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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Satellite measurements of formaldehyde from shipping emissions" *by* T. Marbach et al.

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First of all we want to thank this reviewer the important comments to our study. They stimulated us to investigate in more detail the possible source mechanisms for the observed enhanced HCHO values. Together with the suggestions of the other reviewers, these comments lead to major revisions of our paper. Before we address the reviewer comments in detail, we give a short overview of the two major changes of the revised version.

a) The discussion of the origin of the enhanced HCHO values is completely changed. We now discuss in detail (especially in section 3) the findings of this study compared to those from the previous study on NO2 emissions from ship traffic (Beirle et al. 2004). By comparing the observed absolute values and the peak shapes and distances from

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the ship route, it becomes obvious that neither direct emissions of HCHO, nor direct emissions of NMHC can explain the observed HCHO values. Instead, we conclude that increased degradation of CH4 is the most probable cause for the enhanced HCHO values. Increased CH4 degradation is caused by increased OH concentration inside the ship plume, and the intermediate oxidation products (with lifetimes of several hours) are then transported away from the ship route. In addition, also outside the emission plume enhanced OH concentrations might occur due to increased ozone concentrations. Besides in section 3, we added these findings and conclusions to the abstract and conclusions. We also changed the title to reflect the fact that the observed increase of HCHO is very probable not caused by direct emissions.

b) We investigated the potential influence of aerosols on the satellite observations in more detail and discuss the related findings in the manuscript (section 4). First we carried out additional radiative transfer simulations using various aerosol properties. It turned out that even for rather high aerosol optical depths the change of the AMFs are < 50% and could not explain the observed HCHO increase assuming typical background concentrations of HCHO. It is interesting, however, to note that large enhancements of the AMF occur only for scattering aerosols (single scattering albedo close to unity) which are probably not adequate to describe aerosols from ship emissions. Nevertheless, even if aerosols from ship emissions were purely scattering aerosols with high optical depth, the resulting high top of the atmosphere radiance should be clearly visible, e.g. in aerosol products from satellite observations. Second, we analysed the simultaneous observed O2 absorption in the satellite spectra and applied the same averaging and filtering as for the HCHO data. The resulting maps did not show a similar pattern as found in the HCHO satellite data indicating that the enhanced HCHO values are not an artefact caused by modifications of the tropospheric AMF. We added this information to section 4.

Detailed replies:

Reviewer comment: “This paper describes analysis of data from the GOME satellite

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instrument to extract an estimate of enhanced formaldehyde due to emissions from shipping in the Indian Ocean between Sri Lanka and Indonesia. This paper is similar in many respects to a previously published analysis of NO2 emissions from ships in the same region [Beirle et al., 2004]. However, while the prior NO2 analysis is robust, the same cannot be said for the present analysis of HCHO. Since I don't think the conclusions are supported by the data, I must recommend that this paper not be accepted for publication."

Author Reply: We are aware about the fact that the observed enhanced HCHO absorption over the ship tracks is weak. However, we are confident, that it is not an artefact caused by other effects (like effects of aerosol or clouds, see also above). To make this clearer, we performed additional sensitivity studies on the possible effects of aerosols and added this information to the revised version of our manuscript). It turned out that the HCHO signal can not be caused by the potential effects of aerosols and/or clouds.

Reviewer comment: "The mean enhancement in the HCHO column is 2.0e15 molec/cm2, where the authors state that this is entirely in the MBL which is 700 meters high (AMF=0.4). For sea level pressure and 30_C, this translates to an average mixing ratio enhancement over background of about 1.1 ppbv. This is a substantial amount of HCHO, especially given the geographical extent (40 km by 320 km) of one pixel."

Author Reply: We agree that 1.1 ppbv is a substantial amount of HCHO. However, it might be good to put this value in perspective to HCHO mixing ratios which could be expected from other sources, in particular from CH4 oxidation. Assuming a CH4 mixing ratio of 1800 ppb and a lifetime of 3650 days for the reaction with OH results in a daily destruction of about 0.5 ppb CH4, even more in the Tropics (note that this value is in good agreement with results from the EMAC-model, see Figure below).With a HCHO lifetime of a few hours (with respect to destruction by OH and photolysis) we can expect about a few tens of ppb HCHO (which is not very far from the 1.1 ppbv HCHO derived from the enhanced HCHO absorptions over the ship tracks. It should be also noted that it is close to the typical background HCHO mixing ratio of about 0.3

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ppb (Wagner et al, 2001). Enhanced OH concentrations due to ship emissions were also found by a recent modelling study (Hoor et al., 2009). It is now interesting to note that increased OH concentrations in the plume of the ship emissions will further increase the HCHO concentration from CH4 destruction, because the HCHO production depends mainly on the OH concentration, whereas the HCHO destruction depends on both OH concentration and photolysis (see figure below).

Reviewer comment: "A similar calculation for the peak NO2 (VCD=2.0e14 molec/cm2; Figure 4) yields about 0.1 ppbv. If we accept for the moment that this enhanced HCHO value is correct, can it be explained by ship emissions? There are two possibilities - direct emissions and secondary production. That direct emissions cannot account for this can be seen in the ratio of the HCHO VCD (using AMF=0.4) to the NO2 VCD from Figure 4. Since the MBL heights are the same, and the lifetimes are similar, a direct ratio of VCDs is an approximate measure of the HCHO emissions (or enhancements) relative to NO2 emissions. Ship emission factor data from the Lloyd's Engineering study [1995], converted from mass units, show that this ratio is about 0.03, assuming all of the emitted HC is formaldehyde. The authors estimate that only 0.4% of total HC ship emissions is formaldehyde, thus the HCHO/NO2 molar emission ratio would be about 0.0001. Using a value of 1.0e14 molec/cm2 for the average NO2 enhancement, this gives an estimate of HCHO enhancement from direct emissions of about 1.0e10 molec/cm2 with an uncertainty of about an order of magnitude. However, this emission is about five orders of magnitude lower than the observed average HCHO enhancement of 2.0e15 molec/cm2. Clearly, there must be other sources for the HCHO signal."

Author Reply: We are thankful for these comments, which stimulated us to investigate the involved chemistry in more detail. We completely agree with the reviewer that the observed HCHO enhancement can not be caused by direct emission of HCHO or NMHC. We made this clearer in the revised version of our manuscript (abstract, section 3, and conclusions). .

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Reviewer comment: “The authors suggest that, rather than direct emissions, the observed enhancement in HCHO is likely a mix of direct emissions and secondary production, where the latter is indicated by the latitudinal breadth of the HCHO signal compared to that from NO2. Evidence in support of this is presented in the form of output from a chemistry-transport model with a weak ship emission source included in the region of interest. Only qualitative agreement was found (Figure 5). Moreover, total HCHO from the model was more than a factor of two lower than the HCHO enhancement seen in the satellite data. They argue that perhaps the emission source estimate is too low or that the actual chemistry is not well-represented by the coarse grid of the model. It seems that the strongest argument they propose is that the pattern of enhanced HCHO seen in the model output agrees with the pattern of the apparent HCHO signal seen in the GOME data. I don’t think this is sufficient evidence to demonstrate that what is observed by the satellite is HCHO from shipping emissions.”

Author Reply: We agree with the reviewer that the comparison of the satellite observations with the model data is only of limited value, because of the coarse model resolution (similar arguments were also raised by reviewer #2). Nevertheless, we still think it is interesting to perform such a comparison, especially because these models are often used to investigate the impact of emission sources on the global trace gas concentrations. Such models also allow to study the effect resulting from switching on or off specific emission sources (see Hoor et al., 2009). In view of the coarse model resolution, we consider a deviation by only a factor of 2 as a rather nice result. Besides that, we agree that the comparison with model data is not sufficient to support the conclusions of our study. Thus we added a much more detailed discussion of the involved chemistry to the revised version of our manuscript including the comparison with the simultaneously measured NO2 data (see also point 1 above).

Reviewer comment: “While I do not understand all the nuances of satellite data retrieval, it is clear that the AMF calculation has significant impact on the derived VCDs. The authors provide an estimate of this on page 10497 where they show the variation

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in VCD with AMF, given a peak SCD of 8.0e14 molec/cm2. Calculating approximate mixing ratios from the VCDs, as above, surface HCHO can be as low as 0.5 ppbv (MBL=1000 m; AMF=0.6) or as high as 5.8 ppbv (MBL=200 m; AMF=0.3). Since the AMF is calculated from a complex model with estimated inputs that are assumed to be homogeneous in the region of interest, it would not be surprising that errors in the input data (AOD, SSA, etc.) caused by, for example, other emissions from ships would influence the AMF."

Author Reply: This is an important comment (in agreement with reviewer #1). We performed additional sensitivity studies in order to better quantify the associated uncertainties. It turned out that potential aerosol effects on the HCHO AMF can not explain the observed enhancements (see point 2 above). We added discussion of this point in section 4 of the revised version of our manuscript.

Reviewer comment: "On the other hand, the very similar analysis of GOME NO2 data in this region [Beirle et al., 2004] is quite reasonable, as are the HCHO comparison results (GOME and MAXDOAS) from the FORMAT mission in the polluted Po River valley near Milan, Italy. This suggests that there might be some unrecognized problems with detection of HCHO at the lower levels expected over the Indian Ocean."

Author Reply: We can not exclude unrecognised problems for the HCHO detection, and we also stated more clearly now in our manuscript that the deviation between measurements and model results might be also partly due to the measurement uncertainties. However, in our opinion there are strong arguments that the observed HCHO signal is not an artefact. First, it is systematically oriented with respect to the ship tracks, and it changes according to the wind direction. Second, we can also rule out that it is an artefact due to the potential effects of clouds and aerosols (see point 2 above). As stated above, we think that our observations are an indication for increased CH4 degradation, and that the order of magnitude is not in disagreement with simple calculations and model simulations (see figure above).

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Reviewer comment: “Whatever the issues are, it is clear that a 5.8 ppbv HCHO enhancement over background in this region is completely unreasonable, and the 1.1 ppbv value (derived from the VCD stated in the abstract) is excessive as well. While it’s likely that ship emissions do contribute, in some way, to elevated formaldehyde in this region, I don’t think this paper presents a convincing argument for what that contribution might be.”

Author Reply: We hope we could convince the reviewer that a) our observations are very probably not an artefact, and b) that the findings allow sound and interesting conclusions on the chemistry in ship plumes and the related formation of HCHO.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 10487, 2009.

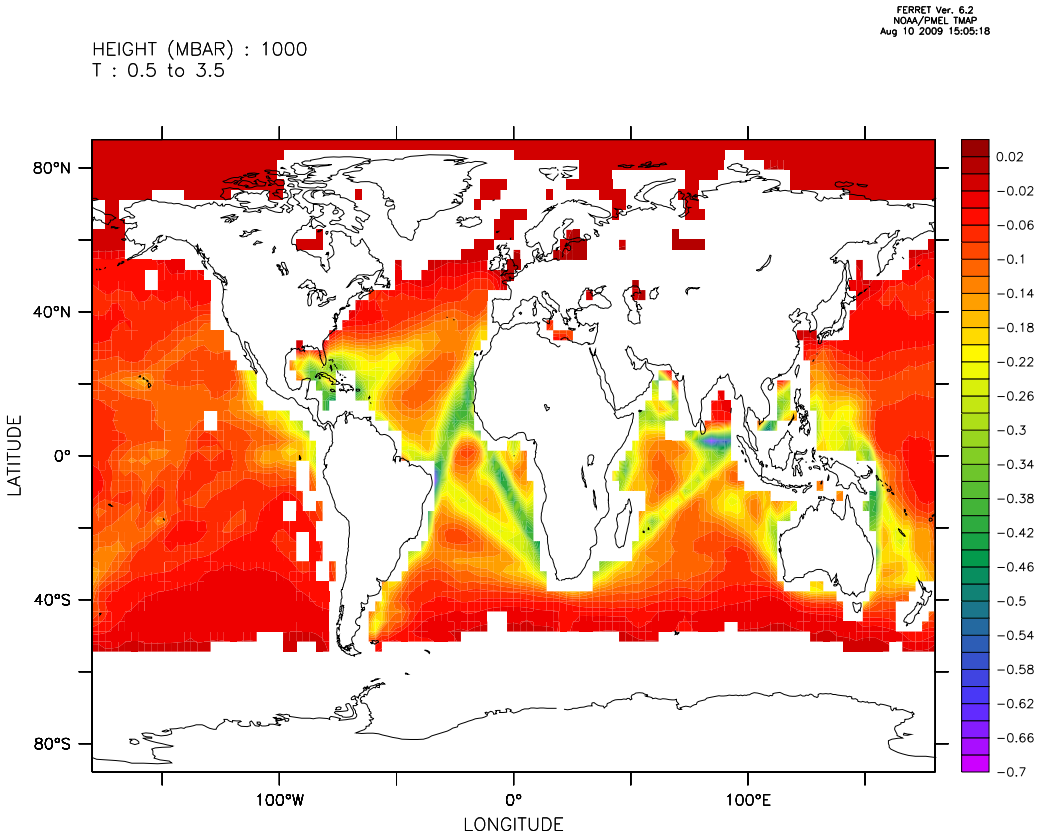

Fig. 1.

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