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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Emission ratios of trace gases and particles for Siberian forest fires on the basis of mobile ground observations" *by* Anastasia Vasileva et al.

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The authors thank the Referee 2 for a careful examination of the the manuscript and a favorable general comment. We also thank for a constructive discussion and valuable suggestions which helped us to clarify presentation of the results. The comment on the plume age forced us to revise the source-receptor relationships for F1 and F2 plumes which affected interpretation of the estimated ER variability. Please find below the answers to all the critical comments and the relevant changes in the manuscript.

1 General comments

Comment: Age and source of smoke. This paper reports observations of normalized excess mixing ratios (NEMR) which they classify as emission ratios (ER) based on the assertion that the smoke plumes sampled were less than 24 hours old. A NEMR is only an ER if the smoke has not undergone significant chemical transformation. ER may be used to derive emission factors (EF) for estimating mass emissions when combined with estimated of fuel mass consumed. Often 24 hours is used as an arbitrary threshold for classifying NEMR as ER (see below). However, the authors have not provided evidence demonstrating that the plumes sampled were less than 24 hours old. Figure 2 maps back trajectories, plume transects, and CO emissions totaled over a two month period. Figure 2 provides no insight into where fires were active during the day of sampling or the preceding few days which may have contributed to the emissions measured. The authors need to provide a better demonstration of the rough plume age. For example map MODIS active fire detections for the day of and preceding few days of the plume samples. Use larger figures with focused on the area of interest with back trajectories labeled for time. I suggest something similar to the presentation in the supplementary material of (Collier et al., 2016). With only two samples periods (2 plumes) this should not be difficult to do. In its current state, the paper doesn't demonstrate the approximate plume age or reasonably identify the source regions; therefore the assertion that the smoke samples may be used as ER is cannot be accepted.

Comment: Normalized excess mixing ratios, emission ratios, and uncertainties. The Methods section needs a more complete description of emission measurements along the line alluded to at P12 L33-P13, L2. The authors need to distinguish between excess mixing ratios, normalized excess mixing ratios, and the conditions under which a normalized excess mixing ratio may be considered an emission ratio (ER). A few points (Akagi et al., 2011; Yokelson et al., 2013): The excess mixing ratio of species X in a plume is dX = dXplume – dXbackground. The normalized excess mixing ratio

(NEMR) is dX/dY, where Y is a long-lived reference species co-emitted with X, CO or CO2, to normalize for dilution (Equation 1 in manuscript). If “fresh emissions” are measured, then the NEMR is an “emission ratio” (ER) which can be used to derive emission factors (EF) which may be used to estimate emissions per unit mass of fuel consumed. To be characterized as fresh emissions there must be no significant photochemical loss or other removal or production of either X or Y (Yokelson et al., 2013). Assigning a simple age since emission as a threshold for when a NEMR may be considered an ER that can be used to derive EF involves much uncertainty. The destruction or creation of an emitted species X depends on a host of factors including the chemical reactivity, volatility, and photolability of X, the composition of the emissions, the plume dilution rate and dispersion conditions, composition of the background air that mixes with the plume, and solar insolation. Additionally, it should be noted for readers that field measurements from aircraft platforms have observed changes in smoke plume chemical composition within 0.5 to 5 hours after emissions (Akagi et al., 2013, 2012; Liu et al., 2016; May et al., 2015) I do not argue that smoke which is one day old cannot be used to report ER. The “one day” threshold, while somewhat arbitrary, has been widely used (Hornbrook et al., 2011; O’Shea et al., 2013; Simpson et al., 2011). However, it is important that readers that when smoke is not sampled at the source there are significant uncertainties when using these smoke samples to assign ER and/or EF.

Response to the comments. Thank you for these essential comments. Here we reply to them both. We’ve edited Fig. 1–2 and Fig. 3–4 to demonstrate the source-receptor relationships for F1 and F2 fire plumes. Now in Fig. 1–2 the MODIS active fires are shown as circles with the size proportional to fire radiative power (FRP) and color indicating the day o fire detection. Possible origins of the air sampled within the plumes are shown in Fig. 1–2 with HYSPLIT model three-day backward three-dimensional Lagrangian air parcel trajectories started from 50 m a.g.l. at geographical locations along the railway with 1 h time intervals covering the total time duration of the plume crossing events. The trajectories are colour coded in gray scale according to approximate time of air transport from areas of possible emission sources to the points

of observation, with the time stamps along the trajectories shown with black circles at 12 h intervals. In Fig. 3a and Fig. 4a we show geographical longitudes of the train in the tick labels for the upper X axis to relate location of MODIS active fires in Fig. 1–2 to the measured concentrations.

The analysis of Fig. 1–2 and Fig. 3–4 supplemented by examination of dairy records allowed us to conclude that the smoke measured within F1 and F2 plumes has originated from multiple small active fires that burned directly near the railway. Thus, we may confidently assume that the measured smoke characterizes the original emissions with negligible transformations of the constituents, and the measurements can be used to derive emission ratios. For details, please refer to the revised manuscript.

Changes. Fig. 1–2 are substantially edited. Discussion of Fig. 1–2 is added to the "Plume crossing episodes" section which therefore was substantially extended.

In the section "Methods of data analysis", definitions of normalized excess mixing ratios and emission ratios are added to the description of equation (1).

In Fig. 3a and Fig. 4a we show geographical longitudes of the train in the tick labels for the upper X axis to relate location of MODIS active fires in Fig. 1–2 to the measured concentrations as discussed in "Results and discussion" section in the following paragraphs:

"Beyond the data segments corresponding to the train stops..."

"In the remaining parts of the plumes..."

Further, in the discussion of $ER_{NOx/CO}$ variations: "Nevertheless, from Table 5 we see that the estimated average $ER_{NOx/CO}$ are very stable within each plume, thus indicating a similar photochemical "age" of the two plume segments in each plume. The analysis of Fig. 1–2 and Fig. 3–4 above showed that the peak excess levels of the biomass burning products measured in the F1 and F2 events have originated most probably from fires located in the vicinity of the measurement route. Therefore, we

can safely assume that all (not the peaks only) the measurements used to derive ERs in our study are heavily dominated by smoke from fresh fire plumes with a negligible average effect of chemical transformations."

In the "Conclusions" section:

"The analysis of MODIS active fire detections and HYSPLIT backward trajectories, accompanied by visual observations of many smoldering fires near the train route, shows that the excess levels of the biomass burning products measured within the plumes in the present study refer to a fresh fire smoke with negligible average effect of chemical transformations. Consequently, the estimated ERs can be safely assumed to characterize the initial chemical composition of wildfire emissions."

"The derived gas ERs are generally stable within the plumes, with the differences between the ERs estimated for different plume segments being statistically insignificant, which supports the general idea of a common fire smoke age throughout each plume, as well as a negligible effect of the changing environment on the measurements."

"The uncertainties in the ER estimates are associated mainly with variability of wildfire emissions (combustion phase, nitrogen content in the fuel) as well as with the choice of the regression approach as different assumptions on independent variables inevitably affect the final statistical inference. Chemical transformations (photochemical loss of NO_X and oxidation of NMHC) of the initial wildfire emissions during their transport to the measurement route seem to have no effect on the reported average ERs and their uncertainties because of the proximity of fire emission sources to the TROICA route."

Comment: Treatment of observations. P10, L3-7: “The observed strong scattering of some data subsets is clearly attributable to highly complex measurement environment and the supposed strong spatial heterogeneity of the emission sources contributed to the smoke plumes. Consequently, we exclude from the analyzes the measurements producing extremely high or low dY/dX values to make our final estimates more robust with respect to various disturbing factors.”

This is not an appropriate manner to handle the data. One cannot simply toss data points because they introduce scatter and reduce the correlation coefficient and increase the uncertainty of the slope in the assumed relationship. The authors should have an objective criteria for identifying data segments that are treated as the biomass smoke plume. Rejection of observations taken within the biomass plume should only be rejected using a clear, objective criteria that is based on sound reasoning – e.g. a significant influence of a local anthropogenic, instrument malfunction, or failed calibration.

Response. You are certainly right. To our experience, a significant influence of local (anthropogenic or biogenic) emissions is the main cause of short-term (several minutes long) fluctuations in the analyzed data sets because the events related to an instrument failure or calibration are recorded in the dairy and filtered out first at a data quality control stage. Thus we had to explain the outliers this way. The dY/dX criteria is just a technical approach to filter out fluctuations caused by non-fire sources using programmable scripts. Thus “various disturbing factors” means various local non-fire sources. Thus, we remove the lines cited above and add discussion of possible non-fire contamination.

Changes. In the "Results and discussion" section, we add the following paragraphs:

"Before the top of the ridge (02:50–04:00 UTC)..." and till the end of the paragraph.

"In Fig. 4a two broad CO_2 peaks in the western F2 plume part are observed..."

2 Specific Comments

Comment. P3, L23-24: “Both the plumes were observed in Transbaikalia – a mountainous area in the south Siberia east to the Lake Baikal known for its severe wildfire activity during warm seasons which start early in spring due to exceptionally dry

weather conditions" This sentence is awkward and I do not understand the last portion.

Response and Changes. We have divided this sentence into two: "Both the plumes were observed in Transbaikalia – a mountainous area in the south Siberia east to the Lake Baikal known for its severe wildfire activity. Due to dry weather conditions during winter, fire season in the region usually starts early in spring and can last from April to October."

Comment: Measurements and instrumentation. Grimm calibration PM3 was measured by light scattering which depends in part on the particle size distribution, chemical composition, and morphology. Please clarify if the PM3 mass density reported is based on the instrument's factory calibration or if it was calibrated for biomass burning aerosols (Aurell and Gullett, 2013; Yokelson et al., 2007) and (Nance et al., 1993). If the instrument's factory calibration was used do you anticipate any systemic bias for biomass smoke aerosols?

Response. We kindly thank Referee 2 for this notice. We then admit some bias due to the lack of calibration. We've added information about the PM_3 instrument calibration in to the "Measurements and instrumentation" section and revised interpretation of the observed PM_3 variability in the "Results and discussion" section. For details, please refer to the revised manuscript.

Changes. In the "Measurements and instrumentation" section:

"To measure PM_3, the Dust Indicator and Tunnel System (model 1.411), designed by GRIMM Corporation (Germany), was used. This instrument was calibrated by nephelometer PHAN-A (photoelectric photometer for aerosols) produced in Russia and calibrated by the manufacturer using the methods which are state-approved in Russia (Kopeikin et al., 2008). Calibrations were performed immediately before and after each train route. To perform the calibration, synchronous measurements by both the instruments were made during approximately 1 month both in urban and rural regions. The proper zero and span coefficients were obtained and then applied to recalculate the

measurements made along the train route. Such the calibration include a wide range of aerosol types from various sources which might partly compensate a possible systematic bias in the measurements of biomass smoke aerosol due to specific particle size distribution, chemical composition, and morphology which may influence the PM_3 mass density measured by light scattering (Aurell et al., 2013; Yokelson et al., 2007; Nance et al., 1993)."

In the "Results and discussion" section:

"The estimated $ER_{PM3/CO}$ varies within 320–385 $\frac{\text{ng m}^{-3}}{\mu\text{g m}^{-3}}$ with the relative uncertainties of 4–8% caused mainly by variability in the measured concentrations which, in turn, may come either from natural variability of fire emissions or from aerosol specific measurement errors. The latter are most probably related to the specific features of biomass smoke aerosol which were not completely accounted for during the instrument calibration as pointed above."

"...the $ER_{PM3/CO}$ which varies by 50–55 $\frac{\text{ng m}^{-3}}{\mu\text{g m}^{-3}}$ within each plume. The latter may be due to the incomplete calibration of the PM_3 measurement instrument for biomass smoke aerosol as pointed above, therefore we may suggest to use the average $ER_{PM3/CO}$ for each plume (which is about 360 ± 30 $\frac{\text{ng m}^{-3}}{\mu\text{g m}^{-3}}$ for F1 and 350 ± 32 $\frac{\text{ng m}^{-3}}{\mu\text{g m}^{-3}}$ for F2) to address this issue."

Comment: NMHC detection of OVOC. In biomass smoke a significant fraction of VOC are oxygenated-VOC (OVOC) (Akagi et al., 2011; Gilman et al., 2015). Please comment on the sensitivity of the study's NMHC detection method to OVOC, in particular the possible under-sampling of these compounds, e.g. Trabue et al., 2013.

Response. Thank you very much as you drew our attention for an interesting phenomenon. Indeed, burning of different substances (like OVOCs) in FIDs of different constructions used for NMHC detection may differ somewhat. So, the measured NMHC concentration may depend on VOC composition (and in particular on OVOC fraction)

as it was pointed out by Trabue et al. Although, our measurements of some oxygenated VOCs (acetic acid, acetone, ethanol, methanol, methacrolein, methyl-vinyl-ketone) during TROICA campaigns performed with PTR-MS (see, for example, Timkovsky et al. (2010)) showed that concentration of all these compounds are within few ppb. Concentrations of NMHC generally reach hundreds of ppb (see Table 3 and Fig. 3–4 in the manuscript) that is two orders more. The accuracy of NMHC analyzer Horiba APHA-360 is 2%, while total variability of the measurements in the analyzed fire plumes is higher. So, to our opinion, the influence of oxygenated VOCs on the NMHC analyzer readings in our case is not significant.

Changes. In the "Measurements and instrumentation" section, see the following paragraph:

"Previous studies show that a significant fraction of volatile organics in a biomass smoke are oxygenated compounds (OVOC)..."

3 Results and discussion

Comment. Please describe how the smoke plume boundaries were identified /selected. Were they selected based on PM_3 level, coincident increases in PM_3 and CO, or some other criteria?

Response. The smoke plume boundaries were selected as the segment with coincident and pronounced increases in ALL the measured compounds well correlated with each other (see P9,L4-8 in the discussion paper). Hence, high correlation of a measured specie with CO generally means high correlation with each other measured specie within the plume. Low background concentrations of the compounds before and after the plume (see Table 3 and Fig. 3–4) suggest the absence of large sources interfering with biomass burning (the exceptions are now described in the text, see response to the next comment).

Comment. How did the authors assign observations to the different plume segments? Do the plume segments, e.g. F1-1 and F1-2, correspond to different stretches of the sample path? Please clarify.

Response. Yes, they do. The different plume segments were initially selected on the basis of varying correlations between excess levels of the major biomass burning products, CO and CO_2 (see Table 6 and P9,L24-26 in the discussion paper). Please refer to the revised text.

Changes. In the "Results and discussion" section:

"Variations of the excess levels of all the measured gases and particulate matter are generally well correlated with each other within the plumes, thus supporting the notion on their common emission source. The few exceptions are discussed further."

Then, see the following paragraphs:

"Thus, Fig. 3 shows a distinct decrease in all excess mixing ratios..."

"In Fig. 4a two broad CO_2 peaks in the western F2 plume part are observed..."

"Given all of the above, one can see that the continuously changing environment of the measurements from the moving platform results in appreciable variations in excess mixing ratios and correlation between the major biomass burning products, CO and CO_2 (as well as between CO_2 and other measured compounds that are correlated with CO in this study). These variations, associated with changing surface heights in a mountainous region, as well as with non-fire emission sources as shown above, interfere with the fluctuations in the measured concentrations attributed to local forest fire emissions. To deal with the heterogeneity in the measurements conditions, we split each of the F1 and F2 plume crossing episodes into two consequent time intervals (parts, or segments, see Table 4) for further analysis according to the observed differences in excess mixing ratios and the rate of correlation between CO and CO_2."

Comment. The different plume segments need to be identified on Fig. 3–4.

Response. The suggestion is reasonable but Fig. 3–4 do already contain much information, therefore we do not like to overload them. Thus the reader may identify the different plume segments with the UTC time stamps listed in Table 4 using the X axis in Fig. 3 and 4.

Comment. P9,L9-11: Simpson et al. (2011) data show dNO2/dNOx of about 70%.

Response. Sorry, but we can not find such a value in the cited publication. Their Table 1 suggests a "plume average" of about 88% which is 100*(1228-173)/(182-40 + 1228-173) if appropriate.

Comment. P9,L13-17 and Fig. 3–4 Do the "train stops" regions highlighted at the top of the plots correspond to regions excluded from the analysis?

Response. Thanks for your attention. Please see P5, L28-29 in the discussion paper: "The measurements during extra events (oncoming trains, tunnels, populated areas along the road) according to the records in the dairy were not used in the analysis." The train stops generally occur within the populated areas therefore the corresponding data segments were excluded as suspected for anthropogenic contamination. We've added train stops into the list of excluded events in the revised text.

Changes. In the "Measurements and instrumentation" section:

"Thus, the measurements during extra events (oncoming trains, tunnels, populated areas along the road, train stops) according to the records in the diary are not used in the analysis."

Comment. P9, L15-17: Please explain how/why these criteria for identifying anthropogenic contamination were selected.

Response. The NO_X thresholds were selected to filter out short-term (several minutes long) peaks in NO_X measurements, which are most likely associated with local anthropogenic emissions, according to our experience of the analysis of TROICA measurements. The CO threshold was selected to filter out the measurements made during

the train stop at the railway station within the rural settlement (according to the records in the dairy). There is only one episode in each plume which satisfy all these criteria (about 05:30 UTC in F1 and about 02:30 UTC in F2) and we have rejected them as suspicious.

Comment. Fig. 3–4. Do the dashed background lines correspond to the plume sample period? Please clarify. Fig. 3–4 should be plotted with local time or note the offset in the caption.

Response. Yes, they do. The offset of 8 h (see Table 1) is now in the caption.

Changes. In the "Results and discussion" section:

"Time series of gas mixing ratios and particle mass concentrations measured within F1 and F2 forest fire plumes are shown in Fig. 3–4 along with the estimated background levels of the measured species plotted for the period of plume crossing."

Fig. 3–4 captions are changed.

Comment. P9, L19: I assume "500 to 800 m a.g.l." should be "500 to 800 m a.s.l." i.e. meters above sea-level. Tables 5–6 should be merged.

Response. You are certainly right. Thank you.

Comment. P10, L1-3: NO_X and BC are associated with flaming combustion and may correlate better with CO_2. Did the authors check for correlation vs. CO_2 and if so how does it compare with that vs. CO?

Response. It is reasonably to expect that. However, correlation with CO_2 is lower than with CO for ALL the measured species. That is why we choose CO as a reference specie (P6, L13-16 in the discussion paper). Thus, outliers are really outliers. The high NO_X are most likely associated with local anthropogenic emissions and therefore are excluded. Other outliers that were excluded from the analysis are also suspected for contamination by non-fire sources. We've added description of the episodes of possible

contamination by non-fire emissions within the F1 and F2 fire plumes as follows.

Changes. Thus, in the "Results and discussion" section, we remove the following lines:

"... although a limited number of outliers persist for each particular data group with the largest scattering observed for..." and till the end of paragraph.

Instead, please refer to:

"The highest concentrations in F1 and F2 events were measured during the train stops at railway stations..." and till the end of the paragraph.

"Thus, Fig. 3 shows a distinct decrease in all excess mixing ratios..." and till the end of the paragraph.

"In Fig. 4a two broad CO_2 peaks in the western F2 plume part are observed..." and till the end of the paragraph.

Comment. P10, L3-7: "The observed strong scattering of some data subsets is clearly attributable to highly complex measurement environment and the supposed strong spatial heterogeneity of the emission sources contributed to the smoke plumes. Consequently, we exclude from the analyzes the measurements producing extremely high or low dY/dX values to make our final estimates more robust with respect to various disturbing factors."

This is not an appropriate manner to handle the data. One cannot simply toss data points because they introduce scatter and reduce the correlation coefficient and increase the uncertainty of the slope in the assumed relationship. The authors should have an objective criteria for identifying data segments that are treated as the biomass smoke plume. Rejection of observations taken within the biomass plume should only be rejected using a clear, objective criteria that is based on sound reasoning – e.g. a significant influence of a local anthropogenic, instrument malfunction, or failed calibration.

Also, it is unclear what is meant by: ". . .more robust with respect to various disturbing factors"

Response. You are certainly right. To our experience, a significant influence of local (anthropogenic or biogenic) emissions is the main cause of short-term (up to several minutes long) fluctuations in the analyzed data sets because the events related to an instrument failure or calibration are recorded in the dairy and filtered out first at a data quality control stage. Thus the dY/dX criteria is just a technical approach to filter out fluctuations caused by non-fire sources using programmable scripts. Thus "various disturbing factors" means various local non-fire sources.

Changes. See the changes related to the previous comment.

Comment. P10, L8-16: I suspect a portion of the plume F2-2 was influenced by a biogenic CO_2 source. Examination of Fig 6d and Fig 4a leads me to believe that F2-2 corresponds to the second portion of the plume around 3:30 to 5:30 UTC, which exhibits to broad peaks in CO_2 between 4:00 and 5:30 UTC for which there is not coinciding response in the CO. Additionally, the NO_X does not show not increase during these broad CO_2 peaks (Figure 4c). Since NO_X is associated with flaming combustion one would expect it to correlate with CO_2. Since it does not, this is further evidence that the CO_2 mixing ratio sampled during this plume stretch is noticeably influenced by a non-fire source. Also, the $\Delta NO_X/\Delta CO$ ratio for F2-1 and F2-2 are the same within uncertainties (2.8 ± 0.2 versus 3.1 ± 0.4). If the source of plume segments F2-1 and F2-2 was really a fires with MCE of 0.91 and 0.97, respectively, one would expect a difference in $\Delta NO_X/\Delta CO$. I strongly disagree with the authors' interpretation of Figure 7b. It appears that dBC/dPM3 are very similar for F2-1 and F2-2. What are the plume segment average values for these ratios? I find it difficult to believe they are significantly different. In fact, I interpret Fig 7b as evidence that segments F2-1 and F2-2 originated from fires with very similar MCE. The authors should consider the CO_2 during this stretch to be highly suspect and not report $\Delta CO/\Delta CO_2$ or MCE for this segment.

Response. Thank you for this suggestion. The F2-2 indeed corresponds to the second portion of the F2 plume (F2-2, 03:40–5:20 UTC, see Table 4). The plume segment MEDIAN values (based on 5 min concentrations) for dBC/dPM are about 2.6% for both F2-1 and F2-2 but the scattering is strong. Thus we remove Fig. 7 and its discussion from the manuscript. We also do not report dCO/dCO2 and MCE for F2-2 following your recommendation.

We've also reconsidered the whole F2-2 part of the data and clarified the discussion of the variability in the measurements. According to the dairy records, during 04:00–04:20 UTC and 05:00-05:10 UTC, when the CO_2 peaks were observed and not correlated with CO, the train passed through a town and a rural settlement, respectively. Such the passage in not always associated with elevated measured concentrations, but it seems to be the case for the considered event. Thus we suggest a contribution from anthropogenic emissions into the measurements of CO_2, CH_4, NMHC, and NO_X within the F2-2 plume part. For details, please refer to the paragraph in the revised manuscript cited below.

Changes. In the "Resulst and discussion" section:

Fig. 7 with scatter plots of BC vs. NOx and MCE vs. dBC/dPM3 and its discussion are deleted. Instead, a paragraph is added:

"In Fig. 4a two broad CO_2 peaks in the western F2 plume part are observed..." and till the end of the paragraph.

Comment. P10, L32–P11, L2: Based on my comments, I do not believe F2-2 should be considered flaming. I would limit comparison to F1-2 and F2-1, since these have valid MCE.

Response. We agree and revised discussion following your recommendations (see the response to the previous comment).

Comment. P11, L14-16: The authors have not demonstrated the sampled plumes are

likely less than 1 day old (see general comments).

Response. Now refer to the revised "Resulsts and discussion" section:

"Atmospheric NO_X is also prone to higher variability compared to..." and till the end of paragraph. Please also see the response to the general comment related to plume age.

Comment. P13, Ln 27-29: I believe these were not included in Akagi et al. (2011) as they did not measure "fresh smoke" samples or the smoke age was uncertain.

Yes, it is true for the studies of Kondo et al. (2011) and Warneke et al. (2009). Meanwhile, Paris et al. (2009) reports the measurements in two Siberian plumes of 1 day old (on the basis of FLEXPART model estimates). Pirjola et al. (2015) reports the measurements of fresh emissions from an experimental fire but this study certainly could not be considered by Akagi et al. (2015) just because of the date of publication. Anyway, as far as we removed the discussion of most of the estimates from the lower left part of the plot in Fig. 7d (of the revised manuscript) following your recommendations, the following lines are abundant and we remove them as well: "The "flaming" $ER_{CO/CO2} = 2.8 \pm 0.6\%$ from the present study falls within the range of low values $ER_{CO/CO2} = 1.5 - 6\%$ in Fig. 7d. The latter corresponds to the most recent works (Paris et al, 2009; Warneke et al., 2009; Kondo et al., 2011; Pirjola et al., 2015) that apparently were not included in the compilation of Akagi et al. (2011)."

Comment. P16, Ln32-33 While the authors report the train operator observed some fire activity, they are clear in stating that the plumes sampled likely resulted from multiple fires, all of which were not observed. Therefore, the authors cannot relate their measured MCE to any specific observed combustion type. I agree that visual observations of fire behaviour tend to be a poor metric for classifying combustion type and MCE, especially since both flaming and smoldering typically occur simultaneously for naturally burning forest fires. However, given that EF for many species are correlated with MCE, it does have utility for extrapolating measured EF to other fire types with

different MCE regimes.

Response. As we understand, you reason that if visual observations of fire state do not agree with MCE – the problem is with visual observations but not with MCE. We agree. Although, visual classification of combustion regimes seems to be usual in studies that use experimental fires. We'd like to point that such the classification may give confusing results (for example, see P12, L1-4 and P12, L7-11 in the discussion paper). Therefore we have revised this part of the "Conclusions" section as follows.

Changes. In the "Conclusions" section:

"The authors did not find any definite relation between the visually observed combustion type (smoldering or flaming) and MCE values neither in this study, mainly because of the lack of detailed information on fire state, nor in the previous studies where emissions from experimental fires were attributed to flaming or smoldering combustion on the basis of visual inspections (Cofer et al., 1998; Pirjola et al., 2015). Thus, we are cautious in using visual observations to attribute fire emissions to a specific combustion type since both flaming and smoldering typically occur simultaneously for naturally burning forest fires."

4 Comparison with other published results

Comment. The discussion and figures are a bit confusing. The authors seem to include studies where the plumes sampled were older than 1 day and therefore are not emission ratios and not appropriate for comparison with the current work. I strongly recommend the authors limit the comparison to studies where the plume samples were <= 1 day old and result from boreal fires.

Response and Changes. This also seems reasonably. Although, there are only three publications (known to the authors of the present study) that report both BC and CO

emissions for boreal fires. Therefore, we cite them all, with a warning about differences in plume age. And in Fig. 9b in the discussion paper, there is no clear relation between the plume age and $ER_{BC/CO}$, with ER from Paris et al. (2009) for plume of 1 day old being close ERs from Kondo et al. (2011) and Warneke et al. (2009) for boreal fire plumes of several days old. Following your recommendation, we remove discussion of $ER_{CO/CO2}$ from Kondo et al. (2011) and Warneke et al. (2009) but we'd like to keep the $ER_{BC/CO}$ from these publications.

Comment. NMHC comparison and Figure 8b: The NMHC EF based on Laursen et al. (1992) and Urbanski et al. (2009) are the sum of only a handful of compounds and not comprehensive VOC measurement like that constructed in the current study. This should be clarified in the text.

Response and Changes. We agree. Although it does not decrease the value of the data for the comparison. See in the revised text: "Thus, Laursen et al. (1992) and Urbanski et al. (2009) report the measurements of a very limited number of individual NMHC compounds which can not be directly compared to the comprehensive NMHC measurements employed in the present study but are shown in Fig. 7b because of the deficit of NMHC observations in boreal forest fire plumes."

5 Technical Corrections

Comments. The authors should define chemical formulas when first introduced. P1, L16: Insert "the" between (btw) "and" and "boreal"

P1, L16: change "became" to "become"

P1, L18: insert "the" btw "including" and "global"

P2, L3: Insert "the" btw "In" and "future"

P2, L14: Change “OH-” to “OH” it’s a radical not an ion. No charge.

P2, L17: change “is” to “are”

P2, L19: change “on the basis” to “by”

P2, L21: delete “,Canada, and Alaska as a ....”

P3, L1: insert “of’ btw “all” and “these”

P3, L17: change “substantia amount” to “many”

P3, L32: insert “that” before “originated”.

There are many similar errors in English usage throughout the remainder of the manuscript that need correction.

Response. Done, thanks.

Comment. Figure 3a – The CO and CO2 background lines have wrong colors

Response. Thanks for your attention. It should be ok now.

Comment. Table 6 change “PM1” to “PM3”

Response. Table 6 is merged with Table 5 according to your recommendation.

Comment. Fig. 8–9: The plotted symbols do not all match the legend, Vasileva et al., 2017 and Pirjola et al., 2015 are different.

Response and Changes. We removed the results of Kondo et al. (2011) and Warneke et al. (2009) from Fig. 7 of the revised manuscript following you suggestion. The legend and symbols in Fig. 7 and Fig. 8 are rearranged. Although, note that ig. 7 and Fig. 8 have independent legends, and the symbols are used independently.

References

Timkovsky, I. I. and Elanskii, N. F. and Skorokhod, A. I. and Shumskii, R. A., Studying of biogenic volatile organic compounds in the atmosphere over Russia, Izv. AN Fiz. Atmos. Ok+, 2010, 46, 3, 319–327, doi=10.1134/S0001433810030059