

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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We appreciate the positive comments at the beginning of the review. Thank you.

Entrainment:

Entrainment could be included in a parametrised fashion, in much the same way as sea surface emissions of both Hg⁰ and other gases have been included in previous versions of the model (Hedgecock and Pirrone, 2004, <http://pubs.acs.org/doi/abs/10.1021/es034623z>). We did consider this possibility, but had a number of doubts regarding the assumptions which would have needed to

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have been made, in order to implement it in the model. The boundary layer height over the open Mediterranean is reasonably stable under summer anticyclonic conditions, however in the Adriatic, and particularly near the coast, it is not simple to estimate its variation due to the complex terrain, and the intensity of the heating of the land during the day which results from the high intensity of the solar radiation. The presence of breezes from land to sea during the evening/night would lead one to suspect the concentrations of Hg measured over the sea at night are more influenced by air originating from the remains of the terrestrial boundary layer than exchange with the free troposphere. It is this, in fact, that we believe we have identified in the instances at which high RGM and / or Hg^P were observed during the hours of darkness, with the help of the back trajectory calculations.

As to measurements above the MBL, we could not agree more, and this leads us to the other uncertainty in including entrainment into the model. What are the concentrations of Hg⁰, RGM and Hg^P above the boundary layer? There are so few measurements, that we felt that any value chosen would be open to valid questioning and criticism. There are some places in the Mediterranean near the coast or on islands where it might be possible to sample air above the boundary layer, however many of these are volcanoes and therefore Hg sources. There are national and international initiatives to begin systematic Hg measurements on board aircraft, and the CARIBIC (<http://www.caribic-atmospheric.com/>) project has already furnished valuable data, it is to be sincerely hoped that in the near future we will have more information available to reduce this major area of uncertainty.

Back trajectories:

The back trajectories are of course subject to inaccuracies and we could have been clearer in stating that the attribution of a given 'plume' was a suggestion and not by any means a hard and fast fact. Checking the trajectories again, we can state however, that where we have suggested a possible source for the observed high values of RGM or Hg^P, the time between the hypothetical source and the measurement is in

all cases less than 12 hours (and in some cases much less). In the case of the high concentrations observed on the 28th / 29th this is actually mentioned specifically in the text. We have added the approximate time between potential source and observation suggested by the back trajectories in each of the descriptions of the high RGM / Hg^P events. Regarding the possible influence of Mt Etna on the measurements between the 28th and the 29th, we find it improbable that emissions from above 3000 m would have such a clear (and apparently short-lived) influence at sea level.

We have included a couple of back trajectory figures to illustrate the reasons behind our attribution of possible sources of the high RGM / Hg^P events. We have also changed the wording in the text to avoid the possibility that the word plume could be interpreted as a conclusive identification of an individual source.

OH concentration:

As this question has been raised by both referees we have extended the description of our methods and included comments on the results of some sensitivity runs. Further references to works describing measurements of OH and CO over the Mediterranean, albeit in a different area, however at a similar time of year under similar meteorological conditions, have been added. The model concentrations of O₃ and water vapour are constrained by the observations and updated every five minutes from an input file containing the measurement data. The solar zenith angle and photolysis rate constants are also recalculated every five minutes, a clear sky was assumed (during the measurement campaign there was fine weather almost all the time). In our sensitivity tests we varied CO, NO_x and VOC input concentrations (and NO emissions from the sea surface). As described in our reply to referee #1 increasing NO_x results in increased model RGM as a result of more efficient acidification of the sea salt aerosol and thus release of reactive halogen compounds. Under the high O₃ conditions encountered, assuming a CO concentration of 100 ppb gives a maximum OH concentration of 3.2×10^7 molecules cm⁻³, 200 ppb CO (the value used in the simulations) a maximum of 2.3×10^7 and 300 ppb CO a maximum

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of 1.8×10^7 molecules cm^{-3} . If the reaction between Hg^0 and OH is assumed to give a gas phase product it is necessary to increase the CO concentration to 1000 ppb in order to obtain RGM values similar to observations (using the $\text{Hg} + \text{OH}$ rate constant from Sommar et al., ([http://dx.doi.org/10.1016/S1352-2310\(01\)00108-X](http://dx.doi.org/10.1016/S1352-2310(01)00108-X)). Measurements made during the MINOS campaign (Berresheim et al., 2003, <http://www.atmos-chem-phys.net/3/639/2003/acp-3-639-2003.html>, Salisbury et al., 2003, <http://www.atmos-chem-phys.net/3/925/2003/acp-3-925-2003.html>) found CO concentrations between 100 and 200 ppb and OH concentrations which peaked at around 2×10^7 molecules cm^{-3} . We are therefore reasonably confident that the model is reproducing the OH concentration with a fair degree of accuracy. See also our reply to Referee #1

We have changed the word 'comprehensively' to 'detailed' to reflect the referee's point that box models are relatively simple. We entirely agree with the referee concerning the difficulty of including Br chemistry in 3-d models, appreciate the fact that the referee considers our statement regarding the problems of identifying RGM as poignant and also agree that the atmospheric redox reactions involving Hg have yet to be conclusively identified. We hope that this article provides further evidence which will prove useful in the eventual resolution of the processes involved in atmospheric Hg cycling.

We have changed the manuscript according to the editorial comments.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24815, 2009.

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