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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements and modelling of ozone in the Mediterranean MBL: an investigation of the importance of ship emissions to local ozone production" *by* I. M. Hedgecock et al.

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1 Reply to Referee #1

We thank the referee for their useful and thought provoking comments.
Below is our reply, point by point, to the referee's concerns:

My main concern with the manuscript is that the model does a rather poor job of repro-

ducing the ozone data collected on the ships and by stations on land (EMEP). Absolute mean biases are as high as 30-40 %, which are often higher than your model estimate of the impact of ship emissions on ozone.

The model bias is particularly high in the modelling results for the 2004 oceanographic campaign, and is quite high for the 2006 and 2009 campaigns. Over the sea the mean bias values are 6.8, 6.1, 28.7, 4.7, 16.6, 14.8 and 1.4 % of the observed mean ozone concentrations for the individual campaigns. The 28.7% value is the 2004 campaign which took place in the Spring, and most models have difficulty reproducing the spring-time Mediterranean ozone maximum. Over land the values are mostly between 5 and 20%, although again 2004 was not well reproduced and generally nor was the Italian EMEP station on the outskirts of Rome.

The average difference in ozone concentrations over the modelling domain when ship emissions are removed from the emissions database are 11.4, 9.3, 9.5, 10.5, 11.7, 16.3 and 9.0%, (original Table 6), and thus in two cases the modelled percentage change in O_3 concentration is less than the mean bias, as a percentage of the mean measured concentration.

However, when we look at the change in modelled O_3 concentration in those cells of the model domain which are over the sea (or sea + coast) the values are 15.2, 11.7, 13.9, 17.0, 14.4, 19.9, 10.5, (Table 6), which are more than twice as high as the absolute mean bias values in four cases, and almost twice as high in one other (2003).

Undoubtedly, ship emissions have an important impact on pollution in the Mediterranean Sea, but I find it difficult to believe the conclusions concerning the impact of ship emissions on ozone and compliance with the ozone standard.

As we have just described the differences in O_3 concentrations with and without shipping emissions are in a number of instances are more than twice the mean bias between observations and model results. Nevertheless we take the point that

extrapolating over the whole domain and drawing conclusions about ozone standard exceedances. We have therefore plotted the ozone concentrations graphically rather than using maps and illustrate the model concentrations with and without ship emissions along the campaign routes (the new Fig. 10). In this way we manage to show the difference the ship emission make in the specific areas where measurements were made, and we have included the mean bias for the campaign in the figure caption so that the reader can judge more easily the results. We have obviously changed the text describing the figures accordingly, and described the findings in the conclusions in a more circumspect manner.

My first reaction to this model output is that more thought needs to be put into understanding the source of the model's poor performance. Have you investigated the source of the temperature high bias? Could the chemical and aerosol mechanisms be the issue? Aerosol chemistry within the ship plume? This wonderful shipboard dataset will allow you to explore these issues with your model.

One source of the temperature bias is the input dataset which comes from the 1 degree by 1 degree NCEP FNL Operational Model Global Tropospheric Analyses. This is particularly noticeable in the Adriatic as we mention in the text. We have rerun the model with alternative chemical mechanisms, see the specific comment referring to RADM2 below, and the results are no better. So we do not think the model chemical mechanism has a major influence on the results. The general performance of the model in terms of reproducing ozone concentrations is not dissimilar to the references which we cited in the article (Schürmann et al., 2009; de Meij et al., 2009; Misenis and Zhang, 2010; Grell et al., 2005; Tie et al., 2007; Tuccella et al., 2012; Fast et al., 2006; Zhang and Dubey, 2009; Geng et al., 2007). The nature of the measurements themselves adds a degree of variability to the observations which is not possible to reproduce. The position of the R.V. Urania with respect to other vessels and their emissions does on a number of occasions cause the ozone concentration to decrease

dramatically and rapidly. This was highlighted in during the most recent oceanographic campaign in 2012 when the route actually passed through the Strait of Gibraltar and back again. The observed concentrations of ozone were so low that at one point there was some concern that the analyser was faulty. Therefore while generally speaking our approach of interpolating the EMEP shipping emissions directly on to the modelling domain seems to function reasonably, there are occasions during all the campaigns when the measurements are directly influenced by other vessels. This is clearer now that we have included some figures in the article which illustrate the times series of measurements vs. model results. There are times when the measured ozone concentration is very low, and the model obviously cannot capture emissions from individual ships as they navigate the Mediterranean.

General Comments

There are quite a few grammatical errors throughout the manuscript.

We have gone through the text again, and made a number of corrections. Referee #2 pointed out a number of errors as well.

The manuscript is too verbose. Please make your points more concisely.

We have rewritten a large number of sections and as asked by referee #2 shortened a number of sentences which were somewhat unwieldy.

Introduction: The literature is well cited and the study is well justified. However, the scientific objective of the paper is lost in the confusing text of the final paragraph.

The last paragraph has been rewritten ....

It is unclear whether you are citing earlier work or saying what the objective of your work is. Please make this clearer. Also, please make it clear what is new and exciting about your work.

.... and a couple more sentences added to highlight what we believe to be the most important and innovative results and outcomes of our work.

Sec. 3.1.3. The RADM2 mechanism is very, very old and dated. Could this contribute to your model's problem simulating the observed ozone?

Perhaps tried and tested would be a more generous description. We have run the 2005 simulation using both CBM4 and CBM-Z, the results actually proved to compare less well with observations than those obtained with RADM2. Interestingly the modelling literature cited previously in this response six of the chemistry schemes used RADM2, two used CBM-Z, and one used CHIMERE.

Sec. 3.2. There are newer emission estimates of biogenic fluxes from Guenther. Why do you use emissions developed in the 1990s?

We have since run a number of the simulations again using the bio_emiss pre-processor to create MEGAN input for WRF-Chem (http://www.acd.ucar.edu/wrf-chem/). The results are actually very similar, but the simulations actually took significantly longer. We did not expect the biogenic emissions parametrisation to have a major effect over the open sea, where the R.V. Urania was for the most part of the time. However little difference was seen even at the terrestrial sites, possibly because the biogenic emissions from Mediterranean vegetation during hot weather have been well known for some time.

Sec. 3.2.1. You don't mention in-plume aerosol chemistry that you use. There is quite

a bit of discussion in the literature on the chemistry in plumes that is not related to the dilution effect that you discuss.

The aerosol in ship plumes is mostly primary aerosol (of most concern is black carbon), looking in the literature I didn't actually find many articles on in-plume aerosol chemistry and those I did were concerned with the plumes of large industrial facilities. The formation of aerosols seemed to be most probable when warm flue gases became trapped for some time in the nighttime residual layer. The fact that ships are generally in movement means that they begin to be diluted from the moment they are emitted. A ship obviously emits far less than an electricity generating plant for example and so the concentrations of sulphate are unlikely to reach concentrations that would promote nucleation, see Zaveri et al. (2010), Nighttime chemical evolution of aerosol and trace gases in a power plant plume: Implications for secondary organic nitrate and organosulfate aerosol formation, NO_3 radical chemistry, and N_2O_5 heterogeneous hydrolysis.

Sec. 4.1.2. Why don't you show a few comparisons of the model and observations along the ship paths for ozone? The same goes for your discussion in Sec. 4.2 and 4.3.

We have included three figures showing time series and scatterplots, the new figures are Figs, 3, 4 and 5.

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