

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

Anonymous Referee #2

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This paper describes an interesting observation and modeling study of atmospheric mercury behavior in the marine boundary layer (MBL) in the Adriatic Sea. The authors describe a number of particular aspects of the Adriatic and Mediterranean Seas that suggest the results obtained here may not be generally applicable to all marine air masses. Nonetheless, this study does bring to light some important issues regarding our present understanding of the reduction-oxidation balance of atmospheric mercury both in marine air and in the overall global atmosphere. Unfortunately, those issues are not at all settled by the results presented. The authors make a poignant statement at the end of the paper that currently deployed measurement technology is not sufficiently resolving the chemical speciation of atmospheric mercury. They have applied a rela-

C8407

tively simple box model using various combinations of controversial chemical reactions and kinetic rates in an attempt to match their observations of atmospheric mercury concentration which continue to provide insufficient chemical speciation to settle the ongoing controversies. Nonetheless, the results and discussion do lend some credence to the growing consensus of opinion that ozone and hydroxyl radical are not the primary oxidants of atmospheric mercury, at least not in the MBL. For that alone, this work is worthy of publication and consideration by the research community. However, the paper does have some shortcomings that need to be addressed to make it more understandable and informative.

In the Introduction, the authors mention the possibility that observed variations in reactive gaseous mercury (RGM) concentration might be the result of the change in boundary layer height from day to night. The AMCOTS modeling would be much improved if it could treat the entrainment of free tropospheric air into the MBL. In the same regard, it would have been very informative to have measurements of mercury species concentrations above the MBL.

In section 4.2, incidents of unusually elevated mercury concentration are sometimes referred to as “plumes” and at other times as “events”. The discussion of back trajectories obtained from the HYSPLIT model is quite specific as to the sources of the air sampled at particular times. If these trajectory analyses could indeed be trusted to be so accurate, I would be more willing to accept these events as interceptions of emission plumes. The paper should provide some graphical representations of these 72-hour back trajectories, especially when they are said to indicate specific sources of primary RGM or particulate Hg (HgP). For example, in the discussion of the 28/29 October 2004 event, the authors describe a trajectory path that moves across the entire island of Sicily as the time of interception of the cruise ship moves from midday on the 28th to midday on the 29th. Depending on how far back in time that trajectory crosses the island, the confidence that one should place in the accuracy of the positioning varies. If the sampled air crossed the island 48 or 72 hours before it was sampled,

C8408

the errors in positioning are much greater than for 12 or 24 hours. In fact, I wonder if mercury emissions from Mt. Etna might be involved, rather than those of the industrial and port areas mentioned. In general, I am worried that errors in the trajectory are simply not considered in the discussion.

In section 4.3, it is stated that OH is effectively constrained by the measured O₃ concentration and the relative humidity. How so? Errors in the assumed OH concentration could have a profound negative effect on the modeling assessment.

In the Conclusions, the authors state that Br chemistry can be explicitly and comprehensively included in box models, but that its inclusion in regional and global models presents far greater problems. First of all, box models do not treat anything comprehensively. The reason Br chemistry can be treated so easily in box models is that they are relatively simple models. Indeed, full 3-dimensional simulation modeling requires accurate definitions for all variables and parameters in 3-d space and in time and this is currently difficult to achieve for Br. Obviously this is why these large-scale models have been slow to include Br.

At the very end of the Conclusions, the authors make the most poignant statement in the paper by stating that our understanding of atmospheric mercury cycling is unlikely to progress significantly without some way to measure air concentrations of the actual chemical compounds of mercury. This too may be one of the reasons that large-scale models have not taken the steps necessary to fully include bromine in their simulations. It is yet to be proven which reactions are truly driving the reduction-oxidation balance of atmospheric mercury.

Specific editorial comments:

Figures 2 and 3 should use the same symbol and line color for RGM (and for HgP). Switching the symbols for RGM vs. HgP is confusing.

Figure 3 caption should show summer 2005, not autumn 2005.

C8409

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