Heavy metals:
transboundary pollution of the environment

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EXECUTIVE SUMMARY

In accordance with the EMEP work-plan for 2004 [ECE/EB.AIR/79/Add.2] the Meteorological Synthesizing Centre – East (MSC-E) and the Chemical Coordinating Centre (CCC) continue research activities in the field of heavy metal atmospheric pollution assessment. The main objective of the work is to evaluate lead, cadmium and mercury pollution levels in Europe on the basis of measurement data and modelling results. Particular attention is paid to cooperation with the effect community on development of the critical load approach, to support of activities on the review of the Protocol on Heavy Metals, and to the evaluation of the MSC-E heavy metal transport model in the framework of preparation to the model review.

National data on anthropogenic emissions of lead, cadmium and mercury for 2002 were submitted to the EN ECE Secretariat by 27 countries. In addition 13 countries presented the revised data for the period of 1990-2001 resulted from the improvement of statistical data, emission factors, calculation methods etc. For the remaining countries expert estimates were used in the assessment. Anthropogenic emissions of lead, cadmium and mercury in 2002 reduced by 11%, 5% and 11% respectively as compared with 2001. The most significant emissions of these heavy metals are from the sources located in Western, Central and Southern Europe.

Heavy metals were included in the EMEP monitoring programme in 1999, though measurements of these substances at individual stations have been carried out since 1988. At present the EMEP monitoring network includes 66 stations measuring lead and cadmium, of which 25 stations measure concentrations of these metals both in the air and precipitation. There are 13 stations, where at least one mercury form is measured. However, the distribution of the monitoring stations over the European territory is not uniform: they are mainly located in Central and Northern Europe. The EMEP monitoring strategy being developed for 2004-2009 will probably improve the spatial coverage of monitoring sites in Europe. Annual analytical intercomparisons of national laboratories processing measurements of heavy metals indicate a substantial improvement of data quality during the period of 1995-2002.

Measurements of heavy metal pollution levels in 2002 showed that the lowest concentrations of lead, cadmium and mercury were observed in Northern Scandinavia. In general concentration levels increase towards the southeast of Europe.

Model estimates of the environment pollution by heavy metals were made by the regional and hemispherical models. According to the modelling results the spatial distribution of environmental pollution levels of heavy metals in Europe is highly non-uniform. The deposition intensity in different parts of Europe can differ by more than an order of magnitude. High deposition levels are characteristic of Central and Southern Europe, the lowest levels – of Northern Europe. Transboundary transport plays an important role in pollution of most of European countries. Contribution of external European anthropogenic sources to depositions in European countries varies from 5 to 85% for lead, 4 – 75% for Cd and 3 – 60% for Hg. The highest contribution is characteristic of the countries with insignificant national emissions and of those bordering powerful emission sources. The most significant contributors of heavy metals to the atmospheric transboundary transport in Europe are the countries with the largest national anthropogenic emissions. The contribution of the transboundary transport to depositions of heavy metals to the European Union varies from 7 to 15%. The bulk of
heavy metals (75%) involved in the transboundary transport is emitted only by 10, 9 and 9 European countries for lead, cadmium and mercury respectively.

Pollution levels vary greatly within a country. For example, the annual deposition of lead can differ 3.5 times in different Lands of Germany. Besides, contribution of the transboundary transport to the deposition of lead to different Lands varies from 14 to 46%.

Atmospheric depositions contribute significantly to heavy metal pollution of marginal seas. The highest mean deposition flux of lead was reported over the Black Sea, of cadmium – over the Baltic Sea, and of mercury – over the North Sea.

Hemispheric modeling was applied to the assessment of heavy metal pollution of the new Parties to the Convention – Kazakhstan and Kyrgyzstan. Levels of mercury and lead depositions in these countries were analyzed. It was obtained that about 65% of mercury and 62% of lead depositions to the territory of Kazakhstan are determined by external anthropogenic and natural sources. For Kyrgyzstan the contribution of external sources is even larger – 90% for mercury and 83% for lead.

The MSC-E regional transport model used for the assessment of pollution levels in Europe was evaluated against available measurement data and compared with other models. The evaluation demonstrates a significant correlation of modelling results with measurements. However, the model underestimates lead and cadmium concentrations both in the air and in precipitation and slightly overestimates mercury deposition with precipitation as compared with the observed values.

The activities under the multi-stage project on the intercomparison of mercury transport models are continued. The third stage of the project dedicated to the comparison of the long-term modelling results with the annual and monthly mean measurements of mercury ambient air concentrations and atmospheric deposition fluxes is under way.

In the framework of cooperation with the Working Group on Effects MSC-E operationally calculates relevant parameters of atmospheric inputs to ecosystems. Ecosystem-specific depositions of heavy metals in Europe were assessed and analyzed. To support a preparatory work of the Working Group on Strategies and Review aimed to review the Protocol on Heavy Metals, in particular the work of the Expert Group on Heavy Metals, MSC-E continues preparations for the modelling of heavy metals of the second priority. Emission and monitoring data for these pollutants were collected; information on physical and chemical properties of these pollutants was prepared.

Besides, the EMEP Centres were involved in cooperation with other international organizations and national programmes (AMAP, EU, HELCOM, OSPAR, WMO). The main results were discussed at a number of scientific conferences, workshops and expert meetings. Detailed information about CCC and MSC-E activities can be found at the EMEP website (www.emep.int) and in CCC Report [Aas and Breivik, 2004].
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INTRODUCTION

Pollution of the environment by heavy metals is the subject of concern of a number of national and international bodies. In 1998 a number of Parties to the Convention on Long-Range Transboundary Air Pollution (hereinafter the Convention) signed the Protocol on Heavy Metals (Protocol). The aim of the Protocol was to control atmospheric emissions of toxic metals (lead, cadmium and mercury). In accordance with the Protocol the Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP) provides the assessment of pollution levels of heavy metals in the European region. Measurements of heavy metal concentrations in the air and precipitation are carried out at the EMEP monitoring network under the methodological guidance of the Chemical Co-ordinating Centre (CCC). Along with that the Meteorological Synthesizing Centre – East (MSC-E) performs the model assessment of depositions and air concentrations of heavy metals throughout the European region as well as the transboundary fluxes between the European countries.

In 2003 the Protocol on Heavy Metals came into force. In order to support the Working Group on Strategies and Review (WGSR), in particular, an Expert Group on Heavy Metals in its preparatory work for the review of the Protocol, MSC-E and CCC initiated preparatory activities on the second priority metals (As, Ni, Cr, Zn, Cu) pollution assessment. The progress of EMEP Centres in the field of the assessment of environmental pollution by heavy metals with respect to the Protocol requirements was described in the special report [EMEP contribution…, 2004].

In order to correlate the existing pollution levels with their effects on the environment and human health, they are compared with the scientifically sound critical values, developed by the Working Group on Effects (WGE). In the framework of the cooperation with WGE, MSC-E evaluated ecosystem-specific depositions of lead, cadmium and mercury for the European region.

For the practical use of the modelling results, e.g. for the development of optimal emission reduction, comparison with the critical values etc., the results should be reliable. According to the decision of the Task Force on Measurements and Modelling (TFMM) (Prague, Czech Republic, April 2004), a workshop on the model review is planned to be held in 2005. The aim of the review is to evaluate the reliability of the modelling results. The review should comprise the comparison of the model results with measurements, model intercomparison studies as well as analysis of the quality of emission and measurement data.

The Status Report describes the progress in the study of air pollution by lead, cadmium and mercury in Europe. The presented results were obtained in studies made by CCC and MSC-E in 2004 according to the EMEP work-plan on heavy metals (Annex A).

Chapter 1 is focused on the monitoring activities in the field of heavy metals. The measurement network is described, and the measured pollution levels (concentrations in the air and precipitation) are presented. Special attention is devoted to the quality of measurement data. Reliable data were suggested for further use in the analysis of pollution levels and model validation. Results of the recent intercomparison of the analytical methods are outlined.

Chapter 2 describes the modelling assessment of the atmospheric transport of lead, cadmium and mercury in Europe as well as the hemispherical transport of mercury and lead. Spatial distribution
patterns of heavy metal deposition to the European region, and information on source-receptor relationships are summarized. In addition to European countries, source-receptor relationships were determined for the European Union. Special attention was paid to the variability of pollution levels within an individual country by the example of Germany. Atmospheric loads of heavy metals to marginal seas were estimated. Hemispheric modelling was used to evaluate the heavy metal pollution of the new Parties to the Convention - Kazakhstan and Kyrgyzstan. Depositions of mercury and lead were assessed and the main contributors to the transboundary pollution were identified. Some aspects of the input information (emission data and measurement results) uncertainties with regard to modelling needs were analysed. Much attention in the report was paid to the validation of the model. Modelled concentrations of lead, cadmium and mercury were compared against the monitoring data and with the outcomes of other models.

Chapter 3 is devoted to cooperation between EMEP and other bodies to the Convention, international organizations, and national programmes. In cooperation with WGE EMEP evaluates ecosystem-dependent depositions of the metals on a regular basis. A short review of emissions, measurements and atmospheric physical properties of the second priority metals was prepared as a part of cooperation with the WGSR. Besides, the results of the cooperation of EMEP with HELCOM, EU, WMO and national programmes are described.

The main results of the EMEP work in the field of heavy metals are summarized in Conclusions. The EMEP work-plan on heavy metals for 2004 and description of the model are presented in the annexes. Detailed information about CCC and MSC-E activities can be found at the EMEP website (www.emep.int).
1. MONITORING OF HEAVY METALS IN EMEP

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 thus also includes older data, even back to 1988 for a few sites. A number of countries have been reporting heavy metals within the EMEP area in connection with different national and international programmes such as HELCOM, AMAP and OSPARCOM.

The locations of the measurement sites, which have delivered data on heavy metals for 2002, are found in Fig. 1. In the figure, the sites are divided in those measuring both concentrations in air and in precipitation, and those measuring only one of them. In 2002 it was 25 sites measuring heavy metals in both compartments, and altogether it was 66 measurement sites. It was 13 sites measuring at least one form of mercury.

It is quite evident from Fig.1 that the spatial distribution of monitoring sites in Europe is unsatisfactory. There are hardly any sites that measure heavy metals in east of Europe, and in southern Europe at the Iberian Peninsula only. In addition, it is too few sites measuring both in air and precipitation. In the new EMEP monitoring strategy for 2004-2009, it states that all EMEP parties should measure heavy metals; this strategy will expectantly help to improve the situation. Detailed information about the sites and the measurement methods are found in EMEP/CCC’s data report on heavy metals and POPs [Aas and Breivik, 2004].

Monitoring of Pb, Cd and Hg in 2002

Annual averages of Pb, Cd and Hg concentrations in precipitation and in air in 2002 are presented in Fig. 2-7. The lowest concentrations for all elements in air as well as precipitation are 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.
The highest cadmium concentrations in precipitation are observed at Preila in Lithuania, Knokke in Belgium and at Chopok in Slovakia; in air the highest concentrations are observed in Slovakia. Also for lead in precipitation, the highest concentrations are seen in Preila in Lithuania and Chopok in Slovakia. The concentrations in air were highest at sites in Belgium, Austria and Spain in addition to Slovakia.

There are only a few stations measuring mercury in Europe, and most of them are related to the OSPARCOM program CAMP. The concentrations of mercury at the different sites are decreasing from north to south, but these differences are quite small.
Data quality

For lead, the precipitation data from EE11, BE04 and GB14 is not included in the map (Fig. 3) due to large uncertainties and/or low data capture. Precipitation data from PL05, Portugal, Ireland and Estonia should be looked as upper limits because most of the data are below the detection limits. The cadmium precipitation measurements in Portugal, Great Britain and the aerosol measurements from Belgium is not included due to high uncertainties. The majority of the precipitation data from Ireland, Island, PL05 and Denmark is below the detection limits, and the annual averages are therefore only an upper estimate of the concentration level. For mercury, the precipitation data from Ireland has too high detection limits and are not useful. The same pattern is seen for the second priority compounds; Ireland, Portugal and Belgium have problems with the measuring low concentrations and the sensitivity of their instruments is too low.

The data quality objectives (DQO) in EMEP states that the accuracy in the laboratory should be better than 15% and 25% for high and low concentrations of heavy metals, respectively. One important measure to check the data quality is laboratory ring test. There is a marked improvement in the laboratory performance for both lead and cadmium since the beginning of the laboratory comparison in 1995. The intercomparison completed last year is representative for the 2002 data [Uggerud and Skjelmoen, 2003]. In Table 1, there is a summary of the results from this laboratory intercomparison. Sweden, Denmark (precipitation) and Iceland were not participating because these measurements were analyzed in Norway. The measurements of high concentration samples are hardly any problems, but these samples are not very representative for many EMEP sites. Several countries have some problems with measuring low concentration samples of Cr, Ni, As and Cd. In addition, there are some countries reporting measurements data without participation in the laboratory intercomparison: Belgium, Ireland, Portugal, and Spain. Data from these countries are of unknown quality; and it is therefore strongly recommended that they take part in the annual laboratory intercomparison.

Table 1. Average per cent error (absolute) in low and high concentration samples, results from the laboratory intercomparison. DQO is EMEPs data quality objectives

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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2. MODEL ASSESSMENT OF ENVIRONMENTAL POLLUTION BY HEAVY METALS

This Chapter is devoted to the model assessment of the long-range transport of heavy metals in the atmosphere of Europe and in the Northern Hemisphere as a whole. The first section contains brief information on emissions of lead, cadmium and mercury to the atmosphere of Europe in 2002 from anthropogenic and national sources. The second section contains the analysis of levels of the environmental pollution by lead, cadmium and mercury in Europe in 2002, information on transboundary fluxes between European countries, and heavy metal atmospheric loads to the regional seas. The third section is devoted to the evaluation of the MSC-E heavy metal model. It includes the analysis of input information (emission and monitoring data), comparison of modelling results with measurements, description of the model development and progress in the mercury models intercomparison study. The fourth section describes the application of the hemispheric modelling approach to the assessment of heavy metal atmospheric pollution. Particularly, levels of mercury and lead pollution in the new Parties to the Convention, Kazakhstan and Kyrgyzstan, that not covered by the EMEP grid are analysed using the available global emission inventories.

2.1. Emissions of heavy metals in Europe

Under the commitments taken in the framework of the Convention the Parties annually submit to the UN ECE Secretariat information on national anthropogenic emissions of heavy metals. National data on heavy metal emissions for the reported year 2002 were submitted by 27 countries. Besides, 13 countries presented revised data for the period 1990-2001 resulted from the improvement of statistical data, emission factors, calculation methods etc. The changes in national emissions are analysed in Section 2.3. For the countries that have not submitted any data or data for some years, a linear interpolation or expert estimates of anthropogenic emissions were used in the modelling process [Berdowski et al., 1998]. National information on the spatial distribution of emission sources at least for one year is submitted by 20 countries. For the rest of them expert estimates [Berdowski et al., 1997] were used to distribute the total national emission over a country.

The resulting maps of the spatial distribution of lead, cadmium and mercury anthropogenic emissions in Europe in 2002 are presented in Figs. 8, 9, and 10 respectively.

According to the available data the most significant sources of lead emissions are located in Central Europe (Poland, Germany), Southern Europe (Italy, Croatia, Serbia and Montenegro, Romania, Greece) and Eastern Europe (Russia). In contrast, emissions of cadmium distributed more or less uniformly over Western, Central and Southern Europe except Poland, where emission levels are significantly higher. Low emissions are in Northern Europe and in some countries of Eastern Europe (Belarus, Ukraine). The most significant emissions of mercury are also located in Western, Central and Southern Europe. The total emission of lead, cadmium and mercury in Europe in 2002 amounts to 8003 t/y, 257 t/y and 180 t/y respectively.

Apart from anthropogenic emissions, heavy metals enter the atmosphere of Europe due to re-emission of previously deposited substances and from natural sources. These types of sources are taken into account on the basis of expert estimates made in MSC-E [Ryaboshapko and Ilyin, 2001; Travnikov and Ryaboshapko, 2002].
Natural emission and re-emission processes are particularly important for the mercury cycle in the environment. The distribution of mercury re-emission from soil in Europe is illustrated in Fig. 11. The most significant re-emission fluxes are in Central Europe in the regions where intensive depositions have been observed for a long time. The spatial distribution of estimated natural emission of mercury in European region is shown in Fig. 12. Rather high emission fluxes are from soil of the geochemical belt in the south of Europe and from coastal seawater with the intensive primary carbon production. According to these estimates the total annual emission of mercury from natural sources and reemission from European soil and marginal seas are 100 and 50 tonnes respectively.
2.2. Air pollution by lead, cadmium and mercury in Europe in 2002

The assessments of atmospheric pollution have been made by the regional (MSCE-HM) and the hemispherical (MSCE-HM-Hem) transport models developed in MSC-E. The regional model covers the EMEP region with the spatial resolution of 50x50 km; the hemispheric model describes the atmospheric transport within the Northern Hemisphere with the spatial resolution of 2.5°x2.5°. Annex A contains brief description of both models. The main outputs of the modelling include data on heavy metal concentration in the air and precipitation as well as levels of deposition to the surface. Since the negative impact of heavy metals on human health and biota is mainly attributed to their long-term accumulation in environmental media particular attention has been given to the assessment of their depositions from the atmosphere.

2.2.1. Pollution levels in Europe

**Lead**

Depositions and concentrations of lead, cadmium and mercury were evaluated on the basis of emissions and meteorological data for 2002. In 2002 anthropogenic emissions of lead in Europe amounted to 8 kt/y. This is about 11% less than in 2001\(^1\). In addition, natural emissions and re-emissions made up 1 kt/y. The total depositions to Europe in 2002 were 6.7 kt.

Spatial distribution of lead depositions in Europe varies to a large extent. Detailed pattern of the spatial distribution is given in Fig.13. In the central and southeastern parts of Europe, e.g. in Belgium, Poland, Italy, Serbia and Montenegro, depositions are the highest and can exceed 2 kg/km²/y. Similar values of depositions are characteristic of the central region of Russia. These high depositions are caused by the significant emission sources located in these regions (Fig. 13).

Atmospheric pollution in different countries can be illustrated by deposition fluxes averaged over the country area (Fig. 14). Serbia and Montenegro is characterized by the highest averaged deposition flux of lead (about 1.5 kg/km²/y). High deposition fluxes are also obtained for other countries in the south-east of Europe: Croatia, Bulgaria, Greece, Romania. As for the western European countries high depositions are noted for Poland and Belgium. These countries are also characterized by relatively high emissions (Fig. 14). The lowest flux was obtained for Scandinavian countries: Norway, Iceland and Sweden.

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\(^1\) All comparisons with the year 2001 are based on the recalculated national emissions data for preceding years and can differ from values published in the previous reports
Serbia&Montenegro
Belgium
Croatia
Poland
Bulgaria
Greece
Romania
Slovakia
Netherlands
Slovenia
Germany
Italy
Hungary
Georgia
Bosnia&Herzegovina
Luxembourg
FYR of Macedonia
Albania
Czech Republic
Switzerland
Cyprus
Lithuania
Turkey
Austria
Ukraine
Russia
Denmark
Belarus
France
United Kingdom
Moldova
Azerbaijan
Latvia
Estonia
Spain
Kazakhstan
Ireland
Malta
Armenia
Portugal
Finland
Sweden
Iceland
Norway

0
1
2
4
6
Average deposition/emission, kg/km
2/y
Deposition
Emissions

Fig. 14. Average lead anthropogenic emission and deposition flux in European countries in 2002

A significant part of depositions over each country is caused by the transboundary transport from external sources. In 2002 the contribution of external European anthropogenic sources to depositions over different countries ranges from 5 to 85% (Fig. 15). The highest contribution was obtained for the Former Yugoslav Republic of Macedonia and Monaco. In 20 countries of Europe the external European anthropogenic sources contribute more than 50% of total deposition. In addition to individual European countries, source-receptor relationships were evaluated for the “composite” region: the European Union\(^2\). The contribution of external anthropogenic sources to EU amounted to 12%.

A significant amount of lead emitted in a country is transported beyond the national borders contributing to the transboundary transport. In 2002 as much as 4.8 kt (around 60% of total anthropogenic emission) of atmospheric lead, emitted in Europe, were involved in transport across state borders. Absolute magnitudes of lead transported outside countries vary substantially from country to country (Fig. 16). It was calculated as difference between national emission and deposition to the country. This magnitude depends on national emission, size of the territory, climatic conditions and spatial distribution of emission sources within the country.

The highest amount of lead transported across the state borders, is coming from Russia, followed by Turkey and Italy (Fig. 16). This can be explained mainly by the significant absolute values of lead atmospheric emissions in these countries. About 1500 t of lead was transported from the European

\(^2\) Although the present-day European Union includes 25 states, we consider only 15 member states constituting the EU in 2002 (EU15)
Union. It should be noted that more than 75% of lead mass involved in the transboundary transport is emitted by 10 major countries-contributors.

**Fig. 16.** Contribution of European countries to the lead transboundary transport in 2002

**Cadmium**

In 2002 anthropogenic emission of cadmium in Europe amounted to 257 t/y, that is 5% lower than in 2001. Emission caused by natural processes (natural emission and re-emission) add up 55 t/y. Depositions to Europe in 2002 were 240 t/y.

Spatial distribution of cadmium deposition in Europe is shown in Fig. 17. The regions with relatively high depositions are Poland with surrounding countries, the south-east of Europe and the area around Belgium. Deposition fluxes in these regions exceed 30 g/km²/y. In the northern part of Europe deposition fluxes are below 10 g/km²/y.

The spatial pattern of national emissions and atmospheric transport from neighbouring countries causes high variability in depositions to different countries (Fig. 18). The highest deposition flux of cadmium averaged over the country area is noted for Poland (almost 100 g/km²/y), followed by Slovakia, Belgium, and Bulgaria. The lowest average deposition flux is in Finland and Norway.

**Fig. 17.** Spatial distribution of cadmium depositions in Europe in 2002

**Fig. 18.** Average cadmium anthropogenic emission and deposition flux in European countries in 2002
The contribution of the external European anthropogenic sources to cadmium depositions in Europe in 2002 varies from 4 to 75% (Fig. 19). In 17 countries it exceeded 50%. The countries most affected by the transboundary transport of cadmium are Belarus, Ukraine, Lithuania, and Czech Republic. These countries are located close to Poland, which is a significant emitter of cadmium. Similar to lead, the lowest contributions are observed in Spain and Iceland. The contribution of the transboundary transport to pollution of the European Union with cadmium is about 15%.

![Fig. 19. Relative contribution of external anthropogenic sources to cadmium depositions in European countries in 2002](image)

Each country is not only a receptor but also a source of the transboundary transport. As much as 153 t (60% of anthropogenic emission in Europe) of cadmium, emitted in Europe, leaves the territory of the counties and is involved in the long-range transport. The highest absolute value – 30 t/y - of cadmium transported across national borders was obtained for Poland (Fig. 20). The significant “exporters” of cadmium are Spain, the Russian Federation, Romania and Italy. Nearly 40 t of cadmium is transported outside the European Union. Besides, only nine countries control more than 75% of cadmium transboundary transport.

![Fig. 20. Contribution of European countries to the cadmium transboundary transport in 2002](image)

**Mercury**

Mercury emissions from European anthropogenic sources in 2002 totalled 180 tonnes; this is 11% lower than those in 2001. The input from natural emission and re-emission from European soils and the marginal seas is estimated at about 150 tonnes. More than 65% of emitted mercury was transported beyond the boundaries of Europe. The total mercury depositions to Europe were about
100 tonnes. Of this amount, 50 tonnes originated from anthropogenic sources of European countries; the rest was the input from natural sources, re-emission and global anthropogenic sources.

The spatial distribution of mercury depositions over Europe is shown in Fig. 21. The highest deposition fluxes are observed in Central and Southern Europe in the countries with significant anthropogenic emissions and their neighbours. In these countries the annual mercury depositions can exceed 30 g/km²/y. The lowest depositions were in Scandinavia and in the northern part of Russia (lower than 5 g/km²/y).

Levels of mercury deposition vary from country to country appreciably. Fig. 22 illustrates the average mercury anthropogenic emissions and deposition fluxes in European countries in 2002. As was mentioned above the most significant depositions are in Central and Western European countries – Poland, Belgium, Germany, Slovakia, Check Republic, Hungary etc. – where average deposition levels exceed 15 g/km²/y. In most of these countries the average anthropogenic emission flux is 2-3 times higher. This means that the greater part of mercury emitted in these countries is transported across the boundaries. On the contrary, there are countries, such as the FYR of Macedonia, Croatia, Norway, Sweden etc., where the average deposition flux significantly exceeds that of national anthropogenic emission.

Contribution of the transboundary flux from external (European) anthropogenic sources to mercury deposition in European countries is illustrated in Fig. 23. More than half the total mercury deposition to such countries as Check Republic, Slovakia, the Netherlands, the FYR of Macedonia and Belarus was determined by external anthropogenic sources. This fact can be explained by the vicinity of these countries to significant emission sources in Poland and Germany. The lowest contribution of external sources was in countries located at the periphery of Europe: Ireland, Spain, Iceland etc. Deposition of mercury from external sources to the European Union did not exceed 7% of total value.
Roles of different European countries in the transboundary transport of mercury in Europe are illustrated in Fig. 24. The diagram shows amount of anthropogenic mercury emitted in a country, which was transported beyond the boundaries. As seen the largest contributors to the transboundary transport in Europe were Germany, Spain and Poland. Transport beyond the boundaries of these countries amounts to 23 t/y, 22 t/y and 18 t/y respectively. Besides, nine major countries-contributors determined more than 75% of mercury involved in the transboundary transport. The total transport from the European Union exceeds 85 t/y.

**2.2.2. National scale pollution**

The distribution of pollution levels over the territory of a country is highly non-uniform. This is caused mainly by the location of national and transboundary emission sources and complex pattern of geographical parameters such as precipitation, orography, land-cover etc. That is the reason that the averaged deposition to the country as a whole can significantly differ from depositions to its administrative units. In Section 2.2.1 information was presented for countries as a whole. This section deals with more detailed information for a specific country.
country, exemplified by lead pollution in Germany.

The average deposition flux of lead for the entire territory of Germany is about 1 kg/km²/y. However, in different lands the average deposition flux can vary from 0.7 (Bayern) to 2.4 (Berlin) kg/km²/y (Fig. 25).

The contribution of the transboundary transport to lead pollution in Germany is about 30%. However, a portion of depositions caused by national emissions, and transboundary pollution varies considerably from one Land to another (Fig. 26). Predominant sources of the transboundary transport are also different in different parts of the country. In the eastern part of the country contribution of national sources normally exceed those in the western part. It is consistent with the spatial distribution of emissions (Fig. 8) and the predominant western wind flows. The main external country-source is Poland, which contribution varies from 7% (Sachsen) to 13% (Mecklenburg-Vorpommern). In the western part the main country-source of transboundary pollution is Belgium, and its contribution is maximum in Nordrhein-Westfalen (19%). In the south a significant effect on lead depositions is made by Switzerland. For example, in Baden-Württemberg its contribution is 25%.

Fig. 26. Contributions of transboundary transport to depositions of lead in lands of Germany in 2002. RNG stands for re-emission, natural and global sources.
On the level of individual grid cells a spatial pattern of long-range transport contributions to depositions is much more inhomogeneous (Fig. 27). In the eastern part of Germany this contribution is the lowest and only in a few regions exceeds 40%. However, in the western and southern parts of the country the contribution can often exceed 60%.

In each region of the country it is possible to analyse the transboundary transport contribution not only from all European sources taken together, but also from individual countries. For example, the main contributor to transboundary depositions of lead in Germany is Belgium. Contributions to depositions from Belgium are the highest near the German-Belgium border, where they exceed 50% (Fig. 28). Even in the central part of Germany these contributions can reach 10%.

A brief review of variations in pollution levels within Germany is presented here as an example. Similar information about pollution on a grid cell level or a province level is also available for other countries and other metals.

2.2.3. Depositions to regional seas

Atmospheric loads to seas surrounding Europe are computed by MSC-E operationally. In 2002 the highest average deposition flux of lead was obtained for the Black and Azov Seas (Fig. 29). This is caused by atmospheric transport from the countries that are significant emission sources of lead such as Romania, Turkey, Russia and others (Fig. 8). The highest deposition flux of cadmium takes place in the Baltic Sea, but the difference in fluxes to other seas is not large. The most significant depositions of mercury occur over the North Sea, the lowest – over the Black and Azov Seas.

The spatial distribution of the contribution from anthropogenic emissions of lead and the total depositions of the main countries-sources are shown in Fig. 30. The highest contribution of anthropogenic sources is observed in the Baltic and Azov Seas. Normally the contribution there exceeds 70%. High contributions of these sources are also experienced in the Baltic, Aegean and

![Fig. 27. Contribution of external anthropogenic sources to depositions of lead in Germany in 2002](image1)

![Fig. 28. Contribution of external anthropogenic sources from Belgium to depositions of lead in Germany in 2002](image2)

![Fig. 29. Averaged deposition fluxes of lead, cadmium and mercury to regional seas in 2002](image3)

![Fig. 30. Spatial distribution of the contribution from anthropogenic emissions of lead and the total depositions of the main countries-sources in 2002](image4)
Adriatic Seas. Relatively low contributions were obtained for the northern part of the North Sea and the southwestern part of the Mediterranean Sea. This is caused by remoteness of the main anthropogenic sources. However, it should be noted that depositions from anthropogenic sources to the Mediterranean Sea are most likely underestimated because the anthropogenic emission sources in northern Africa and the Middle East were not taken into account.

For each sea the contribution of various emission sources to atmospheric depositions was assessed. It is obvious that the countries with high emissions, located close to the seas make the highest contributions to anthropogenic depositions. For example, the most significant contribution to the North Sea comes from the United Kingdom (28%) and Germany (16%). The main anthropogenic contributor to the Caspian Sea is Russia (46%), followed by Azerbaijan (22%) and Turkey (12%). Similar information is also available for cadmium and mercury.

![Figure 30](image)

**Fig. 30.** Contribution of anthropogenic input to total atmospheric depositions of lead in regional seas and contributions from main countries – sources

### 2.3. Evaluation of the regional model

Reliability of the modelling results is one of most important conditions of the pollution assessment. A comprehensive analysis of the MSC-E heavy metal model consistency will be reported at the EMEP Workshop on the model review to be held in 2005 in accordance with recommendation of the 5th TFMM (Prague, Czech Republic, April 2004). It will include the evaluation of the model parameterisation as well as estimation of the uncertainty of input information, the most important parameter of which are emission data. Besides, additional attention is to be paid to the analysis of measurement data as the most important criterion of the modelling results consistency. In this section some preliminary results of the regional model evaluation are presented.
2.3.1. Recalculations of national emission data

Emission data are one of the most important input parameters affecting accuracy of modelling heavy metal air pollution. This is of particular concern for lead and cadmium, which are transported in the composition of primary aerosol particles and characterized by a relatively short residence time in the atmosphere. Anthropogenic emissions of short-lived oxidized mercury forms are also very important for regional pollution by mercury in Europe.

Data on national anthropogenic emissions are submitted by the Parties to the Convention annually. Besides, due to the improvement of statistical data, emission factors, calculation methods etc., some countries recalculate national emissions for the previous years. This revision should improve the assessment of the pollution levels dynamics in Europe in the last decade. However, the uncertainty of emission estimates is still significant and results in the inaccuracy of the pollution assessment. A general idea on the emission data uncertainty could be obtained from the analysis of changes in national emission data for the previous years. The analysis of changes in the emission estimates for the period of 1990-2001 submitted this year by 13 countries is illustrated in Fig. 31. Each column of the diagrams shows the range between the maximum increase and maximum decrease of national emissions for all the countries for each year of the period. For example, the maximum increase of lead emissions in 1993 amounted to about 100%. It means that some European country increased national emissions of lead twice for this year (due to the recalculation only).

![Fig. 31. Maximum changes of lead (a), cadmium (b) and mercury (c) national emission estimates for the period 1990-2001](image)

The maximum changes in the national emission estimates during the whole period vary from 100% of increase to 15% of decrease for lead, from 10% of increase to 45% of decrease for cadmium and from 200% of increase to 40% of decrease for mercury (Fig. 31). These values can characterize to some extent the uncertainty of the anthropogenic emission flux in some parts of Europe. However, one should notice that these changes do not characterize the European anthropogenic emission as a whole. Therefore additional efforts to evaluate the uncertainty of the overall emission field in Europe are required.
2.3.2. Analysis of measurement data

Some aspects of quality of measurement data have already been discussed in chapter 1 of this report. Measurements with high uncertainty and low data capture were not used in the model verification. Stations not used for the model validation are summarised in Table 2.

Table 2. Information from monitoring stations, not used in the model validation

<table>
<thead>
<tr>
<th>Measurements</th>
<th>Station code</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, air</td>
<td>BE4</td>
<td>High uncertainty</td>
</tr>
<tr>
<td>Pb, precipitation</td>
<td>BE4, GB14</td>
<td>High uncertainty</td>
</tr>
<tr>
<td></td>
<td>EE11</td>
<td>Low data capture</td>
</tr>
<tr>
<td></td>
<td>EE9, PL5, IE1, IE2, PT1, PT3, PT4, PT10</td>
<td>Most of values below detection limit</td>
</tr>
<tr>
<td>Cd, air</td>
<td>BE4</td>
<td>High uncertainty</td>
</tr>
<tr>
<td>Cd, precipitation</td>
<td>BE4, GB14, GB90, GB91, PT1, PT3, PT4, PT10</td>
<td>High uncertainty</td>
</tr>
<tr>
<td></td>
<td>EE9</td>
<td>Low data capture</td>
</tr>
<tr>
<td></td>
<td>EE11, IE1, IE2, IS90, IS91, PL5</td>
<td>Most of values below detection limit</td>
</tr>
<tr>
<td>Hg, precipitation</td>
<td>IE1</td>
<td>Too high detection limit</td>
</tr>
</tbody>
</table>

In addition, the lead and cadmium concentrations in precipitation at station LT15 (Preila, Lithuania) are very high, and it is suspected that these data are influenced by contamination, either from local sources or in the laboratory. Measured concentrations in precipitation from this station were therefore not used in the validation.

Another station, which data seem very high, is SK2 (Chopok). The station is located at the altitude of about 2000 meters. Normally, at such high latitudes the air is expected to be relatively clean. However, concentrations of lead and cadmium in precipitation at this station are several times higher than those at other stations (Fig. 32). So far this station was used in the validation procedure.

![Fig. 32. Measured mean annual concentrations in precipitation of lead and cadmium in 2002](image)

At station DE2 (Langenbrüger) heavy metals are measured by both bulk and wet-only samplers. For lead the difference in the concentrations is not high. However, for cadmium the concentrations in precipitation are about three times higher in the bulk collector, which is probably due to influence of dry deposition. According to the EMEP Manual (1996) heavy metals in precipitation should be measured using a wet-only collector and this sampler is therefore the official EMEP data at DE2. This
dataset is therefore used for validation of the model. More details on this comparison is shown in the EMEP Quality Assurance report [Aas et al., 2004].

Precipitation amounts collected at monitoring stations require special consideration. The precipitation amounts are usually measured in the same collector as the heavy metals, bulk or wet-only sampler. At some sites the precipitation amount from the mercury collector is also measured. At sites where different collectors are used one can compare the precipitation amount. Annual sums of precipitation, collected by different methods, do not differ much (Fig. 33). Monthly sums of precipitation at some stations can also be consistent (Fig. 34a), but at other stations vary considerably (Fig. 34b). Since precipitation amount is crucial parameter for estimation of wet deposition flux, such high differences in monthly precipitation amounts at some stations introduce additional uncertainty in calculation of wet deposition fluxes. It is recommended to use an official rain gauge at all EMEP sites to control the precipitation amount [EMEP, 1996] and these data should be reported to CCC as well.

![Fig. 33. Annual sums of precipitation amounts, collected by different samples at EMEP monitoring stations](image)

![Fig. 34. Monthly sums of precipitation amounts, collected by different samples at station DE2 Langenbrüger (a) and SE5, Rörvik (b)](image)

Special attention was devoted to the comparison of precipitation amounts measured at the stations and used in the model. To make the interpretation of the comparison outcomes more reliable only stations, where modelled and observed precipitation amounts differed less than 1.5 times, were selected. Differences in precipitation amounts do not characterise the quality of measurement data as such or that of the model. However, in case of a large difference it would be difficult to explain either a good agreement or discrepancy between modelling results and measurement data. The stations left out by this reason are CZ1, CZ3, DE1, IS90, FI8, FI9, FI53, NO99, SK2, SK4, and SK6. Ultimately 28 stations measuring lead and 26 stations measuring cadmium in precipitation were used in the comparison.
2.3.3. Model evaluation against measurements

The most important part of the model review is the comparison of the model outcomes with the measurement data. In 2002 information on lead and cadmium concentrations in the air was submitted from 38 stations, in precipitation – from 51 stations. These include 25 stations measuring lead and cadmium in both in air and in precipitation. Following the criteria mentioned in 2.3.2 the model was compared with the measured Pb, Cd and Hg concentrations in air and precipitation.

**Lead and cadmium**

The comparison for all the stations measuring air concentrations of lead shows that the model underestimates observations almost twofold (Fig. 35a). Similar underestimation was obtained for concentrations in precipitation (Fig. 35b). The correlation coefficients were relatively high: about 0.9 for air and 0.6 for precipitation.

![Graph](image)

**Fig. 35. The comparison of modelled concentrations of lead against observations for 2002 in air (a); in precipitation (b)**

The comparison results for all the stations measuring cadmium similar to those measuring lead (Fig. 36a and b). Both concentrations in the air and in precipitation are underestimated by the model to nearly equal extent. Keeping in mind that the correlation coefficients are significant: 0.8 for air and 0.6 for precipitation, it is likely that the most probable reasons for the underestimation have to do with uncertainties of the emission data.

![Graph](image)

**Fig. 36. The comparison of modelled concentrations of cadmium against observations for 2002 in air (a); in precipitation (b)**
The significant correlation coefficients indicate that the model was able to capture a spatial pattern of the pollution levels. However, a twofold underestimation of concentrations in both the air and in precipitation implies that the mass of the pollutant in the air is insufficient. This can be caused by a number of reasons. Among those are uncertainties of the emission data, model parameterisations and quality of monitoring data. The forthcoming procedure of the model review including the revision of the model itself, revision of measurement data and emission data should explain the existing differences between the measurements and the model.

Since one of the possible reasons for the underestimation could be the underestimated emission data, a simple test was performed. According to this test the emission data were multiplied by a factor of 2. The aim was to obtain the sufficient mass of the pollutant in the atmosphere, so that regression slopes for both air and precipitation concentrations were equal to 1.

To analyse the results stations that measure concentrations in both the air and precipitation were selected. Ultimately 12 stations were selected. The regression slope for these stations is close to unity (Fig. 37a). The correlation coefficient is about 0.95. Similar slope was also obtained for concentrations in precipitation (Fig. 37b). The correlation coefficient for concentrations in precipitation is about 0.6.

![Graphs showing modelled vs observed concentrations for lead in air and precipitation.](image)

**Fig. 37.** The comparison of modelled concentrations of lead against observations for 2002 (doubled emission) in air (a); in precipitation (b)

This experiment demonstrates that the model adequately responds to the changes in emission data, and a significant increase of the emission data can sufficiently improve the model performance, at least for the set of selected stations. Nevertheless, other possible sources of discrepancies between the model and measurements should also be studied in the forthcoming procedure of the model review.

**Mercury**

The evaluation of mercury modelling results against measurements differs considerably from that of lead and cadmium due to the fact that a number of monitoring stations measuring this pollutant is much smaller. Among these only 10 sites measured mercury concentration in precipitation, 5 sites – gaseous mercury in the air, and 5 sites – mercury in aerosol. Besides, all of them are located in Northern and Western Europe (see Chapter 1, Fig. 1). Therefore, the comparison is limited in character. Wider coverage of mercury measurements is required. Another distinctive feature of mercury is that direct anthropogenic emissions in Europe determine mercury pollution levels not as significantly as in the case of lead and cadmium. This is due to more considerable contribution of the intercontinental transport and natural emission.
Fig. 38 illustrates the comparison of the modelled and measured total gaseous mercury concentrations in the ambient air. As seen both calculated and measured concentrations do not vary significantly and are in agreement within the limits of ±20%. In contrast to lead and cadmium, the model does not underestimate the observed concentrations noticeably. This fact can be explained by the appropriate consideration of natural emission and global sources (taken into account by the boundary conditions) rather than by more reliable anthropogenic emission estimates.

The comparison of the typical modelled and observed within-a-year variability of the total gaseous mercury concentration in the ambient air is illustrated in Fig. 39 for the monitoring site Råö (Sweden). As is seen mean monthly concentrations vary within the range of 1.4-2.1 ng/m$^3$ with the moderate correlation between calculated and measured values.

Monitoring of different mercury species is very important for the understanding of mercury behaviour in the atmosphere. Measurements of mercury concentration in aerosol became recently available at some EMEP monitoring sites. Fig. 40 shows the comparison of measured and calculated total particulate mercury concentrations. The concentration values vary in the range of 3-22 pg/m$^3$. At two sites (IS91 and NO99) the observed concentrations significantly exceed the modelled ones, for other sites the agreement is reasonable.

The analysis of mean monthly concentrations of the total particulate mercury at the sites, where the agreement between calculations and measurements is the worst (Storhofdi (IS91) and Lista (NO99)) is illustrated in Fig 41. As seen from Fig. 41a the model cannot reproduce the abnormally high observed concentrations in first months of the year. During the rest of the year the agreement between calculations and measurements is good. Similar situation is with the other site (Fig. 41b): The model outcomes agree with observations in all the months reasonably except the one when the measured mean monthly concentration was very high.
Modelling of wet deposition or concentration in precipitation of any pollutant depends to a large extent on the model precipitation amount. Input precipitation data supplied by the meteorological preprocessor are not always in the satisfactory agreement with the measurement data. Nevertheless, in the case of mercury we did not exclude the sites with significant discrepancies between measured and model precipitation amounts from the primary comparison because of the limited number of the measurements.

Fig. 42 shows measured vs. modelled precipitation amounts, mercury concentration in precipitation and wet deposition flux at all the available monitoring sites. As is seen at four sites (DE1, NO99, SE11, SE14) the model precipitation amounts considerably exceed the measured values (Fig. 42a). The significant underestimation of the observed concentration in precipitation by the model is characteristic of these sites (Fig. 42b). This fact could be easily understood if it is supposed that the total mass mercury was washed out from the air during rainfall events and the solution is diluted by extra precipitation. At other sites the modelled concentrations either agree with or slightly overestimate the measured ones. As a result the correlation between calculated and observed wet deposition fluxes is better (Fig. 42c).
The final comparison of modelled and observed mercury concentrations in precipitation and wet deposition flux at monitoring sites, where predicted and measured precipitation amounts do not differ more than 1.5 times (DE2, DE9, FI96, NL91 and SE5) is illustrated in Fig. 43. As is seen in both cases the correlation coefficients are significant but some overestimation is observed. One of the possible reasons for this is the underestimation of dry deposition of oxidized mercury forms, in particular, reactive gaseous mercury.

![Graphs showing modelled versus measured values of weighted mean annual mercury concentration in precipitation and wet deposition flux at selected monitoring sites.](image)

**Fig. 43. Modelled versus measured values of weighted mean annual mercury concentration in precipitation (a) and wet deposition flux (b) at selected monitoring sites**

### 2.3.4. Model development and sensitivity study

Main directions of the model development during the reporting year were the improvement of the model description of the atmospheric transport and enhancement of the wet deposition parameterisation.

To improve the atmospheric transport parameterisation a new vertical structure of the model domain was developed. It consists of 15 terrain-following layers (see Annex B) and allows taking into account the Earth surface orography. Higher vertical resolution makes it possible to more adequately describe the pollutant advective transport especially in the atmospheric boundary layer. The sensitivity analysis of the changes showed the significant improvement of the correlation of the calculated lead and cadmium concentrations in the ambient air with those obtained from measurements.

Wet removal of heavy metals from the atmosphere was enhanced by developing new parameterisations of precipitation scavenging. Both in-cloud and sub-cloud wet removal were modified on the basis of the up to date scientific literature data. The study of the model sensitivity to the wet deposition parameterisation showed that new scavenging parameters allow the disbalance of lead and cadmium concentrations in precipitation and in the ambient air characteristic of the previous version to be avoided. However, lead and cadmium concentrations both in the air and in precipitation are still underestimated. One of the possible reasons for this is the considerable underestimation of emissions of these metals.

General structure of low-resolution multi-compartment model of mercury circulation in the environment was formulated. Atmospheric part of the model was developed and tested. Analysis of available data on mercury cycling in the marine environment was performed for the development of the marine module.

More detailed information on the models development and sensitivity study is to be included in the comprehensive model description planned to be published for the model review.
2.3.5. Intercomparison of Hg models

MSC-E continues its activities in the framework of the mercury transport models intercomparison project. The final third stage of the project was started in 2004. It is devoted to the comparison of modelling results with annual and monthly mean measurements of mercury concentration in the ambient air and atmospheric deposition fluxes. Besides, deposition budgets for selected European countries (UK, Poland, Italy) predicted by different models are to be compared. The intercomparison involves seven models of mercury atmospheric transport and deposition at regional and global levels:

- GKSS-Forschungszentrum Geesthacht GmbH (Germany), the European mercury version of the Acid Deposition and Oxidants Model (ADOM).
- U.S. Environmental Protection Agency (USA), the Community Multi-Scale Air Quality (CMAQ) model.
- Environment Canada (Canada), Global/Regional Atmospheric Heavy Metals Model (GRAHM).
- National Ocean and Atmosphere Administration (USA), Hybrid Single Particle Lagrangian Integrated Trajectory model, version 4 (HYSPLIT_4)
- National Institute of Meteorology and Hydrology (Bulgaria), Eulerian Model for Air Pollution (EMAP)
- National Environmental Research Institute (Denmark), Danish Eulerian Hemispheric Model (DEHM)
- Meteorological Synthesizing Centre-East of EMEP, MSC-E Heavy Metal model (MSCE-HM).

Fig. 44 shows an example of the comparison of measured and calculated by different models concentration of total gaseous mercury (TGM) in the ambient air (a) and mercury concentration in precipitation (b) at the monitoring site Rörvik (Sweden) in February 1999. As seen all the models slightly overestimate air concentration of TGM (within 30% of magnitude). The maximum discrepancy of calculated concentrations in precipitation with regard to observations does not exceed a factor of two.

![Comparison of modelled and measured monthly mean air concentration of total gaseous mercury (a) and concentration in precipitation (b) at monitoring site Rörvik (Sweden) in February 1999](image)

Preliminary results of the third stage of the comparison are published in the Progress report [Ryaboshapko et al., 2004].
2.4. Application of the hemispheric modelling for the assessment of heavy metal pollution in new Parties to the Convention

Recently new countries joined the Convention on Long-Range Transboundary Air Pollution. Among them are the countries located mostly outside the traditional EMEP region such as Kazakhstan and Kyrgyzstan. The assessment of air pollution of these countries requires modification of the traditional regional approach to the atmospheric transport modelling – the extension of the EMEP domain or application of the hemispheric/global scale approach. In both cases the assessment needs supplementary input information and, in particular, additional emission data. Kazakhstan and Kyrgyzstan are located in Central Asia and have long boundaries with China, Asian part of Russia, Uzbekistan and Tajikistan. Emissions from these countries as well as the long-range transport from the whole Asian region can significantly affect pollution levels in Kazakhstan and Kyrgyzstan. Therefore data on anthropogenic and natural emissions in Asian region are necessary for the assessment of heavy metal pollution in these countries.

Pollution of Kazakhstan and Kyrgyzstan by mercury and lead has been initiative assessed by means of hemispheric modelling using the available global emission inventories of the considered heavy metals. The outcomes of the assessment are presented in this section.

**Mercury**

Anthropogenic emission of mercury to the atmosphere in the considered countries and in the Northern Hemisphere as a whole is assessed with the global emission inventory for 1995 [Pacyna et al., 2003]. According to these data the total anthropogenic emission of mercury in the Northern Hemisphere was about 1900 t/y, the emissions of mercury in Kazakhstan and Kyrgyzstan were 49 and 2.6 t/y respectively. Fig. 45 illustrates the spatial distribution pattern of anthropogenic emission of mercury in the Northern Hemisphere as well as in Kazakhstan and Kyrgyzstan. The highest density of emission sources of the Northern Hemisphere is in South-Eastern Asia, Europe, and the eastern part of North America (Fig. 45a). Emission fluxes in the countries of concern (Fig. 45b) are relatively low in comparison with those in European and Eastern Asian countries. Mercury emissions from natural sources were considered using the parameterisation developed in [Travnikov and Ryaboshapko, 2002].

![Fig. 45. Spatial distribution of mercury anthropogenic emission in the Northern Hemisphere (a) and in Kazakhstan and Kyrgyzstan (b) in 1995. Black line in the left figure delineates the EMEP region](image-url)
The calculated maps of the annual mercury deposition in the Northern Hemisphere and over the considered countries are shown in Fig. 46. A high transport ability of mercury enables it to be transported in the atmosphere over long distances. A significant part of mercury emitted in the polluted regions is deposited far from major emission sources (e.g. in the Central Pacific). On the other hand, national emissions of short-lived mercury forms are responsible for local depositions of this pollutant in a country. Thus, mercury contamination in Kazakhstan and Kyrgyzstan is caused both by national and by remote sources. The highest depositions of mercury in the considered countries are in the areas with intensive emissions located in Northern Kazakhstan near the border between these two states.

Fig. 46. Spatial distribution of annual mercury deposition in the Northern Hemisphere (a) and in Kazakhstan and Kyrgyzstan (b) in 1995

The contribution of different regions and countries of the Northern Hemisphere to mercury deposition to Kazakhstan and Kyrgyzstan is illustrated in Fig. 47. In the analysis Russia and China are separated from Europe and Asia as the most important neighbours of the considered countries. As seen from the diagram 47a the most significant depositions of mercury to Kazakhstan are from national sources (35% of the total). Russia contributes about 14% of the total deposition that is equal to the joint contribution of the rest of Europe and Asia. On the contrary, national sources contribute only 10% to the total mercury deposition to Kyrgyzstan (Fig. 47b). About one third of the total deposition is from Kazakhstan and 10% is from other Asian sources. In both cases about 20% is contributed by natural sources. The total annual deposition of mercury to Kazakhstan amounts to 28 t/y and to Kyrgyzstan - 2.9 t/y.

Fig. 47. Contribution of different regions and countries of the Northern Hemisphere to the total annual mercury deposition to Kazakhstan (a) and Kyrgyzstan (b) in 1995. The last column of the chart – contribution of the Southern Hemisphere
**Lead**

The assessment of lead contamination in Kazakhstan and Kyrgyzstan is based on the global lead emission inventory for 1990 [Pacyna et al., 1995], the only available dataset at the moment. Despite the fact that lead emissions have considerably changed worldwide in the last fourteen years, the outcomes of the assessment can illustrate the general character of the long-range lead pollution in the countries under consideration.

The spatial distribution of lead anthropogenic emissions in the Northern Hemisphere and particularly in Kazakhstan and Kyrgyzstan in 1990 is shown in Fig. 48. As is seen the major emission sources were located in Europe. Some significant emissions were also in Eastern Asia and in North America. The total anthropogenic emission of lead in the Northern Hemisphere was about 146 kt/y, the emissions of lead in Kazakhstan and Kyrgyzstan were 5.8 kt/y and 0.7 kt/y respectively.

![Fig. 48. Spatial distribution of lead anthropogenic emission in the Northern Hemisphere (a) and in Kazakhstan and Kyrgyzstan (b) in 1990](image)

Fig. 49 shows the calculated maps of the annual lead deposition both in the Northern Hemisphere and in the countries of concern (Fig. 49) in 1990. Lead is characterized by significantly lower ability to the long-range transport as compared with mercury and for the most part it determines regional pollution. As seen from Fig. 49a the most significant depositions of lead occurred in the regions with high emission intensity – Europe, Eastern Asia and North America, where deposition fluxes can exceed 10 kg/km²/y. Depositions in Kazakhstan and Kyrgyzstan were significantly lower and mostly did not exceed 3 kg/km²/y (Fig. 49b). Higher depositions were observed in the northern part of Kazakhstan because of the transboundary transport from the Russian Federation as well as near the boundary between Kazakhstan and Kyrgyzstan, where significant emission sources are located. The total deposition of lead to Kazakhstan and Kyrgyzstan amounted to 3.5 kt/y and 0.43 kt/y respectively.

The contribution of different regions and countries of the Northern Hemisphere to the total annual deposition of lead to Kazakhstan and Kyrgyzstan is shown in Fig. 50. National sources made the most significant contribution to lead deposition to Kazakhstan (38% of the total). Russia was the most important contributor among external sources. It contributed about 27% of the total deposition. The contributions of other European and Asian countries were 15% and 18% respectively. Depositions of lead over Kyrgyzstan were mostly determined by Asian sources (more than 70%). Among them the greatest contributor was Kazakhstan (40% of the total deposition). The contribution of the national Kyrgyz sources did not exceed 17%.
Fig. 49. Spatial distribution of annual lead deposition in the Northern Hemisphere (a) and in Kazakhstan and Kyrgyzstan (b) in 1990

Fig. 50. Contribution of different regions and countries of the Northern Hemisphere to the total annual lead deposition to Kazakhstan (a) and Kyrgyzstan (b) in 1990
3. CO-OPERATION

Investigations of the environmental pollution by heavy metals are carried out by the EMEP Centres in co-operation with subsidiary bodies to the Convention: the Working Group on Strategies and Review (WGSR) and the Working Group on Effects (WGE); with the World Meteorological Organization (WMO), the European Union (EU), Helsinki Commission (HELCOM) and with national programmes of the Parties to the Convention.

3.1. Working Group on Effects

MSC-E presented information on the progress of the EMEP activities with regard to the priorities of the effect community at the recent CCE workshop and the 20th meeting of the Task Force on Modelling and Mapping (Laxenburg, Austria, May 2004). The following issues were jointly discussed in depth: ecosystem-dependent depositions, speciation of mercury depositions, mercury concentrations in precipitation. It was assumed that deposited metals exist in geochemically reactive forms. Special attention at the meeting was devoted to the land-cover data. It was agreed that the land-use data would be based on CORINE database. In the areas of the EMEP region that are not covered by CORINE, SEI database will be used. It was also stressed at the workshop that the model evaluation of historical and future (scenario) depositions of lead, cadmium and mercury were of a great importance for the dynamic modelling of the heavy metal behavior in soil.

In the framework of cooperation with the WGE MSC-E operationally calculates relevant parameters of atmospheric inputs to ecosystems. One of the most important types of information is ecosystem-dependent atmospheric depositions. The method to estimate critical load is based on the balance of a metal in soil. Atmospheric deposition is one of the important components of this balance. For each ecosystem critical load is calculated separately. Atmospheric deposition, in its turn, also depends on the characteristics of the underlying surface. For example, dry deposition to the areas covered by forests can be significantly larger than that to grasslands or arable lands. That is why it is necessary to differentiate deposition fluxes between land-cover categories (ecosystems). It is especially true for the areas with relatively low precipitation amounts.

To confirm this idea two examples are given in Figs. 51a and 51b: ecosystem–dependent depositions of lead in South Norway and in Central Spain in 2002. Depositions are split in wet and dry. Wet deposition fluxes are assumed to be the same for different categories of ecosystems. Annual precipitation amounts in these regions are about 1400 (Norway) and 510 (Spain) mm.

In Norwegian region dry deposition to forests is higher than that to arable lands. However, due to the large amount of precipitation, wet deposition prevails and total deposition (sum of wet and dry) does not differ much between forests and arable lands.

In Spain the situation is opposite. Dry deposition to forests is higher than that to arable lands as much as 4.5 times. Moreover, unlike Norway, at this station dry deposition to forests significantly higher than wet deposition. The total depositions fluxes to arable lands and to forests also differ almost twofold. Similar effects are also observed for cadmium and mercury.
Variable geographical conditions and distribution of emission source causes highly uneven distribution of ecosystem-specific deposition patterns across Europe. From the viewpoint of the adverse effects it appears that the most interesting ecosystems are forests, arable lands, grasslands, and freshwaters. In Fig. 52 depositions of cadmium to forests and to arable lands are exemplified. As seen, in areas where there are both forests and arable lands, deposition fluxes to forests are substantially higher than to arable lands.

Similar information is also available for lead and mercury, and not only for forests and arable lands, but also for other land-cover categories. This information is presented on the Internet [www.msceast.org].
3.2. Working Group on Strategies and Review

3.2.1. Progress in heavy metal assessment activity

Progress in the EMEP activities on emission inventories, monitoring and modelling of heavy metals was reported jointly by MSC-E and CCC at the second meeting of the Expert Group on Heavy Metals (Brussels, Belgium, April 2004). Particularly it was noticed that approximately two thirds of the Parties to the Convention currently reported national annual emissions of cadmium, lead and mercury; expert estimates were used for others. The monitoring network for heavy metals covers Northern and Central Europe only. To improve the spatial coverage of the European territory by monitoring sites the EMEP monitoring strategy for 2004-2009 has been developed. MSC-E has assessed country-specific deposition balances. EMEP is ready to provide national and area-related heavy metals atmospheric export and import maps.

3.2.2. Second priority heavy metals

To support the Working Group on Strategies and Review in its preparatory work for the review of the Protocol on Heavy Metals, in particular the work of the Expert Group on Heavy Metals, MSC-E continues preparatory activities for the modelling of the second priority heavy metals (As, Cr, Ni, Zn, Cu). Emission and monitoring data for these pollutants were collected; information on physical and chemical properties of these pollutants was prepared.

Emissions

National data on emissions of the second priority heavy metals at least for one year of the period 1990-2002 were submitted by 31 countries. For the aims of modelling it is possible to fill in the gaps in the emission data by expert estimates from [Berdowski et al., 1997]. An example of the resulting maps of anthropogenic emission of arsenic and nickel is shown in Fig. 53. As is seen the spatial distributions of emission of these two pollutants differ from each other significantly. However, the most significant hot spots in such countries as Poland, Germany, Spain, Russia, etc. coincide in both cases.

![Fig. 53. Spatial distribution of arsenic (a) and nickel (b) anthropogenic emission in Europe in 2002](image-url)
**Monitoring data**

Most of the sites measuring Pb and Cd also measure the second priority metals. In Figs. 54-58 the annual concentrations in precipitation are shown. The general distribution pattern is similar for most of heavy metals with increasing concentrations in south and east. But there are some sites with very high concentrations, may be due to the local influence or contamination. Especially for zinc which is very easy to contaminate both in field and laboratory.

![Maps showing annual weighted mean concentration of metals](image)

**Physical and chemical properties**

Modelling of the atmospheric transport of any of the substances requires knowledge of atmospheric properties and behaviour of this substance. Similar to lead and cadmium, the second priority metals (Zn, Ni, Cr, As and Cu) are particulate species. Some fraction of atmospheric arsenic might present in a gaseous phase in the atmosphere, but this fraction is likely not high [Matschullat, 2000]. Transport and scavenging of these metals from the atmosphere are determined by the properties of particles-carriers. The main characteristic of a particle determining its scavenging parameters is its size (or spectrum of sizes). On the basis of literature data it is possible to conclude that Ni, Cr, Zn and As for the most part are concentrated on particles with a size of about 1 μm. In case of copper, various literature sources give different mass median diameters, ranging from 1 to about 1.8 μm. The spectrum of the particles is normally characterised by several maximums. At least 50% of the
The atmospheric mass of these metals, except for copper, is bound to particles below 2.5 μm. For copper this fraction is 30%.

For the evaluation of the atmospheric budget of heavy metals for the EMEP countries information on background levels is highly important. Concentrations of Ni, Cr, As, Cu and Zn in remote regions of the Earth have been summarised on the basis of available literature data. The ranges of concentrations are given in Table 3. As seen from the table variations of background concentrations can be as high as two orders of magnitude. The highest variation of background concentrations is found for arsenic (see Table 3), the lowest – for chromium. Median values can be used as boundary concentrations in future modelling of atmospheric transport and depositions of these metals.

Table 3. Range and median value of concentrations of second priority metals measured in background locations

<table>
<thead>
<tr>
<th>Metal</th>
<th>Range, ng/m$^3$</th>
<th>Median, ng/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.17 – 11</td>
<td>1.6</td>
</tr>
<tr>
<td>Zn</td>
<td>0.6 – 43</td>
<td>4.3</td>
</tr>
<tr>
<td>Cu</td>
<td>0.04 – 3.9</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr</td>
<td>0.06 – 3.5</td>
<td>0.8</td>
</tr>
<tr>
<td>As</td>
<td>0.02 – 3.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3.3. Helsinki Commission

In the framework of co-operation between EMEP Centres and Helsinki Commission MSC-E continues its work on the evaluation of airborne pollution load of selected heavy metals to the Baltic Sea. Information on the atmospheric transport and depositions of lead, cadmium, and mercury to the Baltic Sea and its catchment area for 2001 has been prepared. The results are published in the EMEP Centres’ joint report for HELCOM [Bartnicki et al., 2004].

MSC-E has also contributed to the Forth HELCOM Pollution Load Compilation Report (PLC-4). The report is to summarize the results of the assessment of the Baltic Sea airborne pollution by lead, cadmium, and mercury in the period of 1996-2000 [Bartnicki et al., 2002].

Another important HELCOM activity on the assessment of the Baltic Sea pollution is the preparation of annually updated environmental indicator reports. MSC-E has contributed to two annual indicator reports on temporal variations of heavy metals emissions and depositions to the Baltic Sea and its sub-basins. The reports are available at the web site of Helsinki Commission (www.helcom.fi).

Annual emissions of heavy metals from the anthropogenic sources of HELCOM countries significantly decreased during the period of 1990-2001. In particular, annual emissions of cadmium decreased by 45%, whereas lead and mercury emissions reduced by 60%. Following this reduction and also due to the changes of heavy metals emissions in other European countries the level of atmospheric depositions to the Baltic Sea has also significantly decreased (Fig. 59). Compared to 1990 atmospheric depositions to the Baltic Sea in 2001 are lower by 70% for lead, by 40% for mercury, and by 30% for cadmium.

Fig. 59. Decrease of cadmium, mercury, and lead depositions to the Baltic Sea in 1990-2001
The highest depositions of heavy metals over the Baltic Sea can be noted in the south-western part of the Baltic Sea within the Belt Sea and the Baltic Proper sub-basins (Fig. 60). Significant levels of lead and cadmium depositions can also be noted in the Gulf of Riga. The total contribution of HELCOM countries to the heavy metals deposition over the Baltic Sea in 2001 amounts to 40%.

On the request of the Contracting Parties to HELCOM MSC-E has additionally included to the indicator reports the information on fractions of the HELCOM countries’ national emissions of lead, cadmium and mercury deposited to the Baltic Sea (Fig. 61).

MSC-E in 2004 participated in the EU EMECAP project (QLK4-CT-2000-00489). The project is focused on the combined epidemiological and environmental studies of human health risks from mercury emissions of Mercury Cell Chlor-Alkali (MCCA) plants. In the framework of the project MSC-E assessed the effect of mercury emissions from chlor-alkali plants in Europe on the levels of air concentration and atmospheric deposition of this pollutant on a regional (European) scale.

Mercury emissions from chlor-alkali plants estimated under the project are shown in Fig. 62. It should be noted that in some countries (Ukraine, Bulgaria, Slovenia, Austria etc.) emissions from this sector are treated as area sources and distributed according to the population density due to the lack of more detailed information. According to the estimates the total annual emission of mercury from chlor-
alkali production in Europe in 2000 amounted to 15 tonnes (about 7% of the total emission of mercury in Europe).

The contribution of chlor-alkali industry to mercury deposition in Europe is illustrated in Fig. 63. The long-range atmospheric transport of mercury from these emission sources leads to the increase of mercury depositions in the background regions by 0.1-0.2 g/km$^2$/y (5-7% of the total deposition). In the industrial regions of Western Europe the relative contribution can be lower because of a significant influence of other emission sources. However, in the areas contiguous with chlor-alkali plants the contribution of this industrial sector can exceed 10 g/km$^2$/y (50% of the total deposition).

MSC-E also takes part in the EU ESPREME project (SSPI-CT-2003-502527) launched in 2004. The project aims to develop methods and tools to support European environmental policy making in the specific case of reducing the harmful impacts of heavy metals in a harmonised way across Europe. The role of MSC-E in the project is to assess by means of its chemical transport models the atmospheric dispersion of selected heavy metals (Hg, Pb, Cd, As, Ni and Cr) and their deposition to water and soil.

### 3.5. National programmes

MSC-E continues co-operation with national experts under the multi-stage project on the mercury transport models intercomparison. Models of long-range atmospheric transport of mercury developed by different scientific groups from Germany, the USA, Canada, Bulgaria, Denmark and MSC-E participate in the project. In 2004 the third stage of the project was started – it is devoted to the comparison of the long-term modelling results with annual and monthly mean measurements of mercury concentration in the ambient air and atmospheric deposition fluxes. A special issue of this stage is the comparison of mass balances of mercury export-import for selected European countries (Poland, Italy and the United Kingdom) calculated by different models.

Preliminary results of the third stage of the comparison are analyzed and presented in the Progress report [Ryaboshapko et al., 2004]. The outcomes of the previous stages were reported at the 7th International Conference on Mercury as a Global Pollutant (Lubljava, Slovenia, June-July 2004).
CONCLUSIONS

The EMEP Centres’ activities in the field of monitoring and modelling of heavy metals in 2004 were aimed at investigation of the pollution of the European region and the Northern Hemisphere as a whole. Besides, particular attention was paid to validation of the MSC-E heavy metal model and support of Working Group on Strategies and Review in its preparatory work for the review of the Protocol on Heavy Metals. The main conclusions of the studies are formulated below.

Monitoring of heavy metals

1. Measurements of heavy metal pollution levels in 2002 showed that the lowest concentrations of lead, cadmium and mercury were observed in Northern Scandinavia. In general concentration levels increase towards the southeast of Europe.

2. At present the EMEP monitoring network contains 66 stations measuring lead and cadmium, of which 25 stations measure concentrations of these metals both in air and precipitation. There are 13 stations where at least one mercury form is measured. The monitoring stations, however, are non-uniformly distributed over European territory: they are mainly located in Central and Northern Europe.

3. Annual analytical intercomparisons of national laboratories processing measurements of heavy metals indicate a substantial improvement of data quality during the period of 1995-2002.

Model assessment of pollution levels

1. According to the national data on heavy metal emissions and expert estimates anthropogenic emissions of lead, cadmium and mercury in 2002 were reduced by 11%, 5% and 11% in comparison with 2001. The most significant emissions of these heavy metals are located in Western, Central and Southern Europe.

2. The spatial distribution of environmental pollution levels of heavy metals is highly non-uniform. The deposition intensity in different parts of Europe can differ by more than an order of magnitude. High deposition levels are characteristic of Central and Southern Europe, the lowest levels – of Northern Europe.

3. The transboundary transport plays an important role in pollution of most of European countries. Contribution of the external European anthropogenic sources to depositions ranges from 5 to 85% for lead, 4 – 75% for Cd and 3 – 60% for Hg. The highest contribution is characteristic of the countries with insignificant national emissions and of those bordering powerful emission sources. The contribution of the transboundary transport to depositions of heavy metals to the European Union varies from 7 to 15%.

4. The most significant contributors of heavy metals to the atmospheric transboundary transport in Europe are countries with the largest national anthropogenic emissions. The bulk of heavy metals (75%) involved in the transboundary transport is emitted only by 10, 9 and 9 European countries for lead, cadmium and mercury respectively.
5. Pollution levels vary greatly within a country. For example, annual deposition of lead can differ 3.5 times in different Lands of Germany. Besides, the contribution of the transboundary transport to lead deposition to different Lands varies from 14 to 46%.

6. Atmospheric depositions contribute significantly to heavy metal pollution of marginal seas. The highest mean deposition flux of lead is observed over the Black Sea, of cadmium – over the Baltic Sea, and of mercury – over the North Sea.

7. Hemispheric modeling was initiatively applied to the assessment of heavy metal pollution of the new Parties to the Convention – Kazakhstan and Kyrgyzstan. Levels of mercury and lead depositions in these countries were analyzed. It was obtained that about 65% of mercury and 62% of lead depositions to Kazakhstan are determined by external anthropogenic and natural sources. For Kyrgyzstan the contribution of external sources is even larger – 90% for mercury and 83% for lead.

Model evaluation

1. The MSC-E regional transport model used for the assessment of the pollution levels in Europe was evaluated against the available measurement data and through the comparison with other models. The evaluation demonstrates a significant correlation of calculations with measurements. However, the underestimation of the observed concentrations of lead and cadmium both in the air and in precipitation is noted. Besides, the model slightly overestimates the observed values of mercury deposition with precipitation.

2. The activities under the multi-stage project on the intercomparison of mercury transport models are continued. The third stage of the project dedicated to the comparison of long-term modelling results with annual and monthly mean measurements of mercury concentration in the ambient air and atmospheric deposition fluxes is under way.

Co-operation

1. In the framework of cooperation with the Working Group on Effects MSC-E operationally calculates relevant parameters of atmospheric inputs to ecosystems. Ecosystem-specific depositions of heavy metals in Europe were assessed and analyzed.

2. To support the Working Group on Strategies and Review in its preparatory work for the review of the Protocol on Heavy Metals, in particular the work of the Expert Group on Heavy Metals, MSC-E continues preparatory activities for the modelling of heavy metals of the second priority. Emission and monitoring data for these pollutants were collected; information on physical and chemical properties of these pollutants was prepared.

3. The EMEP Centres were also involved in cooperation with other international organizations and national programmes (AMAP, EU, HELCOM, OSPAR, WMO).
REFERENCES


EMEP WORK-PLAN FOR 2004

Description/objectives

Provide monitoring and modelling data on concentrations, depositions and transboundary fluxes of cadmium (Cd), lead (Pb) and mercury (Hg). Develop further the Pb, Cd and Hg transport models in parallel with the development of heavy metal critical limits under the Working Group on Effects. Develop reliable emission data for Cd, Pb and Hg, as well as a preliminary data set for other metals. Support preparatory work for the review of the Protocol on Heavy Metals, in particular the work of the Expert Group on Heavy Metals.

Main activities and time schedule

(a) MSC-E will prepare information for 2002 for Pb, Cd and Hg on: deposition and air concentrations fields in Europe with a resolution of 50 km x 50 km; country-to-country deposition matrices; and deposition to the regional seas. It will compare model results for concentrations in air and precipitation and deposition fluxes with measurements, and study model sensitivity and uncertainty. It will, furthermore, present estimates for Hg atmospheric transport on a hemispheric scale and, in cooperation with CCE, critical load exceedance maps for Pb and Cd. In cooperation with CCC, it will prepare a report on new model developments and model evaluation for discussion by the Task Force on Measurements and Modelling at its fifth meeting in April 2004 and present a status report to the Steering Body at its twenty-eighth session;

(b) MSC-E will further develop its models and its input databases. It will, in particular, improve the parameterization of ocean and soil modules for the hemispheric multicompartment modelling of Hg transport. It will also initiate work for the modelling of other metals (arsenic, copper, chromium, nickel, selenium and zinc). Work on data will include: meteorological data (including sea currents and ice dynamics) and, together with CCC, emission data (including on gridded and natural emissions) and measurement data (including concentrations in different media);

(c) MSC-E will continue the Hg model intercomparison study. At stage III, the modelled annual and monthly mean concentrations will be compared with measurements. At stage IV export-import balances for Italy, Poland and the United Kingdom will be compared. A fifth expert meeting will be organized in Moscow;

(d) In cooperation with Parties, CCC will enhance the establishment of new sites to meet the requirements of the draft monitoring strategy. Together with MSC-E, it will complement EMEP data with data from other international programmes. CCC will report on the intercomparison for analytical techniques for seven heavy metals measured in precipitation.
**MSC-E activity in the field of heavy metals**

<table>
<thead>
<tr>
<th>Activity</th>
<th>Results</th>
</tr>
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</table>
| Modelling the transport of heavy metals    | Fields of deposition and air concentrations of Cd, Pb and Hg are calculated with spatial resolution 50x50 km for 2002  
|                                             | Transboundary fluxes of Cd, Pb and Hg between European countries and fluxes to regional seas are specified.                                                                                             |
|                                             | Deposition fluxes of Cd, Pb and Hg to different surface types are computed for the assessment of critical load exceedance in different ecosystems.                                                       |
|                                             | Hg airborne transport within the Northern Hemisphere is studied. The contribution of Hg intercontinental transport to the pollution of Europe is estimated.                                                    |
| Model evaluation                            | Calculated concentrations of Cd, Pb and Hg in the surface air and precipitation are evaluated against available measurements.                                                                             |
|                                             | Sensitivity                                                                                                                                |
|                                             | The intercomparison of Hg transport models is continued. The final third stage of the comparison is in progress. Preliminary results of the stage are presented in the progress report. |
|                                             | Plan for the MSC-E models review was elaborated and discussed at the Task Force on Measurements and Modelling at its fifth meeting in April 2004.                                                     |
| Development of model approaches             | The advection scheme of the regional model is improved to take into account the surface orography. Terrain-following vertical structure of the model domain with higher resolution was incorporated |
|                                             | Wet removal of heavy metals from the atmosphere was enhanced by developing new parameterisations of precipitation scavenging. Both in-cloud and sub-cloud wet removal were modified on the basis of the up to date scientific literature data |
|                                             | General structure of low-resolution multi-compartment model of mercury circulation in the environment was formulated                             |
| Preparation of data for modelling          | Data on Cd, Pb and Hg anthropogenic emission are prepared on the basis of the submitted official data and expert estimates.                                                                           |
|                                             | Meteorological data (sea currents and ice dynamics)                                                                                         |
DESCRIPTION OF MSC-E ATMOSPHERIC TRANSPORT MODELS

Model assessment of heavy metal pollution of the environment was performed by means of regional (MSCE-HM) and hemispheric (MSCE-Hg-Hem) models developed in MSC-E. Short description of the models is presented below.

Model domains

Both MSCE-HM and MSCE-Hg-Hem are three-dimensional models of Eulerian type. The regional model operates within the EMEP region (Fig. B.1). The EMEP region covers the area from approximately 35°W to 60°E and from the North Pole to about 20°N, and includes Europe, the northern part of Africa, a part of Middle East, the North Atlantic and a part of the Arctic. The MSCE-HM model grid has spatial resolution 50 km × 50 km at 60°N (135x111 gridcells). The model vertical structure consists of fifteen irregular terrain-following layers (Fig. B.2) and covers the entire troposphere (up to 16 km altitude). The hemispheric model domain covers the whole Northern Hemisphere with resolution 2.5°×2.5° (Fig. B.1). Along the vertical it consists of eight terrain-following layers up to the lower stratosphere.

Main processes

Both models consider emissions of heavy metals from anthropogenic and natural sources, transport in the atmosphere and deposition to the underlying surface (Fig. B.3). It is assumed that lead and cadmium are transported in the atmosphere only as a part of aerosol particles. Besides, chemical transformations of these metals do not change removal properties of their particles-carriers. On the contrary, mercury enters the atmosphere in different physical and chemical forms and undergoes numerous transformations during its pathway in the atmosphere.

Fig. B.1. Horizontal structure of the regional and hemispheric model domains. Red line depicts the EMEP region

Fig. B.2. Vertical grid structure of the regional model domain

Fig. B.3. The model scheme of heavy metal behaviour in the atmosphere
**Atmospheric transport**

The transport of heavy metals in the atmosphere is described by means of monotone version of Bott's advection scheme in both models. Pressure based $\sigma$-coordinate in the vertical makes possible to take into account an effect of the underlying surface elevation. Vertical eddy diffusion is described in the models to consider air mass mixing in the atmospheric boundary layer.

**Mercury transformation scheme**

Both models apply the same chemical scheme of mercury transformations. It is assumed that mercury occurs in the atmosphere in two gaseous forms – gaseous elemental Hg$^0$, gaseous oxidized Hg(II); particulate oxidized Hg$_{part}$, and four aqueous forms – elemental dissolved Hg$^0_{dis}$, mercury ion Hg$^{2+}$, sulphite complex Hg(SO$_3$)$_2^{2-}$, and aggregate chloride complexes Hg$_n$Cl$_m$. Physical and chemical transformations include dissolution of Hg$^0$ in cloud droplets, gas-phase and aqueous-phase oxidation by ozone and chlorine, aqueous-phase formation of chloride complexes, reactions of Hg$^{2+}$ reduction through the decomposition of sulphite complex, and adsorption by soot particles in droplet water.

**Removal processes**

Heavy metals are removed from the atmosphere by means of surface uptake and precipitation scavenging. Ecosystem-specific dry deposition scheme is based on the resistance analogy approach and distinguishes 16 land use types. Wet removal by precipitation considers both in-cloud and sub-cloud scavenging.

**Model development**

The following modifications of the models have been conducted this year:

- The advection scheme of the regional model is improved to take into account the surface orography. Terrain-following vertical structure of the model domain with higher resolution was incorporated
- Wet removal of heavy metals from the atmosphere was enhanced by developing new parameterisations of precipitation scavenging. Both in-cloud and sub-cloud wet removal were modified on the basis of the up to date scientific literature data
- General structure of low-resolution multi-compartment model of mercury circulation in the environment was formulated. Atmospheric part of the model was developed and tested.

More detailed information on the model development and sensitivity study is to be included in the comprehensive model description planed to be published for the model review.