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Atmospheric
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Discussions

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

D. B. Millet et al.

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Response to comment by Anonymous Referee 2

Our responses are given below in bold italics.

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 Anthropogen versus Biogenic Sources") but this is not clear in the abstract as this sentence follows a global statement about terrestrial plant sources.

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Discussion Paper

The reviewer is correct, we were referring to the ICARTT dataset (as is made clear later in the text). We modified the abstract to clarify this point.

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 and methanol during the growing season as well as during BB events.

CO and methanol would certainly correlate in biomass burning plumes, but we have filtered such plumes from the datasets used, so this is not an issue here.

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 do not 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).

As we now note in the abstract, we were referring to summertime observations over land. The correlation is driven by the fact that both species have a similar array of terrestrial sources (biogenic + urban/industrial), though in differing proportion. The methanol lifetime is also sufficiently long that it will persist as CO is produced photochemically from VOC precursors (e.g., biogenic isoprene), which can also contribute to a correlation. Outside of the growing season (though there is limited data), any correlation in the continental boundary layer should be due to the common urban/industrial source and similar vertical gradients. We added a discussion of these points to the text (Sect. 3.3).

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?

In general, yes, to the extent that there is data available. We added the following discussion of this point (Section 3.3): "On the other hand, we find that methanol and CO are in general not as well-correlated in the non-urban surface datasets or over the ocean (and this is also captured by the model)."

We also modified the sentence the reviewer mentions to in order to clarify that the statement refers specifically to the ICARTT observations.

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.

The reviewer is correct that the slope is the more critical test. We see from Figure 10 that changing the biogenic methanol source by a factor of 2 significantly changes the modeled methanol:CO slope but not the R value. We clarified this point by specifying (e.g.), "we reproduce this correlation AND SLOPE" at relevant points in the abstract and in Section 3.3.

We believe that we have demonstrated convincingly that the anthropogenic methanol source is small. Our calculation of the anthropogenic source is derived by scaling CO emissions to observed methanol:CO enhancement ratios in polluted air. The CO emissions are independently constrained (Hudman et al., 2008). The methanol:CO relationship observed in the aircraft data and shown in our paper is consistent both with the optimized model and with prior understanding of the methanol:CO emission ratio.

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).

We inserted the following discussion of this point into the text describing Figure 4: "The model generally reproduces the observed concentrations over the remote ocean, in a region where marine emissions are the dominant model source of methanol (50 to >90%), though in fact the ocean acts as a net sink here (Figure 3). Atmospheric production is the main other source (5 to 35%, according to the model), with a small contribution from transported terrestrial emissions (generally <10%)."

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, 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).

The reviewer is correct that methanol exhibits a seasonal cycle, with higher concentrations in spring/summer and lower in fall/winter. In Section 3.2, we expanded the discussion of the Blodgett Forest dataset, which is the only published full annual cycle for methanol: "The measured and simulated concentrations at this site (not shown) both peak in spring-summer and exhibit a fall-

winter minimum, reflecting the seasonality of the biogenic source (plant decay emissions and photochemical production are also lower in winter).”

With regards to the need for more such data, we added the following comment in the Conclusions: “More extensive measurements defining how methanol emissions depend on PFT and season would help to resolve these issues and further refine the overall budget.”

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).

We made a mention of the different measurement techniques in the text (section 3.1).

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.

We have re-worked this paragraph and do not believe the revised discussion is unbalanced. The modeled vertical profile shape agrees with observations for 4 of the 6 datasets. As we point out, the model does not do well for the other two. These are both from the eastern Pacific, and we speculate as to the reasons for

the difference.

We disagree that C130-INTEX-B and ITCT-2K2 datasets are further removed from continental sources and hence more representative for looking at air-sea exchange. PEM-TB and DC8-INTEX-B are more remote, in the central Pacific. Though we have filtered out polluted air and only use data over the ocean, ITCT-2K2 and C130-INTEX-B are near the North American coast and hence can be influenced by re-circulated emissions from the North American continent.

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.

At the reviewer's suggestion, we have replotted Figure 6 after filtering out polluted air (diagnosed by CO > 150 ppb).

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

We choose to leave this figure as-is to emphasize the relative seasonal cycles, which is the only point of the figure.

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

Agreed, important uncertainties do remain for both oceanic and terrestrial sources. We inserted the following statements to emphasize this fact at relevant points in the Conclusions: "Our analysis is based on the only published

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dataset of methanol concentrations in the surface ocean (Williams et al., 2004), though these measurements do agree with inferred levels elsewhere (Singh et al., 2003). More process-level information on methanol in the OML is needed to build on the initial work presented here."

"More extensive measurements defining how methanol emissions depend on PFT and season would help to resolve these issues and further refine the overall budget."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7609, 2008.

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