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Atmospheric Chemistry and Physics Discussions

Interactive comment on "New constraints on terrestrial and oceanic sources of atmospheric methanol" *by* D. B. Millet et al.

Anonymous Referee #2

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This is a well written and well organized paper. The overall quality is high as the authors did a good job of researching the subject and the authors deserve much credit for the significant effort that went into this paper. Some comments are given below.

The authors state in the abstract that the aircraft measurements show a strong correlation with CO (r2 = 0.51-0.61). They may be referring to the ICARTT aircraft measurements (this range appears in the discussion under the 'Importance of Anthropogenic versus Biogenic Sources') but this is not clear in the abstract as this sentence follows a global statement about terrestrial plant sources. Because of co-emission of isoprene and methanol by vegetation during the growing season, and the subsequent oxidation of isoprene to 'ultimately' yield CO, and the fact the biomass burning co-produces both methanol and CO, one might reasonably expect a significant correlation between CO

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and methanol during the growing season as well as during BB events. Since methanol has a lifetime of ~5 days or so (according to this paper), one would expect that this co-variance would break down rather rapidly when the sampling period is removed a week or more from the event (BB or growing season). (One still might expect some minor correlation due to co-atmospheric production of methanol and CO). However, the authors don't discuss this in the paper to any significant degree. If there is significant correlation of CO and methanol in other data sets, a significant ocean source of CO could help explain this in the absence of BB or growing season influence. However, to my knowledge it is believed that the ocean is a small source for CO (e.g., Duncan et al., 2007). The paper states that the model reproduces the correlation with CO in the model with the reduced vegetation source but then the questions become: 1) is it reproduced during all seasons and at all times? and 2) is it (CO:methanol) expected to correlate less well with the reduced vegetation source if the model is not correct or merely have a different slope? Also, this, in itself, does not confirm that the anthropogenic source of methanol is small.

A good deal of insight into the question of relative sources would be data from the southern hemisphere since the majority of vegetation is in the northern hemisphere and the authors were able to find some data in the SH and compare with model results. Figure 4 helps with demonstrating some robustness with the model. However, since the ocean is a net sink for methanol and since there are apparently no continental sources of methanol here, it is perhaps surprising, without further explanation, why methanol is 100-400 pptv (model 100-200 pptv).

It would also be instructive to compare (or at least discuss) the methanol mixing ratio distribution in the northern hemisphere in the winter with the summer. Since, as proposed in the paper, the ocean is a source as well as a sink and is, in total, close to a net zero for methanol globally, the methanol present in the atmosphere should be due mainly to terrestrial plant growth, decay and atmospheric production. All three of these will be significantly slowed in the winter so that methanol mixing ratios in the winter,

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based on the results from this paper (and others), should be much lower than in the summer. (Gas phase oxidation by OH will also be lower in the winter but this will be relatively less significant). Data to this effect may not be available but again it would be germane to the subject to discuss the need for such data (and also possibly show what the model predicts in winter).

It is stated that the air-sea flux parameterization yields a vertical profile shape that is consistent with observations over the Pacific Ocean ((PEM-TB) and DC-8-INTEX-B). However, the INTEX-B and ITCT-2K2 results differ. It is stated in the paper that this may be due to enhanced biological activity or upwelling of cold, methanol-depleted water. The authors should state that the techniques used for these measurements are different ((PEM-TB and DC-8-INTEX-B) and (INTEX-B and ITCT-2K2)), faster techniques being employed in the latter data sets (this is possibly key in understanding boundary layer runs). It could be construed as unbalanced to assume that the model agrees with the measurements because of one set of data and then rationalize away the other set of data. Measurements during INTEX-B and ITCT-2K2 were not over highly productive sections of the ocean but they were further removed from continental sources which should make them more representative for gaining insight into the air-sea exchange processes. This is an important point and goes to the crux of one of the theses in the paper. Another factor to consider when looking at vertical profiles and boundary layer runs is the CO and methanol relationship; to isolate the effect of air-sea exchange it is important to be in air masses that are not largely influenced by pollution sources and that are far removed from other sources that could mask the effect of air-sea exchange. To this end, air masses that show little correlation between CO and methanol would be desirable.

In Figure 8 perhaps the authors could consider showing the actual concentrations rather than the normalized concentrations.

In summary, this is a solid paper but questions remain about some of the arguments presented. I believe that there is considerably more uncertainty in the methanol budget

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as presented than the authors seem willing to recognize and more measurements are clearly desirable.

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