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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 1 for a favourable attention to the manuscript as well as for useful comments which helped us to improve presentation of the results.

1 Primary comments

Comment. 1) A serious problem is that there is insufficient information about the uncertainties of the measurements – especially the aerosol and black carbon mea-

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Discussion paper

surements. Essentially all background information about instruments and measurement uncertainty are only referenced via citations, and the citations are insufficient to demonstrate the level of control over the measurements necessary to provide convincing evidence of its value (both because they are hard to find, and because the ones I found did not have enough information). a. For example, Kopeikin 2008 was cited for the GRIMM PM measurements. The entirety of its discussion was: “The nephelometer “Dust Indicator and Tunnel System” designed by GRIMM Corporation (Germany) with the concentration measurement range from 0.01 to 15 $\mathrm{mg\ m^{-3}}$ was used in expeditions in 2004-2007.” Then there is some discussion of a different system (with limited calibration information) for different missions that are not relevant here. This is entirely inadequate. For BC, I was not able to get the corresponding Kopeikin paper via interlibrary-loan, but I saw that it did not contain any references that were relevant to major corrections and uncertainties typically applied and associated with Aethalometer measurements. The current ACPD paper: Comparison of different Aethalometer correction schemes and a reference multi-wavelength absorption technique for ambient aerosol data, by Jorge Saturno et al., gives a good introduction to these issues, which must be dealt with before the data can be considered final.

Response. We have essentially expanded the "Measurements ans instrumentation" section to address your comment. Here we may add that natural variability of wildfire emissions is significant and cause variability in the measured concentrations (see Fig. 3–4) that is much higher than potential instrument errors. Anyway, the high correlations between ΔPM_3 and ΔCO reported in the study suggest that we should not expect significant errors due to the PM3 measurements technique in the estimated fire plume $\Delta PM_3/\Delta CO$ ratios. Yes, a sort of a systematic bias in the PM3 vs. CO scatter plots seen in Fig. 5e and Fig. 6e may be caused by either the lack of calibration or by natural variations of the emissions as well. Therefore, we suggest using the plume average $ER_{PM3/CO}$ in the revised manuscript to compensate this potential issue. Same is true for the BC measurements. As we can see from the relevant papers, the corrections of BC measurements by multi-wave method, as well as the correction of

nephelometer calibration with respect to particle size distribution, chemical composition and morphology in biomass smoke may be within several percents that is considerably lower than variability of the measurements caused by natural factors (changies in intensity of burning, flaming vs. smoldering combustion, dilution during dispersion in the atmosphere) that are addressed during the analysis. Note also the relatively low temporal resolution (5 min) of the BC measurements contributing to high (20%) uncertainties in the $ER_{BC/CO}$ estimates as well. To our opinion, the principal value of the TROICA measurements is their transcontinental extent and uniqueness because the TROICA routes covered the regions for which very little observational data is available today. This somewhat compensates the fact that the TROICA's measurements may be not as precise as the up-to-date ones.

Changes. The "Measurements ans instrumentation" is essentially expanded to provide information on the measurements instrument calibration. See also 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. 2) The focus of the paper is on coarsely segregated averages of the two plumes measured, with variability within each section treated more as a "uncertainty

source" than as an important feature in its own right. I suggest that the authors attempt to share more information about the variability, perhaps merely via slightly increased discussion, and highlight that component of the results as valuable in their own right to expand the value of these within the whole. In this vein, I wonder if Figures 3 and 4 could be made more useful by showing the ratios, in addition or instead of the simple concentrations.

Response. Thank you for this very important comment. Although the physical causes (including natural variability) of uncertainty for each ER estimate are considered in the manuscript, the topic needs additional discussion. Thus we've extended the discussion of the variability and revised the interpretation: indeed, variability of gas ERs within the plumes is small (the exceptions are discussed), while variability between the plumes is noticeable. We've also revised the interpretation of variations in the estimated ERs with respect to the source-receptor relationships for the F1 and F2 plumes (to address the Referee 2 comments) and concluded that the effect of physical and chemical transformations related to plume ageing on the ER variability was not significant. For details please refer to the changes in the manuscript listed below.

We have also considered showing the time series of emission ratios in Fig. 3-4 but addition of new lines makes plots difficult to read. At the same time, we'd really like to show the original measurements data and the observed magnitudes of real concentrations, because it is the base for all the research. Therefore, we have decided to show the original data in Fig.3-4, and the scattering of the emission ratios in Fig. 5-6. We would leave Fig. 3-4 as they are, if you don't mind.

Changes. Additional potential causes of the variability (uncertainty) in individual ERs are pointed at the end of the corresponding paragraphs in "Results and Discussion" section. We've also added three paragraphs at the end of the "Results and Discussion" section with an additional discussion of the ER variability within and between different plume segments, as well as between different plumes:

"In the following paragraphs we summarize the uncertainty and variability in the ER estimates reported in Table 5. In the individual ER estimates the ranges of relative variations..."

"The variability of the reported ER_{avg} between different plume segments within each plume generally does not exceed the variability..."

"We note finally, that the variability of ERs between F1 and F2 plumes is more pronounced than within each plume..."

See also:

"Herewith the term "uncertainty" means the precision of a model estimate as well as natural variability of the estimated quantity, because both these meanings are closely related in the present study."

In the "Conclusions" section see the following paragraphs:

"Between the plumes, the estimated gas ERs vary appreciably due to..."

"The uncertainties in the ER estimates are associated mainly with..."

Also see:

"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."

Comment. 3) The connection between the observations of fire state by the scientist on the train, and the actual (mixed) state of the fires at the positions and times actually sourcing the pollution sampled is extremely weak. I did not understand how the line-of-sight of the observer were relevant to large and wide-spread fires. Hence, unless this can be strengthened, I suggest removing the conclusions about lack of connection between flame state and MCE.

Response. The remark is rather true for the present study, although the source-receptor relationships were revised in the manuscript following the critical comments of the Referee2. Anyway, the authors cite previous publications where atypical combination of MCE and visual observations were reported (see page 12, lines 17-24 of the discussed non-revised manuscript) and yield confusing results with high MCE attributed to smoldering (Pirjola et al., 2015) and low MCE attributed to flaming (Cofer et al., 1998). To clarify this issue, we have changed this pat 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."

See also the revised source-receptor relationships in the "Plume crossing episodes" section (discussion of Fig. 1–2) which has been substantially changed following critical comments of the Referee 2. In the "Results and discussion" section, see the TWO paragraphs starting at "Beyond the data segments corresponding to the train stops described above, peak excess levels within both the plumes were observed near the locations of active fires detected exactly in the day of the plume observation directly close to the railway..."

Comment. 4) I did not understand the rationale to omit the CO2 data from a large segment of the F1 plume. How do the authors know that this is not some variability from the fire? Why would CO_2 be differently mixed than other trace gases?

Response. We suspect contribution from a non-fire CO_2 emissions during 02:50–04:35 UTC in F1 plume and 03:40–05:20 UTC in F2 plume, with the latter suggested by the Referee 2. Therefore we do not report $ER_{CO/CO2}$ and MCE for those plume parts (F1-1 and F2-2). Please see details in the revised manuscript.

Changes. Two paragraphs are added into the "Results and discussion" section to describe episodes of possible contamination by non-fire emissions within the plumes:

"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..."

2 Secondary comments

Comment. 1) The work of the authors in analyzing the relationships between different species using different fitting techniques was welcome to see. However, the results (and supporting literature) support the idea that the orthogonal distance regression is both the most appropriate approach, and pretty much represented the mean between the other two linear regressions. Once this was clear, I thought the paper might benefit from this discussion being moved to supplemental material, and the graphs simplified by omission of the two simple linear regression lines. After all, this is not the main thrust of the paper.

Response. Thank you for an interesting suggestion. However, we can not say that the orthogonal distance regression (ORD) method is the most appropriate (see P7, L22–25 in the discussion manuscript). If you look at Fig. 5-6 you'll see that the ODR line also does not lay between the other two regression lines in the most controversial cases (Fig. 6a,c,e,f, Fig. 5f). Further research of this topic refers to the study of mathematical methods which is interesting but falls beyond the scope of the discussed manuscript. Hence we had to keep the three lines at the graphs to enable the skeptical readers to

visually assess the representativeness of the average ERs listed in Table 5.

Comment. 2) The authors present PM/CO correlations in units of $(\text{ng m}^{-3})/(\mu\text{g m}^{-3})$ "for easy comparison to other studies". However, this makes it difficult to compare the other ERs and PM_3 to CO correlations, and makes PM_3/CO a "odd man out". Perhaps it is clearer to leave PM_3/CO in ng m^{-3} ppm^{-1}, and adjust the other studies.

Response. It is reasonable to do that, but the PM_3 emissions in the cited studies are expressed as emission factors (g kg^{-1}), thus calculation of $ER_{PM3/CO}$ in units of ng m^{-3} ppm^{-1} requires information about atmospheric pressure and temperature which was not available in all the cited studies and therefore introduces additional uncertainty. In our study, the $ER_{PM3/CO}$ in units of ng m^{-3} ppm^{-1} seemed to depend on the changing altitude in the F1 plume, therefore we chose the unit of $(\text{ng m}^{-3})/(\mu\text{g m}^{-3})$ as the more robust one.

Comment. 3) In figures 8 and 9 I suggest referring to the new analysis as "this work" rather than Vasileva et al., 2017.

Response. Thanks. Done.

Comment. 4) The paper is clear and well written, but has numerous small English errors (mostly missing "the"s or extra "thes". Here are some examples:

a. Page 2 line 3: "in THE future"

b. Line 13: "alter the OXIDATIVE capacity"

c. Line 14: "and disturb THE background chem"

d. Line 27: "... can SERIOUSLY DETERIORATE the .. "

e. Line 28: "... and contribute to Arctic haze" ("the" should be left out)."

These, and others, should be corrected.

Response. Many thanks for your attention. We have tried to do our best.