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Heavy Metals: Transboundary Pollution of the Environment

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Heavy Metal Transboundary Pollution of the Environment

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EXECUTIVE SUMMARY

Heavy metals are known for their toxicity for human health and biota. Because of their ability to dispersion in the atmosphere over long distances (up to hundreds or thousands of kilometres) heavy metals are within the scope of the UNECE Convention on Long-range Transboundary Air Pollution (hereafter, CLRTAP or the Convention). Protocol on Heavy Metals to the Convention (hereafter, Protocol on HMs or the Protocol), signed and ratified by most of the European countries, the USA and Canada, is aimed at reduction of heavy metal emissions and decrease of the environment pollution by these contaminants. Heavy metals targeted by the Protocol include lead, cadmium and mercury.

According to the Protocol the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) provides Parties to the Convention with information about modelled and observed pollution levels, their trends and transboundary fluxes. This information allows assessing effectiveness of regulations on emission reduction posed by the Protocol. Outcome of the EMEP Centres research activity in the field of heavy metals is regularly reported and discussed at meetings of the EMEP Task Force on Measurements and Modelling (TFMM).

This report is focused on main results of the EMEP programme aimed at support of the implementation of the Protocol on HMs. The report summarizes information about current status of emissions, modelled and observed pollution levels and transboundary transport in 2012. Besides, long-term pollution trends are characterized. New directions in development of the modelling tools used for assessment of heavy metal pollution are overviewed. Finally, significant attention is paid to dissemination and exchange of information with subsidiary bodies to the Convention, national and international organizations and programmes.

Data on atmospheric emissions are among the key information required for model pollution assessment. Emission data for heavy metal modelling are jointly generated by the Centre on Emission Inventories and Projections (CEIP) and the Meteorological Synthesizing Centre-East (MSC-E). CEIP collects official emissions data reported by Parties to the Convention and provides gridded emissions for the latest year of the assessment (2012). MSC-E prepares historical data for the trend assessment based on both official data and expert estimates. Besides, the updated global inventory of mercury anthropogenic emissions (prepared as a part of the UNEP Global Mercury Assessment 2013) is used for the assessment. According to available data, emissions of heavy metals have been considerably decreased in the EMEP region over the last two decades. Lead emissions have dropped by 90% since 1990, whereas emissions of cadmium and mercury have decreased approximately by 60%.

Atmospheric monitoring of pollutants under EMEP is supervised by the Chemical Coordinating Centre (CCC). In 2012 measurements of heavy metals are carried out at 71 stations. The lowest concentrations for all contaminants in air as well as in precipitation are generally found in Northern Scandinavia. Relatively high levels are noted for few sites in Eastern Europe and the Benelux region. Most of the EMEP monitoring stations measuring heavy metals are located in the northern, western and central parts of Europe. There is still a need for better coverage in the eastern and southern parts of Europe and in Central Asia, especially, in the countries of Eastern Europe, Caucasus and Central Asia (EECCA) and South-eastern Europe (SEE). Monitoring data coverage could be improved through more active involvement of national data as well as data from international programmes and projects, such as Global Mercury Observation System (GMOS). In addition to this, alternative monitoring approaches could be used, e.g., biomonitoring, passive sampling methods etc.

Model evaluation of heavy metal pollution levels is carried out by MSC-E. Long-term trends of lead, cadmium and mercury are analyzed based on both measurements and model calculations and

applying a novel statistical approach. This information is important for understanding effectiveness of environmental policy in the EMEP countries, and in particular, for the implementation of the Protocol on HMs. Pollution levels of lead, cadmium and mercury in the EMEP region have been reducing since 1990 at rate 6.7 %, 3.4% and 2.3% per year, respectively. However, in particular countries the characteristics of the long-term changes vary significantly. Three major factors account for these changes: reduction of anthropogenic emissions, changes in secondary emission sources and inter-annual variability of meteorological conditions. In the beginning of the considered period the main factor controlling long-term changes is anthropogenic emission. In the end of the period the effects of meteorological variability and secondary sources become as important as the effect of anthropogenic emission reduction.

In spite of reduction of pollution since 1990 relatively high levels of lead, cadmium and mercury in 2012 are noted for countries in the central (Poland, Germany, north of Italy) and in the south-eastern (the Balkan region, east of Ukraine) parts of Europe. Besides, comparatively high levels of lead and cadmium in the southern part of Russia, the western part of Kazakhstan and the Caspian region are caused mostly by influence of re-suspension from desert areas of Central Asia. Poland, Monaco, Slovakia, Slovenia, Italy, Belgium and Bulgaria are characterized by the highest country-averaged deposition flux of heavy metals.

Transboundary transport plays an essential role in pollution of the EMEP countries. In 36 countries out of 51 the contribution of foreign sources to lead anthropogenic deposition exceeds 50%. For cadmium this contribution exceeds 50% of total deposition in 37 countries, and for mercury – in 32 countries. Emission sources of each country contribute to transboundary pollution in other countries of the EMEP region. The contribution of national sources to transboundary transport between countries, expressed in relative terms varies from 60% to almost 100%. More detailed information about source-receptor relationships for the EMEP countries in 2012 is available on the MSC-E website (www.msceast.org).

Mercury differs from other heavy metals by its ability to long-range dispersion in the atmosphere. Therefore, mercury pollution levels in the EMEP countries are largely affected by emission sources in other regions. On the other hand, mercury originated from the EMEP countries contributes to contamination of other regions and continents. Atmospheric dispersion of mercury on a global scale and its transport between different continents and regions are simulated for 2012. It is obtained that mercury deposition in the EMEP countries is largely determined by emissions from both EMEP domestic sources (15-50%) and sources located in East Asia (11%) and Africa (4%). However, relative contribution of these source types differs significantly over the EMEP region. In addition to this, about 50% on average is contributed by natural and legacy sources.

Global EMEP Multi-media Modelling System (GLEMOS) has been developed for the last several years by MSC-E as a new generation model for the EMEP operational modelling of the environment pollution by heavy metals, POPs and other contaminants. Recent updates and development of the modelling system performed during the last year include preparation to transition of the EMEP regular modelling to the new gridding system, pilot simulations on the new EMEP grid, elaboration of multi-media model approach for mercury (oceanic module) and preparation of GLEMOS distribution for public use.

Following decisions of the Executive Body for CLRTAP (*ECE/EB.AIR/113/Add.1*) MSC-E initiated preparatory work for transition of the EMEP operational modelling of heavy metal and POP pollution to the new EMEP grid. These activities are associated with adaptation of the model for applications in the new domain, collection and processing variety of input information and overall testing of the modelling system. The pilot simulations performed with GLEMOS on the new EMEP grid for mercury demonstrate reasonable model performance for the EMEP operational modelling. Increased spatial

resolution of the model grid allows reproduction of pollution dispersion on a national scale. Nevertheless, the model testing and evaluation on the new grid will be continued to cover other heavy metals (lead and cadmium) and POPs.

Investigation of the effects of modelling with finer spatial resolution is also continued within the framework of the EMEP country-specific case studies focused on heavy metal pollution assessment on a country scale. It has been shown that modelling with fine spatial resolution leads to higher variability of pollution levels over country's territory. Furthermore, effect of Large Point Sources (LPS) on national and transboundary pollution is revealed when calculations with fine spatial resolution are applied.

Further development of the GLEMOS modelling system also includes elaboration of the multi-media approach for mercury. The current activities in this direction are focused on development of the oceanic module describing mercury transformations and cycling in seawater. Elaboration of the oceanic module has been started with a comprehensive literature survey of available information on physical and chemical transformations of mercury in the ocean. The developed parameterisations have been tested with an empirically constrained box model for simulations of mercury concentration in seawater.

Dissemination of the assessment results and other relevant information aimed at support of political decisions is of high importance. Annual reports containing current status of heavy metal pollution within the EMEP region are supplemented by presentation of information on the MSC-E website (www.msceast.org), where detailed information on heavy metal pollution is given for both the whole EMEP region and each EMEP country individually. Besides, to support the EECCA countries in their efforts on the implementation of the Protocol on HMs and development of national environmental programs a full-scale Russian version of the MSC-E website has been developed (ru.msceast.org). Another important aspect is the information exchange with subsidiary bodies to the Convention, other international organizations and programmes as well as with national experts.

MSC-E and the Task Force on Emission Inventories and Projections (TFEIP) jointly discussed current problems regarding heavy metal emissions and formulated priority directions to analyze and improve quality of the emission data. Completeness and consistency of emission data, information on the range of uncertainty of reported emissions, generation and updates of emission expert estimates and collaboration with other international programmes (e.g. the UNEP Minamata Convention on Mercury and the Arctic Monitoring and Assessment Programme - AMAP) are needed for improving emission data quality and further progress in assessment of heavy metal pollution in the EMEP domain.

Analysis of heavy metal pollution levels in the EMEP domain has been performed in close co-operation with the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP-Vegetation) of the Working Group on Effects (WGE). Measurements of heavy metals in mosses, as biomonitoring data, are very valuable information for assessment of spatial distribution of pollution levels and their trends, especially in areas with scarce monitoring network. Significant spatial correlation between simulated heavy metal deposition and concentrations in mosses is found for Scandinavia and some countries in the central part of Europe. Besides, modelled long-term deposition trends of lead, cadmium and mercury agree reasonably well with the trends of heavy metal concentrations in mosses.

Pilot results of model assessment of intercontinental transport and source-receptor relationships of mercury were presented by MSC-E as possible contribution to the on-going numerical experiments under the Task Force on Hemispheric Transport of Air Pollution (TF HTAP). It was demonstrated that both regional sources and contribution of long-range transport played significant role in mercury

pollution of many industrial regions. It was also concluded that the multi-media dispersion character of this contaminant required source apportionment of secondary emissions over longer period.

MSC-E participates in various activities aimed at scientific support of international efforts to abate mercury pollution on global and regional scales. In particular, MSC-E took part in preparation of the Global Mercury Assessment 2013 for negotiations of the Minamata Convention on Mercury. Estimates of mercury pollution on a global scale have been recently updated by the Centre. Levels of mercury air concentration and deposition in different terrestrial and aquatic regions of the globe were assessed for present conditions by means of the GLEMOS model. Particular attention was paid to evaluation of mercury deposition to major fishing areas of the ocean keeping in mind the primary role of the fish consumption in human health exposure to mercury.

A new scientific cooperative initiative GMOS (Global Mercury Observation System) Mercury Modelling Task Force (MMTF) has been launched recently as a part of the EU GMOS project. GMOS MMTF is aimed at model studies supplemented by comprehensive monitoring data for improvement of current understanding of the key mercury atmospheric processes and evaluation of present and future levels of mercury pollution. MSC-E performs general coordination of the Task Force and leads the mercury model assessment on a global scale. Research activities under MMTF will improve quality of model assessment of mercury pollution within the EMEP domain. Besides, the model studies within MMTF closely correlate with the current activities carried out within TF HTAP and the UNEP efforts to support implementation of the Minamata Convention on Mercury.

MSC-E continued cooperation with national experts from the EMEP countries. First of all, the EMEP case study on lead pollution assessment in the Netherlands has been completed. Information on pollution levels, contribution of emission source categories and source-receptor relationships on national scale was prepared. Fine spatial resolution made possible evaluation of pollution levels in particular provinces of the country. In addition, the Centre carried out calculations of air concentrations of lead, cadmium, arsenic, nickel and mercury over Italy in order to support national scale modeling of heavy metals in ENEA (Italian national agency for new technologies, energy and sustainable economic development). The results were verified by comparison of modelled heavy metal levels with the EMEP measurements.

Future directions of MSC-E research will be focused on assessment of heavy metal pollution levels in the EMEP region and support of the EMEP countries with information required for the implementation of the Protocol on Heavy Metals. Special efforts will be undertaken to characterize status of heavy metal pollution in the EECCA countries. The model testing and evaluation on the new EMEP grid will be continued to cover other heavy metals (lead, cadmium) and POPs. Investigation of effects of transition to finer spatial resolution will be also performed in the framework of the EMEP country-specific case studies in close cooperation with national experts from Belarus and Poland. It is planed to examine the effects of large point sources on national and transboundary pollution. Development of the multi-media approach for mercury in the GLEMOS modelling system will be continued with focus on aquatic and terrestrial environments. Besides, it is planned to refine mercury chemistry modules to reduce the existing uncertainties and improve quality of the assessment. Finally, the GLEMOS source code will be distributed for public use to support development of country-scale modelling approaches by national experts.

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INTRODUCTION

Heavy metals are known for their toxicity for human health and biota. Because of their ability to dispersion in the atmosphere over long distances (up to hundreds or thousands of kilometres) heavy metals are within the scope of the UNECE Convention on Long-range Transboundary Air Pollution (hereafter, CLRTAP or the Convention). Protocol on Heavy Metals to the Convention (hereafter, Protocol on HMs or the Protocol), signed and ratified by most of the European countries, the USA and Canada, is aimed at reduction of heavy metal emissions and decrease of the environment pollution by these contaminants. Heavy metals targeted by the Protocol include lead, cadmium and mercury.

Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) provides the Executive Body for the Convention with information on effectiveness of emission control measures and on pollution changes of a range of contaminants including heavy metals. Different aspects of the assessment of heavy metal pollution in the EMEP region are covered by the EMEP Scientific Centres. Centre on Emission Inventories and Projections (CEIP) is responsible for collection, processing and quality control of data on emissions reported by countries, Chemical Co-ordinating Centre (CCC) provides methodological support of the EMEP monitoring network, Meteorological Synthesizing Centre – East (MSC-E) performs model assessment of pollution levels and transboundary transport. The work of the Centres is conducted in collaboration with the Task Force on Measurements and Modelling (TFMM), the Task Force on Hemispheric Transport of Air Pollution (TF HTAP), the Task Force on Emission Inventories and Projections (TFEIP) and the Working Group on Effects (WGE).

This report presents an overview of recent assessment results on heavy metal pollution in the EMEP region. The report includes information on heavy metal atmospheric emissions used in the model assessment. Besides, it gives analysis of pollution levels in 2012 and their temporal trends based on both model calculations and measurements. Furthermore, it describes further development of the Global EMEP Multi-media Modelling System (GLEMOS). Much attention is paid to exchange of information between MSC-E and subsidiary bodies to the Convention, as well as dissemination of output information to national and international organizations.

Information on long-term trends of heavy metals and analysis of factors affecting trends are important for understanding effectiveness of the environmental policies in the EMEP countries and, in particular, for the implementation of the Protocol on Heavy Metals. Analysis of heavy metal pollution trends in the EMEP region over the last two decades is presented in the report. Besides, deposition fluxes to different types of land-cover categories and their long-term changes are overviewed. This information is needed for evaluation of critical load exceedances. Special attention is also paid to evaluation of contribution of intercontinental transport to mercury pollution in the EMEP countries. Finally, pilot simulations of lead and cadmium levels in 2013 were carried out and analysed (so-called “near-real time” calculations based on the latest available emission data).

In order to improve quality and reliability of output information submitted to the EMEP countries MSC-E continues development of the modelling tools. Following the decision of the Executive Body for CLRTAP (*ECE/EB.AIR/113/Add.1*) a preparatory work for transition of the EMEP operational modelling to the new EMEP grid has been initiated for heavy metals and POPs. In particular, pilot simulations of heavy metal pollution were performed on the new grid and the model results were evaluated against measurements. Effects of the modelling grid refinement were further examined in the framework of the EMEP country-specific case studies. This year the study has been focused on assessment of lead pollution levels in the Netherlands. Further development of the GLEMOS modelling system also includes elaboration of the multi-media approach for mercury. The current activities in this direction are focused on development of the oceanic module describing mercury transformations and cycling in seawater.

Particular attention is paid to dissemination of the assessment results and exchange of information with subsidiary bodies to the Convention, international and national organizations. In addition to the annual Status reports a variety of information on heavy metal pollution levels in the EMEP region, individual countries, marginal seas etc. is distributed via the Internet at the MSC-E website (www.msceast.org). It can be used by national authorities of the EMEP countries for development and implementation of the environment protection policies on both national and international levels. Information exchange with other international organizations and programmes (the UNEP Minamata Convention on Mercury, the Arctic Monitoring and Assessment Programme, Helsinki Commission etc.) broaden dissemination of the scientific and policy oriented information generated within EMEP and strengthen the status of the program on international level.

Finally, along with the most important results of the EMEP activities in 2014 the report overviews the main challenges and directions of future work in the field of heavy metal pollution. More detailed scientific information is presented in Annexes, Joint MSC-E/RIVM Report 1/2014 [*Ilyin et al.*, 2014] and MSC-E Technical Report 4/2014 [*Shatalov et al*., 2014].

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1. POLLUTION OF THE EMEP REGION

1.1. Emission data for model assessment

Heavy metal emissions at least for one year of the period 1990-2012 were reported by 41 out of 51 Parties to the Convention. Data for the base year 1990 and the year 2012 were provided by 30 countries and 27 countries submitted gridded emissions of lead, cadmium and mercury.

The data on heavy metal emissions for modelling within the EMEP domain for the period 1990-2012 were generated by CEIP and MSC-E. CEIP provided datasets of gridded emissions for 2012. MSC-E prepared gridded emission data for the base year 1990 using official emissions reported by countries, emission expert estimates made by TNO [*Denier van der Gon et al.*, 2005] and expert estimates of emissions for the EECCA countries prepared by MSC-E.

Information on emission distribution with height is important for modelling of atmospheric transport of heavy metals. Pollutants emitted at higher altitude tend to be transported further due to increase of wind velocity with height. Vertical distribution of the pollutant concentration in the vicinity of emission sources also depends on height of the emission source. In order to estimate distribution of emissions with height MSC-E utilized sector-split emission information provided by the EMEP countries. Height distributions for different emission sectors were averaged taking into account a sector contribution to the total emission. It was assumed that heavy metal emission was distributed between three lowest model layers (0-70 m; 70-150 m and 150-300 m).

Mercury is emitted to the atmosphere in elemental, gaseous oxidized and particulate forms. Atmospheric behaviour of mercury strongly depends on its form. Gaseous oxidized and particulate mercury are removed relatively quickly, whereas elemental mercury persists in the atmosphere over long time (around a year) and is involved in intercontinental transport. The speciation of mercury emissions is not included in the information reported by the Parties to the Convention. Therefore, expert estimates of mercury emission speciation have been used by MSC-E. Detailed information on speciation of mercury emissions for 1990-2010 and vertical distribution of the emission data are presented in [*Travnikov and Ilyin*, 2005]. For calculations of mercury levels in 2012 speciation of mercury emissions derived from global emission dataset [*AMAP/UNEP*, 2013] was applied.

Information about uncertainties of emission data is important for understanding and interpretation of the model results. However, only few countries report uncertainties of their national emission data.

Changes of heavy metal emissions in the EMEP countries in the period 1990-2012

Emissions of heavy metals have considerably decreased in the EMEP region over the last two decades. Lead emissions have dropped by 90% since 1990, whereas emissions of cadmium and mercury have decreased approximately by 60% (Fig. 1.1).

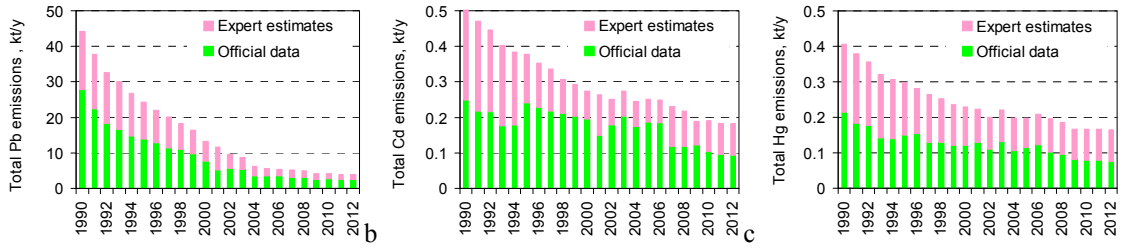


***Fig. 1.1**. Temporal changes of lead (a), cadmium (b), and mercury (c) anthropogenic emissions in the EMEP region from 1990 to 2012*

In 2012 total emission of lead from the EMEP domain made up about 3893 tonnes. The emission reductions between 1990 and 2012 took place in all EMEP countries, except for Azerbaijan, Georgia, Armenia and Malta (Fig. 1.2). The most noticeable emission decreases (more than 95%) were in Republic of Moldova, the Russian Federation, Monaco, Montenegro, Hungary, the United Kingdom, Luxembourg, Norway, France, Iceland, Lithuania, Sweden, Croatia, Latvia, Ukraine and Liechtenstein.

In the period from 1990 to 2012 lead emissions in the EMEP region reduced by 90%, and cadmium and mercury emissions – by about 60%

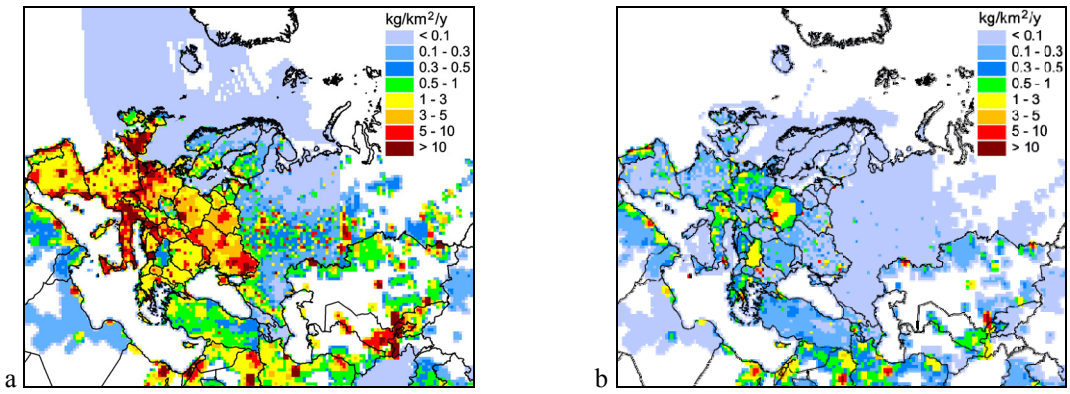


Fig. 1.2. *Spatial distribution of lead anthropogenic emissions over the EMEP domain in 1990 (a) and 2012 (b).*

Total emission of cadmium in the EMEP domain in 2012 was 182 tonnes. Compared to 1990, lower cadmium emissions for 2012 were seen in 38 EMEP countries (Fig. 1.3). The highest emission decreases compared to 1990 took place in Malta (96%), Republic of Moldova (95%), Ukraine (95%), Luxembourg (92%), Monaco (91%), Hungary (91%), the United Kingdom (91%) and Romania (91%). Increases in emissions indicated in Cyprus (62%), Belarus (36%), Latvia (35%), Georgia (32%), Azerbaijan (25%), Liechtenstein (16%) and Turkey (9%).

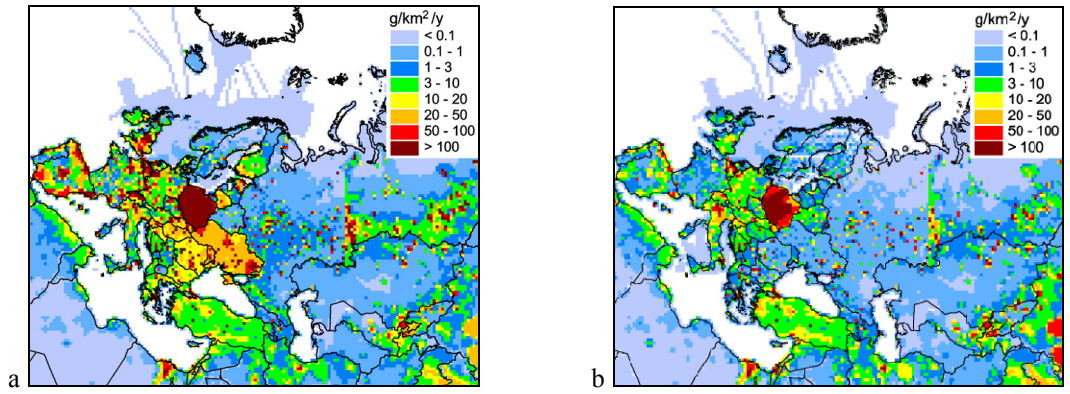


Fig. 1.3. *Spatial distribution of cadmium anthropogenic emissions over the EMEP domain in 1990 (a) and 2012 (b).*

Emission of mercury in the EMEP domain in 2012 amounted to 164 tonnes. During the period from 1990 to 2012, mercury emissions decreased in 39 countries and increased in 6 countries (Fig. 1.4). The most substantial decreases of mercury emission values took place in Malta (99%), Republic of Moldova (94%), the Russian Federation (94%), Hungary (90%), Slovakia (90%) and Denmark (90%).

Higher levels of emissions in 2012 (compared to 1990) were noticed in Iceland (119%), Liechtenstein (40%), Turkey (27%), Georgia (25%), Azerbaijan (23%) and Montenegro (19%).

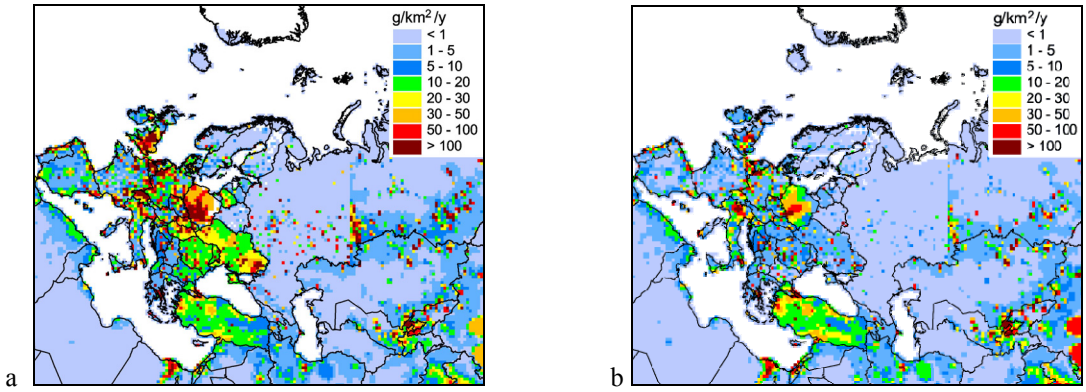


Fig. 1.4. *Spatial distribution of mercury anthropogenic emissions over the EMEP domain in 1990 (a) and 2012 (b).*

Mercury emissions on a global scale

Mercury is well known as a pollutant capable of intercontinental transport in the atmosphere [*HTAP*, 2010]. Therefore, assessment of mercury pollution in the EMEP countries requires data on mercury anthropogenic emissions on a global scale. The updated global inventory of mercury anthropogenic emissions for 2010 has been prepared as a part of the UNEP Global Mercury Assessment 2013 [*AMAP/UNEP*, 2013]. A new improved methodology has been developed for the inventory that allows better characterization of differences between countries in terms of fuels and raw materials used as well as technologies and practices applied. Figure 1.5 presents the global distribution of anthropogenic emissions of mercury in 2010 in accordance with the new inventory. Areas with elevated mercury emissions correspond to highly industrialized regions (China, India, Europe, the eastern part of the United States) and areas of artisanal and small-scale gold mining (East and Southeast Asia, South America, Sub-Saharan Africa).

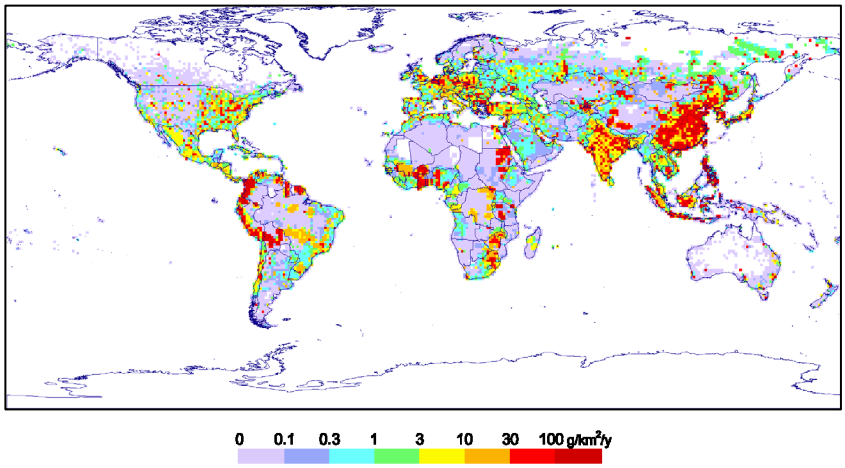


Fig. 1.5. *Global distribution of anthropogenic emissions of mercury in 2010*

The global mercury inventory in 2010 is estimated at 1960 tonnes and comprises emissions from artisanal and small-scale gold mining (ASGM), combustion of fossil fuels (mainly coal) in power plants,

industrial and residential boilers, metal production (ferrous and non-ferrous), cement production, product use, and cremation. The largest emissions of mercury to the global atmosphere in 2010 are associated with ASGM (727 tonnes) and stationary combustion of fossil fuels (484 tonnes, 474 tonnes from coal combustion). Other major emission sectors include non-ferrous metal production (303 tonnes) and cement production (173 tonnes). Figure 1.6 summarizes contribution of various anthropogenic activities to the global mercury emission.

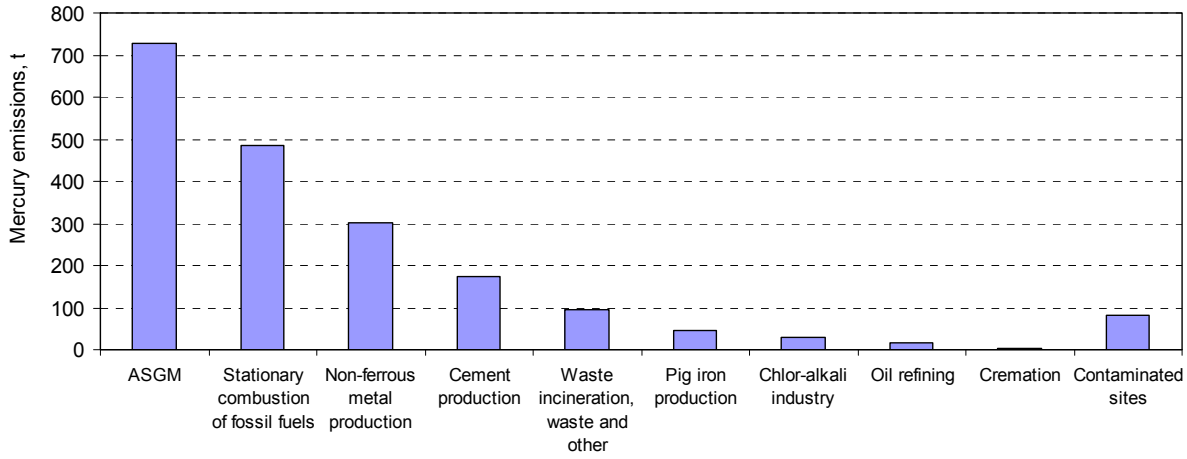


Fig. 1.6. *Global anthropogenic emissions of mercury to air in 2010 from various sectors*

Contribution of different regions to total mercury emissions on a global scale in 2010 is shown in Fig. 1.7. As seen, the Asian emission sources contribute about 47% to the global mercury emissions whereas the contribution of the European and North American sources does not exceeded 15% in sum.

It should be noted that expert estimates of mercury anthropogenic emissions included to the UNEP global emissions inventory can differ significantly from national data reported by some EMEP countries because of different methodologies and statistical data applied [*AMAP/UNEP*, 2013].

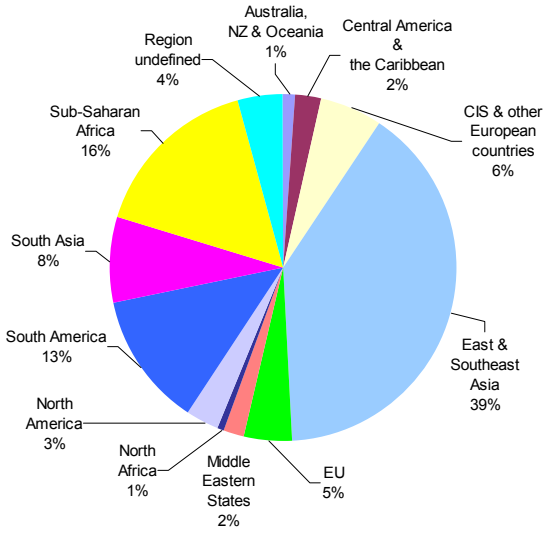


Fig. 1.7 *Contribution of different regions to the global anthropogenic mercury emissions in 2010*

Further improvement of heavy metal emissions

EMEP/MCS-E current activities in the field of heavy metal (HM) emissions were the subject of the note (Annex A) which had been prepared to respond to the questions posed by the EMEP Task Force on Emission Inventories and Projections (TFEIP) and to support discussions focused on the quality of HM emissions and their improvement.

Concluding comments on further improvement of HM emission data were drawn in that note. In particular, it was emphasized that the major issues with regard to the quality of officially reported

emission data for the assessment of HM pollution were connected with the completeness and consistency of inventories in line with the Emission Reporting Guidelines with special attention to the EECCA countries. Additionally, it was indicated that information on the range of uncertainty of reported emission data was needed to prepare scenarios of emissions for the evaluation of possible maximum and minimum levels of pollution of the EMEP domain. Generating and updating of emission expert estimates, applied for the preparation of HM emission data for modeling, is highly appreciated. Collaboration with the UNEP Minamata Convention on Mercury and AMAP is of mutual importance for further work on the evaluation of non-EMEP emission sources affecting pollution of the EMEP domain.

Completeness and consistency of emission data, information on the range of uncertainty of reported emissions, generating and updating of emission expert estimates and collaboration with the UNEP Minamata Convention on Mercury and AMAP are needed for improving emission data quality and further progress in assessment of heavy metal pollution in the EMEP domain.

1.2. EMEP monitoring network for heavy metals

Measurement network

Heavy metals were included in EMEP's monitoring program in 1999. However, earlier data has been available and collected, and the EMEP database [http://ebas.nilu.no] thus also includes older data, even back to 1987 for a few sites. A number of countries have been reporting heavy metals within the EMEP area in connection with different national and international programmers such as HELCOM, AMAP and OSPARCOM.

Detailed information about the sites and the measurement methods are found in EMEP/CCC's data report on heavy metals and POPs [*Aas and Nizzetto*, 2014]. In 2012, there were 35 sites measuring heavy metals in both air and precipitation, and altogether there were 71 measurement sites, 4 more than previous year. 14 sites were measuring mercury in both air and precipitation. In total, 9 Parties to the Convention fulfil their monitoring obligations as defined in the EMEP monitoring strategy [*UNECE*, 2009] with at least one level 2 site with both air and precipitation measurements of heavy meals and mercury in air and precipitation.

During June 2012 (and January 2013), the EMEP intensive measurement periods included measurements of mineral dust at 18 sites across Europe. These dust measurements include several trace element analysis. These analyses can be used as tracers of anthropogenic sources (local/external) at regional sites. Some preliminary results are presented in the last year EMEP PM Status report 4/2013 [*Aas and Breivik*, 2013] as well as this year status report EMEP 1/2014 [*Aas and Nizzetto* [2014]. Further results in respect of heavy metals will be presented in next year HM status report.

Observed concentration level of Pb, Cd and Hg in 2012

Annual averages of Pb, Cd and Hg concentrations in precipitation and in air in 2012 are presented in Fig. 1.8-1.13. Note that Cyprus with measurements of heavy metals in air is outside the map domain so included as a dislocated point south of Turkey. The lowest concentrations for all elements in air as well as precipitation are generally found in northern Scandinavia. An increasing gradient can in general be seen southeast, but the concentration levels are not evenly distributed, there are some

"hotspots" for some elements, i.e. in the BeNeLux countries for lead and cadmium in air. The relatively high concentrations indicated at the few sites in Eastern Europe show the importance of getting more sites with continuous measurements in this region to get better knowledge of the pollution level here. The spatial distribution of elemental mercury in air does not follow a general pattern; though somewhat elevated level in central Europe. In precipitation there are several sites (in PT, LV, IE) with high detection limits and these only give an indicative measure for the upper limit. A more detailed discussion of temporal and spatial resolution of heavy metals in Europe is found in *Tørseth et al.* [2012].

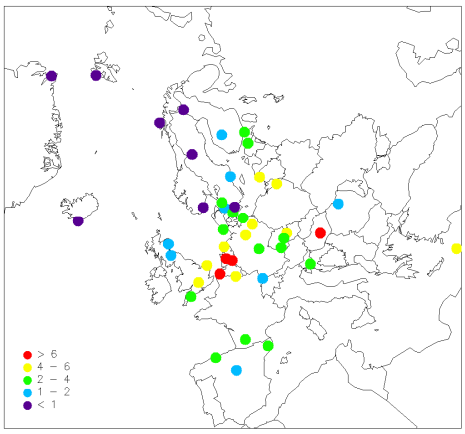


Fig. 1.8. *Pb in aerosol, ng/m^3*

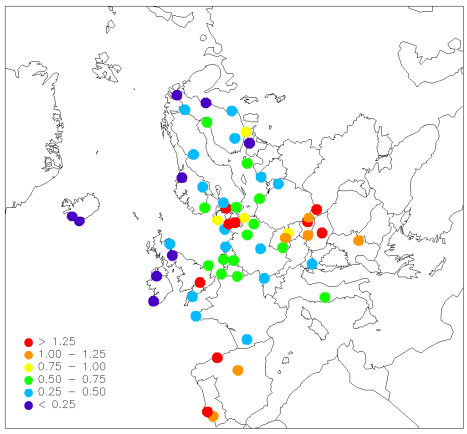


Fig. 1.9. *Pb in precipitation*

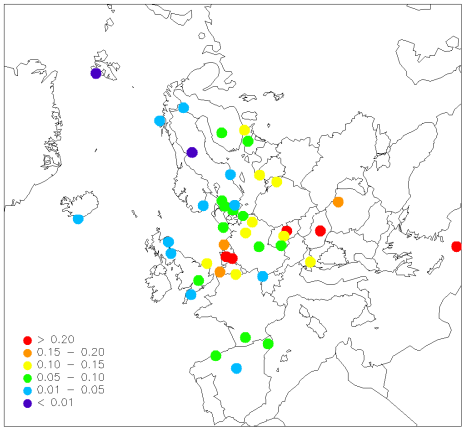


Fig. 1.10. *Cd in aerosol, ng/m^3*

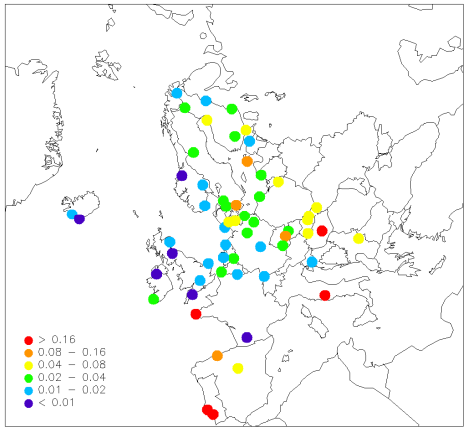


Fig. 1.11. *Cd in precipitation, µg/L*

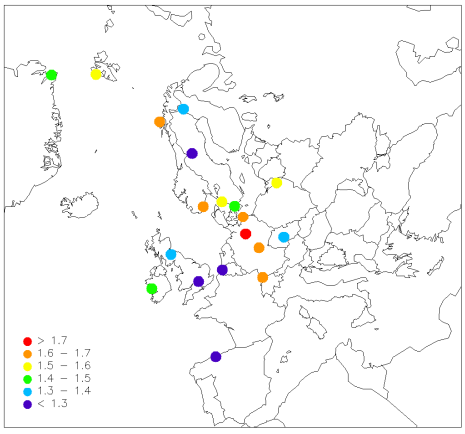


Fig. 1.12. *Hg (g) in air, ng/m^3*

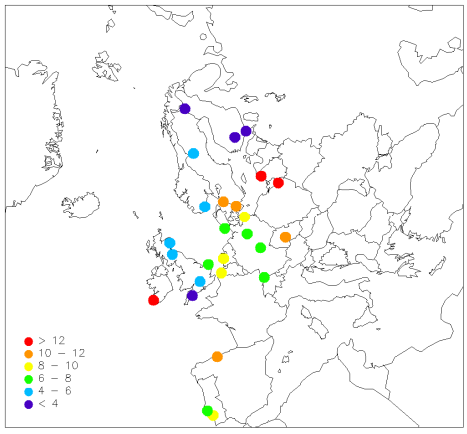


Fig. 1.13. *Hg in precipitation, ng/L*

1.3. Pollution levels and long-term trends for 1990-2010

Information on long-term trends of heavy metals and analysis of factors affecting trends are important for understanding effectiveness of environmental policy in the EMEP countries, in particular, implementation of the Protocol on Heavy Metals. This section is focused on the analysis of heavy metal pollution trends in the EMEP region taken place in the last two decades. Information about calculated and observed trends, their analysis and evaluation of factors responsible for long-term changes of heavy metal pollution were reported at the TFMM meeting held in April, 2014 in Bologna, Italy.

Available information for trend analysis

Long-term trends of heavy metal pollution levels can be evaluated using EMEP monitoring data and model calculations. Observed concentrations and wet deposition fluxes represent real values of pollution levels in particular points where monitoring stations are located. Modelling results are available for every grid cell of the EMEP domain, but these data require verification through comparison with observations. Therefore, modelling and monitoring data complement each other.

Information on calculated and observed heavy metal pollution levels in the EMEP region is available for the period from 1990 to 2012. However, for the trend analysis calculated time series of pollution levels should be consistent. It means that the entire time series should be simulated on the same version of the model and using emissions reported in one year. However, this condition is often not fulfilled completely because of changes in the model parameterizations and re-calculations of national emissions in many EMEP countries. The consistent calculated time series are available for 1990 – 2010 period [*Travnikov et al.*, 2012]. Therefore, trends are analyzed for this period.

Because of re-calculations of official emissions, changes in model parameterizations and other input data, the analysis of long-term trends should be repeated periodically for the whole period, e.g., once in few years.

For evaluation of modelling results calculated concentrations and wet deposition fluxes are compared with the levels observed at the EMEP stations. 15 stations measuring lead and cadmium and 6 stations measuring mercury with long time series are selected for the analysis (Fig. 1.14). As seen, the stations are located mostly in the central and the northern parts of Europe. In these areas long-term trends can be described on the base of both monitoring information and modelling results. Trends in the other parts of the EMEP region are characterized entirely by the modelling.

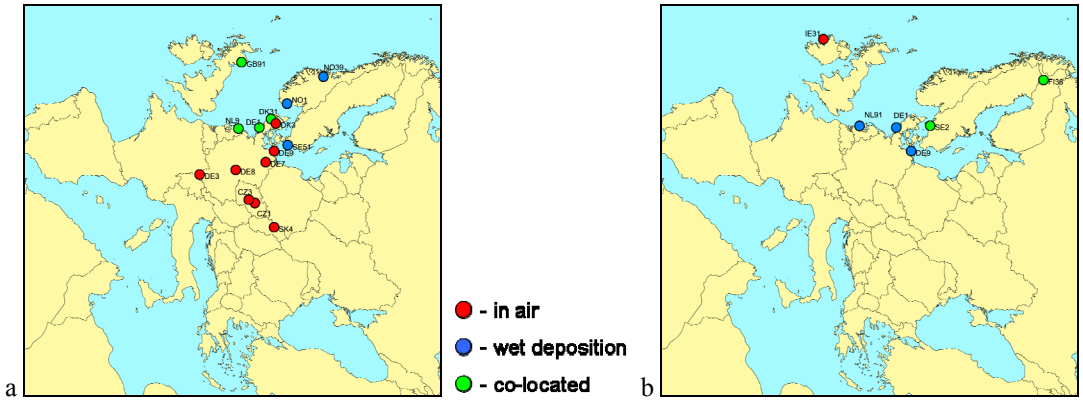


Fig. 1.14. *Location of measurement stations with long time series selected for the analysis of long-term trends of lead and cadmium (a) and mercury (b).*

Long-term trends in the EMEP region can be examined by means of modelling and monitoring. In the southern, eastern and south-eastern parts of Europe and in Central Asia, where EMEP measurements are not available, evaluation of trends is based entirely on modelling.

Trend analysis approaches

Two aspects of the long-term trend analysis are considered in this chapter: approximation of observed or calculated time series of concentrations and deposition, and statistical parameters characterizing trends.

As a rule, the rate of long-term changes of heavy metal levels recorded at monitoring stations is not constant. In the beginning of the considered period the decline of the levels is usually relatively fast, due to significant reduction of anthropogenic emissions, followed by decline of pollution levels. In the end of the period the decrease is slow. In order to describe this behaviour, bi-exponential approximation of trend is suggested:

$$y = C_1 \cdot e^{-\frac{t}{\tau_1}} + C_2 \cdot e^{-\frac{t}{\tau_2}}$$

Here t is time (years), τ_1 and τ_2 ($\tau_1 \geq \tau_2$) – characteristic times, and C_1 and C_2 – constants. The first term of this formula describes 'fast', whereas the second – 'slow' decline. This approach can be applied both for emissions and for pollution level trends based on measurements or modelling. Example of application of this approximation to emissions of lead in Germany and annual air concentrations of lead at station DE3 (Germany) is demonstrated in Fig. 1.15. More detailed description regarding this approximation is presented in the MSC-E Technical report [*Shatalov et al.*, 2014].

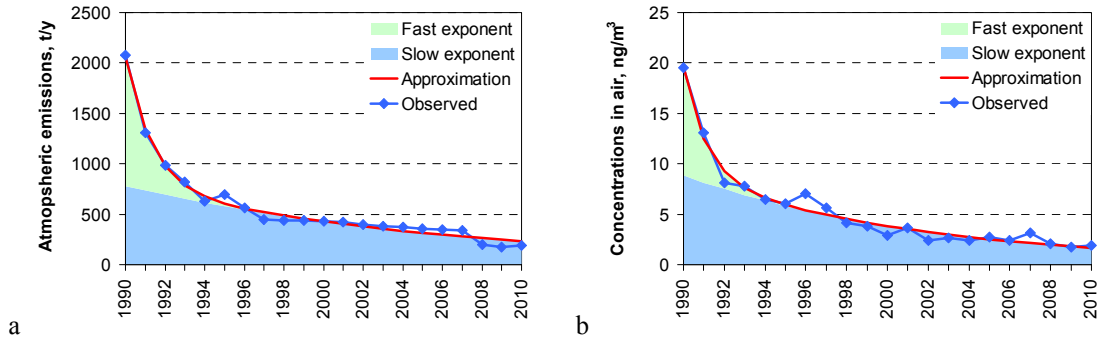


Fig. 1.15. *Reported and approximated lead emission data (a) and observed and approximated concentrations of lead in air at German station DE3 (b) in 1990-2010.*

In order to characterize statistical significance of long-term trends the Mann-Kendall test is applied [*Hirsch et al.*, 1982]. Agreement between modelled and observed levels at stations is assessed via the Pearson's correlation coefficient (R_c) and the Normalized Root Mean Square Error (NRMSE). Magnitude of long-term changes is characterized by characteristic times τ_1 and τ_2 and by mean relative reduction rate (% per year). Mean relative reduction rate for the whole period is calculated as geometric mean of annual reduction rates [*Shatalov et al.*, 2014].

Analysis of pollution trends in the EMEP region and its countries

Analysis of trends has been applied to calculated time series of total deposition to the European part of the EMEP region and in individual countries. Deposition of lead and mercury are described by two components: fast exponent and slow exponent. The latter is often reduced to zero or a constant value (Fig. 1.16). The nature of this constant 'base' may be explained by presence of sources which do not change in time. Cadmium time series is described only by one exponential term, while the second term is reduced to zero. Mean reduction rates for the whole period for lead, cadmium and mercury are 6.7%, 3.4% and 2.3% per year, respectively.

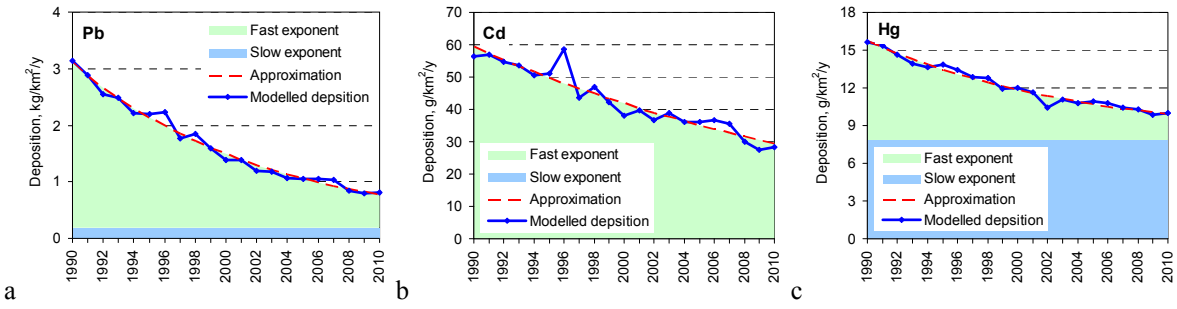


Fig. 1.16. *Long-term trends of lead (a), cadmium (b) and mercury (c) in Europe for 1990-2010 period.*

In particular countries long-term deposition trends may differ significantly from the trend in Europe as a whole. For example, in Sweden the changes of lead deposition are described by two exponents: fast reduction, caused by phasing out of leaded gasoline, is noted for 1990-1995, followed by relatively slow reduction after 1995 (Fig. 1.17a). In some countries, e.g., in Switzerland, the decline of deposition is characterized by one exponent (Fig. 1.17b). It means that the rate of relative changes of lead levels in this country is constant over the considered period. In some countries (e.g., Belarus) the reduction is described by one exponent approaching a constant 'base' (Fig. 1.17c). It means that approximated trend of pollution levels can not reach zero value.

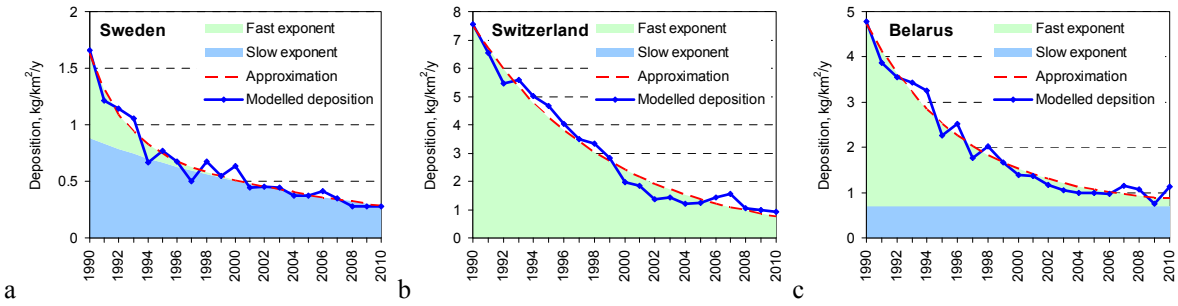


Fig. 1.17. *Long-term trends of lead in Sweden (a), Switzerland (b) and Belarus (c) for 1990-2010 period*

Relative reduction rates for lead, cadmium and mercury averaged over the considered period are summarized in Fig. 1.18. The highest reduction rate is noted for lead. In most of the EMEP countries lead deposition has been reducing at rate about 5-10% per year (Fig. 1.18a). For cadmium the rate is smaller – about 2 – 5% per year (Fig. 1.18b), which is explained by lower rate of emission reduction [*Travnikov et al.*, 2012]. Rate of reduction of mercury deposition varies from 0.5 to 6% per year (Fig. 1.18c). In most of the countries the rate of mercury reduction is lower compared to that of lead and cadmium. It is caused by large contribution of intercontinental transport of mercury to the EMEP

region, which variability over the considered period is relatively small. In some countries, e.g., Armenia and Azerbaijan, the reduction of heavy metal levels is negligible. These countries are strongly affected by atmospheric transport from non-EMEP sources located in the Asian part of the EMEP region (e.g., Iran, Iraq, Syria etc.). Emission data in this part of the EMEP region are uncertain and need refinement.

Since the rate of reduction in many countries is not constant (fast in the beginning and slow in the end of the period), information on range of the reduction rate (from maximum to minimum) for each country is also included in Fig. 1.18. The wider ranges indicate higher difference of rates of deposition decline between 1990 and 2010. For example, in the beginning of the considered period rate of lead deposition reduction in Spain is almost 28% per year, while by the end of the period it slows down to 7% per year (Fig. 1.18a). For a number of countries the range is not seen. It means that the rate of reduction is constant over the period (e.g., Switzerland or Slovenia in Fig. 1.18a).

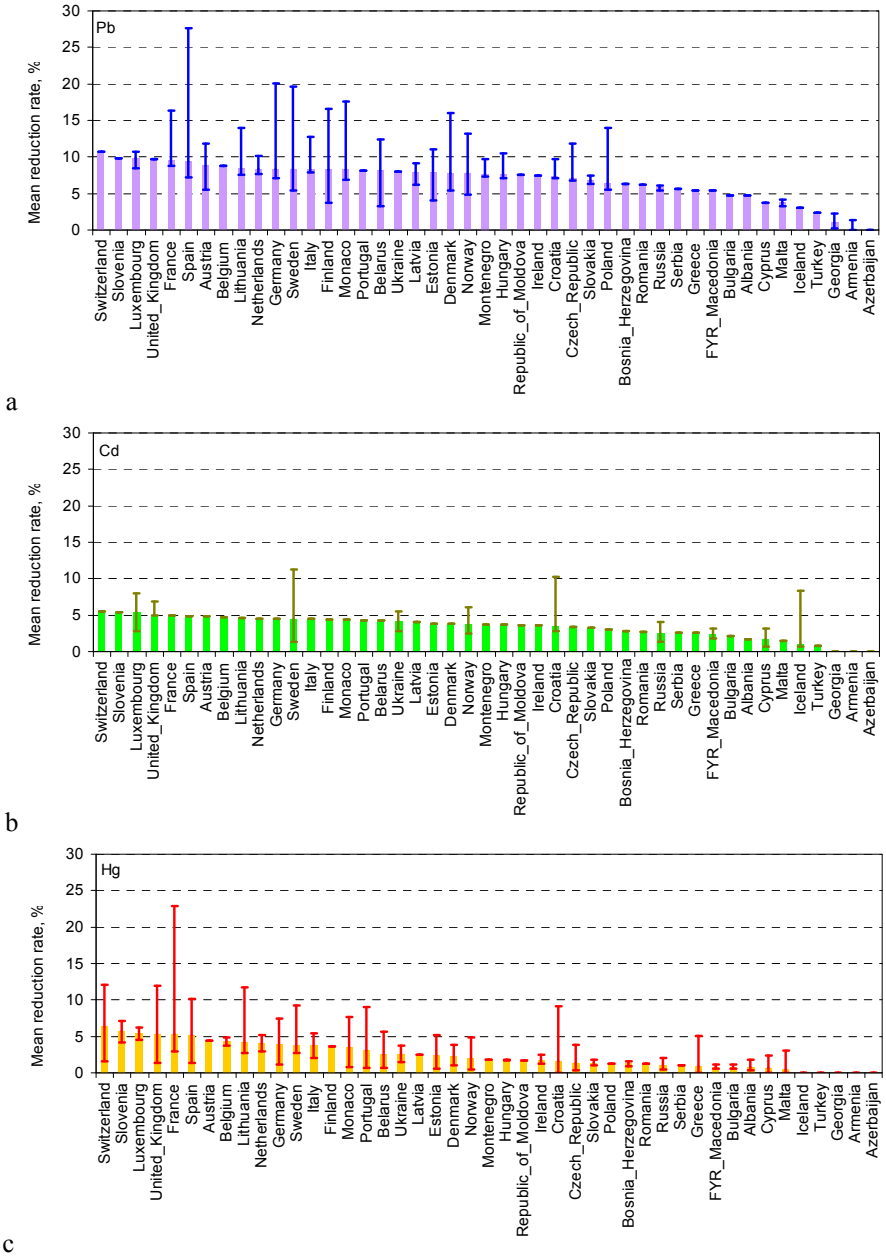


Fig. 1.18. *Mean reduction rate of lead (a), cadmium (b) and mercury (c) deposition in the EMEP region and ranges of the rates (from maximum to minimum) for 1990-2010 period.*

Pollution levels of lead, cadmium and mercury in the EMEP region have been reducing since 1990 at rate 6.7 %, 3.4% and 2.3% per year, respectively. However, in particular countries the characteristics of long-term trends vary significantly

Evaluation of modelled trends at monitoring stations

Calculated heavy metal pollution trends are evaluated in particular grid cells where measurement stations are situated. This evaluation includes calculation of significance of long-term trends using the Mann-Kendall test, comparison of modelled and observed concentrations in air and wet deposition fluxes and comparison of characteristics of long-term changes (mean reduction rate and characteristic times).

The Mann-Kendall test is applied for modelled and observed concentrations in air and wet deposition for every selected monitoring station. Results of application of the test to all considered heavy metals and stations are summarized in Table 1.1. Details of application of this test are available in MSC-E Technical report [*Shatalov et al.*, 2014]. For lead and cadmium long-term trends are statistically significant for both modelled and observed levels. For mercury at some stations the trends are statistically significant, and at the others the trend are not determined.

Table 1.1. *Results of significance test for the selected stations. ('+' – significant for all stations, '–' – not significant for all stations, '±' – significant for some stations)*

	Obs (in air)	Obs (wet dep.)	Mod (in air)	Mod (wet dep.)
Pb (15 stations)	+	+	+	+
Cd (15 stations)	+	+	+	+
Hg (5 stations)	–	±	±	±

Comparison of modelled and measured levels is carried out on monthly basis in order to take into account seasonal variability over the long-term period. At the majority of the stations both observed levels and their seasonal changes are captured by the model with reasonable accuracy. The comparison of modelled and observed concentrations of lead at the station DE1 is demonstrated as an example (Fig. 1.19). Temporal correlation coefficient is 0.81. Approximated observed and modelled trends also almost coincide.

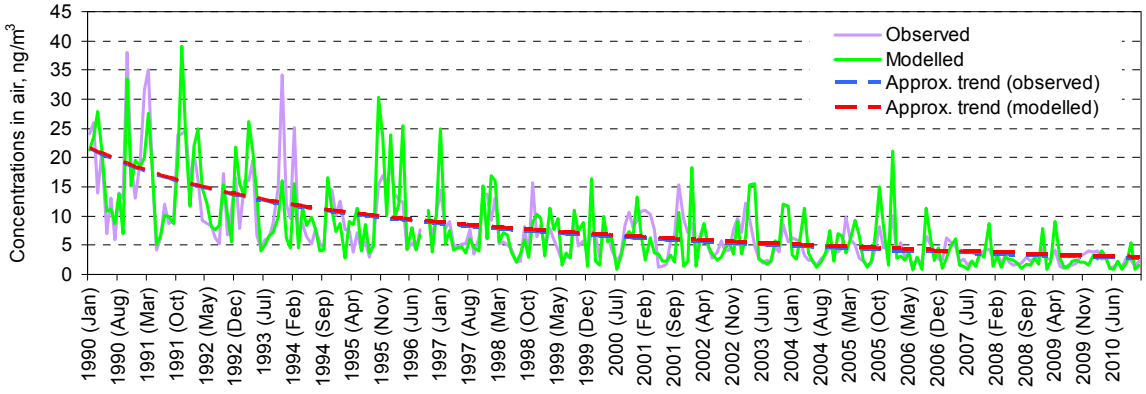


Fig. 1.19. *Modelled and measured monthly mean concentrations of lead and their long-term approximated trends at station DE1 (Germany)*

At some other stations the discrepancies between the calculated and observed pollution levels are noted. For example, at the German station DE8 relatively high air concentrations of cadmium in the beginning of the considered period (1993-1996) are not reproduced by the model (Fig. 1.20). Because of this fact the approximated trends differ largely in this period. In the second part of the period both levels and seasonal changes are captured by the model. Temporal correlation for the entire period is 0.45.

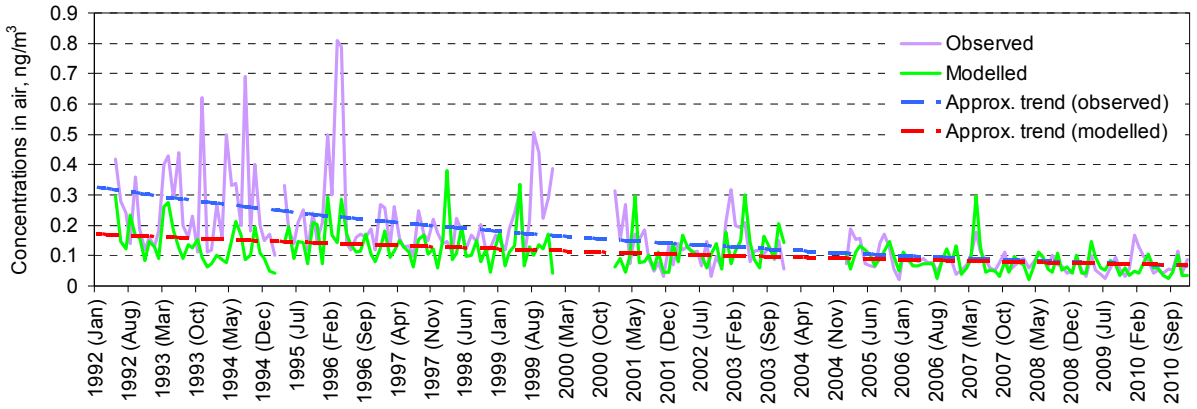


Fig. 1.20. *Modelled and measured monthly mean concentrations of cadmium and their long-term approximated trends at station DE8 (Germany)*

Parameters characterizing agreement between modelled and observed levels are calculated for each of the selected stations. Calculated levels of lead are characterized by the highest correlation with observations (Fig. 1.21a,c). Relatively low correlation is noted for mercury concentrations in air, which is explained by relatively weak temporal variability of mercury air concentrations. However, NRMSE for mercury concentrations is very low (Fig. 1.21b). It means that its levels are satisfactory reproduced by the model. NMRSE for lead and cadmium does not exceed a value of 2. It can be interpreted as the agreement of modelled and observed levels within a factor of two.

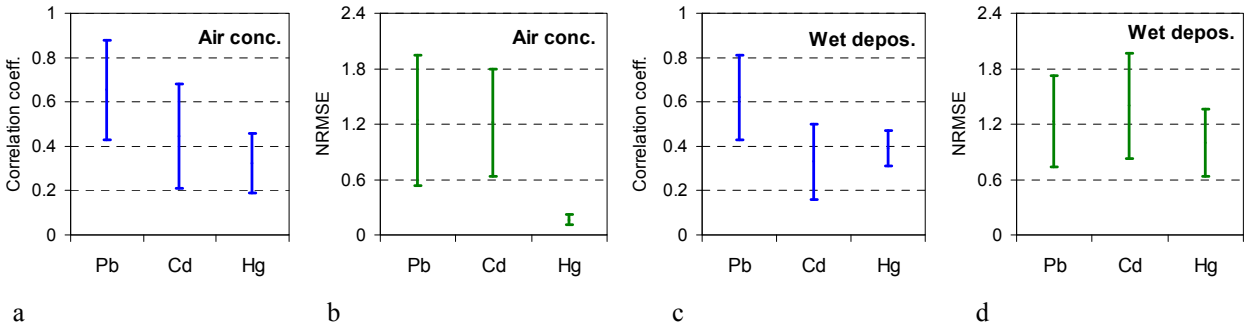
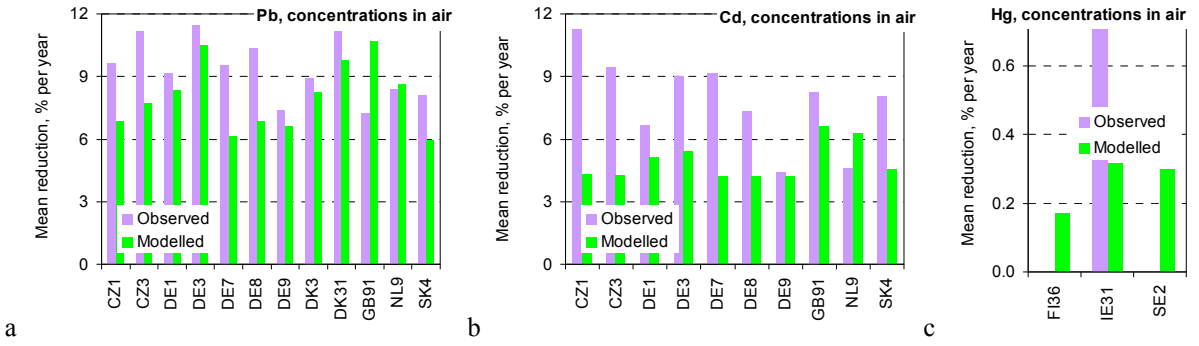


Fig. 1.21. *Ranges of correlation coefficients (a, c) and NRMSE (b, d) for monthly mean air concentrations and monthly wet deposition.*

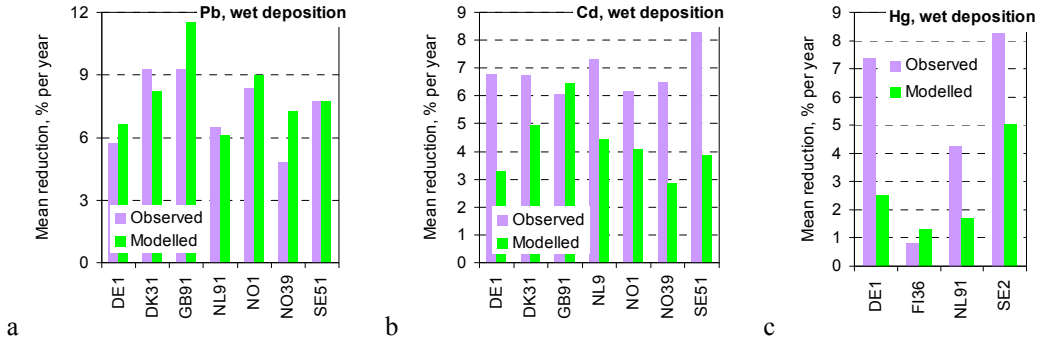
Mean relative reduction of heavy metal levels is estimated for every selected station (Fig. 1.22). Modelled and measured air concentrations of lead decline at average rate of 6 – 11% per year (Fig. 1.22a). For observed cadmium concentrations this rate is similar - 5 – 11% per year, while for modelled concentrations it is smaller and ranges from 4 to 6% per year (Fig. 1.22b). Long-term reduction of mercury levels is relatively small and statistically not significant (Fig. 1.22c).



a b c

Fig. 1.22. *Mean relative reductions of lead (a), cadmium (b) and mercury (c) concentrations in air at the selected EMEP monitoring stations*

Reductions of observed wet deposition of lead are similar to those obtained by modelling (Fig. 1.23a). The same is correct for the stations measuring wet deposition fluxes of cadmium in Denmark and the United Kingdom (Fig. 1.23b). Underestimated magnitude of deposition reduction of cadmium at the Scandinavian stations is explained by high levels of observed fluxes not captured by the model. Smaller rate of reduction of modelled wet deposition at the DE1 station is caused by somewhat underestimation of the observed levels in the beginning, and overestimation in the end of the considered period. Differences in modelled and observed reduction rates of mercury fluxes can be caused by uncertainties of mercury speciation in anthropogenic emissions, and by complexity of parameterization of atmospheric chemistry of mercury (Fig. 1.23c).



a b c

Fig. 1.23. *Mean relative reductions of lead (a), cadmium (b) and mercury (c) wet deposition fluxes at the selected monitoring stations*

Long-term trends of heavy metal levels observed at the EMEP monitoring stations are reproduced by the model reasonably well.

In general, the model reasonably well reproduces observed levels of lead, cadmium and mercury over the considered long-term period. Magnitudes of modelled and observed concentrations and wet deposition agree within a factor of two. The model favourably reproduces seasonal variations of the observed levels. Mean rates of reduction of modelled and observed values are comparable.

Factors affecting long-term trends

Comparison of long-term emission trend of lead in the European part of the EMEP region with trend of calculated deposition demonstrates that the reduction of deposition is smaller than that of emission (Fig. 1.24). Besides, long-term changes of deposition are less smooth compared to the changes of emissions. In order to explain the reasons of these changes the effects of three factors are evaluated: long-term changes of anthropogenic emissions, inter-annual meteorological variability and temporal changes of wind re-suspension of heavy metals.

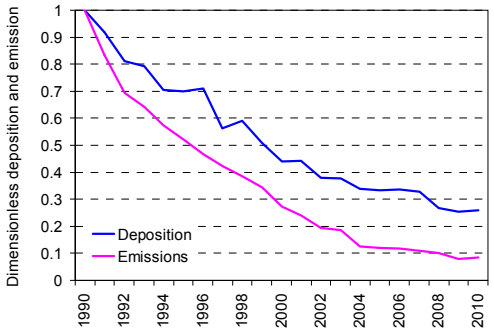


Fig. 1.24. *Dimensionless emission and deposition of lead in Europe*

The effects of these three factors have been estimated. Details regarding the approach are available in the Technical report [*Shatalov et al.*, 2014], while the main outcomes are summarized in this chapter. The main factor conditioning the decline of lead levels in the EMEP region is reduction of anthropogenic emissions (Fig. 1.25). Its role is more essential in the beginning of the considered period. In the end of the period the reduction of emissions is relatively low and thus this effect is also weaker. Meteorological variability is responsible for about ±10% variation of deposition in Europe, and it does not exhibit long-term trend. This effect is relatively small in the beginning of the considered period, but it increases as the effect of decline of anthropogenic emissions weakens. The effect of changes of re-suspension is expressed as a declining trend because of the assumed long-term decrease of lead concentrations in soils. Its magnitude is comparable with that of the effect of meteorological variability.

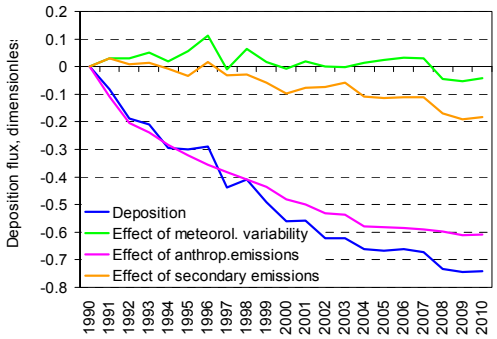
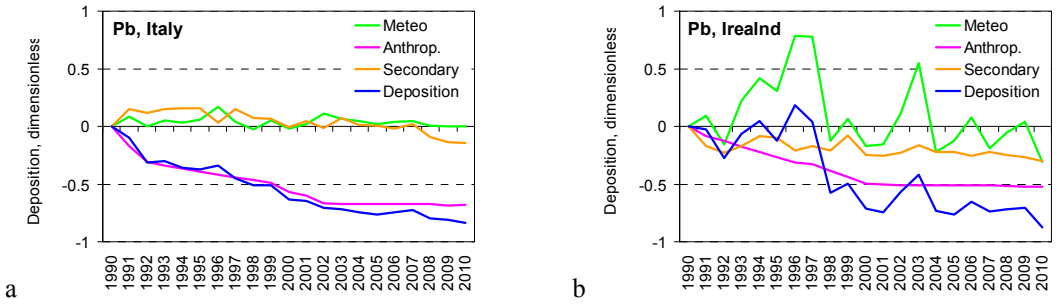


Fig. 1.25. *Relative lead deposition changes in Europe caused by different factors*

In the beginning of the considered period (1990-2010) the main factor controlling long-term changes is anthropogenic emission. In the end of the period the effects of meteorological variability and secondary sources become as important as the effect of anthropogenic emission reduction.

The effects of anthropogenic emission changes, meteorological variability and changes of wind re-suspension estimated for particular countries may differ from those for Europe as a whole, both in terms of their magnitude and temporal variations. These effects have been estimated for each European country. In most of the countries reduction of anthropogenic emissions is the main factor governing long-term changes of lead, whereas the role of changes of wind re-suspension and annual meteorological variability become comparable with the effect of anthropogenic emissions in the second half of the considered period. It can be exemplified by Italy (Fig. 1.26a). In some countries (e.g., in Ireland, Fig. 1.26b) the effect of meteorological variability is comparable with the effect of anthropogenic emission changes throughout the entire period 1990 – 2010.



a b

Fig. 1.26. *Relative lead deposition changes in Italy (a) and Ireland (b) caused by different factors.*

Long-term trends of pollution levels of lead, cadmium and mercury in the EMEP region for the period from 1990 to 2010 are examined using modelling results and monitoring data. Pollution levels of lead, cadmium and mercury in the EMEP region have been reducing since 1990 at rate 6.7 %, 3.4% and 2.3% per year, respectively. However, in particular countries the rate of long-term changes differs significantly from the rate averaged for the EMEP domain as a whole. Long-term reduction rate of heavy metal pollution in countries is not constant. As a rule, it is fast in the beginning of the considered period, due to significant reduction of anthropogenic emissions. In the end of the period the decline of anthropogenic emission is relatively slow, and its contribution to pollution changes becomes comparable with the contributions of annual meteorological variability and long-term changes of secondary sources.

1.4. Pollution levels and transboundary fluxes in 2012

Heavy metal pollution levels in 2012

Modelling information about pollution levels of lead, cadmium and mercury in the EMEP region and in the individual countries in 2012 has been prepared and allocated in the Internet [www.msceast.org]. The main features of pollution levels and atmospheric transboundary transport of heavy metals are overviewed in this section.

Spatial distribution of heavy metal pollution levels is mostly determined by location of emission sources and meteorological parameters responsible for atmospheric dispersion and scavenging of the pollutants. Relatively high levels of concentrations in air (Fig. 1.27a) and total deposition (Fig. 1.27b) of lead in 2012 are noted for countries in the central (Poland, Germany, north of Italy) and in the south-eastern (the Balkan region, east of Ukraine) parts of Europe and for the southern part of Kazakhstan. These levels are caused by significant anthropogenic and secondary sources in these regions. Besides, comparatively high levels in the southern part of Russia, the western part of Kazakhstan and the Caspian region are caused mostly by influence of wind re-suspension from desert areas of Central Asia. Similar spatial distribution of concentrations and deposition is noted for cadmium.

Annual mean concentrations of mercury in air are distributed almost homogeneously over the EMEP region. The lowest concentrations (1.3 – 1.4 ng/m^3) take place over Scandinavia, the most part of Russia and the north-western part of Kazakhstan. The highest levels (> 1.8 ng/m^3), associated with industrial activity, are noted for northern Italy, the Balkans region, Turkey, south-east of Central Asia. This low spatial variability is explained by significant influence of intercontinental transport of mercury due to long residence time of mercury in the atmosphere. Spatial pattern of mercury in the western

and central parts of Europe is similar to that of cadmium and lead. However, there is no elevated deposition in the southern part of Russia, western Kazakhstan and the Caspian region, since re-suspension of particulate mercury has likely low effect on deposition and thus it is not considered in modelling.

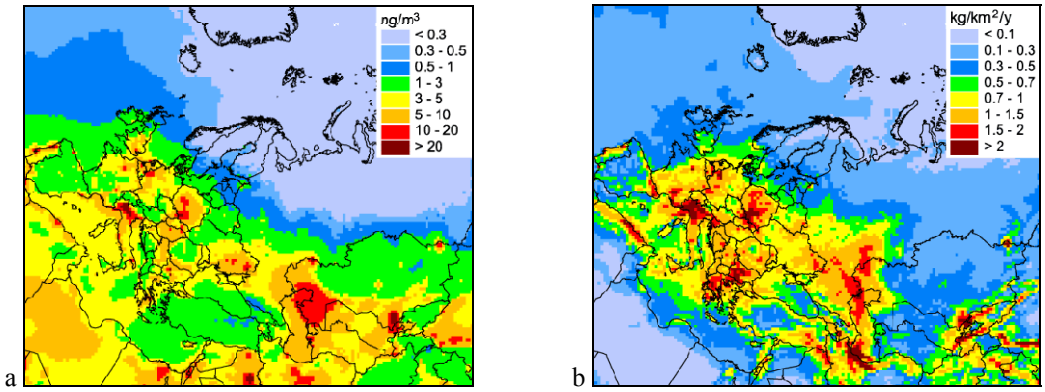


Fig. 1.27. *Annual mean concentrations in air (a) and total deposition (b) of lead in 2012*

Country-averaged deposition of cadmium in 2012 ranges from 5 to 80 g/km^2/y (Fig. 1.28). Deposition range for lead is 0.1 – 2.4 kg/km^2/y, and for mercury - 4 - 21 g/km^2/y. The highest country-averaged deposition fluxes of the considered metals take place in Poland, Monaco, Slovakia, Slovenia, Italy, Belgium and Bulgaria. The lowest heavy metal deposition fluxes are noted in Norway, Sweden, Finland, Russia, Iceland, Ireland, Turkmenistan, and Kazakhstan.

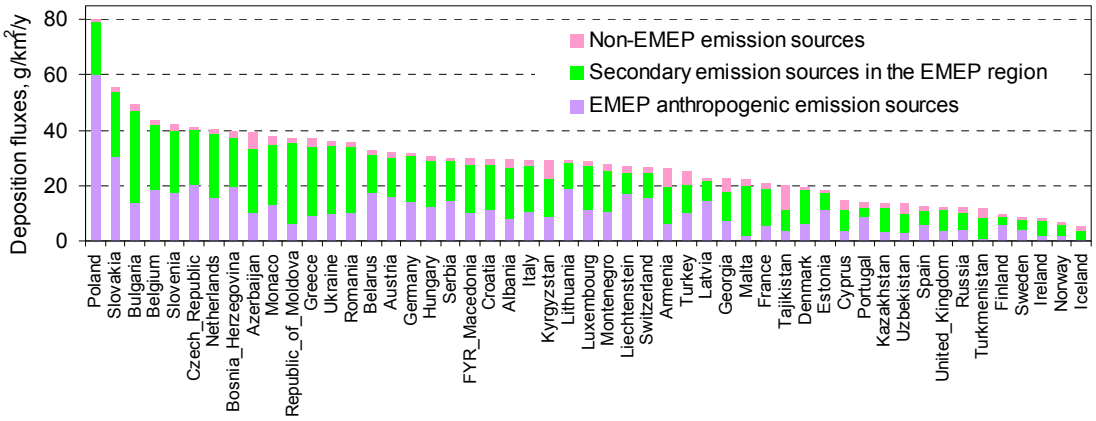


Fig. 1.28. *Country-averaged deposition fluxes of cadmium from the European and Central Asian anthropogenic, secondary and non-EMEP emission sources in 2012*

Deposition fluxes of heavy metals are caused by three groups of sources. They are anthropogenic emissions in the EMEP countries, secondary (natural emission and re-suspension) emissions in the EMEP region and sources (both anthropogenic and secondary) located outside the EMEP countries (non-EMEP sources). Deposition fluxes of lead and cadmium to the EMEP countries in 2012 are mostly caused by anthropogenic and secondary emission sources (Fig. 1.28). Since the anthropogenic emissions of lead and cadmium substantially have reduced for the last two decades, the role of secondary sources in pollution of the EMEP countries becomes more important. The contribution of secondary sources ranges from 10% to 80% for lead and from 20% to 80% for

cadmium. The contribution of non-EMEP sources to lead and cadmium total deposition is 2 – 15% in the most of countries. However, the contribution is higher in the Trans-Caucasian and the Central Asian countries (up to 40%) because of influence of sources of non-EMEP Asian countries within the EMEP region (e.g., Iran, Iraq, Syria etc.). Mercury deposition fluxes are mainly presented by anthropogenic component (1 - 55%) and by contribution of intercontinental transport of both anthropogenic and secondary emissions (43 - 97%). Contribution of domestic secondary sources of the EMEP region is relatively low (2 - 5%).

Transboundary transport in 2012

Anthropogenic deposition of lead, cadmium and mercury is split in two components: deposition caused by national emission sources and those coming from atmospheric transboundary transport. The contribution of foreign sources is significant in most of the EMEP countries. For example, in 36 countries of total 51 the contribution of foreign emission sources to lead deposition exceeds 50% (Fig. 1.29). For cadmium the contribution of foreign sources exceeds 50% in 37 countries, and for mercury – in 32 countries. However, even if the contribution of anthropogenic sources to deposition is relatively low for a country as a whole, it can be high in particular grid cells, for example, nearby state borders. Information about spatial distribution of contribution of foreign sources to pollution levels for each EMEP country is available in the Internet at MSC-E website (http://www.msceast.org/index.php/emep-countries).

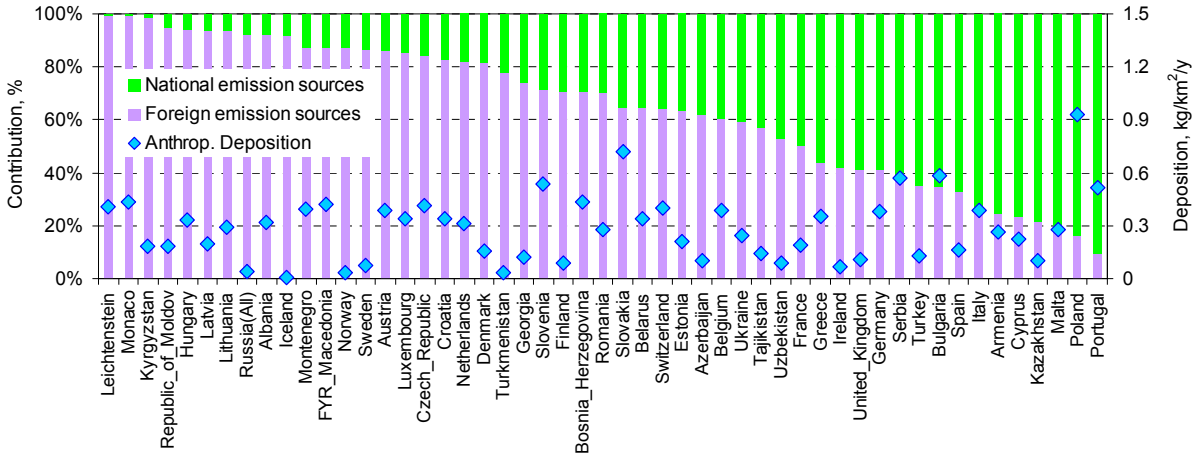


Fig. 1.29. *Relative contribution of the transboundary transport and national sources to anthropogenic lead deposition in the European and the Central Asian countries and deposition values from anthropogenic emission sources in 2012*

Emission sources of each country contribute to transboundary pollution in other countries of the EMEP region. The countries which contribution to transboundary transport, expressed in absolute terms, is the highest are Poland, Turkey, Italy and Kazakhstan. These countries are characterized by significant national emissions and thus contribution of their sources to transboundary transport is dominating. Besides, Germany and Russia are significant contributors to long-range transport of cadmium and mercury. Spain is one of the largest contributors of lead and cadmium to long-range transport.

The contribution of countries to transboundary transport can be expressed in relative terms, e.g., as a fraction of emitted mass transported outside state borders. For cadmium this fraction is more or less similar for most of the EMEP countries and it varies from 60% to almost 100% (Fig. 1.30). The

exception is Russia: due to vast territory most of emitted lead and cadmium are deposited within the country's territory, and relatively small fraction (24% for Pb and 23% for Cd) enters transboundary transport. Mercury persists longer in the atmosphere compared to lead and cadmium. Therefore, its fraction of emissions involved in transboundary transport is rather high and ranges from 80 to almost 100%.

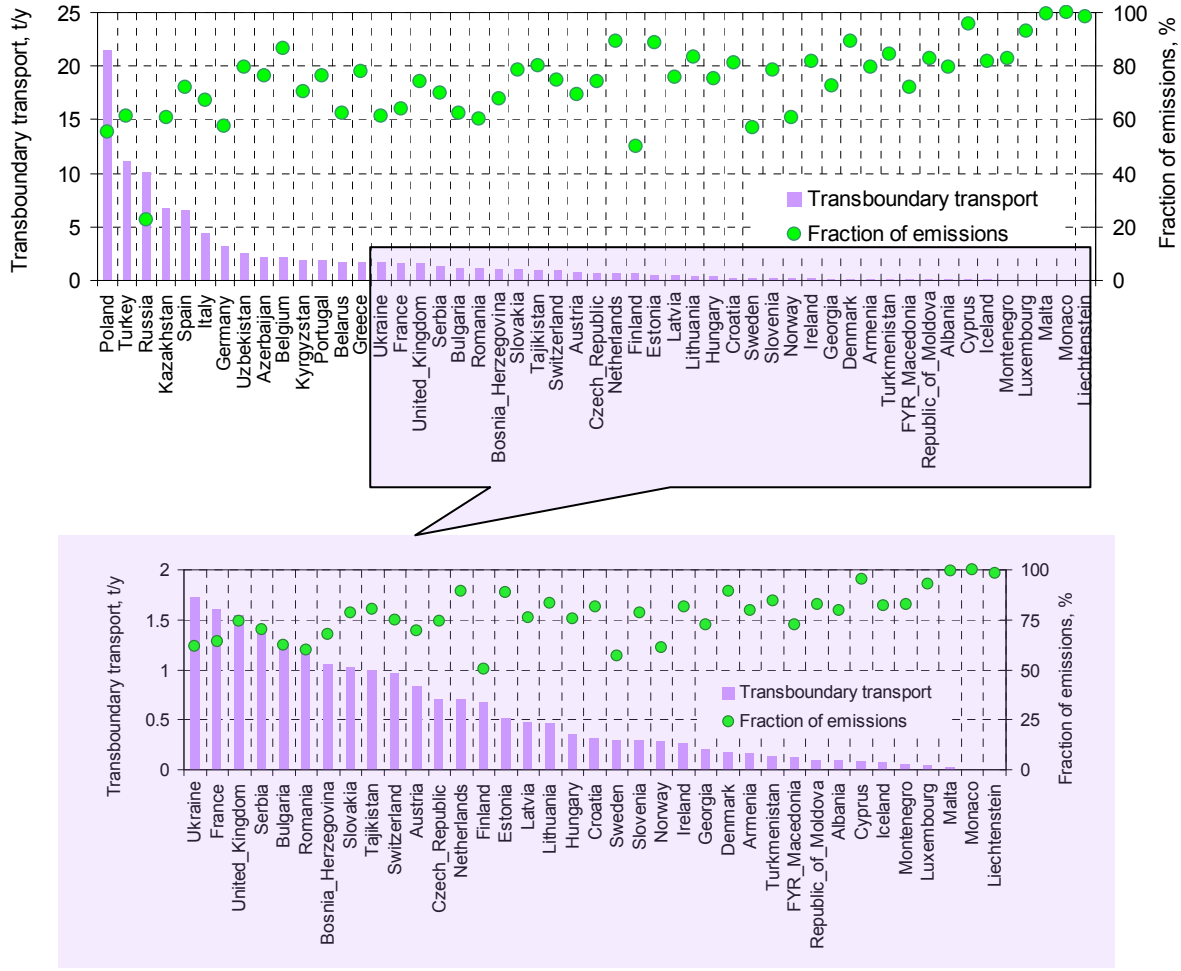


Fig. 1.30. *Absolute contribution of the European and the Central Asian countries to cadmium transboundary transport in 2012 and relative fraction of national emissions involved into the transboundary pollution*

This section provides an overview of the heavy metal pollution levels in the EMEP region as a whole and its particular countries. More detailed information as well as original modelling data on spatial distribution of concentrations and deposition of the metals in the EMEP region, country-specific information about pollution levels and source-receptor relationships are available in the Internet at the MSC-E website http://www.msceast.org/.

1.5. Ecosystem-dependent deposition

In order to evaluate harmful effect of deposition of heavy metals for biota and human health the deposition is compared with their threshold levels (so-called critical loads). If the critical loads are exceeded the harmful effects likely occur. Evaluation of critical load exceedances is carried out by the Coordinating Centre for Effects (CCE) of WGE. For this purpose deposition data specific for different ecosystems are required. Deposition of lead, cadmium and mercury to 18 types of underlying surface is calculated annually and allocated at the MSC-E website (http://www.msceast.org/index.php/emep-countries). An example of lead deposition to forests in 2012 is presented in Fig. 1.31. As seen, spatial distribution of deposition to forests is similar to grid-cell averaged deposition in the EMEP region. However, deposition fluxes to forest are generally higher due to larger contribution of dry deposition.

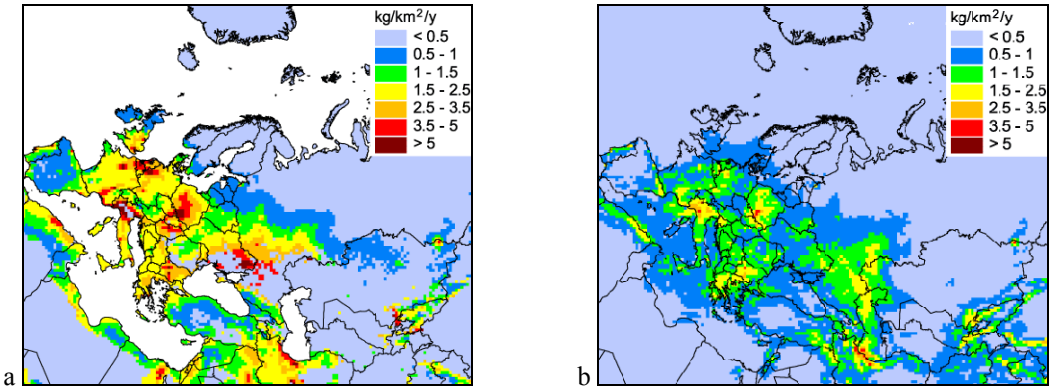


Fig. 1.31. *Deposition of lead to coniferous forests (a) and gridcell-averaged deposition (b) in 2012.*

Long-term changes of ecosystem-dependent deposition are analyzed applying the approach described in section 1.3 of this Chapter. Information on long-term trends of ecosystem-dependent deposition is available for any land cover type in each EMEP country as well as for the entire EMEP region. Few examples of deposition trends to the EMEP region are presented in Fig. 1.32. Reduction of lead to crops is described by two exponential components: slow component with τ_1 = 40 years, and fast component with τ_2 = 11 years. In case of cadmium deposition to root crops one exponent with τ = 30 years is sufficient. Mercury decline to sea surface within the EMEP domain is approximated by two components: exponential term (τ = 14 years) and a constant 'base'.

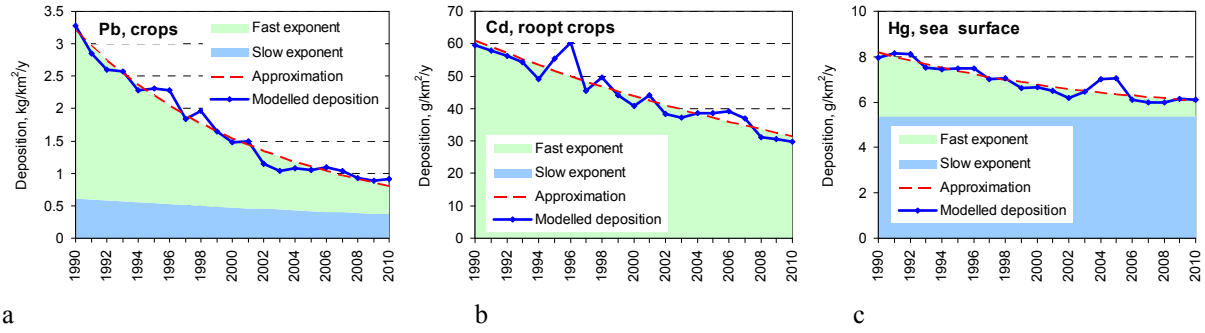


Fig. 1.32. *Long-term trends of deposition of lead to crops (a), cadmium to root crops (b) and mercury to sea surface (c) in the EMEP region for 1990-2010 period*

Deposition reduction rate to different types of underlying surface depends on properties of the surface and location of emission sources. The highest rate (5 – 8% per year) is noted for lead, due to phasing out of leaded gasoline in Europe (Fig. 1.33). The lowest rates of reduction take place for mercury because of significant and almost constant contribution of non-EMEP sources to mercury deposition in the EMEP region. The highest rates of mercury reduction are indicated for land-cover types 'urban', 'crops', 'root crops', which are typically located close to regions of anthropogenic activity. As a rule, the contributions of non-EMEP sources to these types of surface are lower, and of anthropogenic sources are higher compared to the other types of surfaces. Therefore, reduction of mercury anthropogenic emissions causes stronger decline of mercury deposition to these surfaces. However, it should be noted that in particular countries or regions of the EMEP domain the rates can differ markedly from the averaged ones.

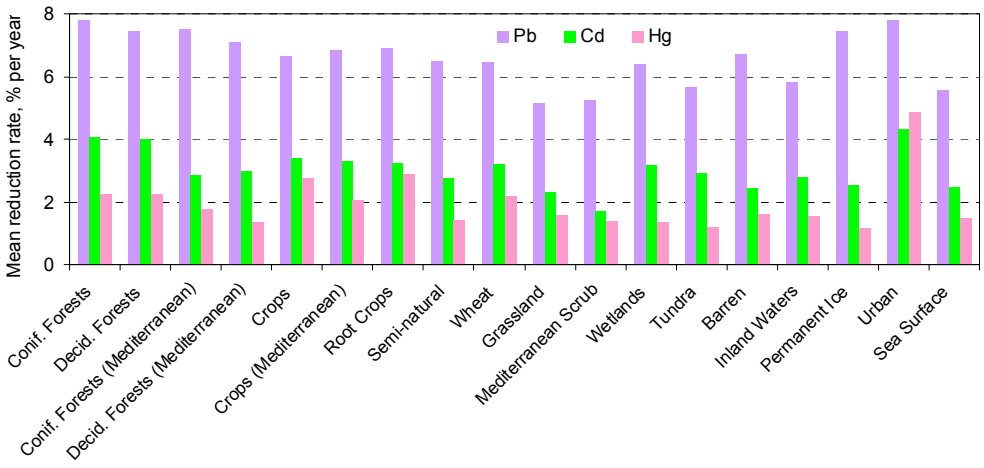


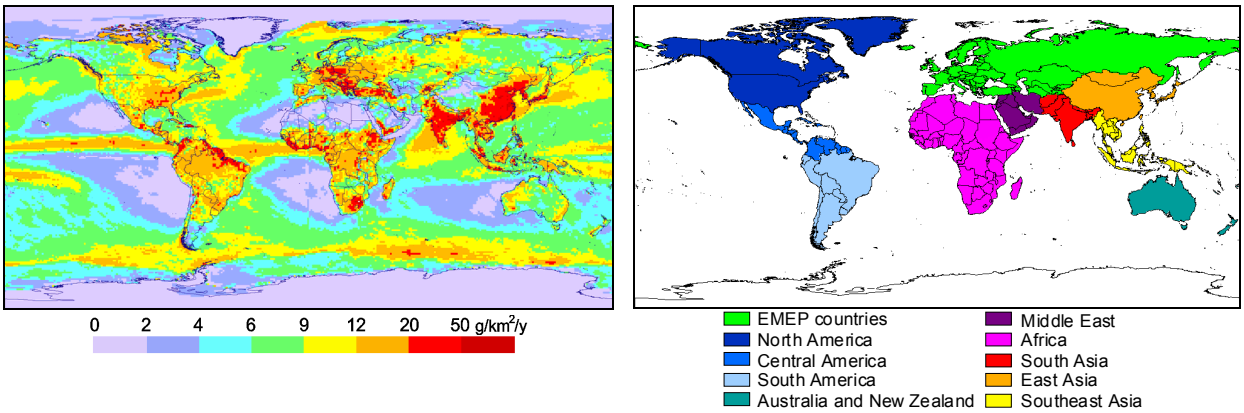
Fig. 1.33. *Mean reduction rate of lead, cadmium and mercury deposition to different types of the underlying surface between 1990 and 2010.*

1.6. Mercury intercontinental transport and its impact on pollution of the EMEP countries

Mercury differs from other heavy metals by its ability to long-range dispersion in the atmosphere. The bulk mercury atmospheric form – gaseous elemental mercury (Hg^0) – which is a poorly soluble and relatively inert gas can drift in the atmosphere for months making possible transport over thousands of kilometres. After that it can be oxidized and deposited to the ground or water surfaces contributing to local pollution of terrestrial and aquatic ecosystems. Therefore, mercury pollution levels in the EMEP countries are largely affected by emission sources from other regions (see Section 1.4). On the other hand, mercury originated from the European sources contributes to contamination of other regions and continents.

Mercury atmospheric dispersion on a global scale and its transport between different continents and regions in 2012 were simulated with GLEMOS. The model assessment is based on the UNEP global inventory of mercury anthropogenic emissions for 2010 [*AMAP/UNEP*, 2013]. Calculated global distribution of mercury deposition is shown in Fig. 1.34a. Along with high mercury deposition fluxes over industrial regions (East and South Asia, Europe, North America etc.) and regions with significant artisanal and small-scale gold mining (Southeast Asia, South America, Sub-Saharan Africa) relatively large deposition is also detected in some remote areas of the oceans and the polar regions. The latter

are characterized by intensive oxidation of Hg^0 in the lower troposphere leading to increased Mercury deposition during springtime (Atmospheric Mercury Depletion Events, AMDE). Definition of the source/receptor regions considered in the study is shown in Fig. 1.34b.



a b

Fig. 1.34. *Global distribution of mercury deposition flux in 2012 and definition of source regions used in the source-receptor analysis.*

Figure 1.35 presents source attribution of mercury deposition to various regions of the world. Size of each pie-chart diagram corresponds to average mercury deposition flux to the region. As seen mercury deposition to the EMEP countries (including the whole territory of the Russian Federation) consists of almost equal contributions of contemporary anthropogenic emissions and emissions from natural and legacy sources. A half of the anthropogenic part is contributed by domestic emission sources and the other half is by transport from sources located in other regions. The largest external contributors include East Asia (11%), Africa (4%), Southeast Asia (2%) and South America (2%).

Contribution of domestic sources to mercury deposition to North America (13%) is roughly equal to contribution of East Asia (11%). The EMEP countries (5%), Africa (5%) and Central America (2%) are among other contributors of deposition from contemporary anthropogenic emissions. At the same time, natural and legacy sources contribute up to 58% of average deposition to this continent. In contrast, current anthropogenic emissions account for two thirds of mercury deposition to East Asia, which is dominated by contribution of domestic sources (56%). Moderate mean deposition flux to this region (17 $g/km^2/y$) is explained by averaging between the heavily industrialized eastern part of China and relatively clean western part of the region (Fig. 1.35a). Even higher average mercury deposition in South Asia (about 20 $g/km^2/y$) is also largely affected by domestic sources (35%) but also includes considerable contributions of other regions: East Asia (7%), Africa (4%) and EMEP (3%).

As it has been mentioned above, mercury deposition to the EMEP countries is largely defined by emissions from the EMEP domestic sources, as well as from sources located in East Asia and Africa. However, contribution of these source groups differs significantly over the EMEP region. Contribution of the EMEP emissions significantly exceeds 25% of mercury total deposition over most of the central, western and southern European countries as well as over some regions of the EECCA countries (Fig. 1.36a). In some industrial areas, contribution of domestic sources can exceed 50%. On the other hand, contribution of the EMEP sources does not exceed 15% in Northern Europe and in the easternmost part of the domain. Contribution of East Asian emissions is below 6% in Central and Southern Europe, however, is growing above 12% in Eastern Russia and over the Arctic (Fig. 1.36b). Emission sources located in Africa contribute more than 5% of total mercury deposition in some countries of Southern Europe, whereas their contribution over the rest of the EMEP region does not exceed a few percents (Fig. 1.36c).

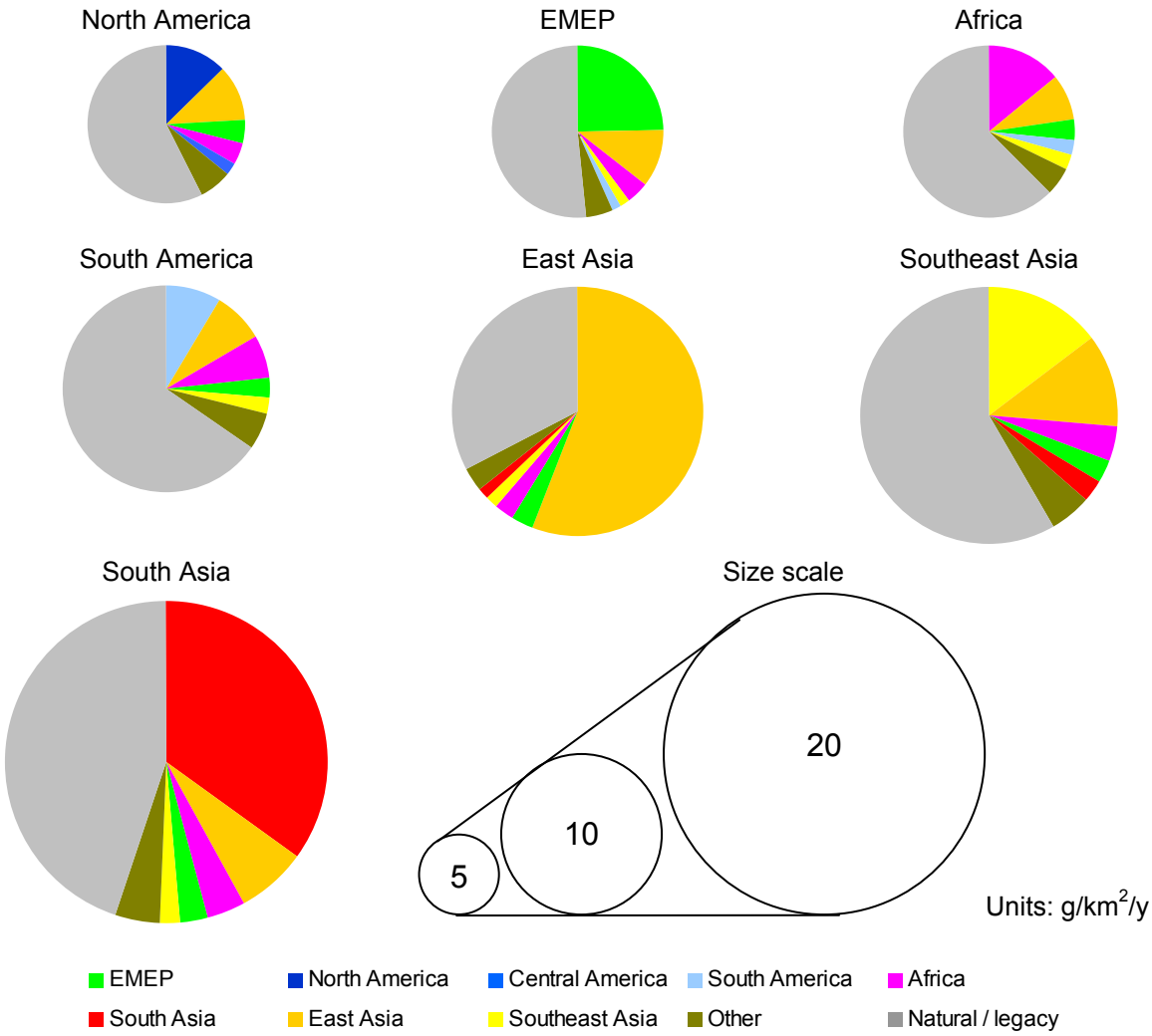


Fig. 1.35. *Source attribution of average mercury deposition to various regions of the world in 2012. Linear size of the pie-chart diagrams corresponds to average mercury deposition flux to appropriate region.*

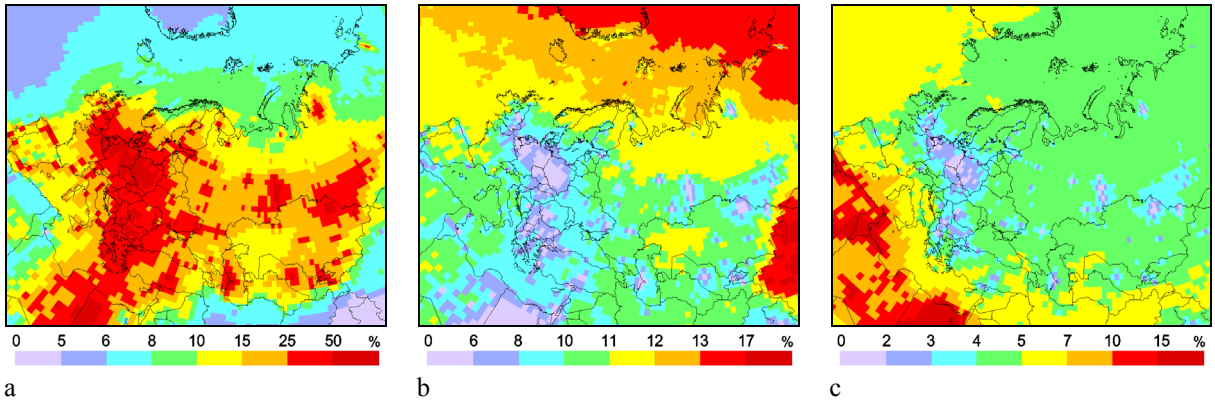


Fig. 1.36. *Relative contribution of the different source regions to mercury deposition over the EMEP domain: (a) - EMEP domestic sources; (b) - East Asia, (c) - Africa.*

Mercury deposition in the EMEP countries is largely defined by emissions from the EMEP domestic sources (15-50%), as well as from sources located in East Asia and Africa. However, contribution of

these source groups differs significantly over the region. In addition, about 50% on average is contributed by natural and legacy sources.

1.7. "Near-real time" estimates of pollution levels

According to current practice adopted in the Convention, submission of emissions and information about pollution levels becomes available for the EMEP countries with two-year delay. However, recent changes of emissions in the EMEP countries are relatively low. Therefore, this two-year temporal gap can be reduced (up to a few months), if previously reported emissions are used. In particular, preliminary information about heavy metal pollution levels in 2013 can be obtained on the base of emissions reported in 2011 and meteorological data for 2013. It should be noted that in this case changes between 2011 and 2013 are explained by meteorological variability.

"Near-real time" modeling of pollution levels of lead and cadmium was carried out for the EMEP region. This information was provided to the EMEP countries in February, 2014. Compared to 2011, significant decline (> 50%) of deposition in 2013 takes place in Scandinavian countries, in Pyrenees, in the northern and southern parts of Russia (Fig. 1.37). The increase is noted in the western and central parts of Europe (France, the United Kingdom, Switzerland, Austria etc.), and in the central part of Russia. Similar distribution of the changes is calculated for lead.

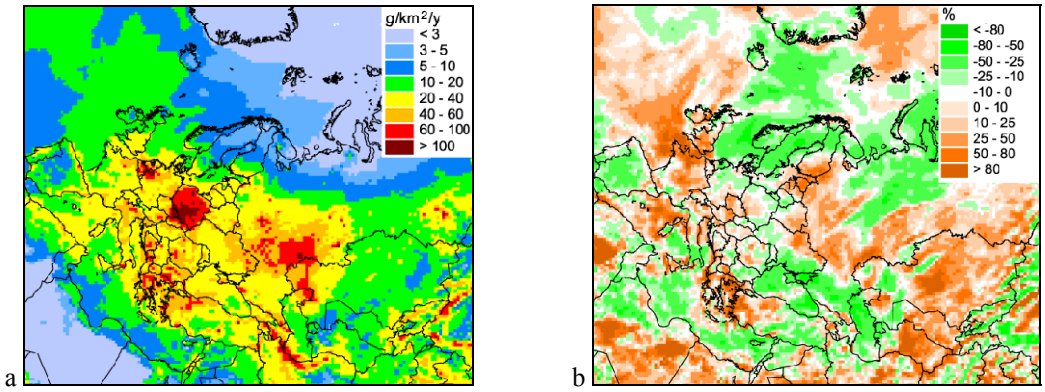


Fig. 1.37. *Annual deposition of cadmium in 2013 (a) and relative change between deposition in 2011 and 2013 (b) (positive values mean increase from 2011 to 2013).*

For the EMEP region as a whole deposition of lead increased by 5%, and of cadmium – by 0.2%. Country-averaged deposition changes are different: increase in some countries and decline in the others (Fig. 1.38). As a rule, magnitudes of changes for lead are higher than those for cadmium. In some countries direction of the change for lead and cadmium deposition differs. For example, in Bulgaria, Ukraine and Republic of Moldova deposition of lead increased and deposition of cadmium decreased deposition from 2011 to 2013.

Results of "near-real time" modeling of lead and cadmium levels are allocated at MSC-E website (www.msceast.org).

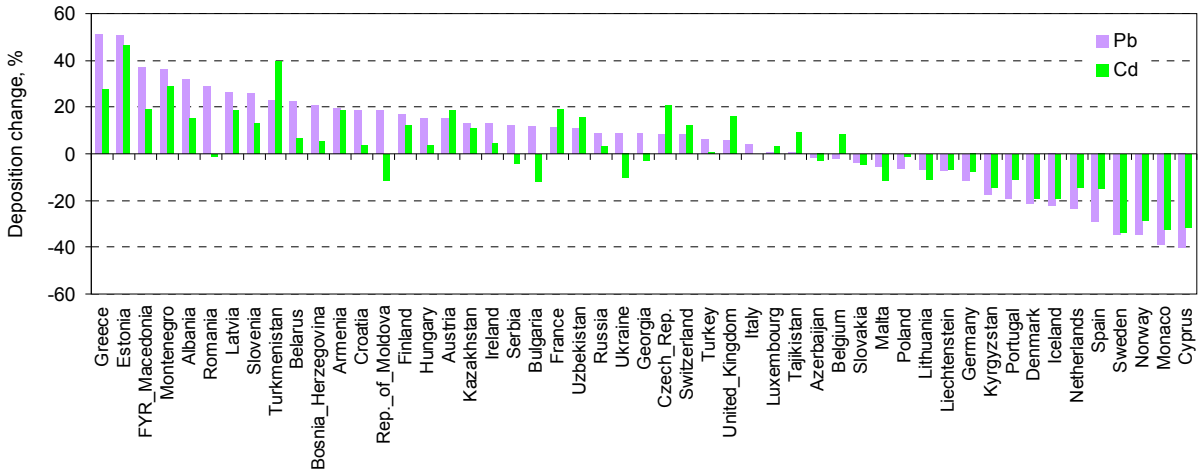


Fig. 1.38. *Country-averaged changes of deposition of lead and cadmium between 2011 and 2013. Positive values mean increase from 2011 to 2013*

2. DEVELOPMENT OF GLEMOS MODELLING SYSTEM

Global EMEP Multi-media Modelling System (GLEMOS) has been developed for the last several years by MSC-E as a new generation model for the EMEP operational simulations of the environment pollution by heavy metals, POPs and other contaminants. The current progress of GLEMOS development is discussed below.

2.1. Overview and current status of GLEMOS development

GLEMOS is a multi-scale multi-pollutant simulation platform recently developed for operational and research applications within the EMEP programme. The framework allows modelling of dispersion and cycling of different classes of pollutants (e.g. mercury and other heavy metals, POPs) in the environment with a flexible choice of the simulation domain (from global to national scale) and spatial resolution. In addition, GLEMOS supports multi-media description of pollutants' cycling in the environment. A modular architecture of the modelling system allows flexible configuration of the model set-up for particular research task and pollutant properties. The modular architecture is a key feature of the modelling system aimed at providing flexibility for multi-media simulations of pollutants with diverse properties. Each environmental medium is presented in the model by a set of procedures describing general processes in the medium which are combined into the program modules. Development of the modelling system was documented in a series of MSC-E and MSC-W Technical reports [*Tarrason and Gusev*, 2008; *Travnikov et al*., 2009; *Jonson and Travnikov*, 2010; *Travnikov and Jonson*, 2011; *Jonson and Travnikov*, 2012; *Shatalov et al*., 2013].

Resent updates and development of the modelling system performed during the last year include the following directions:

- Preparation to transition to the new EMEP gridding system
- Pilot simulations on the new EMEP grid
- Elaboration of multi-media model approach for mercury (oceanic module)

- Refinement of multi-media model approach for POPs (effect of direct releases to soil)
- Parameterizations of POP sorption on aerosols and degradation in particulate phase
- Preparation of GLEMOS for public use

General aspects of the GLEMOS development and the model updates related to heavy metals are briefly discussed below. The model improvements specific for POP modelling are considered in other EMEP Status Report [*Gusev et al.*, 2014]. Besides, more information on GLEMOS developments is available in the MSC-E Technical Report [*Shatalov et al*., 2014].

2.2. Preparation to transition to the new EMEP gridding system

Following decisions of the Executive Body for CLRTAP (*ECE/EB.AIR/113/Add.1*) MSC-E initiated preparatory work for transition of the EMEP operational modelling of heavy metal and POP pollution to the new EMEP grid. The grid changes include movement from the polar-stereographic to the regular geographic (latitude-longitude) projection of the Earth surface, appropriate transformation of the EMEP domain and increase of the grid spatial resolution. The changes of the projection are motivated by possibility of consistent model studies on different scales (from national to global), better consistency with common databases of input data (emissions, meteorology, land cover etc.) and improved data exchange with other scientific and environment protection communities [*EMEP/SB*, 2012].

The new EMEP domain defined on the latitude-longitude projection is shown in Fig. 2.1 (red line) in comparison with the old standard EMEP domain (green line). The new domain covers almost the same territory as the old one including Europe, Central Asia, the Mediterranean and surrounding areas and spreading from 30°W to 90°E and from 30°N to 82°N. The change of the EMEP domain is accompanied by increase of spatial resolution of the model grid (from 50×50 km^2 up to 10×10 km^2 in the angular equivalent) that aimed at better presentation of physical and chemical processes responsible for pollution dispersion and transformations in the atmosphere, increased details and, ultimately, enhanced accuracy of the assessment results. However, the additional accuracy to be gained from higher resolution depends on the quality of appropriate input data (meteorology, emissions data etc.), indicating therefore that refinement of the model grid should be accompanied by a corresponding increase in input data quality and resolution [*EMEP/SB*, 2012].

Fig. 2.1. *The old standard EMEP domain (green line) and the new EMEP domain (red line).*

Additional accuracy to be gained from higher resolution depends on the quality of appropriate input data, indicating therefore that refinement of the model grid should be accompanied by a corresponding increase in input data resolution and quality.

Transition of the model assessment to the new EMEP grid is associated with adaptation of the model code for applications in the new domain, collection and processing of variety of input information and the overall testing of the modelling system. The GLEMOS modelling system is updated to include

possibility of simulations on the new EMEP grid. Input information prepared for the new domain includes high spatially resolved meteorological data, detailed topography and land cover characteristics, air concentration of chemical reactants, data on sea currents etc. (Fig. 2.2). It should be noted that preparation of gridded anthropogenic emission data for modelling requires changes of national emission reporting for the new grid by all EMEP countries. In the meantime, for the transition period the gridded emissions can be produced by interpolation of emissions reported by countries in the old EMEP grid.

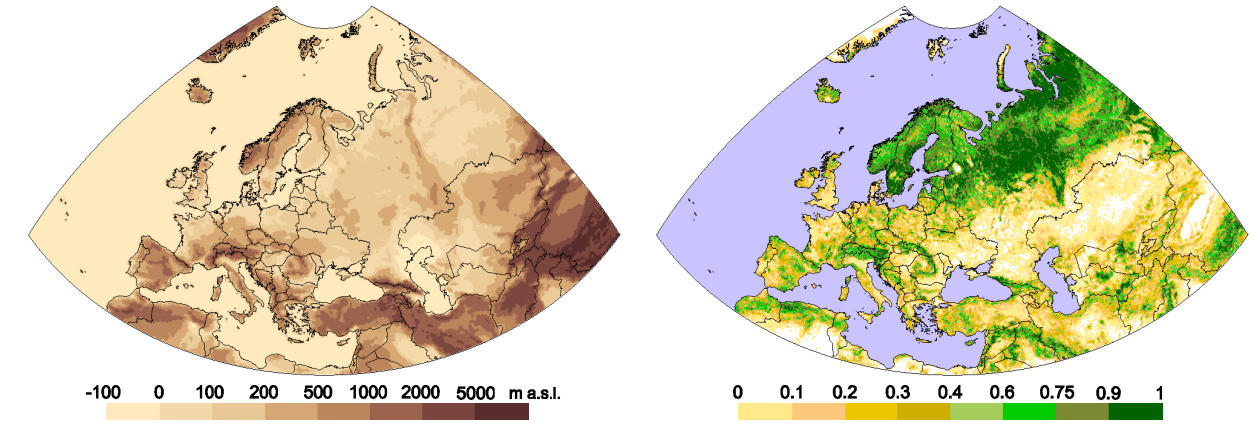


Fig. 2.2. *Some elements of input information prepared for modelling on the new EMEP grid: (a) – topography (height above sea level); (b) – land cover (fraction of forests and shrubs).*

Pilot simulations aimed at testing the whole modelling system on the new EMEP grid are discussed below.

2.3. Pilot simulations on the new EMEP grid

The updated version of GLEMOS was applied to pilot simulation of heavy metal atmospheric transport and deposition over the new EMEP domain. For the sake of testing mercury atmospheric dispersion was calculated with spatial resolution 0.2°×0.2° for two months of 2010 – January and July. To keep consistency between the regional and global simulations the most recent expert estimates of mercury anthropogenic emissions on a global scale [*AMAP/UNEP*, 2013] were used for the simulations instead of the official emission data. The original emission fields with spatial resolution 0.5°×0.5° were interpolated into the model native grid. Boundary conditions for regional modelling with 6-hour temporal resolution were retrieved from the GLEMOS simulations on a global scale.

Results of the pilot simulations are shown in Figs. 2.3 and 2.4. The figures present calculated spatial distribution of mercury deposition over the whole domain and over one of the EMEP countries (Germany) in January and July 2010. As seen mercury deposition over Europe and Central Asia is significantly higher in July due to more intensive mercury oxidation chemistry during summertime and somewhat higher precipitation over Central and Northern Europe. In general, spatial distribution of deposition flux is largely determined by the precipitation pattern due to prevailing contribution of wet deposition. Areas with very low mercury deposition flux commonly correspond to areas with low precipitation. In contrast, high deposition levels are defined by several competing factors including anthropogenic emissions of oxidized mercury forms, mercury oxidation in the atmosphere and removal by precipitation or surface uptake.

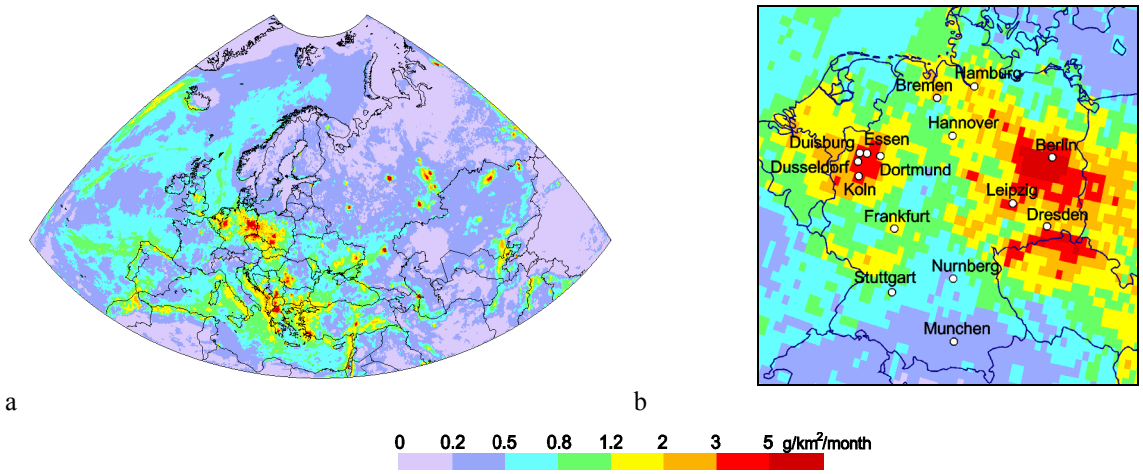


Fig. 2.3. *Monthly mean mercury deposition flux over the new EMEP domain (a) and over Germany (b) simulated for January 2010.*

The pilot simulation results demonstrate considerable improvement of spatial resolution of calculated deposition patterns. Figures 2.3(b) and 2.4(b) show enlarged patterns of mercury deposition over Germany. Implemented finer spatial resolution of the model grid (0.2°×0.2°) allows reproduction of detailed mercury deposition patterns on a national scale. In particular, high deposition fluxes are characteristics of industrialized and urbanized areas in North Rhine-Westphalia, Saxony and around Berlin. Seasonal variation of deposition in these areas is relatively low due to prevailing impact of local anthropogenic sources. In contrast, seasonal changes of mercury deposition are larger in Southern Germany, where deposition flux is largely affected by mercury oxidation in the atmosphere that is more intensive during summer time. It should be noted that accuracy and reliability of detailed deposition patterns are limited to significant extent by quality of spatially resolved input data used for the modelling – first of all, by meteorological and emissions data. Specifically for mercury, chemical speciation of anthropogenic emissions highly affects simulated deposition fields on national and regional scales. Therefore, increased spatial resolution of EMEP operational modelling requires improved quality standards for anthropogenic emissions reporting and other input data for modelling.

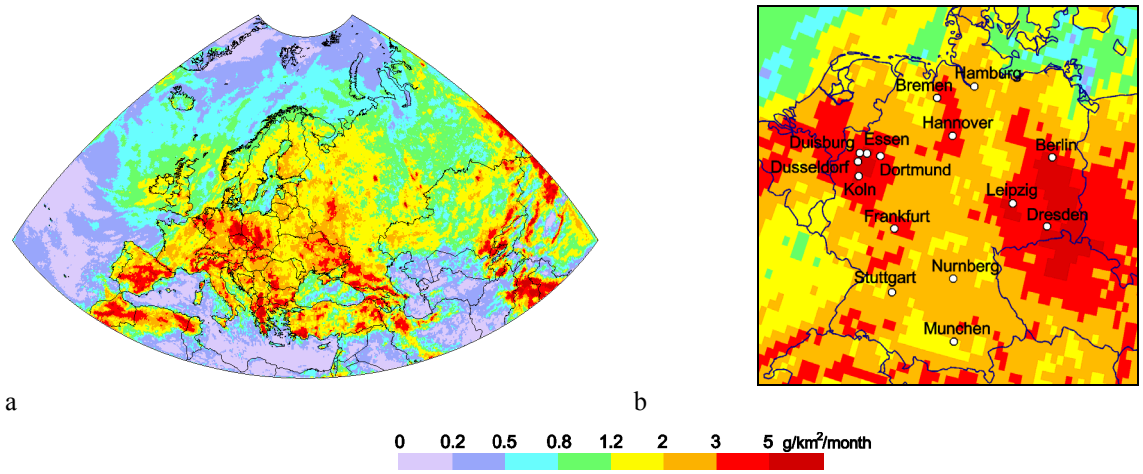


Fig. 2.4. *Monthly mean mercury deposition flux over the new EMEP domain (a) and over Germany (b) simulated for July 2010.*

The pilot modelling results were evaluated against the EMEP monitoring data. Figure 2.5 shows simulated monthly mean distribution of air concentration and wet deposition of mercury in July 2010. Coloured markers present mercury measurements at sites of the EMEP monitoring network. Both

modelled and observed data show that air concentration of gaseous elemental mercury (Hg^0) in Central and Northern Europe mostly varies from 1.5 to 1.8 ng/m^3 (Fig. 2.5a). The model predicts elevated Hg^0 concentration (over 2 ng/m^3) in Southern Europe, over the Baltic and Northern Seas in summer time due to high natural/secondary emissions from soil and seawater. However, absence of EMEP measurement data in these regions complicates evaluation of the model results. Elevated mercury wet deposition fluxes in July (more than 1 g/m^2/month) are estimated over the most territory of Central and Southern Europe (Fig. 2.5b). High deposition levels are determined by intensive oxidation of mercury in summer and significant precipitation. The model tends to overestimate wet deposition in Southern Europe, most probably, due to uncertainties in parameterization of atmospheric chemistry.

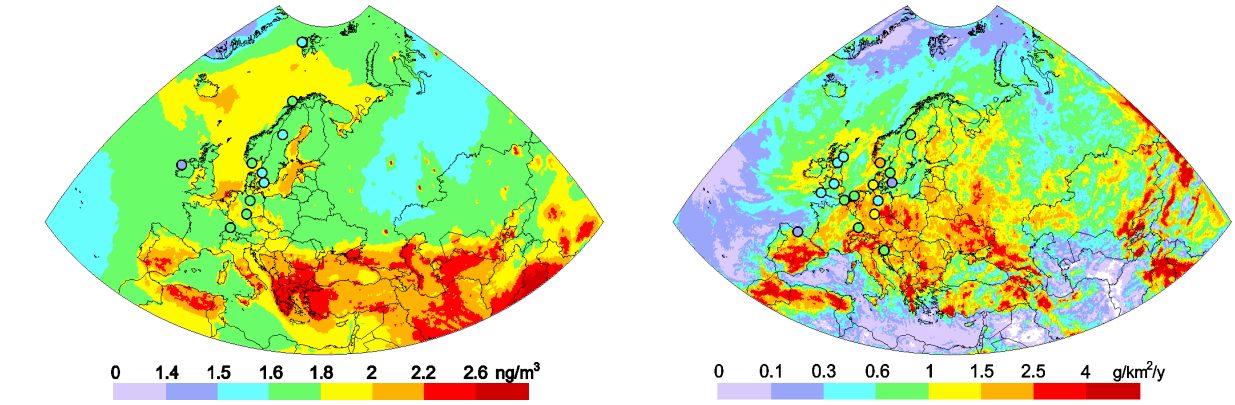


Fig. 2.5. *Monthly mean air concentration (a) and wet deposition (b) of mercury over the new EMEP domain in July 2010. Coloured circles show mercury observations from the EMEP monitoring network.*

Detailed evaluation of the model results against observations is shown in Fig. 2.6 in the form of scatter plots. As seen simulated air concentration of Hg^0 well agrees with measurement data (Fig. 2.6a). The model-to-measurement difference does not exceed 10% for both January and July. The deviation is larger for wet deposition. As it has been mentioned above the model tends to overestimate observed values in July (Fig. 2.6b). Taking into account no evident overestimation in January, one can expect that the model overpredicts summertime oxidation of Hg^0 in the troposphere. It leads to excess of mercury oxidized species in the atmospheric air and high levels of wet deposition. It should be noted that current understanding of mercury atmospheric chemistry in the troposphere is still incomplete in terms of both the major oxidation mechanisms and reaction products.

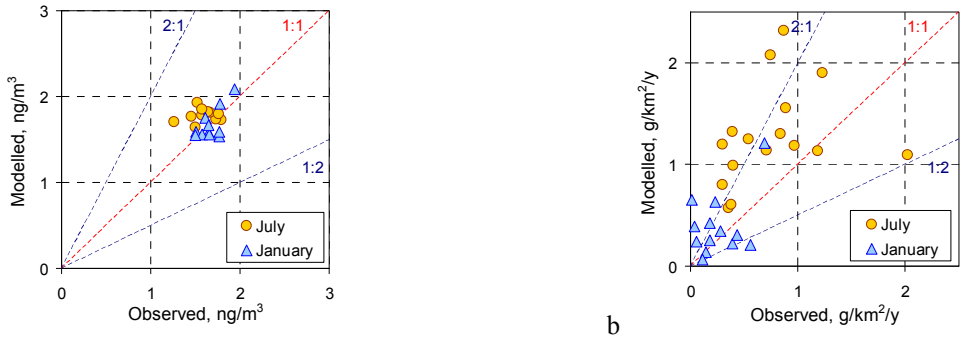


Fig. 2.6. *Evaluation of simulated monthly mean air concentration (a) and wet deposition (b) of mercury against observations for January and July 2010.*

To evaluate the model performance at fine spatial scales the simulation results were compared with mercury observations with high temporal resolution at one of the EMEP monitoring sites – Waldhof, Germany (DE2). Hourly mean model results were evaluated against observed hourly air concentration of Hg^0 and 3-hourly mean concentration of particulate mercury (Fig. 2.7). The monitoring site is located in Northern Germany and is affected by direct anthropogenic emissions from national sources. The model successfully reproduces short-term variation of both measured mercury species. In particular, the model catches three observed episodes of high Hg^0 concentration (days 5-8, 12-16 and 19-25). Hg^0 concentration during the episodes considerably exceeds the global background values (1.5-1.7 ng/m^3) and is most probably caused by plumes transported from regional anthropogenic sources (Fig. 2.7a). This is also confirmed by concurrent episodes of elevated concentrations of particulate mercury (50-150 pg/m^3), which have been successfully captured by the model as well (Fig. 2.7b).

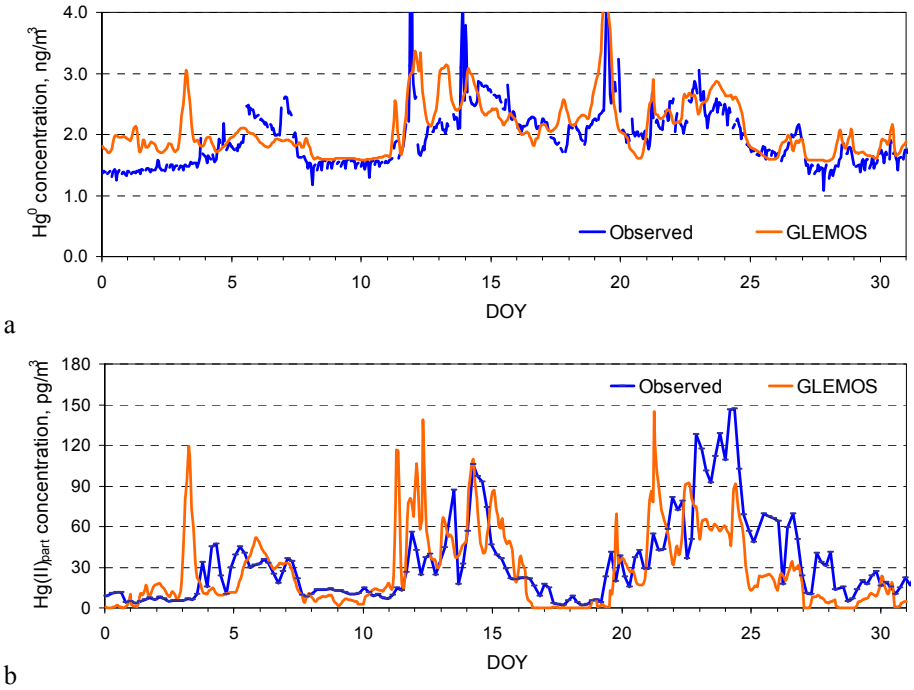


Fig. 2.7. *Evaluation of simulated hourly mean air concentration of gaseous elemental mercury (Hg^0)(a) and particulate mercury ($Hg(II)_{part}$) (b) against observations at EMEP site Waldhof (DE2) in January 2010.*

Figure 2.8 presents a set of back-trajectories for air masses coming to the Waldhof site during the three high concentration episodes simulated with the HYSPLIT model [*Draxler and Rolph*, 2013; *Rolph*, 2013]. As seen the back-trajectories confirm the idea of the origin of elevated mercury concentrations from regional emission sources located in Germany. During the first episode (days 5-8) air masses came from the industrial region North Rhine-Westphalia trough the area with emission sources around Hannover. During the second and the third episodes air masses arriving the site were influenced by emission sources located around Berlin, Leipzig and in the northern part of the Czech Republic.

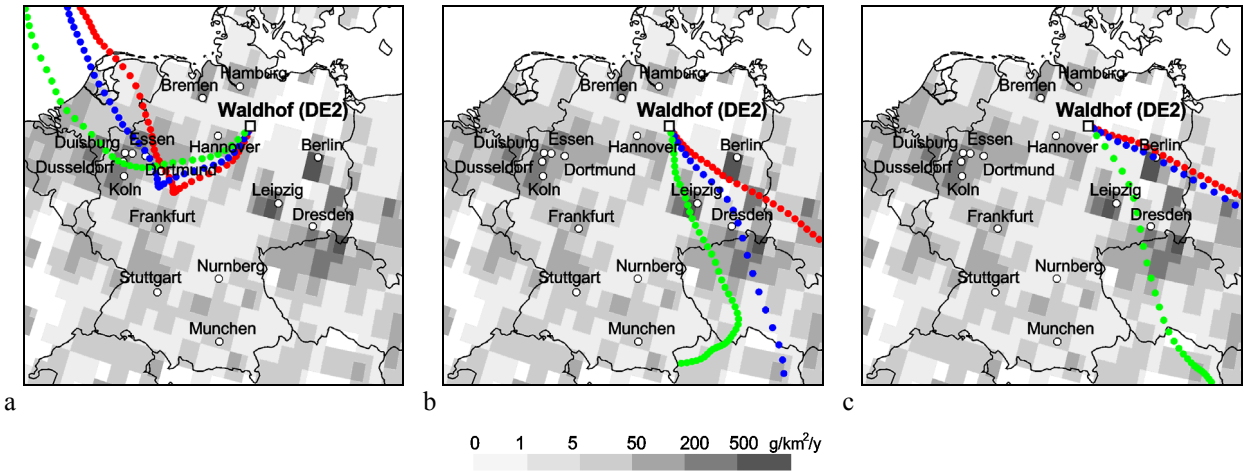


Fig. 2.8. *Back-trajectories for air masses coming to Waldhof on 05 January (a), 15 January (b) and 25 January (c) 2010 plotted with the HYSPLIT model. Arrival heights are 10 m (red), 100 m (blue) and 500 m (green). Underlying map shows mercury anthropogenic emissions in 2010.*

Thus, the pilot simulations performed with GLEMOS on the new EMEP grid demonstrate reasonable performance for the EMEP operational modelling. Increased spatial resolution of the model grid allows reproduction of pollution dispersion on a national scale. Nevertheless, the model testing and evaluation on the new grid will be continued to cover other heavy metals (lead, cadmium) and POPs. Besides, detailed comparison with the model results obtained on the old EMEP grid will be performed to ensure succession of the EMEP assessment after transition to the new grid.

MSC-E initiated preparatory work for transition of the EMEP operational modelling of heavy metal and POP pollution to the new EMEP grid. Pilot simulations performed with GLEMOS on the new EMEP grid demonstrate reasonable model performance for the EMEP operational modelling. Increased spatial resolution of the model grid allows reproduction of pollution dispersion on a national scale.

2.4. Development of the mercury multi-media approach: Oceanic module

The role of the ocean in the biogeochemical cycling of mercury is critical. Ocean emissions contribute approximately 30–40% of the current mercury input to the atmosphere. Once it enters the ocean water, mercury is subject to various biogeochemical processes that include association and dissociation, oxidation and reduction, methylation and demethylation, adsorption and desorption to suspended particulate matter, etc. (Fig. 2.9) Among others methylation plays a special role because of its influence on human health; methylmercury, which is bioaccumulated in fish, is a potent neurotoxin. Furthermore, increased exposure to methylmercury during gestation may result in neurobehavioral disorders in children. Thus, transformations of mercury in the ocean are an important part of the global mercury cycle and its adverse impact on human health and the environment.

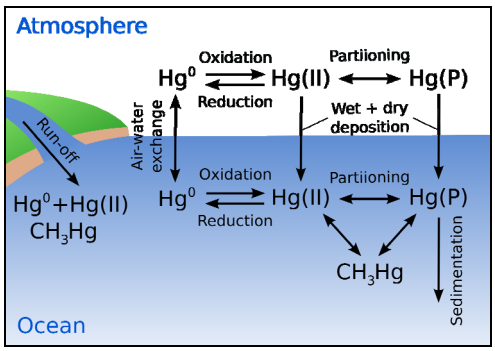


Fig. 2.9. *General scheme of Hg transformations in seawater*

To facilitate development of the oceanic module for the GLEMOS modelling system a comprehensive literature survey of available information on physical and chemical transformations of mercury in the ocean has been performed including description of the mechanisms and compilation of reaction rate constants. Based on collected information the following parameterisations have been developed for the GLEMOS oceanic module of mercury:

- Air-water exchange of mercury between the atmosphere and the ocean
- Mercury oxidation and reduction under solar and dark conditions
- Mercury adsorption by suspended particulate matter and colloids
- Methylation and demethylation in water column (biotic and abiotic)

To test the developed parameterisation, an empirically constrained box model was applied for simulation of dissolved gaseous mercury (DGM) concentration in the surface seawater. As a reference points, measurement sites of one of oceanographic cruises in the Adriatic Sea were selected (Fig. 2.10). As seen elevated surface DGM concentrations were obtained along the Italian coast from Ancona to Venice, and in the Gulf of Trieste. The sensitivity analysis shows that simulated DGM concentrations in surface waters under the considered conditions are weakly sensitive to the processes of oxidation, reduction and sedimentation, but are largely defined by deposition flux of bivalent mercury and air-water exchange of elemental mercury. In addition to this, the Monte Carlo simulation was applied for the estimation of the effect of input parameters variability on modelled DGM concentrations. It was observed that maximum uncertainty was introduced by deposition flux of mercury oxidized forms and the mass transfer coefficient of Hg^0 air-surface exchange. Nevertheless, other processes, such as reduction, oxidation, and sedimentation can largely affect mercury concentration in deeper layers and over longer periods.

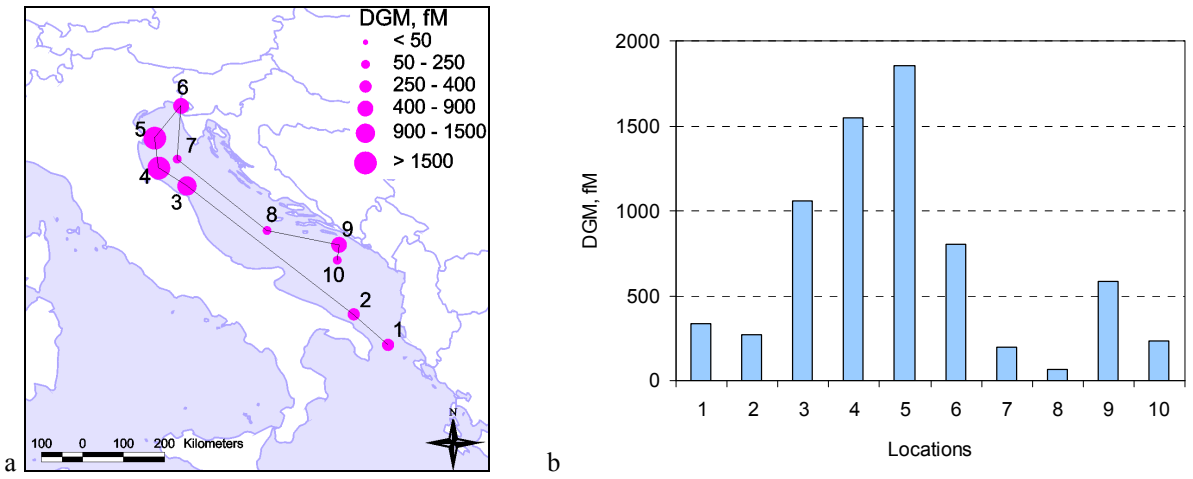


Fig. 2.10. *Simulated DGM concentration in seawater of the Adriatic Sea*

Development of mercury oceanic module for GLEMOS has been started with a comprehensive literature survey of available information on physical and chemical transformations of mercury in the ocean. The developed parameterisations have been tested with an empirically constrained box model for simulations of mercury concentration in seawater.

2.5. Preparation of GLEMOS distribution for public use

GLEMOS is developed as a multipurpose flexible modelling system for both research and policy oriented applications. Research tasks require state-of-the-art model formulation combined with a flexible choice of the model domain and parameterisations of physical and chemical processes. On the other hand, policy applications and operational modelling make high demands to the model performance and computer resources. The modular structure of GLEMOS allows flexible configuring the modelling system for conditions of particular task.

As it was demonstrated in a series of the Case Studies on heavy metal pollution in selected EMEP countries (e.g. the Czech Republic, Croatia, and the Netherlands), the model application on a national scale with involvement of country specific information gives significant benefits to pollution assessment on both national and the entire EMEP scales. In order to share the EMEP modelling experience and involve national experts to the assessment process MSC-E is preparing the GLEMOS modelling system for distribution for public use. In particular, the current stable version of GLEMOS is adapted for possibility of flexible compilation and run by third-party users. A collection of the model source codes, auxiliary scripts, input data and documentation are prepared for distribution under a free software licence (GPLv3). The model distribution contains the following components:

- GLEMOS source code and collection of scripts;
- Model documentation and user guide;
- Input data for test model runs (meteorology, land use, chemical reactants, etc.);
- Examples of the model applications (benchmarks for mercury and PCB)
- Web portal for support of public access to the model and its application by national experts.

The first version of GLEMOS public distributive is currently under extensive verification and testing and will be available through the MSC-E website soon.

3. DISSEMINATION OF INFORMATION

Dissemination of the assessment results and other relevant information aimed at support of political decisions is of high importance. Annual reports containing current status of heavy metal pollution within the EMEP region are supplemented by presentation of information on the MSC-E website (www.msceast.org). It provides more flexible and targeted assistance to national experts and authorities with data required for the environment protection regulations. In particular, detailed information on heavy metal pollution is given for both the whole EMEP region and for each EMEP country individually. The country-specific information includes variety of data on emissions, measurements and model assessment for particular country collected in one place to make easier access to the information and its analysis by national experts. Besides, to support the EECCA countries in their efforts on the implementation of the Protocol on HMs and development of national environmental programs a full-scale Russian version of the MSC-E website has been developed (ru.msceast.org).

Another important aspect is the information exchange with subsidiary bodies to the Convention and other international organizations and programmes. There is a wide interest outside the Convention to the data products and analysis performed by the EMEP scientific Centres. EMEP is the unique instrument within the LRTAP Convention providing regular pollution assessment and supporting

Parties to the Convention with information on pollution levels of heavy metals and other contaminants in Europe and other regions. In the context of the co-operation MSC-E regularly exchanges information on heavy metal pollution with different international bodies including UNEP, AMAP, European Commission, HELCOM etc. These and other aspects of the information dissemination are discussed below.

3.1. Subsidiary bodies to the Convention

3.1.1. Working Group on Effects (ICP-Vegetation)

Evaluation of modelled pollution levels is performed via comparison of simulated concentrations and deposition with the values observed at the EMEP monitoring network. Most of the EMEP monitoring stations are situated in the northern, western and central parts of Europe, whereas in the southern and eastern parts density of the network is low. Lack of measurement information in these regions can be partly compensated by the usage of supplementary information such as measurements of heavy metal content in terrestrial mosses.

Monitoring of heavy metals in mosses in the EMEP region is coordinated by the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP-Vegetation) of the Working Group on Effects (WGE). EMEP countries report data on moss surveys every five years. Sampling, storage and chemical analysis of heavy metals are carried out following methodology described in [*Harmens*, 2010]. This year ICP-Vegetation has provided MSC-E with data on moss concentrations of heavy metals for 1990, 1995, 2000, 2005 and 2010. Calculated deposition of lead, cadmium and mercury were compared with concentrations of these metals in mosses. Results of the comparison were presented at the 27th ICP-Vegetation Task Force meeting, held in January 2014, in Paris, France.

Data on measured concentrations of HMs are important supplementary information for analysis of pollution levels in the EMEP region, especially in areas with scarce monitoring network.

Concentrations in mosses and deposition can not be compared directly. However, there are two possible approaches of comparing these two parameters. Firstly, it is possible to compare long-term tendencies of concentrations in mosses and deposition. And, secondly, it is also possible to compare spatial distributions of modelled deposition and observed concentrations in mosses via analysis of spatial correlation.

Number of countries participating in moss monitoring programme may differ from one survey to another. Besides, even if a country takes part in the regular moss surveys, area covered by moss monitoring activity within the country in different surveys often differs. Therefore, in order to analyze trends of concentrations of metals in mosses and to compare them with deposition trends in the EMEP region, it is necessary to select gridcells where measurements of heavy metal concentrations in mosses are available from the entire period from 1990 to 2010. Area, satisfying this condition is depicted in Fig.3.1. Concentrations of lead and cadmium in mosses were measured in all five surveys in Scandinavia and some countries of Central Europe (Fig. 3.1a), and concentrations of mercury – in Finland, Norway, Austria and the Czech Republic (Fig. 3.1b).

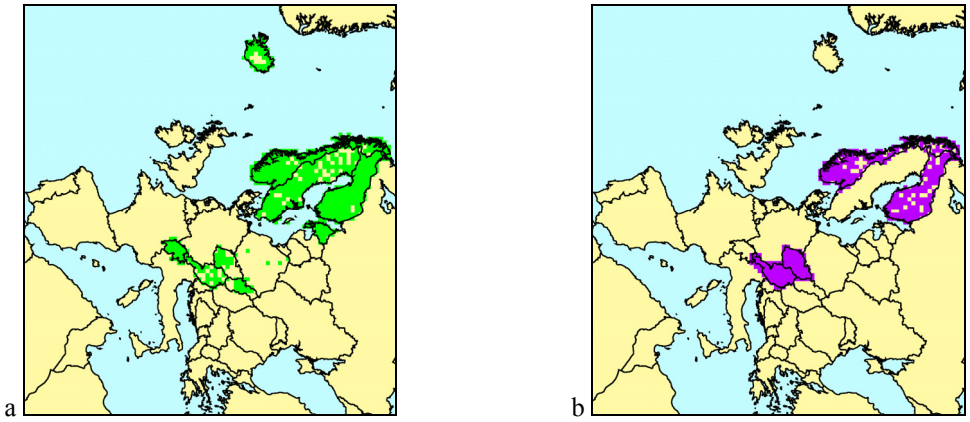


Fig. 3.1. *Area, selected for analysis of long-term trends of lead and cadmium (a) and mercury (b).*

Simulated trends of lead, cadmium and mercury deposition reduction are similar to those based on monitoring of concentrations in mosses (Fig. 3.2). The highest reduction is noted for lead, followed by the reduction of cadmium levels (Table 3.1). The decline of mercury levels is relatively low, compared to lead and cadmium. It is explained by significant contribution of anthropogenic and natural sources located outside the EMEP region.

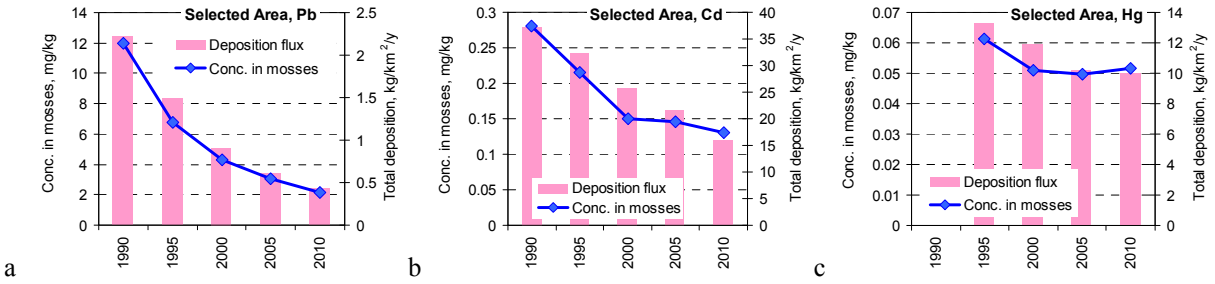


Fig. 3.2. *Long-term trends of lead (a), cadmium (b) and mercury (c) in the selected area for 1990 - 2010 period*

Table 3.1. *Long-term changes (times) of deposition and concentrations in mosses of lead, cadmium (1990/2010) and mercury (1995/2010).*

	Pb, times	Cd, times	Hg, times
Concentrations in mosses	5.5	2.1	1.3
Deposition	5.1	2.3	1.2

In addition to the selected area, the trends were estimated for individual countries. Magnitudes of changes between periods of 1990-2010, 1990-2005 and 1995-2010 in various countries are summarized in Fig. 3.3. As seen, the reductions of concentration in mosses and deposition of lead for the considered periods are similar in most countries (2 – 7 times). The reductions are the highest in the central part of Europe (e.g., Austria, the Czech Republic, and Switzerland) and the lowest in South-Eastern Europe (Bulgaria) as well as in Iceland.

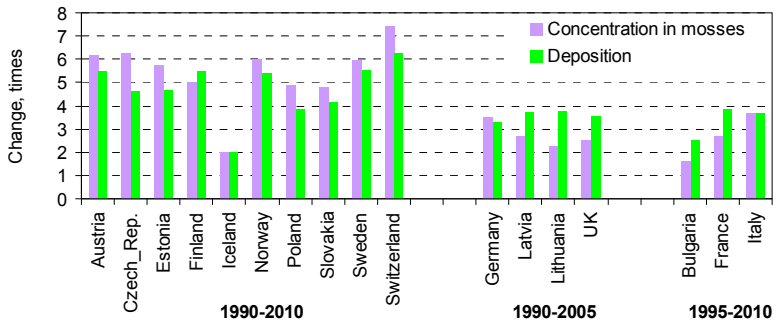


***Fig. 3.3**. Long-term changes of concentrations of lead in mosses and total deposition in countries for the specified periods*

Reduction of the calculated and measured cadmium levels for the considered periods is around 1.5-2.5 times in most countries. The magnitudes of long-term changes of concentrations in mosses and simulated deposition differ for a number of countries. For example, in Norway, Poland, Slovakia, Latvia, Bulgaria and France the decline of cadmium deposition is substantially stronger than the decline of concentrations in mosses (Fig. 3.4). In Iceland and the United Kingdom the situation is the opposite: concentrations in mosses dropped much stronger (4-9 times) than the calculated deposition (1.3-1.7 times). The reasons of these differences need special investigation in cooperation with experts working in the field of biomonitoring.

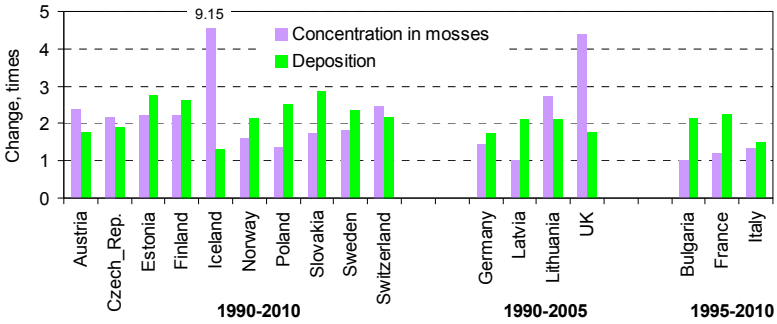


***Fig. 3.4.** Long-term changes of concentrations of cadmium in mosses and total deposition in countries for the specified periods*

Changes of mercury levels are lower compared to those of lead and cadmium. Between 1995 and 2010 deposition of mercury and its concentration in mosses reduced by about 1.6 times in the Czech Republic and by 1.1-1.2 times in Finland (Fig. 3.5). In Austria concentrations in mosses reduced somewhat stronger than total deposition. In Norway deposition declined by 1.3 times, while concentrations in mosses only by 1.1 times. The reduction of deposition of mercury in Norway is in line with the tendency of declining of mercury levels in the EMEP region due to reduction of anthropogenic emissions [*Travnikov et al.,* 2012].

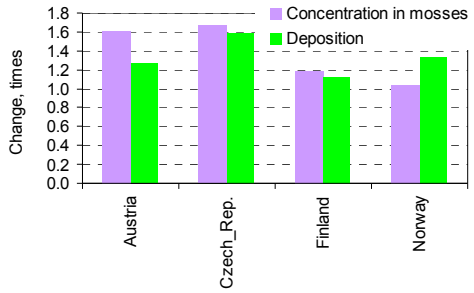


***Fig. 3.5.** Long-term changes of concentrations of mercury in mosses and total deposition in countries for the 1995-2010 period*

Second approach to comparing measured concentrations in mosses and simulated deposition consists of comparison of their spatial distributions.

These two parameters characterize different aspects of heavy metal pollution (and their units are also different). Therefore, to make them comparable it is worth normalizing them. Each value of gridcell-averaged concentration in mosses or deposition flux is divided by their median values. It allows producing comparable dimensionless fields of concentrations in mosses and deposition. For example, spatial distributions of lead concentration in mosses and deposition are quite similar in a number of regions of the EMEP domain (Fig. 3.6). Modelled deposition reproduces south-to-north gradient in Scandinavia and Poland, and east-to-west gradient in France. However, normalized concentrations in the south-eastern part of Europe look higher than the normalized deposition, especially in Romania. Emission data, officially reported by Romania, are not so high compared to emissions in surrounding countries, and the same is true for deposition. Similar situation takes place for cadmium levels. Most likely, this discrepancy is caused by uncertainties of emission data, or by methodological issues of moss sampling and analysis.

Long-term trends of modeled total deposition and concentrations of heavy metals in mosses agree reasonably well.

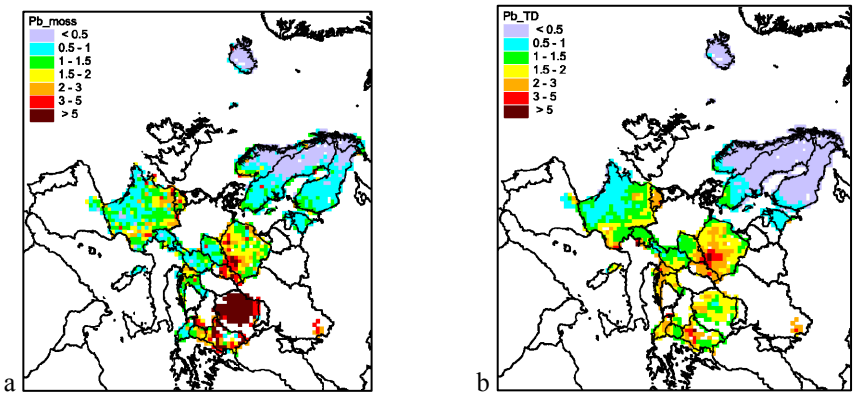


Fig. 3.6. *Normalized observed concentrations of lead in mosses (a) and total deposition (b) in 2010.*

For the analysis of spatial distribution of pollution levels within individual countries liner regressions between modelled deposition and observed concentration in mosses are plotted and Spearman's correlation coefficients are calculated [*Holy at al.*, 2010]. Non-parametric Spearman's rank correlation coefficient is used because the metal concentrations in mosses mostly proved to be not normally distributed [*Holy at al.*, 2010].

An example of comparison of lead, cadmium and mercury normalized total deposition and concentrations in mosses is given for Finland (Fig. 3.7). For lead and cadmium the agreement between spatial distributions of concentrations in mosses and deposition is significant because correlation is high (0.8). Relatively high correlation is obtained also for some other countries, located mainly in Scandinavia (Sweden, Norway) and in the central part of Europe (e.g., the Czech Republic, Switzerland). Mercury is more complicated pollutant for this analysis. Correlation for mercury in Finland is not high (0.22) which is typical also for the other countries. One of possible reasons for this is ability of mercury, unlike lead and cadmium, to participate in bi-directional exchange between moss tissue and atmospheric air [*Holy et al.*, 2010]. Therefore, other factors, in addition to atmospheric deposition, are likely to be important for accumulation of mercury in mosses.

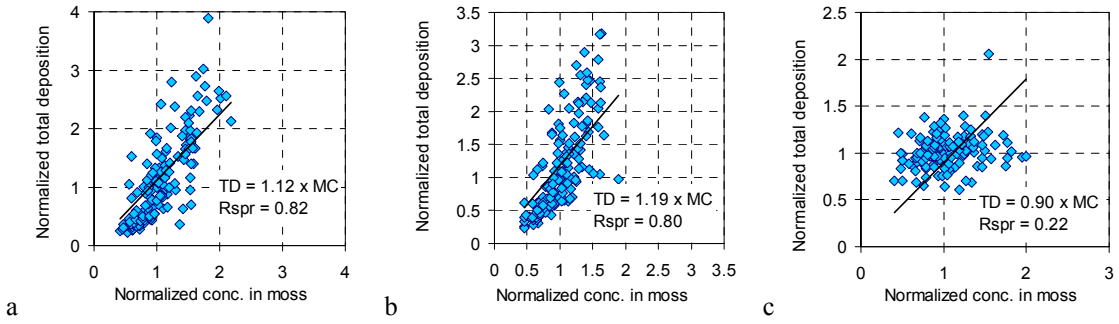


Fig. 3.7. *Scatter plots of normalized calculated total deposition vs. observed concentrations in mosses of lead (a), cadmium (b) and mercury (c) in Finland. Rspr – Spearman's correlation coefficient, TD – total deposition and MC – concentration in mosses*

The results presented in this section provide a short overview of the joint usage of simulated deposition and observed concentrations of heavy metals in mosses. It demonstrates that the model successfully reproduces long-term pollution trends of heavy metals in most of the EMEP countries. Besides, spatial distribution of lead and cadmium deposition simulated by the model generally well agrees with that of measured concentrations in mosses in a number of the countries.

Significant spatial correlation between HM modelled deposition and concentrations in mosses was found for Scandinavia and some countries in the central part of Europe

In order to explain the identified similarities and differences in long-term trends and spatial distributions between results based on these two approaches, more detailed investigation is needed. Possible directions of further research may include more sophisticated statistical analysis, similar to that which has been done jointly by experts from German University of Vechta and MSC-E [*Holy et al.*, 2010; *Schröder et al.*, 2010]. In some regions of the EMEP domain, first of all, in countries of the eastern and south-eastern part of Europe, monitoring of concentrations in air and deposition is scare. Low monitoring coverage in these regions can partly be compensated by measurements in mosses. In addition to this, it is worth to perform comparison of measured concentrations in mosses and wet deposition fluxes observed at the EMEP monitoring stations.

Further cooperation between EMEP and WGE in the field of HM pollution levels and trend analysis is appreciated

3.1.2. Task Force on Hemispheric Transport of Air Pollution

MSC-E continued co-operation with the Task Force on Hemispheric Transport of Air Pollution (TF HTAP). It took part in the Task Force workshop held in San Francisco, USA in December 2013. The Centre presented an overview of ongoing activities within EMEP and relevant research projects focused on the assessment of mercury and POP pollution. In particular, it reported results of process studies and model experiments, aimed at the improvement of current knowledge of mercury atmospheric chemistry and performed within the EU project Global Mercury Observation System (GMOS). The Centre also informed TF HTAP participants about future plans in that field as a part of the newly organized GMOS Mercury Modelling Task Force (GMOS MMTF). As possible contribution to the forthcoming TF HTAP numerical experiments MSC-E presented pilot results of model assessment of intercontinental transport and source-receptor relationships of mercury and selected POPs (PCB-153). It was demonstrated that both regional sources and contribution of long-range transport played

significant role in mercury and POP pollution of many industrial regions. It was also concluded that the multi-media dispersion character of these contaminants required source apportionment of secondary emissions over longer period. Particular attention was paid to evaluation of mercury deposition to various aquatic regions.

TF HTAP recognises the importance of a closer cooperation with relevant on-going activities within international bodies including the Minamata Convention on Mercury and the Stockholm Convention on POPs.

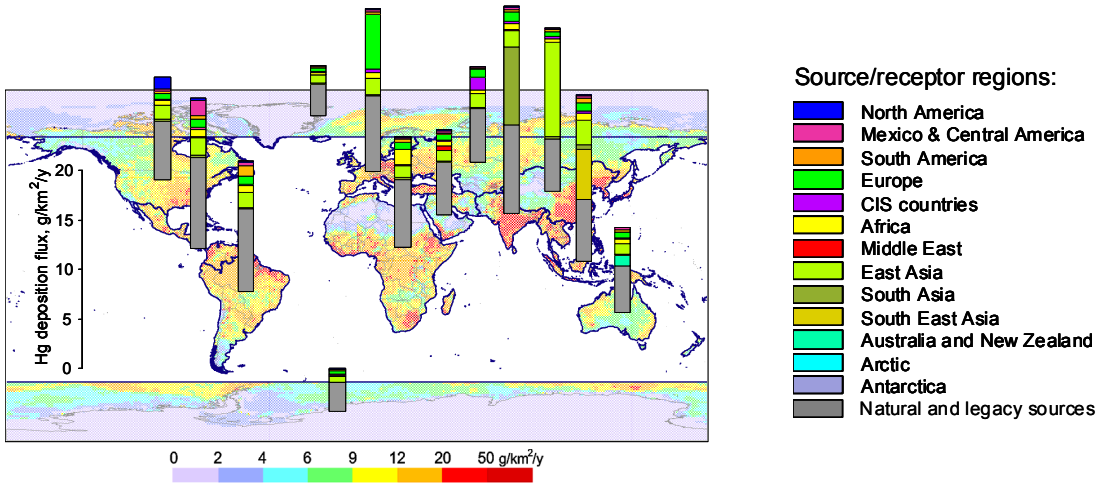


Fig. 3.8. *Source apportionment of mercury deposition on a global scale in 2010*

3.1.3. Task Force on Emission Inventories and Projections

The Task Force on Emission Inventories and Projections (TFEIP) supports the EMEP countries in the official reporting of air pollutant emissions and projection data to the Convention. It also provides a technical forum and expert network to identify emission factors, establish methodologies for the estimation of emissions, and identify problems related to data reporting.

In 2014 MSC-E continued cooperation with TFEIP. In particular, the Task Force invited EMEP modeling Centres to give their thoughts on what emission information they use, wishes concerning reported emissions, and how improvements might be made to the current datasets. In the framework of this activity MSC-E has prepared the note to respond to the questions posed by TFEIP and to support discussions focused on the quality of heavy metal emissions and their improvement (Annex A).

Completeness and consistency of emission data, information on the range of uncertainty of reported emissions, generation and updates of emission expert estimates and collaboration with the UNEP Minamata Convention on Mercury and the Arctic Monitoring and Assessment Programme (AMAP) are necessary for improving emission data quality and further progress in the assessment of heavy metal pollution in the EMEP domain. Tight cooperation between TFEIP and modelling community is needed to find the optimal solutions of the emission-related problems.

3.2. International organizations

3.2.1. UNEP Minamata Convention on Mercury

EMEP participates in various activities aimed at scientific support of international efforts to abate mercury pollution on global and regional scales. In particular, MSC-E took part in preparation of the Global Mercury Assessment 2013 for negotiations of the Minamata Convention on Mercury. Estimates of mercury pollution on a global scale have been recently updated by the Centre. Levels of mercury air concentration and deposition in different terrestrial and aquatic regions of the globe were assessed for present conditions by means of the GLEMOS model. Particular attention was paid to evaluation of mercury deposition to major fishing areas of the ocean keeping in mind the primary role of the fish consumption in human health exposure to mercury. The work was partly funded by the EU FP7-ENV-2010 project "Global Mercury Observation System" (GMOS, Grant Agreement N 265113). Results of the study were presented at the Diplomatic Conference for the Minamata Convention (Japan, October 2013).

Model simulations of mercury atmospheric dispersion on a global scale were performed for 2010. Two-years model spin-up was carried out to fill up the atmosphere with mercury. Simulated spatial distributions of Hg^0 concentration in ambient air and mercury wet deposition fluxes are shown in Fig. 3.9.

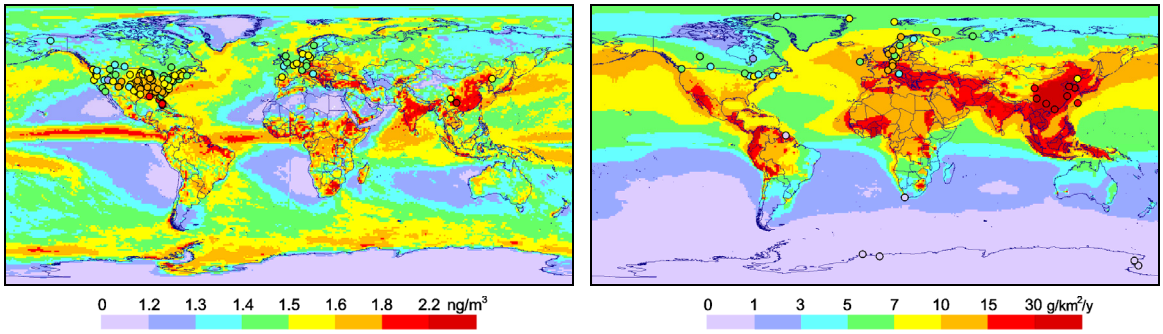


Fig 3.9. *Global distribution of mean annual Hg^0 concentration in ambient air and wet deposition in 2010. Circles present long-term observations*

The simulation results were evaluated against long-term observations. Deviation of simulated Hg^0 concentrations from observed values is mostly within ±20%, whereas for wet deposition it does not exceed a factor of 2. The Pearson's correlation coefficient between the simulated and measured pairs exceeds 0.7 for both Hg^0 concentration and wet deposition (Figs. 3.10, 3.11).

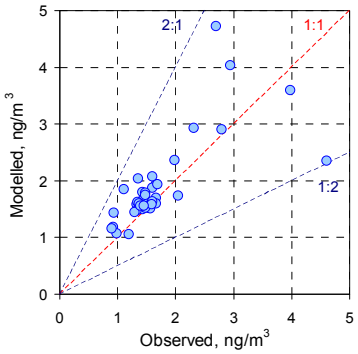


Fig. 3.10. *Model-to-measurement comparison for mean annual Hg^0 concentration in 2010*

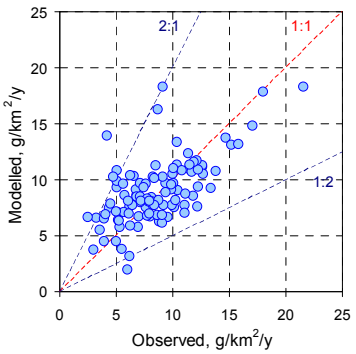


Fig. 3.11. *Model-to-measurement comparison for annual wet deposition flux of mercury in 2010*

Mercury deposition in different regions of the world differs significantly depending on geographical location of the region with respect to emission sources and local environmental conditions (oxidation ability of the atmosphere, precipitation etc.) The highest fluxes are characteristics of South, Southeast and East Asia. Somewhat lower deposition is in Europe, Central and South America. Almost twice as lower deposition is estimated in Middle East, Australia and New Zealand (3.12). The lowest average deposition fluxes are over the polar regions even taking into account locally significant deposition over the Atmospheric Mercury Depletion Events (AMDE) areas.

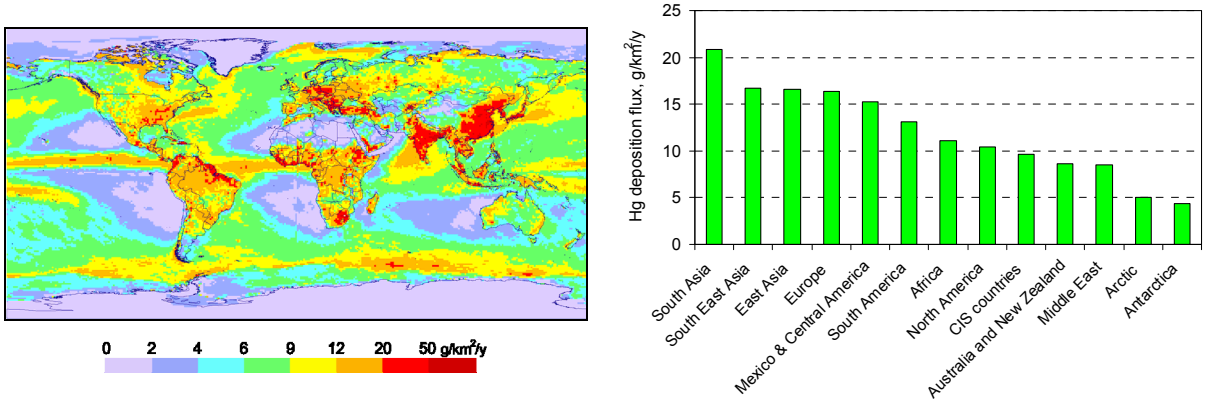


Fig. 3.12. *Spatial distribution of mercury total deposition and average deposition flux over various regions in 2010*

In regions not impacted by industrial point sources of contamination, most human exposure to mercury is through fish consumption. Mercury coming to freshwater and marine ecosystems from atmospheric deposition and other sources is converted by biotic and/or abiotic processes to methylmercury (MeHg), which is biomagnifies in aquatic food webs. To estimate mercury loads to different aquatic regions and potential accumulation in fish mercury deposition to the major fishing areas according to classification by Food and Agriculture Organization [*FAO,* 2013a] were calculated.

In accordance with the FAO statistics for 2010 [*FAO*, 2013b], total capture fisheries production takes place in the Northwest Pacific, Western Central Pacific and Northeast Atlantic. These areas are also characterized by significant average mercury deposition (Fig. 3.13). It is particularly important that the highest deposition fluxes within the Northwest Pacific are estimated over the off-shore sea areas and marginal seas of East Asia (Yellow Sea, East and South China Seas, Sea of Japan), where intensive capture fisheries are expected. Tuna fisheries production is dominated by fisheries in the Western Central Pacific [*FAO,* 2013b]. It is also affected by high mercury deposition. Other regions of tuna fisheries with considerable mercury deposition include the Western Indian Ocean, Eastern Central Pacific, Eastern Indian Ocean and Eastern Central Atlantic (Fig. 3.13).

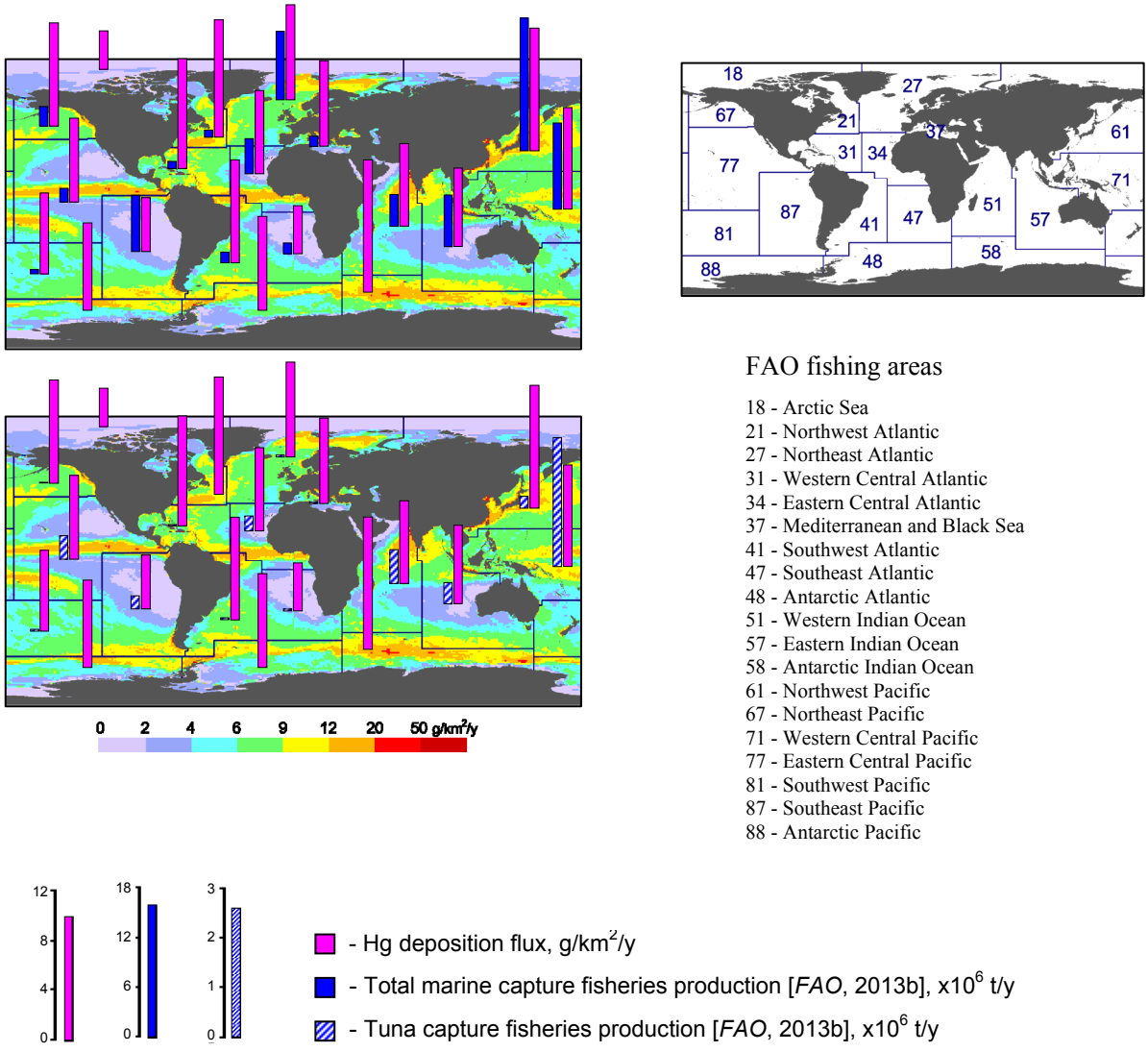


Fig. 3.13. *Annual mercury deposition to the FAO major fishing areas and marine capture fisheries production in 2010 [FAO, 2013b].*

3.2.2. European Union and GMOS project

A new scientific cooperative initiative GMOS Mercury Modelling Task Force (GMOS MMTF) has been launched recently as a part of the EU funded GMOS (Global Mercury Observation System) project and with support of the UNEP Mercury Air Transport and Fate Research Partnership (UNEP F&T) and the Group on Earth Observation (GEO, Task HE-02-C1). GMOS MMTF is aimed at model studies supplemented by comprehensive monitoring data for improvement of current understanding of the key mercury atmospheric processes and evaluation of present and future levels of mercury pollution. MSC-E, as a GMOS partner and coordinator of global-scale modelling activities within the project, takes an active part in the work of MMTF. In particular, it performs general coordination of the Task Force and leads the mercury model assessment on a global scale. All aspects of MMTF activities were discussed at the kick-off meeting held in April 2014 in Rome, Italy.

Main objectives of GMOS MMTF:

- To organize and coordinate model studies of mercury atmospheric processes, emission inventories, and the overall model performance making use of the GMOS measurement data.
- To provide multi-model assessment of mercury pollution levels in Europe and other selected regions as well as over the globe and evaluation of future pollution changes according to different emission control scenarios.
- To facilitate co-operation in the field of mercury model assessment between GMOS, EMEP and other international programmes including UNEP, AMAP and the Minamata Convention.

The work of MMTF is organized in the form of multi-model experiments aimed at answering particular scientific questions related to mercury atmospheric chemistry, speciation, anthropogenic and natural/secondary emissions etc. The simulation results will be evaluated against observations from the GMOS land-based network as well as measurement network of external partners, aircraft and ship-based measurements (Fig. 3.14).

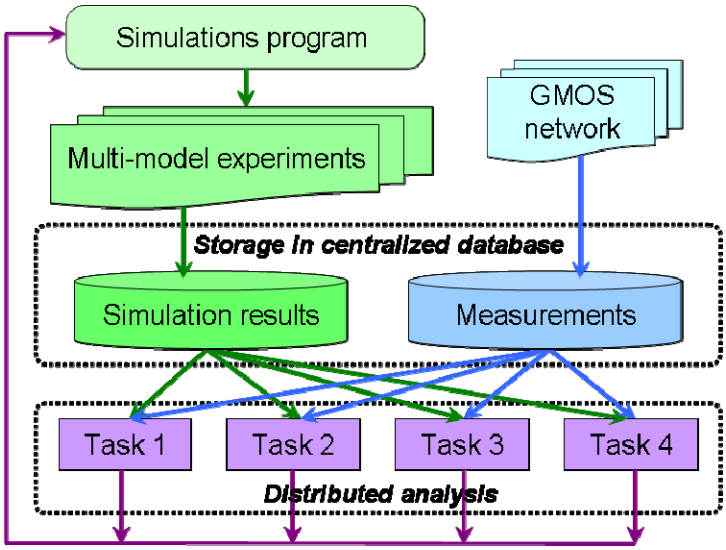


Fig. 3.14. *General scheme of MMTF informational flows*

In order to facilitate the analysis of the results a number of Tasks is to be organized with a focus on particular scientific problems. Each of the Tasks will get access to all available measurement data and simulation results though the centralized database. To ensure that the set of model experiments covers all aspects of the analysis the Tasks contribute both to formulation of the original simulation program and to possible updates of the program after initial analysis.

Tasks of MMTF distributed analysis:

Task 1. Global mercury concentration and deposition patterns. Analysis of spatial patterns and temporal variations on a global scale, inter-hemispherical gradients, chemical mechanisms.

Task 2. Regional mercury patterns in Europe. Analysis of mercury levels in the surface air and free troposphere of Europe, emissions speciation, oxidation pathways.

Task 3. Regional mercury patterns in Asia. Analysis of mercury spatial and temporal patterns in Asia, anthropogenic emissions, emission scenarios.

Task 4. Mercury dispersion and processes in the Polar regions. Analysis of mercury processes in the Arctic and Antarctica, oxidation chemistry, air-snow exchange.

Task 5. Inverse modelling and evaluation of mercury emissions. Application of both inverse and direct modelling for evaluation of mercury emissions in different regions of the globe.

Research activities performed under MMTF will improve quality of model assessment of mercury pollution within the EMEP domain. Besides, the model studies within MMTF closely correlate with the current activities carried out within TF HTAP and the UNEP efforts to support implementation of the Minamata Convention on Mercury.

GMOS MMTF model studies closely correlate with the activities carried out within the EMEP/TFHTAP and the UNEP efforts to support implementation of the Minamata Convention on Mercury.

3.2.3. Helsinki Commission

Information on atmospheric pollution of marginal seas by heavy metals within the EMEP region is of interest for the marine conventions (e.g., HELCOM, OSPAR). In cooperation with other EMEP Centres, MSC-E performs regular model assessment of atmospheric pollution of the Baltic Sea by various pollutants including heavy metals. This work is carried out in accordance with the Memorandum of Understanding between HELCOM and the Convention and based on the long-term EMEP/HELCOM contract.

Recent assessment of airborne pollution load to the Baltic Sea [*Bartnicki et al.*, 2013] includes information on long-term trends in heavy metal deposition for the period 1990-2011 and source apportionment of heavy metal deposition for 2011. Short summary of information on the Baltic Sea pollution by heavy metals is available also in a form of indicator fact sheets published in the Internet on the HELCOM website [http://www.helcom.fi]. Anthropogenic heavy metal emissions in the HELCOM countries have substantially dropped from their levels in 1990 (by 90% for lead, 65% for cadmium, and 74% for mercury). Among the HELCOM countries Poland, Russia and Germany are the biggest contributors to heavy metal emissions in 2011.

Model evaluation of pollution levels indicates essential decrease of annual total atmospheric deposition of heavy metals to the Baltic Sea in the period from 1990 to 2011. The most significant drop in heavy metal deposition is obtained for lead (76%), followed by cadmium (55%), and mercury (35%) (Fig. 3.15a). Changes of heavy metal pollution in different parts of the sea are not homogeneous. Particularly, significant decrease in cadmium and lead deposition is noted for the eastern sub-basins (by 70-80%), while mercury deposition has decreased the most significantly in the western sub-basins (by 50-70%).

Spatial distribution of heavy metal pollution of the Baltic Sea in 2011 is exemplified by cadmium deposition fluxes in Fig. 3.15b. Elevated levels of pollution can be seen in the southern and western parts of the Baltic Sea (the Baltic Proper and the Western Baltic sub-basins). The largest contributions among the HELCOM countries to heavy metal pollution of the Baltic Sea are made by Poland, Germany, and Russia.

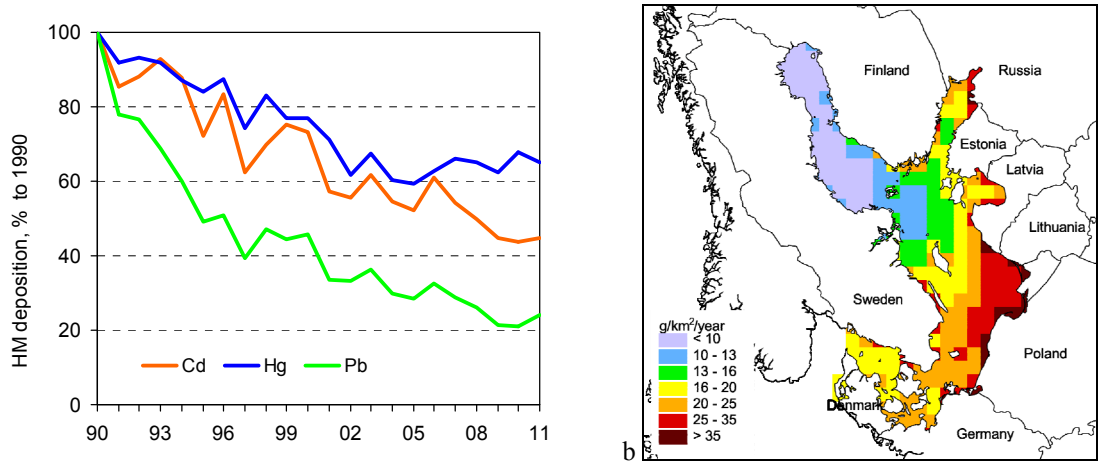


Fig. 3.15. *Relative changes of total annual atmospheric deposition of cadmium, mercury, and lead to the Baltic Sea for the period 1990-2011 (a) and spatial distribution of cadmium deposition over the Baltic Sea in 2011 (b)*

3.3. Cooperation with Parties to the Convention

Information on pollution levels regularly produced by EMEP can be extended by an assessment performed at a country-scale level. MSC-E and the Task Force on Measurements and Modelling (TFMM) of EMEP carried out a number of country–specific case studies on heavy metal pollution assessment in several individual countries: Croatia [*Ilyin et al.*, 2011], the Czech Republic [*Ilyin et al.*, 2012] and the Netherlands [*Ilyin et al.*, 2014]. Similar work has been initiated for Belarus and Poland. Country-specific case studies assume the integrated analysis of factors affecting quality of the assessment including emissions, measurements, and modelling with fine spatial resolution in the selected countries as well as detailed analysis of pollution levels. The studies allow taking into account specific features of countries' orography, meteorological conditions, distribution of emission sources across a country and additional data from national monitoring programmes. This section includes the results of assessment of lead pollution levels in the Netherlands in 2007 and results of model simulations of lead, cadmium, mercury, arsenic and nickel for Italy.

3.3.1. Assessment of pollution levels of lead in the Netherlands

The work was fulfilled in close cooperation with national experts from the Netherlands. The experts presented detailed national emission data with fine spatial resolution from emission source categories. In addition to the EMEP monitoring information the data from national monitoring programmes were involved in the study. Experts from MSC-E and the Netherlands jointly analyzed the obtained results.

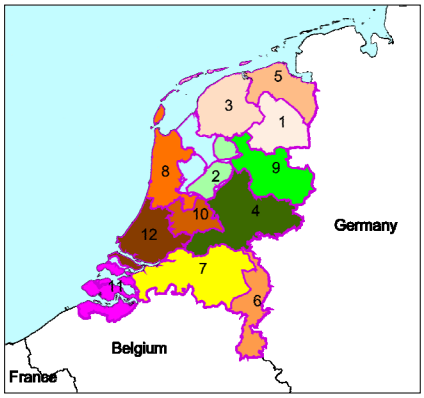


Fig. 3.16. *Provinces of the Netherlands*

Dutch provinces:

1. Drente
2. Flevoland
3. Friesland
4. Gelderland
5. Groningen
6. Limburg
7. Noord-Brabant
8. Noord-Holland
9. Overijssel
10. Utrecht
11. Zeeland
12. Zuid-Holland

Air concentration, deposition and transboundary fluxes were simulated with fine spatial resolution (5x5 km^2) for 2007. Results of this work were compared with information annually prepared by EMEP for the Netherlands. In

particular, in addition to the annual EMEP data, the country is informed about pollution levels with fine spatial resolution, contribution of emission source categories to lead pollution, and transboundary transport between the provinces of the country (Fig. 3.16).

In addition to the annual EMEP data, country-specific studies produce information on pollution levels with fine spatial resolution, contribution of emission source categories to pollution, and transboundary transport between the provinces of a country.

Spatial distribution of lead levels over the Netherlands is not uniform. In the northern part of the country (provinces Groningen, Friesland, Drente, Flevoland, Overijssel) the range of air concentrations is 4-5 ng/m^3, and that of deposition - 1-2 kg/km^2/y (Fig. 3.17). The highest air concentrations (more than 30 ng/m^3) and deposition (more than 4 kg/km^2/y) levels are noted for the province Noord-Holland. The levels obtained for 50-km resolution are generally similar to those for 5x5 km^2, but ranges between maximum and minimum values are smaller.

Modelling with fine spatial resolution results to higher variability of pollution levels over country's territory than modelling with coarse resolution.

The highest pollution levels noted in the Noord-Holland province are caused mostly by one large point source (LPS) 'Corus Staal BV'. According to available emission inventories it contributes more than 60% to total national emission of lead in 2007. It should be noted also that the influence of this LPS is revealed when modelling with high spatial resolution is applied. Evaluation of role of particular LPS in national and transboundary pollution requires more detailed attention in future.

Modelling with fine spatial resolution allows revealing effect of LPS on national and transboundary pollution.

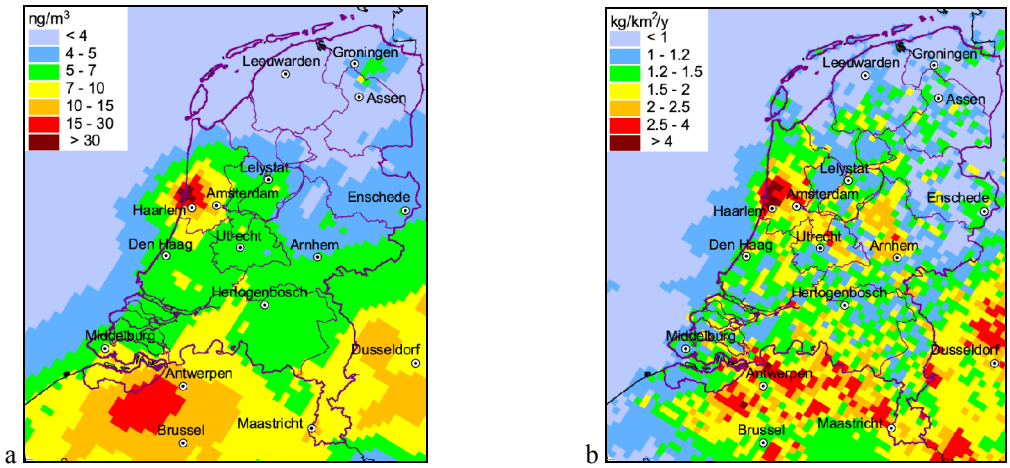


Fig. 3.17. *Calculated concentrations of Pb in air (a) and total deposition (b) in the Netherlands in 2007 with resolution 5x5 km^2*

Contribution from national anthropogenic sources to total deposition of lead (48 tonnes) in the Netherlands in 2007 is 18%, from foreign anthropogenic sources – 27%, from secondary sources (wind re-suspension) – 52%, and from non-EMEP sources – 3% (Fig. 3.18). When pollution levels are simulated with coarse (50x50 km^2) resolution, contributions of re-suspension (55%) and foreign

sources (29%) to deposition in the Netherlands are similar to those modelled with fine resolution. However, the contribution of national emission sources is considerably lower (12%).

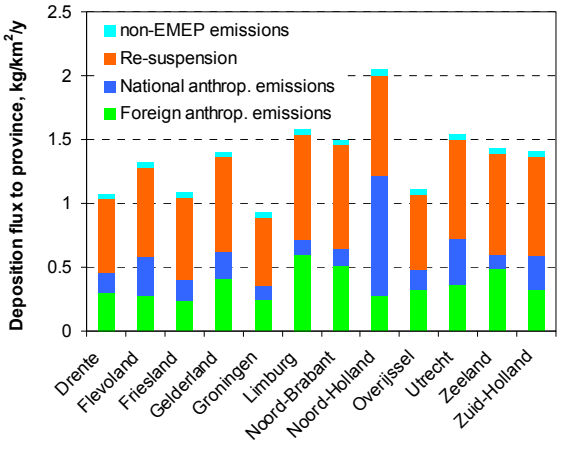


Fig. 3.18. *Contribution of foreign anthropogenic emission sources, national emission sources, wind re-suspension and non-EMEP emission sources to lead deposition in the Netherlands in 2007*

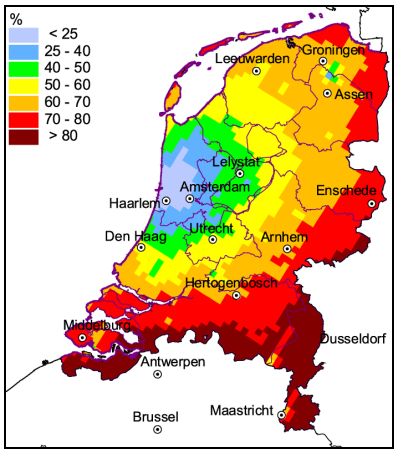


Fig. 3.19. *Contribution of foreign emission sources to anthropogenic deposition of lead in the Netherlands in 2007*

Contribution of foreign emission sources to deposition from the anthropogenic sources in the Netherlands ranges from 25% to 80% over the most part of the country (Fig. 3.19). The highest contribution is noted for the Dutch-Belgian border, while the lowest – for the central part of the country (province Noord-Holland). The main foreign contributors to lead pollution in the Netherlands are emission sources of Belgium, Germany, the United Kingdom, and France. The main national contributor – sources of the Noord-Holland province.

From 5% to 12% of lead is deposited to a territory of a province where it is emitted, and from 4 to 19% - to the other provinces (Fig. 3.20). The most of lead (72-90%) emitted in the Dutch provinces is transported through the state borders to other countries. For the country as a whole 19% of emitted lead are deposited to the country's territory. When modelling with 50x50 km resolution, this fraction is around 13%.

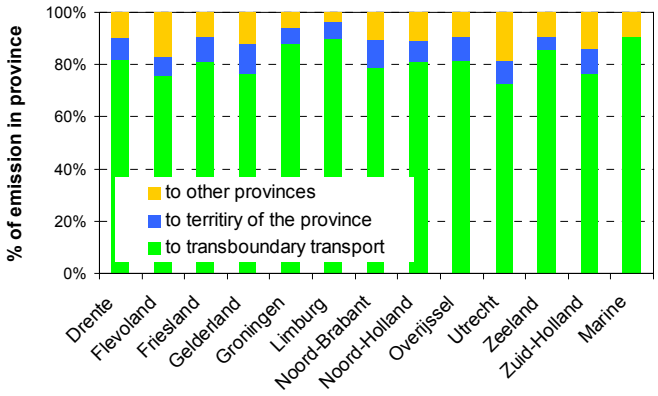


Fig. 3.20. *Fractions of lead emitted in the Dutch provinces and deposited to territory of a province, to other provinces of the country and transport abroad*

Contributions of emission source categories to deposition from national sources in the Netherlands were estimated. The main contribution (63%) to deposition in the country is caused by "*Iron and steel production*", followed by "*Transport (except aviation)*" (16%), "*Industrial processes*" (9%), "*Small combustion installations*" (6%) and "*Aviation*" (5%) (Fig. 3.21). In provinces the contributions of different source categories vary substantially. Contribution of the source category "*Iron and steel*

production" is the main in most of provinces, ranging from 24% to 91%. In the Limburg province the main contributor is "*Industrial processes*" (34%).

Refinement of spatial resolution leads to general reduction of discrepancies between modelled and measured pollution levels in the Netherlands. Besides, the correction of wind re-suspension parameterization favours further improvement of the modelled concentrations in air in the Netherlands. For the other parts of the EMEP region additional research is needed to achieve the improvements.

Detailed assessment of lead pollution levels in the Netherlands was possible due to availability of highly detailed and diverse national data on emissions and monitoring and due to close co-operation with national experts from this country. Similar work can be carried out for other countries interested in detailed national-scale information on heavy metal pollution.

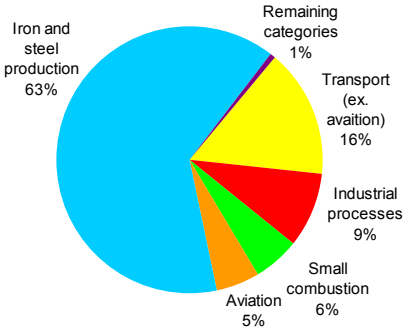


Fig. 3.21. *Contribution of different emission source categories of the Netherland to lead deposition in the country from national sources as a whole in 2007*

3.3.2. Evaluation of pollution levels of heavy metals over Italy and surrounding areas

This year MSC-E continued cooperation with Italian experts from ENEA (Italian national agency for new technologies, energy and sustainable economic development). In order to support national scale modeling of heavy metals Italian experts were provided with 3D air concentrations of lead, cadmium, arsenic, nickel and three mercury forms (elemental, particulate and gaseous oxidized) over the agreed area. For example, calculated concentration of arsenic in air in 2010 is demonstrated in Fig. 3.22. Spatial resolution of modelled data is 50x50 km^2 and temporal resolution is 6 hours. It was planned that these data would be utilized as boundary concentrations for the national MINNI modelling system.

Information about emission total values in the EMEP countries and their spatial distribution were derived from official emission data received from the EMEP Centre on Emission Inventories and Projections [*Mareckova et al*, 2013]. If officially reported data were not available, emission expert estimates for 2010 produced by the Dutch TNO institution [*Denier van der Gon et al.,* 2005] were used. Speciation of mercury emissions was based on global-scale mercury emission data for 2010 prepared under UNEP [*AMAP/UNEP*, 2013].

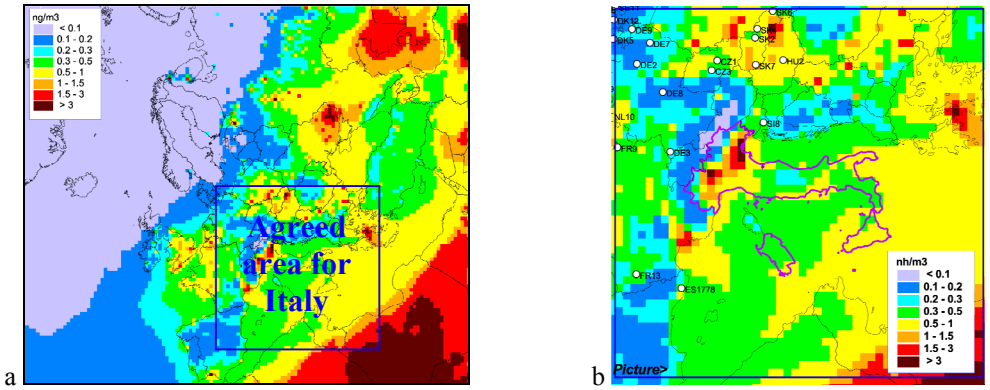


Fig. 3.22. *Annual mean concentrations of arsenic in 2010 in the EMEP domain (a) and in the agreed area (b). White circles denote location of EMEP monitoring stations.*

The comparison of modelled and observed levels was carried out both for the entire EMEP domain and for the agreed area. Observations involved in the comparison were derived from the EMEP/CCC monitoring database. Lead levels were reproduced relatively well both for the EMEP region as a whole and for the agreed area: the bias did not exceed 10% (Fig. 3.23). For cadmium the deviation was higher both for air concentrations and wet deposition. This fact indicated that atmospheric emissions from anthropogenic or secondary emission sources could be underestimated. Calculated air concentrations of mercury matched well the observed levels (the bias was about 1%), while wet deposition was overestimated by about 45-50%. It could be caused by complexity of atmospheric chemistry of mercury as well as lack of officially reported information on speciation of mercury in anthropogenic emissions. Modelled levels of arsenic were below the observed ones in the EMEP domain by 20-30%. But within the agreed area the arsenic air concentrations underestimated, and wet deposition - overestimated the observed levels, whereas for nickel the situation was opposite. Air concentrations of nickel matched well the observed levels both for entire domain and within the agreed area, and wet deposition were underestimated by 20-40%.

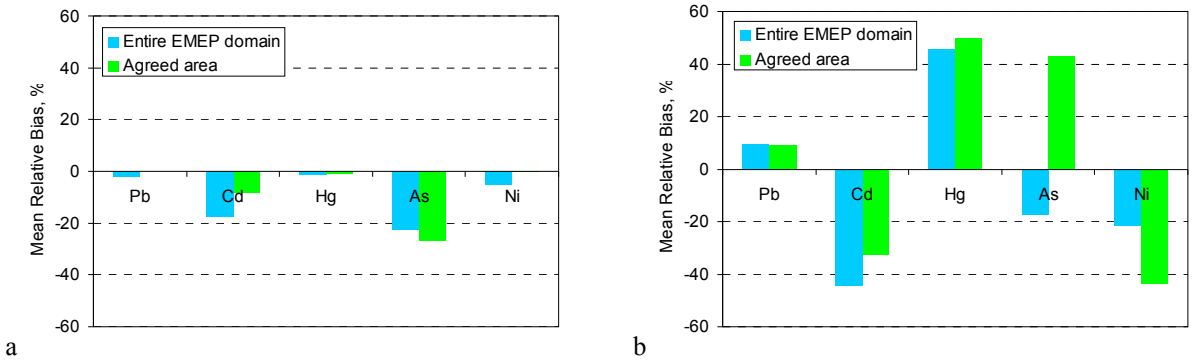


Fig. 3.23. *Mean relative bias for annual concentrations in air (a) and wet deposition fluxes (b)*

Evaluation of modeling results for the agreed area was performed on the base of the EMEP data only. It should be noted that EMEP stations are mostly located in the northern part of the considered area, while in the southern and central parts measurement data are not available. Therefore, involvement of national monitoring data could be very helpful for better understanding of origin of atmospheric heavy metal pollution levels in Italy and for improving both national and the EMEP transport models.

4. MAIN CHALLENGES AND DIRECTIONS OF FUTURE RESEARCH

Main activities of the EMEP Centres MSC-E and CCC in 2015 will proceed in line with the "2014-2015 workplan for the implementation of the Convention" [ECE/EB.AIR/122/Add2] and will focus on assessment of heavy metal pollution levels in the EMEP region and support of the EMEP countries with information required for the implementation of the Protocol on Heavy Metals. Special efforts will be undertaken to characterize status of heavy metal pollution in the countries of Eastern Europe, Caucasus and Central Asia (EECCA). The main challenges of heavy metal pollution assessment, needed particular attention and further research in 2015, are summarized below.

- MSC-E and the Task Force on Emission Inventories and Projections (TFEIP) jointly discussed current problems regarding heavy metal emissions and formulated priority directions to analyze and improve quality of the emission data. Completeness and consistency of emission data, information on the range of uncertainty of reported emissions, generating and updating of emission expert estimates and collaboration with other international programmes (e.g. the UNEP Minamata Convention on Mercury and the Arctic Monitoring and Assessment Programme) are necessary for improving emission data quality and further progress in assessment of heavy metal pollution in the EMEP domain.

- The EMEP monitoring network for heavy metals includes more than sixty sites which are located mostly in the northern, western and central parts of Europe. However, there is still a need for better coverage in the eastern and southern parts of Europe and in Central Asia, especially, in the EECCA countries. Monitoring data coverage could be improved through more active involvement of national data as well as data from international programmes and projects, such as Global Mercury Observation System (GMOS). In addition to this, alternative monitoring approaches could be used, e.g., biomonitoring, passive sampling methods etc.

- Further cooperation with the Working Group on Effects (WGE) is appreciated. In particular, analysis of long-term heavy metal pollution trends based on modeling results and regular moss surveys will be continued. In addition to this, involvement of moss monitoring data in the analysis of pollution levels in the EECCA and South-eastern Europe (SEE) countries is highly important, taking into account limited EMEP monitoring data from these countries.

- Information on long-term trends of heavy metals and analysis of factors affecting trends are useful for understanding effectiveness of environmental policy in the EMEP countries, in particular, for the implementation of the Protocol on Heavy Metals. Long-term trends of lead, cadmium and mercury were analyzed for the period 1990-2010 using a novel methodological approach. This approach can be applied also for other pollutants within the scope of EMEP. The trend analysis is to be periodically repeated (e.g. once in a few years) to take into account both re-calculations of national emissions by countries and updates of the model parameterizations.

- Analysis of factors affecting long-term changes of heavy metal pollution demonstrates that the relative contribution of secondary emission sources to lead and cadmium pollution levels in the EMEP region has increased due to significant reduction of anthropogenic emissions since 1990. Investigation of the processes governing wind re-suspension of heavy metals will be continued to update parameterisations applied in the model. This work is to be performed in cooperation with the Task Force on Measurements and Modelling (TFMM) and national experts.

- Further development of the Global EMEP Multi-media Modelling System (GLEMOS) will be undertaken. Pilot simulations of mercury levels carried out with GLEMOS on the new EMEP grid demonstrate reasonable model performance for the EMEP operational modelling. The model testing and evaluation on the new grid will be continued to cover other heavy metals (lead, cadmium) and POPs. In order to investigate effects of transition to finer spatial resolution, the EMEP country-specific case studies focused on heavy metal pollution assessment on country scale will be continued. In particular, the investigation in 2015 will be fulfilled in close cooperation with national experts from Belarus and Poland.

- Modelling with fine spatial resolution allows revealing effect of Large Point Sources (LPS) on national and transboundary pollution. Evaluation of role of particular LPS requires particular attention in future. It is planned to present calculation results and analysis of pollution levels caused by LPS of selected countries at the 16th TFMM meeting in 2015.

- Development of the multi-media approach for mercury in the GLEMOS modelling system will be continued with focus on aquatic and terrestrial environments. Besides, it is planned to refine mercury chemistry modules to reduce the existing uncertainties and improve quality of modelled concentrations and deposition. Finally, the GLEMOS source code will be distributed for public use to support development of country-scale modelling approaches by national experts.

- MSC-E will continue support and development of English and Russian versions of the MSC-E website to facilitate access to various types of information on pollution levels in the EMEP region and in particular countries. In order to enhance exchange of relevant information it is planned to continue cooperation with subsidiary bodies to the Convention, international and national organizations.

REFERENCES

Aas W. and K. Breivik [2013] Heavy metals and POP measurements. EMEP/CCC-Report 4/2013.

Aas W. and Nizzetto P.B. [2014]. Heavy metals and POP measurements 2012, Norwegian Institute for Air Research. EMEP/CCC-Report 3/2014.

AMAP/UNEP [2013] Technical Background Report for the Global Mercury Assessment 2013. Arctic Monitoring and Assessment Programme, Oslo, Norway/UNEP Chemicals Branch, Geneva, Switzerland. vi + 263 pp. http://www.amap.no/documents/download/1265.

Aulinger A., V. Matthias and M. Quante [2010] An Approach to Temporally Disaggregate Benzo(a)pyrene Emissions and Their Application to a 3D Eulerian Atmospheric Chemistry Transport Model, *Water, Air, & Soil Pollution*, vol. 216, No. 1-4, pp. 643-655.

Bartnicki J., A.Gusev, W.Aas, S. Valiyaveetil [2013] Atmospheric supply of nitrogen, lead, cadmium, mercury and dioxins/furans to the Baltic Sea in 2011. Summary Report for HELCOM. MSC-W Technical Report 2/2012.

Breivik K., R. Alcock, Y.-F.Li, R. E. Bailey, H. Fiedler, J.M. Pacyna [2004] Primary sources of selected POPs: regional and global scale emission inventories. *Environmental Pollution* 128, 3–1.

Breivik K., Sweetman A., Pacyna J.M., Jones K.C. [2007] Towards a global historical emission inventory for selected PCB congeners - A mass balance approach-3. An update. *Science of the Total Environment*, vol. 377, pp. 296-307.

Cao Z., H. Fiedler, B. Wang, T. Zhang, G. Yu, J. Huang, S. Deng [2013] Economic status as a determinant of national PCDD/PCDF releases and implications for PCDD/PCDF reduction, *Chemosphere* 91, 328-335.

Denier van der Gon D. H.A.C., van het Bolscher M., Visschedijk A.J.H. and Zandveld P.Y.J. [2005] Study to the effectiveness of the UNECE Heavy Metals Protocol and costs of possible additional measures. Phase I: Estimation of emission reduction resulting from the implementation of the HM Protocol. TNO-report B&O-A R 2005/193.

Draxler R.R. and Rolph G.D. [2013] HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, College Park, MD.

EMEP Status Report 2/2012. Long-term Changes of Heavy Metal Transboundary Pollution of the Environment (1990-2010).

EMEP Status Report 2/2013. Heavy Metals: Transboundary Pollution of the Environment.

EMEP Status Report 3/2012. Persistent Organic Pollutants in the Environment.

EMEP Status Report 3/2013. Persistent Organic Pollutants in the Environment.

EMEP/MSC-E Technical report 1/2013. Heavy Metals and Persistent Organic Pollutants: Model Assessment of Pollution and Research Activities.

EMEP/MSC-E Technical Report 1/2014. Assessment of Heavy Metal Pollution Levels in the Netherlands (EMEP case study).

EMEP/MSC-E Technical Report 6/2005. Regional Model MSCE-HM of Heavy Metal Transboundary Air Pollution in Europe.

EMEP/SB [2012] Consideration of changing the EMEP grid. Informal Document №3, 36th session of the EMEP Steering Body, Geneva, Switzerland, 2012. (http://www.unece.org/fileadmin/DAM/env/documents/2012/air/EMEP_36th/n_3_EMEP_note_on_grid_scale__projection_and_reporting.pdf.

FAO [2013a] Search Geographical Information. FAO Major Fishing Areas (http://www.fao.org/fishery/area/search/en).

FAO [2013b] Fishery Statistical Collections. Global Capture Production (http://www.fao.org/fishery/statistics/global-capture-production/en).

Fiedler H. [2007] National PCDD/PCDF release inventories under the Stockholm Convention on Persistent Organic Pollutants, Chemosphere 67, S96–S108.

Gusev A., M. Vagygina, O.Rozovskaya, W. Aas, P. Nizzetto [2014] Persistent Organic Pollutants in the Environment. EMEP Status Report 3/2014.

Harmens H. [2010] Monitoring of atmospheric deposition of heavy metals, nitrogen and POPs in Europe using bryophytes. Monitoring manual. 2010 survey. 12p. http://icpvegetation.ceh.ac.uk .

Hirsch R.M., Slack J.R. and Smith R.A. [1982] Techniques of trend analysis for monthly water quality data. *Water Resources Research,* 18, 1, pp 107-121.

Holy M., Pesch R., Schröder W., Harmens H., Ilyin I., Alber R., Aleksiayenak Y., Blum O., Coşkun M., Dam M., De Temmerman L., Fedorets N., Figueira R., Frolova M., Frontasyeva M., Goltsova N., González Miqueo, L., Grodzińska K., Jeran Z., Korzekwa S., Krmar M., Kubin E., Kvietkus K., Larsen M., Leblond S., Liiv S., Magnússon S., Maňkovská B., Mocanu R., Piispanen J., Rühling Å., Santamaria J., Steinnes E., Suchara,I., Thöni L., Turcsányi G., Urumov V., Wolterbeek H.T., Yurukova L., Zechmeister H.G. [2010]. First thorough identification of factors associated with Cd, Hg and Pb concentrations in mosses sampled in the European Surveys 1990, 1995, 2000 and 2005. *Journal of Atmospheric Chemistry* 63, 109-124.

HTAP [2010] HTAP 2010 Assessment Report. Geneva: UN–Economic Commission for Europe. (available at www.htap.org).

Ilyin I., Rozovskaya O., Travnikov O., Varygina M., Aas W., Uggerud H.T. [2011]. Heavy Metals: Transboundary Pollution of the Environment. EMEP Status Report 2/2011. 78p.

Ilyin I., Travnikov O., Varygina M., Vana M., Machalek P. and Hnilikova H. [2012]. Assessment of Heavy Metal Pollution Levels in the Czech Republic (EMEP case study) Joint MSC-E/CHMI Report. EMEP/MSC-E Technical Note 1/2012. 34 p.

Ilyin I., Varygina M., van der Swaluw E., Jimmink B. and Leekstra A.J. [2014]. Assessment of Lead Pollution Levels in the Netherlands (EMEP case study) Joint MSC-E/RIVM Report. EMEP/MSC-E Technical Report 1/2014, 40 p.

Jonson J.E. and O.Travnikov (Eds.) [2010] Development of the EMEP global modeling framework: Progress report. Joint MSC-W/MSC-E Report. EMEP/MSC-W Technical Report 1/2010.

Jonson J.E., Travnikov O. [2012] Global scale modelling within EMEP: Progress report. Join MSC-E/MSC-W Report EMEP/MSC-E Technical Report 1/2012.

Tørseth K., Aas W., Breivik K., Fjæraa A.M., Fiebig M., Hjellbrekke A.G., Lund Myhre C., Solberg S. and K.E. Yttri [2012]. Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009. *Atmos. Chem. Phys. Discuss*., 12, 1733-1820.

Mareckova K., R. Wankmueller, L. Moosmann, M. Pinterits [2013] Inventory Review 2013, Technical Report 1/2013, CEIP, ISBN 978-3-99004-248-9.

Mareckova K., R. Wankmueller, R. Whiting, and M. Pinterits [2012] Inventory Review 2012, Technical Report 1/2012, CEIP, ISBN 978-3-99004-201-4.

Pacyna E.G., J.M. Pacyna, J. Fudala, E. Strzelecka-Jastrzab, S. Hlawiczka, D. Panasiuk, S. Nitter, T. Pregger, H. Pfeiffer, R. Friedrich [2007] Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. *Atmospheric Environment* 41, 8557–8566.

Rolph G.D. [2013] Real-time Environmental Applications and Display sYstem (READY) Website (http://www.ready.noaa.gov). NOAA Air Resources Laboratory, College Park, MD.

Schaap M., M. Roemer, F. Sauter, G. Boersen, R. Timmermans, and P. G. H. Builtjes [2005] LOTOS-EUROS: documentation, TNO report B&O-A R 2005/297.

Schröder W., Holy M., Pesch R., Harmens H., Ilyin I., Steinnes E., Alber R., Aleksiayenak Y., Blum O., Coşkun M., Dam M., De Temmerman L., Frolova M., Frontasyeva M., González-Miqueo L., Grodzińska K., Jeran Z., Korzekwa S., Krmar M., Kubin E., Kvietkus K., Leblond S., Liiv S., Magnússon S., Maňkovská B., Piispanen J., Rühling Å., Santamaria J., Spiric Z., Suchara I., Thöni L., Urumov V., Yurukova L., Zechmeister H.G. [2010]. Are cadmium, lead and mercury concentrations in mosses across Europe primarily determined by atmospheric deposition of these metals. *Journal of Soils and Sediments* 10: 1572-1584.

Shatalov V., Ilyin I., Gusev A., Rozovskaya O., Travnikov O. [2014] Heavy Metals and Persistent Organic Pollutants: Model Assessment of Pollution and Research Activities. EMEP/MSC-E Technical report 4/2014.

Shatalov V., Ilyin I., Gusev A., Rozovskaya O., Sokovykh V., Travnikov O. [2013] Heavy Metals and Persistent Organic Pollutants: Model Assessment of Pollution and Research Activities. EMEP/MSC-E Technical report 1/2013.

Solorzano-Ochoa G., D.A. de la Rosa, P. Maiz-Larralde, B.K. Gullett, D.G. Tabor, A. Touati, B. Wyrzykowska-Ceradini, H. Fiedler, T. Abel, W.F. Carroll Jr. [2012] Open burning of household waste: Effect of experimental condition on combustion quality and emission of PCDD, PCDF and PCB. *Chemosphere* 87, 1003–1008.

Tarrasón L. and A. Gusev Ed. [2008] Towards the development of a common EMEP global modelling framework EMEP/MSC-W Technical Report 1/2008.

Travnikov O. and I.Ilyin [2005] Regional Model MSCE-HM of Heavy Metal Transboundary Air Pollution in Europe. EMEP/MSC-E Technical Report 6/2005, p.59.

Travnikov O. and Jonson J.E. (Eds.) [2011] Global scale modelling within EMEP: Progress report. Joint MSC-W/MSC-E Report. EMEP/MSC-E Technical Report 1/2011.

Travnikov O., Ilyin I., Rozovskaya O., Varygina M., Aas W., Uggerud H.T., Mareckova K. and Wankmueller R. [2012]. Long-term Changes of Heavy Metal Transboundary Pollution of the Environment (1990-2010). EMEP Status report 2/2012, 53 p.

Travnikov O., J.E. Jonson, A.S Andersen, M. Gauss, A. Gusev, O. Rozovskaya, D. Simpson, V. Sokovykh, S. Valiyaveetil and P. Wind [2009] Development of the EMEP global modelling framework: Progress report. Joint MSC-E/MSC-W Report. EMEP/MSC-E Technical Report 7/2009.

UNECE [2009] EMEP monitoring strategy. ECE/EB.AIR/GE.1/2009/15.

UNEP [2010] Final review of scientific information on cadmium.

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

Wenborn M., K. King, D. Buckley-Golder, and J A Gascon [1999] Releases of Dioxins and Furans to Land and Water in Europe, Report AEAT-4703, AEA Technology Environment, EC DG Environment.

Annex A

EMEP/MSC-E CURRENT ACTIVITIES IN THE FIELD OF HM AND POP EMISSIONS

Introduction

Emission data currently provided by the EMEP countries in their national inventories cover only part of the information that is required for model assessment of HM and POP pollution. To provide reliable levels of concentrations and deposition fluxes within the EMEP domain officially reported data need to be complemented by various expert estimates as shown in Table A.1.

Table A.1. *Information on HM and POP emissions officially provided by EMEP countries. Additional emission data required for model assessment of pollution levels*

Information on HM (Pb, Cd, Hg) and POP (PAHs, HCB, PCBs, PCDD/Fs) emissions	**Official emission data (CEIP)**	**Emission data for modelling (MSC-E)**
Time-series of national total emissions (annually)	X	
Gridded sectoral emissions (once in five years)	X	
Emissions of Large Point Sources (once in five years)	X	
Gridded total emissions for the latest reported year generated by CEIP (annually)	X	
Time-series of gridded annual emissions 1990-2012		X
Vertical distribution of emissions		X
Speciation of Hg forms (Hg°, $Hg(II)_{gas}$, $Hg(II)_{part}$)		X
Congener composition for POPs (PCDD/Fs – 17 congeners, PCB-153)		X
Intra-annual variations of emissions		X
Historical emissions of PCBs, HCB, PCDD/Fs up to 1990		X
Emissions to other environmental compartments (PCDD/Fs, HCB)		X
Emissions for the non-EMEP countries within the EMEP domain. (North Africa and Middle East).		X
Natural emissions		X
Re-suspension, re-emissions		X
Global emission inventories (PCDD/Fs, HCB, PCBs, Hg)		X

The preparation of HM and POP emission data for the EMEP domain includes gap-filling of officially submitted data and generation of gridded time-series of annual emissions. Part of this work is currently carried out by CEIP, namely, gap-filling and gridding the emissions for the latest reported year.

At the same time, preparation of gridded *time-series* of emissions for the whole period of time from the base year to the latest reported year is performed at MSC-E including also *gap-filling and providing emissions for the non-EMEP countries within the EMEP domain* [*EMEP Status Report 2/2012*, Section 1.5; *EMEP Status Report 3/2013, Section 1.1*]. Along with this, model assessment requires evaluation of various parameters and characteristics of these gridded emissions, in particular, their *vertical distribution, chemical composition, and intra-annual variations* [*EMEP/MSC-E Technical Report*

6/2005, Section 2.2; *EMEP Status Report 3/2012*, Sections 1.2.2, 1.2.3]. This information is not provided by the EMEP countries and generated on the basis of expert estimates.

A number of HMs and POPs are the pollutants of global scale dispersion (e.g. Hg, PCBs, PCDD/Fs, HCB). Evaluation of pollution of non-EMEP emission sources, located outside of the EMEP domain, requires application of *global inventories of anthropogenic and natural emissions.*

Pollution levels of HMs and POPs are subject of the influence of *secondary emissions (re-suspension and re-emission)*. For long-lived pollutants it is important to take into account their *historic emissions and emissions to surface waters and land* which have essential effect on contemporary levels of pollution.

Requested by the TFEIP information on various aspects and issues related to the use of officially submitted emissions and expert estimates is given below.

1. Which pollutant(s) is/are your priority for improvement?

Priority for the improvement could be given to cadmium and PCDD/Fs which are characterized by essential uncertainties in emissions and the largest disagreement between modeling results and measurements. Particularly, the discrepancies (under-prediction) for cadmium are about a factor of 2 and for PCDD/Fs about a factor of 5 on the average.

A number of studies performed recently for these two pollutants have noted the uncertainties and incompleteness of available emission inventories for these two pollutants. In particular, analysis of anthropogenic HM emissions in Europe, carried out in the framework of the EU ESPREME project [*Pacyna et al*., 2007], indicated that officially submitted cadmium emissions were significantly lower (by more than a factor of 2) comparing to expert estimates made under the project. It was noted that official data on cadmium released from fuel combustion in various industrial, residential, and commercial units could be *underestimated by more than a factor of 3.* Model assessment of cadmium pollution in Europe performed on the basis of the expert estimates of the project showed satisfactory agreement with measurements.

The under-prediction of observed cadmium pollution levels, obtained in most of modeling studies, was also pointed out in the UNEP review on cadmium [*UNEP*, 2010]. The review indicated that the most likely reason of this under-prediction could be the underestimation of anthropogenic cadmium emissions and uncertainties in data on natural *releases and re-emission of former cadmium deposition* which required further improvement.

As to PCDD/Fs, it was noted in the review of *Breivik et al*. [2004], that a number of recently made mass balance studies for PCDD/Fs indicated incompleteness and missing of significant sources in the available emission inventories. The incompleteness of PCDD/F emissions reported officially can be connected with the *underestimation of releases from diffuse and unregulated sources such as open burning of biomass or waste [Fiedler, 2007; Mareckova et al., 2012]*. According to the data of global PCDD/F inventory of the UNEP Stockholm Convention (SC) (more than 60 national inventories) the open burning is one of the most significant sources of PCDD/F pollution. In particular, in almost 25% of countries open burning contributed more than 80% of national total PCDD/F emissions [*Solorzano-Ochoa et al.,* 2012]. This type of information is very limited in officially reported emission data in the EMEP countries.

Along with anthropogenic emissions to the atmosphere the PCDD/F pollution levels are also affected by the secondary emission sources which are formed by the atmospheric deposition and direct emissions to land and surface waters. *Direct releases of PCDD/Fs to land, water, and residues are taken into account in the national emission inventories within the UNEP SC*. At the same time, the methodology on the inventory of POP emissions applied in the CLRTAP is oriented on the atmospheric emissions. Thus, the collaboration with the UNEP SC can be important for further improvement of the assessment of PCDD/F emissions.

2. For HMs and POPs, is the current issue poor geographical coverage? Lack of completeness of the national inventories currently being submitted? Or lack of consistency between Parties?

The completeness and consistency of national inventories of HMs and POPs are still the issues and require further improvement. Complete time-series of annual total emissions are reported by only 55% of the countries for HMs and 43% for POPs. The most complete datasets of emissions are currently available for the countries of the Northern and Western parts of Europe, while for the rest EMEP countries the information on emissions is much more incomplete. In particular, 9 countries for HMs and 8 countries for POPs (most of them are the EECCA countries) do not yet report any data on their national emissions. [*Mareckova et al.*, 2013].

In this respect it is important to mention the proposal of Belarus made at the recent session of the Executive Body for the Convention (December, 2013) to set up a project "Proposal on providing technical assistance to the EECCA countries on methodological and practical issues in preparing emission inventories of POPs, HMs, and TSP". The session recognized significance of supporting of this Belarusian capacity-building activity and technical assistance in the EECCA countries.

Besides in the EMEP Status report on emissions [*Mareckova et al.*, 2013], it was noted that recalculations of their emissions were made by 28 of 40 countries (Annex B). It should be mentioned also that the information on the range of uncertainty of reported emission data estimates (max-min) is essential for model assessment of pollution. However, at present only 8 countries provide the information on uncertainties of their national emissions in the informative inventory reports.

3. Have we solved the issue with metal emissions? If not, what needs to be done next?

Though the quality of officially reported data on emissions of heavy metals is slowly improving, they are still subject of deficiencies listed above. Along with these issues particular attention should be given also to the refinement of *information on emission temporal variations, speciation of mercury forms and congener compositions for POPs, vertical distribution of emissions, time-series of gridded annual emissions, contribution of wind re-suspension and etc.*

Wind re-suspension significantly contributes to heavy metal pollution in the EMEP region. Parameterization of re-suspension process is included in the model assessment of heavy metal pollution levels in the EMEP domain. It is likely that estimates of wind re-suspension currently used in the model are characterized by considerable uncertainties and partly compensate possible underestimation of the anthropogenic emissions. Therefore, further refinement of dust suspension parameterization and information on concentrations of HMs in soils, road dust etc. is needed.

Inverse modeling approach can be useful for evaluation and improving quality of emission data. The approach allows identifying regions where emissions may need special examination. MSC-E started to

use inverse modelling for refinement of re-suspension from the urban territories [*EMEP/MSC-E Technical Report 1/2014*]. Similar approach may be also implemented for analysis of the anthropogenic emissions.

4. Can you give us a couple of paragraphs on how you make "expert estimates" to fill the gaps in the reported POPs/HM emissions data?

Filling of the gaps in the officially reported time-series of HM and POP emissions is performed on the basis of available emission inventories made by various experts and estimates of emissions carried out by MSC-E. To fill in the gaps of the officially reported data (time-series, spatial distribution, and distribution by sectors) MSC-E uses emission expert estimates worked out by TNO [*Denier van der Gon et al.*, 2005]. For some of the EECCA countries there is no emission data in the TNO inventory. In these cases emissions are derived from available global inventories or estimated from the emissions of other EMEP countries using relationship between emissions and gross domestic products. Details can be found in the *EMEP Status Report 2/2013* and *EMEP Status Report 3/2013*.

Additionally, expert estimates are essentially important in the preparation of emissions for the non-EMEP countries within the EMEP domain. For this purpose available global emission inventories are used (e.g. for Pb, Hg, and PCBs). These data are also applied for the evaluation of contributions of intercontinental transport and secondary emission sources (re-volatilization to the atmosphere) to the EMEP pollution levels. For the evaluation of HCB pollution historic HCB emission scenarios were prepared using available information on the application of HCB in various activities (e.g. agriculture, industry). Elaborated scenarios covered the period starting from 1940s and included low, average and high estimates of emissions. Gridded data were based on the distribution of cropland area for the emissions from agricultural use and on population density for other sources of HCB emissions [*EMEP Status Report 3/2012*, Section 1.2.4].

For PCBs a global emission inventory for the period from 1930 to 2010 [*Breivik et al.*, 2007] is applied for evaluation of the effects of historical emissions and intercontinental transport on the pollution in the EMEP countries.

There is ongoing work at the MSC-E on the development of scenarios for the PCDD/F emissions to the atmosphere and other media based on the inventories of the EU project "Releases of Dioxins and Furans to Land and Water in Europe" [*Wenborn et al.*, 1999; *EMEP/MSC-E Technical report 1/2013*, Section 1.2] and data of the UNEP SC PCDD/F emission inventory [*Cao et al.*, 2013].

Compilation of global PCDD/F emissions, using the UNEP Standardized Dioxins Toolkit [*UNEP*, 2013] is under preparation within the SC now.

A certain progress in the elaboration of global emission inventories is achieved for Hg. Particularly, during the preparation of the Minamata Convention the new global inventory of mercury emission was developed for the year 2010 by UNEP and AMAP [*AMAP/UNEP*, 2013]. These data have been applied for the recent model assessment of pollution levels of Hg for the EMEP region and on the global scale. Thus, collaboration with the UNEP Minamata and Stockholm Conventions as well as with AMAP is of importance and of mutual interest.

5. Do countries then submit these data in subsequent years?

Expert estimates used for the model assessment of pollution levels are available on the MSC-E website [*EMEP/MSC-E Technical report 1/2013*, *EMEP Status Report 3/2013*, *EMEP Status Report 2/2012*, *EMEP Status Report 3/2012*, *EMEP/MSC-E Technical Report 6/2005*].

It would be good to address this question to the countries to start dialogue on this issue.

6. Do you just use data at an annual resolution? If no, can you provide us with a brief description of how you generate the fine timescale emissions?

At present we consider intra-annual variations of emissions for PAHs and PCDDF/s, while for lead, cadmium, mercury, HCB, and PCBs annual resolution of emissions is applied for modeling of pollution levels. Temporal distribution of PAH emissions is made for several aggregated emission source groups. Particularly, fine timescale PAH emissions from residential heating source category are generated using the approach based on the assumption of the dependence of heating power supply on ambient temperature [*Aulinger et al.*, 2010]. Monthly, weekly, and diurnal variations of PAH emissions from road transport and industrial processes source categories are constructed in accordance to the emission temporal profiles used in LOTOS/EUROS model [*Schaap et al.*, 2005]. For other source categories annual emissions are used. Simplified description of seasonal changes of PCDD/F emissions is constructed on the basis of available measurements of air concentrations and variations of emissions of pollutants emitted by similar groups of sources, namely, PAHs [*EMEP Status Report 3/2012*, Section 1.2.2].

Concluding comments on further improvement of HM and POP emission data

1. The major issues with regard to the quality of officially reported emission data for the assessment of HM and POP pollution are connected with the completeness and consistency of inventories in line with the Emission Reporting Guidelines with special attention to the EECCA countries. Cd and PCDD/Fs are pollutants of a first priority.

2. Information on the range of uncertainty of reported emission data is needed to prepare scenarios of emissions for the evaluation of possible maximum and minimum levels of pollution of the EMEP domain.

3. Generating and updating of emission expert estimates, applied for the preparation of HM and POP emission data for modeling, is highly appreciated. (see Table A.1).

4. Collaboration with the UNEP Minamata and Stockholm Conventions as well as with AMAP is of mutual importance for further work on the evaluation of non-EMEP emission sources affecting pollution of the EMEP domain.

QUALITY OF THE MODEL ASSESSMENT

One of advantages of modelling approach in assessing pollution levels is ability to produce calculation-based information in every gridcell of the modelling domain and at any required temporal resolution. However, quality of the modelling results has to be evaluated. Comparison of modelled and observed pollution levels in gridcells where monitoring stations are located is one of ways to evaluate calculation results. Calculated concentrations in air and wet deposition fluxes of lead, cadmium and mercury are compared with values measured at the EMEP monitoring stations. Results of monitoring of heavy metal levels in the EMEP region are described in Chapter 1 of this report.

All components of the assessment of pollution levels, such as emissions, model parameterizations, and measurements are subject to various uncertainties. Therefore, modelled values of pollution levels can hardly fully coincide with the observed levels. However, if the difference between modelled and observed levels at a station is significant, e.g., exceeds factor of 2 or 3, analysis of these deviations is required. Table B.1 summarises the main statistical indicators of comparison of modelled and measured concentrations in air and wet deposition fluxes. More detailed information about the comparison is available in the MSC-E Technical Report [*Shatalov et al*., 2014].

Table B.1. *Main statistical indicators of agreement between annual modelled and measured levels of air concentrations and wet deposition fluxes for 2012.*

	Lead		Cadmium		Mercury	
	C_{air}	Wet Dep	C_{air}	Wet Dep	C_{air}	Wet Dep
Relative bias, %	-4.1	6.4	-18.5	-38.7	-3.7	40.1
Correlation coefficient	0.80	0.55	0.73	0.63	0.36	0.52
NRMSE	0.49	0.53	0.58	0.59	0.09	0.56
F2, %	71	83	65	66	100	76
F3, %	88	98	93	85	100	95

C_{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

For lead the modelled levels match the observed levels relatively well. Relative bias, calculated for totality of stations, is quite low: -4% for air concentrations and 6% for wet deposition (Table B.1). It means that the model does not overestimate or underestimate lead levels in general. This idea is also confirmed by high percentage of modelled values agreeing with observations within a factor of 2 or factor of 3. However, at different stations the agreement between modelled and measured values varies considerably (Fig B.1 a, b). Underestimation (50-60%) of lead levels in Scandinavian countries, especially in Finland, can be linked with insufficient contribution from transboundary transport

Modelled levels of lead match observations relatively well in the EMEP region. Special attention should be paid to overestimation of concentrations in the Netherlands and Spain, and underestimation of lead pollution levels in Scandinavia.

from emission sources of some neighbouring countries. Overestimation at some stations in Spain and the Netherlands is likely caused by overestimation of influence of secondary emission sources in these regions. In particular, in the framework of the EMEP country-specific case study of pollution level assessment for the Netherlands it is shown that re-suspension from urban territories assumed in the model is likely overestimated and needs correction [*Ilyin et al.,* 2014]. Pilot calculations with corrected re-suspension are discussed in the MSC-E Technical Report [*Shatalov et al*., 2014].

Over most part of the EMEP region cadmium modelled levels agree well with the observed concentrations and deposition. However, in some regions (Scandinavia, the eastern and south-eastern parts of Europe) underestimation of the observed levels takes place, likely because of emission uncertainties. Inverse modelling approach and country-specific research with fine spatial resolution are possible ways to further examine and resolve the problem.

Cadmium levels are calculated with higher uncertainty compared to lead. Underestimation of air concentrations is relatively low – around 20%, whereas wet deposition is underpredicted by almost 40%. Relatively good agreement between modelled and observed wet deposition fluxes takes place for most of stations in Germany, the United Kingdom, Norway, Poland, the Netherlands, Estonia and Slovakia. Significant underestimation (2-3 times) is noted for Scandinavian stations, mostly for those that are located in Finland, but also for some stations in Norway, Denmark and Sweden (Fig. B.2). Besides, the underestimation is considerable at stations of the Czech Republic, Serbia and Latvia. These discrepancies can be caused by uncertainties of emission data or by influence of local sources. Inherent model uncertainty for deposition is around 40%. It means that the uncertainty of the model cannot explain 2-3 fold difference between modelled and observed levels, and effect of other factors influencing quality of modelling results should be considered. Inverse modelling approach can be applied in order to investigate sensitivity of modelled levels at particular stations to emissions in different parts of the EMEP domain. This approach is useful to identify areas where emissions need more detailed analysis. In order to single out the influence of local sources emission data with fine spatial resolution are needed, and modelling with fine spatial resolution should be applied. This approach has already been used in examination of measured and modelled levels of heavy metals in the Czech Republic [*Ilyin et al*., 2012] and in the Netherlands [*Ilyin et al*., 2014]. Another source of uncertainties could be monitoring data. For example, the highest observed wet deposition fluxes are noted for station FR90 (France), which measurements are subject to influence of marine aerosol.

Atmospheric chemistry of mercury is the major source of uncertainties. In order to improve model assessment of mercury levels in the EMEP counties, more research activity in this field is needed.

Annual mean concentrations of mercury in air exhibit low spatial variability. Both modelled and measured levels range within 1.3 – 1.7 ng/m^3 (Fig. B.3a). The model tends to overestimate wet deposition fluxes of mercury (Fig. B.3b). Relatively low (±30%) discrepancies are noted for stations in Norway, Belgium, Spain, the Netherlands and most of Swedish stations. At some German and British stations the model overestimates observed wet deposition fluxes by 50-80%. The highest overestimation – 2.7 – 3.6 times - takes place for Finnish sites. Wet deposition depends on air concentrations of readily wet-scavenged mercury forms, which, in turn, are mostly products of atmospheric chemical transformations. Mercury chemistry is known to be highly uncertain at present.

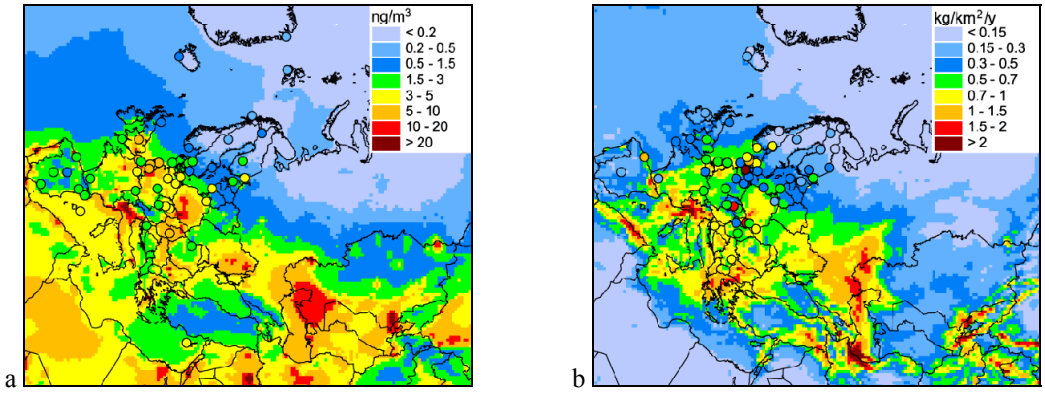


Fig. B.1. *Modelled and observed air concentrations of lead air concentrations (a) and wet deposition (b) in 2012*

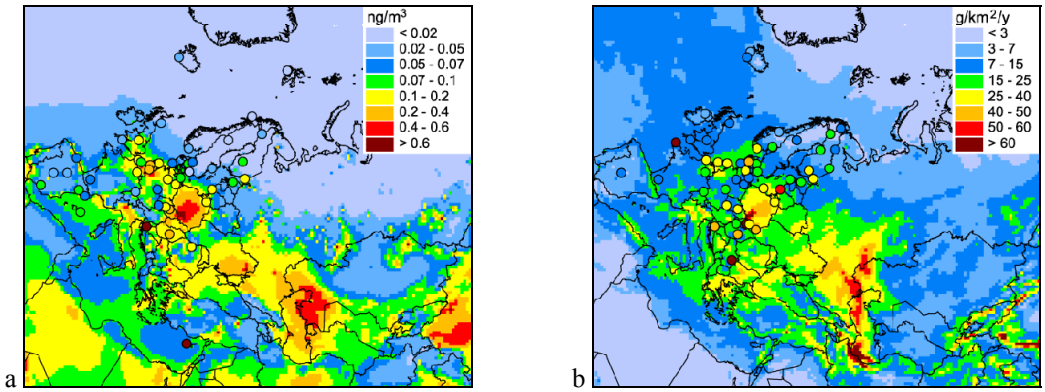


Fig. B.2. *Modelled and observed air concentrations of cadmium air concentrations (a) and wet deposition (b) in 2012*

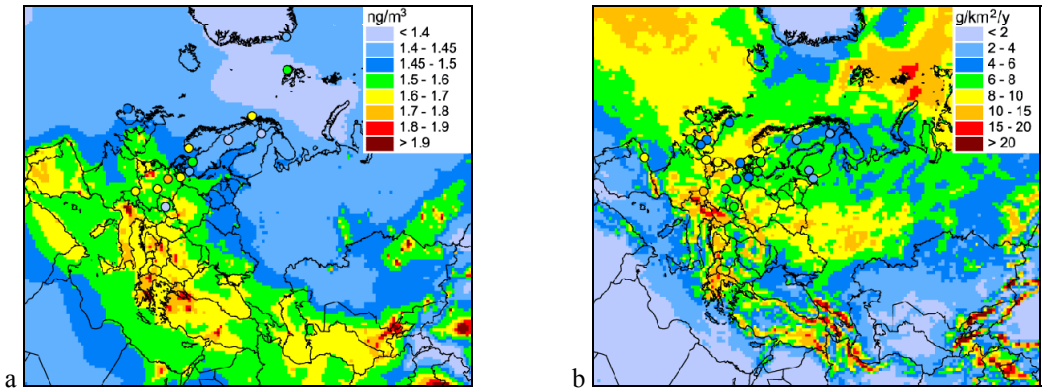


Fig. B.3. *Modelled and observed air concentrations of mercury air concentrations (a) and wet deposition (b) in 2012*