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

Anonymous Referee #3

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This paper describes analysis of data from the GOME satellite 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.

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. 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.

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.

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 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. 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 MAX-DOAS) 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. 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.

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