Heavy Metals and Persistent Organic Pollutants: Multi-scale modelling and trend analysis methodology.

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## CONTENTS

Introduction 5

1. Trend analysis of HM and POP 9
   1.1. Methodology of trend analysis of air quality data 9
   1.2. Trend analysis results 21
      1.2.1. Heavy metals (HMs) 21
      1.2.2. Persistent organic pollutants (POPs) 35
   1.3. Concluding remarks 45

2. Multi-model assessment of mercury pollution on a global scale 47
   2.1. Global patterns of mercury air concentration and deposition 47
   2.2. Estimates of mercury intercontinental transport 51
   2.3. Mercury deposition from different emission sectors 56
   2.4. Concluding remarks 58

3. Future changes of mercury pollution 59
   3.1. Future mercury emission scenarios 59
   3.2. Changes of mercury deposition levels 60
   3.3. Changes of source apportionment of mercury deposition 62
   3.4. Concluding remarks 64

4. Model assessment of global scale POP pollution POP pollution levels 65
   4.1. Emission data for model assessment 65
   4.2. Evaluation of POP pollution levels and comparison with measurements 69
   4.3. Concluding remarks 77

Conclusions 78
References 80
Annex A. 83
INTRODUCTION

Heavy metals (HMs) and persistent organic pollutants (POPs) are persistent toxic substances characterized by high ability to dispersion in the atmosphere over long distances (up to hundreds or thousands of kilometres). These substances are within the scope of the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP). Protocols on HMs and POPs are aimed at reduction of HM and POP emissions and decrease of the environmental pollution by these contaminants.

Heavy metals are chemical elements naturally occurring in the environment. Their concentration and deposition levels have increased significantly since pre-industrial times due to anthropogenic activities causing a risk of adverse health effects in humans and wildlife. Heavy metals targeted by the Protocol on HMs include lead, cadmium and mercury.

Persistent organic pollutants are semi-volatile persistent toxic substances (mainly of anthropogenic character) that are characterized by significant potential to accumulation in the environmental media. Despite the measures to reduce their usage, they are still found in the environment and pose risk to human health and ecosystems. POPs involved in the EMEP modelling activity according to Protocol on POPs are polyaromatic hydrocarbons (PAHs), dibenzo-para-dioxins and dibenzofurans (PCDD/Fs), polychlorinates biphenils (PCBs) and hexachlorobenzene (HCB),

Along with routine work on evaluation of environmental levels and transboundary transport of HMs and POPs in the EMEP domain for 2013, MSC-E undertakes activities for both model development (refinement of model design and parameterization and evaluation of input data) and for generating additional information required for the implementation of the Protocols on HMs and POPs (such as long-term trends of pollution). The information on long-term trends of pollution by HMs and POPs is submitted to WGE assessment report and TFMM assessment report on trends.

In this context, the following activities have been undertaken in the current year (2014).

Long-term trends

Information on long-term trends of HMs and POPs is important for understanding effectiveness of environmental policy in the EMEP countries, in particular, implementation of the Protocols on Heavy Metals and POPs. This year the evaluation of long-term trends of HM contamination has been done for three species: lead, cadmium and mercury. For POP pollution trend analysis has been fulfilled for PAHs (using benzo(a)pyrene B[a]P as an indicator compound), PCDD/Fs (total toxicity), PCBs (using PCB-153 as an indicator congener), and HCB. According to the recommendations of the TFMM Trend Analysis Workshop, the analysis of trends has been performed for the period from 1990 (reference year) to 2012. Taking into account insufficient coverage of the EMEP domain by measurement sites with sufficiently long time periods, modelling was used as main source for input data for trend analysis. In addition, combined evaluation of trends using modelling and monitoring data was performed at location of monitoring sites suitable for the analysis of long-term tendencies of contamination. Modelling of contamination by the above listed pollutants was done using consistent set of emission data available for this period. For all pollutants except for B[a]P initial and boundary conditions for modelling were generated by running global modelling system GLEMOS for sufficiently long time.

Analysis of trends in pollution levels is based on the methodology elaborated by MSC-E. Short description of the methodology can be found on the TFMM wiki page (https://wiki.met.no/emep/emep-experts/start). According to the methodology, initial time series (annual and/or monthly means of POP concentrations) are decomposed to the regular component (trend) and irregular component (residue). In turn, regular component is split into main component describing general decrease/increase of air
concentrations during the considered period and seasonal component describing intra-annual variations of air concentrations. This methodology was discussed at TFMM Trend Analysis Workshop (Paris, November 2014). Results of research and development activities in the field of trend analysis are presented and discussed at the EMEP Task Force on Measurements and Modelling (TFMM) (http://www.msceast.org/index.php/presentations). Along with this, contributions to the WGE Assessment Report on trends in POP pollution and to the EMEP Assessment Report were prepared. The description of the elaborated approach and of the obtained results is given in Section 1 of this report.

Global modelling in long-lat grid

Following 2014 – 2015 Workplan for the implementation of the Convention [ECE/EB AIR/122/Add. 2], MSC-E has continued the development of the GLEMOS model in order to improve quality and reliability of output information submitted to the EMEP countries. The main directions of research and developments include the preparation of the GLEMOS modelling system for the transition of the EMEP operational modelling to the new EMEP grid, testing and refinement of GLEMOS capabilities to perform multi-scale model simulations for POPs, incorporation of gridded data on aerosols and atmospheric reactants provided by various chemistry transport models, as well as further refinement of the GLEMOS multi-media modelling approach for POPs. The results of this work are reflected in Sections 2 – 4 of the current Report. Model assessment of POP pollution of the EMEP countries is carried out using the multi-media modelling approach, which comprises nested global and regional model calculations.

Section 2 of the Report is aimed at multi-model simulations of mercury atmospheric transport performed as a part of the Mercury Modelling Task Force (MMTF), a scientific cooperative initiative under the Global Mercury Observation System (GMOS, www.gmos.eu), aimed at improvement of current understanding of the key mercury atmospheric processes and evaluation of present and future levels of mercury pollution. In this study, an ensemble of three chemical transport models (GLEMOS, GEOS-Chem, GEM-MACH-Hg) was applied for evaluation of mercury atmospheric dispersion and deposition on a global scale in 2013. The models differ significantly in their formulation including different horizontal and vertical spatial resolution, description of mercury atmospheric chemistry and parameterization of specific processes and phenomena (e.g. the Atmospheric Mercury Depletion Events (AMDEs) in the polar regions). Thus, the multi-model ensemble reflects variety of contemporary approaches applied for simulations of mercury contamination and partly characterizes uncertainties associated with gaps in knowledge on mercury processes in the environment. In line with evaluation of spatial patterns of mercury air concentrations and deposition fluxes, mercury intercontinental transport and contributions of emissions from various emission sectors are estimated.

Assessment of future levels of Hg pollution and evaluation of different abatement scenarios carried out in Section 3 is the key information for development of future mitigation measures. It is particularly topical in the context of the recently adopted Minamata Convention for Mercury – a global treaty to protect human health and the environment from the adverse effects of mercury (http://www.mercuryconvention.org/). Mercury differs from other heavy metals by its ability to long-range dispersion in the atmosphere. Therefore, changes of Hg pollution in the EMEP countries are largely affected by emission dynamics in other geographical regions and require assessment on a global scale. Evaluation of future Hg pollution levels in the EMEP and other regions has been performed as a part of collaborative MSC-E activities within the EU GMOS project. Section 3 presents results of application of the GLEMOS model for assessment of future Hg atmospheric concentration and deposition levels as well as source-receptor relationships. For this purpose a number of model simulations have been performed for selected Hg emission scenarios for 2035.
Section 4 is aimed at the assessment of global transport of some POPs (PCDD/Fs, PCBs and HCB). In the evaluation of global transport of POPs it should be taken into account that POP pollution is formed not only by anthropogenic releases to the atmosphere but also by releases to the other media and secondary emissions (re-mobilization of pollutant from soil, water bodies, etc.) so that model assessment of POP pollution of the EMEP region is carried out using the multi-media multi-scale modelling approach. This approach is realized with the use of GLEMOS modelling system. It should be noted that such modelling requires historical emission data for sufficiently long time period. In order to evaluate relative contributions of secondary and non-EMEP sources, scenarios of global HCB, PCDD/F and PCB emissions (including historical emissions) were updated and used for the evaluation of POP global transport and fate. The Section contains the description of emission scenarios used in modelling and evaluation of modelling results against the measurements collected in the UNEP SC GMP Data Warehouse
1. TREND ANALYSIS OF HM AND POP

One of the most important topics of the assessment of air pollution of EMEP countries by HMs and POPs is the analysis of long-term tendencies of contamination. Such analysis allows evaluating effectiveness of abatement measures taken under LRTAP Convention, on the one hand, and to reveal contemporary tendencies of pollution dynamics, on the other.

When analyzing long-term tendencies of contamination on the long time scale (decades), one should exclude from consideration variations of contamination due to short-scale factors such as year-to-year variations of meteorological parameters, random variations of pollutant emissions, etc., and concentrate on regular tendencies of contamination dynamics characteristic of the entire period. In doing so, peculiarities of contamination dynamics of the considered pollutant (or group of pollutants) should be taken into account. In particular, for HMs and POPs seasonal variations are of importance, since these variations lead to significant intra-annual variations of pollution.

The tool for the investigation of regular long-term tendencies of pollution is trend analysis. Applying this method initial time series (values of pollution levels for a number of points of time within the considered period) is decomposed into two components: regular component (trend) and residues. The residues may be conditioned by short-term and/or random perturbations of the investigated series whereas the trend represents these series free from these perturbations. The form of the considered trend depends to a great extent on a nature of the pollutant under consideration. The methodology of the trend analysis proposed for examination of HMs and POPs is described below.

The necessity of trend analysis for evaluation of pollution levels of airborne pollutants was recognized under CLRTAP. In particular, results on trend analysis of airborne pollutants shall be considered in Assessment Report on Trends that is under preparation by the Task Force on Measurements and Modelling (TFMM). Further, topics related to trend analysis should be included into the Assessment Report of Working Group on Effects (WGE). Here the current status of the research on trends of the contamination of the EMEP region by HMs and POPs is given.

1.1. Methodology of trend analysis of air quality data

Here the methodology of the trend analysis for operational evaluation of trends of air quality data (air concentrations and deposition fluxes of airborne pollutants) in the framework of CLRTAP is proposed. This methodology is worked out following the decision of TFMM Workshop on trend analysis held in Paris (France) 17 – 18 November 2014. To be definite, the methodology is illustrated below by the examples of air concentrations.

Typical measurement data on air quality for sufficiently long period (1990 – 2012) is exemplified in Fig. 1.1, where air concentrations of B[a]P and lead at EMEP sites CZ3 and DE7, respectively, are shown.

Fig. 1.1. Air concentrations of B[a]P and lead at EMEP sites CZ3 and DE7, 1990 – 2012, monthly means
It is seen that the dynamics of air concentrations can be decomposed to the following three components:

\[ C(t) = C_{\text{main}}(t) + C_{\text{seas}}(t) + C_{\text{res}}(t), \tag{1.1} \]

where \( t \) is time, \( C_{\text{main}} \) (main component) describes general decrease of air concentrations during the considered period and \( C_{\text{seas}} \) (seasonal component) correspond to seasonal variability of concentrations. These two tendencies are perturbed by \( C_{\text{res}} \) – variations not described by the two above components (residual component). The sum of the two first components will be referred to as full trend\(^1\).

For the evaluation of the above components a number of methods were described in literature. The main three of them are:

**Deterministic trend.** Under this approach, explicit formulas for the trend compartments including a set of parameters that can be chosen for the best fit with the investigated data are used (linear or non-linear regression). The parameters can be calculated by least squares procedure. This is the most traditional and simple approach to the trend analysis.

**Digital filtration technique** (DF). Roughly speaking, this technique cuts off high frequency component from the considered series so that only “smooth component” rests. In application of this approach, no parameters are calculated, and no explicit formula for trend is obtained. It should be noted that the choice of particular DF method can essentially change the results of the analysis (see [Pickers and Manning, 2013]).

**Time variable parameters** (TVP). Here trend parameters are considered as stochastic time-variable parameters. Such an approach is, in particular, realized in dynamic harmonic regression (DHR) method (see, for example, [Venier et al., 2012]).

The comparative analysis of these approaches is presented in [Venier et al., 2012]. In conclusions to this paper the authors claim that the first approach, “despite of its simplicity and ease of use, provide valuable information on the overall rates of increase or decrease in the concentrations”. In addition, they mention that the first and third approaches “are more complex methods and they require more sophisticated software” and “the choice between approaches might also be influenced by software availability and user capabilities to run the models and interpret the results”. In what follows, the second approach will be considered as the most simple and straightforward.

For the sake of simplicity, we begin with the consideration of trends of annual averages. Consideration of trend analysis including seasonal variations of pollution will be considered later. In this case the decomposition of time series \( C(t) \) is as follows:

\[ C(t) = C_{\text{main}}(t) + C_{\text{res}}(t), \tag{1.2} \]

The example of such decomposition is given by plots in Fig. 1.2.

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\(^1\) In some literature sources main component is referred to as trend, and the sum of main and seasonal components – as seasonal trend.
The following steps are to be performed:

**Step 1.** Detection of the trend and determination of its character. At this step, one makes certain that the trend exists and determines the character of the trend (increasing, decreasing, or mixed).

**Step 2.** Identification of trend type. At this step, one chooses the type of trend suitable for the description of general tendencies of the considered time series (e.g., linear trend, exponential trend, etc.). Possible types of trends are considered below.

**Step 3.** Quantification of trend. At this step choice of main output parameters for the trend of the chosen type is performed.

**Step 4.** Calculations and the interpretation of the obtained results.

**Detection of the trend and its character (step 1).** To determine the existence of the trend Mann-Kendall test is often used (see, e.g., [Hirsch et al., 1982]). We recall that Mann-Kendall test is based on the statistics $Z$ calculated as the difference between increasing and decreasing pairs of values in the time series under investigation (see Fig. 1.3).

After normalization by $(N \cdot (N - 1) \cdot (2N + 5) / 18)^{1/2}$, this statistics has the normal (0,1) distribution and can be used for the determination of the existing of the trend with the following thresholds:

- 1.44 at confidence level 85%;
- 1.65 at confidence level 90%;
- 1.96 at confidence level 95%;
- 2.57 at confidence level 99%

(95% confidence level is mostly used). If the calculated value of the statistics $Z$ exceeds the corresponding threshold in absolute value, then the series are assumed to have trend at the corresponding confidence level. In this case, positive values of $Z$ correspond to the increasing trend, and negative – to decreasing one. In some cases, the value of $Z$ is considered as the indicator of the rate of increase (decrease).

**Fig. 1.2.** Decomposition of the time series to the regular component (trend) and residues for calculated annual means of B[a]P air concentrations in Germany for the period from 1990 to 2012.

**Fig. 1.3.** Increasing and decreasing pairs of values used for calculation of Mann-Kendall statistics $Z$. 
Let us make two remarks to the application of the Mann-Kendall test. First, in the case when the corresponding threshold is not exceeded, one cannot conclude that there is no trend in the investigated time series; additional consideration is required. For example, calculation of $Z$ for the series shown in Fig. 1.3 gives the value of - 1.49 showing decreasing trend only at 80% significance level. Nevertheless, more detailed analysis shows the presence of decreasing trend for this series. Second, it refer to the entire series whereas in many cases the series can be increasing on one its part and decreasing on another; such situation is typical for POPs and HMs. Such trends we shall refer as mixed. The example of this situation is given in Fig. 1.4.

For this series, Mann-Kendall test calculated for the period from 1990 to 2003 shows statistically significant decrease ($Z$ value is – 4.27) at 99% confidence level, and increase for the period from 2004 to 2010 at confidence level 95% ($Z$ value is 1.98). The methodology of the investigation of trends of mixed type is presented below.

**Identification of trend type (step 2).** The following three forms of trend are most common:

- **linear trend:**
  \[ C_{\text{main}}(t) = a \cdot t + b \]  
  (1.3)

- **exponential trend:**
  \[ C_{\text{main}}(t) = a \cdot \exp(-t/\tau) \]  
  (1.4)

- **polynomial trend:**
  \[ C_{\text{main}}(t) = a + b \cdot t + c \cdot t^2 \]  
  (1.5)

Let us consider the application of trends of these three types to the investigation of time series shown in Fig. 1.5 (annual means of B[a]P concentrations in Germany from 1990 to 2012). Natural requirement to trend type is that residual component does not show any statistically significant trend on any of sufficiently long sub-periods (with length over 7 years).

The series with linear trend and the corresponding residues are displayed in Fig. 1.5.

**Fig. 1.5. Application of linear trend to time series of annual means of B[a]P concentrations in Germany from 1990 to 2012: time series and trend (a) and residues (b).**

Application of Mann-Kendall test to the two sub-periods of the entire period (from 1990 to 2001 and from 2001 to 2012) indicates statistically significant decreasing trend on the first sub-period and statistically significant increasing trend on the second one at 95% confidence level. This manifests that the applied linear trend does not describe well the dynamics of pollution on the whole period, so that
some “residual trend” remains. Thus, another trend type should be applied for the description of behaviour of pollution within the considered period.

The attempt of applying exponential trend to the same time series leads to the same results (see Fig. 1.6).

![Fig. 1.6. Application of exponential trend to time series of annual means of B[a]P concentrations in Germany from 1990 to 2012: time series and trend (a) and residues (b).](image)

Better approximation can be obtained by polynomial trend of second order (Fig. 1.7).

![Fig. 1.7. Application of polynomial trend to time series of annual means of B[a]P concentrations in Germany from 1990 to 2012: time series and trend (a) and residues (b).](image)

For this trend type Mann-Kendall test shows no statistically significant trend on the first sub-period but on the second period statistically significant trend is indicated. So, even in this case there exists residual trend.

One of possible solutions of this problem is to use poly-exponential trend of the form:

\[
C_{\text{main}}(t) = a_1 \cdot \exp\left(-\frac{t}{\tau_1}\right) + a_2 \cdot \exp\left(-\frac{t}{\tau_2}\right) + \ldots + a_m \cdot \exp\left(-\frac{t}{\tau_m}\right),
\]  

(1.6)

where \( m \) is a number of exponentials included into trend representation. This parameter can be evaluated for the considered series using F-statistics (see [Smith, 2002]). This statistics for evaluation of statistical significance of second term in (1.6) for \( m = 2 \) can be calculated as:

\[
F = (SS_1 - SS_2) / (2 \cdot s),
\]

where \( SS_1 \) and \( SS_2 \) are sums of squares of residual component for approximations with one and two exponential terms, respectively, and \( s \) is the estimate of standard deviation of residual component. This statistics follows approximately to Fisher distribution with 2 and \( N - 2 \) degrees of freedom.
Second exponential is considered to be significant if $F$ exceeds the corresponding threshold value at the chosen significance level.

Trend representation (1.6) allows take into account the change of reduction rates within the considered period. It was found that for the considered time series third exponential normally is not statistically essential, so that bi-exponential trend ($m = 2$) should be used. The possibility of evaluating confidence intervals for parameters $\tau_1$ and $\tau_2$ is also discussed in [Smith, 2002]. Application of bi-exponential trend to the above series is illustrated in Fig. 1.8.

Application of Mann-Kendall test shows the absence of statistically significant trend on the above two sub-periods of the considered period, which manifests the absence of the “residual trend” for the chosen trend type.

It should be noted that bi-exponential trend is non-linear in parameters $\tau_1$ and $\tau_2$. The application of non-linear trends is considered in many scientific publications (see, e.g., [Smith 2002; dos Santos and Porta Nova, 2007; Seber and Wild, 2003]).

Since a lot of trend analyses use linear (with respect to time) trends, the measure of the deviation of the obtained trends from the linear ones could be of interest. The following characteristic of non-linearity can be used for enumeration of such inclination (Fig. 1.9):

$$NL = \max[\text{abs}(\Delta_i/C_{\text{chord}})] \cdot 100\%$$  \hspace{1cm} (1.7)

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**Fig. 1.8.** Application of bi-exponential trend to time series of annual means of B[a]P concentrations in Germany from 1990 to 2012: time series and trend (a) and residues (b).

**Fig. 1.9.** Criterion on non-linearity of the trend
It is supposed that the threshold level of 10% is suitable to distinguish between linear and non-linear (in time) trends. Examples of trends for calculated B[a]P concentrations in two EMEP countries together with linear trends and calculated non-linearity are presented in plots in Fig. 1.10.

![Graph showing B[a]P concentrations in the United Kingdom and Norway with trend lines and non-linearity values NL = 78% for the UK and NL = 8.7% for Norway.]

Fig. 1.10. Examples of non-linear (a) and linear (b) trends.

It is seen that for the UK trend is essentially non-linear, so that linear trend even shows negative values in the end of the considered period. At the same time bi-exponential trend well represents the dynamics of B[a]P air concentrations in the country. For Norway b-exponential trend is rather close to the linear one, so that linear trend can be used for this country in line with bi-exponential trend. It should be mentioned that for HMs and POPs trends of contamination on most of countries are non-linear.

It can be claimed that bi-exponential (or, in some cases, three-exponential) form of trend is suitable for HMs and some POPs (namely, for PAHs and PCDD/Fs). However, for PCBs and HCB the trend form needs modification. This is illustrated by plots in Fig. 1.11 where PCB-153 air concentrations together with bi-exponential trend and the corresponding residues for the period from 1990 to 2012 are shown.

![Graph showing PCB-153 concentrations in Europe with bi-exponential trend and residues.]

Fig. 1.11. Application of bi-exponential trend to time series of annual means of PCB-153 concentrations in Europe from 1990 to 2012: time series and trend (a) and residues (b).

For the considered time series application of Mann-Kendall test for the two sub-periods shows that in the first half of the period (namely, from 1990 to 2001) statistically significant increasing trend (at confidence level 90%) takes place, so that “residual trend” is obtained. The reason for this is that in the definition of bi-exponential trend (1.6) it is supposed that relative annual reduction for each particular trend component is not changed within the entire period. However, for some types of dependence of initial time series on time this supposition can be violated. For such series the form of trends can be modified by the assumption that parameters $\lambda_i = 1 / \tau_i$ can slowly depend on time. For the description of such trends polynomial approximation of first or second order can be used. So, the form of main component should be changed to:
\[ C_{\text{main}}(t) = a_1 \cdot \exp(-\lambda_1(t) \cdot t) + a_2 \cdot \exp(-\lambda_2(t) \cdot t) + \ldots + a_m \cdot \exp(-\lambda_m(t) \cdot t), \]  

(1.8)

where, as above, \( m \) is a number of exponentials included into trend representation. It was found that it is sufficient to use the linear dependence of \( \lambda_i(t) \) on time:

\[ \lambda_j(t) = A_j \cdot t + B_j, \quad j = 1, \ldots, m, \]  

(1.9)

and the parameters \( A_j \) and \( B_j \) are determined by least square procedure together with the rest parameters involved in (1.8). The results of application of this method to the series of PCB-153 air concentrations in the EMEP region is illustrated in Fig. 1.12.

Here Mann-Kendal test applied to two sub-periods of the considered period indicates the absence of "residual trend".

Let us consider now trend analysis of monthly averages of concentrations. To do that one should take into account that a lot of air contaminants are characterize by pronounced seasonal variations of pollution. Examples of seasonal variations of pollution for persistent organic pollutants (B[a]P) and heavy metals (Pb) are presented by plots of measured values of air concentrations at some EMEP sites are given in Fig. 1.1 above. The presence of seasonal variations can essentially increase peak concentrations of the pollutant under consideration.

To include seasonal variations of pollution into trend analysis, a number of harmonic components are added to the trend, so that (see formula (1.1) above):

\[ C(t) = C_{\text{main}}(t) + C_{\text{seas}}(t) + C_{\text{res}}(t), \]  

(1.10)

where main component \( C_{\text{main}}(t) \) is defined by formula (1.5) (or formula (1.8) is modified trend form is used), and seasonal component is given by:

\[ C_{\text{seas}}(t) = \exp(-\lambda_1(t) \cdot t) \cdot (b_{11} \cdot \cos(2\pi \cdot t - \phi_{11}) + \ldots + b_{1k} \cdot \cos(2k\pi \cdot t - \phi_{1k})) + \ldots \]  

\[ + \exp(-\lambda_m(t) \cdot t) \cdot (b_{m1} \cdot \cos(2\pi \cdot t - \phi_{m1}) + \ldots + b_{mk} \cdot \cos(2k\pi \cdot t - \phi_{mk})), \]  

(1.11)

or, more generally,

\[ C_{\text{seas}}(t) = \exp(-\lambda_1(t) \cdot t) \cdot (b_{11} \cdot \cos(2\pi \cdot t - \phi_{11}) + \ldots + b_{1k} \cdot \cos(2k\pi \cdot t - \phi_{1k})) + \ldots \]  

\[ + \exp(-\lambda_m(t) \cdot t) \cdot (b_{m1} \cdot \cos(2\pi \cdot t - \phi_{m1}) + \ldots + b_{mk} \cdot \cos(2k\pi \cdot t - \phi_{mk})), \]  

(1.12)
where $k$ is the number of multiple harmonics used. Number of harmonics to be included into each of exponential components can again be evaluated using F-statistics (see the discussion after formula (1.5)). Calculations made for HMs and POPs manifest that two harmonic components is normally sufficient for the description of trends for these pollutants. The usage of higher harmonics allows avoiding in some cases such artifacts as negative values of calculated trend for air concentrations. For example, the trend calculated for monthly means of B[a]P concentrations measured at the site CZ3 with the use of one harmonic includes negative values of concentrations (Fig. 1.13).

However, essential negative values do not appear in calculations including two-harmonic trend (Fig. 1.14).

Besides, representation of time series with two-harmonic trend is normally much more accurate than one-harmonic representation. This is illustrated by trend calculations for average B[a]P concentrations over Europe made with one-harmonic and two-harmonic approaches (Fig. 1.15).

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**Fig. 1.13.** Trend calculated for monthly means of B[a]P concentrations measured at the site CZ3 with the use of one harmonic component for each exponential.

**Fig. 1.14.** Trend calculated for monthly means of B[a]P concentrations measured at the site CZ3 with the use of two harmonic components for each exponential.

**Fig. 1.15.** Trend calculated for average B[a]P concentrations over Europe (monthly means) with the use of one- and two-harmonic trends.
It should be noted that the applied approach smoothes meteorological variability between various years (such as in winter of 1996/1997 and 2009/2010).

Note. The considerations above were performed for variations with main period 1 year. The same approach can be applied for consideration of variations with any other period $T$; to do this, harmonic components with frequencies $2\pi k/T$, $k = 1, \ldots, N$ should be used. For example, inclusion of diurnal variations requires adding harmonic components of the form

$$\cos(2\pi j \cdot 365.25 \cdot t - \varphi_j), j = 1, \ldots, k,$$

where $k$ is the number of harmonic components included into the trend expression.

So, the proposed methodology of trend analysis leads to the following decomposition of initial time series (Fig. 1.16).

**Quantification of trend (step 3).** Since for time series with bi-exponential trend is characterized by reduction rates changing in time, for trend characterization annual reduction for all years should be used together with general reduction within the entire period. To be able to compare reduction rates for various contaminants, relative reductions for the entire periods and for each year within this period should be calculated. So, the following parameters can be introduced (for notation see Fig. 1.17):

- **total reduction:** $R_{tot} = (C_{beg} - C_{end}) / C_{beg} = 1 - C_{end} / C_{beg}$,
  \hspace{1cm} (1.14)

- **annual reduction for year $i$:** $R_i = \Delta C_i / C_i = 1 - C_{i+1} / C_i$,
  \hspace{1cm} (1.15)

where $C_i$ are concentration values along the main component in the year $i$. 

![Fig. 1.16. Decomposition of time series (B[a]P concentrations in Germany).](image-url)
Besides, average annual reduction rate within the considered period can be calculated. Since the ratio \( C_{i+1} / C_i \) is a multiplicative quantity, geometrical mean of ratios should be used, so that average annual reduction can be calculated as follows:

\[
R_{av} = 1 - \left( \frac{C_{\text{end}}}{C_{\text{beg}}} \right)^{1/(N-1)},
\]

(1.16)

where \( N \) is the number of years in the series.

Now main component of representation (1.10) can be characterized by the following parameters:
- total reduction over the entire period \( R_{\text{tot}} \);
- average annual reduction \( R_{\text{av}} \);
- reduction in the last year of the considered period \( R_{\text{last}} \).

The latter parameter can be of interest since it characterizes “contemporary” value of reduction rate.

Confidence intervals for reduction/increase rates can be obtained at small sub-periods (about 7 years) by application of linear regression. Below this procedure is illustrated by evaluation of confidence interval for the above series (B[a]P annual means for air concentrations in Germany) for the period from 2005 to 2012, where calculated trend shows increase of concentrations. Application of Mann-Kendall test does not confirm statistically significant increasing trend at this period for confidence level 95% (Fig. 1.18a).

However, this cannot be viewed as the confirmation of the absence of the increase within this period. Additional investigations can be performed by application of linear regression to the residues of the trend. Standard estimates of the slope of linear regression give confidence interval for this parameter.
Combining this with the slope of the obtained trend (0.01) confidence interval of the trend slope on the considered sub-period at confidence level 95% occurs to be (0.004, 0.028) (Fig. 1.18c). Since trend remains increasing even for the lower bound of the confidence interval, the increase of concentrations within the period from 2005 to 2012 can be viewed as statistically significant.

For quantification of seasonal component we first note that the amplitude of this component follows the magnitude of main component (see Fig. 1.16). So, it is reasonable to normalize this component by division of its values by values of main component (Fig. 1.19).

![Fig. 1.19. Normalization of seasonal component.](image)

After such normalization, the values of seasonal component will show the fraction of main component by which it can be modified with seasonal one. Further, the amplitude of the normalized seasonal component for each year can be calculated as:

$$A_i = \left( \max(C_{\text{seas}} / C_{\text{main}}) - \min(C_{\text{seas}} / C_{\text{main}}) \right) / 2,$$

where max and min are taken within the year $i$. Average of these amplitudes over all years of the considered period can characterize the change of trend main component due to seasonal variations:

$$F_{\text{seas}} = \text{Aver}(A_i),$$

where average Aver is taken over all years of the considered period. Threshold value of 10% is proposed for determination whether seasonal component is essential.

One more important characteristic of seasonal variations is the shift of maximum value of contamination with respect to the beginning of the year (phase shift). This shift varies from year to year, and for its characterization the average value of annual phase shifts can be used:

$$S = \text{Aver}(S_i),$$

where $S_i$ are phase shifts (in months) within the year $i$. Maximum of the trend values is searched using its analytical expression (see formulas (1.11) and (1.12)).

Quantification of residue component $\omega$ is made similar to quantification of seasonal component. Namely, since the values of residual component $C_{\text{res}}$ follows also the magnitude of main component, $C_{\text{main}}$, the following quantity can be used as a characteristic of residual component in comparison to the main one:

$$F_{\text{res}} = \sigma(C_{\text{res}}(t) / C_{\text{main}}(t))$$

where $\sigma$ stands for standard deviation.
So, full characterization of the trend includes following parameters:

<table>
<thead>
<tr>
<th>Main component</th>
<th>Total reduction over the period $R_{\text{tot}}$</th>
<th>formula (1.14)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reduction in the last year $R_{\text{last}}$</td>
<td>formula (1.15)</td>
</tr>
<tr>
<td></td>
<td>Average annual reduction $R_{\text{av}}$</td>
<td>formula (1.16)</td>
</tr>
<tr>
<td>Seasonal component</td>
<td>Seasonality parameter $F_{\text{seas}}$</td>
<td>formula (1.18)</td>
</tr>
<tr>
<td></td>
<td>Phase shift of maximum contamination $S$</td>
<td>formula (1.19)</td>
</tr>
<tr>
<td>Residual component</td>
<td>Relative residues $F_{\text{res}}$</td>
<td>formula (1.20)</td>
</tr>
</tbody>
</table>

### 1.2. Trend analysis results

Applying the above described methodology, trend analysis of air quality data on HMs (lead, cadmium and mercury) and POPs (PAHs, PCBs, PCDD/Fs and HCB) included into the EMEP operational activity was performed. For the analysis of chemical groups containing large number of substances such as PAHs and PCBs, indicator compounds are used. Specifically, B[a]P is considered as an indicator compound of PAHs, and PCB-153 – as such of PCBs. These species were selected for the analysis due to large amount of information on their physical-chemical properties needed for modelling. The analysis of PCDD/Fs is made with respect to their total toxicity (calculated using NATO toxicity equivalents).

For the analysis, monitoring data and model calculations were applied in combination. Due to poor coverage of the EMEP domain by monitoring sites, especially with measurement periods sufficient for trend analysis, main source of information on air contamination by the considered pollutants occurs to be modelling.

So, the following information on temporal changes of POP contamination is presented below:

- long-term trends of POP contamination in the EMEP region and individual EMEP countries obtained on the basis of model calculations;
- long-term trends of POP contamination in the EMEP region and individual EMEP countries obtained on the basis of model calculations.

#### 1.2.1. Heavy metals (HMs)

Trends of pollution levels were analyzed for the EMEP region (Europe, Caucasus and Central Asia) and particular countries. Table 1.1 summarizes main characteristics of long-term trends in the EMEP region: total reduction, average, maximum and minimum reductions per year and seasonality. As seen, lead was characterized by the highest, and mercury – by the lowest magnitude of total reduction and average rate of reduction. Rates of deposition reduction of lead and mercury were higher in the beginning and lower in the end of the two-decade period, while the rate of cadmium annual decline remained constant. Deposition trends of all three metals were characterized by seasonality of around 30-40%. Since emission data did not include information on seasonal variations of heavy metal releases to the atmosphere, this seasonality could be attributed to the effect of meteorological variability.
### Table 1.1. Main characteristics of long-term deposition trends of lead, cadmium and mercury for the period 1990-2012

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pb</th>
<th>Cd</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total reduction, %</td>
<td>78.3</td>
<td>52.8</td>
<td>23.4</td>
</tr>
<tr>
<td>Average reduction, % per year</td>
<td>6.4</td>
<td>3.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Maximum reduction (beginning of the period), % per year</td>
<td>6.8</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Minimum reduction (end of the period), % per year</td>
<td>5.9</td>
<td>3.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Seasonal variations, %</td>
<td>33.7</td>
<td>36.4</td>
<td>41.6</td>
</tr>
</tbody>
</table>

For simplicity time series and trends of total deposition over the EMEP region were given for annual mean values. As seen, the reduction of lead deposition is faster in the beginning of the considered period, and the lowest – in the end. The same is noted for mercury, but its reduction rate is smaller than that for lead (Fig. 1.20).

![Fig. 1.20. Long-term changes of total deposition flux and of main component of its trend for lead (a), cadmium (b) and mercury (c). Dashed line indicates confidence intervals at 95% level.](image)

The changes of pollution levels in particular countries could differ considerably from averaged values for the entire EMEP region. For example, lead deposition in Sweden were reducing with rate 19% per year in the beginning of the period, which was much faster than the average for EMEP value (Fig. 1.21a). Another situation is exemplified by trend of total deposition of mercury in Greece. From 1990 to 1996 the deposition were declining, with starting rate of 3.5% per year (Fig. 1.21b). However, the decline stopped in 1996 and was changed by growth, which rate reached 3% per year in 2012.

![Fig. 1.21. Total deposition, trend and main component of lead in Sweden (a) and mercury in Greece (b)](image)
For analysis of long-term pollution changes the EMEP countries were divided in three groups: EU28, EECCA, and the remaining countries related to the group ‘other’. In most of countries of all three groups reduction rate of lead deposition was similar ranging from 4% to 8% per year (Fig. 1.22). The exceptions were Turkey and the Transcaucasian countries – Armenia, Georgia and Azerbaijan, where reduction rates were substantially lower – 1.4 – 2.7%. However, the highest rates of the reduction in the beginning of the considered period (15% – 18%) were noted for a number of the EU28 countries (Finland, Denmark, Germany, Spain etc…), for Monaco and for Norway from the group ‘Other’. This fast decline followed by rapid reduction of anthropogenic emissions in these countries took place due to phasing out of leaded gasoline.

Fig. 1.22. Country-averaged deposition reductions in countries of EU28 (left), EECCA (middle) and remaining regions (right) of lead (a), cadmium (b) and mercury (c). Negative values of reduction mean increase. Whiskers indicate range of annual reduction rates
The main typical characteristic of reduction of cadmium deposition was its uniformity in time. Only in few countries (e.g., Estonia, Finland, Denmark, Russia etc.) annual reduction rate varied over the period. In the EU28 countries mean rate of annual reduction ranged from 2% to 6%. In the EECCA countries similar rate was noted only for countries in the European part of the region: Russia, Ukraine, Belarus and Moldova. In the Transcaucasian and the Central Asian countries the reduction was less than 1.3% per year, and in Armenia and Azerbaijan even slow growth (0.1%-0.2% per year) was indicated. Minor long-term changes of cadmium transboundary pollution in these countries was explained by relatively low rate of reduction or even growth of national emissions, and partly by contribution of non-EMEP sources, which long-term changes were neglected.

Mercury deposition rates were the lowest compared to those of lead and cadmium. In most of the countries they were lower than 3% per year. As a rule, annual reduction rates in the EU28 countries were higher than those in the EECCA countries. Although mean rates of deposition decline were low, they ranged substantially from year to year. In some countries (Belgium, Slovakia, the Netherlands etc.) the rates in the beginning of the considered period made up 10%-17% due to rapid reduction of anthropogenic emissions in these and neighbouring countries. In some countries (e.g., Belarus) even some long-term increase of deposition was noted followed by growth of national emissions.

Besides main component of trend describing gradual long-term changes of pollution levels, another important parameter is seasonality. Trends of cadmium deposition in Belgium and Kazakhstan were used to exemplify countries with low and high seasonalities (Fig. 1.23). Seasonality of cadmium deposition in Belgium was relatively low (24%) (Fig. 1.24a). In spite of marked month-to-month variability of deposition, the applied statistical methods did not deduce significant seasonality. The most probable reason for this is that seasonal variations were disturbed by strong episodic short-term variability of deposition. Kazakhstan is characterized by continental climate with marked seasonal variations of meteorological conditions. This meteorological variability resulted to strong (more than 60 %) seasonality of deposition levels (Fig. 1.24b).

In particular countries seasonality ranged from 8% to 95% for the considered metals (Fig. 1.24). On average it amounted to 30-40%. Seasonality for mercury was somewhat lower than that for lead and cadmium, mostly due to long (about a year) atmospheric life time of mercury.
Factors affecting trends

Long-term trends of pollution levels depend on a number of factors including changes of anthropogenic and secondary emission data, long-term climatic trends, changes of land-use etc. However, the main factors affecting the changes of heavy metal levels in the EMEP region from 1990 to 2012 seem to be anthropogenic and secondary emissions.

Reduction of anthropogenic emission of lead and cadmium for the period 1990-2012 resulted to decline of deposition from anthropogenic sources up 90% and 64%, respectively (Fig. 1.25). However, total deposition reduction to the EMEP region was smaller (Table 1.1). The reason of this was significant contribution of secondary sources to pollution levels in the EMEP region. Reduction of sum of anthropogenic and secondary sources within the region made up 80% for lead and 57% for cadmium, which was very close to the reductions of deposition, because most of lead or cadmium emitted from the EMEP region was deposited within the region.

Situation with mercury differed from that for lead and cadmium. First of all, very large amount of mercury entered the region due to intercontinental transport from non-EMEP sources. Contribution of non-EMEP sources (both anthropogenic and secondary) ranged from 40% to almost 60% over the considered period (Fig. 1.26). However, in absolute terms their contribution remained almost the same for the whole period, because global emissions of mercury had not changed much. And secondly, mercury speciation of emissions was very important factor affecting its transport and deposition. Since significant part of mercury was emitted as long-living elemental form (around 70% for anthropogenic sources and 100% for secondary sources), most of elemental mercury was transported outside the EMEP region. These two reasons resulted to relatively low (23%) reduction of mercury deposition in the region.

![Fig. 1.24. Seasonality of lead, cadmium and mercury deposition averaged among the EMEP countries. Whiskers indicate range of seasonalities among particular countries](image)

![Fig. 1.25. Time series of anthropogenic and secondary emission fluxes of lead (a) and cadmium (b) within EMEP region](image)
Similar to the EMEP domain, changes of pollution levels within each country could also be expressed through changes of anthropogenic and secondary sources. Anthropogenic sources were split into national and foreign ones. For example, deposition change of cadmium in the United Kingdom was around 75% (Fig. 1.26). This reduction was combined of deposition reductions due to national sources and EMEP secondary sources (around 35% each) and of deposition reduction from foreign emission sources (5%). There were countries, e.g., the Republic of Moldova, where the main factor responsible for cadmium deposition reduction was change of contribution of transboundary transport. In some countries, e.g., Latvia and Belarus, deposition from national emission sources even increased from 1990 to 2012. It was explained by increase of national emissions in these countries for the considered period. In some countries (e.g., Azerbaijan, Cyprus, Tajikistan) the increase of deposition was caused by growth of contribution of secondary sources. Although deposition from secondary sources tended to decline in the EMEP region, the increase in these particular countries was conditioned, most likely, by meteorological variability.

![Fig. 1.26. Cadmium deposition change between 1990 and 2012 due to reduction of anthropogenic (national and foreign) and secondary emission sources within EMEP region](image)

Analysis of long-term trends of lead, cadmium and mercury pollution levels in the EMEP region demonstrates that the levels have been declining since 1990. The highest reduction of pollution was noted for lead, followed by cadmium and then by mercury. The main reason of the decline was reduction of atmospheric emissions in the EMEP countries. However, other factors such as long-term changes of secondary emissions of lead and cadmium and contribution of intercontinental transport of mercury to pollution in the EMEP region were also important. Main characteristic of long-term changes (total reduction, annual reduction rate and seasonality) demonstrated considerable geographical variability, which was confirmed by analysis of modelled and observed levels at monitoring stations and of calculated deposition in particular EMEP countries.

**Trends in observed and modelled levels of pollution in particular grid cells**

There were 19 EMEP stations measuring lead and cadmium and 8 stations measuring mercury over last two decades. Measurement data on lead and cadmium concentrations in air and wet deposition fluxes at these selected stations were available for the period started in 1992 or earlier and finished in 1998 or later. For mercury starting year for the selection was 1995, because earlier measurements were either unavailable or unreliable. For example, at Swedish station SE2/SE14 air concentrations in
1990-1992 were significantly higher compared to other years (Fig. 1.27 Most likely it is connected with measurement uncertainties. The selected stations were located mostly in the central and the northern parts of Europe (Fig. 1.28). Trends in the other parts of the EMEP region were characterized entirely by the modelling. Analysis of observed and modelled heavy metal levels at each selected station was performed on monthly basis in order to account for seasonal variability.

Analysis of modelled and observed trends of heavy metal pollution was based on monthly-mean values. At some stations there are measured values which look suspiciously high, e.g., concentrations of Pb in air at station SK4 in 1991 and 1997-1999, or Cd in air at CZ1 in 1993 and 1995 (Fig. 1.29). Similar peaks are noted for some other stations too. Most likely, these high concentrations are caused by measurement problems or irregular effects of local emission sources. Since these data may look somewhat unrealistic, they were excluded from validation of the modelling results by means of filtering procedure.
This filtering procedure is documented in MSC-E report [Ilyin and Travnikov, 2005]. Briefly, the values of time series which exceed mean value (averaged over the entire time series) plus three standard deviations are excluded from the validation. However, in order to take into account long-term decline of pollution levels the mean value was replaced by linearly approximated trend. Because of application of this procedure to time series of air concentrations and wet deposition fluxes, only less then 3% of monthly mean values were excluded from the analysis of modelled and observed trends.

Verification of the modelling results was performed for each considered station with long period of measurements. Statistical indices applied for the verification were: mean relative bias (MRB), correlation coefficient and normalized root mean square error (NRMSE). The formulae to calculate MRB and NRMSE are as follows:

\[
MRB = \left( \frac{\overline{M} - \overline{O}}{\overline{O}} \right) \cdot 100\% \tag{1.21}
\]

\[
NRMSE = \frac{1}{\overline{O}} \sqrt{\frac{\sum_{i=1}^{N} (M_i - O_i)^2}{N}} \tag{1.22}
\]

Here \( M_i, O_i \) – modelled and observed values at \( i^{th} \) station. \( \overline{M}, \overline{O} \) - averaged modelled and observed values, \( N \) – number of model-measurement pairs.

The same statistical parameters were implemented for individual stations. Besides, the comparison was carried out not only for modelled and observed time series, but also for their trends. From the comparison it is seen, that the modelled and observed trends have smaller deviations than the original time series. For example, correlation coefficients for time series of lead air concentrations vary from 0.3 to 0.9, while the coefficients for trends range from 0.6 to almost 1 (Fig. 1.30a). The same could be noted for NRMSE: for trends this indicator is lower than for original time series. The better statistical indicators for trends compared to time series is explained by the fact that the trends do not include random component.

Values of mean relative biases for trends and original time are almost the same. As seen (Fig. 1.30b), for most of stations the biases lie within ±50% range. The exception is station DE3 (Schauinsland, Germany). For this station the model tends to overestimate monthly mean observed air concentrations of lead by up to an order of magnitude (Fig. 1.31a), and annual mean concentrations – by 1.5 – 3.6 times (Fig. 1.31b). Partly the overestimation could be linked with overestimated contribution of secondary sources. However, even if only anthropogenic component of modelled air concentrations is compared with the observed concentrations, the overestimation still remains in the first half of the period. Analysis of emission data in areas which affect pollution levels at this station, is needed.

![Fig. 1.30. Correlation coefficient (a), mean relative bias (b) and NRMSE (c) for monthly-mean time series and their trends of lead concentrations in air](image-url)
Another point is significant difference in periods of maximums and minimums of observed and modelled trends at this station. Modelled values reach maximum in winter period, while the observed values – in spring or summer. Information on seasonal variability, which is not available now, could contribute to improvement of agreement between modelled and observed levels. Besides, it is worth mentioning that the station is situated in the mountainous region at altitude 1205 m. Theoretically, in cold period air, polluted by higher winter-time anthropogenic emissions, could be trapped within surface layer because of temperature inversions. Therefore, this air does not reach the station, and observed levels at the station are relatively low. In warm period of time near-surface inversions occur less often than in cold period, and air from pollution sources reaches the station. The model, in its turn, has spatial resolution 50x50 km², which favours “smoothing” relief and leads to missing the described effect. However, this theoretical idea require more detailed investigation. Transition to finer spatial resolution may help to improve the agreement between modelled and observed concentrations at this station.

Current spatial resolution 50x50 km² may be insufficient to fully reproduce peculiarities of local meteorological situation, which could also affect the quality of modeling.

Correlation coefficients for wet deposition of lead vary from 0.3 to 0.7 (time series) and from 0.7 to 0.9 (trends) (Fig. 1.32a). Like for air concentrations, relative bias for most of stations is within ±50% range (Fig. 1.32b). Notable (a factor of two on average) overestimation of the observed levels is noted for station DE1 (Westerland, Germany). Most likely, the main factor lading to the overestimation is too high contribution of secondary sources (Fig. 1.33a). In other regions the contribution of secondary sources of lead seems to be correct, for example, at station GB91 (Fig. 1.33b). In general, it is possible to conclude that further work is needed on evaluation of contribution of secondary lead emissions to pollution levels in order to further improve quality of the model assessment.

**Fig. 1.32.** Correlation coefficient (a), mean relative bias (b) and NRMSE (c) for monthly-mean time series and their trends of lead wet deposition fluxes
Compared to lead, calculation results for cadmium exhibit somewhat higher discrepancies relative to observed values. For concentrations correlation coefficients vary from 0.2 to 0.7, and for wet deposition – from 0.2 to 0.5. Mean relative bias for concentrations in air ranged within ±70% (Fig. 1.34b). For wet deposition general underestimation of the observed values up to 60% is noted (Fig. 1.35b).

For some stations relatively high biases for long-term time series is caused by underestimation of observed levels for the beginning of the considered period. For example, this situation is noted for wet deposition at station GB91 (Fig. 1.36), and at some other stations (SE51, NL91, DK31). At Scandinavian stations (NO39, NO1) some underestimation is noted throughout the entire period.
Validation results for mercury concentrations in air look contradictory. On one hand, correlation coefficients are comparatively low, and even negative (Fig. 1.37a). On the other hand, bias and NRMSE are also low compared to similar indicators for lead or cadmium. For example, modeled concentrations of elemental mercury in air on average agree with observed levels with ±8% accuracy.

First of all, lifetime of elemental mercury in the atmosphere is estimated at several months to a year. This time is quite enough to disperse over the entire globe. Therefore, temporal and spatial variability of background levels of atmospheric mercury is relatively low compared to other metals, such as lead or cadmium. In background or rural regions of Europe typical levels of mercury are around 1.4 – 1.6 ng/m$^3$. As a result, magnitude of variability of mercury concentrations is comparable with modeling and measured uncertainties, which leads to low correlation coefficients.

Another point is the decrease of correlation coefficients of modelled and measured trends compared to original time series (Fig. 1.38a). The main reason is that seasonal variability of modelled values differs from the observed ones: maximum of modelled air concentrations of mercury takes place in the end of summer or beginning of autumn, while the observed concentrations reach maximum in winter or beginning of spring. This situation is exemplified by time series and trends of mercury at Swedish station SE14 (Fig. 1.38). When random component of time series is removed, the phase shift in maximums/minimums becomes more explicit, and thus the temporal correlation coefficient declines.

There are two main reasons explaining the shift. The first one is seasonal variations of the emission data. Currently information about seasonal variations of mercury anthropogenic emissions is not available. Another reason is atmospheric chemistry of mercury which is one of the main sources of uncertainties of mercury transport modeling [Lin et al., 2006, Subir et al., 2011; 2012].

**Fig. 1.36.** Observed and modelled wet deposition fluxes of cadmium at station GB91 (the United Kingdom).
Uncertainties of mercury chemical transformations in the atmosphere are likely to be a reason of overprediction of wet deposition fluxes at some stations, namely at DE1 and FI36. While for most of stations the difference between modelled and measured fluxes is within ±20% (Fig. 1.39), for DE1 it reaches 60%, and for FI36 – around 150%. Partly this overestimation could be explained by inconsistencies of precipitation amounts, measured at stations and simulated by meteorological driver MM5. Simulated precipitation amount at station FI36 exceeds on average two-fold the observed ones, and by 30% - at DE1 station. However, calculated precipitation amounts for station FI36 agree much better (within ±25%) with those observed at meteorological station Muonio located in the same grid cell (Fig. 1.40) (http://www.gosic.org).

Fig. 1.38. Time series and main components of trends (a) and trends of modelled and observed air concentrations of mercury at station SE14.

Fig. 1.39. Correlation coefficient (a), mean relative bias (b) and NRMSE (c) for monthly-mean time series and their trends of mercury wet deposition fluxes
Values of statistical indices for totality of annual mean values at the selected stations are summarized in Table 1.2. Values for non-filtered tie series are given in brackets. As seen, the filtering out of outlying values, as a rule, results to improvement of results of comparison modelled and measured values. As follows from the table, lead is characterized by the lowest relative bias: both for air concentrations and wet deposition fluxes it is below ±15%. For most of model-observation pairs of values difference between modelled and observed levels lies within a factor of two. For cadmium the discrepancies between modelled and observed levels are somewhat higher than those for lead. The bias for air concentrations is -26% and -35% for wet deposition. The reason for this is underestimation of the observed levels at some stations in the beginning of the period. Most likely, these high concentrations are caused by uncertainties of measurement approaches.

For mercury concentrations in air mean relative bias is the lowest (0%), and all modelled values agree with the observed ones within a factor of two. Relatively low correlation for mercury in air is explained by its small spatial and temporal variability. Bias for wet deposition of mercury is positive which means that the model tends to overestimate the observed levels. It could be connected with uncertainties in current understanding of mercury atmospheric chemistry.

### Table 1.2. Main statistical indicators of agreement between annual modelled and measured levels of time series of air concentrations and wet deposition fluxes the period 1990-2012

<table>
<thead>
<tr>
<th></th>
<th>Lead</th>
<th>Cadmium</th>
<th>Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C\textsubscript{air}</td>
<td>Wet Dep</td>
<td>C\textsubscript{air}</td>
</tr>
<tr>
<td>Relative bias, %</td>
<td>-6.6 (-9.9)</td>
<td>13.4 (6.2)</td>
<td>-23.6 (-26.2)</td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>0.66 (0.66)</td>
<td>0.68 (0.77)</td>
<td>0.63 (0.58)</td>
</tr>
<tr>
<td>NRMSE</td>
<td>0.69 (0.74)</td>
<td>0.66 (0.57)</td>
<td>0.80 (0.93)</td>
</tr>
<tr>
<td>F2, %</td>
<td>83 (83)</td>
<td>83 (85)</td>
<td>81 (80)</td>
</tr>
<tr>
<td>F3, %</td>
<td>96 (95)</td>
<td>99 (99)</td>
<td>96 (95)</td>
</tr>
<tr>
<td>N</td>
<td>324</td>
<td>151</td>
<td>257</td>
</tr>
</tbody>
</table>

\(C_{\text{air}}\) – concentration in air  
Wet Dep – wet deposition flux  
NRMSE – Normalized Root Mean Square Error  
F2 – fraction of values fitting to factor of 2 difference  
F3 – fraction of values fitting to factor of 3 difference  
N – number of values (stations x years)
Main characteristics of trends at individual stations, such as reduction and seasonality, were also characterized. On average, mean annual reduction of observed and modelled concentrations and wet deposition of lead for the period from 1990 to 2012 amounted to about 7-9% (Fig. 1.41a). For cadmium the reduction of modelled levels was around 4%, and that of observed levels – about 5-8% (Fig. 1.41b). Somewhat higher reduction of observed compared to modelled levels was caused by underestimation of high observed values in the beginning of the considered period. Reduction of modelled and measured mercury air concentrations was low (less than 0.5%) (Fig. 1.41c). Reduction of observed mercury wet deposition was higher (about 3% per year) than that of modelled levels. However, range of reductions of observed mercury deposition was quite high and fully overlapped the range for modelled values.

![Fig. 1.41. Average annual reduction rates for modelled and observed air concentrations and wet deposition fluxes of lead (a), cadmium (b) and mercury (c) over selected monitoring stations. Whiskers mean range of average reduction rates among stations](image)

Average seasonality of measured and observed lead and cadmium levels was about 40 - 50% (Fig. 1.42a and b). In case of mercury seasonality of air concentrations was low compared to the other heavy metals, amounting to about 10% (Fig. 1.42c). Observed seasonally of mercury wet deposition, ranging from 20 to 110%, was higher than modelled one, which could be linked with uncertainties of understanding of mercury chemical transformations as well as lack of data on seasonal variation of emissions.

![Fig. 1.42. Mean seasonality of modelled and observed air concentrations and wet deposition fluxes of lead (a), cadmium (b) and mercury (c). Whiskers mean range of seasonalities among stations](image)
1.2.2. Persistent organic pollutants (POPs)

**POP pollution trends in the EMEP region and in individual EMEP countries.** Trends of average POP air concentrations in the EMEP region for the period from 1990 to 2012 are shown in Fig. 1.43. To describe general tendencies in changes of air concentrations, trends of annual averages of pollution (not taking into account seasonal variations) are considered.

**Fig. 1.43.** Trends in annual mean air concentrations of (a) B[a]P, (b) PCDD/Fs, (c) PCB-153 and (d) HCB in the EMEP region for the period from 1990 to 2012. Negative reduction in the legend denotes increase of air concentrations. Dashed lines show 95% confidence intervals.

Calculated trends allow evaluation total reduction of pollution for the considered period, average annual reduction and reduction in 2012 (negative reduction denotes increase of air concentrations). Estimates of rates for the year 2012 illustrate current state of contamination changes (decrease or increase). It was obtained that B[a]P air concentrations in the EMEP region tend to be growing beginning from 2005; this growth occurred to be statistically significant at 90% confidence level. For PCDD/F air concentrations in the end of the period become to be almost stable. For PCB-153 and HCB reduction of air concentrations is diminished to the end of the period but remains noticeable. The values of average annual reductions for the entire period and reduction rates in 2012 for all considered pollutants are summarized in Fig. 1.44.

In addition estimate of the residual component of the calculated trend allows the construction of confidence intervals for trend. Such intervals at 95% confidence level are shown in Fig. 1.43 by dashed lines. This information can be of use when applying trends for projections of contamination levels to future periods.

**Fig. 1.44.** Average reduction of air concentrations of the considered pollutants, 1990 – 2012, and reduction in 2012 in the EMEP region.
Following the decisions of the TFMM Workshop on trends, MSC-E performed the analysis for the period from 2001 to 2012. It was found that trends calculated for this period well agree with those for the whole period (1990 – 2001), see Fig. 1.45.

Seasonal variability of concentrations is important characteristic in the evaluation of long-term trends of POPs. Trends of air concentrations of B[a]P, PCDD/Fs and PCB-153 in the EMEP region on the level of monthly means are demonstrated by plots in Fig. 1.46. For correct evaluation of seasonal variations of HCB additional refinement of physical-chemical properties and model description of exchange processes is required.

Calculations show that seasonality parameter for B[a]P equals about 100%, for PCDD/Fs – about 20%, and for PCB-153 – about 30%. It is worth noting that for EMEP countries and, especially, for particular locations this parameter can be larger (see below).

Further, calculations show that due to substantial seasonal variability B[a]P air concentration in cold period of year can exceed several times the annual average value, whereas for PCDD/Fs and PCB-153 the situation is opposite (maximum concentrations are calculated for summer months). This is conditioned by the fact that seasonal variations of B[a]P are determined mainly by the degradation in the atmosphere while for the other two pollutants main factor determining seasonal variations is exchange with environmental media (soil, seawater, vegetation).

Along with changes of POP pollution in the EMEP region as a whole the analysis of trends can be performed also for individual EMEP countries. This year such analysis was done for B[a]P air concentrations. The results of the analysis are presented below.

Average annual reduction rates for the period from 1990 to 2012 and reduction rates in the last year of the period (2012) for all EMEP countries are shown in Fig. 1.47 (a – c). For the analysis of long-term
changes of pollution the EMEP countries were considered for the following three groups: EU28, EECCA, and remaining countries specified as the group 'other'.

**Fig. 1.46.** Trends of air concentrations of (a) B[a]P, (b) PCDD/Fs and (c) PCB-153 in the EMEP region (monthly means)

**Fig. 1.47.** Estimated average annual reduction rates of B[a]P air concentrations for the period from 1990 to 2012 and reduction rates in the last year (2012) of the period in the EMEP countries: a) the EU28 countries, b) the EECCA countries, c) other EMEP countries. Negative values denote growth of pollution.
Calculation results indicate that for most of the EU28 countries reduction of B[a]P pollution levels in the end of the considered period was changed to growth. For most of the EECCA countries negative rates of average annual reduction are obtained that indicates the increase of air concentrations on the average. Other countries are generally characterized by slower decline of contamination levels from 1990 to 2012 as compared to the EU countries.

Examples of trends for two EMEP countries (Germany and Belgium), with different types of B[a]P air concentration trends are displayed in Fig. 1.48 together with confidence intervals at 95% significance level. Along with large total reduction (68%), the growth of contamination in Germany in the end of the period (from 2005) takes place, reaching 4.5% in the last year 2012 (here reduction rates refer to the trend). It should be noted that the growth of B[a]P air concentrations from 2005 to 2012 is statistically significant (see Fig. 1.18 above and discussion therein).

In contrast, for Belgium, though total reduction is slightly lower, decline of contamination took place throughout the entire period being less in the end of the period (1.4%) than average reduction rate (about 4.4%).

Calculated trends of B[a]P air concentrations were compared with the trends of annual emission totals (Fig. 1.49). It was found that trends of air concentrations and emission totals well agree with one another. Differences in values of reduction parameters for modelled air concentrations and emissions are conditioned by transboundary transport.
It should be taken into account that air concentrations of POPs are subject to strong spatial variability and varies to high extent between different parts of a country. For example, essential number of people can live in regions where EU target value of 1 ng/m³ (Directive 2008/50 EC) is exceeded (Fig. 1.50) in spite of the fact that for all these countries average annual air concentrations over the entire country area is less than 1 ng/m³.

Let us now consider seasonal variations of air concentrations in the EMEP countries. The values of seasonality parameter for particular EMEP countries are presented in Fig. 1.51.

As was indicated above, seasonality parameter for the entire EMEP domain is about 100%. However, the values of this parameter vary strongly between countries (from 45% for Spain to over 150% for Turkmenistan). Nevertheless, seasonal variations of air concentrations remain to be essential in all EMEP countries. Examples of trends in the above two EMEP countries taking into account seasonal variations of air concentrations are given in Fig. 1.52.

Differences of seasonal variation intensity among the countries can be explained by their geographical location (the influence of seasonal variations is higher in continental countries than in coastal ones).
Trends in observed and modelled levels of pollution in particular grid cells

Performing trend analysis it is important to apply “integrated approach” that combines emission inventories, models and measurement data. Such an approach allows one to compose a complete picture of environmental contamination by POPs, reveals inconsistencies in available information, and helps set priorities for further research that will support decision-making. So, it is necessary to compare trends calculated on the basis of measurement data and on calculation results at locations of measurement sites. It should be taken into account, however, that measurement data reflects the values of air concentrations / deposition fluxes in a single location whereas model calculates average value of pollution over relatively large grid cell. This can be a source of disagreement between measurements and model output.

Measurements of B[a]P, PCB-153 and HCB air concentrations for sufficiently long time period were available for the following EMEP monitoring sites: CZ3 (Kosetice), FI96 (Pallas), IS91 (Storhofdi), NO42 (Zeppelin), NO99 (Lista) SE2/14 (Rövik/Råo) and SE12 (Aspvreten). Location of these sites is shown in Fig. 1.53. Since time periods of measurements for different sites are different, average annual reduction rates are used to evaluate decline of pollution levels. Not all of the considered pollutants are measured at all listed sites.

For evaluation of the agreement between measurement data and calculation results from point of view of long-term tendencies of contamination it is reasonable to compare trends rather than initial time series. Such approach allows obtaining more detailed information on disagreements between calculation results and observations. This is illustrated below by the comparison of measured and calculated PCB-153 air concentrations at site FI96 for the period from 1996 to 2012 (see Fig. 1.54).

Traditional statistical parameters of comparison of model results with observations (Fig. 1.54a) are: correlation coefficient equals to 0.45, relative bias is about 60%, and normalized root square error is 1.35. More details on the comparison can be obtained from the comparison of trends calculated on the base of monitoring data and model results and measured values (Table 1.3).
Table 1.3. Main trend parameters of the comparison of trends of PCB-153 air concentrations at FI96 site calculated on the basis of measurements and modeling results.

<table>
<thead>
<tr>
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<th>Total reduction (from 1996 to 2012)</th>
<th>Average annual reduction</th>
<th>Seasonality</th>
<th>Residual component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurements</td>
<td>72%</td>
<td>7.4%</td>
<td>50%</td>
<td>54%</td>
</tr>
<tr>
<td>Calculations</td>
<td>69%</td>
<td>6.6%</td>
<td>100%</td>
<td>57%</td>
</tr>
</tbody>
</table>

It is seen that the model well reproduces total reduction of contamination (and, consequently, average annual reduction) at FI96 though the dynamics of the reduction is slightly different for measurements and calculations (Fig. 1.54b). The relative values of residual component (normalized by the values of main component) are rather close for measurements and calculations. However, seasonal variations normalized by main component (seasonality parameter) differ two times (see Fig. 1.55).

This shows that for refinement of the agreement of measurements and model results it is necessary to refine model parameterization of degradation and exchange with environmental media and, possibly, to refine seasonal variations of emissions.

The statistical parameters (correlation coefficient, relative bias and normalized root square error NRMSE) of the comparison between measured and calculated PCB-153 air concentrations calculated on the basis of initial values and of trends is shown in Fig. 1.56.

It can be seen that statistical parameters calculated on the basis of trends are always better than those calculated on the basis of initial values. This shows that the model well enough reproduces long-term tendencies of air pollution by PCB-153. Further, the agreement between measurements and calculations is well enough at all sites except for NO42 and IS91. The reason of the disagreement at these two sites is connected with that the levels of pollution here are likely influenced by the emission sources outside the EMEP domain. Thus refinement of description of global scale emissions and their temporal changes in various regions of the world is needed. At present these two sites are excluded from the trend comparison.
Average annual reduction rates of PCB-153 air concentrations estimated on the basis of combined trend analysis of measurements and modelling results are shown in Fig. 1.57a. It is seen that measurements and model results indicate similar reduction rates of PCB-153 for all the sites except for CZ3 (Kosetice).

Fig. 1.57. Average annual reduction rates (a) and seasonality parameter (b) of PCB-153 calculated by trend analysis of measurement and modelling data.

Difference in the reduction rates for CZ3 site is caused by disagreement between modelled and measured values of PCB-153 air concentrations in the period 1997-1999 (see Fig. 1.58). It may be conditioned by several factors, including uncertainties in the emission data applied in model simulations as well as changes in measurement techniques during the monitoring period. This issue should be further analyzed with joint participation of experts in modelling, measurements and emissions.

The comparison of seasonal variability parameters for the considered sites calculated on the basis of observations and modelling are shown in Fig. 1.57b. It is seen that the values of the parameter calculated by the model well agree with those given by measurements except for the site FI96. The discussion on disagreement at this latter site was given above.

For B[a]P the analysis was carried out for four sites, namely, CZ3, FI96, SE2/14 and SE12. Similar to the case of PCB-153, measurements obtained at the site NO42 were not included since levels of concentrations at this site might be affected by the emission sources located outside the EMEP domain, which were not taken into account in model simulations. The statistical parameters of the comparison between measured and calculated B[a]P air concentrations calculated on the basis of initial values and of trends is shown in Fig. 1.59.

It is seen that, in general, the agreement between trends of measurements and calculations is well enough at all sites except for NO42 and SE12. High value of relative bias at the site SE12 can be conditioned by the closeness of this site to Stockholm city and by peculiarities of location of the site. Low correlation between measurements and observations at FI96 (at the level of air concentration values) will be discussed later.

Fig. 1.58. Comparison of modelled and measured concentrations of PCB-153 at site CZ3 (Kosetice).
Average annual reduction rates of B[a]P air concentrations and seasonality parameter estimated on the basis of combined trend analysis of measurements and modelling results are shown in Fig. 1.60.

It is seen that the model reasonably determine seasonal variations of B[a]P pollution. Analysis of both measurement and calculation data shows that seasonal variations of B[a]P air concentrations can change pollution levels up to several times from annual average value (see Fig. 1.61).
It is also seen that the results on reduction rates at FI96 differ from each other. Specifically, calculated trend show growth in the end of the period, whereas measurement trend does not. Such situation can be obtained at low values of reduction (calculations show about 1.5% growth on the average, and observations – about 0.7% decrease). However, both measurements and calculations show growth of maximum annual concentrations in the end of the period. The results of the analysis of maximum B[a]P concentrations at location of the EMEP measurement sites are displayed in Fig. 1.62, where average annual reductions of air concentrations and their reductions in the last year of the period (2012) are given.

For HCB, long enough time series of measured air concentrations were available for the following EMEP monitoring sites CZ3, NO42, NO99 and IS91. The results of the analysis of trends for the sites CZ3 and NO99 are summarized in Fig. 1.63, where average annual reduction for the entire period and reduction in the last year of the period are displayed.

Analysis of temporal variations of HCB air concentrations for the two remote sites, NO42 and IS91, indicates larger difference in estimates of trends. Particularly, model overestimates annual average reduction for the period 1990-2012 and does not capture the growth of HcCB air concentrations in the end of the period. The reason of the differences is connected with that the levels of pollution at these sites are likely influenced by the emission sources outside the EMEP domain. Thus refinement of description of global scale HCB emissions and their temporal changes in various regions of the world is needed.

Regular measurements of dioxins and furans air concentrations at the EMEP monitoring sites are not currently performed. At the same time, it is possible to use available long-term measurements of PCDD/F air concentrations in the EMEP countries reported in literature for the analysis of long-term changes of pollution. A number of studies provided results of long-term measurements of dioxins and furans concentrations in air. Significant decrease of PCDD/F air concentrations (about 70%) was observed in Spain in the period 1994-2004 [Abad et al., 2007]. Monitoring of PCDD/F air concentrations in the UK at urban and rural sites indicated sharp decline in early 1990s and smaller decline in later period of time [Katsoyiannis et al., 2010]. Pronounced decrease of PCDD/F air concentrations and deposition (about a factor of 5) was also observed in Germany from 1988-1992 to 2005 [Bruckmann et al., 2013] which was almost leveled off since 2005. In general, results of model simulations are in line with available measurements and demonstrate similar decline of PCDD/F pollution in the EU countries from 1990 to 2012 (about 80%).
1.3. Concluding remarks

The analysis of HM and POP trends for the period from 1990 to 2012 has been performed based on simulation results of MSC-E models. In addition, for locations of EMEP monitoring sites with sufficiently long observation period (at least from 1996 to 2010) combined measurement-modelling analysis is carried out. For POPs, to take into account the influence of secondary and non-EMEP sources multi-scale and multi-compartment modeling is applied.

The major conclusions of the study are summarized below.

General conclusions

- The methodology of the analysis of long-term trends accounting non-homogeneous reduction within the period and seasonal variation of pollution was elaborated by MSC-E and discussed at TFMM Trend Analysis Workshop (Paris, November 2014) (see TFMM wiki-page https://wiki.met.no/emep/emep-experts/start).
- According to the methodology, initial time series (annual and/or monthly means of air concentrations / deposition fluxes) are decomposed to the regular component (trend) and irregular component (residue). In turn, regular component is split into main component describing general decrease/increase of pollution during the considered period and seasonal component describing intra-annual variations of air concentrations.
- For all considered pollutants reduction of contamination in the beginning of the considered period is larger than in the end of the period.

Heavy metals

- Analysis of long-term trends of lead, cadmium and mercury pollution levels in the EMEP region demonstrates that the levels have been declining since 1990. The highest reduction of pollution was noted for lead (78%), followed by cadmium (53%) and then by mercury (23%). Lead and mercury are characterized by higher reduction in the beginning, and smaller in the end of the 1990-2012 period, while rate of cadmium reduction remains stable. In particular countries the values of total reduction and reduction rates can significantly differ from the averaged ones.
- The main factor responsible for the long-term decline of heavy metal concentrations and deposition in the EMEP region is reduction of atmospheric emissions in the EMEP countries. However, other factors such as long-term changes of secondary emissions of lead and cadmium and contribution of intercontinental transport of mercury to pollution in the EMEP region are also important.
- Seasonality of total deposition trends of lead, cadmium and mercury in countries of the EMEP region amounts to 30-40% on average. However, regional differences are significant. Since the data on seasonal changes of anthropogenic emissions are currently not available, seasonal variability of heavy metal pollution levels is caused by variability meteorological conditions.
- Comparison of modelled and measured values over long period of time (1990-2012) demonstrated that the model in general was capable of reproducing observed levels, as well as main characteristics of the observed trends (reduction rate and seasonality). However, analysis of modelled and observed levels at some stations revealed main directions of further investigation. They include analysis of uncertainties of heavy metal anthropogenic and secondary emissions, influence of spatial resolution on the model performance and atmospheric chemistry of mercury.
Persistent organic pollutants

- B[a]P air concentrations in the EMEP region tend to be growing beginning from 2005; this growth occurred to be statistically significant at 90% confidence level. For PCDD/F air concentrations in the end of the period become to be almost stable. For PCB-153 and HCB reduction of air concentrations is diminished to the end of the period but remains noticeable. These results are in line with the data from EMEP monitoring sites.

- Seasonal variability of POP air concentrations was evaluated for B[a]P, PCDD/Fs and PCB-153. For correct evaluation of seasonal variations of HCB additional refinement of physical-chemical properties and model description of exchange processes is required.

- Seasonality parameter (average amplitude of seasonal component normalized by main component) for B[a]P equals about 100%, for PCDD/Fs – about 20%, and for PCB-153 – about 30%. Due to substantial seasonal variability B[a]P air concentration in cold period of year can exceed several times the annual average value, whereas for PCDD/Fs and PCB-153 the situation is opposite (pollution in summer exceeds that in winter).

- Air concentrations of POPs are subject to strong spatial variability and varies to high extent between different parts of a country. For example, essential number of people can live in regions where EU target value of 1 ng/m³ (Directive 2008/50 EC) is exceeded in spite of the fact that for these countries average annual air concentrations over the entire country area is less than the target value.
2. MULTI-MODEL ASSESSMENT OF MERCURY POLLUTION ON A GLOBAL SCALE

The character of mercury dispersion in the atmosphere and transport from one region to another is largely affected by physicochemical properties of mercury atmospheric species. Poorly soluble and relatively stable gaseous elemental mercury (GEM) can drift in the air for months providing transport of mercury mass between different regions of the planet. In contrast, oxidized mercury species – gaseous oxidized mercury (GOM) and particle bound mercury (PBM) – are easily removed from the air by precipitation scavenging or the surface uptake [Selin, 2009; Travnikov, 2011; AMAP/UNEP, 2013]. Therefore, levels of mercury deposition and its source apportionment in each region are determined by the strength and speciation of domestic emissions, emissions in other regions and by the oxidative capacity of the atmosphere that transforms globally dispersed GEM to deposited GOM and PBM. As it has been shown in previous studies [Seigneur et al., 2004; Travnikov and Ilyin, 2009; Selin et al., 2008; Corbitt et al., 2011; Lei et al., 2013; Chen et al., 2014], atmospheric transport from distant sources can significantly contribute to mercury deposition, particularly, in regions with low domestic emissions. On the other hand, proportion of anthropogenic emissions that deposits locally or regionally depends on emissions speciation that differs significantly for different emission sectors. Besides, impact of long-range transport on mercury deposition can vary seasonally due to change in air concentrations of mercury oxidizing agents (e.g. Br, O3, OH) that leads to change in GEM oxidation intensity and subsequent deposition.

The current study is based on multi-model simulations of mercury atmospheric transport performed as a part of the Mercury Modelling Task Force (MMTF), a scientific cooperative initiative under the Global Mercury Observation System (GMOS, www.gmos.eu), aimed at improvement of current understanding of the key mercury atmospheric processes and evaluation of present and future levels of mercury pollution. Simulation results of the multi-model ensemble (see Annex A) are used to quantify global patterns of mercury concentration and deposition, source apportionment of mercury deposition to major geographical regions and aquatic areas of the global ocean as well as seasonal variation of the source-receptor relationships, and deposition from different emission sectors.

2.1. Global patterns of mercury air concentration and deposition

An ensemble of three chemical transport models (GLEMOS, GEOS-Chem, GEM-MACH-Hg) was applied for evaluation of mercury atmospheric dispersion and deposition on a global scale in 2013. A brief summary of characteristics of participating models is given in Annex A. The models differ significantly in their formulation including different horizontal and vertical spatial resolution, description of mercury atmospheric chemistry and parameterization of specific processes and phenomena (e.g. the Atmospheric Mercury Depletion Events (AMDEs) in the polar regions). Besides, two of three models (GLEMOS and GEM-MACH-Hg) are mainly atmospheric models simulating mercury transport in the atmosphere and exchange with the Earth’s surface (deposition and re-emission), whereas the other model (GEOS-Chem) presents full multi-media description of mercury cycling in the environment. The models also differ in their estimates of natural and secondary emissions of mercury to the atmosphere. Thus, the multi-model ensemble reflects variety of contemporary approaches applied for simulations of mercury contamination and partly characterizes uncertainties associated with gaps in knowledge on mercury processes in the environment.

The global inventory of mercury anthropogenic emissions for 2010 [AMAP/UNEP, 2013] was used in the study. The dataset consists of gridded emission data with spatial resolution 0.5°×0.5° for three mercury species (GEM, GOM, PBM). Total global emissions of mercury from anthropogenic sources are estimated at 1875 tonnes per year with the overall proportion of GEM, GOM, and PBM emissions equal to 81%, 15%, and 4%, respectively. This value is somewhat lower than total mercury emission
given in GMA 2013 (1920 tonnes per year), because it does not include emissions from contaminated sites [AMAP, 2014]. Besides, it should be noted that some models of the ensemble applied changed speciation of anthropogenic emissions (Annex A, Table A.1) in accordance with the model formulation. The emissions dataset is also sub-divided into three classes of source heights: (1) h < 50 m; (2) 50 m < h < 150 m; (3) h > 150 m. There is no information on temporal variation of emissions available in the dataset.

Spatial distribution of Hg total annual emission over the globe in 2010 is illustrated in Fig. 2.1a, whereas emission speciation in different geographical regions is shown in Fig. 2.1b (see Section 2.2 for definition of the source regions). Significant Hg emissions are characteristics of industrial regions in East and South Asia, Central Europe and the eastern part of North America. These regions are also characterized by increased share of oxidized mercury forms (GOM and PBM). Besides, high emission fluxes are typical for some areas of Central and South America, Sub-Saharan Africa and Southeast Asia due to mercury releases from artisanal and small-scale gold mining (ASGM) mostly as GEM. Almost no emissions are expected in the Arctic and Antarctic regions.

Simulated spatial distributions of GEM concentration in ambient air and total mercury deposition fluxes are shown in Fig. 2.2. As seen concentration of GEM has a pronounced south-to-north gradient (Fig. 2.2a). Mercury concentrations in the Southern Hemisphere are mostly below 1.2 ng/m³, whereas in the Northern Hemisphere they range between 1.3 and 1.4 ng/m³ over the ocean and commonly exceed 1.4 ng/m³ over land. As seen GEM concentrations in East and South Asia are higher than those in Europe, which, in turn, are somewhat larger than concentrations in North America. This pattern generally reflects spatial distribution of mercury emissions (Fig. 2.1a). Elevated concentration levels simulated by the models in the northern part of South America and in Sub-Saharan Africa are caused by large contribution of emissions from ASGM.

![Fig. 2.1. Global distribution of mercury anthropogenic emissions in 2010 (a) and speciation of mercury emissions in different geographical regions (b).](image)

![Fig. 2.2. Global distribution of ensemble mean annual GEM concentration in ambient air (a) and annual total mercury deposition (b) in 2013.](image)
Calculated global distribution of Hg deposition in 2013 is shown in Fig. 2.2b. Along with high Hg deposition fluxes over large industrial regions (East and South Asia, Europe, North America etc.) and regions with significant mercury emissions from ASGM (Southeast Asia, Central and South America, Sub-Saharan Africa) relatively large deposition is also predicted over some remote areas of the oceans and in the polar regions. The former include, for instance, elevated mercury deposition in the Intertropical Convergence Zone (ITCZ) due to high precipitation intensity. The latter are characterized by intensive oxidation of GEM in the lower troposphere during AMDEs leading to increased Hg deposition in springtime.

Atmospheric deposition of mercury includes significant contribution of natural and legacy sources. The shares of contemporary anthropogenic emission sources and natural/legacy emissions are shown in Fig. 2.3. The diagram also presents average Hg deposition fluxes in various geographical regions. As seen relative contributions of these two types of emissions are comparable only in three source regions – South Asia, East Asia and Europe. In other regions the share of current anthropogenic sources varies between 20% and 35%. Contribution of natural and legacy sources is generally higher in remote regions with lower atmospheric deposition. It should be noted that models relatively well agree in simulation of the current anthropogenic deposition. In contrast, estimates of mercury deposition from legacy and natural sources vary within a factor of 2 indicating higher uncertainty of the multi-model results for this deposition component.

The main pathway of human exposure to mercury is through fish consumption [Mahaffey et al., 2004; 2009; Sunderland et al., 2010]. Mercury enters marine and freshwater ecosystems through direct anthropogenic releases, atmospheric deposition, riverine run-off and other pathways. In water bodies and bottom sediments it is converted by biotic and/or abiotic processes to methylmercury, a highly toxic mercury organic compound, which accumulates and biomagnifies in aquatic food webs [Wiener et al., 2003; Cossa et al., 2009; Sunderland et al., 2004; 2009; 2010]. It is suggested that most methylmercury accumulating in ocean fish is derived from in situ production within the upper waters, with the main source of mercury in the open ocean being from atmospheric deposition [Mason et al., 2012]. To estimate mercury loads to different aquatic regions and connect them with potential accumulation in fish we have calculated mercury deposition to the major fishing areas according to the classification of Food and Agriculture Organization [FAO, 2014a]. It should be noted that these rough estimates do not reflect chain of processes leading to mercury accumulation in fish (aquatic chemistry, methylation, movement through the trophic web etc.) but rather indicate aquatic regions with potential risk of fish contamination by mercury.
Figure 2.4a shows spatial distribution of annual mercury deposition over the ocean and location of the FAO major fishing areas (specifications of the areas are given in Table 2.1). In addition, global distribution of total mercury concentration in seawater simulated by one of the models (GEOS-Chem) is shown in Fig. 2.4b. The highest deposition fluxes are over the Northwest Pacific (area 61), Northwest Atlantic (area 21), Western Central Atlantic (area 31) and Western Central Pacific (area 71). Besides, significant fluxes are predicted also over the Antarctic Indian Ocean and Antarctic Pacific (areas 58 and 88). The simulated pattern of mercury concentration in seawater generally follows the deposition distribution. The highest concentrations are characteristics of the equatorial parts of the Atlantic and Pacific Oceans, the Northeast Atlantic, and some areas of the Southern Ocean. High concentrations are also predicted for the Mediterranean and Black Seas.

![Fig. 2.4. Spatial distribution of ensemble mean annual mercury deposition over the ocean in 2013 (a) and total mercury concentration in seawater simulated by GEOS-Chem (b). Lines show boundaries of the FAO major fishing areas [FAO, 2014a].](image)

### Table 2.1. Specifications of FAO major fishing areas [FAO, 2014a]

<table>
<thead>
<tr>
<th>Code</th>
<th>Fishing area</th>
<th>Code</th>
<th>Fishing area</th>
<th>Code</th>
<th>Fishing area</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.5 shows annual mercury deposition and concentration in seawater averaged over the FAO major fishing areas. The diagram also includes total annual marine capture fisheries production according to FAO statistics for 2012 [FAO, 2014b]. As seen the largest total capture production takes place in the Northwest Pacific (area 61), Western Central Pacific (area 71) and Northeast Atlantic (area 27). These areas are also characterized by significant mercury deposition (10-15 g/km²/y on average). Besides, mercury concentration in some locations of these aquatic areas reaches maximum values (more than 1.5 pM). Total fisheries production is also significant in the Southeast Pacific (area 87) and the Eastern Indian Ocean (area 57), where both mercury atmospheric deposition and concentration in seawater are relatively low.
Fig. 2.5. Average annual mercury deposition and total mercury concentration in the FAO major fishing areas in 2013. Total annual marine capture fisheries production in 2012 are given for the same areas for comparison [FAO, 2014b].

2.2. Estimates of mercury intercontinental transport

Source apportionment of mercury deposition, illustrating atmospheric transport of mercury between different continents and regions, was evaluated by the model ensemble. Definition of source and receptor regions adopted in the study is shown in Fig. 2.6. The considered regions include the continents (Europe, North, Central and South America, Africa, Australia), large sub-continents (Middle East, countries of the Commonwealth of Independent States (CIS), South, East and Southeast Asia) and the Polar Regions (Fig. 2.6a). Total anthropogenic emission of mercury from the selected geographical regions is shown in Fig. 2.6b. As seen the largest anthropogenic emissions are estimated for East Asia (616 t/y) and Africa (329 t/y). Considerable emissions (120-170 t/y) are also assessed for South America, Southeast and South Asia, and Central America. The smallest emissions are characteristics of Australia, Middle East and the Arctic [AMAP/UNEP, 2013].

Fig. 2.6. Definition of source and receptor regions used in the analysis (a) and share of global Hg anthropogenic emissions among the source regions (b).

As it was mentioned above mercury deposition in all regions consists of contribution of contemporary anthropogenic emissions and large contribution of natural and legacy sources. The former includes deposition from domestic emissions and mercury transported from sources located in other regions. Comparison of relative contributions of domestic and foreign anthropogenic sources to total mercury deposition in various regions simulated by the model ensemble is illustrated in Fig. 2.7. The share of domestic sources varies from zero in Antarctica to 36% in East Asia. In most regions (except for East
Asia) contribution of foreign sources is within the range 15-30%. In general, it well agrees with conclusions drawn in GMA 2013. In two regions (East and South Asia) contribution of domestic sources (25-36%) exceeds contribution of sources located outside the region (12-18%). It is determined by significant anthropogenic emissions in these regions and by dominating role of emissions from industrial and combustion sources, which include essential fraction of Hg in oxidised forms (Section 2.3). In Europe both domestic and foreign emissions contribute almost equally (20%) to total mercury deposition. It should be noted that the models somewhat differ in estimates of relative contributions of domestic and foreign sources. The main reason for that is the difference in chemical speciation of anthropogenic emissions used by the models.

On the other hand, some large contributors to global mercury emission – Africa, South America and Southeast Asia – are characterized by considerably lower contribution of domestic sources (6-11%). It can be explained by considerable portion of emissions from ASGM in these regions, which contain mercury in gaseous elemental form. The majority of these emissions contribute to the global transport instead of deposition within the region. The lowest contribution of domestic sources was estimated for Middle East (3%), Australia (2%) and the Arctic (1%), which are characterized by the lowest anthropogenic emissions (Fig. 2.6b). It should be noted that presented above average characteristics of Hg deposition can noticeably vary within the regions due to uneven spatial distribution of emission sources. In particular, contribution of domestic source can be significantly higher in the vicinity of large point sources and industrial areas.

![Fig. 2.7. Relative contribution of domestic and foreign anthropogenic sources to total Hg deposition over various regions](image)

Figure 2.8 presents source apportionment of mercury deposition from contemporary anthropogenic sources to various geographical regions of the world. As it has been mentioned above mercury anthropogenic deposition to Europe consists of almost equal contributions of domestic and foreign anthropogenic emissions. The largest external contributors include East Asia (20%), Africa (8%), CIS countries (5%), and South Asia (3%). Contribution of domestic sources to mercury deposition to North America (23%) is smaller than contribution of East Asia (32%). Africa (12%), CIS countries (6%) and Central America (6%) are among other significant contributors of deposition from contemporary anthropogenic emissions. In contrast, anthropogenic deposition of mercury to East and South Asia is dominated by contributions of domestic sources (76% and 58%, respectively). Mercury deposition to remote regions such as the Arctic and Antarctica is determined by long-range atmospheric transport from major source regions. The major contributors for both regions are East Asia and Africa. The Arctic is also affected by emission sources located in Europe and the CIS countries, whereas Antarctica is influenced by South and Central Americas.
Fig. 2.8. Source apportionment of mercury deposition from contemporary anthropogenic emissions to various geographical regions in 2013.

Mercury deposition to aquatic regions is affected by both littoral emission sources and long-range atmospheric transport. As seen from Fig. 2.9 East Asia is the largest contributor to mercury deposition in almost all the aquatic regions. Its contribution to mercury deposition from contemporary anthropogenic sources varies from 25% to 53%. It is followed by sources located in Africa (11-26%). The exception is the Mediterranean and Black Seas, which are dominated by European emissions. As it has been mentioned above, the regions where considerable mercury deposition is accompanied by large total capture fisheries production include the Northwest Pacific, the Western Central Pacific and the Northeast Atlantic (Section 2.1). Anthropogenic deposition of mercury in these regions is mostly determined by emissions from East Asia, Africa, Europe, CIS countries, South and Southeast Asia.
Both absolute and relative contributions of different source regions to mercury deposition vary in time during a year. Figure 2.10 presents estimated by the model ensemble mean seasonal variation of source apportionment of mercury deposition to various geographical regions. As seen, seasonal variation of deposition from domestic sources is considerably smaller than that from foreign and natural/legacy sources. It is particularly seen in Europe, the CIS countries, North and Central Americas (Figs. 2.10a-2.10d). It should be noted that temporal variation of direct anthropogenic emissions is not taken into account in the study. Given that local and regional mercury deposition is largely caused by removal of directly emitted oxidized mercury forms (GOM and PBM), variation of deposition from domestic sources is mostly determined by changes of the environmental conditions affecting removal processes (precipitation amount, stability of atmospheric boundary layer, vegetation height etc.)

In contrast, deposition of Hg transported from other regions is highly affected by oxidation chemistry, which converts GEM transported in the atmosphere to GOM and PBM deposited to the ground by wet removal and surface uptake. Therefore, contribution of foreign sources is larger in summer when mercury oxidation is more intensive. In case of natural and legacy sources, the seasonal pattern is also affected by intensity of Hg evasion from the surface. During the warm season natural and legacy emission of mercury are higher due to increased temperatures and solar radiation as well as absence of snow cover. Similar to the Northern Hemisphere the seasonal variation of mercury deposition is also well pronounced in regions located in the Southern Hemisphere (South America and Australia) with maximum deposition in summer and minimum deposition in winter (Figs. 2.10g-2.10h). Deposition in the Arctic and Antarctica has pronounced maximums in springtime of the respective hemisphere, due to intensive mercury oxidation and removal during the Atmospheric Mercury Depletion Events (Figs. 2.10i-2.10j).

![Fig. 2.9. Source apportionment of mercury deposition from contemporary anthropogenic sources to various aquatic regions in 2013](image-url)
Fig. 2.10. Seasonal variation of source attribution of average Hg deposition to various regions in 2013.
2.3. Mercury deposition from different emission sectors

The model ensemble was also applied for simulation of mercury deposition from different anthropogenic emissions sectors. An additional subset of the global mercury emissions inventory 2010 that provides sector specific emissions data was used for this purpose [AMAP, 2014]. In the subset the sectors of mercury anthropogenic emissions were aggregated into three general groups:

- Stationary combustions sources including power plants and distributed heating;
- Industrial sources including stationary combustion for industry;
- Intentional use and product waste associated sectors including artisanal and small-scale gold mining.

Spatial distribution of mercury emissions from the sector groups is shown in Fig. 2.11. The majority of emissions from stationary combustion sources are located in the largest industrial and populated regions of the Northern Hemisphere – East and South Asia, Europe and North America – as well as in Southern Africa in the Southern Hemisphere (Fig. 2.11a). Emissions from industrial sources are sporadic but are distributed somewhat wider then stationary combustion sources (Fig. 2.11b). Significant part of mercury emissions from intentional use and product waste relates to South America, Sub-Saharan Africa and East and Southeast Asia (Fig. 2.11c). Total emissions from the three sector groups amount to 379, 642 and 854 t/y for stationary combustion, industrial sources and intentional use and product waste, respectively.

Chemical speciation of mercury emissions differs considerably between different sector groups (Fig. 2.11c). According to the applied inventory [AMAP/UNEP, 2013; AMAP, 2014], emissions from stationary combustion consists of approximately equal contributions of elemental mercury (GEM) and oxidized forms (GOM, PBM). Proportion of oxidized mercury is much smaller in emissions from industrial sources (20%). More than 95% of mercury emissions from intentional use and product waste are in elemental gaseous form. It should be noted that estimates of mercury emissions speciation are associated with significant uncertainties [Amos et al., 2012; Zhang et al., 2012; Kos et al., 2012] that can affect results of the analysis.

![Fig. 2.11. Spatial distribution of mercury emissions from three groups of emission sectors: (a) - stationary combustion sources; (b) - industrial sources; (c) - intentional use and product waste. (d) - presents chemical speciation of Hg emissions from the sector groups.](image)
Simulated global patterns of relative contributions of the three sector groups to total mercury deposition are shown in Fig. 2.12. Impact of stationary combustion sources is mostly limited by large industrial regions in East and South Asia, Europe, the eastern part of North America and South Africa, where contribution of this group of sectors exceeds 20-30% of total mercury deposition (Fig. 2.12a). On the other hand, its contribution is below 10% in other regions. This spatial character is determined by significant proportion of short lived oxidized mercury forms in emissions from this sector group. It leads to intensive mercury deposition in the vicinity of the source regions. Emissions from industrial sources affect the whole Northern Hemisphere, where its contribution to deposition exceeds 10% (Fig. 2.12b). Mercury released from intentional use and product waste (mostly as GEM) can be transported globally. Contribution of this sector group varies between 10% and 30% everywhere over the world with maximum impact in the equatorial zone (Fig. 2.12c).

Fig. 2.12. Ensemble mean relative contribution of different groups of emission sectors to total mercury deposition in 2013: (a) - stationary combustions sources; (b) - industrial sources; (c) - intentional use and product waste.

The sectoral composition of mercury deposition in different geographical regions is illustrated in Fig. 2.13. As seen anthropogenic mercury deposition in the major source regions is largely determined by stationary combustion and industrial sources. These emission sectors dominate in Asia, Europe, North America and the CIS countries. In contrast, regions with smaller emissions (Central and South America, Australia and New Zealand, the Arctic etc.) are significantly affected by mercury from intentional use and product waste associated sectors.

Fig. 2.13. Contribution of the groups of emission sectors to average mercury deposition from contemporary anthropogenic sources over various regions in 2013 simulated by the model ensemble.
2.4. Concluding remarks

Assessment of mercury atmospheric dispersion and deposition on a global scale as well as evaluation of intercontinental transport and source apportionment of mercury deposition have been performed based on simulation results of the ensemble of global scale models. The major conclusions of the study are summarized below.

- High mercury deposition fluxes are characteristics of the large industrial regions (East and South Asia, Europe, North America etc.) and regions with significant mercury emissions from artisanal and small-scale gold mining (Southeast Asia, Central and South America, Sub-Saharan Africa). Relatively large deposition is also detected over some remote areas of the oceans and in the Polar Regions.

- Mercury deposition in all geographical regions consists of contribution of anthropogenic emissions from the regions’ domestic sources, mercury transported from sources located in other regions, and significant contribution of natural and secondary sources. The share of current anthropogenic emissions varies between 20% and 50%. Contribution of natural and legacy sources is generally higher in remote regions with lower atmospheric deposition.

- Contribution of domestic source varies from zero (Antarctica) to 36% (East Asia). In all the regions contribution of foreign sources is within the range 12-30%

- Mercury anthropogenic deposition to Europe consists of almost equal contributions of domestic and foreign anthropogenic emissions. The largest external contributors include East Asia (20%), Africa (8%), CIS countries (5%), and South Asia (3%). Contribution of domestic sources to mercury deposition to North America (23%) is much smaller than contribution of other source regions, the largest of which include East Asia (32%), Africa (12%), CIS countries (6%) and Central America (6%). In contrast, anthropogenic deposition of mercury to East and South Asia is dominated by contributions of domestic sources (76% and 58%, respectively).

- Oceanic regions characterized by both significant Hg deposition and the highest total capture fisheries production include the Northwest Pacific, Western Central Pacific and Northeast Atlantic. Anthropogenic deposition of mercury in these regions is mostly determined by emissions from East Asia, Africa, Europe, CIS countries, South and Southeast Asia.

- Estimated seasonal variation of deposition from domestic sources is considerably smaller than that from foreign and natural/legacy sources and it is mostly determined by changes of environmental conditions affecting removal processes. Contribution of foreign sources is larger in summer when mercury oxidation is more intensive. In case of natural and legacy sources, the seasonal pattern is also affected by intensity of Hg emission from the surface.

- Anthropogenic mercury deposition in industrial regions is largely determined by emissions from stationary combustion and industrial sources. In contrast, regions with smaller emissions are significantly affected by mercury emissions from intentional use and product waste associated sectors.
3. FUTURE CHANGES OF MERCURY POLLUTION

Assessment of future levels of Hg pollution and evaluation of different abatement scenarios are the key information for development of future mitigation measures. It is particularly topical in the context of the recently adopted Minamata Convention for Mercury – a global treaty to protect human health and the environment from the adverse effects of mercury (http://www.mercuryconvention.org/). Mercury differs from other heavy metals by its ability to long-range dispersion in the atmosphere. The bulk mercury atmospheric form – gaseous elemental mercury – can drift in the atmosphere for months moving over distances of thousands of kilometres. Therefore, changes of Hg pollution in the EMEP countries are largely affected by emission dynamics in other geographical regions and require assessment on a global scale.

Evaluation of future Hg pollution levels in the EMEP and other regions has been performed as a part of collaborative MSC-E activities within the EU GMOS project. GMOS as an integrated research project focused on various aspects of mercury pollution assessment provides a platform for evaluation of both contemporary and future levels of Hg content in the environment on a global scale. Along with establishment of a global scale observational network for Hg and performing ad-hoc oceanographic and tropospheric measurements the project provides up-to-date inventories of Hg anthropogenic emissions and future emission scenarios. In addition, an important component of the project consists of development and application of global and regional scale models for assessment of Hg air concentrations and deposition, source apportionment and evaluation of future emission scenarios.

The current study is focused on application of the GLEMOS model for assessment of future Hg atmospheric concentration and deposition levels as well as source-receptor relationships. For this purpose a number of model simulations have been performed for selected Hg emission scenarios for 2035. Main results of the study are discussed below.

3.1. Future mercury emission scenarios

The global inventory of mercury anthropogenic emissions for 2010 [AMAP/UNEP, 2013] was used as a reference point for evaluation of future changes. Spatial distribution of Hg anthropogenic emissions over the globe in 2010 is shown in Fig. 1a. As seen significant Hg emission fluxes were characteristics of industrial regions in East and South Asia, Central Europe and the eastern part of North America. Besides, high emissions are typical for some areas of Central and South America, Sub-Saharan Africa and Southeast Asia due to mercury releases from artisanal and small-scale gold mining. Definition of the geographical regions used in the study was based on the specifications adopted in the Phase II of the multi-model experiments under the CLRTAP Task Force on Hemispheric Transport of Air Pollution, TF HTAP (Fig. 3.1b).

![Fig. 3.1. Global distribution of mercury anthropogenic emissions in 2010 (a) and definition of source and receptor regions used in the analysis (b).](image-url)
A number of future emission scenarios for 2035 have been developed within the EU GMOS project based on current and newly planned emission measures and energy consumption patterns. They consider the prospects for reducing Hg emissions from Hg specific measures or as a co-benefit from climate, pollutant and energy policy. The scenarios used in the study include:

- The ‘Current Policy’ scenario (CP 2035) assuming that governmental policies and measures existing in 2010 have been adopted, including those that have not been fully implemented. It gives a baseline vision on energy, industrial production as well as the use of air pollution control devices and waste management practices that are likely to change given no additional effort with regard to policy making.

- The ‘New Policy’ scenario (NP 2035) assuming that policy commitments and plans announced by countries worldwide to reduce greenhouse gas emissions, as well as phase out fossil-energy subsidies, were fully implemented.

- The ‘Maximum Feasible Reduction’ scenario (MFR 2035) set out a target of all counties reaching the highest feasible reduction efficiency in each emission sector. The scenario illustrates the maximum possible Hg emission reductions that could be achieved if no other constraints have been taken into account, such as economy and increased demand.

Figure 3.2 shows total Hg anthropogenic emissions in various geographical regions according to the reference year 2010 and three selected emission scenarios for 2035. In the EMEP region as well as in the majority of other regions the CP 2035 scenario implies from weak to moderate reduction of Hg emissions between 2010 and 2035. Exceptions are East Asia and South Asia where the ‘Current Policy’ scenario expects emissions increase. The MFR 2035 scenario predicts essential Hg emissions decrease in all regions of the world. The NP 2035 presents an intermediate case with moderate reduction.

![Fig. 3.2. Total Hg anthropogenic emissions in various geographical regions in 2010 and 2035 according to selected emission scenarios.](image)

### 3.2. Changes of mercury deposition levels

Long-term changes of Hg pollution in future have been evaluated with the GLEemos model. Model simulation results for the three emissions scenarios of 2035 (CP2035, NP2035 and MFR2035) were compared with the reference case of 2010 to predict changes of Hg atmospheric dispersion and deposition on a global scale. Meteorological data for 2013 were used in all simulations to exclude the influence of inter-annual meteorological variability. Each model run consisted of the multi-year spin-up to reach the steady-state conditions and a one-year control simulation for the ultimate results.
Geogenic and legacy sources were taken unchangeable over the considered period. Thus, the presented results reflect response of Hg atmospheric deposition to changes of direct anthropogenic emissions and do not take into account possible feedback of the ocean and terrestrial reservoirs to these changes.

Figure 3.3a shows global distribution of Hg deposition flux simulated by GLEMOS for the reference year 2010. The largest deposition levels are characteristics of East and South Asia, which agrees with the spatial distribution of anthropogenic emissions (Fig. 3.1a). There are also significant deposition fluxes over the ocean, in the so called ‘Inter Tropical Convergence Zone’, which is characterized by enhanced precipitation. The model also predicts increased deposition fluxes in the polar regions due to the effect of the Atmospheric Mercury Depletion Events, AMDEs [Schroeder et al., 1998; Lindberg et al., 2002; Steffen et al., 2008].

Projections of future changes in Hg deposition on a global scale simulated GLEMOS for three emissions scenarios of 2035 are illustrated in Figs. 3.3b-3.3d. The ‘Current Policy’ scenario (CP2035) supposes considerable decrease (20-30%) of Hg deposition in Europe and North America and strong (up to 50%) increase in South and Eastern Asia (Fig. 3.3b). In most of other parts of the Northern Hemisphere no significant changes (±5%) are expected, whereas slight decrease (5-15%) of deposition will take place in the Southern Hemisphere.

According to the ‘New Policy’ scenario (NP2035) moderate decrease of Hg deposition (20-30%) is predicted over the whole globe except for South Asia (India), where some deposition increase (10-15%) is expected due to the growth of regional anthropogenic emissions (Fig. 3.3c). Model predictions based on the ‘Maximum Feasible Reduction’ scenario (MFR2035) demonstrate consistent Hg deposition reduction on a global scale with somewhat larger decrease in the Northern Hemisphere (35-50%) and smaller decrease (30-35%) in the Southern Hemisphere (Figs. 3.3d). Thus, the most significant changes in Hg deposition (both increase and decrease) during the next 20 years for all considered scenarios are expected in the Northern Hemisphere and, in particular, in the largest industrial regions, where the majority of regulated emission sources are located.

**Fig. 3.3.** Global distribution of Hg deposition in 2013 (a) and relative deposition changes by 2035 according to three emission scenarios: (b) – CP 2035; (c) – NP2035; (d) – MFR 2035.
Dynamics of Hg deposition between 2010 and 2035 in various geographical regions according to the selected emission scenarios is illustrated in Fig. 3.4. As it was mentioned above, the model predicts that the highest contemporary fluxes and the most significant changes in Hg deposition are characteristics of South, East and Southeast Asia. Mercury deposition will increase or decrease up to a factor of two in these regions depending on realized scenario. All other regions are characterized by insignificant changes (CP2035) or deposition reduction (NP2035 and MFR2035). The smallest changes are expected in regions remote from significant emissions sources (e.g. the Arctic and Antarctica).

![Fig. 3.4. Average Hg deposition flux in various geographical regions for 2010 and 2035 corresponding to the selected emission scenarios.](image)

### 3.3. Changes of source apportionment of mercury deposition

Source apportionment of Hg deposition from direct anthropogenic sources in different geographical regions is illustrated in Fig. 5. Contributions of natural and legacy emissions are not shown in the figure. Both CP 2035 and MFR 2035 scenarios suppose considerable reduction of Hg deposition in the EMEP region, North America and some other regions during the next 20 years (Figs. 3.5a and 3.5d). Relative contribution of various source regions to Hg deposition slightly changes for the both scenarios. The only exception is enhanced deposition from South Asia to these regions according to CP 2035. In contrast, in East and South Asia the CP 2035 scenario leads to substantial increase of Hg anthropogenic deposition due to increase of domestic emissions (Figs. 3.5h and 3.5i).
Fig. 3.5. Source apportionment of average Hg deposition from direct anthropogenic sources in 2013 and 2035 in various geographical regions: (a) – EMEP region; (b) - Arctic; (c) – Africa; (d) – North America; (e) – Central America; (f) – South America; (h) – East Asia; (i) – South Asia; (j) – Australia and New Zealand.
3.4. Concluding remarks

Future changes of Hg pollution levels on a global scale as well as source-receptor relationships of Hg deposition in different geographical regions have been evaluated for three emission scenarios for 2035 using two GMOS consortium global models (GLEMOS and ECHMERIT). Despite considerable deviations in deposition levels the models substantially agree in predictions of relative changes of Hg atmospheric loads over the considered period. The major conclusions of the study are summarized below:

- The most significant changes in Hg deposition (both increase and decrease) during the next 20 years for all considered scenarios are expected in the Northern Hemisphere and, in particular, in the largest industrial regions, where the majority of regulated emission sources are located.

- The ‘Current Policy’ scenario (CP2035) supposes considerable decrease (20-30%) of Hg deposition in Europe and North America and strong (up to 50%) increase in South and Eastern Asia, whereas no significant changes are expected in other regions.

- According to the ‘New Policy’ scenario (NP2035) moderate decrease of Hg deposition (20-30%) is predicted over the whole globe except for South Asia (India), where some deposition increase (10-15%) is expected due to the growth of regional anthropogenic emissions.

- Model predictions based on the ‘Maximum Feasible Reduction’ scenario (MFR2035) demonstrate consistent Hg deposition reduction on a global scale with somewhat larger decrease in the Northern Hemisphere (35-50%) and smaller decrease (30-35%) in the Southern Hemisphere.
4. MODEL ASSESSMENT OF GLOBAL SCALE POP POLLUTION LEVELS

Model assessment of POP pollution levels in the EMEP domain is based on multi-media modelling approach being developed in the framework of the Global EMEP Multi-media Modelling System (GLEMOS). This approach takes into account peculiarities of POP transport and fate in the environment (e.g. phase partitioning, degradation in media, multi-hop transport). For long-lived POPs it is important to evaluate global scale transport and contribution of non-EMEP sources to the pollution levels in the EMEP countries.

This year MSC-E has continued development and application of the GLEMOS modelling system for POPs in several directions. Further work was carried out to prepare the GLEMOS for the transition of the EMEP operational modelling of HM and POP pollution to the new EMEP grid including preparation of meteorological and geophysical data. There is ongoing work on the incorporation of gridded data on aerosols and atmospheric reactants based on the output of chemistry transport models to describe gas-particle partitioning of POPs and their degradation in the atmosphere. On subsequent stages it is planned to develop simplified chemical modules for the GLEMOS modelling system, which can provide necessary information on atmospheric aerosols and reactants in course of modelling of POP transport and fate. Further refinement of the GLEMOS multimedia modelling approach for POPs is being continued. Current activities in this direction include collection of measurements obtained in various campaigns aimed at parallel monitoring of POP concentrations in the atmosphere, water and soil compartments to perform testing and improving of multi-media modelling of POP transport and fate. Results of these activities will be reported on further stages of the work.

This chapter provides results of model simulations of global scale dispersion of selected POPs, namely, PCDD/Fs, HCB, and PCBs, using geographic (latitude-longitude) projection and their comparison with measurements of the EMEP monitoring network and measurements of the UNEP SC Data Warehouse.

4.1. Emission data for model assessment

Long-term variations of POP pollution in the EMEP region depend on temporal changes of releases from anthropogenic and secondary emission sources. Secondary emissions are represented by the re-mobilization of POPs from surface media (e.g. soil, water bodies), where they have been previously accumulated due to legacy (historical) emissions. Significant contribution to the pollution of the EMEP countries can be made by non-EMEP anthropogenic and secondary emission sources, taking place in other regions outside the EMEP domain. In order to evaluate relative contributions of these sources scenarios of global HCB, PCDD/F and PCB emissions (including historical emissions) were updated and used for the evaluation of POP global transport and fate.

**PCB emissions**

Assessment of global scale transport and fate of PCBs was made on the basis of the inventory of global PCB emissions [Breivik et al., 2007] and emissions officially reported by the EMEP countries. The inventory of Breivik et al. [2007] provided consistent set of historical and future emissions of 22 individual PCB congeners from 1930 up to 2100. It included three scenarios of emissions, namely, minimum, average, and maximum, which represented the range of emission variations. For the evaluation of pollution levels maximum scenario of emissions was chosen since it permitted to obtain modelling results with more reasonable agreement with measurements comparing to average and minimum scenarios. Modelling of pollution levels for 1990 and 2013 was carried out for indicator congener PCB-153. Estimates of global PCB-153 emissions for the period 1930-2013 are shown in
Fig. 4.1a. It is seen that peak of global emissions was reached in late 1970s. After that significant decrease of global emission took place due to the banning of PCB production and use. In the period 1990-2013 the rate of decrease was slowing down (Fig. 4.1b). Emissions of PCB-153 congener decreased from its maximum in 1975 to 2013 by 13 times. The decline from 1990 to 2013 is estimated to 9 times.

Fig. 4.1. Scenario of temporal variations of global emission of PCB-153 to the atmosphere in the period 1930-2013 (a) and in the period 1990-2013 (b)

The spatial distribution of PCB-153 emissions for 1990 and 2013, used for global modelling with resolution 1°x1°, is illustrated in Fig. 4.2. It can be seen that considerable levels of PCB-153 emission fluxes are the characteristic of the EMEP region. Other regions are characterised by comparatively lower annual emissions.

Fig. 4.2. Spatial distribution of PCB-153 emissions in 1990 (a) and in 2013 (b) over global domain with resolution 1°x1°

HCB emissions

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. Three scenarios of historical HCB emissions (maximum, average and minimum), elaborated previously [Shatalov et al., 2010], were updated and used for modelling of long-term accumulation of the pollutant in the environmental media. Model simulations carried out for this report were made applying the maximum emission scenario, which allowed to get better agreement with available measurements of HCB air concentrations. Following available information the application of HCB, largely in agricultural activities as a fungicide, was started from 1945 and reached its maximum in 1980-s. Estimates of global HCB emissions for the period 1945-2013 are given in Fig. 4.3a. Starting from 1980-s the agricultural use of HCB was banned in many countries world-wide resulting in considerable decrease of primary emission of HCB and the increase of relative importance of HCB re-volatilization. Changes of estimated global HCB emissions in the
period 1990-2013 are shown in Fig. 4.3b). According to constructed scenario emissions of HCB decreased from its maximum in 1978 to 2013 by more than 400 times. The decline of HCB emission from 1990 to 2013 is estimated to 7 times.

Spatial distributions of global HCB emission fluxes for 1990 and 2013 are shown in Fig. 4.4. The largest HCB emission fluxes took place in Southern and Eastern Asia. Releases of HCB to the atmosphere in the EMEP region were relatively lower.

PCDD/F emissions

Modelling of global scale transport and fate of PCDD/Fs has been carried out using experimental emission scenario constructed on the basis of the data of the UNEP SC inventory. This inventory is being compiled under SC using the methodology of the UNEP Standardized Dioxins Toolkit [Fiedler, 2007; Fiedler et al., 2012; UNEP, 2013]. The inventory comprises data on national emissions of dioxins and furans reported by 68 countries characterizing the level of emissions during the recent decade. For other countries, which did not provide information on their emissions, releases of PCDD/Fs were estimated using the analysis of compiled national inventories carried out by Cao et al. [2013] (Fig 4.5a).

It was found that the intensity of PCDD/F emissions in the countries correlated with their economic status. Obtained regression relationship between the national PCDD/F emissions and the data on Gross Domestic Product and total population of the countries was applied to estimate emissions for the other countries, for which the information on emissions was not available (Fig. 4.5b).
Fig. 4.5. Distribution of countries submitted their PCDD/F emission data to the SC (blue) and countries for which regression analysis (grey) and other data on emissions (green) were used (a) and regression relationship between annual PCDD/F releases of the countries and their Gross Domestic Product (b).

Compiled inventories covered main modes of entry of emissions to the environment (the atmosphere, land, water, residues, and products), among which major releases were indicated to the atmosphere (45%). Releases of PCDD/Fs to the atmosphere and land compartments were taken into account in the constructed scenario for modeling, while other vectors were neglected. More detailed description of this experimental scenario can be found in the MSC-E Technical Report [Shatalov et al., 2014]. Elaborated emission scenario was based on the inventories reported by countries for different years of the period 2000-2010 and thus represents the level of emissions during the recent decade.

Spatial distribution of PCDD/F emissions to air and soil with resolution 1°x1°, which was used in model simulations, is shown in Fig.4.6. Elevated levels of emissions are estimated for countries of Central Africa, Southern and Eastern Asia, and Europe. Relatively low emissions are characteristic of North and South America, and Australia.

Fig. 4.6. 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.
4.2. Evaluation of POP pollution levels and comparison with measurements

Polychlorinated biphenyls (PCBs)

Model assessment of PCB pollution levels in the EMEP countries was carried out using combination of global and regional scale modelling. Model simulations were made for the indicator congener PCB-153. In order to perform evaluation of transboundary transport of PCB-153 between the EMEP countries global model simulations were used to prepare initial and boundary conditions for regional modelling within the EMEP region. Results of global scale model simulations were compared with measurements of the EMEP monitoring network and of the UNEP SC GMP Data Warehouse.

Global distributions of annual mean PCB-153 air concentrations evaluated for 1990 and 2013 are presented in Fig. 4.7. The figure illustrates significant decline of global scale pollution levels from 1990 to 2013. According to available data on PCB emissions about 90% of PCBs during the period of its production and use were released into the environment in the Northern Hemisphere. Elevated levels of pollution can be seen in the Northern Hemisphere which is explained by the location of major emission sources of PCBs in the European region and in North America.

In 2013 elevated air concentrations are seen in Europe (1-10 pg/m$^3$) and North America (0.25-2.5 pg/m$^3$), while the other regions are characterized by low air concentrations (0.01-0.1 pg/m$^3$) which is generally confirmed by measurements.

![Fig. 4.7. Spatial distribution of global annual mean PCB-153 air concentrations (pg/m$^3$) for 1990 (a) and 2013 (b) with spatial resolution 1°x1°.](image)

![Fig. 4.8. Location of monitoring sites performed measurements of PCB-153 air concentrations (a) and comparison of annual mean modelled PCB-153 concentrations with measurements made in the period 1995-2013. Solid lines denote the area of agreement within a factor of 5, and dashed line – a factor of 10.](image)
Results of model simulation for PCB-153 were compared with available measurements performed from the beginning of 1990s up to 2013 in various regions of the world in the remote, background, and rural areas (Fig. 4.8). Measurement data were obtained from the UNEP SC GMP Data Warehouse and included measurements made using active and passive sampling of POP air concentrations. Location of the monitoring sites which belong to the EMEP monitoring network as well as to other networks is illustrated in Fig. 4.8a. Comparison indicates that for more than 70% of model predictions the difference between modelled and observed air concentrations is within a factor of five and for about 40% of them it is within a factor of two (Fig. 4.8b). The spatial correlation of model predictions and measurements is better for the European and North American regions, while for other regions the level of correlation is lower.

Comparison of model predictions and measurements of PCB-153 air concentrations in several regions of the world is illustrated in Fig. 4.9.

Model generally captures the spatial distribution of observed levels of pollution. Results of model simulations reasonably well agree with measurements carried out in the European countries as well as in the countries of Central Asia and the Caucasus region. At the same time, significant differences between the modelling results and measurements are obtained for South America, Africa, Asia, and Australia. It is seen that about a half of model predictions for these regions are in reasonable agreement with measurements, while some of the measurements are significantly underestimated by
the model exhibiting the tendency to underpredict levels of PCB-153 air concentrations in the Southern Hemisphere. This underprediction can be attributed to larger uncertainties in the emissions for these regions comparing to the Northern Hemisphere.

![Graphs showing observed and modeled PCB-153 air concentrations for different locations over time.](image)

**Fig. 4.10.** Comparison of annual mean modelled PCB-153 air concentrations with long-term measurements of the EMEP monitoring sites (NO42, IS91, FI96, SE12, SE2/14) for the period 1990-2013.

In general, the model closely describes temporal variations of observed pollution levels during the two recent decades. In particular, time-series of PCB-153 annual mean air concentrations measured at the EMEP monitoring sites NO42, IS91, FI96, SE12, and SE2/14, were reasonably well reproduced by the model, especially for the recent decade (2004-2013). At the same time, higher differences can be seen for the period 1994-2003 due to more significant uncertainties in the estimates of emissions and results of monitoring of PCB air concentrations.
Fig. 4.11. Comparison of monthly mean modelled PCB-153 air concentrations (pg/m$^3$) with long-term measurements of the EMEP monitoring sites SE12, SE2/SE14, and FI96.

Along with long-term variations of annual mean concentrations the model satisfactorily described seasonal variations of PCB-153 concentrations in air observed at the EMEP sites. Examples of comparison of modelling results with monthly mean measured concentrations for the sites SE2/14, SE2, and FI96 are shown in Fig. 4.11.

**Hexachlorobenzene (HCB)**

Evaluation of HCB pollution of the EMEP region was performed using nested global and regional scale model simulations. Experimental scenario of global contemporary and historical HCB emissions was updated taking into account official emission data reported by the EMEP countries for the period 1990-2013. Global dispersion of HCB and its accumulation in the environmental media were evaluated for the period 1945-2013. Results of global model simulations were used to generate initial and boundary conditions for regional modelling in order to evaluate levels of pollution in the EMEP region with higher spatial resolution and to estimate transboundary transport of pollution between the EMEP countries. Modelled air concentrations of HCB were evaluated against measurements of the EMEP monitoring sites and observations collected in the UNEP SC GMP Data Warehouse.
Estimates of spatial distribution of annual mean HCB concentrations in air obtained for 1990 and 2013 are illustrated in Fig. 4.12. As seen from the figure, levels of HCB air concentrations substantially decreased from 1990 to 2013.

**Fig. 4.12. Spatial distribution of global annual mean HCB air concentrations (pg/m³) for 1990 (a) and 2013 (b) with spatial resolution 1°x1°.**

According to modelling results major sources of HCB pollution include Southeast Asia, Europe, Central Asia, and North America. In 2013 elevated air concentrations can be seen in Southeast Asia and Eastern Europe (30-100 pg/m³), while the other regions are characterized by relatively lower concentrations (5-30 pg/m³) which is consistent with observed levels.

To evaluate modelling results available measurements of HCB air concentrations carried out in the period 1990-2013 were used. Observed concentrations were obtained from the UNEP SC GMP Data Warehouse. Measurements performed in the remote, background, and rural areas using active and passive sampling were selected. Location of the monitoring sites which belong to the EMEP monitoring network as well as to other networks is illustrated in Fig. 4.13a. Comparison of modelled and observed HCB annual mean air concentrations is shown in Fig. 4.13b. Evaluation of model predictions shows that almost 90% of modelled concentrations agree with observed air concentrations within a factor of five and for about 45% of them the agreement is within a factor of two. In general, the model captures spatial distribution of observed HCB pollution levels.

Level of agreement between the modelled and measured HCB air concentrations in several regions of the world is shown in Fig. 4.14.

**Fig. 4.13. Location of monitoring sites performed measurements of HCB air concentrations (a) and comparison of annual mean modelled HCB concentrations with measurements made in the period 1990-2013 (b). Solid lines denote the area of agreement within a factor of 5, and dashed line – a factor of 10.**
It is seen that model predictions reasonably agree with measurements made in most of the regions. At the same time, the model slightly underestimates HCB air concentrations in North America, Western Europe, Central and Eastern Europe.

The underestimation of HCB air concentrations is likely caused by the uncertainties of emission scenario applied in model simulations and requires further analysis in cooperation with experts in the field of POP emissions and measurements.

Long-term variations of HCB air concentrations observed during the two recent decades at two EMEP sites (CZ3, NO99) and three Canadian sites (Eagle Harbour, Sleeping Bear Dunes, and Sturgeon Point) of IADN monitoring network were reasonably reproduced by the model (Fig. 4.15). At the same time, it is seen that the model overestimate levels of HCB air concentrations in early 1990s about a factor of 2-3.

Fig. 4.14. Comparison of annual mean modelled HCB air concentrations with measurements made in different regions in the period 1990-2013. Solid lines denote the area of agreement within a factor of 5, and dashed line – a factor of 10.
Fig. 4.15. Comparison of annual mean modelled HCB air concentrations with long-term measurements of the EMEP monitoring sites (CZ3, NO99) and the IADN sites (Eagle Harbour, Sleeping Bear Dunes, Sturgeon Point) for the period 1990-2013.

Measurements of Canadian monitoring sites demonstrate increase of HCB content in air in recent years (2010-2012) which is not captured by the model. These differences indicate the need of further refinement of the scenario of global historical HCB emissions.

Analysis of temporal variations of HCB air concentrations for the two remote sites, NO42 and IS91, indicates larger difference between the model predictions and measured values (Fig.4.16). Particularly, model overestimates annual average reduction for the period 1990-2013 and does not capture the growth of HCB air concentrations observed at NO42 in the end of the period. The reason of the differences is connected with that the levels of pollution at these sites are likely influenced by the emission sources outside the EMEP domain.
Polychlorinated dioxins and furans (PCDD/Fs)

This year model evaluation of global scale transport and fate of dioxins and furans was continued on the basis of the experimental emission scenario based on the emission inventory of the UNEP SC described in [Gusev et al., 2014a; Shatalov et al., 2014]. Model simulations were performed with the meteorological data for 2012 and spatial resolution 1° x 1°. Initial conditions to evaluate pollution levels in 2012 were obtained using long-term spin-up model run for the period from 1930s to present time. Spatial distribution of annual mean PCDD/F air concentrations for 2012 is presented in Fig. 4.17.

Results of model simulations indicated elevated levels of PCDD/F air concentrations (> 10 fg TEQ/m³) in Africa and South and East Asia. Lower levels of pollution were characteristic of Europe, North and South America, and Australia. Comparison of model predictions with measurements of PCDD/F air concentrations in Europe, North America, and East Asia showed reasonable agreement between modelled and observed air concentrations [Gusev et al., 2014b].

Fig. 4.16. Comparison of annual mean modelled HCB air concentrations with long-term measurements of the EMEP monitoring sites (NO42, IS91) for the period 1990-2013.

Fig. 4.17. Spatial distribution of modelled annual mean PCDD/F concentrations in air (fg TEQ/m³) obtained for 2012.

Fig. 4.18. Comparison of modelled annual mean PCDD/F air concentrations for 2012 (fg TEQ/m³) with measurements performed in South America region. Dashed lines denote the area of agreement between modelled and measured values within a factor of 2, solid lines – within a factor of 5.
In 2015 results of global scale model simulations were evaluated against the measurements of dioxins and furans air concentrations carried out in South America [Schuster et al., 2015]. Monitoring of PCDD/Fs in air was performed in the period 2011-2013 using a passive air sampling network established on the basis of Global Atmospheric Passive Sampling (GAPS) sites and six additional sites in the Group of Latin American and Caribbean Countries region (GRULAC).

Model predictions obtained for 2012 are in reasonable agreement with measured air concentrations (Fig. 4.18). For more than a half of the sites, modelled values are within a factor of two with measurements and are found to correlate with observed levels. For some of the urban and rural sites model predictions are lower than observed air concentrations, which is likely caused by the uncertainties in the spatial distribution of PCDD/F emissions, which is based on the density of population. Along with this comparison, there is ongoing work on the evaluation of modelling results for PCDD/Fs using the measurements collected in the UNEP SC GMP Data Warehouse. Results of this activity will be reported on further stages of the work.

To improve evaluation of PCDD/F pollution further co-operation with relevant activities on the assessment of PCDD/F emissions and monitoring of their content in the atmosphere, performed under the UNEP SC, is of importance.

4.3. Concluding remarks

In this chapter results of ongoing work on the transition of the EMEP operational modelling of HM and POP pollution to the new EMEP grid in latitude-longitude projection are summarized. Particularly, further work was performed with the GLEMOS modelling system to evaluate global scale distribution of PCDD/Fs, HCB, and PCB-153 using the longitude-latitude projection. Model predictions were evaluated against available measurements of the EMEP monitoring network and measurement data collected in the UNEP SC GMP Data Warehouse. Main outcome of this work is summarized below:

- Comparison of PCB-153 global modeling results indicated satisfactory agreement of model predictions with measurements made at monitoring sites of the EMEP network as well as of other networks based on the active and passive sampling. However, levels of PCB-153 air concentrations observed in Africa and Central Asia are underestimated by the model, which can be attributed to the uncertainties in the emissions for these regions.

- Model estimates of global HCB air concentrations generally agree with the results of monitoring campaigns performed in different regions of the world. At the same time, the model slightly underestimates observed HCB air concentrations in North America, Western Europe, Central and Eastern Europe. The underestimation is likely caused by the uncertainties of emission scenario applied in model simulations and further analysis of observed and modelled HCB concentrations in cooperation with experts in the field of POP emissions and measurements is needed.

- Studies of global scale transport and fate of PCDD/Fs has been continued out using experimental scenario of global emissions, constructed on the basis of the data of the UNEP SC inventory. Comparison of modelling results with measurements performed in countries of Latin America indicated reasonable agreement between the modelled and observed PCDD/F air concentrations.

- In order to improve estimates of POP cycling between different ecosystem compartments parameterizations of air-water, air-soil, and air-vegetation exchange in GLEMOS need to be further developed. Analysis and refinement of model parameterizations of processes governing POP fate in the terrestrial and aquatic environmental compartments will be carried out to link transport and fate of POPs to the exposure and improve understanding of bioaccumulation/biomagnification in food chains.
CONCLUSIONS

This year along with routine work on evaluation of environmental levels and transboundary transport of HMs and POPs in the EMEP domain for 2013, MSC-E undertakes activities for both generating additional information required for the implementation of the Protocols on HMs and POPs (such as long-term trends of pollution) and for model development (refinement of model design and parameterization and evaluation of input data). The results of these activities are briefly summarized below.

Long-term trends analysis

- The methodology of the analysis of long-term trends was elaborated by MSC-E and discussed at TFMM Trend Analysis Workshop (Paris, November 2014).

- For all considered pollutants reduction of contamination in the beginning of the considered period is larger than in the end of the period. Moreover, B[a]P air concentrations in the EMEP region tend to be growing beginning from 2005. For PCDD/F air concentrations in the end of the period become to be almost stable. For PCB-153 and HCB reduction of air concentrations is diminished to the end of the period but remains noticeable. Lead and mercury are characterized by higher reduction in the beginning, and smaller in the end of the 1990-2012 period, while rate of cadmium reduction remains stable. These results agree with the data from EMEP monitoring sites.

- The main factor responsible for the long-term decline of heavy metal concentrations and deposition in the EMEP region is reduction of atmospheric emissions in the EMEP countries. However, other factors such as long-term changes of secondary emissions of lead and cadmium and contribution of intercontinental transport of mercury to pollution in the EMEP region are also important.

- Due to substantial seasonal variability B[a]P air concentration in cold period of year can exceed several times the annual average value, whereas for PCDD/Fs and PCB-153 the situation is opposite (pollution in summer exceeds that in winter).

- Air concentrations of POPs are subject to strong spatial variability and vary to high extent between different parts of a country. For example, essential number of people can live in regions where EU target value of 1 ng/m$^3$ (Directive 2008/50 EC) is exceeded in spite of the fact that for these countries average annual air concentrations over the entire country area is less than the target value.

- Comparison of modelled and measured values over long period of time (1990-2012) demonstrated that the model in general was capable of reproducing observed levels, as well as main characteristics of the observed trends (reduction rate and seasonality).
Global modelling in long-lat grid

- High mercury deposition fluxes are characteristics of the large industrial regions (East and South Asia, Europe, North America etc.) and regions with significant mercury emissions from artisanal and small-scale gold mining (Southeast Asia, Central and South America, Sub-Saharan Africa). Relatively large deposition is also detected over some remote areas of the oceans and in the Polar Regions.

- Mercury anthropogenic deposition to Europe consists of almost equal contributions of domestic and foreign anthropogenic emissions. The largest external contributors include East Asia (20%), Africa (8%), CIS countries (5%), and South Asia (3%).

- Anthropogenic mercury deposition in industrial regions is largely determined by emissions from stationary combustion and industrial sources. In contrast, regions with smaller emissions are significantly affected by mercury emissions from intentional use and product waste associated sectors.

- The most significant changes in Hg deposition (both increase and decrease) during the next 20 years for all considered scenarios are expected in the Northern Hemisphere and, in particular, in the largest industrial regions, where the majority of regulated emission sources are located.
REFERENCES


UNEP [2013] Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs.


### CHARACTERISTICS OF CHEMICAL TRANSPORT MODELS PARTICIPATED IN THE MULTI-MODEL EXPERIMENTS

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>GEM-MACH-Hg (^{(a)})</th>
<th>GEOS-Chem</th>
<th>GLEMOS</th>
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<tr>
<td>Institution</td>
<td>Environment Canada</td>
<td>Massachusetts Institute of Technology</td>
<td>Meteorological Synthesizing Centre - East</td>
</tr>
<tr>
<td>Domain</td>
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<td>Global</td>
<td>Global</td>
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<tr>
<td>Spatial resolution</td>
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<td>2.5° × 2°</td>
<td>1° × 1°</td>
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<tr>
<td>Vertical</td>
<td>58 levels, top 7 hPa</td>
<td>47 levels, top 0.01 hPa</td>
<td>20 levels, top 10 hPa</td>
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<tr>
<td>Type</td>
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<td>Multi-media</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Emissions</td>
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<td>1875</td>
<td>1875</td>
</tr>
<tr>
<td>Speciation (average), GEM : GOM : PBM</td>
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<td>81 : 19 : 0</td>
<td>81 : 15 : 4</td>
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<tr>
<td>Natural and legacy, t/y</td>
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<td>5070</td>
<td>3995</td>
</tr>
<tr>
<td>Atmospheric chemistry</td>
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<td>Br</td>
<td>OH, O₃, Cl₂</td>
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<tr>
<td>Oxidation (air)</td>
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<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Reduction (air)</td>
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<td>none</td>
<td>OH, O₃, HOCI/OCl⁻</td>
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<tr>
<td>Oxidation (cloud water)</td>
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<td>none</td>
<td>SO₅²⁻</td>
</tr>
<tr>
<td>Reduction (cloud water)</td>
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<td>none</td>
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<td>Parameterization of AMDEs based on Br chemistry, re-emission from snow</td>
<td>Gas-particle partitioning of Hg(II). Parameterization of AMDEs based on Br chemistry, re-emission from snow</td>
<td>Parameterization of AMDEs based on Br chemistry, re-emission from snow, chemical reactants imported from MOZART and p-TOMCAT</td>
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<td>References</td>
<td>Durnford et al. [2012], Kos et al. [2013], Dastoor et al. [2014]</td>
<td>Holmes et al. [2010]; Amos et al. [2012]</td>
<td>Travnikov et al. [2009]</td>
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</table>

\(^{(a)}\) GEM-MACH-Hg is a new chemical transport model for mercury that is based on the GRAHM model developed in Environment Canada.