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Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury

Stage III. Comparison of modeling results with long-term observations and comparison of calculated items of regional balances

Alexey Ryaboshapko, Richard Artz, Russell Bullock, Jesper Christensen, Mark Cohen, Ashu Dastoor, Didier Davignon, Roland Draxler, Ilia Ilyin, John Munthe, Jozef Pacyna, Gerhard Petersen, Dimiter Syrakov, Oleg Travnikov

METEOROLOGICAL SYNTHESIZING CENTRE - EAST

Ul. Arhitektor Vlasov, 51, Moscow 117393 Russia
tel.: 7 095 128 90 98
fax: 7 095 125 24 09
e-mail: msce@msceast.org
Internet: www.msceast.org

THE AUTHORS (THE MODELS):

Richard S. ARTZ (HYSPLIT) Deputy Director NOAA Air Resources Laboratory 1315 East West Highway, SSMC3, R/ARL, Room 3316, Silver Spring MD 20910 USA tel: 301 713 09 72; fax: 301 713 01 19 e-mail: richard.artz@noaa.gov	**O. Russell BULLOCK, Jr.** (**CMAQ**) U.S. Department of Commerce, NOAA, Air Resources Laboratory (on Assignment to the U.S. EPA Office of Research and Development), Mail Drop 80 Research Triangle Park NC 27711 USA tel: 919 5411349; fax: 919 5411379 e-mail: bro@hpcc.epa.gov
Jesper CHRISTENSEN (**DEHM**) National Environmental Research Institute Department of Atmospheric Environment P.O.Box 358 DK-Roskilde DENMARK tel: 45 46 301175; fax: 45 46 301114 e-mail: jc@dmu.dk	**Mark COHEN** (**HYSPLIT**) NOAA Air Research Laboratory 1315 East West Highway SSMC 3 Room 3316, R/ARL Silver Spring MD 20910 USA tel: 301-7130295 x122; fax: 301-7130119 e-mail: mark.cohen@noaa.gov
Ashu DASTOOR (GRAHM) Modelling and Integration Research Division, Air Quality Research Branch, Meteorological Service of Canada, Environment Canada 2121 Trans-Canada Highway, 5th Floor Dorval, H9P 1J3 Quebec CANADA tel: 514 421 4766; fax: 514 421 2106 e-mail: ashu.dastoor@ec.gc.ca	**Didier DAVIGNON (GRAHM)** Modelling and Integration Research Division, Air Quality Research Branch, Meteorological Service of Canada, Environment Canada 2121 Trans Canada Highway, 5th Floor Dorval, Quebec H9P 1J3 CANADA tel: 514 421 7242; fax: 514 421 2106 e-mail: didier.davignon@ec.gc.ca
Roland R. DRAXLER (HYSPLIT) NOAA Air Research Laboratory 1315 East West Highway SSMC 3, Room 3316, R/ARL Silver Spring, MD 20910 USA tel: 301 713 02 95 x117; fax: 301 713 01 19 e-mail: roland.draxler@noaa.gov	**Ilia ILYIN** (**MSCE-Hg**) Meteorological Synthesizing Center “East” Ul. Arhitektor Vlasov, 51, Moscow 117393 RUSSIA tel.: +7 095 1289621; fax: +7 095 1252409 e-mail: ilia.ilyin@msceast.org
John MUNTHE (Measurements) Swedish Environmental Research Institute Dagjamningsgatan 1, P.O. Box 47086 S-40758 Goteborg SWEDEN tel: 46 31 725 62 00; fax: 46 31 725 62 90 e-mail: john.munthe@ivl.se	**Jozef PACYNA (Emission)** Norwegian Institute for Air Research NILU P.O.Box 100 2007 Kjeller NORWAY tel. 47 63 89 81 55; fax 47 63 89 80 50 jozef.pacyna@nilu.no
Gerhard PETERSEN (**ADOM**) GKSS - Research Centre, Institute of Hydrophysics Max-Planck-Strasse 1 D-21502 Geesthacht GERMANY tel: 49 41 52871847; fax: 49 41 52871888 e-mail: Petersen@gkss.de	**Alexey RYABOSHAPKO** (**MSCE-Hg**) Meteorological Synthesizing Center “East” Ul. Arhitektor Vlasov, 51, Moscow 117393 RUSSIA tel: +7 095 1289621; fax: +7 095 1252409 e-mail: alexey.ryaboshapko@msceast.org
Dimiter SYRAKOV (**EMAP**) National Institute of Meteorology and Hydrology Tzarigradsko chaussee 66 1784 Sofia BULGARIA tel: 3592 9753986; fax: 3592 9880380 e-mail: Dimiter.Syrakov@meteo.bg	**Oleg TRAVNIKOV** (**MSCE-Hg**) Meteorological Synthesizing Center “East” Ul. Arhitektor Vlasov, 51, Moscow 117393 RUSSIA tel.: +7 095 1289621; fax: +7 095 1252409 e-mail: oleg.travnikov@msceast.org

CONTENT

1. INTRODUCTION

Recently it was widely recognized that mercury is a hazardous heavy metal, which possesses unique characteristics in the environment. It enters the atmosphere from both anthropogenic and natural sources. It migrates through the environment in different physical-chemical states. It is chemically and biochemically active in soils, water bodies and in the atmosphere. Finally, mercury in the forms of its organic compounds can be accumulated it trophic chains. In these forms it is the most dangerous for human and animals whose diet is connected with fish and other fresh water or oceanic food.

Taking into account high jeopardy of mercury and its high mobility in the environment the 1979 Convention on Long-Range Transboundary Air Pollution included this metal into its consideration. The Protocol on Heavy Metal, which came into effect on December 2004, determines mercury as on of three metals of the first priority. A number of investigations shown that anthropogenic activity of recent centuries led to long-term accumulation of mercury in all main geospheres – the atmosphere, the pedosphere, the Ocean. To assess global biogeochemical aspects of mercury environmental cycle and pollution UNEP launched a project “Global Mercury Assessment”.

Complicated mercury behavior in the environment and diversity of its form make study of this metal especially difficult. In such cases numerical modeling becomes a powerful tool of investigations. One should also bears in mind that routine monitoring of mercury is very expensive, and that density of monitoring networks cannot be high. All these facts were recognized by a number of researchers and decision-makers. The Protocol on Heavy Metals considers the modeling approach as a basis for assessment of mercury transboundary pollution in Europe. It determined the main task for the European Monitoring and Evaluation Program (EMEP) in this field as follows: “EMEP shall, using appropriate models …., provide to the Executive Body for the Convention calculations of transboundary fluxes and depositions of heavy metals within the geographical scope of EMEP”. According to the Protocol, Meteorological Synthesizing Centre “East” (MSC-E) of EMEP has a responsibility to perform model calculations of transboundary transport and deposition of heavy metals over Europe.

By the moment many numerical models of different types were developed to evaluate mercury atmospheric transport and deposition on local, regional and global levels. They are widely used as purely scientific instruments or as applied methods to solve problems of local or national levels. It is understandable that the models can differ from each other depending on their complexities, their tasks and disposable financial potential. Natural questions arise: Can the models produce reliable results? How far are the modeling results from the available observations? To what extent different models are commensurable between each other?

Recognizing the importance of these questions the Steering Body of EMEP at its 18th session decided (EB.AIR/GE.1/24, 1994) that MSC-E had to organize an intercomparison study of atmospheric long-range transport models for heavy metals. Such a study is considered by the Steering Body to be one of the essential prerequisites for development and application of EMEP operational models. The mercury model intercomparison study was launched in 1999. The mercury intercomparison study is focused on:

- an evaluation of parameterizations of the main physical-chemical processes of mercury transformations in the gaseous and the liquid phase;

- a comparison of modeling results with measurements obtained from both short-term campaigns and from the EMEP monitoring network and other international and national programs;
- a comparison of the main features of long-range transport of different mercury forms.

Taking into account significant complexity of mercury models, necessity to consider main modeling processes separately it was decided to divide the program of the mercury model intercomparison study into three stages:

Stage I. Comparison of modules for physico-chemical transformations of mercury species in a cloud/fog environment with prescribed initial mercury concentrations in ambient air and other physical and chemical parameters relevant for atmospheric mercury transformations.

Stage II. Comparison of model results with observations during 1-2 weeks episodes. Hourly and daily averages and event based averages of mercury concentrations in air, obtained from the joint Swedish/Canadian/German field campaign TRANSECT 1995 and from the European Union Environment & Climate project Mercury Species Over Europe (MOE-1999) will be used.

Stage III. Comparison of model results with observed monthly and annual means of mercury concentrations in air and precipitation and deposition fluxes available from European monitoring stations in 1999. Comparison of model predicted atmospheric budgets of mercury species in the entire EMEP domain and for selected European countries (UK, Poland and Italy), including dry and wet deposition within and outside the area of the countries.

The first stage of the intercomparison study was started in 1999 and finished in 2001. In addition to the MSC-East four scientific groups from Germany, Sweden and the USA took part in the study. The results were presented in a MSC-East technical report [*Ryaboshapko et al.,* 2001] and published in scientific literature [*Ryaboshapko et al*., 2002].

The second stage started in 2001 is focused on comparison of modeled and observational results. The observations were performed at five measurement sites in Europe during two short-term campaigns in 1995 and 1999. In the first case main attention was paid to the mercury elemental form. In 1999 reactive gaseous and aerosol mercury were measured in addition to the elemental form. Seven scientific groups involved in atmospheric mercury modeling participated in the second stage. They represent all the most advanced scientific and operational mercury models of regional and global types known by the moment. The results of the second stage were analyzed and discussed in MSC-East reports (MSC-E 10/2002) and (MSC-E 1/2003). A corresponding scientific article is under preparation.

The last stage of the mercury model comparison combined performances of seven models of atmospheric mercury transport and deposition of regional and global levels. They are:

- GKSS-Forschungszentrum Geesthacht GmbH (Germany), the European mercury version of the Acid Deposition and Oxidants Model (ADOM).
- U.S. Environmental Protection Agency (USA), the Community Multi-Scale Air Quality (CMAQ) model.
- Environment Canada (Canada), Global/Regional Atmospheric Heavy Metals Model (GRAHM).
- National Ocean and Atmosphere Administration (USA), Hybrid Single Particle Lagrangian Integrated Trajectory model, version 4 (HYSPLIT_4)

- National Institute of Meteorology and Hydrology (Bulgaria), Eulerian Model for Air Pollution (EMAP)
- National Environmental Research Institute (Denmark), Danish Eulerian Hemispheric Model (DEHM)
- EMEP Meteorological Synthesizing Centre-East, MSCE Heavy Metal model, Hg version (MSCE-Hg).

In this case the EMEP model was presented by two versions: regional one – for EMEP domain, and global one – for the Northern Hemisphere.

The program of the third stage of the study met to the greatest degree the requirements of the 1979 Convention on Long-Range Transboundary Air Pollution. It was focused on answering two very important questions:

- To what extent can the current atmospheric mercury models of regional and global levels reproduce annual and monthly mean values of mercury concentrations and depositions observed in Central Europe at monitoring stations?
- What is accuracy of model assessment of separate items of mercury atmospheric balances for individual European countries?

To discuss the program of the third stage a workshop was organized in Moscow in April 2003. The participants discussed the volume of calculations, methods of their statistical processing, and formats of reporting data. All details were agreed and accepted as a working plan. The results of the last stage and the study as a whole were considered by the participants at the final workshop held in Moscow in April 2004 (MSC-East).

2. PROGRAM OF THE THIRD STAGE

The third stage of the mercury model intercomparison study aims to provide comparison of model results with monthly and annual mean measurements in 1999 and comparison of model predicted deposition budgets for selected European countries (UK, Poland, Italy). The participants of the workshop in Moscow (April 15-16, 2003) discussed and agreed the following program of the stage.

All the models, both regional and global ones consider Europe as the main modeling domain. The reference year is 1999.

The calculating parameters are:

- TGM in air (ng/m^3)
- Hg concentration in precipitation (ng/L)
- Precipitation amount (mm/month)
- Hg wet deposition (g/km^2/month)
- Hg dry deposition (g/km^2/month)
- Hg total deposition (g/km^2/month for a given geographical point or g/y for a given country).

Temporal resolution of the calculating parameters is 1 month for each selected monitoring station. Total depositions over selected countries are presented as monthly and annual values. The modelers are free to calculate the parameters for the whole year (12 months) or for some selected months. In the last case winter and summer months are chosen for the calculations.

Common subsidiary input parameters are:

- sulfur dioxide field with 50x50 km resolution (monthly mean values);
- ozone field with 50x50 km resolution (monthly mean values);
- soot field with 50x50 km resolution (monthly mean values);
- chlorine in the gas phase – fixed value of 100 ppt – within the lowest hundred meters over the ocean at night; zero above 100 m over the ocean at night; zero - during daytime; zero - over the continents;
- fixed value of pH of cloud water equal to 4.5;
- fixed value of chloride concentration in cloud water equal to 2.5 mg/l or $7x10^{-5}$ M;
- OH radical in cloud water - midday (maximum) concentration of OH radical – 10^{-12} M; at night-time the radical concentration is zero; sinusoidal trend during daytime.

Subsidiary input parameters to be used individually are:

- meteorological data sets;
- global concentration fields of SO_2, CO, NO_x, VOC_s, soot;
- boundary conditions (concentrations of modeled species at domain boundaries) for the regional models;
- initial concentration values for global (hemispheric) models.

The following monitoring stations are used for comparison of total gaseous mercury concentrations (TGM) in air:

- Pallas, FI96, Finland
- Mace Head, IE31, Ireland
- Zeppelinfjell, NO42, Norway
- Lista, NO99, Norway
- Rörvik, SE2, Sweden
- Zingst, DE9, Germany

The following monitoring stations are used for mercury concentrations in precipitation (total mercury):

- Westerland, DE1, Germany
- Zingst, DE9, Germany
- Pallas, FI96, Finland
- Rörvik, SE2, Sweden
- Lista, NO99, Norway
- Bredkälen, SE5, Sweden
- Vavihill, SE11, Sweden
- Aspvreten, SE12, Sweden

The following sets of emission data are commonly used:

- anthropogenic Hg^0, Hg^{+2} and HgP emission fields (50x50km) within EMEP domain for 2000, three vertical layers;
- global anthropogenic Hg^0, Hg^{+2} and HgP emission fields (1x1 degree) for 1995 in accordance with (Pacyna and Pacyna, 2002), one vertical layer;
- natural Hg^0 emissions from the land and the sea surface within EMEP domain, spatial resolution 50x50 km (prepared by MSC-E);
- global natural emission of Hg^0 from the continents and the World ocean, spatial resolution 1x1 degree (prepared by MSC-E);
- re-emission from land within EMEP region, spatial resolution 50x50 km (prepared by MSC-E)

The emission values are given as annual mean values without any seasonal variations.

For quantitative characterization of the comparison the following parameters are used:

- mean arithmetic value;
- correlation coefficient (measurements against calculations);
- relative bias;
- mean deviation factor.

3. THE MEASUREMENT DATA

There were only several monitoring sites where mercury concentrations were measured in 1999 in the framework of EMEP monitoring program. At five sites total gaseous mercury was measured in air. Sampling of precipitation to measure wet deposition of mercury was organized at nine EMEP sites. Unfortunately, only one site provides measurements of mercury in aerosol form (TPM). Moreover, this site was located far from European continent (Iceland). The locations of the measurements sites are given in Table 3.1.

Table 3.1. *Locations of the monitoring sites*

Station name	EMEP code	Country	Latitude	Longitude	Height, m
Total gaseous mercury concentrations in air					
Pallas	FI96	Finland	67° 58´ N	24° 07´ E	566
Mace Head	IE31	Ireland	53° 19´ N	10° 17´ W	5
Zeppelin	NO42	Norway	78° 54´ N	11° 53´ E	474
Lista	NO99	Norway	58° 06´ N	06° 34´ E	13
Rörvik	SE02	Sweden	57° 25´ N	11° 56´ E	10
Total mercury concentrations in precipitation					
Westerland	DE01	Germany	54° 55´ N	08° 18´ E	12
Zingst	DE09	Germany	54° 26 N	12° 44´ E	1
Rörvik	SE02	Sweden	57° 25´ N	11° 56´ E	10
Bredkälen	SE05	Sweden	63° 51´ N	15° 20´ E	404
Vavihill	SE11	Sweden	56° 01´ N	13° 09´ E	172
Aspvreten	SE12	Sweden	58° 48´ N	17° 23´ E	20
De Zilk	NL91	Netherlands	52° 18´ N	04° 30´ E	4
Lista	NO99	Norway	58° 06´ N	06° 34´ E	13
Pallas	FI96	Finland	67° 58´ N	24° 07´ E	566
Total particulate mercury (TPM)					
Storhöfdi	IS91	Iceland	63° 24´ N	20° 17´ W	118

Very conditionally the monitoring sites can be divided into 3 groups. The sites of Germany (DE01, DE09) and The Netherlands can be considered as “polluted” because they are located relatively close to strong anthropogenic sources. The second group is the “regional” sites located in southern Scandinavia (NO99, SE02, SE11, SE12) where anthropogenic effects caused by European anthropogenic sources are noticeable. The rest are “background” sites located in the Arctic and in the Atlantic.

Measured values of monthly mean concentrations of total gaseous mercury (TGM) in 1999 are presented in Table 3.2 and in Fig. 3.1 [*Ilyin et al*., 2001]. It should be mentioned that generally TGM concentrations reached their minimum during warm season.

Table 3.2. *Monthly mean concentrations of total gaseous mercury (TGM) in 1999, ng/m^3*

Station: code, name, country	Analyzer type	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec	Year
FI96 Pallas Finland	CV-AFS	1.50	1.60	1.85	1.60	1.40	1.30	1.23	1.33	1.10	1.30	1.38	1.50	1.42
IE31 Mace Head, Ireland	Tekran	1.83	1.70	1.85	1.64	1.60	1.69	1.57	1.51	1.54	1.90	1.96	2.10	1.74
NO42 Zeppelin Norway	Tekran	2.13	2.93*	1.83	2.60*	1.60	ND	ND	ND	1.75	1.20	ND	1.65	1.69*
NO99 Lista Norway	Tekran	1.80	1.70	2.10	1.90	1.60	ND	ND	ND	2.60*	1.50	1.80	1.70	1.76*
SE02 Roervik, Sweden	CV-AFS	1.35	1.33	1.43	1.47	ND	1.35	1.35	1.44	1.62	1.30	1.48	1.28	1.40

Note: ND – No Data

* - outliers

** - outliers are removed

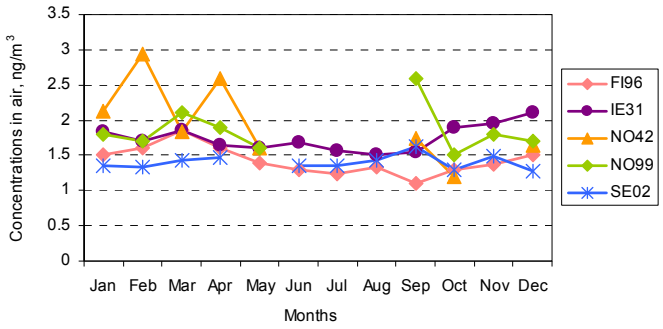


Fig. 3.1. *Measured values of monthly mean concentrations of total gaseous mercury (TGM) at EMEP sites in 1999, ng/m^3*

Consideration of Fig. 3.1 shows that the values measured at Norwegian sites NO42 and NO99 are very variable. At the Arctic site Zeppelin the mean concentration in February was extremely high - about 3 ng/m^3. This fact compels to have some doubts as to quality of the measurements. In accordance with advice of experts, who is responsible for EMEP data quality, it was decided to regard these values as outliers to remove them from database for the comparison (Torunn Berg, private communication). The TGM concentrations measured at SE02 stations seem to be relatively low, however, there are no ground to remove them from the database.

The measurement data have some uncertainty connected with terminology used. It is believed that Terkan method gives a possibility to measure "gaseous elemental mercury" (GEM) only. However, some experts think that in reality “total gaseous mercury” (TGM) is measured (Torunn Berg, private communication).

Concentrations of TPM measured at site Storhoefdi, Iceland in 1999 are shown in Table 3.3 and Fig. 3.2. The values are extremely low and make up less than 0.05% of mercury is the gaseous form. There is an obvious seasonal cycle of the TPM concentrations – the minimum values of 0.2-0.3 pg/m^3 are measured during autumn while the maximum – during winter and spring (0.8-0.9 pg/m^3).

Mercury concentrations in precipitation were measured only in Northern Europe – at one site in the Netherlands, at two sites of northern Germany and at six Scandinavian sites. All measurement results as mean monthly values are presented in Table 3.4 and Fig. 3.3.

Table 3.3. *Monthly mean concentrations of total particulate mercury (TPM) in 1999, pg/m^3*

Station: code, name, country	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec	Year
IS91 Storhoefdi, Iceland	0.78	0.92	0.78	0.79	0.41	0.78	0.49	0.24	0.31	0.23	0.19	0.49	0.53

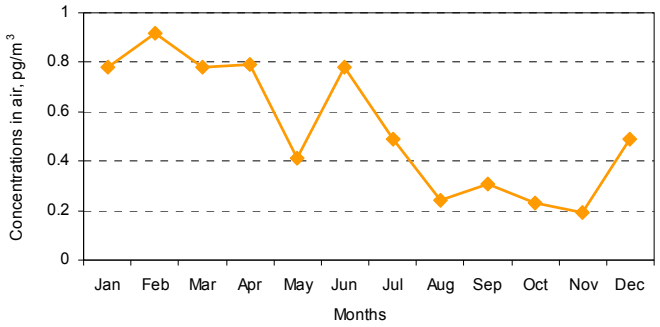


Fig. 3.2*. Concentrations of total particulate mercury (TPM) measured at EMEP site Storhoefdi (IS91), Iceland in 1999, pg/m^3*

Table 3.4. *Monthly mean concentrations of mercury in precipitation at EMEP monitoring sites in 1999, ng/L*

Month	DE01	DE09	NL91	NO99	SE02	SE11	SE12	SE05	FI96
January	16.7	12.0	8.4	8.8	7.3	13.0	4.5	4.8	2.4
February	12.5	11.0	8.7	8.1	8.9	10.8	8.5	2.4	3.3
March	6.7	8.3	11.9	9.1	11.4	20.5	11.7	4.5	4.9
April	12.2	14.7	13.9	11.8	9.0	13.2	7.2	3.8	5.8
May	9.2	19.8	23.0	17.5	18.7	9.7	9.0	6.6	4.5
June	35.8*	11.7	12.6	ND	11.1	9.9	ND	3.6	7.1
July	60.6*	13.0	16.6	8.5	12.7	11.6	36.9*	6.6	7.6
August	10.6	8.5	13.1	14.1	6.4	6.9	10.3	3.0	4.9
September	6.9	11.8	13.4	14.3	9.1	12.0	7.8	5.4	3.6
October	7.5	18.4	10.3	6.5	6.8	8.2	16.1	2.0	3.2
November	6.4	15.6	8.1	14.1	13.8	11.9	16.6	3.4	2.3
December	6.6	7.6	7.1	6.1	ND	9.3	7.6	4.3	3.3
Annual (without outliers)	9.5	12.7	12.3	10.8	10.5	11.4	9.9	4.2	4.4

ND – No Data;
* - outliers

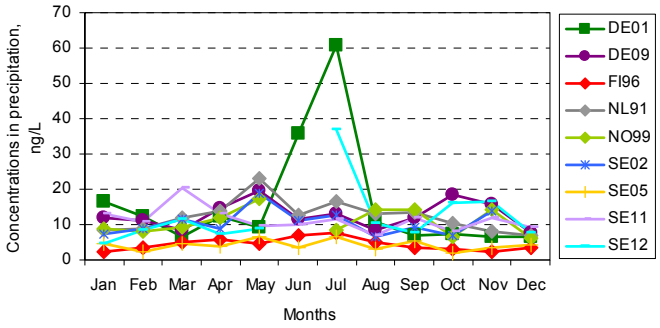


Fig. 3.3. *Monthly mean concentrations of mercury in precipitation at EMEP monitoring sites in 1999, ng/L*

Fig. 3.3 demonstrates that two values from German site DE01 and one value from Swedish site SE12 overstep the limits of typical variations. One can assume that these values are measuring outliers connected with any sampling or analytical problems (Torunn Berg, private communication). Removing the outliers from our consideration shows (Fig. 3.4) that the bulk of the measurement data is within the range from 2 to 20 ng/L. The curve of mean values for the whole region reveals no obvious seasonal trend.

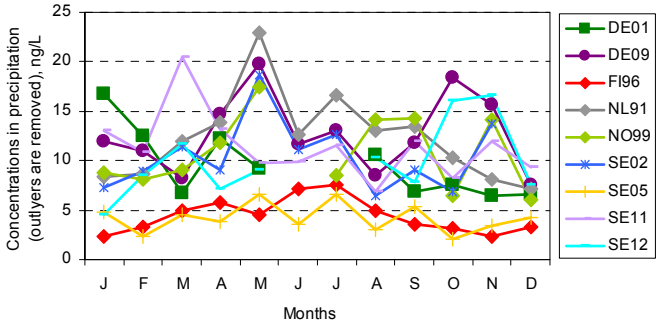
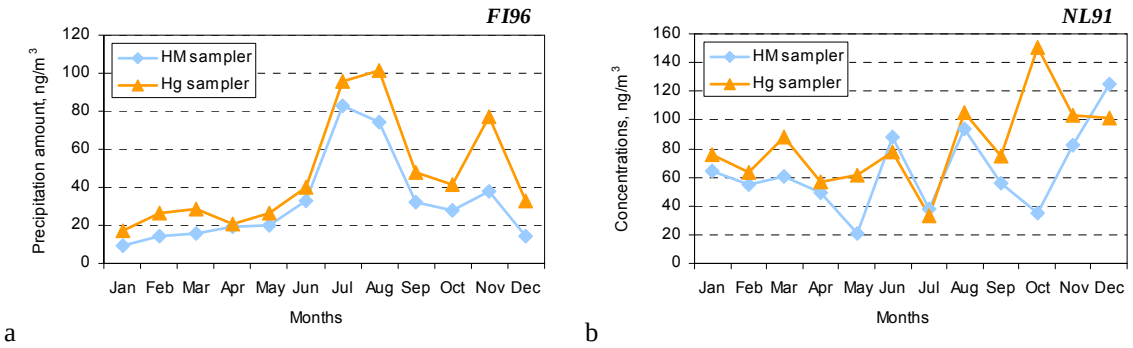


Fig. 3.4. *Monthly mean concentrations of mercury in precipitation at EMEP monitoring sites in 1999 without outliers, ng/L*

Northern location of the monitoring sites restricts considerably possibilities to reveal any spatial trends at different distances from the main European mercury sources. Nevertheless, annual values (without outliers) display higher concentrations at the polluted sites of Germany and The Netherlands while the minimum concentrations are characteristic of the most northern sites SE05 and FI96.

There are two problems, which can seriously complicate the procedure of comparison of the measured values and the modeling results for mercury wet deposition. The first one is connected with the fact that the sampling of precipitation was provided by two types of the instrument – bulk sampler and wet-only sampler. The experience obtained for acidifying compounds demonstrated that for remote sites of Northern Europe there was no statistically reliable difference between wet-only samplers and bulk samples [*Soederlund*, 1982; *Brukhanov et al*., 1991; *Jorander and Pedersen*, 1992; *Steadman et al*., 1990; *Granat,* Stockholm University, private communication]. One may assume that this is also true for heavy metals, however, there is no experimental evidence for this assumption. It is impossible to say what contribution of dry deposition is characteristic of the bulk samplers for mercury.

The second problem seems to be even more dramatic. The EMEP manual for sampling and analyzing (EMEP/CCC, 1995) prescribes strictly to use the precipitation amount data obtained only by a standard meteorological precipitation gauge. However, in practice the precipitation amounts are determined by different samples. Their designs can be very different. For example, at some sites four types of samplers are used: for acidifying compounds, for heavy metals (but mercury), for mercury and for POPs. In this work the precipitation amount data obtained by mercury sampler are used (as they have been published in EMEP reports). However, one can see how serious can be difference in precipitation amounts measured by different samplers from consideration of Fig.s 3.5 (a and b). At sites FI96 and NL91 the precipitation amounts were measured by samplers for mercury and for other heavy metals separately. For FI96 there is high correlation (r=0.95) but the total annual amounts differ very considerably (380 mm for HMs and 556 mm for Hg). At site NL91 the correlation is poor (r=0.30), however the total difference is smaller (769 and 991 mm, accordingly). For some individual months the difference between the samplers can exceed 2 times. It also should be mentioned that the measured annual precipitation amount at site SE12 (340 mm) seems to be atypically low for Central Sweden. Very probably this value was underestimated.



a b

Fig. 3.5. *Precipitation amounts collected by sampler for heavy metals (blue) and by sampler for mercury (orange): a) – site FI96; b) – site NL91*

Below for the comparison the precipitation amount values obtained by samplers for mercury will be used. Naturally, uncertainty in determination of precipitation amounts inevitably leads to corresponding uncertainty in determination of mercury wet deposition fluxes. It is understandable that a mercury transport / deposition model cannot produce output data better than the quality of the input information. This fact should be kept in mind when the measurement data are compared with the modeling results.

4. THE EMISSION DATA

Modern ideas on mercury cycling assume occurrence of three pathways of mercury into the atmosphere: natural emission, current anthropogenic emission and secondary anthropogenic re-emission from previously contaminated environmental compartments. Naturally, that all emission types can contribute to concentration and deposition values over Europe. There is an important difference between the emission types. It is believed that natural emission and re-emission are presented only by gaseous elemental mercury (GEM). Industrial high-temperature sources can emit mercury in three forms: GEM, reactive gaseous mercury (RGM) and mercury within particulate matter. The latter is called as usual "total particulate mercury" or TPM.

Direct anthropogenic emission over European continent for 2000 was estimated by *J.Pacyna* and his colleagues [*Pacyna et al*, 2003]. It was decided that the difference in emissions of 1999 and 2000 should be insignificant. Hence, the 2000 emission data can be applied for the modeling result comparison with the 1999 measurement data without any corrections. The data consist of mercury emissions from individual point sources within Europe and national total emission values for area sources in European countries. It was assumed that all area sources emit mercury into the lowest atmospheric layer near the ground. All the emission height data for point sources are divided into three vertical layers: below 50 m, 50-100 m and upper than 100 m. All the area sources have the same mercury speciation ratio: GEM - 80%, RGM - 15%, and TPM - 5%. As for the point sources, each of them has its individual mercury speciation ratio. It this case Hg^0 contribution can vary from 20% (waste disposal) to 80% (cement production). The emission data are estimated on annual basis believing in absence of any seasonal cycle of the anthropogenic activity.

The direct anthropogenic emission was spatially distributed over the EMEP domain with 50x50 km resolution (the EMEP grid). The emission field is shown in Fig. 4.1. Naturally, that all point sources were strictly attributed to the corresponding grid cells. National area sources were distributed over the grid in proportion to population density. Generally, the European direct anthropogenic emission in 2000 made up 239 t/y including 162 t/y from individual point sources (power plants, non-ferrous and ferrous foundries, cement kilns, caustic soda plants) and 77 t/y from area sources (combustion in residential heat boilers, oil combustion, waste disposal and other sources).

The intercomparison program suggests consideration of atmospheric mercury balances for three individual countries: UK, Italy and Poland. For this task the anthropogenic emission field should be obtained individually for all these countries. To do this the emissions of area sources in all boundary cells were divided between neighboring countries in proportion to the territory share. Naturally, the individual point sources were attributed to this or that country in accordance with their co-ordinates. Total national anthropogenic mercury emissions in 2000 were 8.54 t/y in the UK, 9.78 t/y in Italy and 25.6 t/y in Poland [*Pacyna et al.*, 2003].

Assessment of global distribution of mercury emission was done for 1995 [*Pacyna and Pacyna,* 2002]. On the global level the total anthropogenic emission changed between 1995 and 1999 insignificantly [*Pacyna et al*., 2003). Rather high increase of the emission in South-Eastern Asia was compensated by emission reduction in developed countries. Taking this fact into account it was decided to use for the comparison study the 1995 global emission data for 1999 without any corrections. The global emission was also shared between three mercury forms, however, the data were not divided according to emission heights. Over the globe the emission was distributed with spatial resolution of

1x1 geographical degree. The map of the anthropogenic mercury emission distribution for the globe in 1995 is presented in Fig. 4.2. *E.Pacyna and J.Pacyna* [2002] estimated the worldwide anthropogenic emission by value of 1913 t/y in 1995.

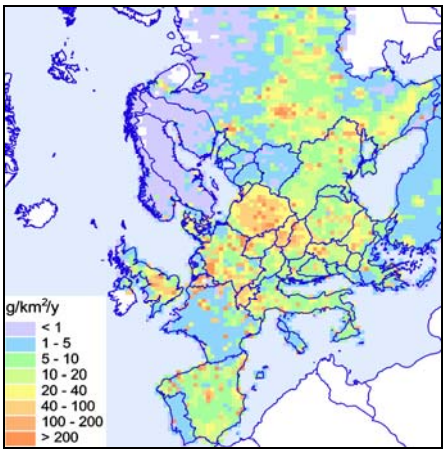


Fig. 4.1. *Spatial distribution of mercury anthropogenic emission over Europe with 50x50 km resolution in 2000, g/km^2/y*

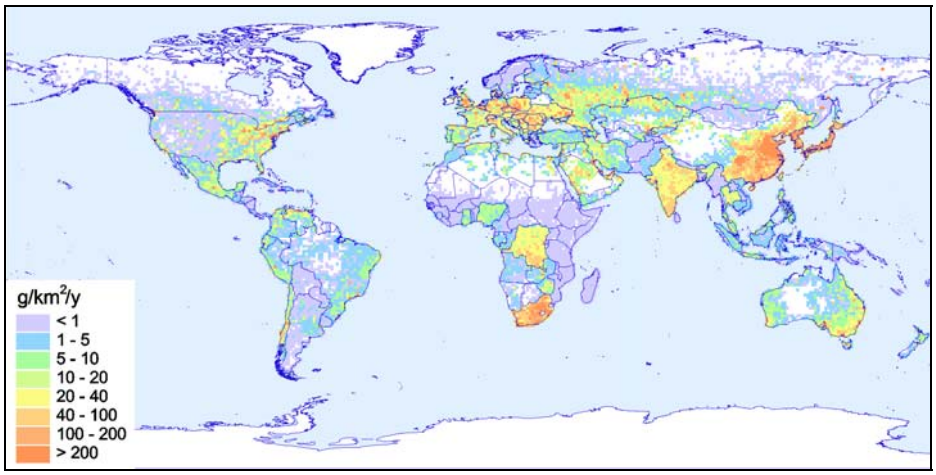


Fig. 4.2. *Spatial distribution of mercury anthropogenic emission over the globe with 1x1 degree resolution in 1995, g/km^2/y*

It is well known that the oceanic surface is permanent source of elemental mercury to the atmosphere. The current global mercury emission from the oceanic surface was estimated by the value of 2000 t/y [*Seigneur et al*., 2001]. There are some evidences that the emission intensity from water surface depends on biological activity within the surface water layer [*Kim and Fitzgerald*, 1986, *Costa and Liss*, 1999]. Taking this fact into account *O.Travnikov and A.Ryaboshapko* [2002] distributed the emission from the Ocean spatially based on spatial distribution of primary biological production of organic carbon [*Behrenfeld and Falkowski*, 1997, available through http://marine.rutgers.edu/opp].

Mercury always was presented in the surface layer of the lithosphere (soils, rocks). Accordingly always occurred natural flux of mercury to the atmosphere from continental surfaces. *C.Seigneur et al.* [2001] estimated this mercury flux as 2000 t/y. Measurements of the intensity of this flux in different places under different conditions show that the main controlling factors are mercury content in

soils/rocks and surface temperature [*Gustin et al.*, 1999]. On this basis *O.Travnikov and A.Ryaboshapko* [2002] distributed the emission from the continents. The map of spatial distribution of annual natural mercury emissions from oceanic and land surfaces over the globe is presented in Fig. 4.3. Because natural emission intensity is a function of temperature such maps were constructed separately for each month.

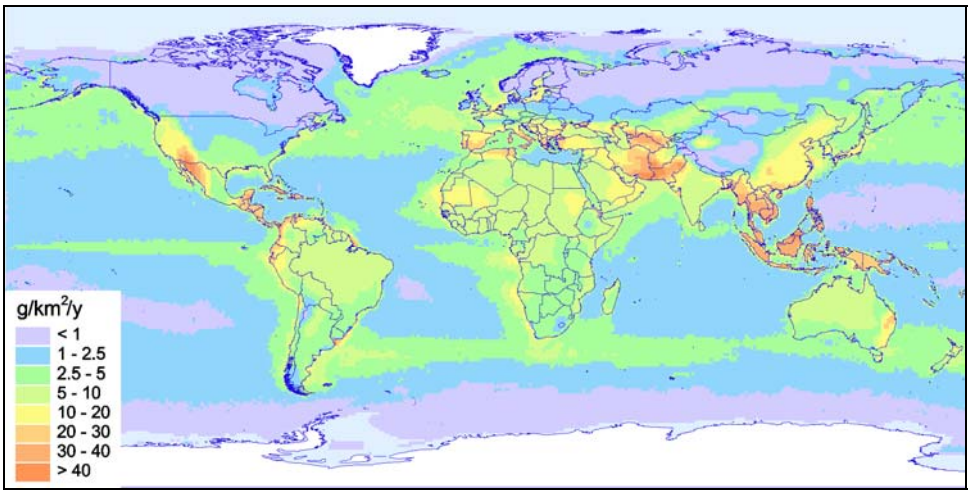


Fig. 4.3. *Spatial distribution of mercury natural emissions from oceanic and land surfaces over the globe with 1x1 degree resolution, g/km²/y*

Natural emission in Europe is distributed unevenly. The main reason of that is occurrence of mercury geochemical anomaly in southern part of the continent where mercury content in soils can be an order of magnitude higher than in the North. Because this study is focused on comparison with European monitoring sites, the natural emission field for the EMEP domain was obtained with finer resolution – 50x50 km in the EMEP grid. Such an emission field (on annual basis) is shown in Fig. 4.4.

Intensive anthropogenic emissions of mercury over Europe and consequent depositions during at least two centuries led to mercury accumulation in European soils. In its turn elevated mercury content in soils leads to mercury re-emission to the atmosphere. *A.Ryaboshapko and I.Ilyin* [2001] estimated the current re-emission flux for Europe as 50 t/y. Assuming that re-emission intensity should be proportional to cumulative depositions they distributed this value over Europe. The map of re-emission over Europe is shown in Fig. 4.5. One can mention that for some grid cells in Central Europe the re-emission intensity is of the same values as the current anthropogenic emission (see Fig. 4.1). It is reasonable to think that the re-emission intensity should be a function of temperature and, consequently, should have a seasonal cycle. However, in this work the intensity is accepted to be constant through the year.

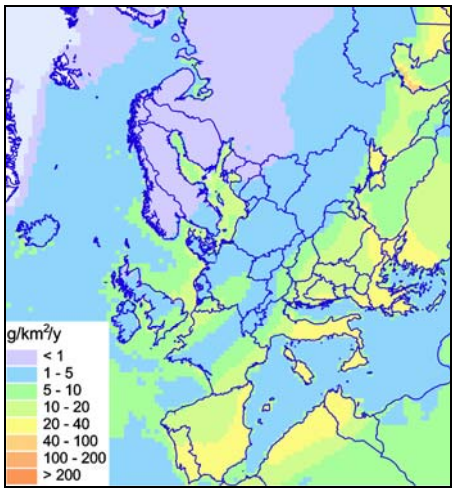


Fig. 4.4. *Spatial distribution of mercury natural emissions from oceanic and land surfaces over the EMEP domain with 50x50 km degree resolution, g/km^2/y*

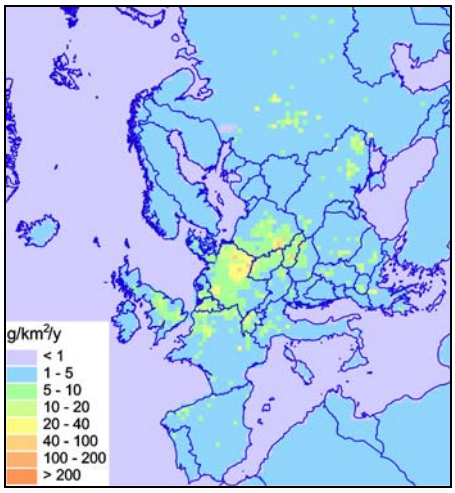


Fig. 4.5. *Spatial distribution of mercury re-emission over Europe for the end of XX century with 50x50 km degree resolution, g/km^2/y*

For the calculations of mercury transport and depositions the corresponding fields of mercury emissions in different physico-chemical forms have been added. It is extremely difficult to assess degree of uncertainty of the total emission in individual grid cells. One can believe that the most accurate data are for European anthropogenic sources, which are the main contributors to the mercury emission within the area of locations of monitoring sites.

5. METEOROLOGICAL DATA AND OTHER INPUT INFORMATION

It was agreed that all the models should use their own input meteorological data. Model ADOM is based on the meteorological data, produced by HIRLAM meteorological model, which uses ECMWF analyses. Model GRAHM is based on Canada's operational Global Environmental Multiscale (GEM) model at Canadian Meteorological Centre [*Dastoor and Larocque*, 2004]. MSCE model uses data of NCEP/NCAR Re-analysis project. The same source of meteorological data is used by HYSPLIT, EMAP, and CMAQ. DEHM model also based on analyses fields of ECMWF, which are processed by MM5 meteorological system.

All the models use different chemical schemes of mercury transformations in the atmosphere. To avoid additional uncertainties it was decided to use the same information on concentrations of different reactants. Common subsidiary input parameters are:

- sulfur dioxide field with 50x50 km resolution (monthly mean values);
- ozone field with 50x50 km resolution (monthly mean values);
- soot field with 50x50 km resolution (monthly mean values);
- chlorine in the gas phase – fixed value of 100 ppt – within the lowest hundred meters over the ocean at night; zero above 100 m over the ocean at night; zero - during daytime; zero - over the continents;
- fixed value of pH of cloud water equal to 4.5;
- fixed value of chloride concentration in cloud water – 2.5 mg/L or 7×10^{-5} M;
- OH radical in cloud water - midday (maximum) concentration of OH radical – 10^{-12} M; at night-time the radical concentration is zero; sinusoidal trend during daytime.

Some input parameters should be chosen by the modelers. Subsidiary input parameters to be used individually are:

- boundary conditions (concentrations of modelled species at domain boundaries) for the regional models;
- initial concentration values for global (hemispheric) models.

6. DESCRIPTIONS OF THE PARTICIPATING MODELS AND THE CALCULATION RESULTS

The participating models were designed to solve different problems of mercury pollution of the environment. Depending on the tasks solved the models operate with different domains. Such models like ADOM, EMAP, MSCE-Hg deal with European region. CMAQ and HYSPLIT models were developed to simulate mercury transport over North American continent. The other models (GRAHM, DEHM and MSCE-Hg-Hem) can be considered as models of global type. The participating models comprise a regional Lagrangian formulation as well as Eulerian approaches employing extensive gas- and aqueous phase chemical mechanisms and explicitly tracking numerous species concentrations. Lagrangian models are usually formulated under assumptions of simplified turbulent diffusion, no convergent flows and no wind shear. In these approaches only first-order chemical reactions can be treated rigorously. However, the Lagrangian approach avoids many of the computational complexities associated with the simultaneous solution of many differential equations; this generally results in requiring significantly less computational resources and can facilitate an understanding of problems that do not require descriptions of interactive non-linear processes. However, the most of the models are based on Eulerian approach. These approaches employ extensive gas- and aqueous phase chemical mechanisms and explicitly track numerous species concentrations. Also, a more detailed numerical formulation of physical and chemical processes occurring within and below precipitating and non-precipitating clouds is included. Typically, these models contain modules designed to calculate explicitly the chemical interactions that move gas-phase species into and among the various aqueous phases within clouds as well as calculate the aqueous-phase chemical transformations that occur within cloud- and precipitation droplets. The main properties of the participating models are presented in Table 6.1.

Table 6.1. *Main properties of the participating models*

Model	Type	Model height, m	Resolution	Boundary concentrations			Oxidants		Reductants
				Hg^0, ng/m^3	RGM, pg/m^3	TPM, pg/m^3	Gas phase	Liquid phase	Liquid phase
CMAQ-Hg	Eulerian - Regional	15,000	36x36 km	1.67*	18*	10*	O_3, H_2O_2, Cl_2, $OH^•$	O_3, $OH^•$, Cl_2	$SO_3^=$, hv, HO_2
ADOM	Eulerian - Regional	10,000	55x55 km	1.88	0.2	20	O_3	O_3	$SO_3^=$
HYSPLIT	Lagrangian - Regional	15,000	36x36 km 108x108 km	-	-	-	O_3, H_2O_2, Cl_2, HCl	O_3, $OH^•$, Cl_2	$SO_3^=$, HO_2
EMAP	Eulerian - Regional	5,000	50x50 km	1.5	No	No	O_3, $OH^•$	O_3	$SO_3^=$
GRAHM	Eulerian - Global	30,000	1x1 degree	Calculated by the global model			O_3	O_3	$SO_3^=$
DEHM	Eulerian - Hemispheric	15,000	50x50 km 150x150 km	Calculated by hemispheric model			O_3	O_3	$SO_3^=$
MSCE-Hg	Eulerian - Regional	3,900	50x50 km	Calculated by hemispheric model			O_3	O_3	$SO_3^=$
MSCE-Hg-Hem	Eulerian - Hemispheric	12,000	2.5x2.5 degree	No	No	No	O_3	O_3, $OH^•$, Cl_2	$SO_3^=$

* - these values for the lowest modeling atmospheric layer

By the moment of preparation of the final report (July 2004) not all modeling groups have carried out the whole program of calculations. It was decided by the inter-comparison participants to present in this progress report the calculation data for one month of the modeled period (February 1999). Estimates of mercury atmospheric balance should be given only for Poland. A detailed presentation of the modeling results is done below only for ADOM model as an example. For the other models only generalized tables of the results are presented. Besides, very preliminary comparison of the modeling data for February 1999 is given for ADOM, EMAP, CMAQ, MSCE, and DEHM. A detailed analysis of the comparison results will be done later when results of all participating models are available.

6.1. Acid Deposition and Oxidants Model (ADOM)

ADOM was used to simulate concentrations and depositions at the site locations during two months of cold season (February and March) and two months of warm season (June and July). Accordingly, the items of mercury atmospheric balances for the selected countries were calculated for these four months.

The measured and calculated concentrations of total gaseous mercury (TGM) are presented in Fig. 6.1. The highest deviation of a modeled mean monthly value from a measured one is 27% (site Lista in March). Average deviation for all considered sites and months is only 5.5%.

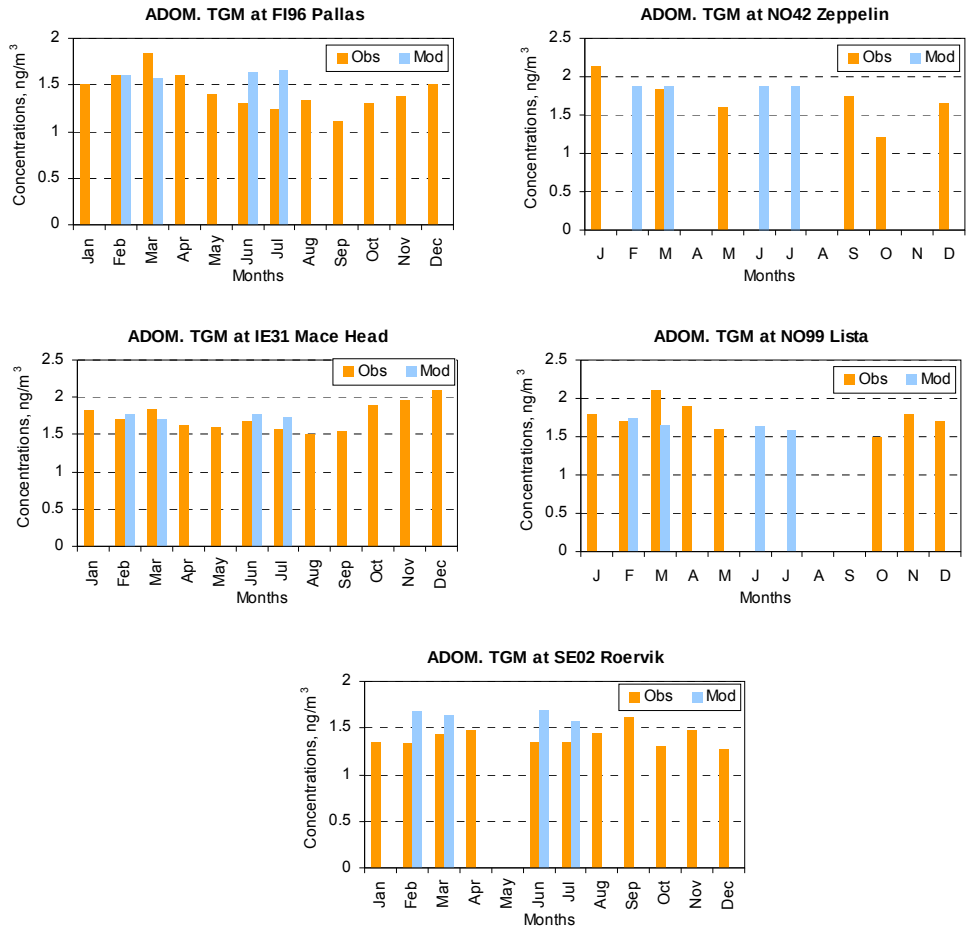


Fig. 6.1. *Comparison of measured and calculated by ADOM concentrations of total gaseous mercury (TGM) and EMEP sites*

Comparison of measured and calculated mercury concentrations in precipitation on monthly basis is presented in Table 6.2. In general, the modeled values are about 9.4% lower than the measured ones. However, for an individual station and for a separate month the disagreement can reach 4 times. There is no correlation between the modeled and observed values.

Table 6.2. *Measured concentrations of Hg in precipitation at EMEP sites in 1999 (obs) and modeled by ADOM (mod), ng/L*

Month / Site	Obs/Mod	Jan	Feb	Mar	Apr	May	June	July
DE01	Obs	16.7	12.5	6.7	12.2	9.2		
	Mod		**3.8**	**9.8**			**6.5**	**7.5**
DE09	Obs	12.0	11.0	8.3	14.7	19.8	11.7	13.0
	Mod		**5.5**	**7.4**			**8.9**	**12.0**
FI96	Obs	2.4	3.3	4.9	5.8	4.5	7.1	7.6
	Mod		**13.6**	**12.7**			**13.4**	**8.6**
NL91	Obs	8.4	8.7	11.9	13.9	23.0	12.6	16.6
	Mod		**7.3**	**11.2**			**8.9**	**12.2**
NO99	Obs	8.8	8.1	9.1	11.8	17.5		8.5
	Mod		**3.9**	**4.3**			**7.1**	**11.6**
SE02	Obs	7.3	8.9	11.4	9.0	18.7	11.1	12.7
	Mod		**7.0**	**8.8**			**10.2**	**14.0**
SE05	Obs	4.8	2.4	4.5	3.8	6.6	3.6	6.6
	Mod		**7.0**	**11.4**			**7.0**	**12.2**
SE11	Obs	13.0	10.8	20.5	13.2	9.7	9.9	11.6
	Mod		**7.3**	**8.2**			**10.5**	**10.6**
SE12	Obs	4.5	8.5	11.7	7.2	9.0		
	Mod		**4.3**	**6.8**			**7.7**	**16.9**

It was mentioned above that the measured precipitation amounts could differ from the values used by the model as the input meteorological information. To assess uncertainty of the main modeled parameter – mercury wet deposition flux – one should have an idea about uncertainty, which is introduced by deviations between measured and forecasted precipitation amounts. Table 6.3 demonstrates that the measured and forecasted values are highly correlated (r = 0.86), however, in general the forecasted precipitation amounts are significantly higher than the values measured at the stations (a factor of 1.5). It means, that the deposition values can be correspondingly overestimated. In some cases the difference exceeds 5 times.

Table 6.4 presents the mercury wet deposition fluxes at the sites obtained on the basis of the observations and by the model. In the many cases the model overestimates the depositions (the ratio for the totality of the results is 1.14). The maximum deviation between the observed and modeled values can reach an order of magnitude. However, the measured and modeled values are correlated (r = 0.44).

Mercury dry deposition fluxes cannot be measured but can be modeled. Table 6.5 gives an idea about relative importance of wet and dry deposition fluxes. For the totality of the stations mean relative contribution of dry deposition to the total deposition amounts for 24%. However, for individual months at separate stations such contribution can reach 47%. During wintertime role of dry deposition is somewhat lower (22%) than during summer (27%).

The comparison of the modeling results with observations of total particulate mercury (TPM) at Iceland site IS91 discovers very significant difference – the model predicts concentrations higher than

the observed ones by an order of magnitude (Fig. 6.2). The site is situated in the middle of the Atlantic, so any European anthropogenic influence can be ignored in this case. Most probably the reasons of the disagreement are connected either with the accepted boundary concentration values or with any sampling/analytical problems. The last assumption seems to be more reasonable because in 2000-2002 the station reported much higher values of TPM concentrations.

Table 6.3. *Measured and forecasted values of monthly precipitation amounts for EMEP sites in 1999, mm*

Month / Site	Obs/Pred	Jan	Feb	Mar	Apr	May	June	July
DE01	Obs	42.3	53.8	79.6	16.6	27.3	79.3	41.3
	Predict		**128.1**	**121.9**			**125.3**	**83.6**
DE09	Obs	40.4	28.5	64.0	35.7	22.1	92.1	32.0
	Predict		**83.3**	**97.5**			**98.7**	**43.6**
FI96	Obs	9	14	16	19	20	33	83
	Predict		**37.9**	**54.3**			**50.0**	**134.9**
NL91	Obs	64.5	54.5	60.3	49.2	21.0	87.8	38.3
	Predict		**92.7**	**81.6**			**71.4**	**29.9**
NO99	Obs	122.7	115.1	157.8	67.0	46.9	172.9	64.2
	Predict		**152.8**	**205.2**			**249.4**	**141.3**
SE02	Obs	69.8	58.3	63.5	54.3	35.5	146.7	62.7
	Predict		**93.9**	**115.2**			**151.8**	**111.7**
SE05	Obs	43.7	49.1	28.3	42.2	27.3	80.8	63.5
	Predict		**72.5**	**59.7**			**122.3**	**105.1**
SE11	Obs	74.4	67.3	22.8	42.6	56.4	87.5	46.0
	Predict		**81.2**	**95.0**			**114.8**	**91.0**
SE12	Obs	30.8	17.0	26.0	13.9	16.3	75.0	3.0
	Predict		**49.4**	**83.9**			**59.0**	**15.4**

Table 6.4. *Mercury wet deposition fluxes at EMEP sites in 1999 obtained on the basis of observations and by ADOM, g/m^2/mo*

Month / Site	Obs/Mod	Jan	Feb	Mar	Apr	May	June	July
DE01	Obs	0.71	0.67	0.53	0.20	0.25		
	Mod		**0.49**	**1.17**			**0.81**	**0.63**
DE09	Obs	0.48	0.31	0.53	0.52	0.44	1.08	0.42
	Mod		**0.46**	**0.72**			**0.88**	**0.52**
FI96	Obs	0.02	0.05	0.08	0.11	0.09	0.23	0.63
	Mod		**0.52**	**0.69**			**0.67**	**1.16**
NL91	Obs	0.54	0.47	0.72	0.68	0.48	1.11	0.64
	Mod		**0.68**	**0.91**			**0.64**	**0.36**
NO99	Obs	1.08	0.93	1.44	0.79	0.82		0.55
	Mod		**0.60**	**0.88**			**1.77**	**1.64**
SE02	Obs	0.51	0.52	0.72	0.49	0.66	1.63	0.80
	Mod		**0.66**	**1.01**			**1.55**	**1.56**
SE05	Obs	0.21	0.12	0.13	0.16	0.18	0.29	0.42
	Mod		**0.51**	**0.68**			**0.86**	**1.28**
SE11	Obs	0.97	0.73	0.47	0.56	0.55	0.87	0.53
	Mod		**0.59**	**0.78**			**1.21**	**0.96**
SE12	Obs	0.14	0.14	0.30	0.10	0.15		
	Mod		**0.21**	**0.57**			**0.45**	**0.26**

Table 6.5. *Mercury wet and dry deposition fluxes at EMEP sites in 1999 calculated by ADOM, g/m^2/mo*

Month / Site	Wet/Dry	Jan	Feb	Mar	Apr	May	June	July
DE01	Wet		0.49	1.17			0.81	0.63
	Dry		0.11	0.18			0.27	0.30
DE09	Wet		0.46	0.72			0.88	0.52
	Dry		0.09	0.11			0.24	0.27
FI96	Wet		0.52	0.69			0.67	1.16
	Dry		0.36	0.39			0.39	0.41
NL91	Wet		0.68	0.91			0.64	0.36
	Dry		0.10	0.16			0.26	0.32
NO99	Wet		0.60	0.88			1.77	1.64
	Dry		0.36	0.38			0.62	0.98
SE02	Wet		0.66	1.01			1.55	1.56
	Dry		0.26	0.23			0.56	0.75
SE05	Wet		0.51	0.68			0.86	1.28
	Dry		0.33	0.35			0.35	0.77
SE11	Wet		0.59	0.78			1.21	0.96
	Dry		0.05	0.10			0.14	0.13
SE12	Wet		0.21	0.57			0.45	0.26
	Dry		0.03	0.03			0.03	0.04

Results of calculations of mercury depositions over the individual countries caused by different emission sources are presented in Table 6.6. The values show that own anthropogenic sources contribute 30-50% to the total depositions over the UK, 15-25% over Italy and 50-65% over Poland. Obviously, the contributions depend mainly on two factors – intensity of own anthropogenic emission and geographical configuration of a given country. It should be mentioned, that in accordance with ADOM results 92-94% of anthropogenic mercury emission in the UK is transported outside the country. For Italy and Poland the corresponding values are 94-96% and 82-88%.

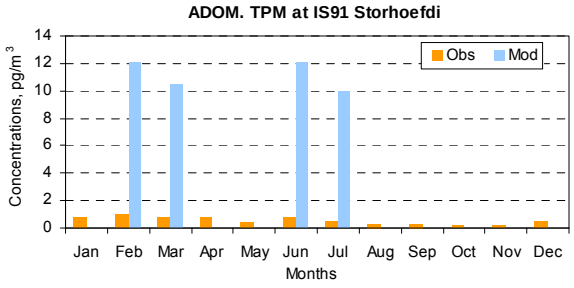


Fig. 6.2. *Comparison of measured and calculated by ADOM concentrations of total particulate mercury (TPM) and site IS91*

Table 6.6. *Atmospheric mercury depositions for individual countries in 1999 calculated by ADOM, kg*

Country	Deposition source	Jan	Feb	Mar	Apr	May	Jun	Jul
UK	National antropogenic. sources		43	60			53	60
	European antropogenic sources		52	78			117	65
	All sources		**95**	**138**			**170**	**125**
Italy	National antropogenic sources		33	48			45	43
	European antropogenic sources		110	185			255	243
	All sources		**143**	**233**			**300**	**283**
Poland	National antropogenic sources		258	328			393	300
	European antropogenic sources		145	168			325	265
	All sources		**403**	**496**			**718**	**565**

6.2. Community Multi-Scale Air Quality (CMAQ)

Calculations of concentrations and depositions at the site locations performed by CMAQ are restricted by two months: February (cold season) and August (warm season). Accordingly, the items of mercury atmospheric balances for the selected countries were calculated for these two months. Besides, the CMAQ domain does not cover the most northern sites: FI96 Pallas, NO42 Zeppelin and SE05 Bredkaelen. The calculated values of mercury concentrations, wet and dry depositions for February 1999 are presented in Table 6.7.

Results of CMAQ calculations of mercury depositions over Poland caused by different emission sources are presented in Table 6.8. The values show that own anthropogenic sources contribute 61% to the total depositions over Poland. In accordance with CMAQ results 39% of anthropogenic mercury emission in Poland is transported from external European anthropogenic sources.

Table 6.7. *CMAQ data on mercury concentrations, wet and dry depositions for February 1999*

Station	TGM, ng/m^3	Concentrations in precipitation, ng/L	Amount of precip used in calculations, mm	Wet deposition, g/km^2/month	Dry deposition, g/km^2/month	Total particulate mercury, pg/m^3
FI96	x	x	x	x	x	
IE31	1.53					
NO42	x					
NO99	1.57	12.5	87.6	1.10	0.25	
DE01		13.0	62.8	0.81	0.24	
DE09		17.0	46.3	0.79	0.37	
SE02	1.61	12.6	33.3	0.42	0.27	
SE05						
SE11		18.7	38.7	0.71	0.60	
SE12		7.2	18.0	0.13	0.28	
NL91		13.5	59.3	0.80	0.56	
IS91						x

x - Stations are outside the CMAQ modeling domain

Table 6.8. *Atmospheric mercury depositions for Poland in 1999 calculated by CMAQ, kg*

Country	Deposition source	February 1999
Poland	National anthropogenic sources	510
	European anthropogenic sources	325
	All sources	**835**

6.3. Eulerian Model for Air Pollution model (EMAP)

EMAP was used to simulate concentrations and depositions at the site locations during all 1999. Accordingly, the items of mercury atmospheric balances for the selected countries were calculated on monthly and yearly basis. The calculated values of mercury concentrations, wet and dry depositions for February 1999 are presented in Table 6.9.

Table 6.9. *EMAP data on mercury concentrations, wet and dry depositions for February 1999*

Station	TGM, ng/m^3	Concentrations in precipitation, ng/L	Amount of precip. used in calculations, mm	Wet deposition, g/km^2/ month	Dry deposition, g/km^2/ month	Total particulate mercury, pg/m^3
FI96	2.00	18.6	22.5	0.42	2.58	
IE31	1.27					
NO42	1.91					
NO99	2.05	10.9	77.4	0.84	2.92	
DE01		11.0	51.9	0.57	2.73	
DE09		13.0	30.7	0.40	5.19	
SE02	1.94	10.4	42.8	0.44	2.88	
SE05		15.8	17.2	0.27	1.98	
SE11		11.0	40.8	0.45	3.72	
SE12		12.8	34.9	0.45	2.40	
NL91		11.4	48.0	0.55	2.19	
IS91						1.6

Results of EMAP calculations of mercury depositions over Poland caused by different emission sources are presented in Table 6.10. The values show that own anthropogenic sources contribute 54% to the total depositions over Poland. In accordance with EMAP results 46% of anthropogenic mercury emission in Poland is transported from external European anthropogenic sources.

Table 6.10. *Atmospheric mercury depositions for Poland in 1999 calculated by EMAP, kg*

Country	Deposition source	February 1999
Poland	National anthropogenic sources	1477
	European anthropogenic sources	1279
	All sources	**2756**

6.4. Danish Eulerian Hemispheric Model (DEHM)

DEHM was used to simulate concentrations and depositions at the site locations during February 1999. Accordingly, the items of mercury atmospheric balances for Poland were calculated for February 1999. The calculated values of mercury concentrations, wet and dry depositions for February 1999 are presented in Table 6.11.

Results of DEHM calculations of mercury depositions over Poland caused by different emission sources are presented in Table 6.12. The values show that own anthropogenic sources contribute 59% to the total depositions over Poland. In accordance with DEHM results 41% of anthropogenic mercury emission in Poland is transported from external European anthropogenic sources.

Table 6.11. *DEHM data on mercury concentrations, wet and dry depositions for February 1999*

Station	TGM, ng/m^3	Concentrations in precipitation, ng/L	Amount of precip used in calculations, mm	Wet deposition, g/km^2/month	Dry deposition, g/km^2/ month	Total particulate mercury, pg/m^3
FI96	1.45	10.8	30.8	0.33	0.03	
IE31	1.43					
NO42	1.43					
NO99	1.43	14.0	49.1	0.69	0.05	
DE01		16.9	75.7	1.28	0.14	
DE09		25.0	49.8	1.25	0.24	
SE02	1.45	16.8	40.7	0.68	0.12	
SE05		6.5	56.9	0.37	0.02	
SE11		23.5	59.2	1.39	0.23	
SE12		14.3	35.7	0.51	0.09	
NL91		28.2	46.7	1.32	0.25	
IS91						2.6

Table 6.12*. Atmospheric mercury depositions for Poland in 1999 calculated by DEHM, kg*

Country	Deposition source	February 1999
Poland	National anthropogenic sources	332
	European anthropogenic sources	234
	All sources	**566**

6.5. MSCE Heavy Metal model, Hg version (MSCE-Hg)

MSCE-Hg model was used to simulate concentrations and depositions at the site locations during all 1999. Accordingly, the items of mercury atmospheric balances for the selected countries were calculated on monthly and yearly basis. The calculated values of mercury concentrations, wet and dry depositions for February 1999 are presented in Table 6.13.

Table 6.13. *MSCE data on mercury concentrations, wet and dry depositions for February 1999*

Station	TGM, ng/m^3	Concentrations in precipitation, ng/L	Amount of precip used in calculations, mm	Wet deposition, g/km^2/month	Dry deposition, g/km^2/month	Total particulate mercury, pg/m^3
FI96	1.9	7.1	14.0	0.10	0.02	
IE31	1.7					
NO42	1.7					
NO99	1.7	6.9	69.6	0.48	0.05	
DE01		12.8	32.0	0.41	0.10	
DE09		19.6	20.4	0.40	0.13	
SE02	1.8	12.3	22.8	0.28	0.07	
SE05		7.5	8.0	0.06	0.02	
SE11		25.8	24.8	0.64	0.19	
SE12		11.4	17.6	0.20	0.06	
NL91		23.5	34.4	0.81	0.20	
IS91						4.1

Results of MSCE calculations of mercury depositions over Poland caused by different emission sources are presented in Table 6.14. The values show that own anthropogenic sources contribute 78% to the total depositions over Poland. In accordance with MSCE modeling results 22% of anthropogenic mercury emission in Poland is transported from external European anthropogenic sources.

Table 6.14. *Atmospheric mercury depositions for Poland in 1999 calculated by MSCE, kg*

Country	Deposition source	February 1999
Poland	National anthropogenic sources	832
	European anthropogenic sources	236
	All sources	**1068**

7. COMPARISON OF INDIVIDUAL MODEL RESULTS AGAINST OBSERVATIONS

Since the calculation data of come models are not ready yet, there is no reason to carry out detailed analysis for all monitoring stations and for each month. Below comparison is done only for February 1999. To obtain a generalized picture the data of individual stations are averaged. Because CMAQ model did not provide calculations for some stations (NO42, FI96, SE05), they were excluded from this preliminary consideration.

Fig. 7.1 demonstrates the comparison of the modeled values against mean regional value for total gaseous mercury concentration in February 1999. All the results are within +/- 10%.

Comparison of modeling results with observations of mercury in precipitation at 7 monitoring stations is shown in Fig. 7.2. The variations of the modeling results are rather high, however, all the modeled values are within a factor of two: ADOM underpredicts the observations (43%) while DEHM overpredict them 2 times.

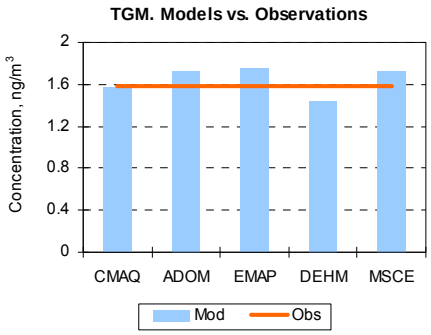


Fig. 7.1. *Comparison of the modeled values against mean regional value for total gaseous mercury concentration in February 1999*

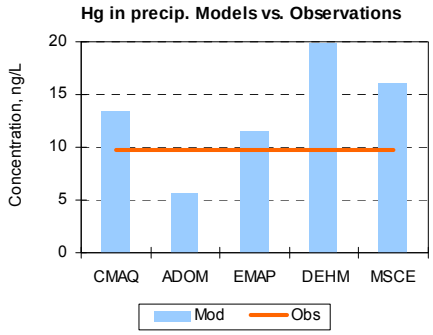


Fig. 7.2. *Comparison of modeling results with observations of mercury in precipitation (mean value for 7 monitoring stations) in February 1999*

The input meteorological data on forecasted precipitation amounts are a very significant source of uncertainty of mercury wet deposition assessments by transport/deposition models. Fig. 7.3 shows a degree of such uncertainty for the participating models. Averaged value of precipitation amount for the whole region in February 1999 was 56.4 mm. ADOM had to use the value of 97.3 mm (73% higher) while MSCE used much lower forecasted value (31.7 mm). Naturally, the accuracy of modeled values of mercury depositions cannot be higher than the accuracy of the input information in principle.

Fig. 7.4 presents the comparison of measured (mean for the region) mercury wet deposition in February 1999 and the values calculated by the models. One can mention a very good agreement obtained by four models but DEHM, which overpredicted the measured value by 88%. The agreement for wet deposition is higher than the agreement for mercury concentrations in precipitation. It can be explained by compensating the errors in concentration evaluation and in precipitation amounts. Thus ADOM underpredicted the concentration values but used overpredicted values of precipitation amounts.

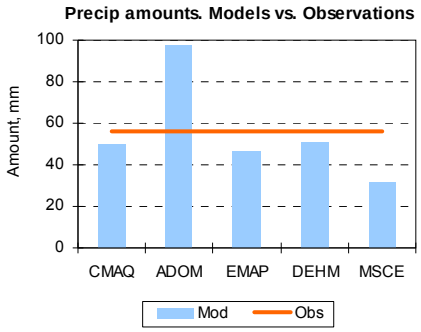


Fig. 7.3. *Comparison of precipitation amounts measured at monitoring station (mean for the region in February 1999) and amounts forecasted by meteorological models*

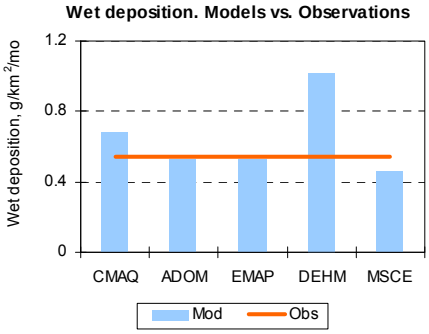


Fig. 7.4. *Comparison of measured (mean for the region) mercury wet deposition in February 1999 and the values calculated by the models*

CONCLUSIONS

By July 2004 four models of seven fulfilled the agreed programmes of calculations within the third stage of the intercomparison study. At that, calculations by ADOM model were performed for four months of 1999, while by CMAQ - for two months. EMAP and MSCE models calculated all months of 1999. DEHM presented the results only for February 1999. Results for the other months will be prepared by September. It is planned that HYSPLIT and GRAHM will fulfil the calculation program by October 2004.

Very preliminary results of calculations (obtained only for February 1999) shown that the models (at least, 5 of 7) could predict concentrations of total gaseous mercury in air with high accuracy. The deviations from the measured values lie within +/-10%. The uncertainty of the modelling results for mercury concentrations in precipitation and for mercury wet deposition is within a factor of two.

Comparison of mercury deposition values will be done when results of all the models are available. It is planned that the final analysis of the comparison of the models will be done by the end of 2004.

REFERENCES

Behrenfeld M.J. and P.G. Falkowski [1997] Photosynthetic derived from satellite-based chlorophyll concentration. *Limnol. Oceanogr*., vol. 42, No.1, pp.1-20.

Brukhanov P.A., Korolev S.M. and A.V. Lysak [1991] Comparison of composition of atmospheric precipitation samples collected in parallel by two types of rain water samplers at Soviet stations of the transboundary atmospheric pollution monitoring network (EMEP). In: «Monitoring of Background Environmental Pollution», Issue 7, Eds. Yu.Izrael and F.Rovinsky, Leningrad, «Gidrometeoizdat», pp.243-246 (in Russian).

Costa M. and Liss P.S., 1999. Photoreduction of mercury in sea water and its possible implications for Hg^0 air-sea fluxes. *Marine Chemistry*, vol. 68, pp. 87-95

Dastoor A.P. and Y. Larocque [2004] Global circulation of atmospheric mercury: a modeling study. *Atmospheric Environment*, vol. 38, pp.147 – 161.

EMEP/CCC [1995] EMEP manual for sampling and chemical analysis. http://www.nilu.no/projects/ccc/index.html

Gustin M. S., Lindberg S., Marsik F., Casimir A., Ebinghaus R., Edwards G., Hubble-Fitzgerald C., Kemp R., Kock H., Leonard T., London J., Majewski M., Montecinos C., Owens J., Pilote M., Poissant L., Rasmussen P., Schaedlich F., Schneeberger D., Schroeder W., Sommar J., Turner R., Vette A., Wallschlaeger D., Xiao Z., and Zhang H., [1999] Nevada STORMS project: Measurement of mercury emissions from naturally enriched surfaces. *J. Geophys. Res*., vol. 104, No. D17, pp. 21831-21844.

Ilyin I., Ryaboshapko A., Afinogenova O., Berg T., A.-G. Hjellbrekke [2001]. Evaluation of transboundary transport of heavy metals in 1999. Trend analysis. EMEP Report 3/2001. MSC-East and CCC, http://www.msceast.org.

Jorander E., and U. Pedersen [1992] Comparison of bulk vs. wet-only weekly precipitation sampling, Nordmoen, Norway, 1987-1989. In: EMEP/CCC Report 5/91, pp. 287-291.

Kim J. and W. Fitzgerald [1986] Sea-Air Partioning of Mercury in the Equatorial Pacific Ocean. *Science*, vol. 231, No.4742, pp.1131-1133.

Pacyna E.G. and J.M. Pacyna [2002] Global emission of mercury from anthropogenic sources in 1995. *Water, Air and Soil Pollution*, v. 137, No. 1, pp.149-165.

Pacyna J., Pacyna E., Steenhuisen F., Wilson S. [2003] Global mercury emissions. Long Range Workshop, Ann Arbor, Michigan, USA, September 16-17, 2003.

Ryaboshapko A., Bullock R., Ebinghaus R., Ilyin I., Lohman K., Munthe J., Petersen G., Seigneur C. and I.Waengberg [2002] Comparison of mercury chemistry models. *Atm. Environ.,* vol. 36, pp. 3881-3898.

Ryaboshapko A. and I. Ilyin [2001] Mercury re-emission to the atmosphere in Europe. In: Proceedings of EUROTRAC Symposium 2000 Transport and Chemical Transformation in the Troposphere. (Eds.) Pauline M. Midgley, Markus J. Reuther, Marilee Williams, Springer-Verlag Berlin Heidelberg (CD-annex).

Ryaboshapko A., Iliyin I., Bullock R., Ebinghaus R., Lohman K., Munthe J., Petersen G., Seigneur C., I. Waengberg [2001] Intercomparison study of numerical models for long-range atmospheric transport of mercury. Stage I. Comparison of chemical modules for mercury transformations in a cloud/fog environment. EMEP MSC-E Technical Report 2/2001. http://www.msceast.org.

Seigneur C., Karamchandani P., Lohman K., Vijayaraghavan K. and R.-L. Shia [2001] Multiscale modelling of the atmospheric fate and transport of mercury. *J. Geophys. Res.,* vol. 106, No.D21, pp.27795-27809.

Soederlund R. [1982] A note to the difference between bulk and wet-only precipitation collectors. In: EMEP expert meeting on chemical matters. EMEP/CCC Report 1/82.

Steadman J.R., Heyes C.J. and J.G. Irwin [1990] A comparison of bulk and wet-only precipitation collectors at rural site in the United Kingdom. WASP, 52, pp. 377-395.

Travnikov O. and A. Ryaboshapko [2002] Modelling of Mercury Hemispheric Transport and Depositions. MSC-E Technical Report 6/2002, 67 p., www.msceast.org.