We would like to thank the referees for their careful review and useful questions. In the revision we have addressed all comments, in particular the remark of the second referee related to the in-plume formation of formic acid. To verify the results, we have in addition to brightness temperature derived retrievals, now also carried out independent (optimal estimation) retrievals of formic acid. The retrieved columns with this alternative method are around a factor two lower than the brightness temperature derived ones, clearly showing the difficulty in the measuring accurate concentrations for this species. However, even in this case, the large enhancement ratios point to secondary formation. As outlined below, we have expanded the manuscript with a detailed discussion of these different retrieval approaches and estimated uncertainties.

Please find our detailed answers below (in blue) to the referees' questions and also to the interactive comment of Yokelson et al. (in black).

Referee #1:

Comment 1:

Fig 2 (y-axis) presents the total columns of all 3 gases in molec cm^{-2}, but no explanation is given why the authors choose to write an "X" before the label TC-max and TC-mean. Explain or correct

→ X represents the corresponding species CO, NH_3 and HCOOH. We agree that the label is unnecessary and confusing; we therefore removed it from figure 2.

Comment 2:

Large fires have repeatedly occurred in the past, but might have not been measured in such detail as remote sensing techniques have not been available for such a long time. A reference to "typical background values" is made in the abstract (l7) and (p31565 l19), does this refer to values outside the plume or to other times or years observed within the same region and with the same instrument? Please specify.

→ We have clarified this in the text; which now reads: "The typical background values were calculated as the mean of the daily minimum columns measured with IASI before the fire period (from 1-26 July)."

Comment 3:

Where are the highest values on 2, 10 and 15 August to be seen?

→ For NH_3 the maximum columns have been observed close to the sources, at around 500 km southeast of Moscow. For CO and HCOOH these were observed somewhat further, at around 1000 km southeast of Moscow. This has been added in the text.

Comment 4:

P31563 l9, cite previous articles where "large spatial and temporal" studies of NH_3 and HCOOH have been performed (Lieven 2009, Grutter 2010)

→ The case study presented here focuses on a specific large scale fire event as opposed to the two general global studies of Clarisse et al. (2009) and Grutter et al. (2010). These two papers are, however, cited elsewhere in the text (at the end of Section 2 where we discuss seasonality).

Comment 5:

p31566 l4, cite and compare qualitatively with the seasonal evolution observed by MIPAS in the UT.

→ Grutter et al. (2010) reported a marked seasonality of formic acid at 8 km in the mid latitudes of the Northern Hemisphere (20°-60°N), which was attributed to plant growth and corresponding biogenic emissions; reaching a maximum in summer and decreasing by a factor 2 to 3 in early winter. This seasonality is also clearly seen in the IASI data (figure 2.b). Note however, that the maximum in the summer is partly hidden by the strong fire emission. We have added the reference to Grutter et al. (2010) in the discussion of the seasonality (end of Section 2).

Comment 6:

P31567 l9, can background or urban CO contribute to what is seen here? Was it removed from the linear regression to avoid the offset?

→ Following also the comment of the second referee, we found that most of the observations with a large CO column, but a small NH_3 column are the result of spectral fits with a large residual. We have removed all such measurements from our calculations. (see our detailed reply to the first comment of the second referee below). A few observations with a large CO column, but a small NH_3 column remain, but these have a negligible impact on the enhancement ratio.

Comment7:

P31570 l10, "possibly coupled"? .. the authors should know.

→ This word was confusing indeed. The point is that an atmospheric transport model was applied in some studies (e.g. Krol et al 2012), but not all (e.g. Huijen et al 2012). We replaced the word 'possibly' with 'sometimes'.

Comment 8:

P31570 l16. Specify if the adjustments are made with averaging kernels or something else.

→ The adjustments in Yurganov et al. (2011) and Fokeeva et al. (2011) simply consisted in adding a boundary layer offset as explained in the text. As far as we can tell averaging kernels were not taken into account. We have clarified this in the text.

Comment 9:

P31572 l12, please clarify if the enhancement ratios are not affected by the errors in the total columns. Would the uncertainty in TC propagate all the way to the emission calculation? Please be clear.

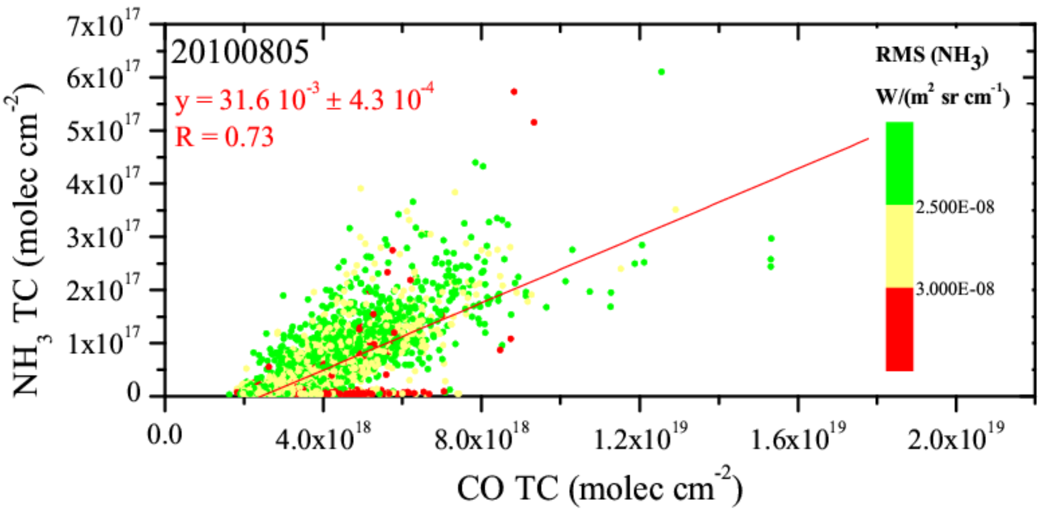
→ Enhancement ratios are affected by errors in the total columns, however, the point we want to make in the text is that errors due to limited boundary layer sensitivity partially cancel each other out, as sensitivity of the different trace gases in the boundary layer will be similar. Other sources of errors will not cancel out and therefore will propagate in the error of the enhancement ratios. As for the emissions, systematic errors will propagate to the emission calculation, but not random retrieval errors as these cancel each other out when we integrate total columns over a large area. We have added this explanation now in the text (end of Section 5).

Referee #2:

Comment 1:

Pg. 31567, line 8. In Figure 3a, were the low ammonia points included in the slope determination? I don't think they should be because the low values look more like some sort of retrieval failure or at least a very marginal result. Please clarify in the paper.

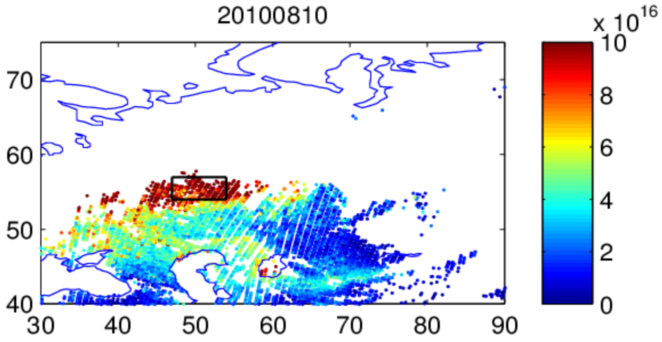
→ Thank you for pointing this out. To investigate the effect of retrieval failures we have remade Figure 3a (see below) but this time indicating the root mean square of the fit residual (RMS) of NH_3. It indeed turns out that most of the observations with a high CO and low NH_3 value have a large NH_3-fit residual (>3 10^{-6} (W/(m^2 sr m^{-1})). In the revised manuscript, we have excluded such retrievals from further processing and updated all affected figures and derived values. The effect of removing these retrievals is however not very large. For instance for the 5th August, the enhancement ratio changes from 31.6 10^{-3} to 32.2 10^{-3}; while the correlation coefficient changes from 0.73 to 0.76. The only exception is the enhancement ratio around the 20th August (two days after the end of the fires) which is now close to zero (before it was around 25.0 10^{-3}) and now much more in line with what is expected for a species with a short lifetime.



Comment 2:

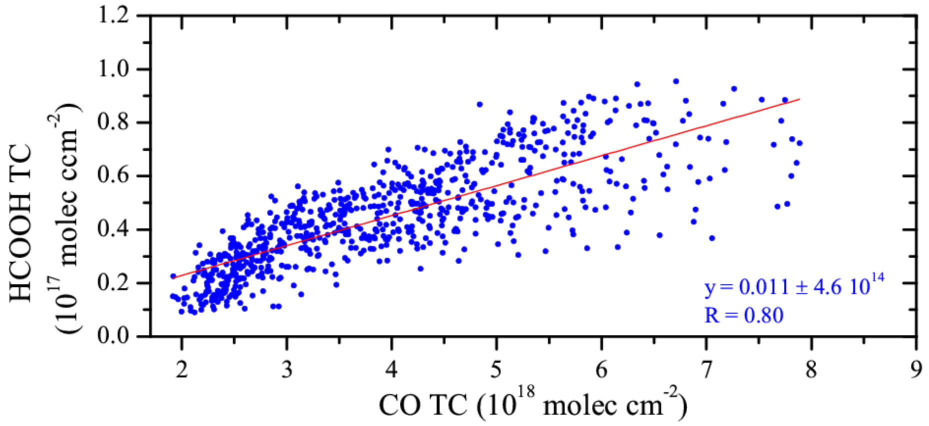
Pg. 31567, near line 25. I find the values for the emission ratios of formic acid to be surprisingly high. Although references to higher values are cited, there exist several un-cited references to lower values including one by one of the co-authors (Coheur et al. ACP 7, 5437, 2007). The suggestion of secondary production during aging is also not very convincing because there is a recent paper by Tereszchuk et al. ACPD 12, 31629, 2012 (see also Tereszchuk et al. ACP 11, 12169, 2011) with emission ratios for formic acid that decline as the fire plume ages. Furthermore, the calculation of emission ratios from total columns is also somewhat dubious because CO, formic acid and ammonia all have very different vertical profiles, and the averaging kernels of IASI therefore sample them in different ways. I realize that the authors are well aware of these problems, but they should be brought to the attention of the readers. In other words, I think the authors should point out potential problems in the methodology and the values (at least for formic acid), even if they do not provide solutions.

→ We agree with the referee that the reported enhancement ratios of formic acid are large. To investigate possible retrieval effects, we have performed independent optimal estimation retrievals (OEM) for HCOOH. Since these are computationally heavy, these were carried out only over a selected area (delimited by the black box indicated in the figure below) and only for a few days (from July 27 to August 10 of 2010). Note that this area is not fully representative for the large spatial extent of the fire plumes but allows to compare the columns retrieved using the OEM with the retrieval scheme applied in the paper (which is based on BTDs).



The OEM retrievals yield total columns which are on average a factor two smaller than the BTDs retrievals (around 1.5 for columns higher than $5\ 10^{16}$ molec cm^{-2} and 2.3 for columns lower than $5\ 10^{16}$ molec cm^{-2}). This analysis has been included in the third paragraph of section 2.

As an illustration all OEM retrievals (from July 27 to August 10 of 2010) are shown vs. the corresponding CO retrievals in the figure below. The average enhancement ratio for these observations equals 0.011 compared to an average of 0.025 for the same time period using the BTD method. So also the resulting enhancement ratio's are about a factor two lower.



If we consider a factor two, the range of enhancement ratios would shift from (0.010-0.032) to (0.005-0.016). This is still much higher than the tabulated emission ratios given by Akagi et al. (2011), which are $2.73\ 10^{-3}$, $2.69\ 10^{-3}$ and $1.80\ 10^{-3}$ respectively for the typical Boreal, Extratropical and Peat forests fire emissions. Therefore even in this scenario, there is evidence of secondary formation of formic acid.

The observed differences could point to limitations of the BTD approach for this specific event. On the other hand also OEM retrievals are prone to errors (including the important smoothing errors when the sensitivity is low). As far as we know, there have been no independent measurements of formic acid in the Russian fires, so that we cannot resolve this uncertainty at this stage. We discuss these now in details in the manuscript (in the formic acid discussion's paragraph in section 3).

As for the comment on the smaller enhancement ratios reported in other studies. Firstly, formic acid emissions are known to have a large dependency on VOCs co-emissions, so that it is not unusual to find large variations between different events. Secondly, the rapid secondary formation (in less than six hours, as reported in numerous studies, e.g. see the interactive comment of Yokelson et al.), should not be confused with the gradually depletion of formic acid (with an atmospheric lifetime of 3-4 days) observed in e.g. Tereszchuk et al. (2011, 2012). Also note that we do not directly observe secondary formation (as the overpass of IASI does not allow high temporal resolved measurements), but instead infer it from the elevated enhancement ratios.

As for the comment of the estimation of the “emission ratios from total columns”, it is true that there are differences both in vertical profile and in the vertical sensitivity of the different species, which will impact the calculation of the enhancement ratios. We now bring this more clearly to the attention of the readers (at the end of section 3).

Interactive comment of Yokelson et al.:

We would like to warmly thank B. Yokelson et al. for their important and enthusiastic comment to the paper. The comments concern on one hand the use of reference spectroscopy for formic acid (and the way it impacts on previous literature results) and on the other hand the formation of formic acid in the downwind plumes. They point to previous studies where a secondary production was clearly observed. The corresponding references have been included in our revised manuscript. This is especially important given that the range of enhancement ratios reported in these earlier studies is in very good agreement with our results, strengthening one of the conclusions of this paper, which is the in-plume formation of HCOOH during the Russian fires. There is obvious complementarity between field and satellite measurements of the gaseous species released by fire, which hopefully will trigger further research and lead to important new results.

List of other changes to the manuscript

4 references have been modified/updated:

Akagi, S. K., Craven, J. S., Taylor, J.W.,McMeeking, G. R., Yokelson, R. J., Burling, I. R., Urbanski, S. P., Wold, C. E., Seinfeld, J. H., Coe, H., Alvarado, M. J., and Weise, D. R.: Evolution of trace gases and particles emitted by a chaparral fire in California, Atmospheric Chemistry and Physics, 12, 1397–1421, doi: 10.5194/acp-12-1397-2012, 2012.

Goode, J. G., Yokelson, R. J., Ward, D. E., Susott, R. A., Bab bitt, R. E., Davies, M. A., and Hao, W. M.: Measurements of excess O3, CO2, CO, CH4, C2H4, C2H2, HCN, NO, NH3,HCOOH, CH3COOH, HCHO, and CH3OH in 1997 Alaskan biomass burning plumes by airborne Fourier transform infrared spectroscopy (AFTIR), Journal of Geophysical Research: Atmospheres, 105, 22 147–22 166, doi:10.1029/2000JD900287, 2000.

Konovalov, I. B., Beekmann, M., Kuznetsova, I. N., Yurova, A., and Zvyagintsev, A. M.: Atmospheric impacts of the 2010 Russian wildfires: integrating modelling and measurements of an extreme air pollution episode in the Moscow region, Atmospheric Chemistry and Physics, 11, 10 031–10 056, doi:10.5194/acp-11-10031-2011, 2011.

Krol, M.; Peters, W.; Hooghiemstra, P.; George, M.; Clerbaux, C.; Hurtmans, D.; McInerney, D.; Sedano, F.; Bergamaschi, P.; El Hajj, M.; Kaiser, J. W.; Fisher, D.; Yershov, V. & Muller, J.-P., How much CO was emitted by the 2010 fires around Moscow?, Atmospheric Chemistry and Physics Discussions, 12, 28705-28731, doi: 10.5194/acpd-12-28705-2012, 2012.

And those 5 references have been added:

Coheur, P.-F.; Herbin, H.; Clerbaux, C.; Hurtmans, D.; Wespes, C.; Carleer, M.; Turquety, S.; Remedios, C. P. R. A.; Hauglustaine, D.; Boone, C. D. and Bernath, P. F., ACE-FTS observation of a young biomass burning plume: first reported measurements of C_2H_4, C_3H_6O, H_2CO and PAN by infrared occultation from space, Atmos. Chem. Phys., 7, 5437–5446, doi: 10.5194/acp-7-5437-2007, 2007.

Grutter, M., Glatthor, N., Stiller, G. P., Fischer, H., Grabowski, U., Höpfner, M., Kellmann, S., Linden, A., and von Clarmann, T.: Global distribution and variability of formic acid as observed by MIPAS-ENVISAT, J. Geophys. Res., 115, D10303, doi: 10.1029/2009JD012980, 2010.

Kerzenmacher, T., Dils, B., Kumps, N., Blumenstock, T., Clerbaux, C., Coheur, P.-F., Demoulin, P., García, O., George, M., Griffith, D. W. T., Hase, F., Hadji-Lazaro, J., Hurtmans, D., Jones, N., Mahieu, E., Notholt, J., Paton-Walsh, C., Raffalski, U., Ridder, T., Schneider, M., Servais, C., and De Mazière, M.: Validation of IASI FORLI carbon monoxide retrievals using FTIR data from NDACC, Atmos. Meas. Tech., 5, 2751-2761, doi:10.5194/amt-5-2751-2012, 2012.

Tereszchuk, K. A.; González Abad, G.; Clerbaux, C.; Hurtmans, D.; Coheur, P.-F. & Bernath, P. F. ACE-FTS measurements of trace species in the characterization of biomass burning plumes Atmospheric Chemistry and Physics, 11, 12169-12179, doi: 10.5194/acp-11-12169-2011, 2011.

Tereszchuk, K. A.; González Abad, G.; Clerbaux, C.; Hadji-Lazaro, J.; Hurtmans, D.; Coheur, P.-F. and Bernath, P. F. ACE-FTS observations of pyrogenic trace species in boreal biomass burning plumes during BORTAS Atmospheric Chemistry and Physics Discussions, 12, 31629-31661, doi: 10.5194/acpd-12-31629-2012, 2012.

Other minor changes in the manuscript:

p31563 l16: add a brief description of the BTD meaning: “based on brightness temperature difference between a perturbed and a reference channel (BTD)”.
p31563 l9: specify that this study corresponds to a fire case analysis.
p31565 l14: modify to “a two month period”
p31567 l4: “shows an example of the enhancement ratio's calculation” instead of “shows an example of the calculation of the enhancement ratio”
p31569 l7: add the unit of the emission fluxes “(in Tg day^{-1})”
p31571 l2: modify to “have taken several possible effective lifetimes, as to obtain a range of reasonable”.