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Heavy metals:

transboundary pollution of the environment

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EXECUTIVE SUMMARY

In accordance with the EMEP work-plan for 2003 [ECE/EB.AIR/77/Add.2] Meteorological Synthesizing Centre-East (MSC-E) and Chemical Co-ordinating Centre (CCC) proceed with investigations the environmental pollution by heavy metals (HM). The main objective of the work is the assessment of lead, cadmium and mercury pollution levels in Europe made on the basis of measurement data obtained at the EMEP monitoring network and modelling results.

National data on anthropogenic emissions of lead, cadmium and mercury for 1990–2001 were submitted to the UN ECE Secretariat by 34 countries. For the remained countries expert estimates were used in calculations. In the majority of European countries emissions of heavy metals tend to decline in the period of 1990–2001. The total emission in Europe has reduced approximately 3.3 times, cadmium – 1.8 times and mercury – 2 times.

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 contains 65 stations measuring lead and cadmium, of which 22 stations measure concentrations of these metals both in air and precipitation. There are 15 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.

Measurements of heavy metal pollution levels in 2001 show that the lowest concentrations of lead, cadmium and mercury are observed in northern Scandinavia. In general concentration levels increase towards the southeast of Europe. The analysis of available long-term measurements demonstrates an essential decrease of concentration levels of lead and cadmium during 1989-2001. Annual analytical intercomparisons of national laboratories treating measurements of heavy metals indicate an essential improvement of data quality during the period of 1995-2002.

Model estimates of the environment pollution by heavy metals were made by the regional and hemispherical models developed in MSC-E. According to the modelling results the emission reduction resulted in the decrease of heavy metal depositions over the major part of European territory. On the whole in the period from 1990 to 2001 lead deposition in Europe decreased 2.7 times, cadmium and mercury – 1.5 times. Less essential decrease of depositions in comparison with the anthropogenic emission reduction is conditioned by the contribution of natural sources, re-emission as well as by global sources of heavy metals.

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.

Non-uniform emission reduction of heavy metals in different European countries brings about strengthening the role of the transboundary transport in countries where the reduction rate is most essential. The highest absolute values of the transboundary transport are estimated for countries with large territories and for countries bordering powerful emission sources. In countries with insignificant national emission relative contribution of the transboundary transport to deposition of lead can exceed 70% of the total value, cadmium – 50% and mercury – 40%.

Mercury is a pollutant capable to global transport. The contribution of the intercontinental transport to mercury depositions over Europe is about 40% of the total value. Asian sources and mercury emission from the ocean surface play the most important role.

About half the mercury deposition to such a remote region as the Arctic is due to the transport from anthropogenic emission sources, of which the greatest contribution make European and Asian sources. A special role in the contamination of the Arctic region plays the phenomenon of mercury depletion events, which are responsible for up to 50% of total deposition in the coastal regions of the Arctic Ocean.

In accordance with the “EMEP strategy for 2000-2009” (EB.AIR/GE.1/2000/5) MSC-E has started the preparatory work of evaluation of the environment pollution by heavy metals of the second priority. Pilot calculations of nickel and zinc transport were performed. The computation results were presented at the meeting of the Expert group

on heavy metals (Working Group on Strategy and Review).

This year MSC-E proceeds with the assessment of atmospheric pollution loads on different ecosystems in Europe. The obtained results are meant for the Working Group on Effects for the development of critical loads approach.

The activity within the framework of the multi-stage project on the comparison of mercury transport models is also continued. The second stage of the project dedicated to the comparison of modelling results with short-term measurements of mercury in the atmosphere is finished.

The activity of the EMEP Centres was carried out in co-operation with national experts, international organizations and programmes (AMAP, HELCOM, OSPAR, UNEP, WMO, UN ECE/WGEM). The main results were discussed at a number of scientific conferences, workshops and expert meetings.

CONTENTS

INTRODUCTION

In the environmental community the notation of heavy metals implies stable high-density metals (lead, cadmium, mercury, copper, nickel etc.) and some metalloids (e.g. arsenic). These elements are natural constituents of the Earth's crust. As a result of anthropogenic activity the input of heavy metal to the environment has increased sufficiently and resulted in the increase of their content in air, water, soil and tissues of living organisms.

Heavy metals are chemical elements capable of spreading in the environmental compartments and circulating between them. Indeed, heavy metals emitted to the atmosphere in the composition of fine particles or in the gaseous form are transported by atmospheric fluxes at considerable distances and enter ecosystems of remote regions.

The majority of heavy metals and their compounds possess pronounced properties of toxicants. Entering living organisms during a long period of time by means of inhalation, ingestion and absorption through the skin heavy metals accumulate there and adversely affect vital functions (metabolism, reproductivity etc.). Besides, the accumulation is intensified due to biomagnification, when heavy metals content in living organisms increases as they move up the food chain.

Prevention of the environment pollution by heavy metals is a topical problem various aspects of which are studied in different international organizations. In the framework of the Convention on Long-Range Transboundary Air Pollution the Protocol on Heavy Metals was signed in 1998 (hereinafter the Convention). It is aimed at the control of atmospheric emissions of heavy metals. According to the Protocol lead, cadmium and mercury are metals of the first priority. Apart from that the Governing Council of the United Nations Environment Programme (UNEP) at its 22nd Session (February 2003) adopted the Programme of International Actions on restriction of negative impact of mercury on the environment and human health. Besides, the problem of the environment pollution by heavy metals is one of the priorities for international organizations and programmes investigating pollution of such regions as the Arctic (AMAP[1]) and marginal seas (HELCOM[2], OSPAR[3]).

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 these substances in European region. Measurements of heavy metal concentrations in air and precipitation are carried out at the EMEP monitoring network under the methodological guidance of Chemical Co-ordinating Centre (CCC). Alongside this Meteorological Synthesizing Centre – East (MSC-E) performs the model assessment of depositions and air concentrations of heavy metals throughout European region as well as the transboundary fluxes between the European countries.

The Status Report describes the progress in the study of air pollution by lead, cadmium and mercury both in Europe and in the Northern Hemisphere as a whole (mercury only). The presented results were obtained in studies made by CCC and MSC-E in 2003 according to the EMEP work-plan on heavy metals (Annex A). More detailed information about CCC and MSC-E activities can be found in EMEP Technical Reports [*Ilyin and Travnikov*, 2003; *Aas and Hjellbrekke*, 2003] and at EMEP website (www.emep.int).

Chapter 1 of the Status report describes monitoring of heavy metals within EMEP. Short characteristics of the measurement network are presented, results of heavy metal measurements in air and precipitation in Europe in 2001 are discussed, and trends of measured concentrations in the period of 1989 - 2001 are analyzed. Besides, the quality of measuring data is briefly outlined.

Chapter 2 is devoted to the model assessment of atmospheric pollution by heavy metals. Modelling results of heavy metals dispersion in the atmosphere and their deposition to the ground are considered. The main attention is given to the pollution of European region. Deposition levels and air concentrations of heavy metals in different parts

[1] Arctic Monitoring and Assessment Programme (www.amap.no)
[2] Baltic Marine Environment Protection Commission (www.helcom.fi)
[3] Commission for the Protection of the Marine Environment of the North-East Atlantic (www.ospar.org)

of Europe in 2001 as well as the transboundary fluxes between European countries are discussed; changes in the levels of pollution within the period of 1990 – 2001 are also analyzed. Special attention is given to the comparison of modelling results with measurement data. Apart from that, the distribution of such a global pollutant as mercury is considered within the whole Northern Hemisphere. The contribution of intercontinental transport of mercury to the pollution of Europe is evaluated as well as the influence of the European sources on the pollution of remote regions such as the Arctic.

The Report contains preliminary results of the assessment of pollution levels in Europe by some second priority heavy metals (nickel, chromium). These results were presented for the consideration to the Expert Group on Heavy Metals (Working Group on Strategies and Review). Heavy metals deposition to different surface types (forests, arable lands etc.) is considered. This information is meant for the Working Group on Effects for development of critical load approach. Besides, there is also a review of the results of co-operation with other bodies to the Convention, international organizations and national experts.

The Conclusions give the summary of the EMEP Centres' activities in the field of studies of environmental pollution by heavy metals and outline the perspective directions of further research.

1. MONITORING OF HEAVY METALS

1.1. Measurement network

Heavy metals were included in EMEP's monitoring program in 1999. However, earlier data have 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 AMAP, HELCOM and OSPAR.

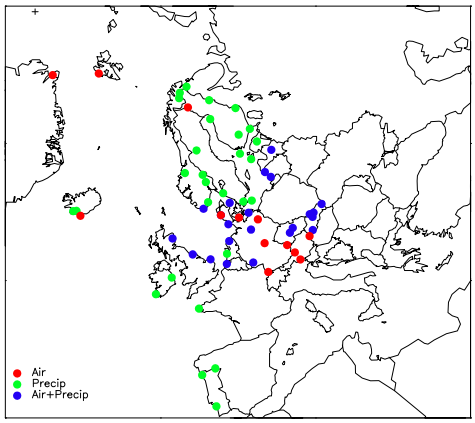
The locations of the measurement sites, which have delivered data on heavy metals for 2001, are found in Fig. 1. Detailed information about the sites and the measurement methods are found in EMEP/CCC's data report on heavy metals and POPs [*Aas and Hjellbrekke*, 2003]. In the figure, the sites are divided in those measuring both concentrations in air and in precipitation, and those measuring only one of them. In 2001 it was 22 sites measuring heavy metals in both compartments, and altogether it was 65 measurement sites. In addition Spain started heavy metal measurements in particles at two sites during 2001. It was 15 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 neither south nor east of Europe. In the new EMEP monitoring strategy for 2004-2009 new monitoring requirements are given where heavy metals shall be a compulsory part of the monitoring program for all EMEP Parties, this will hopefully improve the distribution network. The sites will be differentiated into three levels, "Core sites level 1" is the basic group of EMEP sites and these shall include measurements of heavy metals in precipitation, about 80 sites in Europe. At "Core sites level 2" (supersites), heavy metals in both air and precipitation should be measured simultaneously at around 20 stations evenly distributed over the domain. "Core sites level 3" should be established to carry out more specialized measurements, which are voluntary under the EMEP program. At these sites could be organized campaign studies and more detailed studies on e.g. size distribution and chemical speciation of the different mercury compounds.

1.2. Monitoring of lead, cadmium and mercury in 2001

Annual averages of Pb, Cd and Hg concentrations in precipitation and in air in 2001 are presented in Figs. 2 – 7. The cadmium measurements in Portugal (for precipitation) and Belgium (for air) are not included because the methods used have too high detection limits. In addition, the precipitation data for all elements at the Belgium site are inconsistent with parallel measurements and are therefore rather unreliable. The precipitation results from the UK are not shown on the maps because these data have been reported as deposition fluxes and not concentrations in precipitation.

a



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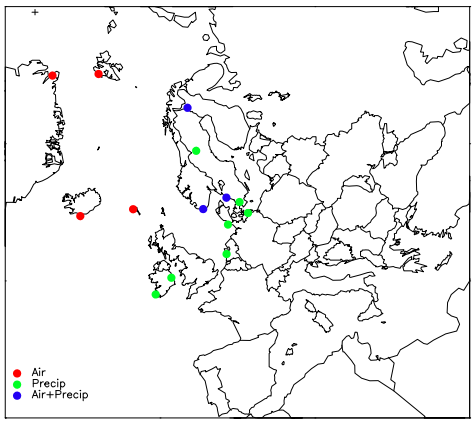

Fig. 1. *Measurement network of lead, cadmium (a) and mercury (b) in 2001*

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 air are observed at Illmiz in Austria, Rucava in Latvia and at the two sites in the Czech Republic. For cadmium in precipitation, the concentrations are highest at Chopok and Stara Lesna in Slovakia. For lead in air the highest concentrations are seen in Belgium, at Illmiz in Austria and at three sites in Slovakia; for lead in precipitation the highest concentrations are at the two sites in the Czech Republic, Preila in Lithuania and Chopok in Slovakia.

There are only a few stations measuring mercury in Europe, and most of them are related to the OSPAR program CAMP. The concentrations of mercury at the different sites are quite comparable for both air and precipitation. Further details of the measurements results are found in the EMEP/CCC data report on heavy metals and POPs [*Aas and Hjellbrekke*, 2003].

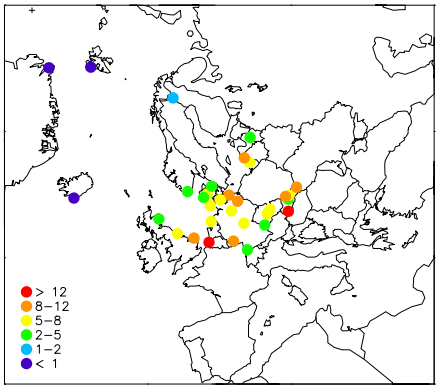

Fig. 2. *Lead in aerosol, ng/m^3*

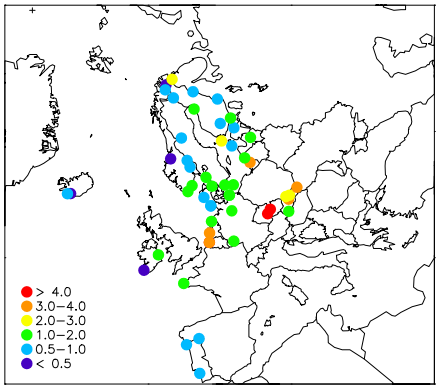

Fig. 3. *Lead in precipitation, µg/l*

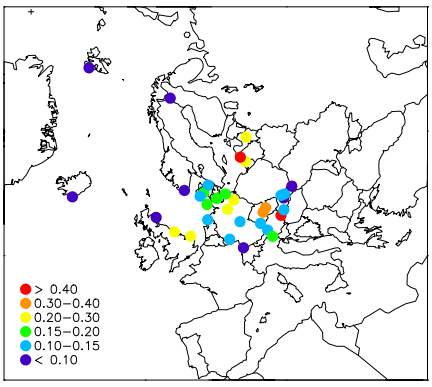

Fig. 4. *Cadmium in aerosol, ng/m^3*

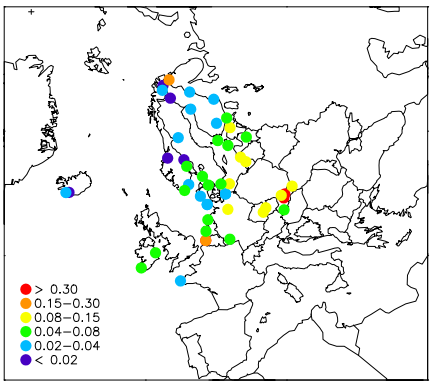

Fig. 5. *Cadmium in precipitation, µg/l*

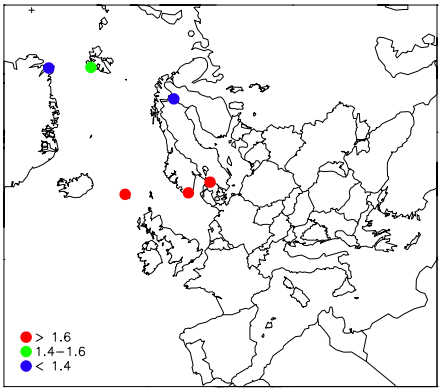

Fig. 6. *Mercury in air, ng/m^3*

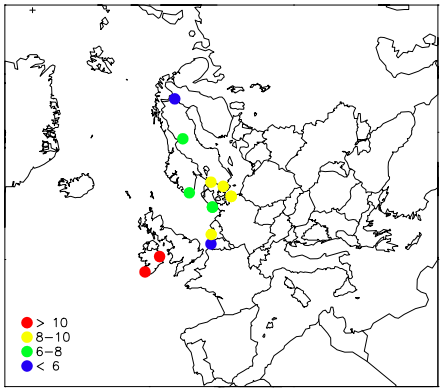

Fig. 7. *Mercury in precipitation, µg/l*

1.3. Measured trends for 1989 - 2001

Fig. 8 shows temporal trends for Cd and Pb in atmospheric aerosols at a few selected stations for which there have been measurements for a longer period. The emissions of Cd and Pb have decreased in Europe in recent years and the concentration levels of both elements show a significant reduction in air concentrations at sites in Germany, Slovakia and UK (Fig. 8). In Norway it there is no significant trend for these two elements in air after 1990. A Mann Kendall test has been run to calculate the Sen's slope estimate for the time period 1989-2001, Table 1 [*Gilbert*, 1987; *FMI*, 2002].

Table 1. *Annual changes in air concentration and total percentage change for lead and cadmium in aerosols at three selected EMEP sites, 1989-2001 using the Sen's slope estimate*

Site	Pb		Cd	
	ng/m^3/y	%	ng/m^3/y	%
DE01	-1.068	76	-0.019	67
GB90	-1.193	64	-0.021	63
SK04	-1.788	72	-0.047	65

The annual average changes in air concentrations of Pb and Cd are calculated and as seen in Table 1 the highest reductions in absolute quantities for both elements are seen at the Slovakian site, but the percentage decrease in concentrations are relatively similar, 63-67% for cadmium and 64-76% for lead. Similar reductions in the concentrations in precipitation are also seen at those sites with long measurement program for precipitation.

1.4. Data quality

Laboratory inter-comparisons of heavy metals in precipitation has been arranged annually since 1995. The data quality objectives (DQO) in EMEP [*EMEP/CCC*, 1996] states that the accuracy in the laboratory should be better than 15% and 25% for high and low concentrations of heavy metals, respectively. As can be seen from Fig. 9 there is a marked improvement in the laboratory performance for both lead and cadmium in low concentration samples. In 2001 and 2002, all values reported for determination of lead in low concentration samples were within the DQO, compared to 65% in 1999 when heavy metals became part of the EMEP measurement program. For cadmium, 76% of the reported values were within the DQO in 2002, compared to 44% in 1999. A marked improvement in laboratory performance is also seen for determination of lead and cadmium in high concentration samples. Further details from the EMEP analytical inter-comparison of heavy metals in precipitation is found in [*Uggerud and Skjelmoen*, 2003].

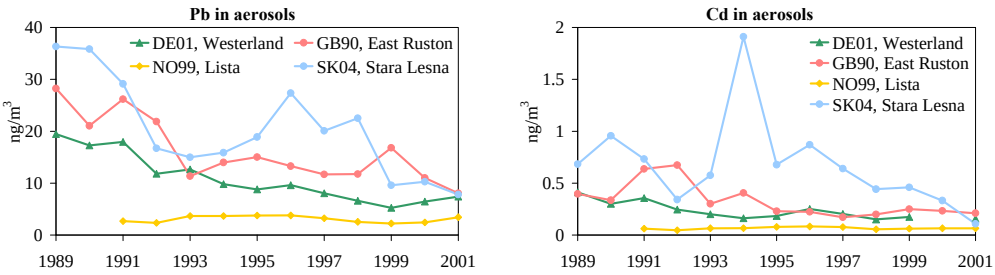

Fig. 8. *Annual average concentrations of Pb and Cd in aerosols at four selected EMEP sites, 1989 – 2001*

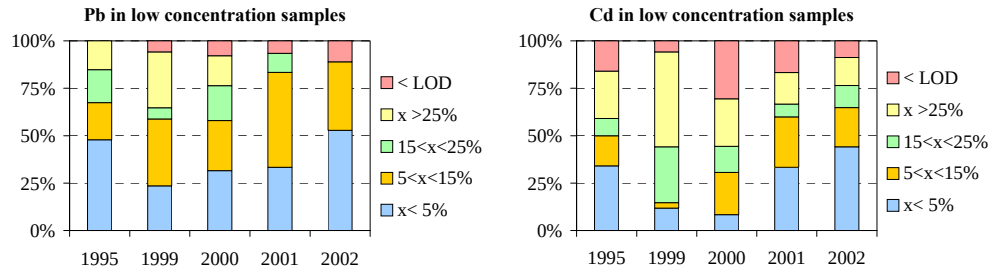

Fig. 9. *Results in laboratory inter-comparison for lead and cadmium in precipitation (low concentration samples) from 1995 to 2002. The laboratories are categorized depending on the relative standard deviations compared with theoretical values; LOD is results below the detection limit*

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 European atmosphere and in the Northern Hemisphere as a whole. The first section contains the analysis of trends of lead, cadmium and mercury pollution of Europe in 1990–2001, spatial distribution of depositions and also transboundary fluxes between European countries in 2001. The second section describes mercury pollution levels in the Northern Hemisphere. Particular emphasis has been placed on the evaluation of intercontinental transport contribution to European mercury pollution as well as on the impact of European sources on pollution of remote regions such as the Arctic.

The assessments were made by the regional (MSCE-HM) and the hemispherical (MSCE-HM-Hem) transport models developed in MSC-E. The regional model covers the territory of Europe with spatial resolution 50x50 km; the hemispherical model describes the atmospheric transport within the Northern Hemisphere with spatial resolution of 2.5ºx2.5º. Annex A contains brief description of both models. The main outputs of modelling include data on heavy metal concentration in air and precipitation as well as levels of deposition to the ground surface. Since the negative impact of heavy metals on human health and biota is mainly due to their long-term accumulation in environmental media particular attention has been given to the assessment of their depositions from the atmosphere.

2.1. Air pollution by lead, cadmium and mercury in Europe

2.1.1. *Pollution trends in 1990–2001*

Under the commitments taken in the framework of the Convention participating countries submit to UN ECE Secretariat information on national anthropogenic emissions of heavy metals. National data on lead, cadmium and mercury emissions for the period of 1990 – 2001 was submitted by 34 countries. For the rest of them expert estimates were used in the modelling process [*Berdowski et al.*, 1997]. There is a common trend of heavy metal emission reduction in the majority of European countries though in some countries a temporary increase of the emission level can be noted. For example, in Poland, Spain and in a number of other countries cadmium emissions increased in 2001 in comparison with the level of 2000.

Apart from anthropogenic emissions heavy metals enter European atmosphere from natural sources due to emissions of previously deposited substances (re-emissions) and also from sources located outside Europe (global sources). More specific information on emission and spatial distribution used for modelling is presented in the Technical Report [*Ilyin and Travnikov*, 2003].

Lead

Anthropogenic lead emissions reduced in 1990–2001 as much as 3.3 times in Europe – from 36000 to 10800 tons per year mainly due to the reduction of leaded gasoline consumption. Unlike the anthropogenic emissions, natural emissions and re-emission assumed to be practically unchanged in time and amount to about 3000 tons for the territory of Europe.

Due to the anthropogenic emission reduction in European countries the decrease of lead depositions is noted. In 1990–2001 depositions declined 2.7 times (Fig. 10). The reduction of depositions is slightly slower than the emission reduction because of permanent contributions of re-emission, natural and global sources.

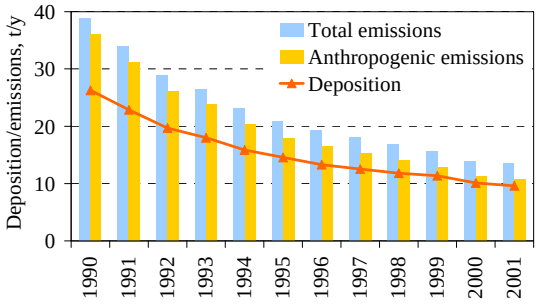

Fig 10. *Trends of lead emissions and depositions in Europe in the period of 1990-2001*

Changes of deposition levels in different parts of Europe significantly differ from the common continental trend. The major reduction of depositions took place in Western and Northern

Europe. Decrease in the levels of pollution in these parts of Europe can be explained by a significant reduction of national emissions. Less significant reduction is characteristic of Eastern and South-Eastern Europe where the emission level reduced slower.

In Europe the reduction rate of national lead emission and deposition differs significantly from country to country. Fig. 11 illustrates the rate of pollution changes in the countries with the highest and lowest emission reduction. It is seen that in the countries that reduced emissions by more than 20 times (Luxemburg, Norway, Monaco, Sweden etc.) the level of deposition decline is much lower and it does not exceed 10 times (Fig. 11a). The reason for it is transboundary transport from countries with insignificant emission reduction.

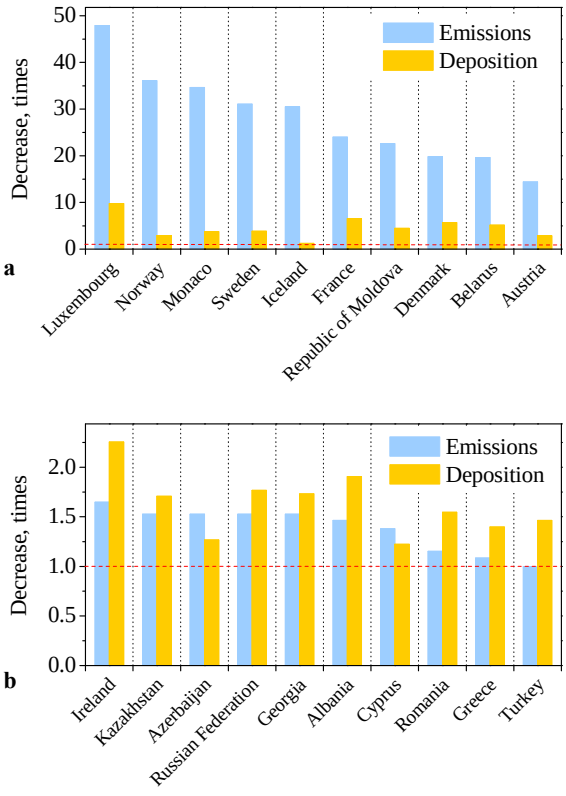

***Fig. 11**. Change of national lead emissions and depositions in 1990–2001 in countries with the highest (a) and lowest (b) emission reduction*

On the other hand, in the countries with moderate emission reduction decrease (Greece, Romania, Albania etc.) the decline of deposition exceeds the national emission reduction (Fig. 11b). This results from the reduction of transboundary component of pollution in these countries because of more intensive emission reduction in neighboring countries.

Thus, in general the level of lead emission and deposition significantly reduced in Europe during the period of 1990 - 2001. However, the irregularity of emission reduction rates in different parts of Europe resulted in the increased relative contribution of transboundary transport to the contamination of countries with essential emission reduction.

Cadmium

Anthropogenic cadmium emission is reduced 1.8 times in Europe during the last decade (1990–2001) and in 2001 it amounted to 290 t/y (Fig. 12). Natural sources and re-emission in addition to anthropogenic emissions provide continuous input of cadmium to the atmosphere of Europe. The estimates show that this additional contribution amounts to about 150 tons annually.

Fig. 12 shows that the anthropogenic emission reduction resulted in the decrease of atmospheric cadmium depositions. In Europe as a whole depositions decreased 1.5 times – from 530 to 350 t/y during the period of 1990–2001. The comparison of cadmium emission and deposition reduction rate in Europe shows that the anthropogenic emission level reduces slightly faster than depositions due to the continuous contribution from natural sources and re-emission.

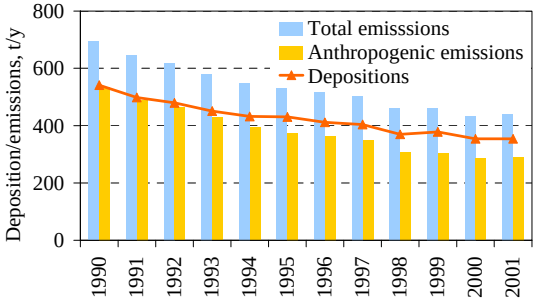

***Fig. 12.** Trends of cadmium emissions and depositions in Europe in the period of 1990-2001*

Fig. 13 illustrates the rate of anthropogenic emission and deposition reduction in some European countries. Countries with the highest emission reduction level are shown on Fig. 13a and countries with the lowest reduction rate (or even with the increase of emissions) are presented in

Fig. 13b. The comparison of the two figures shows that a significant emission reduction does not lead to an adequate deposition reduction. For example, cadmium emissions in Moldova decreased more than 20 times during the last ten years and at the same time depositions reduced only 2.5 times.

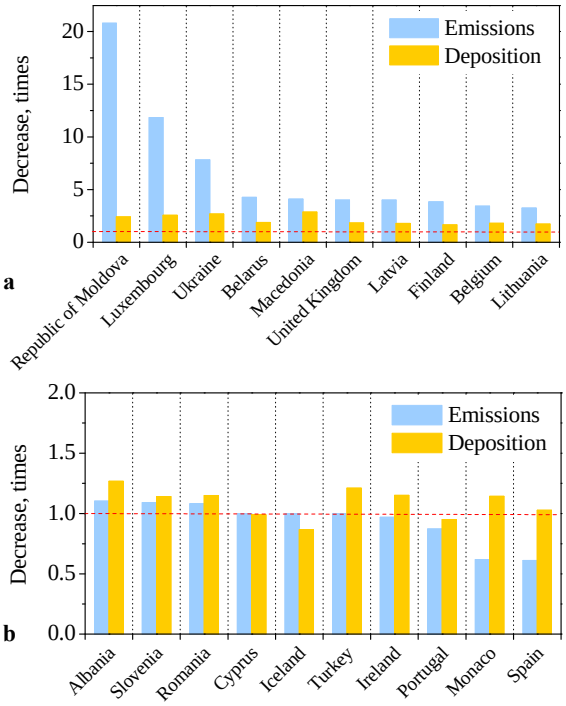

Fig. 13. *Change of national cadmium emissions and depositions in 1990–2001 in countries with the highest (a) and lowest (b) emission reduction*

The difference between emission ad deposition reduction rates is mainly caused by a significant impact of transboundary transport. In Moldova the role of cadmium airborne transport from neighboring Romania increased significantly since there was practically no emission reduction. In general it is possible to say that significant emission reduction in a number of countries (Moldova, Luxembourg, the Ukraine, Belarus etc.) did not have an adequate effect due to actual invariability of the transboundary transport input from the countries with insignificant level of emission reduction.

In general cadmium deposition in Europe reduced slower than that of lead because of the lower rate of anthropogenic emission reduction and more important role of natural emission and re-emission.

Mercury

In contrast to lead and cadmium, mercury is a global pollutant, i.e. it can be transported by atmospheric flows all around the globe. That is why mercury emission sources located on other continents have a significant impact on pollution of Europe. Apart from that, natural emission sources and re-emission contribute significantly to mercury penetration to the atmosphere. Section 2.2 of this Chapter contains more detailed consideration of the impact of global anthropogenic and natural mercury emission sources on pollution of Europe.

During the period of 1990–2001 anthropogenic mercury emissions in Europe reduced approximately 2 times – from 420 to 195 t/y (Fig. 14). At the same time total mercury deposition on the territory of Europe reduced only 1.5 times. It comes about due to the impact of global sources as well as natural component of emissions and mercury re-emission assumed to be unchanged during this period.

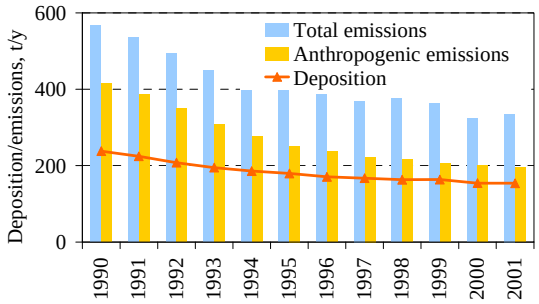

Fig. 14. *Trends of mercury emissions and depositions in Europe in the period of 1990-2001*

Rates of mercury emission reduction do not differ significantly in the majority of European countries and do not exceed the fourfold reduction level during the period indicated. The exceptions are Macedonia, Moldova, Armenia, Lithuania and the Netherlands where the emission level reduced more significantly (Fig. 15a). Besides, in a number of countries (Lithuania, Monaco, Ireland etc.) a certain increase in the level of emissions is observed (Fig. 15b). Nevertheless, moderate reduction of mercury deposition (up to 3.3 times) is characteristic practically of all European countries. Upon the whole, like in the case of lead and cadmium, in the countries with significant emission reduction the deposition reduction lags behind due to the transboundary transport.

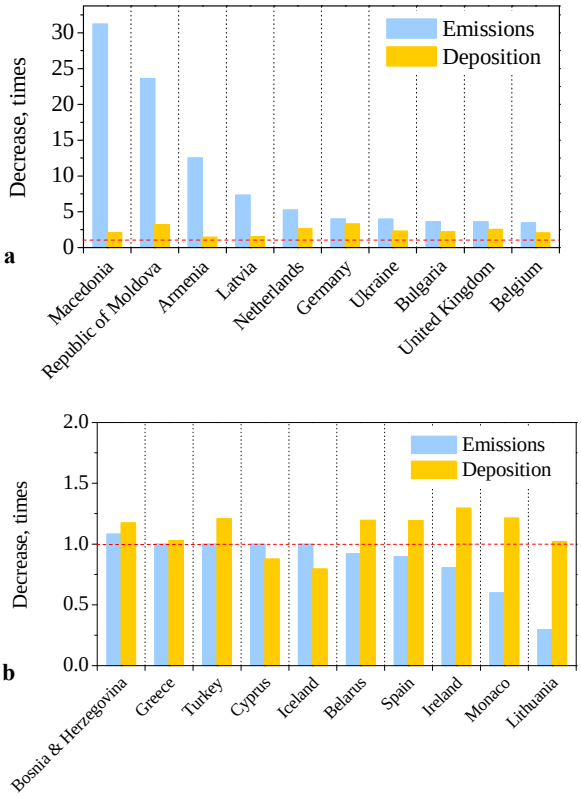

Fig. 15. *Change of national mercury emissions and depositions in 1990–2001 in countries with the highest (a) and lowest (b) emission reduction*

Thus, during the period of 1990-2001 levels of European pollution by heavy metals demonstrate a stable declining trend. The greatest deposition decrease is characteristic of lead due to effective emission reduction. Cadmium and mercury deposition decrease is smaller due to less significant emission reduction as well as due to the impact of natural and global anthropogenic sources. Besides, unequal emission reduction in different countries of Europe leads to the increase of the role of transboundary transport in the countries with the most significant reduction.

Detailed information on trends of heavy metal pollution for each European country in the period of 1990-2001 can be found in the Internet (www.emep.int; www.msceast.org/countries/).

2.1.2. *Pollution levels in 2001*

The detailed assessment of the heavy metal pollution levels in Europe was made for the year 2001. The analysis of spatial distribution of depositions and assessment of the role of transboundary transport in the formation of pollution levels in Europe is given below.

Lead

Total lead anthropogenic atmospheric emissions from European countries in 2001 amounted to 10800 tons and 3000 tons were supplied by natural sources and re-emission. About 30% of lead emitted to the atmosphere is transported beyond the boundaries of Europe. Total lead depositions on the territory of Europe in 2001 approximately amounted to 10000 tons, depositions from European anthropogenic sources made up 7200 tons.

Spatial distribution of anthropogenic emissions is characterized by high non-uniformity (Fig. 16). Significant emissions are observed in Italy, Poland, Spain, and in a number of countries of South-Eastern Europe. Relatively low emission intensity is characteristic of France, Belarus, and Scandinavian countries.

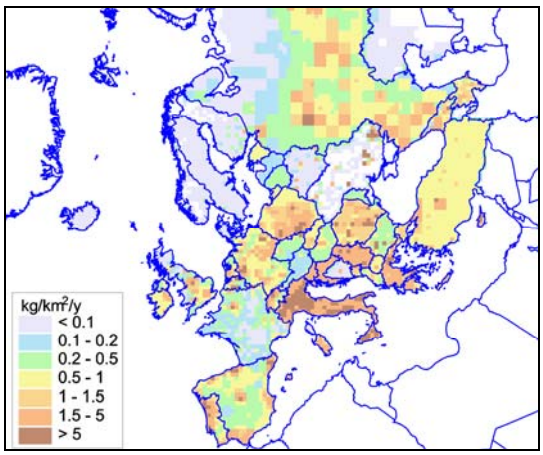

Fig. 16. *Spatial distribution of lead anthropogenic emission flux*

In contrast to the emission field the spatial distribution of deposition levels is more uniform (Fig. 17). Deposition intensity values range from 0.5 to 1.5 kg/km^2/y on the most part of European territory. However in a number of countries significantly higher values are obtained (more than 10 kg/km^2/y).

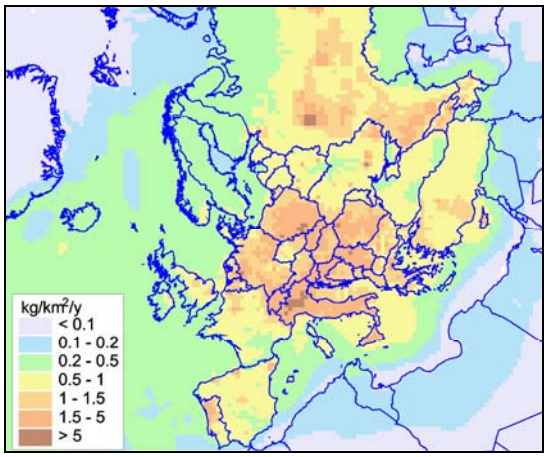

Fig. 17. *Spatial distribution of lead deposition flux*

Levels of pollution for this or that country can be characterized by average values for the territory of the country as well as by maximum local values in different regions of the country (Fig. 18). Local deposition levels are determined with the accuracy of the model grid cell size (50x50 km). As a rule they reflect the impact of powerful local sources. Deposition values on such local territories can significantly (up to an order of magnitude) differ from average values for a country.

The highest values of average deposition (up to 3 kg/km^2/y) are obtained in Italy, Switzerland, Slovenia (Fig. 18). At the same time values of local fluxes can exceed average values as much as several times. Thus, in Italy and Romania maximum deposition fluxes reach 14 kg/km^2/y.

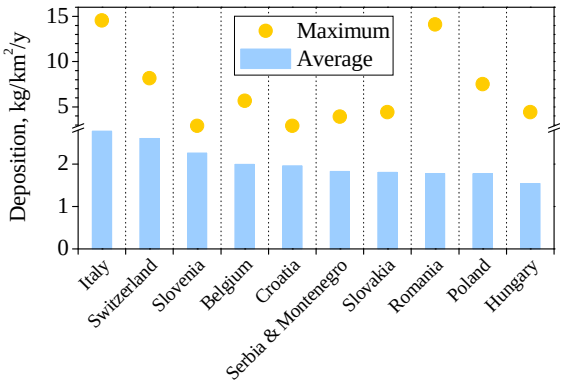

Fig. 18. *Average and maximum lead deposition fluxes in some European countries*

In many European countries lead deposition levels are defined to a great extent by transboundary transport. For example, transboundary transport in 2001 contributed about 360 tons of lead depositions to the territory of Russia, 180 tons to the Ukraine, 170 tons to France (Fig. 19). An essential quantity of lead from external sources is deposited to other relatively large European countries.

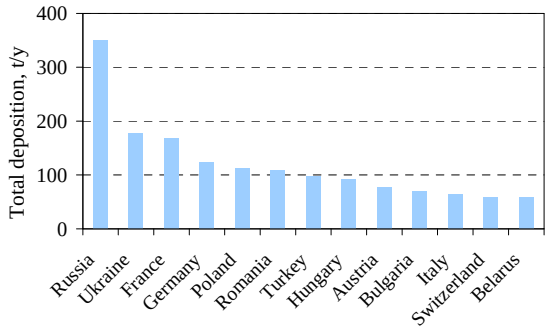

Fig. 19. *Total lead depositions from external anthropogenic sources to some European countries*

A relative input of lead transboundary transport to the pollution of some countries with comparatively low level of national emissions can be significant (Fig. 20). For example, in small countries (Monaco, Bosnia and Herzegovina, Austria etc.) the input of lead transboundary pollution can exceed 70%.

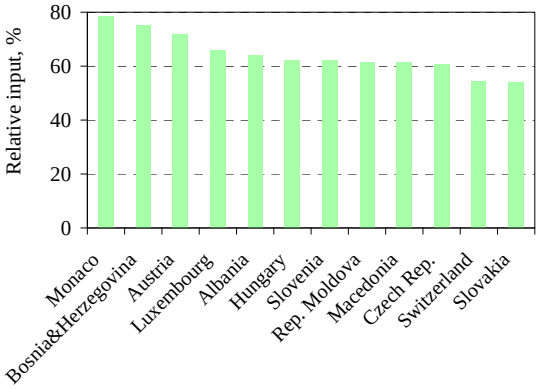

Fig. 20. *Relative inputs of external anthropogenic sources to lead depositions to some European countries*

Values of lead transport beyond national boundaries differ from country to country (Fig. 21). The major source of lead transboundary transport is Italy – more than 1000 tons of lead emitted falls out beyond its national borders. It is related both to significant values of national anthropogenic emissions and to geographical configuration of the country. The level of 100-300 t/y of lead transport beyond the national borders is characteristic of other large industrial countries.

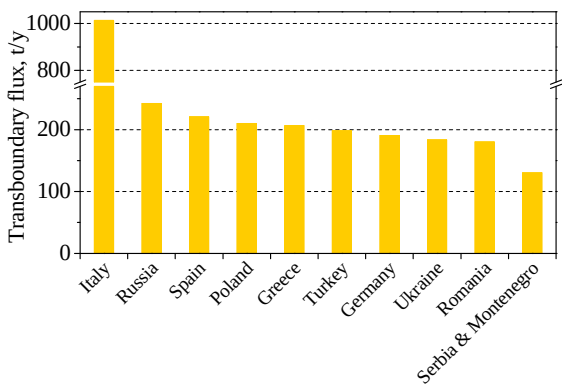

Fig. 21. *Lead transboundary transport from some European countries*

Cadmium

Cadmium anthropogenic emissions in European countries amounted to 290 tons in 2001. A relative input of natural emission and re-emission in the total cadmium inflow to the atmosphere is slightly higher than that for lead and amounts to 150 tons. More than 25% of cadmium emitted to the atmosphere is transported beyond the European boundaries. The atmospheric cadmium deposition to European territory is 360 tons. About 60% of the total is due to the impact of European anthropogenic sources; the rest is the contribution of natural emission, re-emission and global sources.

Spatial distribution of cadmium anthropogenic emission is shown in Fig. 22. The most powerful emission sources are located in Poland. Relatively high emission intensity is characteristic of Northern Italy, Central Russia, Spain and some countries of South-Eastern Europe. The lowest cadmium emission values are in Scandinavian countries and in the North Russia. The Ukraine is a special case. According to the official data cadmium emissions do not exist on the most part of the country except for regions with powerful local sources.

The most part of European territory is characterized by cadmium deposition intensity ranging between 10-50 g/km^2/y (Fig. 23). High deposition levels are characteristic of some countries of Central Europe, Italy and Russia. The lowest values of atmospheric cadmium depositions are obtained for Northern Europe.

Fig. 24 illustrates cadmium deposition levels averaged over a country and maximum local depositions for some European countries. The highest deposition values are characteristic of Poland and Slovakia (about 130 g/km^2/y). At the same time in Poland, Bulgaria and the Czech Republic local depositions exceed average values as much as several times. The highest local deposition value is observed in Romania (1740 g/km^2/y) that can be explained by the presence of a powerful point source in this country.

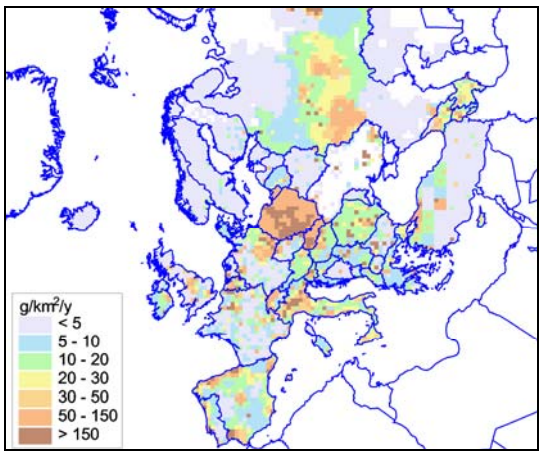

Fig. 22. *Spatial distribution of cadmium anthropogenic emission flux*

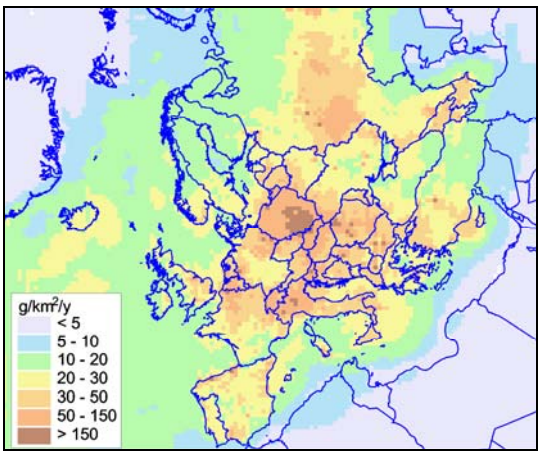

Fig. 23. *Spatial distribution of cadmium deposition flux*

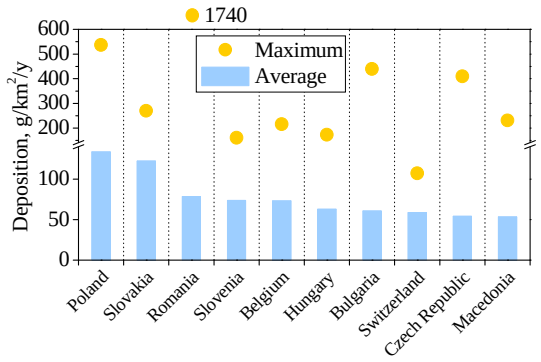

Fig. 24. *Average and maximum cadmium deposition fluxes in some European countries*

In some European countries transboundary transport contributes significantly to the total cadmium depositions. The greatest amount about 10 tons of cadmium from external anthropogenic sources is imported to Russia (Fig. 25). Transboundary deposition levels are also significant in the Ukraine, Poland, France, Germany etc.

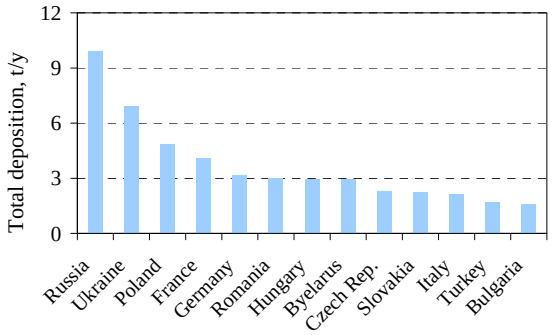

Fig. 25. *Total cadmium depositions from external anthropogenic sources to some European countries*

Fig. 26 shows a relative input of external anthropogenic sources to cadmium depositions to the territory of countries where the role of transboundary transport is most significant. The input of transboundary transport to the pollution of Monaco, Luxemburg and the Czech Republic overcomes 50%. Besides, it is possible to mention that the share of cadmium depositions from external anthropogenic sources is more than 20% in almost all European countries.

The export of cadmium beyond the national borders is most significant in Poland and Italy (Fig. 27). A significant input to the transboundary pollution of Europe is also made by Spain, Romania, Russia etc. As in the case of lead, the level of transport beyond the national borders is determined both by total national emission and country's geographical peculiarities.

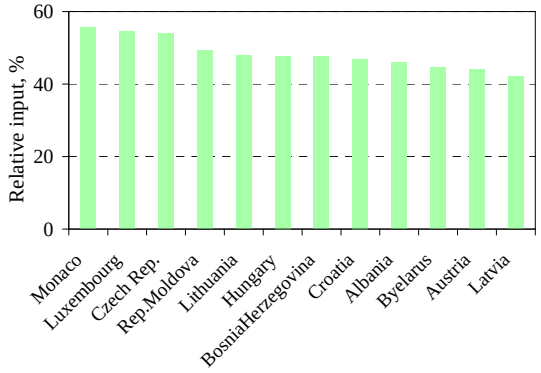

Fig. 26. *Relative inputs of external anthropogenic sources to cadmium depositions to some European countries*

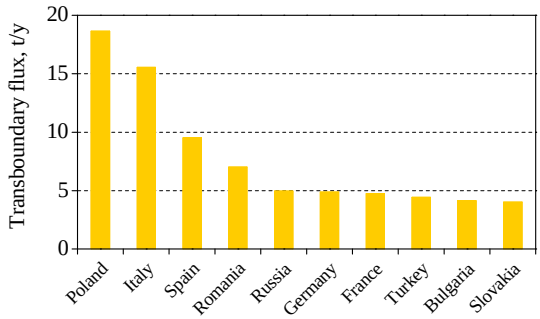

Fig. 27. *Cadmium transboundary transport from some European countries*

Mercury

Mercury emissions from European anthropogenic sources amounted to 195 tons in 2001; the input from natural emission and re-emission is estimated at about 150 tons. More than 60% of emitted mercury is transported beyond the boundaries of Europe. Total mercury depositions to Europe are about 160 tons. Of this amount, 70 t (45%) originates from anthropogenic sources of European countries; all the rest is the input from natural sources, re-emission and global anthropogenic sources.

Spatial distribution of mercury anthropogenic emission intensity is shown in Fig. 28. High emission intensity is characteristic of Poland, East Germany, Hungary, Greece, some regions of Italy and Spain (above 100 g/km^2/y). Besides, high values of local emission are estimated in such countries as France, the United Kingdom, Russia, the Ukraine, Turkey where average emission levels are not very high. Low emissions are also observed in Belarus, Bosnia and Herzegovina, Scandinavian countries (not more than 5 g/km^2/y).

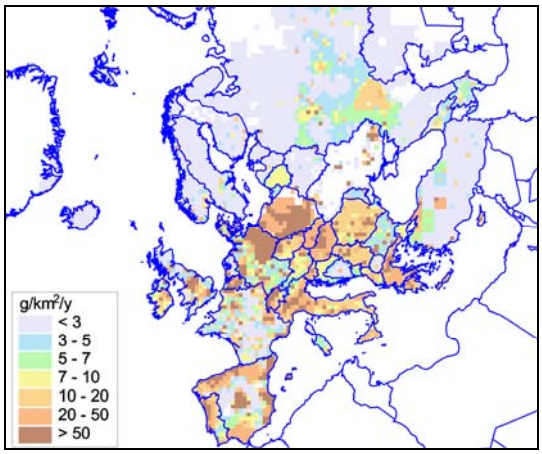

Fig. 28. *Spatial distribution of mercury anthropogenic emission flux*

Mercury depositions are distributed more uniformly than emissions throughout the territory of Europe. On the most part of European region levels of mercury deposition fluxes are between 5-20 g/km^2/y (Fig. 29). In the central part of Scandinavia, in Russia, Belarus and Baltic countries deposition fluxes as a rule do not exceed 10 g/km^2/y. High deposition levels are characteristic of countries with high emission levels and also of the Arctic regions of Norway, Sweden, Finland and Russia due to *mercury depletion events*. This phenomenon and its impact on atmospheric mercury deposition are considered in Section 2.2 of this Chapter.

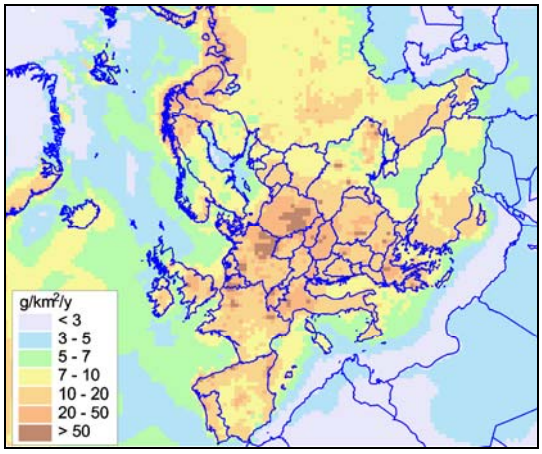

Fig. 29. *Spatial distribution of mercury deposition flux*

The highest values of average mercury deposition per country – about 40 g/km^2/y are observed in Slovakia, Poland and Belgium (Fig. 30). This is caused both by high national emissions and transboundary transport from neighboring countries.

In these or other countries local deposition values can exceed average ones by an order of magnitude. The maximum local mercury deposition flux is determined in Greece (260 g/km^2/y).

The highest absolute input of transboundary transport to mercury pollution of the territory (above 1 t/y) is characteristic of countries with large territories such as Russia, Poland, France, etc. (Fig. 31). Besides, a considerable amount of mercury is transported to small countries (the Czech Republic, Hungary, Romania etc.) bordering the countries with high emission density.

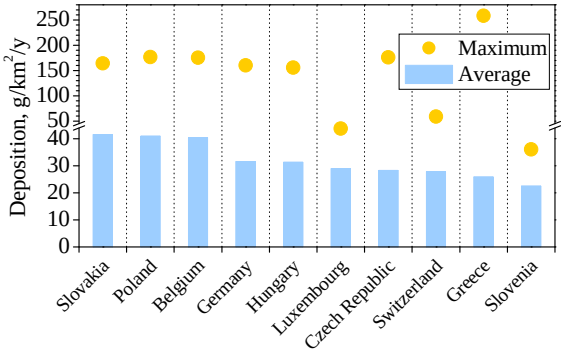

Fig. 30. *Average and maximum mercury deposition fluxes in some European countries*

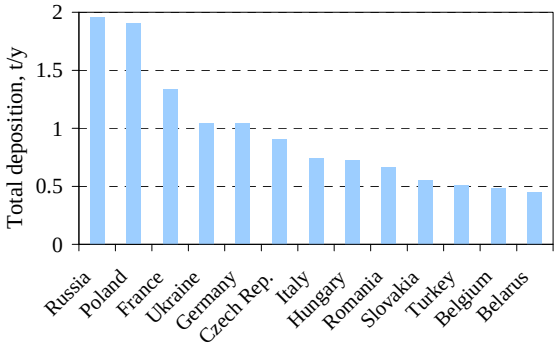

Fig. 31. *Total mercury depositions from external anthropogenic sources to some European countries*

For countries with low national emission intensity (Monaco, the Netherlands, Macedonia, the Czech Republic etc.) the relative input of transboundary transport to mercury deposition to a country can exceed 40% of the total (Fig. 32).

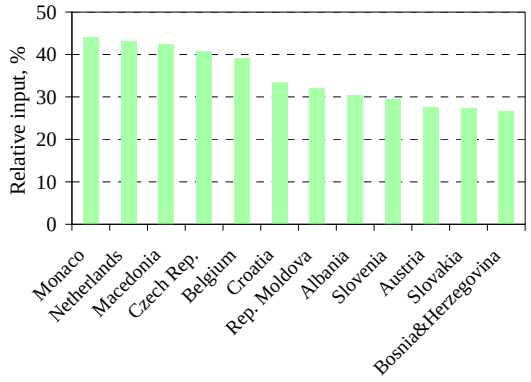

Fig. 32. *Relative inputs of external anthropogenic sources to mercury depositions to some European countries*

The most significant sources of transboundary transport are Germany, Spain, Greece and Poland (Fig. 33). More than 2.5 t of mercury was transported from the territory of each of these countries in 2001.

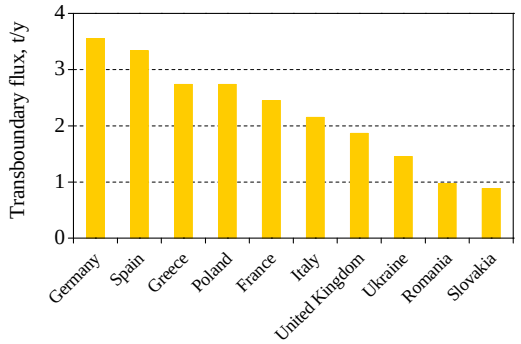

Fig. 33. *Mercury transboundary transport from some European countries*

On the basis of this analysis it is possible to conclude that HM pollution levels of European countries are specified both by national sources and transboundary transport. The highest absolute values of transboundary transport from external sources are characteristic of large countries (Russia, Germany, France, the Ukraine, Poland) and also of such countries as Romania, Hungary, the Czech Republic, Belarus bordering the most powerful emission sources. The most significant relative input of transboundary transport to the pollution is observed in the countries with low national emissions (Luxemburg, Monaco, the Netherlands, Austria etc.). The input of different countries to the transboundary transport is defined by the total value of national emissions as well as by the location of emission sources in the country.

2.1.3. *Transboundary transport analysis on the example of one country*

A detailed analysis of transboundary pollution of one of European countries (exemplified in France) can be found below. Information on pollution of any other European country is available in the Internet: (www.msceast.org/countries/).

Fig. 34 illustrates the input of national and external sources to annual cadmium deposition to France in 2001. Depositions from national sources amount to about 30% of the total. The highest input from external anthropogenic sources is made by Spain (9%) and Italy (5%). Besides, taking into account that France is situated close to Atlantic coast, a significant input (above 40%) is made by re-emission, natural and global anthropogenic sources.

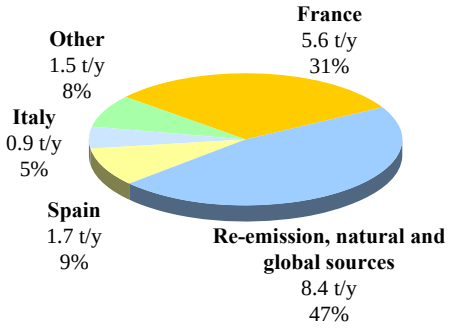

Fig. 34. *Diagram of the input of national and external sources to the total cadmium deposition to France in 2001*

The contribution of transboundary transport is non-uniformly distributed over the country (Fig. 35). Regions neighboring the countries with powerful emission sources (Italy, Spain) are most impacted by external anthropogenic sources. The lowest input of the transboundary transport is characteristic of central regions and regions with significant levels of national emission.

France in its turn is a source of cadmium deposition to other European countries. Fig. 36 illustrates spatial distribution of cadmium depositions of French anthropogenic sources to Europe domain in 2001. The prevailing direction of transport is to the East and South-East towards Germany, Belgium and Italy. Besides, transboundary transport from French sources reaches other neighboring countries – Spain and the United Kingdom.

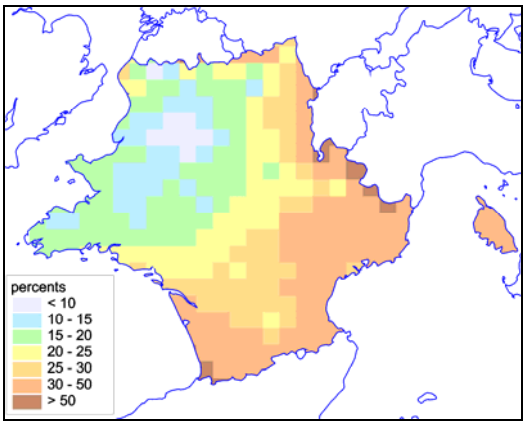

Fig. 35. *Spatial distribution of inputs of external anthropogenic sources to cadmium deposition to France in 2001*

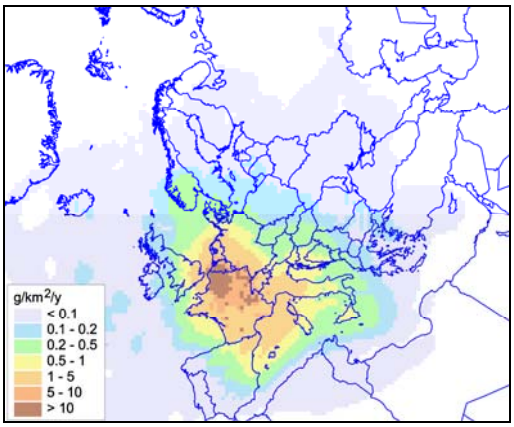

Fig. 36. *Spatial distribution of cadmium deposition levels from French anthropogenic sources in 2001*

Total deposition values from French anthropogenic emission sources in European countries in 2001 are shown in Fig. 37. More than half the cadmium emitted to the atmosphere in France is deposited to its own territory (5.6 t/y). The highest depositions to other countries are obtained in Germany (0.5 t/y), Belgium (0.5 t/y) and Italy (0.4 t/y).

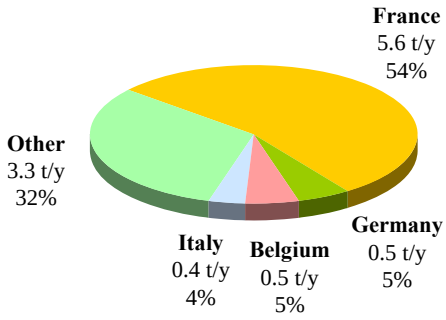

Fig. 37. *Diagram of total deposition from French anthropogenic emission sources to European countries in 2001*

2.1.4. Validation of the regional model

The validation of the regional model consisted of the comparison of modelling results against measurements, the analysis of model sensitivity to the variability of input parameters and the comparison of calculation results of the MSCE-HM model with other models.

For the ***comparison of model results with measurements*** monitoring data on lead, cadmium and mercury are used for the period from 1990 to 2001. Monitoring stations are located mainly in the Northern and Central parts of Europe. The numbers of calculated values consistent with measured ones within a factor of 2 make up 85% for lead and 74% for cadmium (Fig.38). Correlation coefficients are 0.7 and 0.6 respectively. It should be mentioned that as a rule the model somewhat underestimates air concentrations of lead, cadmium as well as wet deposition fluxes [*Ilyin and Travnikov*, 2003].

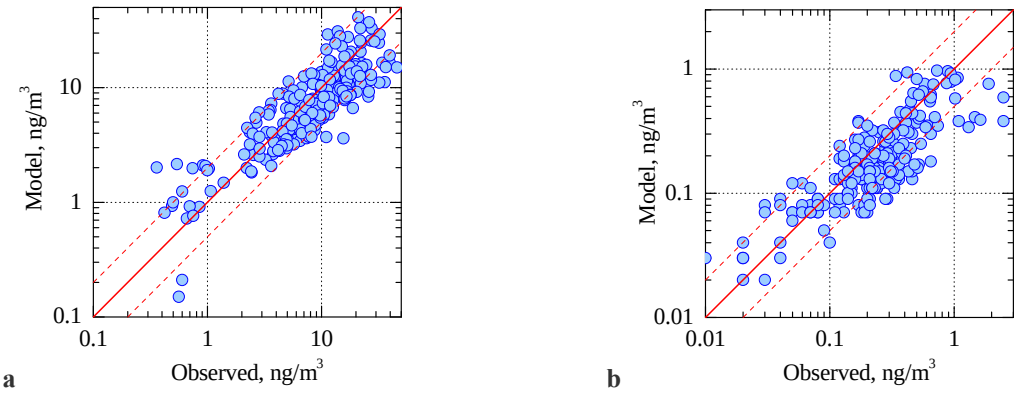

Fig. 38. *The comparison of calculated air concentrations of lead (a) and cadmium (b) with monitoring data for 1990-2001. The dashed lines indicate the limits of factor 2 for measured and calculated values*

The difference between measured and calculated mercury air concentrations are mainly within the limit of 30% (Fig. 39). Upon the whole the calculated air concentrations and wet deposition fluxes are higher than measured values [*Ilyin and Travnikov*, 2003]. Calculated and measured concentrations of total gaseous mercury vary in narrow limits both in space and time. The variability of concentration values is comparable with measurement and model uncertainties. For these reasons the correlation is actually absent.

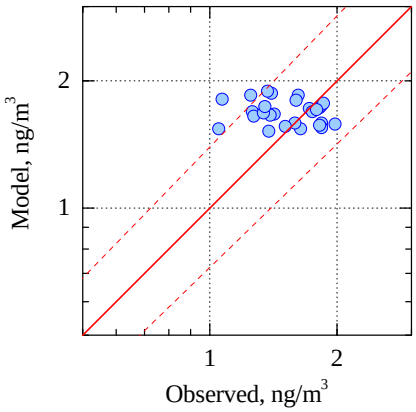

Fig. 39. *The comparison of calculated air concentrations of mercury with monitoring data for 1990-2001.The dashed lines indicate the difference by 30% between measured and calculated values*

An important feature of the model is its capability to display long-term variations of pollution levels in Europe. The model provided data on the dynamics of concentrations in air, precipitation and wet deposition fluxes of lead, cadmium and mercury for 1990-2001. These data are compared with available monitoring data.

Measurement data and calculated values demonstrate the decline of lead depositions in various parts of Europe. In Central Europe this trend is more pronounced than in Northern Europe. As an example Fig. 40 shows long-term variations of wet depositions for German (Fig. 40a) and Finish stations (Fig. 40b).

In Chapter 1, dedicated to monitoring, it was mentioned that cadmium air pollution decreases in countries located in Central in Western Europe. Similar trends are reproduced by the model (Fig. 41a). In Northern Europe long-term trends of air concentrations are practically absent. It is testified by monitoring data (see Chapter 1) and calculation results (Fig. 41b). The same peculiarity is characteristic of wet depositions [*Ilyin and Travnikov*, 2003]. Interannual variations of pollution levels in Northern Europe are mainly defined by the variability of meteorological parameters from year to year.

Only two stations in Europe have sufficiently long series of observations of mercury wet depositions. Fig. 42 illustrates examples of mercury wet deposition dynamics at Westerland station (Germany) and Rörvik station (Sweden). Measured deposition values at Westerland station for 1990-2001 demonstrate a considerable variability. As to the calculated values, they decrease corresponding to a general pattern of mercury pollution level variation in Europe. Both calculated and measured wet deposition fluxes observed at Rörvic station display a trend of decrease.

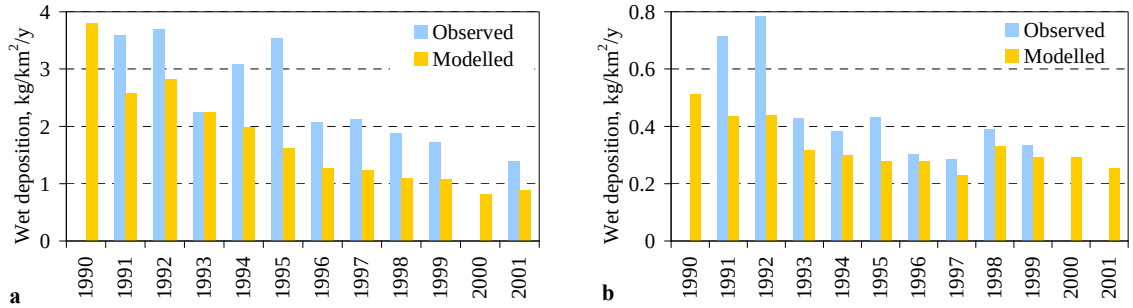

Fig. 40. *Lead wet deposition at Deuselbach station (DE4), Germany (a) and at Pesosjarvi station (FI94), Finland (b)*

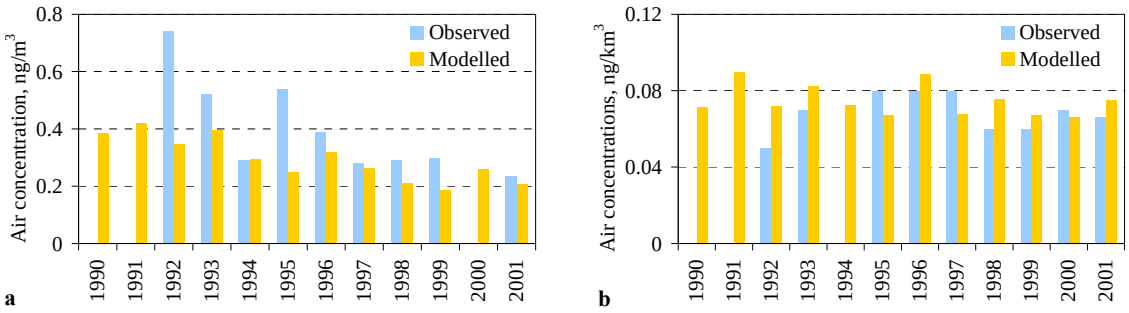

Fig. 41. *Cadmium air concentration at Neuglobsow station (DE7), Germany (a) and at Lista station (NO99), Norway (b)*

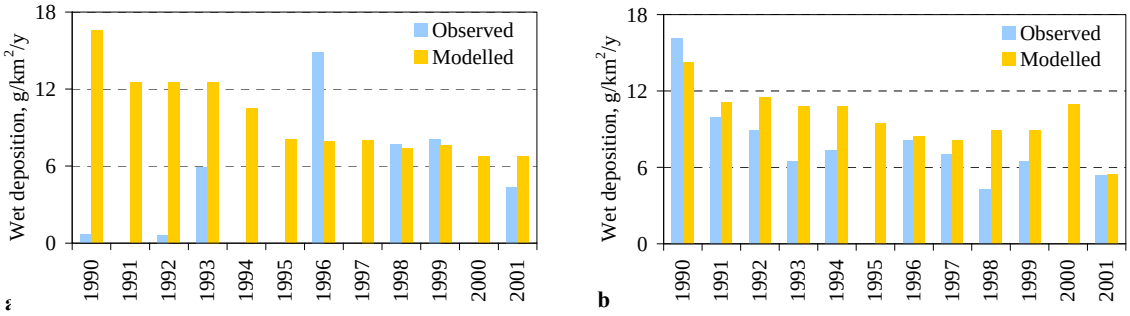

Fig. 42. *Mercury wet deposition at Westerland station (DE1), Germany (a) and at Rörvic station (SE2), Sweden (b)*

The comparison of modeling and monitoring results show that in general calculated results satisfactory describe lead, cadmium and mercury pollution levels in Central and Northern Europe and long-term trends of these levels in the period of 1990-2001. For the remained regions of Europe data on heavy metal monitoring are practically absent. Special attention should be given to the fact that model underestimates lead and cadmium deposition and concentration in comparison with measurement data. Most likely the reason for it is incompleteness of emission data. Experts in the field of emission inventories and modeling pointed out [*Proceedings of EMEP Workshop…*, 2002] that in many countries the inventories does not cover all the sources of heavy metals emissions and that the emission is the key source of uncertainties in model results.

Contrary to lead and cadmium calculated values of air concentration and wet deposition of mercury are somewhat higher than measured values. Most probably it is connected with uncertainties of estimated natural emission, chemical transformation processes of mercury as well as with boundary conditions.

The analysis of model uncertainty relative to its input parameters was made in a special study [*Travnikov*, 2000]. This analysis demonstrates that the model uncertainty does not exceed 25% for the major part of the calculation domain without taking into consideration the impact of anthropogenic emission. Boundary areas of the calculation region are the only exception. Anthropogenic emissions make the greatest contribution to the uncertainty of calculated air concentrations and depositions.

An important stage of model validation is ***the comparison of MSCE-HM model results with those of other models***. The MSCE-HM model participated in the comparison of calculation results of lead and cadmium concentration and deposition [*Gusev et al.*, 2000]. During this comparison it was shown that the results of the operational MSCE-HM model and of other models agree with measurement data within a factor of 2. The results of participating models demonstrated a satisfactory agreement (within a factor of 2).

At present the activity within the framework of multi-stage project “Intercomparison study of numerical models for long-range atmospheric transport of

mercury" is being continued. The first two stages – the comparison of chemical models and the comparison of air concentrations during short-term episodes are finalized. A detailed description of this investigation can be found in the works [*Ryaboshapko et al.*, 2002; *Ryaboshapko et al.*, 2003].

MSC-E approach to model validation including the comparison with observations, model sensitivity analysis and model intercomparison studies was overviewed and discussed at 4th meeting of TFMM (Valencia, Spain, April 2003). The Task Force recognized that model review had to remain a continuous activity to be pursued as emission and measurement data availability and quality and model performance, were improved.

2.2. Atmospheric transport of mercury in the Northern Hemisphere

Mercury differs considerably from other heavy metals, such as lead or cadmium, by its unique ability to be transported over great distances in the atmosphere. The reason for this phenomenon lies in the fact that the predominant part of mercury in the atmospheric air (up to 99%) is represented by slightly soluble and relatively inert mercury vapour (elemental gaseous mercury). As a result, mercury is capable of remaining in the atmosphere for a long time, being transported by airflows over continents and oceans. In addition, after entering the soil or surface water (mainly, in the oxidised form), mercury can be reduced again to the volatile elemental form that is emitted into the atmosphere once again (so-called re-emission). Re-emission processes increase considerably the capability of mercury for dispersion in the environment.

2.2.1. *Mercury emission to the atmosphere*

Mercury enters the atmosphere owing to both the anthropogenic activity (combustion of coal and other fossil fuels, ferrous and non-ferrous metal production, cement production, waste incineration etc.) and natural processes (volcanic activity, evasion from mercury enriched soils, etc).

To assess the anthropogenic emission of mercury into the atmosphere, we have used global emission inventory for 1995 [*Pacyna & Pacyna*, 2002]. According to these data, the total global anthropogenic emission of mercury is about 2400 t/y. In the Northern Hemisphere, the anthropogenic emission of mercury reaches 1900 t/y. The distribution pattern of anthropogenic emission fluxes of mercury in the Northern Hemisphere is shown in Fig. 43. The highest densities of emission sources are found in South-eastern Asia, Europe, and the eastern part of North America.

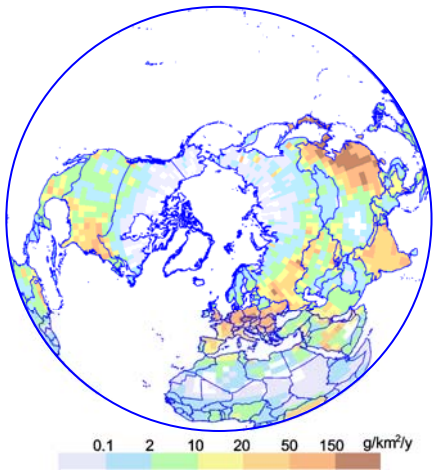

Fig. 43. *Spatial distribution of anthropogenic mercury emission in the Northern Hemisphere*

Available data on the natural emission of mercury into the atmosphere are rather discrepant. Published estimates of the global natural emission of mercury vary within wide limits. In our model calculations, we have used expert estimates of the natural mercury emission based on the work [*Lamborg et al.*, 2002]. According to this study, the global emission of mercury from natural sources (including re-emission) reaches about 2300 t/y. In order to obtain spatial distribution of natural emission fluxes the total emission value was scattered throughout the globe depending on the type of the earth's surface. Fig. 44 shows the obtained distribution of natural emission fluxes of mercury in the Northern Hemisphere. The highest emission values are typical of the so-called geochemical mercuriferous belts with an increased content of mercury in soils and surface deposits. The total natural emission of mercury (including re-emission) in the Northern Hemisphere constitutes about 1600 t/y.

Contributions of particular regions to the total (anthropogenic and natural) emission of mercury in the Northern Hemisphere are shown in Fig. 45. The predominant contributors are Asian sources (55% of the total emission). Besides, European (11%) and American (10%) sources make the significant inputs as well as mercury evasion from the ocean surface (17%).

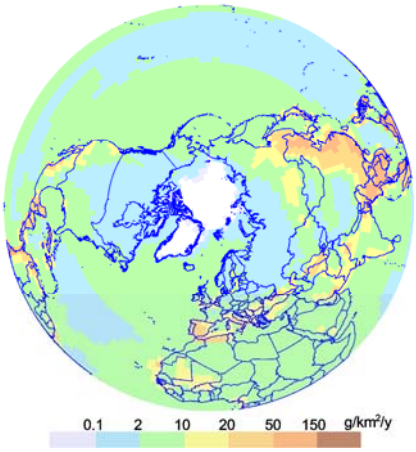

Fig. 44. *Spatial distribution of natural mercury emission in the Northern Hemisphere*

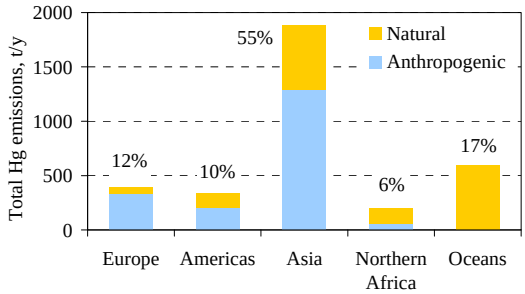

Fig. 45. *Contribution of different regions to the total annual mercury emission in the Northern Hemisphere*

2.2.2. *Background mercury concentrations*

According to modern views, the mean residence time of mercury in the atmosphere is about one year. This is a long period, during which mercury can be transported by airflows around the planet several times. As a result of mixing processes, the levelling of mercury concentrations in the troposphere takes place, and the global mercury background concentration of in the air is established. Numerous measurements have proved that the background concentration of mercury in the surface air varies from 1 to 2 ng/m^3, though local mercury concentrations in industrial regions can be several times higher. Fig. 46 displays the calculated distribution pattern of mercury concentrations in the surface air for the Northern Hemisphere. The highest concentrations (above 2.2 ng/m^3) are typical of Europe and South-eastern Asia. However, even in the remote parts of the Atlantic and Pacific oceans, as well as in the Arctic, mercury concentration in the surface air does not fall below 1.4 ng/m^3. Lower concentrations are only obtained for high-altitude regions and territories near the equator.

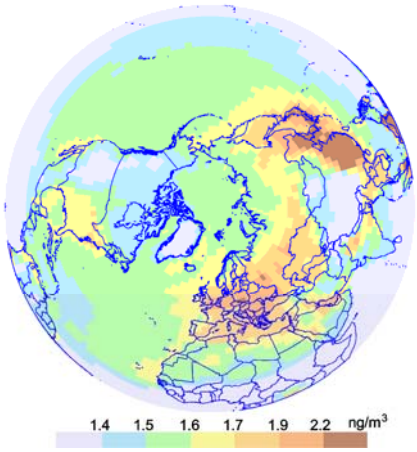

Fig. 46. *Mean annual concentration of total gaseous mercury in the surface air of the Northern Hemisphere*

The global character of mercury transport in the atmosphere means that any source of mercury emission can affect very remote regions. In this context, environmental pollution with mercury is not restricted to the effect of local and regional emission sources but also includes the intercontinental transport of mercury.

2.2.3. *Intercontinental transport*

Europe is one of the main sources of mercury emission in the Northern Hemisphere. Therefore, mercury depositions in this region is largely controlled by internal (European) emission sources. However, mercury transport from anthropogenic and natural sources in other regions also affects the mercury deposition levels in Europe. The distribution of mercury deposition fluxes (except for those from European emission sources) in the Northern Hemisphere is shown in Fig. 47.

Mercury transport from external sources influences entire Europe; mercury deposition levels in Europe from non-European sources amount to 10 g/km^2/y, which are comparable with those from European sources. Fig. 48 illustrates the relative contribution of external sources to mercury deposition in Europe. In the central part of Europe with the highest density of mercury emission, this contribution does not exceed 25% of the total mercury deposition. In northern and southern Europe, as well as over the adjacent seas, the contribution of external sources to mercury deposition exceeds 50%.

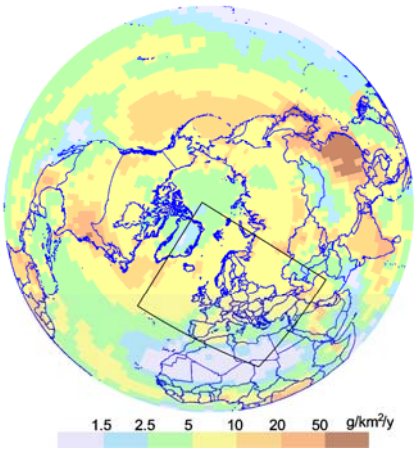

Fig. 47. *Spatial distribution of annual deposition fluxes of mercury in the Northern Hemisphere (except for the fluxes from European emission sources). Black line delineates the EMEP region*

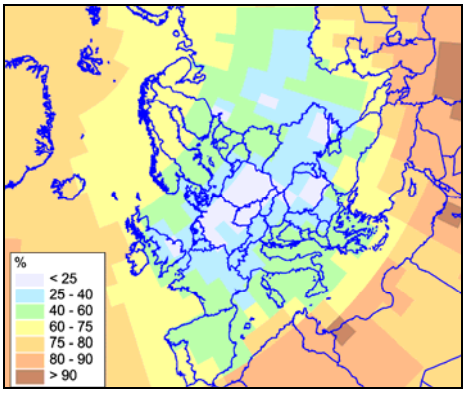

Fig. 48. *Relative contribution of external sources to mercury deposition in Europe*

In general, the contribution of external sources to mercury deposition in Europe is assessed at 40% (Fig. 49). The most significant input is made by Asian sources (15%) and mercury evasion from the ocean surface (12%). American sources contribute to about 5%. It should be noticed that the anthropogenic component of mercury deposition to Europe considerably exceeds the natural one and amounts to 75% of the total.

At the same time, European sources of mercury emission also contribute to mercury pollution in other regions of the Northern Hemisphere. The levels of mercury deposition from European sources in the Northern Hemisphere are shown in Fig. 50. The mercury transport from Europe affects vast areas in the Northern Hemisphere and leads to noticeable levels of mercury deposition from European sources in Asia and North America (up to 5 g/km^2/y).

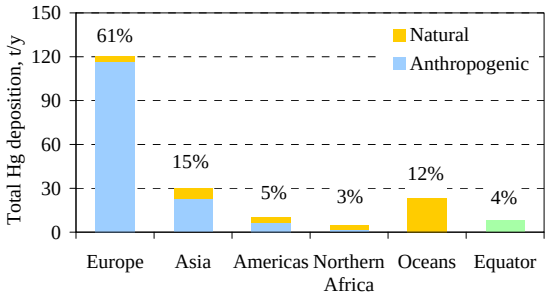

Fig. 49. *Contribution of different regions to the total annual mercury deposition to the European region. The last column of the chart – contribution of mercury transported through the equator*

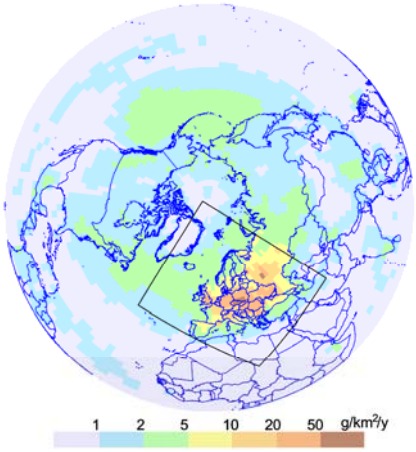

Fig. 50. *Spatial distribution of annual deposition fluxes of mercury from European sources in the Northern Hemisphere. Black line delineates the EMEP region*

The total mercury deposition from European sources to North America amounts to 33 t/y (Fig. 51); in Asia, the maximum mercury depositions from European sources falls on Asian Russia (28 t/y).

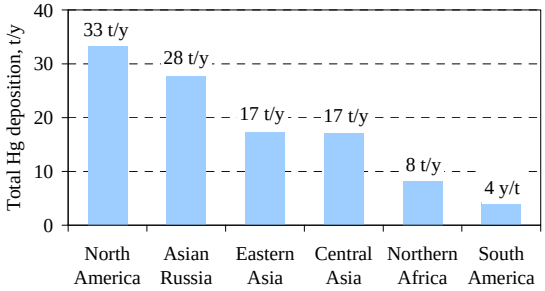

Fig. 51. *Annual deposition of mercury from European sources to different regions of the Northern Hemisphere*

2.2.4. *Arctic pollution*

The Arctic is a special region of the Northern Hemisphere. It has no significant sources of mercury emission. However, the Arctic environment is subjected to a considerable pollution owing to mercury transport from distant industrial areas of Europe, south-eastern Asia, and other regions. The phenomenon of Mercury Depletion Events (MDE) accompanied by the active deposition and accumulation of mercury in the snow plays a special role in the mercury pollution of the Arctic ecosystems [*AMAP*, 2002]. The essence of this phenomenon is in a rapid transformation of long-lived elemental mercury into short-lived forms, which takes place in the surface air of the Arctic during the spring season. As a result, the levels of mercury deposition in the Arctic during this season may be very significant and comparable to the levels typical of industrial regions.

Fig. 52 displays the calculated mercury deposition levels in the Arctic region. According to model estimates, these levels vary from 2 to 20 g/km^2/y. The highest levels of mercury deposition are predicted for coastal areas of the Arctic Ocean, where the effect of MDE is believed to be very significant. Fig. 53 illustrates the net effect of MDE on the annual deposition of mercury in the Arctic. As seen from this figure, the contribution of MDE (lasting for several weeks) to the annual mercury deposition may be as high as 50% in coastal Arctic regions (Queen Elisabeth Islands, coastal areas of the White, Kara, and Laptev Seas etc.).

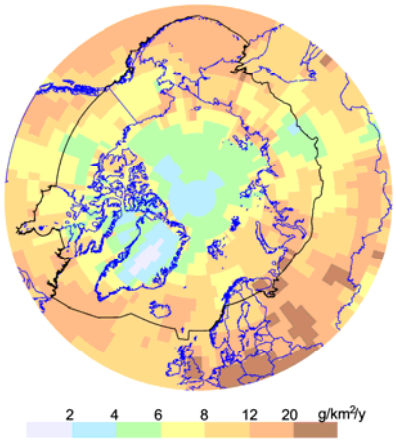

Fig. 52. *Spatial distribution of annual mercury deposition fluxes in the Arctic. Black line delineates the Arctic boundary as specified by AMAP*

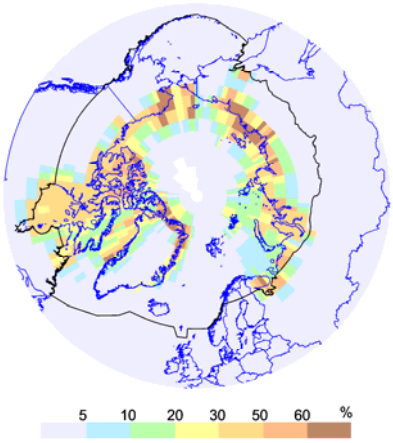

Fig. 53. *Contribution of MDE to the total annual mercury depositions in the Arctic region. Black line delineates the Arctic boundary as specified by AMAP*

The contribution of particular regions of the Northern Hemisphere to the mercury pollution of the Arctic environment is shown in Fig. 54. The most significant contribution is made by Asian (33%) and European (22%) sources. The total mercury deposition to the Arctic is assessed at about 270 t/y. Of this amount, about 50% is contributed by anthropogenic emission sources.

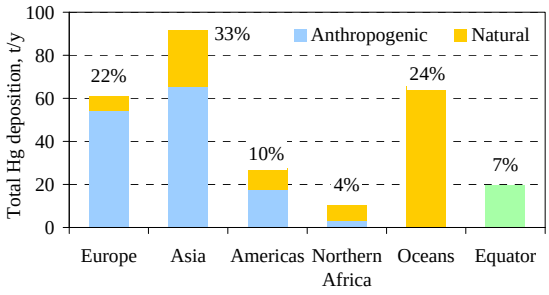

Fig. 54. *Contribution of different regions to the total annual deposition of mercury to the Arctic. The last column of the chart – contribution of mercury transported through the equator*

2.2.5. *Validation of the hemispheric model*

The foregoing assessment of mercury airborne transport and deposition in the Northern Hemisphere has been performed by means of hemispheric model MSCE-Hg-Hem developed at MSC–E. An important criterion of the modelling approach reliability is the degree of correspondence between predicted and measured values of mercury concentration in air and deposition with precipitation (wet deposition). The comparative analysis of these data is given below.

Long-term measurements performed at stations of the EMEP monitoring network [*Berg and Hjellbrekke*, 1998] and the North American NADP/MDN monitoring network [*NADP/MDN*, 2002] were used in the analysis. In addition, we also used data of short-term measurements performed during episodic measurement campaigns. The location of monitoring stations and sites of episodic measurements is shown in Fig. 55.

The results of the comparison of predicted and measured mean annual mercury concentrations in the surface air are given in Fig. 56. As seen from these data, the model predicts air concentrations of mercury in background regions (~1.5 ng/m^3) rather accurately. Some underestimation of measured values takes place in the regions with an increased concentration of mercury (South-eastern Asia). In general, the difference between measured and predicted values does not exceed 30%.

The difference between predicted and measured values of the annual wet deposition of mercury is displayed in Fig. 57. The accuracy of model prediction in this case is somewhat lower, because deposition fluxes highly depend on the precipitation amount, the model input parameter with a considerable degree of uncertainty. However, in general, the ratio between measured and predicted values is close to unity; the maximum difference between them does not exceed a factor of two.

Fig. 55. *Location of monitoring stations and sites of episodic measurements*

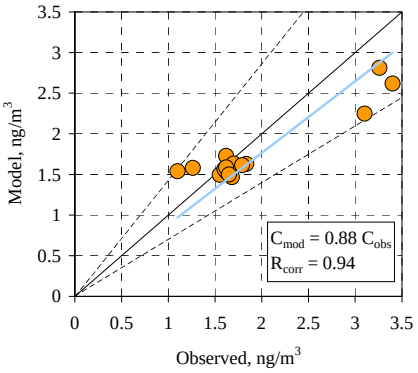

Fig. 56. *Predicted versus measured values of mercury concentration in the air. Dashed line shows the 30% discrepancy*

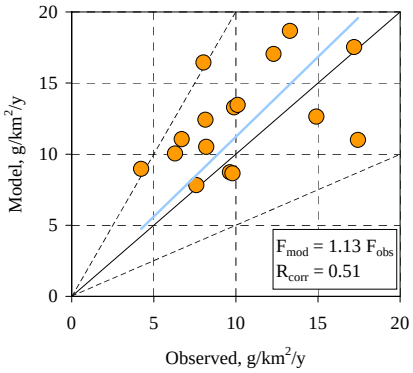

Fig. 57. *Predicted versus measured values of annual wet deposition of mercury. Dashed line shows the two-fold difference*

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: Working Group on Strategies and Review (WGSR), Working Group on Effects (WGE); with international organisations and programmes: Arctic Monitoring and Assessment Programme (AMAP), United Nations Environment Programme (UNEP), World Meteorological Organization (WMO) and Helsinki Commission (HELCOM). Besides, special attention was given to the interaction with national experts of the Parties to the Convention.

3.1. Co-operation with subsidiary bodies to the Convention

Expert Group on Heavy Metals (Working Group on Strategies and Review)

In conformity with the "EMEP Strategy 2000-2009" (EB.AIR/GE.1/2000/5) MSC-E started the preparation for the assessment of environmental pollution by the second priority heavy metals (arsenic, chromium, nickel, zinc, copper). A preliminary stage dealt with parameterization of model processes and tentative computations of airborne transport of nickel and chromium for 1996. The results were presented at the meeting of the Expert Group on Heavy Metals (Geneva, Switzerland, March 2003).

The computations are made with the use of data on nickel and chromium emissions to the atmosphere submitted by Parties to the UN ECE Secretariat. When official data are not available expert estimates are used [*Berdowski et al.*, 1997]. The spatial distribution of annual nickel depositions in 1996 is illustrated in Fig. 58. On the major part of Europe nickel deposition values are within 0.1–1.5 kg/km^2/y. Deposition levels on marginal sea basins do not exceed 0.5 kg/km^2/y.

The highest depositions are estimated in countries located in the Southern, Central and Eastern parts of Europe. The highest values (about 1 kg/km^2/y) of depositions averaged over the country are determined for Italy, Slovenia, Luxembourg and the Ukraine (Fig. 59). At the same time maximum deposition levels (with the accuracy of grid cell size 50x50 km) can essentially exceed average values and reach levels of about 10 kg/km^2/y in such countries as the Ukraine, Russia, Belarus, Bulgaria etc. Relatively low deposition levels are estimated in Northern Europe: Denmark and Norway where the annual deposition does not exceed 0.5 kg/km^2/y.

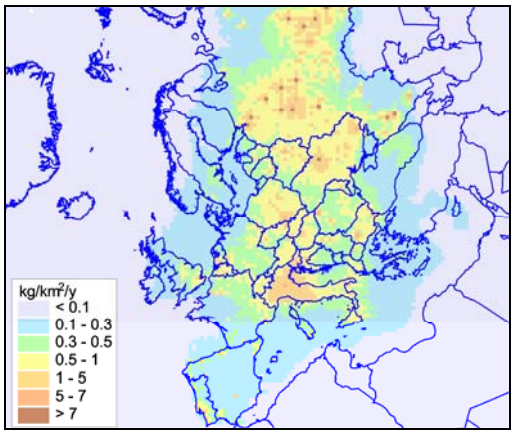

Fig. 58. *Spatial distribution of nickel deposition flux in 1996*

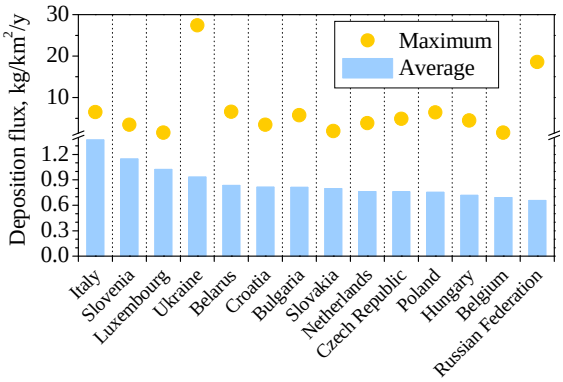

Fig. 59. *Average and maximum nickel deposition fluxes in some European countries in 1996*

Fig. 60 demonstrates chromium deposition fluxes in Europe in 1996. In the major part of Europe deposition levels vary within 0.03–0.5 kg/km^2/y. High levels are estimated in countries located in the Southern and Central parts of Europe. Depositions to marginal sea basins do not exceed 0.15 kg/km^2/y.

The highest mean values chromium deposition (about 0.4 kg/km^2/y) is estimated in Luxembourg, Belgium and Germany (see Fig. 61). At the same time maximum deposition fluxes in some regions of Germany, Poland, Russia, the Ukraine and the Netherlands exceed 2 kg/km^2/y.

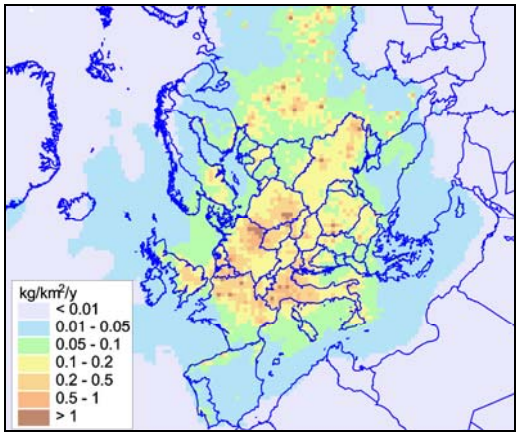

Fig.60. *Spatial distribution of chromium deposition flux in 1996*

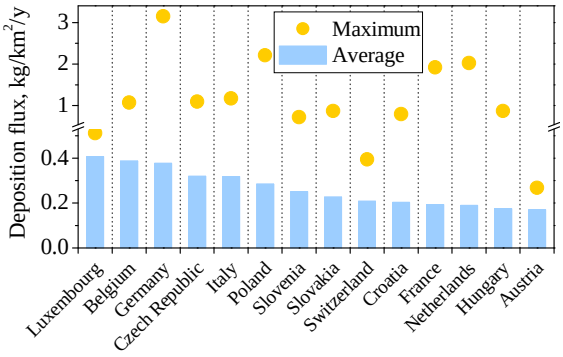

Fig. 61. *Average and maximum chromium deposition fluxes in some European countries in 1996*

Working Group on Effects

MSC-E in 2003 continued the assessment of cadmium, lead and mercury deposition to different surface types (forests, arable lands, pastures, water surface etc.) agreed with Coordination Center for Effects. Deposition levels of heavy metals to each type of the surfaces within the EMEP domain are estimated for the period of 1990-2001. The obtained results are meant for the Working Group on Effects for the elaboration of critical load approach for different ecosystems.

Fig. 62 illustrates the distribution of total annual cadmium deposition between different ecosystems of Europe in 2000. For the sake of comparison the internal circle of the diagram shows fractions of European territory occupied by different ecosystems. Half the total cadmium deposition is accounted for agricultural lands; an essential part is also accounted for forests due to vast areas covered by these ecosystems in Europe. Cadmium deposition to other ecosystem types is not higher than 15% of the total value.

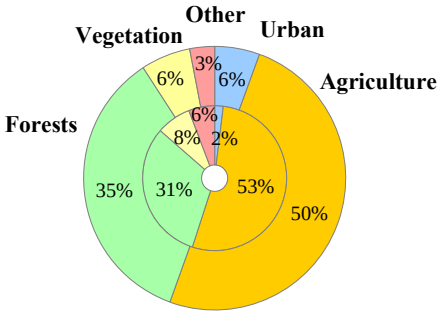

Fig. 62. *The fraction of total annual cadmium deposition to different ecosystems in Europe in 2000. The internal circle illustrates the share of relevant ecosystems in European territory*

Fig. 63 illustrates spatial distribution of cadmium annual deposition intensity to agricultural land of Europe in 2000. High deposition levels are estimated in countries of the Central, Southern and Eastern Europe. It is in line with a general pattern of cadmium deposition to European region. The deposition value does not exceed 80 g/km^2/y over 65% of territory covered with agricultural lands (see the incut).

Fig. 64 shows the distribution of cadmium deposition intensity over European forests. Upon the whole the pattern is similar to that of cadmium deposition to agricultural lands though in this case the levels are somewhat higher. It is connected with the fact that forests more efficiently capture atmospheric aerosols carrying cadmium. On the major part of the territory (more than 60%) covered with forests deposition levels vary within the range of 40–120 g/km^2/y.

Detailed information on cadmium, lead and mercury depositions to different European ecosystems is presented in EMEP/MSC-E Technical Report [*Ilyin and Travnikov*, 2003].

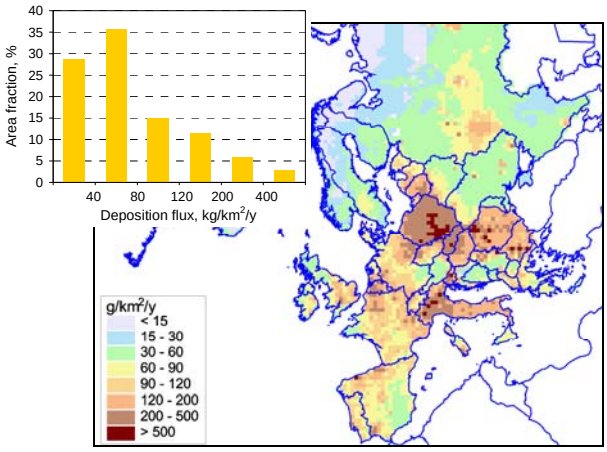

Fig. 63. Spatial distribution of cadmium annual deposition flux to agricultural land of Europe in 2000. The incut illustrates quantitative distribution of deposition value over agricultural land area

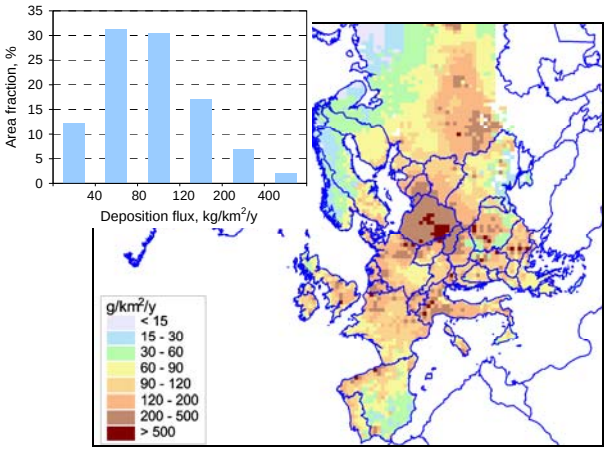

Fig. 64. Spatial distribution of annual cadmium deposition flux to European forests in 2000. The incut illustrates quantitative distribution of deposition to the forest area

3.2. Co-operation with international organization and programmes

Helsinki Commission

MSC-E in 2003 continued its co-operation with the Baltic Marine Environment Protection Commission. Under the Contract between EMEP Centres and HELCOM the assessment of cadmium, lead and mercury depositions to the Baltic Sea and its catchment area was carried out for the period from 1996 - 2001. The results are to be presented in EMEP Centres' joint report for HELCOM.

Spatial distribution of lead deposition fluxes to the Baltic Sea basin in 2000 is shown in Fig. 65. The highest depositions are characteristic of the Gulf of Finland, coast of Poland and Kaliningrad Region as well as the Kattegat. The figure shows the contribution of different countries to lead deposition in these Baltic regions. The highest contribution to depositions to the Gulf of Finland is made by Russia (45%) and Estonia (30%); to the South-Eastern coast of the Baltic Sea – Poland (60%) and Germany (17%); to the Kattegat – Germany (22%) and the United Kingdom (18%).

In addition the assessment of lead, cadmium and mercury depositions to other regional seas (the North Sea, the Mediterranean Sea, the Black Sea, the Sea of Azov and the Barents Sea) is made. Fig. 66 shows mean values of depositions of the three metals to the sea basins of marginal seas. As it is evident the highest deposition of lead is estimated for the Black Sea and the Sea of Azov. It is explained by the proximity of emission sources located in Eastern and Central Europe. Cadmium deposition to the Baltic Sea is also comparatively high due to the effect of Polish emission sources (see Section 2.1). The lowest lead and cadmium deposition to the Barents Sea is explained by its remote location from major emission sources. Mercury depositions to all the marginal seas are comparable by the value. It is explained by its high capability to be transported.

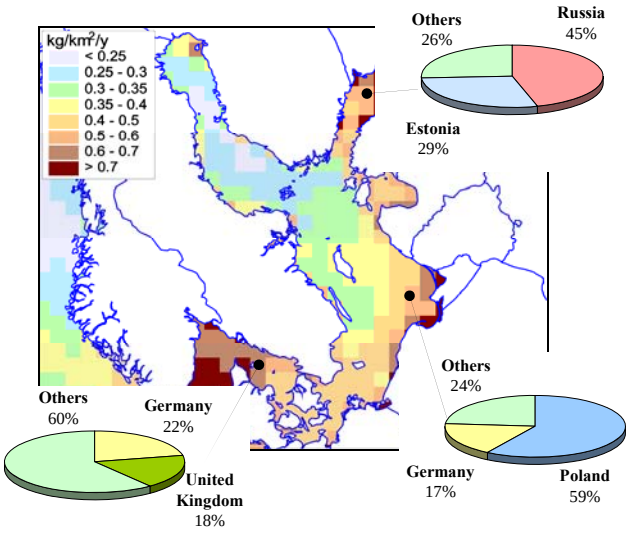

Fig. 65. Spatial distribution of annual lead deposition flux to the Baltic Sea basin area. The incuts illustrate individual countries' contribution to the pollution of different parts of the Baltic

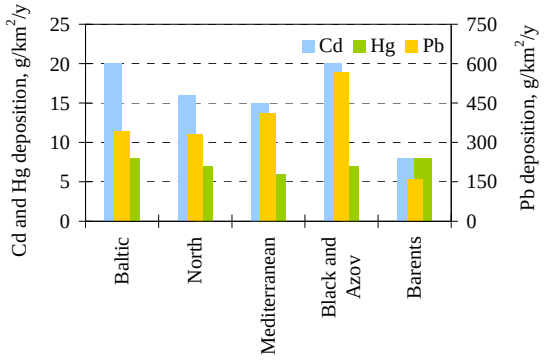

Fig. 66. *Mean deposition to regional sea areas of lead, cadmium and mercury*

Arctic Monitoring and Assessment Programme and World Meteorological Organization

On the basis of the Agreement between EMEP, AMAP and WMO MSC-E participated in the GEF[4] Project on Persistent Toxic Substances, Food Security and Indigenous People of the Russian North. Technical Report on Assessment of Long-Range Transport of Mercury, PCBs and γ-HCH to the Russian North [*Dutchak et al*., 2002], prepared by MSC-E under the Project, was approved by independent experts from Canada and Norway and accepted by the AMAP Secretariat in January 2003. The results obtained allowed to evaluate the levels of atmospheric mercury pollution in five Northern regions of the Russian Federation and the Arctic as a whole. Apart from that, the regions of the Northern Hemisphere contributing greatly to the pollution of the Arctic were revealed. The Technical Report and its Executive summary were discussed at the 4th Meeting of EMEP Task Force on Measurements and Modelling (Valencia, Spain, April 2003).

United Nations Environment Programme

A representative of MSC-E participated as a member of Global Mercury Assessment Working Group organized under UNEP. In the framework of this activity MSC-E carried out the assessment of mercury dispersion in the Northern Hemisphere, and evaluated air concentration levels as well as deposition fluxes of mercury to the ground surface. The calculation results were included in the Global Mercury Assessment, which was presented and approved at the 22nd Session of UNEP Governing Council (Nairobi, Kenya, February 2003).

3.3. Co-operation with national experts

MSC-E continued the activities on the development and verification of MSCE-HM model in the framework of the multi-stage project on the intercomparison of mercury transport models, elaborated by experts representing different scientific groups. In 2003 the second stage of the project was finalized – it was devoted to the intercomparison of modelling results with short-term (1-2 weeks) atmospheric mercury measurements. Scientific groups of experts from Germany, the USA, Canada, Bulgaria, Denmark and MSC-E took part at this stage of the comparison. The intercomparison results of model assessments with the use of measurement data were analyzed, the reasons for discrepancies were revealed, and the ways to improve model approaches were suggested. The results of the second stage of the comparison were presented in the EMEP/MSC-E Technical Report [*Ryaboshapko et al.*, 2003].

MSC-E exchanges information with national experts and programmes in the field of assessment of environmental pollution by heavy metals. The calculated data on lead, cadmium and mercury depositions to the territory of Germany were provided to the Karlsruhe University (Germany) and were used for the assessment of heavy metals inflow to German river basins.

On the request of UN ECE Working Group on Environmental Monitoring MSC-E prepared and presented data on emissions and transboundary heavy metal pollution of Kazakhstan (Almaty, Kazakhstan, May 2003).

[4] Global Environmental Facility (www.gefweb.org)

CONCLUSIONS

The EMEP Centres' activities in the field of monitoring and modelling of heavy metals in 2003 were aimed at investigation of the pollution of the European region and the Northern Hemisphere as well as at the assessment of pollution trends in the last decade. The main conclusions and perspective directions of the studies are formulated below.

Emissions of heavy metals

In the majority of European countries emissions of heavy metals tend to decline in the period of 1990-2001. The total emission in Europe has reduced approximately 3.3 times, cadmium – 1.8 times and mercury - 2 times.

Monitoring of heavy metals

1. The analysis of available long-term measurements demonstrated an essential decrease of concentration levels of lead and cadmium during 1989-2001

2. Measurements of heavy metal pollution levels in 2001 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.

3. At present the EMEP monitoring network contains 65 stations measuring lead and cadmium, of which 22 stations measure concentrations of these metals both in air and precipitation. There are 15 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.

4. Annual analytical intercomparisons of national laboratories treating measurements of heavy metals indicate an essential improvement of data quality during the period of 1995-2002.

Model assessment of pollution levels

1. According to the modelling results the emission reduction resulted in the decrease of heavy metal depositions over the major part of European territory. On the whole in the period from 1990 to 2001 lead deposition in Europe decreased 2.7 times, cadmium and mercury – 1.5 times. Less essential decrease of depositions in comparison with the anthropogenic emission reduction is conditioned by the contribution of natural sources, re-emission as well as by global sources of heavy metals.

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. Non-uniform emission reduction of heavy metals in European countries brings about strengthening the role of the transboundary transport in countries where the reduction rate is most essential.

4. The highest absolute values of the transboundary transport are estimated for countries with large territories and for countries bordering powerful emission sources. In countries with insignificant national emission the relative contribution of the transboundary transport to deposition of lead can exceed 70% of the total value, cadmium – 50% and mercury – 40%.

5. Mercury is a pollutant capable to the global transport. The contribution of the intercontinental transport to mercury depositions over Europe is about 40% of the total value. Asian sources and mercury emissions from the ocean surface play the most important role.

6. About half the mercury deposition to such a remote region as the Arctic is due to the transport from anthropogenic emission sources, of which the greatest contribution make Asian and European sources. The phenomenon of Mercury Depletion Events plays a special role in the contamination of the Arctic region and it is responsible for up to 50% of total deposition in the coastal regions of the Arctic Ocean.

7. The regional and hemispheric transport models used for evaluation of the pollution levels are validated by means of comparison with

measurement data, sensitivity analysis and intercomparison with other models. The validation results demonstrate applicability of the models for the assessment of heavy metals pollution in Europe and in the Northern Hemisphere.

Co-operation

1. Pilot calculations of European pollution by the second priority heavy metals (nickel and zinc) were performed. The computation results were presented at the meeting of the Expert group on heavy metals (Working Group on Strategy and Review).
2. Atmospheric pollution loads on different ecosystems in Europe were assessed. The obtained results are meant for the Working Group on Effects for the development of critical loads approach.
3. Deposition levels of heavy metal to marginal seas were estimated. The obtained data on Baltic pollution were used in joint EMEP Centres' Report for HELCOM.
4. Levels of mercury pollution of the Arctic region were assessed in the framework of co-operation between EMEP, AMAP and WMO.
5. The activity within the framework of multi-stage project on the intercomparison of mercury transport models is continued. The second stage of the project dedicated to the comparison of modelling results with short-term measurements of mercury in the atmosphere is finished.
6. On the request of UN ECE Working Group on Environmental Monitoring MSC-E prepared and presented data on emissions and transboundary heavy metals pollution of Kazakhstan (Almaty, Kazakhstan, May 2003).

Perspective directions

The following directions of the development of heavy metal pollution modelling are considered to be important.

1. Development of the multi-compartment approach to mercury transport modeling. Such approach is essential for the evaluation of mercury circulation and accumulation in the environment.
2. Development of the model parameterization and assessment of the environment pollution by heavy metals of the second priority (arsenic, chromium, nickel, zinc, copper).
3. Further activities connected with the composite model validation including the comparison with measurement data, sensitivity analysis and intercomparison with other models.

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Annex A

EMEP WORK-PLAN FOR 2003

EMEP work-plan elements in 2003 [ECE/EB.AIR/77/Add.2]

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.

Main activities and time schedule

(a) MSC-E will prepare information for 2001 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 furthermore present: 1990-2000 pollution trends for Pb, Cd and Hg; estimates for Hg atmospheric transport on a hemispheric scale; and, in co-operation with CCE, critical load exceedance maps for Pb and Cd. In co-operation with CCC, it will compare modelling results with monitoring data;

(b) MSC-E will further develop its models and its input data. It will, in particular, improve the parameterization of: Hg behaviour in environmental compartments; Pb, Cd, Hg dry deposition to different underlying surfaces; wet removal processes; and mercury atmospheric chemistry. 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;

(c) In co-operation with Parties, CCC will enhance the completion of the superstation network (about ten monitoring sites in defined areas). It will complement EMEP data with data from other international programmes. It will report on the intercomparison for sampling and analytical techniques for Hg and on the analytical intercomparison of the other seven heavy metals measured in precipitation. An intercomparison study on mercury will, if possible, be organized by Germany;

(d) MSC-E will prepare gridded anthropogenic emission data, based on officially submitted data and expert estimates, and collect available data on natural emissions. CCC and MSC-E, in consultation with national experts, will adjust European Hg emission inventories to modelling requirements. CCC will develop profiles of chemical species of heavy metal emissions.

MSC-E activity in the field of heavy metals

Activity	Results
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 2001 • Transboundary fluxes of Cd, Pb and Hg between European countries and fluxes to regional seas are specified. • Levels of pollution by Cd, Pb and Hg in European countries from 1990 to 2001 are analyzed. • 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 validation	• Cd, Pb and Hg calculated and measured concentrations in the surface air and precipitation in European region for the period from 1990 to 2001 are compared. • Modelling results of Hg transport in the Northern Hemisphere are compared with data measured at the EMEP monitoring stations, NADP/MDN and during short-term measuring campaigns. • The intercomparison of Hg transport models is continued. The second stage of the comparison is finalized and preparatory work for III and IV stages is done.
Development of model approaches	• Parameterization of Cd, Pb and Hg dry deposition to different underlying surfaces is refined. • Hg chemical scheme and the parameterization of Hg transformation processes in the atmosphere are refined. • An approach to the parameterization of Hg behavior in the marine environment is developed. • The advection scheme of the regional model providing a way to consider the surface orography is improved. Provisional calculations are made. • The parameterization of model processes is made and tentative calculations of two metals of the second priority (nickel and chromium) are performed.
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. • Parameterization of Hg natural emission is refined.

Annex B

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 five non-uniform layers and covers the entire planetary boundary layer and a part of the free troposphere (up to 4 km). 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 irregular terrain-following layers up to the lower stratosphere (Fig. B.2).

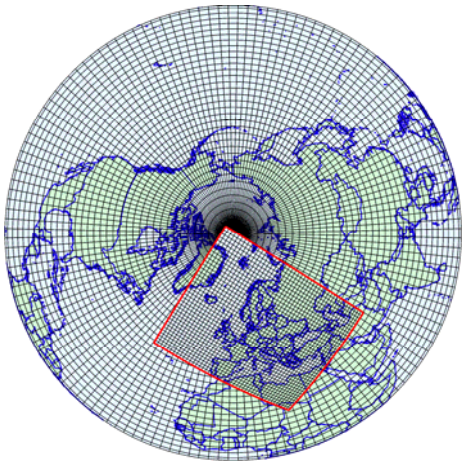

Fig. B.1. *Horizontal structure of the regional and hemispheric model domains. Red line depicts the EMEP region*

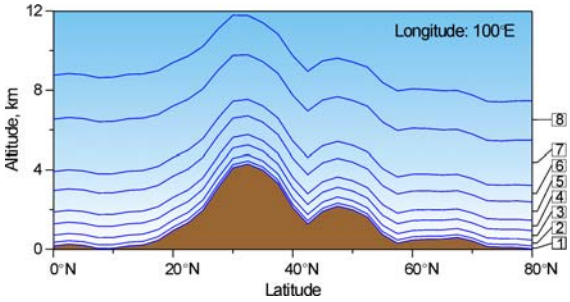

Fig. B.2. *Vertical grid structure of the hemispheric model domain*

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.

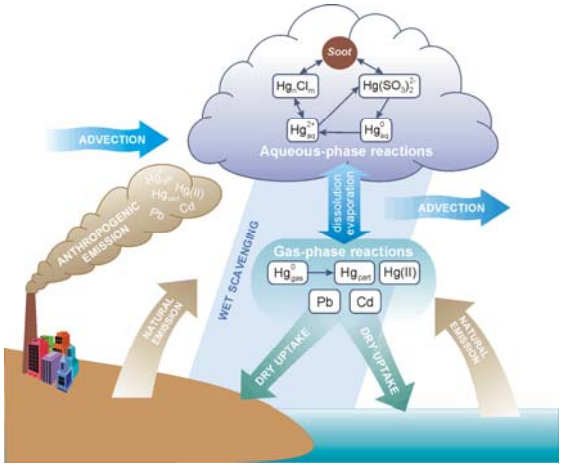

Fig. B.3. *The model scheme of heavy metal behaviour in the atmosphere*

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 dissolved forms – elemental dissolved Hg^0_{dis}, mercury ion Hg^{2+}, sulphite complex $Hg(SO_3)_2^{2-}$, and aggregate chloride complexes Hg_nCl_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 formation of sulphite complex, and adsorption by soot particles in droplet water. Mercury forms are removed from the atmosphere by means of surface uptake and precipitation scavenging.

Model modifications

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

- The model parameterization of dry uptake of Pb, Cd, and Hg by the underlying surface is been improved. The underlying surface specification of 15 types is included in the models.
- The model scheme of Hg chemical transformations is enhanced. Chemical reactions of Hg oxidation by chlorine over marine surface are incorporated.
- Preliminary work on parameterization of Hg behavior in the marine environment is conducted.
- Advection scheme of the regional model is improved to take into account the surface orography. Pilot calculations are performed.
- Model parameterization of the atmospheric transport of two heavy metals of the second priority (nickel and chromium) is developed. Pilot calculations are conducted.

Detailed description of MSC-E regional and hemispheric models as well as their modifications can be found in the EMEP/MSC-E Technical Report [*Ilyin et al.*, 2003].