## CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

### TASK FORCE ON MEASUREMENTS AND MODELLING
### WORKSHOP ON THE REVIEW OF THE EMEP MODELS ON HEAVY METALS AND PERSISTENT ORGANIC POLLUTANTS

# M i n u t e s

## I. INTRODUCTION

1. The workshop to review and evaluate the EMEP MSC-E models on heavy metals and persistent organic pollutants took place on 13-14 October 2005 in Moscow. It was organized by the Task Force on Measurements and Modelling and supported by the Meteorological Synthesizing Centre East (MSC-E) and the World Meteorological Organization (WMO).

2. The workshop was attended by 48 experts from Bulgaria, Croatia, Czech Republic, Denmark, France, Germany, Hungary, Japan, Latvia, Netherlands, Norway, Poland, Russian Federation, Slovak Republic, Sweden, Switzerland, United Kingdom, USA, and the European Community. Representatives of Chemical Coordinating Centre (CCC), Meteorological Synthesizing Centre West (MSC-W), Meteorological Synthesizing Centre East (MSC-E) and ESPREME project (Estimation of willingness-to-pay to reduce risks of exposure to heavy metals and cost-benefit analysis for reducing heavy metals occurrence in Europe) also attended.

3. The main aim of the workshop was to establish whether the EMEP MSC-E models on heavy metals (HMs) and persistent organic pollutants (POPs) are state-of-the-art and fit for the purpose of evaluating the contribution of long-range transport to the environmental impacts caused by heavy metals and persistent organic pollutants.

4. The objective of the workshop was to review the performance of MSC-E HM and MSC-E POP models. The review considered the ability of the EMEP models to provide concentration and deposition data, to determine trends in regional air concentration and deposition data over Europe, and to establish the response of regional air quality to emission changes for use in the development of emission reduction strategies (source-receptor relationship), to facilitate the evaluation of the effects of air quality on ecosystems, support the assessment of health effects by providing regional concentrations of health-relevant pollutants; and to support the preparatory work for the review of the Protocols on HMs and POPs.

5. The review and evaluation of the MSC-E HM and MSC-E POP models were based on three elements:

- examination of the model formulation, description and parameterization of main environmental processes, and model sensitivity study to main parameters;

- evaluation of the model performance against monthly and annual measurements of HM and POP air concentrations and deposition levels from EMEP and national monitoring networks;
- intercomparison of the MSC-E models with other numerical models simulating HM and POP fate in the environment.

6. The workshop was preceded by an open process involving participation and close cooperation with national experts as well as with the subsidiary bodies to the Convention (WGE, WGSR) and with relevant international organizations (AMAP, EC, HELCOM, OSPAR, UNEP).

7. The following background documentation was sent out to participating experts prior the Workshop and was made available on the Internet :

- "Regional model MSC-E HM of heavy metal transboundary air pollution" (EMEP/MSC-E Technical Reports 6/2005);
- "Modelling of heavy metal airborne pollution in Europe: Evaluation of the model performance" (EMEP/MSC-E Technical Reports 8/2005);
- "Intercomparison Study of Numerical Models for Long-Range Atmospheric Transport of Mercury" (EMEP/MSC-E Technical Reports 1/2005);
- "Regional Multicomparment Model MSC-E POP" (EMEP/MSC-E Technical Reports 5/2005);
- "Modelling of POP Contamination in European Region: Evaluation of the Model Performance" (EMEP/MSC-E Technical Reports 7/2005);
- "POP Model Intercomparison Study. Stage II. Comparison of mass balance estimates and sensitivity studies" (EMEP/MSC-E Technical Reports 4/2005).

A number of peer-reviewed papers have also been published in the scientific literature.

8. The Workshop was organized in plenary sessions and two working groups (Working Group on HMs and Working Group on POPs). Conclusions regarding the development and fitness of the MSC-E HM and MSC-E POP models as well as recommendations for future work are presented in paragraphs 43-47 below.

9. The presentations given at the Workshop can be found on the Internet at: www.emep.int.

## II. SUMMARY OF THE PLENARY SESSIONS

10. Mr. Knut Breivik (EMEP/CCC) informed the workshop of an evaluation of emission data for POPs and HMs with emphasis on model applications.

It was concluded that:

- Official emission data are of limited value in terms of model applications because insufficient emphasis had been given to temporal and spatial resolution, speciation and media coverage.

- Most emission data for HMs and POPs suffer from significant uncertainties and poor accuracy.
- Further improvement of official emission data through the TFEIP is the most sensible way to proceed .
- Knowledge of the sources and emissions are likely to remain the least understood feature with respect to the overall behaviour and fate of many of these compounds. This needs to be taken into account when evaluating the MSC-E models.
- Great care needs to be taken when selecting, adjusting and combining emission inventories for the purpose of model application and data interpretation.
- Certain features of emission inventories are robust including spatial patterns, temporal patterns, congener and isomer patterns and model evaluation exercises should take advantage of these features.

11. Ms. Torunn Berg and Mr. Knut Breivik (EMEP/CCC) presented an evaluation of the monitoring data for HMs and POPs with emphasis on model applications. The attention of the Workshop was drawn to the work of the UNEP Global Convention on POPs as its activities are complementary to those of EMEP. Care must however be exercised in using monitoring data from different laboratories in the context of model evaluation because of different QA/QC procedures. A campaign using passive samplers for POPs is planned for the EMEP network during the summer of 2006.

It was concluded that:

- EMEP monitoring data are particularly suited for model evaluation purposes because of their QA/QC procedures and their coverage of seasonal and long-term trends and of congener and isomer patterns.
- EMEP monitoring data, however, suffer from limited spatial and temporal coverage, lack of speciation for mercury, limited coverage of environmental media and the presence of significant uncertainties.

12. Mr. Jesper Christensen (National Environmental Research Institute, Denmark) described the processing of meteorological data for use in the modelling of HMs and POPs. Comparisons were made between the use of the MM5 model to generate meteorological fields for the DEHM and MSC-E models.

It was recommended that MSC-E:

- provide some validation of the meteorological fields generated;
- consider increasing the number of vertical layers and time resolution of the meteorological fields employed.

13. Mr. Armin Aulinger (GKSS Research Centre, Germany) presented the results of applying the CMAQ model to B[a]P. Gas-to-particle partitioning with the dry and wet

aerosol phase was described using the Junge-Pankow concept. Model and observations agreed closely for Aspreveten, Sweden but larger discrepancies were noted for Kosetice, Czech Republic. The next phase of this study will address shipping emissions, chemical degradation mechanisms for airborne POPs and boundary conditions.

14. Mr. Alexey Gusev (MSC-E) followed on with a presentation on the application of the CMAQ model to Pb and Cd. From his results and the results of the CMAQ-B[a]P study peformed by GKSS, it was concluded that the CMAQ model could be a valuable tool for MSC-E to stand alongside the MSC-E HM and POP models. CMAQ could provide self-consistent $O_3$ and OH concentrations for the MSC-E mercury and POP models.

15. Mr. Yelva Roustan (ENPC/EDF, France) gave a presentation concerning a methodological development for sensitivity analysis and inverse modeling. It was applied to mercury chemistry in the framework of the Polyphemus/Polair3D chemistry-transport model. The model was found to perform reasonably well for total gaseous mercury and wet deposition fluxes. The adjoint method was presented. Examples of applications to sensitivity analysis were given in the form of sensitivity maps to the emissions throughout Europe, of Hg concentrations in Germany and of deposition fluxes at Rörvik station. Inverse modeling, using concentration measurements of gaseous elemental mercury, was performed to improve boundary conditions. Future work will involve inverse modeling of air concentrations and deposition fluxes to ascertain European scale emission fields.
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## III. MODELS FOR HEAVY METALS AND MERCURY

16. Mr. Oleg Travnikov (MSC-E) provided a description of the MSC-E HM model and provided an introduction to the documents that described them in detail (MSC-E Technical Reports 6/2005 and 8/2005), focusing on long-range transport, dry and wet deposition and chemistry.

17. Mr. Dimitr Syrakov (National Institute of Meteorology and Hydrology, Bulgaria) presented a review of various advection schemes used in chemistry-transport models, noting that none are perfect. He applauded the use of Bott`s scheme in the MSC-E models.

18. Mr. Russell Bullock (Department of Commerce, NOAA, USA) reviewed the dry and wet deposition formulations in the MSC-E HM model, noting that the formulations are appropriate given the uncertainties in the definitions of the atmospheric processes.

19. Mr. John Munthe (Swedish Environmental Research Institute, Sweden) reviewed the state-of-science in Hg chemistry. He presented results from Stage I of Hg model intercomparison at MSC-E.

20. Mr. Alexey Ryaboshapko (MSC-E) discussed the Cd and Pb model intercomparison studies carried out in 1994 and 1997 and repeated in 2005. He demonstrated that all

participating models were close to each other and to observations when the high ESQUAD emission scenario was used for 1990. The MSC-E model and CMAQ model underestimated air concentrations and deposition of Cd and Pb when official emission inventories for 2000 were used.

21. Mr. Addo van Pul (Netherlands Environmental Assessment Agency/RIVM, Netherlands) described the EUTREND model for Pb and Cd. Compared with the MSC-E model, EUTREND gives higher concentrations and smoother horizontal patterns. However, both models underestimated air concentrations and deposition of Pb and Cd when official emission inventories were used.

22. Mr. Mark Cohen (NOAA Air Resources Laboratory, USA) described the three stages of mercury model intercomparison at MSC-E, involving ten different atmospheric mercury models from research groups around the world. The study was carried out from 1999-2005 in three separate phases, involving comparison of simulations of: (I) atmospheric chemistry; (II) atmospheric concentration for short-term episodes, and (III) long-term deposition and transboundary fluxes. Where comparisons could be made against ambient measurements, the MSC-E mercury model generally performed as well, and in many cases better, than the other participating models. In general, the MSC-E model showed quite satisfactory agreement with measured concentrations and deposition. In the few cases where the MSC-E model had difficulty matching observations, it was generally found that other models had similar difficulties. For results with no available measurements for direct comparison, for example dry deposition and transboundary fluxes, it was found that the MSC-E model typically gave values close to the average of those obtained by the other models. Thanks were offered to MSC-E for their scientific leadership in organizing the study, in which significant advances in atmospheric mercury modeling were made.

23. Mr. Ilya Ilyin (MSC-E) presented results from the analysis of monitoring data for 1990 – 2003 and their further use in the HM model validation exercises. It was shown that the evaluation of the observed data is an important step in the verification of MSC-E HM model. Some unconventional data from moss bag surveys were presented for the discussion with national experts.

24. Ms. Marta Mitosinkova, (Slovak Hydrometeorological Institute, Slovakia) described the results of weekly air and monthly precipitation monitoring in Slovakia for a wide range of HMs, including: Pb, Cd, Cu, Zn, Cr, Ni, As and Mn. Distributions of Pb and Cd in air across Slovakia were presented for 2003.

25. Ms Marina Frolova, (Latvian Environment, Geology and Meteorology Agency, Latvia) described how HMs including: Pb, Cd, Cu and Zn, have been measured in air and precipitation in Latvia since 1974, with As, Ni and Mn added in 2001. Annual averages for all metals in air were presented for 2002-2004. As and Mn were below the detection limit for 60-80% of the cases.

26. Mr Oleg Travnikov (MSC-E) summarized the availability of official emission estimates for HMs. Estimates were available for only 14 member states. Wet deposition of Pb and Cd to land surfaces far exceeds anthropogenic emissions and hence model fluxes markedly underestimate observations by up to a factor of 2 to 3. If national annual emissions are adjusted to minimize deviations from observations, then some of the required adjustments are quite severe.

27. Mr Ilya Ilyin (MSC-E) described the results of the model verification for mercury. Spatial and temporal variability of mercury in air and in precipitation was reasonably well reproduced by the model. The comparison showed that majority of modeled concentrations agreed with measurements to a significant level of accuracy. The importance of the intercontinental transport of Hg for pollution levels in Europe was emphasized.

28. Mr John Munthe (IVL Swedish Environmental Research Institute, Sweden) introduced the concept of critical loads for Hg. Two concepts are presently used: one for Hg in fish (related to concentration of Hg in precipitation) and one for Hg in forest soils (related to total deposition to the forest floor). Limited measurements of Hg in litterfall and throughfall (i.e. dry + wet deposition to the forest floor) are available from research projects in Sweden, Finland and Germany. The sum of measured Hg in litterfall and throughfall is much higher than that due to modeled wet and dry deposition. The explanation may be insufficient knowledge of dry deposition processes to forest canopies although Hg cycling within the forest ecosystem may also occur. This complicates the application of the critical loads approach to Hg. Modelled total deposition to forests can be regarded as minimum fluxes when evaluating critical loads exceedances.

29. Mr Oleg Travnikov (MSC-E) presented the results of the model evaluation for Pb and Cd when adjusted emission inventories were used. The MSC-E HM model showed slight underestimations for Pb and Cd in precipitation at the stations in Germany and large underestimations in Finland and Norway. In general, the agreement between observed and modeled air concentrations was good over much of Europe, though concentrations in precipitation were generally underestimated. Cd was overestimated in both air and precipitation at the Preila station in Lithuania.

## III. MODELS OF PERSISTENT ORGANIC POLLUTANTS

30. Mr. Viktor Shatalov (MSC-E) presented an overview of the MSC-E POP model including an introduction to model structure, input/output and model parameter sensitivity. He covered aspects of the model which modeled multimedia compartments, gas phase partitioning and air surface exchange.

31. Mr. Alexey Gusev (MSC-E) presented an overview of the comparison studies between model prediction and measurement data. This included information on long-term trends, spatial distribution and seasonal reliability. Chemicals covered were B[a]P, PCB-153 and 2,3,4,7,8 PeCDF. Measurement data were taken from EMEP stations and national networks from Germany, Czech Republic and the UK. Overall, model

performance was encouraging with predictions of air concentrations generally within a factor of 3.

32. Ms. Eva Brörstrom-Lünden (Swedish Environmental Research Institute, Sweden) presented data from long-term monitoring studies in Sweden and Finland. The data included air concentrations and precipitation fluxes calculated from bulk deposition samplers. The data covered the period 1996 to 2000 although data from two sites has been collected since 1989. Long-term trend data has shown a decrease over the period 1989 to 1996 but since then, levels have flattened and show no overall decline. Chemicals included were PAHs, PCBs, HCHs, PBDEs, chlordanes and DDTs.

33. Mr. Andy Sweetman (Lancaster University, United Kingdom) presented data from passive sampling campaigns across Europe. Although the data provided by these samples is semi-quantative, it provide a methodology that allows simultaneous sampling for spatial surveys without the drawbacks and costs of active sampling techniques.

34. Mr. Ivan Holoubek (RECETOX, Czech Republic) presented a summary of a large body measurement data from the Czech Republic and other Balkan countries. These included air data that were obtained using passive and active techniques and covered a range of spatial scales from local or regional. He also presented comparison between the data and MSC-E model predictions for Central Europe. Although the comparisons were generally good, he provided some explanation as to why this was not always the case where there were strong local influences and sources

35. Mr. Viktor Shatalov (MSC-E) provided a further presentation about some recent developments carried out using the MSC-E POP model, which involved changing model inputs and parameterisations in order to improve model comparison with measurement data. This work focused on seasonality of B[a]P concentrations and investigated improvements in the description on emission seasonality, inclusion of photodegradation and changing the spatial distribution of emissions. When all three factors were combined, a substantial improvement resulted in the comparison between observations and model predictions.

36. Andy Sweetman (Lancaster University, United Kingdom) presented an overview of Stage I of the POP model intercomparison exercise. This study compared physico-chemical data and other model parameters/processes such as air-surface exchange.

37. Bertrand Bessagnet (INERIS, France) presented an overview of recent developments to the CHIMERE 3D atmospheric transport model. The CHIMERE model is currently being adapted to provide predictions of POP fate and behaviour. Initial results for B[a]P were presented.

38. Elena Mantseva (MSC-E) presented data from the POP model intercomparison exercise from Stage I and II. This included comparison of processes and parameterizations, mass balance estimates and spatial variability. There was a good level

of agreement between the models for some processes and predictions but notable differences were also evident.

39. Dik van de Meent (RIVM, Netherlands) presented the results of a comparison exercise between spatial and non-spatial POP models. He demonstrated that it is possible to get spatial information from box type models by using Monte Carlo sampling of the model input parameters. He concluded by that it is only necessary to use a spatial model if geographical information is required. Otherwise non-spatial models will provide an adequate picture of environmental fate and behaviour.

40. Michel Roemer (TNO, Netherlands) provided an overview of the atmospheric non-spatial model ADEPT. The model is primarily intended as part of a risk assessment process for point sources. Hence, the model can be used to predict receptor concentrations based on an understanding of sources and chemical data. The model does not currently consider air-surface re-emission and treats only atmospheric dispersion and deposition.

41. Martin Scheringer (ETH, Switzerland) provided some insights into how a mechanistic interpretation of the output from the model intercomparison study might be achieved. He demonstrated several processes where model disagreement was evident, and suggested that an in-depth analysis was required to understand why this was occurring. Hence, further investigations and explanations are required to explain the agreement between model simulations as well as discrepancies.

42. Viktor Shatalov (MSC-E) presented some further developments and investigations into the prediction of POP seasonality and the factors that may control it. These factors included temperature dependent degradation rates and partition coefficients.

## IV. RECOMMENDATIONS FOR FUTURE WORK

43. There are a number of long-term strategic issues that may need to be taken into account in the future development of the MSC-E modeling, some of which were raised at the 7$^{th}$ meeting of the Task Force on Measurement and Modelling in Zagreb, Croatia. There are the questions of extending the scale of the mercury and POP modeling to the global scale and involvement of MSC-E with the Task Force on the Hemispheric Transport of Air pollution. There are issues involved with the description of those emission processes that are driven by meteorology such as resuspension and volatilization from soils. There may be potential advantages from moving to meteorological data from the European Centre for Medium Range Weather Forceasting ECMWF, particularly for the global scale. There may be advantages from a closer cooperation between MSC-E and MSC-W and harmonizing their activities on the hemispheric and global scales.

44. It is recommended that MSC-E consider the following issues for scientific investigation in the long term in their forward work-plan:

- extension of the MSC-E HM model to the consideration of other elements and heavy metals, including: Ni, Cu, Cr, As, Zn and Se.
- the application of the MSC-E POP model to screening a wider range of POPs for their potential environmental significance.
- development of emission algorithms and models for the representation of emissions that are driven by meteorological processes, such as resuspension and volatilization from soils.
- inverse modelling using passive sampling campaign data.
- extension of the MSC-E models to the global scale.
- investigate the potential influence of climate change on the fate and behaviour of mercury and POPs.

## V. CONCLUSIONS OF THE REVIEW AND EVALUATION

45. Based on an evaluation of the model formulations, an examination of intercomparisons between monitored data as well as with other models, the workshop drew the following conclusions regarding the performance of the MSC-E models with respect to policy applications.

46. Concerning the MSC-E HM model, it was concluded that:

- the model parameterizations of atmospheric transport were appropriate for the operational modeling of HMs at the regional scale. However, the inclusion of a shallow lowest layer was recommended to represent better the emission heights of the HMs from road traffic.

- The descriptions of wet and dry deposition processes in the model were relevant for the reliable evaluation of HM deposition at the regional scale. The wet scavenging approach, used by many other models as well, was deemed an appropriate approach to simulate cloud physics and chemistry, even though some models utilize a more elaborate approach. There appear to be significant measurement and modeling uncertainties in quantifying dry deposition of mercury to forests. Further scientific progress is needed to quantify the magnitude of dry deposition to forests, to evaluate the ability of the models to simulate it, and to improve the models if necessary.

- The model chemistry scheme is appropriate for the description of the principal Hg transformations in the atmosphere. However, analytical solutions need to be flexible as new chemical kinetics data become available and as new species are introduced into mechanisms. There are major uncertainties concerning the completeness of the description of the chemical kinetics of the reactions of atmospheric Hg.

- The HM air concentrations and deposition levels eastimated with the MSC-E HM model were found to be in good agreement with those estimated with other transport models in the various intercomparison exercises.

- The transboundary fluxes of HMs calculated with the MSC-E HM model corresponded well with and were within the range of those obtained with other transport models.

- Other models underestimate air and precipitation concentrations of Pb and Cd when using official emission data as has been found with the MSC-E HM model. For the 1990s, the model underestimations for Pb are ± 40%, whereas for more recent years, they are much larger and may be up to a factor of 3 to 7. The origins of these discrepancies need to be investigated and may involve the omission of key source categories in official statistics, neglect of the emission heights of some sources, the neglect of resuspension from soils and the inadequate treatment of particle size distributions in the treatment of deposition processes. In one model, it has been possible to eliminate underestimation for Pb in the 1990 case.

- The monitoring data and adjusted emission scenarios employed in the evaluation of model performance were largely appropriate, however, some concerns were expressed about the adjustment of emissions data for Pb and Cd. Because of the difficulties associated with the official emission estimates, it has been difficult to test the performance of the MSC-E HM and other models against observations in an objective manner. Subject to these limitations, the MSC-HM models satisfactorily reflected the observed spatial distribution of HMs in air and precipitation in Europe. They also adequately reproduced the temporal variations characterized by the observations.

- Model performance would be improved by employing meteorological fields with a $1^o$ x $1^o$ spatial resolution rather than the $2.5^o$ x $2.5^o$ currently used.

- The MSC-E HM model is suitable for the evaluation of the long range transboundary transport and deposition of HMs in Europe. However, significant difficulties still remain with official emissions data for Pb and Cd. Furthermore, significant uncertainties are associated with the chemistry of elemental Hg in all models and with the representation of HM dry deposition.

47. Concerning the MSC-E POP model, it was concluded that:

- Results from the MSC-E POP model demonstrated its ability to provide spatially resolved air concentrations and depositions of POPs across Europe. Similarities between measurements and model predictions were encouraging, given the constraints with emission and measurement data.

- Future emission data will need to provide improved spatial, temporal and speciation information to allow better comparisons between model predictions and measurements. Further measurement studies of long term and seasonal air concentration data across the whole of the EMEP region are also essential.

- Although the model provided reasonable agreement with long-term temporal trends of air pollution at most EMEP monitoring sites, there are aspects about the measurement data that are as yet unclear concerning the importance of location and local sources.

- There was limited confidence in the model's ability to represent the observed seasonal variations of air concentrations and depositions of PCB-153, B[a]P, PCDD/Fs. The main reason for this discrepancy is that the emissions data employed do not represent adequately the seasonal variations that arise from domestic heating. Possible additional reasons include the degradation of gas-phase and particle-bound POPs, scavenging by snow and the seasonal dependence of soil volatilisation.

- The currently existing POPs monitoring network is not sufficient for model development and validation purposes. Full implementation of the EMEP monitoring strategy will give up to 50 monitoring sites for POPs across Europe and this will allow a better understanding to be formed of model performance.

- Strong support should be given to the organization of a pilot study using passive and active air samplers to monitor POPs across the EMEP domain to provide spatially and temporally resolved air concentration data. It is especially important that southern European countries participate.

- Boundary conditions of the MSC-E model, as determined by the EMEP grid, need further improvement. This can be achieved using the hemispheric model which provides information on air concentrations beyond the EMEP domain.

- The parameterizations in the MSC-E POP model are based on up-to-date information and conform with those employed in most of the other models used to simulate the behaviour of POPs in the environment. Remaining differences in process descriptions are caused by several specific assumptions underlying the set-up of each particular model. A main goal of the POP model intercomparison exercise is to make these assumptions transparent.

- The general level of agreement found between the different POP models in the model intercomparison exercise was encouraging given the wide range of model approaches and structures employed. Nevertheless, a number of significant discrepancies were identified that will require further investigation.

- MSC-E POP model predictions of concentrations at the interfaces between the main environmental media are in reasonable agreement with the results of other models. There are some discrepancies in the mass fluxes between environmental compartments calculated by different models. Again, it is an objective of the POP model intercomparison exercise to analyze the causes of such discrepancies.

- Within the limitations of current understanding of the sources and emissions of POPs and of their fate and behaviour in the environment, the MSC-E POP model represents the state-of-the-science. It is also considered fit for the purpose of evaluating the contribution of long range transport to the environmental impacts caused by POPs.