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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An investigation of the origins of reactive gaseous mercury in the Mediterranean marine boundary layer" *by* F. Sprovieri et al.

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High Hg *species event analysis:*
The referee is concerned with the way in which the high Hg concentration phenomena are discussed in section 4. The events described are periods during the measurement campaign in which one or more of the three chemical atmospheric forms of Hg (Hg^0, RGM or Hg^P) is, in our opinion, unusually high. We have added a preamble to this section in which we describe our reasoning for classifying these events as 'unusual', these include Hg^0 concentrations notably background level, RGM concentrations above a few $pg\,m^{-3}$ at times which do not correspond to maximum photochemical activity,

and Hg^P over 5 $pg\,m^{-3}$. Such occurrences stand out from the rest of the measurement data and have therefore been investigated.
The events described in section 4 are listed in chronological order, and are clearly either form the autumn in 2004 or the summer in 2005. It is not really feasible to group them according to similar back trajectories as the synoptic conditions between seasons are notably different. Also, the fact that the research vessel was moving most of the time, means that almost each day was unique either because of the ship's position or the meteorological conditions encountered, or both. There does not much to be gained from considering back trajectories for ship positions on opposite sides of the Italian peninsula, particularly given the presence of the Apennines running from north to south, which create a natural geographic barrier between the Tyrrhenian and Adriatic Seas. To give an example, winds from the north when the R.V. Urania is off the north coast of Sicily, is a very different situation from one in which northerly winds are encountered while the ship is crossing the bottom of the Ionian or Sea or in the Gulf of Trieste.
There is the added complication during the summer that the prevalent anticyclonic conditions result in local land-sea breezes, which have an important influence on wind direction and velocity. We do not think that there is really enough data for an analysis of wind sector/air mass (particularly given the moving ship), but it appears that when the trajectories indicate that the air mass has spent little time over the sea (less than 6-12 hours) the model overestimates RGM. However that is an impression which we intend to investigate further but is not something which we would be comfortable stating in a published article. We have reworded the introduction to section 4.2 to make it as clear as possible why the periods discussed have been chosen and what (for each season) we have considered to be unusual. We have also avoided the use of the word 'plume' in the revised manuscript because of the uncertainties in back trajectory calculations, and make clear that our suggestions as to possible sources of the high Hg species concentration 'events' are hypotheses (see Reply to Referee #2).

Concerning the calculation of the concentration of the hydroxyl radical:
One of the main reasons we felt that the studies presented in our article were of importance is the fact that the high O_3 values and the humidity of the marine atmosphere would allow us to investigate by proxy the role of OH in the oxidation of atmospheric Hg^0. In light of the referee's comments we have performed some tests with the model varying the concentrations of NO_x, VOC's (ethane, ethene, propane, propene and C4 hydrocarbons) and also CO. The NO_x concentration affects the model results because higher concentrations of oxidised N compounds increase the rate at which the sea salt aerosol is acidified and therefore promotes the release of reactive halogen compounds to the atmosphere. Using an initial value of 50 ppt of NO_2 (compared to 20 ppt) and an NO emission flux 5×10^9 molecules cm^{-2} s^{-1} rather than 1.5×10^9 molecules cm^{-2} s^{-1} has the result of increasing the model RGM well beyond the observed concentrations. If we assume that the reaction between Hg^0 and OH produces oxidised gas phase Hg compounds, concentrations of CO above 1000 ppt are necessary to curb the production of RGM from oxidation by OH and give model RGM concentrations similar to those observed. Combining high NO_x and CO concentrations gives model results higher than observations. The VOC concentration affects both halogen (Toyota et al., http://www.atmos-chem-phys.net/4/1961/2004/acp-4-1961-2004.html) and OH concentrations and it is difficult to be precise as to the effect, however the influence on the modelling results is small in comparison to NO_x or CO when the $Hg + OH$ reaction is assumed to give a gaseous product.
The average modelled concentration of the OH maxima during the simulations is around 2×10^7 molecules cm^{-3}, comparing this value to measurements made in northern Crete during the MINOS campaign, (Berresheim et al., 2003, http://www.atmos-chem-phys.net/3/639/2003/acp-3-639-2003.html) in which it should be noted that CO concentrations between 100 and 200 ppb were observed, Salisbury et al., 2003, http://www.atmos-chem-phys.net/3/925/2003/acp-3-925-2003.html), OH concentrations were seen to peak in the range $1.5 - 2.0 \times 10^7$ molecules cm^{-3} with some individual peaks as high as 2.4×10^7 molecules cm^{-3}. We are therefore reasonably confident that

the model is reproducing the atmospheric OH concentration variation with reasonable accuracy. And that therefore $Hg + OH$ does not produce RGM.
We have expanded section 4.3 where the influence of NO_x is discussed to include the comments above regarding VOCs and CO. See also our reply to Referee #2.

Quantification of primary and secondary RGM*:*
This is the point of the comments in section 4.4, where we have looked at the discrepancy between the model predictions and the measurements. Clearly the differences are more obvious at night, and clearly the model (being zero-dimensional) assumes that there is no transport. However the point of the study was to examine the capacity of the MBL to produce RGM per se, and identify those periods where the model and observations disagreed and find a reason for it. As to the magnitude of primary RGM sources we would hesitate to be categorical because of the nature of the measurements; a cruise campaign cannot provide the time series necessary to adjudicate the impact of individual sources either in terms of flux, or speciation, because of the limited sampling time in any one location, the distance between the measurement site and the potential source and also the uncertainty introduced by dispersion and dilution during the transport between the two.

How sensitive are the model results are sensitive to aerosol loading, aerosol composition, replacement time?
Some of these questions were addressed in one of our previous articles, the reference has been included, and we have also re-run the model to ensure that our previous results are comparable with the results from similar tests, given that in this instance where some of the model concentrations have been dictated by observed data. We have added a paragraph to section 3.1 summarising the influence of the variables mentioned specifically by the referee.

We have changed the figure caption, and included the table requested by the referee.

Comparison with previous modelling results:
Our previous simulations used a different chemical mechanism. It was important to check that the suggestions made here for the 2005 dataset were applicable to the 2000 dataset, because it too was a summertime campaign in the Mediterranean, with the last two weeks enjoying typical anticyclonic conditions not dissimilar to those encountered in 2005. If the mechanism employed in this study had produced results for the 2000 campaign which were very different from those in Hedgecock et al., (http://dx.doi.org/10.1016/j.atmosenv.2005.09.002) we would not have submitted the article. The point being that the mechanism employed here to attempt to reproduce the observations of the 2005 campaign, is not incompatible with the observations from a previous campaign undertaken under similar circumstances. It seemed opportune to include this section for completenesses' sake.

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