Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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

Anastasia Vasileva[1], Konstantin Moiseenko[1], Andrey Skorokhod[1], Igor Belikov[1], Vladimir Kopeikin[1], and Olga Lavrova[1,2]

[1]A.M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences, Moscow, 119017, Russia
[2]Russian Research Institute of Railway Transport, Moscow, 107996, Russia

Correspondence to: Anastasia Vasileva (av@ifaran.ru)

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 a lack of information about 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, with several assumptions, to calculate the mass of species emitted into the atmosphere due to combustion of a known mass of biomass fuel. We analyze observations of CO_2, CO, CH_4, total nonmethane hydrocarbons (NMHC), nitrogen oxides (as 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 $ER_{CO/CO_2} = 3-15\%$, $ER_{CH_4/CO} = 8-10\%$, $ER_{NMHC/CO} = 0.11-0.21\%$ ppmC ppmC^{-1}, $ER_{NO_X/CO} = 1.5-3.0$ ppb ppm^{-1}, $ER_{PM_3/CO} = 320-430$ $\frac{\text{ng m}^{-3}}{\mu\text{g m}^{-3}}$, 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 uncertainties are associated with natural factors as well as computational issues and comprise 5–15% of $ER_{CH_4/CO}$, $ER_{NMHC/CO}$ and $ER_{PM_3/CO}$ and 10–45% of $ER_{NO_X/CO}$, ER_{CO/CO_2} and $ER_{BC/CO}$, which is lower than in many other similar studies.

1 Introduction

Boreal forests and boreal climate zone, located within approximately 50–70°N, have became 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 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 of boreal forests with two-thirds of it attributed to Russia (Tchebakova et al., 1994; Shvidenko and Nilsson, 2003). Under predicted climate change scenarios, this terrestrial carbon may be released into the atmosphere in form of gases (mainly CO_2, CO, and CH_4) and particulate matter through different ways, including forest fires. Rapid release of large stocks of carbon into the atmosphere by biomass burning occurs during immediate combustion of organic matter as

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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 future, the frequency, severity and spread of boreal fires may increase in response to climate changes resulting in increase of atmospheric contamination by 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 wildfires in north Eurasia (mostly in Siberia) which are considered as 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).

Locally, forest fires during severe fire seasons may significantly affect regional air quality, decreasing visibility and causing respiratory problems (see for example Popovicheva et al. (2014) and references therein) and make a noticeable contribution into regional air pollution (Cheng et al., 1998; Wotawa and Trainer, 2000). In remote regions, emissions (local or transported) from boreal forest fires may 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 oxidation capacity via chains of chemical reactions with OH^- radicals (Seinfeld and Pandis, 1997; Stockwell et al., 2012), and disturb background chemistry of the atmosphere in the regions (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 is 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 on the basis of 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, Canada and Alaska as a result of large scale transport of biomass burning products (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 depends on many factors and may vary 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 deteriorate seriously the air quality in Europe under suitable meteorological conditions (Saarikoski et al., 2007) and contribute to the Arctic Haze events (Stohl, 2006; Stohl et al., 2007; Cubison et al., 2008; Warneke et al., 2009, 2010) changing radiation budget of the earth surface and 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 may have important effect on energy exchange in the Arctic (Hansen and Nazarenko, 2004; Kim et al., 2005). According to Generoso et al. (2007), Russian biomass fires in an extreme fire year 2003 contributed about 40–56% of the total BC mass deposited north of 75ºN.

The ability of aerosol particles to act as a cloud condensation nuclei causes modifications of the microphysical and optical properties of clouds, changes cloud lifetime and precipitation patterns (see references in Langmann et al. (2009)).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

In all these problems, accurate estimation of the amount of carbon released from biomass fires into the atmosphere in form of gases and particles is important and requires knowledge about emission factors (mass of a specie emitted per unit mass of fuel burned) or emission ratios (amount of species 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 of emission ratios (ERs) which may be converted, when necessary, into emission factors (EFs) using 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 more reliable estimates of ERs.

Despite the growing scientific attention to biomass fires in boreal zone, data from direct observations in Siberian ecosystems is still very limited (Cofer et al., 1998; McRae et al., 2006; Paris et al., 2009). The results presented in this paper are based on 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 complex constructed 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 roughly 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 TROICA-9 and TROICA-11 expeditions were used earlier in substantial amount of studies (see for example (Kuokka et al., 2007; Vartiainen et al., 2007; Berezina et al., 2014)) as they provide a unique insight into the spatial distribution of various pollutants in the near-ground atmosphere and atmospheric 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 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 during warm seasons which start early in spring due to exceptionally dry weather conditions (Sukhinin et al., 2004; Vivchar et al., 2010; Vivchar, 2011; Giglio et al., 2013; van der Werf et al., 2010). The latitudes of observation (51–53°N) approximately correspond to the southern border of the boreal forest zone. During the plume crossing episodes the train route passed through hills and 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 are widely spread in the midlatitudes of Eurasia (Klochko and Romanovskaya, 2004).

The F1 and F2 plume crossing events were about 200 km long. True color MODIS images from Terra satellite shown in Fig. 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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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 and F2 plumes represent mixtures of emissions from several adjacent fires of the type similar to that observed by the operator.

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). Possible origins of the air sampled within the plumes are shown in Fig. 2 with ensembles of HYSPLIT model five-day backward three-dimensional Lagrangian air parcel trajectories started from 300 $\mathrm{m\,a.g.l.}$ at geographical locations along the railway with 1 h time intervals covering the total time duration of the plume crossing events (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 (this results in 27 ensemble members for all possible shifts) to assess a combined impact of various uncertainties on backward trajectory calculations (Stohl, 1998).

Calculation of ERs in the F1 and F2 events requires correct assessment of atmospheric background concentrations of analyzed species which are used commonly as reference levels in the regression analysis of the measurement data. Previous studies of fire plume events in remote Siberia based on the continuous CO measurements at ZOTTO Tall Tower suggest an appreciable anthropogenic signal 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 CO and $\mathrm{CH_4}$ and, therefore, must be discriminated against the true wildfire signal for correct interpretation of the measurements data (Vasileva et al., 2011; Chi et al., 2013). Visual inspection of backward trajectories (Fig. 2) suggests the air sampled within F2 plume could spend more time over territories near the railway with both wildfire and appreciable anthropogenic activity. This may explain elevated background levels of CO, NMHC, $\mathrm{NO_X}$, $\mathrm{PM_3}$ and BC outside F2 plume compared to the F1 plume (see Table 3 in the next section). The Fig. 1b also suggests that elevated levels of the measured species beyond the area directly affected by F2 plume are probably associated with patches of wildfire contaminated air, so we use only the measurements from upwind side of F2 plume affected area to setup reference state species concentrations for this event. In the F1 event, the whole set of measurements immediately outside the area affected by the fire plume was used to setup the reference state concentration levels, as there were no significant nearby anthropogenic sources affecting the measured air in this event.

The $\mathrm{CO_2}$ and $\mathrm{CH_4}$ are the long-lived atmospheric constituents with high background levels that are presumably less disturbed by local and regional emissions. Meanwhile, pronounced diurnal cycles of $\mathrm{CO_2}$ and $\mathrm{CH_4}$ 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 $\mathrm{CH_4}$ 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 $\mathrm{CO_2}$ was negligible within F2 plume which was observed in daytime well after the breakdown of the inversion, but appeared to be important within F1 plume, therefore we discarded a part of the measurements in that case.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

During the fire plume observations, air temperature and humidity measured from the lab carriage were 6–12°C and 40–55% for F1 plume, and 24–29°C and 30–50% for F2. The weak winds of 0.3–0.5 $\mathrm{m \cdot s^{-1}}$, 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 and 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 $\mathrm{NO_X}$ as well as transformation and removal of aerosol particles 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.

3 Measurements and instrumentation

The key characteristics of the measurement instruments used in TROICA campaigns are listed in Table 2 where $\mathrm{PM_3}$ are particles with aerodynamic diameters less than $3 \cdot 10^{-6}$ m. Methane and NMHC were measured with a single flame ionization detector, with separation of NMHC by selective absorber. The NMHC mixing ratios were measured in parts per million by carbon (ppmC) while mixing ratios of other gases were measured in parts per million (ppmv or ppm) or parts per billion (ppbv or ppb) by volume. Nitrogen oxides were measured with TE42C-TL (TROICA-9) and M200AU (TROICA-11) instruments which register chemiluminescent radiation from reaction of NO with $\mathrm{O_3}$, with catalytic conversion of $\mathrm{NO_2}$ to NO.

All the measurements within the TROICA campaigns 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. 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). No systematic influence of the train speed on the trace gas and aerosol observations was revealed in the present study as well as by 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 $\mathrm{PM_3}$ concentrations over 60 s intervals for subsequent analysis. The BC concentrations were averaged over 300 s intervals. 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.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

4 Methods of data analysis

The emission ratio 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. 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 a choice in our study was found to be 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, as well as the ratios of aerosol mass concentrations to CO volume mixing ratios 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.

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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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), 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 will be 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 measurements $(X_i,\ Y_i)$ 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 and the measurement uncertainties from Table 2 summed in quadrature.

Trial calculations does 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 resulting 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):

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

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

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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

where $(ER_k, \delta ER_k)$ for $k = 1, 2, 3$ are the model slopes and their uncertainties estimated with three different approaches described above, and $n = 3$ is the number of the approaches used in this study. The implemented method provides a conservative estimate of δER_{avg} as far as covariances among the three algorithms are neglected.

For comparison with other studies, conversion of units is performed, when necessary, with the data provided in original publications. Specifically, the 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 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 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 photochemical efficiency via thermal and photochemical processes leading to the formation of oxidation products and ozone (Friedli et al., 2001). Thus, more heavy and "photochemically efficient" NMHC compounds contribute more to the $ER_{NMHC/CO}$ reported in the present study.

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

The EFs for particulate matter and BC are converted into ERs ($\frac{\text{ng m}^{-3}}{\mu\text{g m}^{-3}}$) by dividing EF_{PM3} or EF_{BC} 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 (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 (ng m^{-3}) is the excess mass concentration of X in biomass burning plume, and C_T (µg m^{-3}) is 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 a relation $\frac{EF_Y}{EF_X} = \frac{C_Y}{C_X} = ER_{Y/X}$.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

5 Results and discussion

Time series of gas mixing ratios and particle mass concentrations measured within F1 and F2 forest fire plumes are shown at Fig. 3–4 along with the estimated background levels of the measured species. The NO_2/NO_X ratio is shown at Fig. 3c and 4c as an indicator of a "photochemical state" of the plumes. One can see substantial increases in CO, NMHC and NO_X mixing ratios and aerosol concentrations within F1 and F2 plumes compared to those in the ambient air. For long-lived gases CO_2 and 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. 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.

It can be seen from Fig. 3c 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 boreal forest fire plumes, which is probably due to rapid NO to NO_2 conversion by 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 contamination was suppressed through additional filtering of the original data based on some characteristic chemical signatures of the air subjected to local anthropogenic contamination. Namely, data samples with $\Delta CO > 1.3$ ppm for both the plumes, as well as with $\Delta NO_X > 2.5$ ppb and $NO_2/NO_X < 0.82$ for F1 and $\Delta NO_X > 3$ ppb and $NO_2/NO_X < 0.75$ for F2, were excluded from the analysis.

Fig. 3 shows a distinct decrease in all excess mixing ratios and mass concentrations during ascend of the railway from 550 to 800 m a.g.l. Changing elevation does not affect significantly CO-based ERs (Fig. 5) but lead to dramatic decrease in $ER_{CO/CO2}$ and rate of correlation between CO and CO_2. The latter may be due to incomplete vertical mixing of the CO_2 accumulated during nighttime which is difficult to account for in the present study. Therefore, we simply discard CO_2 observations within F1 plume made during the 02:50–04:35 UTC railway ascend.

Scatter plots of excess trace gas and aerosol levels versus excess mixing ratios of CO and CO_2 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 each of the F1 and F2 plume crossing episodes into two consequent time intervals (parts, see Table 4) according to the differences in $\Delta CO/\Delta CO_2$ ratios (discussed later in this section) seen in Fig. 5d and 6d.

The final estimates of ERs values (ER_{avg}) and corresponding standard deviations ($(\delta ER)_{avg}$) calculated with formulas (3)–(5) for each plume part from Table 4 are shown in Table 5. Here, three sources of uncertainty in the derived estimates are considered: internal variability of the measurements data with the uncertainties ($\delta ER_1, \delta ER_2, \delta ER_3$) estimated within the regression algorithms, 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 F1 and F2 plumes as well as within each plume. All the uncertainties in Table 5 represent the range of possible variability of the ER estimates at 68% level of confidence assuming normal distribution of the ERs around the estimated values which is typical for all studies reporting ER or EF estimates.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

The corresponding coefficients of correlation R^2 between various X and Y variables are shown in Table 6. The R^2 are high for both trace gas ($R^2 > 0.7$) and gas–particle ($R^2 > 0.5$) correlations, although a limited number of outliers persist for each particular data group with the largest scattering observed for NO_X vs. CO and BC vs. CO 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. T

From Table 5 one can see that estimated average $ER_{CO/CO2}$ is $15.2 \pm 0.7\%$ (MCE $= 0.87 \pm 0.04$) for F1-2 plume and varies from $10.0 \pm 0.6\%$ (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 about 5% of the 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 $ER_{CO/CO2}$ 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 measurements suggest a noticeable contribution from flaming combustion in the F2-2 plume part. As it follows from the laboratory study of Yokelson et al. (1996), estimated MCE $= 0.91$ suggests that a mixture of emissions from flaming and smoldering combustion was sampled within the F2-1 plume part, while MCE $= 0.87$ for F1-2 indicates the dominance of smoldering. In the studies of real wildfires (see Ward et al. (1992), Cofer et al. (1998) and Pirjola et al. (2015) for example) the relationship between the combustion type and MCE may not be so explicit. Yet, admitting insufficient amount of a priori information, we retain hereafter the terms "smoldering", "mixed", and "flaming" 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.

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

Estimated average $ER_{NMHC/CO}$ increases with increasing MCE, from 0.11–0.12 $\mathrm{ppmC\ ppmC^{-1}}$ for F1 plume to 0.16–0.21 $\mathrm{ppmC\ ppmC^{-1}}$ for F2 plume, with the uncertainties of 4–9% coming mainly from variability of the measurement data. The observed increase of $ER_{NMHC/CO}$ is probably due to decrease in ΔCO because 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;

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

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.

Estimated $ER_{NOx/CO}$ are about 1.7 $\mathrm{ppb\ ppm^{-1}}$ for F1 and 3.0 $\mathrm{ppb\ ppm^{-1}}$ for F2 plume, with the uncertainties up to 10–20% of the ERs coming mainly from the scattering of the measurement data whereas differences among the ERs obtained with each particular regression method are relatively small. The increase in $ER_{NOx/CO}$ with increasing MCE in F1 and F2 plumes is consistent with the laboratory study of Yokelson et al. (1996) although, as mentioned above, this relationship is not always observed in real wildfires (Laursen et al., 1992). Higher variability of $ER_{NOx/CO}$ compared to ERs for other gases in our study can be explained by higher variability in wildfire emissions which generally 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 the 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 middle latitudes (Seinfeld and Pandis, 1997). Nevertheless, the estimated average $ER_{NOx/CO}$ are very stable within each plume. Noting rather short (less than a day) transport time of the emissions in F1 and F2 plumes, the derived estimates of $ER_{NOx/CO}$ may be safely considered as reliable characteristics of fresh boreal wildfire emissions with negligible average effect of chemical transformations.

Estimated $ER_{PM3/CO}$ varies within 320–430 $\frac{\mathrm{ng\ m^{-3}}}{\mathrm{\mu g\ m^{-3}}}$ with the uncertainties of 4–8% of the ERs coming mainly from the variability in the measurements. Estimated $ER_{BC/CO}$ for the two plumes is about 6.2 $\mathrm{\mu g\ m^{-3}\ ppm^{-1}}$ with the uncertainties up to 20% coming equally from differences among the regression slopes as well as from the standard uncertainties in the slopes. Additional factor 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 $ER_{BC/CO}$ seem to reflect correctly the linear dependencies between BC and CO seen in Fig. 5f and 6f.

6 Comparison with other published results

6.1 Gases

The derived ERs of trace gases are compared against other published estimates for boreal forest fires (Fig. 8). It should be noted that most of 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 ER_{CO/CO_2} 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 less than 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 2009. The burning area of about 0.8 ha contained predominantly slash (64%) and humus-layer (32%), with surface vegetation composing only

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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 and 6d), whereas peak ΔCO values of 1–4 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 (same as for the F2-2 plume part in the present study) 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 unusually high $ER_{CO/CO2} = 11.3 \pm 2.7\%$ (MCE = 0.90) from vigorous crowning (flaming) stages of an experimental fire in Siberia (Bor Island, 60°45'N, 89°25'E; 50 ha of live 20 m high pine forest burned in July 1993, with fresh smoke measured from helicopter) which is comparable to the $ER_{CO/CO2} = 9.4 \pm 1.0\%$ for flaming wildfires in Canada and $ER_{CO/CO2} = 12.3 \pm 1.9\%$ for smoldering boreal logging slash fires in North America, but vastly exceeds $ER_{CO/CO2} = 6.7 \pm 1.2\%$ 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 via MCE 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) $ER_{CO/CO2} = 10.0 \pm 0.6\%$ from the present study.

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 ΔCO = 0.1 ppm and ΔCO_2 = 5 ppm (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 CO to CO_2 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.

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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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).

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). Most of the $ER_{CO/CO2}$ in Fig. 8d are 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 three estimates obtained from helicopter (Cofer et al., 1998; McRae et al., 2006) and ground (this study) observations in Siberia. There are also three outliers not shown in Fig. 8 corresponding to $ER_{CO/CO2} = 18 - 34\%$ and MCE = 0.85–0.75 related to emissions from smoldering wildfires in North America and Siberia (Cofer et al., 1998; Kondo et al., 2011). The $ER_{CO/CO2}$ estimates from the present study for "mixed" and "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.

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 GFED4.1 utilized in the present study as well (Fig. 2). Although Andreae and Merlet (2001) provides 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 $50 - 70°$) and "temperate forest" (TEMF). One can see from Fig. 8d 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" $ER_{CO/CO2} = 15.2 \pm 0.7\%$ from the present study, while $ER_{CO/CO2} = 8.5 \pm 3.1\%$ for TEMF is close to the "mixed" $ER_{CO/CO2} = 10.0 \pm 0.6\%$. 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. 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).

The $ER_{CH4/CO} = 8 - 10\%$ reported in this study are at the top of the published range (Fig. 8a) 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 the 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 $ER_{CH4/CO}$ of $3.8 \pm 3.6\%$ and $4.3 \pm 2.2\%$ for two fires in Canada (Laursen et al., 1992; Cofer et al.,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

1998). The relationship between $ER_{CH4/CO}$ and MCE is not evident in Fig. 8a. All the $ER_{CH4/CO}$ from the present study lay within the range of uncertainties of $ER_{CH4/CO} = 7.7 - 8.2\%$ 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 is 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 $ER_{NMHC/CO} = 0.21$ ppmC ppmC^{-1} for forest fire in Alaska from Urbanski et al. (2009). In the middle of the range are $ER_{NMHC/CO} = 0.08-0.09$ ppmC ppmC^{-1} derived from 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. 8b 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. 8b are $ER_{NMHC/CO} = 0.03-0.08$ ppmC ppmC^{-1} derived from 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 of the $ER_{NMHC/CO}$ estimates are associated with natural variability of biomass burning emissions of individual NMHC compounds, chemical transformations of the compounds during the plume transport (see Friedli et al. (2001) and references wherein), as well as with differences among the measurement techniques (Rasmussen et al., 1974).

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 $ER_{CH4/CO}$ 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}, with the uncertainties exceeding 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 $ER_{NOx/CO} = 7.6 \pm 4.9$ ppb ppm^{-1} 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. 8c is $ER_{NOx/CO} = 33.9 \pm 4.5$ 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 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}. 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 a 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, in contrast with $ER_{CH4/CO}$ and $ER_{NMHC/CO}$, the $ER_{NOx/CO}$ from different studies seems to increase with MCE thus supporting the assumption that NO_X and a group of CO, CH_4, and NMHC compounds are emitted from different (flaming for NO_X and smoldering for the others) combustion processes.

Note that the uncertainties in the ERs (where available) shown in Fig. 8 can be as large as 50–150% and more and represent natural variability of the emissions within a single fire event (Laursen et al., 1992), variability between different fires in a region (Cofer et al., 1998; Kondo et al., 2011; Simpson et al., 2011), variability of the measurements due to chemical transformation of measured compounds (NO_x, NMHC) during the plume transport, as well as the uncertainties associated with measurement technique (as in the case of NMHC) and data analysis.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

6.2 Aerosols

There are only a limited amount of the published data 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 $2.5-3.5\cdot10^{-6}$ 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 (Reid et al., 2005; Akagi et al., 2011; Pirjola et al., 2015; Popovicheva et al., 2015).

The $ER_{PM3/CO} = 320-430$ $\frac{ng\,m^{-3}}{\mu g\,m^{-3}}$ (Fig. 9a) 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 $ER_{PM3/CO} = 196-265$ $\frac{ng\,m^{-3}}{\mu g\,m^{-3}}$ estimated for three forest fires in Canada (Ontario and British Columbia) and Alaska (Nance et al., 1993; Urbanski et al., 2009). The $ER_{PM2.5/CO} = 122-143$ $\frac{ng\,m^{-3}}{\mu g\,m^{-3}}$ from Akagi et al. (2011) and Andreae and Merlet (2001), as well as the $ER_{PM2.5/CO} = 35-130$ $\frac{ng\,m^{-3}}{\mu g\,m^{-3}}$ 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 $ER_{PM2.5/CO} = 557\pm92$ $\frac{ng\,m^{-3}}{\mu g\,m^{-3}}$ 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 $ER_{BC/CO} = 6.2\pm1.3$ $\mu g\,m^{-3}\,ppm^{-1}$ from the present study falls within the range of uncertainty of the previous estimates (Fig. 9b). So far the authors know only two studies reporting BC ERs for plumes sampled less than a day after emissions. Paris et al. (2009) reports $ER_{BC/CO}$ of 4.1 and 6.8 $\mu g\,m^{-3}\,ppm^{-1}$ for two forest fires in Siberia, which are within double standard uncertainties of the ERs from the present study. Chi et al. (2013) estimated $ER_{BC/CO} = 10$ $\mu g\,m^{-3}\,ppm^{-1}$ (not shown at Fig. 9b because of the lack of an MCE estimate) for forest fires in West Siberia in July 2007, some of which were located very close to the ground measurements cite. The other studies report BC ERs for plumes of several days old. For example, Warneke et al. (2009) provides $ER_{BC/CO}$ of 7 ± 4 $\mu g\,m^{-3}\,ppm^{-1}$ for forest fire plumes from Siberia near Lake Baikal and of 10 ± 5 $\mu g\,m^{-3}\,ppm^{-1}$ for agricultural fire plumes from Kazakhstan sampled over Alaska in April 2008, which are within the range of uncertainty of the $ER_{BC/CO} = 8.5\pm5.4$ $\mu g\,m^{-3}\,ppm^{-1}$ 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 Kondo et al. (2011). Chi et al. (2013) also provides overall average $ER_{BC/CO} = 9.3$ $\mu g\,m^{-3}\,ppm^{-1}$ (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 $ER_{BC/CO}$ for forest fire plumes.

The lowest $ER_{BC/CO} = 1.7\pm0.8$ $\mu g\,m^{-3}\,ppm^{-1}$ was obtained by Kondo et al. (2011) for smoldering fire plumes in Canada in summer 2008. The results of Kondo et al. (2011) for flaming ($ER_{BC/CO} = 3.4\pm1.6$ $\mu g\,m^{-3}\,ppm^{-1}$, MCE > 0.95) and mixed ($ER_{BC/CO} = 2.3\pm2.2$ $\mu g\,m^{-3}\,ppm^{-1}$, 0.90 < MCE < 0.95) fire plumes in North America are also lower than, or the bottom edge of, standard uncertainties of the $ER_{BC/CO}$ from the present study. The highest $ER_{BC/CO} = 21.8-29.8$ $\mu g\,m^{-3}\,ppm^{-1}$ published for agricultural fires in southern Russia are based on the measurements at the ground cite

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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).

For comparison with Andreae and Merlet (2001), we estimated $ER_{BC/CO}$ of 5.6 ± 0.6 and 6.2 ± 1.2 $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ for F1-2 and F2-1 plume parts, respectively, which agree with $ER_{BC/CO} = 5.2 \pm 2.5$ $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ 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 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 rapidly with transport time. Finally we conclude that the estimates $ER_{PM3/CO} = 320 - 430$ $\frac{\mathrm{ng\,m^{-3}}}{\mathrm{\mu g\,m^{-3}}}$ 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 analysed time series of ground measurements of near-surface chemical air composition in two Siberian forest fire plumes to estimate emission ratios for the primary biomass burning products. In both the plumes, pronounced increase above background concentrations of all the measured species was observed with excess levels of individual compounds well correlated with each other. The plume transects were about 200 km long and located in areas with minor anthropogenic activity. The amount of 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 suggested that the measured smoke was a mixture of emissions from several fires with transport time from the sources of less than a day.

We report 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 through three different approaches. The derived ERs vary appreciably between and within the plumes. 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 NO_X, oxidation of NMHC, and wet deposition of PM_3 and BC), as well as with the choice of the regression method as different assumptions on independent variables inevitably affect the final statistical inference. All the uncertainties are summed to represent the overall uncertainty of each ER estimate which comprises 5–15% of $ER_{CH_4/CO}$, $ER_{NMHC/CO}$ and $ER_{PM_3/CO}$ and 10–45% for $ER_{NO_X/CO}$, ER_{CO/CO_2}, and $ER_{BC/CO}$. The resulting uncertainties are generally lower than those reported in many other similar studies. The reported ERs generally fall within the range of uncertainty of the previous estimates including those incorporated into widely used wildfire emission models, notwithstanding the fact that the ERs from the present study are higher compared to most of the previously published $ER_{CH_4/CO}$, $ER_{NMHC/CO}$, and $ER_{PM_3/CO}$ and are much lower than most of the previous $ER_{NO_X/CO}$.

The authors did not find any definite relation between the observed combustion type (smoldering or flaming) and MCE neither in this study nor in the previous ones. Thus, we are cautious in using MCE to attribute fire emissions to a specific com-

bustion type as previous studies show marked discrepancy between the classification based on MCE and visual observations made during the measurement experiments. 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.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

References

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039–4072, doi:10.5194/acp-11-4039-2011, 2011.

Alvarado, M. J. and Prinn, R. G.: Formation of ozone and growth of aerosols in young smoke plumes from biomass burning: 1. Lagrangian parcel studies, J. Geophys. Res., 114, D09 306, doi:10.1029/2008JD011144, 2009.

Amiro, B. D., Cantin, A., Flannigan, M. D., and de Groot, W. J.: Future emissions from Canadian boreal forest fires, Can. J. Forest Res., 39, 383–395, doi:10.1139/X08-154, 2009.

Anderson, E., Bai, Z., Bischof, C., Blackford, L. S., Demmel, J., Dongarra, J. J., Du Croz, J., Hammarling, S., Greenbaum, A., McKenney, A., and Sorensen, D.: LAPACK Users' Guide, Society for Industrial and Applied Mathematics, Philadelphia, PA, USA, third edn., 1999.

Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochem. Cy., 15, 955–966, doi:10.1029/2000GB001382, 2001.

Arnold, S. R., Emmons, L. K., Monks, S. A., Law, K. S., Ridley, D. A., Turquety, S., Tilmes, S., Thomas, J. L., Bouarar, I., Flemming, J., Huijnen, V., Mao, J., Duncan, B. N., Steenrod, S., Yoshida, Y., Langner, J., and Long, Y.: Biomass burning influence on high-latitude tropospheric ozone and reactive nitrogen in summer 2008: a multi-model analysis based on POLMIP simulations, Atmos. Chem. Phys., 15, 6047–6068, doi:10.5194/acp-15-6047-2015, 2015.

Balshi, M. S., McGuire, A. D., Zhuang, Q., Melillo, J., Kicklighter, D. W., Kasischke, E., Wirth, C., Flannigan, M., Harden, J., Clein, J. S., Burnside, T. J., McAllister, J., Kurz, W. A., Apps, M., and Shvidenko, A.: The role of historical fire disturbance in the carbon dynamics of the pan-boreal region: a process-based analysis, J. Geophys. Res.-Biogeo., 112, G02 029, doi:10.1029/2006JG000380, 2007.

Belikov, I. B., Brenninkmaier, K. A. M., Elansky, N. F., and Ral'ko, A. A.: Methane, carbon monoxide, and carbon dioxide concentrations measured in the atmospheric surface layer over continental Russia in the TROICA experiments, Izv. AN Fiz. Atmos. Ok+, 42, 46–59, doi:10.1134/S000143380601004X, 2006.

Bell, S.: A beginner's guide to uncertainty of measurement, Measurement Good Practice Guide, 11, 1–33, 1999.

Berezina, E. V., Elansky, N. F., Moiseenko, K. B., Safronov, A. N., Skorokhod, A. I., Lavrova, O. V., Belikov, I. B., and Shumsky, R. A.: Estimation of biogenic CH_4 and CO_2 emissions and dry deposition of O_3 using ^{222}Rn measurements in TROICA expeditions, Izv. AN Fiz. Atmos. Ok+, 50, 583–594, doi:10.1134/S000143381406005X, 2014.

Bertschi, I. T. and Jaffe, D. A.: Long-range transport of ozone, carbon monoxide, and aerosols to the NE Pacific troposphere during the summer of 2003: Observations of smoke plumes from Asian boreal fires, J. Geophys. Res.-Atmos., 110, D05 303, doi:10.1029/2004JD005135, 2005.

Bertschi, I. T., Jaffe, D. A., Jaeglé, L., Price, H. U., and Dennison, J. B.: PHOBEA/ITCT 2002 airborne observations of transpacific transport of ozone, CO, volatile organic compounds, and aerosols to the northeast Pacific: Impacts of Asian anthropogenic and Siberian boreal fire emissions, J. Geophys. Res.-Atmos., 109, D23S12, doi:10.1029/2003JD004328, 2004.

Boggs, P. T. and Rogers, J. E.: Orthogonal Distance Regression, in: Contemporary Mathematics: Statistical Analysis of Measurement Error Models and Applications, edited by Brown, P. J. and Fuller, W. A., pp. 183–194, American Mathematical Society, Providence, RI, USA, doi:10.1090/conm/112, 1990.

Bossioli, E., Tombrou, M., Karali, A., Dandou, A., Paronis, D., , and Sofiev, M.: Ozone production from the interaction of wildfire and biogenic emissions: a case study in Russia during spring 2006, Atmos. Chem. Phys., 12, 7931–7953, doi:10.5194/acp-12-7931-2012, 2012.

Burling, I. R., Yokelson, R. J., Akagi, S. K., Urbanski, S. P., Wold, C. E., Griffith, D. W. T., Johnson, T. J., Reardon, J., and Weise, D. R.: Airborne and ground-based measurements of the trace gases and particles emitted by prescribed fires in the United States, Atmos. Chem. Phys., 11, 12 197–12 216, doi:10.5194/acp-11-12197-2011, 2011.

Cahoon, D. R., Stocks, B. J., Levine, J. S., Cofer, W. R., and Pierson, J. M.: Satellite analysis of the severe 1987 forest fires in northern China and southeastern Siberia, J. Geophys. Res.-Atmos., 99, 18 627–18 638, doi:10.1029/94JD01024, 1994.

Cantrell, C. A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmos. Chem. Phys., 8, 5477–5487, doi:10.5194/acp-8-5477-2008, 2008.

Cheng, L., McDonald, K. M., Angle, R. P., and Sandhu, H. S.: Forest fire enhanced photochemical air pollution. A case study., Atmos. Environ., 32, 673–681, 1998.

Chi, X., Winderlich, J., Mayer, J.-C., Panov, A. V., Heimann, M., Birmili, W., Heintzenberg, J., Cheng, Y., and Andreae, M. O.: Long-term measurements of aerosol and carbon monoxide at the ZOTTO tall tower to characterize polluted and pristine air in the Siberian taiga, Atmos. Chem. Phys., 13, 12 271–12 298, doi:10.5194/acp-13-12271-2013, 2013.

Cofer, W. R., Levine, J. S., Sebacher, D. I., Winstead, E. L., Riggan, P. J., Stocks, B. J., Brass, J. A., Ambrosia, V. G., and Boston, P. J.: Trace gas emissions from chaparral and boreal forest fires, J. Geophys. Res.-Atmos., 94, 2255–2259, doi:10.1029/JD094iD02p02255, 1989.

Cofer, W. R., Winstead, E. L., Stocks, B., Goldammer, J. G., and Cahoon, D. R.: Crown fire emissions of CO_2, CO, H_2, CH_4, and TNMHC from a dense Jack pine boreal forest fire, Geophys. Res. Lett., 25, 3919–3922, doi:10.1029/1998GL900042, 1998.

Conny, J. M. and Slater, J. F.: Black carbon and organic carbon in aerosol particles from crown fires in the Canadian boreal forest, J. Geophys. Res.-Atmos., 107, AAC 4–1–AAC 4–12, doi:10.1029/2001JD001528, 2002.

Cristofanelli, P., Fierli, F., Marinoni, A., Calzolari, F., Duchi, R., Burkhart, J., Stohl, A., Maione, M., Arduini, J., and Bonasoni, P.: Influence of biomass burning and anthropogenic emissions on ozone, carbon monoxide and black carbon at the Mt. Cimone GAW-WMO global station (Italy, 2165 m a.s.l.), Atmos. Chem. Phys., 13, 15–30, doi:10.5194/acp-13-15-2013, 2013.

Cubison, M. J., Sueper, D., Dunlea, E., Jimenez, J. L., Weinheimer, A., Knapp, D., Dibb, J., Schauer, E., Diskin, G., Sachse, G., Anderson, B., Thornhill, L., Wisthaler, A., Mikoviny, T., Wennberg, P., and Crounse, J.: Submicron Aerosol Composition during the ARCTAS campaign: Arctic Haze, Biomass Burning, and California Pollution, pp. A11A–0081, AGU Fall Meeting, San Francisco, California, USA, http://abstractsearch.agu.org/meetings/2008/FM/A11A-0081.html, 2008.

Elansky, N. F., Belikov, I. B., Berezina, E. V., Brenninkmeijer, C. A. M., Buklikova, N. N., Crutzen, P. J., Elansky, S. N., Elkins, J. V., Elokhov, A. S., Golitsyn, G. S., Gorchakov, G. I., Granberg, I. G., Grisenko, A. M., Holzinger, R., Hurst, D. F., Igaev, A. I., Kozlova, A. A., Kopeikin, V. M., Kuokka, S., Lavrova, O. V., Lisitsyna, L. V., Moeseenko, K. B., Oberlander, E. A., Obvintsev, Y. I., Obvintseva, L. A., Pankratova, N. V., Postylyakov, O. V., Putz, E., Romashkin, P. A., Safronov, A. N., Shenfeld, K. P., Skorokhod, A. I., Shumsky, R. A., Tarasova, O. A., Turnbull, J. C., Vartiainen, E., Weissflog, L., and Zhernikov, K. V.: Atmospheric composition observations over Northern Eurasia using the mobile laboratory : TROICA [transcontinental observations into the chemistry of the atmosphere] experiments, International Science and Technology Center, Moscow, 2009.

Flanner, M. G.: Arctic climate sensitivity to local black carbon, J. Geophys. Res.-Atmos., 118, 1840–1851, doi:10.1002/jgrd.50176, 2013.

Friedli, H. R., Atlas, E., Stroud, V. R., Giovanni, L., Campos, T., and Radke, L. F.: Volatile organic trace gases emitted from North American wildfires, Global Biogeochem. Cy., 15, 435–452, doi:10.1029/2000GB001328, 2001.

Fromm, M., Alfred, J., Hoppel, K., Hornstein, J., Bevilacqua, R., Shettle, E., Servranckx, R., Li, Z., and Stocks, B.: Observations of boreal forest fire smoke in the stratosphere by POAM III, SAGE II, and lidar in 1998, Geophys. Res. Lett., 27, 1407–1410, doi:10.1029/1999GL011200, 2000.

Fromm, M. D. and Servranckx, R.: Transport of forest fire smoke above the tropopause by supercell convection, Geophys. Res. Lett., 30, 1542, doi:10.1029/2002GL016820, 2003.

Generoso, S., Bey, I., Attiè, J.-L., and Brèon, F.-M.: A satellite- and model-based assessment of the 2003 Russian fires: Impact on the Arctic region, J. Geophys. Res.-Atmos., 112, D15 302, doi:10.1029/2006JD008344, 2007.

Giglio, L., Randerson, J. T., and van der Werf, G. R.: Analysis of daily, monthly, and annual burned area using the fourth-generation global fire emissions database (GFED4), J. Geophys. Res.-Biogeo., 118, 317–328, doi:10.1002/jgrg.20042, 2013.

Goetz, S. J., Mack, M. C., Gurney, K. R., Randerson, J. T., and Houghton, R. A.: Ecosystem responses to recent climate change and fire disturbance at northern high latitudes: observations and model results contrasting northern Eurasia and North America, Environ. Res. Lett., 2, 045 031, 2007.

Goode, J. G., Yokelson, R. J., Susott, R. A., and Ward, D. E.: Trace gas emissions from laboratory biomass fires measured by open-path Fourier transform infrared spectroscopy: Fires in grass and surface fuels, J. Geophys. Rese.-Atmos., 104, 21 237–21 245, doi:10.1029/1999JD900360, 1999.

Goode, J. G., Yokelson, R. J., Ward, D. E., Susott, R. A., Babbitt, R. E., Davies, M. A., and Hao, W. M.: Measurements of excess O_3, CO_2, CH_4, C_2H_4, C_2H_2, HCN, NO, NH_3, HCOOH, CH_3COOH, HCHO, and CH_3H in 1997 Alaskan biomass burning plumes by airborne Fourier transform infrared spectroscopy (AFTIR), J. Geophys. Res.-Atmos., 105, 22 147–22 166, doi:10.1029/2000JD900287, 2000.

Guyon, P., Frank, G. P., Welling, M., Chand, D., Artaxo, P., Rizzo, L., Nishioka, G., Kolle, O., Fritsch, H., Silva Dias, M. A. F., Gatti, L. V., Cordova, A. M., and Andreae, M. O.: Airborne measurements of trace gas and aerosol particle emissions from biomass burning in Amazonia, Atmos. Chem. Phys., 5, 2989–3002, doi:10.5194/acp-5-2989-2005, 2005.

Hansen, J. and Nazarenko, L.: Soot climate forcing via snow and ice albedos, P. Natl. Acad. Sci. USA, 101, 423–428, doi:10.1073/pnas.2237157100, 2004.

Hecobian, A., Liu, Z., Hennigan, C. J., Huey, L. G., Jimenez, J. L., Cubison, M. J., Vay, S., Diskin, G. S., Sachse, G. W., Wisthaler, A., Mikoviny, T., Weinheimer, A. J., Liao, J., Knapp, D. J., Wennberg, P. O., Kürten, A., Crounse, J. D., Clair, J. S., Wang, Y., and Weber, R. J.: Comparison of chemical characteristics of 495 biomass burning plumes intercepted by the NASA DC-8 aircraft during the ARCTAS/CARB-2008 field campaign, Atmos. Chem. Phys., 11, 13 325–13 337, doi:10.5194/acp-11-13325-2011, 2011.

Hobbs, P. V., Sinha, P., Yokelson, R. J., Christian, T. J., Blake, D. R., Gao, S., Kirchstetter, T. W., Novakov, T., and Pilewskie, P.: Evolution of gases and particles from a savanna fire in South Africa, J. Geophys. Res.-Atmos., 108, doi:10.1029/2002JD002352, 8485, 2003.

Honrath, R. E., Owen, R. C., Val Martín, M., Reid, J. S., Lapina, K., Fialho, P., Dziobak, M. P., Kleissl, J., and Westphal, D. L.: Regional and hemispheric impacts of anthropogenic and biomass burning emissions on summertime CO and O_3 in the North Atlantic lower free troposphere, J. Geophys. Res.-Atmos., 109, D24 310, doi:10.1029/2004JD005147, 2004.

Hsu, N. C., Herman, J. R., Bhartia, P. K., Seftor, C. J., Torres, O., Thompson, A. M., Gleason, J. F., Eck, T. F., and Holben, B. N.: Detection of biomass burning smoke from TOMS measurements, Geophys. Res. Lett., 23, 745–748, doi:10.1029/96GL00455, 1996.

Jacob, D. J., Crawford, J. H., Maring, H., Clarke, A. D., Dibb, J. E., Emmons, L. K., Ferrare, R. A., Hostetler, C. A., Russell, P. B., Singh, H. B., Thompson, A. M., Shaw, G. E., McCauley, E., Pederson, J. R., and Fisher, J. A.: The Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) mission: design, execution, and first results, Atmos. Chem. Phys., 10, 5191–5212, doi:10.5194/acp-10-5191-2010, 2010.

Jaffe, D., Bertschi, I., Jaeglé, L., Novelli, P., Reid, J. S., Tanimoto, H., Vingarzan, R., and Westphal, D. L.: Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America, Geophys. Res. Lett., 31, L16 106, doi:10.1029/2004GL020093, 2004.

Jaffe, D. A. and Wigder, N. L.: Ozone production from wildfires: A critical review., Atmos. Environ., 51, 1–10, doi:10.1016/j.atmosenv.2011.11.063, 2012.

Jaffe, D. A., Honrath, R. E., Zhang, L., Akimoto, H., Shimizu, A., Murano, K., Hatakeyama, S., and Merrill, J.: Measurements of NO, NO_Y, CO and O_3 and Estimation of the Ozone Production Rate at Oki Island, Japan, during PEM-West, J. Geophys. Res., 101, 2037–2048, 1996.

Kasischke, E. S.: Boreal Ecosystems in the Global Carbon Cycle, pp. 19–30, Springer New York, New York, NY, USA, doi:10.1007/978-0-387-21629-4_2, 2000.

Kasischke, E. S. and Turetsky, M. R.: Recent changes in the fire regime across the North American boreal region, Geophys. Res. Lett., 33, L09 703, 2006.

Kasischke, E. S., Christensen, N. L., and Stocks, B. J.: Fire, global warming and the carbon balance of boreal forests, Ecol. Appl., 5, 437–451, 1999.

Kasischke, E. S., Hyer, E. J., Novelli, P. C., Bruhwiler, L. P., French, N. H. F., Sukhinin, A. I., Hewson, J. H., and Stocks, B. J.: Influences of boreal fire emissions on Northern Hemisphere atmospheric carbon and carbon monoxide, Global Biogeochem. Cy., 19, GB1012, doi:doi:10.1029/2004GB002300, 2005.

Keene, W. C., Lobert, J. M., Crutzen, P. J., Maben, J. R., Scharffe, D. H., Landmann, T., Hély, C., and Brain, C.: Emissions of major gaseous and particulate species during experimental burns of southern African biomass, J. Geophys. Res.-Atmos., 111, D04 301, doi:10.1029/2005JD006319, 2006.

Kim, Y., Hatsushika, H., Muskett, R. R., and Yamazaki, K.: Possible effect of boreal wildfire soot on Arctic sea ice and Alaska glaciers, Atmos. Environ., 39, 3513–3520, doi:10.1016/j.atmosenv.2005.02.050, 2005.

Klochko, A. A. and Romanovskaya, M. A.: National atlas of Russia. Vol. 2. Nature and the environment, FGUP "GOSGIGCENTRE", Moscow, in russian, 2004.

Kondo, Y., Matsui, H., Moteki, N., Sahu, L., Takegawa, N., Kajino, M., Zhao, Y., Cubison, M. J., Jimenez, J. L., Vay, S., Diskin, G. S., Anderson, B., Wisthaler, A., Mikoviny, T., Fuelberg, H. E., Blake, D. R., Huey, G., Weinheimer, A. J., Knapp, D. J., and Brune, W. H.: Emissions of black carbon, organic, and inorganic aerosols from biomass burning in North America and Asia in 2008, J. Geophys. Res.-Atmos., 116, D08 204, doi:10.1029/2010JD015152, 2011.

Kopeikin, V. M.: Monitoring of the soot aerosol of the atmosphere over Russia the TROICA international experiments, Atmospheric and oceanic optics, 20, 641–646, 2007.

Kopeikin, V. M.: Monitoring of the submicron aerosol content of the atmosphere over Russia the TROICA international experiments, Atmospheric and oceanic optics, 21, 970–976, 2008.

Kuokka, S., Teinilä, K., Saarnio, K., Aurela, M., Sillanpää, M., Hillamo, R., Kerminen, V.-M., Pyy, K., Vartiainen, E., Kulmala, M., Skorokhod, A. I., Elansky, N. F., and Belikov, I. B.: Using a moving measurement platform for determining the chemical composition of atmospheric aerosols between Moscow and Vladivostok, Atmos. Chem. Phys., 7, 4793–4805, 2007.

Langmann, B., Duncan, B., Textor, C., Trentmann, J., and van der Werf, G. R.: Vegetation fire emissions and their impact on air pollution and climate, Atmos. Environ., 43, 107–116, doi:10.1016/j.atmosenv.2008.09.047, 2009.

Laursen, K. K., Hobbs, P. V., Radke, L. F., and Rasmussen, R. A.: Some trace gas emissions from North American biomass fires with an assessment of regional and global fluxes from biomass burning, J. Geophys. Res.-Atmos., 97, 20 687–20 701, doi:10.1029/92JD02168, 1992.

Lavoué, D. C., Liousse, C., Cachier, H., Stocks, B. J., and Goldammer, J. G.: Modelling of carbonaceous particles emitted by boreal and temperate wildfires at northern latitudes, J. Geophys. Res.-Atmos., 105, 26 871–26 890, 2000.

Le Canut, P., Andreae, M. O., Harris, G. W., Wienhold, F. G., and Zenker, T.: Airborne studies of emissions from savanna fires in southern Africa: 1. Aerosol emissions measured with a laser optical particle counter, J. Geophys. Res.-Atmos., 101, 23 615–23 630, doi:10.1029/95JD02610, 1996.

Marlon, J. R., Bartlein, P. J., Carcaillet, C., Gavin, D. G., Harrison, S. P., Higuera, P. E., Joos, F., Power, M. J., , and Prentice, I. C.: Climate and human influences on global biomass burning over the past two millennia, Nat. Geosci., 1, 697–702, doi:10.1038/ngeo313, 2008.

McGuire, A. D., Anderson, L. G., Christensen, T. R., Dallimore, S., Guo, L., Hayes, D. J., Heimann, M., Lorenson, T. D., Macdonald, R. W., and Roulet, N.: Sensitivity of the carbon cycle in the Arctic to climate change, Ecol. Monogr., 79, 523–555, doi:10.1890/08-2025.1, 2009.

McRae, D. J., Conard, S. G., Ivanova, G. A., Sukhinin, A. I., Baker, S. P., Samsonov, Y. N., Blake, T. W., Ivanov, V. A., Ivanov, A. V., Churkina, T. V., Hao, W. M., Koutzenogij, K. P., , and Kovaleva, N.: Variability of fire behavior, fire effects, and emissions in scotch pine forests of Central Siberia, Mitigation and Adaptation Strategies for Global Change, 11, 45—74, doi:10.1007/s11027-006-1008-4, 2006.

Myers-Smith, I. H., McGuire, A. D., Harden, J. W., and Chapin, F. S.: Influence of disturbance on carbon exchange in a permafrost collapse and adjacent burned forest, J. Geophys. Res.-Biogeo., 112, G04 017, doi:10.1029/2007JG000423, 2007.

Nance, J. D., Hobbs, P. V., Radke, L. F., and Ward, D. E.: Airborne measurements of gases and particles from an Alaskan wildfire, J. Geophy. Res.-Atmos., 98, 14 873–14 882, doi:10.1029/93JD01196, 1993.

Olsen, M., Shearer, R., Wrona, F., Klint, M., Mähönen, O., Jensson, H., Døvle, P., Lundberg, T., Tsaturov, Y., and Armstrong, T.: AMAP Assessment 2015: Black carbon and ozone as Arctic climate forcers. Arctic Monitoring and Assessment Programme (AMAP), Tech. rep., Arctic Council, Oslo, Norway, http://www.amap.no/documents/doc/AMAP-Assessment-2015-Black-carbon-and-ozone-as-Arctic-climate-forcers/1299, 2015.

Paris, J.-D., Stohl, A., Nédélec, P., Arshinov, M. Y., Panchenko, M. V., Shmargunov, V. P., Law, K. S., Belan, B. D., and Ciais, P.: Wildfire smoke in the Siberian Arctic in summer: source characterization and plume evolution from airborne measurements, Atmos. Chem. Phys., 9, 9315–9327, doi:10.5194/acp-9-9315-2009, 2009.

Pirjola, L., Virkkula, A., Petäjä, T., Levula, J., Kukkonen, J., and Kulmala, M.: Mobile ground–based measurements of aerosol and trace gases during a prescribed burning experiment in boreal forest in Finland, Boreal Environment Research, 20, 105–119, 2015.

Popovicheva, O., Kistler, M., Kireeva, E., Persiantseva, N., Timofeev, M., Kopeikin, V., and Kasper-Giebl, A.: Physicochemical characterization of smoke aerosol during large-scale wildfires: Extreme event of August 2010 in Moscow, Atmos. Environ., 96, 405–414, doi:10.1016/j.atmosenv.2014.03.026, 2014.

Popovicheva, O. B., Kozlov, V. S., Engling, G., Diapouli, E., Persiantseva, N. M., Timofeev, M. A., Fan, T.-s., Saraga, D., and Eleftheriadis, K.: Small-Scale Study of Siberian Biomass Burning: I. Smoke Microstructure, Aerosol Air Qual. Res., 15, 117–128, doi:10.4209/aaqr.2014.09.0206, 2015.

Quinn, P. K., Shaw, G., Andrews, E., Dutton, E. G., Ruoho-Airola, T., and Gong, S. L.: Arctic haze: current trends and knowledge gaps, Tellus B, 59, 99–114, doi:10.1111/j.1600-0889.2006.00238.x, 2007.

Quinn, P. K., Bates, T. S., Baum, E., Doubleday, N., Fiore, A. M., Flanner, M., Fridlind, A., Garrett, T. J., Koch, D., Menon, S., Shindell, D., Stohl, A., and Warren, S. G.: Short-lived pollutants in the Arctic: their climate impact and possible mitigation strategies, Atmos. Chem. Phys., 8, 1723–1735, doi:10.5194/acp-8-1723-2008, 2008.

Randerson, J. T., Liu, H., Flanner, M. G., Chambers, S. D., Jin, Z., Hess, P. G., Pfister, G., Mack, M. C., Treseder, K. K., Welp, L. R., Chaplin, F. S., Harden, J. W., Goulden, M. L., Lyons, E., Neff, J. C., Schuur, E. A. G., and Zender, C. S.: The impact of boreal forest fire on climate warming, Science, 314, 1130–1132, doi:doi:10.1126/science.1132075, 2006.

Randerson, J. T., Chen, Y., van der Werf, G. R., Rogers, B. M., and Morton, D. C.: Global burned area and biomass burning emissions from small fires, J. Geophys. Res.-Biogeo., 117, G04 012, doi:10.1029/2012JG002128, 2012.

Rasmussen, R. A., Westberg, H. H., and Holdren, M.: Need for Standard Referee GC Methods in Atmospheric Hydrocarbon Analyses, J. Chromatogr. Sci., 12, 80–84, doi:10.1093/chromsci/12.2.80, 1974.

Reid, J. S., Koppmann, R., Eck, T. F., and Eleuterio, D. P.: A review of biomass burning emissions part II: intensive physical properties of biomass burning particles, Atmos. Chem. Phys., 5, 799–825, doi:10.5194/acp-5-799-2005, 2005.

Rolph, G. D.: Real-time Environmental Applications and Display sYstem (READY), http://ready.arl.noaa.gov, accessed: 10 January 2017, 2017.

Saarikoski, S., Sillanpaa, M., Sofiev, M., Timonen, H., Saarnio, K., Teinila, K., Karppinen, A., Kukkonen, J., and Hillamo, R.: Chemical composition of aerosols during a major biomass burning episode over northern Europe in spring 2006: experimental and modelling assessments, Atmos. Environ., 41, 3577–3589, 2007.

Saarnio, K., Aurela, M., Timonen, H., Saarikoski, S., Teinilä, K., Mäkelä, T., Sofiev, M., Koskinen, J., Aalto, P. P., Kulmala, M., Kukkonen, J., and Hillamo, R.: Chemical composition of fine particles in fresh smoke plumes from boreal wild-land fires in Europe, Sci. Total Environ., 408, 2527–2542, doi:10.1016/j.scitotenv.2010.03.010, 2010.

Schuur, E. A. G., Bockheim, J., Canadell, J. G., Euskirchen, E., Field, C. B., Goryachkin, S. V., Hagemann, S., Kuhry, P., Lafleur, P. M., Lee, H., Mazhitova, G., Nelson, F. E., Rinke, A., Romanovsky, V. E., Shiklomanov, N., Tarnocai, C., Venevsky, S., Vogel, J. G., and Zimov, S. A.: Vulnerability of Permafrost Carbon to Climate Change: Implications for the Global Carbon Cycle, BioScience, 58, 701, doi:10.1641/B580807, 2008.

Screen, J. A. and Simmonds, I.: The central role of diminishing sea ice in recent Arctic temperature amplification, Nature, 464, 1334–1337, doi:10.1038/nature09051, 2010.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: from Air Pollution to Climate Change, Wiley, New York, New York, USA, second edn., 1997.

Shvidenko, A. and Nilsson, S.: A synthesis of the impact of Russian forests on the global carbon budget for 1961–1998, Tellus, 55B, 391–415, 2003.

Simpson, I. J., Rowland, F. S., Meinardi, S., and Blake, D. R.: Influence of biomass burning during recent fluctuations in the slow growth of global tropospheric methane, Geophys. Res. Lett., 33, L22 808, doi:10.1029/2006GL027330, 2006.

Simpson, I. J., Akagi, S. K., Barletta, B., Blake, N. J., Choi, Y., Diskin, G. S., Fried, A., Fuelberg, H. E., Meinardi, S., Rowland, F. S., Vay, S. A., Weinheimer, A. J., Wennberg, P. O., Wiebring, P., Wisthaler, A., Yang, M., Yokelson, R. J., and Blake, D. R.: Boreal forest fire emissions in fresh Canadian smoke plumes: C_1-C_{10} volatile organic compounds (VOCs), CO_2, CO, NO_2, NO, HCN and CH_3CN, Atmos. Chem. Phys., 11, 6445–6463, doi:10.5194/acp-11-6445-2011, 2011.

Singh, H. B., Anderson, B. E., Brune, W. H., Cai, C., Cohen, R. C., Crawford, J. H., Cubison, M. J., Czech, E. P., Emmons, L., Fuelberg, H. E., Huey, G., Jacob, D. J., Jimenez, J. L., Kaduwela, A., Kondo, Y., Mao, J., Olson, J. R., Sachse, G. W., Vay, S. A., Weinheimer, A.,

Wennberg, P. O., and Wisthaler, A.: Pollution Influences on Atmospheric Composition and Chemistry at High Northern Latitudes: Boreal and California Forest Fire Emissions, Atmos. Environ., 44, 4553–4564, 2010.

Soja, A. J., Cofer, W. R., Shugart, H. H., Sukhinin, A. I., Stackhouse, P. W., McRae, D. J., and Conard, S. G.: Estimating fire emissions and disparities in boreal Siberia (1998–2002), J. Geophys. Res.-Atmos., 109, D14S06, doi:10.1029/2004JD004570, 2004.

Soja, A. J., Tchebakova, N. M., French, N. H. F., Flannigan, M. D., Shugart, H. H., Stocks, B. J., Sukhinin, A. I., Parfenova, E. I., Chapin, III, F. S., and Stackhouse, P. W.: Climate-induced boreal forest change: predictions versus current observations, Global Planet. Change, 56, 274–296, 2007.

Spichtinger, N., Wenig, M., James, P., Wagner, T., Platt, U., and Stohl, A.: Satellite detection of a continental-scale plume of nitrogen oxides from boreal forest fires, Geophys. Res. Lett., 28, 4579–4582, 2001.

Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., and Ngan, F.: NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System, B. Am. Meteorol. Soc., 96, 2059–2077, doi:10.1175/BAMS-D-14-00110.1, 2015.

Stockwell, W. R., Lawson, C. V., Saunders, E., and Goliff, W. S.: A Review of Tropospheric Atmospheric Chemistry and Gas-Phase Chemical Mechanisms for Air Quality Modeling, Atmosphere, 3, 1–32, doi:10.3390/atmos3010001, 2012.

Stohl, A.: Computation, accuracy and applications of trajectories – a review and bibliography, Atmos. Environ., 32, 947–966, doi:10.1016/S1352-2310(97)00457-3, 1998.

Stohl, A.: Characteristics of atmospheric transport into the Arctic troposphere, J. Geophys. Res.-Atmos., 111, D11 306, doi:10.1029/2005JD006888, 2006.

Stohl, A., Berg, T., Burkhart, J. F., Fjæraa, A. M., Forster, C., Herber, A., Hov, Ø., Lunder, C., McMillan, W. W., Oltmans, S., Shiobara, M., Simpson, D., Solberg, S., Stebel, K., Ström, J., Tørseth, K., Treffeisen, R., Virkkunen, K., and Yttri, K. E.: Arctic smoke – record high air pollution levels in the European Arctic due to agricultural fires in Eastern Europe in Spring 2006, Atmos. Chem. Phys., 7, 511–534, 2007.

Sukhinin, A. I., French, N. H. F., Kasischke, E. S., Hewson, J. H., Soja, A. J., Csiszar, I. A., Hyer, E. J., Loboda, T., Conrad, S. G., Romasko, V. I., Pavlichenko, E. A., and Miskiv, S. I.: AVHRR-based mapping of fires in Russia: New products for fire management and carbon cycle studies, Remote Sens. Environ., 93, 546–564, doi:10.1016/j.rse.2004.08.011, 2004.

Tanimoto, H., Kajii, Y., Hirokawa, J., Akimoto, H., and Minko, N. P.: The atmospheric impact of boreal forest fires in far eastern Siberia on the seasonal variation of carbon monoxide: Observations at Rishiri, A northern remote island in Japan, Geophys. Res. Lett., 27, 4073–4076, doi:10.1029/2000GL011914, 2000.

Tanimoto, H., Furutani, H., Kato, S., Matsumoto, J., Makide, Y., and Akimoto, H.: Seasonal cycles of ozone and oxidized nitrogen species in northeast Asia 1. Impact of regional climatology and photochemistry observed during RISOTTO 1999–2000, J. Geophys. Res.-Atmos., 107, ACH 6–1–ACH 6–20, doi:10.1029/2001JD001496, 2002.

Tchebakova, N. M., Monserud, R. A., and Leemans, R.: A Siberian vegetation model based on climatic parameters, Can. J. Forest Res., 24, 1597–1607, 1994.

Urbanski, S. P., Hao, W. M., and Baker, S.: Chemical Composition of Wildland Fire Emissions, 8, 79–107, doi:10.1016/S1474-8177(08)00004-1, 2009.

Urbanski, S. P., Hao, W. M., and Nordgren, B.: The wildland fire emission inventory: western United States emission estimates and an evaluation of uncertainty, Atmos. Chem. Phys., 11, 12 973–13 000, doi:10.5194/acp-11-12973-2011, 2011.

Val Martín, M., Honrath, R. E., Owen, R. C., Pfister, G., Fialho, P., and Barata, F.: Significant enhancements of nitrogen oxides, black carbon, and ozone in the North Atlantic lower free troposphere resulting from North American boreal wildfires, J. Geophys. Res.-Atmos., 111, doi:10.1029/2006JD007530, 2006.

Val Martín, M., Logan, J. A., Kahn, R. A., Leung, F., Nelson, D. L., and Diner, D. J.: Smoke injection heights from fires in North America: Analysis of 5 years of satellite observations, Atmos. Chem. Phys., 10, doi:10.5194/acp-10-1491-2010, 2010.

van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009), Atmos. Chem. and Phys., 10, 11 707–11 735, doi:10.5194/acp-10-11707-2010, 2010.

Vartiainen, E., Kulmala, M., and Ehn, M.: Ion and particle number concentrations and size distributions along the Trans-Siberian railroad, Boreal Environ. Res., 12, 375–396, 2007.

Vasileva, A. V., Moiseenko, K. B., Mayer, J. C., Jurgens, N., Panov, A., Heimann, M., and Andreae, M. O.: Assessment of the regional atmospheric impact of wildfire emissions based on CO observations at the ZOTTO tall tower station in central Siberia, J. Geophys. Res.-Atmos., 116, D07 301, doi:10.1029/2010JD014571, 2011.

Vivchar, A.: Wildfires in Russia in 2000–2008: estimates of burnt areas using the satellite MODIS MCD45 data, Remote Sensing Letters, 2, 81–90, doi:10.1080/01431161.2010.499138, 2011.

Vivchar, A. V., Moiseenko, K. B., and Pankratova, N. V.: Estimates of carbon monoxide emissions from wildfires in northern Eurasia for airquality assessment and climate modeling, Izv. AN Fiz. Atmos. Ok+, 46, 281–293, doi:10.1134/S0001433810030023, 2010.

Ward, D. E., Setzer, A., Kaufman, Y. J., and Rasmussen, R. A.: Characteristics of Smoke Emissions from Biomass Fires of the Amazon Region-BASE-A Experiment, in: Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications, edited by Levine, J. S., pp. 394–402, MIT Press, Cambridge, MA, USA, 1991.

Ward, D. E., Susott, R. A., Kauffman, J. B., Babbitt, R. E., Cummings, D. L., Dias, B., Holben, B. N., Kaufman, Y. J., Rasmussen, R. A., and Setzer, A. W.: Smoke and fire characteristics for cerrado and deforestation burns in Brazil: BASE-B Experiment, J. Geophys. Res.-Atmos., 97, 14 601–14 619, doi:10.1029/92JD01218, 1992.

Warneke, C., Bahreini, R., Brioude, J., Brock, C. A., de Gouw, J. A., Fahey, D. W., Froyd, K. D., Holloway, J. S., Middlebrook, A., Miller, L., Montzka, S., Murphy, D. M., Peischl, J., Ryerson, T. B., Schwarz, J. P., Spackman, J. R., and Veres, P.: Biomass burning in Siberia and Kazakhstan as an important source for haze over the Alaskan Arctic in April 2008, Geophys. Res. Lett., 36, L02 813, doi:10.1029/2008GL036194, 2009.

Warneke, C., Froyd, K. D., Brioude, J., Bahreini, R., Brock, C. A., Cozic, J., de Gouw, J. A., Fahey, D. W., Ferrare, R., Holloway, J. S., Middlebrook, A. M., Miller, L., Montzka, S., Schwarz, J. P., Sodemann, H., Spackman, J. R., and Stohl, A.: An important contribution to springtime Arctic aerosol from biomass burning in Russia, Geophys. Res. Lett., 37, L01 801, doi:10.1029/2009GL041816, 2010.

Wiedinmyer, C., Quayle, B., Geron, C., Belote, A., McKenzie, D., Zhang, X., O'Neill, S., and Wynne, K. K.: Estimating emissions from fires in North America for air quality modeling, Atmos. Environ., 40, 3419–3432, doi:10.1016/j.atmosenv.2006.02.010, 2006.

Wotawa, G. and Trainer, M.: The Influence of Canadian Forest Fires on Pollutant Concentrations in the United States, Science, 288, 324–328, 2000.

Wotawa, G., Novelli, P. C., Trainer, M., and Granier, C.: Interannual variability of summertime CO concentrations in the Northern Hemisphere explained by boreal forest fires in North America and Russia, Geophys. Res. Lett., 28, 4575–4578, 2001.

Yokelson, R., Goode, J., Ward, D. E., Susott, R. A., Babbitt, R. E., Wade, D. D., Bertschi, I., Griffith, D. W. T., and Hao, W. M.: Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy, J. Geophys. Res.-Atmos., 104, 30 109–30 125, doi:10.1029/1999JD900817, 1999.

Yokelson, R. J., Griffith, D. W. T., and Ward, D. E.: Open–path Fourier transform infrared studies of large–scale laboratory biomass fires, J. Geophys. Res.-Atmos., 101, 21 067–21 080, doi:10.1029/96JD01800, 1996.

Yokelson, R. J., Susott, R., Ward, D. E., Reardon, J., and Griffith, D. W. T.: Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy, J. Geophys. Res.-Atmos., 102, 18 865–18 877, doi:10.1029/97JD00852, 1997.

Yokelson, R. J., Burling, I. R., Urbanski, S. P., Atlas, E. L., Adachi, K., Buseck, P. R., Wiedinmyer, C., Akagi, S. K., Toohey, D. W., and Wold, C. E.: Trace gas and particle emissions from open biomass burning in Mexico, Atmos. Chem.and Phys., 11, 6787–6808, doi:10.5194/acp-11-6787-2011, 2011.

Yurganov, L. N., Duchatelet, P., Dzhola, A. V., Edwards, D. P., Hase, F., Kramer, I., Mahieu, E., Mellqvist, J., Notholt, J., Novelli, P. C., Rockmann, A., Scheel, H. E., Schneider, M., Schulz, A., Strandberg, A., Sussmann, R., Tanimoto, H., Velazco, V., Drummond, J. R., and Gille, J. C.: Increased Northern Hemispheric carbon monoxide burden in the troposphere in 2002 and 2003 detected from the ground and from space, Atmos. Chem. Phys., 5, 563–573, doi:10.5194/acp-5-563-2005, 2005.

Zimov, S. A., Schuur, E. A. G., and Chapin, F. S.: Permafrost and the Global Carbon Budget, Science, 312, 1612–1613, doi:10.1126/science.1128908, 2006.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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 1.400 (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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

Table 5. Average emission ratios (with standard uncertainties) for trace gases and particles in F1 and F2 forest fire plumes estimated with linear regression.

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	427 ± 18	–
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	2.8 ± 0.6	9.9 ± 1.5	21.4 ± 1.0	3.1 ± 0.4	321 ± 20	–

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

Table 6. Correlation coefficients (R^2) from linear regressions of excess levels of trace gases and particles onto excess mixing ratios of CO or CO_2.

Plume part	CO / CO_2	CH_4 / CO	NMHC / CO,	NO_X / CO	PM_1 / CO	BC / CO
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	0.70	0.83	0.94	0.81	0.89	–

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

Atmospheric Chemistry and Physics Discussions

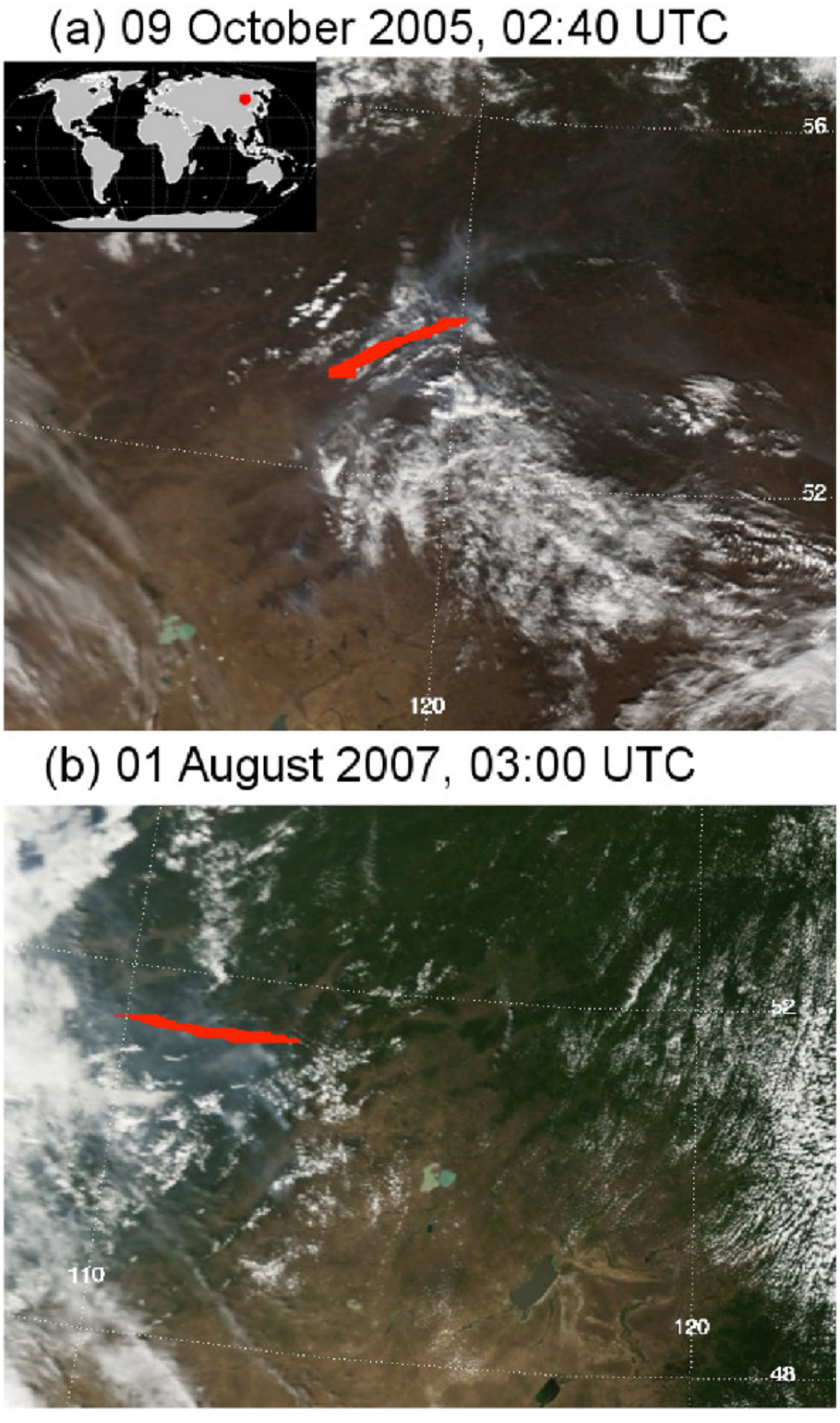

Figure 1. Parts of MODIS Terra MOD021KM true color (spectral bands 1, 4, 3 as red, green, blue) scenes for (a) 9 October 2005 02:40 UTC and (b) 1 August 2007 03:00 UTC. Downloaded from https://modis-atmos.gsfc.nasa.gov/IMAGES. Red lines show approximate locations of plume transects.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

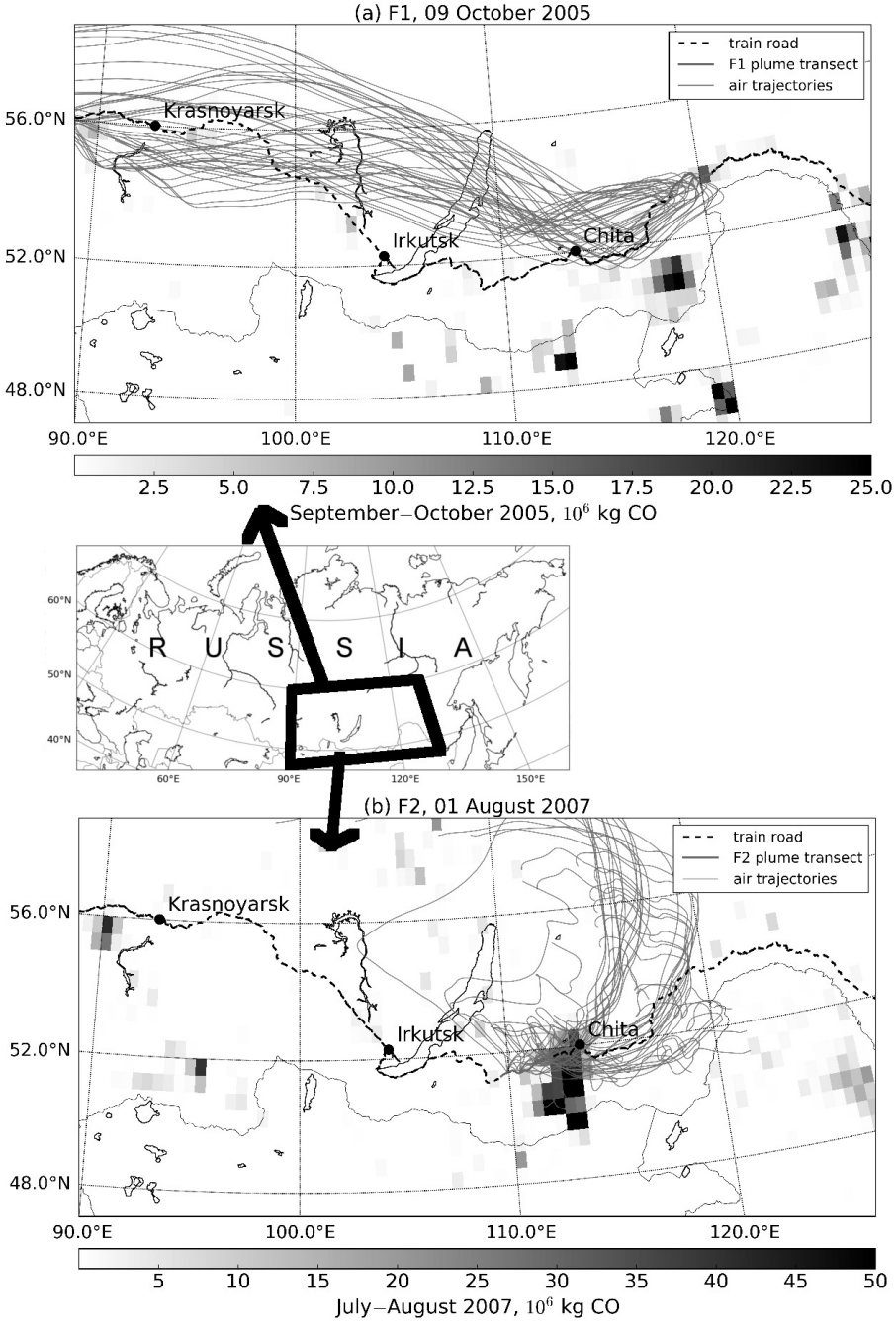

Figure 2. TROICA expedition train routes and ensembles of five-day HYSPLIT backward trajectories started from 300 m a.g.l. each hour within each plume crossing superimposed on two-month CO emissions from biomass burning according to GFEDv4.1s model.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

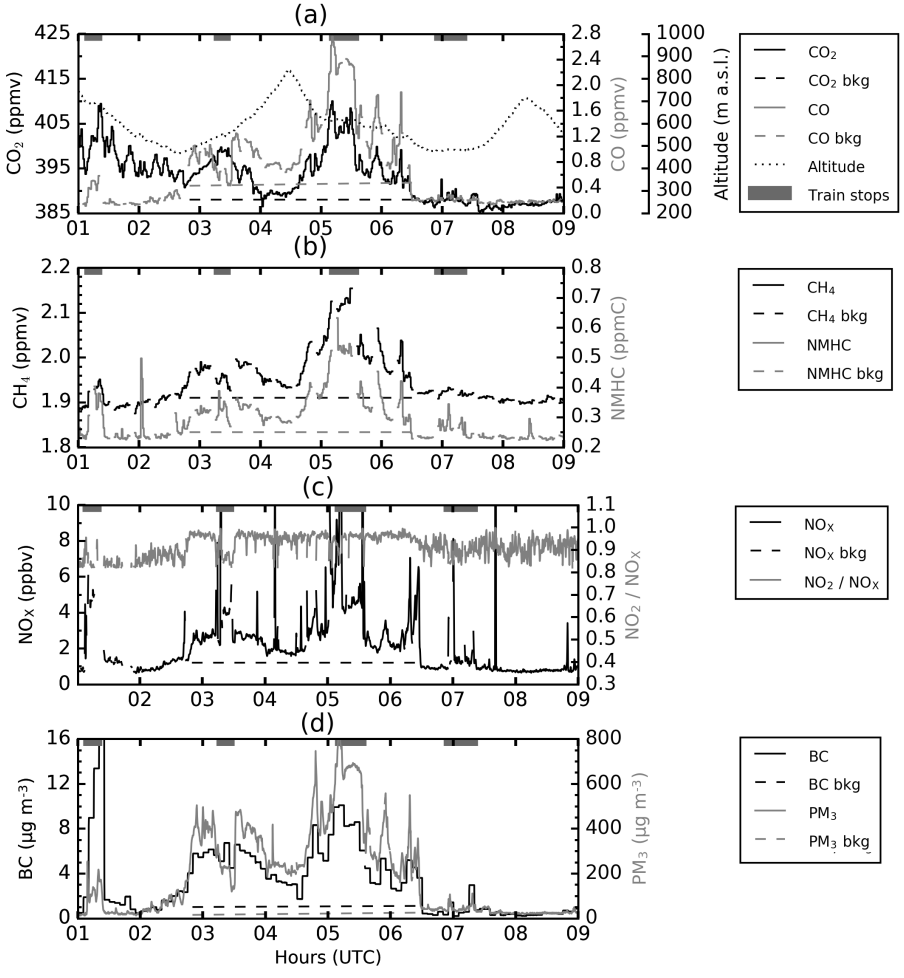

Figure 3. Measured 10 s trace gas mixing ratios and aerosol mass concentrations observed in vicinity of F1 forest fire plume during TROICA-09 expedition in 9 October 2005.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

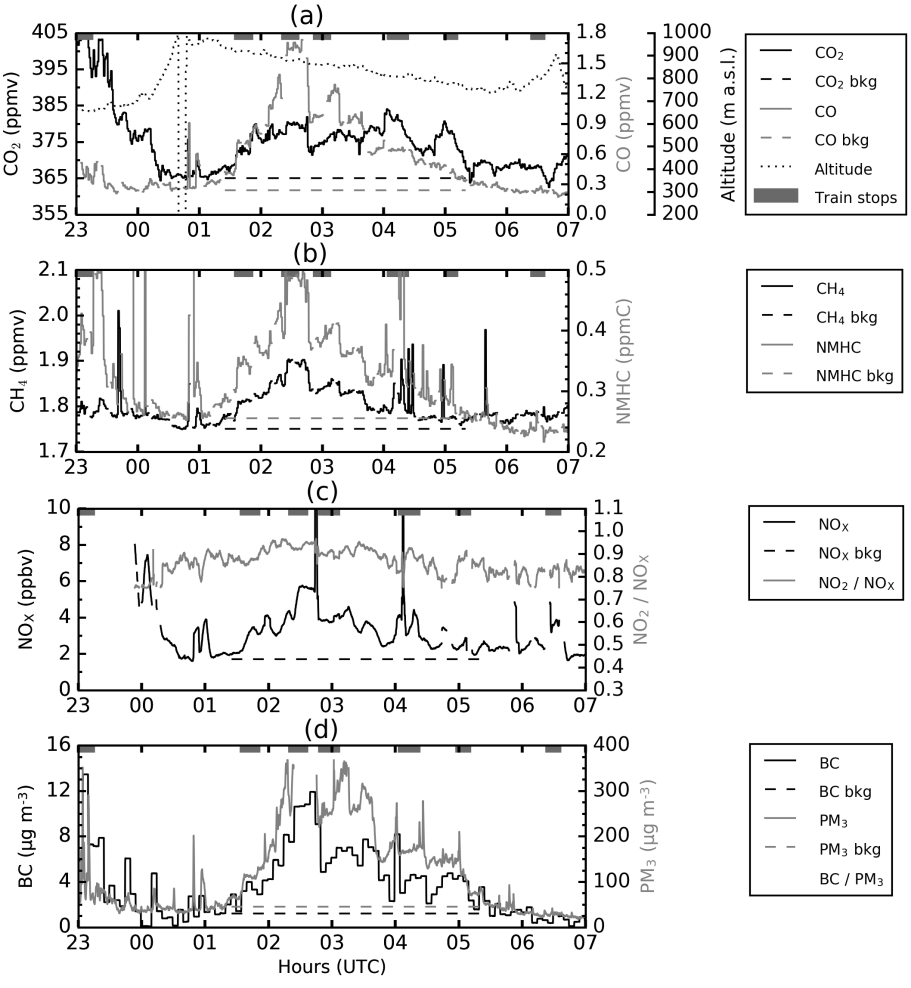

Figure 4. Measured 10 s trace gas mixing ratios and aerosol mass concentrations observed in vicinity of F2 forest fire plume during TROICA-11 expedition in 1 August 2007.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

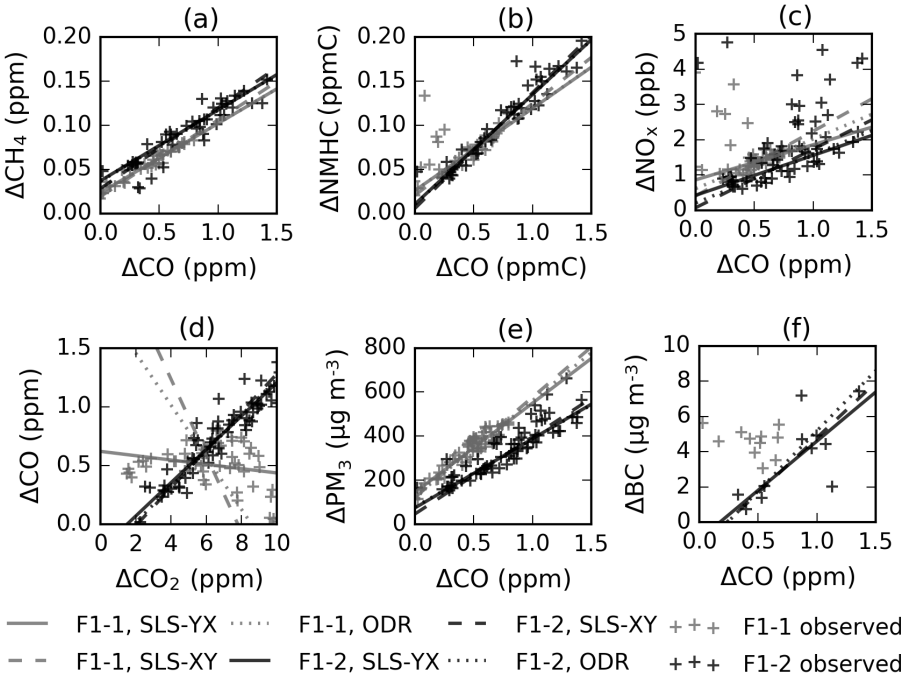

Figure 5. Excess levels of trace gases and particles versus excess mixing ratios of CO or CO_2 for F1 plume parts, with lines fitted to the data by different regression methods (see explanations in the text).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

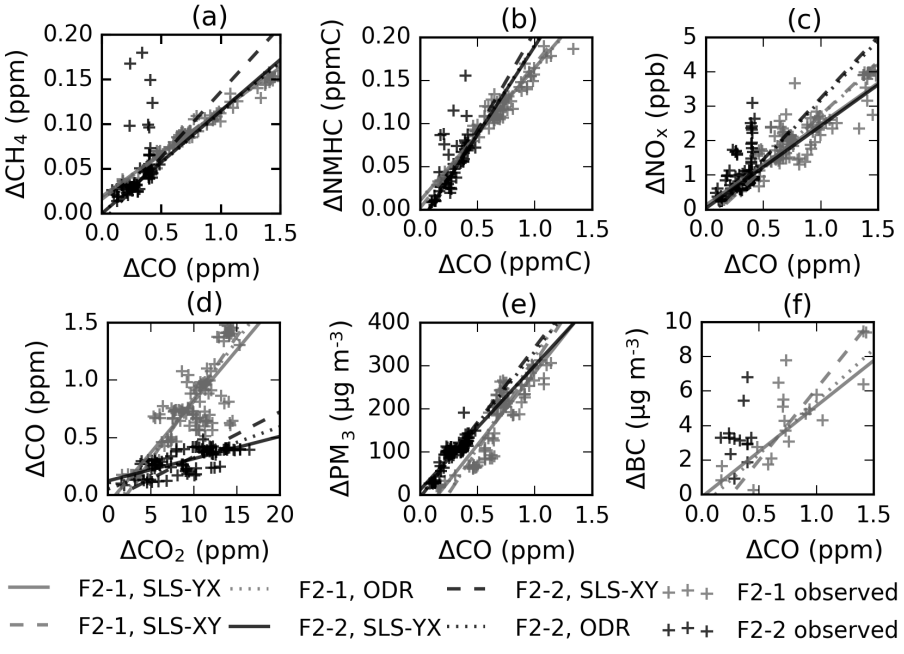

Figure 6. Same as Fig. 5 but for F2 plume parts.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

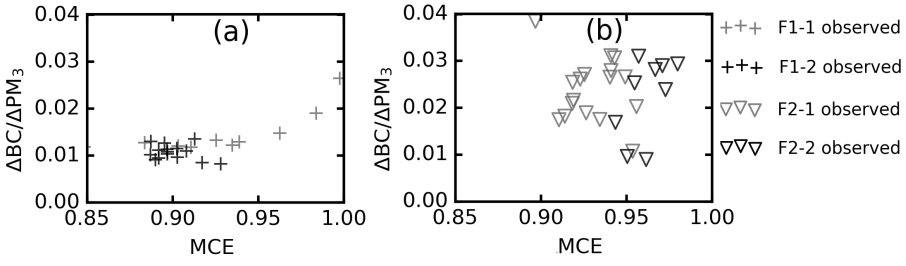

Figure 7. Excess ratio of $\Delta BC/\Delta PM3$ versus MCE for F1 and F2 plume parts.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

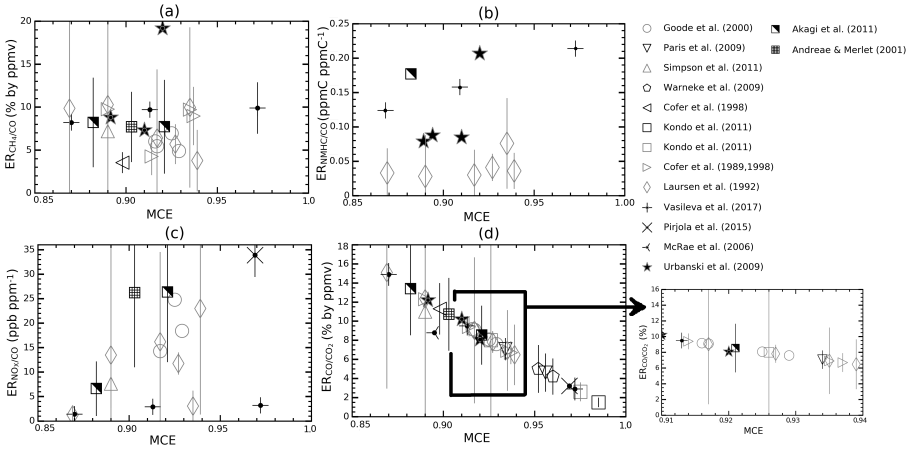

Figure 8. Scatter plots of trace gas $ER_{Y/X}$ with standard uncertainties (where available) versus MCE for this study and previous publications.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-362, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 4 May 2017

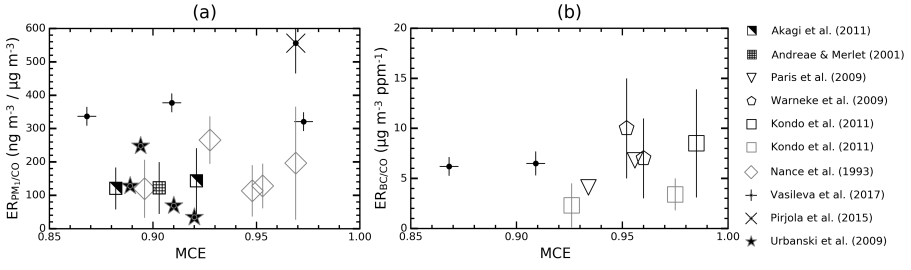

Figure 9. Scatter plots of particle $ER_{Y/X}$ with standard uncertainties (where available) versus MCE for this study and previous publications.