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# Persistent Organic Pollutants in the Environment

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# Persistent Organic Pollutants in the Environment


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# EXECUTIVE SUMMARY

According to the Article 9 (3) of the Protocol on Persistent Organic Pollutants (hereafter the POP 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***". Following the EMEP Work-plan for 2012 – 2013, Meteorological Synthesizing Centre East (MSC-E) and Chemical Coordinating Centre (CCC) continued the investigations of the contamination by persistent organic pollutants (POPs) within the EMEP region. This year the evaluation of POP pollution in 2010 were made for ***polycycling aromatic hydrocarbons (PAHs), polychlorinated dibenzo(p)dioxins and dibenzofurans (PCDD/Fs) and hexachlorobenzene (HCB)***. Emission data for modelling were prepared by MSC-E on the basis of the data provided by the EMEP Centre on Emission Inventories and Projections (CEIP). Main emphasis was made on the assessment of POP pollution levels within the EMEP domain and their comparison with existing EU regulations (for PAHs), evaluation of congener composition of complex chemical mixtures (for PCDD/Fs), further developing of the global scale modelling of POPs (exemplified by HCB) and exploring the links between the climate change and POP pollution.

Evaluation of POP contamination in the EMEP region is carried out using the integrated measurement/modelling/emission approach (see ***HTAP Assessment Report 2010***). Under this approach information on emissions, physical-chemical properties of substances and monitoring/ modelling data is complementary used to provide a consistent picture of pollution of the environment. A complete, self-consistent description of chemical properties, emissions, transport pathways and environmental concentrations provides a quantitative basis for making regulatory decisions designed to reduce environmental and human exposure in regions remote from sources.

In evaluation of POP environmental levels it should be taken into account that they are characterized by semi-volatility, persistence, toxicity, bioaccumulation, and long-range transport potential [*Jones and de Voogt*, 1999]. POPs can be accumulated in the environmental compartments such as soil and seawater, persist in these compartments for years and decades and be then re-emitted back to the atmosphere. Besides, some POPs (like HCB and, in less extent, PCDD/Fs) are pollutants of global concern. Taking this into account, modelling of the considered POPs is performed by ***multicompartment*** chemical transport model MSCE-POP. The influence of global POP sources is accounted by application of ***global/hemispheric*** calculations. To consider the affect of long-term accumulation of a pollutant in the environmental media, simulations for a long enough period of time (depending on a pollutant in question) are carried out to generate initial and boundary conditions for regional simulations for 2010.

The outcome of these studies is summarized below.

## *Polycyclic aromatic hydrocarbons (PAHs)*

PAHs are subject to a lot of national and international regulations. In particular, a lot of substances containing PAHs are listed in EU Regulation (EC) No 1907/2006 of the European Parliament and of the Council on **R**egistration, **E**valuation, **A**uthorisation and restriction of **CH**emicals (REACH), Annex VII "Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles". Further, Directive 2004/107/EC of the European Parliament and of the Council (fourth daughter directive for Air Quality Framework Directive 96/62/EC) establishes target value for B[a]P as 1 ng/m$^3$ (B[a]P is used as a marker for the carcinogenic risk of polycyclic aromatic hydrocarbons in ambient air). Here target value is "a concentration in the ambient air fixed with the aim of avoiding, preventing or reducing harmful effects on human health and the environment as a whole, to be attained where possible by 31 December 2012". Similar activities are undertaken in Northern America (CEPA 1999 and CMP in Canada; FIFRA and TSCA in the US; Canadian and US Strategy GLBTS). In this report evaluation of B[a]P environmental levels relative to EU target value is performed.

Emission data for modelling have been prepared on the basis of the official emissions complemented when necessary by expert estimates presented by CEIP. Taking into account that temporal variations of emissions from sources of different categories are different, MSC-E has prepared gridded emission data for main categories contributing to B[a]P emissions (Residential heating, Industrial processes, Waste incineration, Road transport and other categories). Modelling results together with measurements at the EMEP monitoring network provide a consistent picture of contamination in the EMEP region.

The analysis of contamination in 2010 allows selecting several areas with essential exceedances of EU target value for B[a]P, equal to 1 ng/m$^3$ (annual average), which are populated by at least 15 million people.

Further, it has shown that B[a]P contamination is characterized by essential spatial and temporal variability. In particular, winter concentrations of B[a]P can exceed annual averages several times. The variations of air concentrations between neighbouring areas of different character (from urban to background) can be even more essential and reach an order of magnitude. Hence, further evaluation of contamination in heavy polluted regions by modelling with finer spatial resolution is reasonable. For such modelling more detailed information on emissions with finer temporal and spatial resolution is required.

The analysis of long-term trends in B[a]P contamination shows general reduction of B[a]P air concentrations in Europe since 1990 by about 30%. However, this reduction is spatially inhomogeneous. Particularly, significant reduction of pollution (twice and more) is characteristic of 8 countries, moderate reduction (from 50% to 25%) takes place in 10 countries, and in 10 countries air concentrations either have not been changed since 1990 or even become higher. The contamination of the EMEP countries in considerable extent is determined by transboundary transport. Particularly, 12 countries are responsible for 80% of total value of B[a]P deposition to the consolidated area of all EMEP countries. Further, the contributions of transboundary transport (import) exceed 60% for 23 EMEP countries. Besides it should be stressed that contributions of transboundary transport in a country are subject to strong spatial variations. For example, average contribution of transboundary transport to deposition flux over Germany is 30%, though in some regions this contribution can reach 90% and more.

For the description of gas-particle partitioning of PAHs and their degradation in the particle-bound form the information on concentrations and chemical composition of the atmospheric aerosol is crucial. The inter-linkages between POP behaviour in the environment and chemical composition of atmospheric aerosol are examined from the viewpoint of reaction rates of POP degradation due to various atmospheric reactants (ozone and NOx) of PAHs sorbed on aerosol particles of different chemical nature. In future these data will be used for the refinement of model description of PAH behaviour in the atmosphere.

Further improvement of evaluation of B[a]P contamination in the EMEP region imply application of modelling with finer spatial resolution in particular regions and elaboration of tools for POP inverse modelling.

## *Polychlorinated dibenzo(p)dioxins and dibenzofurans (PCDD/Fs)*

The problem of environmental contamination by PCDD/Fs is recently in the focus of a lot of national and international organizations and programs (the Stockholm Convention, HELCOM, SEPA and others). Evaluation of environmental pollution by PCDD/Fs under CLRTAP is currently characterized by essential uncertainties connected with the following:

- Emission data on PCDD/Fs is reported by countries in total toxicity units. However, for model evaluation of PCDD/F contamination the congener composition of emission should be taken into account since the behaviour of particular PCDD/F congeners in the environment is different due to differences in their physical-chemical properties.

- Monitoring of PCDD/F levels is not included into regular EMEP monitoring program. For evaluating PCDD/F contamination of the EMEP region the results of national and international measurement campaigns found in literature are used.

Taking this into account, evaluation of PCDD/F contamination of the EMEP region is performed using compilation of available congener-specific measurement data on PCDD/F air concentrations in background and remote regions and developing inverse modelling approach. Results of model simulations show that the use of available official emission data lead to underestimation of observed PCDD/F concentrations by approximately 5 times which is in line with estimates of uncertainties of available PCDD/F emission inventories for European region. These uncertainties may be caused by incompleteness of emissions, missing source categories, underestimation of uncontrolled emissions, emissions from natural sources, etc.

On the basis of selected measurement data, correction of emission data for particular congeners is carried out using inverse modelling. The correction concerns both total toxicity and contributions of particular congeners. It is found that enlargement of PCDD/F emissions lead to better agreement between measurements and model predictions of total PCDD/F toxicity.

Due to rather high persistence of PCDD/Fs in the environmental media other than the atmosphere (particularly in soil) long-term accumulation in the environmental media can essentially affect PCDD/F air concentrations. To take this accumulation into account and simultaneously evaluate the influence of non-EMEP emission sources, model simulations for the period from 1970 to 2010 are performed for all 17 PCDD/F toxic congeners by means of the hemispheric scale modelling. The evaluation of environmental pollution in 2010 within the EMEP region is carried out by means of regional modelling (with resolution 50×50 km) using initial and boundary condition generated by hemispheric simulations.

Correction of emission data allows to achieve reasonable agreement of calculated and measured values of PCDD/F air concentrations. The agreement between calculated and measured total toxicities within a factor of two is obtained for more than 50% of available measurements at background locations.

Relatively high levels of PCDD/F air concentrations (20 fg TEQ/$m^3$ and higher) are characteristic of some regions in Central and Eastern Europe. In clean regions of Europe (the Scandinavian Peninsula and northern part of the UK) PCDD/F levels are considerably lower (less than 5 fg TEQ/$m^3$). Source-receptor relationships for PCDD/Fs long-range transport and deposition in 2010 are evaluated using corrected emission data. Model results indicate that the contribution of re-emission (that is, re-volatilization of pollutant accumulated previously in the underlying surface) exceeds the half of total deposition to the area of the EMEP countries. Similar to the B[a]P over 80% of total deposition to the area of all EMEP countries from anthropogenic sources is determined by 12 countries. The overall contribution of all the rest EMEP countries does not exceed 20%.

For 22 countries 50% and more of deposition from anthropogenic sources to their area are determined by external emission sources (transboundary transport). Similar to B[a]P contributions of transboundary transport in a country are subject to strong spatial variations. For example, average contributions of external sources in air concentrations in France is about 65%, but these contributions in some regions may be essentially higher (up to 90% and more).

## *Hexachlorobenzene (HCB)*

This year global scale modelling of HCB cycling in the environment is performed by the GLEMOS multi-scale multi-compartment modelling system for the period from 1945 to 2010 with spatial resolution $3^0$x$3^0$. Further, regional-scale calculations for the period from 2009 to 2010 with 50×50 km resolution have been performed with initial and boundary data prepared on the basis of global modelling. The data on HCB historical emissions are prepared and tested by MSC-E during 2009 – 2011 [*Gusev et al.*, 2009; *Shatalov et al.*, 2010; *Gusev et al.*, 2011]. During this work three scenarios of historical HCB emissions (maximum, average and minimal) were constructed [*Shatalov et al,.* 2010]. Preliminary calculations made with the use of GLEMOS system show that calculation results obtained with maximum scenario agree best of all with available measurement data.

Spatial pattern of HCB atmospheric concentrations in 2010 is determined mainly by secondary emission sources, that is, by re-emission of HCB historically accumulated in the underlying surface. Hence, for simulations of HCB contamination levels both in the EMEP region and over the entire globe consideration of historical HCB accumulation is of particular importance. According to emission data used in modelling, the influence of contemporary anthropogenic emissions in the EMEP region to air concentrations is relatively small.

Maximum HCB concentrations (> 30 pg/$m^3$) in the atmosphere have been found in some regions in Europe, India and China. Outside highly contaminated regions air concentrations are close to background ones that depend on latitude. In particular, background HCB air concentrations in low and temperate latitudes of the Northern Hemisphere amount to 10-15 pg/$m^3$.

In the course of global modelling of HCB the evaluation of contamination of main environmental media accumulating HCB (soil and seawater) is carried out. In particular, the spatial pattern of HCB soil concentrations is found to reflect the peculiarities of historical accumulation of the pollutant. Maximum contamination in soil takes place in areas with high emissions and in regions with high latitudes due to

cold condensation. Highest soil concentrations are characteristic of Europe and Russia where they exceed 50 – 100 pg/g. Seawater concentrations are characterized by latitudinal dependence of pollution levels. The highest values of HCB concentrations in seawater (more then 3 pg/L) are obtained for high-latitude regions. The reason for this is connected with the strong temperature dependence of HCB gaseous flux from air to water, particularly, lower air temperatures correspond to higher air-water flux.

## *POP pollution and climate change inter-linkages*

This year MSC-E has continued analyzing the influence of meteorological parameters on the POP contamination. The relationships between inter-annual variability of meteorological and environmental factors and variations of POP concentrations levels are studied by the example of the data for two years 2009 and 2010. This comparison allows examining the influence of extreme events (high temperature levels in Russia during July and August of 2010) on the fate of POPs with different physical-chemical properties.

Two pollutants are used for the analysis. It is found that under the assumption of equal emissions the extreme conditions of 2010 have led to the increase of air concentrations of PCDD/Fs in western part of Russia. On the opposite, the increase of temperature in the considered areas in 2010 has led to the decrease of B[a]P concentrations.

However, measurements of B[a]P contamination levels in Russian cities in 2010 showed the increase of air concentrations. This increase was conditioned by additional emissions from forest fires that occurred in the region due to extreme temperature conditions. Thus the projections of POP fate under the changing climate should take into account not only meteorological changes but also attendant circumstances such as the probability of increased forest fires due to temperature increase.

The analysis of variability of meteorological and environmental factors and variations of POP concentrations indicates that main meteorological processes determining POP fate in the environment are gaseous exchange with underlying surface and atmospheric degradation. The influence of these processes is highly temperature-dependent and is strongly affected by physical-chemical properties of the considered pollutant.

Thus, this year the information on environmental contamination by PAHs, PCDD/Fs and HCB in 2010 has been elaborated including the comparison of B[a]P contamination levels with target value established in the EU, source-receptor relationships for B[a]P and PCDD/Fs and investigation of the role of historical emissions in examination of HCB pollution. Emission data necessary for modelling of the three above pollutants were elaborated. The investigations on the impact of climate change to POP contamination was continued. More detailed information can be found in [*Shatalov et al.*, 2012].

## CONTENTS

# INTRODUCTION

According to the POP Protocol, EMEP should annually provide Executive Body of the Convention with information on the long-range transport and deposition of persistent organic pollutants (Article 9(3)). This year the work on evaluation of pollution levels and deposition for polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo(p)dioxins and dibenzofurans (PCDD/Fs) and HCB is continued. Main results of this work are presented in the present Report.

It should be noted that PAHs and PCDD/Fs are not single pollutants but complex chemical mixtures with great number of individual chemicals inside them. So, particular representatives of these groups should be selected for the assessment. For PAHs B[a]P is selected as such representative since it is used as a marker for the carcinogenic risk of polycyclic aromatic hydrocarbons in ambient air according to the EU regulations. The required information on PCDD/Fs is total toxicity of their mixture in air and deposition. Since difference in physical-chemical properties of particular PCDD/F congeners leads to their different behaviour in the environment, simulations for each of 17 toxic PCDD/F congeners are used for the evaluation of total toxicity of PCDD/F mixture.

Emissions for modelling are prepared by MSC-E on the basis of the data provided by CEIP and complemented, when necessary, by the corresponding expert estimates. Further preparation of emission data for modelling includes:

- For B[a]P – preparation of spatial distribution of emissions from main source categories contributing to B[a]P emissions (residential heating, industrial processes, road transport, waste incineration and other source categories altogether). The necessity of the usage of emission data split by source categories for modelling is conditioned by the differences in temporal variations of emissions originated from different source categories. The issues concerning temporal variations of B[a]P emissions are discussed in Section 1.2.2. The work on investigation of emission temporal variations is performed in collaboration with national experts from Germany.
- For PCDD/Fs – preparation of emission data for 17 toxic congeners. Since congener composition of emissions is not reported by countries, the developing inverse modelling approach is applied for the construction of congener-specific emission data. For this purpose available measurements obtained by MSC-E from literature are used. Simultaneously, emission data for total toxicity are corrected within the range of emission data uncertainty in order to provide realistic levels of PCDD/F pollution. Due to high persistence of PCDD/Fs in surface media, simulations for a long period of time are required to take into account secondary emission sources (re-emissions). Thus, preparation of emission data is carried out for the period from 1970 to 2010. The procedure of evaluation of PCDD/F congener composition in emissions is described in Section 1.2.3.
- For HCB – preparation of historical emission data, which occurs to be a key point in the evaluation of pollution levels in 2010. Besides, due to global character of the pollutant fate, modelling of HCB is performed on the global scale. Global emissions of HCB for these simulations are prepared for the period from 1945 to 2010. Brief description of the results is given in Section 1.2.4.

Evaluation of environmental levels of the above pollutants in 2010 is performed using integrated monitoring/modelling/emission approach (see [*HTAP Assessment*, 2010]) based on application of multiscale modelling using regional and hemispheric MSCE-POP model along with the GLEMOS multi-scale modelling system.

Main focus of the investigations of B[a]P pollution in the EMEP region is the comparison of environmental pollution with target values established in EU Directive 2004/107/EC of the European Parliament and of the Council. The second important issue addressed here is the evaluation of trends of B[a]P pollution from 1990 to 2010. Particular attention is paid also to seasonal variations of B[a]P concentrations since they may noticeably affect annual averages of air concentrations used for the comparison with the target value. Further, spatial variability of B[a]P concentrations within the EMEP region is evaluated. The results are discussed in Section 3.1. Besides, possibilities of further refinement of model description of gas/particle partitioning for B[a]P are examined (Section 4.3).

The investigations of PCDD/F pollution are aimed at the influence of congener composition of emissions on total toxicity of PCDD/F mixture and the contribution of secondary emissions to air concentrations. The study of PCDD/F congener composition has been ongoing for several years in close collaboration with experts from Sweden. Due to the fact that according to the EMEP monitoring strategy regular measurements of PCDD/F are not included into the EMEP measurement program, measurement data from national and international measurement campaigns obtained by literature search are used. The results of these investigations are presented in Section 3.2.

For B[a]P and PCDD/Fs evaluation of source-receptor relationships within the EMEP region is performed. It is shown that for these pollutants transboundary transport plays an important role and contributes essentially to the contamination of the EMEP countries.

Pilot modelling of HCB dispersion on global scale is described in Section 3.3. Due to high persistence and long-range transport potential of HCB in the environment, long-term simulations of transport and accumulation of this contaminant in the environment on global scale are performed for the period from 1945 to 2010 with spatial resolution $3^0x3^0$ using the GLEMOS multi-scale multi-compartment modelling system and global emission data (Section 1.2.4). For the refinement of spatial distribution of HCB contamination, regional-scale calculations for the period from 2009 to 2010 with 50×50 km resolution are performed with initial and boundary data prepared on the basis of global modelling. Relative contributions from contemporary HCB anthropogenic emission sources within the EMEP domain, secondary emissions, and transport from non-EMEP regions are evaluated.

The influence of meteorological variability on POP pollution with linkages to climate change issues is considered in Section 4. Particularly, the difference between POP air concentrations in 2009 and 2010 induced by meteorological variability is analyzed for B[a]P and PCDD/Fs. This comparison allows examining the influence of extreme meteorological conditions (high temperatures in the western part of the Russian Federation) on the fate in the environment of POPs with different physical-chemical properties. In addition, various environmental processes (degradation, scavenging and transport) are compared from the viewpoint of their influence on POP pollution on the basis of seasonal variations of contamination levels within a year.

Finally, MSC-E plans for future activities are described in Section 5.

Main results of the investigations are briefly summarized in the Executive Summary.

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# 1. EMISSION OF POPs

## 1.1. Emission set prepared by CEIP

The data on persistent organic pollutant emission totals from the EMEP countries for 2010 used for modelling were based on the official data received from the EMEP Centre on Emission Inventories and Projections (CEIP) [http://www.emep-emissions.at/ceip/]. If countries did not report their national emission data, emission totals for 2010 were taken from the projections made by TNO [*Denier van der Gon et al.*, 2005]. Information about spatial distribution of POP emissions at least for one year of the period 1990-2010 was provided by 28 countries (Austria, Belarus, Belgium, Bulgaria, Croatia, Cyprus, the Czech Republic, Denmark, Estonia, Finland, France, Germany, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Netherlands, Norway, Poland, Slovakia, Slovenia, Spain, Sweden, Switzerland, the Ukraine and the United Kingdom). 21 countries from them submitted gridded data for 2010. The gridded emissions for 2010 were prepared by CEIP for the EMEP countries with spatial resolution $50\times50$ km$^2$.

## 1.2. Preparation of emissions for modelling

### *1.2.1. Emission totals*

Modelling of POP long-range transport and deposition presented in this report is based on the hemispheric/global and regional scale emission data. Gridded emission data are constructed on the basis of official emission data and expert estimates. The official information on POP emission totals for the Asian part of the EMEP domain, the USA, China and Japan was not available. Therefore, emissions for modelling for these regions are based on non-Party emission estimates. Additionally the analysis of official information on POP emissions by source categories and uncertainties is performed by MSC-E.

Benzo[a]pyrene, polychlorinated dibenzo-p-dioxins and dibenzofurans and hexachlorobenzene emission totals for Kazakhstan and Kyrgyzstan are derived from the TNO emission inventory [*Denier van der Gon et al.*, 2005] using the projections for 2010. B[a]P and PCDD/F emissions in the Asian part of Russia are estimated using official emission data for the European part of the country and the ratio between the population of the European and the Asian parts of the country. HCB emissions for the Asian part of the EMEP domain are derived from the TNO emission inventory [*Denier van der Gon et al.*, 2005]. B[a]P emissions in Tajikistan, Turkmenistan and Uzbekistan are taken from the global atmospheric emission inventory of PAHs prepared by *Y.Zhang and S.Tao* [2009]. PCDD/F emissions in Tajikistan, Turkmenistan and Uzbekistan are taken from the unofficial inventory of PCDD/F emissions in the Central Asian countries made in the framework of the global International POPs Elimination Project (IPEP) [*Hodjamberdiev,* 2006]. Total emissions of HCB from Tajikistan, Turkmenistan and Uzbekistan are assessed using the gross domestic product of these countries. Relationship between the gross domestic product and unofficial HCB emissions for these countries is obtained on the basis of the data for Kazakhstan and Kyrgyzstan taken from the TNO emission inventory [*Denier van der Gon et al.*, 2005].

Spatial distribution of POP emissions in the Central Asian countries and the Asian part of Russia is determined on the basis of data on population density [*Li*, 1996] obtained from the web site of Canadian Global Emissions Interpretation Centre [*http://www.ortech.ca/cgeic*].

The latest available information on PCDD/F emissions in the USA is taken from the dioxin and furan inventories prepared by [*UNEP*, 1999] for 1995. PCDD/F emissions in China are taken from the

inventory of potential PCDD and PCDF emission sources in the mainland of China [*Jin et al.*, 2004]. PCDD/F emissions of Japan are derived from national dioxins emission inventory [*Government of Japan*, 2009].

On the basis of the above information spatial distributions of POP emission totals in 2010 for use in modelling are prepared (Fig. 1.1).

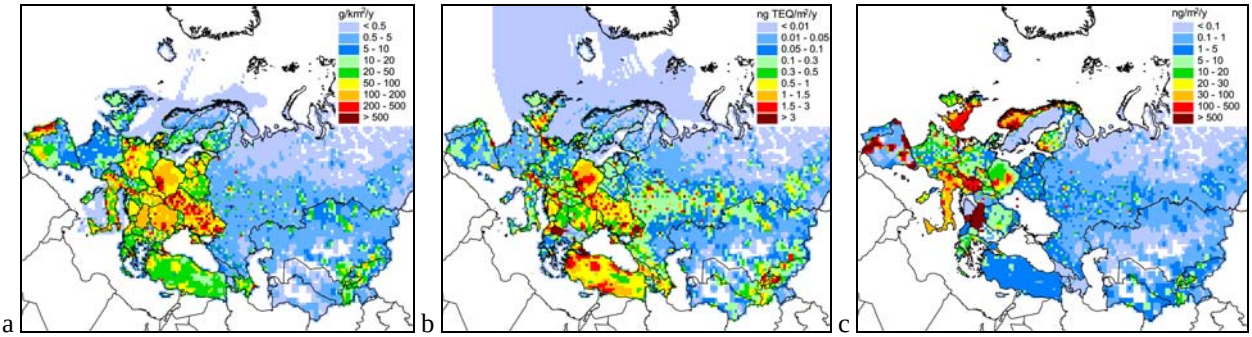



***Fig. 1.1.*** *Spatial distribution of B[a]P (a), PCDD/Fs (b) and HCB (c) emissions over the EMEP domain in 2010*

Total emission of B[a]P in Europe and Central Asia in 2010 (595 tonnes) was 93 tonnes higher than that for 2009. This value includes 563 tonnes from emission sources located in the European countries and 32 tonnes – from the Central Asian region. Emission values for Ukraine, Italy, Serbia, Poland and Germany used in modelling for 2010 are higher than those for 2009 by 60, 10, 5.8, 5.8 and 5.5 tonnes, respectively. The maximum decrease of emission is found for Portugal (3.6 tonnes).

According to the official and unofficial emission data, total emissions of B[a]P within the EMEP domain decreased by 20% in the period from 1990 to 2010. Among the countries submitted official data on B[a]P emissions for 2010, maximum emission reduction within the considered period took place in the United Kingdom (95%), Germany (78%), Republic of Moldova (77%) and the Netherlands (76%). At the same time in Denmark, Iceland, Estonia, Latvia, Cyprus, Bulgaria and Sweden B[a]P emissions increased in comparison with the level of the emission in 1990.

Total anthropogenic emission of PCDD/Fs from the EMEP domain for 2010 accounted for 6468 g TEQ, which was 144 g TEQ lower than that in 2009. Emission from the European part of the EMEP domain (excluding a part of the Kazakhstan territory) amounted to 5630 g TEQ, and from the extended part (Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan, Uzbekistan, the eastern part of Russia) - 838 g TEQ. The highest decrease of emission values (in absolute terms) compared to 2009 took place in Bulgaria (145 g TEQ), Serbia (115 g TEQ) and Hungary (30 g TEQ). At the same time in many countries there was an increase of emissions in comparison to 2009. The greatest increase in PCDD/F emissions occurred in the following countries: the Russian Federation (39 g TEQ), Italy (29 g TEQ), Poland (27 g TEQ), Romania (17 g TEQ) and Croatia (12 g TEQ).

Emission of HCB in the European and the Central Asian countries in 2010 amounted to 1616 kg, which was 85 kg higher than that for 2009. European emissions accounted for 1609 kg, and the emissions from Central Asia and the Asian part of Russia – 7 kg. Most significant increase of emission values in individual countries took place in the Ukraine, Serbia, Spain, Belgium and Montenegro (243, 69, 20, 9.2 and 8.5 kg, respectively). The highest decrease is indicated for the Netherlands, Finland, Italy, Hungary and Bulgaria (122, 18, 6.3, 5.1 and 3.5 kg, respectively).

Official information on B[a]P and PCDD/F emissions by source categories for 2010 is available for 33 and 38 countries, respectively. According to these data the sector *1A4bi Residential - Stationary plants* represents the most significant source category of B[a]P and PCDD/F emissions (Table 1.1 and 1.2) followed by mobile sources for B[a]P emissions and by iron and steel production for PCDD/F emissions.

***Table 1.1.*** *Key source categories for B[a]P emissions in 2010 and their contributions to total emission, %*

| NFR Code | NFR Category | Contributions to emission total, % | Cumulative Total, % |
|---|---|---|---|
| 1 A 4 b i | Residential: Stationary plants | 46.1% | 46.1% |
| 1 A 4 b ii | Residential: Household and gardening (mobile) | 14.1% | 60.2% |
| 1 A 4 c ii | Agriculture/Forestry/Fishing: Off-road vehicles and other machinery | 12.1% | 72.3% |
| 1 A 3 b iii | Road transport: Heavy duty vehicles | 9.9% | 82.2% |
| 1 A 3 c | Railways | 3.4% | 85.6% |
| 1 B 1 b | Fugitive emission from solid fuels: Solid fuel transformation | 2.4% | 88.0% |
| 2 C 3 | Aluminium production | 2.2% | 90.2% |
| 1 A 2 f ii | Mobile Combustion in manufacturing industries and construction | 1.9% | 92.1% |
| 1 A 3 b ii | Road transport: Light duty vehicles | 1.2% | 93.3% |

***Table 1.2.*** *Key source categories for PCDD/F emissions in 2010 and their contributions to total emission, %*

| NFR Code | NFR Category | Contributions to emission total, % | Cumulative Total, % |
|---|---|---|---|
| 1 A 4 b i | Residential: Stationary plants | 36.4% | 36.4% |
| 2 C 1 | Iron and steel production | 13.1% | 49.5% |
| 1 A 2 a | Stationary combustion in manufacturing industries and construction: Iron and steel | 6.6% | 56.1% |
| 1 A 2 f i | Stationary combustion in manufacturing industries and construction: Other | 6.0% | 62.1% |
| 6 D | Other waste | 5.9% | 68.1% |
| 6 C e | Small scale waste burning | 4.4% | 72.5% |
| 1 A 1 a | Public electricity and heat production | 4.4% | 76.9% |
| 6 C b | Industrial waste incineration | 4.1% | 81.0% |
| 1 A 2 b | Stationary Combustion in manufacturing industries and construction: Non-ferrous metals | 2.9% | 83.9% |

***Table 1.3.*** *Key source categories of HCB emission in 2010 and their contributions to total emission, %*

| NFR Code | NFR Category | Contribution to Total Emission, % | Cumulative Total, % |
|---|---|---|---|
| 2 C 2 | Ferroalloys production | 28.3% | 28.3% |
| 2 C 1 | Iron and steel production | 23.6% | 51.9% |
| 2 C 5 e | Other metal production | 14.4% | 66.3% |
| 2 G | Other production, consumption, storage, transportation or handling of bulk products | 10.4% | 76.7% |
| 1 A 2 f i | Stationary combustion in manufacturing industries and construction: Other | 7.7% | 84.4% |
| 2 C 3 | Aluminium production | 4.3% | 89.1% |
| 1 A 4 b i | Residential: Stationary plants | 2.8% | 91.9% |
| 4 G | Other Agricultural processes | 1.6% | 93.5% |
| 1 A 1 a | Public electricity and heat production | 1.6% | 95.1% |
| 6 C b | Industrial waste incineration | 1.2% | 96.3% |

Official information on HCB emissions by source categories for 2010 is available for 32 countries. According to these data the most significant source category of HCB emissions is *2C2 Ferroalloys production* sector (Table 1.3) followed by *2C1 Iron and steel production* sector.

Analysis of source category data of individual countries shows that the contribution of key categories to total HCB emissions can vary essentially among the EMEP countries. Detailed information on relative contribution of key source categories listed above to national emission totals is exemplified by several countries in Table 1.4. It can be seen that data of a number of countries do not consider the key source categories given Table 1.3. Particularly, the information on contribution of *Ferroalloys production* and *Iron and Steel production* source categories to the emissions of the most of countries is not presented. Besides, the most part of HCB emissions of the countries is determined by a few source categories and information on some HCB sources is absent in national inventories. More significant contribution to HCB emissions originated from the production of chlorinated solvents and pesticides, wastes and sewage sludge incineration, metals smelting, sintering process, steel manufacturing, production of magnesium and cement as well as combustion of fossil fuel can be expected. Thus, it is possible to assume that officially reported HCB emissions can be underestimated.

***Table 1.4.*** *Contributions of key source categories to total HCB emissions of the EMEP individual countries*

| NFR Code | AL | BG | CY | EE | IE | LV | ME | RS | ES | UA | GB |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 C 2 | | | | | | | | | | 47% | |
| 2 C 1 | | 98% | | | | | | | 99% | 1% | |
| 2 C 5 e | | | | | | | 99% | | | 23% | |
| 2 G | | | | | | | | | | 17% | |
| 1 A 2 f i | 19% | | 97% | 12% | | 18% | | | | 12% | |
| 2 C 3 | | | | | | | | 99% | | | |
| 1 A 4 b i | 70% | 1% | 2% | 56% | | 59% | | | | | |
| 4 G | | | | | 99% | | | | | | 70% |
| 1 A 1 a | | | | 31% | | 10% | | | 1% | | 29% |
| Total | 89% | 99% | 99% | 99% | 99% | 87% | 99% | 99% | 100% | 100% | 99% |

AL – Albania; BG – Bulgaria; CY – Cyprus; EE – Estonia; IE – Ireland; LV – Latvia, ME – Montenegro; RS – Serbia; ES – Spain; UA – Ukraine; GB – United Kingdom.

Uncertainties of the emissions of the EMEP countries can be caused by missing emission sources, uncertainties of emission factors, insufficient information on activities, etc. Official information on uncertainties of country's POP emission totals for 2010 is available from seven countries: Croatia, Cyprus, Denmark, Finland, France, Sweden and the United Kingdom (Table 1.5). As follows from the table, the uncertainty of PAHs is maximum almost in all countries reported this information. In Denmark POP emission uncertainties are the largest and in France are the smallest. The uncertainty values for Finland and the United Kingdom are similar.

***Table. 1.5.*** *Uncertainties of POP emission totals for 2010, %*

| | Croatia [*Poljanac et al.*, 2012] | Cyprus [*Savvydes and Tsekme*, 2012] | Denmark [*Nielsen et al.*, 2012] | Finland [*SYKE*, 2012] | France [*CITEPA*, 2012] | Sweden [*SEPA*, 2012] | United Kingdom [*Passant et al.,* 2012] |
|---|---|---|---|---|---|---|---|
| PAHs | 393 | 215 | 948* | -78 to +170 | 75 | 719 | -70 to +150* |
| PCDD/Fs | 396 | 92 | 701 | -42 to +54 | 66 | 117 | -40 to +80 |
| HCB | --- | 197 | 717 | -73 to +134 | 60 | --- | -70 to +110 |

* B[a]P

The information on B[a]P emission seasonal variations is of importance for the evaluation of pollution of the EMEP region. Considerable contribution of the Residential category to the total B[a]P emissions determines pronounced seasonal emission variation. However seasonal variations of emissions are not currently reported by the EMEP countries. To construct temporal variability of emissions it is necessary to take into account that this variability depends on the type of emission source (emission sector). To model this variability, the contributions of various emission source categories to the overall B[a]P emissions are assessed. MSC-E has prepared the spatial distribution of emissions from main source categories contributing to B[a]P emissions (residential heating, road transport, industrial processes, waste incineration and other source categories altogether). The issues concerning temporal variations of B[a]P emissions are discussed in Section 1.2.2 below.

The emissions of particular PCDD/F congeners are not included in the information submitted by the Parties to the Convention. The emission data on PCDD/Fs are reported by countries as total toxicity of the mixture of 17 toxic congeners. Every toxic congener has specific physical-chemical properties and thus different behaviour in the environment. Therefore, for model evaluation of PCDD/F contamination the congener composition of the emission should be taken into account. Detailed information on PCDD/F emission congener composition is described in Section 1.2.3.

### *1.2.2. Temporal variations of B[a]P emissions*

This section presents the results of further refinement of model description of seasonal variability of B[a]P content in air and the analysis of the influence of this variability on annual mean B[a]P air concentrations.

Seasonal variability of B[a]P air concentrations can be conditioned by both environmental factors and variability of emissions. Among the environmental factors temperature dependence of physical-chemical properties of the most POPs is of particular importance. This dependence strongly affects seasonal variations of POP contamination through seasonal changes of such important processes as dry and wet deposition and degradation of POPs. These factors are already taken into account in modelling approach implemented in the MSCE-POP model by usage temperature-dependent air-water and octanol-water partitioning coefficients and degradation rates where available. Further, usage of temporally resolved data for atmospheric reactants (OH radicals, organic carbon in the atmospheric aerosol, etc.) allows describing temporal variability of the above listed processes more accurately. Finally, to refine the description of B[a]P pollution seasonal variations the process of photodegradation of this pollutant is involved into the model.

However, in addition to temporal variability caused by environmental factors there exists temporal variability of contamination levels due to that of emissions. Such variability is particularly important for the pollutants which are emitted to the atmosphere by burning processes. Most typical examples of such pollutants are PCDD/Fs and PAHs. Taking into account that the latter group of pollutants is much more investigated (from the viewpoint of data on environmental levels and physical-chemical properties) it is chosen for the analysis of seasonal variability of POPs at this stage of investigations.

Brief description of approaches to the description of temporal variability of emissions in the MSCE-POP model is presented below. More detailed information on these approaches can be found in the EMEP/MSC-E Technical Report [*Shatalov et al.*, 2012].

Temporal variations of emissions for three main source categories (residential heating, industrial processes and road transport) are introduced into the model.

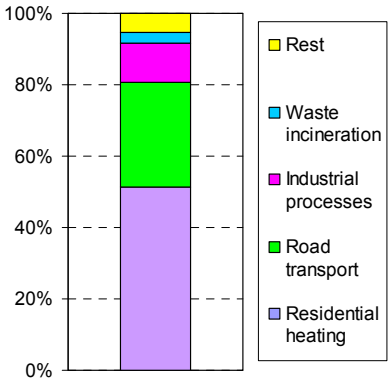



***Fig. 1.2.*** *Main source categories of B[a]P emissions*

To construct temporal variability of emissions one should take into account that this variability depends on the type of emission source (emission source category). So, prior to modelling this variability, the contributions of various emission source categories to the overall B[a]P emissions should be assessed. According to the official emission data for 2010 complemented by the data from TNO emission inventory when necessary, the main contribution to the emissions is made by residential heating (about 50%), followed by road transport (30%), industrial processes (11%) and waste incineration (3%). The contribution of the rest emission source categories is accounted for about 5%. Main source categories of B[a]P emissions are shown in Fig. 1.2.

The approach to modelling temporal variations of emissions from ***residential heating*** based on the data on the dependence of power supply on temperature is worked out by [*Aulinger et al.*, 2010]. This approach is based on the data on power supply dynamics during 2005 – 2006 in Hamburg, Germany. In *Beecken* [2007] it is shown that the quantity of heat that is supplied to consumers linearly decreases with the increase of the ambient temperature up to 18º C where the supplied heat reaches a minimum and remains constant for higher temperatures. Under the assumption that B[a]P emissions are directly proportional to the supplied heat, it can be concluded that B[a]P emissions drop linearly with the temperature increase up to 18º C and remain constant at higher temperatures. On the basis of this assumption, the dependence of B[a]P emissions on temperature are calculated and distributed over the year for each grid cell according to the ambient temperature in such a way that redistribution does not change total annual emissions.

It should be stressed that the parameters of temperature dependence of emissions can be different for different regions of the EMEP domain. The parameters of temperature dependence of emissions can also vary depending on the implemented technology of power supply. The dependence of emissions on the parameters of temperature dependence is investigated in [*Aulinger et al.*, 2010]. It is shown that the usage of temperature-dependent emission variations improves the agreement between measurements and model predictions.

Up to now factors 1.2 for autumn and winter months and 0.8 for summer and spring months (proposed by [*Baart et al.,* 1995]) are applied in the MSCE-POP model to take into account seasonal variation of emissions. The example of emission temporal variations at some location in Central Europe is given in Fig. 1.3 in comparison with earlier used intra-annual emissions variations.

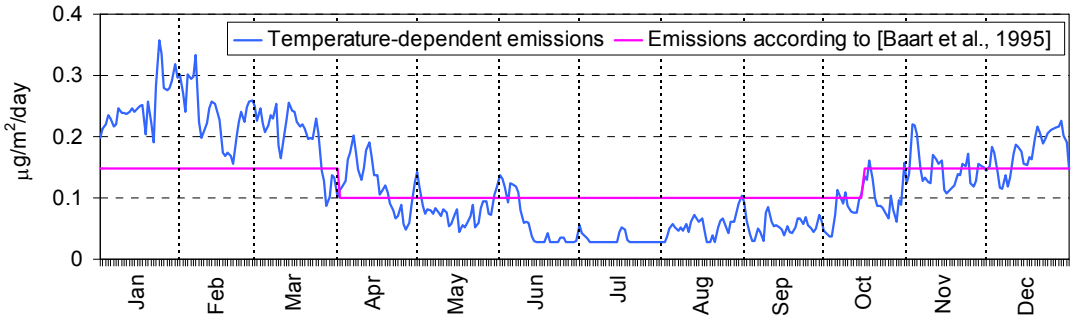



***Fig. 1.3.*** *Temporal variations of B[a]P emissions at a particular location in Central Europe.*

It is seen that usage of temperature dependent scheme of emission seasonal variations leads to essentially higher emissions (by 44% on the average) in cold season (from December to March) and lower emissions (by 51% on the average) in warm season (from June to September). In April, May and October temperature-dependent emissions are oscillating around values predicted by the estimates of [*Baart et al.,* 1995].

Temporal variations of emissions for ***road transport*** and ***industrial processes*** categories are constructed in accordance to the coefficients used in LOTOS/EUROS model [*Schaap et al.,* 2005]. Seasonal variations of emissions from road transport are illustrated in Fig. 1.4a, where fractions of annual emissions for each month are shown. Besides, variations of emission from road transport within a week are taken into account (Fig. 1.4b).

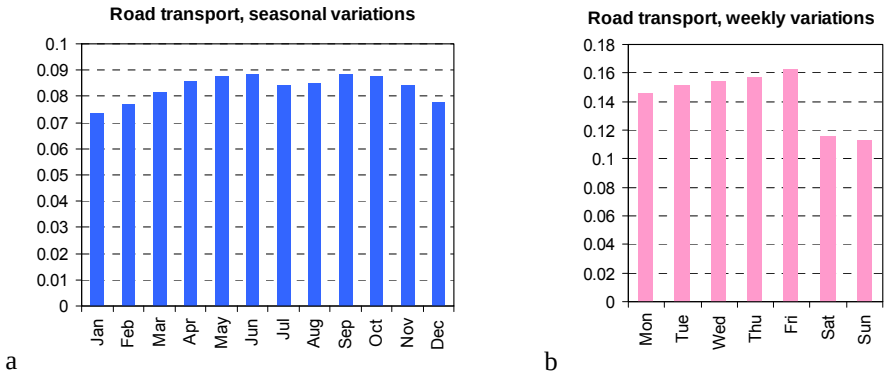



***Fig. 1.4.*** *Monthly fractions of annual emissions (a) and daily fractions of weekly emissions (b) for emissions from road transport.*

Similar diagrams for emissions from industrial processes are presented in Fig. 1.5.

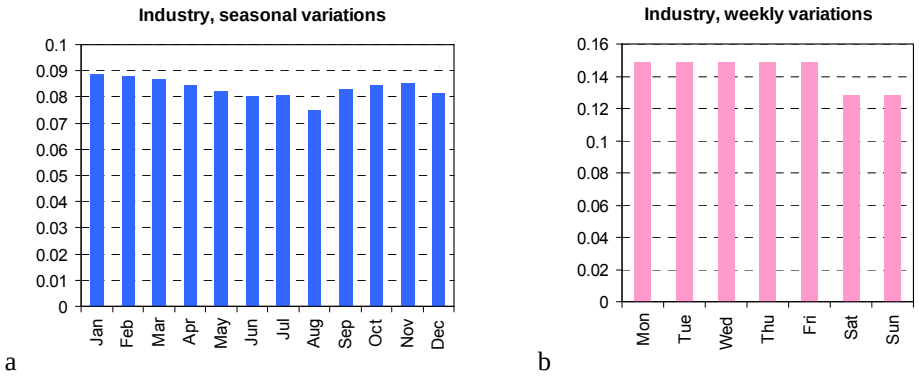



***Fig. 1.5.*** *Monthly fractions of annual emissions (a) and daily fractions of weekly emissions (b) for emissions from industrial sources.*

The diagrams show that the supposed seasonal variations of emissions from industry sources and road transport are low enough in comparison with those used for emissions from residential heating. For industry sources and road transport weekly variations of emissions are taken into account in the model. Emissions of all other source categories are supposed to be constant over the year.

### *Influence of emission seasonal variations*

For evaluation of the influence of seasonal variations of emissions (SV), model simulations for 2009 using previous and modified seasonal variations are carried out. The data on annual emission totals for the considered year are presented by CEIP.

The comparison of simulations of B[a]P transport and accumulation taking into account temperature dependence of emissions (modified SV) with calculations using coefficients proposed by [*Baart et al.,* 1995] (previous SV) allows evaluating the influence of this dependence on B[a]P concentration levels. The comparison of correlation coefficients between measurements and model predictions for these two calculation schemes made over sites where all monthly averages are available is presented in Table 1.6.

***Table 1.6.*** *Correlation coefficients between measurements and model results based on previous seasonal variations scheme (previous SV) and modified one (modified SV) for some EMEP measurement sites.*

| | BE13 | CZ3 | DE1 | DE9 | NO42 | SI8 |
|---|---|---|---|---|---|---|
| Previous SV | 0.91 | 0.77 | 0.71 | 0.87 | 0.42 | 0.89 |
| Modified SV | 0.94 | 0.82 | 0.72 | 0.83 | 0.47 | 0.97 |

The comparison shows that almost for all measurement sites correlation between measured and calculated concentrations enlarges due to implementation of temperature dependence of B[a]P emissions. The comparison of the results of these two simulation schemes with measurements at CZ3 (where correlation coefficient becomes better) and DE9 (where correlation coefficient becomes worse) is given in Fig. 1.6.

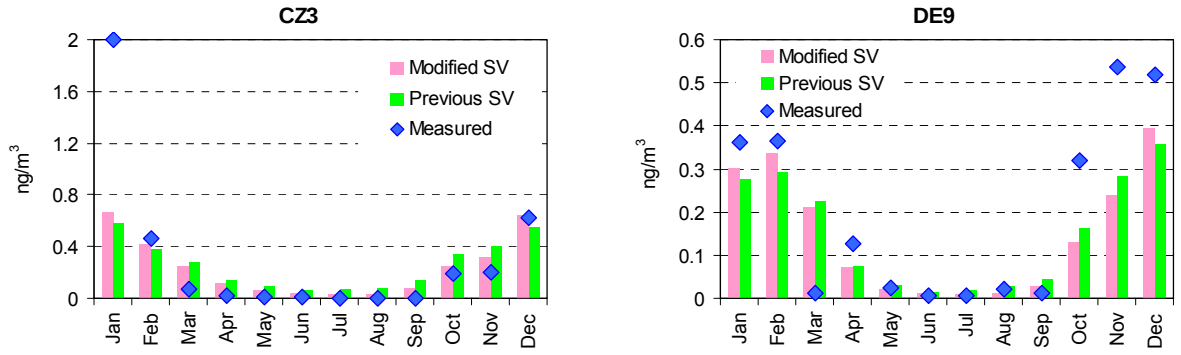



***Fig. 1.6.*** *Comparison of measured values of B[a]P concentrations at CZ3 and DE9 with calculation results using previous and modified scheme of emission seasonal variations.*

It is seen that some improvement of the agreement between measurements and model predictions takes place at CZ3. At the site DE9 in some cases the agreement becomes even worse. This shows that temporal variations of emissions may depend on a particular country.

The improvement of the agreement for warm season is considered separately. For example, at BE13 measurement-to-calculation ratio for air concentrations in warm months has risen from 0.38 to 0.61, at DE1 – from 0.22 to 0.41 and at DE9 – from 0.42 to 0.79 (see Fig. 1.7).

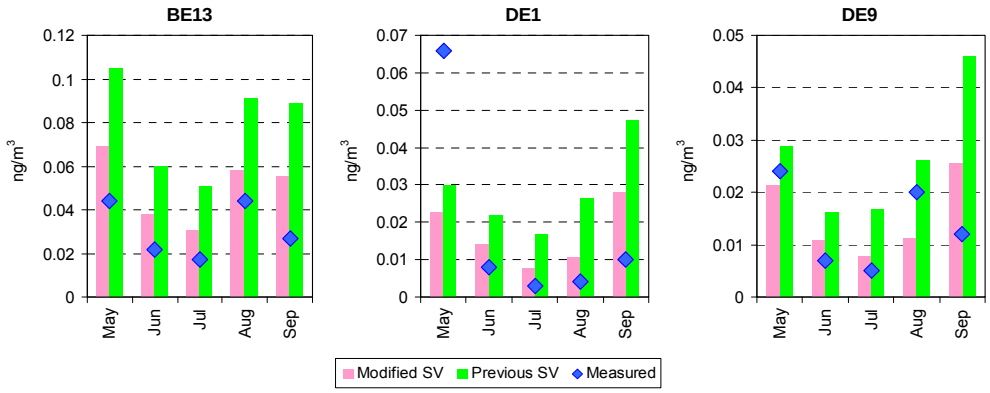



***Fig. 1.7.*** *Comparison of measured values of B[a]P air concentrations with calculated ones for previous and modified emission seasonal variations for the period from June to September at three EMEP sites.*

Thus, in most cases calculations using modified seasonal variations of emissions better agree with measurements than calculations made with the use of previous emission seasonal variations. However, the agreement is improved differently for sites located in different regions.

It is interesting also to evaluate the difference between annual averages of B[a]P air concentrations calculated with previous and modified emission seasonal variations over the whole EMEP grid. Spatial distribution of this difference is shown in Fig. 1.8.

According to the model estimates, differences in calculations of ***annual means*** of air concentrations due to ***emission seasonal variations*** may reach 40% and more. These differences can be essential in regions of Eastern Europe where exceedances of the EU target value threshold take place. This shows that the information on emission seasonal variations is required for reliable assessment of exceedances of target values in the EMEP domain.

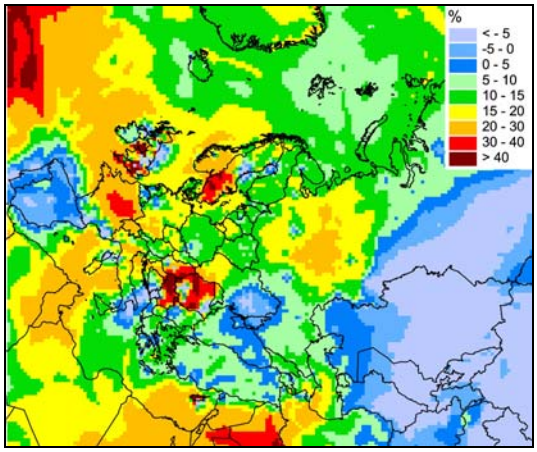



***Fig. 1.8.*** *Difference between calculations with previous and modified schemes of emission seasonal variations.*

## *Concluding remarks*

The above investigation shows that:

- Modification of model description of emission seasonal variations refines the agreement between measured and calculated values of B[a]P air concentrations.
- Temporal variability of B[a]P emissions can considerably (up to 40% and higher) affect annual means of air concentrations. This variability strongly depends on emission composition from the viewpoint of source categories.
- Information on temporal variations for various emission source categories is desirable for correct assessment of B[a]P contamination levels.

### *1.2.3. Evaluation of congener composition of PCDD/F emissions*

Evaluation of PCDD/F fate in the environment should take into account that PCDD/F is a complex chemical mixture and, hence, its total toxicity is composed from toxicities of 17 individual toxic congeners. Essential differences in environmental behaviour of different PCDD/F congeners imply the use of separate simulations for each of 17 toxic congeners for more reliable evaluation of their total toxicity.

Since Parties to the Convention report the emission data on total toxicity of PCDD/Fs only, to assess environmental pollution by PCDD/Fs the congener composition of emissions should be evaluated. To perform this task, the following approach is used.

At the first stage initial model simulations for each of 17 toxic congeners based on the available emission data are performed. For these calculations congener-specific emissions are generated on the basis of official emission data on total toxicity of PCDD/F mixture provided by CEIP. To split the data on total toxicity to emissions of particular congeners the expert estimates from POPCYCLING-Baltic project [*Pacyna et al.,* 2003] are used. According to these data congener composition does not essentially vary between the countries. To take into account remote emission sources (located outside the EMEP domain) and the influence of long-term accumulation of PCDD/F congeners in the environmental media other than the atmosphere, hemispheric simulations for the period from 1970 to 2010 are carried out. Then calculations of environmental levels of 17 toxic congeners are done on the regional level for 2010.

At the second stage the results of initial simulations are compared with available measurement data on atmospheric concentrations of PCDD/F congeners. This task is complicated by the fact that regular measurements of PCDD/Fs at the EMEP measurement sites are currently performed. To obtain monitoring data for the comparison MSC-E performed literature search of congener-specific PCDD/F measurements obtained by national and international monitoring campaigns. These data reported for different years and time periods are compared with calculation results obtained for corresponding periods. The comparison shows essential underestimation of total toxicity of PCDD/F mixture and disagreement between measured and calculated congener composition.

At the third stage correction of emissions of individual congeners is done on the basis of minimization of Root Mean Square Error (RMSE) for each of the considered 17 toxic congeners under the assumptions of a small observation noise and neglecting uncertainties in atmospheric transport model. This correction (being in line with estimates of emission uncertainties up to 700% reported by countries) leads to the refinement of the agreement between both measured and calculated total toxicity of PCDD/F mixture and between fractions of individual congeners in total toxicity in modelling results and observations.

Below short summary of the results of these activities is given. More detailed information can be found in EMEP/MSC-E Technical Report [*Shatalov et al*., 2012].

#### *Measurement data*

Here the monitoring data used for the correction of PCDD/F congener composition are described. A lot of measurement data on PCDD/Fs for the period from late 1980$^{th}$ to 2009 were found in the literature. These data includes measurements in European countries (Austria, Belgium, Denmark, France, Germany, Greece, Italy, Ireland, Luxembourg, the Netherlands, Poland, Portugal, Slovakia, Spain, Sweden and the United Kingdom), Asian countries (China, Japan and Korea) and North America (USA

and Canada). These measurements characterize environmental levels of PCDD/Fs for different locations from background ones (up to 15 – 20 fg TEQ/$m^3$) to urban/industrial regions (about several hundreds of fg TEQ/$m^3$). Extremely high contamination levels of PCDD/Fs (more than 1000 fg TEQ/$m^3$) were obtained at some urban/industrial locations in China, Korea and Poland.

For the comparison measurements in background/rural regions with congener composition of air concentrations were selected. The following data are used: measurements in France (Thau lagoon) for 2005 and 2007; measurements at Swedish sites SE12 and SE14 for 2009, measurements in Spain (Arenys de Mar) made in November 2008, measurements in Italy (Ispra IT04 JRC EMEP site) made in March 2005 and measurements at the UK sites (London, Manchester, Middlesbrough, Stoke Ferry and Hazelrigg) for the period from 2004 to 2008. The site High Muffles was not considered due to large number of measurements being below the detection limit. In addition, measurements at Great Lakes (sites Eagle Harbor, Sleeping Bear Dunes, Sturgeon Point and Chicago) for the period from 2004 to 2007 were used for the comparison.

### *Comparison of initial calculations with measurements*

As mentioned above, for each of 17 PCDD/F toxic congeners separate calculations for the period from 1970 to 2010 (at the hemispheric scale) and for 2010 (at the regional scale) with the use of official emission data and preliminary congener composition of emissions were carried out (initial calculations).

Below the comparison of measured congener composition of PCDD/F mixture in the atmosphere (that is, fractions of individual congeners in total toxicity of PCDD/F mixture) with that obtained by initial calculations was performed for all measurements mentioned above. Here only some examples will be considered; more detailed description of the comparison can be found in [*Shatalov et al*., 2012].

To begin with, measured and calculated congener composition of PCDD/F mixture will be compared. By congener composition the set of fractions of individual congeners in total toxicity of PCDD/F mixture is meant. One of the characteristics of PCDD/F congener composition, which is often used in the literature, is dioxin-to-furan ratio (D/F ratio). It is defined as the ratio of contribution of dioxins to total toxicity to that of furans. Measured and calculated D/F ratios for some locations and time periods in Europe are given in Table 1.7. The table contains both background and urban measurements. The latter can be used for direct evaluation of PCDD/F congener composition in the corresponding region since measurement locations are for these sites close to emission sources and congener composition in the atmosphere is not subject to modifications during the long-range transport due to differences in physical-chemical properties of particular congeners.

It can be noticed that higher measured values of D/F ratio are characteristic of western European countries (locations) whereas lower value of the ratio were measured at the locations situated in the Eastern/Southern Europe (Italy and Poland). It is interesting to note that measurements for China show rather low fraction of dioxins (measured value of D/F ratio in Beijing, February 2006, is only 0.12). At the same time calculated D/F ratio does not vary essentially since initial congener composition in emissions does not vary between particular countries.

The differences in congener composition of PCDD/F toxicity in emissions are conditioned by the differences of congener composition in emissions from different emission source categories and by the differences in the distribution of country emissions by source categories. Average values of D/F ratios for some emission source categories are presented in Table 1.8.

***Table 1.7.*** *Measured and calculated values of D/F ratio for some locations in Europe*

| Period and location | D/F ratio | |
|---|---|---|
| | Measured | Calculated |
| Hazelrigg (the UK), 2004 – 2008 | 1.02 | 0.22 |
| Thau lagoon (France), 2005 | 0.97 | 0.27 |
| London (the UK), 2004 – 2008 | 0.75 | 0.22 |
| Stoke Ferry (the UK), 2004 – 2007 | 0.71 | 0.22 |
| Arenis de Mare (Spain), November 2008 | 0.67 | 0.21 |
| SE14 (Sweden), 2009 | 0.57 | 0.38 |
| Middlesbrough (the UK), 2004 – 2008 | 0.55 | 0.22 |
| Thau lagoon (France), 2007 | 0.48 | 0.21 |
| Manchester (the UK), 2004 – 2008 | 0.48 | 0.22 |
| SE12 (Sweden), 2009 | 0.43 | 0.40 |
| Ispra, IT04 (Italy), March 22 – 30, 2005 | 0.23 | 0.20 |
| Krakow (Poland), June and December 2002 | 0.12 | 0.22 |

***Table 1.8.*** *Average D/F ratios for some emission source categories*

| | D/F ratio | | |
|---|---|---|---|
| | Average | Median | SqD |
| Marine transport | 0.99 | 0.73 | 0.45 |
| Road transport | 0.92 | 0.48 | 1.20 |
| Fuel burning | 0.79 | 0.51 | 0.99 |
| Waste incinerators | 0.47 | 0.27 | 0.58 |
| Cement kilns | 0.44 | 0.33 | 0.23 |
| Metallurgy | 0.26 | 0.18 | 0.20 |

It can be seen that high values of D/F ratios (that is, predominance of dioxins in emissions) is characteristic of source categories connected with fuel burning such as marine transport, road transport, etc. On the opposite, emissions from waste incinerators and industry seem to be characterized by lower value of D/F ratio. Unfortunately, gaps in the information on the distribution of country emissions by source categories and uncertainties in emission factors for individual congeners hamper the construction of correct congener composition of country-specific emissions.

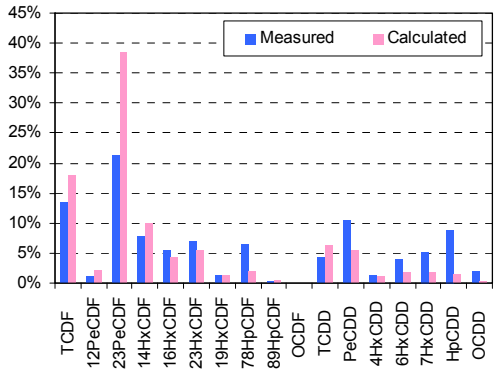



***Fig. 1.9.*** *Comparison of calculated and measured congener composition at Stoke Ferry (the UK) averaged over 2004 – 2007.*

Of course, D/F ratio is just an averaged characteristic of congener composition. To see more detailed information on congener composition, fractions of each particular congener in the total toxicity of PCDD/F mixture (congener profile) should be considered. As an example, the comparison of measured and calculated congener profiles of PCDD/F toxicity in the atmosphere at the UK site Stoke Ferry averaged from 2004 to 2007 is shown in Fig. 1.9 (the list of short names of PCDD/F congeners used in the plot is given in Table 1.9 below).

***Table 1.9.*** *Short names of PCDD/F toxic congeners used in diagrams*

| | | | | | |
|---|---|---|---|---|---|
| 2,3,7,8-TCDD | TCDD | 1,2,3,4,5,6,7,8-OCDD | OCDD | 1,2,3,7,8,9-HxCDF | 19HxCDF |
| 1,2,3,7,8-PeCDD | PeCDD | 2,3,7,8-TCDF | TCDF | 2,3,4,6,7,8-HxCDF | 23HxCDF |
| 1,2,3,4,7,8-HxCDD | 4HxCDD | 1,2,3,7,8-PeCDF | 12PeCDF | 1,2,3,4,6,7,8-HpCDF | 78HpCDF |
| 1,2,3,6,7,8HxCDD | 6HxCDD | 2,3,4,7,8-PeCDF | 23PeCDF | 1,2,3,4,7,8,9-HpCDF | 89HpCDF |
| 1,2,3,7,8,9-HxCDD | 7HxCDD | 1,2,3,4,7,8-HxCDF | 14HxCDF | 1,2,3,4,5,6,7,8-OCDF | OCDF |
| 1,2,3,4,6,7,8-HpCDD | HpCDD | 1,2,3,6,7,8-HxCDF | 16HxCDF | | |

As seen from the plots, the model overestimates fractions of most of furans and underestimates the fractions of most of dioxins, but in different extent. Such differences, in particular, lead to the difference of D/F ratio (0.71 for measurements and only 0.22 for calculations at Stoke Ferry).

The underestimation of D/F ratio is even more pronounced for measurements in Canada (Great Lake district). For example for Eagle Harbor measured D/F ratio is 1.08 whereas calculated ratio is 0.26. Similar, D/F ratios for Chicago are: measured – 0.79, and calculated – 0.22. So, from this comparison it is clear that the model overestimates furans contribution to total toxicity in the Great Lakes district similar to the situation in the western part of Europe.

In addition to the comparison of fractions of individual congeners in total toxicity, it is interesting to compare measured and calculated absolute values of toxicities of particular congeners. As an example, the comparison of measured and calculated toxicities of PCDD/F congeners at the site SE14 in September 2009 is shown in Fig. 1.10. It is seen that the model underestimates toxicities of almost all PCDD/F congeners but in different extent. This, in particular, leads to underestimation of total toxicity of PCDD/F mixture at the considered site about 3.8 times. Similar situation is characteristic of all considered measurement sites. For example, the comparison of measured and calculated values of total PCDD/F toxicity (calculated as the sum of toxicities of individual congeners) in France (near Thau lagoon) for 9 months in 2007 – 2008 shows the underestimation about 5 – 6 times (Fig. 1.11). The underestimation is as much as 5 times on the average.

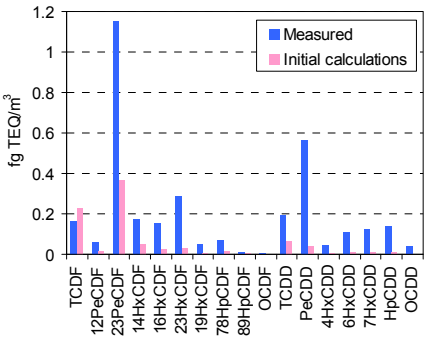



***Fig. 1.10.*** *Comparison of calculated and measured toxicities of PCDD/F congeners composition at SE14 in September 2009 (initial calculations).*

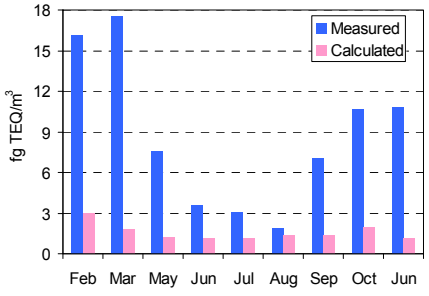



***Fig. 1.11.*** *Measured and calculated PCDD/F toxicity near Thau lagoon (France) in nine months in 2007 – 2008*

Poor coverage of Europe by PCDD/F measurement sites does not allow performing comprehensive analysis of congener composition of total toxicity in the atmosphere at various locations. Some information on spatial distribution of PCDD/F congener composition can be obtained from the analysis of measurements at Aspvreten (SE12, Sweden) [*Sellström et al.*, 2009]. These are one-day measurements for selected days in the end of 2006 and first half of 2007. They are accompanied by information on the compass sectors within which the pollutant is predominantly transported (see Fig. 1.12).

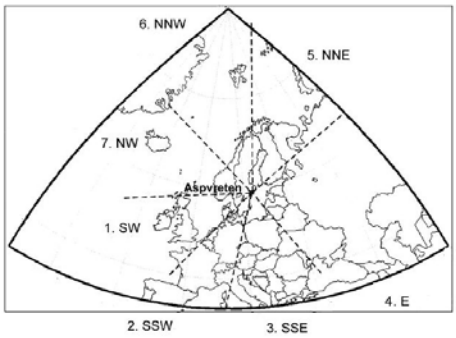



***Fig. 1.12.*** *Compass source categories used in the interpretation of SE12 measurements*

D/F ratios calculated on the basis of measurements at SE12 are 1.13 for North-north-west (NNW) sector, 1.10 for North-west (NW) sector, 0.92 for South-west (SW) sector, 0.49 for South-south-west (SSW) sector, 0.44 for North-north-east (NNE) sector, 0.33 for East (E) sector and 0.26 for South-south-east (SSE) sector. This information agrees with that obtained from measurements at other European sites discussed above.

Additional source of uncertainties in emission data is the formation of PCDD/F congeners from other pollutants due to chemical transformation in the atmosphere. In particular, heavy dioxin congeners can be formed from other air pollutants such as PCP in the course of reactions with atmospheric reactants. As said in Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases used under the Stockholm Convention "The homologue and congener profiles and patterns strongly indicate that PCP is the source of dioxin contamination". In present, there are not enough data to take this source of PCDD/F into account due to deficiency of emission and measurement data on PCP.

So, it can be concluded that:

1. Congener composition of emissions strongly depends on the structure of emissions from the viewpoint of source categories.
2. Measurements show predominance of dioxins in emissions of countries from Northern and Western Europe.
3. Congener composition of emissions used in modelling is subject to essential uncertainties and needs correction.

## *Correction of emission data*

The correction of emission data for modelling is performed with the help of inverse modelling approach using available measurement data and atmospheric concentrations at the considered sites calculated by initial model runs ("synthetic observations" in the terminology of [*Villani et al.,* 2010]). Correction of congener composition of PCDD/F emissions is carried out by multiplying emissions of each of 17 toxic congeners by *correction coefficients* depending on a congener. These coefficients are determined by minimizing root mean square error (RMSE) between measurements at all considered sites and calculation results for each particular congener under the assumptions of a small observation noise and neglecting uncertainties in atmospheric transport model. It should be mentioned that one and the same correction coefficients are used for emissions of all regions. Such rough assumption is used due to deficiency of measurement data on congener composition of total toxicity of PCDD/F mixture in various regions within the globe. Besides, both enlargement of emission totals and refined congener composition is assumed to be one and the same for the whole EMEP domain. The calculated set of correction coefficients for each of 17 toxic congeners determines also changing of total toxicity of emissions.

The result of the above described procedure is as follows. First, enlargement coefficient for total toxicity of emissions is found to be 5.4, which is in accordance to the underestimation of air concentrations by initial calculations obtained above. The difference between congener profile used in initial calculations and corrected congener profile is shown in Fig. 1.13. In the plot short names of PCDD/F congeners are used (see Table 1.9 above).

As a result of this modification, agreement between measured and calculated congener profiles at locations of the considered measurement sites is essentially refined. For example, the comparison of measured congener profiles at sites Råö (SE14, Sweden) and Hazelrigg (the UK) with calculations made with initial and corrected emission data are presented in Fig. 1.14.

The calculations show that Root Mean Square Error (RMSE) between measured and calculated congener profiles has decreased 2.6 times at SE14 and 1.5 times at Hazelrigg.

The comparison of calculation results obtained with corrected emission data with available measurements from the viewpoint of total toxicity of PCDD/F mixture will be considered in Section 3.2 below.

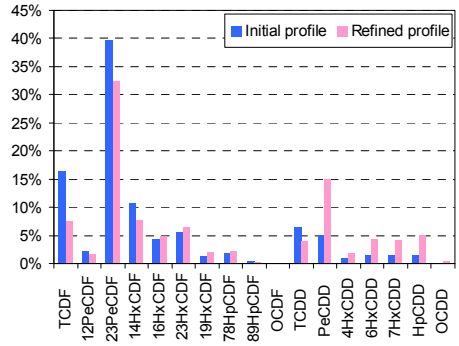



***Fig. 1.13.*** *Change in congener profile in emissions obtained in the optimization procedure based on European measurement data.*

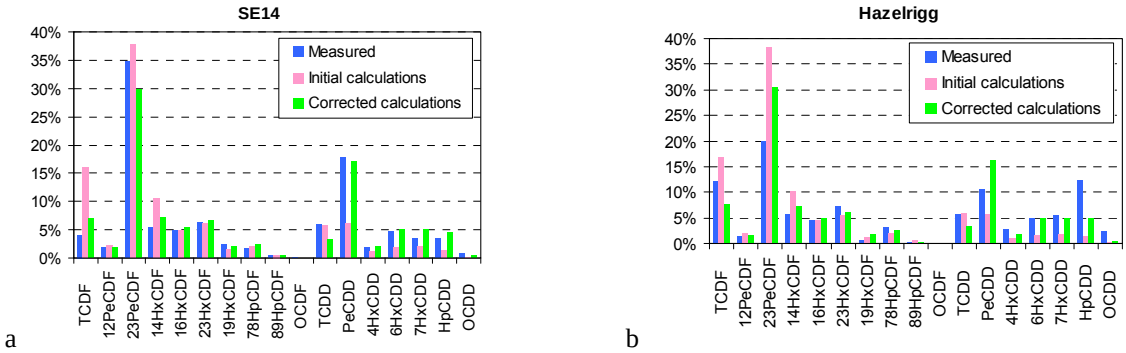



***Fig. 1.14.*** *Comparison of measured congener profiles at SE14 and Hazelrigg with initial and corrected calculations.*

## *Concluding remarks*

- Since the behaviour of different PCDD/F congeners in the environment is different due to their specific physical-chemical properties, separate model evaluation of all 17 PCDD/F toxic congeners is required for obtaining correct information on total toxicity of PCDD/F mixture.
- Congener composition of emissions in a country strongly depends on contributions of particular source categories to total emission. To further refine evaluation of environmental contamination by PCDD/Fs sector split information on emissions for particular countries is essential along with splitting of emissions by individual congeners.
- Preparation of congener-specific emission data for modelling together with corrections of total toxicity of emissions is made using inverse modelling approach based on the measurement data on congener composition collected from the literature. It has been found that for reasonable agreement between measurements and calculations of total toxicity of PCDD/F mixture in the atmosphere emission data should be enlarged about 5 times, which is in line with the estimates of emission uncertainties.

### *1.2.4. Historical HCB emissions*

Due to high persistence of HCB in the environment historical accumulation of this pollutant in main media (soil, seawater) essentially influences HCB contamination levels. So, for calculation of HCB air pollution levels historical emissions for sufficiently long period should be used.

Three scenarios of historical HCB emissions (maximum, average and minimal) are constructed earlier for modelling of long-term accumulation of the pollutant in the environmental media [*Shatalov et al,.* 2010]. Preliminary calculations made with the use of the GLEMOS system show that modelling results obtained with maximum scenario agree best of all with available measurement data. Thus, this particular scenario is used in long-term global simulations with resolution 3°×3°. In modelling it is supposed that half of emissions enter to the atmosphere and other half – in soil.

According to this scenario, global HCB emissions are increasing during the period from 1945 to 1978 reaching 18 thousand tonnes in the end of the period (Fig. 1.15). Further, in 80$^{th}$ of the previous century emissions have been reduced rapidly with subsequent moderate decrease (about 10% a year on the average) beginning from 1987. Total emissions of HCB in 2010 amount to 55.5 tonnes.

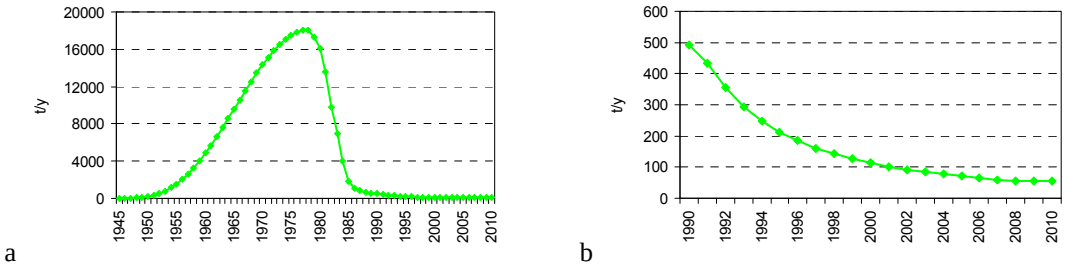



***Fig. 1.15.*** *Time trend of HCB global atmospheric emissions: 1945-2010(a), 1990-2010(b)*

During the period of active HCB use main contributors to the environmental contamination by HCB were Europe and Asia. However, the spatial pattern of contamination changed in time. Spatial distributions of emissions in 1978 (the year with maximum emissions) and in 2010 are shown in Fig. 1.16. In particular, the share of European emission sources decreased from 17% in 1978 to 12% in 2010 whereas the share of Asian sources increased fro 26% to 51% during the same period.

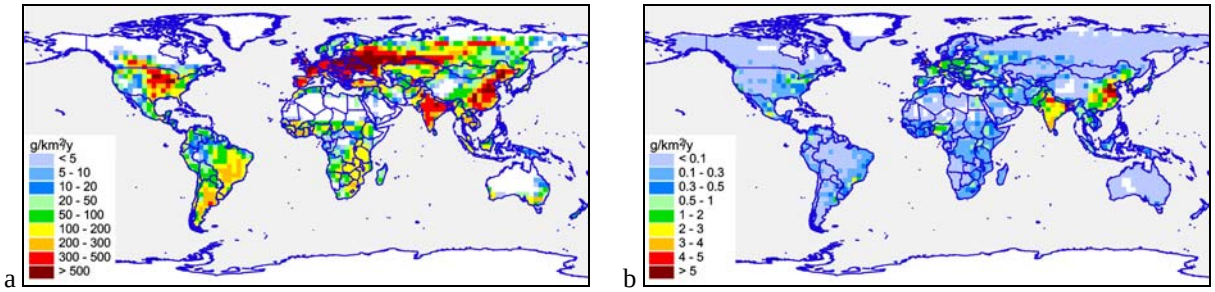



***Fig. 1.16.*** *Spatial distribution of HCB emissions in 1978 (a) and in 2010 (b) over global domain with resolution $3^0x3^0$*

### *Concluding remarks*

- According to estimates of HCB emissions its release reach maximum in the end of 70$^{th}$. Further emissions rapidly drop with subsequent moderate decrease (~10% per year) beginning from 1987.
- Spatial distribution of HCB emissions is different for different years. In particular, the share of European emissions drop from 17% in 1978 to 12% in 2010. On the opposite, share of Asian sources increased from 26% to 51% within the same period.

# 2. MONITORING OF POP POLLUTION LEVELS

## *EMEP measurements of POPs in 2010*

POPs were included in the EMEP's monitoring program in 1999. However, earlier data has been available and collected, and the EMEP database thus also includes older measurements (see http://ebas.nilu.no)). A number of countries have been reporting POPs within the EMEP area in connection with different national and international programmes such as HELCOM, AMAP and OSPARCOM. Data from the open scientific literature are also used for model validation and complements the EMEP data. Detailed information about the sites and the measurement methods used in 2010 are found in EMEP/CCC's data report on heavy metals and POPs [*Aas and Breivik,* 2012].

In 2010 there were twelve sites measuring POPs in both compartments (air and deposition), and altogether there were twenty six measurement sites reporting POPs in either air or deposition, which are three more than in 2009. Two of the new sites are in Moldova and Kazakhstan, but these are only one year campaign measurements where part of 2010 is covered. There has been an increase in EMEP sites measuring PAHs the last years because these compounds are required according to the EUs air quality directive [*EU*, 2004]. Benzo[a]pyrene (B[a]P), which is a by-product of incomplete combustion processes, is the most frequently measured POP component in EMEP. These results are therefore highlighted herein, whereas additional results for other compounds can be found in the annual data report [*Aas and Breivik*, 2012].

***Table 2.1.*** *Measurement sites and program in 2010*

| Country | Code | Name | POPs in air and aerosol | POPs in precipitation |
|---|---|---|---|---|
| Belgium | BE0014R | Koksijde | | PCBs, pesticides, HCH |
| | BE0013R | Houtem | PAHs | |
| Cyprus | CY0002R | Ayia Marina | PAHs | |
| Czech Republic | CZ0003R | Kosetice | PAHs, PCBs, pesticides, HCB, HCHs | PAHs, PCBs, pesticides, HCH |
| Denmark | DK0010G | Nord, Greenland | PAHs, pesticides, HCB, HCHs | |
| Germany | DE0001R | Westerland | PAHs, PCBs, pesticides, HCB, HCHs | PAHs, PCBs, pesticides, HCB, HCHs |
| | DE0003R | Schauinsland | PAHs | |
| | DE0008R | Schmücke | PAHs | |
| | DE0009R | Zingst | PAHs, PCBs, pesticides, HCB, HCHs | PAHs, PCBs, pesticides, HCB, HCHs |
| Spain | ES0008R | Niembro | PAHs | PAHs |
| Finland | FI0096R | Pallas | PAHs, PCBs, pesticides, HCB, HCHs | PAHs, PCBs, HCHs |
| Great Britain | GB0014R | High Muffles | PCBs | |
| Island | IS0091R | Storhofdi | PCBs, pesticides, HCB, HCHs | PCBs, pesticides, HCB, HCHs |
| Kazakhstan | KZ0001R | Borovoe | PAHs, PCBs, pesticides, HCB, HCHs | |
| Latvia | LV0010R | Rucava | PAHs | |
| Moldova | MD0013R | Leova II | PAHs, PCBs, pesticides, HCB, HCHs | |
| Netherlands | NL0009R | Kollumerwaard | PAHs | |
| | NL0091R | De Zilk | PAHs | $\gamma$-HCH |

| Country | Code | Name | POPs in air and aerosol | POPs in precipitation |
|---|---|---|---|---|
| Norway | NO0042G | Spitsbergen | PAHs, PCBs, pesticides, HCHs, HCB | |
| | NO0002R | Birkenes | | PCBs, HCB, HCHs |
| | NO0090R | Andøya | | |
| Poland | PL0005R | Diabla Gora | PAHs | PAHs |
| Sweden | SE0011R | Vavihill | PAHs | PAHs |
| | SE0012R | Aspvreten | PAHs, PCBs, pesticides, HCHs, HCB | PAHs, PCBs, HCHs |
| | SE0014R | Råö | | |
| Slovenia | SI0008R | Iskrba | PAHs | |

## *Benzo[a]pyrene (B[a]P) measurements*

The spatial pattern of the average annual concentration level of B[a]P is shown in Fig. 2.1, where air concentrations seem to decrease when moving towards more remote areas in Europe. The sites in Cyprus, Moldova and Kazakhstan are not included in the plot due to low data coverage over the whole year. Notable differences in air concentrations can be seen between some adjacent sites suggesting that some EMEP sites may be influenced by local emissions of PAHs. In general, elevated concentrations of POPs are often seen in central parts of Europe [*Aas and Breivik*, 2012; *Tørseth et al.* 2012] reflecting proximity to major emission sources in Europe [*Halse et al*, 2010; *Denier van der Gon et al*, 2005].

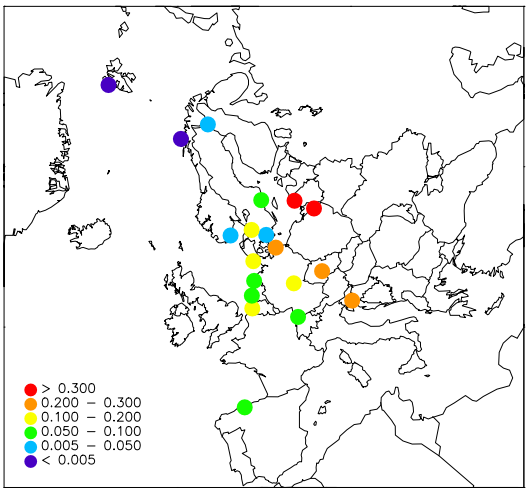



***Fig. 2.1.*** *Spatial distribution of the annual average concentrations of benzo[a]pyrene in 2010, ng/m$^3$.*

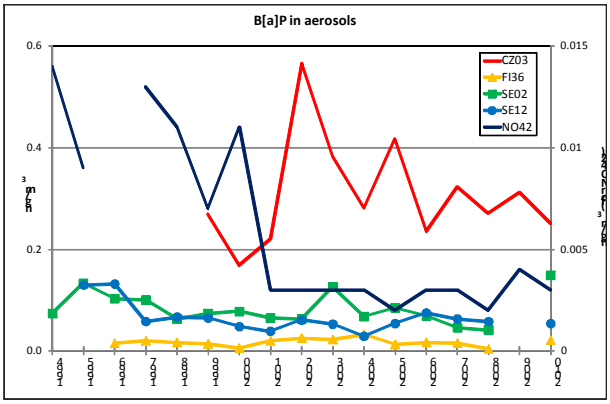



***Fig. 2.2.*** *Trends of B[a]P in aerosols and precipitation, from 1994-2010. Note different y axis for NO42.*

B[a]P has been measured in precipitation and/or aerosols since the mid nineties at five sites(Fig. 2.2). Trend analysis done for the period up to 2009 [*Tørseth et al.*, 2012] show no immediately obvious trend for this compound, except a significant decrease at Zeppelin mountain at Svalbard (NO42) for B[a]P in aerosols, and a significant decrease in total deposition of B[a]P at Rørvik in Sweden (SE02). One should note that the concentration level at Zeppelin, Svalbard is very low and the higher level in the

nineties is due to some high episodes each year causing the relative high annual average. There is quite large inter-annual variability in the observed concentration, especially in precipitation. One should note that the total deposition measurements in Sweden and Finland are not comparable to the regular precipitation measurements, but for trend analysis at the individual sites, they are suitable.

It is difficult to quantify the uncertainty in the POP measurements since it depends on several factors (methodology, sample handling and preparation etc) and the component in question. Also the analytical determination is associated with relative large uncertainties. EMEP together with the Northern Contaminants Program (NCP) in Canada, which is coordinated by the Laboratory Services Branch (LaSB) of the Ontario Ministry of the Environment (MOE), performed a common laboratory intercomparison in 2010. All the laboratories participating in EMEP, HELCOM, OSPAR or AMAP was invited to participate. This interlaboratory study aimed to assess variability in analyzing two standards (one high and one low) and one real air sample for four classes of trace organic chemicals, namely, polycyclic aromatic hydrocarbons (PAHs); polybrominated diphenyl ethers (PBDEs); polychlorinated biphenyls (PCBs); and organochlorine pesticides (OCPs). The results for B[a]P is presented in Fig. 2.3 and it is taken from *Schlabach et al.* [2011]. It is quite clear that some labs have outliers, but the general picture is quite satisfactory. When excluding the outliers, the relative standard variations are 23% for the standard solution and only 15% for the real air sample. Note that not all the laboratories shown in the figure are part of EMEP.

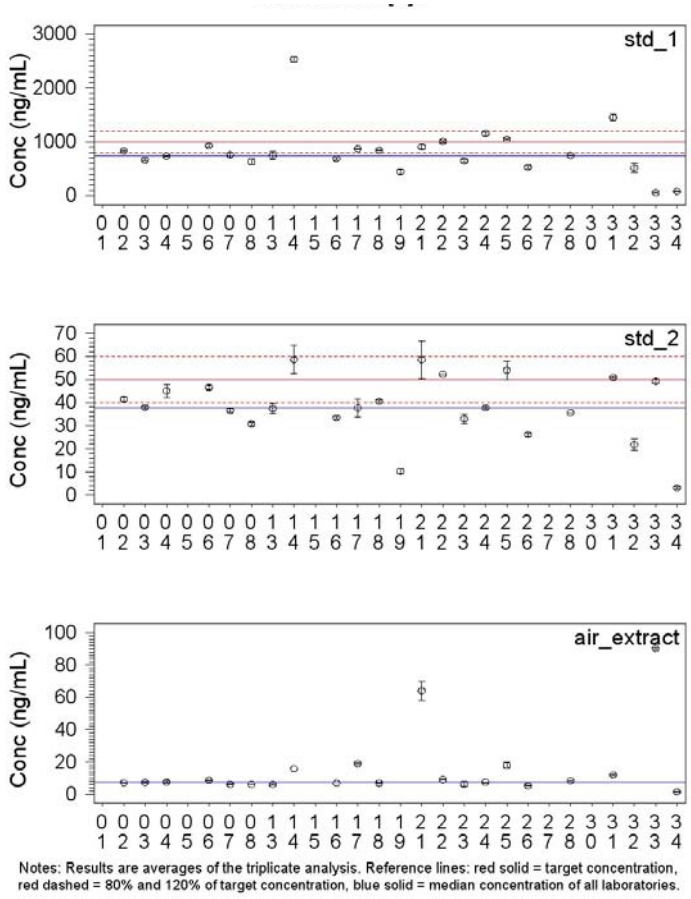



***Fig. 2.3.*** *Analytical performance of B[a]P in standard solutions and real air samples in EMEP/AMAP/NCP laboratory intercomparison [Schlabach et al, 2011]*

# 3. ASSESSMENT OF POLLUTION LEVELS AND TRANSBOUNDARY TRANSPORT OF POPs

## 3.1. Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of chemicals that occur naturally in coal, crude oil and gasoline. PAHs are also contained in products made from fossil fuels, such as coal-tar pitch, creosote and asphalt. When coal is converted to natural gas, PAHs can be released. Therefore, some former coal-gasification sites may have elevated levels of PAHs. PAHs can also be released into the air during the incomplete burning of fossil fuels and garbage. The less efficient the burning process is the more PAHs are released into environment. Forest fires and volcanoes can produce PAHs naturally.

PAHs are widely known as substances posing serious risk for the human health. The risk of PAH adverse effects for humans is intensively investigated. In particular, it is found that "Based on epidemiological data from studies in coke-oven workers, a unit risk for B[a]P as indicator air constituent for PAHs is estimated to be $8.7 \times 10^{-5}$ per ng/m$^3$, which is the same as that established by WHO in 1987. The corresponding concentrations of B[a]P producing excess lifetime cancer risks of 1/10000, 1/100000 and 1/1000000 are 1.2, 0.12 and 0.012 ng/m$^3$, respectively" [*Air quality guidelines for Europe. Second edition*, 2000].

In accordance to EU Regulation (EC) No 1907/2006 on **R**egistration, **E**valuation, **A**uthorisation and restriction of **CH**emicals (REACH), 8 PAH species (benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[b]fluoranthene, dibenz[a,h]anthracene, chrysene and benzo[e]pyrene) are considered as carcinogens of category 2; benzo[a]pyrene is considered in addition as mutagen and toxic to reproduction substance of category 2. Since 2005, benzo[a]pyrene has been included in the list of carcinogens of category 1 by the International Agency for Research on Cancer (IARC) (see Some Non-heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, vol. 92, 2010).

A lot of substances containing PAHs are listed in the REACH Legislation, Annex VII "Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles". In particular, the Annex states that "Extender oils shall not be placed on the market and used for the production of tyres or parts of tyres, if they contain:

- more than 1 mg/kg B[a]P, or
- more than 10 mg/kg of the sum of all listed PAHs.

Taking into account possible risk for human health, a number of countries have introduced target values of air quality objectives for PAHs in the ambient air. Benzo[a]pyrene is often used as a marker for the carcinogenic risk of polycyclic aromatic hydrocarbons in the ambient air (Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004).

According to this Directive, EU target value for B[a]P is established as 1 ng/m$^3$ (annual average). Here ***target value (TV)*** means "a concentration in the ambient air fixed with the aim of avoiding, preventing or reducing harmful effects on human health and the environment as a whole". Besides, upper and lower assessment thresholds (0.6 and 0.4 ng/m$^3$ respectively) are established. Here ***upper assessment threshold (UAT)*** means a level below which a combination of measurements and modelling techniques can be used to assess ambient air quality. ***Lower assessment threshold (LAT)*** is the level below which sole use of modelling or objective estimation techniques can be sufficient.

PAH contamination is of high interest worldwide. In addition to the above EU environmental levels, PAH concentrations are subject to various national legislations. For example, air quality objective in Australia is 0.3 ng/m$^3$. Russian legislation assumes the assessment of ***diurnal means*** of B[a]P concentrations instead of annual ones. B[a]P measurements are carried out in a lot of countries. In particular, the EU database (AirBase) contains measurement data for a number of years in the European Union (see, e.g. Fig. 3.1a where measured levels of B[a]P in the atmosphere in 2009 are presented).

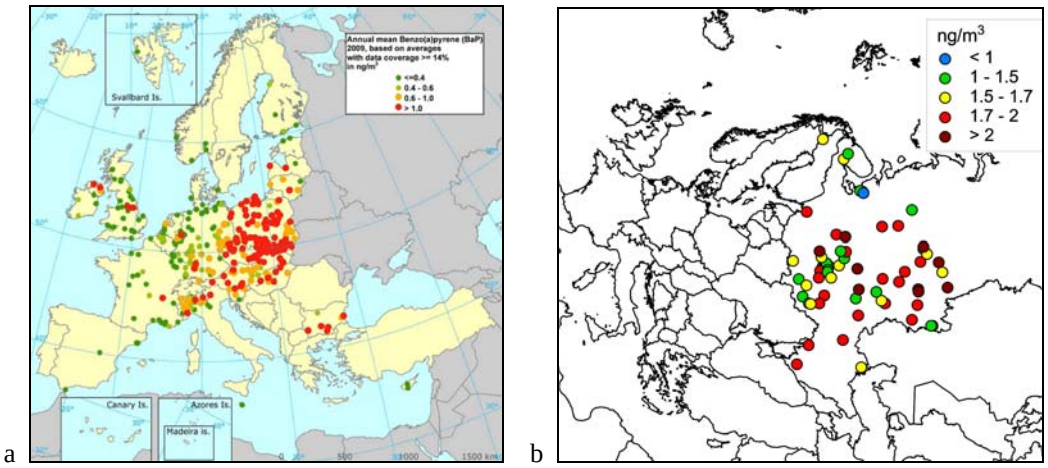



***Fig. 3.1.*** *Annual means of B[a]P concentrations in the surface air: a – measurements from AirBase database (EEA) for 2009 taken from Air Quality Europe 2009 report, b – measurements in Russian cities for 2008 – 2010.*

Measurements in the EU show that there exist a lot of areas where B[a]P concentration levels exceed target values of 1 ng/m$^3$. However, these data do not cover eastern part of the EMEP domain. For the analysis of contamination levels in these areas national measurement data can be used. For example, the data on B[a]P concentrations in Russian cities obtained by Voeikov Main Geophysical Observatory for 2008 – 2010 (http://voeikovmgo.ru) are shown in Fig. 3.1b (see e.g. [*Bezuglaya,* 2009]).

Since B[a]P is considered as a marker of carcinogenic risk of PAHs in most of world-wide legislations the investigations below are focused at this species.

### *3.1.1. Contamination in 2010*

The aim of this section is to evaluate B[a]P contamination levels in the EMEP region in 2010 and to compare them with EU standards. The evaluation of B[a]P air concentrations is made here on the basis of model calculations together with available measurement data.

***Spatial distribution.*** Basic measurement data used for the evaluation of pollution levels in the EMEP region are obtained at the EMEP monitoring network. The results of these measurements together with calculated annual means of B[a]P air concentrations in the surface layer are presented in Fig. 3.2. In addition to the EMEP measurements, data from national networks and monitoring campaigns for the assessment of B[a]P contamination in the EMEP domain are used. Calculated spatial distribution of B[a]P concentrations correlates well with measurements from the EEA AirBase database (Fig. 3.1a). Higher values of observed concentrations are conditioned by the fact that measurements have been performed not only at background sites but also at urban background, rural, traffic and industrial sites as well as by rough resolution of the model (50×50 km).

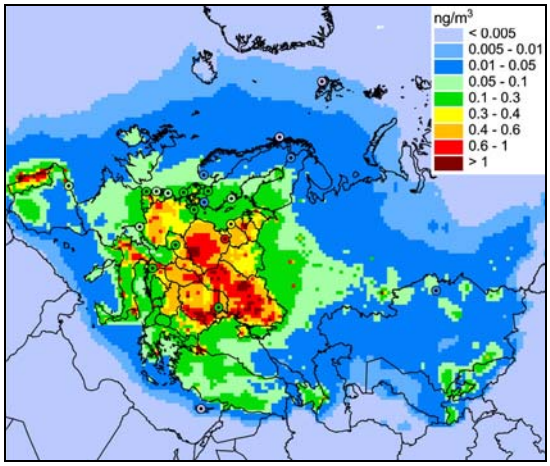



***Fig. 3.2.*** *Calculated annual means of B[a]P concentrations in surface air in 2010 together with measurements at the EMEP monitoring network.*

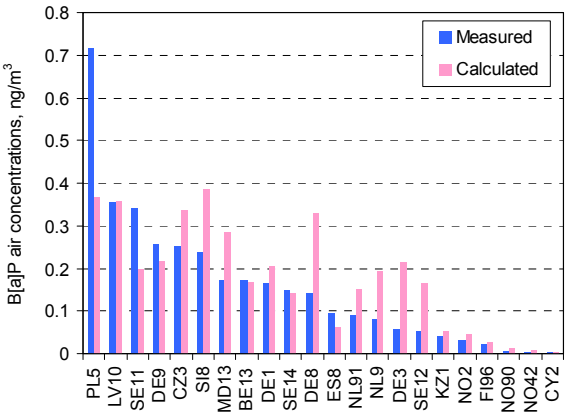



***Fig. 3.3.*** *Comparison between calculation results and measurement data at the EMEP monitoring sites (annual averages)*

In 2010 measurements of B[a]P air concentrations were performed at 19 EMEP measurement sites (BE13, CZ3, DE1, DE9, ES8, FI96, KZ1, LV10, MD13, NL9, NL91, NO2, NO42, NO90, PL5, SE11, SE12, SE14 and SI8). It should be mentioned that spatial coverage of the EMEP measurement network in 2010 has been widened. In particular, measurements of B[a]P concentration were carried out at sites KZ1 (Kazakhstan) and MD13 (the Republic of Moldova). The comparison of measurements and calculation results at the above sites is presented in Fig. 3.3.

The comparison shows that about 70% of modelled concentrations agree with measurements within a factor of 2, and correlation coefficient between modelled and measured values at the EMEP monitoring sites is 0.73. Normalized mean bias is – 0.14, which meets the threshold ± 0.2 used for the evaluation of agreement between measurements and model predictions. So, it can be concluded that measurement data and calculations are in reasonable agreement with each other showing close estimates of contamination levels.

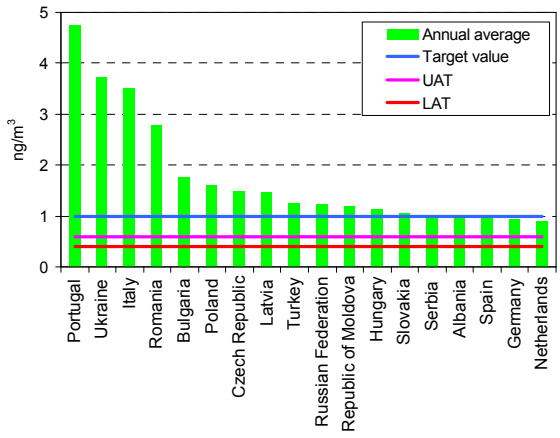



***Fig. 3.4.*** *Maximum values of B[a]P air concentrations over EMEP countries in comparison with UAT and LAT*

Let us proceed with the characterization of contamination levels in the EMEP countries. Calculated values of air concentrations averaged over particular EMEP countries are lower than the EU target value. However, strong spatial variability of annual means of air concentrations inside a country takes place (see Fig. 3.2). Fig. 3.4 shows maximum values of air concentrations within some EMEP countries obtained by calculations. It is seen that air concentrations at particular locations inside these countries can be essentially higher than country averages. The example of spatial variability of B[a]P air concentrations in the Ukraine is shown in Fig. 3.5.

In spite of the fact that average B[a]P air concentrations over the Ukraine is about 0.7 ng/m$^3$, concentration levels can exceed target value of 1 ng/m$^3$ over wide areas in the country. In particular, maximum value of air concentrations in the Ukraine is about 3.7 ng/m$^3$.

***So, for 15 EMEP countries target value is reached or exceeded at some locations***. The exceedance of UAT takes place for 26 countries that is, about 50% of all EMEP countries.

In general, it can be concluded that measurement/modelling assessment of B[a]P air concentrations shows essential exceedances over target value threshold (1 ng/m$^3$ annual average). The highest exceedances are found in Central and Eastern Europe. The analysis allows selecting "hot spots" of pollution in the EMEP region, that is, areas where air concentrations exceed target value. They are some regions of the Ukraine and Poland, southern part of Romania, western part of Portugal and northern and southern parts of Italy (see Fig. 3.6 where areas with exceedances of target value are marked red, and with exceedances of UAT – blue).

The population living within zones where B[a]P air concentrations exceed target value (see Fig. 3.6) was estimated to about 15 million people. The calculated numbers of people living in zones where UAT and LAT are exceeded are given in Table 3.1.

It should be taken into account that these values are obtained using annual averages of B[a]P air concentrations. The consideration of spatial variability of air concentrations leads to the assumption that modelling with finer spatial resolution can reveal additional areas with exceedances of B[a]P contamination levels over target value.

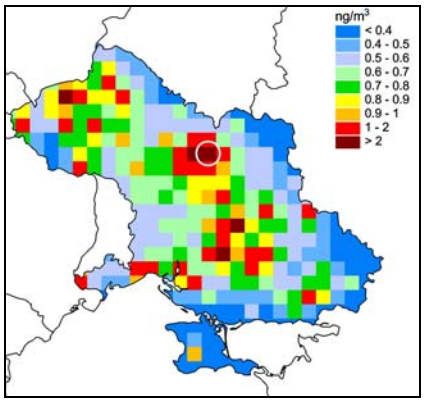



***Fig. 3.5.*** *Spatial distribution of B[a]P air concentrations in the Ukraine. The oval indicates the location with highest concentration level (3.7 ng/m$^3$).*

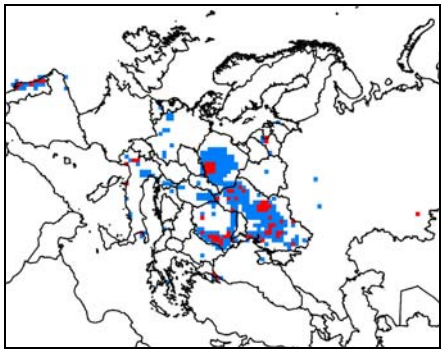


***Fig. 3.6.*** *Areas with exceeded B[a]P target value (red) and UAT (blue)*

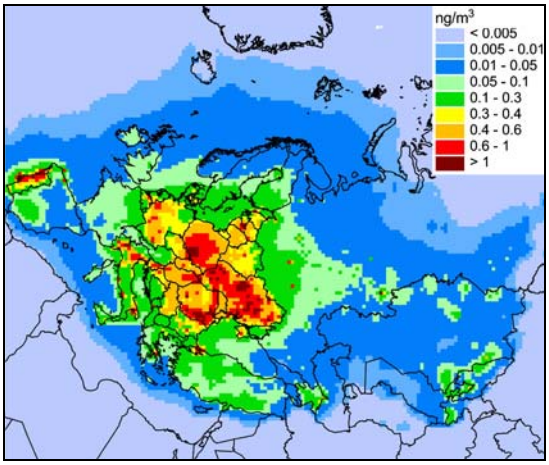
***Table 3.1.*** *Number of people living in zones with exceedances of target value, UAT and LAT (see Fig. 3.6)*

| Levels exceeded | Population |
|---|---|
| Target value (1ng/m$^3$) | 15 mln |
| UAT (0.6 ng/m$^3$) | 75 mln |
| LAT (0.4 ng/m$^3$) | 180 mln |

## *Temporal variability of contamination levels*

Temporal variability of emission leads to essential differences between B[a]P air concentrations in cold and warm seasons. In particular, the comparison of annual averages of air concentrations in the surface atmospheric layer with those in February is shown in Figs. 3.7a and b.

a




b

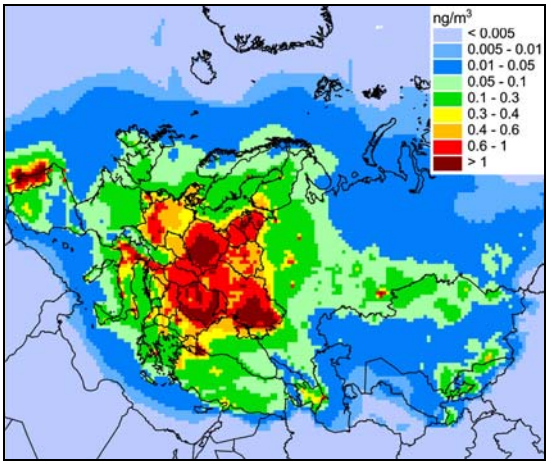
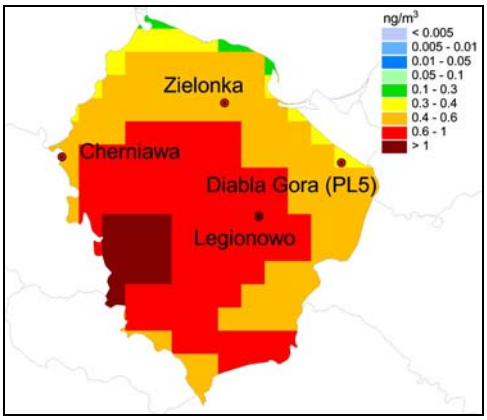



***Fig. 3.7.*** *Calculated B[a]P concentrations in the surface air for 2010: a – annual means, b – means over February.*



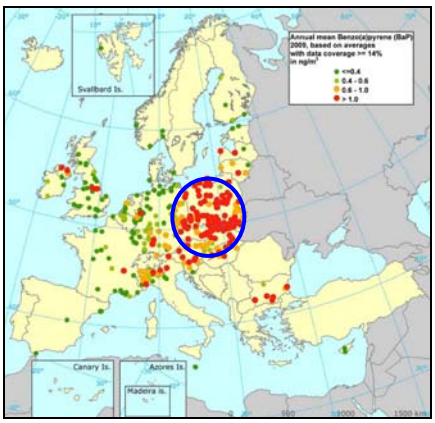



***Fig. 3.8.*** *European area with high B[a]P air concentrations (marked by blue oval), ng/m$^3$.*

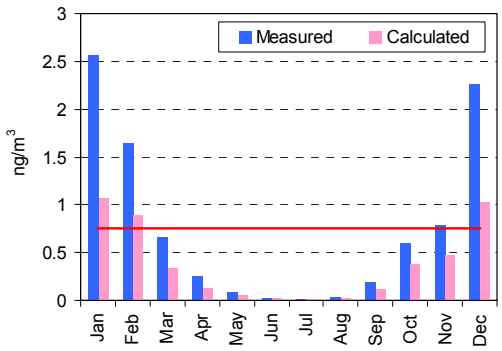



***Fig. 3.9.*** *Calculated and measured monthly means of B[a]P concentrations in the surface air at PL5. Red line shows annual average.*

The location of high concentration area in February is similar to that of annual means but absolute values of air concentrations are essentially higher. In particular, the area where air concentrations exceed EU target value (1 ng/m$^3$) is much wider for concentrations averaged over February in comparison with annual means of air concentrations. Since the degradation of B[a]P is slower in cold period, seasonal variations of air concentrations can affect annual averages in noticeable extent.

Temporal variations of B[a]P air concentrations are analysed in the area with maximum exceedances of EU target value (marked by blue oval in Fig. 3.8). There is one EMEP monitoring site Diabla Gora (PL5, rural background) in this region (see Fig. 3.8). For the comparison annual average of air concentrations at this site is shown by red line (Fig 3.9).

The comparison of seasonal variations of raw measurements and calculation results with ambient temperature at this site is displayed in Fig. 3.10. It is seen that underestimation of B[a]P air concentrations by the model takes place mainly in cold months (from January to March and from November to December).

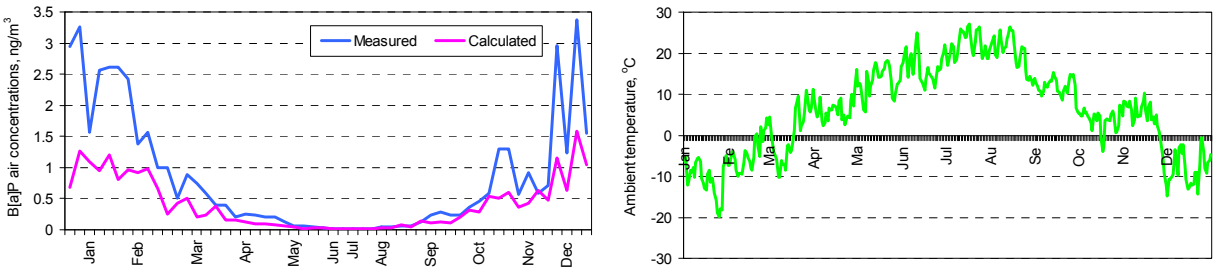



***Fig. 3.10.*** *Calculated and measured B[a]P concentrations in the surface air at PL5, in comparison with ambient temperature.*

Evidently, underestimation of air concentrations at the considered site occurs in the periods with low temperatures. In periods with high temperatures both model results and measurements show strong decrease of contamination levels. This is conditioned by combined influence of seasonal variations of emissions and more intensive degradation process.

For additional information measurements from three sites from EEA AirBase are included into consideration. They are: Cherniawa (rural), Zielonka (rural background) and Legionowo (suburban background), see Fig. 3.8. At the sites Cherniawa and Zielonka situation similar to that at PL5 take place (see Fig. 3.11, where annual averages of measured concentrations are shown at the plots by red lines). Concentration levels found at these two sites are close to those obtained at PL5. Annual average at the site Cherniawa is underestimated since measurements for November and December are not available.

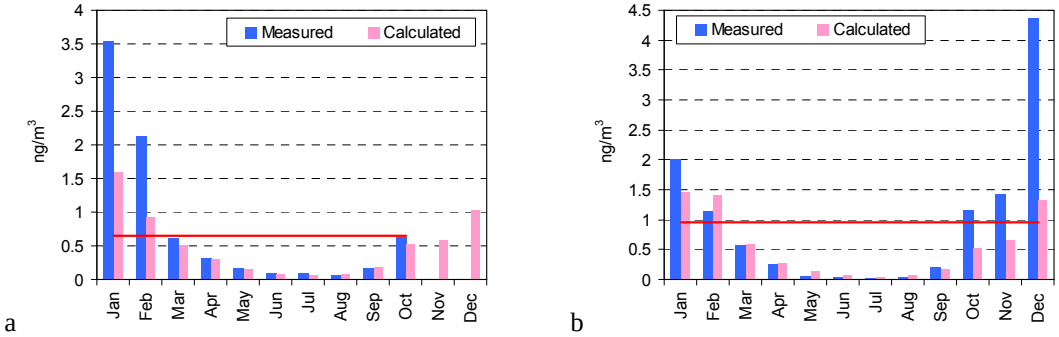



***Fig. 3.11.*** *Calculated and measured monthly means of B[a]P concentrations in the surface air at Cherniawa (a) and Zielonka (b). Annual averages of measured values are shown by red lines.*

At these sites the agreement of calculated and measured values of air concentrations is out of factor 2 in January and February at Cherniawa and for October, November and December at Zielonka. Similar to PL5, the underestimation of air concentrations by the model takes place at low ambient temperatures.

Suburban background site Legionowo (Fig. 3.12) is characterized by essentially higher levels of contamination (up to 17 ng/m$^3$ in January with annual average 5.2 ng/m$^3$) in comparison with the above considered three sites. The model shows

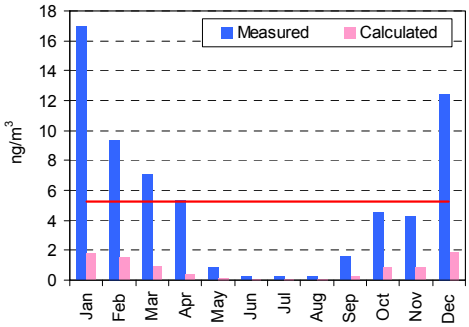



***Fig. 3.12.*** *Calculated and measured monthly means of B[a]P concentrations in surface air at Legionowo (suburban background)*

essentially lower values of concentrations comparable with those obtained at three above sites (with annual average 0.72 ng/m$^3$, see Fig.3.8). The reason of this can be underestimation of spatial variations of B[a]P concentration levels by the model with 50×50 km cells which leads to smoothing of concentrations. Modelling with higher spatial resolution inside a country complemented by the analysis with the help of inverse modelling can give more correct description of pollution levels.

Thus, several areas with exceedances of the EU target values were determined by model simulations. Total population in these areas is estimated as about 15 million people. This estimate is a lower one; for further refinement of determination of "hot spots" modelling with finer spatial resolution is needed. It should be also taken into account that for evaluation of B[a]P contamination in the EMEP region both spatial and temporal variability should be taken into account.

### *3.1.2. Long-term trends of pollution*

This section is devoted to the consideration of long-term trends in B[a]P pollution of the EMEP countries. The evaluation of pollution levels during the period from 1990 to 2010 is made on the basis of integrated use of measurement data and model estimates.

Within the EMEP measurement network there are four such sites measuring B[a]P from 1996 to 2010. They are CZ3 (Košetice), FI96 (Pallas), NO42 (Zeppelin) and SE12 (Aspvreten). Long-term variations of measured and calculated B[a]P concentrations in the ambient air at some of these sites are presented in plots in Fig. 3.13.

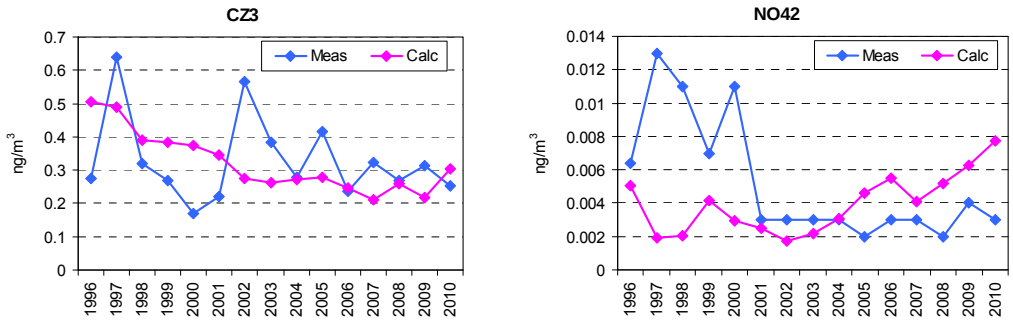



***Fig. 3.13.*** *Comparison of measured and calculated B[a]P air concentrations at CZ3 and NO42.* ***Scales are different!***

Considered sites are located in different parts of Europe and are characterized by quite different levels of contamination. The site CZ3 is located in Central Europe. Measured annual mean air concentrations of B[a]P here range from 0.15 to 0.65 ng/m$^3$. Concentration levels at the site NO42, located in remote region, are essentially lower with concentration range from 0.003 to 0.015 ng/m$^3$. For both sites the model reproduces reasonably concentration levels of B[a]P. More smooth character of time dependence of calculated concentrations can be explained by averaging of calculated concentrations over 50×50 km grid cells. The disagreement between measurements and calculations in the beginning of the considered period (1996-2000) can be conditioned by uncertainties of emission data. Quite another situation takes place at the site SE12 (Fig. 3.14). Here model results occur to be essentially higher than measurements. The difference between calculated and measured air concentrations can be conditioned by peculiarities of the site location. For better agreement the modelling with finer spatial resolution is required

Model calculations allow evaluating average reduction of B[a]P contamination in the whole EMEP domain. The trend of emissions in comparison with the trend of air concentrations is shown in Fig. 3.15, where relative reductions of air concentrations and emissions with respect to 1990 are shown.

Calculations show that emission reduction in the EMEP region as a whole is about 30%, and the reduction of air concentrations is the same on the average. However, this reduction is spatially inhomogeneous. Contamination decrease in different countries is quite different, and for some countries increase of air concentrations takes place. For example, in the UK and Germany contamination by B[a]P has been reduced more than 4 times since 1990. On the opposite, in ten EMEP countries contamination either has not been changed since 1990 or even become higher.

To demonstrate long-term trends of contamination in particular countries, two countries with different changes of emission are chosen, namely, France and Denmark. It should be stressed that emissions of these countries are based on the data officially submitted by countries to CEIP.

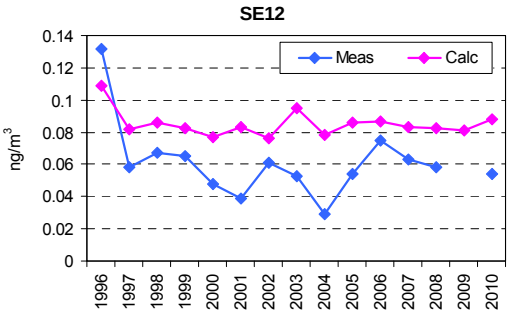



***Fig. 3.14.*** *Comparison of measured and calculated B[a]P air concentrations at SE12.*

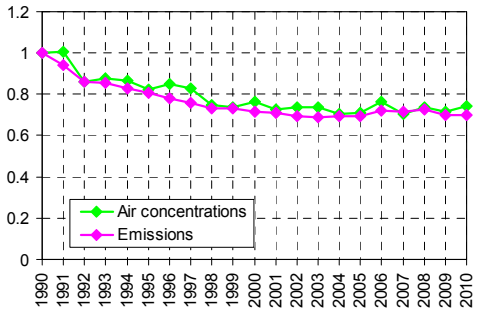
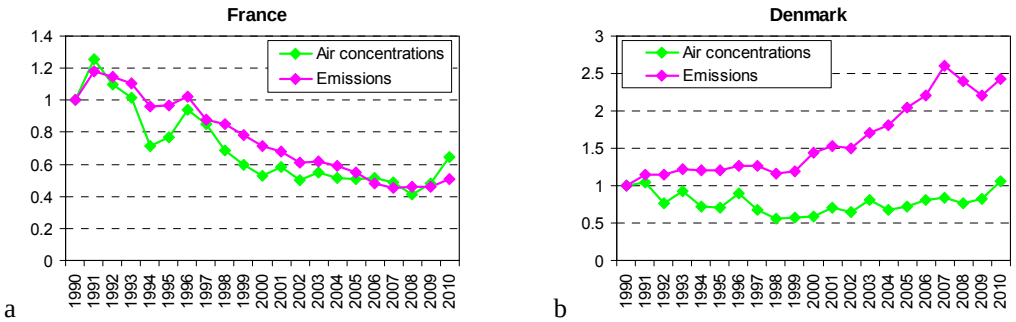



***Fig. 3.15.*** *Relative reductions of B[a]P emissions in comparison with that of average concentrations in the EMEP domain with respect to 1990.*

Strong emission reduction is characteristic of France accounting for 2.2 times during the whole period (see Fig. 3.16a where relative values in comparison with 1990 are shown). The reductions of air concentrations are slightly lower (about 2.1 times). The difference of reduction rates of emissions and air concentrations is conditioned by transboundary transport. Small difference in these rates shows that the reductions of air concentrations in France are governed mainly by the reductions of national emissions.




a b

***Fig. 3.16.*** *Relative reductions of B[a]P emissions in comparison with that of average concentrations with respect to 1990 for France (a) and Denmark (b).*

On the opposite, emissions in Denmark (Fig. 3.16b) are increasing by about 2.5 times within the considered period. At the same time air concentrations in the country are approximately at one and the same level during the whole period due to the reduction of emissions in neighbouring EMEP countries.

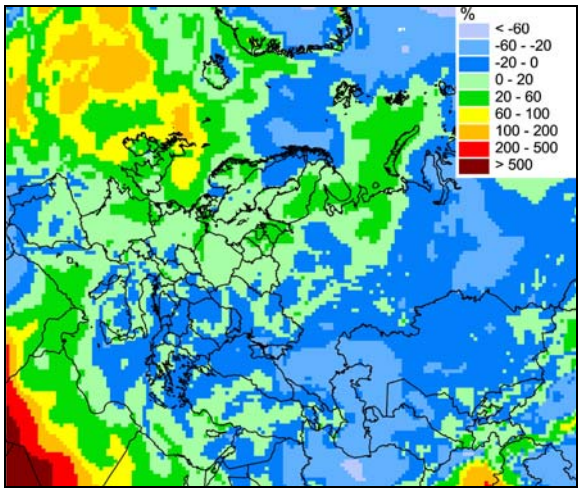



***Fig. 3.17.*** *Relative differences between B[a]P air concentrations calculated with meteorological data for 2009 and 2010 with one and the same emissions.*

It should be stressed that year-to-year variations of pollution due to meteorological variability should be taken into account in the consideration of long-term trends of pollution. These variations may cause random differences from the pollution trend. As an example, the difference between spatial distributions of pollution with one and the same emission data but with different meteorological data of 2009 and 2010 are shown in Fig. 3.17.

It can be seen that the variations in B[a]P concentrations due to meteorological variability in the EMEP domain are typically about 20% - 30%. More detailed analysis of the influence of meteorological variations on POP concentration levels is presented in Section 4.1 aimed at the investigation of the influence of meteorology on POP pollution.

### *3.1.3. Transboundary transport*

This section is devoted to model evaluation of source-receptor relationships within the EMEP region. Traditionally, source-receptor matrices are calculated for deposition originated from sources of particular EMEP countries. Calculated deposition to the EMEP domain due to emission sources of each country in 2010 is presented in Fig. 3.18.

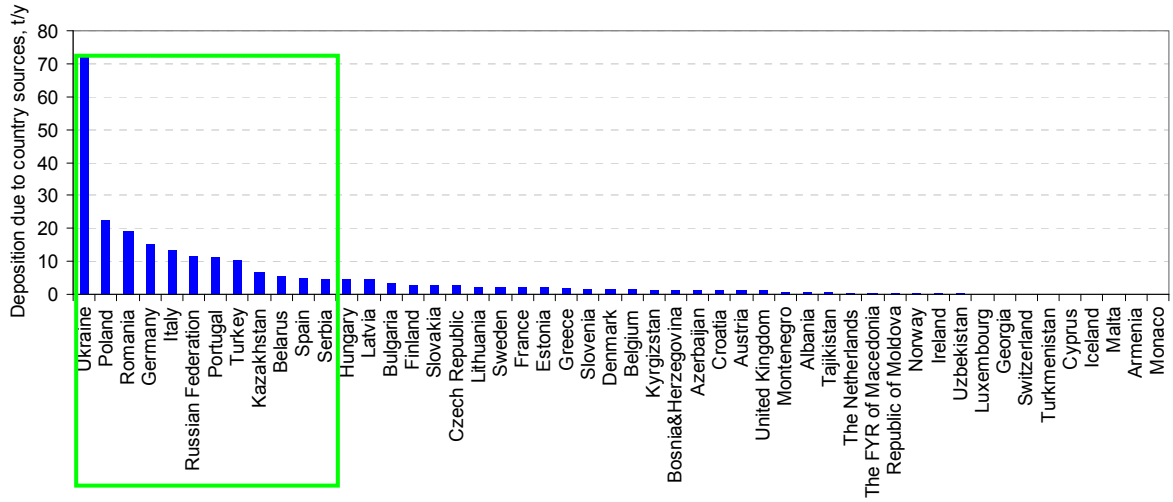



***Fig. 3.18.*** *Deposition from sources of particular EMEP countries to the aggregated area of all EMEP countries in 2010. The countries contributing by 80% of total deposition are marked by the green rectangle.*

The analysis of calculation results shows that deposition to the whole EMEP region are originated mostly from few countries. Particularly, 12 countries are responsible for 80% of total value of deposition (marked by green rectangle on the plot). It should be mentioned that the contributions of country emissions to total deposition over the aggregated area of the EMEP countries differ from their contributions to total emissions in the domain. The differences are determined by locations of the EMEP countries and meteorological conditions. In particular, contributions to deposition are less than

contributions to emissions for Italy, Portugal, Turkey, Kazakhstan and Spain. For all these countries noticeable part of emissions is transported outside the areas of the EMEP countries. For example, the pollutant emitted from sources of Italy is deposited partly to the marine areas (Fig. 3.19a) whereas all deposition from Czech sources occur at the area of the EMEP countries (Fig. 3.19b). The pollutant emitted in Turkey and Kazakhstan is transported partly outside the EMEP region due to west-east prevailing transport.

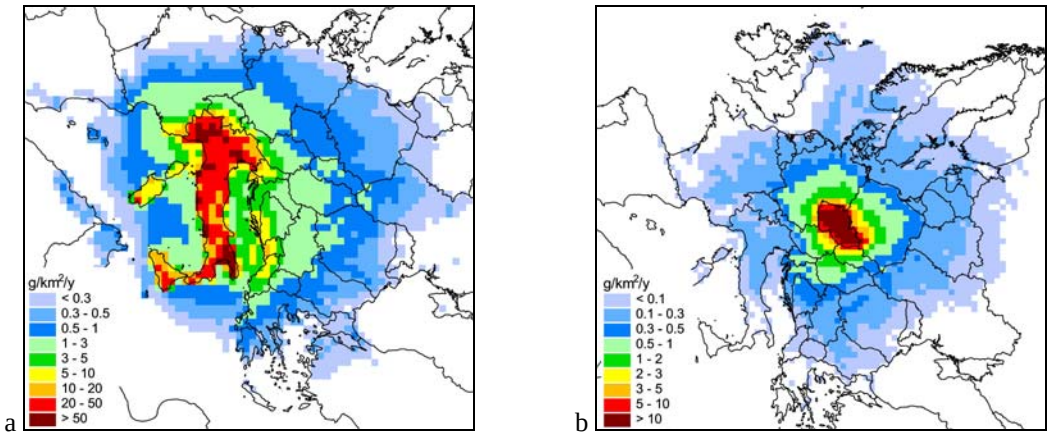



***Fig. 3.19.*** *Deposition flux originated from Italian (a) and Czech (b) sources.*

More detailed analysis allows describing the area affected by deposition originated by a particular country. For example, deposition from Ukrainian emission sources mainly takes place over the own area of the country (about 70%), over the Russian Federation (about 10%), and over areas of Romania, Belarus and Poland (3% to each country). The deposition from Ukrainian sources to the areas of all the rest countries altogether amounts only to 9%, see Fig. 3.20.


***Fig. 3.20.*** *Distribution of deposition from Ukrainian emission sources between other EMEP countries in 2010.*

Further, calculations allow selecting main countries for which deposition to their areas are determined by sources of other countries. The fractions of deposition of the other EMEP countries to the area of the considered country (import) are presented in Fig. 3.21.

It is seen that for 6 countries deposition to their own areas are determined by 80% and more by external sources (transboundary transport). The contributions of transboundary transport exceed 60% for 23 EMEP countries.

Calculations of source-receptor relationships allow obtaining more detailed information on countries mainly contributing to deposition to the area of a particular country. This is exemplified by two countries (Switzerland and Norway) with high contributions of transboundary transport (Fig. 3.22).

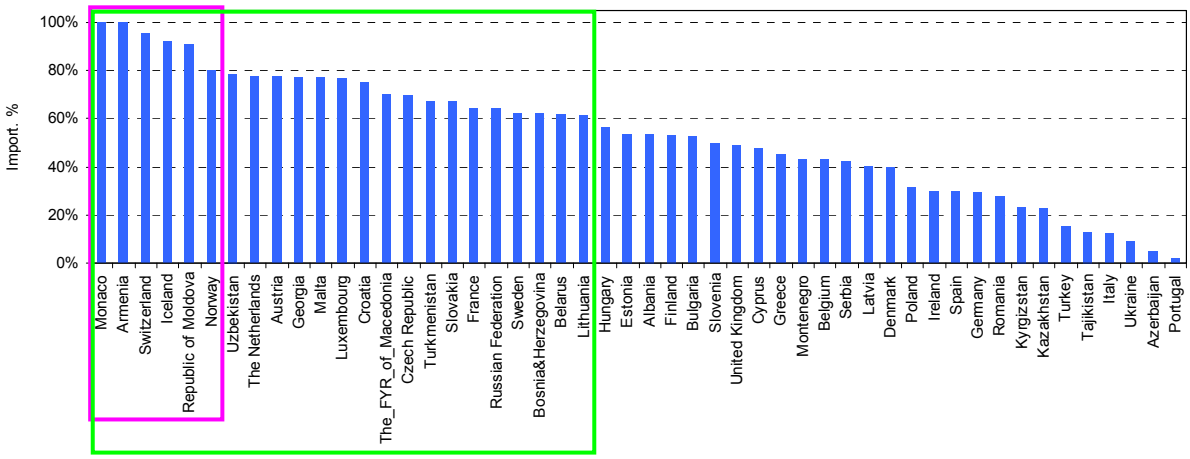



***Fig. 3.21.*** *Fractions of deposition to the area of a given country originated from sources of other countries (import). Red – import ≥ 80%, green – import ≥ 60%.*

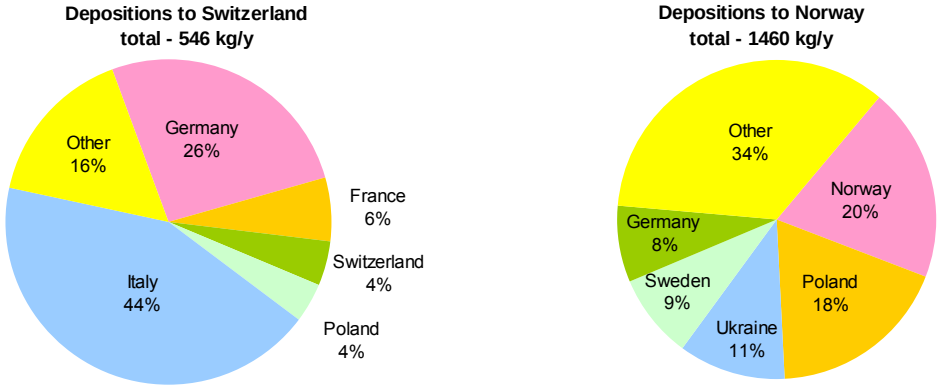



***Fig. 3.22.*** *Fractions of transboundary transport in total deposition to the area of a given country in 2010.*

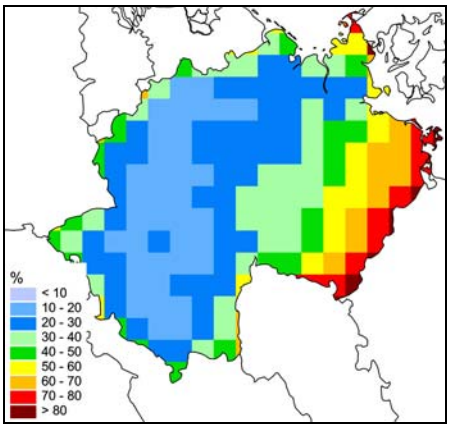



***Fig. 3.23.*** *Spatial distribution of fractions of transboundary transport in total deposition to Germany.*

For Switzerland, the fraction of deposition originated from own sources is only 4% of total deposition to the country. The rest part of deposition is originated from Italy (44%), Germany (26%), France (6%), Poland (4%) and other countries (16%). For Norway main external contributors to deposition over the country's area are Poland (18%), the Ukraine (11%), Sweden (9%), Germany (8%) and other countries (34% altogether).

It should be stressed that contributions of transboundary transport in a country are subject to strong spatial variations. For example, average contribution of transboundary transport to deposition flux to Germany is 30%, though in some regions this contribution can be 90% and more (Fig. 3.23).

The examination of changes in source-receptor relationships for the period from 1990 to 2010 is planned to be performed in the next year.

## *Further development*

For further improvement of the assessment of pollution by PAHs in the EMEP domain the following activities are planned:

- Simulation of PAH transport and deposition in selected regions with the use of modelling with finer spatial resolution.
- The analysis of changes in source-receptor relationships in the EMEP region for the period from 1990 to 2010.
- Working out the modelling tools for the analysis of disagreements between measurements and model predictions on the basis of application of inverse modelling approach (adjoint models).

## *Concluding remarks*

The above investigation shows that:

- Environmental contamination by PAHs is a subject of a lot of national and international legislations. In most cases B[a]P is viewed as an indicator of PAH contamination. In particular, target value for B[a]P of 1 ng/m$^3$ (annual average) is established in the EU. Besides, admissible B[a]P levels are established in a lot of national legislations in Europe, the US and Canada.
- The analysis of contamination in 2010, performed on the basis of combined use of modelling and monitoring information, shows several areas with essential exceedances of B[a]P concentrations over EU target value, which are populated by at least 15 million people.
- Temporal variability of B[a]P emissions is essential for the assessment of B[a]P contamination. As a result of emission variability together with seasonal variations of environmental processes (degradation, gas/particle partitioning, wet deposition, gas exchange with underlying surface, etc.), winter concentrations of B[a]P can exceed annual averages several times.
- Spatial variations of air concentrations can be even more valuable. According to measurement data, the differences of B[a]P air concentrations between neighbouring areas of different character (from urban to background) can reach an order of magnitude. Further evaluation of contamination in heavy polluted regions by modelling with finer spatial resolution can improve evaluation of pollution levels.
- The analysis of temporal trends of B[a]P contamination in the EMEP region for the period from 1990 to 2010 shows overall reduction of air concentrations by about 30%. However, this reduction is not homogeneous among the EMEP countries. For countries with large area and strong national emissions air concentrations are reduced mainly due to reduction of national emissions. For small countries with low emission intensity the reduction of air concentrations is determined by emission changes in neighbouring countries due to transboundary transport. In particular, strong decrease of air concentrations (more than 75% that is, about 4 times) is characteristic of two countries, namely, the UK and Germany. Reduction by 75% – 50% (2 – 4 times) takes place in 8 countries. In 10 countries air concentrations either have not been changed since 1990 or even became higher.
- Transboundary transport plays considerable role in contamination of the EMEP region by PAHs. In particular, 12 countries are responsible for 80% of total value of deposition of B[a]P to the combined area of all EMEP countries. Further, the contributions of transboundary transport to deposition exceed 60% for 23 EMEP countries. It should be noted that even for countries with low average value of the contributions of transboundary transport, locally these contributions may be essential.

## 3.2. Polychlorinated Dibenzo(p)dioxins and Dibenzofurans (PCDD/Fs)

This section is devoted to evaluation of environmental pollution by dibenzo(p)dioxins and dibenzofurans (referred below as PCDD/Fs) in 2010. The results of evaluation are presented in the form of total toxicity of PCDD/F mixture. Since the behaviour of particular congeners in the environment is different due to differences in their physical-chemical properties, for evaluation of total toxicity of PCDD/F mixture simulation of long-range transport for each of 17 toxic congeners have been carried out. Total toxicity of PCDD/Fs is determined as a sum of those of 17 toxic congeners.

For such simulations emission data for each of 17 toxic congeners is used. The procedure of evaluation of congener-specific data is described above in Section 1.2.3. It is important to note that this procedure leads not only to recalculating relative contributions of individual congeners to the total toxicity but also to the enlargement of total toxicity of emissions approximately 5 times, which is in line with estimates of uncertainties of PCDD/F toxicity made by countries. Emission uncertainties may occur due to incompleteness of emissions, missing source categories, underestimation of uncontrolled emissions, emissions from natural sources, etc.

To take into account contributions of distant emission sources (those located outside the EMEP region) and the influence of long-term accumulation of PCDD/Fs in the environmental media with subsequent re-emissions[1] (secondary sources), preliminary calculations with the help of hemispheric modelling for the period from 1970 to 2010 are performed for each of 17 toxic PCDD/F congeners. On the basis of these calculations boundary and initial conditions for the evaluation of PCDD/F toxicity in 2010 at regional level are generated.

Below spatial distribution of the contamination by PCDD/F including the information on source-receptor relationships is presented and the comparison of calculated values with measurements from national monitoring sites and campaigns is given. The comparison is hampered to some extent by the absence of measurement data on PCDD/Fs within the EMEP measurement network.

### *3.2.1. Spatial distribution of PCDD/F contamination*

This section is aimed at evaluation of PCDD/F contamination in the EMEP region for 2010. Model simulations are carried out for each of 17 toxic PCDD/F congeners using the prepared congener-specific emission data and generated boundary and initial conditions. Total toxicity of PCDD/F mixture is evaluated as a sum of toxicities of all toxic congeners. Calculated spatial distribution of total toxicity of PCDD/Fs in the EMEP domain is presented in Fig. 3.24.

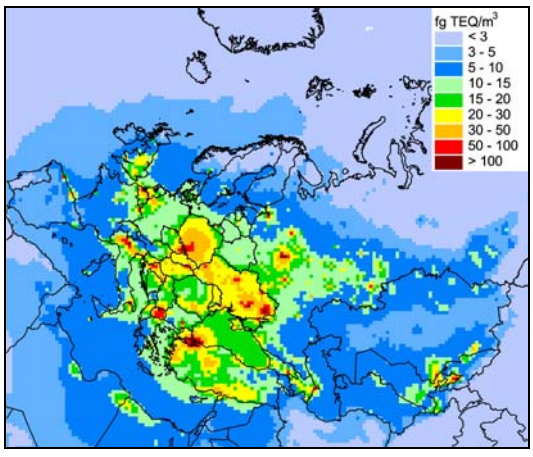



***Fig. 3.24.*** *Spatial distribution of PCDD/F total toxicity in Europe in 2010, fg TEQ/m$^3$*

According to the calculations, relatively high levels of PCDD/F air concentrations (20 fg TEQ/m$^3$ and higher) are characteristic of some regions in Central and Eastern Europe (Hungary, Poland, Slovakia, the Ukraine and parts of the Czech Republic and Turkey).

[1] For the evaluation of re-emission net flux between the atmosphere and underlying surface is split into two components: flux from the atmosphere to the underlying surface (direct gaseous deposition) and flux fro the underlying surface to the atmosphere (re-emissions). Thus, net flux is calculated as superposition of these two components.

In remote regions of Europe (the Scandinavian Peninsula and northern part of the UK) PCDD/F levels are considerably lower (5 fg TEQ/$m^3$ and lower).

Since measurements of PCDD/Fs are not included in the regular EMEP measurement program, MSC-E has performed literature search of available measurement data from national and international projects and campaigns. More than 750 measurements made in various years and at various locations within the Northern Hemisphere have been found. The summary of these measurements is given in Table 3.2.

***Table 3.2.*** *Measurement data on PCDD/Fs found in literature.*

| Country | Years | Station type | Number of measurements | Including congener profile | Value range (fg TEQ/$m^3$) |
|---|---|---|---|---|---|
| Italy | 1990 – 2005 | Contaminated | 14 | 10 | 13 – 480 |
| | | Clean | 9 | 9 | 1.48 – 54 |
| Greece | 1999 – 2006 | Contaminated | 12 | 1 | 4 – 482 |
| | | Clean | 2 | 1 | 2 – 178 |
| Portugal | 1999 – 2004 | Contaminated | 10 | – | 2 – 816 |
| | | Clean | 5 | – | 1.7 – 59.6 |
| Spain | 1994 – 2008 | Contaminated | 57 | 23 | 5 – 1196 |
| | | Clean | 3 | 1 | 5 – 45 |
| Austria | 1992 – 2000 | Contaminated | 24 | – | 1.3 – 587 |
| | | Clean | 1 | – | 10.8 – 110 |
| Belgium | 1992 | Contaminated | 4 | – | 59 – 296 |
| | | Clean | 4 | – | 53 – 197 |
| Germany | 1990 – 1996 | Contaminated | 56 | – | 3 – 1600 |
| | | Clean | 3 | – | 3.3 – 88 |
| Luxembourg | 1992 – 1994 | Contaminated | 2 | – | 54 – 77 |
| | | Clean | 2 | – | 30 – 64 |
| Netherlands | 1989 – 1993 | Contaminated | 4 | – | 10 – 150 |
| | | Clean | 2 | – | 9 – 63 |
| Slovakia | 1996 – 1997 | Contaminated | 1 | – | 50 – 130 |
| | | Clean | 1 | – | 40 – 70 |
| Sweden | 1986 – 2009 | Contaminated | 12 | – | 0.16 – 29 |
| | | Clean | 10 | 8 | 0.08 – 55 |
| Poland | 1995 – 2002 | Contaminated | 14 | 9 | 39 – 12000 |
| | | Clean | 3 | 3 | 71 – 3200 |
| France | 2005 – 2008 | Clean | 20 | 20 | 2 – 135 |
| Denmark | 2002 – 2005 | Contaminated | 22 | – | 3 – 57 |
| | | Clean | 56 | – | 3 – 180 |
| United Kingdom | 1997 – 2009 | Contaminated | 75 | 75 | 2 – 168 |
| | | Clean | 127 | 91 | 0.1 – 320 |
| China | 1997 – 2010 | Contaminated | 148 | 64 | 17 – 3030 |
| | | Clean | 7 | – | 3 – 247 |
| Japan | 1992 – 2007 | Contaminated | 30 | – | 4 – 1700 |
| USA | 1987 – 2007 | Contaminated | 8 | – | 15 – 2200 |
| | | Clean | 15 | 8 | 2 – 60 |

About 65% of available measurements are made in contaminated regions, and the rest 35% – in relatively clean regions. Here rural and background regions are viewed as clean, and regions from urban and industrial to suburban – as contaminated. Essential amount of measurements made in clean regions (over 100 individual measurements) are reported together with congener composition of total PCDD/F mixture. In particular, such data (not reported to EMEP) are available at two EMEP sites (SE12 and SE14) for particular periods.

Measurement data indicate PCDD/F levels in the EMEP domain similar to calculated ones. Below examples of the comparison between calculation results and the above measurement data are presented; more detailed information can be found in the EMEP/MSC-E Technical Report [*Shatalov et al.*, 2012]. It should be taken into account that measurements used for the comparison were carried out for different years and with different averaging period (monthly, quarterly or annual).

The comparison of measurements made in France near Thau lagoon for 9 months in 2007 – 2008 with model calculations for these months is presented in Fig. 3.25.

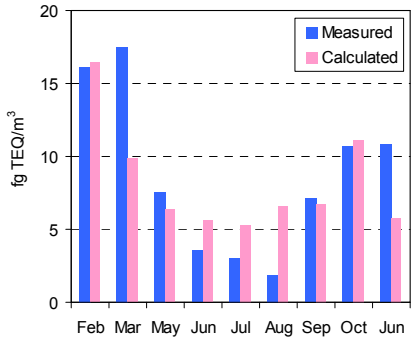



***Fig. 3.25.*** *Comparison of calculated PCDD/F air concentrations in surface atmospheric layer with measurements made in France near Thau lagoon in 2007 – 2008.*

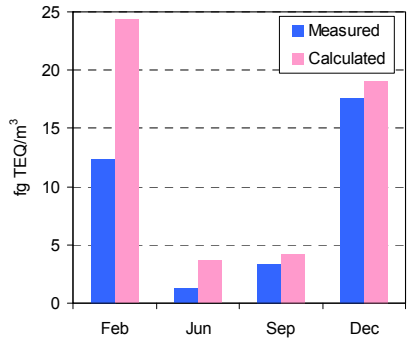



***Fig. 3.26.*** *Comparison of calculated PCDD/F air concentrations in surface atmospheric layer in 2009 with*

It can be seen that the model provides results close to measurements at this location (only in one case the agreement is out of the factor of 2). However, in summer months some overestimation of air concentrations takes place. It can be conditioned by rough reflection of seasonal emission variations used in the model.

The comparison of calculated concentrations with measurements at Swedish site SE14 in 2009 is presented in Fig. 3.26. It can be seen that reasonable agreement takes place at this site. It should be mentioned that though the site SE14 is included into the EMEP monitoring network, measurements on PCDD/Fs are not reported to the CCC and cannot be viewed as EMEP data.

Further, the calculated values of PCDD/F toxicity are compared also with quarterly measurements at five UK sites (London, Manchester, Middlesbrough, Stoke Ferry and Hazelrigg) averaged over years 2006 – 2008. At these sites about 65% of measurements agree with model predictions within a factor of 3, among them over 50% agree within a factor of 2. The examples of the comparison between monitoring data and model results for three sites (Manchester, Middlesbrough and Hazelrigg) are presented in Fig. 3.27. Since the data of these sites for some quarters and some congeners are below the detection limit, it is reasonable to compare annual averages of PCDD/F air concentrations at these sites.

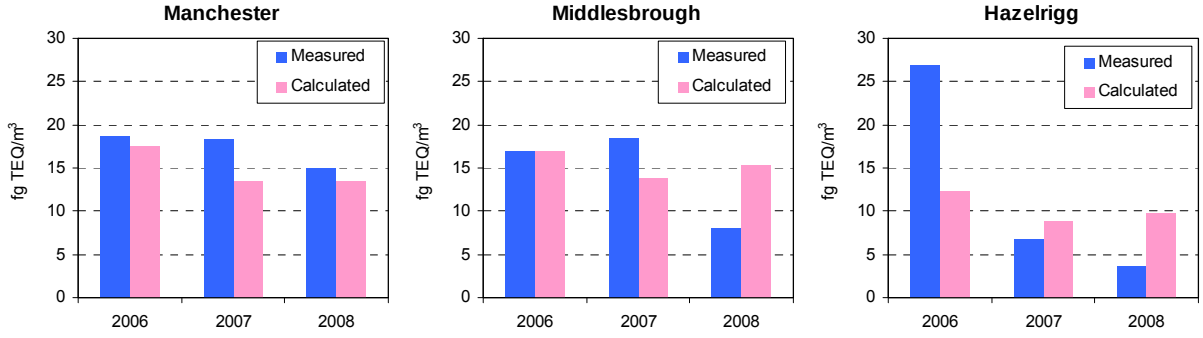



***Fig. 3.27.*** *Comparison of calculated PCDD/F air concentrations in surface atmospheric layer in 2006 – 2008 with measurements made at three the UK sites.*

Reasonable agreement is obtained between measurements in Spain (Arenys de Mar) in November 2008 and model predictions. Namely, measured value of PCDD/F total toxicity is 7.6 fg TEQ/$m^3$ whereas the model shows the level of 8.7 fg TEQ/$m^3$.

The agreement between measurements and model predictions seems to be reasonable taking into account uncertainties in model design and emission inventories. For the improvement of the agreement between measurements and calculations, more information on emission congener composition and seasonal variations is required.

### *3.2.2. Source-receptor relationships*

In evaluation of source-receptor relationships for POPs their ability to be accumulated in the surface media (soil, seawater, vegetation) with subsequent re-emission to the atmosphere should be taken into account. Besides, contribution of anthropogenic sources located outside the EMEP domain is noticeable for PCDD/Fs. So, the sources contributing to deposition over the aggregated area of the EMEP countries can be split into three groups: primary sources from the ***EMEP countries***, primary sources from ***non-EMEP countries*** and secondary sources (***re-emissions***), see Fig. 3.28. By primary sources direct emissions to the atmosphere are meant. Secondary sources include re-emission of pollutant accumulated in the surface media during some period prior to the considered moment. The period of time that should be taken into account for evaluation of re-emission fluxes depends on physical-chemical properties of the pollutant considered, mainly on the persistence of the pollutant in soil. Since half-lives for PCDD/F congeners in soil are evaluated as tens of years, for these pollutants emissions/deposition during 40 – 50 years prior to the considered moment can be essential for the evaluation of re-emissions.

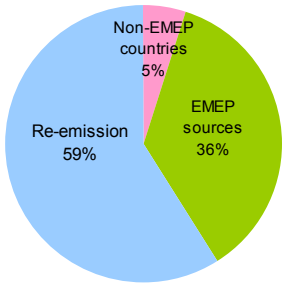



***Fig. 3.28.*** *Contribution of various source groups to deposition over the aggregated area of EMEP countries for 2010.*

From calculations it is seen that the contribution of the EMEP sources to the contamination of the EMEP countries is accounted for 35%; secondary emission sources play essential role in contamination of the EMEP region by PCDD/Fs (about 60%). The contribution of non-EMEP sources to deposition over the area of the EMEP countries is about 5% of total deposition.

It is also of interest to consider in more detail the contribution of internal EMEP sources to the contamination of the EMEP region (without re-emission and contribution of non-EMEP sources).

Similar to B[a]P, over 80% of all deposition to the aggregated area of the EMEP countries are determined by sources of 12 countries, namely the Russian Federation, the Ukraine, Turkey, Poland, Kazakhstan, Italy, Romania, the FYR of Macedonia, the UK, the Czech Republic, Uzbekistan and Spain. The overall contribution of all the rest EMEP countries does not exceed 20%.

For example, deposition from emission sources of Poland mainly fall to the own area of the country (about 60%), to the Russian Federation (about 6%), Germany (5%), the Ukraine (4%), and the Czech Republic (3%). The fraction of total deposition from Polish sources to the areas of the rest countries amounts to 24%, see Fig. 3.29.

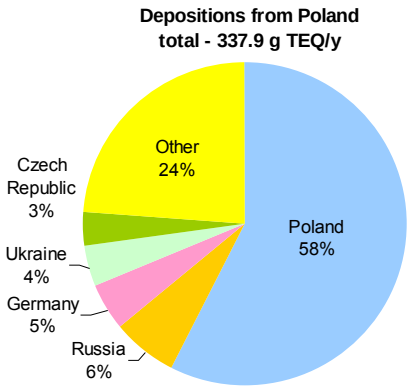



***Fig. 3.29.*** *Distribution of PCDD/F deposition from Polish emission sources between other European countries.*

It is found that for 22 countries over 50% of deposition from anthropogenic sources to their own area are determined by external sources (transboundary transport). Calculations allow evaluating the fractions of deposition to each EMEP country originated from sources of other countries. Such information is exemplified by the diagrams for Finland and France where four main contributors to deposition to the considered countries are specified (Fig. 3.30).

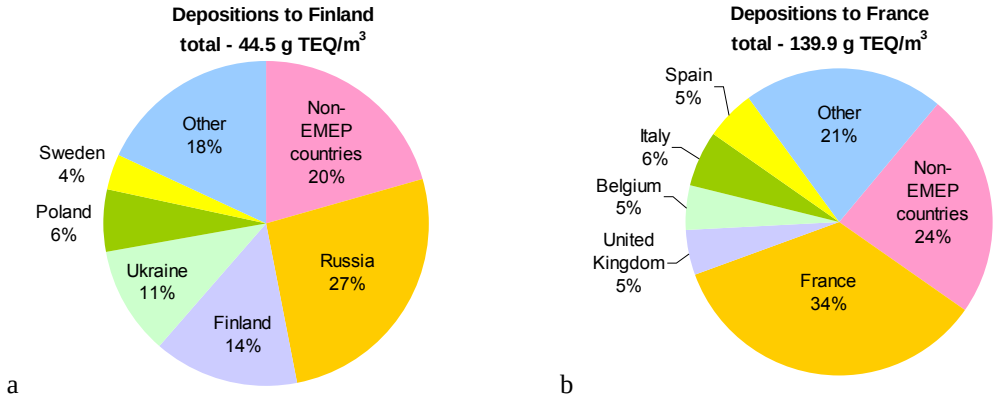



***Fig. 3.30.*** *Contribution of various EMEP countries to deposition to Finland (a) and France (b).*

It is seen that internal sources are responsible for about 14% of deposition to Finland. The rest 86% are due to transboundary transport within the EMEP domain. Main contributors to the contamination of Finland among the EMEP countries are the Russian Federation (27%), the Ukraine (11%), Poland (6%) and Sweden (4%). The combined contribution of the rest EMEP countries is about 20%. The contribution of non-EMEP countries is also noticeable (20%). Such picture is characteristic of countries with relatively small emissions.

For countries with relatively large emission contribution of internal sources can be higher. For example, contributions of internal sources in France are about 35% (Fig. 3.30b).

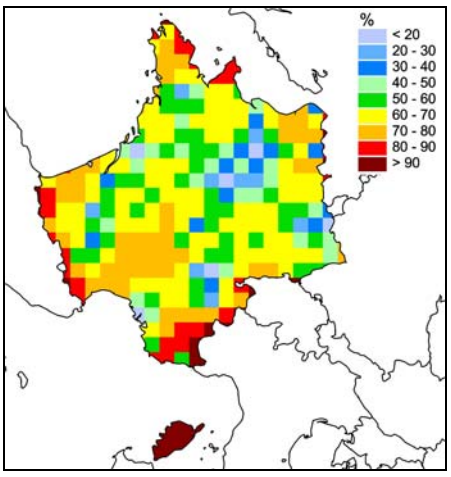



***Fig. 3.31.*** *Spatial distribution of contributions of external EMEP sources to PCDD/F air concentrations in France, in %.*

However, the contributions of external sources undergo strong spatial variations (see Fig. 3.31). In spite of the fact that average contribution of external sources in air concentrations in France is about 65%, this contributions in some regions may be essentially higher (up to 90%). However, since calculation agree with measurements within a factor of two for all measurements but one in a location in France (Thau lagoon, see Fig. 2 above), the results of this preliminary analysis seem reasonable. In fact, spatial distribution of external contributions is determined by spatial distribution of emissions in France and neighbouring countries. For more detailed evaluation of external contributions modelling with finer spatial resolution can be of interest. For carrying out such modelling emission data with the corresponding resolution in France and neighbouring countries and additional measurement data from national experts are required.

### *Concluding remarks*

- Since the behaviour of different PCDD/F congeners in the environment is different due to their specific physical-chemical properties, separate model evaluation of each of 17 PCDD/F toxic congeners was performed for obtaining the information on total toxicity of PCDD/F mixture.
- Preparation of congener-specific PCDD/F emission data for modelling was made using inverse modelling approach. It was found that for reasonable agreement between measurements and calculations of total toxicity of PCDD/F mixture in the atmosphere emission data should be enlarged about 5 times, which was in line with the estimates of emission uncertainties.
- Since measurements of PCDD/Fs are not included into regular EMEP monitoring programme, to refine monitoring/modelling/emission evaluation of PCDD/F toxicity MSC-E has performed literature search of available measurement data from national and international projects and campaigns.
- Modelling of 17 PCDD/F congeners in 2010 is performed by MSCE-POP regional model using corrected congener-specific emissions. Initial and boundary conditions for regional simulations are generated by hemispheric model runs for the period from 1970 to 2010. These simulations showed reasonable agreement with measurement data. The agreement between calculated and measured total toxicities within a factor of 2 is obtained for more than 50% of available measurements at background locations.
- Relatively high levels of PCDD/F air concentrations (20 fg TEQ/$m^3$ and higher) are obtained for some regions in Central and Eastern Europe (Hungary, Poland, Slovakia, the Ukraine and parts of the Czech Republic and Turkey). In the remote regions within the EMEP domain (the Scandinavian Peninsula and northern part of the UK) PCDD/F levels are considerably lower (less than 5 fg TEQ/$m^3$).
- Evaluation of source-receptor relationships for PCDD/Fs in 2010 shows that the contribution of re-emission exceeds the half of total deposition over the area of the EMEP countries. Similar to B[a]P it is found that over 80% of total deposition from anthropogenic sources over the area of all EMEP countries are determined by 12 countries only. For about 20 countries contribution of external sources (transboundary transport) to deposition from anthropogenic sources is accounted for 50% and more. Similar to B[a]P contributions of transboundary transport in a country are subject to strong spatial variations.

## 3.3. Hexachlorobenzene (HCB)

This section describes the progress in the evaluation of HCB pollution levels on global scale and within the EMEP domain.

Experimental modelling of HCB transport and accumulation in the environment is carried out by MSC-E during a number of recent years. The results of the investigations show the following peculiarities of HCB fate in the environment:

- high life-time in the atmosphere leading to global character of HCB pollution;
- essential influence of re-emission on the contemporary HCB atmospheric concentrations due to HCB historically accumulated in the underlying surface (soil, seawater).

The data on HCB historical emissions are rather scarce and are subject to high uncertainties. To overcome this difficulty, during 2009 – 2011 MSC-E has performed the activities on the construction of HCB emission scenarios and testing them using hemispheric and regional modelling [*Gusev et al.*, 2009; *Shatalov et al.*, 2010; *Gusev et al.*, 2011].

Due to the above mentioned peculiarities of HCB fate, long-term simulations of transport and accumulation of this contaminant in the environment on global scale should be performed. To do that HCB global emission data were prepared (see Section 1.2.4 above). Using these data global scale modelling of HCB cycling in the environment is carried out by the GLEMOS multi-scale multi-compartment modelling system for the period from 1945 to 2010 with spatial resolution $3^0$x$3^0$. Based on these global model simulations regional-scale modelling for the period from 2009 to 2010 with 50×50 km resolution is performed using initial and boundary conditions. It should be noted that currently the GLEMOS modelling system does not include vegetation compartment. Usage of two-year period of regional modelling allows obtaining more reasonable results for 2010 taking into account accumulation of HCB in vegetation. The results of these simulations are briefly described in this section.

### *Long-term accumulation in the environment*

According to simulation results, the ocean contains about a half of total environmental content of HCB in 2010. Soil content is about 30% – 40%. The share of HCB in the atmosphere is continuously decreasing from 30% – 35% in the end of 40$^{th}$ of previous century to less than 1% after 2000 (Fig. 3.32).

The most part of HCB mass is removed from the environment due to ocean degradation and sedimentation (Fig. 3.33). These processes are responsible for ~70-80% of total removal in the last years. The contributions of soil degradation amount to ~15-20%. The relative importance of the removal from air decreases from 55% in 1945 to 3% in 2010.

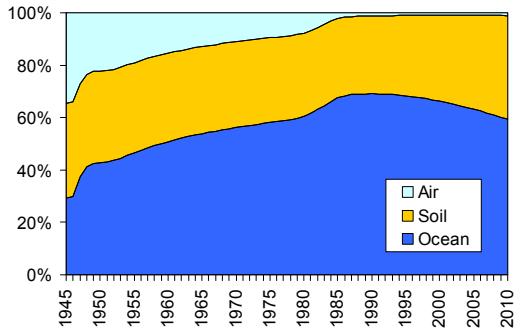



***Fig. 3.32*** *The percentage ratio of HCB content in environmental media for the period from 1945 to 2010*

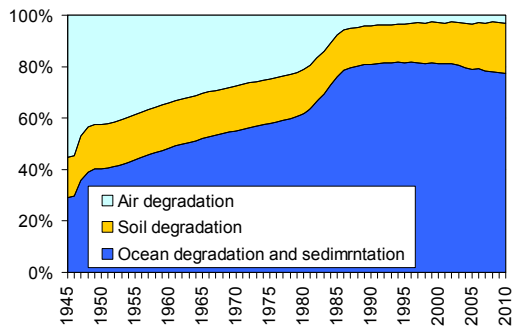



***Fig. 3.33.*** *The percentage ratio of different ways of HCB removal from environmental media for the period from 1945 to 2010*

Annual HCB fluxes between environmental media are shown in Fig. 3.34. It is seen that the fluxes from soil to the atmosphere and from the atmosphere to ocean are prevailing. So, globally HCB mass is transported from soil to ocean through the atmosphere. In the ocean HCB is partially accumulated and partially removed from the environment via sedimentation and degradation processes.

Annual mass flux integrated over the year is directed from soil to the atmosphere (lower curve in Fig. 3.34). However, in some particular regions this flux can have opposite direction. Spatial distribution of HCB gaseous flux from the atmosphere to soil in 1978 (the year with maximum emissions) is shown in Fig. 3.35. It can be seen that in the areas with relatively small emissions this flux is directed from the atmosphere to soil. This is particularly characteristic of high-latitude regions where HCB is intensively accumulated in soil (the effect of ***cold condensation***).

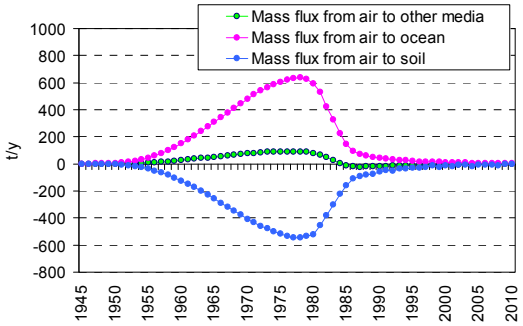



***Fig. 3.34.*** *Time trends of HCB mass fluxes from air to other media (negative values correspond to the flux of reverse direction)*

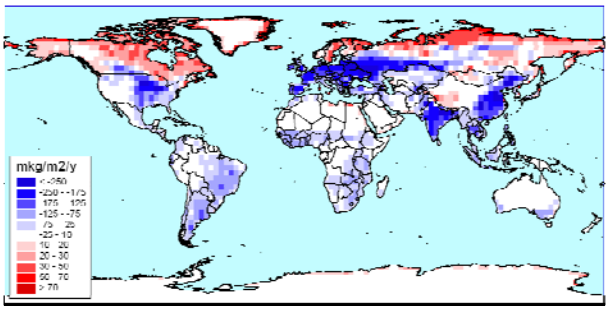



***Fig. 3.35.*** *Spatial distribution of HCB gaseous flux from air to soil in 1978 (negative values correspond to the flux of reverse direction)*

## *Results for 2010*

Let us consider in more detail the results of global modelling concerning the last year of the calculation period (2010).

***HCB content in the atmosphere.*** Maximum HCB concentrations (> 30 pg/m$^3$) in the atmosphere have been found in Europe, India and China. Outside highly contaminated regions air concentrations are close to background ones that depend on latitude. In particular, background HCB air concentrations in low and temperate latitudes of the Northern Hemisphere amount to 10-15 pg/m$^3$ (Fig. 3.36).

The results of modelling are compared to measurement data on HCB concentrations in air at the EMEP monitoring network. Annual mean concentrations are considered. The results are presented in Fig. 3.37.

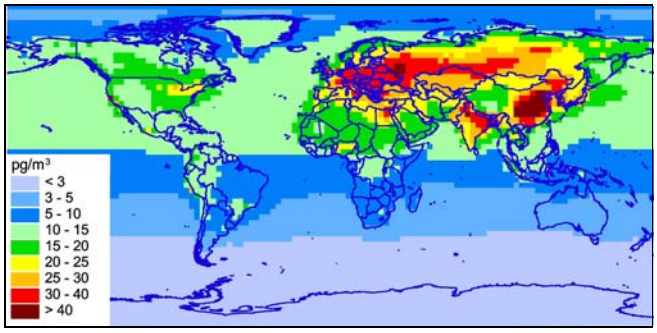



***Fig. 3.36.*** *Spatial distributions of HCB annual mean concentration in surface air for 2010*

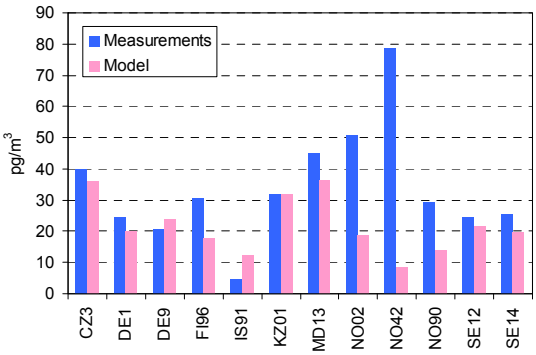



***Fig. 3.37.*** *Comparison of calculated annual mean HCB concentrations in air with measurements of the EMEP monitoring sites in 2010*

In general, calculation results agree reasonably with measurements. About ¾ of measurements agree with calculations within a factor of two. The exceptions are Norwegian sites (particularly NO2 and NO42) where measurements essentially exceed calculated values. One of possible reasons of such disagreement may be local emission sources near Spitsbergen island (NO42) and near Skagerrak straight (NO2). This assumption can be indirectly confirmed by the comparison of measurements at

*Bjornoja* (Bear Island) [*Kallenborn et al.,* 2007] located between the North Norwegian mainland and the Svalbard archipelago (Fig. 3.38) with calculated results. Air concentrations measured at this location agree well with calculation data (Fig. 3.39) being essentially lower than concentrations measured at NO2 and NO42.

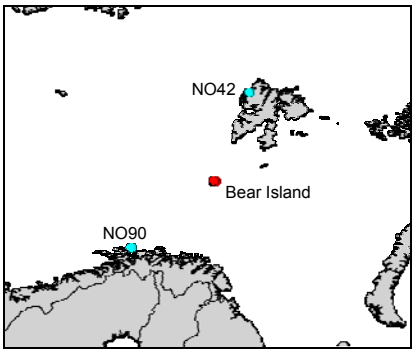



***Fig. 3.38.*** *Relative locations of Bear Island and EMEP monitoring sites NO90 and NO42*

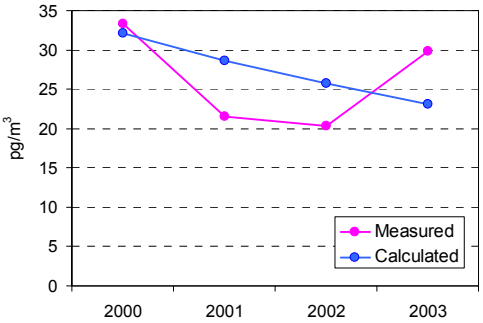



***Fig. 3.39.*** *Comparison of calculated annual mean HCB concentrations in air with measurements at Bjornoja (Bear Island)*

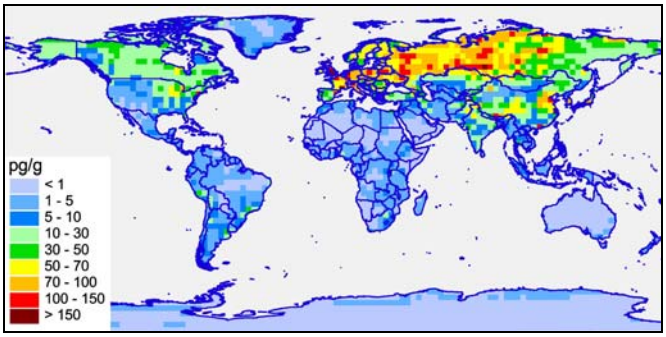



***Fig. 3.40.*** *Spatial distributions of HCB annual mean concentration in soil for 2010*

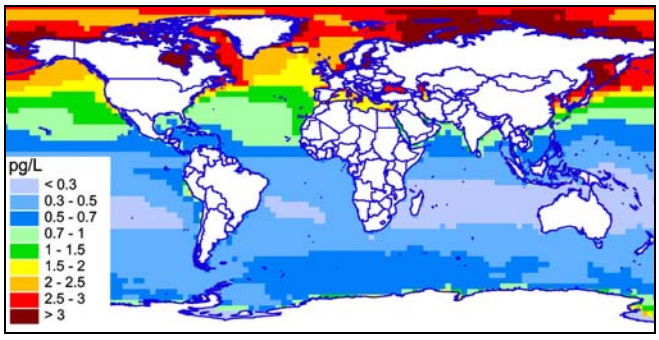



***Fig. 3.41.*** *Spatial distributions of HCB annual mean concentration in seawater for 2010*

***HCB content in soil.*** Spatial pattern of HCB soil concentrations reflects the peculiarities of historical accumulation of the pollutant. Maximum contamination in soil takes place in areas with high emissions and in regions with high latitudes due to cold condensation mentioned above. Highest soil concentrations are characteristic of Europe and the Russian Federation where they exceed 50 – 100 pg/g (see Fig. 3.40).

***HCB content in seawater.*** The distribution of HCB concentrations in surface layer of seawater is given in Fig. 3.41. There is evident latitudinal dependence of pollution level. The highest values of HCB concentrations in seawater (more then 3 pg/L) are obtained for high-latitude regions. The reason for this is strong temperature dependence of the gaseous flux from air to water: lower air temperatures correspond to higher air-water flux. Seawater HCB concentrations in the Antarctic region are higher than those in the temperate latitudes of the Southern Hemisphere.

## *Regional-scale simulations*

Modelling of HCB transport in the EMEP region is carried out by regional version of MSCE-POP model using official emission data complemented with TNO emission estimates where necessary. Calculated HCB air concentrations in 2010 are shown in Fig. 3.42. Maximum concentration levels (> 20 – 25 pg/m$^3$) are obtained for Central and Eastern Europe and in European part of the Russian Federation.

Model results agree with EMEP measurement data in general (Fig. 3.43). Essential underestimation of HCB atmospheric concentrations at Norwegian sites is discussed above during the analysis of global calculations. The differences in the values of air concentrations obtained by regional model from that calculated at the global scale can be conditioned by different resolution used in modelling.

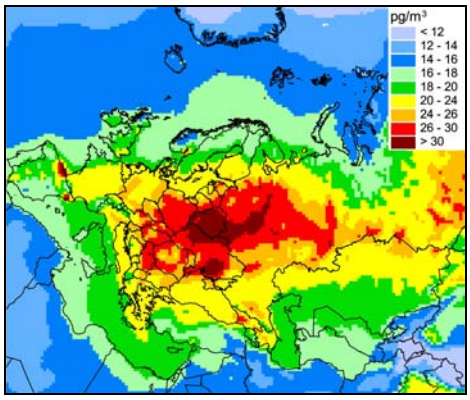



***Fig. 3.42.*** *Spatial distributions of HCB annual mean concentration in surface air in the EMEP region for 2010*

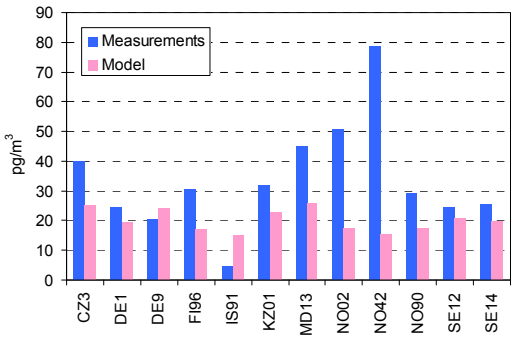



***Fig. 3.43.*** *Comparison of calculated annual mean HCB concentrations in air with measurements at the EMEP monitoring sites in 2010*

To evaluate relative contributions of re-emission (initial conditions), non-EMEP sources (boundary conditions) and anthropogenic sources located within the EMEP region, separate modelling with these emission source groups is made. It should be taken into account that re-emission from surface media outside the EMEP region is included into the second group (boundary conditions). Spatial distribution of HCB air concentrations originated from the above source groups is shown in Fig. 3.44. The sum of these contributions equals to concentration levels presented by the map in Fig. 3.42.

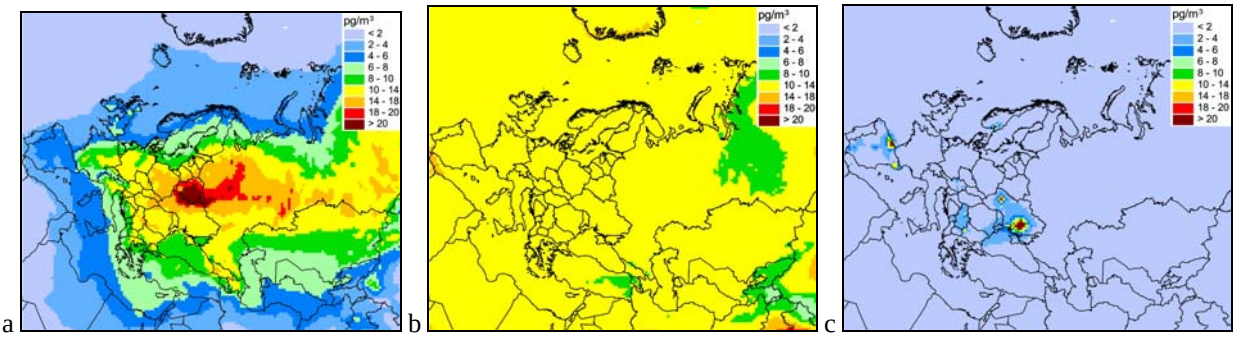



***Fig. 3.44.*** *Contributions from different sources to HCB annual mean concentration in surface air in the EMEP region originated from: a – initial conditions, b – boundary conditions, c – EMEP emissions*

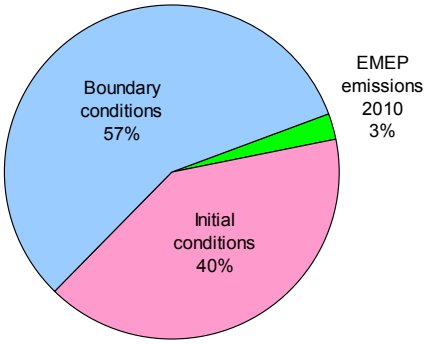



***Fig. 3.45.*** *Averaged contributions from different source groups to HCB concentration in ground-level air in the EMEP region*

It can be seen that spatial pattern of HCB air concentrations is determined mainly by initial conditions (Fig. 3.44a). Boundary conditions are determining the background level of contamination. This level amounts to 10 – 15 pg/m$^3$, which corresponds to background level for temperate latitudes of the Northern Hemisphere calculated in the course of global calculations (see Fig. 3.36 above). The contribution of anthropogenic emissions to air concentrations within the EMEP region is comparably small. The exception is Donets Basin region where contribution of contemporary anthropogenic emissions is 20 pg/m$^3$ and higher.

Contributions of initial conditions, boundary conditions and EMEP anthropogenic sources to air concentrations amount to 40%, 57% and 3%, respectively (Fig. 3.45). Comparably large contribution of boundary conditions to average air concentrations over the EMEP domain is conditioned by homogeneous character of background HCB levels. The contributions of initial conditions (re-emission) in some regions of Central and Eastern Europe are higher than contribution of boundary conditions.

## *Concluding remarks*

- The spatial pattern of HCB atmospheric concentrations is determined mainly by secondary emission sources, that is, by re-emission of HCB historically accumulated in the surface media. Hence, for simulations of HCB contamination levels both in the EMEP region and over the entire globe consideration of historical HCB accumulation is of particular importance.
- Emission scenario for historical and contemporary emissions worked out by MSC-E allows obtaining reasonable agreement between calculated and measured HCB air concentrations at the sites of the EMEP monitoring network.
- Air concentrations of HCB in the regions free from emission sources for low and temperate latitudes in the Northern Hemisphere (10 – 15 pg/m$^3$) are comparable in order of magnitude with concentration levels in contaminated regions. This is conditioned by extremely high persistence of HCB in the atmosphere.
- According to emission data used in modelling, the influence of contemporary anthropogenic emissions in the EMEP region on air concentrations is relatively small. Maximum contribution of contemporary emissions to air contamination in the EMEP domain exceeds 20 pg/m$^3$ (the level which is comparable with air concentrations in highly polluted regions of Central and Eastern Europe).
- Among important directions of further investigation of HCB transport and accumulation in the environment the following activities should be mentioned: elaboration of vegetation module for GLEMOS modelling system, collection of measurement data on contamination levels of HCB in various environmental media and usage of these data for model validation and refinement of emission scenarios.

# 4. POP POLLUTION AND CLIMATE CHANGE INTER-LINKAGES

This section outlines the status and progress in the MSC-E activity with respect to investigating potential effects of projected climate changes on POP long-range transport and fate. The Centre continues to work in this direction studying relationships between temporal variability of pollution levels and variations of meteorological and environmental factors, which can be potentially affected by climate change.

As it is stressed in [*HTAP Assessment*, 2010] changing climate may alter POP exposure pathways and increase vulnerability of ecosystems and human health to POPs. Potential changes in POP dispersion resulted from projected changes of climate are associated with changing of primary and secondary emissions rates, atmospheric circulation and distribution of atmospheric constituents affecting POPs, efficiency of removal processes, characteristics of underlying surface including snow/ice cover, ocean currents, and increase of extreme weather events. Interaction of these factors and complex nature of POP cycling in the environment imply the use of POP models in order to evaluate responses of pollution to the climate variability. Application of models allows performing modelling experiments based on the climate change scenarios and predicting possible reaction of POP levels on future climatic changes. Besides, it is of importance to analyze sensitivity of current and past levels of POP concentrations to temporal variations of meteorological and environmental factors including the influence of extreme weather events which can provide insight into directions and extent of possible future changes in POP pollution.

## 4.1. Variations of spatial distribution of POP concentrations generated by meteorological variability

To analyze the influence of meteorological parameters on the POP contamination, MSC-E has studied relationships between inter-annual variability of meteorological and environmental factors and variations of POP concentration levels on the example of the data for two years 2009 and 2010. This comparison allows examining the influence of extreme events to the fate of POPs with different physical-chemical properties. The year 2010 was characterized by outstandingly high temperatures in western Russia in July and August. So, the comparison of POP behaviour in the environment under the extreme conditions in 2010 with that in 2009 allows evaluating the influence of heat waves to POP concentrations in air. To illustrate the influence of heat waves to behaviour of pollutants with different physical-chemical properties two pollutants (B[a]P and PCDD/Fs) are used.

The differences between monthly averages of air temperature in eastern part of the EMEP domain in 2009 and 2010 are shown by maps in Fig. 4.1.

The increase of temperatures in 2010 in comparison with 2009 begun in July in some areas of western Russia and reached 6 ºC and more. In August the area with increased temperature was widened and shifted to the south-west occupying eastern part of the Ukraine. To reveal the influence of such differences in air temperature the simulations of transport and accumulation of PCDD/Fs and B[a]P with meteorology of the above two years were carried out (to exclude the influence of emission changes emissions were taken the same in 2009 and 2010 for each pollutant). Differences in air concentrations in the surface air for PCDD/Fs are shown in Fig. 4.2.

It is seen that the increase of ambient temperatures in 2010 in comparison with those in 2009 have led to the increase of air concentrations of PCDD/Fs in western part of Russia in July. According to further dynamics of temperature, the increase of air concentrations in August have been widened and took place in south-western part of the Russian Federation and partly in eastern part of the Ukraine.

Generally, the increase of air concentrations reached in August 70% and more. This increase is determined by higher volatilization of PCDD/Fs from soils under higher temperatures.

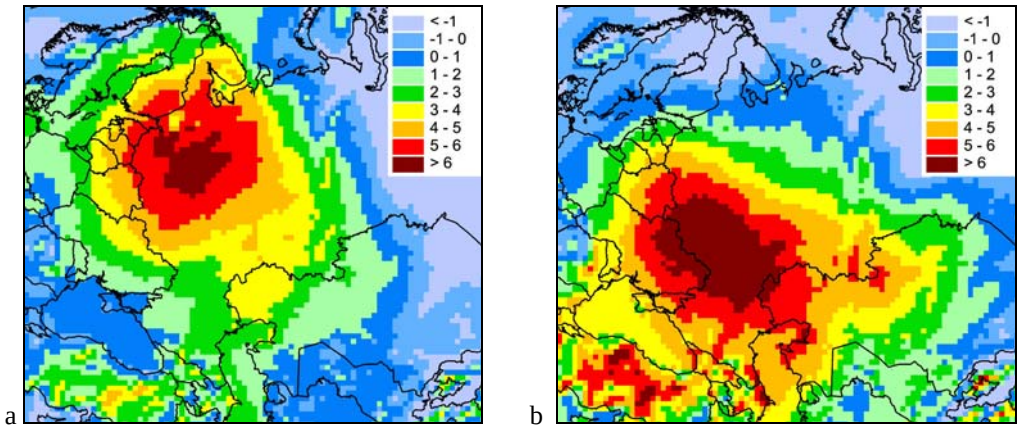



***Fig. 4.1.*** *Spatial distribution of changes in monthly mean surface air temperature (ºC) between 2010 and 2009 for July (a) and August (b). Positive values correspond to the increase of temperature in 2010 in comparison with that in 2009.*

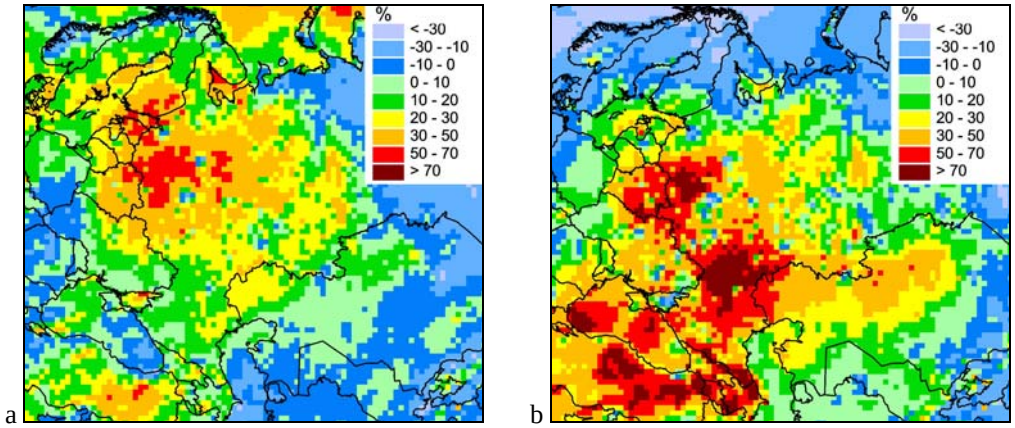



***Fig. 4.2.*** *Spatial distribution of changes in PCDD/F monthly mean air concentrations between 2010 and 2009 for July (a) and August (b).*

Quite another effect of the increase of ambient temperature takes place for B[a]P (Fig. 4.3).

The increase of air temperature has led to the ***decrease*** of B[a]P concentrations. The reason for this is that the change in air concentrations of a POP is determined by two concurrent processes: gaseous exchange between the atmosphere and underlying surface (leading to the increase of air concentrations under temperature increase) and degradation in the atmosphere (having the opposite effect on air concentrations). According to the model parameterization degradation half-life of B[a]P in the atmosphere is about 2 days whereas for PCDD/Fs this half-life equals several tens of days depending on congener. So, the decrease of B[a]P concentrations due to increase of temperature is determined by prevailing influence of degradation process for this pollutant. The evaluation of relative importance of environmental processes for B[a]P behaviour in the atmosphere is considered below.

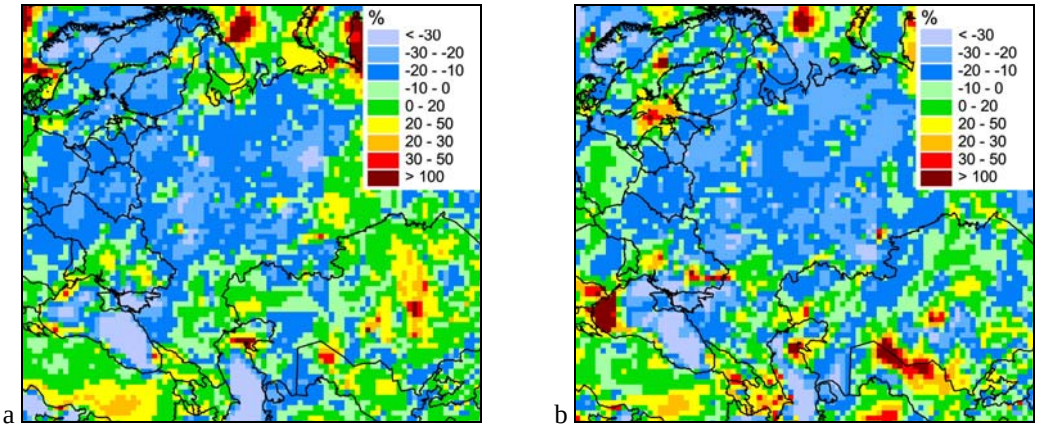



***Fig. 4.3.*** *Spatial distribution of changes in B[a]P monthly mean air concentrations between 2010 and 2009 for July(a) and August (b).*

It should be noted that the above considerations of the influence of meteorological conditions on B[a]P concentrations are performed under the assumption of equal emissions of the pollutant in the two considered years (2009 and 2010). However, measurement data in cities in the Russian Federation obtained by NPO Typhoon (http://www.typhoon.obninsk.ru) show the increase of B[a]P concentrations in July and August of 2010 in comparison with 2009 (Fig. 4.4).

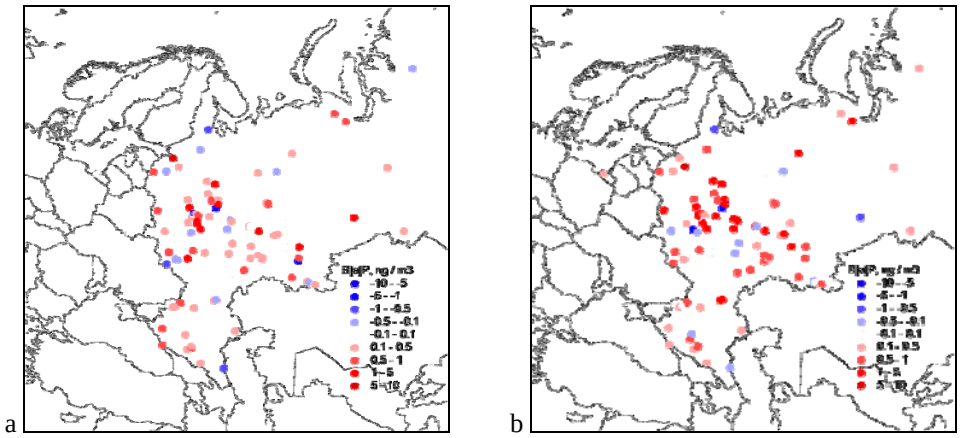



***Fig. 4.4.*** *Difference between monthly mean B[a]P concentrations in surface air in cities located in the western part of Russia observed in July (a) and August (b) of years 2010 and 2009. Calculated on the basis of data of NPO Typhoon.*

It can be seen that over the most part of western Russia levels of B[a]P air concentrations measured in 2010 were significantly higher than that for 2009. This may probably be conditioned by additional emissions from forest fires that took place in these months over the considered area. For example, map of forest fires at July 27 taken from *www.kosmosnimki.ru* is shown in Fig. 4.5.

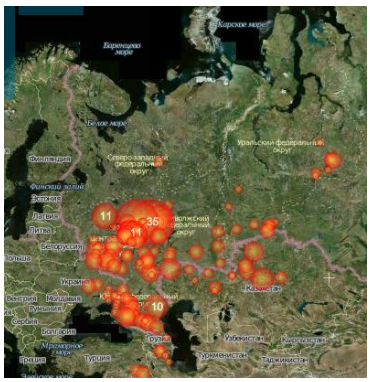


***Fig. 4.5.*** *Forest fires in western part of Russia at July 27, 2010 (taken from www.cosmosnimki.ru). White figures indicate the number of burning points within shown location.*

So, in the projections of the fate of POPs due to climate changes not only meteorological change but also attendant circumstances such as the probability of forest fires due to temperature increase in particular locations should be taken into account.

### *Future activities*

Important contribution to the investigation of climate change effects on air pollution is expected from the activities under the TF HTAP. Importance of this issue is taken into account in course of planning the next phase of work of the Task Force on 2011-2015. Following the discussions at the recent meetings in Arona (2011) and in Pasadena (2012) the Task Force defined several thematic working areas. One of these areas considers the impact of climate change on intercontinental transport and levels of pollution of different substances including POPs.

## 4.2. Analysis of seasonal variations of POP concentrations

Investigation of potential effects of changes of meteorological parameters on POP pollution levels, performed by MSC-E at previous stage of the work, was focused on the analysis of seasonal variations of B[a]P and PCB-153 air concentrations in Europe and their relationships with changes of different meteorological and environmental factors [*Gusev et al.*, 2011]. Particularly, such factors as temperature, precipitation amount, wind speed and direction, and vegetation cover, can in most cases explain 90% – 95% of seasonal variability of POP air concentrations. Besides, sensitivity of POP pollution levels to variations of meteorological and environmental parameters is different in different parts of Europe which can be also reflected in varied response to the climatic changes across Europe. At present stage in framework of this activity MSC-E carries out further analysis of seasonal changes of B[a]P air concentrations analyzing the influence of concentrations of atmospheric reactants (OH radical, organic matter) and concentrations of atmospheric aerosol matter together with meteorological parameters evaluating relationships with their perturbations for the year 2009.

The distribution of POPs in the environment depends on their physical-chemical properties and is governed by environmental processes and variations of meteorological and environmental factors (meteorology, land use, atmospheric reactants, etc.). The subset of the processes and corresponding meteorological and environmental factors included in the analysis are given in Table 4.1.

***Table 4.1.*** *Main processes influencing POP fate in the environment and corresponding meteorological and environmental factors.*

| Process | Meteorological and environmental factors |
|---|---|
| Wet deposition and dry particulate deposition | Temperature (T), precipitation intensity (P), wind speed (Sp), type of underlying surface (Veg) |
| Degradation in the environmental media (particularly, the atmosphere) | Temperature (T), OH radical concentrations (OH) |
| Gas-particle partitioning | Temperature (T), specific aerosol surface (SRF), organic content in the atmospheric aerosol (ORG) |
| Atmospheric transport | Wind speed (Sp) |
| Gaseous exchange with the underlying surface | Temperature (T) , type of underlying surface (Veg) |

Most of the processes listed in the table have direct influence on POP atmospheric concentrations. Particularly, wet deposition process removes the pollutant from the atmosphere during precipitation events characterized by precipitation intensity. Dry deposition flux of the POP in particulate form depends first of all on the wind speed in the atmospheric surface layer and on the type of underlying surface. Most essential differences in dry deposition rates take place between vegetation-covered surfaces and bare soil. On the other hand, the process of wet deposition of the POP in gaseous form is strongly temperature-dependent due to temperature dependence of Henry's law constant. Following the same reason there is strong temperature dependence of gaseous exchange flux between the atmosphere and underlying surface. POP degradation in the atmosphere is temperature-dependent and is influenced in addition by variations of concentrations of atmospheric reactants that undergo chemical reactions with the considered pollutant. For B[a]P, such reactants can be OH radical, ozone and nitric oxides (see Section 4.3). However, at present only the reactions of gaseous form of POPs with OH-radical and generalized description of photodegradation of B[a]P are considered in model simulations.

The process of gas-particle partitioning changes the relation between gaseous and particulate forms of the pollutant in the atmosphere. Since the processes of POP deposition, degradation and exchange strongly depend on the form of the pollutant, gas-particle partitioning indirectly affects the contribution of these processes to changes of concentrations. The model considers two mechanisms of gas-particle partitioning – adsorption and absorption. The environmental parameters governing these two mechanisms of sorption are specific aerosol surface and organic matter content in the atmospheric aerosol.

Finally, long-range transport of POPs in the atmosphere can be roughly characterized by average wind speed over the considered region. Most likely, pollution in the regions with strong wind speed should be lower than in those with low wind speed due to higher value of pollution amount transported outside the region.

The set of factors considered in this study is given below:

- ambient temperature;
- precipitation intensity;
- wind speed;
- leaf area index for vegetation-covered surface;
- OH radical concentration in the atmosphere;
- specific aerosol surface;
- organic matter concentrations in atmospheric aerosol.

Since the study is country-oriented, all these parameters are averaged over the area of each EMEP country.

The method applied to the analysis of the influence of meteorological and environmental parameters on the contamination levels is regression analysis of the pollutant air concentration (target parameter) with respect to the chosen parameters. In the analysis it should be taken into account that the chosen parameters are not independent, and the values of one of the parameters cannot be modified without changing other parameters. The method of conducting sensitivity study with respect to such set of parameters is described in the previous MSC-E reports [*Shatalov et al.,* 2010; *Gusev et al.,* 2011]. This year extended set of parameters including reactant's concentrations in the atmosphere is used.

We recall that the method is based on successive regression analysis. Input data for this analysis is the set of B[a]P air concentrations calculated by MSCE-POP model for 2009 averaged over each EMEP country and each month and environmental parameters used in calculations with same averaging. The analysis is performed stepwise for each country separately. At the first step a parameter explaining highest part of variations of air concentrations is chosen by means of regression analysis. At each next step one more parameter is added. This parameter is chosen again in such a way that the constructed subset of parameters explains concentration variations in maximum extent. For the bulk of countries three parameters explain 85% or more of concentration variations.

Ranking of the priority of the considered parameters may be performed on the basis of the order in which they are selected. This approach was applied in the previous investigations. However, regression coefficients for earlier chosen parameters may be changed at next steps of the process. In this study the ranking according the regression coefficients obtained at the last stage of the process is used. For the comparison of regression coefficients for various parameters normalization was performed to exclude the differences in units used. More exactly, each parameter (both target parameter and environment parameter) was centred by extracting its average and normalized by division by its standard deviation. Under such an approach each regression coefficient shows sensitivity of the target parameter to changes of the corresponding environmental parameters, that is, relative change of target parameter (in %) due to relative change by 1% of the environmental parameter.

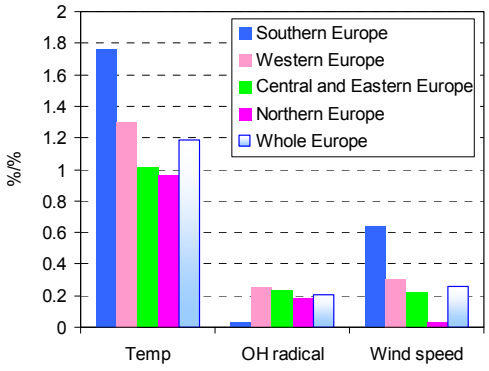



***Fig. 4.6.*** *Sensitivity of B[a]P surface air concentrations to changes of meteorological and environmental factors in various parts of Europe, %/%.*

These sensitivities were averaged over all EMEP countries and over countries of Northern, Central and Eastern, Southern and Western Europe with weights proportional to country areas.

Calculation showed that main processes affecting B[a]P contamination in Europe and its parts are degradation and transport with air masses. These processes are governed by temperature, OH radical concentrations and wind speed. Sensitivities of B[a]P air concentrations to changes of the listed parameters are shown in Fig. 4.6 The sensitivities to other parameters such as precipitation intensity, specific aerosol surface and organic matter content averaged over the whole Europe are found to be relatively small (0.06%/%, 0.04%/% and 0.05 %/%, respectively).

For the analysis of the obtained results it should be taken into account that two parameters (temperature and OH radical concentrations) are highly correlated. So, the impact of degradation process on B[a]P air concentrations should be evaluated by simultaneous change of both these parameters. Calculation shows that maximum influence of degradation process on air concentrations is characteristic of Southern Europe, and minimum influence – in Northern Europe. The second (in importance) process is atmospheric transport characterized by wind speed. This parameter affects air concentrations in two concurrent ways. The increase of wind speed leads, from one hand, to the increase of B[a]P transport from remote sources to the country's area (import), and, from the other hand, to increase of transport of B[a]P emitted from national sources outside the country's area (export). The combined result of these two opposite-directed processes depends on spatial distribution of emissions inside Europe. For the current emission spatial distribution highest influence of atmospheric transport was found for Southern Europe (where export is prevailing) and lowest – in Northern Europe (where the prevailing process is import).

The previous analysis of the influence of environmental processes to environmental parameters was based on the %/% sensitivities. However, it is also interesting to evaluate the decrease of B[a]P concentrations caused by temperature increase by 1º C. Sensitivity coefficients of B[a]P concentrations to the value of ambient temperature in %/ºC are shown in Fig. 4.7.

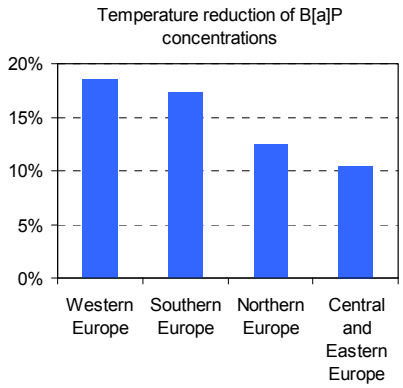



***Fig. 4.7.*** *Sensitivity of B[a]P surface air concentrations to changes of ambient air temperature, %/ºC*

As follows from the analysis, the reduction of B[a]P air concentrations in Europe due to increase of air temperature by 1 degree can be about 14% on the average. The extent to which B[a]P content in air is decreasing depends on geographical location of the considered region varying from about 10% in Central and Eastern Europe to about 19% in Western Europe. It should be noted that these estimates represent the response to the changes of temperature only, without taking into account its relationship with other factors. Besides, they are given for particular meteorological situation of the year 2009, including variations of air temperature, precipitation amount, and transport pathways, and therefore can be slightly different for different years.

## 4.3. Influence of atmospheric reactants

As it has been shown above, consideration of seasonal variations of B[a]P concentrations in the atmosphere is very important for the assessment of contamination levels for this pollutant. These variations are conditioned by two reasons: variations in emissions and seasonal variations of degradation rates. Since B[a]P is mostly present in the atmosphere in particulate form, the processes of degradation of particle-bound B[a]P may strongly affect the contamination levels. These processes are governed by two factors: atmospheric concentrations of the reactants involved in chemical and photochemical reactions with B[a]P and chemical composition of the atmospheric aerosol.

In *A. Gusev et al.* [2006a,b] a parameterization of B[a]P degradation on particles based on averaged information on atmospheric reactants and aerosol chemical composition was proposed. It was shown that even such rough parameterization of B[a]P particulate degradation allows essentially improve the agreement between measurements and model predictions on the level of monthly averages. However, both reactants concentrations and aerosol chemical composition are subject to strong spatial variations, so that the proposed scheme does not describe seasonal variations of pollution in different parts of Europe in the full extent. To further improve the description of particulate degradation of B[a]P it is reasonable to examine reactions of B[a]P with particular atmospheric pollutants, mainly with ozone and nitrogen oxides.

One more important feature of B[a]P degradation in the atmosphere is that reactions with the above atmospheric reactants not only reduce B[a]P content in the atmosphere but also lead to formation of degradation products that may be even more harmful that B[a]P itself [*Organic chemistry of the atmosphere*, 1991]. In particular, this relates to oxy- and nitro-derivatives of B[a]P. The most common reaction with ozone that is characteristic for all polycyclic aromatic hydrocarbons is electrophilic substitution. This reaction leads to formation of different oxy-derivatives of PAHs such as quinones, phenols, dihydrodioles and oxides [*Calvert et al.*, 2002]. Oxygenated polycyclic aromatic hydrocarbons are considered to be the second compound class identified for combustion processes. They are known to have carcinogenic, neoplastigenic, tumorigenic and mutagenic properties. The sources of these

pollutants could be both primary (from direct emissions) and secondary (as oxidative products of the corresponding PAHs) [*Lazzati,* 2009]. Particular attention should be paid to B[a]P diones due to their harmful effects to human health. The atmospheric concentrations of these compounds are well-correlated with those of B[a]P, which can be indicative of their secondary origin.

The consideration of the theory of chemical transformations of PAHs and, in particular, B[a]P in the atmosphere was carried out in a lot of papers and monographs. Here we mention only the classical monograph [*Harvey*, 1991; *Finlayson-Pitts and Pitts,* 2000]. This section is aimed at the review of the theory of chemical interactions between particle-bound B[a]P and gaseous atmospheric reactants. This class of reactions is known as heterogenic ones. Reaction rates and reaction products for this class are dependent on a number of factors such as ambient temperature, moisture, reactants concentrations and chemical composition of particles-carriers.

***Chemical composition of atmospheric aerosol*** strongly affects the process of PAH long-range transport in the atmosphere. There are two processes that go differently for PAHs sorbed at atmospheric aerosol of different chemical nature. First, this is the process of gas/particle partitioning, which determines PAH fraction existing in the atmosphere in particle-bound form. Second, chemical nature of particles-carriers strongly affects various atmospheric processes such as light absorption and reactions with various gaseous atmospheric reactants, particularly, with ozone and NOx. The present section describes the results of literature search of information on rate constants of B[a]P reactions with such important atmospheric reactants as ozone and nitrate compounds at particles-carriers of various nature including elemental carbon.

According to the measurements obtained at the EMEP monitoring network [*Yttri et al.,* 2011; *Hjellbrekke and Fjræaa,* 2011a,b], in consideration of chemical composition of atmospheric aerosol the following classes of compounds are distinguished: inorganic matter (mineral matter, sulphates, nitrates, ammonium salts), organic matter and elemental carbon. Since the rates of heterogenic reactions with PAHs are strongly dependent on the chemical nature of particles-carriers, chemical composition of the atmospheric aerosol is important for the description of PAH degradation in the atmosphere.

Measurements show that mineral compounds are constituents of both rough and fine particles. They are formed mainly due to soil and rock erosion and its composition is similar to that of the earth's crust consisting mainly of silicon dioxide.

According to [*Yttri et al.,* 2011], average fraction of mineral matter in the atmospheric aerosol within the period from 1996 to 2007 lie in wide range. The fraction of mineral compound in $PM_{10}$ amounts to about 15% in Southern Europe and 4% in Northern and Western Europe, whereas in $PM_{2,5}$ it constitutes from 5% in Central and North-western Europe to about 10% in Southern Europe. However, at some locations mineral part may be predominant (Fig. 4.8). For particles from $PM_1$ mineral fraction presents at about 4%.

Further, the content of elemental carbon in the atmospheric aerosol is comparably small (1% – 5%) depending on particle size and considered location. The fraction of organic matter in aerosol particles is essentially higher – from 25% to 50%. It should be mentioned that chemical composition of organic aerosol fraction is rather complicated. Atmospheric aerosol organic fraction includes alkanes, alkanals, ketones, alcohols, polycycling aromatic hydrocarbons, alkanoic acids, alkenoic acids, mono- and dicarboxilic acids, etc. (see e. g. [*Williams et al.,* 2006]). There are few data on chemical composition of this fraction, seasonal variations and source-receptor relationships defining contributions of individual compounds to this fraction.

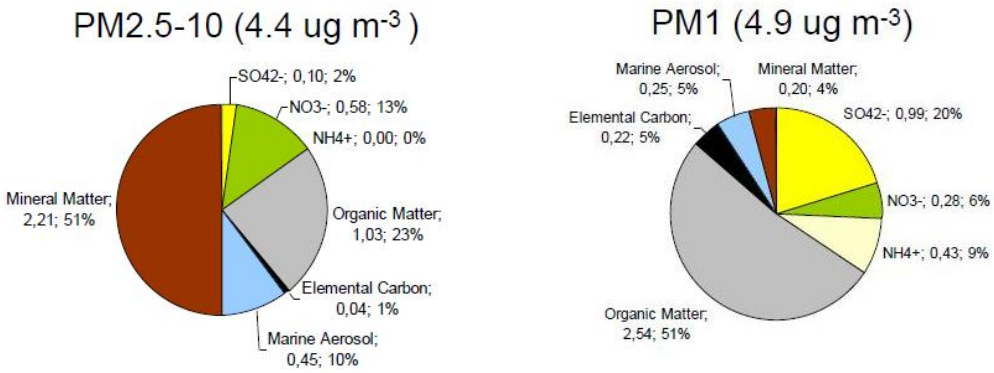



***Fig. 4.8.*** *Annual average composition of $PM_{2,5-10}$ and $PM_1$ at regional background of Montseny (NE, Spain)*

The information on chemical composition of atmospheric aerosol will be used in modelling in future.

In laboratory investigations of reaction rates for B[a]P sorbed on particles of various chemical nature- (mineral matter, elemental carbon and organic carbon) silicagel ($SiO_2$), grafite, soot and some organic species (such as acelaic acid and n-octanol) are often used as surrogates. It is also reasonable to use non-organic particles with organic films for investigation of kinetics of heterogenic reactions [*Zhou et al,* 2011].

***Heterogenic reactions of B[a]P with ozone.*** A number of experimental studies show the ability of B[a]P to photochemical and/or chemical oxidation under the conditions close to the environmental ones [*Pitts et al*., 1986; *Kamens et al*., 1988; *Calvert et al*., 2002, and others].

Unfortunately, only few data on measurements of B[a]P oxidation products were found in literature. In particular, in [*Koeber et al*., 1999] measurements of a number of oxy-B[a]P in the atmosphere over Munich were described. Main analytically determined compounds were B[a]P-1,6-dione, B[a]P-3,6-dione and B[a]P-6,12-dione. Summer measurements of B[a]P and its oxy-derivatives in the atmosphere over Milan in 2006 [*Lazzati,* 2009] where the same compounds as in [*Koeber et al*., 1999] are detected. The relation between concentrations of B[a]P and its oxy-derivatives in Milan is presented in Fig. 4.9.

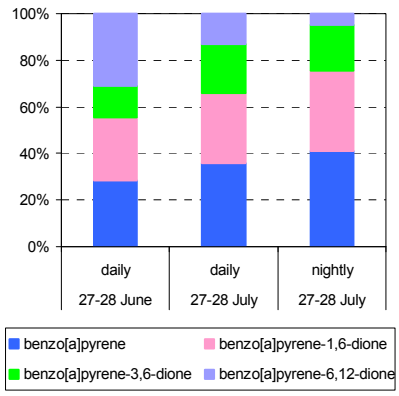



***Fig. 4.9.*** *Relative content of B[a]P and its oxy-derivatives in the atmosphere over Milan for various dates in day and night.*

All B[a]P-diones concentrations correlate well with ozone concentrations ($r^2$ from 0.47 to 0.58). In addition for B[a]P-6,12-dione high enough correlation with solar radiation level takes place ($r^2$ = 0.44). The results of [*Lazzati,* 2009] show that B[a]P oxy-derivatives are (at least partly) formed due to atmospheric oxidation, and the oxidation process is affected by different environmental parameters (ozone concentrations, solar radiation, etc.).

The investigations of kinetics of heterogenic oxidation reaction for particle-bound B[a]P are documented in a number of papers ([*Alebić-Juretić*, 2000; *Pöschl et al*., 2001; *Kwamena et al.,* 2004; *Kahan et al.,* 2006; *Perraudin et al.,* 2007] and others). It is worth noting that model experiments described in the original papers were devoted to the determination of reaction rates with pure ozone with concentrations being much higher that environmental ones. The presence of other atmospheric reactants can essentially change the results.

The heterogenic reaction between atmospheric ozone and particle-bound B[a]P goes into two stages. First, ozone is absorbed from gaseous phase and then the reaction with sorbed ozone takes place on the aerosol surface [*Lazzati,* 2009]. For the description of absorption the Langmuir – Hinshelwood model can be used. For such reaction mechanism non-linear dependence of reaction rate of pseudo-first order on atmospheric ozone concentrations takes place as shown in Fig. 4.10a [*Pöschl et al.*, 2001, *Kwamena et al.,* 2004*, Kahan et al.,* 2006].

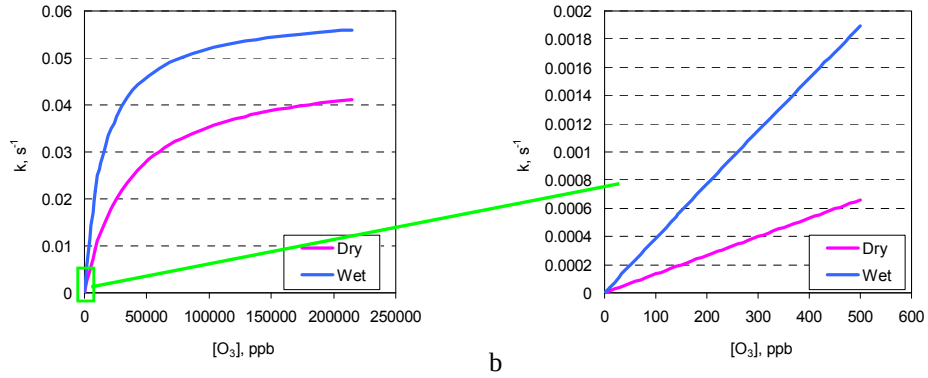



***Fig. 4.10.*** *Dependence of reaction rate of pseudo-first order on ozone concentrations and air moisture (dry – RH=1%, wet – RH = 72%) on acelaic acid aerosol: a – wide range of ozone concentrations, b – range of ozone concentrations typical for the atmosphere (according to [Kwamena et al., 2004]).*

Besides, the plot demonstrates essential influence of air moisture on reaction rate – the difference between reaction rates for dry conditions (*RH* = 1%) and wet conditions (*RH* = 72%) reaches 3 times and more.

It should be stressed that the experiments described in [*Kwamena et al.,* 2004] were performed for very high ozone concentrations (over 5000 ppb). At the same time according to CCC data [*Hjellbrekke and Fjæraa,* 2011b] ozone concentration levels measured at sites of the EMEP monitoring network do not exceed 50 ppb. In the urban and neighbouring regions ozone concentrations can raise up to 100 – 200 ppb and sometimes higher (the sub-range marked green in Fig. 4.10a). The plot of the dependence of reaction rates on ozone concentrations in this range is linear with high accuracy (Fig. 4.10b). So, under environmental conditions the oxidation process can be described by reaction rate of the second order with respect to atmospheric ozone concentrations. This approach is used directly in some investigations [*Alebić-Juretić et al.,* 1990; *Wu et al.,* 1984].

On the basis of the data from various literature sources [*Kwamena et al.*, 2004, *Zhou et al*., 2011, *Perraudin et al.*, 2007] reaction rates of pseudo-first order for oxidation of B[a]P sorbed on particles of various origin with the atmospheric ozone were calculated. The results are summarized on the plot in Fig. 4.11.

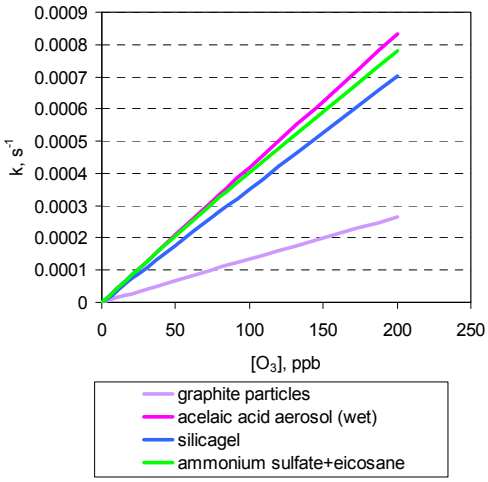



***Fig. 4.11.*** *Reaction rates of pseudo-first order for the oxidation of B[a]P sorbed on particles of various nature by ozone (calculated by literature data).*

It is seen that the interaction of particle-bound B[a]P with ozone is most intensive at organic aerosol (acelaic acid). Among non-organic aerosols maximum reaction rate is obtained for silicagel. For particles containing elemental

carbon (graphite) reaction rate is considerably lower (2 – 5 times) than for silicagel particles but is comparable with reaction rate on the particles containing ammonium sulfate. Evidently, the presence of organic matter in the aerosol particles makes a considerable impact on the rate of the reaction between B[a]P and ozone.

The above degradation rates for reactions of B[a]P with ozone were tested by several models [*Friedman and Selin,* 2012; *Mattias et al*., 2009; *Kwamena et al*., 2007].

These investigations show that reactions of B[a]P with ozone play considerable role in the environmental fate of this pollutant. Inclusion of description of these reactions in transport model can additionally refine the agreement between measurements and model predictions of B[a]P pollution levels in Europe. This work is planned to be done in the nearest future.

***Heterogenic B[a]P reactions with atmospheric nitrogen compounds.*** Similarly to Oxy-PAHs, nitrated polycyclic aromatic hydrocarbons (Nitro-PAHs) can be either directly emitted from combustion sources (vehicle exhaust; industrial emissions and emissions from domestic residential heating/cooking and wood burning [EHC 229: Selected Nitro-and Nitro-oxyPAHs, 2003]) or by chemical reaction with atmospheric reactants.

In [*Bamford et al.,* 2003] urban dust was investigated from the viewpoint of presence of wide spectrum of nitro-PAHs. The results of this work manifest that the content of 6-Nitrobenzo[a]pyrene in urban dust considerably exceeds the content of other nitro-derivatives - 1-Nitrobenzo[a]pyrene и 3-Nitrobenzo[a]pyrene. So, it can be concluded that only one of possible nitro-derivatives of B[a]P (6-Nitrobenzo[a]pyrene) is mostly identified in the atmosphere. It should be noted that according to International Agency for Research on Cancer (IARC) this pollutant is classified as a carcinogen of Category 3 with reported human mutagen data.

Measured 6-Nitrobenzo[a]pyrene concentrations in the atmosphere over Tokyo according to data from [*Matsushita and Iida,* 1986] was found to be 270 pg/m$^3$, or, according to more recent investigations [*Ishii et al*., 2000], from 200 to 470 pg/m$^3$. In Kanazava downtown this compound was detected with concentrations about 2.3 pg/m$^3$ [*Araki et al*., 2009]. In the atmosphere of Tieling (China) in the period from June 2003 to May 2004 annual averages of 6-Nitrobenzo[a]pyrene concentrations ranged from 30.9 to 56.2 pg/m$^3$ [*Tang et al*., 2009]. Similar levels of this pollutant (from 0 to 92 pg/m$^3$ in PM10 and 0 to 71 pg/m$^3$ in PM2.5) are measured in Europe (Montolibretti, Italy, 2005) [*Cecinato et al,* 2008].

There is much less information on rates of reactions with nitrogen compounds compared with those with ozone. Only reaction rates on silicagel (mineral aerosol) and several types of elemental carbon were found in literature. Second order rate constants for B[a]P interaction with $NO_2$ are given in Table 4.2.

***Table 4.2.*** *Second order rate constants for B[a]P reaction with $NO_2$ on aerosol of different types, cm$^3$/molecule/s.*

| Source | Silicagel | Graphite | Soot |
|---|---|---|---|
| *Calvert et al.,* 2002 | | | $3.7 \times 10^{-18} – 6.2 \times 10^{-19}$ |
| *Perraudin et al.,* 2007 | $9.3 \times 10^{-15}$ | $7.7 \times 10^{-17}$ | |
| *Cazaunau et al.,* 2010 | $5.8 \times 10^{-16}$ | | |
| *Guo and Kamens,* 1991 | | | $5.7 \times 10^{-19}$ |

It is seen that the values of second-order rate constants for one and the same particle type can differ by one or two orders of magnitude. The book [*Calvert et al.,* 2002] presents also rate constants for reactions with $HNO_3$ ($3.4\times10^{-19}$) and $N_2O_5$ ($2.9\times10^{-18}$ – $4.7\times10^{-18}$). The scattering between different literature data on first order rate constants for reactions between B[a]P and $NO_2$ can be seen from Table 4.3.

Here scattering between rate constants obtained by different authors reaches four orders of magnitude.

***Table 4.3.*** *First order rate constants for B[a]P reaction with $NO_2$ on elemental carbon aerosol, 1/s.*

| Solid surface in experiment | Rate constant | Source |
|---|---|---|
| Ethylene flame soot | $2.5 \times 10^{-8}$ | *Buthlet and Crosley,* 1981 |
| Wood smoke particles | $1.3 \times 10^{-5}$ | *Kamens et al.,* 1985 |
| Diesel soot | $1.0 \times 10^{-4}$ | *Esteve et al.,* 2006 |
| Kerosene flame soot | $2.1 \times 10^{-7}$ | *Nguyen et al.,* 2009 |
| Graphite particles | $1.9 \times 10^{-4}$ | *Esteve et al.,* 2004 |
| | $1.9 \times 10^{-4}$ | *Perraudin et al.,* 2007 |

Comparison of reaction rates of oxidation and nitration as well as of concentrations of reaction products allows one to suppose that nitration goes much slower than oxidation. Besides, the information on nitration reactions is far of being complete. So, it can be concluded that at present state of knowledge involving nitration reactions to model description of B[a]P long-range transport is not reasonable.

## *Concluding remarks*

- Main meteorological processes determining POP fate in the environment are gaseous exchange with underlying surface and degradation in the atmosphere. Both these processes are strongly temperature-dependent. Since these two processes are concurring, joint effect of them may be different for different pollutants. Thus, temperature increase leads to the increase of PCDD/F concentrations in the atmosphere, but B[a]P concentrations are decreasing with temperature increase.
- Along with the change of meteorological conditions, attendant circumstances such as the probability of forest fires due to temperature increase in particular locations should be taken into account for evaluating the influence of climate change at environmental contamination by POPs.
- The influence of temperature changes to pollution levels for B[a]P is spatially inhomogeneous. Calculations show that maximum sensitivity to temperature changes is characteristic of Western Europe and minimal – of Central and Eastern Europe.
- Interaction of B[a]P with active atmospheric reactants can play essential role in its long-range transport.
- Degradation products (nitro- and oxy-derivatives of B[a]P) are also dangerous for human health and the environment. Measurements show the presence of these products in the atmosphere in Europe and Asia.
- Reaction rates of oxidation and nitration are essentially dependent on the nature of atmospheric aerosol, as well as environmental conditions (humidity, ambient temperature, etc.). Experimental data for these rate constants found in the literature are subject to strong variability. Rate constants for nitration are known only for mineral particles and elemental carbon.

# 5. FUTURE ACTIVITIES

In order to further improve evaluation of POP pollution of the EMEP region the following activities of MSC-E and CCC are proposed for 2013:

### *Ongoing activities*

- Review, store and make available EMEP monitoring data for the modelling centres and Parties;
- Publish the validated annual data and contribute to preparation, review and assessments of observation data presented in the series of EMEP reports;
- Provide training/guidance to Parties to establish monitoring activities in compliance with the EMEP monitoring strategy;
- Address global scale integration of quality assessment/quality control (QA/QC) activities of regional monitoring programmes, including standards for metadata provision and intercomparisons (in collaboration with the Task Force on Hemispheric Transport of Air Pollution);
- Maintain close interaction with relevant organizations and bodies in relation to integration of observations, including monitoring efforts under other Convention bodies e.g., the ICPs and national monitoring obligations to European Commission Directives, as well as activities undertaken by EEA, WMO, the OSPAR Commission, the Baltic Marine Environment Protection Commission (HELCOM), the United Nations Environment Programme (UNEP), AMAP, Nitrogen in Europe(NinE), GMES/GEOSS and others;
- Evaluate air concentrations, deposition fluxes and transboundary transport of POPs (PAHs, PCDD/Fs, and HCB) for 2011 with spatial resolution 50km × 50km;
- Calculate POP dispersion on a global scale with the help of global EMEP model (GLEMOS) for the evaluation of initial and boundary conditions and contributions of intercontinental transport to pollution levels in the EMEP domain and in remote regions (the Arctic) with spatial resolution 1°x 1°;
- Prepare input data required for global/regional/local modelling (emission, meteorological, and geophysical data);
- Contribute to the effect community work with information on ecosystem-dependent deposition fluxes of POPs to different land use types to support evaluation of the pollutants adverse effect on human health and the environment;
- Support countries with information required for air quality management and implementation of the CLRTAP Protocol on POPs with special emphasis to EECCA countries;
- Cooperate with the CLRTAP subsidiary bodies (WGSR, WGE), EMEP task forces (TFHTAP, TFMM), and relevant international organizations.

### *New (research and development) activities*

Monitoring of POPs:

- Improve the EMEP database to include more statistical opportunities for aggregated data, further develop the plotting routines and develop improved export routines for data download for modellers;

- Evaluate new measurements data of POPs from Eastern Europe, the Caucasus and Central Asia to assess the relative importance of the different pollutants and the main source regions;

Global/regional/local modelling:

- Further develop the GLEMOS multi-scale modelling system including improvement of the multi-media approach and refinement of the pollutant specific processes;

- Incorporate data on aerosols and atmospheric reactants based on external datasets or simplified chemical modules for improving evaluation of POP pollution levels;

- Further develop and test the integrated monitoring/modelling/emission approach for POPs including the adjoint modelling;

- Initiate model assessment of POP pollution on a country scale;

Climate change impact on POP long-range transport and fate:

- Perform modelling of climate change effects on POP transport and fate for selected periods using the climate change scenarios data.

# CONCLUSIONS

This Status Report presents the progress in the evaluation of pollution levels and transboundary transport of POPs within the EMEP region in 2012. The main conclusions of the work carried out by CCC and MSC-E are summarized below.

## *Polychlorinated aromatic hydrocarbons*

- Environmental contamination by PAHs is a subject of a lot of national and international legislations. In most cases B[a]P is viewed as an indicator of PAH contamination. In particular, target value for B[a]P of 1 ng/m$^3$ (annual average) is established in the EU Directive 2004/107/EC of the European Parliament and of the Council. Besides, admissible B[a]P levels are established in a lot of national legislations in Europe, the US and Canada.

- The analysis of contamination in 2010 based on the combined use of modelling and monitoring information indicates several areas with essential exceedances of B[a]P concentrations over EU target value which are populated at least by 15 million people.

- Temporal variability of B[a]P emissions is essential for the assessment of B[a]P contamination. As a result of emission variability together with seasonal variations of environmental processes (degradation, gas/particle partitioning, wet deposition, gas exchange with underlying surface, etc.), winter concentrations of B[a]P in air can exceed annual averages several times. Emission variability can also noticeably change annual averages of air concentrations (up to 40% – 50%). For evaluating emission temporal variations the information on emissions from various source categories is required.

- Spatial variations of air concentrations can be even more valuable. According to measurement data, the differences of B[a]P air concentrations between neighbouring areas of different character (from urban to background) can reach an order of magnitude. Further evaluation of contamination in heavy loaded regions by modelling with finer spatial resolution could improve evaluation of pollution levels.

- The analysis of temporal trends of B[a]P contamination in the EMEP region for the period from 1990 to 2010 shows overall reduction of air concentrations by about 30%. However, this reduction is not homogeneous among the EMEP countries. In particular, strong emission reduction (more than 75% that is, about 4 times) is characteristic of two countries (the UK and Germany). Reduction by 75% – 50% (2 – 4 times) takes place in 8 countries. In 10 countries air concentrations either have not been changed since 1990 or even become higher.

- Transboundary transport plays considerable role in the contamination of the EMEP region by PAHs. In particular, only 12 countries are responsible for 80% of total value of deposition of B[a]P to the combined area of all EMEP countries. Further, the contributions of transboundary transport to deposition exceed 60% for 23 EMEP countries. It should be noted that even for countries with low average value of contributions of transboundary transport, locally these contributions may be essential.

- Concentrations and chemical composition of the atmospheric aerosol are essential for evaluation of B[a]P degradation process. Particularly, B[a]P degradation and chemical transformation products may be at least as toxic as B[a]P itself. Reaction rates between particle-bound B[a]P and ozone/NOx strongly depend on chemical nature of particles-carriers.

## *Polychlorinated dibenzo(p)dioxins and dibenzofurans*

- Since the behaviour of different PCDD/F congeners in the environment is different due to their specific physical-chemical properties, model evaluation of 17 PCDD/F toxic congeners is preformed for the evaluation of total PCDD/F toxicity within the EMEP domain.

- Preparation of congener-specific emission data for modelling is made using inverse modelling approach. It is found that for reasonable agreement between measurements and calculations of total toxicity of PCDD/F mixture in the atmosphere emission data should be enlarged about 5 times, which is in line with the estimates of emission uncertainties.

- Since measurements of PCDD/Fs are not included into regular EMEP monitoring programme, to refine monitoring/modelling/emission evaluation of PCDD/F MSC-E has used available measurement data from national and international projects and campaigns obtained by literature search.

- Modelling of 17 PCDD/F congeners in 2010 is performed by MSCE-POP regional model with resolution 50×50 km using corrected emissions of 17 PCDD/F toxic congeners. Initial and boundary conditions for regional simulations are generated by hemispheric model runs for the period from 1970 to 2010. These simulations show reasonable agreement with measurement data. The agreement between calculated and measured total toxicities within a factor of 2 is obtained for more than 50% of available measurements at background locations.

- Relatively high levels of PCDD/F air concentrations (20 fg TEQ/$m^3$ and higher) are calculated for some regions in Central and Eastern Europe. In clean regions of Europe PCDD/F levels are considerably lower (less than 5 fg TEQ/$m^3$).

- The evaluation of source-receptor relationships for PCDD/Fs in 2010 shows that the contribution of re-emission exceeds the half of total deposition to the area of the EMEP countries. More than 80% of total deposition over the area of all EMEP countries from anthropogenic sources are determined by 12 countries only. For about 20 countries the contribution of external sources (transboundary transport) to deposition from anthropogenic sources over their area is accounted for 50% and more. Similar to B[a]P contributions of transboundary transport in a country are subject to strong spatial variations.

## *Hexachlorobenzene*

- Spatial pattern of HCB atmospheric concentrations is formed mainly by secondary emission sources, that is, by re-emission from HCB historically accumulated in the surface media. Hence, for simulations of HCB contamination levels both in the EMEP region and over the entire globe consideration of historical HCB accumulation is of particular importance.

- Emission scenario for historical and contemporary emissions worked out by MSC-E allows obtaining reasonable agreement between calculated and measured HCB air concentrations at the sites of the EMEP monitoring network. About ¾ of measurements agree with calculations within a factor of two.

- Within the Northern Hemisphere there exists background level of air concentrations of HCB in the regions free from emission sources depending on latitude. For low and temperate latitudes

this level amounts to 10 – 15 pg/m$^3$, which is comparable in order of magnitude with concentration levels in contaminated regions (20 – 30 pg/m$^3$). This is conditioned by extremely high persistence of HCB in the atmosphere.

- According to emission data used in modelling, the influence of contemporary anthropogenic emissions in the EMEP region to air concentrations is relatively small. Maximum contributions of contemporary EMEP emissions to air contamination in the EMEP region at one location exceed 20 pg/m$^3$ (the level comparable with air concentrations in highly polluted regions of Central and Eastern Europe).

- Among important directions of further investigation of HCB transport and accumulation in the environment the following activities should be mentioned: elaboration of vegetation module for GLEMOS modelling system, collection measurement data on contamination levels of HCB in various environmental media and usage these data for calibration of the model and refinement of emission scenarios.

## *POP pollution and climate change inter-linkages*

- Main meteorological processes determining POP fate in the environment are gaseous exchange with underlying surface and degradation in the atmosphere. Both these processes are strongly temperature-dependent. Since these two processes are concurring, joint effect of them may be different for different pollutants. Thus, temperature increase leads to the increase of PCDD/F concentrations in the atmosphere but B[a]P concentrations are decreasing with temperature increase.

- Along with the change of meteorological conditions, attendant circumstances such as the probability of originating forest fires due to temperature increase in particular locations should be taken into account for evaluating the influence of climate change at environmental contamination by POPs.

- The influence of temperature changes to pollution levels for B[a]P is spatially inhomogeneous. Calculations show that maximum sensitivity to temperature changes is characteristic of Western Europe and minimal – of Central and Eastern Europe.

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# ANNEX A

# COUNTRY-TO-COUNTRY DEPOSITION MATRICES FOR 2010

***Table A.1***. *Codes of countries*

| Country/Region/Sea | Code | Country/Region/Sea | Code |
|---|---|---|---|
| Albania | AL | Monaco | MC |
| Armenia | AM | Montenegro | ME |
| Austria | AT | Netherlands | NL |
| Azerbaijan | AZ | Norway | NO |
| Belarus | BY | Poland | PL |
| Belgium | BE | Portugal | PT |
| Bosnia and Herzegovina | BA | Republic of Moldova | MD |
| Bulgaria | BG | Romania | RO |
| Croatia | HR | Russian Federation (European part) | RU |
| Cyprus | CY | Russian Federation (Asian part) | RUA |
| Czech Republic | CZ | Serbia | RS |
| Denmark | DK | Slovakia | SK |
| Estonia | EE | Slovenia | SI |
| Finland | FI | Spain | ES |
| France | FR | Sweden | SE |
| Georgia | GE | Switzerland | CH |
| Germany | DE | The Former Yugoslav Republic of Macedonia | MK |
| Greece | GR | Tajikistan | TJ |
| Hungary | HU | Turkey | TR |
| Iceland | IS | Turkmenistan | TM |
| Ireland | IE | Ukraine | UA |
| Italy | IT | United Kingdom | GB |
| Kazakhstan | KZ | Uzbekistan | UZ |
| Kyrgyzstan | KY | Baltic Sea | BAS |
| Latvia | LV | Black Sea | BLS |
| Lithuania | LT | Caspian Sea | CAS |
| Luxembourg | LU | North Sea | NOS |
| Malta | MT | Mediterranean Sea | MDT |

***Table A.2**. Matrix of B[a]P country-to-country deposition in 2010, kg/y*

Receptors ↓ Emitters →

| | AL | AM | AT | AZ | BA | BE | BG | BY | CH | CY | CZ | DE | DK | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AL** | **433.89** | 0.00 | 0.92 | 0.03 | 4.61 | 0.54 | 15.97 | 0.61 | 0.04 | 0.00 | 1.75 | 7.29 | 0.51 | **AL** |
| **AM** | 0.01 | **0.01** | 0.00 | 56.60 | 0.00 | 0.00 | 0.07 | 0.02 | 0.00 | 0.01 | 0.01 | 0.03 | 0.00 | **AM** |
| **AT** | 3.14 | 0.00 | **508.40** | 0.16 | 15.14 | 9.94 | 7.83 | 6.45 | 2.09 | 0.00 | 126.47 | 500.95 | 7.16 | **AT** |
| **AZ** | 0.03 | 0.00 | 0.01 | **862.22** | 0.02 | 0.01 | 0.26 | 0.25 | 0.00 | 0.01 | 0.04 | 0.15 | 0.02 | **AZ** |
| **BA** | 24.98 | 0.00 | 10.88 | 0.07 | **666.61** | 1.47 | 21.50 | 2.60 | 0.13 | 0.00 | 16.21 | 36.69 | 2.28 | **BA** |
| **BE** | 0.07 | 0.00 | 1.99 | 0.02 | 0.31 | **614.46** | 0.22 | 3.19 | 0.35 | 0.00 | 5.39 | 245.04 | 6.66 | **BE** |
| **BG** | 16.13 | 0.00 | 3.14 | 0.71 | 7.23 | 1.20 | **2024.4** | 8.31 | 0.07 | 0.04 | 9.65 | 20.99 | 2.49 | **BG** |
| **BY** | 2.46 | 0.00 | 7.18 | 1.90 | 6.62 | 4.37 | 16.15 | **2629.9** | 0.20 | 0.01 | 27.04 | 78.33 | 18.69 | **BY** |
| **CH** | 0.23 | 0.00 | 11.89 | 0.02 | 1.67 | 4.24 | 0.62 | 1.37 | **24.40** | 0.00 | 6.90 | 141.94 | 1.74 | **CH** |
| **CY** | 0.02 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 | 0.21 | 0.06 | 0.00 | **10.47** | 0.03 | 0.09 | 0.02 | **CY** |
| **CZ** | 2.08 | 0.00 | 69.97 | 0.28 | 7.29 | 8.25 | 7.05 | 16.26 | 0.93 | 0.00 | **1006.6** | 417.15 | 11.53 | **CZ** |
| **DE** | 2.61 | 0.00 | 129.30 | 0.73 | 10.62 | 243.19 | 7.50 | 72.65 | 15.80 | 0.00 | 302.42 | **9675.1** | 160.77 | **DE** |
| **DK** | 0.09 | 0.00 | 1.55 | 0.09 | 0.34 | 9.28 | 0.36 | 7.48 | 0.07 | 0.00 | 6.47 | 79.69 | **513.96** | **DK** |
| **EE** | 0.19 | 0.00 | 1.33 | 0.24 | 0.66 | 1.81 | 1.34 | 52.78 | 0.05 | 0.00 | 4.96 | 25.84 | 10.52 | **EE** |
| **ES** | 0.48 | 0.00 | 2.70 | 0.06 | 1.90 | 16.46 | 1.05 | 3.96 | 0.35 | 0.00 | 5.88 | 90.16 | 10.44 | **ES** |
| **FI** | 0.30 | 0.00 | 3.37 | 0.57 | 1.35 | 6.72 | 2.31 | 106.87 | 0.16 | 0.00 | 12.59 | 78.56 | 27.36 | **FI** |
| **FR** | 2.06 | 0.00 | 24.81 | 0.20 | 10.43 | 216.14 | 5.39 | 20.86 | 10.55 | 0.00 | 50.78 | 1031.5 | 33.29 | **FR** |
| **GB** | 0.19 | 0.00 | 2.36 | 0.14 | 0.56 | 35.04 | 0.98 | 8.94 | 0.28 | 0.00 | 9.41 | 152.24 | 39.07 | **GB** |
| **GE** | 0.14 | 0.00 | 0.03 | 77.59 | 0.06 | 0.03 | 1.06 | 0.40 | 0.00 | 0.03 | 0.09 | 0.34 | 0.04 | **GE** |
| **GR** | 40.57 | 0.00 | 1.73 | 0.32 | 4.68 | 0.89 | 216.23 | 3.04 | 0.06 | 0.02 | 4.68 | 14.17 | 1.58 | **GR** |
| **HR** | 14.54 | 0.00 | 26.75 | 0.09 | 175.63 | 1.80 | 18.81 | 3.36 | 0.17 | 0.00 | 22.73 | 52.53 | 2.30 | **HR** |
| **HU** | 11.25 | 0.00 | 52.63 | 0.30 | 46.98 | 3.26 | 43.09 | 10.92 | 0.24 | 0.00 | 61.72 | 78.81 | 4.66 | **HU** |
| **IE** | 0.06 | 0.00 | 0.15 | 0.02 | 0.08 | 3.20 | 0.31 | 1.68 | 0.01 | 0.00 | 0.62 | 13.18 | 5.35 | **IE** |
| **IS** | 0.07 | 0.00 | 0.46 | 0.09 | 0.19 | 3.22 | 0.46 | 4.33 | 0.04 | 0.00 | 1.91 | 25.28 | 6.57 | **IS** |
| **IT** | 21.47 | 0.00 | 63.14 | 0.19 | 56.69 | 8.58 | 23.07 | 7.46 | 4.49 | 0.00 | 28.67 | 205.37 | 7.16 | **IT** |
| **KY** | 0.02 | 0.00 | 0.01 | 0.99 | 0.02 | 0.00 | 0.11 | 0.08 | 0.00 | 0.00 | 0.03 | 0.08 | 0.02 | **KY** |
| **KZ** | 0.95 | 0.00 | 1.51 | 22.85 | 1.36 | 1.18 | 6.92 | 20.30 | 0.06 | 0.02 | 5.01 | 17.96 | 4.57 | **KZ** |
| **LT** | 0.79 | 0.00 | 3.56 | 0.41 | 2.02 | 2.81 | 2.90 | 223.10 | 0.12 | 0.00 | 14.44 | 50.98 | 15.71 | **LT** |
| **LU** | 0.01 | 0.00 | 0.25 | 0.00 | 0.04 | 6.96 | 0.03 | 0.30 | 0.05 | 0.00 | 0.58 | 29.17 | 0.34 | **LU** |
| **LV** | 0.55 | 0.00 | 2.79 | 0.36 | 1.56 | 3.10 | 3.05 | 148.94 | 0.10 | 0.00 | 11.06 | 49.78 | 18.91 | **LV** |
| **MC** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | **MC** |
| **MD** | 0.94 | 0.00 | 0.48 | 0.70 | 0.87 | 0.27 | 12.45 | 8.44 | 0.01 | 0.01 | 1.79 | 4.78 | 0.61 | **MD** |
| **ME** | 55.95 | 0.00 | 0.93 | 0.01 | 25.91 | 0.35 | 6.25 | 0.49 | 0.03 | 0.00 | 1.61 | 5.80 | 0.44 | **ME** |
| **MK** | 53.03 | 0.00 | 0.76 | 0.03 | 2.59 | 0.32 | 61.32 | 0.88 | 0.02 | 0.00 | 1.88 | 5.22 | 0.48 | **MK** |
| **MT** | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | **MT** |
| **NL** | 0.05 | 0.00 | 1.64 | 0.03 | 0.22 | 175.18 | 0.18 | 2.92 | 0.20 | 0.00 | 4.85 | 277.34 | 12.37 | **NL** |
| **NO** | 0.21 | 0.00 | 3.70 | 0.54 | 0.82 | 13.22 | 1.86 | 46.62 | 0.18 | 0.00 | 17.52 | 112.78 | 82.93 | **NO** |
| **PL** | 6.75 | 0.00 | 45.04 | 2.02 | 18.84 | 22.66 | 28.51 | 375.06 | 1.34 | 0.01 | 405.79 | 623.66 | 117.88 | **PL** |
| **PT** | 0.03 | 0.00 | 0.21 | 0.01 | 0.11 | 2.03 | 0.08 | 0.63 | 0.02 | 0.00 | 0.52 | 9.55 | 1.82 | **PT** |
| **RO** | 25.08 | 0.00 | 11.61 | 2.16 | 30.16 | 3.59 | 450.51 | 32.25 | 0.23 | 0.05 | 33.85 | 71.65 | 7.06 | **RO** |
| **RS** | 62.89 | 0.00 | 9.03 | 0.15 | 89.14 | 1.85 | 142.86 | 5.18 | 0.14 | 0.00 | 20.08 | 41.22 | 3.01 | **RS** |
| **RU** | 11.22 | 0.00 | 27.84 | 126.64 | 20.30 | 29.23 | 81.66 | 1022.0 | 1.02 | 0.20 | 97.20 | 402.88 | 124.57 | **RU** |
| **SE** | 0.52 | 0.00 | 5.79 | 0.83 | 1.52 | 20.83 | 3.52 | 119.30 | 0.31 | 0.00 | 27.19 | 215.54 | 219.91 | **SE** |
| **SI** | 2.77 | 0.00 | 45.33 | 0.05 | 20.36 | 1.06 | 5.23 | 1.75 | 0.13 | 0.00 | 9.95 | 37.14 | 0.98 | **SI** |
| **SK** | 3.79 | 0.00 | 22.61 | 0.25 | 12.14 | 2.20 | 15.13 | 11.04 | 0.18 | 0.00 | 93.98 | 55.68 | 5.10 | **SK** |
| **TJ** | 0.01 | 0.00 | 0.00 | 0.49 | 0.01 | 0.00 | 0.04 | 0.02 | 0.00 | 0.00 | 0.01 | 0.02 | 0.00 | **TJ** |
| **TM** | 0.03 | 0.00 | 0.02 | 4.04 | 0.03 | 0.01 | 0.18 | 0.25 | 0.00 | 0.00 | 0.06 | 0.19 | 0.05 | **TM** |
| **TR** | 5.59 | 0.00 | 2.20 | 16.04 | 3.82 | 1.30 | 124.00 | 20.03 | 0.08 | 4.42 | 6.22 | 20.33 | 2.73 | **TR** |
| **UA** | 15.25 | 0.00 | 13.68 | 17.67 | 23.07 | 6.53 | 123.81 | 390.85 | 0.35 | 0.18 | 50.33 | 120.03 | 20.75 | **UA** |
| **UZ** | 0.06 | 0.00 | 0.05 | 2.42 | 0.06 | 0.03 | 0.40 | 0.51 | 0.00 | 0.00 | 0.13 | 0.42 | 0.10 | **UZ** |
| | **AL** | **AM** | **AT** | **AZ** | **BA** | **BE** | **BG** | **BY** | **CH** | **CY** | **CZ** | **DE** | **DK** | |

***Table A.2**. Matrix of B[a]P country-to-country deposition in 2010, kg/y (continued)*

Receptors ↓ Emitters →

| | EE | ES | FI | FR | GB | GE | GR | HR | HU | IE | IS | IT | KY | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AL** | 0.25 | 0.70 | 0.22 | 1.48 | 0.17 | 0.00 | 50.47 | 2.46 | 4.78 | 0.04 | 0.00 | 127.73 | 0.00 | **AL** |
| **AM** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.24 | 0.05 | 0.00 | 0.02 | 0.00 | 0.00 | 0.07 | 0.00 | **AM** |
| **AT** | 3.00 | 1.98 | 2.69 | 11.60 | 3.74 | 0.01 | 2.29 | 33.50 | 163.39 | 0.78 | 0.01 | 210.98 | 0.02 | **AT** |
| **AZ** | 0.03 | 0.01 | 0.03 | 0.01 | 0.01 | 4.19 | 0.15 | 0.02 | 0.08 | 0.00 | 0.00 | 0.23 | 0.04 | **AZ** |
| **BA** | 1.19 | 1.33 | 1.00 | 2.71 | 0.69 | 0.01 | 12.78 | 113.25 | 83.87 | 0.17 | 0.00 | 187.26 | 0.01 | **BA** |
| **BE** | 1.60 | 4.02 | 1.57 | 39.35 | 10.15 | 0.00 | 0.07 | 0.65 | 3.30 | 1.26 | 0.01 | 10.48 | 0.00 | **BE** |
| **BG** | 1.71 | 0.60 | 1.29 | 1.76 | 0.57 | 0.12 | 98.29 | 5.30 | 40.57 | 0.12 | 0.00 | 54.88 | 0.02 | **BG** |
| **BY** | 37.18 | 1.60 | 16.67 | 3.95 | 2.38 | 0.24 | 4.93 | 7.58 | 52.46 | 0.53 | 0.01 | 35.59 | 0.17 | **BY** |
| **CH** | 0.93 | 3.45 | 0.76 | 34.62 | 2.26 | 0.00 | 0.23 | 3.78 | 5.84 | 0.54 | 0.00 | 235.03 | 0.00 | **CH** |
| **CY** | 0.02 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.27 | 0.01 | 0.07 | 0.00 | 0.00 | 0.18 | 0.00 | **CY** |
| **CZ** | 4.25 | 2.17 | 3.34 | 9.32 | 3.36 | 0.03 | 2.25 | 12.15 | 110.79 | 0.65 | 0.01 | 61.23 | 0.02 | **CZ** |
| **DE** | 29.49 | 26.81 | 24.14 | 170.97 | 46.60 | 0.08 | 2.47 | 17.76 | 104.03 | 8.08 | 0.10 | 250.75 | 0.08 | **DE** |
| **DK** | 6.24 | 0.93 | 6.43 | 3.86 | 4.79 | 0.01 | 0.09 | 0.52 | 5.40 | 0.88 | 0.02 | 4.14 | 0.01 | **DK** |
| **EE** | **681.60** | 0.36 | 42.21 | 1.27 | 1.08 | 0.03 | 0.42 | 0.95 | 6.17 | 0.25 | 0.01 | 4.35 | 0.04 | **EE** |
| **ES** | 2.37 | **4700.2** | 2.36 | 61.27 | 7.56 | 0.01 | 0.39 | 2.85 | 7.30 | 1.92 | 0.02 | 50.85 | 0.01 | **ES** |
| **FI** | 304.44 | 1.17 | **1580.0** | 4.01 | 4.68 | 0.08 | 0.67 | 2.13 | 13.75 | 1.30 | 0.07 | 8.37 | 0.13 | **FI** |
| **FR** | 11.69 | 183.31 | 11.14 | **1718.5** | 51.41 | 0.03 | 1.94 | 19.37 | 41.97 | 11.35 | 0.08 | 560.35 | 0.02 | **FR** |
| **GB** | 8.74 | 15.62 | 9.44 | 36.87 | **705.58** | 0.02 | 0.37 | 0.95 | 6.51 | 56.25 | 0.12 | 10.02 | 0.02 | **GB** |
| **GE** | 0.03 | 0.02 | 0.02 | 0.04 | 0.01 | **62.13** | 0.90 | 0.04 | 0.23 | 0.00 | 0.00 | 1.27 | 0.01 | **GE** |
| **GR** | 0.91 | 1.00 | 0.74 | 1.90 | 0.35 | 0.04 | **1196.6** | 3.37 | 15.32 | 0.08 | 0.00 | 77.15 | 0.01 | **GR** |
| **HR** | 1.20 | 1.52 | 1.03 | 2.98 | 0.83 | 0.01 | 9.32 | **464.98** | 203.93 | 0.21 | 0.00 | 217.51 | 0.01 | **HR** |
| **HU** | 2.36 | 1.47 | 1.91 | 3.52 | 1.53 | 0.03 | 13.34 | 82.59 | **2024.4** | 0.35 | 0.00 | 117.71 | 0.01 | **HU** |
| **IE** | 1.66 | 5.66 | 1.91 | 5.02 | 30.43 | 0.00 | 0.15 | 0.09 | 0.54 | **299.96** | 0.05 | 0.75 | 0.01 | **IE** |
| **IS** | 3.55 | 1.76 | 4.00 | 1.95 | 6.42 | 0.01 | 0.19 | 0.27 | 1.61 | 4.46 | **13.11** | 1.69 | 0.03 | **IS** |
| **IT** | 4.38 | 17.13 | 3.74 | 42.37 | 3.77 | 0.02 | 24.23 | 98.62 | 98.67 | 0.89 | 0.01 | **10009** | 0.03 | **IT** |
| **KY** | 0.02 | 0.01 | 0.02 | 0.01 | 0.00 | 0.05 | 0.08 | 0.02 | 0.07 | 0.00 | 0.00 | 0.22 | **922.43** | **KY** |
| **KZ** | 8.93 | 0.74 | 7.35 | 1.36 | 1.11 | 0.96 | 3.44 | 1.49 | 8.98 | 0.39 | 0.02 | 13.03 | 210.40 | **KZ** |
| **LT** | 24.11 | 0.76 | 10.35 | 2.29 | 1.48 | 0.05 | 1.15 | 2.68 | 17.45 | 0.33 | 0.01 | 12.82 | 0.06 | **LT** |
| **LU** | 0.12 | 0.44 | 0.11 | 5.08 | 0.48 | 0.00 | 0.01 | 0.08 | 0.33 | 0.08 | 0.00 | 1.61 | 0.00 | **LU** |
| **LV** | 99.88 | 0.72 | 19.88 | 2.34 | 1.74 | 0.04 | 0.95 | 2.08 | 13.69 | 0.38 | 0.01 | 10.17 | 0.08 | **LV** |
| **MC** | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.24 | 0.00 | **MC** |
| **MD** | 0.66 | 0.12 | 0.53 | 0.27 | 0.13 | 0.10 | 2.63 | 0.61 | 5.53 | 0.02 | 0.00 | 6.70 | 0.01 | **MD** |
| **ME** | 0.25 | 0.45 | 0.21 | 0.95 | 0.14 | 0.00 | 8.91 | 3.75 | 5.78 | 0.03 | 0.00 | 96.64 | 0.00 | **ME** |
| **MK** | 0.25 | 0.24 | 0.20 | 0.63 | 0.13 | 0.01 | 78.96 | 1.60 | 6.70 | 0.03 | 0.00 | 34.52 | 0.00 | **MK** |
| **MT** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.18 | 0.00 | **MT** |
| **NL** | 1.94 | 2.87 | 1.80 | 14.87 | 9.48 | 0.00 | 0.06 | 0.45 | 2.50 | 1.11 | 0.02 | 6.82 | 0.00 | **NL** |
| **NO** | 30.73 | 3.39 | 51.08 | 8.58 | 17.94 | 0.05 | 0.42 | 1.31 | 13.99 | 4.83 | 0.25 | 7.38 | 0.08 | **NO** |
| **PL** | 33.03 | 5.69 | 21.06 | 20.92 | 10.18 | 0.23 | 10.28 | 27.33 | 204.69 | 2.06 | 0.04 | 136.92 | 0.09 | **PL** |
| **PT** | 0.72 | 147.30 | 0.60 | 2.98 | 1.56 | 0.00 | 0.03 | 0.17 | 0.59 | 0.44 | 0.00 | 2.23 | 0.00 | **PT** |
| **RO** | 4.48 | 1.78 | 3.53 | 4.22 | 1.73 | 0.29 | 53.84 | 19.73 | 274.29 | 0.36 | 0.01 | 145.52 | 0.03 | **RO** |
| **RS** | 1.63 | 1.17 | 1.26 | 2.62 | 0.88 | 0.02 | 55.20 | 39.97 | 137.90 | 0.21 | 0.00 | 127.38 | 0.01 | **RS** |
| **RU** | 790.48 | 11.02 | 578.55 | 24.84 | 22.18 | 16.73 | 31.30 | 24.29 | 148.63 | 6.76 | 0.38 | 155.11 | 17.51 | **RU** |
| **SE** | 123.28 | 3.19 | 254.97 | 11.64 | 14.98 | 0.08 | 0.87 | 2.57 | 23.82 | 4.30 | 0.14 | 14.74 | 0.20 | **SE** |
| **SI** | 0.54 | 0.72 | 0.45 | 1.75 | 0.45 | 0.00 | 1.96 | 92.94 | 85.32 | 0.10 | 0.00 | 152.70 | 0.01 | **SI** |
| **SK** | 1.96 | 0.66 | 1.54 | 2.34 | 1.07 | 0.02 | 5.29 | 17.22 | 290.35 | 0.22 | 0.00 | 47.31 | 0.01 | **SK** |
| **TJ** | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.02 | 0.03 | 0.00 | 0.02 | 0.00 | 0.00 | 0.07 | 35.17 | **TJ** |
| **TM** | 0.07 | 0.01 | 0.06 | 0.02 | 0.01 | 0.08 | 0.09 | 0.03 | 0.13 | 0.00 | 0.00 | 0.33 | 1.23 | **TM** |
| **TR** | 3.37 | 1.14 | 2.52 | 2.12 | 0.63 | 4.32 | 108.46 | 3.16 | 18.76 | 0.09 | 0.00 | 53.43 | 0.05 | **TR** |
| **UA** | 21.99 | 3.02 | 14.36 | 6.83 | 3.14 | 2.93 | 39.05 | 19.93 | 203.68 | 0.63 | 0.01 | 139.43 | 0.25 | **UA** |
| **UZ** | 0.15 | 0.03 | 0.14 | 0.04 | 0.02 | 0.09 | 0.18 | 0.05 | 0.28 | 0.01 | 0.00 | 0.70 | 128.45 | **UZ** |
| | **EE** | **ES** | **FI** | **FR** | **GB** | **GE** | **GR** | **HR** | **HU** | **IE** | **IS** | **IT** | **KY** | |

***Table A.2**. Matrix of B[a]P country-to-country deposition in 2010, kg/y (continued)*

Receptors ↓ Emitters →

| | KZ | LT | LU | LV | MC | MD | ME | MK | MT | NL | NO | PL | PT | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AL** | 0.08 | 0.38 | 0.06 | 0.55 | 0.00 | 0.34 | 104.02 | 29.43 | 0.03 | 0.18 | 0.04 | 8.79 | 0.32 | **AL** |
| **AM** | 0.22 | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.10 | 0.00 | **AM** |
| **AT** | 0.31 | 3.20 | 1.46 | 5.05 | 0.00 | 0.88 | 4.00 | 1.51 | 0.01 | 3.37 | 0.62 | 164.91 | 1.72 | **AT** |
| **AZ** | 3.37 | 0.10 | 0.00 | 0.09 | 0.00 | 0.05 | 0.02 | 0.02 | 0.00 | 0.00 | 0.00 | 0.52 | 0.01 | **AZ** |
| **BA** | 0.18 | 1.41 | 0.16 | 2.20 | 0.00 | 0.82 | 72.67 | 5.83 | 0.03 | 0.62 | 0.18 | 56.12 | 0.96 | **BA** |
| **BE** | 0.09 | 2.77 | 12.46 | 3.84 | 0.00 | 0.11 | 0.08 | 0.03 | 0.00 | 42.79 | 0.74 | 36.67 | 5.37 | **BE** |
| **BG** | 2.03 | 2.98 | 0.12 | 4.15 | 0.00 | 10.42 | 7.88 | 35.60 | 0.02 | 0.48 | 0.29 | 73.73 | 0.33 | **BG** |
| **BY** | 4.08 | 232.86 | 0.39 | 186.25 | 0.00 | 10.90 | 2.64 | 1.69 | 0.00 | 1.82 | 1.41 | 644.74 | 1.75 | **BY** |
| **CH** | 0.05 | 0.75 | 0.85 | 1.35 | 0.00 | 0.11 | 0.27 | 0.11 | 0.00 | 1.19 | 0.20 | 21.53 | 2.14 | **CH** |
| **CY** | 0.01 | 0.03 | 0.00 | 0.03 | 0.00 | 0.02 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.33 | 0.01 | **CY** |
| **CZ** | 0.51 | 7.38 | 1.04 | 9.28 | 0.00 | 1.34 | 2.58 | 1.27 | 0.00 | 3.68 | 0.98 | 1012.8 | 1.69 | **CZ** |
| **DE** | 1.75 | 45.67 | 36.53 | 63.43 | 0.00 | 2.80 | 3.26 | 1.28 | 0.01 | 115.95 | 8.34 | 1363.8 | 26.77 | **DE** |
| **DK** | 0.23 | 5.61 | 0.40 | 10.61 | 0.00 | 0.18 | 0.12 | 0.05 | 0.00 | 5.68 | 4.84 | 81.64 | 1.05 | **DK** |
| **EE** | 0.81 | 41.60 | 0.13 | 277.50 | 0.00 | 0.69 | 0.20 | 0.13 | 0.00 | 0.85 | 1.14 | 88.10 | 0.55 | **EE** |
| **ES** | 0.19 | 3.41 | 1.20 | 5.09 | 0.00 | 0.23 | 0.48 | 0.19 | 0.00 | 5.75 | 0.70 | 39.29 | 1620.8 | **ES** |
| **FI** | 4.12 | 79.91 | 0.46 | 226.69 | 0.00 | 1.72 | 0.33 | 0.23 | 0.00 | 3.30 | 8.76 | 202.62 | 2.03 | **FI** |
| **FR** | 0.64 | 16.84 | 38.04 | 24.79 | 0.01 | 1.19 | 2.35 | 0.91 | 0.01 | 42.58 | 3.17 | 272.37 | 91.78 | **FR** |
| **GB** | 0.57 | 8.29 | 1.65 | 15.95 | 0.00 | 0.35 | 0.19 | 0.10 | 0.00 | 15.07 | 5.95 | 83.02 | 37.12 | **GB** |
| **GE** | 0.76 | 0.18 | 0.00 | 0.13 | 0.00 | 0.18 | 0.07 | 0.08 | 0.00 | 0.01 | 0.01 | 1.19 | 0.01 | **GE** |
| **GR** | 0.72 | 1.47 | 0.10 | 2.13 | 0.00 | 3.05 | 4.94 | 45.37 | 0.08 | 0.31 | 0.16 | 31.34 | 0.47 | **GR** |
| **HR** | 0.22 | 1.55 | 0.22 | 2.28 | 0.00 | 0.87 | 19.95 | 4.23 | 0.02 | 0.70 | 0.21 | 68.31 | 1.32 | **HR** |
| **HU** | 0.45 | 4.44 | 0.36 | 5.41 | 0.00 | 1.94 | 14.79 | 8.13 | 0.01 | 1.30 | 0.47 | 294.93 | 1.30 | **HU** |
| **IE** | 0.11 | 1.60 | 0.12 | 3.23 | 0.00 | 0.08 | 0.05 | 0.03 | 0.00 | 1.45 | 0.84 | 8.49 | 23.32 | **IE** |
| **IS** | 0.56 | 3.27 | 0.21 | 6.23 | 0.00 | 0.14 | 0.07 | 0.04 | 0.00 | 1.43 | 2.28 | 22.87 | 5.64 | **IS** |
| **IT** | 0.49 | 4.46 | 1.36 | 7.57 | 0.00 | 1.56 | 19.71 | 5.95 | 0.41 | 2.80 | 0.68 | 99.86 | 9.23 | **IT** |
| **KY** | 141.91 | 0.02 | 0.00 | 0.04 | 0.00 | 0.02 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.30 | 0.03 | **KY** |
| **KZ** | **4762.2** | 8.05 | 0.10 | 14.84 | 0.00 | 1.56 | 0.77 | 0.61 | 0.00 | 0.53 | 0.68 | 54.79 | 0.94 | **KZ** |
| **LT** | 1.07 | **951.30** | 0.23 | 312.30 | 0.00 | 1.96 | 0.81 | 0.50 | 0.00 | 1.31 | 1.04 | 336.44 | 1.02 | **LT** |
| **LU** | 0.01 | 0.22 | **16.34** | 0.31 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.60 | 0.03 | 3.28 | 0.40 | **LU** |
| **LV** | 1.25 | 222.29 | 0.24 | **1877.2** | 0.00 | 1.74 | 0.57 | 0.37 | 0.00 | 1.46 | 1.40 | 211.34 | 1.06 | **LV** |
| **MC** | 0.00 | 0.00 | 0.00 | 0.00 | **0.00** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | **MC** |
| **MD** | 0.87 | 1.44 | 0.03 | 1.43 | 0.00 | **145.20** | 0.77 | 0.65 | 0.00 | 0.12 | 0.07 | 25.34 | 0.09 | **MD** |
| **ME** | 0.04 | 0.33 | 0.04 | 0.52 | 0.00 | 0.18 | **463.02** | 5.30 | 0.01 | 0.12 | 0.03 | 7.67 | 0.26 | **ME** |
| **MK** | 0.08 | 0.46 | 0.03 | 0.64 | 0.00 | 0.46 | 5.99 | **199.66** | 0.01 | 0.12 | 0.04 | 10.90 | 0.11 | **MK** |
| **MT** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | **0.10** | 0.00 | 0.00 | 0.01 | 0.00 | **MT** |
| **NL** | 0.10 | 2.64 | 1.69 | 4.30 | 0.00 | 0.10 | 0.06 | 0.02 | 0.00 | **167.89** | 0.90 | 30.92 | 4.28 | **NL** |
| **NO** | 2.15 | 34.20 | 0.75 | 60.08 | 0.00 | 0.73 | 0.28 | 0.16 | 0.00 | 6.53 | **288.47** | 268.90 | 8.00 | **NO** |
| **PL** | 3.25 | 148.83 | 2.17 | 108.68 | 0.00 | 11.25 | 7.55 | 4.37 | 0.01 | 10.43 | 6.19 | **12646** | 6.08 | **PL** |
| **PT** | 0.03 | 0.72 | 0.11 | 1.38 | 0.00 | 0.02 | 0.03 | 0.01 | 0.00 | 0.79 | 0.17 | 4.56 | **9352.6** | **PT** |
| **RO** | 3.85 | 7.79 | 0.36 | 9.71 | 0.00 | 77.65 | 23.25 | 20.48 | 0.03 | 1.55 | 0.84 | 293.39 | 1.11 | **RO** |
| **RS** | 0.42 | 2.52 | 0.19 | 3.62 | 0.00 | 2.62 | 94.64 | 64.32 | 0.02 | 0.76 | 0.30 | 91.54 | 0.69 | **RS** |
| **RU** | 1371.1 | 433.18 | 2.29 | 918.54 | 0.00 | 24.39 | 9.91 | 7.13 | 0.02 | 13.27 | 26.62 | 1498.4 | 15.43 | **RU** |
| **SE** | 3.77 | 105.69 | 1.26 | 200.84 | 0.00 | 1.94 | 0.61 | 0.38 | 0.00 | 11.48 | 49.84 | 494.19 | 6.41 | **SE** |
| **SI** | 0.10 | 0.79 | 0.14 | 1.05 | 0.00 | 0.35 | 3.43 | 1.10 | 0.01 | 0.37 | 0.11 | 28.50 | 0.69 | **SI** |
| SK | 0.31 | 4.57 | 0.25 | 5.16 | 0.00 | 1.28 | 4.51 | 2.83 | 0.00 | 0.91 | 0.48 | 644.29 | 0.59 | SK |
| **TJ** | 7.55 | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.01 | **TJ** |
| **TM** | 15.50 | 0.08 | 0.00 | 0.12 | 0.00 | 0.03 | 0.02 | 0.02 | 0.00 | 0.01 | 0.01 | 0.69 | 0.02 | **TM** |
| **TR** | 3.96 | 8.57 | 0.14 | 9.67 | 0.00 | 9.49 | 2.54 | 3.82 | 0.04 | 0.47 | 0.31 | 78.33 | 0.83 | **TR** |
| **UA** | 21.10 | 58.08 | 0.63 | 61.09 | 0.00 | 100.46 | 14.02 | 10.06 | 0.02 | 2.72 | 1.80 | 939.19 | 2.40 | **UA** |
| **UZ** | 121.06 | 0.17 | 0.00 | 0.27 | 0.00 | 0.06 | 0.05 | 0.04 | 0.00 | 0.01 | 0.02 | 1.49 | 0.04 | **UZ** |
| | **KZ** | **LT** | **LU** | **LV** | **MC** | **MD** | **ME** | **MK** | **MT** | **NL** | **NO** | **PL** | **PT** | |

***Table A.2**. Matrix of B[a]P country-to-country deposition in 2010, kg/y (continued)*

Receptors ↓ Emitters →

| | RO | RS | RU | SE | SI | SK | TJ | TM | TR | UA | UZ | Total | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AL** | 19.41 | 90.07 | 0.79 | 0.34 | 1.50 | 1.68 | 0.00 | 0.00 | 9.63 | 16.36 | 0.00 | 938.47 | **AL** |
| **AM** | 0.32 | 0.04 | 0.43 | 0.00 | 0.00 | 0.01 | 0.00 | 0.02 | 25.76 | 1.18 | 0.01 | 87.31 | **AM** |
| **AT** | 90.13 | 48.27 | 3.46 | 3.98 | 146.27 | 63.86 | 0.01 | 0.00 | 1.87 | 89.78 | 0.01 | 2256.37 | **AT** |
| **AZ** | 1.26 | 0.14 | 7.73 | 0.02 | 0.01 | 0.05 | 0.03 | 0.35 | 16.97 | 6.93 | 0.19 | 905.68 | **AZ** |
| **BA** | 104.97 | 228.23 | 2.12 | 1.39 | 18.37 | 19.45 | 0.00 | 0.00 | 5.05 | 55.36 | 0.00 | 1763.80 | **BA** |
| **BE** | 4.11 | 1.02 | 1.34 | 3.13 | 1.33 | 2.36 | 0.00 | 0.00 | 0.31 | 13.97 | 0.00 | 1082.67 | **BE** |
| **BG** | 1018.3 | 224.77 | 14.19 | 2.03 | 3.54 | 16.53 | 0.00 | 0.01 | 158.49 | 410.10 | 0.01 | 4285.59 | **BG** |
| **BY** | 229.19 | 29.08 | 116.34 | 19.31 | 9.59 | 38.39 | 0.08 | 0.02 | 24.17 | 2370.8 | 0.06 | 6881.73 | **BY** |
| **CH** | 7.13 | 3.29 | 0.62 | 0.98 | 8.02 | 2.58 | 0.00 | 0.00 | 0.26 | 11.97 | 0.00 | 545.89 | **CH** |
| **CY** | 0.65 | 0.11 | 0.05 | 0.01 | 0.01 | 0.04 | 0.00 | 0.00 | 6.00 | 1.27 | 0.00 | 20.10 | **CY** |
| **CZ** | 101.38 | 35.40 | 6.29 | 5.33 | 22.99 | 153.18 | 0.01 | 0.00 | 2.84 | 174.01 | 0.01 | 3300.99 | **CZ** |
| **DE** | 127.99 | 38.29 | 24.99 | 49.95 | 34.82 | 74.59 | 0.03 | 0.01 | 6.70 | 410.48 | 0.02 | 13739.54 | **DE** |
| **DK** | 7.59 | 1.55 | 4.15 | 34.99 | 1.03 | 4.34 | 0.00 | 0.00 | 0.52 | 36.23 | 0.00 | 853.53 | **DK** |
| **EE** | 17.02 | 2.59 | 42.89 | 18.07 | 1.45 | 4.62 | 0.01 | 0.00 | 2.51 | 136.33 | 0.01 | 1475.67 | **EE** |
| **ES** | 11.27 | 4.93 | 2.13 | 5.68 | 4.46 | 3.61 | 0.00 | 0.00 | 0.69 | 24.39 | 0.00 | 6705.04 | **ES** |
| **FI** | 38.05 | 5.82 | 154.07 | 162.51 | 3.29 | 10.00 | 0.05 | 0.01 | 5.48 | 303.19 | 0.04 | 3373.68 | **FI** |
| **FR** | 61.17 | 22.87 | 8.72 | 18.76 | 35.88 | 23.37 | 0.01 | 0.00 | 3.09 | 130.24 | 0.01 | 4815.98 | **FR** |
| **GB** | 13.74 | 2.35 | 7.55 | 20.64 | 1.80 | 5.58 | 0.01 | 0.00 | 1.88 | 57.73 | 0.01 | 1379.27 | **GB** |
| **GE** | 4.52 | 0.48 | 11.46 | 0.03 | 0.04 | 0.12 | 0.00 | 0.04 | 91.22 | 19.08 | 0.03 | 274.14 | **GE** |
| **GR** | 133.61 | 64.86 | 5.11 | 1.24 | 2.11 | 6.14 | 0.00 | 0.00 | 165.88 | 132.37 | 0.01 | 2186.87 | **GR** |
| **HR** | 111.43 | 169.82 | 2.37 | 1.36 | 163.17 | 28.25 | 0.00 | 0.00 | 3.90 | 65.77 | 0.00 | 1868.19 | **HR** |
| **HU** | 602.34 | 264.93 | 5.49 | 2.82 | 63.98 | 333.72 | 0.00 | 0.00 | 7.31 | 435.75 | 0.01 | 4612.95 | **HU** |
| **IE** | 2.37 | 0.38 | 1.32 | 3.50 | 0.12 | 0.41 | 0.00 | 0.00 | 0.39 | 9.40 | 0.00 | 428.06 | **IE** |
| **IS** | 4.72 | 0.89 | 5.36 | 5.09 | 0.46 | 1.12 | 0.01 | 0.00 | 1.28 | 19.55 | 0.01 | 162.89 | **IS** |
| **IT** | 117.95 | 88.47 | 5.13 | 4.59 | 206.98 | 26.87 | 0.01 | 0.00 | 12.97 | 98.61 | 0.01 | 11445.02 | **IT** |
| **KY** | 0.50 | 0.09 | 0.79 | 0.02 | 0.02 | 0.04 | 91.56 | 0.26 | 1.38 | 2.41 | 40.31 | 1204.03 | **KY** |
| **KZ** | 46.35 | 6.41 | 384.11 | 4.56 | 1.91 | 6.20 | 41.45 | 2.95 | 36.05 | 416.55 | 36.96 | 6169.42 | **KZ** |
| **LT** | 49.37 | 8.34 | 29.31 | 17.51 | 4.09 | 14.35 | 0.03 | 0.01 | 3.69 | 316.53 | 0.02 | 2441.61 | **LT** |
| **LU** | 0.44 | 0.13 | 0.09 | 0.18 | 0.16 | 0.22 | 0.00 | 0.00 | 0.03 | 1.31 | 0.00 | 69.85 | **LU** |
| **LV** | 42.45 | 6.31 | 40.70 | 23.77 | 3.12 | 10.67 | 0.03 | 0.01 | 3.91 | 291.79 | 0.02 | 3133.86 | **LV** |
| **MC** | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.33 | **MC** |
| **MD** | 399.03 | 6.40 | 8.99 | 0.56 | 0.55 | 3.38 | 0.00 | 0.01 | 18.89 | 1004.9 | 0.01 | 1667.38 | **MD** |
| **ME** | 14.32 | 92.14 | 0.52 | 0.29 | 1.52 | 1.77 | 0.00 | 0.00 | 2.72 | 10.52 | 0.00 | 816.24 | **ME** |
| **MK** | 32.16 | 123.27 | 0.83 | 0.34 | 0.89 | 2.36 | 0.00 | 0.00 | 14.92 | 22.30 | 0.00 | 665.34 | **MK** |
| **MT** | 0.02 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.02 | 0.00 | 0.44 | **MT** |
| **NL** | 3.79 | 0.75 | 1.52 | 4.30 | 0.97 | 2.00 | 0.00 | 0.00 | 0.28 | 14.40 | 0.00 | 757.83 | **NL** |
| **NO** | 28.85 | 4.34 | 34.22 | 125.95 | 2.44 | 13.83 | 0.03 | 0.01 | 3.12 | 156.08 | 0.02 | 1459.54 | **NO** |
| **PL** | 444.36 | 78.28 | 61.42 | 53.73 | 44.39 | 324.82 | 0.05 | 0.02 | 22.63 | 2276.8 | 0.05 | 18381.09 | **PL** |
| **PT** | 0.90 | 0.34 | 0.42 | 1.05 | 0.27 | 0.32 | 0.00 | 0.00 | 0.10 | 2.84 | 0.00 | 9538.29 | **PT** |
| **RO** | **12010** | 383.97 | 36.55 | 5.10 | 13.60 | 85.06 | 0.01 | 0.02 | 130.76 | 2386.2 | 0.03 | 16669.73 | **RO** |
| **RS** | 506.89 | **2381.7** | 4.76 | 1.97 | 9.65 | 30.72 | 0.00 | 0.00 | 21.16 | 150.89 | 0.00 | 4113.22 | **RS** |
| **RU** | 654.72 | 91.06 | **9927.3** | 221.92 | 33.27 | 106.42 | 5.35 | 1.79 | 414.52 | 8111.1 | 4.65 | 27664.88 | **RU** |
| **SE** | 63.69 | 8.08 | 78.40 | **1502.2** | 4.98 | 23.04 | 0.07 | 0.01 | 5.03 | 353.10 | 0.05 | 3985.10 | **SE** |
| **SI** | 42.11 | 37.66 | 1.01 | 0.57 | **633.62** | 13.99 | 0.00 | 0.00 | 1.02 | 29.22 | 0.00 | 1257.54 | **SI** |
| **SK** | 217.13 | 58.28 | 4.29 | 2.70 | 24.24 | **936.48** | 0.00 | 0.00 | 3.47 | 334.33 | 0.00 | 2836.23 | **SK** |
| **TJ** | 0.15 | 0.03 | 0.26 | 0.00 | 0.00 | 0.01 | **400.94** | 0.44 | 0.56 | 0.77 | 14.55 | 461.30 | **TJ** |
| **TM** | 0.91 | 0.14 | 3.79 | 0.04 | 0.03 | 0.08 | 8.56 | **30.48** | 1.72 | 6.96 | 16.24 | 92.38 | **TM** |
| **TR** | 298.06 | 31.57 | 31.90 | 2.79 | 3.17 | 9.80 | 0.01 | 0.03 | **9044.7** | 746.68 | 0.03 | 10691.78 | **TR** |
| **UA** | 1635.3 | 121.26 | 314.15 | 17.39 | 19.00 | 121.43 | 0.12 | 0.18 | 312.40 | **50120** | 0.24 | 55110.59 | **UA** |
| **UZ** | 1.84 | 0.29 | 6.98 | 0.10 | 0.06 | 0.18 | 158.61 | 5.74 | 2.59 | 13.05 | **122.11** | 569.06 | **UZ** |
| | **RO** | **RS** | **RU** | **SE** | **SI** | **SK** | **TJ** | **TM** | **TR** | **UA** | **UZ** | **Total** | |

***Table A.3**. Matrix of PCDD/F country-to-country deposition in 2010, g TEQ/y*

Receptors ↓ Emitters →

| | AL | AM | AT | AZ | BA | BE | BG | BY | CH | CY | CZ | DE | DK | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AL** | **63.72** | 0.01 | 0.26 | 0.06 | 0.96 | 0.17 | 0.99 | 0.04 | 0.09 | 0.00 | 0.64 | 0.24 | 0.05 | **AL** |
| **AM** | 0.03 | **5.61** | 0.02 | 11.36 | 0.03 | 0.01 | 0.04 | 0.01 | 0.01 | 0.00 | 0.04 | 0.02 | 0.01 | **AM** |
| **AT** | 0.44 | 0.10 | **78.70** | 0.13 | 1.71 | 1.60 | 0.30 | 0.23 | 1.78 | 0.00 | 15.45 | 5.21 | 0.36 | **AT** |
| **AZ** | 0.10 | 0.97 | 0.05 | **228.12** | 0.08 | 0.04 | 0.20 | 0.05 | 0.02 | 0.00 | 0.15 | 0.05 | 0.02 | **AZ** |
| **BA** | 2.79 | 0.02 | 1.59 | 0.08 | **105.48** | 0.36 | 0.64 | 0.15 | 0.17 | 0.00 | 3.56 | 0.68 | 0.15 | **BA** |
| **BE** | 0.02 | 0.00 | 0.22 | 0.04 | 0.04 | **90.16** | 0.02 | 0.08 | 0.27 | 0.00 | 0.63 | 6.05 | 0.27 | **BE** |
| **BG** | 2.19 | 0.02 | 0.71 | 0.43 | 1.43 | 0.39 | **110.21** | 0.29 | 0.15 | 0.00 | 3.21 | 0.59 | 0.19 | **BG** |
| **BY** | 0.45 | 0.01 | 0.98 | 0.87 | 0.87 | 0.77 | 0.74 | **84.49** | 0.18 | 0.00 | 7.29 | 1.33 | 0.90 | **BY** |
| **CH** | 0.09 | 0.00 | 1.77 | 0.03 | 0.33 | 0.67 | 0.06 | 0.05 | **24.95** | 0.00 | 1.09 | 1.69 | 0.11 | **CH** |
| **CY** | 0.05 | 0.00 | 0.02 | 0.03 | 0.04 | 0.02 | 0.06 | 0.01 | 0.01 | **0.68** | 0.05 | 0.02 | 0.01 | **CY** |
| **CZ** | 0.25 | 0.05 | 9.54 | 0.17 | 0.82 | 1.10 | 0.25 | 0.42 | 0.58 | 0.00 | **195.55** | 4.80 | 0.51 | **CZ** |
| **DE** | 0.39 | 0.04 | 15.91 | 0.68 | 1.18 | 25.45 | 0.38 | 1.58 | 10.55 | 0.00 | 34.15 | **175.39** | 6.64 | **DE** |
| **DK** | 0.03 | 0.00 | 0.21 | 0.14 | 0.07 | 0.93 | 0.03 | 0.21 | 0.05 | 0.00 | 1.38 | 1.08 | **27.05** | **DK** |
| **EE** | 0.05 | 0.00 | 0.18 | 0.28 | 0.11 | 0.22 | 0.08 | 1.26 | 0.05 | 0.00 | 1.13 | 0.37 | 0.40 | **EE** |
| **ES** | 0.40 | 0.01 | 1.05 | 0.38 | 0.98 | 4.06 | 0.29 | 0.26 | 0.77 | 0.00 | 2.43 | 3.03 | 0.87 | **ES** |
| **FI** | 0.20 | 0.02 | 0.47 | 1.34 | 0.32 | 0.82 | 0.31 | 2.89 | 0.14 | 0.00 | 2.54 | 1.13 | 1.16 | **FI** |
| **FR** | 0.80 | 0.03 | 4.23 | 0.55 | 2.34 | 36.05 | 0.56 | 0.84 | 9.90 | 0.00 | 10.00 | 24.43 | 2.17 | **FR** |
| **GB** | 0.17 | 0.01 | 0.82 | 0.50 | 0.31 | 9.48 | 0.25 | 0.56 | 0.46 | 0.00 | 4.02 | 5.43 | 2.93 | **GB** |
| **GE** | 0.17 | 0.85 | 0.07 | 19.77 | 0.13 | 0.07 | 0.23 | 0.05 | 0.03 | 0.01 | 0.23 | 0.08 | 0.03 | **GE** |
| **GR** | 6.96 | 0.02 | 0.78 | 0.38 | 1.70 | 0.57 | 11.48 | 0.19 | 0.26 | 0.01 | 2.33 | 0.77 | 0.20 | **GR** |
| **HR** | 1.57 | 0.04 | 3.58 | 0.09 | 23.57 | 0.39 | 0.54 | 0.21 | 0.20 | 0.00 | 5.33 | 0.83 | 0.16 | **HR** |
| **HU** | 0.88 | 0.05 | 6.85 | 0.17 | 4.40 | 0.54 | 0.82 | 0.65 | 0.22 | 0.00 | 16.08 | 1.19 | 0.31 | **HU** |
| **IE** | 0.05 | 0.00 | 0.08 | 0.11 | 0.07 | 1.11 | 0.06 | 0.11 | 0.04 | 0.00 | 0.36 | 0.60 | 0.42 | **IE** |
| **IS** | 0.05 | 0.00 | 0.14 | 0.14 | 0.10 | 0.55 | 0.08 | 0.19 | 0.06 | 0.00 | 0.61 | 0.57 | 0.42 | **IS** |
| **IT** | 5.73 | 0.03 | 8.67 | 0.35 | 9.40 | 2.14 | 1.71 | 0.32 | 3.91 | 0.00 | 7.29 | 3.50 | 0.56 | **IT** |
| **KY** | 0.08 | 0.04 | 0.05 | 1.52 | 0.07 | 0.04 | 0.09 | 0.03 | 0.02 | 0.00 | 0.11 | 0.05 | 0.02 | **KY** |
| **KZ** | 1.02 | 0.25 | 0.95 | 14.63 | 1.14 | 1.08 | 2.14 | 1.61 | 0.32 | 0.01 | 3.61 | 1.31 | 0.84 | **KZ** |
| **LT** | 0.11 | 0.00 | 0.49 | 0.28 | 0.29 | 0.47 | 0.14 | 5.50 | 0.09 | 0.00 | 3.94 | 0.84 | 0.69 | **LT** |
| **LU** | 0.00 | 0.00 | 0.03 | 0.00 | 0.01 | 1.21 | 0.00 | 0.01 | 0.05 | 0.00 | 0.07 | 0.80 | 0.02 | **LU** |
| **LV** | 0.10 | 0.00 | 0.37 | 0.36 | 0.23 | 0.41 | 0.14 | 3.52 | 0.08 | 0.00 | 2.65 | 0.71 | 0.75 | **LV** |
| **MC** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | **MC** |
| **MD** | 0.16 | 0.01 | 0.11 | 0.21 | 0.18 | 0.09 | 0.44 | 0.27 | 0.03 | 0.00 | 0.78 | 0.15 | 0.07 | **MD** |
| **ME** | 0.12 | 0.00 | 0.02 | 0.00 | 0.15 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.05 | 0.01 | 0.00 | **ME** |
| **MK** | 7.05 | 0.00 | 0.23 | 0.05 | 0.56 | 0.13 | 2.86 | 0.04 | 0.06 | 0.00 | 0.70 | 0.20 | 0.05 | **MK** |
| **MT** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | **MT** |
| **NL** | 0.02 | 0.00 | 0.24 | 0.08 | 0.05 | 25.58 | 0.02 | 0.10 | 0.15 | 0.00 | 0.83 | 8.68 | 0.61 | **NL** |
| **NO** | 0.22 | 0.02 | 0.85 | 1.16 | 0.41 | 2.07 | 0.33 | 1.98 | 0.26 | 0.00 | 5.56 | 2.34 | 3.86 | **NO** |
| **PL** | 0.83 | 0.05 | 5.01 | 0.95 | 2.22 | 3.02 | 0.92 | 9.49 | 0.84 | 0.00 | 151.99 | 8.71 | 4.81 | **PL** |
| **PT** | 0.04 | 0.00 | 0.09 | 0.05 | 0.09 | 0.55 | 0.03 | 0.03 | 0.06 | 0.00 | 0.23 | 0.34 | 0.12 | **PT** |
| **RO** | 2.82 | 0.03 | 1.85 | 0.94 | 4.43 | 0.77 | 8.60 | 0.95 | 0.30 | 0.01 | 9.14 | 1.34 | 0.48 | **RO** |
| **RS** | 11.41 | 0.02 | 1.51 | 0.18 | 14.36 | 0.46 | 3.58 | 0.24 | 0.20 | 0.00 | 5.25 | 0.84 | 0.22 | **RS** |
| **RU** | 4.56 | 0.89 | 5.41 | 57.56 | 5.60 | 6.36 | 7.87 | 29.57 | 1.67 | 0.05 | 25.10 | 8.48 | 7.32 | **RU** |
| **SE** | 0.32 | 0.02 | 0.98 | 1.81 | 0.56 | 2.46 | 0.45 | 4.15 | 0.29 | 0.00 | 7.50 | 3.46 | 10.17 | **SE** |
| **SI** | 0.23 | 0.02 | 5.34 | 0.04 | 1.62 | 0.17 | 0.14 | 0.07 | 0.11 | 0.00 | 1.93 | 0.41 | 0.06 | **SI** |
| **SK** | 0.41 | 0.03 | 3.04 | 0.15 | 1.27 | 0.37 | 0.39 | 0.47 | 0.15 | 0.00 | 32.27 | 0.82 | 0.28 | **SK** |
| **TJ** | 0.04 | 0.02 | 0.02 | 0.81 | 0.04 | 0.02 | 0.05 | 0.01 | 0.01 | 0.00 | 0.05 | 0.02 | 0.01 | **TJ** |
| **TM** | 0.16 | 0.12 | 0.10 | 7.71 | 0.14 | 0.09 | 0.30 | 0.10 | 0.03 | 0.00 | 0.28 | 0.11 | 0.06 | **TM** |
| **TR** | 3.26 | 1.60 | 1.65 | 8.17 | 2.84 | 1.40 | 10.89 | 0.91 | 0.59 | 0.34 | 5.10 | 1.77 | 0.52 | **TR** |
| **UA** | 2.40 | 0.12 | 2.29 | 5.22 | 3.37 | 1.55 | 5.22 | 9.86 | 0.48 | 0.02 | 15.55 | 2.55 | 1.41 | **UA** |
| **UZ** | 0.15 | 0.07 | 0.10 | 3.21 | 0.14 | 0.11 | 0.26 | 0.11 | 0.04 | 0.00 | 0.33 | 0.13 | 0.06 | **UZ** |
| | **AL** | **AM** | **AT** | **AZ** | **BA** | **BE** | **BG** | **BY** | **CH** | **CY** | **CZ** | **DE** | **DK** | |

***Table A.3**. Matrix of PCDD/F country-to-country deposition in 2010, g TEQ/y (continued)*

Receptors ↓ Emitters →

| | EE | ES | FI | FR | GB | GE | GR | HR | HU | IE | IS | IT | KY | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AL** | 0.01 | 0.49 | 0.01 | 0.46 | 0.33 | 0.07 | 1.71 | 1.35 | 0.32 | 0.02 | 0.00 | 9.37 | 0.00 | **AL** |
| **AM** | 0.00 | 0.09 | 0.00 | 0.03 | 0.03 | 5.94 | 0.06 | 0.04 | 0.02 | 0.00 | 0.00 | 0.19 | 0.01 | **AM** |
| **AT** | 0.02 | 0.96 | 0.04 | 2.48 | 2.42 | 0.13 | 0.16 | 7.69 | 4.70 | 0.11 | 0.01 | 17.01 | 0.01 | **AT** |
| **AZ** | 0.00 | 0.23 | 0.01 | 0.08 | 0.11 | 15.13 | 0.18 | 0.13 | 0.05 | 0.01 | 0.00 | 0.55 | 0.06 | **AZ** |
| **BA** | 0.01 | 0.78 | 0.02 | 0.76 | 0.80 | 0.09 | 0.43 | 34.53 | 2.95 | 0.05 | 0.01 | 12.08 | 0.01 | **BA** |
| **BE** | 0.01 | 0.55 | 0.02 | 9.60 | 5.00 | 0.02 | 0.01 | 0.14 | 0.11 | 0.11 | 0.02 | 0.68 | 0.00 | **BE** |
| **BG** | 0.02 | 0.81 | 0.04 | 0.78 | 0.85 | 0.56 | 3.54 | 2.03 | 1.89 | 0.05 | 0.01 | 6.00 | 0.01 | **BG** |
| **BY** | 0.29 | 0.71 | 0.32 | 1.06 | 1.86 | 0.61 | 0.41 | 1.97 | 2.02 | 0.09 | 0.01 | 2.96 | 0.04 | **BY** |
| **CH** | 0.01 | 1.03 | 0.01 | 3.41 | 1.40 | 0.04 | 0.04 | 1.29 | 0.29 | 0.07 | 0.01 | 23.25 | 0.00 | **CH** |
| **CY** | 0.00 | 0.05 | 0.00 | 0.03 | 0.04 | 0.04 | 0.22 | 0.07 | 0.02 | 0.00 | 0.00 | 0.32 | 0.00 | **CY** |
| **CZ** | 0.03 | 0.59 | 0.04 | 1.66 | 1.90 | 0.14 | 0.12 | 2.58 | 3.64 | 0.08 | 0.01 | 3.78 | 0.01 | **CZ** |
| **DE** | 0.17 | 3.71 | 0.32 | 37.77 | 20.66 | 0.43 | 0.21 | 3.47 | 2.88 | 0.68 | 0.06 | 13.61 | 0.03 | **DE** |
| **DK** | 0.04 | 0.23 | 0.10 | 0.60 | 2.51 | 0.06 | 0.02 | 0.18 | 0.20 | 0.09 | 0.01 | 0.45 | 0.00 | **DK** |
| **EE** | **5.70** | 0.16 | 0.65 | 0.23 | 0.61 | 0.10 | 0.05 | 0.26 | 0.21 | 0.03 | 0.00 | 0.49 | 0.02 | **EE** |
| **ES** | 0.04 | **378.46** | 0.08 | 11.11 | 10.11 | 0.22 | 0.21 | 2.73 | 0.92 | 0.63 | 0.08 | 10.05 | 0.01 | **ES** |
| **FI** | 2.63 | 0.67 | **34.68** | 0.86 | 2.67 | 0.55 | 0.21 | 0.74 | 0.54 | 0.16 | 0.04 | 1.61 | 0.09 | **FI** |
| **FR** | 0.11 | 40.40 | 0.26 | **261.45** | 36.16 | 0.35 | 0.35 | 7.21 | 2.61 | 1.62 | 0.25 | 42.34 | 0.02 | **FR** |
| **GB** | 0.11 | 4.39 | 0.27 | 9.18 | **451.57** | 0.21 | 0.15 | 0.79 | 0.64 | 5.92 | 0.11 | 2.41 | 0.02 | **GB** |
| **GE** | 0.00 | 0.42 | 0.01 | 0.13 | 0.16 | **211.35** | 0.39 | 0.20 | 0.08 | 0.01 | 0.00 | 0.92 | 0.02 | **GE** |
| **GR** | 0.02 | 1.58 | 0.03 | 1.36 | 1.19 | 0.49 | **67.94** | 2.73 | 1.17 | 0.08 | 0.02 | 13.93 | 0.02 | **GR** |
| **HR** | 0.01 | 0.75 | 0.02 | 0.80 | 0.81 | 0.09 | 0.33 | **173.49** | 7.38 | 0.05 | 0.01 | 13.15 | 0.01 | **HR** |
| **HU** | 0.02 | 0.58 | 0.04 | 0.82 | 1.08 | 0.15 | 0.33 | 23.66 | **101.67** | 0.06 | 0.01 | 6.42 | 0.01 | **HU** |
| **IE** | 0.02 | 1.20 | 0.06 | 1.26 | 14.83 | 0.03 | 0.04 | 0.12 | 0.08 | **39.92** | 0.04 | 0.36 | 0.00 | **IE** |
| **IS** | 0.04 | 0.50 | 0.10 | 0.54 | 3.03 | 0.13 | 0.06 | 0.21 | 0.13 | 0.37 | **5.28** | 0.56 | 0.02 | **IS** |
| **IT** | 0.04 | 6.57 | 0.09 | 8.15 | 4.23 | 0.34 | 1.71 | 28.54 | 4.04 | 0.26 | 0.04 | **572.93** | 0.02 | **IT** |
| **KY** | 0.00 | 0.20 | 0.01 | 0.09 | 0.11 | 0.78 | 0.12 | 0.12 | 0.04 | 0.01 | 0.00 | 0.52 | **152.41** | **KY** |
| **KZ** | 0.24 | 3.56 | 0.50 | 1.70 | 3.50 | 6.43 | 1.50 | 1.94 | 1.05 | 0.24 | 0.06 | 6.67 | 45.46 | **KZ** |
| **LT** | 0.16 | 0.28 | 0.18 | 0.50 | 1.11 | 0.13 | 0.08 | 0.70 | 0.59 | 0.05 | 0.01 | 1.04 | 0.01 | **LT** |
| **LU** | 0.00 | 0.06 | 0.00 | 4.98 | 0.24 | 0.00 | 0.00 | 0.02 | 0.01 | 0.01 | 0.00 | 0.10 | 0.00 | **LU** |
| **LV** | 0.64 | 0.29 | 0.34 | 0.43 | 1.07 | 0.15 | 0.08 | 0.59 | 0.47 | 0.05 | 0.01 | 0.94 | 0.02 | **LV** |
| **MC** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | **MC** |
| **MD** | 0.01 | 0.15 | 0.02 | 0.14 | 0.23 | 0.23 | 0.16 | 0.29 | 0.26 | 0.01 | 0.00 | 0.77 | 0.00 | **MD** |
| **ME** | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.02 | 0.13 | 0.06 | 0.00 | 0.00 | 0.13 | 0.00 | **ME** |
| **MK** | 0.01 | 0.31 | 0.01 | 0.31 | 0.27 | 0.06 | 2.73 | 0.79 | 0.40 | 0.02 | 0.00 | 3.53 | 0.00 | **MK** |
| **MT** | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | **MT** |
| **NL** | 0.02 | 0.43 | 0.03 | 3.07 | 6.14 | 0.03 | 0.01 | 0.14 | 0.12 | 0.13 | 0.01 | 0.57 | 0.00 | **NL** |
| **NO** | 0.33 | 1.59 | 1.26 | 2.10 | 9.25 | 0.60 | 0.24 | 0.91 | 0.87 | 0.55 | 0.13 | 2.51 | 0.07 | **NO** |
| **PL** | 0.21 | 1.72 | 0.33 | 3.65 | 6.14 | 0.60 | 0.43 | 6.07 | 6.80 | 0.27 | 0.03 | 8.53 | 0.04 | **PL** |
| **PT** | 0.00 | 11.88 | 0.01 | 0.93 | 1.84 | 0.03 | 0.02 | 0.22 | 0.09 | 0.10 | 0.01 | 0.72 | 0.00 | **PT** |
| **RO** | 0.05 | 1.44 | 0.08 | 1.38 | 1.80 | 0.95 | 1.69 | 6.10 | 10.07 | 0.10 | 0.02 | 10.74 | 0.03 | **RO** |
| **RS** | 0.02 | 0.91 | 0.03 | 0.93 | 0.98 | 0.19 | 1.63 | 13.13 | 6.16 | 0.06 | 0.01 | 12.58 | 0.01 | **RS** |
| **RU** | 9.62 | 14.36 | 11.59 | 8.87 | 20.12 | 56.31 | 6.00 | 10.83 | 6.62 | 1.29 | 0.35 | 30.68 | 6.09 | **RU** |
| **SE** | 1.05 | 1.42 | 6.40 | 2.23 | 8.09 | 0.75 | 0.29 | 1.21 | 1.17 | 0.47 | 0.08 | 2.90 | 0.13 | **SE** |
| **SI** | 0.00 | 0.26 | 0.01 | 0.33 | 0.32 | 0.04 | 0.07 | 22.86 | 2.11 | 0.02 | 0.00 | 9.42 | 0.00 | **SI** |
| **SK** | 0.02 | 0.34 | 0.03 | 0.56 | 0.75 | 0.12 | 0.17 | 3.93 | 14.64 | 0.04 | 0.01 | 3.12 | 0.00 | **SK** |
| **TJ** | 0.00 | 0.10 | 0.00 | 0.04 | 0.05 | 0.38 | 0.06 | 0.06 | 0.02 | 0.00 | 0.00 | 0.26 | 7.44 | **TJ** |
| **TM** | 0.01 | 0.44 | 0.02 | 0.17 | 0.27 | 2.51 | 0.26 | 0.23 | 0.10 | 0.02 | 0.00 | 0.95 | 1.38 | **TM** |
| **TR** | 0.07 | 6.25 | 0.10 | 2.95 | 3.44 | 17.06 | 12.05 | 4.81 | 2.16 | 0.21 | 0.04 | 20.07 | 0.15 | **TR** |
| **UA** | 0.22 | 3.03 | 0.36 | 2.42 | 3.90 | 5.77 | 2.52 | 6.04 | 7.05 | 0.21 | 0.04 | 12.85 | 0.13 | **UA** |
| **UZ** | 0.01 | 0.43 | 0.03 | 0.18 | 0.32 | 1.49 | 0.22 | 0.23 | 0.10 | 0.02 | 0.01 | 0.91 | 27.01 | **UZ** |
| | **EE** | **ES** | **FI** | **FR** | **GB** | **GE** | **GR** | **HR** | **HU** | **IE** | **IS** | **IT** | **KY** | |

***Table A.3**. Matrix of PCDD/F country-to-country deposition in 2010, g TEQ/y (continued)*

Receptors ↓ Emitters →

| | KZ | LT | LU | LV | MC | MD | ME | MK | MT | NL | NO | PL | PT | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AL** | 0.09 | 0.04 | 0.01 | 0.04 | 0.03 | 0.15 | 0.49 | 36.34 | 0.29 | 0.09 | 0.02 | 1.21 | 0.01 | **AL** |
| **AM** | 0.17 | 0.01 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 | 0.12 | 0.02 | 0.01 | 0.00 | 0.12 | 0.00 | **AM** |
| **AT** | 0.17 | 0.36 | 0.05 | 0.15 | 0.08 | 0.19 | 0.04 | 1.56 | 0.24 | 0.80 | 0.15 | 12.61 | 0.02 | **AT** |
| **AZ** | 1.82 | 0.02 | 0.00 | 0.03 | 0.00 | 0.07 | 0.01 | 0.39 | 0.04 | 0.03 | 0.02 | 0.46 | 0.00 | **AZ** |
| **BA** | 0.12 | 0.10 | 0.01 | 0.13 | 0.04 | 0.18 | 1.14 | 5.36 | 0.29 | 0.20 | 0.06 | 4.74 | 0.03 | **BA** |
| **BE** | 0.04 | 0.11 | 0.43 | 0.09 | 0.02 | 0.02 | 0.00 | 0.07 | 0.02 | 9.18 | 0.11 | 1.97 | 0.01 | **BE** |
| **BG** | 0.65 | 0.11 | 0.02 | 0.18 | 0.03 | 1.79 | 0.12 | 44.33 | 0.28 | 0.21 | 0.10 | 7.25 | 0.02 | **BG** |
| **BY** | 0.97 | 3.63 | 0.02 | 4.20 | 0.02 | 1.94 | 0.04 | 2.53 | 0.10 | 0.47 | 0.35 | 49.40 | 0.02 | **BY** |
| **CH** | 0.04 | 0.09 | 0.03 | 0.04 | 0.14 | 0.04 | 0.01 | 0.34 | 0.07 | 0.28 | 0.05 | 2.04 | 0.02 | **CH** |
| **CY** | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.23 | 0.02 | 0.01 | 0.00 | 0.12 | 0.00 | **CY** |
| **CZ** | 0.21 | 0.33 | 0.04 | 0.23 | 0.03 | 0.26 | 0.03 | 1.18 | 0.23 | 0.67 | 0.17 | 61.94 | 0.01 | **CZ** |
| **DE** | 0.70 | 1.58 | 1.01 | 1.33 | 0.18 | 0.55 | 0.04 | 1.53 | 0.37 | 17.92 | 1.23 | 82.42 | 0.08 | **DE** |
| **DK** | 0.09 | 0.10 | 0.01 | 0.27 | 0.01 | 0.04 | 0.00 | 0.12 | 0.01 | 0.87 | 0.63 | 6.68 | 0.01 | **DK** |
| **EE** | 0.19 | 0.61 | 0.00 | 6.91 | 0.00 | 0.12 | 0.00 | 0.27 | 0.02 | 0.15 | 0.20 | 6.23 | 0.00 | **EE** |
| **ES** | 0.32 | 0.20 | 0.07 | 0.26 | 0.22 | 0.20 | 0.04 | 1.40 | 0.16 | 1.99 | 0.36 | 6.11 | 3.74 | **ES** |
| **FI** | 1.70 | 1.27 | 0.02 | 5.66 | 0.02 | 0.36 | 0.02 | 0.96 | 0.08 | 0.56 | 1.50 | 13.81 | 0.02 | **FI** |
| **FR** | 0.54 | 1.18 | 1.73 | 0.85 | 4.40 | 0.44 | 0.08 | 2.88 | 0.47 | 10.50 | 0.96 | 25.78 | 0.39 | **FR** |
| **GB** | 0.33 | 0.35 | 0.09 | 0.78 | 0.06 | 0.22 | 0.01 | 0.70 | 0.06 | 5.79 | 1.65 | 13.24 | 0.15 | **GB** |
| **GE** | 0.63 | 0.02 | 0.00 | 0.03 | 0.01 | 0.11 | 0.01 | 0.66 | 0.08 | 0.04 | 0.02 | 0.65 | 0.01 | **GE** |
| **GR** | 0.69 | 0.15 | 0.02 | 0.13 | 0.07 | 1.03 | 0.15 | 71.42 | 0.88 | 0.29 | 0.09 | 4.81 | 0.03 | **GR** |
| **HR** | 0.13 | 0.11 | 0.01 | 0.25 | 0.05 | 0.19 | 0.21 | 3.66 | 0.24 | 0.22 | 0.07 | 6.29 | 0.04 | **HR** |
| **HU** | 0.20 | 0.18 | 0.02 | 0.25 | 0.03 | 0.38 | 0.11 | 4.79 | 0.18 | 0.32 | 0.13 | 24.06 | 0.03 | **HU** |
| **IE** | 0.05 | 0.07 | 0.01 | 0.17 | 0.01 | 0.05 | 0.00 | 0.20 | 0.02 | 0.66 | 0.28 | 1.60 | 0.06 | **IE** |
| **IS** | 0.30 | 0.08 | 0.01 | 0.23 | 0.00 | 0.06 | 0.00 | 0.25 | 0.02 | 0.35 | 0.54 | 2.65 | 0.03 | **IS** |
| **IT** | 0.50 | 0.40 | 0.06 | 0.28 | 1.95 | 0.54 | 0.42 | 12.86 | 3.28 | 1.04 | 0.26 | 11.61 | 0.13 | **IT** |
| **KY** | 26.74 | 0.02 | 0.00 | 0.02 | 0.01 | 0.04 | 0.01 | 0.30 | 0.04 | 0.02 | 0.01 | 0.31 | 0.01 | **KY** |
| **KZ** | **844.25** | 0.66 | 0.05 | 1.20 | 0.07 | 1.00 | 0.09 | 4.05 | 0.40 | 0.64 | 0.71 | 12.52 | 0.06 | **KZ** |
| **LT** | 0.24 | **20.08** | 0.01 | 7.23 | 0.01 | 0.26 | 0.01 | 0.56 | 0.03 | 0.31 | 0.20 | 26.73 | 0.01 | **LT** |
| **LU** | 0.00 | 0.01 | **0.83** | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.12 | 0.01 | 0.21 | 0.00 | **LU** |
| **LV** | 0.29 | 4.16 | 0.01 | **53.24** | 0.01 | 0.24 | 0.01 | 0.50 | 0.03 | 0.28 | 0.24 | 15.10 | 0.01 | **LV** |
| **MC** | 0.00 | 0.00 | 0.00 | 0.00 | **0.02** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | **MC** |
| **MD** | 0.25 | 0.05 | 0.03 | 0.08 | 0.01 | **40.72** | 0.01 | 0.84 | 0.03 | 0.06 | 0.04 | 3.09 | 0.00 | **MD** |
| **ME** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | **0.04** | 0.75 | 0.00 | 0.00 | 0.00 | 0.09 | 0.00 | **ME** |
| **MK** | 0.08 | 0.03 | 0.00 | 0.04 | 0.02 | 0.13 | 0.08 | **326.72** | 0.14 | 0.07 | 0.02 | 1.31 | 0.01 | **MK** |
| **MT** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | **0.60** | 0.00 | 0.00 | 0.00 | 0.00 | **MT** |
| **NL** | 0.06 | 0.07 | 0.05 | 0.12 | 0.02 | 0.03 | 0.00 | 0.07 | 0.01 | **39.20** | 0.19 | 2.57 | 0.01 | **NL** |
| **NO** | 1.27 | 0.85 | 0.03 | 2.13 | 0.03 | 0.30 | 0.02 | 1.00 | 0.10 | 1.43 | **58.50** | 26.57 | 0.05 | **NO** |
| **PL** | 1.03 | 3.02 | 0.09 | 2.46 | 0.07 | 1.63 | 0.08 | 3.68 | 0.55 | 1.92 | 1.03 | **1046.36** | 0.05 | **PL** |
| **PT** | 0.04 | 0.02 | 0.01 | 0.04 | 0.02 | 0.02 | 0.00 | 0.13 | 0.02 | 0.28 | 0.06 | 0.63 | **19.12** | **PT** |
| **RO** | 1.20 | 0.22 | 0.05 | 0.42 | 0.06 | 13.16 | 0.29 | 17.67 | 0.36 | 0.44 | 0.25 | 24.69 | 0.04 | **RO** |
| **RS** | 0.24 | 0.12 | 0.02 | 0.19 | 0.05 | 0.54 | 4.41 | 74.63 | 0.34 | 0.25 | 0.10 | 8.66 | 0.03 | **RS** |
| **RU** | 238.62 | 8.11 | 0.22 | 22.84 | 0.31 | 6.30 | 0.34 | 19.61 | 1.63 | 3.99 | 6.50 | 116.31 | 0.27 | **RU** |
| **SE** | 1.73 | 2.02 | 0.04 | 6.01 | 0.03 | 0.58 | 0.03 | 1.47 | 0.12 | 1.87 | 10.42 | 43.08 | 0.04 | **SE** |
| **SI** | 0.05 | 0.04 | 0.00 | 0.05 | 0.02 | 0.06 | 0.03 | 0.75 | 0.06 | 0.09 | 0.03 | 2.24 | 0.02 | **SI** |
| **SK** | 0.15 | 0.18 | 0.02 | 0.19 | 0.02 | 0.25 | 0.05 | 2.13 | 0.13 | 0.21 | 0.10 | 45.47 | 0.01 | **SK** |
| **TJ** | 2.69 | 0.01 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 | 0.16 | 0.02 | 0.01 | 0.01 | 0.14 | 0.00 | **TJ** |
| **TM** | 13.36 | 0.04 | 0.00 | 0.06 | 0.01 | 0.11 | 0.01 | 0.64 | 0.06 | 0.05 | 0.04 | 0.90 | 0.01 | **TM** |
| **TR** | 4.49 | 0.39 | 0.04 | 0.47 | 0.15 | 3.17 | 0.19 | 16.11 | 1.56 | 0.73 | 0.28 | 13.80 | 0.10 | **TR** |
| **UA** | 5.85 | 1.21 | 0.13 | 1.96 | 0.09 | 23.81 | 0.20 | 12.18 | 0.52 | 0.91 | 0.68 | 78.53 | 0.07 | **UA** |
| **UZ** | 39.87 | 0.04 | 0.00 | 0.07 | 0.01 | 0.11 | 0.01 | 0.58 | 0.06 | 0.06 | 0.05 | 1.02 | 0.01 | **UZ** |
| | **KZ** | **LT** | **LU** | **LV** | **MC** | **MD** | **ME** | **MK** | **MT** | **NL** | **NO** | **PL** | **PT** | |

***Table A.3**. Matrix of PCDD/F country-to-country deposition in 2010, g TEQ/y (continued)*

Receptors ↓ Emitters →

| | RO | RS | RU | SE | SI | SK | TJ | TM | TR | UA | UZ | Total | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AL** | 1.24 | 3.33 | 0.80 | 0.06 | 0.08 | 0.25 | 0.00 | 0.01 | 3.09 | 3.21 | 0.02 | **132.28** | **AL** |
| **AM** | 0.11 | 0.02 | 0.68 | 0.01 | 0.00 | 0.02 | 0.01 | 0.11 | 14.75 | 0.79 | 0.08 | **40.65** | **AM** |
| **AT** | 2.93 | 1.20 | 1.55 | 0.26 | 5.72 | 5.18 | 0.01 | 0.02 | 1.53 | 7.47 | 0.04 | **184.05** | **AT** |
| **AZ** | 0.45 | 0.07 | 6.98 | 0.03 | 0.01 | 0.07 | 0.04 | 1.36 | 13.88 | 3.65 | 0.94 | **276.80** | **AZ** |
| **BA** | 3.30 | 6.08 | 1.16 | 0.12 | 0.55 | 1.56 | 0.00 | 0.01 | 2.17 | 5.22 | 0.02 | **200.80** | **BA** |
| **BE** | 0.19 | 0.04 | 0.44 | 0.18 | 0.03 | 0.13 | 0.00 | 0.00 | 0.20 | 1.19 | 0.01 | **128.53** | **BE** |
| **BG** | 33.43 | 6.45 | 6.19 | 0.22 | 0.16 | 1.78 | 0.01 | 0.06 | 35.50 | 34.65 | 0.09 | **310.03** | **BG** |
| **BY** | 7.45 | 0.90 | 42.34 | 1.35 | 0.23 | 3.33 | 0.02 | 0.08 | 8.21 | 135.72 | 0.16 | **374.73** | **BY** |
| **CH** | 0.48 | 0.18 | 0.34 | 0.08 | 0.27 | 0.29 | 0.00 | 0.00 | 0.38 | 1.47 | 0.01 | **68.42** | **CH** |
| **CY** | 0.13 | 0.04 | 0.20 | 0.01 | 0.01 | 0.02 | 0.00 | 0.00 | 8.34 | 0.66 | 0.00 | **11.65** | **CY** |
| **CZ** | 3.10 | 0.81 | 2.32 | 0.34 | 0.51 | 8.37 | 0.01 | 0.02 | 1.50 | 12.36 | 0.04 | **323.33** | **CZ** |
| **DE** | 4.42 | 1.01 | 8.53 | 2.76 | 0.77 | 4.17 | 0.02 | 0.07 | 3.65 | 30.39 | 0.13 | **521.17** | **DE** |
| **DK** | 0.38 | 0.06 | 1.55 | 2.34 | 0.04 | 0.32 | 0.00 | 0.01 | 0.47 | 3.41 | 0.02 | **53.13** | **DK** |
| **EE** | 0.65 | 0.09 | 13.78 | 1.14 | 0.04 | 0.34 | 0.01 | 0.02 | 1.05 | 8.18 | 0.05 | **52.71** | **EE** |
| **ES** | 2.00 | 0.65 | 2.45 | 0.90 | 0.39 | 0.85 | 0.01 | 0.03 | 2.44 | 7.88 | 0.06 | **461.92** | **ES** |
| **FI** | 2.14 | 0.30 | 63.50 | 8.97 | 0.10 | 0.81 | 0.05 | 0.13 | 4.76 | 26.52 | 0.30 | **190.35** | **FI** |
| **FR** | 4.29 | 1.69 | 5.43 | 1.80 | 1.22 | 2.60 | 0.01 | 0.05 | 4.11 | 18.94 | 0.11 | **575.47** | **FR** |
| **GB** | 1.75 | 0.28 | 4.97 | 2.21 | 0.16 | 1.05 | 0.01 | 0.04 | 2.73 | 11.47 | 0.07 | **548.89** | **GB** |
| **GE** | 0.73 | 0.12 | 8.28 | 0.04 | 0.02 | 0.11 | 0.01 | 0.25 | 38.72 | 5.27 | 0.21 | **291.42** | **GE** |
| **GR** | 7.37 | 3.09 | 5.44 | 0.23 | 0.22 | 1.03 | 0.01 | 0.06 | 55.56 | 25.13 | 0.09 | **294.19** | **GR** |
| **HR** | 3.63 | 4.61 | 1.26 | 0.13 | 4.30 | 2.50 | 0.00 | 0.01 | 1.91 | 6.07 | 0.03 | **269.34** | **HR** |
| **HU** | 16.38 | 6.23 | 2.46 | 0.24 | 1.63 | 49.04 | 0.00 | 0.02 | 2.45 | 25.61 | 0.04 | **301.78** | **HU** |
| **IE** | 0.35 | 0.06 | 0.80 | 0.41 | 0.02 | 0.11 | 0.00 | 0.01 | 0.43 | 1.89 | 0.01 | **68.25** | **IE** |
| **IS** | 0.39 | 0.08 | 3.10 | 0.40 | 0.03 | 0.18 | 0.01 | 0.03 | 1.32 | 3.21 | 0.07 | **27.20** | **IS** |
| **IT** | 6.59 | 3.83 | 3.94 | 0.53 | 5.28 | 3.09 | 0.01 | 0.05 | 8.63 | 15.90 | 0.10 | **751.86** | **IT** |
| **KY** | 0.26 | 0.06 | 1.64 | 0.03 | 0.01 | 0.05 | 19.70 | 1.06 | 4.37 | 1.66 | 66.09 | **279.01** | **KY** |
| **KZ** | 6.67 | 0.99 | 239.22 | 1.43 | 0.24 | 1.57 | 11.29 | 9.23 | 33.96 | 68.90 | 75.65 | **1416.63** | **KZ** |
| **LT** | 1.39 | 0.24 | 10.40 | 1.09 | 0.10 | 1.09 | 0.01 | 0.02 | 1.46 | 15.53 | 0.06 | **104.70** | **LT** |
| **LU** | 0.02 | 0.01 | 0.04 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.02 | 0.13 | 0.00 | **9.07** | **LU** |
| **LV** | 1.31 | 0.19 | 13.56 | 1.48 | 0.08 | 0.83 | 0.02 | 0.03 | 1.60 | 14.61 | 0.08 | **122.30** | **LV** |
| **MC** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | **0.05** | **MC** |
| **MD** | 14.06 | 0.24 | 3.29 | 0.09 | 0.03 | 0.42 | 0.00 | 0.02 | 4.84 | 51.99 | 0.03 | **124.97** | **MD** |
| **ME** | 0.16 | 0.97 | 0.03 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.06 | 0.13 | 0.00 | **3.04** | **ME** |
| **MK** | 1.49 | 4.51 | 0.70 | 0.05 | 0.06 | 0.31 | 0.00 | 0.01 | 3.63 | 3.10 | 0.01 | **362.89** | **MK** |
| **MT** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | **0.73** | **MT** |
| **NL** | 0.23 | 0.04 | 0.67 | 0.31 | 0.03 | 0.17 | 0.00 | 0.01 | 0.26 | 1.69 | 0.01 | **92.89** | **NL** |
| **NO** | 2.56 | 0.36 | 20.34 | 8.34 | 0.15 | 1.53 | 0.04 | 0.14 | 5.24 | 22.42 | 0.28 | **193.16** | **NO** |
| **PL** | 11.70 | 1.85 | 20.19 | 3.39 | 0.96 | 20.01 | 0.03 | 0.10 | 6.69 | 113.05 | 0.18 | **1463.81** | **PL** |
| **PT** | 0.20 | 0.06 | 0.31 | 0.13 | 0.03 | 0.08 | 0.00 | 0.00 | 0.28 | 0.87 | 0.01 | **39.86** | **PT** |
| **RO** | **420.35** | 11.96 | 13.63 | 0.50 | 0.46 | 8.40 | 0.02 | 0.11 | 27.72 | 124.42 | 0.17 | **732.67** | **RO** |
| **RS** | 15.56 | **96.10** | 2.58 | 0.20 | 0.34 | 3.02 | 0.00 | 0.03 | 5.65 | 13.33 | 0.04 | **301.30** | **RS** |
| **RU** | 38.46 | 5.08 | **4149.12** | 16.29 | 1.38 | 9.92 | 3.12 | 7.50 | 180.19 | 649.24 | 17.79 | **5846.32** | **RU** |
| **SE** | 3.99 | 0.52 | 40.31 | **105.83** | 0.25 | 2.08 | 0.08 | 0.17 | 6.14 | 39.27 | 0.40 | **324.83** | **SE** |
| **SI** | 1.15 | 0.70 | 0.46 | 0.05 | **18.82** | 1.02 | 0.00 | 0.01 | 0.57 | 2.20 | 0.01 | **73.98** | **SI** |
| **SK** | 5.74 | 1.28 | 1.93 | 0.20 | 0.54 | **86.53** | 0.00 | 0.02 | 1.54 | 19.35 | 0.03 | **229.41** | **SK** |
| **TJ** | 0.13 | 0.03 | 0.82 | 0.01 | 0.01 | 0.02 | **97.92** | 1.28 | 2.18 | 0.80 | 30.49 | **146.28** | **TJ** |
| **TM** | 0.70 | 0.12 | 8.96 | 0.08 | 0.03 | 0.13 | 4.56 | **69.82** | 9.47 | 6.41 | 46.12 | **177.28** | **TM** |
| **TR** | 19.12 | 2.97 | 35.94 | 0.63 | 0.50 | 2.39 | 0.07 | 0.48 | **3470.04** | 123.04 | 0.64 | **3805.71** | **TR** |
| **UA** | 54.70 | 3.74 | 126.19 | 1.84 | 0.60 | 11.33 | 0.07 | 0.64 | 81.26 | **2812.94** | 0.90 | **3314.90** | **UA** |
| **UZ** | 0.71 | 0.12 | 9.40 | 0.10 | 0.03 | 0.15 | 43.90 | 13.29 | 6.99 | 6.29 | **261.02** | **419.57** | **UZ** |
| | **RO** | **RS** | **RU** | **SE** | **SI** | **SK** | **TJ** | **TM** | **TR** | **UA** | **UZ** | **Total** | |