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Atmospheric Chemistry and Physics Discussions

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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Reply to Referee #2

We acknowledge the referee for his useful comments which have helped to improve the manuscript. We agree with the referee that the source identifications are too speculative at this stage, and section 5, on the correlation between species, has been removed. More work with model comparisons is ongoing to provide sources attribution and quantification. Detailed answers are provided hereafter.

Specific comments:

Title: It is not true that this work presents the first global distributions of formic acid; however, these are the first global distributions derived from the IASI/MetOP sounder, to my knowledge. I therefore suggest to reword the title of the paper as follows: "Global distributions of methanol and formic acid retrieved for the first time from the IASI/MetOP thermal infrared sounder". Abstract: A similar correction applies to line 5-8 of the abstract. Correction: "In this work, we derive global distributions of these two organic species using for the first time the . . ..".
The title and the abstract have been corrected accordingly.

Introduction: p 21476, l24: which VOC with more that 1 ppmv mixing ratio does exist in the atmosphere (besides methane, which is usually not listed under VOCs)? Please give examples.
The only VOC with mixing ratios exceeding 1 ppm is indeed methane. As different definitions of VOC exist, methane as been included here in a general context but the sentence has been clarified.

Section 1.1: p21477, l 16-20: the following contributions on global distributions of organic compounds should also be mentioned: Moore and Remedios, ACP, 2010; Moore, Remedios, and Waterfall, ACPD, 2010.
The two references have been added in section 1.1.

Section 1.2: p21479, l18/19: The diurnal variation of methanol is mentioned here. Just curious: is it possible to derive the diurnal variation from IASI data?
As IASI provides two measurements per day (9:30 and 21:30 local time), it is theoretically possible to compare the day and night concentrations of methanol. Preliminary

results show similar spatial distribution for night observations but with lower total columns. It is, however, not clear if this is due to a diurnal behavior or to different sensitivities in the retrieval.

Section 1.3, p21482, l19/20: Please note that both Grutter et al., 2010 and Zander et al., 2010 explicitly state that they have used the Vander Auwera et al. (2007) spectroscopic data. Your presumption that previous IR observations of formic acid were likely to high by a factor of 2 is not correct for these two publications.
This has been corrected :
"The updated data set reports $HCOOH$ line intensities larger by about a factor 2 compared to previous studies (Perrin et al.,2007). This implies that concentrations obtained from infrared retrievals before 2007 were likely too high by the same factor."

Section 3.1: p21486, l2: Since you perform a profile retrieval (consisting of 4 layers), you should be able to give the methanol amounts as vmrs as well. How do your retrieved vmrs compare to observations from other instruments as given in the introduction?
Averaged mixing ratios of methanol in the lowermost retrieval layer (ground to 4 km) are between 0.1 and 7.0 ppb for the different selected regions. In the literature, methanol concentrations are found to be a few hundreds of ppt above oceans and increase up to several tens of ppb in fire plumes. This agrees relatively well with the values found by IASI although the highest concentrations in fire plumes are not reached. The following has been added to section 3.1 :
"Retrieved methanol mixing ratios in the lowermost atmospheric layer (0 to 4 km) range from about 0.1 to 7.0 ppb for the different selected regions."

P21486, l18: " . . . very well defined linear correlation . . .": The correlation between ΔTb and O3 does not look linear; if an extrapolation to lower O3 values becomes

necessary, this could introduce considerable errors. Could you comment on this?
It is true that ozone variations below 200 DU could have a different influence on the methanol ΔTb. However, such low concentrations are found only in the Antarctic during the ozone hole period. The linear assumption could therefore only introduce higher methanol total columns during this special event. The following sentences have been added :
"For very low O_3 concentrations, it is possible that the linear assumption introduces errors in the retrieved methanol columns. However, as concentrations below 200 DU for ozone only occur during the antarctic ozone hole period, this will not affect the distributions discussed here."

Section 3.2: p21487, l20: please add: " . . . first global distributions of methanol from IASI."
corrected

Section 3.2, p21488, l15 to p21489, l12: The discussion of sources of methanol is highly speculative. Further evidence is necessary for the assignment to biomass burning and vegetation growth, respectively. Plotting time series for certain regions could help to identify annual cycles.
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 certain 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 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 $10 \times 10^{\circ}$ 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."

Section 4.1: p21491, l14/15: How is τ defined? Where do numbers for τ come from?
The thermal contrast τ is defined here as the temperature difference between the surface and the first atmospheric layer as given in the level 2 IASI data. The following has been inserted in the text :
"The thermal contrast τ corresponds to the difference between the surface temperature and the air temperature at the first retrieved altitude level, located at about 100 m (both included in the IASI level 2 data)."

Section 4.1, general: Could you give any indication to which altitude range the formic acid retrievals from IASI are sensitive?
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."

Section 4.2, p21493, l2-4: Is there any evidence for boreal fires as source of formic acid in Northern Asia and Northern America? What about the vegetation cycle?
By comparing with AATSR fire count distributions, we found that some strong enhancement in HCOOH above Alaska and NE Asia are well correlated with these fire counts during JJA. But the overall increase of formic acid in the northern hemisphere is more probably related to biogenic emission. This has been clarified in the text:
"The overall increase of formic acid in the Northern Hemisphere during JJA is likely caused by the seasonality of its biogenic emissions. However, according to the AATSR fire count distributions, some regions with large $HCOOH$ columns may be associated with boreal fires such as in Eastern Russia and in Alaska."

Section 4.2, general: As for section 3.2, the source attribution of formic acid is highly speculative, and more evidence must be provided for the assignment of biomass burning, boreal fires, biogenic emissions, and anthropogenic activities to the observed enhancements. Again, time series for certain regions might be helpful to identify the annual cycles and to link these cycles to the different sources.
Biomass burning regions were identified according to AATSR fire count distributions. This has been clarified in the text and time series in selected regions have also been added (see comment on section 3.2).

Section 5, general: Before analyzing correlations, it must be clear that all measurements (of CO, CH3OH, HCOOH) represent the same altitude range. Is this the case?
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 same column in the free troposphere are measured and can be compared.

The correlation of global CH3OH versus HCOOH as in Fig. 11 is not very helpful in my opinion. Comparing Figs. 6 and 10 it becomes evident that the emission regions for CH3OH and HCOOH are by far not identical. Enhancements in Africa in Northern tropics as for methanol are not present for formic acid (JJA), Southern American enhancements in JJA methanol are not found in formic acid, enhancements over China and SE-Asia in formic acid are not found in methanol and so on. Why should CH3OH and HCOOH correlate globally then? Even if CH3OH and HCOOH are emitted from the same sources, a linear relationship between both is not to be expected, due to chemical processing in the atmosphere (besides the problem of sensitivity to altitude regions). Besides this, the scatter plots for MAM and JJA are not very indicative of a linear relationship.
P21493, l27 to p21494, l2: This is a contradiction to p21493, l6-8: In the upper sentence, you tentatively exclude biomass burning as source for HCOOH enhancements, while in the lower sentence, you assume biomass burning as the most probable source. Correlations to CO with color-coded latitudinal bands as in Fig. 12 are more helpful. However, the high red values of HCOOH in the lower panel of Fig. 12 challenge the statement that Northern American and Northern Asian HCOOH enhancements were from boreal fires (p21493, l2-4), and, indeed, are claimed to be emitted from biogenic processes now (p21494, l14).

I suggest to proceed in the analysis of CH3OH and HCOOH in the way as it was begun in Fig. 12. It would probably be helpful to analyze the correlations for various geographical regions (not latitude bands) and provide clear evidence from independent observations for either biogenic emissions, boreal fires or biomass burning, or anthropogenic activities for these regions/seasons.
As we agree that more work is needed on the correlations of methanol, formic acid and carbon monoxide, section 5 has been completely modified. It now includes only the comparison between the time series of these three species for selected regions subject to biomass burning (see comment on section 3.2).

Technical comments:

P21485, l25: "Fig. 4" should read "Fig. 3"
corrected

P 21492, l10: Typo "constraint"
corrected

Fig. 3: What are the dashed light green horizontal lines in panel (a)?
They correspond to the RMS of the residue when CH_3OH is taken into account. This has been added to the figure caption.

Fig. 5: Please make clear (by selection of axis range or marking the x=0, y=0 lines) that the linear regression pass through the (0,0) point and the y axis intercept is zero. The figures as presented suggest that the linear regression produces a bias in methanol (CH3OH $\neq$ 0 for ΔTb = 0).
The axis range has been changed and starts now at x=0 and y=0 for more clarity.

Fig. 7: What do negative errors mean in this figure? In particular, do negative errors larger than 100 $\%$ mean that negative total columns have been derived?
Negative errors means that the retrieved total column from ΔTb is below the a priori value inserted in the simulation. Negative errors larger than 100 % correspond indeed to negative retrieved total columns. However, these negative total columns correspond only to HCOOH total column below the limit of detection of IASI ($0.6\,10^{16}\,molec/cm^2$).