

# ***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.**

## **Anonymous Referee #2**

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Review of acp-2017-362

Emission ratios of trace gases and particles for Siberian forest fires on the basis of mobile ground observations

## General Comments

This paper reports emission ratios for Siberian forest fires measured from a mobile ground based platform. The measurements were obtained from a laboratory car on an electric powered train travelling the Trans-Siberian Railway in October 2005 and August 2007. In each year the train passed through smoke plumes from nearby forest fires. Each smoke plume crossing event was  $\sim 200$  km in length and  $\sim 4$  hours in

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duration. Instrumentation on the lab car measured CO<sub>2</sub>, CO, CH<sub>4</sub>, NMHC, NO, NO<sub>2</sub>, PM<sub>3</sub>, and BC. The study provides emission ratios which are an important addition to the limited body of knowledge regarding emissions from boreal forest fires in northern Eurasia. Given the global importance of northern Eurasia as a source of biomass burning emissions and sensitivity the sensitivity of the region to climate and associated likelihood of increased fire in the future, this study presents a potentially important contribution to the biomass burning science literature. However, besides several specific comments, I have found three issues that must be addressed prior to publication:

### 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 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.

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  $dX = dX_{\text{plume}} - dX_{\text{background}}$ . The normalized excess mixing ratio (NEMR) is  $dX/dY$ , where Y is a long-lived reference species co-emitted with X, CO or CO<sub>2</sub>, 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.

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.

#### Specific Comments

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.

#### 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?

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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.

Results and discussion Please describe how the smoke plume boundaries were identified /selected. Were they selected based on PM<sub>3</sub> level, coincident increases in PM<sub>3</sub> and CO, or some other criteria?

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. The different plume segments need to be identified on Figures 3 & 4.

P9, L9-11: Simpson et al. (2011) data show dNO<sub>2</sub>/dNO<sub>x</sub> ~70%.

P9, L13-17 and Figs. 3 & 4 Do the “train stops” regions highlighted at the top of the plots correspond to regions excluded from the analysis?

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

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

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.

P10, L1-3: NO<sub>x</sub> and BC are associated with flaming combustion and may correlate better with CO<sub>2</sub>. Did the authors check for correlation vs. CO<sub>2</sub> and if so how does it compare with that vs. CO?

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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”

P10, L8-16: I suspect a portion of the plume F2-2 was influenced by a biogenic CO<sub>2</sub> 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 broad peaks in CO<sub>2</sub> between 4:00 and 5:30 UTC for which there is not coinciding response in the CO. Additionally, the NO<sub>x</sub> does not show not increase during these broad CO<sub>2</sub> peaks (Figure 4c). Since NO<sub>x</sub> is associated with flaming combustion one would expect it to correlate with CO<sub>2</sub>. Since it does not, this is further evidence that the CO<sub>2</sub> mixing ratio sampled during this plume stretch is noticeably influenced by a non-fire source. Also, the dNO<sub>x</sub>/dCO ratio for F2-1 and F2-2 are the same within uncertainties ( $2.8 \pm 0.2$  versus  $3.1 \pm 0.4$ ). 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 dNO<sub>x</sub>/dCO. I strongly disagree with the authors’ interpretation of Figure 7b. It appears

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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 CO2 during this stretch to be highly suspect and not report dCO/dCO2 or MCE for this segment.

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.

P11, L14-16: The authors have not demonstrated the sampled plumes are likely less than 1 day old (see general comments).

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.

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 behavior 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.

Comparison with other published results 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  $\leq 1$  day old and result from boreal fires.

NMHC comparison and Figure 8b: The NMHC EF based on Laursen et al. (1992) and

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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.

Technical Corrections 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.

Figure 3a – The CO and CO<sub>2</sub> background lines have wrong colors

Table 6 change “PM<sub>1</sub>” to “PM<sub>3</sub>”

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

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