**Atmospheric
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Interactive comment on "First global distributions of methanol and formic acid retrieved from the IASI/MetOp thermal infrared sounder" *by* A. Razavi et al.

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Received and published: 14 December 2010

Reply to Referee #1

We thank the referee for his useful comments and corrections. His major concern is on the section 5 where correlations between methanol, formic acid and carbon monoxide were presented. The 2 other referees were equally skeptical on this short section and have recommended to keep the results for future research. We decided to remove the correlations figures but we alternatively provide comparison between their time series over selected regions. We also agree with the referee's concern about the discussion

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of source attributions which will be addressed more carefully with model comparison in another paper (to be submitted in the coming weeks). A point-by-point response to the referee's comments is provided below.

Major comments:

1. Section 3.1: How were the covariance matrices calculated for methanol (from daily varying IMAGESv2 profiles? Or spatial variability? Or. . .?) and for Section 4.1 what is the error covariance on the a priori profile of formic acid? How sensitive is the retrieval to the specification of the a priori covariances?
The methanol covariances matrices were calculated from monthly averaged IMAGES v2 profiles given on a $4° \times 5°$ grid, over the whole world and one full year. The following has therefore been added to section 3.1 for clarification :
"Methanol a priori profiles and covariance matrices were derived from distributions calculated by the IMAGESv2 global chemistry-transport model (Stavrakou et al., 2009). Monthly averaged model profiles over the whole year 2007 were used globally, on a $4° \times 5°$ latitude-longitude grid to account for the seasonal and spatial variability of the model."

For formic acid the procedure to build the covariance matrix was different because the model profiles are still considered very uncertain. The a priori profile has been constructed from aircraft measurements above the USA for altitude below 8 km and from ACE-FTS profiles for the upper troposphere. In order to perform the simulations that permitted the conversion of ΔTb to total columns the profile has been multiplied by factors ranging from 0.5 to 10 for different atmospheric conditions. This represents a variability of up to 350 %. This has been clarified in section 4.1.

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Table 1. Selected regions and periods for the retrieval of methanol using the Optimal Estimation Method.

Localization	Region boundaries	Date [dd/mm/yyyy]	DOFS range
Congo	0–35° S	20/10/2008	0.29–1.02
	10–50° E		
Chad	0–25° N	05/04/2009	0.77–1.05
	0–30° E		
Brazil	0–20° S	20/10/2008	0.45–1.02
	35–60° W		
India	5–40° S	02/05/2009	0.50–1.06
	70–90° E		
Atlantic ocean	30° S–25° N	11/08/2008	0.12–0.87
	10–40° W		

2. Figure 5 and explanatory text: Please provide more details on the "training set" of full retrievals used. For how many days? Over what time period? Globally or in what regions? Are there seasonal differences in the expressions given by equation 3 and 4? The following table describing the regions selected for the training set has been added to section 3.1.

The regions/periods are selected to correspond to situations of high ΔTb. The retrievals were conducted over these regions for one day of observations. The days were chosen during fall 2008 and spring 2009; no significant seasonal differences were found between the resulting conversion factors used in equation 3 (the standard deviation is equal to $0.4\,10^{16}$ around the conversion factor of $4.48\,10^{16}\,molec\,cm^{-2}/K$). This has been clarified in the text.

3. Section 3.3: In addition to errors, can you comment on detection limits? Is there a minimum concentration of methanol and formic acid that can be retrieved with IASI?

According to its NEDT noise (about 0.2 K), the limits of detection of IASI for methanol and formic acid have been calculated from simulations using a standard atmosphere (1976 U.S. model) to be about $1.60\,10^{16}$ molec/cm^2 and $0.60\,10^{16}$ molec/cm^2, respectively. One should point out, however, that the detection is highly dependent on the species vertical profile and on the thermal state of the atmosphere. This information has been added to section 3.3. for methanol and 4.1. for formic acid.

4. Section 5, 1st paragraph: It's not clear what value there is in looking at global CH3OH v HCOOH correlations. Perhaps the authors could select either enhanced regions to comment on sources or colour these plots regionally as in Figure 12?
As explained on top, more work is needed to identify different emission processed from the global correlations between CH_3OH, $HCOOH$ and CO. Section 5 was modified and compares now the time series of these three species in selected regions (see next comment).

5. Section 5: In order to link the observed concentrations with fire activity, it might be useful to show an annual timeseries of monthly mean CH3OH columns, HCOOH columns, CO columns and fire counts over different fire regions. This would provide a more compelling description of the importance of this source to observed concentrations.
Section 5 has been modified and includes now the figure 1 (in the pdf attachment) which compares time series of methanol, formic acid and carbon monoxide in biomass burning regions. A fair correlation between these three species is observed in Brazil, Congo and SE Asia with a time-lag, however. Although biomass burning is the likely source, it is obvious that more work will be needed in the future to identify/quantify sources by sector. Work in this direction, using the IMAGESv2 model, is ongoing. Section 5 reads now :
"In this section we compare the 2009 time series of methanol, formic acid and carbon

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monoxide for three selected regions subject to biomass burning. The comparisons are most likely to reflect similarities/differences in the free tropospheric columns, as IASI is more sensitive to this altitude range for these three species. Monthly mean total columns of methanol and formic acid are shown in Fig. 11 together with the total columns of carbon monoxide and the AATSR fire counts for three $10 \times 10°$ regions located in Brazil ($15–5°$S, $60–50°$W), Congo ($15–5°$S, $20–30°$E) and South-East Asia ($20–30°$N, $95–105°$E). For each regions, the time series of CO, CH_3OH and $HCOOH$ are similar. An increase in the total columns is observed for the three species just after the month with the maximum fire counts. The highest number of fires (exceeding 700) is found above Congo where methanol, formic acid and carbon monoxide reach high values, with increases of about $1.6\,10^{16}$, $2.5\,10^{16}$ and $1.4\,10^{18}\,molec/cm^2$ in comparison with their mean total column between January and June, respectively. In each cases, the CH_3OH maximum lasts longer than for CO or $HCOOH$ suggesting an additional source. Overall higher concentrations of CH_3OH found above Brazil and Congo might be due to the larger biogenic source in these regions.

In addition to looking into correlations regionally, preliminary global analyses were carried out. Linear correlations ($R^2 = 0.7$) between CH_3OH and $HCOOH$ were found during the DJF and SON periods highlighting specific emissions or fate of these two species."

The conclusion section has also been modified accordingly :
"Time series of methanol, formic acid, carbon monoxide and AATSR fire counts were also compared and found to be fairly well correlated for three different regions (Congo, Brazil and South-East Asia) where biomass burning is their likely common source."

Minor comments:

1. Page 21477, line 11: grammar, "among which are methanol. . ."

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The sentence has been changed into :"Methanol and formic acid, along with a series of other compounds, have been observed in young or aged biomass burning plumes with the ACE-FTS instrument."

2. Page 21477, line 24: grammar, "Other VOC observations. . ."
corrected

3. Page 21479, line 11: grammar, "coordinated measurement campaigns."
corrected

4. Section 1.2: Would be nice to include the Beer et al., TES results in this overview of methanol
The reference has been included in the overview :
"Beer et al.,(2008) has demonstrated the possibility to measure methanol from a nadir infrared sounder and reports lower CH_3OH concentrations in California than near Beijing, where emissions could be caused by local sources."

5. Page 21480, line 24: grammar, "precipitation (Sanheueza et al. . .."
corrected

6. Page 21480, line 25: The primary reason for the decrease in lifetime in the FT is the scarcity of precipitation
This has been corrected :
"The resulting lifetime of $HCOOH$, estimated to be a few days in the boundary layer, increases in the free troposphere because of the scarcity of precipitations (Sanhueza et al.,1996)."

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7. Page 21482, lines 15-20: Could you comment on the uncertainties on the CH3OH and HCOOH line parameters?

The uncertainties on the methanol and formic acid line intensities were inserted in section 1.2 and 1.3, respectively :

"The strongest absorption band of methanol in the infrared is the ν_8 CO-stretching mode centered at $1033\,cm^{-1}$. We have used line parameters of Xu et al. (2004), implemented in the HITRAN database for which a precision of 6% for line intensities is quoted."

"We have used a new set of $HCOOH$ spectroscopic line parameters of (Vander auwera et al.,2007), implemented in the latest versions of HITRAN and GEISA databases. The accuracy on the absolute line intensities is evaluated to be about $7\,\%$."

8. Page 21482, line 23: grammar, "in October 2006 in a. . ."
corrected

9. Figure 1: The a priori is shown with vertical resolution exceeding the retrieval. Could you include the 4-layer version used in the retrieval on Figure 1 as well?
The four points used as a priori for the methanol retrievals were added (see figure 2 in the pdf attachment).

10. Page 21485, line 25 and page 21486, line 2: typo: The text refers to Figure 3 not, Figure 4 as given.
corrected

11. Page 21486, line 8: What is the range in DOFs for the retrievals?
The DOFS for the selected retrieval range from 0.12 above the Pacific ocean to 1.06 above India. The DOFS range for each retrieval regions has been added in table 1

and the following sentence has been added to section 3.1 :

"The resulting DOFS (Degrees Of Freedom for Signal, given by the trace of the averaging kernel matrix) for these retrievals are given in table 1. DOFS values range from 0.29 to 1.06 over land and are found lower above the ocean (between 0.12 and 0.87) where the dependence on the a priori is therefore larger."

12. Page 21486, line 25: Is the ozone contamination in the CH3OH retrieval at all altitude dependent?

Simulation results show that the dependence of CH_3OH ΔTb in O_3 variation at different altitudes is relatively constant for altitudes above 8 km. The behavior in the first kilometers is somewhat different with the ΔTb slightly increasing with ozone concentrations. At this stage the altitude dependence is not explicitly taken into account, with an average O_3-dependent factor being considered. The referee's comment is very valid and will be addressed in future developments.

13. Section 3.2, last paragraph: The statement that 5% of methanol comes from biomass burning emissions requires a citation. While the IASI observations are certainly suggestive of fire emissions, no comparison with models is shown, thus it seems unjustified to claim that models underestimate these emissions. Can you provide some comparison or cite some values for simulated CH3OH columns in these regions?

We agree that the possibility that models were underestimating biomass burning emission is an overstatement with the information provided in the paper. A dedicated paper on source estimates using IASI constraints is in preparation. This part has been modified into:

"Although biomass burning is assumed to be a weak emission source of methanol (accounting for less than 5% of total emissions according to current inventories) (Jacob et al., 2005), the main hot spots in the global distributions appear to be possibly

related to fires. This could be caused by the fact that methanol emitted by fire events is usually transported higher in the troposphere where the IASI sensitivity is larger or by the fact that a better sensitivity near the surface is induced because of higher surface temperatures for burning areas."

14. Page 21489, line 15 and line 17: grammar, replace "estimation" with "estimate"
corrected

15. Section 4.1: It seems a bit arbitrary to not retrieve over oceans, given that concentrations in outflow may be of general interest. Could you justify this a bit more? Is the signal particularly low over this region? Do the oceans meet the minimum 5K thermal contrast requirement? If not, you may be able to use this later criteria to eliminate this data from your analysis in a more justified fashion.
Thermal contrast above oceans does not reach 5K. This is indeed why retrieval above oceans have not been considered for formic acid. It has been clarified :
"We have chosen to consider only the cases for which the thermal contrast is higher than $5\,K$. This conservative criterion excludes all retrievals above oceans."

16. Section 4.1: Can you say anything about vertical sensitivity with this modified retrieval approach? Similarly, how important is the a priori constraint in these retrievals?
The following has been added to section 4.1 to provide an indication about the altitude sensitivity of formic acid retrievals:
"This retrieval approach does not provide information about the vertical sensitivity of the formic acid total column. However, the limited set of full profile retrievals performed give a maximum sensitivity between 4 and 14 km."

17. Section 5: what is the impact of filtering out points with low thermal contrast on

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these correlations?
The filtering of observations with low thermal contrast may indeed introduce a bias which favors the tropical region. Further analyses must be conducted to consider this aspect and other possible influence such as the varying vertical sensitivity. As suggested by another referee, the correlation figures have therefore been removed (see comment 5).

18. Section 5: Comment on the vertical sensitivity of the HCOOH, CH3OH and CO retrievals – do they coincide? Are the observations looking at the same air masses?
The vertical sensitivity of these three species are all maximum in the free troposphere, i.e. between 4 to 14 km, 6 to 10 km and between 3 to 12 km for $HCOOH$, CH_3OH and CO total columns, respectively. Although fine structures in the respective profiles could be missed, the same column in the free troposphere are measured and can be compared.

19. Section 6, final paragraph: Could the authors comment on the challenges of comparing these non-traditional brightness T retrievals with in situ profiles and models? Are averaging kernels routinely estimated for these retrievals, or would characteristic "average" averaging kernels need to be applied when making comparisons?
The following sentences have been added to the conclusion :
"It is anticipated that the assimilation of these data in a global chemistry model will help to improve the determination of the emission fluxes for these two species. Mean averaging kernels for methanol (differentiated for land and ocean) are provided in order to account for the vertical sensitivity of the measurements."