Joint CEIP/MSC-E report on emission inventory improvement for persistent organic pollutants modeling

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INTRODUCTION

According to the “2016-2017 workplan for the implementation of the Convention” (ECE/EB.AIR/133/Add.1, p.1.1.2.5) “Review and assess data, methodologies and competences available to deal with POPs and HM issues in the ECE region and propose a strategy to improve emission inventories”, CEIP and MSC-E have prepared the “Joint CEIP/MSC-E technical report on emission inventory improvement for POPs modeling”. This technical report focus on the current situation, gap filling and methodologies used for gap filling and gridding, discrepancies between reported and expert emission estimates, and identified sources of errors. The report considers approaches used by CEIP and MSC-E and proposals to upgrade the current situation and practice. This report should serve as a basis for the EMEP strategy to alleviate existing problems and guide Parties.

One of the main tasks of the EMEP Centre on Emission Inventories and Projections (CEIP) is the preparation of gridded emission data sets as input for long-range transport models. As data submitted by parties is not always complete and as several parties do not submit data it is necessary to fill in missing information before these emission data sets can be used by modelers. To gap-fill those missing data, CEIP applies different gap-filling methods. These methods are described in Chapter 1. After the gap-filling, sector emissions are used for spatial emission mapping, i.e. the EMEP grid. The gap-filled data sets are also published in the UNECE/EMEP emission database WebDab (CEIP 2017) which contains information on air pollutant emissions and projections from the Parties to the LRTAP Convention (UNECE 1979).

Information on pollutant’s emission to the atmosphere and other environmental media is one of the key parameters required for model assessment of pollution levels and transboundary fluxes. Completeness and uncertainties of emission data can significantly affect the quality of the model estimates. Sensitivity analysis of the modeling results has shown that, in many cases, emission uncertainties largely determine the overall uncertainty of the model assessment. Emission data for POP modeling are described in Chapter 2.

Application of chemical transport models for the assessment of POP pollution levels in the EMEP countries requires anthropogenic emission data spatially distributed (or ‘gridded’) over the regular EMEP grid. It should be noted that modeling of air concentration and deposition fluxes needs emission data covering the entire EMEP domain that includes not only territories of all EMEP countries but also adjacent areas (Northern Africa, Middle East etc.). Along with this, application of the gridded emission data for modeling requires evaluation of additional emission parameters. They comprise chemical composition of emitted pollutants, vertical distribution of emission height and temporal variation of anthropogenic emissions along the year.

Some POPs (e.g. PCDD/Fs, PCBs and HCB) are persistent in the environment and can travel over long distances. In many EMEP countries pollution levels of these substances are significantly influenced by emissions from other parts of the globe. Therefore, emission inventories on a global scale are required for pollution assessment within the EMEP region. Besides, cycling of POPs in the environment has a complex character and includes not only atmospheric transport and transformations but also bi-directional exchange with the earth’s surface. Natural and secondary emission sources should be taken into account when assessing both effectiveness of environment protection policy and human exposure of these contaminants.
1 Data assessment, methodologies and improvements to deal with POPs in the EMEP region (CEIP contribution)

1.1 Gap-filling methods

Data used by CEIP were reported by the Parties to the LRTAP Convention as sectoral emissions (NFR14) and National Total emissions according to the UNECE guidelines for reporting emissions and projections data under the Convention on long-range transboundary air pollution, Annex I (UNECE 2014). The nomenclature for reporting (NFR) foresees 140 different sectors. The reporting template contains guidance how these 140 sectors can be aggregated to 13 GNFR sectors. As gap-filling on NFR level would require very detailed background data the datasets reported by parties were aggregated to the GNFR level before they were gap-filled. All data are available from the CEIP website (CEIP 2017).

1.1.1 Gap-filling of National Total data

The share of reported data ranged between 54 and 71% of National Total data (Table 1). HCB had the highest share of reported data and Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene and Indeno(1,2,3-cd)pyrene had the lowest share of reported data (Figure 1). All reported data up to the 20th March 2017 were included\(^1\) for the CEIP gap-filled data set 2017.

If no submission is available, different estimates were made to fill the gaps. Copy of expert data from different literature sources were used, as well as calculations such as extrapolation of these data or previous reported data, also by using population data. Literature sources comprise:

- the Norwegian final report of the POPCYCLING-Baltic project (Pacyna et al. 1999), were emission data for HCB for the years 1990 and 1995 were given
- emission projections from the Dutch institute TNO (Denier van der Gon et al. 2005) for PCDD/Fs, PAHs and HCB for the year 2000 and 2010
- a study on uncertainties in PCDD/F emission estimates for central Europe (Pulles et al. 2006) that contains data for the year 2000
- a study on the determination of dioxins, furans, PCB sources and anti-POPs campaign in Central Asia (Hodjamberdiev 2006) including dioxin data for 2006
- the global POPs Inventories (Fiedler 2007) including data for PCDD/Fs and HCB for the year 2000
- the global atmospheric emission inventory of PAHs with for the year 2004 (Zhang & Tao 2009)
- PAH emission estimates for the Russian Federation (Shen et al. 2013)
- a primary estimate of global PCDD/F release (Wang et al. 2016) with several PCDD/F data for the years 2000 to 2007
- PCDD/F emission estimates for the Russian Federation (Treger 2011)

\(^1\) Additionally, a resubmission from Luxembourg on 31 March 2017 is included.
Further, a common imputation method – only for the PAHs – was the split of reported Total PAH data into Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene and Indeno(1,2,3-cd)pyrene. This method was used when no data for PAHs were given, but information on Total PAH was available. Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene and Indeno(1,2,3-cd)pyrene data were calculated using a ratio to split Total PAH emissions. This sector splitting ratio was derived using data from other countries by calculating the mean share of the reported PAH data on the Total PAH emissions. Data were only used from countries where the sum of the PAHs equals the reported Total PAH data.

In several cases, not only one estimate is given for a country, and the question rose which estimate fits most. Therefore ratios for each pollutant between emissions and population data, GDP and area size were calculated by using only reported and plausible data. Then, the distance of the different estimates to this ratio is used to determine the best method.

Table 1: Overview of reported data and imputation methods

<table>
<thead>
<tr>
<th></th>
<th>Benzo(a)-pyrene</th>
<th>Benzo(b)-fluoranthene</th>
<th>Benzo(k)-fluoranthene</th>
<th>Indeno(1,2,3-cd)-pyrene</th>
<th>PCDD/Fs</th>
<th>HCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reported data</td>
<td>54%</td>
<td>57%</td>
<td>54%</td>
<td>57%</td>
<td>54%</td>
<td>56%</td>
</tr>
<tr>
<td>Extrapolation of expert/</td>
<td>21%</td>
<td>21%</td>
<td>21%</td>
<td>21%</td>
<td>12%</td>
<td>6%</td>
</tr>
<tr>
<td>reported data using population data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear extrapolation/</td>
<td>8%</td>
<td>8%</td>
<td>8%</td>
<td>8%</td>
<td>13%</td>
<td>12%</td>
</tr>
<tr>
<td>copy of expert data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAH split</td>
<td>13%</td>
<td>16%</td>
<td>13%</td>
<td>16%</td>
<td>13%</td>
<td>17%</td>
</tr>
<tr>
<td>Sector distribution like other countries</td>
<td>25%</td>
<td>24%</td>
<td>24%</td>
<td>24%</td>
<td>25%</td>
<td>23%</td>
</tr>
<tr>
<td>Sector distribution like previous years</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>3%</td>
</tr>
<tr>
<td>Other methods</td>
<td>4%</td>
<td>0%</td>
<td>4%</td>
<td>0%</td>
<td>4%</td>
<td>0%</td>
</tr>
</tbody>
</table>

1.1.2 Gap-filling of sectoral data

The share of reported data ranged between 56 (Indeno(1,2,3-cd)pyrene) and 74% (HCB) of the sectoral data (Table 1). All reported data up to the 20th March 2017 were included.

The most common imputation method to gap-fill sector data was to use the distribution ratio of sector emissions from similar countries. To identify which countries are similar to each other, for all countries where data were available a distance matrix using Euclidean distances was generated using GDP per capita and gap-filled or reported National Total emissions from Total PAH, PCDD/F and HCB as variables (z-transformed).

Further, a common imputation method – only for the PAHs – was the split of reported Total PAH data into Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene and Indeno(1,2,3-cd)pyrene. This method was used when no data for PAHs were given, but information on Total PAH emissions was available.

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2 These countries are: Estonia, Hungary, Ireland, Poland, Romania, Switzerland and the United Kingdom.

3 Additional, a resubmission from Luxembourg on 31 March 2017 is included.
was available. Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene and Indeno(1,2,3-cd)pyrene data were calculated using a ratio to split Total PAH emissions. This sector splitting ratio was derived using data from other countries by calculating the mean share of the reported PAH data on the Total PAH emissions. Data were only used from countries where the sum of the PAHs equals the reported Total PAH data. The only other gap-filling method was the sector distribution like in previous years.

1.2 Identified sources of errors and reasons for replacement of reported data

If a country made a submission, reported data are checked for plausibility by comparing with reported data of other countries, expert data and their ratio to population data, GDP and area in comparison with other countries. Further, the sum of reported Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene and Indeno(1,2,3-cd)pyrene data is compared with reported data on Total PAHs. If plausibility was not given, reported data were replaced.

Most countries submitted data that seem to be complete and plausible – although in some cases no data on the individual PAHs was given but information on total PAHs. Problems occur where no data at all are available, or when submitted data are not plausible. Emissions are not plausible when no data for relevant sectors were reported, when the sum of the sectors differ to the National Total, when submitted data show unusual trends or when they vary strongly to data of emission estimates or projections of other sources. In these cases, data were replaced (Table 2).

For four countries, data submitted in 2017 were replaced: PAH data of Germany, Kazakhstan, Portugal and Serbia and PCDD/F data of Kazakhstan. PAH data were replaced, as the sum of the four PAHs differ strongly with the reported Total PAH data. PCDD/F data of Kazakhstan were replaced, as the reported data were very low compared with expert data.

Table 2: Overview on gap-filled and replaced data
(‘NT’ = National Total data, ‘Sectors’ = Sectoral data)

<table>
<thead>
<tr>
<th></th>
<th>Benzo(a)-pyrene</th>
<th>Benzo(b)-fluoranthene</th>
<th>Benzo(k)-fluoranthene</th>
<th>Indeno(1,2,3-cd)-pyrene</th>
<th>PCDD/Fs</th>
<th>HCB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NT</td>
<td>Sectors</td>
<td>NT</td>
<td>Sectors</td>
<td>NT</td>
<td>Sectors</td>
</tr>
<tr>
<td>reported</td>
<td>50%</td>
<td>53%</td>
<td>50%</td>
<td>55%</td>
<td>50%</td>
<td>54%</td>
</tr>
<tr>
<td>gap-filled</td>
<td>43%</td>
<td>41%</td>
<td>43%</td>
<td>40%</td>
<td>43%</td>
<td>41%</td>
</tr>
<tr>
<td>replaced</td>
<td>7%</td>
<td>6%</td>
<td>7%</td>
<td>5%</td>
<td>7%</td>
<td>5%</td>
</tr>
</tbody>
</table>

However, the methods and checks for plausibility of data need some improvements, as the gridded maps show some inconsistencies. An example is shown in Figure 1, where especially HCB data for the Ukraine seem to be not correct.
1.3 Proposal to upgrade the current situation and practice

1.3.1 Method overview

To gap-fill missing data and also for plausibility checks of reported data, literature or expert data can be used, or data can be calculated using different (imputation) methods.

Literature or expert data

For future versions of the gap-filled WebDab database, the intention is to search for additional and updated data sources, estimates and projections to fill gaps and compare data. Also, the cooperation and possible exchange of information with other organisations dealing with air pollution data, like the task force on Hemispheric Transport of Air Pollution (TF HTAP) or the Task Force on Techno-economic Issues (TFTEI), shall be enhanced.

Imputation methods and emission calculations

To improve imputation methods, first the question raises what influences the quality of the data. Thus a key category analysis was made (see below) to detect if some key categories stand out for certain POPs, and the quality of the submissions was analysed. Further, correlations with population or GDP data were made.

\[http://www.htap.org\]
\[http://tftei.citepa.org\]
1.3.2 Analysis of submissions

Figure 2 shows the quality of the submissions itself for the whole EMEP area (i.e. The number of notation keys or values used for source categories in the NFR reporting templates, and the amount of missing submissions were accumulated over all countries and is shown in percentage values for the 2017 submissions). About 28-32% is missing data, this means the submissions contain empty cells, the value ‘0’, the notation key ‘NE’ (‘not estimated’) or no submission was made.

![Figure 2: Quality of 2017 submissions accumulated over all EMEP countries](image)

The quality of the data submissions vary highly between the different countries. As an example, in Figure 3 the PCDD/F submissions of the individual countries are shown.

![Figure 3: Quality of 2017 submissions for PCDD/Fs](image)

However, in spite of this result gap-filling will be limited mostly to total emissions as before, as the reasons for missing data are often not very transparent, i.e. the notation key ‘NE’ is sometimes used rightly but not documented. Nevertheless, for the review of submitted data such analyses as shown in Figure 3 can help to evaluate the quality and credibility of the data, e.g. for replacement decisions.
1.3.3 Key category analysis

For improving the gap-filling procedure, it is important to evaluate what influences the quality of the data. Therefore, an analysis of the key categories was done to detect if some key categories stand out for certain POPs. If so and if activity data for certain countries become available, it would be possible to calculate emissions of the key categories and gross them up to the total emissions of the respective POP. Table 3 shows the results of the analysis, and Figure 4 shows the distribution of the five most important key categories of HCB as an example.

Table 3: Overview of POPs key categories of the EMEP countries

<table>
<thead>
<tr>
<th>POPs</th>
<th>Number of key categories (all EMEP countries):</th>
<th>Number of key categories per country (min-max):</th>
<th>Five most important categories</th>
<th>Five most important categories</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAHs</td>
<td>17</td>
<td>1-5</td>
<td>1A4bi 34 92%</td>
<td>1A4bi 34 92%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1A3bi 5 14%</td>
<td>1A1a 26 70%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2C1 4 11%</td>
<td>1A4bi 20 54%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2C3 4 11%</td>
<td>5C1bi 5 14%</td>
</tr>
<tr>
<td>PCDD/Fs</td>
<td></td>
<td></td>
<td>1A4bi 34 92%</td>
<td>1A1a 26 70%</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>1-9</td>
<td>2C1 18 49%</td>
<td>1A4bi 20 54%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1A1a 9 24%</td>
<td>5C1bi 5 14%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5E 8 22%</td>
<td>2C1 5 14%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1A2a 5 14%</td>
<td>3Df 4 11%</td>
</tr>
<tr>
<td>HCB</td>
<td>27</td>
<td>1-6</td>
<td>1A1a 26 70%</td>
<td>1A4bi 20 54%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5C1bi 5 14%</td>
<td>2C1 5 14%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3Df 4 11%</td>
<td>1A1a 26 70%</td>
</tr>
</tbody>
</table>

Figure 4: HCB emissions of the individual countries (the five most important key categories are shown)
This analysis showed that reporting is very diverse between the countries, i.e. many different key categories were identified for the individual countries. The HCB example (Figure 4) shows that sources are quite different between the countries, even the distribution of the main key categories differ much.

Anyway, for each POP one or two main key categories seem to be a major source for several countries (compare Table 3). These are the categories ‘1A4bi – Residential: Stationary’ for PAHs and Dioxins and Furans, and ‘1A4bi – Residential: Stationary’ and ‘1A1a – Public electricity and heat production’ for HCB. This information can be used when activity data became available and by using emission factors from the air pollutant emission inventory guidebook (EMEP/EEA 2016). For key categories, usually Tier 2 emission factors or better methods should be used. However, this would be too complex for the gap-filling procedure. In the guidebook, Tier 1 emission factors for the categories ‘1A1a’ and ‘1A4bi’ are given that could be used when activity data became available. In a next step, the calculated amount of the emissions from the key categories can be grossed up for the total emissions.

However, these calculations are very complex due to the gathering of activity data, the calculations and the grossing up, and will involve high uncertainties. Therefore this method will not be implemented for future gap filling.

1.3.4 Correlations with population or GDP data

Within this analysis, the correlation⁶ of National Total emissions with population or GDP data is studied (Figure 5). The intention is to investigate if such data can be used for calculating POP emissions, e.g. by extrapolating older emission data using current population or GDP data, as partly already done within the gap-filling 2017.

The correlation between population or GDP data and National Total emissions was calculated using Pearson correlation and square root transformed Population-, GDP- and PCDD/F emission data. To reach Gaussian distribution of the variables, data from the European Union, Canada, the United States, Russia and Turkey were excluded, as these countries or country groups are outlier. Additionally, data from Albania and Armenia were excluded for the correlation with population data to avoid covariance as these data were gap-filled using population data. Further, data from Liechtenstein and Monaco were excluded for the GDP correlation as no GDP data were available. Emission data from PAH and HCB did not show Gaussian distribution and thus were not included into the analysis.

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⁶ Population and GDP data are from the World Bank Data Base (Indicator Codes: SP.POP.TOTL, NY.GDP.MKTP.PP.KD). Total population is based on the de facto definition of population, which counts all residents regardless of legal status or citizenship. The values shown are midyear estimates. PPP GDP is gross domestic product converted to international dollars using purchasing power parity rates. An international dollar has the same purchasing power over GDP as the U.S. dollar has in the United States. GDP is the sum of gross value added by all resident producers in the economy plus any product taxes and minus any subsidies not included in the value of the products. It is calculated without making deductions for depreciation of fabricated assets or for depletion and degradation of natural resources. Data are in constant 2011 international dollars. PCDD/F emission data are gap-filled data from 2017.
The results of the correlations show that there is a strong correlation (Pearsons $r=0.76$, $p>0.00001$) between Dioxin and Furan and population data (Figure 5). The coefficient of determination ($R^2$) is 0.58, which means 58% of the PCDD/F variance can be explained by the variance of the population data. There is also a correlation shown between Dioxin and Furan and GDP (Figure 6, Pearsons $r=0.56$, $p>0.0001$; $R^2=0.31$).

As the analyses show, relationships exist between Dioxin and Furan emissions and population data and also between those emissions and GDP data – although not that strong. Therefore, to calculate Dioxin and Furan emissions, it is a suitable method to extrapolate data by using population data.
2 EMISSION DATA FOR POPS MODELING (MSC-E CONTRIBUTION)

2.1 Current situation

EMEP Centre on Emission Inventories and Projections (CEIP) is responsible for the preparation of emission data sets as input for long-range transport models. Emission data currently provided by the EMEP countries in their national inventories cover only part of the information that is required for model assessment of POP pollution. The gap filling is performed by the Centre on Emission Inventories and Projections to provide complete sets of gridded emissions over the EMEP domain. Along with this, application of the gridded emission data for modeling requires evaluation of additional emission parameters. They comprise chemical composition of emitted pollutants, vertical distribution of emission height and temporal variation of anthropogenic emissions along the year.

Emission parameters for model application prepared by CEIP and MSC-E are given in Table 4. Assumptions and methodologies used for evaluation of the parameters prepared by MSC-E are discussed below along with characteristics of their major uncertainties.

Table 4: Emission parameters for modeling generated by CEIP and MSC-E

<table>
<thead>
<tr>
<th>Information on POP (PAHs, HCB, PCBs, PCDD/Fs) emissions</th>
<th>Emission data for modeling (CEIP)</th>
<th>Additional emission data for modeling (MSC-E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time-series of national total emissions (annually)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Gridded sectoral emissions (once in five years)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Emissions of Large Point Sources (once in five years)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Gridded total emissions for the latest reported year generated by CEIP (except PCBs) (annually)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Time-series of gridded annual emissions 1990-2012</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Vertical distribution of emissions</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Congener composition for POPs (PCDD/Fs - 17 congeners, PCB-153)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Temporal variation of emissions</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Historical emissions of PCBs, HCB, PCDD/Fs up to 1990</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Emissions to other environmental compartments (PCDD/Fs, HCB)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Emissions for the non-EMEP countries within the EMEP domain. (North Africa and Middle East).</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Natural emissions</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Re-suspension, re-emissions</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Global emission inventories (PCDD/Fs, HCB, PCBs)</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

Additional information on emission data for modeling including approaches of their preparation, methodologies used for gap filling, and discrepancies between officially reported and expert emission estimates is available in the Annexes (p. 30 ff).
2.2 Time-series of gridded annual emission

Nowadays, the gridded data are available for the base year 1990 (only for B[a]P) and for the years of the period from 2009 to 2015. Starting from 2015 data on PAH emissions are prepared separately for different PAH compounds (B[a]P, B[b]F, B[k]F, IP). It should be noted that consistent time series of gridded emission data for the whole period from 1990 to 2015 (including the latest recalculations of all years of the period) are not available for modeling of long-term pollution trends.

For model reproduction of air concentration and deposition fluxes needs emission data covering the entire EMEP domain that includes not only territories of all EMEP countries but also adjacent areas (Northern Africa, Middle East etc.)

It should be also mentioned that further improvement of completeness of officially reported data and expert emission estimates are needed (Figure 7).

![Figure 7: Gridded emissions reporting by Parties in the EMEP area](image)

Besides, for the modeling purpose it is important to have quantitative estimates of emission data uncertainty in a form of error intervals of the reported emission values. This is needed for the evaluation of possible maximum and minimum scenarios of pollution levels in the EMEP region. Range of uncertainties of the officially reported emission data is submitted only by 12 EMEP countries and can differ from 36% (France) to 727% (Denmark).
2.3 Chemical composition of emissions

2.3.1 PCDD/Fs and PCBs

Some of the POPs, defined in the Protocol on POPs, e.g. PCDD/Fs and PCBs, are released into the environment as complex mixtures of different congeners that represents a challenge for the evaluation of their emissions [Breivik et al., 2004]. Individual congeners have their own physical-chemical properties that differ substantially and depend on environmental characteristics (e.g. temperature). In particular, lower chlorinated congeners are semi-volatile, partitioning in the atmosphere between gaseous and particulate phase, and exchange efficiently with terrestrial and aquatic surfaces, while more chlorinated congeners are less volatile and tend to associate with atmospheric aerosol particles that control their transport. Differences in the properties lead to differential removal and fractionation of particular congeners in course of their long-range transport that have been observed in several studies [e.g. Meijer et al., 2003; Schuster et al., 2010] and obtained in model simulations [von Waldow et al., 2010; Gusev et al., 2007].

At present officially reported emission data of the EMEP countries do not provide this kind of information. Particularly, national emission inventories are reporting total PCDD/F emission in the toxicity units and total PCB emission in mass units without splitting on particular congeners. For modeling purposes the information on the congener-specific gridded emissions of PCDD/Fs and PCBs was obtained from expert emission inventories [e.g. Breivik et al., 2007; Pacyna et al., 2003] (Figure 8). However, these estimates characterize the situation for the beginning of 2000s and earlier that might not be applicable for the current period.

![Figure 8: Congener composition of PCDD/Fs emissions (EMEP region).](image)

In course of model assessment of PCDD/F pollution levels in the EMEP countries MSC-E performed a number of studies directed to the analysis of available data on the emissions of dioxins and furans to the environment. These studies were mostly focused on the examination of uncertainties of PCDD/F emissions as well as on elaboration of experimental scenario emissions for modelling that allowed to explain observed pollution levels. Results of these research activities are given in Annex I.
Refinement of estimates of congener composition of emissions is of importance for further progress in the assessment of pollution levels. Further work in this direction could be performed in course of updating of available expert estimates of congener-specific emissions for the EMEP region and for the global scale, including also estimation of emissions from particular source categories.

2.4 Temporal variation of emissions

The contamination levels (air concentrations and deposition fluxes) of POPs are subject to essential temporal variability [Shatalov et al., 2015]. Intra-annual variability of some POPs (e.g. PAHs, PCDD/Fs, PCBs) can be more 50%. For instance, as shown in Figure 9, difference between observed winter time and summer time B[a]P air concentrations can reach an order of magnitude and more.

Temporal variability of POP pollution levels can be conditioned by both environmental factors and temporal variability of emissions from various source categories. Parameterization of emission temporal variability was developed for B[a]P. Temporal variations of emissions were constructed individually for four source categories (residential heating, road transport, industrial processes, waste incineration and other), which determined over 90% of total emissions. Model parameterization of temporal variability of emissions from residential heating used the approach introduced in [Aulinger et al., 2010] based on the dependence of emissions from this sector on ambient temperature. For the other emission sectors temporal variations of emissions were assumed to be such as used in LOTOS/EUR OS model [Schaap et al., 2005]. According to the model estimates, effect of emission seasonal variations on annual means may reach up to 40%. The information on emission temporal variations is required for reliable assessment of exceedances of target values in Europe. Detailed description of this investigation can be found in Annex III and in [Shatalov et al., 2012].

Information on seasonal changes of POP emissions (e.g. for PAHs, PCDD/Fs, and PCBs) can help to reduce uncertainties in the evaluation of POP pollution levels. However, further research is required to quantify the effect of more detailed temporal variability of emissions.
2.5 Vertical distribution of emissions

Vertical distribution of emissions is important for modelling of atmospheric transport of pollutants. Since wind velocity tends to increase with altitude, pollutants emitted at higher altitudes tend to transport over longer distances compared to those at lower layers. Besides, contributions of wet and dry components to total deposition depend on distribution of pollutants in the column of atmosphere along the vertical. When vertical distribution of emissions is taken into account, simulated deposition flux decreases nearby large emission sources and increases in other regions of the EMEP domain. This effect is expected to be even stronger when moving to a finer resolution grid.

Vertical distribution of POP emissions could be updated by linking atmospheric releases from particular source categories to their emission heights (or range of heights). Information on large point sources (LPS) such as physical stack height, gas outflow velocity, top diameter of a stack and gas temperature as well as meteorological information can facilitate improvement of vertical distribution due to considering rise or emission plumes [Briggs, 1984; Houyoux, 1998]. However, for regular operational calculations it seems feasible to use aggregated information of emission height for different source categories [Bieser et al., 2011].

2.6 Global emission inventories

Atmospheric dispersion of a number of pollutants under the scope of the Convention, including some POPs (PCDD/Fs, PCBs and HCB), is not limited by a regional scale. Given their persistence in the environment and long residence time in the atmosphere these substances can travel over long distances. The potential to long-range transport of these pollutants is also enhanced by their ability to be re-emitted after deposition to the ground that leads to multi-hop dispersion. As a result pollution levels in the EMEP region can be significantly affected by emissions from distant sources located in other regions or even continents. Model simulations for selected POPs, performed in the framework of the TF HTAP multi-model assessment, showed that contribution of intercontinental transport from the source regions to the pollution levels in the receptor regions could be about 10% and more for some of the regions [Gusev et al., 2010].

Besides, even deposition of B[a]P with relatively short residence time in the atmosphere is influenced by sources located outside the EMEP region, particularly, in the Asian countries with growing economies. Therefore, correct consideration of these sources is required through evaluation appropriate boundary conditions.

Available emission inventories for POPs on a global scale are summarized in Table 5. Global gridded emission data are available only for PCBs that include historical estimates from 1930 and future projections up to 2100. For HCB, PAHs, and PCDD/Fs available inventories of global emissions provide information on national emission totals without spatial distribution and most of them characterize levels of releases in mid-1990s or beginning of 2000s. For modeling purposes global PCDD/F experimental emission scenario was constructed on the basis of the information on dioxins and furans releases compiled under the UNEP Stockholm Convention (Annex I).
Further improvements of global emission data for POPs should include update of existing inventories with more recent data and development of absent gridded data for HCB, PAHs, and PCDD/Fs.

### 2.7 Historical and natural emissions

POP pollution levels are controlled by various emission sources, particularly, primary anthropogenic emissions to the atmosphere and other media, as well as natural and secondary emissions (re-mobilization of previously deposited pollutants from soils, water bodies, etc.). Along with anthropogenic emissions, the contribution of secondary sources is an important factor that needs to be addressed in studies of contemporary levels of pollution. While primary emissions are decreasing or ceasing due to emission control measures, the role of secondary emissions can increase or they can even dominate.

Secondary emissions of POPs to the atmosphere are in general estimated from primary releases to the media in course of model simulations. The estimates of secondary emissions are characterized by significant uncertainties as they depend on many factors including historical emissions as well as changes of meteorology, climate, and characteristics of environmental compartments over the period of their past use. Among the POPs considered in the EMEP modeling activities global inventory of historical emissions is currently available only for PCBs [Breivik et al., 2007] (Figure 10 a. and b.).

![Figure 10](image-url)

**Figure 10:** a.: Scenario of temporal variations of global emission of PCB-153 to the atmosphere in the period 1930-2015; b.: Spatial distribution of PCB-153 in 2015 over global domain with resolution 1°x1°
For other POPs there is a lack of inventories, that include historical emissions, and thus further work on their elaboration is required to refine model assessment of contemporary levels of pollution. Model evaluation of HCB global transport and fate was performed on the basis of experimental emission dataset, which described contemporary levels of HCB releases as well as historical emissions for the period from 1945 to 2013 (Figure 11). Three scenarios of historical HCB emissions (maximum, average and minimum), had been elaborated previously [Shatalov et al., 2010], were updated and used for modelling of long-term accumulation of the pollutant in the environmental media (Annex II).

![Figure 11: Estimates of historic and current HCB emissions under the three emission scenarios (minimum, average, and maximum) for the period 1945-2013, t/y](image)

For some of the POPs (e.g. for HCB, PCDD/Fs) it is important also to take into account direct emissions to soils and water bodies to evaluate their accumulation in surface media and subsequent re-emission [Theloke et al., 2010]. Direct releases to land, water, and residues are taken into account in the national emissions of global PCDD/F inventory of the UNEP Stockholm Convention (SC). (Figure 12) At the same time, the methodology on the inventory of POP emissions applied in CLRTAP is oriented on the atmospheric emissions. Thus, for further improvement of POP pollution estimates the elaboration of inventories for these emission pathways is appreciated and collaboration with the UNEP SC activities on the evaluation of emissions is of importance.

![Figure 12: Emissions of PCDD/Fs to the atmosphere and other media](image)
2.8 Summary

Emission data for POPs have been characterized from the viewpoint of their use for the operational modeling within EMEP. Various emission parameters which affect quality of the model assessment have been discussed along with characterizing of their uncertainties. Importance of different emission parameters and their influence on quality of the assessment results varies considerably for simulation of different pollutants. This fact should be taken into account when planning improvement of the emission data. Table 6 characterizes the key emission parameters for POPs in terms of their priority for the further improvement. It should be noted that lower priority level does not mean that no improvements are needed for this emission parameter but rather determines order of their implementation.

Table 6: Key emission parameters affecting quality of model estimates

<table>
<thead>
<tr>
<th>Emission parameter</th>
<th>PAHs</th>
<th>PCDD/Fs and PCBs</th>
<th>HCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quality of gridded anthropogenic emissions</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Chemical composition</td>
<td>-</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Temporal variation</td>
<td>2</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Vertical distribution</td>
<td>3</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>Global emissions inventory</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Historical emissions</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Emissions to other media</td>
<td>6</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

- First priority; - Second priority; - Third priority
3 CONCLUSIONS AND RECOMMENDATIONS

3.1 CEIP

- Additional and updated data sources, estimates and projections will be searched to fill gaps and compare data. Cooperation with other organisations dealing with air pollution data will be enhanced.
- The quality of the data submissions vary highly between the different countries. The reasons for missing data are often not very transparent but for the review of submitted data the analysis of the submissions can help to evaluate the quality and credibility of the data, e.g. for replacement decisions.
- Key category distribution is diverse between the countries. To calculate emissions using key category distribution and activity data would be very resource demanding. Calculations are very complex due to the gathering of activity data, the calculations itself and the grossing up of emissions. Further, results would contain high uncertainties. Therefore this method will not be implemented for future gap filling.
- Correlations exist between emissions of PCDD/F and population or GDP data. Especially population data (rather than GDP data) can be used for e.g. extrapolation of previous reported emission data.
- The quality of the database will increase the best, when countries frequently report complete data inventories.

3.2 MSC-E

- Emission data currently provided by the EMEP countries in their national inventories cover only part of the information that is required for model assessment of POP pollution. Consistent time series of gridded emission data for the whole period from 1990 to 2015 (including the latest recalculations of all years of the period) are not available for modeling of long-term pollution trends.
- Modeling of air concentration and deposition fluxes needs emission data covering the entire EMEP domain that includes not only territories of all EMEP countries but also adjacent areas (Northern Africa, Middle East etc.). Further improvement of completeness of officially reported data and expert emission estimates are needed.
- Application of the gridded emission data for modeling requires evaluation of additional emission parameters. They comprise chemical composition of emitted pollutants, vertical distribution of emission height and temporal variation of anthropogenic emissions along the year.
- Refinement of estimates of congener composition of emissions is of importance for further progress in the assessment of pollution levels. Further work in this direction could be performed in course of updating of available expert estimates of congener-specific emissions for the EMEP region and for the global scale, including also estimation of emissions from particular source categories.
- Information on seasonal changes of POP emissions (e.g. for PAHs, PCDD/Fs, and PCBs) can help to reduce uncertainties in the evaluation of POP pollution levels. Further research is required to quantify the effect of more detailed temporal variability of emissions.
• Vertical distribution of POP emissions could be updated by linking atmospheric releases from particular source categories to their emission heights (or range of heights). Information on large point sources (LPS) such as physical stack height, gas outflow velocity, top diameter of a stack and gas temperature as well as meteorological information can facilitate improvement of vertical distribution due to considering rise or emission plumes. However, for regular operational calculations it seems feasible to use aggregated information of emission height for different source categories.

• Pollution levels in the EMEP region can be significantly affected by emissions from distant sources located in other regions or even continents. Therefore, emission inventories on a global scale are required for pollution assessment within the EMEP region.

• Cycling of POPs in the environment has a complex character and includes not only atmospheric transport and transformations but also bi-directional exchange with the earth’s surface. Natural and secondary emission sources should be taken into account when assessing both effectiveness of environment protection policy and human exposure of these contaminants. Along with anthropogenic emissions, the contribution of secondary sources is an important factor that needs to be addressed in studies of contemporary levels of pollution. The estimates of secondary emissions are characterized by significant uncertainties as they depend on many factors including historical emissions as well as changes of meteorology, climate, and characteristics of environmental compartments over the period of their past use.
4 RECOMMENDATION

Quality of gridded emission data (including completeness of reported data and quality of expert estimates used for gap filling) is among the first priority parameters. Other parameters with the highest priority include chemical composition of emissions, temporal variation (for PAHs) and historical emissions (for HCB). Lower priority parameter, which is still important for all the substances, is global emissions inventory. Besides, pollutants with marked multi-media properties (HCB, PCDD/Fs and PCBs) require information on historical emissions and releases to other environmental media (soil, seawater, etc.). On the other hand, predominantly airborne substances (PAHs) can be more affected by temporal variation of emissions and vertical distribution of emission sources. It should be noted that lower priority level does not mean that no improvements are needed for this emission parameter but rather determines order of their implementation.
5 REFERENCES


Joint CEIP/MSC-E report on emission inventory improvement for persistent organic pollutants modeling


Pacyna, J.M., Breivik, K., Wania, F. 1999: *Final report for Project POPCYCLING-Baltic EU DGXII, Environment and Climate Program ENV4-CT96-0214*. NILU, P.O. Box 100, N-2027 Kjeller, Norway.


Polychlorinated dibenzo(p)dioxins and dibenzofurans are unintentional by-products released into the environment during various combustion processes. Along with direct emissions due to anthropogenic activities, dioxins and furans can also be re-mobilized from surface media (e.g. soil, water bodies) where they were accumulated in course of past industrial and agricultural activities. Analysis performed in the studies of K.Breivik et al. [2004], H.Fiedler [2007], and K.Mareckova et al. [2012] indicated that available national inventories of PCDD/F emissions most likely do not cover all potential sources of PCDD/Fs releases to the atmosphere and thus could not explain observed levels of pollution.

In course of model assessment of PCDD/F pollution levels in the EMEP countries MSC-E performed a number of studies directed to the analysis of available data on the emissions of dioxins and furans to the environment. These studies were mostly focused on the examination of uncertainties of PCDD/F emissions as well as on elaboration of experimental scenario emissions for modelling that allowed to explain observed pollution levels. In particular, collection of information on PCDD/F emissions in the EMEP countries and their congener composition was performed in 2001 [Vulykh and Shatalov, 2001]. It was indicated that major source categories of PCDD/F emissions included combustion of organic fuels, incineration of wastes, and secondary processing of non-ferrous metals. Different congeners provide different contributions to overall emission of PCDD/Fs. According to the data collected from literature three homologue groups of PCDD/F congeners, in particular, PeCDFs, HxCDFs, and PeCDDs, contributed more than 70% to the emitted dioxins and furans mixture toxicity. Due to essential differences in physical-chemical properties of toxic PCDD/F congeners it is important to define congener composition of emitted PCDD/F mixture. This information for modelling purpose is obtained from the data of POPCYCLING-Baltic project [Pacyna et al., 1999]. However, these estimates characterize the situation for the beginning of 2000s and earlier that might not be applicable for the current period of time.

Analysis of reported PCDD/F emission data for the Baltic Sea region was performed in framework of the BalticPOPs research program [Shatalov et al., 2012a; Wiberg et al., 2013]. One of the aims of this study was to trace the origin of dioxins and furans in the Baltic Sea region and to evaluate whether the observed PCDD/F air concentrations can be reproduced by the modeling using officially reported PCDD/F emissions. MSC-E has contributing to this study with model assessment of pollution and elaboration of experimental scenario emissions. In particular, combined analysis of air monitoring and modelled data showed that the use of officially reported emissions for modeling lead to underestimation of measured air concentrations and deposition fluxes. The largest disagreement between measurements performed with indication of air masses transport direction and modeled data was obtained for episodes with transport from the south southeast (SSE) and south southwest (SSW) compass sectors. Thus the most important source regions for the Baltic Sea area were likely central and eastern parts of Europe which could be characterized by underestimated emissions. Several modeling experiments with regionally adjusted emission scenarios showed that increase of emissions in these regions could substantially reduce underestimation of observed pollution levels.

Later on this work was continued for 17 toxic congeners of PCDD/Fs on the basis of extended set of measurements [Shatalov et al., 2012b]. Application of this approach and construction of experimental scenario emissions for modeling permitted to improve agreement of modeled values with available measurements and to estimate the likely levels of PCDD/F releases to the environment, which exceeded officially reported emissions about five times. At the same time, further work is required to refine national inventories of dioxins and furans emissions in the countries of Central and Eastern Europe to improve assessment of pollution.
Along with anthropogenic emissions of the EMEP countries, additional contribution to the pollution levels can be made by emissions from non-EMEP sources and secondary emissions from media (e.g. soil, water bodies). For this purpose experimental scenario of global emissions of PCDD/Fs was prepared for modeling using the data of the UNEP SC inventory. This inventory is being compiled under SC using the methodology of the UNEP Standardized Toolkit [Fiedler, 2007; Fiedler et al., 2012; UNEP, 2013]. More detailed description of this experimental scenario can be found below and in the MSC-E Technical Report [Shatalov et al., 2014].

**Experimental scenario of global PCDD/F emissions**

Global PCDD/F experimental emission scenario for modeling was constructed on the basis of the information on dioxins and furans releases compiled under the UNEP SC [Fiedler, 2007; Fiedler et al., 2012]. National inventories of annual PCDD/F emissions were available for 68 countries representing the level of emissions during the recent decade. These inventories include data on total PCDD/F emissions constructed in accordance with the UNEP Toolkit using detailed information on PCDD/F releases from ten source groups. Major contributions of these source groups to PCDD/F emission are shown in Figure A.1.

In addition, results of the research performed by Z. Cao et al. [2013] were used. In this study the correlation between the intensity of PCDD/F emissions in the countries and their economic status was evaluated. It was found that PCDD/F emissions from a country and its gross domestic product (GDP) as well as economic level correlated with each other. The regression relation between annual PCDD/F releases per billion of GDP (Release, g TEQ) and GDP per person (GDPPers, USD) has the form:

\[
\text{Release} = A \times (\text{GDPPers})^{-B}
\]

where the constants \(A\) and \(B\) are defined by linear regression between \(\log(\text{Release})\) and \(\log(\text{GDPPers})\) (Figure A.2).

At first step, global data on PCDD/F emissions to the atmosphere were constructed. For this purpose regression relation was applied to estimate emissions for countries, for which information on their emissions was not available in the SC inventory. Using these data it has been found that the correlation between \(\log(\text{Release})\) and \(\log(\text{GDPPers})\) equals to \(-0.79\) (negative sign shows
that PCDD/F releases are growing when GDPPers drops down). Such high value of correlation between two considered variables shows the reasonability of applying the above regression method for obtaining the global emission data set for model calculations.

Further, confidence intervals at 80% level for coefficients $A$ and $B$ included in the equation (1) were calculated and applied for evaluation of PCDD/F emissions to air for various values of $A$ and $B$ and for estimation of the uncertainty of such emission evaluation. It was found that the total PCDD/F emissions to the atmosphere over the globe varied from 32 to 192 kg TEQ/y with average emission about 75 kg TEQ per year.

Anthropogenic emissions of PCDD/Fs to other media were estimated with the use of the data of the UNEP SC inventory, since it contained the estimates of PCDD/F releases to soil and water along with releases to the atmosphere. Emissions to soil and water for model calculations were obtained using the information on the relation between emission totals to these media taken from [Cao et al. 2013]. This relation strongly varied between countries. The paper presents relationships between emissions to air, soil and water separately for four groups of countries with different economic levels (low income or less, lower middle income, upper middle income, and high income or more). This information was used for generating emissions to all three above media in the emission scenario under construction. The values of total annual emissions to air, soil and water are displayed in Figure A.3. Due to relatively small amount of PCDD/Fs released to water bodies, this pathway of emission was not taken into account.
Spatial distribution of PCDD/F emissions to air and soil on global scale with resolution 1°x1° was made on the basis of gridded data on population density. Obtained spatial distributions of annual emissions to these two environmental media are shown in Figure A.4. Relatively high levels of emissions are estimated for countries of Central Africa, Southern and Eastern Asia, and Europe. Low emissions are characteristic of North and South America, and Australia.

Figure A.4: Spatial distribution of annual PCDD/F emissions (ng TEQ/m²/y) to the atmosphere (a) and to soil (b) constructed on the basis of UNEP global PCDD/F emission inventory

The comparison of total PCDD/F emissions to the atmosphere according to the constructed scenario and to officially reported EMEP emission data is presented in Figure A.5.

Figure A.5: Comparison of PCDD/F emission totals to the atmosphere according to the constructed scenario and to official EMEP emission data for 2005
The comparison is presented for the year 2005 since the significant part of countries developed their inventories for the years around 2005. Total emissions of PCDD/Fs from the EMEP the countries according to the constructed scenario amounted to 14.5kg TEQ/y, at the same time total emissions according to the data submitted to the LRTAP Convention were noticeably lower accounting for 6.3kg TEQ/y.

**Further progress in the developing of national inventories of PCDD/F emissions under the UNEP SC**

There is substantial progress in the development of national inventories of PCDD/F releases to the environment by countries for the UNEP Stockholm Convention. According to the national reports, published at the UNEP SC web site in the beginning of 2016, the estimates of dioxins and furans emissions were available for more than 140 countries\(^7\). The reference years of the emission data varied from about 1998 up to 2014, at the same time most of the inventories were made for years around 2004. Substantial number of countries provided estimates of PCDD/F releases for several years that can be used for the evaluation of temporal changes of emissions.

Geographical distribution of national PCDD/F emissions to the atmosphere reported by countries to the UNEP SC is shown in Figure A.6. In accordance with submitted data the largest contributions to the global emission were made by Africa (36%) and South and East Asia (34%). The EMEP countries contributed 15% and contribution of North and South Americas is accounted for about 13%. It is seen that for some of the countries inventories of emissions were not available and thus actual contributions of particular regions might be somewhat different.

![Figure A.6: Total releases of PCDD/Fs to the atmosphere from anthropogenic emission sources in different countries (g i-TEQ/yr) and contributions of major regions to global PCDD/F emission](http://chm.pops.int/Implementation/NIPs/NIPTransmission/tabid/253/Default.aspx)

Within the EMEP region the most significant annual PCDD/F emissions from anthropogenic sources were reported by 10 countries including Russia, Turkey, Ukraine, Kazakhstan, the UK, Poland, Czech Republic, Romania, Bulgaria, and Serbia (Figure A.7). The share of emissions from these countries in total emission of the EMEP region exceeded 80%.

National inventories of PCDD/F releases provide important information on sector distribution of emission. In accordance with the data reported by countries the largest contribution to global emission is made by uncontrolled open burning processes (42%) followed by metal production (19%) and power generation/heating (16%). At the same time data on emissions for the EMEP

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\(^7\) [http://chm.pops.int/Implementation/NIPs/NIPTransmission/tabid/253/Default.aspx](http://chm.pops.int/Implementation/NIPs/NIPTransmission/tabid/253/Default.aspx)
region demonstrate that major contribution is made by ferrous and non-ferrous metallurgy (37%) and power generation/heating (21%) while open burning contributes only 19%. These three source categories of releases comprise the largest contribution (more than 75%) to overall PCDD/F emissions to the atmosphere.

There is ongoing work in the Stockholm Convention on the refinement of national PCDD/F emission inventories, which includes the application of the most recent version of UNEP Standardized Toolkit and updates of national emission data [Black et al., 2012; Fiedler, 2015]. According to available requirements inventories of national releases need to be revised and updated every five years. Thus, the information reported by countries to the Stockholm Convention is of importance for further studies of environmental pollution by dioxins and furans as in the EMEP region and on the global scale and further co-operation between the LRTAP and Stockholm Conventions in this field is highly appreciable.

![Figure A.7: Ten countries of the EMEP region with largest annual emissions of PCDD/F to the atmosphere, g l-TEQ/yr](image1)

![Figure A.8: Major source categories of PCDD/F emissions to the atmosphere for the EMEP countries and for the global scale emissions](image2)
References


Pacyna J.M. et al. [1999] Final report for Project POPCYCLING-Baltic. EU DGXII, Environment and Climate Program ENV4-CT96-0214. Available on CD-rom including technical report, the emission and environmental databases as well as the POPCYCLING-Baltic model. NILU, P.O. Box 100, N-2027 Kjeller, Norway.


ANNEX II - EMISSION DATA FOR MODEL ASSESSMENT (POP STATUS 3/2010)

HCB emissions

Hexachlorobenzene is highly persistent toxic chemical which was widely used as fungicide from the beginning of 1940s. After restrictions and banning of HCB usage as a fungicide/pesticide in many countries starting from 1970s its atmospheric concentrations significantly declined. However it is still released to the environment in course of manufacturing of various chlorinated compounds as unintentional by-product. Content of HCB in the atmosphere during the two recent decades is largely controlled by secondary emissions from the environmental media previously polluted due to agricultural or industrial activities, while relative contribution of anthropogenic emissions is rather small [Barber et al., 2005].

Importance of secondary HCB emissions was considered in several previous studies performed by MSC-E [Shatalov et al., 2010; Gusev et al., 2011]. It was concluded that further improvement of the evaluation of HCB pollution levels in the EMEP countries could be achieved by the refinement of historical releases of HCB to the environment as well as officially reported HCB emissions. As noted in [Mareckova et al., 2012] anthropogenic HCB emissions reported by the EMEP countries are subject of uncertainties and their estimates require further refinement with regard to spatial and temporal coverage and completeness of information on its releases from various source categories.

Due to its high persistence in the environment long-term accumulation of HCB in environmental media (soil, seawater) substantially influences HCB contamination levels. Thus, for the evaluation of HCB pollution levels historical emissions for sufficiently long period of time should be used. There is a lack of global inventories of HCB emissions to the atmosphere and other media. Therefore, to evaluate global distribution and fate of HCB, three experimental scenarios of historical global HCB emissions were constructed for modelling of long-term accumulation of the pollutant in the environmental media using the approach described in [Shatalov et al., 2010].

Following available information the application of HCB in various activities was started from 1945 and reached its maximum in 1980-s. The major source of its release into the environment in that period was the application in the agriculture as a fungicide. Additional sources contributing to the emissions of HCB were the production of chlorinated solvents and pesticides, wastes and sewage sludge incineration, metals smelting, sintering process, steel manufacturing, production of magnesium and cement as well as combustion of fossil fuel. Following the information on agricultural use of HCB in [Food and Agriculture Production Yearbook, 1989] Vulykh and Putilina [2000] estimated that the global HCB emissions in 1980-s could ranged approximately from 7 kt to 18 kt per year with average annual emission about 12 kt. It should be noted that these estimates are subject of essential uncertainties as they do not cover all the countries where the HCB was applied.

Starting from 1980-s the agricultural use of HCB was banned in many countries world-wide resulting in substantial decrease of HCB use and emissions. According to the estimates of Bailey et al. [2001] annual global emissions of HCB in the middle of 1990-s were about 23 t per year varying in the range from 12 t to 92 t. Using these estimates three simple scenarios (maximum, average, and minimum) of global HCB emission temporal development in period 1945-2013 were elaborated. For two recent decades it was assumed that global emissions were gradually decreasing by about 10% a year on average. Temporal variation of global HCB emission according to
maximum scenario is shown in Figure A.9. Spatial distribution of global emission was prepared with the spatial resolution 1°×1° degree using the distribution of cropland area [Li, 1999] for the emissions from agricultural use and population density [Li, 1996] for other sources of HCB emissions (Figure A.9).

![Figure A.9: Scenario of temporal variations of global emission of HCB to the atmosphere in the period 1945-2013 (a) and spatial distribution of HCB emissions to the atmosphere for 2013 over global domain with resolution 1°×1° (b)](image)

Model simulations with the constructed scenarios of HCB emission permitted to evaluate HCB fate in main environmental compartments in line with other modelling studies. In particular, it was indicated that for contemporary period of time major part of HCB mass in media was stored in soil (more than 90%), while other media contained only small share of the total environmental burden. These estimates of HCB distribution in the environment were close to modelling studies of HCB fate of [Zhang et al., 2003], [MacLeod and Mackay, 1999], and [Barber et al., 2005].

Elaboration of scenarios of historic and current HCB emissions resulted in reasonable agreement of modelling results with available measurements and demonstrated essential role of the historic emissions for the evaluation of HCB pollution levels [Shatalov et al., 2010; Gusev et al., 2011; Shatalov et al., 2015]. Further investigations of HCB long-range transport and fate in the EMEP region and on global scale requires further refinement of officially reported emission data of the EMEP countries and elaboration of global gridded emission inventories.

References


ANNEX III - EMISSION DATA FOR MODEL ASSESSMENT
(POP STATUS 3/2012)

Temporal variations of B[a]P emissions

To evaluate seasonal variations of B[a]P pollution levels temporal variations of its emissions from three main source categories (residential heating, industrial processes and road transport) were introduced into the model.

To construct temporal variability of emissions one should take into account that this variability depends on the type of emission source (emission source category). So, prior to modelling this variability, the contributions of various emission source categories to the overall B[a]P emissions should be assessed. According to the official emission data for 2010 complemented by the data from TNO emission inventory when necessary, main contribution to the emissions is made by residential heating (about 50%), followed by road transport (30%), industrial processes (11%) and waste incineration (3%). The contribution of the rest emission source categories is accounted for about 5%. Main source categories of B[a]P emissions are shown in Figure A.10.

![Figure A.10: Main source categories of B[a]P emissions](image)

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

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

Former parameterization of seasonal changes of B[a]P emission to the atmosphere, applied in the MSCE-POP model, assumed the scaling factors for autumn and winter months (1.2) and for summer and spring months (0.8) following the estimates of [Baart et al., 1995]. Comparison of modified and earlier used intra-annual variations of B[a]P emission for the particular location in Central Europe is given in Figure A.11.

Figure A.11: Temporal variations of B[a]P emissions at a particular location in Central Europe

It is seen that usage of temperature dependent scheme of emission seasonal variations leads to significantly higher emissions (by 45% on the average) in cold season (from December to March) and lower emissions (by 50% on the average) in warm season (from June to September). In April, May and October temperature-dependent emissions are oscillating around the values predicted by the estimates of [Baart et al., 1995].

Temporal variations of emissions for road transport and industrial processes categories are constructed in accordance to the coefficients used in LOTOS/EUROS model [Schaap et al., 2005]. Seasonal variations of these emissions are illustrated in Figure A.12 a. and Figure A.13 a., where fractions of annual emissions for each month are shown. Besides, variations of emissions within a week are taken into account (Figure A.12 b. and Figure A.13 b.). Emissions of all other source categories are supposed to be constant over the year.

Figure A.12: Monthly fractions of annual emissions (a) and daily fractions of weekly emissions (b) for emissions from road transport
The diagrams demonstrate that the supposed seasonal variations of emissions from industrial sources and road transport are low enough in comparison with those used for the emissions from residential heating.

### Influence of emission seasonal variations

For evaluation of the influence of seasonal variations of emissions (SV), model simulations for 2009 using previous and modified seasonal variations are carried out.

The comparison of model simulations of B[a]P long-range transport taking into account temperature dependence of emissions (modified SV) with calculations using coefficients proposed by [Baart et al., 1995] (previous SV) allows evaluating the influence of this dependence on B[a]P concentration levels. Table A.1 provides evaluation of temporal correlation between the measurements made at the EMEP monitoring sites and model predictions based on these two calculation schemes of emissions seasonal variations.

#### Table A.1: Correlation coefficients between measurements and model results based on previous seasonal variations scheme (previous SV) and modified one (modified SV) for some EMEP measurement sites

<table>
<thead>
<tr>
<th></th>
<th>BE13</th>
<th>CZ3</th>
<th>DE1</th>
<th>DE9</th>
<th>NO42</th>
<th>SI8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Previous SV</td>
<td>0.91</td>
<td>0.77</td>
<td>0.71</td>
<td>0.87</td>
<td>0.42</td>
<td>0.89</td>
</tr>
<tr>
<td>Modified SV</td>
<td>0.94</td>
<td>0.82</td>
<td>0.72</td>
<td>0.83</td>
<td>0.47</td>
<td>0.97</td>
</tr>
</tbody>
</table>

The comparison shows that almost for all measurement sites correlation between measured and calculated concentrations enlarges due to implementation of temperature dependence of B[a]P emissions. The comparison of the results of these two simulation schemes with measurements at CZ3 (where correlation coefficient becomes better) and DE9 (where correlation coefficient becomes worse) is given in Figure A.14.
It is seen that some improvement of the agreement between measurements and model predictions takes place at CZ3. At the site DE9 in some cases the agreement becomes even worse. This shows that temporal variations of emissions may depend on a particular country.

The improvement of the agreement for warm season is considered separately. For example, at BE13 measurement-to-calculation ratio for air concentrations in warm months has risen from 0.38 to 0.61, at DE1 – from 0.22 to 0.41 and at DE9 – from 0.42 to 0.79 (see Figure A.15).

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

It is interesting also to evaluate the difference between annual averages of B[a]P air concentrations calculated with previous and modified emission seasonal variations over the whole EMEP grid. Spatial distribution of this difference is shown in Figure A.16.
Temporal variability of B[α]P emissions can considerably (up to 40% and higher) affect annual means of air concentrations. This variability strongly depends on emission composition from the viewpoint of source categories.

Thus, information on intra-annual variations of emissions from various source categories is an important factor for correct assessment of B[α]P contamination levels.

References


