

POPs and Hg Intercomparison and Evaluation

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EMEP/MSC-E

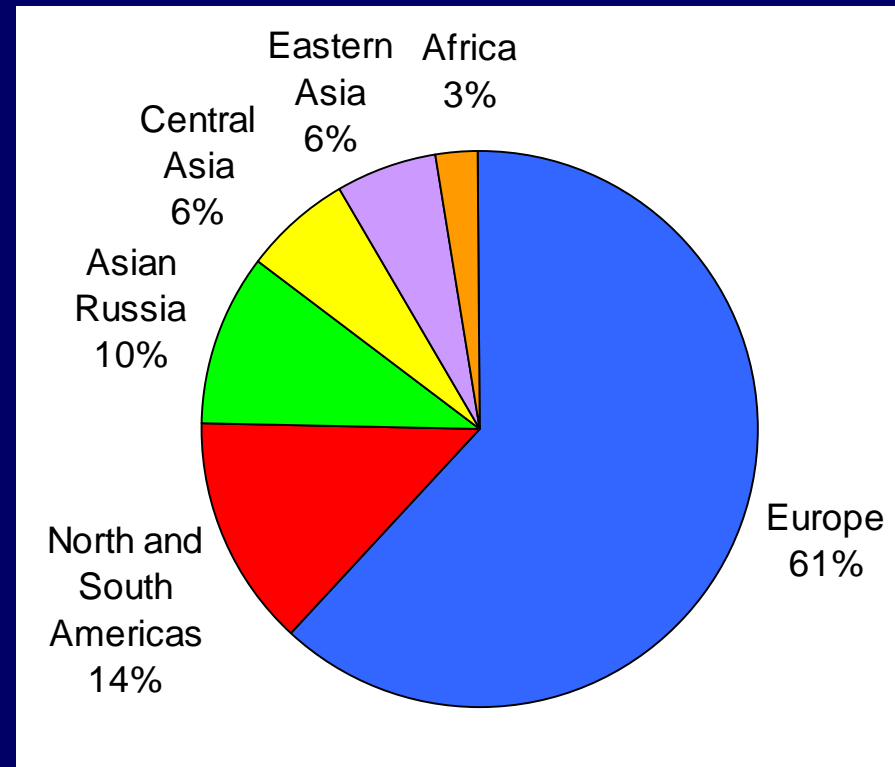
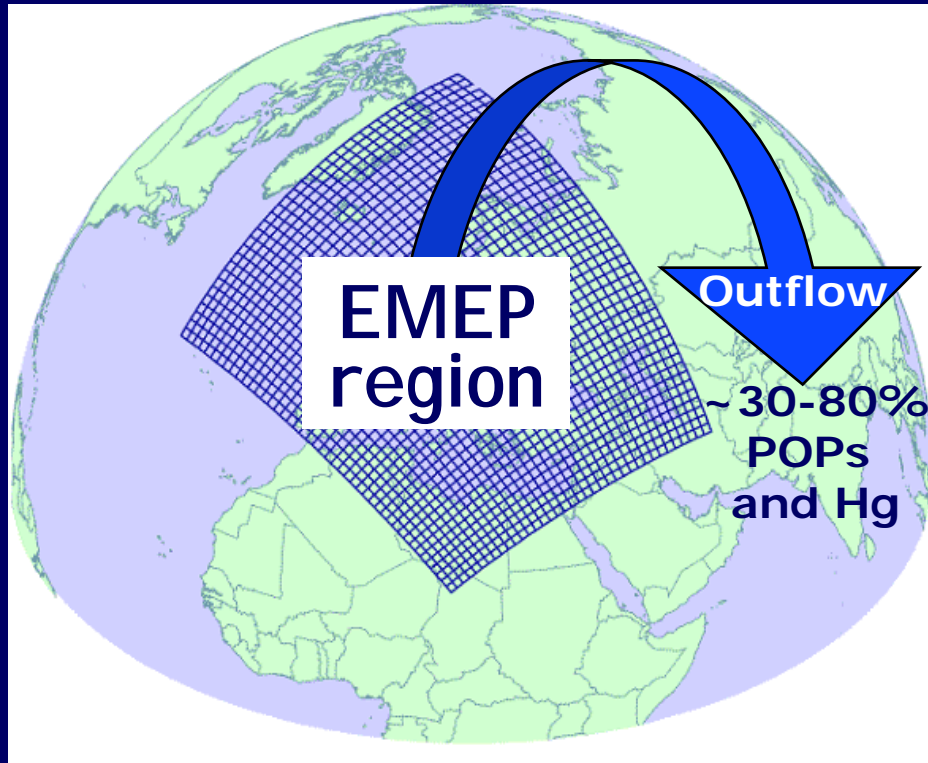


LRTAP Convention requirements for HM and POP model output

HM and POP Protocol (*Articles 8,9*)

EMEP shall provide to the Executive Body calculations of **transboundary fluxes and depositions** of HMs and POPs within the geographical scope of EMEP.

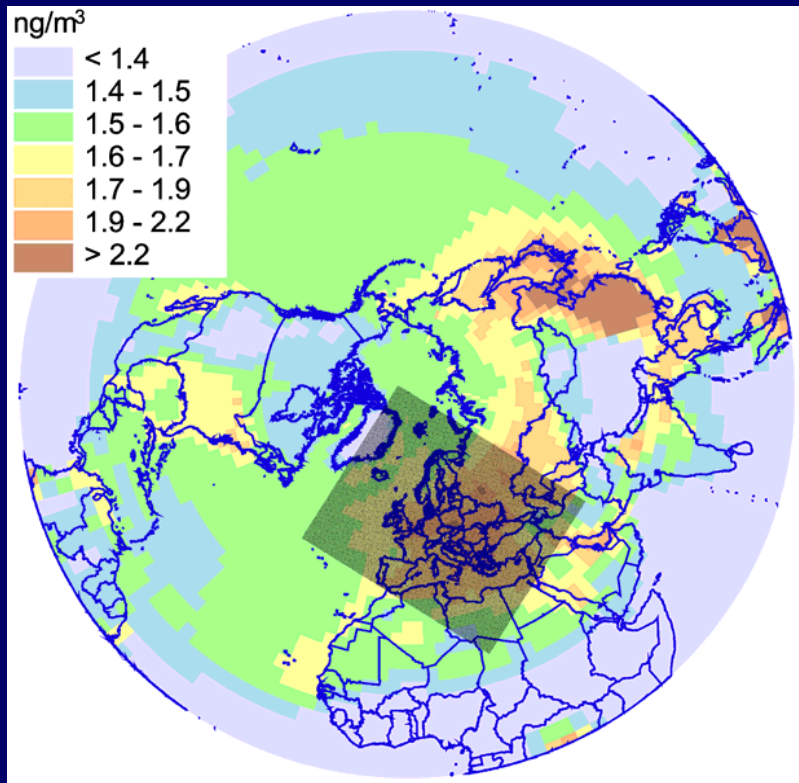
Intercontinental transport



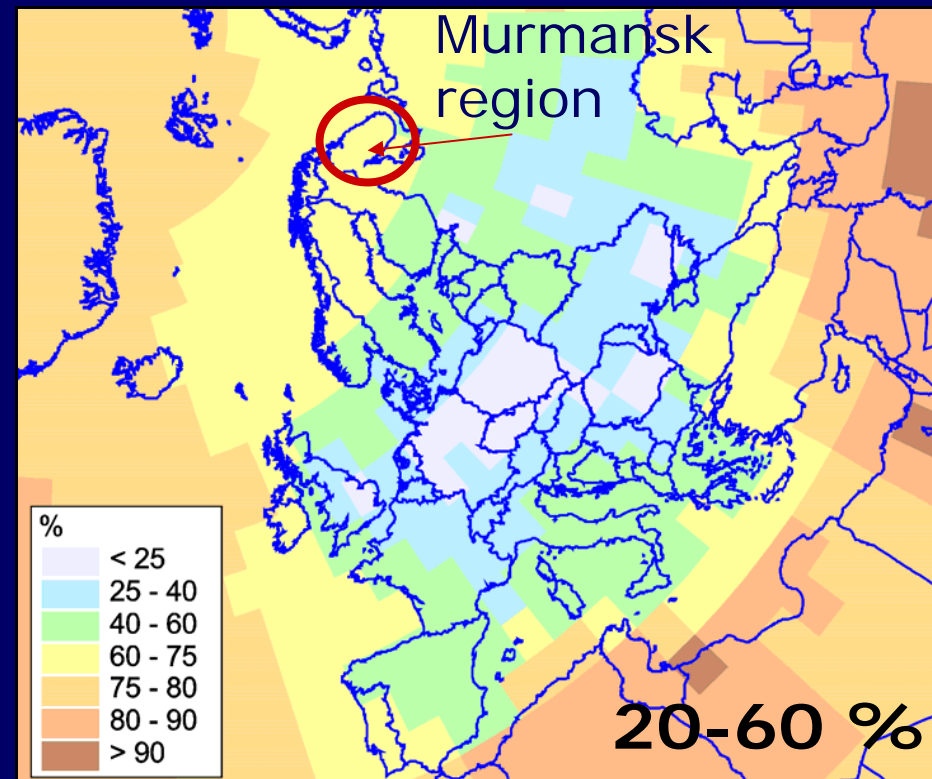
Intercontinental transport from European sources

Intercontinental transport

Contribution of external sources to Hg pollution in Europe



Spatial distribution of total gaseous Hg in the Northern Hemisphere



Relative contribution of external sources to Hg deposition in Europe

HMs and POPs model intercomparison

Main Goal

- Evaluation of models state-of-the-art and ability to produce concentration and deposition fields and long-range transboundary transport of HMs and POPs on the basis of
 - model-to-model comparison
 - model results against measurements

Scientific goals

- Increasing transparency of models of different types and resolution
- Sensitivity study. Evaluation of influence of uncertainties in model parameterization on the model output
- Improvement of model parameterization and description of main physical-chemical processes on the basis of advanced scientific knowledge

EMEP/MSC-E experience in model intercomparison

Model intercomparison study organized by MSC-E for:

| | |
|---------------------------|-------------------------|
| Pb – | 1995 - 1996 (5 models) |
| Cd – | 1997 - 2000 (5 models) |
| Hg – Stage I-III | 2001 - 2005 (10 models) |
| POPs – Stage I-III | 2002 - 2006 (17 models) |



EMEP POP model intercomparison, 2004-2006

Aim: to improve our understanding of POP long-range transport and behaviour in the environmental compartments.

- Evaluation of uncertainties of main physical-chemical parameters used for POP modelling.
- Simulation of basic processes of POP fate in main environmental compartments
- Estimation of mass balance, intermedia fluxes and concentration of POPs in different environmental compartments

Participation - 17 models of different types and resolution including 8 global/hemispheric models (ChemRange, ClimoChem, CAN/POPs, Globo-POP, MEDIA, DEHM-POP, SimpleBox, MSCE-POP)



Experiment conditions:

Input data:

- Emissions (global 1°x1°, *Breivik et al.*, 2002)
- Land cover data
- Leaf area index
- Organic matter content in soil
- Initial concentrations in media

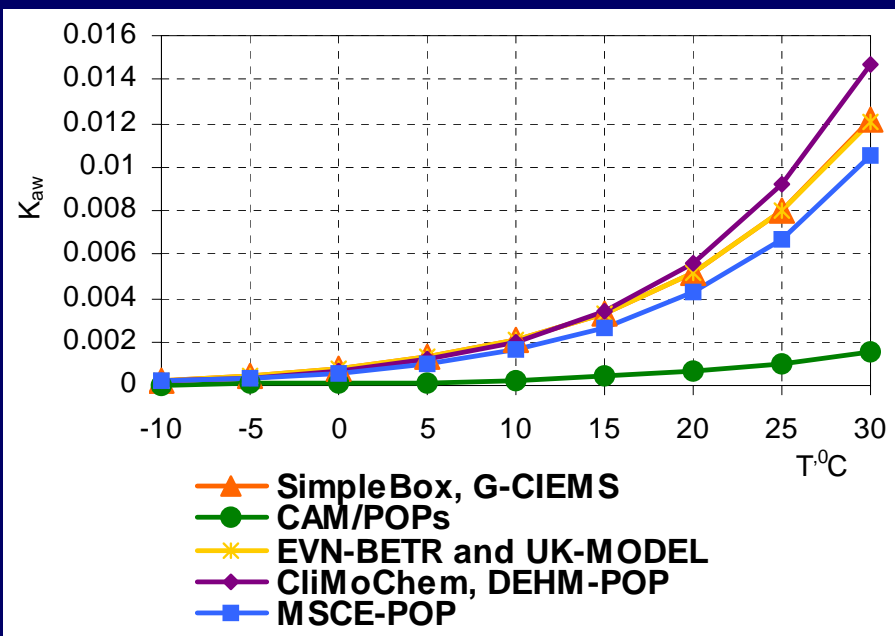
Meteorology: model specific meteorological data

Simulations:

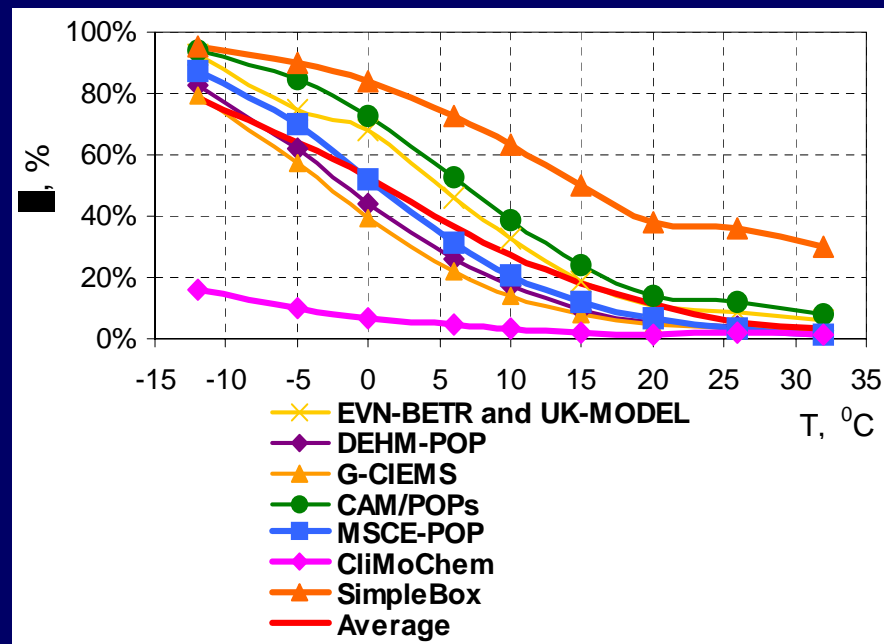
two one-year simulation (2000) and one simulation for 20-year period (1981-2000) for some PCB congeners

Analysis of variability physical-chemical parameters and description of basic processes

air/water partition coefficient
(K_{aw} , dimensionless)



Gas-particle partitioning process
(fraction of particulate phase in air)



| | -10° | 10° | 25° |
|---------|------|-----|-----|
| max/min | 8 | 8 | 9 |

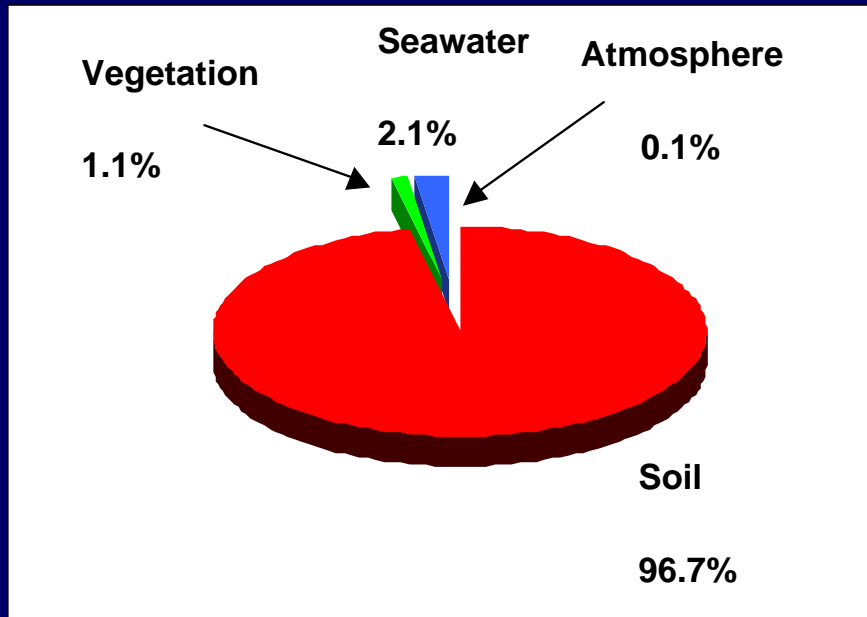
| | -10° | 10° | 25° |
|---------|------|-----|-----|
| max/min | 6 | 21 | 20 |

PCB-153

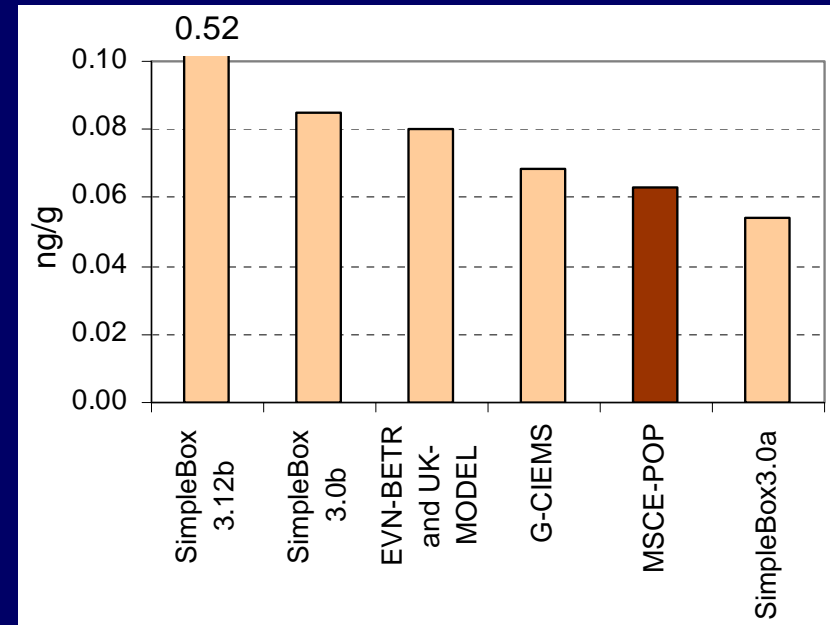


Analysis: POP mass distribution and concentrations in media

Mass distribution between environmental media, %



Concentrations in soil, ng/g



Averaged over participated models

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Main results:

Most participating POP models provide reasonable agreement in:

- model parameterisation and description of main processes;
- simulation of mass distribution and degradation in main environmental media;
- evaluation of concentration levels at interfaces of main environmental media;
- description of spatial distribution of concentrations and depositions.

Publications:

MSC-E Technical Report 1/2004 "POP Model Intercomparison Study. Stage I."

EMEP/MSC-E Technical Report 4/2005 "POP Model Intercomparison Study. Stage II."

One manuscript is under preparation

Mercury model intercomparison study

Aim: A comprehensive analysis of different approaches to simulate mercury dispersion, transformations and removal from the atmosphere; improvement available approaches.

Main elements:

I – comparison of chemical modules

II – modelling monthly and annual means and comparison against observations

III – evaluation and comparison of source-receptor relationships

Participation: 10 models of different types and resolution including 3 global/hemispheric models (GRAHM, DEHM and MSCE-HM-HEM)



Stage I. Comparison of chemical modules

Aim: consideration of evolution of mercury concentrations in a cloud/fog environment for 48 hour period.

Experiment conditions: All participants should use their own individual values of reaction rates, water solubilities, Henry's law constants, etc.

Input parameters for comparison:

| Initial concentrations and parameters | Value, dimension |
|---|----------------------------|
| Liquid water content | 0.5 g/ m ³ |
| Water drop size, diameter | 10 μm |
| Temperature | 278°K |
| Elemental mercury in air | 1.7 ng Hg / m ³ |
| Elemental mercury in water | 0 ng Hg /l |
| Gaseous oxidized mercury in air (as HgCl ₂) | 0.05 ng Hg /m ³ |
| Particulate Hg in air | 0.05 ng Hg /m ³ |
| Oxidized mercury in water | 0 ng Hg /l |
| Mercury adsorbed on soot particles in water | 0 ng Hg /l |
| Sulphur dioxide in air | 1 μg S /m ³ |
| Sulphite ion in water, [SO ₃ ⁼] | 0 M |

The output parameters:

Elemental mercury (Hg^0) in the gas phase

Oxidized mercury (Hg^{2+}) in the gas phase

Mercury in the aerosol particulate phase

Elemental mercury (Hg^0) in the liquid phase

Oxidized mercury (Hg^{2+}) dissolved

Mercury in the particulate phase within droplets

Temporal resolution - 10 min, mercury mass in cubic meter.

Simulation: six 48 hours simulations

| Parameter/case | case 1 | case 2 | case 3 | case 4 | case 5 |
|---|--------|--------|--------|--------|--------|
| Hg ⁰ , ng/m ³ | 1.7 | 1.7 | 1.7 | 1.7 | 1.7 |
| HgCl ₂ (gas), ng/m ³ | 0 | 0 | 0 | 0.005 | 0.005 |
| HgCl ₂ (part), ng/m ³ | 0 | 0 | 0.04 | 0 | 0.04 |
| Soot | No | Yes | No | No | Yes |

Output:

Elemental mercury concentrations (Hg⁰) in the liquid phase averaged for the second day of the calculated evolution, ng Hg/L

| Model | case 1 | case 2 | case 3 | case 4 | case 5 |
|---------|--------|--------|--------|--------|--------|
| CMAQ | 10 | 17 | 10 | 10 | 35 |
| GKSS | 15 | 15 | 75 | 20 | 80 |
| AER | 25 | 35 | 110 | 25 | 115 |
| MSCE-HM | 20 | 45 | 70 | 20 | 120 |
| IVL | 10 | 25 | 80 | 10 | 90 |

Main results:

A comparative evaluation of the chemistry module performances led to main issues:

- in general, results from all models in terms of total aqueous mercury concentrations agree within a factor of about two, suggesting that there are no significant processes missing from their formulations.
- the results do show some differences that indicate important uncertainties regarding the reduction-oxidation balance of aqueous mercury and the fraction of aqueous mercury that is sorbed to suspended particles.

Publications:

EMEP/MSC-E Technical Report 2/2001 "Intercomparison Study of Numerical Models for Long-range Atmospheric Transport of Mercury Stage I"

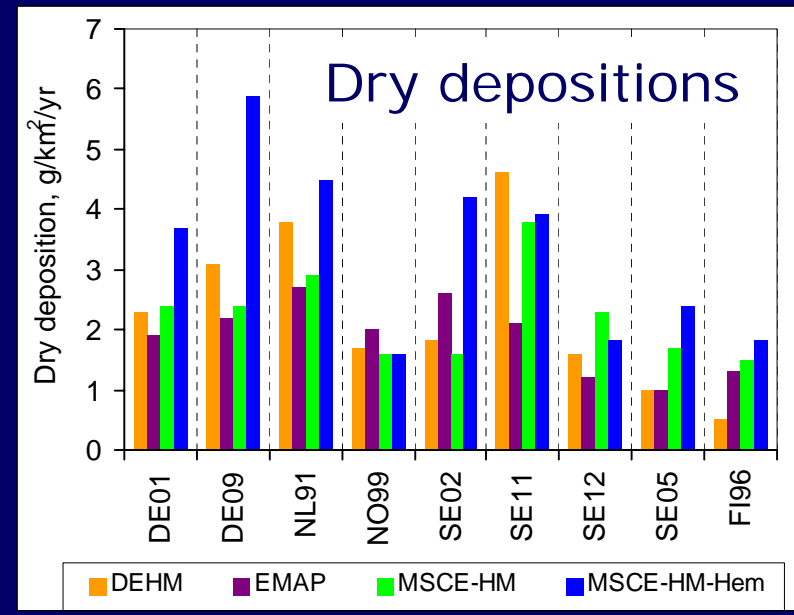
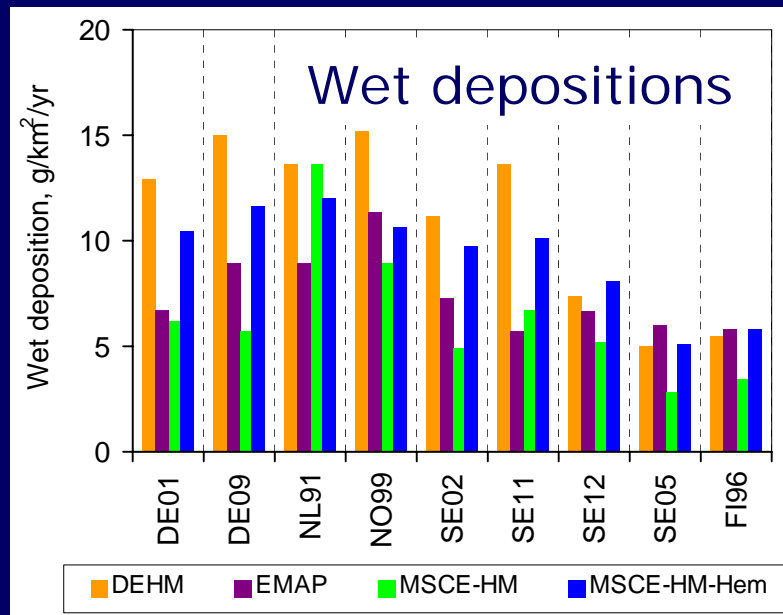
Atmospheric Environment, 2003 "Comparison of mercury chemistry models"

Mercury model intercomparison

Stage II. Comparison of model results with observations

Input data: European scale (50x50 km) Hg emissions for regional models and 1°x1° dataset for global models. Natural Hg emissions prepared by MSC-E

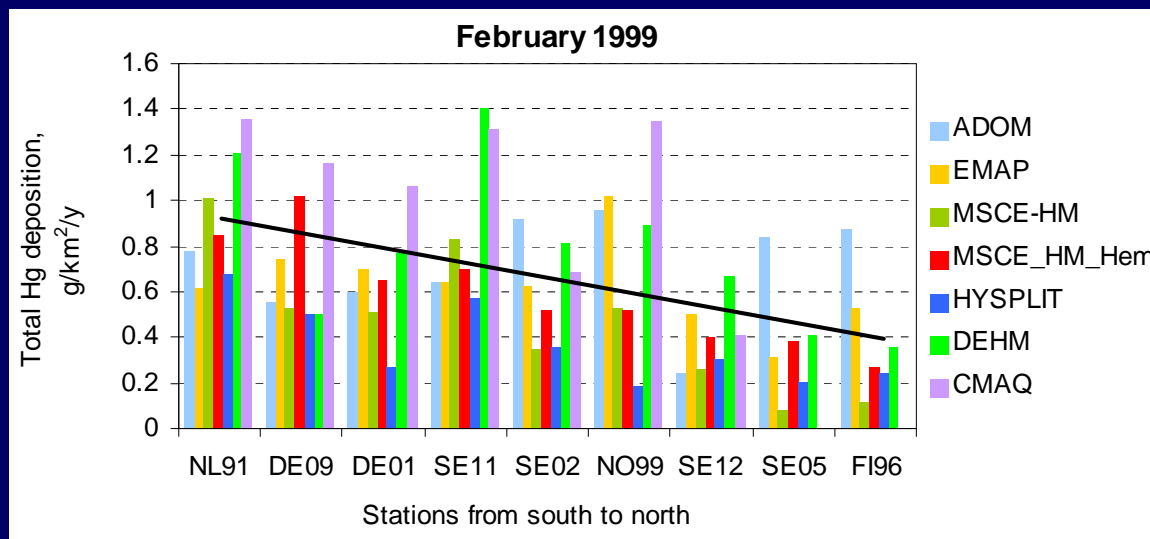
Meteorological data: NCEP, ECMWF, MM5



Model output: annual Hg wet and dry depositions at monitoring stations in 1999

Stage II. Comparison of model results with observations

Model output



Predicted total (wet + dry) Hg depositions at the monitoring stations

Analysis

| | NO99 | SE02 | FI96 | NO42 | IE31 |
|-----------------------------------|------|------|------|------|------|
| Mean modelled | 1.64 | 1.67 | 1.68 | 1.66 | 1.52 |
| Mean deviation of modelled values | 11% | 8% | 12% | 12% | 10% |
| Observed | 1.70 | 1.33 | 1.60 | - | 1.70 |
| Deviation factor for the means | 1.04 | 1.25 | 1.05 | - | 1.12 |

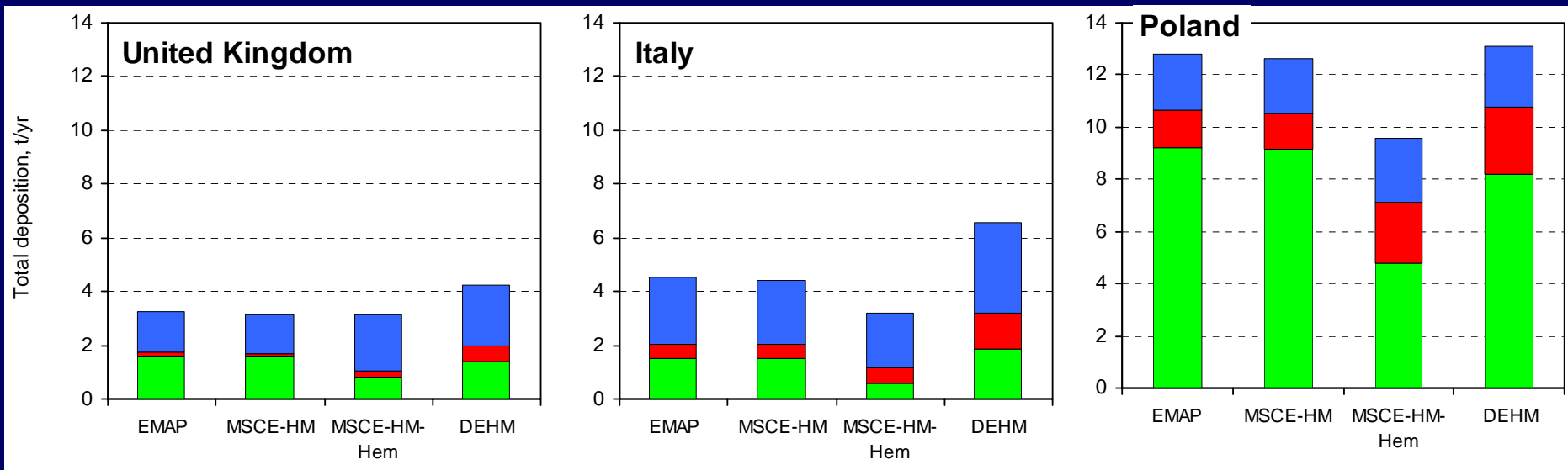
Main results

1. For most of the monitoring stations the models can predict the observations of concentration of Hg with accuracy within a factor of 1.2. Model-to-model variations of the results are within 12%.
2. Model-to-model variations of predicted monthly wet deposition values are within $\pm 50\%$. Variations for annual values are small: from 13% to 40%.
3. Comparison of the modelling results for mercury dry deposition shows that most of the models predict contribution of this process into total deposition on the level of 30%.

Publications: *EMEP/MSC-E Technical Report 1/2003* "Intercomparison Study of Numerical Models for Long-Range Atmospheric transport of Mercury"

Stage III. Evaluation and comparison of source-receptor relationship

Annual Hg depositions in selected countries in 1999



Contribution:

- national anthropogenic sources
- European anthropogenic sources
- global, natural and re-emission sources

Main results

1. Mercury atmospheric balances for three individual countries (UK, Italy, Poland) predict that for the UK and Italy, national anthropogenic sources account for about 1/3 and for Poland more than half of total Hg deposition over country.
2. Contributions of natural sources, re-emission and remote anthropogenic sources are practically equal for the countries ($\sim 8 \text{ g/km}^2/\text{y}$).
3. All the countries are net sources of Hg for the global atmosphere: $\sim 70\text{-}80\%$ of national emissions.
4. Contribution of external global sources to the Hg pollution level in Europe is around 20-60%.

Concluding remarks on model intercomparison

Important elements:

- Clear formulation of model intercomparison aim
- Work programme
- Realistic time-table
- Agreed input data (emissions, meteorology, measurements, physical-chemical properties)
- Agreed format of input and output information
- Agreed statistical procedure
- Centralized analysis team
- Publications
- Financial support of national experts

Concluding remarks

Possible stages of hemispherical model intercomparison for Hg and POPs

1. Tracer experiment
2. Comparison of hemispherical/global model parameterization and description of physical-chemical processes which determine Hg and POPs fate on hemispherical/global level
3. Comparison of Hg and POP deposition and concentrations fields with various sets of measurements
4. Model-to-model comparison of intercontinental transport (source-receptor relationship)

Atmospheric Transport Model Evaluation Study II (ATMES-II)

Aim: comparison of long-range transport model results with measurements of the European Tracer Experiment (ETEX).

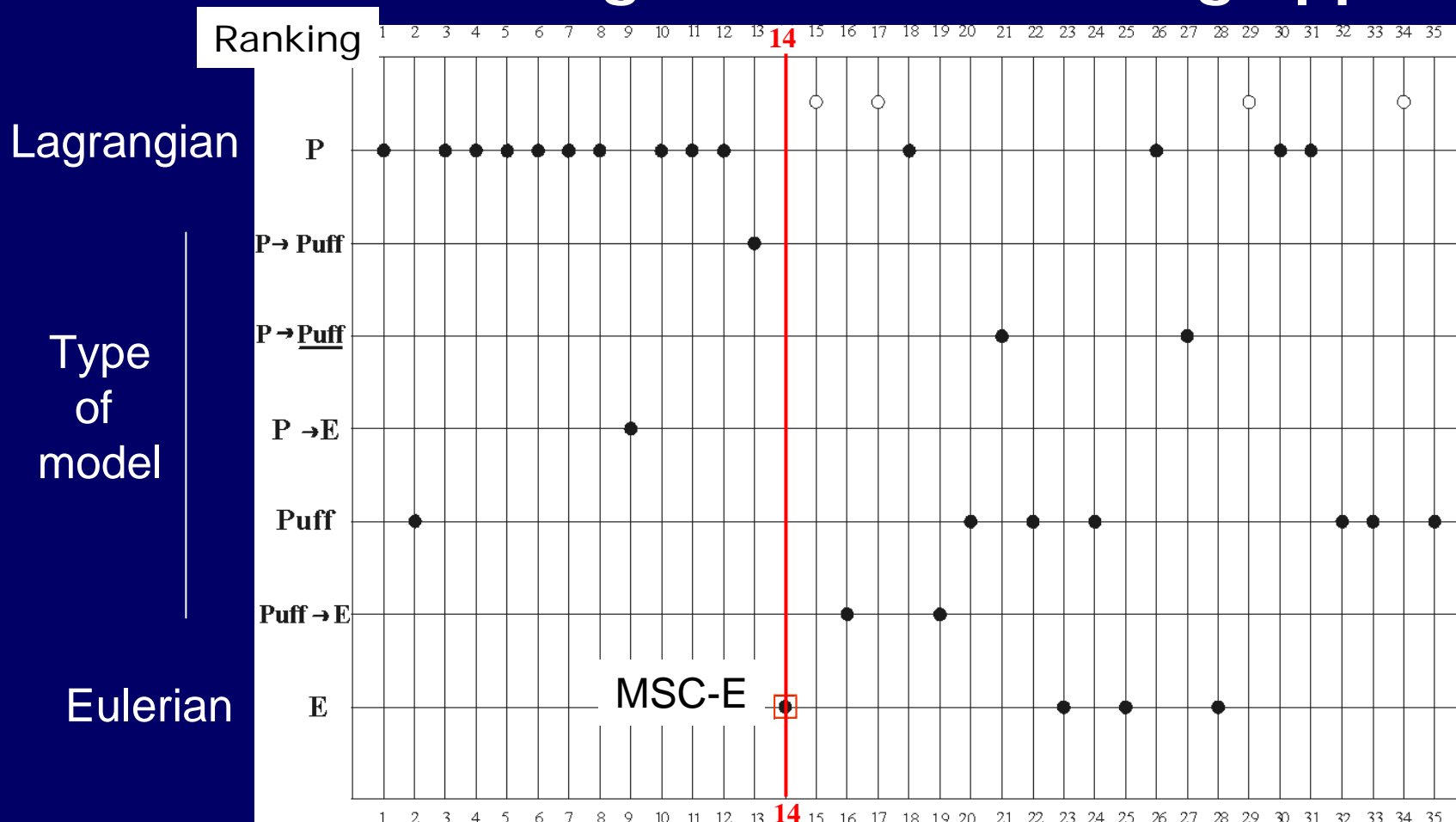
Participation: 35 models participated in ATMES-II used ECMWF meteorological data and 14 models – own meteorology.

Experiment conditions:

Emissions: 340 kg of Perfluoro-Methyl-Cyclo-Hexane (PMCH) was released during 12 hours with speed 7.95 g/s (23-24 Oct. 1994 in Bretagne, France).

Measurement data: 168 sites (with sampling period every 3 hours and duration 72 hours).

Main results: Ranking of models participated in ATMES-II according to their modelling approach



Publications: ATMES II – evaluation of long-range dispersion models using data of the 1st ETEX release [1998] S.Mosca, R.Bianconi, R.Bellasio, G.Graziani, W.Klug