Development of a regional scale atmospheric Hg model based on WRF-Chem: results of preliminary studies

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Abstract. The modelling of atmospheric Hg chemistry, transport and deposition has progressed significantly over the last few years, aided by a number of factors. These include an improved understanding of the processes involved in the atmospheric Hg cycle, advances in computer performance, an ever increasing archive of measurement data with which model results may be compared, and also an increase in the number of models (global, regional and zero-dimensional) currently in use. The increase in the number of models has permitted model intercomparisons to be performed for the first time. The number of global models available to provide initial and boundary conditions for regional models has increased and the possibility of using modelling ensembles to verify emission and deposition fluxes is close to becoming a reality. This abstract describes the development of a mercury chemistry version of the WRF/Chem, which due to the architecture of the model permits a number of chemical mechanisms to be employed within the same model.

Keywords: Mercury, modelling, MBL, Mediterranean

Introduction

Mercury in the gas phase is emitted from natural sources mostly as Hg0(g), and from anthropogenic sources as a mixture of Hg0(g), HgII(g) and Hg(P) (where Hg(P) represents Hg associated with particulate matter). The lifetime of Hg0(g) in the atmosphere (roughly 8 months) is long enough for it to be transported hemispherically and globally. Most atmospheric Hg is deposited as a result of the oxidation of Hg0(g) and subsequent dry or wet deposition of the HgII produced. In order to estimate deposition fluxes of Hg it is therefore necessary to simulate emissions (both natural and anthropogenic), atmospheric transport, chemistry and deposition processes. The fact that Hg0(g) is transported over long distances makes it necessary to give particular attention to the boundary conditions employed when using regional/mesoscale models to simulate Hg concentration fields and deposition fluxes. It has been shown that the Hg0(g) boundary condition is highly correlated with the simulated deposition fluxes, and therefore the output from a global chemical transport model is required to provide time varying boundary conditions (BC) for the regional modelling domain (Pongueska et al., 2008). Model intercomparisons have shown how improvements in modelling skill for regional models can be made by using BC from global models (Bullock et al., 2008).

Global model intercomaprisons have been used to provide ensemble estimates of the links between source and receptor areas on intercontinental scales (HTAP 20010).

The oxidation chemistry of atmospheric Hg0(g) has come under scrutiny in recent years as more field evidence, laboratory kinetic studies and modelling studies have indicated that Br and/or BrO are potentially the major atmospheric Hg oxidants, and that the role of O3 and perhaps OH are secondary, if indeed they play a role at all. Unfortunately it is still not possible to determine the exact nature of the oxidised Hg species in the atmosphere, because of the extremely low concentrations involved, and because the analytical technique used to detect such low concentrations requires the thermal decomposition of the compounds so that they can be detected as Hg0(g). The differences between chemistry mechanisms using different oxidation schemes can be investigated directly using the modelling scheme described in this Abstract.

The amount of measurement data concerning Hg and its compounds in the atmosphere and wet deposition fluxes are increasing and recently with the GMOS project have become far more wide spread on a global scale. Previously there was a very little data available for the Southern Hemisphere, certainly it is still not as well monitored as the Northern Hemisphere, but the situation has improved significantly and this is a major step

forward and of great usefulness in the validation of global modelling studies.

Materials and Methods

WRF-Chem is an on-line model (atmospheric physics and chemistry are solved in the same time-step rather than using pre-calculated meteorological data), and the transport of chemical species is performed using the same vertical and horizontal coordinates (no horizontal or vertical interpolation), and the same physics parametrization with no interpolation in time. This is particularly important when working at high spatial resolution. The numerical weather prediction part of the model includes a number of choices for the parametrisation of the boundary layer, surface layer, the land surface model, microphysics, cumulus parametrisations and long and shortwave radiation.

The WRF-Chem model includes a choice of chemical mechanisms as well as the possibility of including new ad-hoc user defined mechanisms for specific situations. It also includes a choice of aerosol chemistry/physics modules which simulate the nucleation, growth and deposition of both inorganic and secondary organic particulates. A choice of two photolysis schemes is also available.

Anthropogenic emissions input for the chemistry scheme chosen can either be taken from global or regional emissions databases. Biogenic emissions are calculated on-line, the emissions fluxes are calculated according to the land-use categories used in WRF.

The most recent version of the WRF-Chem model includes an expanded version of the emissions pre-processor (Freitas et al., 2011) which allows the inclusion of biomass burning emissions and includes a parametrisation to calculate plume rise so that emissions are placed in appropriate model levels. The emissions from wild or deforestation fires are provided using two methodologies. The first option is based on the Brazilian Biomass Burning Emission Model (3BEM) which makes use of fire detection by remote sensing, and combines derived fire data from the the AVHRR, MODIS and the GOES satellites, with a filter to avoid double counting. The preprocessor already includes emission factors for 102 chemical species as well as PM, elemental and organic carbon, and it will be possible to fine tune these emission factors according to the project results.

The preprocessor also provides the data needed to drive the smoke plume rise model. This plume rise parametrization has been incorporated in the WRF-CHEM model, and is used to interactively determine the effective injection height of vegetation fires emissions during the flaming phase.

Measurements of atmospheric mercury species were conducted aboard the CNR's R.V. Urania during an oceanographic campaign from 15 June to 5 July 2005, mostly in the Adriatic Sea (Sprovieri et al., 2010). Collection and analysis of Hg0(g) , HgII(g) and HgP was performed using an automated Tekran (Toronto, Canada) Model 2537A CVAFS, Tekran Model 1130 speciation unit, and Tekran Model 1135 HgP system. Hg0(g) samples (5 min) were continuously quantified by the 2537A analyser. The integrated Tekran speciation system was configured to collect 2 h HgII(g) and HgP samples on a quartz KCl-coated annular denuder and quartz filter assembly, respectively. The HgP and HgII collected on the quartz filter and annular denuder, respectively, were thermally decomposed (at 800 and 500°C respectively) into the mercury free air stream and detected as Hg0. The detection limit for HgII and HgP under the operating conditions used was less than 2 pgm−3.

The WRF/Chem model (Grell et al., 2005) has been used to simulate atmospheric Hg chemistry. Due to the intention of performing a comparison with results obtained during an oceanographic campaign performed in the Adriatic Sea during the summer, the aqueous phase chemistry of Hg has been greatly simplified, as clouds were rarely present. The model assumes that both Hg0(aq) and O3(aq) come to rapid equilibrium with the gas phase and the rate of the Hg0(aq) oxidation by O3(aq) is calculated from these equilibrium values. Although sea salt aerosol is always present in the MBL compared to clouds the total liquid water content is very low and is therefore most likely of little importance to the oxidation of Hg0(g), however its role as a scavenger of HgII(g) was included for investigation. Two base chemistry schemes were used, the RADM2 (Stockell et al., 1990) and CBM-Z (Zaveri and Peters, 1990) mechanisms. These were combined with an O3/OH oxidation mechanism for Hg0(g), and the same simulations rerun using a Br/BrO oxidation mechanism. The RADM2 mechanism has been used previously to study the formation of O3 and the impact of ship emissions on its production, during this oceanographic campaign (Hedgecock et al., 2012). The comparison between modelled and measured concentrations was found to be very reasonable, hence we are reasonably certain that the basic photochemistry of the model is realistic. The Br/BrO concentrations were not calculated on-line but derived from previous photochemical box modelling studies of the same oceanographic campaign (Sprovieri et al., 2010).

Results and Discussion

The results confirm the likelihood that Br and not O3 or OH is the major oxidant of Hg0(g) in the MBL. In fact it proves impossible to reproduce the atmospheric Hg species concentrations if O3 and OH are assumed to be the oxidant species. Certainly if O3 were the principal oxidant of Hg0(g) a very different temporal variation in the HgII(g) concentration would be expected, given that the average over the whole cruise was slightly over 60 ppb, including the nighttime concentrations.

Routines for the inclusion of biomass burning emissions into WRF-Chem have been made available recently (Freitas et al., 2010) and these have been implemented in these simulations. As well as the VOC, NOx and CO (black carbon (BC) has not been included in these preliminary simulations) associated with biomass burning and particularly with wildfires, Hg has been added. The effect that these fires have on Hg deposition to the sea is extremely dependent on the effective emission height. The summertime Mediterranean MBL is significantly lower than oceanic MBLs because the

Mediterranean region is under the descending arm of the Hadley Circulation, and during anticyclonic conditions in the summer the MBL is typically around 400m asl. Therefore if the plume rise from the fires is sufficient the emissions from wild fires will remain above the MBL, however if an evening offshore breeze or the local circulation conditions are favourable it is possible that the emissions are transported from land over the sea and effectively trapped in the MBL until oxidised and deposited.

During the oceanographic research campaigns performed aboard the R.V. Urania the concentration of Hg dissolved in the surface layer of the sea has been measured. This data can be used with the modelled Hg0(g) concentration, wind speed, sea and air temperature to estimate the evasive flux of Hg0(g) from the sea surface. A number of parametrisations are available in the literature to represent the evasive fluxes of gases from seas and oceans which can be applied to Hg0 (see for example Ci et al., 2011, Wanninkhof et al., 2009). The anticyclonic conditions resulted in generally low wind speeds during the oceanographic campaign period, however in the Mediterranean due to the complex orography complex local circulation patterns can form particularly in the early morning and late afternoon. The model results suggest, as have previous experimental and modelling studies (Andersson et al., 2007, Hedgecock et al., 2006), that the Mediterranean is by far a larger source of Hg to the atmosphere than it is a sink.

Conclusion

Modules and routines to include atmospheric mercury processes in the state of the art numerical weather prediction and atmospheric chemistry model WRF/Chem have been developed. These modules include Hg emission from biomass burning, both from biofuel use and from wildfires and Hg exchange at the sea/ocean surface, with a choice of parametrisations. Atmospheric Hg chemistry may be investigated with a choice of oxidation mechanisms and the development of a detailed aqueous phase Hg chemistry scheme is in progress. Preliminary results indicate that in the Mediterranean MBL Br-containing compounds are the main Hg0(g) oxidant, and also that the Mediterranean Sea is a quite significant Hg source for the region. The influence of biomass burning and particularly wildfires merits further investigation, it is potentially important for local Hg biogeochemical cycle however the complex interactions between the complex local orography, meteorology and eventual transport and/or deposition of Hg from this emission source require the detailed study of a larger number of wildfire events to draw even initial conclusions on it's importance for the region.

Acknowledgements

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