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## Intercomparison study of atmospheric mercury models: 2. Modelling results vs. long-term observations and comparison of country deposition budgets

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### Abstract

Five regional scale models with a horizontal domain covering the European continent and its surrounding seas, two hemispheric and one global scale model participated in the atmospheric Hg modelling intercomparison study. The models were compared between each other and with available measurements from 11 monitoring stations of the EMEP measurement network. Because only a very limited number of long-term measurement records of Hg were available, significant attention was given to the intercomparison of modelling results. Monthly and annually averaged values of Hg concentrations and depositions as well as items of the Hg deposition budgets for individual European countries were compared. The models demonstrated good agreement (within  $\pm 20\%$ ) between annual modelled and observed values of gaseous elemental Hg. Modelled values of Hg wet deposition in Western and Central Europe agreed with the observations within  $\pm 45\%$ . The probability to predict wet depositions within a factor of 2 with regard to measurements was 50–70% for all the models. The scattering of modelling results for dry depositions of Hg was more significant (up to  $\pm 50\%$  at the annual scale and even higher for monthly data). Contribution of dry deposition to the total Hg deposition was estimated at 20–30% with elevated dry deposition fluxes during summer time. The participating models agree in their predictions of transboundary pollution for individual countries within  $\pm 60\%$  at the monthly scale and within  $\pm 30\%$  at the annual scale. For the cases investigated, all the models predict that the major part of national anthropogenic Hg emissions is transported outside the country territory.

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## 1. Introduction

Human activity can significantly disturb the natural environmental Hg cycle and cause enhanced accumulation of Hg in soil, water, and vegetation. Subsequent bio-magnification in food webs may lead to elevated concentrations of Hg in marine fish, mammals and birds, and finally may result in significant human exposure to Hg through the diet. The atmosphere plays an important role in the delivery to and cycling of Hg in ecosystems; understanding and quantifying this role is of critical importance. Modern methods of monitoring are not able to provide spatially comprehensive information on total (both wet and dry) Hg deposition. In addition, by itself, monitoring is not able to provide comprehensive information on source attribution for atmospheric deposition and the extent of transboundary Hg pollution. Numerical chemical transport models must be used to provide the above information. Comparison of modelling results obtained by different chemical transport models as well as comparison of the modelled values with available measurements provides information about the uncertainty in such models.

To this end, an intercomparison project for evaluation of numerical models of Hg long-range atmospheric transport and deposition on the European scale has been carried out under the auspices of EMEP. Results of the first phase of the intercomparison – a study of physical and chemical schemes of Hg transformations applied in the models – were published earlier (Ryaboshapko et al., 2002). Results of the second phase – an intercomparison of modelling results for relatively short-term detailed observations in Europe – are presented in a companion paper (Ryaboshapko et al., 2007–this issue). The final phase of the project – described here – included a comparison of modelling results with long-term observations of Hg deposition fluxes and concentrations in air and precipitation as well as a comparison of model predicted atmospheric budgets of Hg species in the entire EMEP domain and for selected European countries. The major emphasis of the final phase was the evaluation of the model performance in policy-oriented applications and the development of additional information about the uncertainty in modelling results. A summary of the results of the final phase is presented here; additional details are available in report form (Ryaboshapko et al., 2005).

## 2. Program and participating models

The main task of this study was to characterize the ability of contemporary chemical transport models to

predict Hg levels in the atmosphere and depositions on long-term time scales (months to years). The models are a potentially valuable tool in assessing Hg accumulation in the environment and long-term adverse effects on human health, and so it is important to evaluate their accuracy and model-to-model differences. Three types of model results were analyzed via comparison with available measurement data and by intercomparison of the results of the different participating models: Hg concentration in ambient air, wet and dry deposition fluxes, and balances of atmospheric deposition for selected European countries.

In contrast to the short-term (second) phase of the project, only gaseous elemental mercury (GEM) was considered in the atmospheric concentration aspects of the analysis, because there were insufficient long-term data records for other atmospheric Hg forms — reactive gaseous mercury (RGM) and total particulate mercury (TPM). GEM is characterized by a long residence time in the free troposphere (months to a year) and is therefore particularly important in long-range atmospheric transport. Comparison of model predictions with measured GEM concentrations provides important information about how well a given model is able to describe the regional and global transport of Hg in the atmosphere, including an accounting of major sources and sinks of atmospheric Hg. Evaluation of wet and dry deposition processes provides information about the ability of models to estimate Hg atmospheric loads to ecosystems. Finally, intercomparison of model results for country-specific deposition budgets is useful for assessing the current level of model performance in answering policy-relevant source-attribution questions.

Since there is very limited long-term measurement data for atmospheric Hg in Europe (there are only about a dozen sites measuring Hg in air and/or precipitation on a regular basis), it is impossible to perform a comprehensive evaluation of a model performance by comparison of modelling results with measurements. Nevertheless, comparison with the limited available data allows at least an initial characterization of the overall accuracy of the model simulations. In addition, for processes that cannot be routinely measured, e.g., dry deposition and source attribution, comparison of simulation results obtained by different models yields information about the uncertainty in the estimates.

Eight models were involved in this phase of the intercomparison:

- ADOM, GKSS-Forschungszentrum, Germany (Petersen et al., 2001);
- CMAQ, EPA, USA, (Bullock and Brehme, 2002);

- GRAHM, Environment Canada, Canada (Dastoor and Larocque, 2004)
- HYSPLIT, NOAA, USA (Cohen et al., 2004);
- EMAP, Institute of Meteorology and Hydrology, Bulgaria (Syrakov, 1995);
- DEHM, Environmental Research Institute, Denmark (Christensen et al., 2004);
- MSCE-HM, Meteorological Synthesizing Centre-East, EMEP, UN ECE (Ilyin et al., 2002);
- MSCE-HM-Hem, Meteorological Synthesizing Centre-East, EMEP, UN ECE (Travnikov, 2005).

The main properties of the participating models are described in the companion paper in this issue (Ryaboshapko et al., 2007-this issue), and will only be briefly summarized here. First, in this phase, EMEP/MSCE-East participated with two different model versions: the regional model used in previous phases (MSCE—HM) and a new hemispheric model (MSCE—HM-Hem). The hemispheric version has a model domain covering the Northern Hemisphere with spatial resolution  $2.5^\circ \times 2.5^\circ$ , extending vertically to a 12 km height; the other characteristics of the hemispheric version were similar to the regional one, as described in the companion paper. Five of the participating models are of regional (European) scale and three have global or hemispheric domains. One model has a Lagrangian formulation (HYSPLIT) while the others are based on Eulerian approaches. All the models employ extensive chemical schemes describing physical and chemical transformations of Hg species both in gaseous and aqueous phases. The chemical mechanism varies slightly from model to model, but most of the models used the same data regarding key reactant concentrations as described below. Some participating models describe dry deposition processes using the resistance approach, whereas others utilize a simple dry deposition velocity scheme. Only three of the models (GRAHM, MSCE—HM, MSCE—HM-Hem) explicitly consider dry deposition of GEM. Air-surface exchange of this Hg form is poorly known. Therefore, the models that included GEM dry deposition generally utilized a simplified dry deposition approach with deposition velocities ( $V_d$ ) on the order of 0.01–0.03 cm/s to vegetated surfaces. Wet deposition phenomena are simulated in most of the models using a scavenging coefficient approach. Exceptions are ADOM and GRAHM, which consider detailed microphysics of clouds and precipitation.

All but one model utilized pre-processed off-line meteorological data from different datasets, whereas GRAHM is integrated into an operational weather forecasting system and directly uses meteorological data

being simulated on-line in this combined model. ADOM utilized data produced by the weather prediction model HIRLAM. HYSPLIT used re-analysis data from the joint project of the National Centers for Environmental Prediction (NCEP) and National Center for Atmospheric Research (NCAR). The same re-analysis dataset was utilized by MSCE models and EMAP with pre-processing by the System for Diagnosis of the lower Atmosphere (SDA) (Rubinstein and Kiktev, 2000). CMAQ and DEHM utilized the Tropical Ocean and Global Atmosphere dataset of European Centre for Medium-Range Weather Forecasts (ECMWF TOGA) pre-processed by MM5 — Fifth Generation Penn State/NCAR Mesoscale Model (Grell et al., 1995).

Modelling of Hg chemical transformations in the atmosphere requires information on air concentration of important reactants (e.g., ozone, hydroxyl radical, sulphur dioxide, etc.). Several participating models (CMAQ, DEHM, GRAHM) include simulation of transport and fate of these substances in their chemical schemes. Other models utilized pre-simulated concentrations from external sources, similar to the use of off-line meteorological data. Global, gridded monthly mean estimates of the air concentration of chemical reactants involved in reactions with Hg were taken from Wang et al. (1998) for ozone, Chin et al. (1996) for sulphur dioxide, and Spivakovsky et al. (2000) for hydroxyl radical. In addition, all models assumed that the pH of cloud water has a constant value of 4.5 (Acker et al., 1998).

It is well known that mercury is capable of being transported intercontinentally. Therefore, regional models require setting boundary conditions to take into account influence of the intercontinental transport on Hg ambient concentrations and deposition in Europe. Boundary conditions adopted by each of participating models are described in the companion paper (Ryaboshapko et al., 2007-this issue). All Eulerian regional and hemispheric models utilized fixed boundary concentration profiles of GEM corresponding to 1.5–1.7 ng/m<sup>3</sup> under normal conditions. Besides, some models set non-zero boundary concentrations of reactive gaseous mercury (RGM, 2–18 pg/m<sup>3</sup>) and total particulate mercury (TPM, 10–20 pg/m<sup>3</sup>). The Lagrangian model (HYSPLIT) involved in this study used constant background concentrations of Hg species over the model domain as the boundary condition formulation used in Eulerian models cannot be practically applied in this type of model.

For the purposes of this study, all the participating models considered Europe as the primary region of interest. The calculations were made for selected months and for the entire year 1999. Each model

estimated the following parameters at monitoring station locations, to allow for comparisons against measurements: (a) gaseous elemental Hg concentrations in air; (b) Hg concentrations in precipitation; (c) Hg wet deposition; and (d) Hg dry deposition. Three individual countries roughly equal in size but located in different parts of Europe were selected for source-receptor calculations: the UK, Poland and Italy. Due to limited resources, some of the models were not able to simulate the entire year of 1999. In this case, calculations were performed for one winter and one summer month — February and August, respectively. Comparison of simulation results for these two months can reveal some differences in model performance under winter and summer conditions. However, caution must be exercised in generalizing the findings – e.g., to seasonal values – based on the two individual months simulated. Accordingly, in the following, comparison results are presented separately for February, August and the whole year.

### 3. Measurement data

Long-term measurements of Hg concentration in air and precipitation at sites of the EMEP monitoring network (EMEP/CCC, 2006) were used in the study. Within the EMEP monitoring network, there were 5 stations measuring Hg in air and 9 stations measuring Hg in precipitation in 1999. The locations of the measurement sites are shown, along with anthropogenic emissions (described below), in Fig. 1. Additional details of the sites are presented in Table 1. Fig. 1 shows that practically all the stations are located north of the main European Hg anthropogenic source regions. The sites were qualitatively divided into 3 groups. The German and Dutch sites (DE01, DE09 and NL91) were considered as “polluted” since they are located relatively close to strong anthropogenic source areas. The second group is the “regional” sites located in southern Scandinavia (NO99, SE02, SE11, SE12) where anthropogenic effects could be noticeable. The rest were “background”

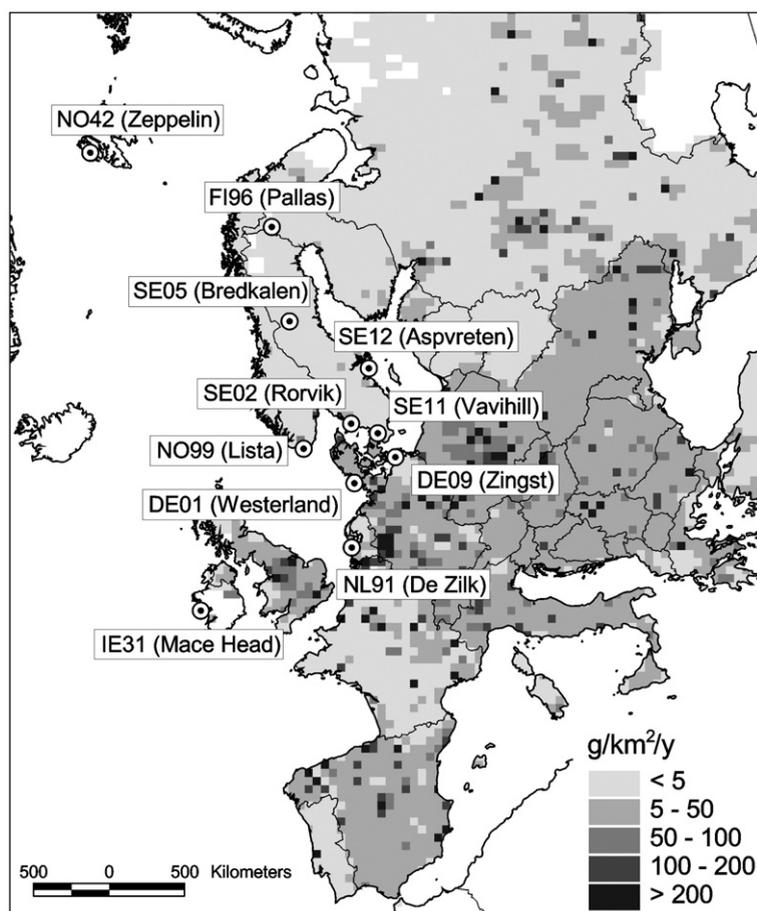


Fig. 1. Locations of the monitoring sites and spatial distribution of Hg anthropogenic emissions in Europe.

Table 1  
Monitoring sites used in this phase of the comparison

Station name	EMEP code	Country	Latitude	Longitude	Height a.s.l., m
<i>Gaseous elemental mercury concentrations in air</i>					
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
<i>Total mercury concentrations in precipitation (type of sampler)</i>					
Westerland (wet only)	DE01	Germany	54° 55' N	08° 18' E	12
Zingst (wet only)	DE09	Germany	54° 26' N	12° 44' E	1
Rörvik (bulk)	SE02	Sweden	57° 25' N	11° 56' E	10
Bredkälen (bulk)	SE05	Sweden	63° 51' N	15° 20' E	404
Vavihill (bulk)	SE11	Sweden	56° 01' N	13° 09' E	172
Aspvreten (bulk)	SE12	Sweden	58° 48' N	17° 23' E	20
De Zilk (wet only)	NL91	Netherlands	52° 18' N	04° 30' E	4
Lista (bulk)	NO99	Norway	58° 06' N	06° 34' E	13
Pallas (bulk)	FI96	Finland	67° 58' N	24° 07' E	566

sites (SE05 and FI96, IE31) located in the Arctic and at relatively remote locations on the Atlantic coast.

A detailed description of methods applied for the sampling and analysis of different atmospheric Hg species at sites of the EMEP monitoring network can be found in Schmolke et al. (1999), Berg et al. (2001), Ebinghaus et al. (2002) and Munthe et al. (2003). Uncertainties in Hg measurements in air and precipitation within the EMEP network have been investigated during a recent field intercomparison campaign (Aas, 2006). In this study, it was found that the uncertainty in monthly mean GEM measurements appears to be on the order of  $\pm 30\%$ . Uncertainty in six-month volume-weighted mean Hg concentrations in precipitation and wet deposition was estimated to be as high as  $\pm 40\%$ , and monthly values were expected to be even more uncertain.

There are two areas of uncertainty in the measurements of Hg wet deposition that should be considered when the modelling results are compared with the measurement data. The first is that the sampling of Hg concentration in precipitation was provided by two types of instruments — bulk samplers and wet-only samplers. In bulk samplers, dry deposition may contribute to the amount of Hg sampled in the continuously open funnel. Wet-only samplers are closed during dry periods and

therefore not vulnerable to this potential artefact. Thus, one might expect to see some effect of sampler type on measurement results (i.e., that bulk samplers overestimate wet deposition). However, the available data regarding comparison of the two methods suggests that the differences in wet deposition measured by the two methods are not significant (Iverfeldt and Munthe, 1993; Aas, 2006).

The second issue concerns the measurements of precipitation amount, a critical parameter for measurement-based estimates of Hg wet deposition. In practice, standardised meteorological precipitation gauges are not always available at the sampling stations and the precipitation amounts are estimated solely by the amounts collected in the pollutant sampling equipment. Analysis of the raw data where methodologies are co-located has shown that for some individual months the difference in precipitation amounts measured by different types of samplers can exceed a factor of 2. These discrepancies may be explained by differences both in sampler construction and the sampling procedure. This uncertainty is therefore important to keep in mind when the model results are evaluated by comparison with the “observed” values.

#### 4. Emissions data

Direct anthropogenic emissions over the European continent for 2000 were estimated by Pacyna et al. (2003a). The data were divided into three emission height classes – below 50 m, 50–150 m and higher than 150 m – and were spatially distributed over the EMEP domain with  $50 \times 50$  km resolution. According to Pacyna et al. (2003a) the proportion of different Hg forms (GEM, RGM, and TPM) emitted from point sources varied for different emission source sectors, whereas emissions from all area sources were assumed to have a fixed speciation. The European direct anthropogenic emission in 2000 totalled 239 tonnes (hereafter metric tonnes are mentioned), including 162 tonnes from individual point sources and 77 tonnes from area sources and had the following overall speciation: GEM — 61%, RGM — 32%, and TPM — 7%. Total national direct anthropogenic emissions of Hg from three selected European countries in 2000 were 8.5, 9.8 and 25.6 tonnes in the UK, Italy and Poland, respectively. For the purposes of this study, it was assumed that the 2000 European inventory was a reasonable approximation of the 1999 emissions. Because of the lack of detailed information on the temporal variations of emissions, anthropogenic emissions were assumed to be constant throughout the year.

The global distribution of anthropogenic Hg emissions for 1995 was estimated by Pacyna and Pacyna (2002), Pacyna et al. (2003b). On the global level, it is believed that overall anthropogenic emissions did not change significantly between 1995 and 1999 (Pacyna et al., 2003a). Increased emissions in South-Eastern Asia were compensated by emission reductions in many developed countries. Therefore, for the purposes of the simulations, it was assumed that the 1995 global inventory was a reasonable approximation of the 1999 global emissions. According to Pacyna and Pacyna (2002) global emissions of total Hg from anthropogenic sources in 1995 was estimated to be on the order of 1900 tonnes. Like the European inventory, the global emissions were apportioned among the three Hg forms and were divided into different emissions heights. Global emissions were spatially distributed with a resolution of  $1^\circ \times 1^\circ$ .

Lamborg et al. (2002) estimated current global Hg emissions from the oceans to be 800 tonnes per year, with approximately half of the flux being “natural” and half representing anthropogenic re-emissions. Natural emissions from land were estimated to be 1000 tonnes per year. Other studies have estimated somewhat higher overall values of global Hg emissions. For example, Mason and Sheu (2002) estimated the total flux of Hg from the ocean (out of the marine boundary layer) to be about 1450 tonnes per year and total evasion of Hg from land (including re-emission) to be 1600 tonnes per year. Seigneur et al. (2004) estimated total natural emission from the ocean and land to be 950 and 1200 tonnes per year, respectively. In addition, they also estimated that 1020 tonnes of anthropogenic Hg re-emitted from the ocean annually and 1110 tonnes re-emitted from land. Thus, available estimates of global natural emission and re-emission vary significantly.

When this study was conducted, the only available spatially resolved estimates of natural Hg emission on a global scale were those of Travnikov and Ryaboshapko (2002) based on the overall estimate of Lamborg et al. (2002) cited above. Therefore these data were adopted for the model intercomparison keeping in mind the significant uncertainty in these estimates and possible underestimation of natural fluxes. This dataset was obtained by distribution of the total values of natural emission over the globe depending on the surface temperature for emissions from land and proportional to the primary production of organic carbon for emissions from the oceans. The temperature dependence was described by an Arrhenius type equation with empirically derived activation energy about 20 kcal/mol (Kim et al., 1995; Carpi and Lindberg, 1998; Poissant and

Casimir, 1998; Zhang et al., 2001). Evasion of Hg from geochemical mercuriferous belts (Gustin et al., 1999) was assumed to be 10 times higher than that from background soils. Monthly mean spatially resolved data on the ocean primary production of carbon (Behrenfeld and Falkowski, 1997) were utilized to distribute the natural Hg emission flux over the ocean. Based on this methodology, it was estimated that approximately 10% of the overall global natural emissions (177 tonnes per year) were emitted from the EMEP domain. The spatial distribution of total Hg emissions (anthropogenic, natural and re-emission) in Europe is shown in Fig. 1.

Lamborg et al. (2002) estimated that on the global level, anthropogenic re-emission from land could account for about 30% of the direct anthropogenic emissions — over 600 tonnes per year. In some recent works, Hg natural emissions and re-emission have been estimated in North America based on a mechanistic approach (Bash et al., 2004) and field measurements (Lin et al., 2005). In this work, only European anthropogenic re-emissions were estimated and taken into account. Ryaboshapko and Ilyin (2001) estimated the current anthropogenic re-emission flux for Europe to be on the order of 50 tonnes per year, and distributed this value over Europe with  $50 \times 50$  km spatial resolution based on estimates of relative cumulative deposition. For this purpose Hg deposition in Europe accumulated during last century was estimated using the regional transport model, and a simple box model considered soil as a reservoir with two output fluxes – re-emission and hydrological leaching – was applied (Ryaboshapko and Ilyin, 2001).

## 5. Concentration of gaseous elemental mercury

The quantitative statistical metrics used in the following analysis are the normalized spread of the ensemble of model simulations

$$NSE = \frac{X_{\max} - X_{\min}}{2\bar{X}} 100\%$$

representing deviation of modelling results from the ensemble average and the normalized deviation of the models ensemble average from the observed value

$$NDE = \left| \frac{\bar{X} - X_{\text{obs}}}{X_{\text{obs}}} \right| 100\% .$$

In the above expressions,  $X_{\max}$ ,  $X_{\min}$  and  $\bar{X}$  are the maximum, minimum, and ensemble averages of the modelled values, and  $X_{\text{obs}}$  is the measured value for any given monitoring station.

Comparison of monthly averaged modelled and observed values of GEM concentration at five monitoring stations in February and August 1999 is presented in Fig. 2. There were no measurement data at stations NO99 and NO42 in August, and the measured value at NO42 in February was classified as an outlier (Ryaboshapko et al., 2005). As seen from the figure the spread of the model results does not exceed  $\pm 30\%$ . This is not surprising considering the relatively low variability of GEM concentration in ambient air. For all the stations except SE02 the normalized deviations of the model ensemble average from the observed values are less than 15%. For Swedish station SE02 most models tend to overestimate observations. The GEM concentrations measured at SE02 station located in southern Sweden appears to be anomalously low ( $1.4 \text{ ng/m}^3$ ) in comparison with the current background GEM concentrations ( $1.5\text{--}1.7 \text{ ng/m}^3$ ) measured in the Northern Hemisphere (e.g., Slemr et al., 2003; Ebinghaus et al. 2002; Munthe et al., 2003). The reason for the unusually low values at SE02 is not presently understood.

On the other hand, most of the models underpredict the relatively high GEM concentration in February ( $1.7 \text{ ng/m}^3$ ) at remote station IE31 located on the Atlantic coast (see Fig. 1). Wängberg et al. (2001) demonstrated that GEM concentrations obtained at this station are higher on average than those measured at remote continental sites. In addition, Ebinghaus et al. (2002)

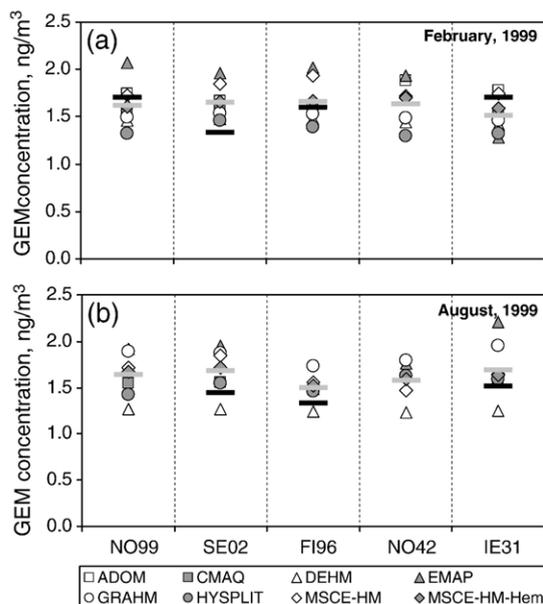


Fig. 2. Modelled and observed monthly GEM concentration at monitoring stations in February (a) and August (b) 1999. Symbols depict modelling results, light grey dashes show the ensemble average, black dashes present observed values.

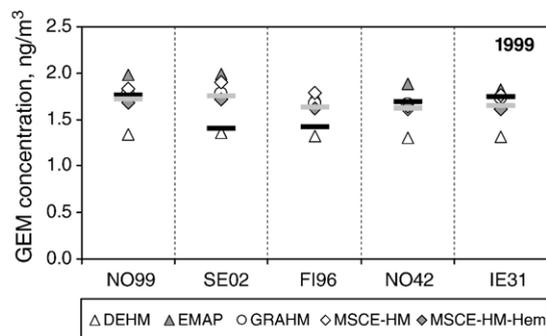


Fig. 3. Modelled and observed annual GEM concentration at monitoring stations in 1999. Symbols depict modelling results, light grey dashes show the ensemble average, black dashes present observed values.

found a significant seasonal cycle of GEM at this station with winter concentrations being 20% higher than summer concentrations. These studies have suggested that: (a) the generally elevated GEM concentrations at this site may be partly explained by Hg emissions to the atmosphere from the ocean into the marine boundary layer; and (b) increased wintertime fossil fuel combustion for domestic heating and/or more intensive summertime Hg oxidation (particularly, by OH radical) may account for the seasonal cycle. Thus, there are a number of potential reasons for the systematic underprediction of GEM concentration at IE31 by the models: underestimation of Hg evasion from the ocean surface, uncertainty in model photochemistry, and the use of constant – rather than seasonally varying – anthropogenic emissions.

The GEM comparison data for the whole year are shown in Fig. 3 for the models that conducted year-long simulations. It is seen that on an annual basis, the spread of the modelled values is lower than the monthly results (below  $\pm 20\%$ ). The lower annual scattering is no doubt a reflection of the fact that fewer models are being compared. In addition, the longer time period may cause some differences to be averaged out. One of the models (DEHM) demonstrates somewhat lower GEM concentrations than other models. For four of the five stations, the deviation of mean modelled values from the observations is less than 15%. Similar to the monthly results the models overestimate the observations at station SE02.

## 6. Wet deposition

The modelled and observed estimates of Hg wet deposition at nine monitoring stations in February and August 1999 are presented in Fig. 4. As seen from the

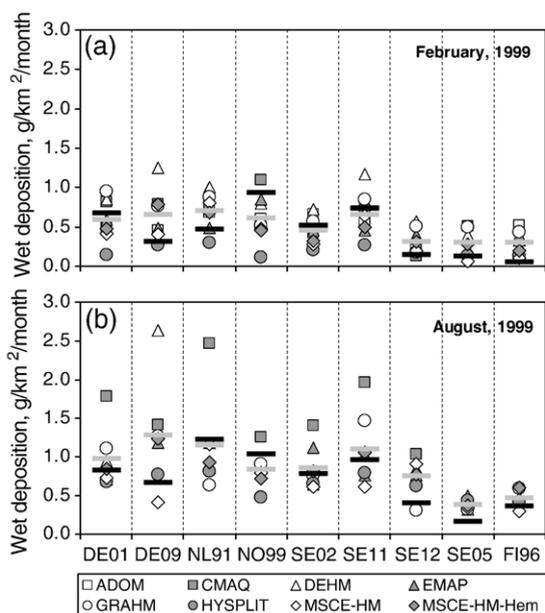


Fig. 4. Modelled and observed monthly Hg wet deposition at monitoring stations in February (a) and August (b) 1999. Symbols depict modelling results, light grey dashes show the ensemble average, black dashes present observed values.

figures both models and observations tend to show lower deposition in February than in August. The spread of modelled wet deposition is significantly larger (up to  $\pm 80\%$ ) than that of GEM concentrations. This is at least partly a consequence of the fact that wet deposition is strongly influenced by short-lived oxidised Hg forms (RGM, TPM), the forms which are most challenging for models (Ryaboshapko et al., 2007-this issue). Another source of uncertainty contributing variation is the estimates of precipitation in the different gridded meteorological datasets used by the models.

Nevertheless, at five of nine stations ensemble-average modelled values agreed with observed ones within 50%. Exceptions are German and Nordic stations DE09, SE12, SE05 and FI96. Most models overestimated wet deposition at DE09, a station located at the Baltic coast (Fig. 1) with relatively low levels of measured wet deposition ( $\sim 0.5 \text{ g/km}^2/\text{month}$ ). A possible explanation is the uncertainty in the spatial distribution or speciation of Hg anthropogenic emissions. In addition, comparison of modelled and measured precipitation shows that the precipitation estimates provided by meteorological models to the chemical transport models tended to be overestimated at this site during wintertime. Almost all the models overpredicted deposition at stations located in Central (SE12) and Northern Scandinavia (SE05, FI96). This region does not contain any significant known emission sources, so errors in emissions are

unlikely to be responsible for the discrepancy. In these cases, reasons for the model overpredictions might include the following: (a) overestimation of  $\text{Hg}^0$  oxidation by existing chemical schemes under the cold conditions of the Arctic; and (b) overestimation of modelled Hg atmospheric wet deposition removal via snow, common in these latitudes.

Comparison of modelled and observed values for the whole year is presented in Fig. 5. The spread of the annual modelled results is lower than that for monthly ones and does not exceed  $\pm 45\%$ . Except for the stations mentioned above, the normalized deviation is less than 40%. As seen from the figure, in general, the models overestimate annual wet deposition of Hg at most stations. The reason for this overestimation may be connected with uncertainties of kinetic constants of chemical reaction responsible for GEM oxidation in the atmosphere. Recently, Calvert and Lindberg (2005) re-evaluated GEM oxidation mechanisms by thermodynamic calculations and chemical modelling. They suggested that the oxidative removal of GEM by ozone and hydroxyl radical currently included in the atmospheric transport models may be significantly overestimated.

To summarize the deviation of the modelling results from the observations we show in Fig. 6 the cumulative distribution of the deviation factor of all modelled monthly wet depositions

$$DF = \max \left( \frac{X_{\text{mod}}}{X_{\text{obs}}}, \frac{X_{\text{obs}}}{X_{\text{mod}}} \right).$$

These plots quantify the probability of model results to reproduce observations within a given degree of deviation from the observed values. As seen from the figure, 50–70% of modelled values are within a factor of 2 of measured values, and 90%–100% are within a factor of 5, depending on the model. However, caution

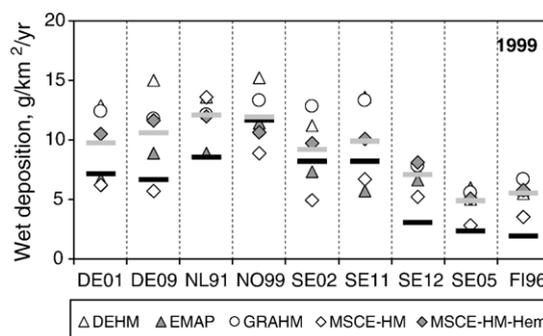


Fig. 5. Modelled and observed annual Hg wet deposition at monitoring stations in 1999. Symbols depict modelling results, light grey dashes show the ensemble average, black dashes present observed values.



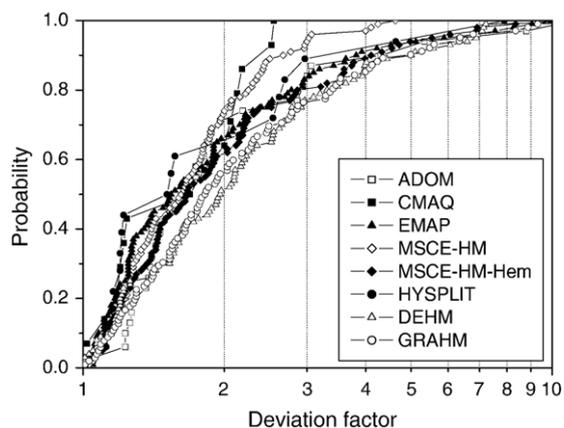


Fig. 6. Cumulative distribution functions of the deviation factor of all monthly modelled and observed pairs of wet deposition at monitoring sites.

should be exercised in model-to-model comparisons based on this figure, as there are differences in the number of months and/or number of stations simulated by the different models.

## 7. Dry and total deposition

As mentioned above, Hg dry deposition fluxes are not routinely measured but can be modelled. Hence, comparison of dry deposition values is possible only between the models. Fig. 7 shows dry deposition estimates obtained by the models at a number of monitoring stations for February (a) and August 1999 (b). Comparison of the 2 months demonstrates that most models predict lower dry deposition in February. This is likely a consequence of more stable atmospheric conditions, increased presence of snow surfaces, and reduced foliage, all of which lead to increased resistance to dry deposition.

As one can see from Fig. 7, the spread of the model results is significant and at some stations exceeds 100%. The spread of the annual values (see Fig. 8) is somewhat lower than that of the monthly ones but is also significant (up to  $\pm 90\%$ ). Particularly large model-to-model scattering is a characteristic of the northern stations. One of the models (GRAHM) predicts significantly higher dry deposition than other models for stations SE05, SE11, SE12 and FI96. This discrepancy is more pronounced in August than in February. GRAHM is one of the few models that included dry deposition of GEM (see Ryaboshapko et al., 2007-this issue, Table 1). Although dry deposition of this Hg form is very slow in comparison with that of other Hg species, the large relative concentration of GEM in the ambient air (more than 95%) can lead to significant dry deposition. This may at least partly

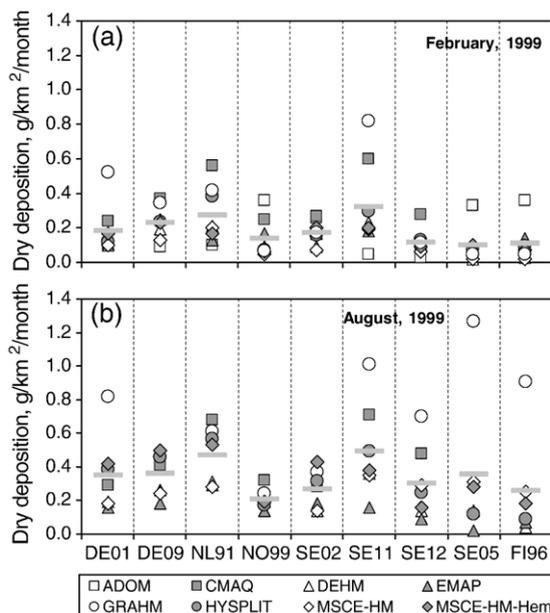


Fig. 7. Modelled monthly Hg dry deposition at monitoring stations in February (a) and August (b) 1999. Symbols depict modelling results, light grey dashes show the ensemble average.

explain the higher dry deposition fluxes estimated by GRAHM for the stations mentioned above, which are located in forested areas. On the other hand, the other two models that considered dry deposition of GEM (MSCE—HM and MSCE—HM-Hem) did not predict such elevated values of total dry deposition. However, in contrast to GRAHM, these models applied a simplified scheme of RGM dry deposition with fixed deposition velocity (0.5 cm/s) instead of the resistance-transfer approach. This scheme may have led to an underestimation of RGM dry deposition, particularly, to forests.

Table 2 presents the model-estimated dry deposition contributions to total Hg deposition (dry+wet) for

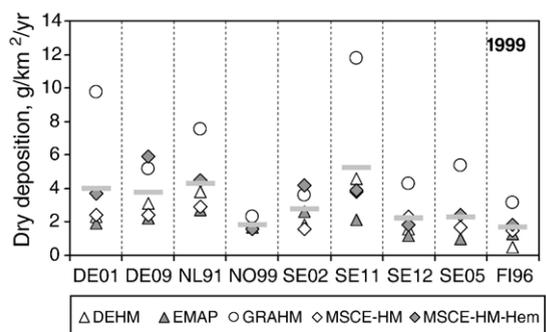


Fig. 8. Modelled and observed annual Hg dry deposition at monitoring stations in 1999. Symbols depict modelling results, light grey dashes show the ensemble average.

Table 2

Mean values and ranges of dry deposition contributions to the total depositions at monitoring stations

Model	Mean value and range of dry deposition contribution to the total deposition, %		
	February 1999	August 1999	1999 as a whole
ADOM	24 (8–41)	30 <sup>a</sup> (12–47)	
CMAQ <sup>b</sup>	30 (18–69)	22 (14–32)	
DEHM	12 (5–17)	19 (9–30)	16 (8–25)
EMAP	25 (16–40)	15 (4–28)	21 (14–29)
GRAHM	24 (9–49)	47 (21–80)	35 (15–49)
HYSPLIT	45 (38–56)	31 (18–41)	
MSCE—HM	20 (9–25)	30 (19–48)	28 (16–38)
MSCE—HM-Hem	24 (11–38)	29 (17–43)	25 (13–32)

<sup>a</sup> Data for July 1999.

<sup>b</sup> Data for 7 stations (stations SE05 and FI96 were outside the model domain).

February, August and the whole year 1999. A relatively large range is expected for any given model, due to differences in meteorology, surface characteristics, and wet deposition at the different locations considered. Nevertheless, the mean values and ranges give some measure of the relative importance of dry and wet deposition. Most models estimate the dry deposition contribution to be roughly 1/5–1/3 of the total at the sites considered in this study. On the other hand, measurements of ecosystem fluxes of Hg at watersheds in Europe and the United States (Munthe et al., 2004) suggest that contribution of Hg dry deposition – estimated as sum of litterfall and net throughfall – may be as large as or even exceed wet deposition. Thus, it is possible that contemporary Hg atmospheric transport models are systematically underestimating dry deposition, e.g., by underestimating or omitting GEM air-vegetation exchange.

In Fig. 9, the stations are ordered according to their latitudes and it is seen that, the models demonstrate a systematic descending trend of total Hg deposition from “polluted” southern sites to “background” northern sites. The modelled total deposition tends to be a factor of 1.5 to 2 higher in August than in February. While not shown here, the south–north trend is also predicted for the annual estimates. Also, while not shown here, the spread of modelled total deposition values for the whole year do not exceed 40%, whereas the spread in the monthly values can be higher — up to 100% for the northern stations.

## 8. Deposition budgets for selected countries

Deposition of Hg to European countries depends not only on regional anthropogenic emissions but also on

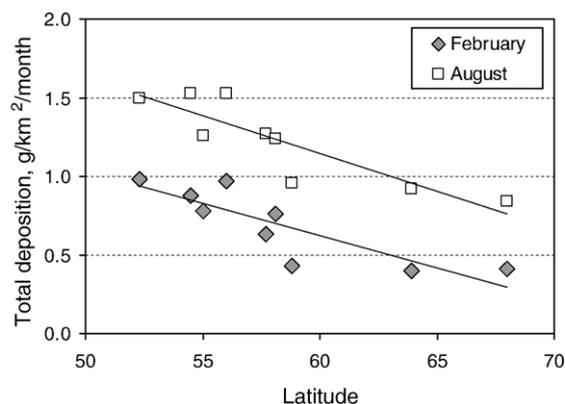


Fig. 9. Spatial descending trend of Hg total depositions (ensemble average of all the models) from “polluted” south to “background” north stations in February and August 1999.

natural sources, re-emissions and global sources. A significant fraction of Hg anthropogenic emissions are in the form of elemental mercury (GEM) and it is believed that essentially all natural sources and re-emissions emit mercury as GEM. This form is long-lived enough to undergo significant intercontinental transport. Deposition from these sources then arises through oxidation of GEM and subsequent removal processes, and as mentioned above, possibly through deposition of GEM itself. Accordingly, the following atmospheric budget quantities were estimated by the models within the comparison:

- NAS deposition caused by National Anthropogenic emission Sources of a given country;
- EAS deposition caused by all European Anthropogenic emission Sources except the anthropogenic sources of a given country (European transboundary pollution);
- GNR deposition caused by Global anthropogenic sources (excluding European ones), Natural sources and Re-emission;
- ROF Relative Out-Flow determined as a fraction of national anthropogenic emissions transported outside a given country.

Three countries – the UK, Italy, and Poland – were selected for analysis in this study as illustrative examples. The three countries are similar in their areas but are very different in their locations relative to the main European sources of Hg. The total value of the estimated national Hg anthropogenic emissions is similar between

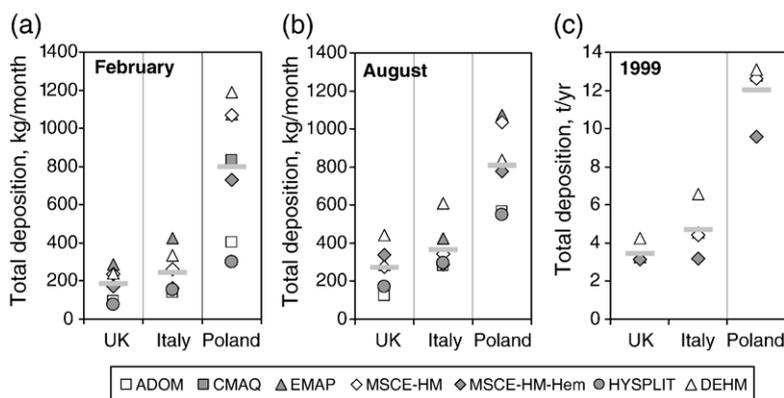


Fig. 10. Total Hg deposition to the UK, Italy and Poland: (a) in February 1999; (b) in August 1999; and (c) in the whole year 1999. Symbols depict modelling results, light grey dashes show the ensemble average.

the UK and Italy but is approximately 3 times higher in Poland. Total Hg deposition to these three countries predicted by different models is shown in Fig. 10 for February, August and the whole year 1999. Total Hg deposition to Poland is 2–3 times higher than deposition to the other countries, which is consistent with the differences in anthropogenic emissions. In addition, deposition is larger in August than in February, most likely due to more intensive oxidative removal of GEM both from national and global sources under summer conditions. It is seen that there is a significant spread of modelling results (up to  $\pm 60\%$ ) for February, while for the whole year, the spread does not exceed  $\pm 35\%$ . The participating models show a relatively wide range in the absolute amounts of total Hg deposition to the selected countries, but as shown below, they are more consistent in their estimates of the relative importance of the different budget items.

The different model's estimates of the atmospheric budget items for the UK, Italy, and Poland are shown in Figs. 11, 12 and 13, respectively. Some models (ADOM, CMAQ) did not estimate all items of the deposition budget; particularly, they did not distinguish EAS and GNR. Therefore, the sum of these parameters (EAS+GNR) is presented in Figs. 11–13 for these models.

Contribution of national sources is the most substantial for Poland (Fig. 11). It is estimated by the different models to be approximately 60%. The model-estimated contribution of global and natural sources generally does not exceed 20%. It is understandable since this country is located in Central Europe and has relatively high emissions. The spread of modelling results does not exceed  $\pm 30\%$  for these two source types but is somewhat higher for other European sources.

Italy is characterized by lowest contribution of national sources (about 30%) among the countries consi-

dered here (Fig. 12). This can be at least partly explained by the elongated form of the country's territory enhancing the outflow of Hg from national sources beyond the borders. The estimated contribution of global and natural sources is more significant in August than in February. This is most likely due to more effective oxidation of elemental Hg during summer time, which, in turn, leads to increased Hg deposition from distant sources. The spread of the estimates obtained by different models can be larger than  $\pm 50\%$  for monthly results but does not exceed  $\pm 30\%$  for annual values.

Contribution of European sources is estimated to be the lowest for the UK (Fig. 13). It varies from about 5% in February to 15% in August. This fact is reasonable because, based on prevailing winds, the UK tends to be on the upwind periphery of Europe. The low absolute contribution amount of these sources results in significant spread of the model estimates (up to 100%). On the other hand, the spread of contributions of national and global/natural sources does not exceed  $\pm 30\%$ .

All the models predict that the majority of national anthropogenic emissions are transported outside the country (parameter ROF in Figs. 11–13). Estimated percentages of Hg transported outside the country are relatively consistent among the models — most models estimate that 85–90% of British and Italian emissions and 70–75% of Polish atmospheric emissions leave their country of origin.

## 9. Summary and conclusions

A five-year, multi-phase project involving a number of Hg atmospheric transport models has been completed. The central feature of the final phase described here was an evaluation and intercomparison of the capabilities of the participating models to simulate long-term

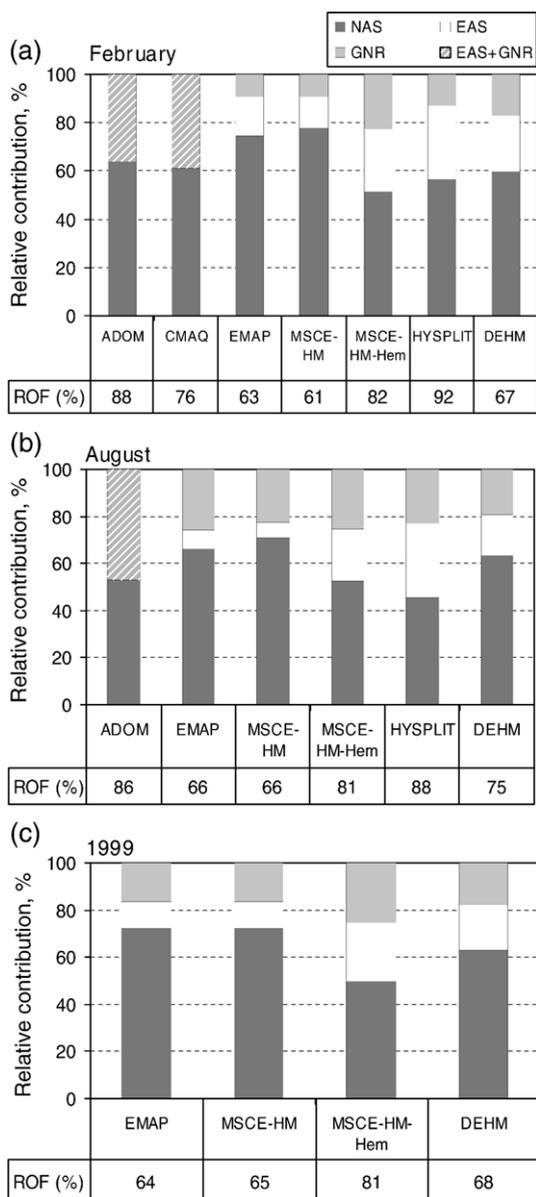


Fig. 11. Contribution of national anthropogenic (NAS), European anthropogenic (EAS), and global, natural and re-emission sources (GNR) to Hg deposition over Poland: (a) in February 1999; (b) in August 1999; and (c) in the whole year 1999. For models, which did not distinguish European and global sources, a sum of EAS and GNR is shown. Relative output flow (ROF) is also presented for each country.

concentrations and deposition of Hg and atmospheric budgets for individual countries. The deposition and budget calculations are of interest in general to environment protection concerns and in particular for the implementation of the Heavy Metal Protocol to the Convention on Long-range Transboundary Air Pollution.

It was found that elemental Hg concentrations in air at the monitoring sites investigated were influenced

primarily by the “hemispheric background”, and only partly by the European anthropogenic emissions. For most of the monitoring stations the models were able to reproduce the monthly observations of GEM with an accuracy of  $\pm 30\%$ . The spread of the annual modelling results does not exceed  $\pm 20\%$ .

Comparison of calculated and measured data on wet Hg deposition shows that for the sites in relatively

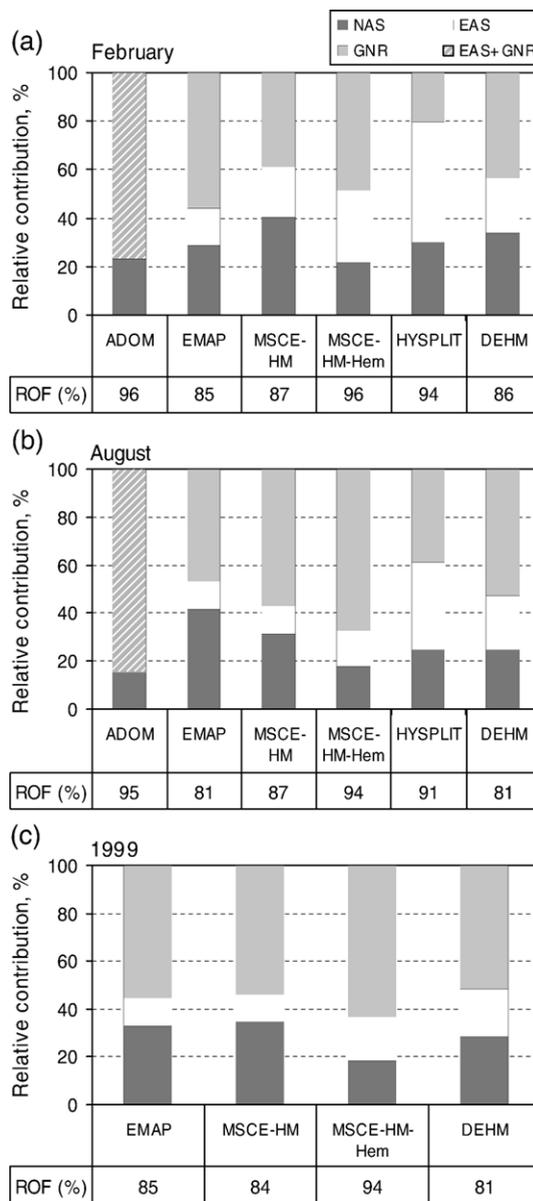


Fig. 12. Contribution of national anthropogenic (NAS), European anthropogenic (EAS), and global, natural and re-emission sources (GNR) to Hg deposition over Italy: (a) in February 1999; (b) in August 1999; and (c) in the whole year 1999. For models, which did not distinguish European and global sources, a sum of EAS and GNR is shown. Relative output flow (ROF) is also presented for each country.

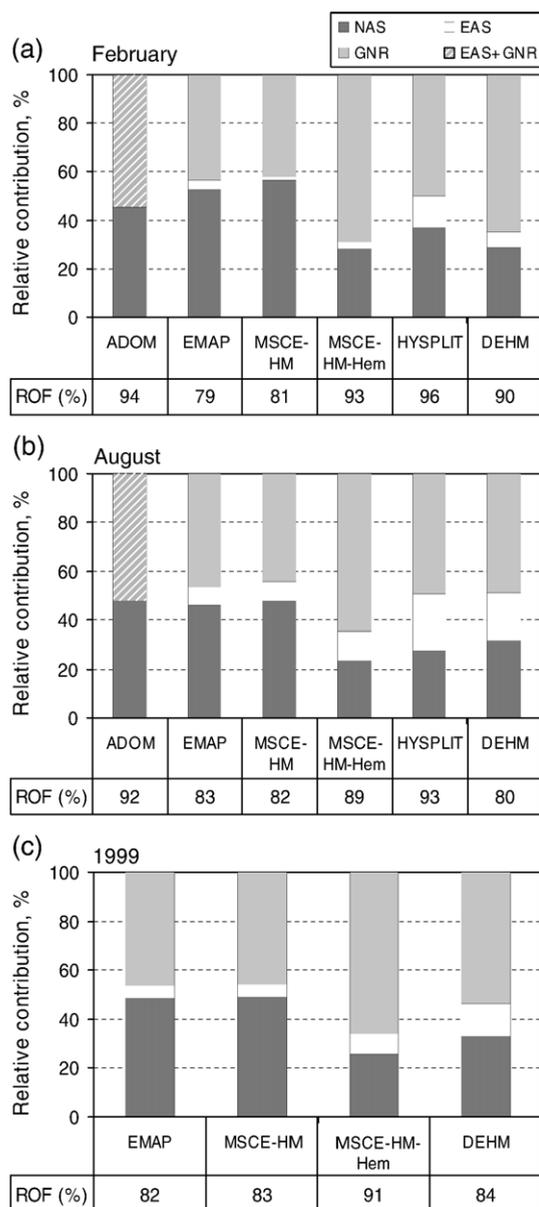


Fig. 13. Contribution of national anthropogenic (NAS), European anthropogenic (EAS), and global, natural and re-emission sources (GNR) to Hg deposition over the UK: (a) in February 1999; (b) in August 1999; and (c) in the whole year 1999. For models, which did not distinguish European and global sources, a sum of EAS and GNR is shown. Relative output flow (ROF) is also presented for each country.

industrialised regions in Germany, The Netherlands, and Southern Scandinavia, the modelled monthly values are in agreement with the observations within  $\pm 50\%$ . However, for the northern background sites, all of the models tend to significantly overestimate the observations. The spread of the annual modelled results

is lower than that for monthly ones and does not exceed  $\pm 45\%$ . Overall, the probability of predicting wet depositions within a factor of 2 of the measurements was 50–70% while the probability of obtaining results more than a factor of 5 different from measurements was less than 10%.

The spread of the modelled Hg dry deposition results is significant (up to  $\pm 100\%$  for the monthly results and  $\pm 50\%$  for the annual results). The highest differences were found at sites in Northern Europe. Most of the models estimate that dry deposition contributes roughly 1/5–1/3 of the total Hg deposition. However, available measurements indicate that this contribution may be significantly higher for Hg deposition to forests.

Comparison of the calculated Hg deposition budgets shows that the participating models agree in simulating monthly values of the budget items for individual countries within a range of  $\pm 60\%$ , whereas the spread of annual results does not exceed  $\pm 30\%$ . As with other parameters, the lower annual scattering is likely due to fewer models being involved and also possibly due to counterbalancing differences over longer time periods, e.g., due to smoothing of highly variable meteorological factors during the year-long period. All the models predict that the majority of national anthropogenic emissions are transported outside the country.

This study has highlighted the likely role of the following factors in creating uncertainty in Hg atmospheric transport modelling. Available estimates of Hg anthropogenic and natural emissions contain significant uncertainties. In particular, the chemical speciation and the temporal variations of anthropogenic emissions are incompletely characterized. There are significant uncertainties in natural and re-emissions, and there are no reliable spatially resolved data on re-emissions of Hg at the global scale. Knowledge of Hg transformations in the atmosphere still remains insufficient. Reaction rate constants of the most important oxidation reactions as well as the reaction products are poorly known. Besides, the characterization and parameterisation of removal processes for different Hg compounds need more accurate definition. This may be of particular importance for Hg dry deposition to forested areas. Finally, there is an urgent need to have reliable monitoring data for different Hg atmospheric forms on a routine basis for model evaluation and improvement.

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