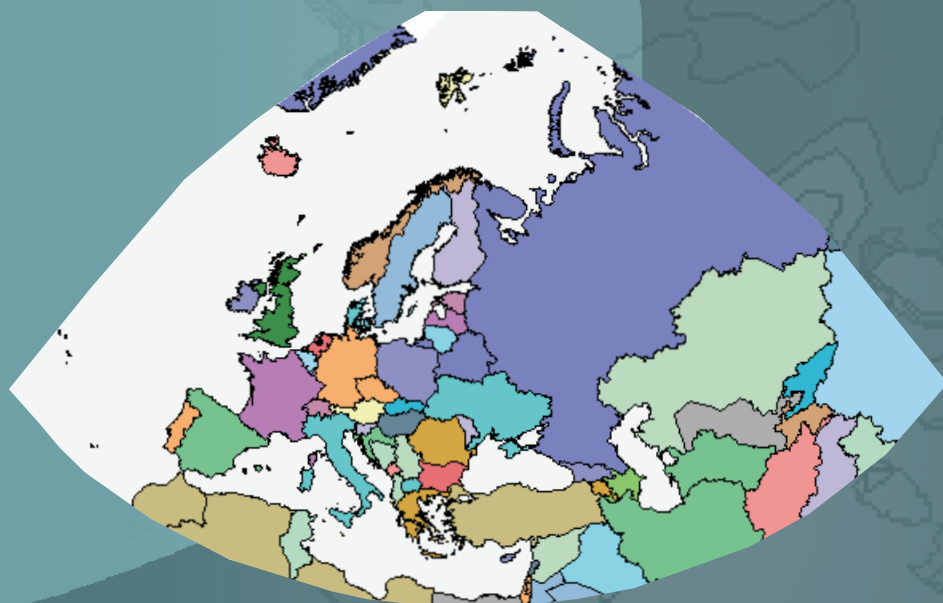


Persistent Organic Pollutants: assessment of transboundary pollution on global, regional, and national scales

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EXECUTIVE SUMMARY

Persistent organic pollutants (POPs) are semi-volatile toxic compounds, resistant to degradation, and causing an array of harmful effects to human health and wildlife. In spite of declining of POP emissions in the past several decades, they still present in the environment and pose risks to humans as well as terrestrial and aquatic ecosystems. Reduction of unintentional releases of POPs is within the scope of the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) activities since 1998, when the Aarhus Protocol on Persistent Organic Pollutants came into force. Monitoring of pollution levels, determination of emissions, and assessment of transboundary transport of POPs is performed within the Convention by scientific Centres of Co-operative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe (EMEP).

This Status Report presents the outcome of recent work of the EMEP Centres in the field of POP pollution assessment, performed in accordance with the bi-annual work-plan of the Convention for 2018-2019 [ECE/EB.AIR/GE.1/2017/20-ECE/EB.AIR/WG.1/2017/13]. Pollution levels of polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo(p)dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB) in the EMEP region were evaluated for 2016 based on national emission inventories, modelling results, and measurements.

Monitoring of POP concentrations in the EMEP region in 2016 was performed by 39 monitoring sites of 17 Parties. While most of these sites reported measurements of PAH concentrations in air, data on HCB and PCBs were provided only by 12 sites of 7 Parties, which were mainly located in Northern and Central Europe. Measurements of POPs in air and precipitation under EMEP are complemented by relevant research and national/regional monitoring activities within Europe and beyond in other regions, which include active air monitoring (e.g. EU national air quality data collected in the EEA AIRBASE, UK network TOMPs) and various passive air sampling (e.g. Spanish POP monitoring network, Global Atmospheric Passive Sampling network (GAPS)).

Analysis of observed POP concentrations was mainly focused on the data for PAHs and PCBs. Levels of observed air concentrations of PAHs across the EMEP sites varied by more than an order of magnitude with relatively higher concentrations measured in Central and Eastern Europe and lower concentrations in other parts of EMEP domain. The highest level of B(a)P air concentrations was observed in the southern part of Poland (more than 10 ng/m³). Unlike other POPs, included in the EMEP program, spatial variations of observed PAH concentrations are characterized by both relatively high and low concentrations reported by the stations in close proximity to each other.

The spatial patterns of observed PCB concentrations showed that lighter and more volatile congeners remained relatively more abundant in air at remote sites at high latitudes, compared to the less volatile ones, which appeared to be more abundant in densely populated areas, suspected to be source regions within Europe. Contemporary PCB concentrations in air may in part be a result of primary emissions which occurred long time ago as well as secondary emissions. While the observed PCBs often show decreasing time trends at monitoring sites within the EMEP domain, it is of importance to sustain the long-term monitoring even long time after intentional PCB production has been banned.

Model assessment of POP pollution in the EMEP countries for 2016 was carried out using the most recent emission data for 2015 available at the moment of the study, which were prepared by the Centre on Emission Inventories and Projections (CEIP)¹. Supplementary characteristics of the emissions (e.g. vertical distribution and seasonal variations) as well as emission scenarios for global scale modelling were elaborated by MSC-E. Though the quality of national POP emission inventories is gradually improving, estimates of emissions of some of the EMEP countries are still subject of considerable uncertainties. To improve the quality of reported emission data detailed analysis of the consistency of applied methodologies and values of emission factors is required. Besides, air quality modelling can be applied as a tool for evaluation of reported emissions with regard to their magnitude and spatial distribution.

Assessment of PAH pollution levels in the EMEP countries has been carried out for the selected PAH compounds, namely, B(a)P, B(b)F, B(k)F, and IP, on the basis of modelling results and measurements. High levels of annual mean PAH air concentrations were predicted for countries in Central and Eastern Europe. Verification of modelling results against measurements at the EMEP monitoring sites demonstrated generally reasonable agreement of modelled and observed concentrations for the sum of 4 considered PAHs. However, model performance for particular PAHs was different, with relatively low deviations from measurements on average for B(a)P, B(b)F, and IP, and more significant under-prediction for B(k)F. The deviations found may indicate both inconsistency between the PAH compounds composition in the reported emission estimates and actual emissions, and uncertainties in physical-chemical properties of PAHs applied for modelling.

More detailed analysis of PAH pollution in the EMEP countries was carried out for B(a)P, which is considered as an indicator compound for the evaluation of exposure to carcinogenic PAHs. Model predictions of annual mean B(a)P air concentrations pointed out exceedances of the EU target value (1 ng/m³) for Poland, Germany, the Czech Republic, Hungary, Romania, Portugal, Spain, northern Italy, the FYR of Macedonia, Bulgaria, and some of the EECCA countries (e.g. Republic of Moldova, Ukraine, and the Russian Federation). According to these results, about 9% of population of the EMEP countries were living in the areas with annual mean B(a)P air concentrations above the EU target level, and almost 75% in the areas with air concentrations above the WHO reference level (0.12 ng/m³).

Evaluation of B(a)P pollution levels at national scale was performed in the framework of country-specific case study for Spain and France. Main emphasis at the current stage of the study was given to the analysis of discrepancies between B(a)P modelling results and observed pollution levels. Particularly, comparison of modelling results, based on official emission data, and observed B(a)P air concentrations revealed significant differences for some of the monitoring sites in Belgium, the Netherlands, Germany, Poland, Portugal, and Spain. Discrepancies found may be attributed to the uncertainties in estimates of B(a)P emissions from the 'Residential Combustion' and 'Field burning of agricultural residues' sectors in the national inventories of these countries. Test model simulations based on scenario emissions, assuming changes of releases for these sectors, showed improvement of the agreement with measurements and indicated the need of refinement of the emission inventories. Another reason of discrepancies may be related to the uncertainties in model parameterization of B(a)P

¹ Update of the modelling results based on the new emission data for 2016 is available at the MSC-E web site [www.msceast.org].

gas-particle partitioning and degradation that is planned to be analyzed at further stages of this B(a)P case study.

Assessment of environmental pollution by PCDD/Fs, PCB-153, and HCB was carried out for regional and global scales using nested model simulations. Model simulations indicate elevated levels of dioxins and furans air concentrations for the UK, northern Italy, countries of Central and Eastern Europe as well as in the Russian Federation, Ukraine, and Azerbaijan. The highest levels of modelled PCB-153 annual mean air concentrations were estimated for the countries in Western Europe (e.g. Germany, France, Belgium). Modelling results for HCB showed low spatial variability of annual mean air concentrations, which can be explained by longer residence time in the atmosphere comparing to other considered POPs.

Major attention in this study was paid to the evaluation of pollution by dioxins and furans. To explore the effect of uncertainties in the officially reported PCDD/F emissions, model simulations were made on the basis of both officially reported emission data and scenario emissions, representing maximum level of releases to the atmosphere. Analysis of modelling results showed that the use of maximum emission scenario led to improvement of agreement between the modelling results and measurements that can be considered as an indication of possible underestimation of officially reported PCDD/F emissions. However, it should be noted that measurement data for the evaluation of PCDD/F model predictions were available for limited amount of countries (Spain, the UK, and Sweden). Therefore, model predictions for other regions in the EMEP domain require further analysis with application of additional PCDD/F monitoring data.

Verification of model predictions for PCB-153 demonstrated reasonable agreement of modelled and measured concentrations with respect to spatial distribution of pollution levels. For 60% of the monitoring sites the difference between measured and modelled concentrations was within a factor of 2. At the same time, modelling results for HCB tended to under-predict observed air concentrations for most of the monitoring sites. The under-prediction was attributed to i) incomplete information on HCB emission sources in the inventories reported by the EMEP countries, ii) possible underestimation of HCB emissions in regions outside the EMEP domain applied in model simulations, and iii) uncertainties of model parameterizations for HCB degradation in media and air-surface exchange.

Source apportionment of PCDD/F, PCB-153, and HCB pollution in the EMEP countries was carried out taking into account primary anthropogenic emission sources and secondary emissions as well as non-EMEP emissions. The largest contribution of contemporary EMEP anthropogenic emission sources was estimated for PCDD/Fs (46%), followed by PCB-153 (36%), and HCB (2%). Secondary emission sources of PCDD/Fs, PCB-153, and HCB contributed to deposition in the EMEP countries about 50% - 70%. The contribution of non-EMEP emission sources was about 4% for PCDD/Fs and PCB-153, and about 30% for HCB.

Co-operation is an important component of research and operational pollution assessment performed by MSC-E to support countries with information on POP pollution levels in Europe and other regions. In this context MSC-E closely collaborates with Parties to the Convention and its Subsidiary Bodies, and exchanges information on POPs with various international organizations. In particular, progress of MSC-E work on the assessment of POP pollution in the EMEP region as well as in the national scale case study of B(a)P pollution was presented at the annual TFMM meeting. The Centre also contributed to

the work of the Task Force on Emission Inventories and Projections (TFEIP) presenting information on uncertainties in the official POP emissions and discussing application of air quality models for the evaluation of reported emissions. In the framework of co-operation with Helsinki Commission (HELCOM), MSC-E performed assessment of PCDD/F atmospheric input to the Baltic Sea.

National inventories of POP emissions, compiled under the Stockholm Convention, as well as development and improvement of methodologies for the estimation of POP emissions, represent important source of information for studies of environmental pollution by PCDD/Fs, PCBs, and HCB in the EMEP region and on the global scale. Therefore, further co-operation and sharing of information between the CLRTAP and the Stockholm Convention is highly appreciated.

Future activities of MSC-E will be directed to further improvement of the quality of POP pollution assessment for the EMEP region. Further development and evaluation of the Global EMEP Multi-media Modelling System (GLEMOS) will include analysis of key factors affecting uncertainties of model estimates of gas-particle partitioning and degradation in the atmosphere for PAHs as well as exchange between environmental compartments for PCDD/Fs, PCBs, and HCB. Country-specific case studies of B(a)P pollution will be continued for Spain and France as well as for some other EMEP countries (e.g. Poland, Croatia, Germany) in close cooperation with national experts. Besides, development and application of methodologies, based on complementary use of multiple regression analysis, fine resolution modelling, and measurements, for the evaluation of B(a)P pollution in urban areas will be continued. Particular attention will be given to the co-operation with subsidiary bodies of the Convention (TFMM, TFHTAP, TFEIP, and WGE), international organizations (AMAP, Stockholm Convention, HELCOM etc.) and national experts. These directions of future research activities are outlined in the MSC-E work-plan for 2018-2019 and the updated Mandate of the Centre.

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INTRODUCTION

Persistent organic pollutants (POPs) constitute a group of toxic compounds, known to have adverse effects to human health and wildlife. Many of POPs are resistant to degradation and globally dispersed in the environment, cycling between the atmosphere and terrestrial and aquatic compartments. Due to these properties reduction of POP releases and pollution levels is among priority tasks of many international and national organizations including UNEP Rotterdam, Basel, and Stockholm Conventions, World Health Organization (WHO), the Arctic Monitoring and Assessment Program (AMAP), Helsinki Commission (HELCOM), and European Union in the framework of EU Regulation concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

POPs were included into activities of the UNECE Convention on Long-range Transboundary Air Pollution (hereafter, CLRTAP or the Convention) since the adoption of the Aarhus Protocol on Persistent Organic Pollutants in 1998. The information on emissions, air pollution levels, and transboundary transport of selected POPs within the geographical scope of Co-operative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe (EMEP) is regularly produced by its scientific Centres and provided to the Executive Body for the Convention (www.emep.int).

The Centre of Emission Inventories and Projections (CEIP) generates gridded POP emission data on the basis of national emission inventories, reported by Parties to the Convention as well as expert estimates and other available data. The Chemical Coordinating Centre (CCC) supports EMEP with monitoring and analytical strategies and guidelines in order to gather quality data to evaluate spatial and temporal trends in air pollution across the EMEP region. The Meteorological Synthesizing Centre East (MSC-E) is responsible for the development and application of modelling tools for the assessment of air pollution levels and transboundary transport of POPs within the EMEP domain.

This Status Report presents the outcome of POP pollution assessment, performed by the EMEP Centres in accordance with the bi-annual work-plan of the Convention for 2018-2019 [ECE/EB.AIR/GE.1/2017/20-ECE/EB.AIR/WG.1/2017/13]. Measurements of POP concentrations in the EMEP region, performed by the EMEP monitoring network, are overviewed in *Chapter 1*. More detailed discussion is provided for the observations of PCBs and PAHs to highlight the importance of long-term monitoring and issues, which may merit further attention. Besides, complementary monitoring activities aimed to assess POP pollution levels in the EMEP region and beyond are described.

Assessment of pollution levels and transboundary transport of PAHs, included into the Protocol on POPs, is described in *Chapter 2*. Analysis of spatial and temporal variability of PAH pollution levels within the EMEP domain is carried out on the basis of modelling results and measurements of the EMEP monitoring network for 2016 as well as national measurements from EEA AIRBASE. Transboundary transport of the selected PAHs is evaluated taking into account anthropogenic emission sources of the EMEP countries as well as influence of non-EMEP emissions. In addition, estimates of PAH pollution for the Arctic area within the EMEP region are also provided. Main emphasis is given to the assessment of B(a)P pollution levels and evaluation of exceedances of EU target value and WHO reference level defined for B(a)P air concentrations.

In *Chapter 3* ongoing activities in framework of country-specific case study of B(a)P pollution in the EMEP countries are outlined. Evaluation of B(a)P pollution levels in Spain is continued. Besides, similar work is initiated for France. Current stage of the study is mainly focused on the analysis of discrepancies between B(a)P modelling results and observed pollution levels taking place for Spain and France as well as for some other EMEP countries. This activity includes construction of experimental emission scenarios and test model simulations in order to evaluate sensitivity of model predictions to possible uncertainties in the officially reported emission data. Particular attention is also paid to possible uncertainties in the applied modelling approach for B(a)P. Model simulations and their analysis are performed in close cooperation with national experts in modelling of B(a)P pollution.

Assessment of PCDD/F, PCB, and HCB pollution levels in the EMEP countries is given in *Chapter 4*. Model simulations are carried out on the basis of officially reported emission data for the new EMEP grid using the multi-media GLEMOS modelling system. Spatial trends of air pollution levels in 2016 on regional and global scales are characterized as well as transboundary transport of pollution is evaluated. Results of model simulations were compared with measurements of the EMEP monitoring sites and data of national monitoring networks. Main emphasis in these activities is given to the evaluation of PCDD/F pollution levels in the EMEP countries.

MSC-E activities related to co-operation and information sharing with subsidiary bodies to the Convention and other international organisations are discussed in *Chapter 5*. Results of recent activities of the Centre with regard to the assessment of POP pollution have been presented and discussed at the meetings of the EMEP task forces, namely, Task Force on Measurements and Modelling (TFMM) and Task Force on Emission Inventories and Projections (TFEIP). Special attention is also paid to the collaboration with other international organizations and programmes including the Stockholm Convention, the Arctic Monitoring and Assessment Programme (AMAP), and Helsinki Commission (HELCOM).

Detailed information on long-range transport and pollution levels of POPs in the EMEP region as well as in particular EMEP countries is presented at the MSC-E website (www.msceast.org). Similar information on POP pollution in the EMEP countries of Eastern Europe, Caucasus and Central Asia (EECCA) is also given at the MSC-E website in Russian (www.ru.msceast.org).

1. EMEP MONITORING DATA FOR POPs IN AIR AND PRECIPITATION IN 2016

Persistent Organic Pollutants (POPs) were included in the EMEP's monitoring program about two decades ago (1999). However, for a few compounds and stations, monitoring data extends back to the early 1990s [Tørseth *et al.*, 2012]. These data provide vital information on observed spatial and temporal trends which, among other, are essential to help evaluate the modelling work carried out under the Convention. The chemical coordinating centre (CCC) supports EMEP with monitoring and analytical strategies and guidelines in order to gather quality data to assess regional scale air pollution across Europe. A long-term goal of CCC is to collect comparable monitoring data to facilitate consistent and comparable data sets for evaluation of spatial and temporal trends. To achieve this goal, CCC attempts to harmonize sampling methodologies and chemical analytical methodologies (EMEP/CCC 2014). Unlike many «classical» air pollutants, EMEP monitoring data on POPs still remain scarce and are only reported by some Parties, especially on other POPs than Polycyclic Aromatic Hydrocarbons (PAHs).

1.1. EMEP data and complementary monitoring activities

In 2016 there were in total 39 sites with POP measurements, from 17 Parties. Most of the sites only include PAHs, 12 sites from 7 Parties measure any of the other POPs, and these are mainly located in Northern- and Central Europe. The spatial distribution of the different sites and measurement program in air and precipitation (or deposition) is illustrated in Fig. 1.1.

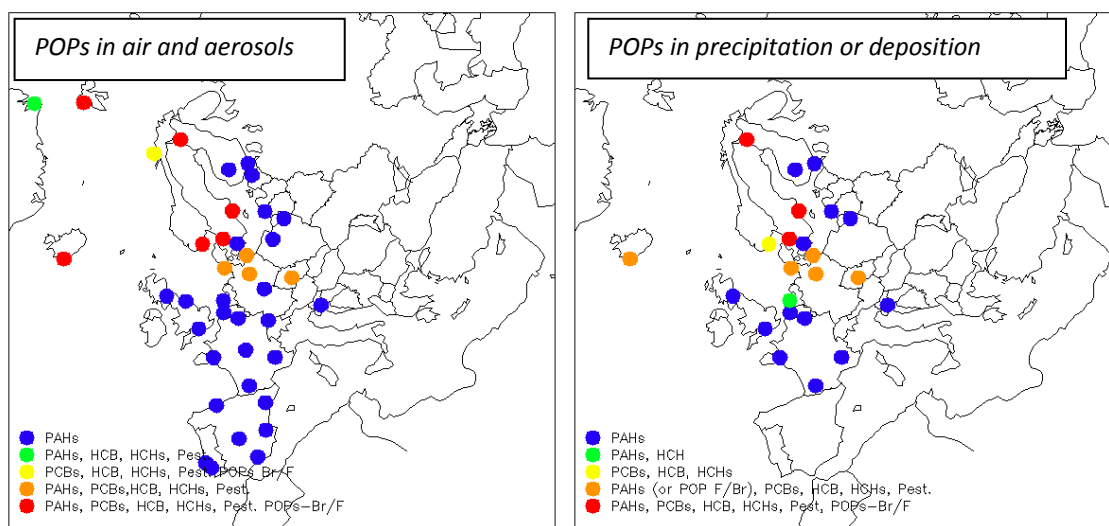


Fig. 1.1. Monitoring network of POPs in EMEP in 2016 . Pesticides are either any DDTs or any of aldrin, dieldrin, endrin, heptachlor, oxychlorane, heptachlorepoxyde, mirex, endosulfan. POPs-F/Br means bromated or fluorinated POPs like BDEs, PFAS etc.

In general terms, limited monitoring data mitigates opportunities for more comprehensive model evaluations within EMEP which, in turn, is required to fully evaluate if source-relationships for POPs are accurately predicted and understood. However, *monitoring data on POPs in air and precipitation under EMEP are complemented by relevant research and national/regional monitoring activities*

within Europe and beyond. Examples of such complementary monitoring activities using active air sampling are the UK TOMPs (Toxic Organic Micro Pollutants) Network performing long-term monitoring of POPs at six urban and rural sites in England and Scotland [Graf et al., 2016]. *Over the last decade and beyond, active air monitoring have increasingly been complemented by various passive air sampling techniques* [Shoeib et al., 2002]. *Examples of passive air sampling studies at various scales include (i) the GAPS programme (Global Atmospheric Passive Sampling network), consisting of more than 50 sites world-wide* [Pozo et al., 2006], *(ii) different initiatives across or within parts of Europe* [Jaward et al., 2004 and Pribylova et al., 2012], some of which often include a goal to complement the EMEP programme [Halse et al., 2011] and/or other national and international programmes and Conventions [Munoz-Arnanz et al. 2016 and Schuster et al., 2011]. *While these passive air monitoring studies have gained valuable complementary information to the data within the EMEP programme, passive air sampling is still considered to be a semi-quantitative method.* It is also incomplete in terms of total atmospheric occurrences for less volatile POPs as it is mainly designed to target the gaseous fraction in air. As a result, passive air sampling data are not fully comparable and consistent with the EMEP data based on active air sampling, although individual passive air sampling initiatives may at the same time offer data which are internally consistent.

In this year's report, the main focus is on polychlorinated biphenyls and polycyclic aromatic hydrocarbons. These measurements will be discussed in some more detail to highlight the importance of long-term monitoring and issues which may merit further attention. For other POPs and more detailed information about the sites and the measurement methods, these are found in EMEP/CCC's data report on heavy metals and POPs [Aas et al., 2018]. All the data are available from the EBAS database (<http://ebas.nilu.no/>).

1.2. Polychlorinated Biphenyls (PCBs)

Polychlorinated Biphenyls (PCBs) are a group of (mainly) industrial chemicals which were deliberately and extensively produced from ~1930 until the early 1990s. Production peaked around 1970, and was followed by various control measures on production and new use. PCBs are among the initial POPs included under the Aarhus protocol on POPs, and also among the compound groups for which monitoring data have been more extensively reported to EMEP. Data for selected PCBs in 2016 are included in Fig. 1.2.

PCBs represent an interesting class of POPs for a more in-depth discussion for several reasons. While most of the initial POPs regulated under CLRTAP were either pesticides (e.g. DDT, HCHs), or combustion by-products (e.g. PCDD/Fs, PAHs), PCBs are mainly an industrial chemical which was extensively used for various purposes and applications ranging from so-called open applications (e.g. carbonless copy paper) and closed systems (capacitors, transformers). Probably, the most extensive historical use in terms of tonnage was for electrical equipment.

While primary emissions are expected to have experienced a general decline over the last decade, as also seen in the EMEP monitoring data, primary emissions may still persist due to the long lifetime of

products and material containing PCBs. PCBs were also used in various building materials, such as paints, and many of these products may still remain in use, causing primary emissions to air and other environmental media even today. Emissions may also occur when material containing PCBs eventually are demolished (e.g. buildings from a certain period) or by accidental releases when old electrical equipment (e.g. containing capacitors) is not properly recycled and/or discarded. PCBs were produced as so-called technical mixtures (e.g. Aroclors), with different isomer (number of chlorines ranging from 1 to 10) and congeneric compositions (1 to 209).

Figure 1.2 shows the annual mean concentrations in 2016 at the EMEP sites for selected PCB congeners (28, 101, 153, 180). These four congeners are among the seven so-called indicator PCBs (or “Dutch PCBs”) which also were among the more abundant in various technical mixtures, and, among the congeners which are more frequently analyzed and reported. However, these and other PCBs represent a wide variety of environmental fate properties, reflecting differences in their temperature dependent physical-chemical properties [Li *et al.*, 2003].

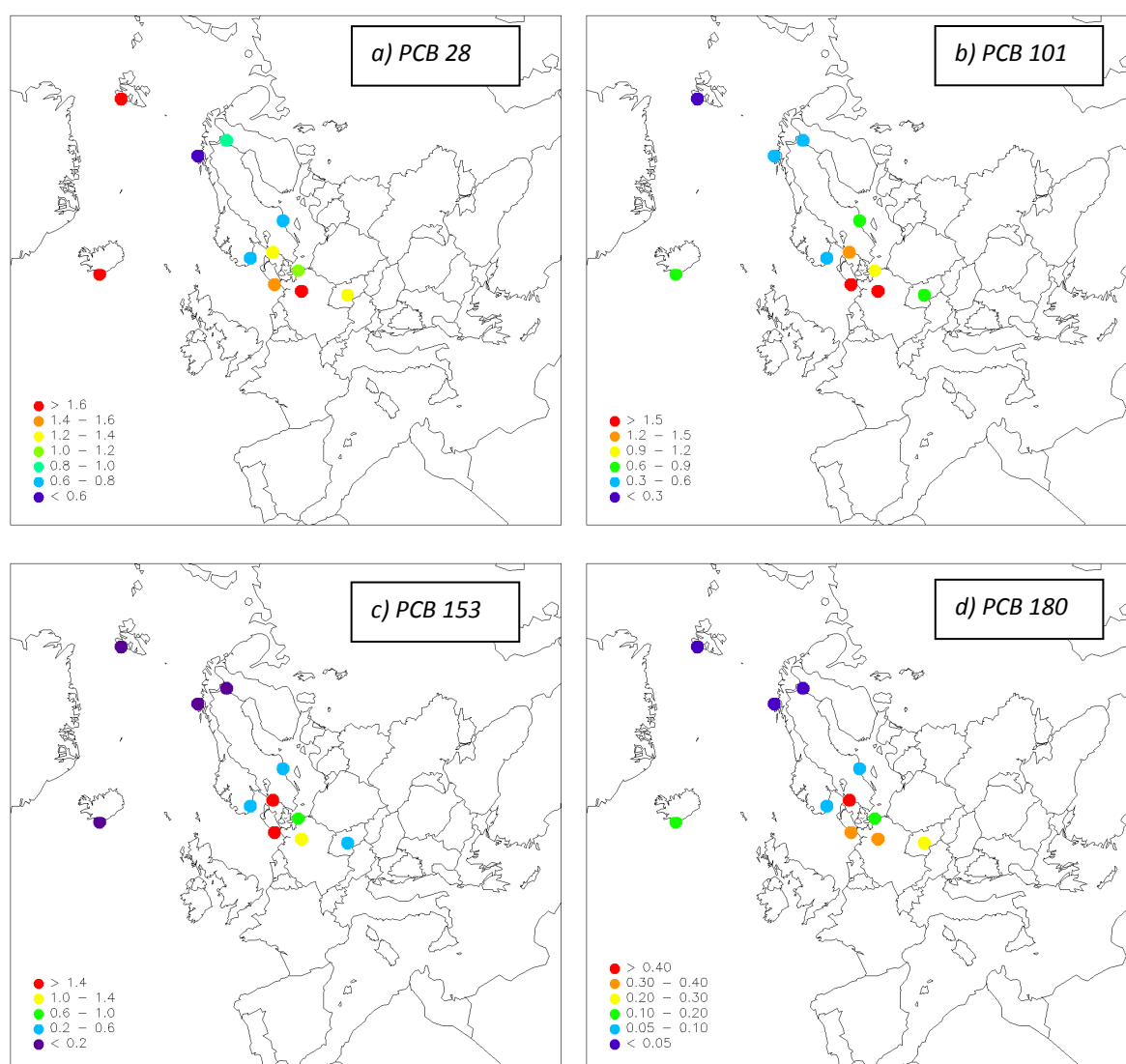


Fig. 1.2. Annual mean concentrations in 2016 for selected polychlorinated biphenyls (PCBs) in air, pg/m^3 .

Because of their semi-volatile properties, PCBs may be present in both the gaseous and particulate fractions in air. Depending on their partitioning between gas and particles, their mobility and persistence in air may hence vary widely, and hence are anticipated to show spatial and temporal variability in air across Europe. There are clues in Figure 1.2 that lighter and more volatile PCBs (e.g. PCB-28) remain relatively more abundant in air at remote sites at high latitudes, compared to the less volatile PCBs which appear more abundant in more densely populated areas which are suspected source regions within Europe.

The example of PCBs illustrates that more information on observed gas-particle partitioning for substances which may be present in both phases is desirable within EMEP for a more in-depth understanding of their atmospheric long-range transport potential and predictions thereof. Another feature associated with PCBs is their potential to undergo reversible atmospheric deposition, i.e. due to secondary emissions from environmental reservoirs as contaminated in the past. Hence, contemporary concentrations in air may in part be a result of primary emissions which occurred long time ago as well as secondary emissions [Nizzetto et al., 2010], which testifies the importance of long-time series of POPs and continued monitoring under the EMEP programme. These are temperature-dependent process, and it has been discussed if the relative significance of secondary emissions may increase as a result of climate change [Ma et al., 2011], e.g. from melting glaciers [Steinlin, 2016].

While this appears plausible, it has nevertheless been observed that PCBs and many other POPs often show decreasing time trends at monitoring sites within the EMEP domain, which testifies to the importance of long-time series of POPs and continued monitoring. Yet, long-term temporal trends of PCBs are rarely always consistent across sites. Nor are temporal trends of individual POP compounds, measured at individual sites, always showing continuous decline, an example being some PCB monitored at the Zeppelin station in Norway [Hung et al., 2016]. *It is therefore interesting and important to sustain the long-term monitoring even long time after intentional PCB production has been banned.*

There are still several important research questions, relevant for control strategies, which remain to be fully understood. One key example is the occurrence and potentially increasing significance of PCB congeners which were not typically associated with technical mixtures. PCBs may also be unintentionally formed and emitted as a result of *de novo* synthesis from the thermal processes, and PCB-118 has been proposed as a marker for such activities [Liu et al., 2013]. *As emissions of PCBs from technical mixtures are expected to decline, the role and possible magnitude of unintentionally produced PCB emissions from thermal processes in controlling contemporary and future PCB concentrations remains an open question.*

Secondly, there are additional PCB congeners which may be unintentional by-products of manufacturing process, including those used to make certain pigments [Grossman, 2013]. Among these, PCB-11 has appeared to be a marker for non-legacy PCB contamination, but PCB-209, PCB-77, PCB-28, and PCB-52 are also implicated manufacturing by-products, according to a recent review [Vorkamp, 2016]. Hence, *recent scientific literature suggest that the number of PCB congeners measured and reported under EMEP should ideally be expanded in order to obtain further knowledge*

about these “new” PCBs, claimed to represent a possible largely overlooked environmental issue [Vorkamp, 2016].

Taken together, the examples may also serve to illustrate the importance of continued monitoring of PCBs in air under the EMEP program, even for substances for which production ceased decades ago. Continued efforts under EMEP to monitoring these relatively data-rich substances may also be to the benefit in terms of expanding sampling, analytical and modelling efforts towards less data-rich substances of more emerging concern, but with similar fate properties.

1.3. Polycyclic Aromatic Hydrocarbons (PAHs)

Unlike PCBs, PAHs are mainly considered as byproducts of incomplete combustion processes. Under EMEP, significant attention has recently been paid to these compounds, including discussions concerning apparent discrepancies between modelled and observed concentration in specific areas. Figure 1.3 summarizes the annual average concentrations of selected PAHs (Anthracene, Fluoranthene, Pyrene and Benzo[*a*]Pyrene) at EMEP sites in 2016. As seen from this Figure, the spatial variability across EMEP sites varies by more than an order of magnitude.

The spatial pattern for selected PAHs in background air may also be seen as different to many other POPs included in the EMEP program, with both relatively high and relatively low concentrations reported for stations in relative close proximity to each other (Fig. 1.3). The absence of a clear spatial pattern mirrors findings from *Halse et al.* [2011], who reported concentrations at 96 European background sites, and who attributed this to a more significant influence of local emission sources, rather than atmospheric long-range transport. Part of the explanation may thus be the relatively short atmospheric half-life of many PAHs in air, compared to e.g. other POPs as hexachlorobenzene (HCB). If this is reasonably correct, *this then represents some additional challenges to accurately determine the spatial and temporal variability of emissions and testifies to the need for high temporal and spatial resolution in the models to improve the understanding of atmospheric source-receptor relationships.*

Clearly, this also implies a need for a more dense network of monitoring stations to better capture some of the anticipated variability in background air, compared to POPs which are more “homogenously” distributed across the EMEP domain (e.g. HCB). *Some PAHs are also, similar to the PCBs, compounds which may partition between the gas and particulate phases. Hence, more data on the observed partitioning between these two phases (i.e. by measuring and reporting both gaseous and particulate concentrations in air) may additionally help to increase confidence in model predictions.*

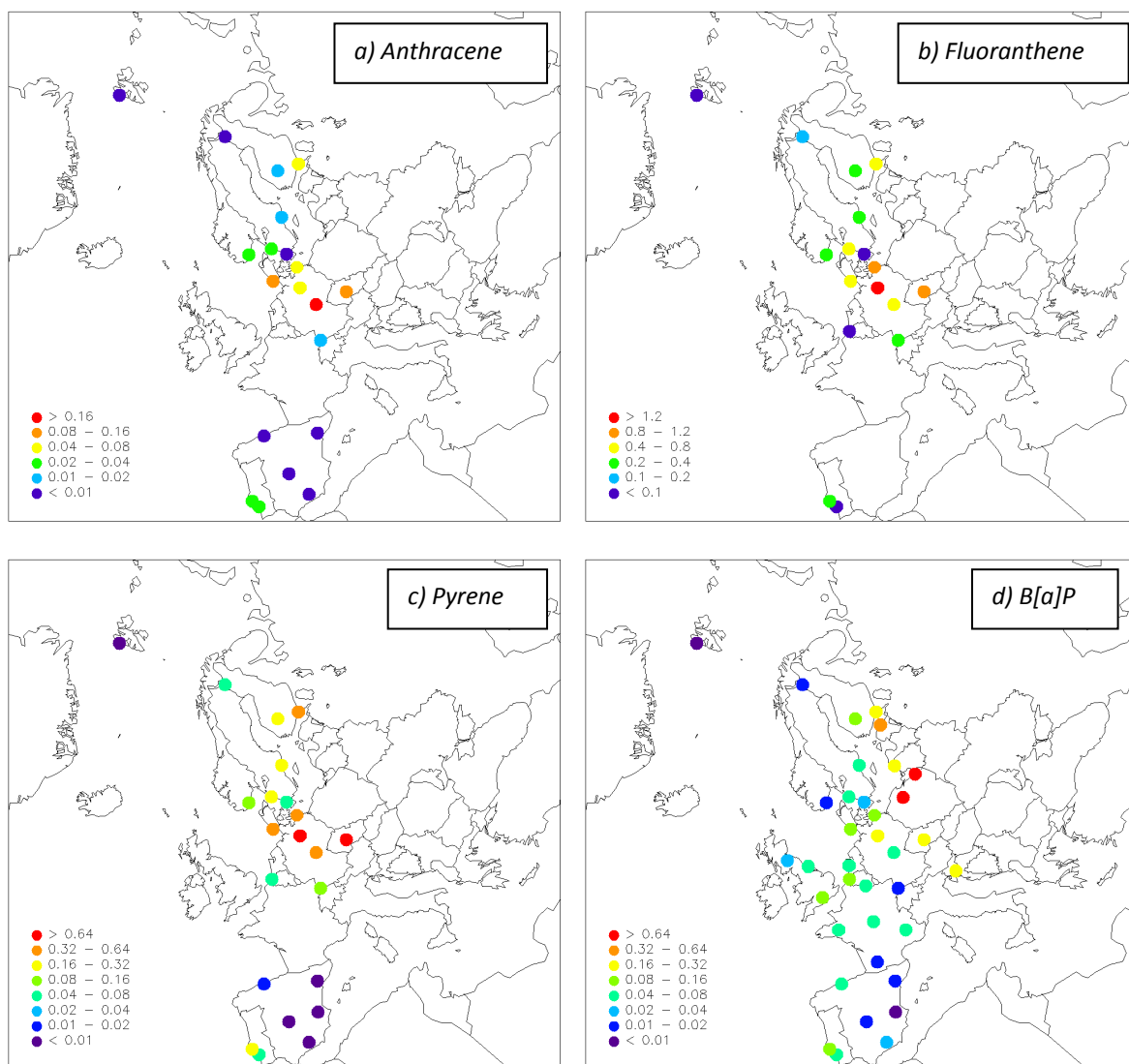


Fig. 1.3. Annual mean concentrations in 2016 for selected polycyclic aromatic hydrocarbons (PAHs) in air and aerosols, ng/m³.

2. ASSESSMENT OF PAH POLLUTION IN THE EMEP REGION

Polycyclic Aromatic Hydrocarbons (PAHs) are a large group of semi-volatile organic compounds some of which are characterized by toxic properties and are known as carcinogens, mutagens, and teratogens. They are released into the environment mainly as a result of anthropogenic activities that include combustion of fossil fuels and biomass burning. Additional contribution to PAH pollution levels can be made by natural sources, namely, forest fires and volcanic activity [Zhang and Tao, 2009]. Being emitted to the atmosphere, PAH undergo complex interactions with other pollutants, including particulate matter and atmospheric reactants, chemical transformations, and dry and wet deposition [Delgado Saborit et al., 2010; Ravindra et al., 2007].

Some of the PAHs are considered as harmful substances for the human health [Theakston, 2000]. Benzo(a)pyrene (B(a)P) has been included in the list of carcinogens of category 1 by the International Agency for Research on Cancer (IARC). According to Classification, Labelling and Packaging (CLP) Regulation², B(a)P is classified as CMR substance (carcinogen, mutagen and reproductive toxicant) of category 1B. In addition it is considered as aquatic toxicant (both acute and chronic) of category 1.

Taking into account possible adverse effects on human health, target values of air quality objectives for B(a)P have been established for European countries³. In particular, EU target value for B(a)P annual mean air concentrations was set to 1 ng/m³. Similar threshold level of B(a)P air concentrations was also established as an air quality standard in a number of other countries in the EMEP domain (e.g. in the EECCA countries). Along with this reference level of 0.12 ng/m³ for B(a)P was defined by WHO as a level of air concentrations corresponding to excess lifetime cancer risk level of 10⁻⁵ [Theakston, 2000].

This chapter provides a summary of the assessment of pollution levels and transboundary transport of four PAHs, included into the Protocol on POPs, namely, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, and Indeno(1,2,3-cd)pyrene). This year for the first time modelling of PAH pollution levels was carried out using fine resolution 0.1°x0.1° emission data reported by the EMEP countries. Analysis of spatial and temporal variability of PAH pollution levels within the EMEP domain was carried out on the basis of modelling results and measurements of the EMEP monitoring network for 2016 as well as national measurements from EEA AIRBASE. Model simulations of PAH transport and fate were performed using multi-media GLEMOS modelling system. Transboundary transport of selected PAHs was evaluated taking into account anthropogenic emission sources of the EMEP countries as well as influence of non-EMEP emissions. Main emphasis was given to the assessment of B(a)P pollution levels and evaluation of exceedances of EU target value and WHO reference level defined for B(a)P air concentrations. To contribute to further improvement of quality of pollution assessment country-specific case study of B(a)P pollution in the EMEP countries was continued in co-operation with national experts from Spain and France.

² Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on the Classification, Labelling and Packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

³ Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004

2.1. PAH emission data for model assessment

Model assessment of PAH pollution requires detailed information on emissions, which have to include chemical speciation of PAH emissions, distribution by sectors, and spatially distributed emission data. Gridded sectoral annual emissions of 4 PAHs with spatial resolution $0.1^\circ \times 0.1^\circ$ were prepared by CEIP on the basis of reported national inventories and available expert estimates. At the moment of preparation of pollution assessment, official emission data were available for the year 2015⁴. Thus, these emissions were used to characterize PAH pollution levels in 2016. Detailed description of PAH emissions for each EMEP country as well as information on applied gap-filling methods can be found in the CEIP Technical Report 01/2017 [Tista *et al.*, 2017]. Spatial distribution of annual total emission fluxes of the sum of 4 PAHs and B(a)P from anthropogenic sources within the new EMEP grid, is illustrated in Fig 2.1.

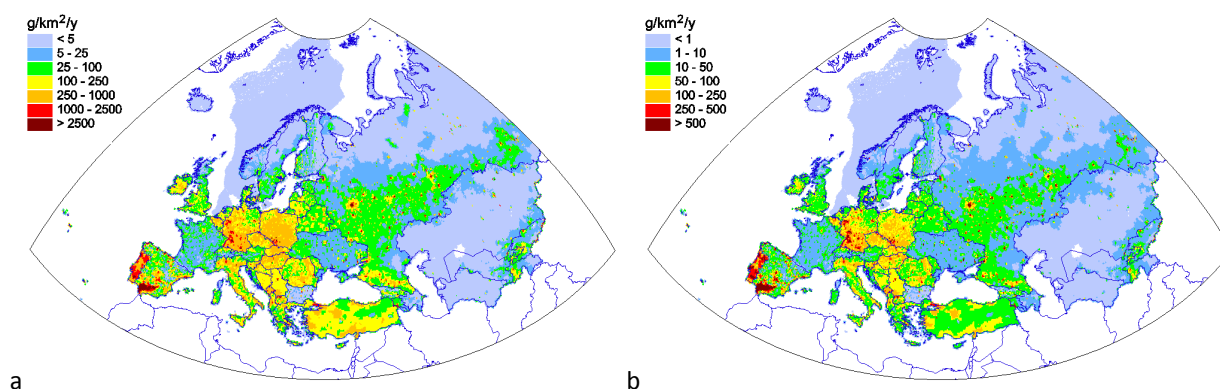


Fig. 2.1. Spatial distribution of annual emission fluxes of 4PAH (a) and B(a)P (b), $\text{g/km}^2/\text{y}$, with spatial resolution $0.1^\circ \times 0.1^\circ$, applied in the model simulations.

Along with gridded emission data the GLEMOS modelling system requires additional information on emissions, namely, intra-annual variations and distribution of emissions with height. Necessary vertical and temporal disaggregation of emissions was generated using emission pre-processing tool, developed by MSC-E for the GLEMOS modelling system. More detailed information on the emission pre-processing procedure is presented in the HM Status Report [Ilyin *et al.*, 2018]. Seasonal variations of PAH anthropogenic emissions were prepared for each emission source sector using monthly temporal factors, adapted from TNO estimates of the MACC project [Denier van der Gon *et al.*, 2011a]. The most pronounced seasonal variations with maximum emission in the cold period of the year are characteristic of the 'Residential Combustion' sector. Distribution of emissions with height within the six lowest model layers is defined on the basis of the calculation results of the SMOKE-EU plume-rise model [Bieser *et al.*, 2011]. The highest emission height is calculated for the 'Public Power', 'Industry', and 'Waste' sectors.

For the evaluation of global scale transport and boundary conditions, required for regional EMEP modelling, expert estimates of global PAH emissions, produced by the research group of Peking University [Shen *et al.*, 2013], were applied. Global PAH emission inventories with $0.1^\circ \times 0.1^\circ$ spatial resolution were developed using a bottom-up approach for the period from 1960 to 2014. Distribution of global emission fluxes of the sum of 4 PAHs and B(a)P is presented in Fig 2.2. According to this

⁴ Update of the modelling results based on the new emission data for 2016 is available at the MSC-E web site [www.msceast.org].

inventory highest level of PAH and B(a)P emissions took place in the countries of Eastern and Southern Asia.

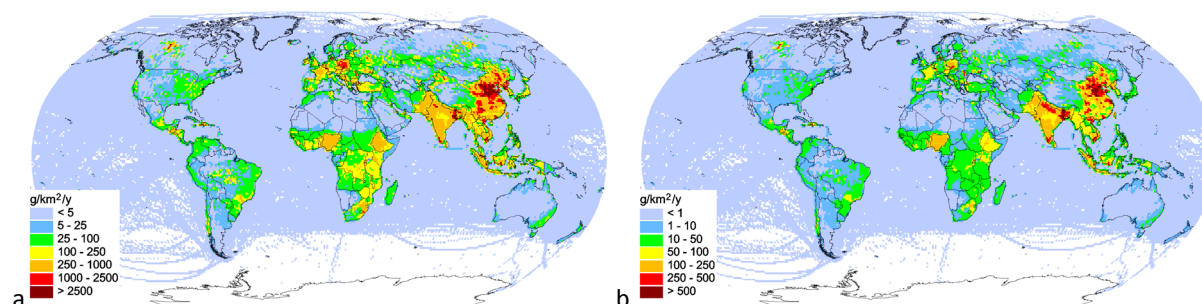


Fig. 2.2. Spatial distribution of global annual emissions of 4PAH (a) and B(a)P (b), g/km²/y, with spatial resolution 1°x1°, applied in the model simulations.

2.2. Evaluation of reported PAH emission data

The quality of model assessment of PAH pollution significantly depends on the completeness and accuracy of PAH emissions, provided by the EMEP countries. Inventories of PAH emissions reported by the EMEP countries are characterized by varying level of uncertainties. In order to contribute to the improvement of assessment of PAH pollution levels, evaluation of some aspects related to the consistency of reported national emissions was performed during the previous year, as described in the POP Status Report [Gusev *et al.*, 2017]. This year the evaluation of reported PAH emission data was continued and included comparison of official PAH emissions with available expert inventories as well as analysis of sector distribution and grid allocation of emissions.

Available expert estimates of PAH anthropogenic emissions provide important information for the evaluation of pollution levels. Besides they can be used for the analysis of national inventories of PAH/B(a)P emissions reported by the EMEP countries. In particular, inventory of B(a)P emissions in the EU countries for 2005, prepared by TNO in framework of TRANSPHORM project [Denier van der Gon *et al.*, 2011b], was compared with the corresponding official emission data. The inventory is based on the bottom-up approach with application of consistent set of emission factors and activity data for the countries within the EMEP region.

Results of the comparison indicate that official emissions of more than 60% of the countries are rather close to the TNO expert estimates for 2005 (Fig. 2.3). At the same time, for some of the countries substantial differences can be seen. In particular, expert estimates of TNO for Poland, France, and Austria are significantly higher than official B(a)P emissions, indicating possible underestimation of B(a)P releases in these countries. Higher values of TNO estimates compared with reported data are also noted for the United Kingdom, Bulgaria, and Finland. Opposite situation is seen for Spain and Portugal where expert estimates are lower comparing to official emissions. Discrepancies found between the TNO and national emission inventories can be used as indication of substantial differences in the methodologies applied by the EMEP countries for the evaluation of PAH emissions.

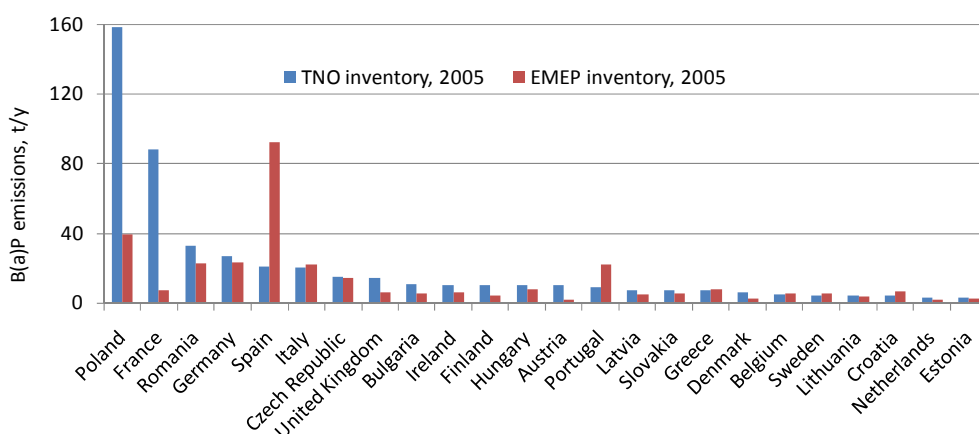


Fig. 2.3. Officially reported national total B(a)P emissions of EU countries for 2005 in comparison with expert estimates, developed by the TNO in framework of TRANSPHORM project.

Analysis of sector distribution of the officially reported PAH emissions shows that in most of the EMEP countries the largest contribution to total PAH emissions belongs to the residential combustion sector. As illustrated in Figure 2.4a for a number of countries, the contribution of this source category to the total national emissions can reach about 90%. At the same time inventories of Spain, Portugal, Greece, are characterized by prevailing contribution of PAH emissions from burning of agricultural residues and wastes. Estimated emissions from agricultural sources of these three countries comprise about 27% of annual total PAH emissions of the EU countries whereas emissions from the same sources of other EU countries account for less than 1% (Fig. 2.4b).

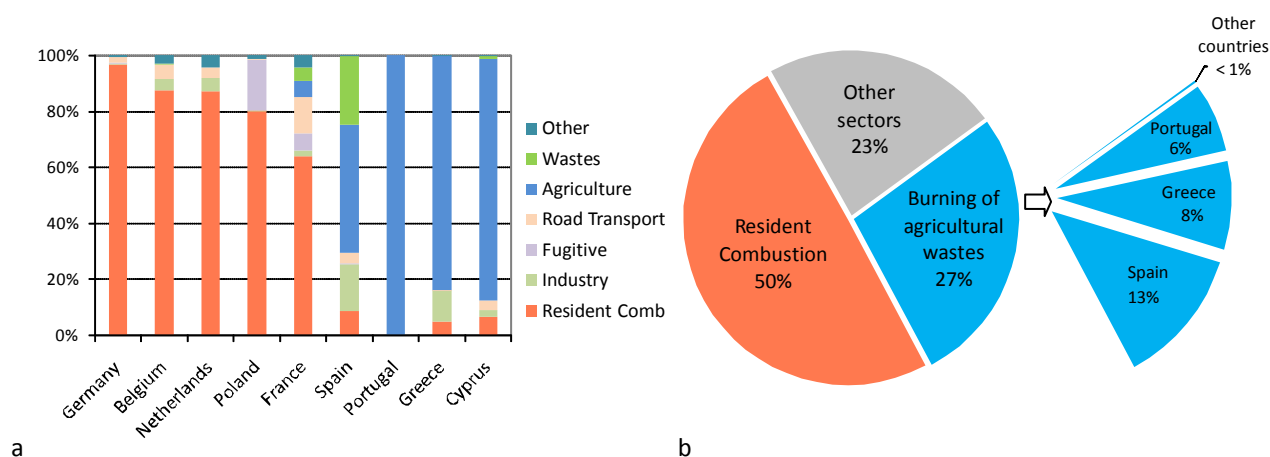


Fig. 2.4. Sector distribution of PAH emissions officially reported by some of the EMEP countries for 2016 (a) and relative contributions of total PAH emissions from the 'Residential combustion' and 'Field burning of agricultural wastes' sectors (along with contributions of Spain, Greece, and Portugal) to total PAH emissions of the EMEP countries (b).

High difference in estimates of PAH emissions from agriculture between this group of countries and the other EU countries indicates considerable uncertainties in the applied methodologies. In particular, high PAH emissions from the field burning of agricultural wastes in Spain were analysed in the framework of the case study on B(a)P pollution in Spain, performed by MSC-E in co-operation with national experts. It

is shown that PAH emissions from this source category can be substantially overestimated by the national emission inventory. More detailed information on this can be found in the subsequent chapter of this report.

To improve the quality of reported PAH emission data further detailed analysis of national PAH inventories is needed, in particular, with respect to the consistency of applied methodologies and values of emission factors. Besides, the analysis can include application of air quality modelling as a tool for evaluation of reported emissions. This work requires cooperation with national experts in emissions as well as CEIP and TFEIP.

2.3. PAH pollution levels in the EMEP region in 2016

Evaluation of PAH pollution levels in the EMEP countries in 2016 was carried out on the basis of model results and measurement data of the EMEP monitoring network as well as data of EU air quality networks collected in the EEA AIRBASE database. Model simulations of PAH long-range transport and pollution levels in the EMEP region were performed using fine resolution anthropogenic emissions reported by the EMEP countries.

Spatial distributions of annual mean air concentrations of the sum of 4 PAHs and B(a)P in 2016, calculated by the GLEMOS model are presented in Fig. 2.5. Modelled PAH air concentrations on the maps are combined with annual mean air concentrations, measured at the EMEP monitoring sites. Most of the stations are located in rural and remote areas characterizing background levels of air pollution. In general, the model reasonably reproduced observed geographical pattern of PAH air concentrations with elevated pollution levels in Central and Eastern Europe and lower levels in Western and Northern Europe. At the same time, for some of the countries predicted B(a)P concentrations noticeably differ from the observed concentrations (e.g. for Central and Southern Germany, Southern Spain, and Portugal).

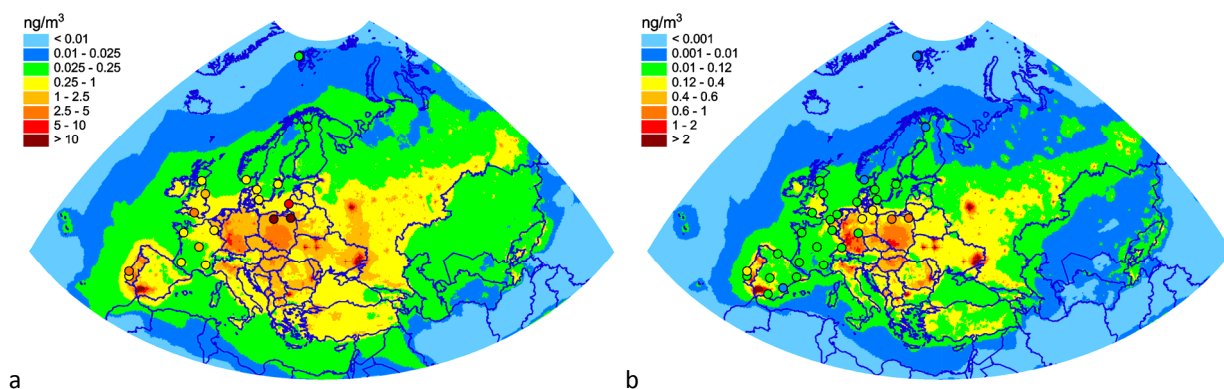


Fig. 2.5. Spatial distribution of modelled and observed annual mean air concentrations of 4PAHs (a) and B(a)P (b) in the EMEP domain for 2016.

Model estimates indicate high levels of annual mean B(a)P air concentrations, exceeding the EU target value (1 ng/m³), in Poland, Germany, the Czech Republic, Hungary, Romania, Portugal, Spain,

northern Italy, the FYR of Macedonia, and Bulgaria (Fig. 2.5b). *Areas of high concentrations (above the EU target value) can also be indicated for some of the EECA countries including Republic of Moldova, the Ukraine, Georgia, Armenia, and the Russian Federation.* For other countries (e.g. France, the UK, and Scandinavian countries) moderate or low levels of B(a)P air concentrations were predicted by the model. *According to these model estimates for 2016, about 9% of population of the EMEP countries lived in the areas with annual mean B(a)P air concentrations above the EU target level, and almost 75% in the areas with air concentrations above the WHO reference level (0.12 ng/m³).*

More detailed observational data on B(a)P pollution levels are collected in the AIRBASE. Spatial distributions of observed annual mean B(a)P air concentrations in 2016, based on the information from the AIRBASE, is shown in Fig. 2.6b. Measurements of EU national air quality stations showed similar geographical pattern of B(a)P air concentrations with elevated levels of pollution in the Central, Eastern, and Southern Europe in comparison with modelling results. Along with monitoring of pollution levels in rural and remote areas, national air quality networks of the EU countries provide information on air concentrations in urban and sub-urban areas as well as in the areas, influenced by industrial sources and traffic. In general, the highest average level of B(a)P air concentrations in 2016 was observed at the urban background stations indicating higher risk of exposure and adverse health effects for the population of urban areas (Fig. 2.6a). Other types of stations reported lower levels of concentrations.

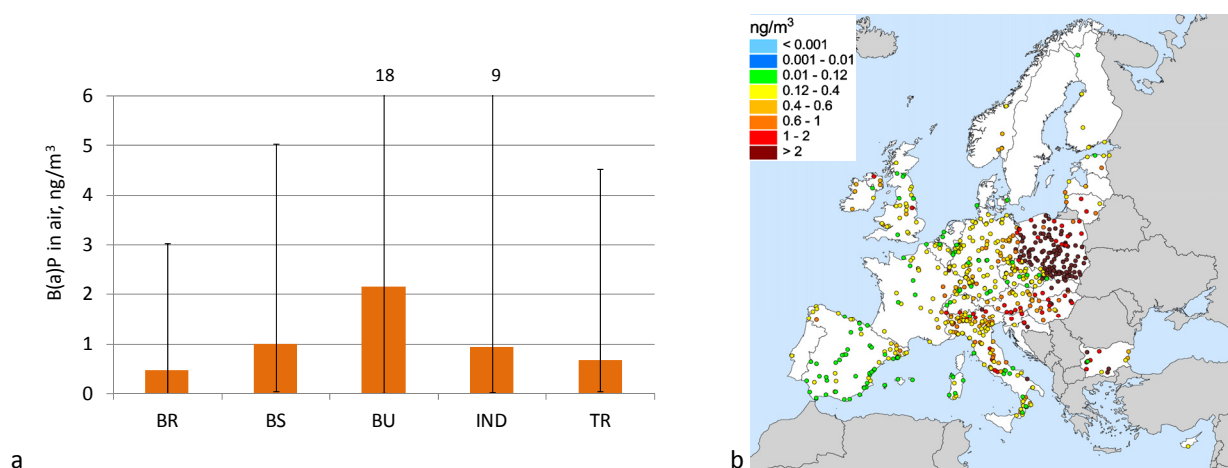


Fig. 2.6. Observed annual mean B(a)P air concentrations in the EU countries in 2016, averaged over the background rural (BR), background suburban (BS), background urban (BU), industrial (IND), and traffic (TR) types of monitoring stations (a), and spatial distribution of observed B(a)P concentrations (b) (AIRBASE). Whiskers denote the range from minimum to maximum of measured concentrations.

Average annual mean B(a)P air concentrations observed in 2016 in the selected European countries, including the range between the minimum and maximum measurements, are illustrated in Fig. 2.7. According to these data *average observed level of B(a)P pollution was above the EU target value in 6 countries, namely, Poland, Slovakia, Croatia, Bulgaria, the Czech Republic, and Hungary.*

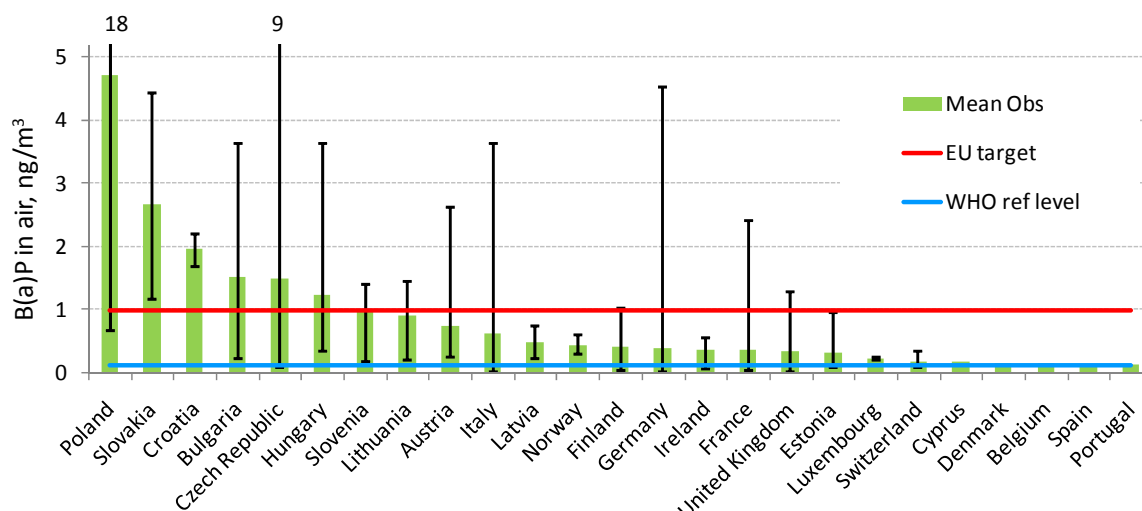


Fig. 2.7. Observed annual mean B(a)P air concentrations in 2016 averaged over the selected EU countries (AIRBASE). Whiskers denote the range from minimum to maximum of measured concentrations

Exceedances of the EU target value were also reported by some of the monitoring stations in Slovenia, Lithuania, Austria, Italy, Finland, Germany, France, and the UK. Most of these high concentrations values were measured at the urban background stations. *The highest level of B(a)P air concentrations was observed in the southern part of Poland (more than 10 ng/m³).* As seen from the Fig. 2.7, *B(a)P concentrations above the WHO reference level, equal to 0.12 ng/m³, were observed across much wider area.* In particular, exceedances of this reference level in 2016 were indicated in 25 European countries.

2.4. Comparison of modelling results with measurements

Evaluation of model predictions of PAH pollution levels for 2016 was made using comparison of modelled air concentrations of 4 PAHs with measurements of the EMEP monitoring network. As long as spatial resolution of reported national emissions increased from relatively coarse (50x50 km) to fine resolution (0.1°x0.1°), additional set of monitoring data, namely, results of national monitoring in the EU countries (AIRBASE), was used for the comparison. Air quality monitoring data of the AIRBASE considerably extend possibilities to analyze model performance for different types of areas.

Current level of spatial resolution in the emission data and model estimates can be applied to evaluate variations of pollution in remote, rural, and partly suburban areas, while urban scale pollution requires finer resolution modelling. Thus, to compare model predictions with observed concentrations measurements of rural and suburban stations were included into comparison. Several aspects were analyzed in course of the evaluation of modelling results. In particular, level of agreement between observed air concentrations of PAHs and model results in terms of relative bias and spatial correlation was examined in general for the whole set of monitoring data. In addition, verification of model predictions on the level of particular countries was performed. Besides, model estimates of the sum of 4 PAHs and fractions of individual PAHs (B(a)P, B(b)F, B(k)F, and IP) in air concentrations in comparison to measured values were evaluated.

Comparison of model results with the EMEP measurements

Comparison of modelled PAH air concentrations with measurements was made for the sum of 4 PAHs (Fig. 2.8a) and for individual PAH compounds (Fig. 2.8b). Monitoring of PAHs in 2016 was carried out at 33 EMEP monitoring sites located in Belgium, Estonia, Finland, France, Germany, Latvia, Netherlands, Norway, Poland, Portugal, Slovenia, Spain, Sweden, and the UK. Statistical indicators, describing the agreement of modelled and observed annual mean PAH air concentrations, are presented in the Table 2.1.

Co-located measurements of 4 PAHs in 2016 were performed at 19 monitoring sites in 8 EMEP countries. Model predictions for the sum of 4 PAHs reproduced in general the observed pattern of annual mean air concentrations with mean relative bias about -7% and spatial correlation 0.55. For more than a half of selected monitoring sites the difference between measured and modelled concentrations is within a factor of 2.

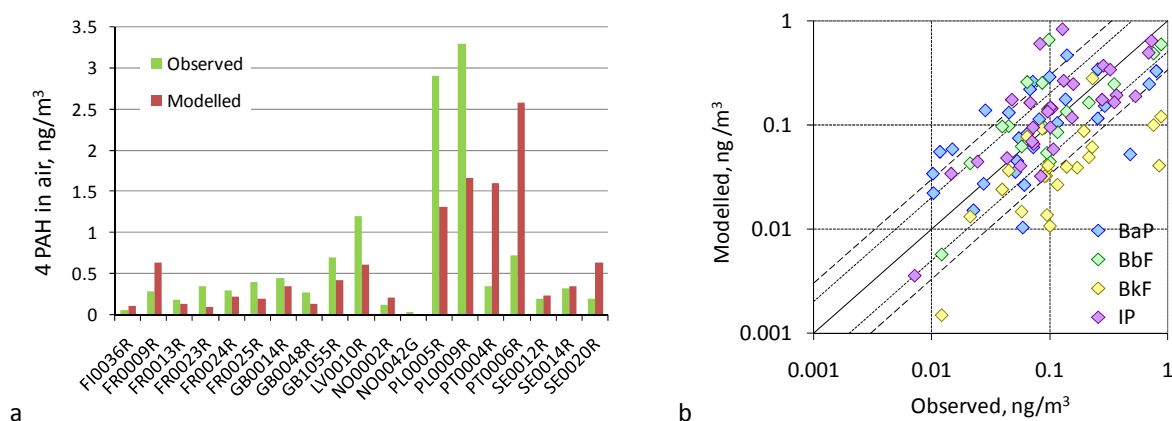


Fig. 2.8. Comparison of modelled and observed air concentrations of $\Sigma 4$ PAHs (a) and scatter plot of modelled and observed B(a)P, B(b)F, B(k)F, and IP air concentrations (b) for 2016. Dashed lines in the right diagram denote the areas of agreement between the modelled and measured values within factors of 2 and 3.

For several monitoring sites, located in France, Norway, Poland, Portugal, and Sweden, the differences between the model predictions and observed concentrations exceeded a factor of 2, with the largest discrepancies (overestimation) for the monitoring sites in Portugal.

Verification of model predictions for individual PAH compounds (B(a)P, B(b)F, B(k)F, and IP) with the EMEP measurements indicated that the model tended to under-predict observed Ba)P and B(k)F air concentrations and over-predict observed concentrations of B(b)F and IP. As seen from the table, better level of agreement with respect to mean bias was obtained for B(a)P (about -11%) followed by IP (about 13%) and B(b)F (about 28%). The lowest level of agreement is seen for B(k)F, for which the modelled concentrations on average were 70% lower comparing to measured values. Spatial correlation of modelled and observed concentrations was about 0.5 for B(a)P, B(b)F, and IP, whereas for B(k)F it was considerably lower (0.3).

Table 2.1. Statistics of the model-to-observation comparison of PAH model simulations for 2016

	<i>B(a)P</i>	<i>B(b)F</i>	<i>B(k)F</i>	<i>IP</i>	4 PAHs
Number of sites	29	19	24	29	19
Mean observed, ng/m ³	0.14	0.19	0.20	0.18	0.65
Mean modelled, ng/m ³	0.12	0.24	0.06	0.20	0.61
Relative bias, %	-11.2	27.7	-70.8	12.6	-7.0
Correlation coefficient	0.47	0.51	0.30	0.52	0.55
Factor 2, %	41	58	29	66	53
Factor 3, %	66	84	50	90	74

Comparison of mean modelled fractions of B(a)P, B(b)F, B(k)F, and IP in sum of air concentrations of 4 PAHs, estimated for 2016, with measurements of 19 EMEP monitoring sites is shown in Fig. 2.9. The fractions of particular PAHs in the concentrations of 4 PAHs depend on both their contributions to total Σ 4PAH emissions and physical-chemical properties of 4 PAHs, governing their transport in and removal from the atmosphere. In particular, the rate of degradation of B(a)P in the atmosphere is more significant comparing to other three PAHs that can affect relative levels of their air concentrations. According to the reported emission data, average fractions of B(a)P, B(b)F, B(k)F, and IP in total emissions are equal to 30%, 35%, 15%, and 20%, respectively. Fractions of B(a)P, B(b)F, B(k)F, and IP in measured air concentrations of 4 PAHs have somewhat different pattern with lower fractions of B(a)P and B(b)F (17% and 30%), and higher fractions of B(k)F and IP (30% and 23%).

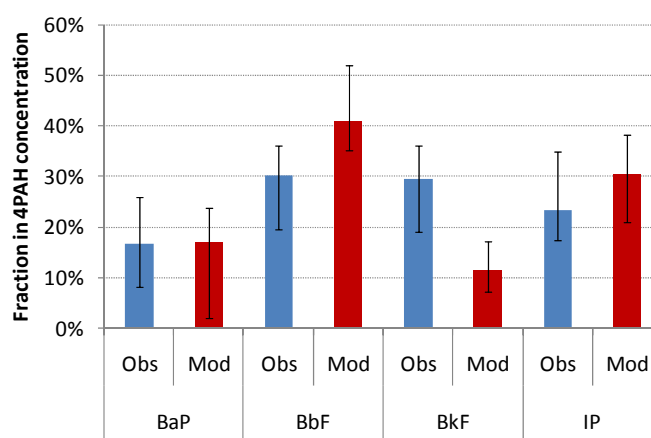


Fig. 2.9. Comparison of mean modelled and observed fractions of B(a)P, B(b)F, B(k)F, and IP in air concentrations of 4 PAHs for 2016 for 19 EMEP monitoring sites. Whiskers indicate the range between the maximum and minimum values of fractions for B(a)P, B(b)F, B(k)F, and IP.

Model predictions for B(a)P are quite close to measured values on average, whereas for other three PAHs the modelled fractions differ from the observed ones, with the most significant difference for B(k)F. The reason of these discrepancies can be related to both the uncertainties of emission inventories for individual PAHs and uncertainties in PAH physical-chemical properties applied in the model. The difference between the estimated and measured PAH compounds distribution was also indicated in the study of PAH pollution levels in Italy [Finardy et al., 2017]. It was noted that *discrepancies found could be attributed to the applied emission factors in the emission inventory that likely did not match the PAH distribution in actual emissions.*

Comparison of model results with the AIRBASE measurements

In this section comparison of model predictions for 2016 with B(a)P measurements of AIRBASE is presented. Measurements of annual mean air concentrations of about 170 background rural and suburban monitoring sites, made in 24 European countries in 2016, were selected for the comparison. Results of the comparison are shown in Fig. 2.10 for the background rural monitoring sites (Fig. 2.10a) and combined set of background rural and suburban monitoring sites (Fig. 2.10b). It is seen that modelling results tend to underestimate annual mean observed B(a)P air concentrations by 39% for the rural monitoring sites and by 46% for the combined rural and suburban monitoring sites. The negative bias can be caused by possible underestimation of anthropogenic emissions reported by some of the EMEP countries. Model predictions in general reasonably correlate with the observed B(a)P concentrations at rural monitoring sites, however in the case of the combined set of rural and suburban monitoring sites the spatial correlation is lower.

Amount of monitoring sites in the AIRBASE allows examining the level of agreement between modelled and observed air concentrations for the particular countries. The scatter plots in Fig. 2.10 highlight the model-observation pairs for the selected EMEP countries, namely, France, Germany, Poland, and Spain, with different colours. Modelling results for these countries are generally characterized by larger extent of disagreement between modelled and observed concentrations comparing to the data for other countries. In particular, it can be seen that model predictions for Poland and France underestimate observed air concentrations. In contrast, overestimation of observed air concentrations is obtained in case of Germany. There is a mixed situation for model predictions for Spain where both underestimation and overestimation take place.

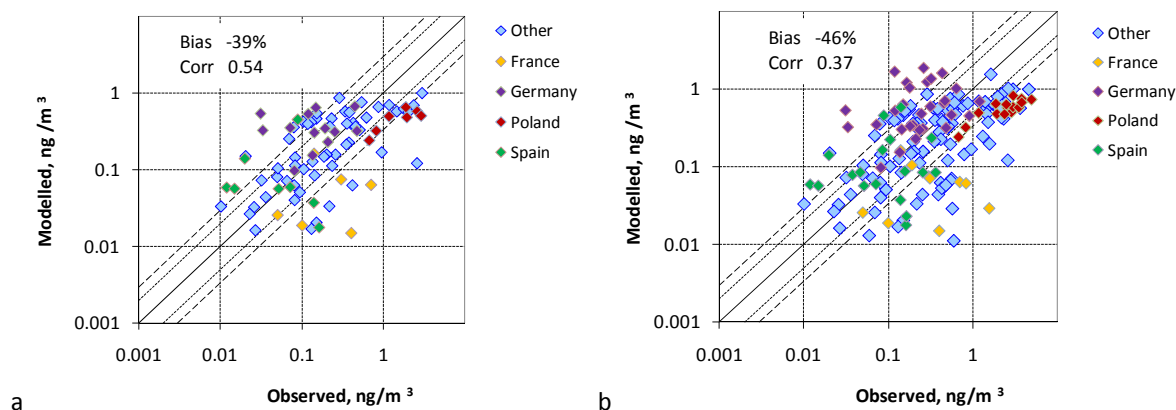


Fig. 2.10. Scatter plots of modelled B(a)P annual mean air concentrations for 2016 versus AIRBASE measurements of background rural (a) and background rural and suburban monitoring sites (b). Dashed lines in the diagram denote the areas of agreement between the modelled and measured values within factors of 2 and 3.

The disagreement found between the measurements of monitoring sites and model estimates for these countries can be attributed to several reasons including uncertainties of national PAH emission inventories as well as to uncertainties in the modelling approach (e.g. parameterization of processes governing B(a)P fate in the atmosphere). Under-prediction of observed B(a)P pollution levels in Poland

and France is likely caused by underestimated levels of B(a)P emissions in these countries. For example, expert estimates of B(a)P emissions in these countries, provided by TNO [Denier van der Gon *et al.*, 2011b], are substantially higher comparing to the national emission inventories.

In case of Germany, overestimation of observed B(a)P concentrations in the model predictions for 2016 can be explained by the assumption made by CEIP in course of generation of gridded B(a)P emissions for Germany. In particular, though the national inventory of PAH emissions in Germany provided estimates of B(a)P releases, gridded B(a)P emissions from the country were calculated from the total emission of 4 PAHs assuming average fraction of B(a)P in the emission of $\Sigma 4\text{PAHs}$. The average fraction of B(a)P was estimated using emission data of other EMEP countries reporting speciated PAH emissions. Thus, B(a)P emissions, calculated in this way, overestimated reported B(a)P emission of Germany that led to higher values of modelled air concentrations.

Over-prediction of observed B(a)P air concentrations in Spain, obtained by model simulations, can be attributed to the overestimated national emissions from the field burning of biomass in agriculture [Gusev *et al.*, 2017]. Levels of B(a)P pollution in Spain and France and agreement between the model predictions and measured air concentrations are being analyzed in more details in course of the ongoing case study. Preliminary results of this activity are outlined in Chapter 3 of this report.

Spatial correlations between the model predictions and observed annual mean B(a)P air concentrations in rural and suburban background sites is shown in Fig. 2.11 for the countries with sufficient amount of measurements (more than five monitoring sites).

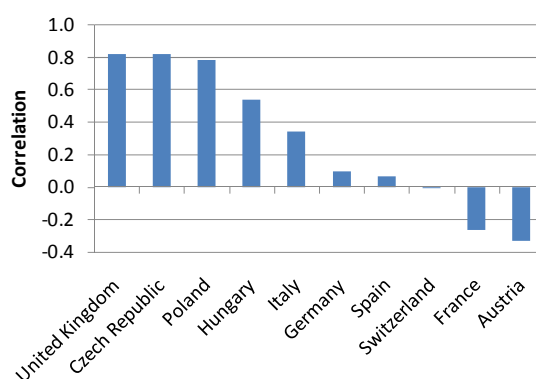


Fig. 2.11. Spatial correlation between modelled B(a)P annual mean concentrations for 2016 and AIRBASE measurements of background rural and suburban monitoring sites for the selected EMEP countries.

It is seen that modelled concentrations reasonably well correlate with the observed pollution levels in the United Kingdom, Czech Republic, Poland, and Hungary. At the same time, low spatial correlation or even negative correlation is found for Italy, Germany, Spain, Switzerland, France, and Austria. The different performance of the model with respect to spatial correlation with observed concentrations is most likely caused by the uncertainties in spatial distribution of PAH emissions in national inventories reported by the EMEP countries. In particular, while some of the background rural monitoring stations in these countries reported elevated B(a)P air concentrations for rural locations (e.g. Fig. 2.10a), gridded emission data for these areas did not provide corresponding emissions that led to the underestimation of observed concentrations.

As an example of this, B(a)P measurements in mountainous areas in northern Spain in Catalonia can be mentioned. Specific case study performed for this area [Viana *et al.*, 2016] showed that high measured B(a)P air concentrations could be result of biomass burning activities for domestic heating and specific meteorological conditions. However, information on biomass burning emissions in this area was not presented in the national PAH emission inventory that caused disagreement with modelling results [Gusev *et al.*, 2017]. Thus, to improve the quality of model assessment of PAH pollution in the EMEP region further refinement of national PAH emission inventories is needed with respect to spatial distribution of emissions.

2.5. Transboundary transport of pollution

Long-range transport and annual total deposition of 4 PAHs within the EMEP region were evaluated for 2016 for each of the selected 4 PAHs. Contribution of non-EMEP emission sources located outside the EMEP domain was taken into account through the application of global scale modelling on the basis of inventory of global PAH emissions developed by the research group of Peking University [Shen *et al.*, 2013]. Annual total deposition fluxes averaged over the EMEP countries for 2016 are presented in Fig. 2.12 with splitting of deposition values into contributions of particular PAHs. In total deposition of 4 PAHs the largest contribution is estimated to B(b)F (43%) followed by B(a)P (20%), IP (20%), and B(k)F (16%).

Annual total modelled PAH deposition fluxes for 2016 and fractions of B(a)P, B(b)F, B(k)F, and IP in the total deposition, estimated for the EMEP countries, are illustrated in the Fig. 2.12. Relatively high level of PAH deposition (more than 200 g/km²/y) is obtained for Portugal, Montenegro, and Slovakia. Substantial values of deposition fluxes (about 50-200 g/km²/y) are estimated for countries of Western and Central Europe (e.g. for Poland, Germany, Spain, and Czech Republic). Countries of Northern and Western Europe, and eastern part of EMEP modelling domain (e.g. Russia, countries in Central Asia) are generally characterized by comparatively low PAH deposition fluxes (below 50 g/km²/y).

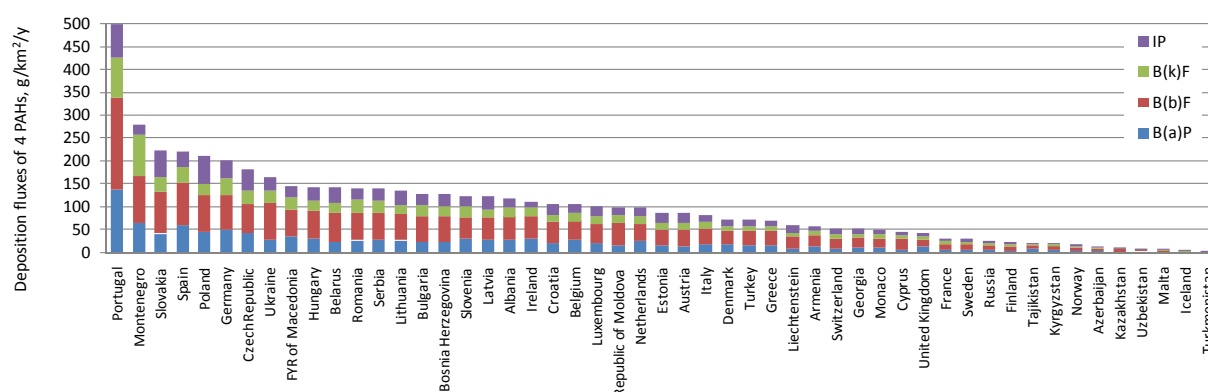


Fig. 2.12. Annual deposition fluxes of 4 PAHs (B(a)P, B(b)F, B(k)F, and IP) in the EMEP countries calculated for 2016, g/km²/y.

Atmospheric transport of PAHs from the emissions of a particular country contributes to deposition over the country itself and deposition to the territories of other countries. The ratio of PAHs deposited within and outside the country boundaries is shown in Fig. 2.13. Assessment of PAH distribution in the EMEP domain indicates importance of the long-range transport of pollution between the EMEP countries as well as influence of non-EMEP emissions. As follows from the Figure, for 28 EMEP countries (55% of the countries) the fraction of PAHs, deposited to other EMEP countries is higher, comparing to the fraction of PAHs, deposited to the country itself.

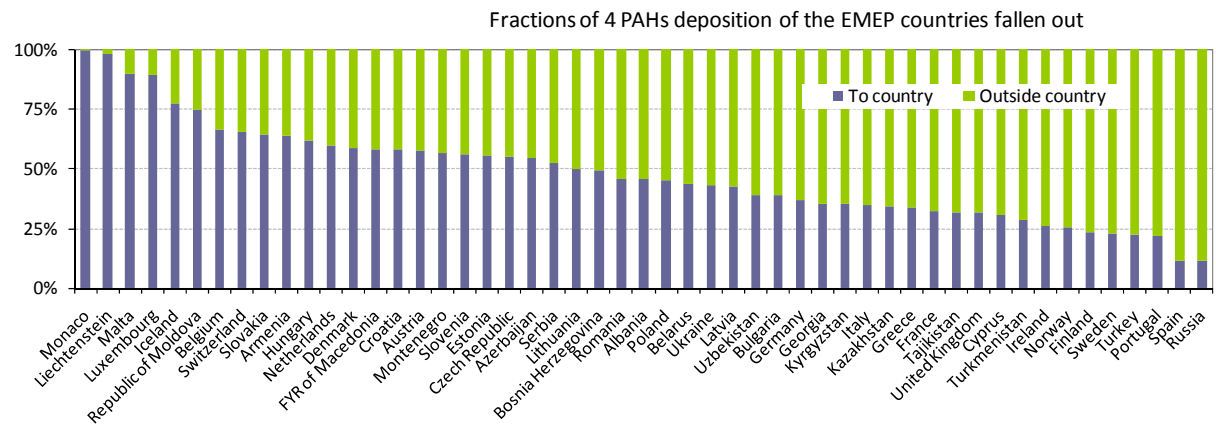


Fig. 2.13. Fractions of total Σ 4PAH deposition, originated from national emissions of the EMEP countries, fallen out to their own territories and outside their boundaries in the 2016.

Source apportionment of PAH deposition showed that for 29 EMEP countries (57% of the countries) the contribution of emission sources, located beyond their territories (transboundary transport), exceeded the contribution of their own national emissions to deposition in the country (Fig. 2.14). Model predictions of transboundary transport of pollution include also contribution of non-EMEP emission sources which was estimated to about 5 - 10% with highest (22%) contribution for Iceland.

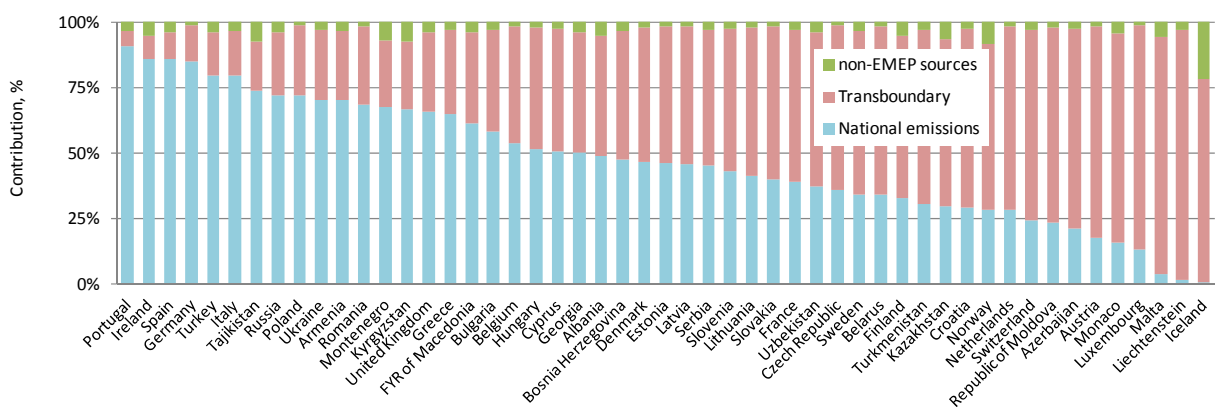


Fig. 2.14. Relative contributions of national emissions, transboundary transport, and non-EMEP emissions to deposition of 4 PAHs from anthropogenic sources in the EMEP countries in the 2016.

2.6. PAH pollution on global scale and in the Arctic region

Evaluation of global scale PAH pollution for 2016 was carried out using the GLEMOS modelling system with application of global inventory of PAH emission [Shen *et al.*, 2013]. Developed gridded inventory of PAH releases to the atmosphere covers the period of time from 1960 to 2014. Model simulations for 2016 were carried out with the latest available emission estimates for 2014 under the assumption that PAH emission rates were not changed much in the subsequent two years. Results of model simulations of PAH pollution on the global scale were used to estimate lateral boundary concentrations for regional EMEP modelling. Besides, these model estimates provide information on the intercontinental transport of PAHs and pollution of remote areas like the Arctic region.

Fig. 2.15 shows spatial distribution of model estimates of B(a)P annual mean air concentrations and annual total deposition fluxes for the year 2016. The highest levels of concentrations, exceeding 1 ng/m³, were estimated for the countries of Eastern and Southern Asia. Relatively high B(a)P air concentrations (0.4-1 ng/m³) were also obtained for the countries of Central and Eastern Europe. Other areas were characterized by relatively low pollution levels (below 0.4 ng/m³). Model predictions of annual mean B(a)P concentrations for the Arctic region varied mostly within the range 0.1-10 pg/m³ which is close to the observed levels of B(a)P air concentrations. Similar pattern of spatial variations was obtained for modelled annual total B(a)P deposition fluxes.

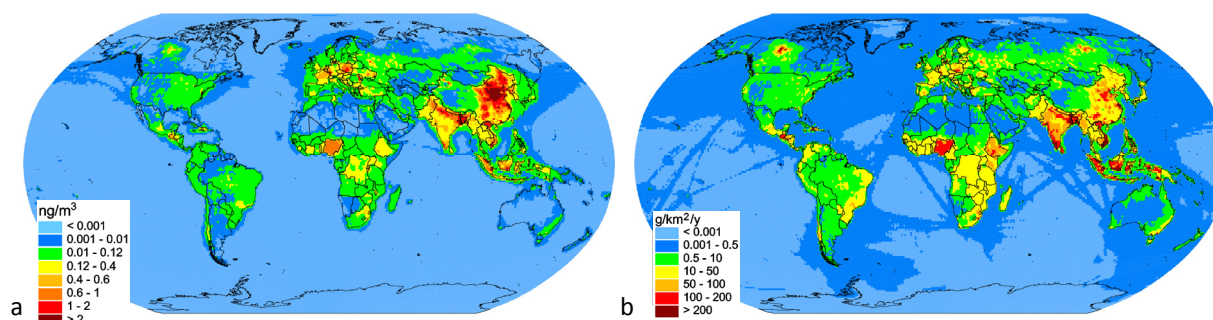


Fig. 2.15. Spatial distribution of global scale annual mean modelled air concentrations, ng/m³ (a) and deposition fluxes, g/km²/y (b) of B(a)P for 2016.

More detailed information on PAH pollution levels and source apportionment of PAH deposition was produced by regional scale EMEP model simulations. Annual total modelled B(a)P deposition fluxes for 2016 are shown in Fig. 2.16a for the northern part of the new EMEP domain, which intersects with the Arctic region. According to the model predictions, B(a)P deposition fluxes gradually decreased northwards from the northern parts of Norway, Sweden, Finland, and Russia to the Arctic area.

Assessment of PAH pollution of this part of the Arctic was made taking into account contributions of EMEP anthropogenic emission sources and non-EMEP emissions outside the EMEP domain. The largest contribution (about 50%) to total B(a)P deposition in the Arctic was made by Russian emissions (Fig. 2.16b). Significant contributions were also estimated for the emissions of Finland (26%) and Norway (6%). The other EMEP countries contributed about 11%. Contribution of non-EMEP emission sources of B(a)P amounted to 4%. Thus, according to the model simulations prevailing contribution to PAH pollution of the European Arctic can be attributed to the EMEP emission sources.

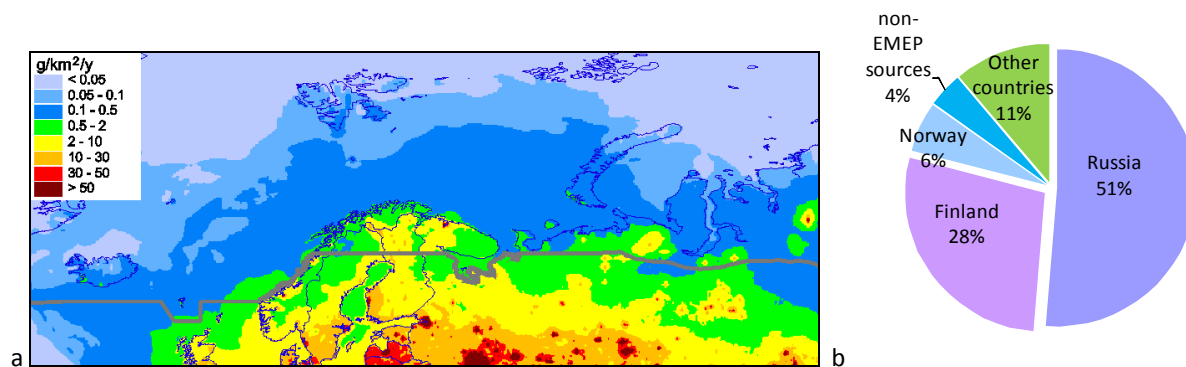


Fig. 2.16. Annual total B(a)P deposition fluxes in 2016 (a) and relative contributions of anthropogenic emission sources of the EMEP countries and non-EMEP emissions to the Arctic region, covered by the EMEP domain (b). Grey line denotes the boundary of the AMAP domain

3. CASE STUDY OF B(a)P POLLUTION IN SPAIN AND FRANCE

This chapter summarizes information on current progress in the case study of B(a)P pollution in the selected EMEP countries. Country-specific studies, performed by MSC-E in co-operation with national experts, represent an important activity that can contribute to further improvement of POP pollution assessment in the EMEP region [Travnikov *et al.*, 2018]. The B(a)P case study was initiated for Spain following the recommendation of the 2nd joint session of the Working Group on Effects and the Steering Body to EMEP. Objectives of the study include:

- Collection of detailed national scale information on emissions and monitoring data;
- Fine resolution modelling of B(a)P pollution levels using GLEMOS and CHIMERE model;
- Evaluation of modelling results against measurements of EMEP and national monitoring stations;
- Model simulations of B(a)P pollution using different scenarios of B(a)P emissions;
- Analysis of model predictions sensitivity to application of different parameterizations of most important processes affecting B(a)P long-range transport and removal from the atmosphere;
- Source-receptor and sector-specific modelling of B(a)P pollution on national scale.

The outcome of initial stage of the B(a)P case study is described in the previous POP Status Report [Gusev *et al.*, 2017]. This year evaluation of national scale B(a)P pollution levels in Spain is continued. In addition, similar work is initiated for France. Main emphasis at the current stage is given to the analysis of discrepancies between B(a)P modelling results and observed pollution levels taking place for Spain and France as well as for some other EMEP countries. This activity includes construction of experimental emission scenarios in order to evaluate sensitivity of model predictions to the uncertainties in the emissions data. Analysis of scenario modelling results can indicate areas of elevated uncertainties and characteristics of emissions that require further refinement. Particular attention is also paid to the effect of possible uncertainties in the applied modelling approach. Thus, different model parameterizations for the evaluation of B(a)P degradation and gas-particle partitioning are planned to be considered and tested. Model simulations and their analysis are performed in close cooperation with national experts in modelling of B(a)P pollution from Spain and France.

3.1. Model domains and emission data for modelling

Modelling of B(a)P pollution levels for this case study is carried out using nesting approach. The configuration of three modelling domains applied in the study is shown in Fig. 3.1. It consists of the coarse domain EU02 with spatial resolution $0.2^{\circ} \times 0.2^{\circ}$ and two nested domains FR005 and SP005 with spatial resolution $0.05^{\circ} \times 0.05^{\circ}$. The year 2015 was selected as a reference year for model simulations.

Emissions for B(a)P modelling were prepared on the basis of the data from different sources. In particular, fine resolution gridded B(a)P emissions for Spain and France were provided by national experts of these countries. In case of Spain it was national inventory of PAH emission with spatial resolution $0.05^{\circ} \times 0.05^{\circ}$. To obtain B(a)P emissions from the PAH emission data a scaling factor 0.14 was

used following the information from national experts of Spain, with reference to the EMEP/EEA Guidebook 2016 [EMEP/EEA Guidebook, 2016]. In case of France national inventory of B(a)P emission with spatial resolution $0.125^\circ \times 0.0625^\circ$ was applied. Both inventories for Spain and France were based on the SNAP sectoral distribution. For other EMEP countries, covered by the defined modelling domains, gridded data on annual B(a)P emissions with spatial resolution $0.1^\circ \times 0.1^\circ$ were obtained from CEIP. To compile consistent emission dataset for modelling, gridded data of CEIP, defined for the NFR sectors, were transformed into the SNAP sectors.

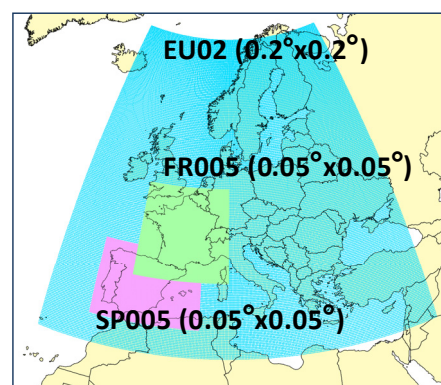


Fig. 3.1. Domains for model simulations: EU02, FR005, and SP005.

Spatial distribution of annual B(a)P emissions from anthropogenic sources for 2015 within the three modelling domains is illustrated in Fig 3.2.

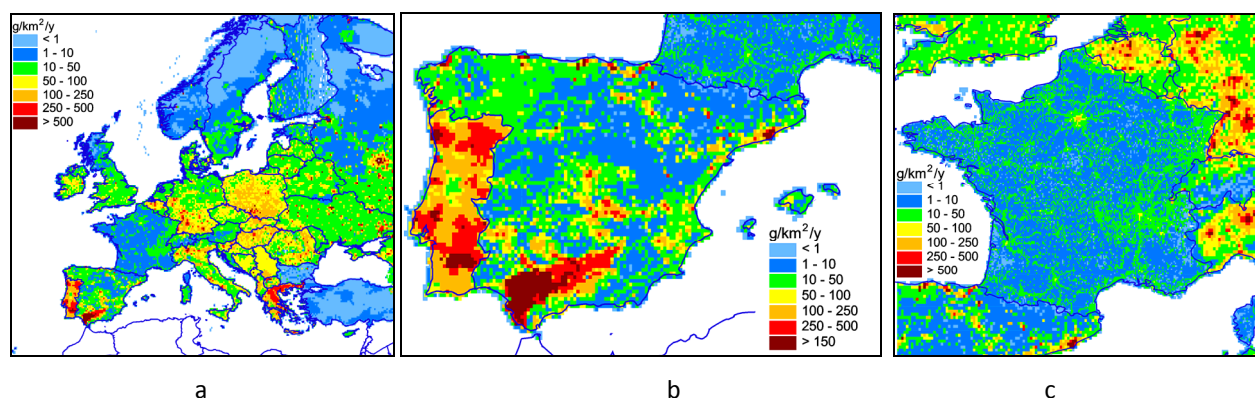


Fig. 3.2. Spatial distribution of annual B(a)P emission fluxes in 2015 for the EU02 domain (a), SP005 domain (b), and FR005 domain (c), $g/km^2/y$

3.2. Preliminary modelling results and their analysis

Preliminary model simulations of B(a)P pollution levels were performed for the coarse resolution domain EU02 using the GLEMOS model and the CHIMERE model [Menut *et al.*, 2013]. Both models have in general similar description of main processes governing B(a)P transport in the atmosphere, in particular, degradation in air, dry deposition of B(a)P in particulate phase, and scavenging with precipitation. At the same time, the models have different parameterizations of gas-particle partitioning. Besides, the CHIMERE model has no parameterization of air-surface gaseous exchange for B(a)P. Thus, these differences can noticeably affect model predictions of B(a)P pollution levels.

Figure 3.3 presents annual mean B(a)P air concentrations in the EU02 domain simulated by the two models for 2015. In general, both models predicted close pattern of B(a)P pollution levels in the European region. The highest B(a)P air concentrations (about $0.6 \text{ ng}/\text{m}^3$ and higher) were estimated for the countries of Central, Southern, and Eastern Europe (e.g. Poland, Slovakia, Hungary, Romania, Serbia,

Italy, and Greece), which in some areas exceeded the EU target level (1 ng/m^3). High levels of pollution were also predicted for southern Spain, Portugal, and some urban areas of Russia. B(a)P concentrations below the WHO reference level 0.12 ng/m^3 were estimated for Scandinavian countries, Denmark, Estonia, the UK, France, and northern Spain.

The spatial pattern of modelled B(a)P air concentrations can be compared with the outcome of mapping of ambient B(a)P concentrations in Europe [Guerreiro *et al.*, 2016]. Model estimates of B(a)P concentrations differ from the results of mapping in some areas of European region. In particular, higher B(a)P concentrations, in comparison to the predictions of the GLEMOS and CHIMERE models, were estimated by ETC/ACM mapping for Poland and France, and lower concentrations for Spain, Portugal, and Germany. The methodology applied for mapping was based on linear regression followed by kriging of the residuals and is largely driven by the observations. Therefore these differences may be explained by uncertainties of national emission inventories used for modelling as well as deficiencies of modelling approaches.

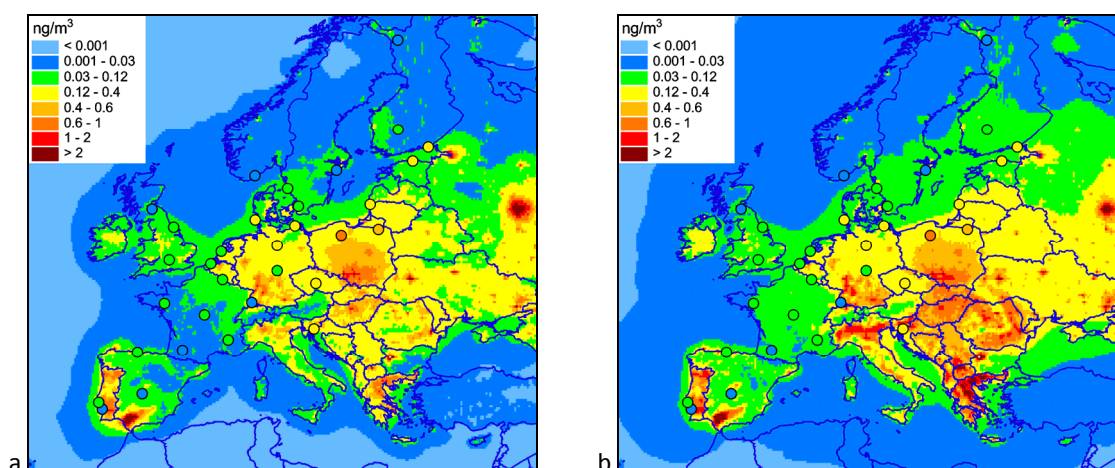


Fig. 3.3. Annual mean B(a)P air concentrations (ng/m^3) in 2015 simulated by the GLEMOS (a) and CHIMERE (b) models for the EU02 domain $0.2^\circ \times 0.2^\circ$; and B(a)P concentrations, observed at the EMEP monitoring sites, overlaid as coloured circles in the same scale as modelled values.

Comparison of model predictions made by the two models showed that B(a)P concentrations simulated by CHIMERE were somewhat higher than the concentrations of GLEMOS. Lower levels of concentrations in the GLEMOS results can be attributed to the difference in the parameterizations applied for B(a)P modelling. As it was mentioned above, mechanisms of gas-particulate partitioning were different in the two models and parameterization of air-surface gaseous exchange was not included in the CHIMERE model.

Evaluation of model results against measurements was carried out using the data of EMEP monitoring network for 2015. Summary of statistical analysis of the agreement between modelled and observed B(a)P air concentrations is presented in Table 3.1. Annual mean measured B(a)P concentrations of 28 EMEP monitoring sites were selected for the comparison. As shown in the Table, statistical metrics, calculated for the GLEMOS and CHIMERE model simulation results, are quite comparable in terms of bias (NMB), correlation (R), and errors (RMSE). Both models tend to under-predict observed B(a)P air concentrations by 25-27%. Geographical pattern of observed B(a)P concentrations is generally

reproduced by the models, which is indicated by the spatial correlation coefficients equal to 0.6-0.7. However, for more than a half of monitoring sites (~60%) B(a)P concentrations, calculated by GLEMOS and CHIMERE, deviate from measurements more than a factor of 2.

Table 3.1. Summary of model performance metrics, calculated for annual mean modelled B(a)P air concentrations of GLEMOS and CHIMERE and measurements of EMEP monitoring stations for 2015.

Model	NMB ^a (%)	R ^a	RMSE ^a (ng/m ³)	F2 ^a (%)	F3 ^a (%)
GLEMOS	-27	0.61	0.13	43	68
CHIMERE	-25	0.69	0.12	36	82

^a NMB is normalized mean bias; R is the spatial correlation between modelled and observed concentrations; RMSE is the root mean square error; F2 and F3 represent fractions of sites for which deviation between modelled and observed values are within a factor of 2 and 3, respectively.

In Figure 3.4 comparison of modelled and observed annual mean B(a)P air concentrations is shown for individual EMEP monitoring sites. The figure illustrates results of the comparison for the two groups, namely, for monitoring sites where deviations between the modelled and observed concentrations are within a factor of 2 (Fig. 3.4a), and where they are higher than a factor of 2 (Fig.3.4b). Model results for the first group of sites are characterized by high level of correlation with measurements (more than 0.9 for both models). The second group includes the sites for which overestimation or underestimation of measured values exceeded a factor of 2. In particular, the models tended to over-predict annual mean B(a)P concentrations observed in Belgium, the Netherlands, southern Germany, northern France, and Portugal. At the same time, B(a)P air concentrations in northern Germany, Estonia, Latvia, Finland, and Poland are underestimated by the models. Besides, the spatial correlation of modelled and measured concentrations for this group of sites is low.

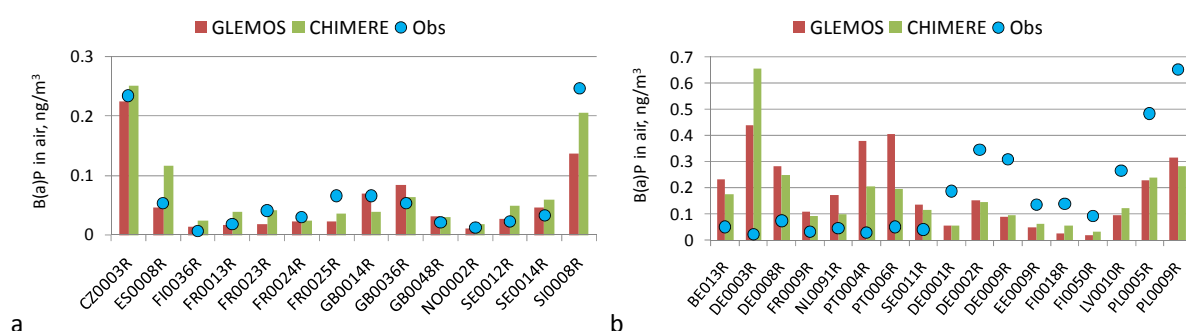


Fig. 3.4. GLEMOS and CHIMERE modelling results for 2015 against the annual mean B(a)P air concentrations, observed at EMEP monitoring sites. Left diagram (a) is for the sites where deviations between the modelled and observed values are within a factor of 2, and right diagram (b) for the sites where deviations for both models exceed a factor of 2.

Results of preliminary model simulations, performed by the GLEMOS and CHIMERE models, indicate significant discrepancies between the modelled and observed B(a)P air concentrations for some of the monitoring sites in Belgium, the Netherlands, Germany, Poland, Portugal, and Spain. Similar deviations with measurements were earlier revealed by the analysis of B(a)P modelling results for 2015 (POP Status Report [Gusev et al., 2017]) as well as of modelling results for 2016 (Chapter 2 of this

report). *These deviations may be explained by the effect of several factors. As it was discussed in the Chapter 2, uncertainties in national emission inventories of the EMEP countries as well as uncertainties in the model parameterizations applied for gas-particle partitioning and degradation of B(a)P can lead to over or under-predictions of observed concentrations by the models.* In particular, a number of recent studies for PAHs suggested that phase partitioning of PAHs may not follow the assumption of instantaneous equilibrium between the gaseous and particle phases (that is applied in currently used parameterization in the GLEMOS model). This process can be influenced by secondary organic aerosols, which might protect particle-phase PAHs from degradation and evaporation [Zelenyuk *et al.*, 2012; Friedman *et al.*, 2014]. Furthermore, it was shown that considering the effects of temperature and humidity variations in the atmosphere on multiphase degradation of PAHs is important for better predicting spatial variability of air concentrations and long-range transport [Mu *et al.*, 2018]. The influence of these factors on model predictions requires more detailed analysis that is planned to be carried out using GLEMOS and CHIMERE models in the framework of this B(a)P case study.

3.3. Experimental scenario of B(a)P emissions in the selected EMEP countries

To explore sensitivity of modelling results to possible uncertainties in the emission inventories of the EMEP countries, experimental model simulations with the scenario of B(a)P emissions were carried out. A simple emission scenario was constructed on the basis of scaling of emissions from particular source categories of selected countries. Two emission source categories, namely, the 'Residential combustion' and 'Field burning of agricultural residues', associated with the most significant level of uncertainties, were considered for the scaling. Changes of emissions were performed for the countries where the most significant deviations between the modelled and observed B(a)P air concentrations were found.

The scaling factors, defined for the selected countries, are given in the Table 3.2. The scenario assumes a factor of 0.5 change of B(a)P emissions from the 'Residential combustion' sector for Belgium, the Netherlands, and Germany following the average difference between the modelled and measured B(a)P air concentrations. In case of Spain and Portugal, emissions from agriculture sector were scaled by a factor of 0.2 and 0.4, respectively, following the ratio of officially reported and TNO emissions [Denier van der Gon *et al.*, 2011b]. Emissions from the 'Residential combustion' sector of Poland and France were increased by a factor of 4 and 3, respectively, following the ratio of officially reported and TNO emissions for Poland, and in accordance with the suggestion of national experts for France.

Table 3.2. Definition of experimental B(a)P emission scenario for selected EMEP countries

<i>Country</i>	<i>Emission source category</i>	<i>Emission scale factor</i>
Belgium	Residential combustion	0.5
The Netherlands	Residential combustion	0.5
Germany	Residential combustion	0.5
France	Residential combustion	3
Poland	Residential combustion	4
Spain	Field burning of agricultural residues	0.2
Portugal	Field burning of agricultural residues (3F)	0.4

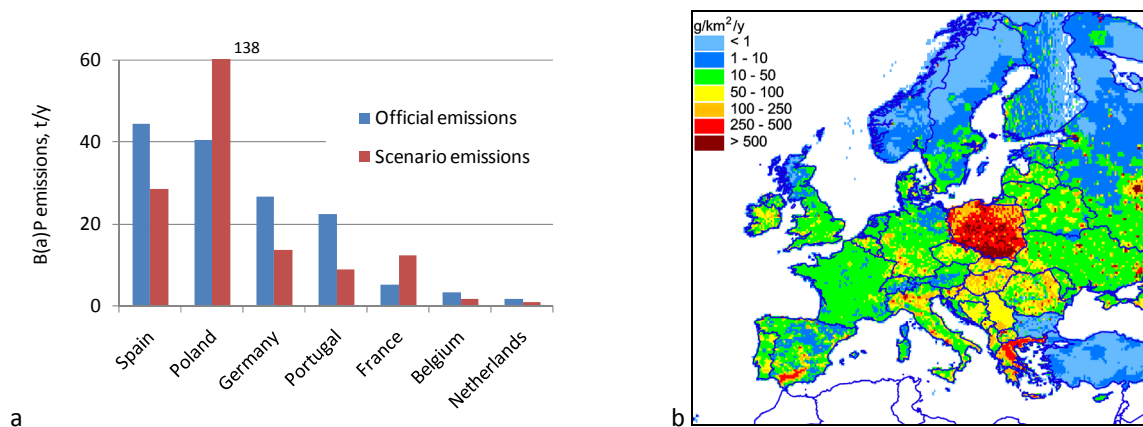


Fig. 3.5. Changes of national emissions (t/y) of selected countries in the experimental scenario of B(a)P emissions (a) and spatial distribution of annual emission fluxes of B(a)P (g/km²/y) in the experimental scenario for 2015.

In Figure 3.5a absolute changes of annual total B(a)P emissions in the selected countries in accordance with the prepared scenario are illustrated. Spatial distribution of resulted B(a)P emission fluxes in the EU02 modelling domain is shown in Figure 3.5b. It is seen that the largest absolute change of B(a)P emissions in the scenario took place for Poland followed by Spain, Portugal, and Germany. At the same time, maximum relative changes of emissions were noted for Poland and France.

Annual mean B(a)P air concentrations, simulated by the GLEMOS and CHIMERE models using experimental emission scenario, and measured concentrations of the AIRBASE background rural and remote monitoring stations are presented in Figure 3.6. Results of reference model runs of the two models, carried out on the basis of officially reported B(a)P emissions, are described in the previous section. Evaluation of the effect of emission scaling on modelling results was carried out using comparison of the scenario and reference model simulations with measurements of AIRBASE (Table 3.3). The Table shows noticeable improvement of all statistical metrics, calculated on the basis of annual mean modelled and observed values.

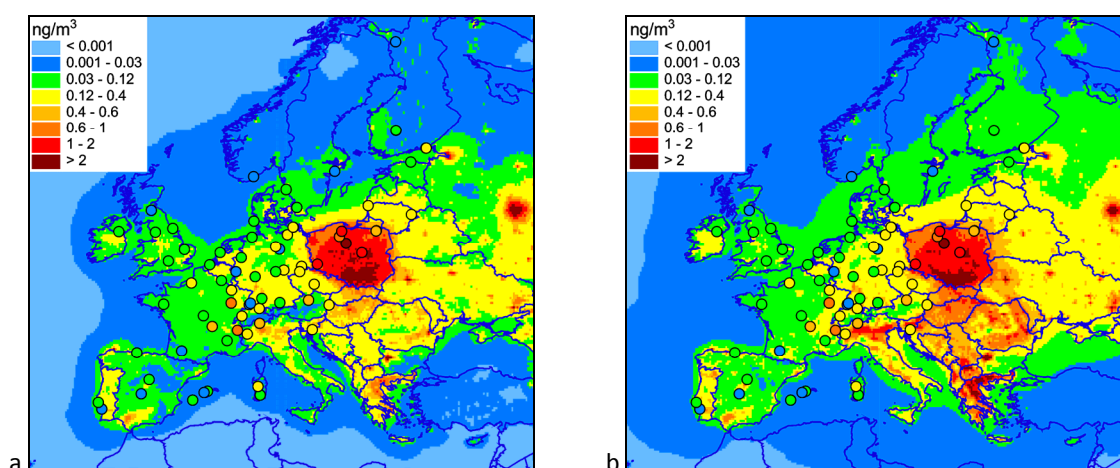


Fig. 3.6. Annual mean B(a)P air concentrations (ng/m³) in 2015 simulated by the GLEMOS (a) and CHIMERE (b) models for the EU02 domain 0.2°x0.2° using scenario emissions; and B(a)P concentrations observed at AIRBASE background rural and remote monitoring sites, overlaid as coloured circles in the same scale as modelled values.

The spatial pattern of B(a)P air concentrations, simulated by GLEMOS and CHIMERE using scenario emissions, better captures the spatial distribution of observed B(a)P air concentrations comparing to reference model runs. Spatial correlation between the simulated concentrations and measurements improved from 0.43 to 0.82 for GLEMOS, and from 0.30 to 0.80 for CHIMERE. Similarly, the values of the bias and RMSE metrics considerably decreased for both models results. Reduction of deviations of model estimates from measurements is also reflected in the increased values of F2 and F3 metrics.

Table 3.3. Summary of statistical metrics, calculated on the basis of annual mean B(a)P air concentrations observed at AIRBASE background rural and remote monitoring stations (n=82) and estimated by GLEMOS and CHIMERE in the scenario and reference model runs for 2015.

Model	NMB^a (%)	R^a	RMSE^a (ng/m³)	F2^a (%)	F3^a (%)
<i>Reference model run with official emissions</i>					
GLEMOS	-39	0.43	0.41	39	59
CHIMERE	-28	0.30	0.43	45	70
<i>Scenario model run with scaled emissions</i>					
GLEMOS	-12	0.82	0.25	51	72
CHIMERE	-2	0.80	0.27	59	83

^a NMB is normalized mean bias; R is the spatial correlation between modelled and observed concentrations; RMSE is the root mean square error; F2 and F3 represent fractions of sites for which deviation between modelled and observed values are within a factor of 2 and 3, respectively.

Model simulations, performed by GLEMOS and CHIMERE using scenario emissions, showed noticeable improvement of agreement between predicted and observed B(a)P air concentrations in European countries. At the same time, though the level of the disagreement is generally decreased, for some of the monitoring sites, located in Austria, Finland, Germany, and France, the deviations remained significant. It should be noted that this simple scenario was based on the scaling of total sectoral emissions, and did not take into account uncertainties of spatial distribution of emissions that could substantially affect model performance for individual monitoring sites.

These results may indicate that officially reported B(a)P emissions of some of the EMEP countries are subject of significant uncertainties that lead to substantial deviations between the model estimates and observations. To improve the quality of model assessment of B(a)P pollution levels, further refinement of national emission inventories with respect to estimates of total emissions and their spatial distribution is appreciated.

3.4. Analysis of B(a)P emissions from agricultural sources in Spain

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Burning of agricultural residues can be important source of toxic pollutants (e.g. PAHs, PCDD/Fs) releases to the atmosphere [Viana *et al.*, 2008; Gonçalves *et al.*, 2011]. In spite of restrictions, introduced by many European countries for open burning of agricultural wastes, this activity still takes place in southern Europe due to permissions given by local and regional authorities [AIRUSE, 2016]. According to the national emission inventory of Spain, emissions from combustion of crop residues accounted for about 45% of national total PAH emitted in 2015 [IIR, 2017]. This emission source category considers the burning of herbaceous agricultural cotton residues⁵, which are, after the harvest, spread but not fixed to land, and stored in a small area for a local burning. Although burning of cotton residues has significantly decreased during the recent years, emissions from this activity are still important since Spain produces ~21% of the European Union's cotton (being the second largest producer after Greece).

Evaluation of emissions from the combustion of agricultural residues to the atmosphere represents difficulties due to dependency on many factors (e.g. type of residue, its moisture content, conditions of combustion, and meteorological conditions) [Oanh *et al.*, 2011; Sanchis *et al.*, 2014; Gonçalves *et al.*, 2011]. The methodology currently used for this purpose contains some uncertainties that can lead to overestimation of PAH emissions from agricultural activities in southern part of Spain (Andalusia). In this section a summary of information on applied methodology, its uncertainties, and results of test model simulations carried out on the basis of national PAH emission inventory and experimental modelling scenarios, is provided.

Estimation of B(a)P emissions from agricultural sources

To estimate emissions from agricultural sources, the Tier 1 methodology and default emission factors of the EMEP/EEA air pollutant emission inventory guidebook [EMEP/EEA Guidebook, 2016] were applied. The Tier 1 methodology optionally points to the generic approach of the IPCC Guidelines [IPCC Guidelines, 2006], which was developed to quantify the amount of burned residues and emissions resulting from biomass burning. According to this approach pollutant emission to the atmosphere from burning of agricultural residues can be evaluated using the following equation:

$$L_{\text{fire}} = A \times M_b \times C_f \times G_{\text{ef}} \times 10^{-3}$$

where:

- | | |
|-------------------|--|
| L_{fire} | the amount of pollutant gaseous emission due to combustion of residues (tons); |
| A | the burnt area (ha); |

⁵ According to the SNAP nomenclature this source category relates to SNAP 10 (Agriculture), subcategory 10.3.5, *burning of herbaceous agricultural crop residue*, and in the NFR nomenclature to the source category 3.F, *field burning of agricultural residues*.

This area is calculated based on the cultivated area, multiplied by the burned fraction specific for each crop type. For cotton a value of 0.333 was used (following the [MAPAMA, 2015]).

M_b the specific mass of residues available for combustion (tons ha^{-1});

C_f the combustion factor defined according to default values of IPCC methodology [IPCC Guidelines, 2006] (dimensionless);

The combustion factor represents a measure of the proportion of biomass fuel that is actually combusted. This value depends on the size and architecture of the fuel load, the moisture content of the fuel as well as on fire intensity and rate of spread.

The burnt dry combustible mass is calculated as $M_b * C_f$ and values of this product were taken from [IPCC Guidelines, 2006]. For the calculation of PAH emissions the value for the aggregated vegetation type 'All Shrublands', equal to 14.3, was selected.

G_{ef} the emission factor for considered pollutant (kg/kg of burnt dry matter).

The Tier 1 default emission factors for NFR source category 3.F [EMEP/EEA Guidebook, 2016] were used for PAHs, which values were based on the study [Jenkins et al., 1996].

Analysis of this methodology, applied for the evaluation of PAH emissions in Spain, indicates that several parameters of this approach can be subject of considerable uncertainties. In particular:

1. The area of burning (A), calculated as a function of the cultivated area, can be overestimated. During the recent years part of the cultivated area in Andalucía has been assigned to an integrated production system, for which the legislation does not allow residues burning. Therefore, calculation of PAH emissions without taking this into account would lead to the overestimation of actual emissions.
2. The value of the burnt dry combustible mass ($M_b * C_f$), selected from the default IPCC estimates [IPCC Guidelines, 2006], is evaluated for the aggregated vegetation type and is not specifically determined for the cotton residues. At the same time, there are estimates for several crops in these guidelines, namely, for wheat, maize, rice, and sugarcane residues. Thus, their use might be more appropriate for the evaluation of this parameter for cotton.
3. Values of default emission factors (G_{ef}) for PAHs in the EMEP/EEA guidebook [EMEP/EEA Guidebook, 2016] are not specific for cotton (for example, for benzo(a)pyrene the value of 67.7 mg/kg dry matter is suggested following [Jenkins et al., 1996] which was estimated for other types of crops).

Experimental emission scenarios and results of model simulations

To examine possible effects of the uncertainties mentioned above on model predictions of B(a)P pollution levels, several experimental emission scenarios were prepared. These scenarios are based on the official PAH emission data for 2015, provided by the Spanish Ministry of the Environment. Inventory of PAH emissions is generated for the sum of 4 PAHs without splitting for particular PAH compounds. Therefore, to obtain emissions of B(a)P, its fraction in the emissions of 4 PAHs was taken equal to 14%. This assumption was made in accordance with the information from national experts on emissions, with

reference to the EMEP/EEA Guidebook 2016. The following modifications of B(a)P emissions were considered in the scenarios:

- Scenario 1: Modification of the spatial distribution of emissions applying a spatial mask for areas assigned to the integrated production system. For these areas no burning of residues is expected, so the emissions in the corresponding grid cells are removed, which reduces total emission from agricultural sources by 62%. In this scenario both the spatial distribution and total emission from agriculture sector are changed.
- Scenario 2: Modification of the fraction of burned area for cotton (A). About 85% of fields for cotton are now part of an integrated production system, where no burning is allowed. Thus, the fraction of burned area can be reduced from 0.333 to 0.15, which leads to 55% reduction of emissions from agricultural sources. This scenario assumes changing of total emission from agriculture sector, while spatial distribution is left the same as it is defined in the national emissions inventory.
- Scenario 3: Modification of the value for burnt dry combustible mass ($M_B * C_f$). Though there is no specific value for burning of cotton residues, the IPCC Guidelines provide the estimates for burning of wheat, maize, rice, and sugarcane crop residues. The average value of these estimates, equal to 6.5, can be used for the evaluation of emissions from agricultural sources (instead of the chosen value 14.3), which equates to a 58% emission reduction.

Preliminary model simulations of B(a)P pollution in Spain were performed for the first scenario with the two air quality models, namely, EMEP GLEMOS and CHIMERE (v2013, [Menut *et al.*, 2013]) models. Modelling of B(a)P pollution using the GLEMOS model was carried out for the year 2015. In case of the CHIMERE model the simulations were made with meteorological data for the year 2017 due to availability of necessary resources. For the evaluation of the impact of emission modifications, model predictions of Scenario 1 (SC1) simulations were compared with the base case (BC) simulations. Besides, level of agreement between modelled and observed B(a)P concentrations was evaluated for both sets of modelling results (BC and SC1). Measurements of 12 monitoring sites in Andalusia of different types, including background urban and suburban, industrial, and traffic sites, were selected for the comparison. The GLEMOS and CHIMERE models are not specifically designed for the evaluation of pollution in urban and industrial areas. However, due to the lack of background rural and remote sites in this area, other types of sites (e.g. urban, industrial, and traffic) were also considered in the comparison for the analysis of spatial distribution of pollution.

Spatial distributions of annual mean B(a)P air concentrations for the BC and SC1 simulations, carried out using the CHIMERE model, are shown in the Fig.3.7. Similar results of the GLEMOS model are presented in the Fig.3.8. Model predictions of the CHIMERE model are slightly higher comparing to the results of the GLEMOS model, which can be explained by several reasons. The CHIMERE model, applied in for these simulations, did not consider degradation of B(a)P by ozone. Furthermore, the GLEMOS model includes parameterization of B(a)P gaseous exchange with underlying surface, whereas in the CHIMERE model this process was not considered. Besides, some differences in modelling results can be due to different model setups (e.g. meteorological and geophysical input data). In spite of this, both models showed similar patterns of B(a)P air concentrations.

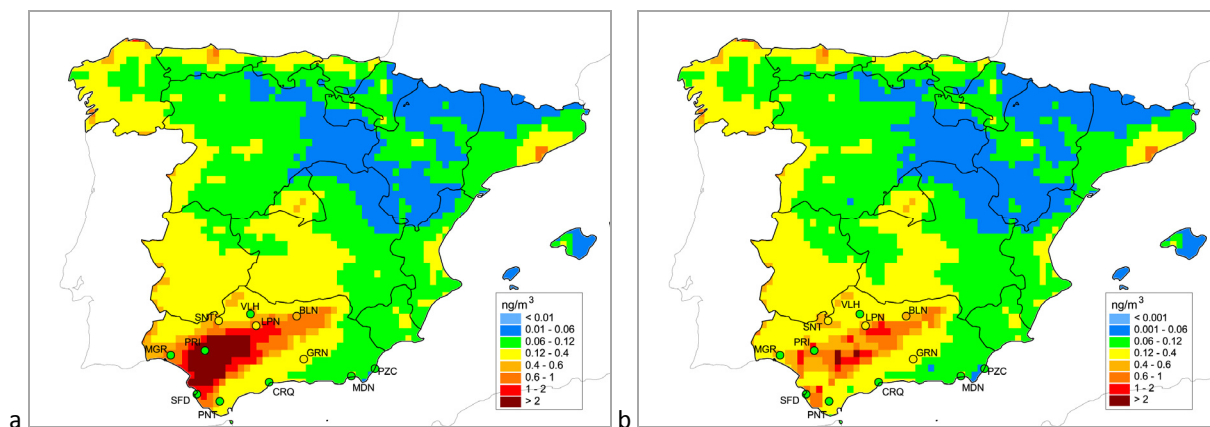


Fig. 3.7. Annual mean B(a)P air concentrations (ng/m^3) in 2017 obtained by the CHIMERE model in the BC and SC1 simulations. B(a)P air concentrations observed at monitoring sites⁶ in Andalusia in 2017, are overlaid as coloured circles in the same scale as modelled values.

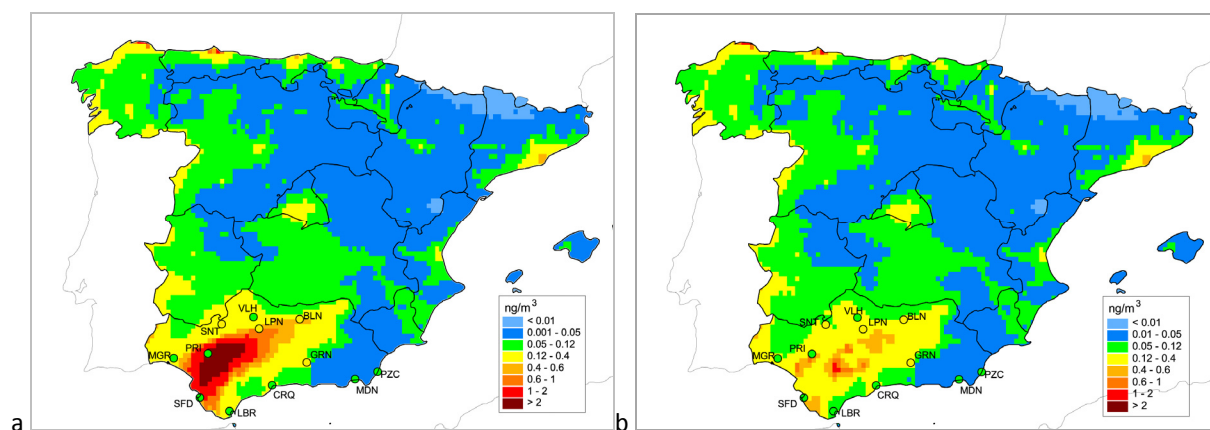


Fig. 3.8. Annual mean B(a)P air concentrations (ng/m^3) in 2015 obtained by the GLEMOS model in the BC and SC1 simulations. B(a)P air concentrations observed at monitoring sites⁶ in Andalusia in 2015, are overlaid as coloured circles in the same scale as modelled values.

In Table 3.4 statistical indicators of the agreement between model predictions of B(a)P air concentrations and measurements are presented. The GLEMOS and CHIMERE models significantly over-predicted observed B(a)P concentrations in the BC simulations. Besides, the spatial correlation between the modelled and measured concentrations was low. The over-prediction can be attributed to possible overestimation of B(a)P emissions from agriculture sector, which is dominating source in this area according to the national emissions inventory. Low correlation might indicate possible inaccuracies in the spatial allocation of emissions.

In case of SC1 simulations both models show substantial decrease of modelled B(a)P air concentrations due to reduction of the burning area and consequently lower emissions from the combustion of cotton residues. The values of average bias (MFB) and error (MFE) decreased comparing to the BC simulations.

⁶ Monitoring sites: Moguer (MGR), Principes (PRI), Sierra Norte (SNT), Villaharta (VLH), Lepanto (LPN), Bailin (BLN), San Fernando (SFD), Puente M (PNT), Los Barrios (LBR), Carranque (CRQ), Mediterraneo (MDN), Pza del Castillo (PZC), Granada Norte (GRN).

Table 3.4. Statistics of the comparison of GLEMOS and CHIMERE modelling results with measurements of B(a)P air concentrations made at 12 monitoring sites in Andalucía in 2015 and 2017

Model (scenario)	Year	Observed, ng/m ³	Modelled, ng/m ³	MFB ^a , %	MFE ^a , %	Correlation
CHIMERE (BC)	2017	0.119	0.718	123	123	0.02
CHIMERE (SC1)	2017	0.119	0.370	106	108	0.25
GLEMOS (BC)	2015	0.125	0.255	39	109	-0.05
GLEMOS (SC1)	2015	0.125	0.134	11	96	-0.01

^a MFB is mean fractional bias; and MFE is mean fractional error following [Boylan and Russell, 2006].

At the same time, changes in spatial distribution of agricultural emissions did not lead to noticeable improvements of spatial correlation between model predictions and measurements. In particular, in the case of the CHIMERE SC1 simulations the spatial correlation was only slightly increased, while no correlation was obtained in the GLEMOS BC and SC1 simulations.

In Fig.3.9 comparison of monthly mean modelled and observed B(a)P air concentrations is illustrated on the example of GLEMOS modelling results for three monitoring sites Principes, Lepanto, and Moguer. The sites are located quite close to the area of cotton agricultural activities. Besides, model predictions for their locations demonstrated the most pronounced response to the changes of emissions in the scenario SC1. It is seen that despite significant decrease of modelled values, the overestimation of observed concentrations for these sites is still significant.

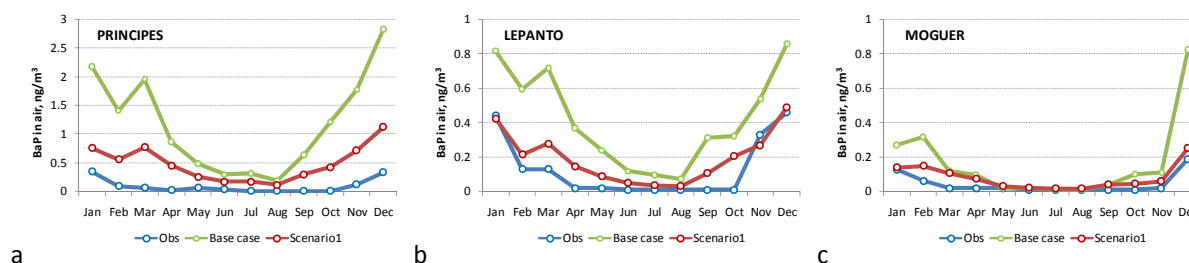


Fig. 3.9. Modelling results of GLEMOS model with base case and scenario emissions.

Concluding, it can be noted that high B(a)P concentrations, modelled with both GLEMOS and CHIMERE in southern Spain (Andalucía), might be directly related to the high emissions from burning of herbaceous crop residues in agriculture. Emission scenario assuming reduction of the burning area for cotton residues permitted to improve the agreement between model predictions and measurements for both models. At the same time, the overestimation of observed B(a)P air concentrations for some of the monitoring sites in the scenario model simulations is still significant. Besides, there is a lack of spatial correlation between the simulated and measured concentrations. Thus, *analysis of B(a)P pollution levels in this area needs to be continued with application of additional emission scenarios. Furthermore, results of test model simulations indicate the need of refinement of methodology applied to the evaluation of the emissions from burning of agricultural residues in Spain.*

4. ASSESSMENT OF PCDD/Fs, PCBs, AND HCB POLLUTION IN THE EMEP REGION

This chapter presents results of the assessment of environmental pollution by PCDD/Fs, PCBs, and HCB performed on the basis of model predictions and measurements. Model simulations were carried out on the basis of officially reported emission data for the new EMEP grid using the multi-media GLEMOS modelling system. Spatial trends of air concentrations and deposition fluxes in 2016 on regional and global scales were characterized. Transboundary transport of pollution between the EMEP countries as well as transport from non-EMEP emission sources was evaluated. Results of model simulations were compared with measurements of the EMEP monitoring sites and data of national monitoring networks. Main emphasis in these activities was given to the evaluation of PCDD/F pollution levels in the EMEP countries. Brief overview of progress and outcome of this work is presented below. Detailed information on modelling results and their analysis is available in the internet on the MSC-E web site (www.msceast.org).

4.1. Emission data for model assessment

Assessment of PCDD/F and HCB pollution in the new EMEP domain was made on the basis of gridded emission data with spatial resolution $0.1^{\circ} \times 0.1^{\circ}$ provided by CEIP. Similar to PAHs, pollution levels of PCDD/Fs and HCB in 2016 were evaluated on the basis of emissions reported for the previous year 2015 due to availability of necessary gridded emission data⁷. Detailed description of estimated PCDD/F and HCB emissions in the EMEP countries, gap-filling methods, and expert estimates applied for preparation of emission inventory, can be found in the Technical report of CEIP [Tista *et al.*, 2017].

Estimates of PCDD/F emissions officially reported by the EMEP countries are most likely subject to considerable uncertainties due to underestimation of releases for some of the source categories (e.g. 'Residential combustion', 'Open burning of wastes') and incomplete coverage of all potential sources [Breivik *et al.*, 2004; Fiedler, 2007; Pulles *et al.*, 2005; Pulles *et al.*, 2006]. For this reason two emission datasets were used in model simulations, namely, officially reported gridded emissions and scenario emissions, representing maximum level of PCDD/F releases to the atmosphere. The maximum emission scenario was prepared on the basis of the uncertainty range reported by 12 EMEP countries in their inventory information reports (namely, Belarus, Belgium, Croatia, Cyprus, Denmark, Estonia, Finland, France, Latvia, Poland, Sweden, and the UK). Difference between the maximum and average estimates of PCDD/F emissions in these countries varied from a factor of 1.5 for the UK up to a factor of 4.1 for Croatia. For other EMEP countries, which did not report uncertainty range in their inventories, the maximum level of national PCDD/F emissions was assumed to be 3-fold higher comparing to the officially reported emissions in accordance with the expert estimates [Pulles *et al.*, 2006; Bogdal *et al.*, 2014]. Thus, total PCDD/F emission in the EMEP countries according to the maximum emission scenario exceeded reported data in the inventories by a factor of 3.5 on average.

Gridded emission data for PCB modelling were based on the available expert estimates and officially reported data of the EMEP countries. Model assessment of PCB pollution levels (total and congener

⁷ Update of the modelling results based on the new emission data for 2016 is available at the MSC-E web site [www.msceast.org].

specific) requires definition of emissions of particular PCB congeners. However, currently reported national inventories of PCB emissions provide total releases of PCBs without distribution by particular congeners. Therefore, to evaluate transport and fate of individual PCB congeners, congener specific emission inventory of *Breivik et al.* [2007] was used for modelling. The indicator congener PCB-153 was selected to characterize transboundary transport and pollution by PCBs. Spatial distribution of PCB-153 emissions was constructed on the basis of gridded PCB emissions officially provided by the EMEP countries. For other EMEP countries, which did not report gridded emission data, gridded population density was used for allocation of emissions.

Maps illustrating spatial distributions of PCDD/F, HCB, and PCB-153 emission fluxes from anthropogenic sources in the EMEP region, used in the model simulations for 2016, are presented in Figs 4.1.

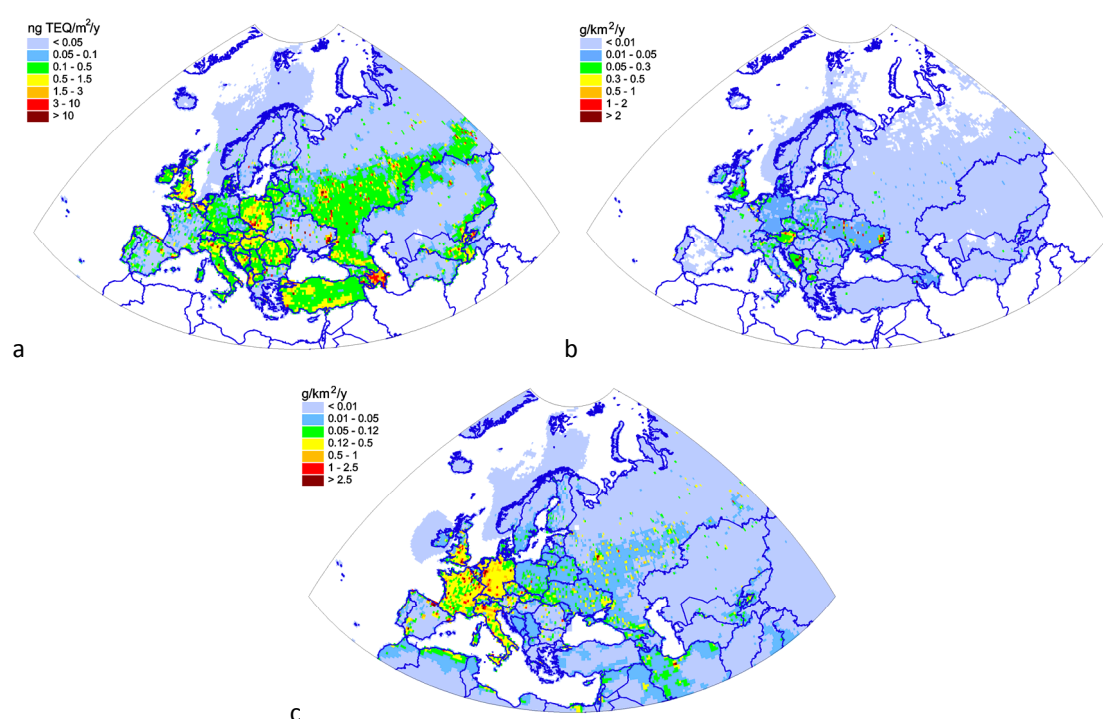


Fig. 4.1. Spatial distribution of PCDD/F, $\text{ng TEQ/m}^2/\text{y}$ (a), HCB, $\text{g/km}^2/\text{y}$ (b), and PCB-153, $\text{g/km}^2/\text{y}$ (c) emissions in the EMEP region used in model simulations for 2016.

For the evaluation of global-scale transport and fate of PCDD/Fs, HCB, and PCBs expert estimates of global emissions were applied. In particular, global gridded emissions of PCDD/Fs to the atmosphere and soil were prepared using the national emission inventories reported by countries to the Stockholm Convention [Gusev et al., 2014; Shatalov et al., 2014]. Model simulations of HCB global-scale transport were carried out on the basis of experimental emission scenario of historical HCB releases during the period covering several recent decades [Shatalov et al., 2010]. For PCB-153 modelling, data on global emissions were derived from the inventory of *Breivik et al.* [2007]. Spatial distributions of PCDD/F, HCB, and PCB-153 emissions, used in the global-scale model simulations for 2016, are shown in Fig.4.2.

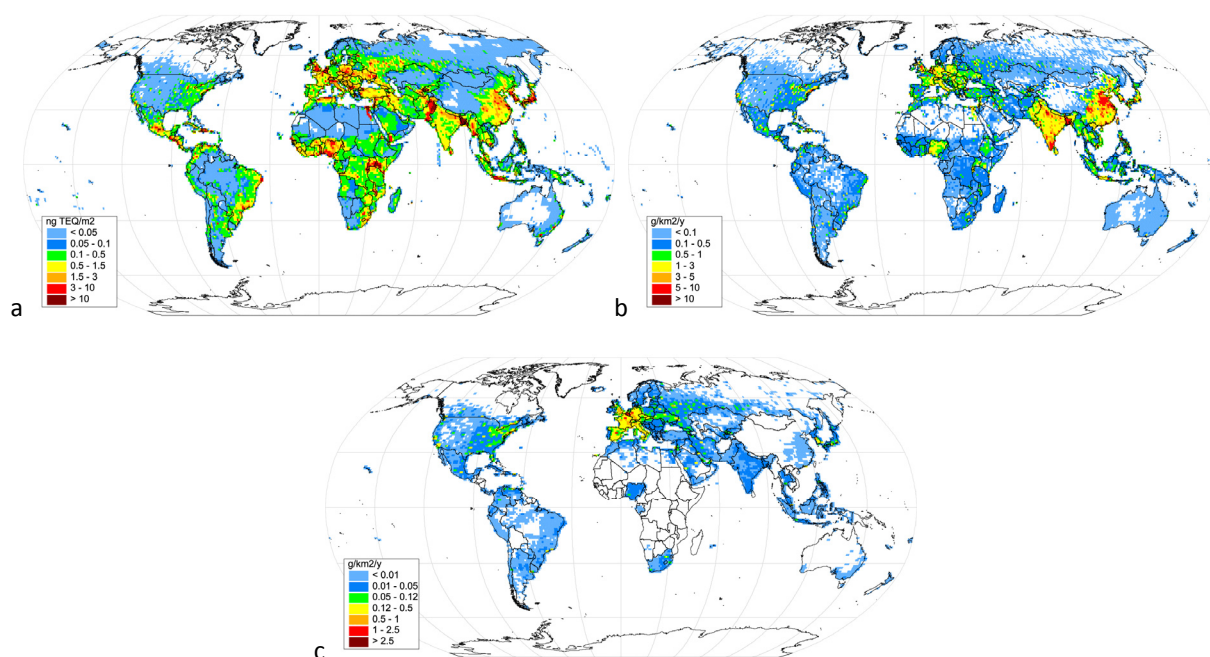


Fig. 4.2. Spatial distribution of global annual emissions of PCDD/Fs, ng TEQ/m²/y (a), HCB, g/km²/y (b), and PCB-153, g/km²/y (c) with spatial resolution 1°x1°, used in model simulations for 2016.

4.2. Pollution levels in the EMEP region

Assessment of PCDD/F, PCB-153, and HCB pollution levels in the new EMEP domain was performed using nested modelling approach. Model simulations were carried out for the global and regional EMEP domains. Results of global scale model runs for 2016 were used to derive lateral boundary conditions for regional model runs. Initial conditions for the evaluation of pollution levels in the EMEP region were prepared on the basis long-term spin-up global model runs. To characterize the spatial variability of PCDD/F pollution levels within the EMEP domain, analysis of modelling results and measurements of national monitoring networks has been carried out.

Regular monitoring of PCDD/F air concentrations is not currently performed at the EMEP network stations. At the same time, long-term measurements of PCDD/F content in air are carried by national monitoring networks in some of the EMEP countries (e.g. in the UK, Spain, and Portugal). In particular, continuous measurements of PCDD/F air concentrations as well as concentrations of some other POPs in the UK are carried out using the Toxic Organic Micro-pollutants Monitoring Network (TOMPs) starting from 1991 up to the present time. The network comprises 6 rural and urban monitoring sites in different parts of the UK. The Spanish Monitoring Program for several POPs including PCDD/Fs was established in 2008 in Spain to explore the effectiveness of existing regulations. Spatial and temporal trends in the observed PCDD/F air concentrations were analyzed using data of national background rural and urban monitoring sites for the period 2008-2015 [Muñoz-Arnanz *et al.*, 2018]. Studies of long-term trends in PCDD/F air concentrations were also carried out in Portugal for the period 2001-2014 [Coutinho *et al.*, 2015]. Along with long-term monitoring activities, concentrations of PCDD/Fs in

ambient air were analysed in the framework of various measurement campaigns in several EMEP countries (e.g. in Sweden, Denmark, and Italy).

In Figure 4.3 model predictions of annual mean PCDD/F air concentrations, calculated using officially reported emissions and maximum emission scenario, are illustrated. The latest available data on the observed PCDD/F air concentrations, namely, measurements for 2015 in Spain, and for 2016 in the UK and Sweden, are shown on the maps (Fig. 4.3).

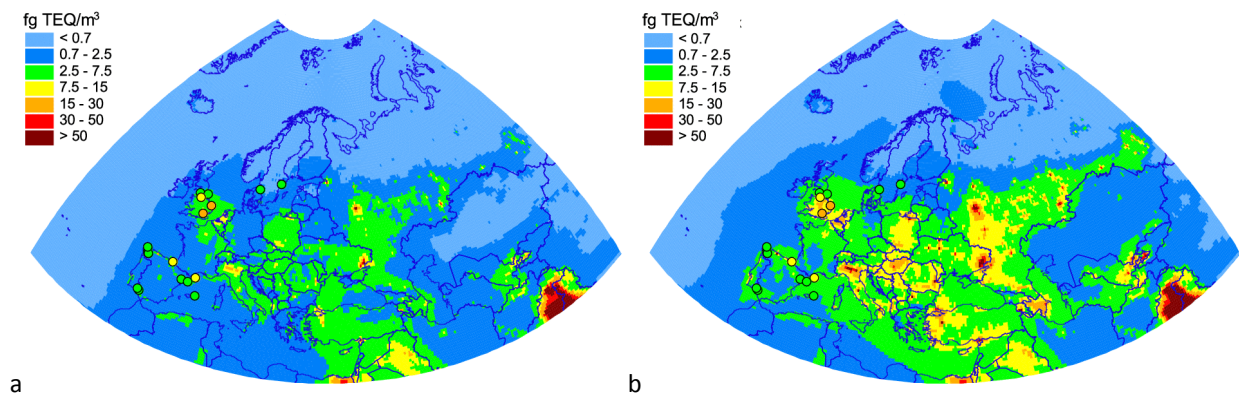


Fig. 4.3. Spatial distribution of modelled and observed annual mean air concentrations of PCDD/Fs (fg TEQ/m³) calculated using official emissions (a) and maximum scenario emissions (b) in the EMEP domain for 2016.

Model predictions with maximum emission scenario (Fig. 4.3b) provided higher levels of pollution in the EMEP countries comparing to the results of simulations with official PCDD/F emissions (Fig. 4.3a). It is seen that maximum scenario results have better agreement with measurements. Model simulations indicate elevated levels of dioxins and furans air concentrations (about 15 - 50 fg TEQ/m³) for the UK, northern Italy, countries of Central and Eastern Europe as well as in the EECCA countries (e.g. the Russian Federation, Ukraine, Azerbaijan). Lower levels of pollution were estimated for France, Spain, Portugal, and countries of Northern Europe (about 1 - 7 fg TEQ/m³).

Model estimates of annual mean PCB-153 and HCB air concentrations for 2016 are illustrated in Fig. 4.4a and 4.4b, respectively. Similar to PCDD/Fs, the maps include overlaid observed annual mean PCB-153 and HCB air concentrations, reported by the EMEP monitoring stations.

The highest levels of modelled PCB-153 annual mean air concentrations (3 - 5 pg/m³ and higher) were estimated for the countries in Western Europe (e.g. Germany, France, Belgium). Simulated PCB-153 concentrations in Northern Europe were generally below 1 pg/m³ that corresponded to the observed concentrations. Similar levels of pollution were also obtained by the model for Eastern Europe and the EECCA countries.

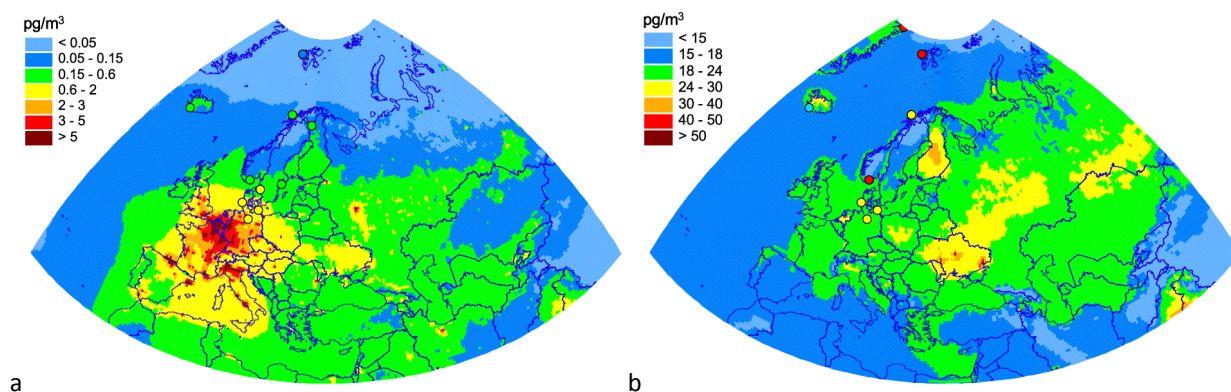


Fig. 4.4. Spatial distribution of modelled and observed annual mean air concentrations (pg/m^3) of PCB-153 (a) and HCB (b) in the EMEP domain for 2016.

Modelling results for HCB showed low spatial variability of annual mean air concentrations, which can be explained by longer residence time in the atmosphere comparing to other considered POPs. Relatively higher levels of pollution were estimated for countries of Central and Eastern Europe (about $20 - 30 \text{ pg}/\text{m}^3$). For other areas model estimates were below $20 \text{ pg}/\text{m}^3$. Contrary to this, measurements of EMEP monitoring sites indicated more significant variability of HCB air concentrations. In particular, high annual mean concentrations (about $60 - 80 \text{ pg}/\text{m}^3$) were observed in Northern Europe and in the Arctic. It is seen that model simulations did not reproduce these high levels of HCB concentrations. Possible reasons of these differences are discussed below in the section related to the comparison of model predictions with measurements (Section 4.3).

4.3. Comparison of modelling results with measurements

Evaluation of PCB-153 and HCB modelling results for 2016 was carried out using measurements of air concentrations of the EMEP monitoring network. Model predictions of PCDD/F air concentrations were evaluated against available measurements of the national monitoring networks in the UK, Spain, and Sweden.

In Figure 4.5 scatter plots of annual mean modelled PCDD/F air concentrations, calculated using official emissions and maximum emission scenario, and measurements of national monitoring sites are presented. It is seen that model simulations with official emissions underestimated observed PCDD/F air concentrations with average bias equal to -51% (Fig. 4.5a). Significant part of model predictions deviated from measurements by more than a factor of 2 (about 60%) and a factor of 3 (about 50%).

Model predictions on the basis of maximum emission scenario showed better agreement with measurements. In particular, the value of average bias (NMB) improved significantly (from 51% to 7%) and values of F2 and F3 indicators increased. For both sets of modelling results the spatial correlation between the modelled and observed PCDD/F air concentrations was about 0.6.

The use of maximum levels of PCDD/F emissions led to improvement of agreement between the modelling results and measurements that could be considered as an indication of possible

underestimation of officially reported PCDD/F emissions. At the same time, amount of available observational data for the evaluation of PCDD/F model predictions was limited to several countries. Therefore, model predictions for other regions in the EMEP domain require further analysis with application of additional PCDD/F monitoring data.

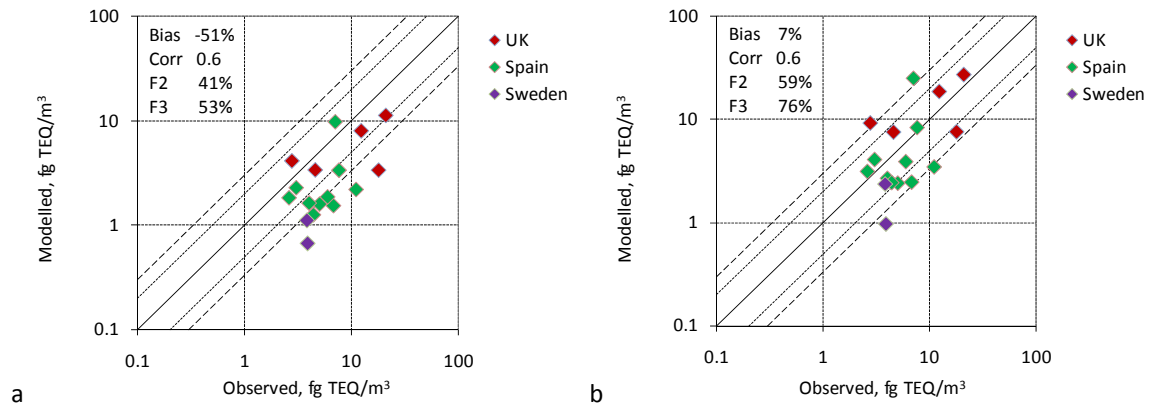


Fig. 4.5. Comparison of annual mean modelled PCDD/F air concentrations, calculated using official emissions (a) and maximum scenario emissions (b), with measurements of national monitoring sites. Dashed lines indicate the area of agreement between the modelled and observed values within a factor of 2 and 3. NMB is normalized mean bias; R is the spatial correlation; F2 and F3 are fractions of sites for which deviation between modelled and observed values are within a factor of 2 and 3, respectively.

Annual mean modelled PCB-153 air concentrations are compared with data of EMEP measurements in Fig. 4.6a. Monitoring of PCB-153 air concentrations in 2016 was carried out at 10 EMEP sites, located in Germany, Finland, Norway, Iceland, and Sweden (Chapter 1). *Model predictions reasonably reproduced spatial distribution of observed PCB-153 levels in ambient air (spatial correlation coefficient was 0.75). For 60% of the monitoring sites the difference between measured and modelled concentrations was within a factor of 2. At the same time, the model tended to under-predict observed concentrations with average bias -23%.* The most significant under-prediction of measured concentrations was obtained for the monitoring sites NO0042R, NO0090R, IS0091R, and SE0014R.

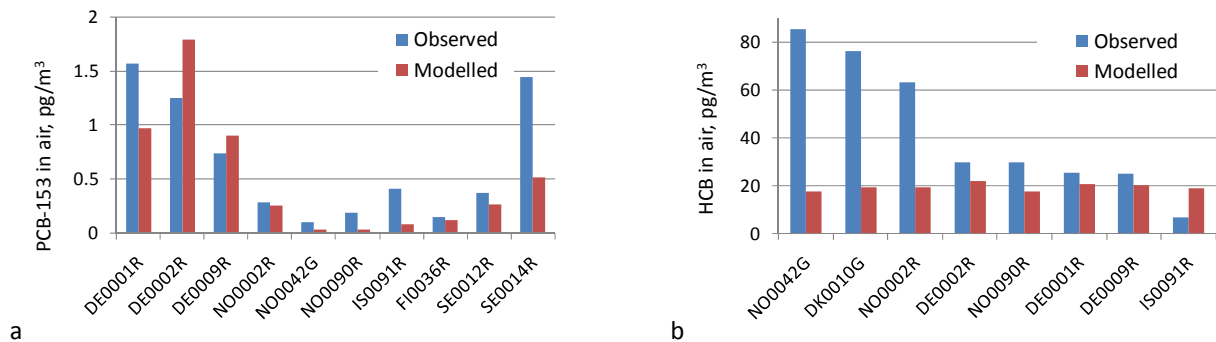


Fig. 4.6. Comparison of annual mean modelled PCB-153 (a) and HCB (b) air concentrations with measurements of the EMEP monitoring sites for 2016.

These deviations might be explained by the use of emission expert estimates in model simulations that might underestimate PCB emissions in some of the areas outside the EMEP domain. For instance, global scale model simulations of PCB-153 in this study were based on the emission inventory of *Breivik et al.* [2007], which estimated atmospheric emissions of intentionally produced PCBs. Refinement of emissions of intentionally produced PCBs in China, carried out by *Cui et al.* [2015], resulted in greater values of emissions for recent two decades comparing to the estimates of *Breivik et al.* [2007] which showed gradual decrease after 1970s. Furthermore, the study indicated importance of contributions of unintentionally produced PCBs from various industrial activities as well as from e-waste re-cycling in China. Thus, refinement of global scale model simulations for PCBs is needed taking into account new information on non-EMEP emissions in different regions of the globe. In addition to this, the deviations might be partly attributed to possible uncertainties of the model parameterizations of air-surface exchange and degradation in soil and seawater compartments. Hence, further analysis of obtained under-prediction of observed PCB concentrations is required in co-operation with national experts.

In Figure 4.6b annual mean modelled HCB air concentrations for 2016 are compared with the observed concentrations. Measurements of HCB air concentrations for 2016 were reported by 8 EMEP sites in Germany, Norway, Denmark, and Iceland. *For most of the monitoring sites the model tended to under-predict observed HCB concentrations in air* with the exception for IS0091R (for which observed concentrations were over-predicted). The most significant under-prediction (more than a factor of 3) is seen for the sites NO0042R and DK0010R in the Arctic region, and NO0002R in the southern part of Norway. Similar differences between the modelled and measured air concentrations for these sites were discussed in the previous Status Report [*Gusev et al.*, 2017].

In particular, *under-prediction of observed HCB concentrations by the model was attributed to i) incomplete information on HCB emission sources in the inventories reported by the EMEP countries, ii) possible underestimation of HCB emissions in the regions outside the EMEP domain applied in model simulations, and iii) uncertainties of the model parameterizations for HCB degradation in media and air-surface exchange.* Besides, measurements of HCB concentrations in ambient air can be subject to considerable uncertainties due to its high volatility ("break-through" effect).

Uncertainties in the HCB emissions, officially reported by the EMEP countries, were discussed during the recent meeting of the Task Force on Emission Inventories and Projections held in 2018 in Sofia (Bulgaria). It was stressed that uncertainties in the reported HCB emissions were still high due to the gaps in coverage of HCB emission sources in national inventories as well as inconsistencies in the methodologies and emission factors used for the evaluation of emissions by different countries. Furthermore, only minor amount of the countries reported HCB emissions due to the application of pesticides containing impurities of HCB (NFR sector 3Df). Thus, the need of further refinement of methodology for estimation of HCB emissions from this source category in the EMEP/EEA Guidebook was highlighted.

4.4. Transboundary transport of pollution

Transboundary transport and source apportionment of PCDD/F, PCB-153, and HCB deposition in the new EMEP domain for 2016 was estimated taking into account the following groups of emission sources, namely, anthropogenic emissions of the EMEP countries, non-EMEP emissions, and secondary emissions. The influence of emissions, located outside the EMEP domain, was evaluated using global-scale model simulations.

Relative contributions of these three groups of emission sources to annual PCDD/F, PCB-153, and HCB deposition in the EMEP countries are shown in Fig. 4.7. The highest contribution of the EMEP anthropogenic emissions was estimated for PCDD/Fs (46%), followed by PCB-153 (36%), and HCB (2%). In the particular EMEP countries these estimates varied for PCDD/Fs from 18% to 66%, for PCB-153 from 14% to 50%, and for HCB from less than 1% to 10%.

Secondary emission sources of PCDD/Fs, PCB-153, and HCB contributed to deposition 50%, 69%, and 70%, respectively. The contribution of non-EMEP emission sources of PCDD/Fs and PCB-153 was relatively low (about 3 - 4%), whereas for HCB it was estimated to almost 30%, varying from 13% to 59% in the particular EMEP countries.

Results of source apportionment of POP deposition in the EMEP countries are exemplified by PCDD/F modelling results for 2016, calculated using the maximum emission scenario (defined in the Section 4.1). Annual PCDD/F deposition fluxes to the EMEP countries are shown in Fig. 4.8. Elevated levels of PCDD/F deposition fluxes in the EMEP countries (above 5 ng TEQ/m²/y) were estimated for Azerbaijan, Armenia, and Belgium. Significant deposition fluxes (about 4 ng TEQ/m²/y) were also characteristic of the Netherlands, Poland, Albania, Turkey, and Slovakia. Relatively low levels of deposition (below 1 ng TEQ/m²/y) were obtained for the Scandinavian countries as well as Iceland, Estonia, the Russian Federation, Kazakhstan, and Malta.

Long-range transport of PCDD/Fs from the emission sources of a particular country contributes to the deposition over the country itself and to the deposition to the territories of other countries. The ratio of PCDD/Fs emitted from anthropogenic emission sources and deposited within and outside the country's boundaries is shown in Fig. 4.9. *Model evaluation of PCDD/F distribution in the EMEP domain indicated that long-range transport between the EMEP countries is an important source of pollution. As follows from the Figure, for 15 EMEP countries (29% of the countries) the fraction of PCDD/Fs, deposited to other EMEP countries is higher than the fraction, deposited to the country itself.*

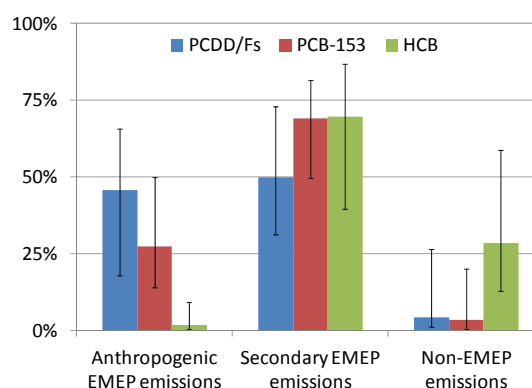


Fig. 4.7. Contributions of three source groups (anthropogenic EMEP, non-EMEP and secondary emission sources) to deposition over the EMEP countries in 2016 for PCDD/Fs, PCB-153, and HCB. Whiskers denote the range of contributions across the EMEP countries.

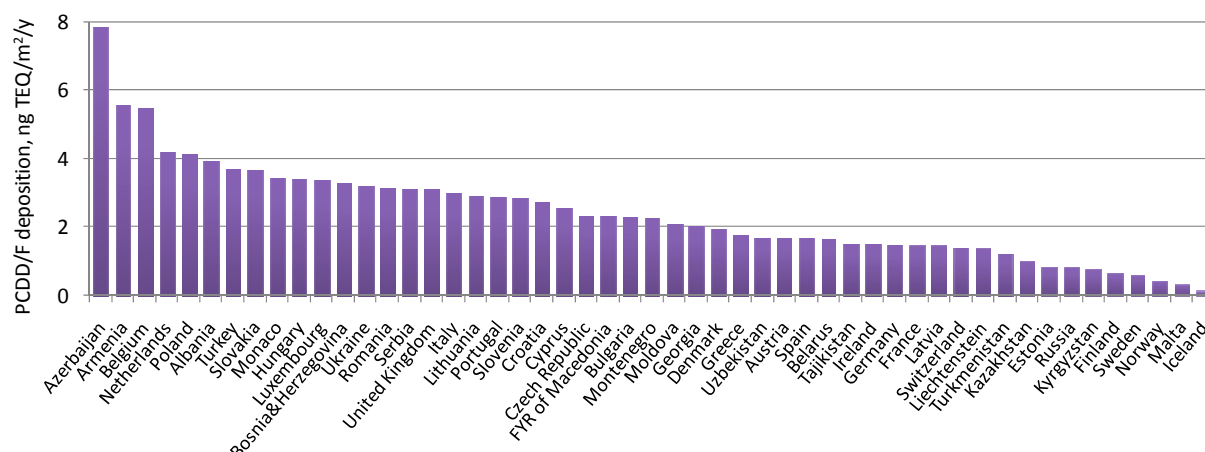


Fig. 4.8. Annual deposition fluxes of PCDD/Fs in the EMEP countries calculated for 2016, ng TEQ/m²/y.

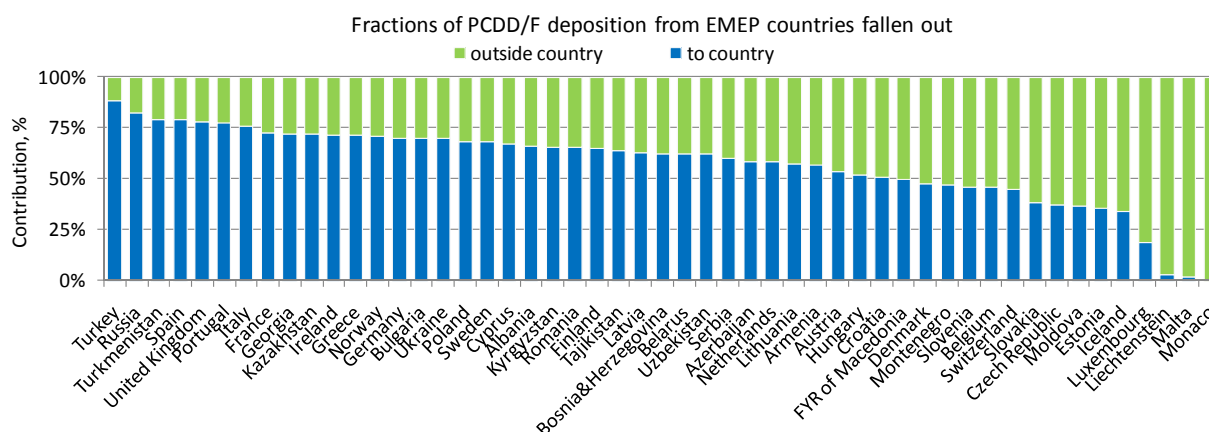


Fig. 4.9. Fractions of PCDD/F deposition, originated from national emissions of the EMEP countries, fallen out to their own territories and outside their boundaries in 2016.

According to model estimates of PCDD/F transboundary pollution, the contributions of emission sources, located outside the boundaries of a particular country, to deposition over this country were higher than the contribution of its own national emissions for 28 EMEP countries (55% of the countries) (Fig. 4.10). Results of nested model simulations provided also information on contributions of non-EMEP emission sources to the pollution levels in the EMEP region. These contributions for particular EMEP countries were in the range from 3% to 69% with the highest contribution estimated for Iceland.

Results of model simulations for 2016 pointed out that the largest contributions in absolute values to the PCDD/F deposition in the EMEP countries due to transboundary transport from anthropogenic emission sources were made by the Russian Federation followed by Ukraine, Azerbaijan, Kazakhstan, and Romania.

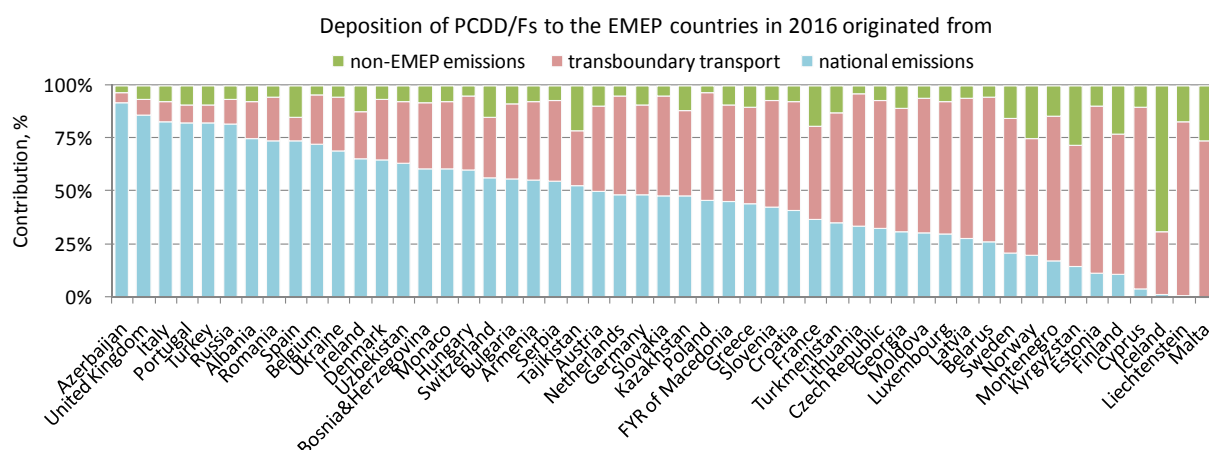


Fig. 4.10. Relative contributions of national emissions, transboundary transport, and non-EMEP emissions to deposition of PCDD/Fs from anthropogenic sources in the EMEP countries in 2016.

4.5. Pollution on global scale and in the Arctic region

Evaluation of global scale transport and pollution of PCDD/Fs, PCB-153, and HCB for 2016 was carried out using the GLEMOS modelling system with application of emission expert estimates (Section 4.1). Results of global scale model simulations were used to estimate lateral boundary concentrations for regional EMEP modelling. Besides, these model predictions provide information on the intercontinental transport and pollution of remote areas like the Arctic region.

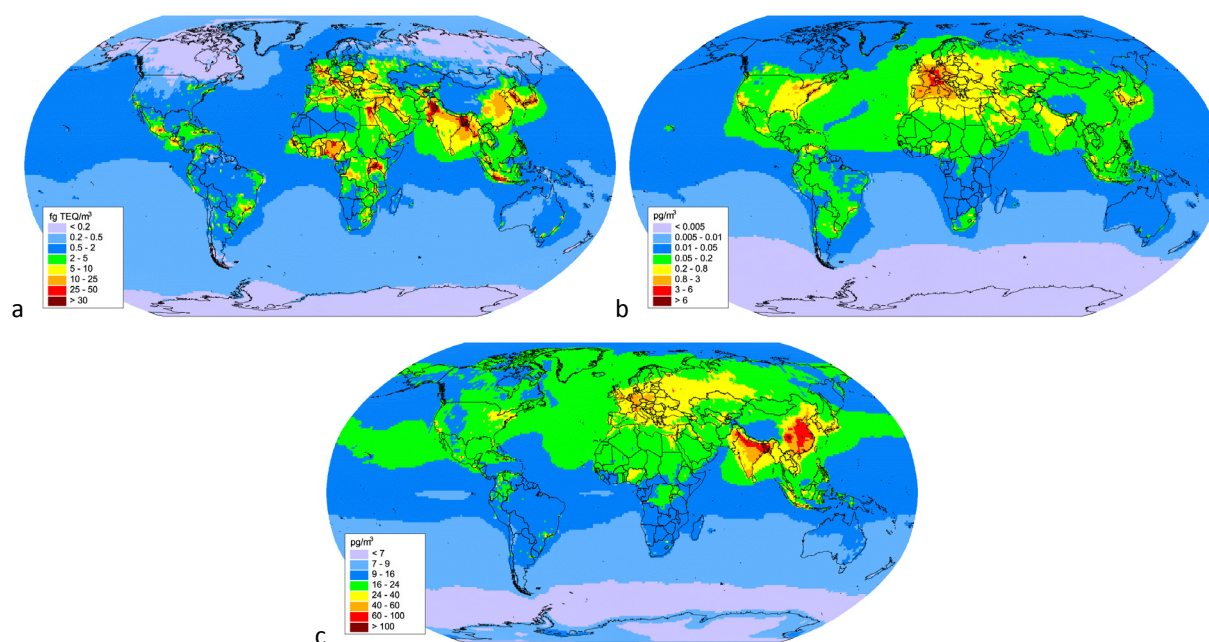


Fig. 4.11. Spatial distribution of global scale annual mean air concentrations of PCDD/Fs, fg TEQ/m³ (a), PCB-153, pg/m³ (b), and HCB, pg/m³ (c) simulated for 2016.

Spatial distributions of global-scale annual mean PCDD/F, PCB-153, and HCB air concentrations simulated for 2016 are presented in Fig. 4.11. The highest levels of PCDD/F air concentrations were estimated for Africa and South Asia ($25 - 50 \text{ fg TEQ/m}^3$), while levels of pollution in Europe, North and South America, and Australia were lower ($1 - 10 \text{ fg TEQ/m}^3$). For PCB-153 elevated air concentrations were obtained for the European region ($0.6 - 6 \text{ pg/m}^3$). For other regions less significant air concentrations were estimated (below 0.2 pg/m^3). Model predicted high annual mean HCB air concentrations for Eastern and Southern Asia ($50 - 100 \text{ pg/m}^3$), and low concentrations for the European countries (about $20 - 40 \text{ pg/m}^3$). Simulated annual mean air concentrations in the Arctic region varied mostly within the range of $0.1\text{-}1 \text{ fg TEQ/m}^3$ for PCDD/Fs, $0.01 - 0.1 \text{ pg/m}^3$ for PCB-153, and $8 - 24 \text{ pg/m}^3$ for HCB. However, it should be noted that the model tended to underestimate levels of PCB-153 and HCB concentrations in the Arctic region (Section 4.3).

Results of regional scale model simulations for the Arctic region are illustrated in the Fig. 4.12a on the example of modelled PCDD/F deposition. As seen from the Figure, relatively high deposition fluxes were estimated for Iceland, and northern parts Scandinavian countries and Russia while lower fluxes were obtained for other areas in the Arctic region.

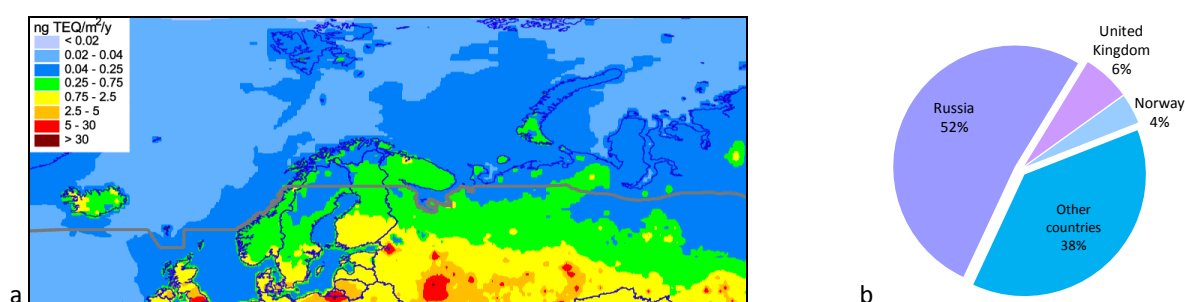


Fig. 4.12. Annual total PCDD/F deposition fluxes in 2016 (a) and relative contributions of anthropogenic emission sources of the EMEP countries to deposition (b) over the Arctic region, covered by the EMEP domain. Grey line denotes the boundary of the AMAP domain

Source apportionment of PCDD/F pollution in the Arctic was carried out taking into account contributions of EMEP anthropogenic, EMEP secondary and non-EMEP sources. According to model estimates, EMEP anthropogenic sources of PCDD/Fs contributed to deposition levels in the Arctic 27%. Substantial contributions were also made by non-EMEP emissions (30%) and secondary emissions (42%).

Results of source apportionment of PCDD/F deposition from anthropogenic emissions of the EMEP countries is illustrated in Fig. 4.12b. It is seen that the largest contribution (52%) was made by Russian emission sources followed by the United Kingdom (6%) and Norway (4%). The other EMEP countries contributed about 38%.

5. CO-OPERATION AND DISSEMINATION OF INFORMATION

Co-operation is an important component of research and operational pollution assessment performed by MSC-E to support countries with information on POP pollution levels in Europe and other regions. In this context MSC-E closely collaborates with Parties to the Convention and its Subsidiary Bodies and exchanges information with various international organizations.

5.1. Task Force on Measurements and Modelling (TFMM)

In the framework of cooperation with TFMM, MSC-E participated in 19th meeting of the Task Force, held in May 2018 in Geneva (Switzerland). The progress in the assessment of POP pollution using the fine resolution POP emission data, reported by the EMEP countries, was outlined and discussed. Model simulations for PAHs, PCDD/Fs, PCBs, and HCB showed in general reasonable level of agreement with measurements. At the same time, significant deviations between observed PAH pollution levels and model predictions for some of the EMEP countries including Spain, France, Germany, and Poland were noted. Substantial under-prediction of measured HCB concentrations was also obtained by the model for several monitoring sites in the northern part of the EMEP domain. Analysis of these discrepancies indicated the need of further refinement of national emission inventories as well as modelling approach for the assessment of pollution levels for these POPs.

The outcome of country-specific case study on B(a)P pollution in Spain and France, performed in co-operation with experts from these countries, was also presented. In particular, preliminary results of GLEMOS and CHIMERE models, simulated B(a)P pollution levels in European region, were demonstrated. It was shown that modelling on the basis of officially reported emissions resulted in significant deviations between modelled and measured B(a)P concentrations for some monitoring sites in several EMEP countries (e.g. France, Germany, Poland and Spain). These deviations were mainly attributed to the uncertainties in currently reported emission inventories. However, the need to analyze the effect of uncertainties of modelling approaches (e.g. parameterizations of B(a)P degradation, gas-particle partitioning, and deposition) was also highlighted.

Besides, analysis of methodologies, used to evaluate PAH/B(a)P emissions in Spain and France, was presented by national experts. In particular, it was shown that underestimation of B(a)P emissions in France could be associated with low values of emission factors used for the estimation of emissions from residential combustion. In case of Spain, overestimation of emission from field burning of agricultural residues was related to the uncertainties of several parameters in the applied methodology (e.g. burning area, crop specific emission factors).

Simulations with experimental emission scenario, based on scaling of sectoral emissions of selected countries, indicated substantial sensitivity of model predictions to the estimates of B(a)P emissions from the 'Residential combustion' and 'Field burning of agricultural residues' sectors. Refinement of emissions from these source categories can be important for the improvement of pollution assessment results. Continuation of B(a)P pollution case study for Spain and France will include analysis of model parameterizations applied for B(a)P degradation and gas-particle partitioning, model simulations with

expert estimates of B(a)P emissions, and fine resolution modelling. Further national case studies on B(a)P pollution might also be carried out for Germany, Poland or Croatia.

5.2. Helsinki Commission

In the framework of cooperation with the Helsinki Commission, MSC-E performs regular evaluation of airborne pollution load of POPs to the Baltic Sea. This work is carried out in accordance with the Memorandum of Understanding between the Baltic Marine Environment Protection Commission (HELCOM) and the United Nations Economic Commission for Europe (UN ECE) and is based on the long-term EMEP/HELCOM contract.

During the recent year this activity was focused on the evaluation of PCDD/F pollution of the Baltic Sea. In particular, long-term variations of PCDD/F deposition fluxes to the Baltic Sea were estimated for the period 1990-2015. Besides, source apportionment of annual deposition was carried out for 2015. Results of the assessment were summarized in the Joint report of the EMEP Centres for HELCOM [Bartnicki *et al.*, 2017] and presented in the indicator fact sheets, published on the HELCOM website [<http://www.helcom.fi>].

Anthropogenic emissions of dioxins and furans in the HELCOM countries declined from 1990 to 2015 by 33%. Russia, Poland, and Germany were the main contributors to the PCDD/F emissions among the HELCOM countries in 2015. The major emission source categories in total PCDD/F emissions of HELCOM countries, according to the officially reported data, were the 'Residential combustion', 'Industry', and 'Waste'.

Results of model simulations indicated considerable decrease (67%) of atmospheric PCDD/F deposition to the Baltic Sea in the period 1990-2015 (Fig. 5.1a). The largest changes of deposition were estimated for the Sound and the Western Baltic sub-basins (decrease by 76% and 73%, respectively). The first decade of the considered period is characterized by more substantial decline of PCDD/F deposition (about 40%), while during the subsequent period decline of deposition was less significant. PCDD/F deposition fluxes to the Baltic Sea are subject to noticeable inter-annual variations due to variability of meteorological conditions (e.g. atmospheric transport pathways). Particularly, deposition in 2015 was lower comparing to the previous year by 22%. Seasonal variations of PCDD/F deposition are characterised by higher values of fluxes in the cold period of the year and lower values of fluxes in the warm period.

Anthropogenic emission sources of the HELCOM countries contributed about 47% to annual PCDD/F deposition to the Baltic Sea in 2015. Russia, Poland, and Denmark were the main contributors of anthropogenic PCDD/F deposition to the Baltic Sea (Fig. 5.1b). Along with anthropogenic emissions significant contribution (more than 50%) to PCDD/F deposition to the Baltic Sea was made by secondary emission sources (e.g. re-emission from soil and sea water compartments) as well as by the long-range transport from the emission sources located outside the HELCOM countries.

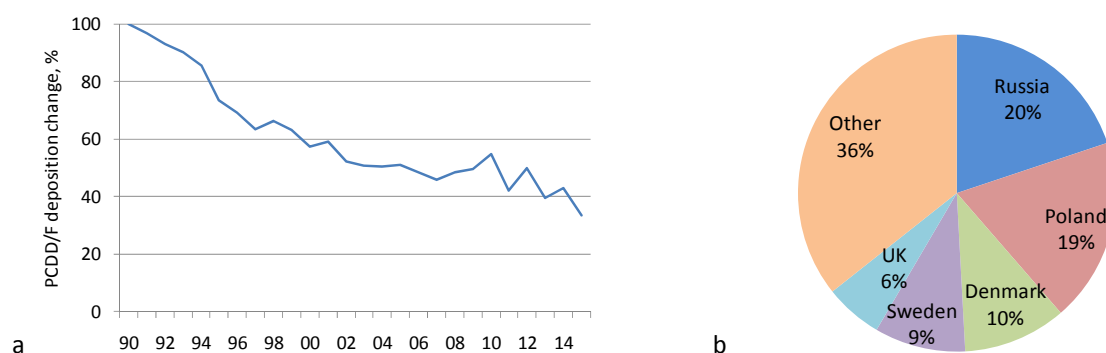


Fig. 5.1. Relative changes of annual atmospheric PCDD/F deposition to the Baltic Sea in the period 1990-2015 (a) and contribution of emission sources from the EMEP countries to total anthropogenic deposition of PCDD/Fs to the Baltic Sea in 2015 (b).

Spatial distribution of annual modelled PCDD/F deposition fluxes in 2015 shows elevated deposition levels in the southern and western parts of the Baltic Sea, located closer to the industrial and densely populated areas of Europe. At the same time, the northern part of the sea was characterised by the lowest deposition fluxes.

5.3. Stockholm Convention

Co-operation and exchange of information with the Stockholm Convention on POPs is of importance for the assessment of environmental pollution of the EMEP region. In the framework of this activity MSC-E continued the use of data on POP emissions, compiled under the Stockholm Convention (SC) on POPs, for the development of global scale scenario of PCDD/F emissions.

There is significant progress in the development and updating of national PCDD/F emission inventories, performed by countries, parties to the Stockholm Convention, on the basis of the Toolkit for Identification and Quantification of releases of unintentional POPs. National emission inventories are being revised due to updating of the Toolkit as well as recalculations of national emission data. Provided data comprise emissions to the atmosphere and other environmental compartments that can be used as additional source of information on PCDD/F emissions in the EMEP region. Similar activities on the collection of information on emissions and improvement of methodology for their evaluation are also performed for other POPs (e.g. PCBs and HCB [Gong *et al.*, 2017a; Gong *et al.*, 2017b]).

According to national reports, provided by the countries, information on dioxins and furans emissions is currently available for more than 140 countries⁸. National PCDD/F emissions were reported for the period of time starting from around 1990 up to 2014 covering several vectors of releases (e.g. to the atmosphere, land, water). Majority of emission data were reported for the recent years. In addition, significant part of inventories included estimates of releases for several years that can be used for the evaluation of temporal changes of emissions. This information was used for the updating of the scenario of global PCDD/F emission developed previously by MSC-E [Shatalov *et al.*, 2014]. In particular,

⁸ List of National Implementation Plan reports
(<http://chm.pops.int/Implementation/NIPs/NIPTransmission/tabid/253/Default.aspx>)

available data permitted to prepare scenario of annual PCDD/F emissions to the atmosphere and to soil for the period 2012 – 2014.

Along with updated information on emissions, different statistical methodology was used for the evaluation of national PCDD/F emissions. In particular, updated emission scenario was constructed using the approach described in [Wang *et al.*, 2016]. The following factors were considered in the regression analysis for the evaluation of PCDD/F emissions, namely, gross national input, country area, gross national input per capita, and CO₂ emissions per million of gross national product. Numerical values for these parameters for each of considered years were taken from the World Bank database (<https://data.worldbank.org/>).

Geographical distribution of national PCDD/F emissions to the atmosphere estimated using regression analysis reported is shown in Fig.5.2a. In accordance with these data the largest contributions to the global emission was made by South and East Asia (49%) followed by Africa (33%). The contributions of the EMEP countries and of North and South Americas were estimates to 9%. It is planned to use updated scenario of global PCDD/F emissions in model simulations for the next year.

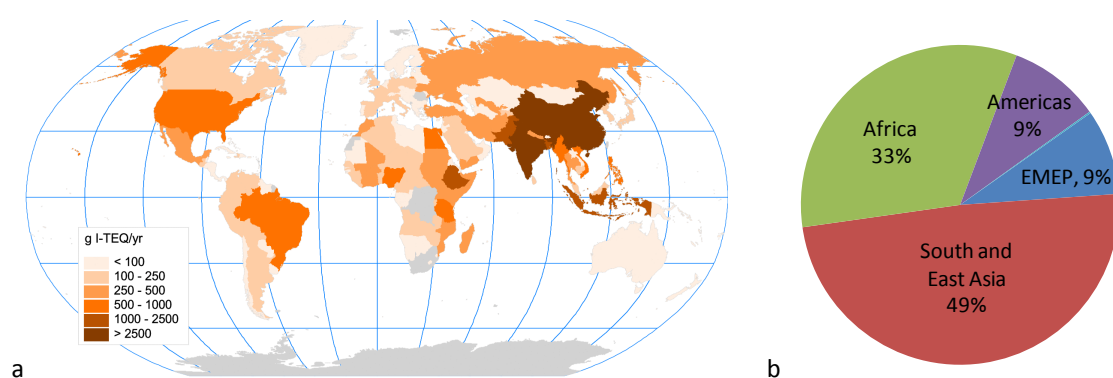


Fig. 5.2. Total releases of PCDD/Fs (a) to the atmosphere from anthropogenic emission sources in different countries (g TEQ/y) and contributions of major source regions (b) to global PCDD/F emissions estimated for 2014.

Another important area of collaboration with the Stockholm Convention is the analysis of global-scale monitoring data on POP concentrations. National POP monitoring activities are performed under the Global Monitoring Plan (GMP) of the Convention, which is established as a global framework for the evaluation of information on POP content in the environmental media [Mogulova and Priceputu, 2016]. Results of long-term monitoring of PCDD/F air concentrations in some of the EMEP countries (e.g. in Spain and the UK) were used in the analysis of pollution levels for the year 2016 in this report (Section 4.3).

MAIN CHALLENGES AND DIRECTIONS OF FUTURE RESEARCH

This Status Report summarizes results of current activities performed by the EMEP Centres, MSC-E and CCC, in the field of the assessment of POP pollution in the EMEP region. Progress in monitoring of pollution levels, modelling of long-range transport and fate, and analysis of POP pollution on global, regional, and national scales are overviewed. Main emphasis of the report is given to the analysis of PAH pollution levels in the EMEP region as well as in particular EMEP countries. Directions of future work and main challenges that need to be addressed are outlined below.

- Accuracy of model assessment of POP pollution significantly depends on the quality of officially reported emissions data. In spite of gradual improving of national inventories, estimates of POP emissions are still subject to considerable uncertainties. Country-scale case studies for B(a)P and scenario simulations of PCDD/Fs pollution showed potential significant uncertainties of the reported POP emissions, particularly, from the source categories 'Residential combustion' and 'Field burning of agricultural residues'. Further improvement of reported POP emissions requires harmonization of methodologies and update of emission factors currently used by the EMEP countries for the evaluation of emissions from these source categories.
- Available expert estimates of POPs anthropogenic emissions are important for the evaluation of pollution levels and can be used for complementary analysis of national inventories. Besides, construction of experimental emission scenarios and test model simulations allows evaluating sensitivity of model predictions to possible uncertainties in the officially reported emission data. Thus, the air quality modelling can be used as a tool for evaluation of reported emissions with regard to their magnitude and spatial distribution.
- Country-specific studies performed by MSC-E in co-operation with national experts present an important activity aimed at improvement of POP pollution assessment in the EMEP region. In the current studies for Spain and France, fine-resolution model simulations with two different models (GLEMOS and CHIMERE) and comparison with measurements allowed revealing inconsistencies in the reported B(a)P emissions and pointed out directions for further improvement of the emission inventories. The case studies for these and some other EMEP countries (e.g. Germany, Poland, Portugal) will be continued including more detailed analysis of B(a)P pollution on a national scale and evaluation of the key processes governing B(a)P atmospheric dispersion (gas-particle partitioning, degradation etc.)
- Recent studies of PAH long-range transport and heterogeneous chemistry suggested that their phase partitioning can be influenced by secondary organic aerosols, which might protect particle-phase PAHs from degradation and evaporation. Furthermore, variations of temperature and humidity in the atmosphere affect multiphase degradation of PAHs and, ultimately, long-range transport and spatial variability of these pollutants. Influence of these factors on the model predictions will be analyzed using test model simulations and the results will be used for updating the GLEMOS modelling system.

- Monitoring and modelling activities indicate high levels of air concentrations of carcinogenic PAHs and exceedances of air quality guidelines for B(a)P in the EMEP countries, especially in areas with high emissions and dense population. To improve evaluation of city pollution by PAHs the methodologies based on complementary use of multiple regression analysis, fine resolution modelling, and measurements will be further developed within the framework of the country-specific case studies in close co-operation with national experts and relevant scientific Centres and Task Forces (TFEIP, CEIP, TFMM, CCC, and EEA).
- The EMEP monitoring network for POP is still very limited and covers mostly Central and Northern Europe. It mitigates opportunities for more comprehensive model evaluation. The spatial coverage can be improved by involvement of data from various passive air sampling studies. However, application of data from passive air sampling is also limited for the analysis of POP pollution as passive air sampling is still considered to be a semi-quantitative method. This is especially important for POPs that mainly are associated with the particulate phase (e.g. benzo(a)pyrene). In addition, since some POPs (PAHs, PCBs, etc.) may partition between the gas and particulate phases, more data on the observed partitioning between these two phases (i.e. by measuring and reporting both gaseous and particulate concentrations in air) may additionally help to increase confidence in the model predictions.
- Environmental dispersion of some POPs (PCDD/Fs, PCBs, HCB) have a pronounced multi-media character and are highly affected by the exchange between and accumulation in the environmental compartments (atmosphere, soil, water, etc.) Model assessment of POP content in the terrestrial and aquatic ecosystems can provide valuable information for the effect community (WGE) for evaluation of possible adverse effects on human health and biota. Further improvement of the GLEMOS model parameterizations for these pollutants requires complementary use of national/regional air monitoring data within EMEP and beyond, as well as measurement data on POP content in other compartments. Strengthening of co-operation with relevant activities of other international organizations (e.g. the Stockholm Convention, AMAP, HELCOM, and OSPAR) is needed to collect appropriate data.
- Exchange of information and the expertise between EMEP and the Stockholm Convention on the evaluation of POP releases to the environment is important for further progress in the assessment of POP pollution in the EMEP region. Development and improvement of methodologies for compilation of national inventories of POP emissions to the atmosphere and other environmental compartments, performed under the Stockholm Convention, can provide valuable information for the studies of environmental pollution by PCDD/Fs, PCBs, and HCB in the EMEP region and on a global scale.

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