Response to Referee 1

Anastasia Vasileva et al.

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The authors thank the Referee 1 for a favorable 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 measurements. 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 inter-library-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 (changes 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 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ 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 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ within each plume. The latter may be due to the incomplete calibration of the $\mathrm{PM_3}$ 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 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ for F1 and 350 ± 32 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ 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 aging 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 $(\mathrm{ng\,m^{-3}})/(\mu\mathrm{g\,m^{-3}})$ "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 $\mathrm{ng\,m^{-3}\,ppm^{-1}}$, 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 ($\mathrm{g\,kg^{-1}}$), thus calculation of $ER_{PM3/CO}$ in units of $\mathrm{ng\,m^{-3}\,ppm^{-1}}$ 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 $\mathrm{ng\,m^{-3}\,ppm^{-1}}$ seemed to depend on the changing altitude in the F1 plume, therefore we chose the unit of $(\mathrm{ng\,m^{-3}})/(\mu\mathrm{g\,m^{-3}})$ 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.

Response to Referee 2

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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 $\mathrm{m\,a.g.l.}$ at geographical locations along the railway with 1 h time intervals covering the total time duration of the plume crossing events. The trajectories are color 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, acompanied 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 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ 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 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ 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 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ for F1 and 350 ± 32 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ 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 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.

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

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

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Abstract. Boreal forest fires are currently recognized as a significant factor in climate change and air quality problems. Although emissions of biomass burning products are widely measured in many regions, there is still [..[1]]lack of information [..[2]]on composition of wildfire emissions in Siberia, the region known for its severe wildfire activity. Emission ratios (ERs) are important characteristics of wildfire emissions as they may be used [..[3]]to calculate mass of species emitted into the atmosphere due to combustion of [..[4]]known mass of biomass fuel. We [..[5]]analyze observations of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), total nonmethane hydrocarbons (NMHC), [..[6]]nitrogen oxides NO_X (=$NO + NO_2$), particulate matter (PM_3) and black carbon (BC) within two forest fire plume transects made by the moving railway observatory during TRanscontinental Observations Into the Chemistry of the Atmosphere (TROICA) expeditions. Slopes in linear regressions of excess levels of pollutants are used to obtain [..[7]]$ER_{CO/CO_2} = 10 - 15\%$, $ER_{CH_4/CO} = 8 - 10\%$, $ER_{NMHC/CO} = 0.11 - 0.21\%$ ppmC ppmC^{-1}, $ER_{NO_X/CO} = 1.5 - 3.0$ ppb ppm^{-1}, $ER_{PM_3/CO} = 320 - 385$ $\frac{\text{ng m}^{-3}}{\mu\text{g m}^{-3}}$, and $ER_{BC/CO} = 6.1 - 6.3$ µg m^{-3} ppm^{-1} which fall within the range of uncertainty of the previous estimates, being at the higher edge for $ER_{CH_4/CO}$, $ER_{NMHC/CO}$, and $ER_{PM_3/CO}$ and at the lower edge for $ER_{NO_X/CO}$. The [..[8]]relative uncertainties comprise 5–15% of the estimated $ER_{CH_4/CO}$, $ER_{NMHC/CO}$, and $ER_{PM_3/CO}$ and 10–20% of $ER_{NO_X/CO}$, ER_{CO/CO_2}, and $ER_{BC/CO}$[..[9]]. The uncertainties are lower than in many other similar studies and associated mainly with natural variability of wildfire emissions.

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1 Introduction

Boreal forests and the boreal climate zone, located within approximately $50-70°$N, have [..[10]]become an object of increasing attention in recent decades. A unique feature of boreal regions is their high sensitivity to global climate changes and ability to provide global climate feedbacks through a variety of mechanisms (Screen and Simmonds, 2010) including the global carbon cycle (Kasischke, 2000; Zimov et al., 2006; Schuur et al., 2008; McGuire et al., 2009). Indeed, current estimates suggest 10–17% of global carbon is stored in vegetation and soil [..[11]]in boreal forests of which two thirds are located on the territory of Russia (Tchebakova et al., 1994; Shvidenko and Nilsson, 2003). Under predicted climate change scenarios, this terrestrial carbon may be released into the atmosphere [..[12]]as gases (mainly CO_2, CO, and CH_4) and particulate matter through different ways [..[13]]including forest fires. Rapid release of large stocks of carbon into the atmosphere by biomass burning occurs during immediate combustion of organic matter as well as by exposing the remaining carbon stocks in the soil to substantial warming and decomposition for years after the fire event (Balshi et al., 2007; Goetz et al., 2007; Myers-Smith et al., 2007; Randerson et al., 2006; McGuire et al., 2009).

In [..[14]]the future, frequency, severity, and spread of boreal fires may increase in response to climate changes resulting in [..[15]]concomitant increase in atmospheric concentrations of biomass burning products (Kasischke et al., 1999; Kasischke and Turetsky, 2006; Soja et al., 2007; Marlon et al., 2008; Amiro et al., 2009). Such a response is now recognized for the wildfires in north Eurasia (mostly in Siberia) which are considered [..[16]]to be a significant extra-tropical source and major driving factor of the variability of climatically important atmospheric species in the northern hemisphere (Lavoué et al., 2000; Kasischke et al., 2005; Yurganov et al., 2005; Simpson et al., 2006; Wotawa et al., 2001).

[..[17]]During severe fire seasons[..[18]], forest fires significantly affect regional air quality, decreasing visibility and causing respiratory problems (see for example Popovicheva et al. (2014) and references therein)[..[19]], and make appreciable contribution into the regional air pollution (Cheng et al., 1998; Wotawa and Trainer, 2000). In remote regions of Siberia, emissions (local or transported) from boreal forest fires [..[20]]can also be an important seasonal source of reactive species in the lower atmosphere (Vasileva et al., 2011; Chi et al., 2013). As an example, excess in CO and NO_X may alter the atmospheric [..[21]]oxidation capacity via chains of chemical reactions with [..[22]]OH radicals (Seinfeld and Pandis, 1997; Stockwell et al.,

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2012) and significantly perturb the background chemistry in the atmosphere (Jaffe et al., 1996; Tanimoto et al., 2000, 2002; Val Martín et al., 2006; Singh et al., 2010).

Rapid transport of combustion products in large scale circulation systems occurs when a significant portion of the products [..[23]]are injected into the free troposphere up to several kilometers or, occasionally, into the lower stratosphere (Fromm et al., 2000; Fromm and Servranckx, 2003; Val Martín et al., 2010). In these cases, smoke plumes from north Eurasia are frequently traced thousands of kilometers downwind over the continent [..[24]]by satellite and aircraft observations (Cahoon et al., 1994; Hsu et al., 1996; Spichtinger et al., 2001; Paris et al., 2009) and may be associated with elevated concentrations of CO_2, CO, NO_X, O_3, and aerosol over North America [..[25]](Bertschi et al., 2004; Bertschi and Jaffe, 2005; Jaffe et al., 2004; Warneke et al., 2009; Singh et al., 2010; Kondo et al., 2011). There is also an evidence of formation of toxic pollutants such as ozone and aerosols in boreal forest fire plumes, although the rate of formation [..[26]]varies broadly with dispersion conditions and original composition of the exhausts (Honrath et al., 2004; Jacob et al., 2010; Bossioli et al., 2012; Jaffe and Wigder, 2012; Alvarado and Prinn, 2009; Arnold et al., 2015).

Atmospheric aerosol particles from biomass fires in Russia can seriously deteriorate the air quality in Europe under suitable meteorological conditions (Saarikoski et al., 2007) and contribute to [..[27]]Arctic Haze events (Stohl, 2006; Stohl et al., 2007; Cubison et al., 2008; Warneke et al., 2009, 2010) changing the radiation budget of the earth surface and the atmosphere in the northern hemisphere high latitudes (Quinn et al., 2007, 2008; Flanner, 2013; Olsen et al., 2015). Particularly, deposition of black carbon on snow and sea ice surfaces decreases their albedo and thereby [..[28]]can have an important effect on the energy exchange in the Arctic (Hansen and Nazarenko, 2004; Kim et al., 2005). According to Generoso et al. (2007), Russian biomass fires in [..[29]]the extreme fire year 2003 contributed about 40–56% of the total BC mass deposited north of 75°N.

The ability of aerosol particles to act as a cloud condensation nuclei causes modifications of the microphysical and optical properties of clouds [..[30]]thus changing the cloud lifetimes and precipitation patterns (see references in Langmann et al. (2009)).

In all [..[31]]of the above mentioned problems accurate estimation of the amount of carbon released from biomass fires into the atmosphere in the form of gases and particles is important and requires knowledge about emission factors (mass of a [..[32]]chemical compound emitted per unit mass of fuel burned) or emission ratios (amount of [..[33]]compounds emitted divided by that of a reference compound) (Wiedinmyer et al., 2006; Soja et al., 2004; van der Werf et al., 2010; Urbanski et al., 2011). In the present study, we provide estimates [..[34]]on the emission ratios (ERs) which may be converted, when necessary,

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into emission factors (EFs) using either the carbon mass balance method (Ward et al., 1991; Laursen et al., 1992) or linear correlations between ERs and EFs (Friedli et al., 2001). Such a conversion, however, introduces additional uncertainties, so we focus on the [..[35]]estimates of ERs.

Despite the growing scientific attention to [..[36]]wildfires in the boreal zone, data from direct [..[37]]measurements of biomass combustion products in Siberian ecosystems is still very limited (Cofer et al., 1998; McRae et al., 2006; Paris et al., 2009). [..[38]]In present study we employ the unique ground-based measurements from TROICA-9 (4–18 October 2005) and TROICA-11 (22 July – 5 August 2007) expeditions along the Trans-Siberian Railway with use of a mobile railway carriage observatory (Elansky et al., 2009). The lab carriage was attached to a passenger train just behind the electric locomotive and equipped with an integrated [..[39]]observation system composed of a large number of precision instruments measuring trace gases, aerosol particles, and meteorological parameters. Each measurement campaign lasted for two weeks, with the train travelling [..[40]]a 10 000 km midlatitude transect of the country, from Moscow to Vladivostok (east route) and from Vladivostok to Moscow (west route). The complex measurements of chemical composition of the near-surface air in [..[41]]the TROICA expeditions were used [..[42]]in many previous studies (see for example (Kuokka et al., 2007; Vartiainen et al., 2007; Berezina et al., 2014)) as they provide [..[43]]the unique insight into the spatial distribution of various [..[44]]air pollutants and allow to distinguish between different anthropogenic and natural air pollution sources in various geographical regions of north Eurasia.

2 Plume crossing episodes

A summary of the two forest fire plumes observed during TROICA-9 and TROICA-11 campaigns (hereinafter referred to as F1 and F2 events or plumes, respectively) is given in Table 1. 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. [..[45]]Due to dry weather conditions during winter, fire season in the region [..[46]]usually starts early in spring [..[47]]and can last from April to October (Giglio et al., 2013; Randerson et al., 2012; Sukhinin et al., 2004; Vivchar et al., 2010). The latitudes of [..[48]]observations

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[48] removed: observation (51–53°

(51 − 53°N) approximately correspond to the southern border of the boreal forest zone. During the plume crossing [..[49]]events the train route passed through [..[50]]low mountain ridges with relative heights up to 400 m. The region of F1 observation is classified as taiga woodlands with *Larix gmelinii* and *Betula fruticosa* which grow in south-east Siberia, while F2 plume was observed in taiga forest steppe with *Larix gmelinii*, *Larix sibirica*, and *Pinus sylvestris* which [..[51]]grow widely in the midlatitudes of Eurasia (Klochko and Romanovskaya, 2004).

[..[52]]Each of the F1 and F2 plume crossing events [..[53]]is about 200 km long. [..[54]]The train routes in the region of plume observations are shown in Fig. [..[55]]1–2 along with the locations of active fires detected by MODIS Terra and Aqua satellites (the MOD14A1 and [..[56]]

[..[57]]MYD14A1, collection 6, data was downloaded through NASA search engine https://search.earthdata.nasa.gov/) on the day of the plume observation and as long as two days before. The size of the circles indicating fire spots is proportional to fire radiative power (FRP, taken from the MODIS data) while the fill color shows the day of fire detection. Possible origins of the air sampled within the plumes are shown in Fig. [..[58]]1–2 with HYSPLIT model (Hybrid Single Particle Lagrangian Integrated Trajectory archive data, available at http://ready.arl.noaa.gov/HYSPLIT.php) three-day backward three-dimensional Lagrangian air parcel trajectories started from [..[59]]50 m a.g.l. at geographical locations of the train along the railway [..[60]]every hour during the time period of each plume crossing event (Stein et al., 2015; Rolph, 2017). For each particular location, ensembles of trajectories were calculated for a range of heights and horizontal shifts relative to the location [..[61]]to assess a combined impact of various uncertainties on backward trajectory calculations (Stohl, 1998). Since all the trajectories in each ensemble follow a similar air transport pattern, we show in Fig. 1–2 only the trajectories arriving at 50 m height and at the exact geographical locations of the train. The trajectories are color coded in gray scale according to the transport time, with the time stamps along the trajectories shown with black circles at 12 h intervals. The train moved from West to East (Fig. 1) and from East to West (Fig. 2) in F1 and F2 events, respectively. In Fig. 1 and 2 one can see active fires burning very close (in 0–12 h of air transport) to the railway within the plume transects (F1 and F2

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[55] removed: 1 suggest that during the time of each plume observation (about 4 h), the train has passed through partially mixed plumes originated from several nearby fires.According to the visual observations made by operator during each of the F1 and F2 plume crossings, a smoldering ground fire with abundance of smoke and sporadic splashes of flame was seen at a forested hill at distance of 500–1500 m from the railway. As it is difficult to estimate contributions from these particular fires into the measurements, we assume that the observed F1

[56] removed: F2 plumes represent mixtures of emissions from several adjacent fires of the type similar to that observed by the operator.

[57] removed: Train courses through the regions of plume observations are shown in Fig. 2, superimposed onto the map of total wildfire emissions of carbon monoxide (CO) according to the GFED4.1s (Global Fire Emissions Database, version 4.1s) model (Randerson et al., 2012; Giglio et al., 2013; van der Werf et al., 2010; Andreae and Merlet, 2001; Akagi et al., 2011) for September–October 2005 for F1 (Fig. 2a) and July–August 2007 for F2 (Fig. 2b)

[58] removed: 2 with ensembles of HYSPLIT model five-day

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[61] removed: (this results in 27 ensemble members for all possible shifts)

events) as well as in more distant (more than 24 h) locations (F2 event, eastern part). Most of the fires affecting the measurements were started no longer than a day before the plume crossing event (although the corresponding fire spot circles are mostly overlapped by the circles on the next day).

Calculation of ERs in the F1 and F2 events requires correct assessment of atmospheric background concentrations of the analyzed species which are used commonly as reference levels in the regression [..[62]]analysis of the measurement data [..[63]][..[64]][..[65]][..[66]]and quantify inputs from various distant emission sources, both natural (including wildfires) and anthropogenic. Such the [..[67]]inputs may be important in F2 event because of more intense wildfire activity compared to the F1 event (note the different FRP scales in Fig. 1 and Fig. 2)[..[68]], with many active fires detected within 24–36 h of air transport to the place of F2 [..[69]]observation according to backward trajectories. These fires might contribute to the elevated background levels of CO, NMHC, NO_X, PM_3, and BC outside the F2 plume [..[70]]seen in Fig. 4 and Table 3 compared to those in the F1 plume[..[71]]. Backward trajectories also suggest that the F1 plume was sampled across the line of dispersion while the F2 plume was sampled along the line starting from the upwind plume margin which is also supported by MODIS true color scenes (not shown, 02:40–02:45 UTC, 04:25–04:30 UTC in October 09 2005 and 03:00–03:05 UTC, 04:45–04:50 UTC in 01 August 2007 for Terra MOD021KM and Aqua MYD021KM, respectively, downloaded from https://modis-atmos.gsfc.nasa.gov/IMAGES) with visible fire smoke for the day and place of each plume observation. As a result, the levels of the measured [..[72]]biomass burning products west (downwind) to the area directly affected by the F2 plume [..[73]]were somewhat elevated compared to the east (upwind) side of the plume, so we use only the [..[74]]upwind measurements to setup reference state [..[75]]concentrations for the F2 plume. In the F1 event, the whole set of [..[76]]the measurements directly outside the area affected by the fire plume was used to setup the reference state concentration levels[..[77]].

During the fire plume observations, the air temperature and humidity measured from the lab carriage were $6-12°$C and 40–55% in the F1 event, and $24-29°$C and 30–50% in the F2 event. The weak winds of 0.3–0.5 $\mathrm{m \cdot s^{-1}}$ were observed during the train stops within both the plumes which is in close agreement with the data form the Mogocha weather station

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[63] removed: . Previous studies of fire plume events in remote Siberia based on the continuous

[64] removed: measurements at ZOTTO Tall Tower suggest an appreciable anthropogenicsignal in air masses arriving at the measurement site. Such a signal can contribute substantial part of the total amount of near-surface abundance of long-lived species like

[65] removed: and

[66] removed: and, therefore, must be discriminated against the true wildfire signal for correct interpretation of

[67] removed: measurements data (Vasileva et al., 2011; Chi et al., 2013). Visual inspection of backward trajectories (

[68] removed: suggests the air sampled within

[69] removed: plume could spend more time over territories near the railway with both wildfire and appreciable anthropogenic activity. This may explain

[70] removed: compared to

[71] removed: (see Table 3 in the next section).The Fig. 1b also suggests that elevated

[72] removed: species beyond

[73] removed: are probably associated with patches of wildfire contaminated air

[74] removed: measurements from upwind side of F2 plume affected area

[75] removed: species concentrations for this event

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(WMO index 30673). Close inspection of the backward trajectories in Fig. 1 and Fig. 2 shows that the air contaminated by biomass burning products was continuously transported in a weak regional wind field during at least two days just before the time of each plume observation. Thus, we can safely assume a negligible contribution of the emissions from fires that burned near the railway in the days prior to the F1 and F2 plume observations into the excess (plume minus background) gas and aerosol levels measured within the plumes. The smoke from active fires detected by MODIS near the railway outside the segment of F1 and F2 plume observations was not measured during the TROICA passes, probably because of insufficient dispersion or a difference between the time of burn and the time of the pass, although emissions from these fires might contribute to the elevated background levels around the F2 plume. On the contrary, the low background levels for the F1 plume suggest that there were no significant [..[78]]emission sources affecting the measured air in this event.

Throughout both the plumes, operators smelled and saw white smoke rising from multiple small fires in the forest on the hillsides approximately 1–1.5 km from the railway. This points to the presence of ground smoldering fires that probably were not detected by MODIS (due to their low radiative temperature, disguise by tree crowns or a difference between time of burn and time of satellite overpass) but contributed to high gas and aerosol concentrations in F1 and F2 plumes alongside the active fires detected by MODIS directly near the railroad within the plumes.

The CO_2 and CH_4 are the long-lived [..[79]]air constituents with high background levels that are presumably [..[80]]much less affected by local and regional emissions[..[81]], in contrast with CO, NO_X, and other biomass burning products. Yet, pronounced diurnal cycles of CO_2 and CH_4 were observed during TROICA campaigns in warm seasons, with the maximas during nighttime surface temperature inversions associated with accumulation of local emissions (Belikov et al., 2006; Berezina et al., 2014). Nevertheless, no influence of diurnal CH_4 variations on the measurements in F1 and F2 plumes was revealed in the present study, probably due to the absence of strong emission sources (wetlands) in the region of observations. The influence of the nighttime accumulation of CO_2 [..[82]]is assumed negligible within F1 and F2 plumes which were observed in daytime well after the breakdown of the inversions. Although, some parts of the plumes [..[83]]are suspected for contributions from [..[84]]non-wildfire emissions and therefore have been excluded from the subsequent analyses (see more discussion below).

[..[85]]Given all of the above, we can safely assume that the peak excess levels of all the chemical compounds measured within F1 [..[86]][..[87]]and [..[88]]F2 plumes have originated from forest fires located directly near the railway and therefore

[78] removed: nearby anthropogenic
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[81] removed: . Meanwhile
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[83] removed: (discussed further)
[84] removed: non-biomass burning emissions , therefore we do not use these parts in the analysis
[85] removed: During the fire plume observations, air temperature and humidity measured from the lab carriage were 6–12°C and 40–55% for
[86] removed: plume, and 24–29°C and 30–50% for F2. The weak winds of 0.3–0.5
[87] removed: , observed during train stops within both the plumes as well as at Mogocha weather station (WMO index 30673), suggest the transport time of smoke to the lab carriage of 1–1.5 h for visible (observed by operator) fires
[88] removed: less than a day for other potential fire plume souses seen at Fig. 1. Thus, for conservative species, the smoke measured from visible fires may be considered as fresh emission fire plume with minimal chemical transformations of the constituents during the transport. For plumes from distant fires, photochemical loss of

represent composition of a fresh wildfire smoke, with negligible effects of photochemical aging as well as transformation and removal of aerosol particles [..[89]](Goode et al., 2000; Hobbs et al., 2003; Stohl, 2006; Paris et al., 2009; Alvarado and Prinn, 2009; Hecobian et al., 2011; Kondo et al., 2011; Chi et al., 2013; Saarnio et al., 2010).

3 Measurements and instrumentation

The key characteristics of the measurement instruments used in TROICA campaigns are listed in Table 2 where PM_3 are particles with aerodynamic diameters less than $3 \cdot 10^{-6}$ m. Nitrogen oxides were measured with TE42C-TL (TROICA-9) and M200AU (TROICA-11) instruments which register chemiluminescent radiation from reaction of NO with O_3, with catalytic conversion of NO_2 to NO. Methane and NMHC were measured with Horiba APHA-360 instrument using a single flame ionization detector, with separation of NMHC by a selective absorber. The details on the CO_2, CO, and CH_4 measurements are given by Belikov et al. (2006). The NMHC mixing ratios were measured in parts per million by carbon ([..[90]]ppmC) while mixing ratios of other gases were measured in parts per million ([..[91]]ppm) or parts per billion ([..[92]]ppb) by volume. [..[93]]

Previous studies show that a significant fraction of volatile organics in a biomass smoke are oxygenated compounds (OVOC) (Akagi et al., 2011; Gilman et al., 2015) which in some cases may be measured as NMHC by flame ionization detectors (Trabue et al., 2013). Our measurements of such OVOCs as acetic acid, acetone, ethanol, methanol, methacrolein, and methylvinylketone performed with proton transfer reaction mass spectrometer (PTR-MS) during TROICA campaigns (see Timkovsky et al. (2010), for example) show that mixing ratios of all these compounds are within few ppb while NMHC mixing ratios generally reach hundreds of ppb (see Table 3 and Fig. 3–4 below) that is two orders more. Thus we expect small sensitivity of the NMHC analyzer to OVOC in our study.

All gas analyzers were calibrated daily during the route. For calibration there were used standards provided by D. I. Mendeleyev Institute for Metrology (Russia), Max Planck Institute for Chemistry (Germany), and Earth System Research Laboratory, NOAA (USA). To perform calibration, gas from standard cylinder was applied to the instrument via a pressure regulator with a proper pneumatic scheme to perform gas supply under atmospheric pressure. The duration of each calibration was approximately 5–10 minutes. The obtained span coefficients were then used for data recalculation and did not exceed the instruments accuracy values provided in their technical specifications. Zero calibrations for the instruments used to measure CO, CH_4, and NMHC were performed every 20 minutes using build-in zero scrubbers. For other instruments, zero air generator was used daily for zero calibrations.

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

[89] removed: are possible (Goode et al., 2000; Hobbs et al., 2003; Stohl, 2006; Paris et al., 2009; Alvarado and Prinn, 2009; Hecobian et al., 2011; Kondo et al., 2011; Chi et al., 2013; Saarnio et al., 2010)but are not measured, therefore we consider all species as conservative when estimating ERs

[90] removed: ppmC

[91] removed: ppmv or ppm

[92] removed: ppbv or ppb

[93] removed: Nitrogen oxides were measured with TE42C-TL (TROICA-9)

in Russia and calibrated by the manufacturer using the methods which are state-approved in Russia (Kopeikin, 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 and Gullett, 2013; Yokelson et al., 2007; Nance et al., 1993).

For black carbon measurements the single-wave (880 nm) aethalometer (model AE-16) was used (Kopeikin, 2007). This instrument was calibrated in Slovenian Institute of Quality and Metrology (www.siq.si) before the train route. The obtained span coefficient 1.06 ± 0.16 was applied to recalculate the data. The accuracy of the single-wave nephelometer used in years 2005 and [..[94]][..[95]][..[96]][..[97]]2007 is not as high as that of the modern instruments such as Multi-Angle Absorption Photometer or Multi-Wavelength Absorbance Analyzer (Saturno et al., 2016), nevertheless the measurements data provides valuable information on wildfire smoke aerosols in boreal Siberia that are still little studied to date.

All the measurements [..[98]]conducted in the TROICA campaigns were fully automated, with all the data available at the central computer. The stability of the measurement system was controlled by operators who also fixed environment settings and some occasional events (oncoming trains, local anthropogenic activity near the railway, biomass burning and industrial plumes, weather conditions, e.t.c.) in electronic dairy. This meta database was then used at a preliminary data quality control stage as well as in subsequent data processing when studying particular atmospheric events. [..[99]]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. No systematic influence of the train speed on the trace gas and aerosol observations [..[100]]is revealed in the present study as well as [..[101]]in the previous analysis of TROICA measurements (Elansky et al., 2009).

Time resolution of the original TROICA data is 10 s. Taking into account a range of the instrument response times (Table 2), we averaged the gas mixing ratios and PM_3 concentrations over 60 s intervals for subsequent analysis. The BC concentrations were averaged over 300 s intervals. [..[102]]

[94] removed: M200AU (TROICA-11)instruments which register chemiluminescent radiation from reaction of

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[99] removed: The instruments were calibrated using standard mixtures provided by manufacturers. The detailed description of the instrumentation has been already published in several studies (Belikov et al., 2006; Elansky et al., 2009; Kuokka et al., 2007; Kopeikin, 2007, 2008)

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[102] removed: 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.

4 Methods of data analysis

The [..[103]]normalized excess ratio (NER) in a biomass burning plume, $ER_{Y/X}$, of a chemical compound Y related to a reference compound X is estimated as the enhancement, above the background, of Y over that of X:

$$ER_{Y/X} = \frac{\Delta Y}{\Delta X} = \frac{Y_{plume} - Y_{background}}{X_{plume} - X_{background}}, \quad (1)$$

where ΔX and ΔY are the excess levels (mixing ratios for gases and mass concentrations for aerosols) of the compounds. In fresh plumes, which do not undergo significant chemical and physical transformations of the initial emissions, the NER is an emission ratio (hereinafter referred to as ER) which may be used to derive emission factors to estimate mass of the products emitted into the atmosphere when combined with estimated mass of a fuel consumed. We assume that the NERs estimated with formula (1) in this study may be safely used as emission ratios because we expect that peak ΔX and ΔY come from fires that burned directly near the measurements route.

The $ER_{Y/X}$ in formula (1) is estimated from the slope of linear regression of ΔY on ΔX (Yokelson et al., 1999). According to a number of studies (Yokelson et al., 1999; Le Canut et al., 1996; Andreae and Merlet, 2001; Guyon et al., 2005; Keene et al., 2006), forcing to zero an intercept term of the linear regression, as stated by (1), can significantly reduce the uncertainty of the resulting ER estimate when the background levels of X and Y are accurately estimated. For F1 and F2 plumes, average background mixing ratios are estimated with the measurements conducted just before and after the plumes (see discussion above) with additional constraints on the upper limits of the measured CO and NO_X to exclude any small scale perturbations caused by local anthropogenic emissions along the railway (Table 3).

We use CO as the reference compound X in (1) as it shows good correlation ($R^2 > 0.70$) with all the measured species within F1 and F2 plumes. Such [..[104]]the choice in our study [..[105]]is preferable compared to CO_2, the other frequently used reference compound, as correlations of the measured species with CO_2 appeared to be substantially smaller. High correlations between ΔY and ΔCO in F1 and F2 events could point to high input of biomass burning products from smoldering combustion process characterized by relatively high emissions of CO, CH_4, NMHC, and particulate matter (Ward et al., 1992; Laursen et al., 1992; Andreae and Merlet, 2001; Hobbs et al., 2003). Noting that many studies provide ERs on the basis of CO_2 which accounts for more than 90% of carbon released into the atmosphere from biomass burning, our estimates of $ER_{CO/CO2}$ provide a basis for recalculating CO-based ERs (see, for example, (Le Canut et al., 1996)) to compare the results presented here with other published data, as well as to estimate emission factors for their implementation in current emission models (Yokelson et al., 1999). We also provide $ER_{PM_3/CO}$ and $ER_{BC/CO}$ as the ratios of mass concentrations and the ratios of aerosol mass concentrations to CO volume mixing ratios, respectively, for easy comparison with other studies. The CO volume mixing ratios were converted into mass concentrations with the use of the ideal gas law by utilizing simultaneous measurements of air temperature and pressure along the TROICA route.

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Additionally, a modified combustion efficiency (MCE) was estimated on the basis of average ER_{CO/CO_2} for each plume:

$$MCE = \frac{1}{1 + ER_{CO/CO_2}} \quad (2)$$

Formula (2) is widely used to approximate combustion efficiency – the molar fraction of carbon emitted in the form of CO_2 in the total amount of carbon emitted from biomass burning including both gaseous phase and particulate matter (Le Canut et al., 1996; Yokelson et al., 1999; Goode et al., 2000; Hobbs et al., 2003).

The MCE is a useful index used to assess relative contributions from flaming and smoldering combustion processes to the measured abundances of species, as well as to compare results of different studies considering large differences between EFs for different types of combustion. Usually emissions of CO, CH_4, most of NMHC, and PM_3 are higher during smoldering combustion, while emissions of CO_2, NO_X, and BC are higher during flaming which is therefore associated with higher MCE (Laursen et al., 1992; Ward et al., 1992; Nance et al., 1993; Le Canut et al., 1996; Yokelson et al., 1996, 1999; Goode et al., 2000). Since CO_2 and CO together contain over 95% of carbon emitted from biomass burning, the difference between real combustion efficiency and its approximation (MCE) is typically only a few percent.

The analysis of Cantrell (2008) showed that using linear least squares approach to calculate the model slope may produce irrelevant results when both variables are measured with significant noise. In this case, a some kind of error-in-variable model would be preferable to account for measurement error in independent variable (ΔX in our case).

In the present study, we calculate emission rations for each measured compound with three different linear regression approaches. Two of them use essentially the same standard linear least squares regression algorithm based on singular value decomposition implemented in Linear Algebra PACKage, LAPACK, (Anderson et al., 1999), with $ER_{Y/X}$ estimated as: a slope in linear regression with Y as a dependent variable (ER_1) [..[106]]and an inverse of the slope in linear regression with X as a dependent variable (ER_2). For algorithms that properly account for uncertainties in both variables, $ER_1 = ER_2$. It [..[107]]is shown below that the latter is not the case in present study, as both X and Y model variables are subject to appreciable (and unknown) amount of uncertainty due to intrinsic inhomogeneity of the emission source as well as various rates of irreversible mixing with the surrounding air during the atmospheric transport. This problem is addressed in present study by estimating $ER_{Y/X}$ with a third approach (ER_3) based on a weighted orthogonal distance regression based on a modified trust region Levenberg–Marquardt algorithm implemented in ORthogonal Distance PACKage, ORDPACK, which accounts for uncertainties in both Y and X variables (Boggs and Rogers, 1990). The weights for each [..[108]]measurement data (X_i, Y_i) pair are then calculated as inverse standard variances of X_i and Y_i. The variances include standard deviations of 10 s data values around 60 s averages (the main part) and the measurement uncertainties from Table 2 (a substantially minor part) summed in quadrature.

Trial calculations [..[109]]do not allow to select a particular regression method (of the three methods described above) as the best candidate for ER estimates on the basis of visual inspection of the residual charts. Hence, we calculate the result-

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ing estimates of ER (ER_{avg}) for each compound as averages of the slopes from three regression approaches, with standard uncertainties (δER_{avg}) calculated according to Bell (1999):

$$ER_{avg} = \frac{1}{3}(ER_1 + ER_2 + ER_3), \tag{3}$$

$$\delta ER_{avg} = \sqrt{U_i^2 + U_{ii}^2}, \tag{4}$$

$$U_i = \frac{1}{n}\sqrt{\sum_{k=1}^{n} \delta ER_k^2},\ U_{ii} = \frac{1}{\sqrt{n(n-1)}}\sqrt{\sum_{k=1}^{n}(ER_k - ER_{avg})^2}, \tag{5}$$

where $n = 3$ and $(ER_k, \delta ER_k)$ [..[110]]are the model slopes and their uncertainties estimated with three different approaches [..[111]]used in the present study. The implemented method provides a conservative estimate of δER_{avg} as far as covariances among the three algorithms are neglected. Henceforth, for convenience we refer to the corresponding averages given by (3) and (4) as ER and δER, correspondingly.

For comparison with other studies, conversion of units is performed, when necessary, with the data provided in original publications. Specifically, [..[112]]CO_2-based ERs (Cofer et al., 1989, 1998) are converted to CO-based through dividing by $ER_{CO/CO2}$, with the relative uncertainties summed in quadrature. The EFs (Laursen et al., 1992; Goode et al., 2000; Andreae and Merlet, 2001; Akagi et al., 2011; Urbanski et al., 2009) are converted to ERs following Andreae and Merlet (2001):

$$ER_{Y/X} = \frac{EF_Y\ MM_X}{EF_X\ MM_Y}, \tag{6}$$

where EF (g kg^{-1}) is the emission factor, and MM (g) is the molecular weight. The MM_{NOx} is set equal to 30 and 42.8 g for publications in which NO_X was assumed to consist of NO by 100% (Goode et al., 2000; Andreae and Merlet, 2001; Akagi et al., 2011) and by 70–90% (Laursen et al., 1992; Pirjola et al., 2015), respectively.

The $ER_{NMHC/CO}$ (ppmC ppmC^{-1}) is calculated from the $ER_{NMHCi/CO}$ (ppmv ppmv^{-1}) for individual NMHC compounds using the relation:

$$ER_{NMHC/CO} = \sum_{i=1}^{N} N_{Ci} ER_{NMHCi/CO}, \tag{7}$$

where N_{Ci} is the number of carbon atoms in the i^{th} NMHC compound ($NMHC_i$), N is the number of NMHC compounds measured in the cited study, and $ER_{NMHCi/CO}$ are either provided in the cited study (Friedli et al., 2001) or calculated from the EF_{NMHCi} and EF_{CO} provided in the cited study (Laursen et al., 1992; Urbanski et al., 2009; Akagi et al., 2011) using the relation (6) with CO as X and $NMHC_i$ as Y. The choice of the unit of measure for $ER_{NMHC/CO}$ in the present study

[110] removed: for $k = 1, 2, 3$

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is related to the technique used to measure NMHC as well as with the fact that molecular weight of a NMHC compound is related to its [..[113]]chemical efficiency via thermal and photochemical processes leading to the formation of oxidation products and ozone (Friedli et al., 2001). Thus, more heavy and "[..[114]]chemically efficient" NMHC compounds contribute more to the $ER_{NMHC/CO}$ [..[115]]values reported below.

When MCE is not provided in [..[116]]an original publication, it is calculated using $ER_{CO/CO2}$ and formula (2) from the present [..[117]]study.

The EFs for particulate matter [..[118]]are converted into ERs ($\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$) [..[119]]dividing EF_{PM3} [..[120]]by EF_{CO}. This approach is justified by the relation from Laursen et al. (1992) for EF estimates on the basis of carbon mass balance approach: $EF_X = F_C\ 1000\ \frac{C_X}{C_T}$, where EF_X ($\mathrm{g\ kg^{-1}}$) is the emission factor for a compound X, F_c is the mass fraction of carbon in the fuel, 1000 is the mass conversion factor (kg to g), C_X ($\mathrm{ng\ m^{-3}}$) is the excess mass concentration of X in biomass burning plume, and C_T ($\mathrm{\mu g\ m^{-3}}$) is the excess mass concentration of carbon in the plume in form of gases and particulate matter. Assuming F_C and C_T to be constant in a plume (or a series of plumes), we obtain [..[121]]the relation $\frac{EF_Y}{EF_X} = \frac{C_Y}{C_X} = ER_{Y/X}$.

5 Results and discussion

Time series of gas mixing ratios and particle mass concentrations measured within F1 and F2 forest fire plumes are shown [..[122]]in Fig. 3–4 along with the estimated background levels of the measured species plotted for the period of plume crossing. The NO_2/NO_X ratio [..[123]]shown in Fig. 3c and Fig. 4c as an indicator of a "photochemical state" of the plumes [..[124]][..[125]][..[126]][..[127]][..[128]][..[129]]

[..[130]]reveals that about 80–95% of NO_X in the plumes is in the form of NO_2. The high relative fraction of NO_2 in NO_X is also reported for other fresh boreal forest fire plumes, which is probably due to rapid NO to NO_2 conversion by

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[128] removed: and
[129] removed: with high background levels in the atmosphere the relative excess levels are much smaller reaching as much as 5–10% of the background levels. Within the plumes, variations of the excess levels of all the measured gases and particulate matter are generally well correlated with each other thus supporting notion on their common emission source.
[130] removed: It can be seen from Fig. 3c that about 80–95

photochemical oxidation (Laursen et al., 1992; Nance et al., 1993). The highest concentrations in F1 and F2 events were measured during the train stops at railway stations (Fig. 3–4). Such local episodes of strong anthropogenic contamination are expected to introduce outliers in the regression analyses whose final effect on the inference may be significant. The perturbing effect of local anthropogenic [..[131]]emissions was suppressed through additional filtering of the original data based on some characteristic chemical signatures of the air subjected to local anthropogenic contamination. Namely, the data samples with $\Delta\mathrm{CO} > 1.3$ ppm for both the plumes, as well as with $\Delta\mathrm{NO_X} > 2.5$ ppb and $\mathrm{NO_2/NO_X} < 0.82$ for F1 and $\Delta\mathrm{NO_X} > 3$ ppb and $\mathrm{NO_2/NO_X} < 0.75$ for F2, were excluded from the analysis.

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 ($119.5°$E–$120.5°$E for F1 and $111°$E–$112°$E for F2, compare longitudes in Fig. 1–2 and Fig. 3–4). This supports the above stated assumption about the dominant contribution of fresh fire smoke to the measurements.

In the remaining parts of the plumes ($118.5°$E–$119.5°$E for F1 and $109.5°$E–$111°$E for F1), the measured excess levels of biomass burning products are still much higher than the background levels, although their origins need special discussion. Throughout both the plumes, operators saw and smelled white smoke rising from many small ground fires in the woods on the hillsides, with the smoke filling the observable area. This indicates the presence of fire emission sources directly near the railroad throughout the whole plume transect in each event, although the fires were probably too small or obscured by tree crowns and therefore were not detected by MODIS. According to Fig. 1 there were no distant emission sources within three days of air transport according to HYSPLIT backward trajectories that could contribute to the measurements in the F1 plume (which is also supported by low background levels of the measured species for the F1 event). Thus we conclude that contribution of emissions from local fires that burned directly near the railway in the day of observation was dominant for the measurements in the F1 plume. In Fig. 2 we see many fires between $112°$E and $114°$E detected by MODIS during the day of the F2 plume observation and in the previous day as well. Some of these fires were located directly near the railway but were not measured by TROICA (probably due to a time mismatch or insufficient dispersion). The more distant fires located between $112°$E and $114°$E within 24–36 h of air transport to the measurements route according to HYSPLIT backward trajectories could contribute to the elevated background levels for the F2 event. These fires also could contribute to the excess levels measured in the F2 plume segment between $109.5°$E and $111°$E. In fact, this segment is the only part of the analyzed plume crossing transects F1 and F2 which can be suspected for some appreciable contamination by aged fire smoke, although the latter is not supported by further analysis of $ER_{NOx/CO}$ variations.

In Fig. 3–4 one can see the substantial and simultaneous increases in CO, NMHC and $\mathrm{NO_X}$ mixing ratios and aerosol concentrations within F1 and F2 plumes compared to those in the ambient air. For long-lived gases $\mathrm{CO_2}$ and $\mathrm{CH_4}$ with high background levels in the atmosphere the relative excess levels are much smaller reaching as much as 5–10% of the background levels. Variations of the excess levels of all the measured gases and particulate matter are generally

[131] removed: contamination

well correlated with each other within the plumes, thus supporting the notion on their common emission source. The few exceptions are discussed further.

Thus, Fig. 3 shows a distinct decrease in all excess mixing ratios and mass concentrations during [..[132]]03:15–04:30 UTC which corresponds to the railway ascend from 550 to 800 [..[133]]m a.s.l. when the railway crossed a mountain ridge. At the top of the ridge (04:00–04:35 UTC), correlation between the measured concentrations of different compounds is very low, therefore we completely exclude the corresponding data segment from further analysis. Before the top of the ridge (02:50–04:00 UTC), correlation of CO_2 with every other measured compound (for example, see gray crosses in Fig. 5d and Fig. 5f, respectively) is also very low while correlation of CH_4, NMHC, NO_X, and PM_3 with CO ($R^2 > 0.7$, Table 5) [..[134]]is as high as in the remaining part (04:35–06:30 UTC) of the F1 plume. This feature suggests that CO_2 observations were influenced by emissions from a non-fire source during that time, therefore we do not report $ER_{CO/CO2}$ [..[135]]for 02:50–04:00 UTC in the F1 plume. We also do not report $ER_{BC/CO}$ for that period because BC shows very low correlation with CO and CO_2. [..[136]]

In Fig. 4a two broad CO_2 [..[137]]peaks in the western F2 plume part are observed during 04:00–04:20 UTC and 05:00–05:10 UTC, accompanied by short-term fluctuations of CH_4 and NMHC (Fig. 4b), as well as an increase in NO_X during 04:00–04:20 UTC (Fig. 4c). The absence of coinciding increases in CO and PM_3 for those periods suggests a non-fire source of these fluctuations, and the diary records indicate the train passage through a town during 04:00–04:20 UTC and a rural settlement during 05:00–05:10 UTC. Since these CO_2 [..[138]]peaks strongly affect the CO–CO_2 ratios for a large F2 plume part from 03:40 UTC till 05:20 UTC, we do not report $ER_{CO/CO2}$ value for that period. We also do not report the $ER_{BC/CO}$ for the same period because of low correlation between BC and CO, also probably due to the anthropogenic contamination. The corresponding short-term variations in CH_4, NMHC, and NO_X produce outliers in scatter plots in Fig.6a–c (black crosses) which were excluded from the regression analysis.

[..[139]]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 [..[140]]and correlation between the major biomass burning products, CO and CO_2 [..[141]](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

[132] removed: ascend of the railway
[133] removed: m a .g.l. Changing elevation does not affect significantly CO-based ERs (
[134] removed: but lead to dramatic decrease in
[135] removed: and rate of correlation between
[136] removed: The latter may be due to incomplete vertical mixing of the
[137] removed: accumulated during nighttime which is difficult to account for in the present study.Therefore, we simply discard
[138] removed: observations within F1 plume made during the 02:50–04:35 UTCrailway ascend.
[139] removed: Scatter plots of excess trace gas and aerosol levels versus
[140] removed: of
[141] removed: in F1 and F2 plumes are shown in Fig. 5–6, along with the regression lines for each regression method and time interval. We subdivided

according to the [..[142]][..[143]]observed differences in excess mixing ratios and the rate of correlation between CO and CO_2. The correlation is high during F1-2 and F2-1 ($R^2 > 0.9$), decreased during F2-2 ([..[144]]$R^2 = 0.7$), and low during F1-1 ($R^2 = -0.24$) plume parts, as shown in Table 5.

Scatter plots of excess gas and aerosol levels versus excess mixing ratios of CO and CO_2 in F1 and F2 plumes are shown in Fig. [..[145]]

5–6, along with the regression lines for each regression method and plume segment. The final estimates of ERs values (ER_{avg}) and corresponding standard deviations ([..[146]]δER_{avg}) calculated with formulas (3)–(5) for each plume part from Table 4 are shown in Table 5. Here [..[147]]three sources of uncertainty in the derived estimates are considered: internal variability of the [..[148]]measurement data with the uncertainties [..[149]]δER_1, δER_2, and δER_3 estimated with the particular regression procedure, variability of the ER estimates due to specific choice of the regression model (estimated as U_{ii} with formula (5)), and variations of the ERs between [..[150]]different plume parts within each plume. 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. All the uncertainties in Table 5 represent the range of possible variability of the final ER estimates at 68% level of confidence assuming a normal distribution of the ERs around the estimated values [..[151]](a common assumption for all the studies reporting ER or EF estimates[..[152]]

[..[153]]). The corresponding correlation coefficients (R^2[..[154]]) for various X and Y variables are shown in Table [..[155]]5 below the ER block. The R^2 are high for both trace gas ($R^2 > 0.7$) and gas–particle ($R^2 > 0.5$) correlations[..[156]][..[157]][..[158]][..[159]][..[160]].

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[142] removed: differences in

[143] removed: ratios

[144] removed: discussed later in this section)seen

[145] removed: 5d and 6d.

[146] removed: $(\delta ER)_{avg}$

[147] removed: ,

[148] removed: measurements

[149] removed: ($\delta ER_1, \delta ER_2, \delta ER_3$) estimated within the regression algorithms

[150] removed: F1 and F2 plumes as well as

[151] removed: which is typical for all

[152] removed: .

[153] removed: The corresponding coefficients of correlation

[154] removed: between

[155] removed: 6.

[156] removed: , although a limited number of outliers persist for each particular data group with the largest scattering observed for

[157] removed: vs.

[158] removed: and

[159] removed: vs.

[160] removed: plots. 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 $\Delta Y/\Delta X$ values to make our final estimates more robust with respect to various disturbing factors

From Table 5 one can see that the estimated average $ER_{CO/CO2}$ is $15.2 \pm 0.7\%$ [..[161]]for F1-2 [..[162]]and $10.0 \pm 0.6\%$ [..[163]]for F2-1 plume parts, with the relative uncertainties about 5% of the [..[164]]$ER_{CO/CO2}$ [..[165]]coming mainly from the internal variability of the measurements. As it follows from the laboratory study of Yokelson et al. (1996), the estimated MCE [..[166]]$= 0.91 \pm 0.05$ suggests that a mixture of emissions from flaming and smoldering combustion was sampled within the F2-1 plume part, while [..[167]]the MCE $= 0.87 \pm 0.04$ for F1-2 indicates the dominance of smoldering. [..[168]]For real wildfires, the relationship between [..[169]]visually observed combustion type and MCE may not be so explicit (for example, see Ward et al. (1992), Cofer et al. (1998) and Pirjola et al. (2015)). Yet, admitting insufficient amount of a priori information, we retain hereafter the terms "smoldering" [..[170]]and "[..[171]]mixed" in our generic classification of the biomass plumes based solely on MCE values, as a particular combustion regime have an important impact on chemical composition of the plumes. Indeed, the reported lower $ER_{CO/CO2}$ for the F2-1 plume part may be due to more severe burning conditions observed in summer compared to those observed in autumn within F1-2 plume part, with more flaming combustion during F2-1 producing more CO_2 and less CO.

[..[172]]The estimated average $ER_{CH4/CO}$ are quite stable within the plumes, being slightly higher (at 68% confidence level) for the F2 plume (9.7–9.9%) compared to the F1 plume (8.1–8.4%), with the [..[173]]relative uncertainties about 5% of the ERs. The relatively high uncertainty in $ER_{CH4/CO}$ for the F2-2 plume part (15% of the average) is most probably due to the [..[174]]accumulation of (X_i, Y_i) data [..[175]]points in the lower left part of the plot [..[176]]in Fig. 6a [..[177]]which affects the results of individual regression methods but not the average $ER_{CH4/CO}$.

[161] removed: (MCE $= 0.87 \pm 0.04$)

[162] removed: plume and varies from

[163] removed: (MCE $= 0.91 \pm 0.05$) to $2.8 \pm 0.6\%$ (MCE $= 0.97 \pm 0.21$) for F2 plume . Total uncertainties of the $ER_{CO/CO2}$ come mainly from variability of the measurements and consist

[164] removed: average $ER_{CO/CO2}$ for F1-2 and F2-1 plumes, and 20% for F2-2 plume. Large uncertainties in MCE arise from the uncertainties in $ER_{CO/CO2}$ and are provided only for consistency. Approximately half of the total uncertainty in the F2-2 average $ER_{CO/CO2}$ comes from large differences between the regression slopes which may be caused by small incline of the regression lines (black lines in Fig. 5d). Indeed, the $ER_{CO/CO2} = 2.8 \pm 0.6\%$ for F2-2 plume is the lowest

[165] removed: estimate reported in this study and lies at the bottom of the range of the ERs for boreal wildfires published anywhere. The high value of MCE (F2-2 plume) is commonly considered as an indicator of emissions from predominantly flaming combustion. The latter assumption is also supported by the observed increase in $\Delta BC/\Delta PM_3$ ratios with increasing MCE ($R^2 = 0.53$) seen at Fig. 7b (black triangles) which is not observed in other parts of F1 and F2 plumes (Ward et al., 1992; Nance et al., 1993; Conny and Slater, 2002; Reid et al., 2005). Hence the measurementssuggest a noticeable contribution from flaming combustion in the F2-2 plume part

[166] removed: $= 0.91$

[167] removed: MCE $= 0.87$

[168] removed: In the studies of real wildfires(see Ward et al. (1992), Cofer et al. (1998) and Pirjola et al. (2015) for example)

[169] removed: the

[170] removed: , "mixed",

[171] removed: flaming

[172] removed: Estimated

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[..[178]]The estimated average $ER_{NMHC/CO}$ [..[179]]is also higher for the F2 plume (0.16–0[..[180]].21 [..[181]]ppmC ppmC^{-1}) compared to that for the F1 plume [..[182]](0.11–0[..[183]].12 ppmC ppmC^{-1}[..[184]]), with the relative uncertainties of 4–9% coming mainly from [..[185]]internal variability in the measurements. The observed increase [..[186]]in $ER_{NMHC/CO}$ [..[187]]may be partially explained by decrease in ΔCO[..[188]], as some previous studies show that excess mixing ratios of most of NMHC in fire plumes decrease when MCE increases (Laursen et al., 1992; Yokelson et al., 2011; Burling et al., 2011). Yet, the measurements by Yokelson et al. (1997) and Goode et al. (1999) showed that, for example, light unsaturated hydrocarbons C_2H_2 and C_2H_4 did not correlate with either CO_2 or CO. Another possible reason is that smoke from flaming combustion in the F2 plume contained more heavy hydrocarbons with higher number of carbon atoms in their molecules which contributed more to the total NMHC mixing ratios measured in TROICA expeditions on the carbon basis. The effect of smoke aging in the F2 plume is a less likely reason of the increasing $ER_{NMHC/CO}$ because of the high correlation ($R^2 > 0.9$) between the measured ΔNMHC and ΔCO (as CO has a lifetime of several months in the atmosphere), as well as the low variability in the estimated $ER_{NOx/CO}$ in the F2 plume discussed below. Noting the above given considerations, we associate the extremely high $ER_{NMHC/CO} = 0.21 \pm 0.01$ ppmC ppmC^{-1} estimate with fresh biomass burning emissions.

[..[189]]The estimated $ER_{NOx/CO}$ are about 1.7 ppb ppm^{-1} for the F1 and 3.0 ppb ppm^{-1} for the F2 plume, with the relative uncertainties up to 10–20% [..[190]]coming mainly from scattering of the measurement data whereas the differences among the ERs obtained with each particular regression method are relatively small. The increase in $ER_{NOx/CO}$ with increasing MCE between F1 and F2 plumes [..[191]]agrees with the laboratory study of Yokelson et al. (1996)[..[192]], although in wildfire plumes NO_X do not always increase with MCE (Laursen et al., 1992). Higher [..[193]]uncertainty of $ER_{NOx/CO}$ compared to ERs for other gases in our study can be explained by [..[194]]substantial variability in wildfire [..[195]]NO_X emissions which depend on the combustion efficiency, nitrogen content of biomass fuel, and even on the deposition of nitrogen (in form of nitrate and ammonium ions in particulate matter) transported from distant pollutant sources onto the fuel surface (tree leaves), with

[178] removed: Estimated
[179] removed: increases with increasing MCE, from 0.11
[180] removed: .12
[181] removed: for
[182] removed: to 0.16
[183] removed: .21
[184] removed: for F2 plume
[185] removed: variability of the measurement data
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[191] removed: is consistent
[192] removed: although, as mentioned above, this relationship is not always observed in real wildfires
[193] removed: variability
[194] removed: higher
[195] removed: emissions which generally

[..[196]]subsequent volatilization during combustion (Nance et al., 1993). Atmospheric NO_X is also prone to higher variability compared to CO and CH_4 because NO and NO_2 are involved in chains of photochemical reactions limiting their atmospheric lifetime to several days in the [..[197]]midlatitudes (Seinfeld and Pandis, 1997). Nevertheless, from Table 5 we see that the estimated average $ER_{NOx/CO}$ are very stable within each plume[..[198]], thus indicating a similar photochemical age of the two plume segments in the events considered, in a close agreement with the results of analyses of Fig. 1–2 and Fig. 3–4 above showing that the peak excess levels of the biomass burning products measured in the F1 and F2 [..[199]]events have been originated most probably from the fires located in the vicinity of the measurement route. Consequently, we can safely assume in our calculations that all 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.

[..[200]]The estimated $ER_{PM3/CO}$ varies within [..[201]]320–385 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ with the relative uncertainties of 4–8% [..[202]]caused mainly by variability in the [..[203]]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 estimated $ER_{BC/CO}$ for the two plumes is about 6.2 [..[204]]$\mathrm{\mu g\,m^{-3}\,ppm^{-1}}$ with the relative uncertainties up to 20% coming equally from differences among the regression slopes as well as from the standard uncertainties in the slopes [..[205]]for each particular regression model. An important reason of the observed high uncertainties is a limited number of BC observations (8–15 sample pairs against 30–80 for gases and PM_3). Yet, the estimated average $ER_{BC/CO}$ for each plume seem to reflect correctly the linear dependencies between BC and CO [..[206]]shown in Fig. 5f [..[207]]and Fig. 6f.

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 $\delta ER_{avg}/ER_{avg}$ comprise 5–15% for $ER_{CH4/CO}$, $ER_{NMHC/CO}$, and $ER_{PM3/CO}$ and 10–20% for $ER_{NOx/CO}$, $ER_{CO/CO2}$, and $ER_{BC/CO}$. The variations come mostly from scattering of data points around the regression lines (via model slope uncertainties δER_1, δER_2, δER_3, see equation (5)) due to natural variability of wildfire emissions since the measurement uncertainties listed in Table 2 are small. In some cases, variations of the ER estimates from different regression methods (ER_1, ER_2, ER_3) around the average ER_{avg} also contributes to the total uncertainty either due to the limited number of observations (in case of $ER_{BC/CO}$) or due to the scattering of data (in case of $ER_{NOx/CO}$) because different regression methods treat scattering of the observed data

[196] removed: the
[197] removed: middle latitudes
[198] removed: . Noting rather short (less than a day) transport time of the emissions in
[199] removed: plumes, the derived estimates of $ER_{NOx/CO}$ may be safely considered as reliable characteristics of fresh boreal wildfire emissions with
[200] removed: Estimated
[201] removed: 320–430
[202] removed: of the ERs coming mainly from the
[203] removed: measurements. Estimated
[204] removed: with the
[205] removed: . Additional factor
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points around the model line differently. In total, variations of individual ER estimates reported in this study are generally lower than those reported in other studies (see Fig. 7–8 below) although in the latter case it is often difficult to separate natural variability from the measurement and analytic uncertainty.

The variability of the reported ER_{avg} between different plume segments within each plume generally does not exceed the variability δER_{avg} within each plume segment. The exceptions are $ER_{CO/CO2}$ and $ER_{BC/CO}$ for which we do not have enough data, the $ER_{NMHC/CO} = 0.21 \pm 0.01$ ppmC ppmC^{-1} for the F2-2 plume part discussed above, and 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. In other cases, the absence of statistically significant differences between the ERs estimated for different plume segments within each plume supports the assumption about the common photochemical smoke age throughout the plumes, as well as the acceptably small effect of the changing environment on the observations, as discussed above.

We note finally, that the variability of ERs between F1 and F2 plumes is more pronounced than within each plume, with $ER_{CO/CO2}$ decreasing by about 35%, and $ER_{NOx/CO}$ increasing by about 45% in the F2 plume compared to the F1 plume, probably due to more intensive burning processes related to the F2 plume observed in summer contrary to the F1 plume observed in autumn. The $ER_{CH4/CO}$ and $ER_{NMHC/CO}$ also increase from F1 to F2 event by about 15% and more than 35%, respectively. The increase of $ER_{CH4/CO}$ may be explained by moderate decrease in the observed ΔCO, while the increase of $ER_{NMHC/CO}$ may be also caused by the changes in chemical composition of NMHC emissions as assumed above. Variations of $ER_{BC/CO}$ and $ER_{PM3/CO}$ between the plumes are not seen probably because of high variations within the plumes.

6 Comparison with other published results

6.1 Gases

The derived [..[208]]gas ERs are compared against other published estimates for boreal forest fires (Fig. [..[209]]7). It should be noted that most of the previous studies provide estimates for the region of boreal North America (Northern US and Canada) (Cofer et al., 1989, 1998; Laursen et al., 1992; Simpson et al., 2011; Kondo et al., 2011) and Alaska (Goode et al., 2000; Laursen et al., 1992) on the basis of aircraft observations of predominantly fresh plumes (less than a day after emissions). Contrary, there are only a few relevant studies on boreal Eurasia, which we refer to below.

Paris et al. (2009) reports the ER_{CO/CO_2} values of of 7.1% and 4.6% for two forest fire plumes in north–east Siberia in July 2008 sampled from aircraft at heights of 1–3 km a.g.l. in [..[210]]a day after emissions. Pirjola et al. (2015) reported $ER_{CO/CO2}$ from a prescribed burning experiment conducted in southern Finland about 200 km north-west to Helsinki in June

[208] removed: ERs of trace gases
[209] removed: 8
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2009. The burning area of about 0.8 ha contained predominantly slash (64%) and humus-layer (32%), with surface vegetation composing only 4%. The highest CO_2 concentrations in the smoke near the ground measured with a mobile laboratory during the smoldering phase of the fire exceeded the background level by 80–100 ppm which is several times higher compared to the ΔCO_2 of 10–20 ppm measured in F1 and F2 plumes in the present study (Fig. 5d [..[211]]and Fig. 6d), whereas peak ΔCO values of [..[212]]1–3.5 ppm were comparable to peak ΔCO of 1–1.5 ppm in F1 and F2 plumes. The resulting $ER_{CO/CO2} = 3.2\%$ reported by Pirjola et al. (2015) yields MCE = 0.97 [..[213]]typical for predominantly flaming emissions, although this result was attributed by the authors to smoldering combustion on the basis of visual observations.

Cofer et al. (1998) reported an unusually high $ER_{CO/CO2} = 11.3 \pm 2.7\%$ value (MCE = 0.90) from vigorous crowning (flaming) stages of an experimental fire in Siberia (Bor Island, [..[214]]60.75°N, 89.42°E; 50 ha of live 20 m high pine forest burned in July 1993, with the fresh smoke measured from helicopter) which is comparable to the $ER_{CO/CO2} = 9.4 \pm 1.0\%$ value for flaming wildfires in Canada and the $ER_{CO/CO2} = 12.3 \pm 1.9\%$ for smoldering boreal logging slash fires in North America, but vastly exceeds the $ER_{CO/CO2} = 6.7 \pm 1.2\%$ for flaming logging slash fires in North America reported in the same study. The $ER_{CO/CO2} = 10.0 \pm 0.6\%$ associated with "mixed" combustion [..[215]]in our study is within the range of uncertainty of the Bor Island flaming experiment value for $ER_{CO/CO2}$. The accompanying $ER_{CH4/CO2}$ and $ER_{NMHC/CO2}$ estimates of Cofer et al. (1998) are consistent with, or even lower than, the typical ERs in flaming related plumes.

The $ER_{CO/CO2} = 8.8\%$ reported by McRae et al. (2006) from helicopter flights over experimental ground fires in Siberian pine forest is in the middle range of the published estimates and is compared to the "mixed" (F2-1 plume part) $ER_{CO/CO2} = 10.0 \pm 0.6\%$ from the present study.

[..[216]][..[217]][..[218]][..[219]][..[220]][..[221]][..[222]]

[211] removed: and

[212] removed: 1–4

[213] removed: (same as for the F2-2 plume part in the present study)

[214] removed: 60°45‘N, 89°25‘

[215] removed: via MCE

[216] removed: Kondo et al. (2011) reported low $ER_{CO/CO2} = 1.5 \pm 0.5\%$ for Asian (from Siberia and Kazakhstan) biomass burning plumes sampled over Alaska in April 2008 and attributed it to flaming emissions on the basis of MCE = 0.98 which was derived directly from the $ER_{CO/CO2}$ estimate. The results were obtained from aircraft sampling of aged plumes transported from the origin in 4.5 ± 2.1 days according to backward trajectories, with low

[217] removed: = 0.1

[218] removed: and

[219] removed: = 5

[220] removed: (see their Fig. 11). Although the authors warn that $ER_{CO/CO2}$ may be underestimated due to dilution of the plumes through mixing with ambient air during the long range transport in the free troposphere, the reported uncertainty of the derived ER value itself is insufficient to explain the low

[221] removed: to

[222] removed: ratios compared to other studies. Noting that "flaming" $ER_{CO/CO2}$ values for the fresh fire plumes from Canada and California $2.6 \pm 1.0\%$ are in close agreement with present estimates $ER_{CO/CO2} = 2.8 \pm 0.6\%$, the atmospheric dilution process does not seem to be the major factor contributing to low $ER_{CO/CO2}$ estimates reported by Kondo et al. (2011). The "mixed" North American $ER_{CO/CO2} = 8.0 \pm 11.0\%$ is comparable to the "mixed" $ER_{CO/CO2} = 10.0 \pm 0.6\%$ from the present study, although the uncertainties in the estimates of Kondo et al. (2011) are large exceeding 50–100% of the reported ERs. Using the same measurements data but employing a Lagrangian particle dispersion model to identify the plume source regions, Warneke et al. (2009) estimated $ER_{CO/CO2}$ of $5.0 \pm 2.5\%$ for agricultural fires in Kazakhstan and $4.2 \pm 1.9\%$ for forest fires in Siberia which are both higher than the accompanying estimates of Kondo et al. (2011) but lower compared to the most of other published estimates for boreal wildfires (Fig. 8d) considered in the present study.

[..[223]]

[..[224]]Most of the $ER_{CO/CO2}$ in Fig. [..[225]]7d fall within the range of 6–16%, with 22 estimates obtained from aircraft measurements of forest fire plumes in Northern US, Canada and Alaska (Cofer et al., 1989, 1998; Goode et al., 2000; Laursen et al., 1992; Simpson et al., 2011; Urbanski et al., 2009) and [..[226]]two estimates obtained from helicopter [..[227]]observations in Siberia (Cofer et al., 1998; McRae et al., 2006). The $ER_{CO/CO2}$ from the present study for "mixed" and "smoldering" combustion fall within the middle range (6–16%) of the previous estimates. There are also [..[228]]two outliers not shown in Fig. [..[229]]7 corresponding to the $ER_{CO/CO2}$ values of 18% and 34% (MCE = 0.85–0.75[..[230]]) related for emissions from smoldering wildfires in [..[231]]Canada and Siberia (Cofer et al., 1998). In the lower right part of the scatter plot in Fig. 7d are the $ER_{CO/CO2}$ [..[232]]of 3.2% and [..[233]]$4.6 \pm 2.0\%$ from Pirjola et al. (2015) (Finland) and Paris et al. (2009) (Siberia), respectively.

It is important to compare the results of the present study with compilations of EFs for bioclimatic zones made by Andreae and Merlet (2001) and Akagi et al. (2011) as the latter values are often used in wildfire emission models including [..[234]]Global Fire Emissions Database (GFED, www.globalfiredata.org). Although Andreae and Merlet (2001) [..[235]]provide EFs for "extratropical forest" (EXTF) on the basis of the substantial amount of studies, in fact only a couple of them provides reliable data for boreal Eurasia. The inventory of Akagi et al. (2011) inherits the results of Andreae and Merlet (2001) with the updates available at the time of publication and the EXTF zone separated into "boreal forest" (BORF, high latitudes about $50-70^{\circ}$) and "temperate forest" (TEMF). One can see from Fig. [..[236]]7d that the $ER_{CO/CO2} = 8.5-13.4\%$ from the inventories reside at the top half of the estimates. The $ER_{CO/CO2} = 13.4 \pm 4.9\%$ for BORF is close to the "smoldering" $ER_{CO/CO2} = 15.2 \pm 0.7\%$

[223] removed: It should be also noted that the estimates of Kondo et al. (2011) and Warneke et al. (2009) are actually the enhancement ratios characterizing enhancement above a background level of one compound relative to the other in a highly aged plume subjected to substantial dilution and chemical processing. The latter quantity is obviously different from the true emission ratios (characterizing essentially the original chemical composition of burning products) which are predominantly shown in Fig. 8. Nevertheless, the enhancement ratios of Kondo et al. (2011) and Warneke et al. (2009) are close to the "flaming" $ER_{CO/CO2} = 2.8 \pm 0.6\%$ from the present study and smoldering $ER_{CO/CO2} = 3.2\%$ from Pirjola et al. (2015) which are both estimated with the ground based observations of fresh plumes (in contrast to most of the other estimates show in Fig. 8 that are based on aircraft or helicopter measurements).

[224] removed: Below, we summarize ER's comprising the lower right part of the scatter plot in Fig. 8d ($ER_{CO/CO2} = 1.5-6\%$): three for aged "flaming" Siberian and Kazakhstanian plumes, one for more fresh "flaming" plume from North America based on aircraft observations (Kondo et al., 2011; Warneke et al., 2009), two for fresh plumes in Scandinavia and Siberia based on ground observations from Pirjola et al. (2015) and the present study, and one for fresh fire plume in Siberia sampled from the aircraft (Paris et al., 2009).

[225] removed: 8d are

[226] removed: three

[227] removed: (Cofer et al., 1998; McRae et al., 2006) and ground (this study) observations in Siberia

[228] removed: three

[229] removed: 8 corresponding to $ER_{CO/CO2} = 18-34\%$ and

[230] removed: related to

[231] removed: North America and Siberia (Cofer et al., 1998; Kondo et al., 2011). The

[232] removed: estimates from the present study for "mixed"

[233] removed: "smoldering" combustion fall within the middle range (6–16%) of the previous estimates, while $ER_{CO/CO2}$ for "flaming" combustion is at the bottom range (1.5-6%) of the previous estimates

[234] removed: GFED4.1 utilized in the present study as well (Fig. 2

[235] removed: provides

[236] removed: 8d

from the present study, while the $ER_{CO/CO2} = 8.5 \pm 3.1\%$ for TEMF is close to the "mixed" $ER_{CO/CO2} = 10.0 \pm 0.6\%$. [..[237]]

The $ER_{CH4/CO}$ from different studies in Fig. [..[238]]

[..[239]]7a somewhat decreases with MCE, though not very much, because both CO and CH_4 are the products of predominantly smoldering combustion (Nance et al., 1993). Herewith, the $ER_{CH4/CO} = 8-10\%$ reported in this study are at the top of the published range[..[240]], along with the $ER_{CH4/CO}$ for boreal North America attributed to different combustion phases (Laursen et al., 1992; Cofer et al., 1989, 1998; Simpson et al., 2011). The $ER_{CH4/CO}$ of $3.5 \pm 1.2\%$ and $3.9 \pm 0.8\%$ reported by Cofer et al. (1998) for flaming and smoldering stages of [..[241]]an experimental fire in Siberia are much lower compared to ERs from the present study and are at the bottom of the published estimates, along with the $ER_{CH4/CO}$ of $3.8 \pm 3.6\%$ and $4.3 \pm 2.2\%$ for two fires in Canada (Laursen et al., 1992; Cofer et al., 1998). [..[242]]All the $ER_{CH4/CO}$ from the present study lay within the range of uncertainties of the $ER_{CH4/CO} = 7.7-8.2\%$ values from Andreae and Merlet (2001) and Akagi et al. (2011).

The $ER_{NMHC/CO} = 0.12-0.21$ ppmC ppmC^{-1} reported in this study [..[243]]are at the top of the range of previous estimates along with the $ER_{NMHC/CO} = 0.18$ ppmC ppmC^{-1} for BORF from Akagi et al. (2011) and the $ER_{NMHC/CO} = 0.21$ ppmC ppmC^{-1} for a forest fire in Alaska from Urbanski et al. (2009). In the middle of the range are the $ER_{NMHC/CO} = 0.08-0.09$ ppmC ppmC^{-1} [..[244]]values derived from the sum of EFs for C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6, and C_3H_4 for two forest fires in Canada and one in Alaska (Urbanski et al., 2009). Not shown (because of the lack of MCE) in Fig. [..[245]]7b is the $ER_{NMHC/CO} = 0.11$ ppmC ppmC^{-1} estimated with a composite of aircraft observations of C_2-C_{10} hydrocarbons in four plumes from vegetation fires in temperate forests of the US (Montana, Colorado) (Friedli et al., 2001). At the bottom of the plot in Fig. [..[246]]7b are the $ER_{NMHC/CO} = 0.03-0.08$ ppmC ppmC^{-1} [..[247]]values derived from the sum of EFs for C_2H_6, C_2H_2, C_3H_8, C_3H_6, i-butane C_4H_{10}, and n-butane C_4H_{10} for five forest fires in Canada and one in Alaska (Laursen et al., 1992). The observed variations [..[248]]in the $ER_{NMHC/CO}$ estimates are large and associated with natural variability of [..[249]]wildfire emissions of individual NMHC compounds [..[250]](see Friedli et al. (2001) and references [..[251]]therein), as well as with differences among the measurement techniques (Rasmussen et al., 1974). Thus, Laursen et al. (1992) and Urbanski

[237] removed: The "flaming" $ER_{CO/CO2} = 2.8 \pm 0.6\%$ from the present study falls within the range of low values $ER_{CO/CO2} = 1.5-6\%$

[238] removed: 8d. 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).

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[242] removed: The relationship between $ER_{CH4/CO}$ and MCE is not evident in Fig. 8a.

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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. Also, the relation between $ER_{NMHC/CO}$ and MCE is difficult to see in Fig. 7b because of the large differences between the few $ER_{NMHC/CO}$ estimates.

The $ER_{NOx/CO} = 1.6-3.1$ ppb ppm^{-1} reported in this study are at the bottom range of the published estimates, along with the $ER_{NOx/CO}$ of 1.2 ± 1.7 and 3.1 ± 3.2 ppb ppm^{-1} obtained from aircraft observations of two fires in Ontario (which also have the $ER_{CH4/CO}$ comparable to the results of the present study) derived from Laursen et al. (1992). Other four estimates from Laursen et al. (1992) for fires in Canada and Alaska yield $ER_{NOx/CO} = 11-22$ ppb ppm^{-1} [..[252]]with the uncertainties [..[253]]over 100–150%. The $ER_{NOx/CO}$ from the present study are also at the bottom of the range of uncertainty (which is about 100%) of BOR $ER_{NOx/CO} = 6.6 \pm 5.6$ ppb ppm^{-1} derived from Akagi et al. (2011) and the $ER_{NOx/CO} = 7.6 \pm 4.9$ ppb ppm^{-1} values derived from the EFs of Simpson et al. (2011) obtained from airborne measurements of predominantly smoldering fires in Canada in 2008. A distinct outlier in Fig. [..[254]]7c is the $ER_{NOx/CO} = 33.9 \pm 4.5$ ppb ppm^{-1} of Pirjola et al. (2015) obtained from ground-based observations of predominantly smoldering fire smoke in Finland, which is several times higher compared to the upper limit of other published estimates and was derived by dividing the relatively high $EF_{NOx} = 2.7 \pm 0.3$ g kg^{-1} by very low $EF_{CO} = 52.1 \pm 2.7$ g kg^{-1}. [..[255]]Such the high variability of the published estimates is typical for NO_X emissions and seems to reflect natural variability rather than the uncertainties associated with different methods of measurements and analysis. Thus, within [..[256]]the single study of Laursen et al. (1992), a series of measurements in different fire plumes in Canada yielded EF_{NOx} varying by an order of magnitude. Herewith, [..[257]]the $ER_{NOx/CO}$ from different studies [..[258]]increase with MCE [..[259]]because NO_X and [..[260]]CO [..[261]][..[262]][..[263]]are emitted from different (flaming [..[264]][..[265]]and smoldering, respectively) combustion processes.

Note that the uncertainties in the ERs (where available) shown in Fig. [..[266]]7 can be as large as [..[267]]100–200% and more and represent natural variability of the emissions within a single fire event (Laursen et al., 1992), variability between different

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[257] removed: in contrast with $ER_{CH4/CO}$ and $ER_{NMHC/CO}$,
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[259] removed: thus supporting the assumption that
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fires in a region [..[268]][..[269]][..[270]](Cofer et al., 1998; Simpson et al., 2011), as well as the uncertainties associated with measurement [..[271]]techniques (as in the case of NMHC) and data analysis.

6.2 Aerosols

There are only a limited amount of [..[272]]data published on aerosol emissions from boreal biomass fires. We compare our estimates for $ER_{PM3/CO}$ and $ER_{BC/CO}$ with previously published data noting that the results from other studies are actually based on the measurements of particles with aerodynamic diameters less than [..[273]]$2.5 \cdot 10^{-6} - 3.5 \cdot 10^{-6}$ m ($PM_{2.5} - PM_{3.5}$). We consider this difference not significant for our quantitative comparison as $PM_{2.5}$ particles contribute most of the total particle mass in fresh biomass burning plumes [..[274]](Reid et al., 2005; Akagi et al., 2011; Pirjola et al., 2015; Popovicheva et al., 2015).

The [..[275]]$ER_{PM3/CO} = 320 - 385$ $\frac{\text{ng m}^{-3}}{\text{µg m}^{-3}}$ (Fig. [..[276]]8a) with standard uncertainty of 4–8% from the present study are at the top of the standard uncertainty ranges (which are 25–85% where available) of the $ER_{PM3/CO} = 196 - 265$ $\frac{\text{ng m}^{-3}}{\text{µg m}^{-3}}$ estimated for three forest fires in Canada (Ontario and British Columbia) and Alaska (Nance et al., 1993; Urbanski et al., 2009). The $ER_{PM2.5/CO} = 122 - 143$ $\frac{\text{ng m}^{-3}}{\text{µg m}^{-3}}$ from [..[277]]Akagi et al. (2011) and Andreae and Merlet (2001), as well as the $ER_{PM2.5/CO} = 35 - 130$ $\frac{\text{ng m}^{-3}}{\text{µg m}^{-3}}$ for other six forest fires in Canada and Alaska (Nance et al., 1993; Urbanski et al., 2009), are 2–10 times lower compared to the $ER_{PM3/CO}$ reported in the present study. The $ER_{PM2.5/CO} = 557 \pm 92$ $\frac{\text{ng m}^{-3}}{\text{µg m}^{-3}}$ derived from Pirjola et al. (2015) for a prescribed forest fire in Finland is about 1.5 times higher compared to the values obtained in the present study.

The $ER_{BC/CO} = 6.2 \pm 1.3$ µg m^{-3} ppm^{-1} from the present study falls within the range of uncertainty of the previous estimates (Fig. [..[278]]8b). So far the authors know only two studies reporting BC ERs for plumes sampled less than a day after emissions. [..[279]]Thus, Paris et al. (2009) reports the $ER_{BC/CO}$ values of 4.1 and 6.8 µg m^{-3} ppm^{-1} for two forest fires in Siberia, which are within double standard uncertainties of the ERs from the present study. Chi et al. (2013) estimated the

[268] removed: (Cofer et al., 1998; Kondo et al., 2011; Simpson et al., 2011), variability of the measurements due to chemical transformation of measured compounds (

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[273] removed: $2.5 - 3.5 \cdot 10^{-6}$

[274] removed: (Reid et al., 2005; **?**; Pirjola et al., 2015; Popovicheva et al., 2015)

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$ER_{BC/CO} = 10$ μg m^{-3} ppm^{-1} (not shown [..[280]]in Fig. [..[281]]8b because of the [..[282]]lacking MCE estimate) for forest fires in West Siberia in July 2007, some of which were located very close to the ground [..[283]]measurement cite.

The other studies report BC ERs for plumes of several days old. [..[284]]Thus, Warneke et al. (2009) provides the $ER_{BC/CO}$ value of 7 ± 4 μg m^{-3} ppm^{-1} for forest fire plumes originated from Siberia near Lake Baikal and of 10 ± 5 μg m^{-3} ppm^{-1} for agricultural fire plumes [..[285]]originated from Kazakhstan and sampled over Alaska in April 2008, which are within the range of uncertainty of the $ER_{BC/CO} = 8.5 \pm 5.4$ μg m^{-3} ppm^{-1} obtained by Kondo et al. (2011) for the plumes originated from wildfires in the same geographical areas and sampled at an earlier stage of their evolution similar to the study of [..[286]][..[287]]Warneke et al. (2009).

The lowest $ER_{BC/CO} = 1.7 \pm 0.8$ μg m^{-3} ppm^{-1} was obtained by Kondo et al. (2011) for fresh smoldering fire plumes in Canada in summer 2008. The results of Kondo et al. (2011) for flaming ($ER_{BC/CO} = 3.4 \pm 1.6$ μg m^{-3} ppm^{-1}, MCE > 0.95) and mixed ($ER_{BC/CO} = 2.3 \pm 2.2$ μg m^{-3} ppm^{-1}, 0.90 < MCE < 0.95) fire plumes in North America are also lower than, or the bottom edge of, the standard uncertainties of the $ER_{BC/CO}$ from the present study. The highest $ER_{BC/CO} = 21.8 - 29.8$ μg m^{-3} ppm^{-1} published for agricultural fires in southern Russia are based on the measurements at the ground cite in central Siberia in April 2008 (Chi et al., 2013) and at the Mount Cimone (2165 m a.s.l.) station in Italy in May 2009 (Cristofanelli et al., 2013).

Chi et al. (2013) also provides an overall average $ER_{BC/CO} = 9.3$ μg m^{-3} ppm^{-1} (R^2 = 0.55) for winter air masses measured at the background cite in central Siberia since September 2006 till December 2011 that have been previously affected by anthropogenic emissions in south and south–west Siberia. While Chi et al. (2013) states that their $ER_{BC/CO}$ "is higher than values normally found at rural sites and even at the higher end of the literature range for cities in Asia", the provided value also falls within the range of published $ER_{BC/CO}$ estimates for forest fire plumes.

We should note that most of the $ER_{BC/CO}$ estimates considered above (Kondo et al., 2011; Warneke et al., 2009; Chi et al., 2013; Cristofanelli et al., 2013) are actually the enhancement ratios characterizing the enhancement above a background level of one compound relative to an other in a highly aged plume (of several days old) subjected to substantial dilution and physical or chemical processing. The enhancement ratio is obviously different from the emission ratio characterizing essentially the original chemical composition of an emission plume. Nevertheless, considering the extremely limited number of studies reporting BC and CO emissions from boreal wildfires, we decide to include all the available data into our comparison.

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[286] removed: Kondo et al. (2011). Chi et al. (2013) also provides overall average $ER_{BC/CO} = 9.3$

[287] removed: (R^2 = 0.55) for winter air masses measured at the background cite in central Siberia since September 2006 till December 2011 that have been previously affected by anthropogenic emissions in south and south–west Siberia. While Chi et al. (2013) states that their $ER_{BC/CO}$ "is higher than values normally found at rural sites and even at the higher end of the literature range for cities in Asia", the provided value also falls within the range of published $ER_{BC/CO}$ for forest fire plumes

For comparison with Andreae and Merlet (2001), we [..[288]]estimate the $ER_{BC/CO}$ of 5.6 ± 0.6 and 6.2 ± 1.2 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ for the F1-2 and F2-1 plume parts, respectively, which agree with the $ER_{BC/CO} = 5.2 \pm 2.5$ $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ derived from the above cited study.

Hence, the published ERs for particulate matter and black carbon from biomass fires in boreal regions vary in a broad range. The most probable reasons for such the strong variability are variations in combustion efficiency of the source fire (which seems to be higher for agricultural fires compared to forest fires) as well as variations in atmospheric dispersion and deposition conditions during the plume transport, as the effects of plume dilution and chemical aging increase [..[289]]with transport time (Kondo et al., 2011). Finally we conclude that the estimates [..[290]]$ER_{PM3/CO} = 320 - 385$ $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ and $ER_{BC/CO} = 6.1 - 6.3\ \mathrm{\mu g\,m^{-3}\,ppm^{-1}}$ reported in the present study fall into the middle of the range of the published estimates.

7 Conclusions

We [..[291]]analyze the time series of ground measurements of the near-surface [..[292]]air chemical composition in two Siberian boreal forest fire plumes to estimate the emission ratios for the primary biomass burning products. In both the plumes, a pronounced increase above the background concentrations of all the measured species [..[293]]is observed, with the excess levels of individual compounds well correlated with each other. [..[294]]Each plume transect is about 200 km long and located in [..[295]]the area affected by only very weak anthropogenic activity. The amount of the measurement data collected within the plumes proves to be sufficient for reliable statistical inference. Consequently, the derived ER estimates are found to be steady with respect to a particular choice of the regression model and robust to some amount of outliers arising in measurement data due to a range of sampling conditions. The analysis [..[296]]of MODIS active fire detections and HYSPLIT backward trajectories, acompanied 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.

We report the CO-based ERs for CH_4, NMHC, NO_X, PM_3, and BC, as well as CO to CO_2 ratios obtained from slopes of linear regression of the excess levels of the species calculated through three different approaches to quantify the effect that different assumptions on errors in the regresoin variables have on the final estimates. The derived [..[297]]gas ERs are

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[297] removed: ERs vary appreciably between and

generally stable within the plumes[..[298]], 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.

Between the plumes, the estimated gas ERs vary appreciably due to the changes in combustion processes manifested via changes in MCE. The high MCE $= 0.91 \pm 0.05$ observed in the F2 summer event probably indicates more intensive burning and flaming combustion compared to the MCE $= 0.87 \pm 0.04$ for the F1 autumn event which may be dominated by smoldering combustion process from fires of lower intensity according to the MODIS data. Consequently, the $ER_{CO/CO2}$ decreases by 35% and $ER_{NOx/CO}$ increases by 45% in the F2 plume compared to the F1 plume, since CO is the product of smoldering combustion while CO_2 and NO_X are the typical products of flaming combustion. The $ER_{CH4/CO}$ and $ER_{NMHC/CO}$ also increase from F1 to F2 plume by 18% and more than 35%, respectively, although the CH_4, [..[299]]NMHC and CO are the typical products of smoldering combustion. Such the increase in $ER_{CH4/CO}$ value can be explained by decrease in CO while the corresponding increase in $ER_{NMHC/CO}$ is probably associated with the accompanying changes in chemical composition of NMHC [..[300]]emissions as well. Compared to the gaseous ERs, variability of the gas-particle ERs is more affected the precision of the PM_3 and BC [..[301]]measurements, therefore we finally report only one $ER_{PM_3/CO}$ and $ER_{BC/CO}$ value with relatively high total uncertainty for each plume.

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 [..[302]]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. All the uncertainties are summed to represent the [..[303]]total variability of each ER estimate which comprises 5–15% of the reported $ER_{CH_4/CO}$, $ER_{NMHC/CO}$, and $ER_{PM_3/CO}$ [..[304]]values and 10–20% of the reported $ER_{NO_X/CO}$, ER_{CO/CO_2}, and $ER_{BC/CO}$ values. The resulting uncertainties are generally lower than those reported in many other similar studies. The reported ERs generally fall within the range of [..[305]]variability of the published estimates including those incorporated into some widely used wildfire emission models, [..[306]]although the ERs from the present study are higher compared to most of the previously published $ER_{CH_4/CO}$, $ER_{NMHC/CO}$, and $ER_{PM_3/CO}$ values and are much lower than most of the previous $ER_{NO_X/CO}$ values.

[298] removed: . The uncertainties of the derived estimates are associated with natural variability of the emissions (combustion phase), transformation of the originally emitted species during transport (photochemical loss of

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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 [..[307]]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 [..[308]]visual observations to attribute fire emissions to a specific combustion type [..[309]]since both flaming and smoldering typically occur simultaneously for naturally burning forest fires. More detailed analysis can not be conducted within the present study as the employed measurement data were not designed originally to study wildfire emissions and the plumes were measured by accident. Nevertheless, the scarcity of information about wildfires in southern Siberia encouraged us to publish the ER estimates with the available measurements which are unique in that sense.

Author contributions. A. Vasileva designed the study and prepared the manuscript. K. Moiseenko formulated the problem and took an active part in preparation of the manuscript. A. Skorokhod prepared and managed TROICA expeditions. I. Belikov prepared and supported the measurement instrumentation for TROICA expeditions. V. Kopeikin was completely responsible for the PM_3 and BC measurements during TROICA expeditions. O. Lavrova conducted the measurements and was responsible for diary observations during TROICA expeditions, contributing to the description of the analysed plume crossing episodes.

Acknowledgements. The authors thank Shumsky R. A. for an active participation in designing of the measurement set of the mobile laboratory and controlling its correct work. This study was supported by the Russian Science Foundation (grant no. 14-47-00049), by the Russian Foundation for Basic Research (grant no. 17-05-00245_A), and contributes to the Pan-Eurasian Experiment (PEEX) Program research agenda.

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Table 1. Two forest fire plumes observed during TROICA expeditions.

Plume ID	Date	UTC time (hh:mm)	Local time (hh:mm)	Latitude (deg)	Longitude (deg)
F1	9 October 2005	02:50–06:30	10:50–14:30	53.5	118.5–120.5
F2	1 August 2007	01:25–05:20	09:25–13:20	51.5	109.5–112.0

Table 2. Instruments used for trace gas and aerosol measurements in TROICA expeditions.

Specie	Model and manufacturer	Measurement method	Measurement range	Measurement uncertainty	Response time
CO_2	LI6262 (LICOR, USA)	non-dispersion infrared spectrometry	0.2–3000 ppmv	± 1 ppmv	10 s
CO	TE48S (Thermo Environmental Inc., USA)	non-dispersion infrared spectrometry	0.05–50 ppmv	± 0.01 ppmv	60 s
CH_4	APHA-360 (Horiba, Japan)	flame ionization	0.05–50 ppmv	± 1%	60 s
NMHC	APHA-360 (Horiba, Japan)	flame ionization with selective adsorption	0.05–50 ppmC	± 1%	60 s
NO, NO_2	TE42C-TL (Thermo Electron Corp., USA); M200AU (Teledyne API, USA)	chemiluminescence	0.05–200 ppbv	± 1%	60 s
PM_3	Grimm Dust Indicator [..[310]]1.411 (GRIMM Aerosol Technik GmbH & Co. KG)	90° scattering light nephelometry	0.01–15 $\mathrm{mg\,m^{-3}}$	±5%	10 s
BC	AE-16, (Magee Scientific, Berkeley, USA)	optical attenuation	$0.01 - 10^4$ $\mathrm{\mu g\,m^{-3}}$	± 20%	300 s

Table 3. Background levels of trace gases and aerosols outside the F1 and F2 plumes.

Plume ID	CO_2 (ppmv)	CO (ppmv)	CH_4 (ppmv)	NMHC (ppmC)	NO_X (ppbv)	PM_3 ($\mu g\,m^{-3}$)	BC ($\mu g\,m^{-3}$)
F1	390	0.15	1.900	0.250	1.2	20	1.0
F2	365	0.24	1.755	0.255	1.7	40	1.2

Table 4. Time intervals (plume parts) within F1 and F2 plumes used for the analysis of emission ratios.

Abbreviation	Date	Time (UTC)
F1–1	09 October 2005	02:50–04:00
F1–2	09 October 2005	04:35–06:30
F2–1	01 August 2007	01:25–03:40
F2–2	01 August 2007	03:40–05:20

Table 5. Average emission ratios (with standard uncertainties) estimated with linear regression and corresponding coefficients of correlation (R^2) for excess levels of trace gases and particles in F1 and F2 forest fire plumes.

	Emission ratios					
Plume part	CO / CO_2 (ppm ppm^{-1} in %)	CH_4 / CO (ppm ppm^{-1} in %)	NMHC / CO (ppmC $ppmC^{-1}$ in %)	NO_X / CO (ppb ppm^{-1})	PM_3 / CO ($\frac{ng\,m^{-3}}{\mu g\,m^{-3}}$)	BC / CO ($\mu g\ m^{-3}/ppm$)
F1–1	–	8.1 ± 0.4	11.5 ± 1.0	1.8 ± 0.3	385 ± 17	–
F1–2	15.2 ± 0.7	8.4 ± 0.5	12.4 ± 0.5	1.6 ± 0.3	337 ± 26	6.1 ± 0.6
F2–1	10.0 ± 0.6	9.7 ± 0.2	15.8 ± 0.6	2.8 ± 0.2	377 ± 24	6.3 ± 1.3
F2–2	[..[311]]–	9.9 ± 1.5	21.4 ± 1.0	3.1 ± 0.4	321 ± 20	–
	Coefficients of correlation					
F1–1	–	0.95	0.94	0.74	0.94	–
F1–2	0.94	0.94	0.97	0.76	0.95	0.94
F2–1	0.92	0.98	0.96	0.87	0.94	0.80
F2–2	[..[312]]–	0.83	0.94	0.81	0.89	–

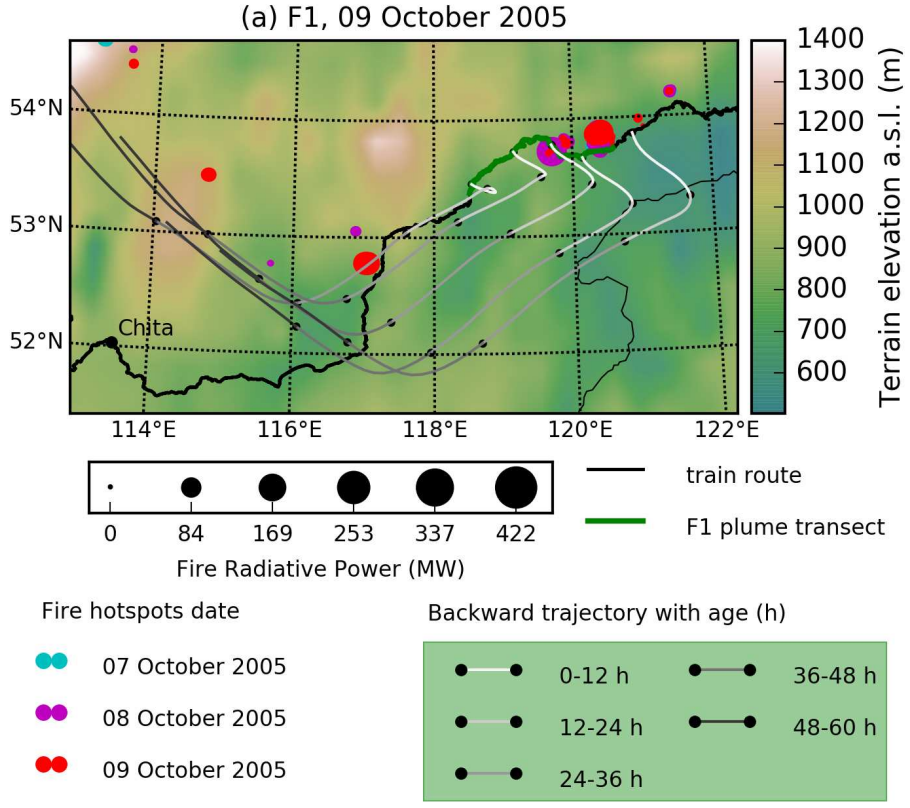


Figure 1. [..[313]]Map of [..[314]]the train route with the F1 plume transect location. [..[315]]The train course is from West to East. [..[316]]Circles show [..[317]]active fires detected by the MODIS satellite during the day of plume [..[318]][..[319]]observation and two days before that and are colored by date and sized by fire radiative power (FRP). Gray lines with open markers show the ensembles of [..[320]]HYSPLIT model backward air parcel trajectories started [..[321]]with hourly time increments along the train route within the plume and the time stamps coded by the number of hours before arrival of an air parcel at the point of observation. [..[322]]Chita is a town with population of 343 511 (Russian Government Statistical Service, 2016).[..[323]]

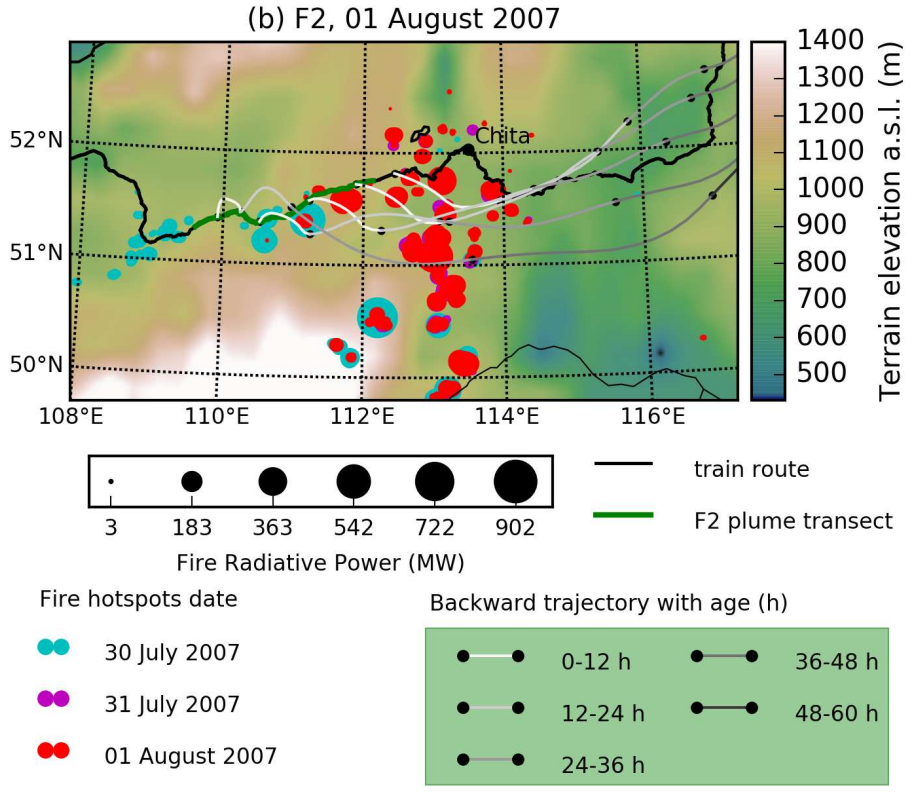


Figure 2. Same as Fig.[..[324]] 1 but for the F2 plume[..[325]]. The train course is from [..[326]]East to [..[327]]West.

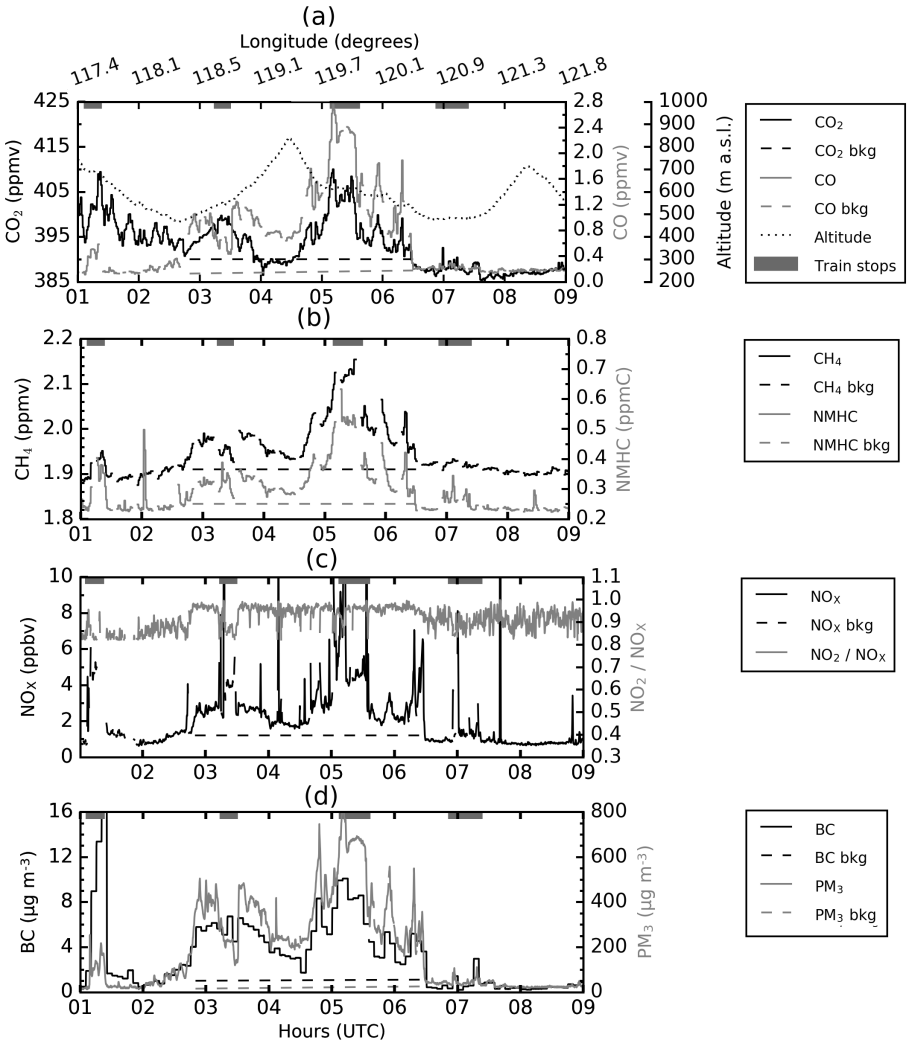


Figure 3. Measured 10 s trace gas mixing ratios and aerosol mass concentrations observed in vicinity of F1 forest fire plume during TROICA-09 expedition in 9 October 2005. Local time is UTC+8.

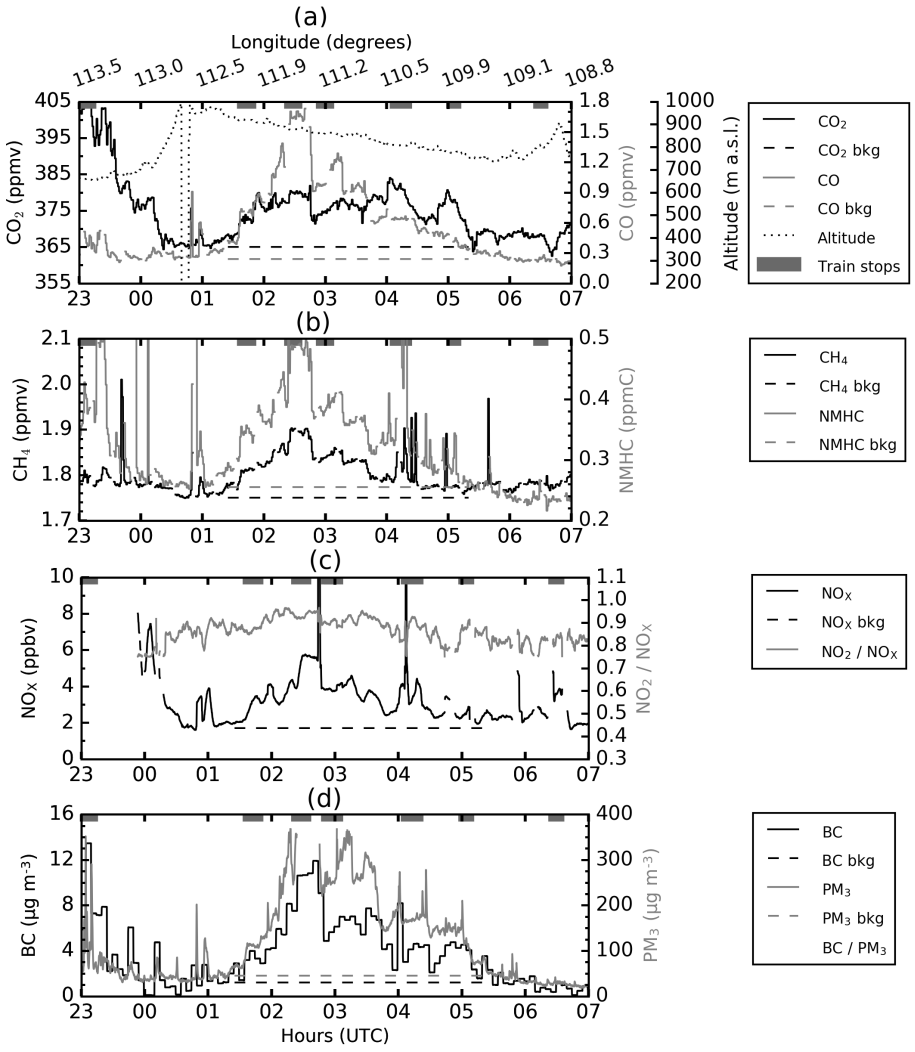


Figure 4. Measured 10 s trace gas mixing ratios and aerosol mass concentrations observed in vicinity of F2 forest fire plume during TROICA-11 expedition in 1 August 2007. Local time is UTC+8.

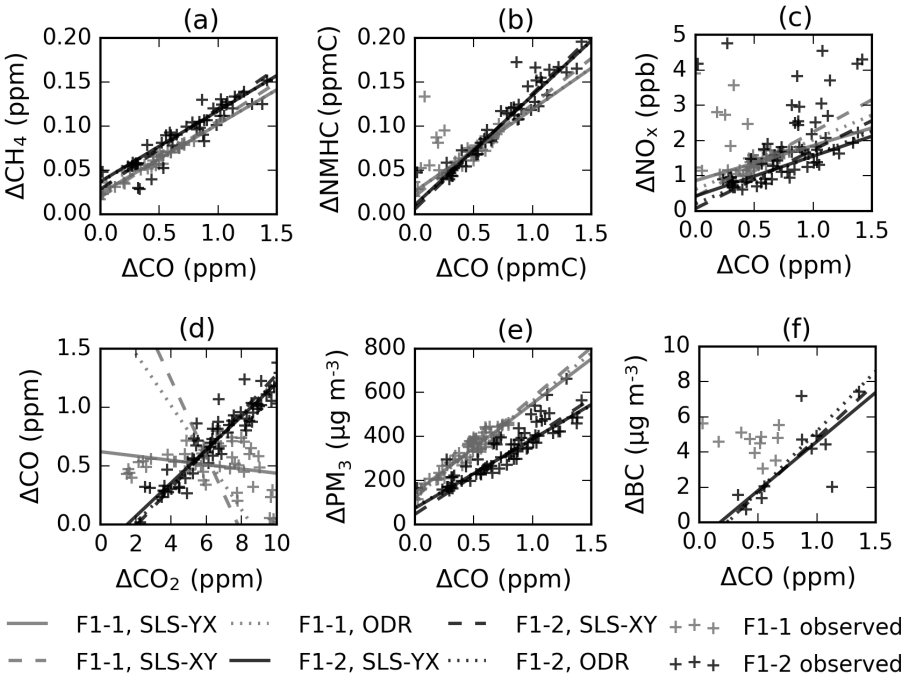


Figure 5. Excess levels of trace gases and particles versus excess mixing ratios of CO or CO_2 for F1 plume parts, with lines fitted to the data by different regression methods (see explanations in the text).

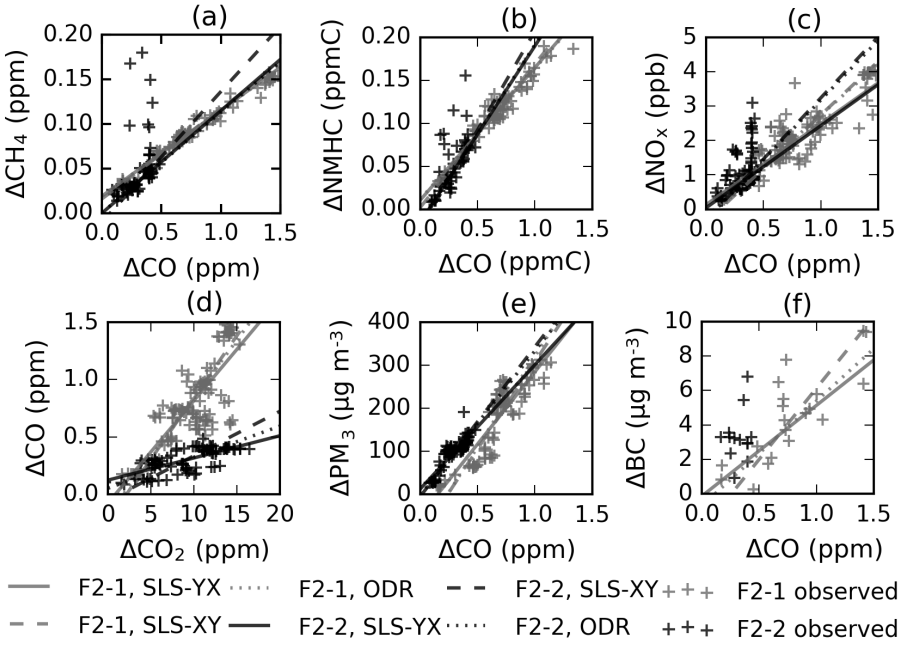
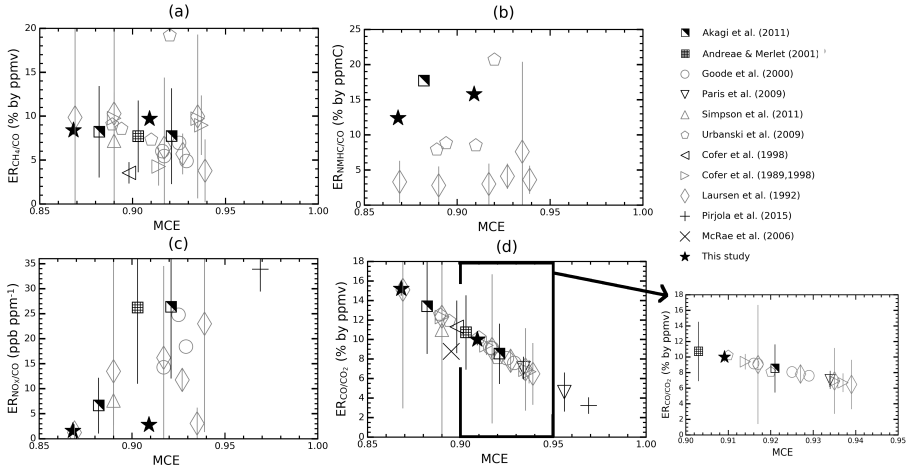


Figure 6. Same as Fig. 5 but for F2 plume parts.



[..328]

Figure 7. Scatter plots of trace gas $ER_{Y/X}$ with standard uncertainties (where available) versus MCE for this study and previous publications.

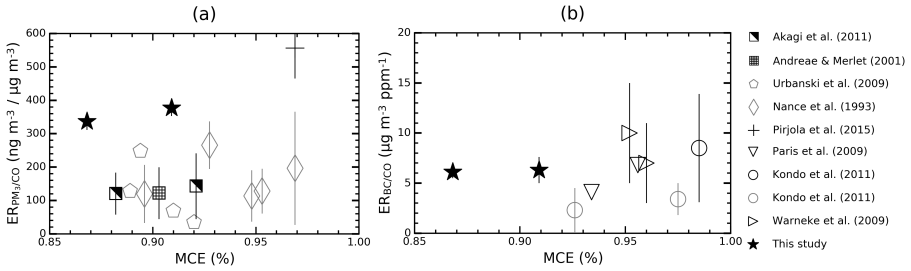


Figure 8. Scatter plots of particle $ER_{Y/X}$ with standard uncertainties (where available) versus MCE for this study and previous publications.