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Comparison of the chemical evolution and characteristics of 495 biomass burning plumes intercepted by the NASA DC-8 aircraft during the ARCTAS/CARB-2008 field campaign

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ACPD
11, 18589–18631, 2011

Abstract

This paper compares measurements of gaseous and particulate emissions from a wide range of biomass-burning plumes intercepted by the NASA DC-8 research aircraft during the three phases of the ARCTAS-2008 experiment: ARCTAS-A, based out of Fairbanks, Alaska USA (3 April to 19 April 2008); ARCTAS-B based out of Cold Lake, Alberta, Canada (29 June to 13 July 2008); and ARCTAS-CARB, based out of Palmdale, California, USA (18 June to 24 June 2008). Extensive investigations of boreal fire plume evolution were undertaken during ARCTAS-B, where four distinct fire plumes that were intercepted by the aircraft over a range of down-wind distances (0.1 to 16 hr transport times) were studied in detail. Based on these analyses, there was no evidence for ozone production and a box model simulation of the data confirmed that net ozone production was slow (on average 1 ppbv h^{-1} in the first 3 h and much lower afterwards) due to limited NO_x. Peroxyacetyl nitrate concentrations (PAN) increased with plume age and the box model estimated an average production rate of ~80 pptv h^{-1} in the first 3 h. Like ozone, there was also no evidence for net secondary inorganic or organic aerosol formation. There was no apparent increase in aerosol mass concentrations in the boreal fire plumes due to secondary organic aerosol (SOA) formation; however, there were indications of chemical processing of the organic aerosols. In addition to the detailed studies of boreal fire plume evolution, about 500 smoke plumes intercepted by the NASA DC-8 aircraft were segregated by fire source region. The normalized excess mixing ratios (i.e. $\Delta X/\Delta CO$) of gaseous (carbon dioxide, acetonitrile, hydrogen cyanide, toluene, benzene, methane, oxides of nitrogen (NO_x), ozone, PAN) and fine aerosol particulate components (nitrate, sulfate, ammonium, chloride, organic aerosols and water soluble organic carbon) of these plumes were compared.

ACPD

11, 18589–18631, 2011

1 Introduction

Bio-fuels, prescribed burns and natural fires are sources of biomass burning smoke. Fire emissions are an important source for a wide range of atmospheric trace gases and aerosol particles that can have important impacts on biogeochemical cycles, air quality, human health, and direct and indirect effects on the climate through influencing the global radiation budget (Crutzen et al., 1979; Crutzen and Andreae, 1990; Yamasoe et al., 2000; Guyon et al., 2003; Bein et al., 2008). Extensive burning episodes (e.g., wildfires) and the persistence of these emissions in the atmosphere for weeks mean that smoke can be transported over great distances and have both regional and global impacts (LeCanut et al., 1996; Scholes and Andreae, 2000; Dickerson et al., 2002; Allen et al., 2004; Duan et al., 2004; Honrath et al., 2004; Engling et al., 2006; Fu et al., 2009). The frequency and intensity of biomass burning events and their effects are expected to be amplified in the future due to anticipated increases in global temperatures and alterations in precipitation patterns resulting from climate change (Penner et al., 1994; Narukawa et al., 1999; Reddy and Boucher, 2004; Stocks et al., 2004; Turetskey et al., 2011).

In recent years, many studies have been conducted to clarify the emissions and physicochemical evolution of various trace gases and aerosols from fires (e.g., Andreae et al., 2001; Decesari et al., 2006). Using a variety of sampling methods, both laboratory and direct studies of biomass burning have characterized fire emissions in differing environments with various fuels and under diverse burning and meteorological conditions (Lacaux et al., 1995; Andreae and Merlet, 2001; Abel et al., 2003; Ludwig et al., 2003; Haywood et al., 2003; Iinuma et al., 2007; Cao et al., 2008; Schmidl et al., 2008; Yokelson et al., 2009; Lee et al., 2010). The emission ratio, where the emission of a species of interest (in the gas or particle phase) is normalized by a co-emitted, non-reactive species (typically CO or CO_2) is one important parameter used to represent fire emissions in model simulations (Helas et al., 1995; LeCanut et al., 1996; Andreae et al., 2001; Andreae and Merlet, 2001). The term emission ratio is used when

ACPD
11, 18589–18631, 2011

sampling occurs near the fire, whereas normalized excess mixing ratios (NEMRs) are used to describe conditions after the plume has aged (Yokelson et al., 2009). NEMRs relative to CO are used in this paper where NEMR is defined as $\Delta X/\Delta CO$. X is the species of interest and ΔX (or ΔCO) is calculated by subtracting the mixing ratios of X (or CO) outside the plume from those inside the plume.

Studying the direct emissions from fires through measurements close to the burning sites and comparing such emissions with the more aged smoke from the same fire to infer physical and chemical evolution can improve our understanding of the effects of fires on regional and global scales (Formenti et al., 2003; Dusek et al., 2005; Falkovich et al., 2005; Hoyle et al., 2007).

Emissions from biomass burning undergo a range of chemical and physical transformations over time (Johnson and Miyanishi, 2001 and references therein). When compared to a relatively non-reacting co-emitted tracer, such as CO, primary gaseous and particulate emissions may be expected to be depleted as the plume ages due to photochemical or physical processes; whereas secondary trace gases and aerosols are expected to increase relative to CO due to production. However, many of the secondary gases have reduced vapor pressures and can partition to the aerosol phase resulting instead in a net increase of secondary aerosols with plume age and depletion of gas phase components. It has also been proposed (Grieshop et al., 2009) that the evaporation of primary aerosol components in the diluting smoke plume may produce gas-phase compounds that subsequently can be photo-chemically converted to lower vapor pressure products that also contribute to secondary aerosol mass at the expense of primary aerosol species.

There are differing data regarding secondary organic aerosol (SOA) formation following the initial emissions of gases and aerosols from fires. Some laboratory studies suggest secondary organic aerosol formation in biomass-burning plumes might readily occur (Grieshop et al., 2009; Hennigan et al., 2011; Heringa et al., 2011). Some ambient studies report evidence of SOA formation (Clarke et al., 2007; Bein et al., 2008; Lee et al., 2008; DeCarlo et al., 2010); whereas, in other cases no or little evidence

ACPD
11, 18589–18631, 2011

of net SOA mass addition in an aging smoke plume has been observed (Capes et al., 2009). Cubison et al. (2011) have recently summarized observations from seven aircraft campaigns and estimated that net SOA formation from biomass burning plumes may be an appreciable contributor (~5 %) to the global OA budget.

Jaffrezo et al. (1998), using fine aerosol potassium as a biomass burning tracer, found elevated concentrations of secondary compounds such as oxalate and sulfate in central Greenland, which they believed were due to the transport of aged biomass burning plumes from Northern Canada. Production of sulfate and nitrate has also been reported in other studies of aged biomass burning plumes (Formenti et al., 2003; Bein et al., 2008).

The wide range of observations for different chemical species reported in ambient smoke plumes may be due to a number of reasons. Emissions of both gaseous and particulate species can vary due to fuel type (duff, pine, etc.) (Koppmann et al., 1997), fuel condition (wet/dry) (Johnson and Miyanishi, 2001), meteorological conditions in the burning region and down-wind (cloudy/clear sky/RH) (Hoffa et al., 1999), fire temperature (Cofer et al., 1996), combustion phase of the fire (Gao et al., 2003) and the location and distance where the data are collected from the fires (Trentmann et al., 2003; Reid et al., 2005). Compounding the complexity of the emissions is the mixing of plumes from various regions or even the variability within the region of burning itself, resulting in the mixing of species of various chemical ages and/or species that may have been emitted under different combustion conditions. Given that organic species comprise most of the smoke aerosol mass, this large variability in emissions from fires can make extracting evidence for SOA formation in a plume difficult (de Gouw and Jimenez, 2009). A host of physical and chemical processes in the plumes can also further complicate the analysis as the plumes age.

Fires studied under controlled conditions, such as micro-combustion or the use of pyrolysis devices (Stankiewicz et al., 1998), and introducing smoke into environmental chambers (Johnson and Miyanishi, 2001 and references therein) can eliminate many of these uncertainties. However, these approaches cannot simulate the chemical aging

ACPD
11, 18589–18631, 2011

of plumes over extended time periods in a manner similar to what occurs in the atmosphere.

One way to acquire a clearer picture of the fire plumes and their evolution is the study of fire emissions from mobile airborne platforms. Here, we report on a wide range of smoke plumes and ambient fires studied during the ARCTAS (Arctic Research of the Composition of the Troposphere from Aircraft and Satellites) experiment undertaken by the National Aeronautics and Space Administration (NASA). Jacob et al. (2010) provide detailed information on the various phases of the study and the range of platforms and instrumentation deployed. Fuelberg et al. (2010) present a complete overview of detailed meteorological conditions during ARCTAS-2008, while Singh et al. (2010) illustrate the general trends of the air masses encountered during the mission.

In this paper we compare and contrast measurements of all biomass-burning plumes intercepted by the NASA DC-8 research aircraft during the three ARCTAS phases: ARCTAS-A, based out of Fairbanks, Alaska, USA (3 to 19 April, 2008); ARCTAS-B, based out of Cold Lake, Alberta, Canada (29 June to 13 July, 2008); and ARCTAS-CARB, based out of Palmdale, California, USA; from 18 to 24 June, 2008. A statistical summary of plume NEMRs based on the DC-8 ARCTAS data is provided through contrasting various smoke emissions by broadly separating the plumes into categories according to their source and age (where available). Since ARCTAS-B focused on boreal wildfire emissions, this data set is discussed first to investigate evolution of plumes with age and to provide a basis for comparison with all other plumes intercepted during ARCTAS. During the ARCTAS-CARB phase of the study, where measurements focused on California emissions, extensive local wildfires provide a contrast to the boreal fires of ARCTAS-B, both in the type of material burned and variety of other atmospheric species present in the burning region (i.e. pristine versus anthropogenic-influenced California plumes). In addition, smoke from fires that had been transported great distances and were periodically intercepted at various times during the three phases of this study, are included in the analysis; these types of plumes were most often encountered in the high Arctic during ARCTAS-A. Characteristics of all the various plumes

ACPD
11, 18589–18631, 2011

are compared, acknowledging that they often may represent very different classes of plumes due to their origins and the different processes that may have affected them during short or long transport times.

2 Experimental methods

2.1 Aircraft instrumentation

Jacob et al. (2010) provided a complete list of measurements made aboard the NASA DC-8 aircraft during ARCTAS. In this analyses the following aircraft data were used: carbon monoxide (CO), carbon dioxide (CO_2), acetonitrile (CH_3CN), hydrogen cyanide (HCN), toluene (TU), benzene (BZ), oxides of nitrogen (NO_x and NO_y), ozone (O_3), peroxyacetyl nitrate (PAN), methane (CH_4), PM_1 (particulate matter with aerodynamic diameter less than 1 µm) water soluble organic carbon (WSOC), PM_1 aerosol non-refractory chemical components including sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), chloride (Cl), and organic aerosol (OA). The hydroxyl radical (OH) and meteorological data and aircraft position measurements (such as latitude, longitude, altitude, etc.) were also used. A list of the instruments, corresponding references to more detailed instrument descriptions and data collection rates are provided in Table 1.

2.2 Plume analysis

To synchronize data used in the following analyses, timing of all data was checked and adjusted, if necessary, to match that of ambient water vapor (H_2O_v) concentrations. Differences can arise due to errors or drift in individual instrument clocks, lag times in sample transport from inlet to detector, and instrument response time. For species where measurements were performed in discrete intervals (e.g., HCN) data were interpolated over the midpoint times of the measurement for CO. Additionally, HCN and CH_3CN data were compared with each other for all flights and adjusted for better peak alignment where values increased for both species. The data were then averaged to a 10-s timeline to obtain a uniform time-base.

ACPD
11, 18589–18631, 2011

The two main trace gases emitted from biomass burning are CO and CO_2 (Crutzen et al., 1979). To identify all burning smoke plumes in the ARCTAS data set, all flights were checked for CO and CO_2 enhancements. For this analysis, plumes were defined as an increase in concentration equivalent to twice that of the uncertainty of the measurement when the enhancement was sustained for at least 4 s. The uncertainty values for CO and CO_2 measurements were reported as 2 ppb and 0.25 ppm (Vay et al., 2011), respectively. Once the plumes were identified, CH_3CN and HCN were used as biomass burning tracers to determine if CO and CO_2 enhancements were mainly due to biomass burning or from other sources. If r^2 values for CO and CH_3CN, or CO and HCN were higher than 0.6 during the period of enhanced CO and CO_2 measurement, the plume was designated as biomass burning. To estimate background values, the measurements outside each plume were averaged and used as the background measurement for that specific plume. The duration of the background measurements were different for each plume and depended on factors such as the location of the next plume, time of flight in the same altitude as the plume, etc. From this data set, the plumes were initially separated by phase of study (ARCTAS-A, ARCTAS-B and ARCTAS-CARB). Further analyses were performed on these plumes to identify the source of the smoke. This analysis was performed using location of the fires (where available), the approximate transit time from the fire to the measurement, and evaluation of other emissions in the region (e.g., urban) to assess possible mixing of smoke with other emissions during transport.

2.2.1 Identification of fire source, smoke trajectory, plume age, and possible mixing with other emissions

For all the plumes identified, plume trajectory from fire to measurement point and an estimate of transport age of the identified fire plume were determined through a combination of back trajectory and forward plume movement estimation (using wind direction and speed) analyses. Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) analyses (http://www.arl.noaa.gov/ready/hysplit4.html) were conducted within

ACPD
11, 18589–18631, 2011

each smoke plume, at 10 s intervals (i.e. for each data point present in the plumes), starting from the location where the aircraft first intercepted the plume. These back trajectories were extended for up to 5 days prior to the measurement. The back trajectory analyses, for each measurement point, were repeated for 3 different altitudes (the altitude where the plume was intercepted ±20 %). Using the Fire Information for Resource Management System (FIRMS) (Justice et al., 2002; Giglio et al., 2003; Davies et al., 2009) website, a combination of the results from FLEXPART (Stohl et al., 2005) and HYSPLIT analyses were used to predict the plume's trajectory. FLEXPART (http://transport.nilu.no/flexpart) dispersion model runs for up to 6 days were used to locate the potential path of the emission from the fires to their intersection with the DC-8 flight path for each isolated plume. When both FLEXPART and HYSPLIT analyses were available, the results were compared, and if the general direction of the plume did not agree, the wind direction and speed at the location of the data collection were checked for further verification. These two methods provided similar results in all but three plumes which were excluded from further analysis.

For plumes intercepted near specific fires (boreal fires), based on visual verification from the aircraft video files and FIRMS data, transport age was estimated using wind direction and wind speed and the location of the fire and plume. The uncertainties associated with this calculation depend on a number of factors. The errors associated with the measurements of the meteorological variables (i.e. wind speed and wind direction) were added to the uncertainties in FIRMS fire data location reports. The uncertainties of transport age for ARCTAS-B were calculated to be roughly 40 %. However, it is important to note that this uncertainly is slightly less when closer to the fires (as visual verification is possible) and higher further away from the biomass burning sources as our inability for visual verification increases the level of uncertainty.

In some cases, especially in the ARCTAS-CARB portion of the experiment, the air masses intercepted, either contained fire plumes emitted within or advected over somewhat rural regions with minor anthropogenic influence, or smoke plumes were transported over regions heavily impacted by urban emissions. These two types of cases

ACPD
11, 18589–18631, 2011

were separated by inspecting and comparing the trajectories of the smoke plumes and trajectories of the urban emissions. If these trajectories intersected prior to the measurement, these plumes were categorized into a different class (CARB BB + Urban).

Overall, 495 aircraft intersects with biomass burning plumes from ARCTAS-A, ARCTAS-B and ARCTAS-CARB were isolated from the seventeen DC-8 flights performed during ARCTAS-2008. The locations of the plumes are shown in Fig. 1. The plumes were separated into nine different categories based on fire source and mixing with urban emissions. For some fires, there were multiple transects through what appeared to be the same smoke plume at different times and downwind distances (e.g., boreal fires). A list and description of each plume category is given in Table 2.

2.2.2 Data processing and analysis

For each smoke plume identified, NEMRs were determined relative to CO for all gaseous and aerosol components of interest (Table 1). CO has been previously used as an inert tracer for biomass burning and other emissions (e.g., Sullivan et al., 2006; Yokelson et al., 2008). The lifetime of CO in the atmosphere has been estimated to range from 1–4 months (Seinfeld and Pandis, 1998). Production of CO from VOCs in fire plumes is thought to be minor compared to the primary emitted CO. As the analysis with respect to transport time was only performed on the boreal fire data for plumes less than 16 h old, any loss of CO would be negligible; however, CO loss could influence the NEMRs reported here for smoke transported over longer distances. NEMRs were determined in two ways; from the slope of a linear regression fit, or by using the mean plume concentrations and subtraction of background values. The two methods generally agreed when the component of interest (X) and CO were well correlated ($r > 0.6$). When the correlation coefficient was smaller ($r < 0.6$), the averaged plume concentrations were used to determine the ratio, as this method is thought to be more robust.

Averaging the data for each species over a 10 s time period minimized some differences between instrument response times (e.g., time smearing). However, this was

ACPD
11, 18589–18631, 2011

still a concern when data were collected close to the fires where plumes could be extremely narrow; resulting from short plume widths and fast aircraft speed (the typical range of speed for the NASA DC-8 was 500–850 km h^{-1} for an altitude range of 1.5–12 km). For data (such as WSOC) from instruments with slower time response, the correlation was generally poor and so the averaged plume concentrations were used exclusively.

2.3 Analyses complications and simplifications

2.3.1 Detailed data segregation versus counting statistics

The 495 plumes analyzed in this study were segregated by fire location, (which is likely related to the type of material burned) and mixing with other emissions (e.g., urban). The result of this categorization is that some groups contain fewer plumes, making their statistical analysis weaker. However, the plume categorization enabled us to study emissions from different sources; this advantage is thought to override the possible statistical shortcoming.

2.3.2 Transport age vs. photochemical age

In the analysis of age for the boreal fire plumes, transport age (i.e. time elapsed from emission to measurement) was calculated, which is different from the plume photochemical age. These two times may differ due to the time of day when the smoke was emitted and when the plume was intercepted by the aircraft or the meteorological conditions in the region (cloudy/clear sky) and the smoke surrounding the region of the measurement. Transport age was used in this analysis instead of photochemical age as the variability in the emissions produced inconsistent results for the photochemical age estimates. The use of visual verification through aircraft videos and simultaneous back-trajectory analyses using HYSPLIT and FLEXPART reduces the transport time uncertainty as much as possible within the scope of this study.

ACPD
11, 18589–18631, 2011

2.3.3 Mixing of various emissions into single smoke plumes

Identifying the source of a plume, either visually when close to the fire or based on back trajectories, and assuming this source is representative of a specific fire, is somewhat uncertain for a number of reasons. First, even within a single region of burning there could be differences in material burned and burning conditions. This was visually observed in the boreal fires as areas of white and black smoke mixing within a single plume. Second, as the plume moves away from the fire, other smaller nearby fires may add fresh emissions to the plume, mixing in smoke of different ages and possibly emission characteristics. Evidence of such events was also observed in the boreal fires. Because of the averaging approach used in this analysis, these issues add uncertainty and likely some scatter to the calculated NEMRs.

2.3.4 Different losses of species relative to CO and the effect of mixing plumes of differing background concentrations

Accounting for dilution of both trace gas and aerosol particle emissions by normalizing to CO assumes that dilution is the main process leading to the loss of primary emissions as the plume moves away from the fire. This is not the case if the species in the plume experience substantial dry or wet deposition losses. For example, soluble trace gases or hydrophilic particles are likely to be much more efficiently lost in wet scavenging events compared to CO or other insoluble/hydrophobic species. Model studies have also shown that NEMRs calculated for diluting plumes can have larger uncertainty due to background concentrations (McKeen et al., 1996). This effect is most prominent when the difference between in-plume and background concentration is low, either due to a very diffuse plume and/or a species with high background concentrations. Both of these effects are not considered here, but should mostly lead to larger relative uncertainties for the more aged and dilute plumes.

ACPD
11, 18589–18631, 2011

3 Results and discussion

3.1 Boreal forest fires (ARCTAS-B)

During the final phase of ARCTAS, smoke plumes from many active boreal fires in Northwestern Canada were investigated. In Fig. 2 black squares represent the locations of all active fires in North America during ARCTAS-B. The most substantial fires were located near Lake Athabasca (59.27° N, −109.45° W) and Lake Mackay (63.94° N, −111.16° W) and were extensively sampled during flights on 1 and 4 July 2008, respectively. The average altitude where these boreal fire plumes were intercepted was approximately 1500 ± 300 m a.g.l. and ranged between 700 m a.g.l. close to the fires, to about 3000 m a.g.l. further downwind.

To investigate the evolution of various gaseous species and secondary aerosol formation in boreal fires as a function of plume age, smoke plumes from four distinct fires were studied. These fires were encountered during four different flights on different days (29 June 2008, 1 July 2008, 4 July 2008 and 8 July 2008). Figure 3a to n show the NEMRs for each of these fires as a function of plume age; with time scales varying from less than approximately 30 min since emission, to plumes with estimated transport times of 16 h encountered at considerable distances (e.g., ~320 km) downwind of the fires.

CH_3CN and HCN concentrations relative to CO show some variability, but do not show a trend transport age (Fig. 3a and b), consistent with the long lifetimes of these compounds. These results are further confirmed in Table 3, where the high correlation coefficients (for values inside each plumes) between these two species and CO provide further support for their emission from the fires. Variability in emissions within the same fire or between different fires can result from variability in fire temperature (e.g., Maleknia et al., 2009) and nitrogen content of the biomass (Yokelson et al., 2007).

Similar trends were observed for CO_2 and CH_4 (Fig. 3c and d), which are also stable compounds on these time scales. Mauzerall et al. (1998) report increasing NEMRs of CH_4 with plume age. As CH_4 has a long atmospheric lifetime and is emitted from

ACPD
11, 18589–18631, 2011

fires, the lack of a correlation between CO and CH_4 may result from mixing of the different boreal fire plumes. Additionally, Simpson et al. (2010) noted CH_4 and CO_2 enhancements in this region due to the presence of oil sand emissions, which may have contributed to the scatter in the reported NEMRs of these compounds.

Benzene and toluene enhancements relative to CO ranged from 0.01 to 2.2 ppbv ppmv^{-1} and 0.001 to 0.5 ppbv ppmv^{-1}, respectively (Fig. 3e and f). Trends in NEMRs for these two compounds were similar to the other stable species.

There was also no clear trend in the evolution of NO_x, NO_y (not shown) and O_3 relative to CO (Fig. 3g and h). O_3 levels were only slightly higher in many of the plumes relative to the regional background concentrations (O_3/CO typically 50 ppbv ppmv^{-1}). Thus, O_3 enhancement relative to CO was mostly low (NEMRs < 80 ppbv ppmv^{-1}), with a few plume intercepts occurring on three of the four days where ratios were high (NEMRs between 600 to 1200 ppbv ppmv^{-1}). These infrequent high ozone episodes were not associated with clear enhancements of other species, either gaseous or aerosol phase. Overall, no clear O_3 enhancement was observed in most boreal fires as also noted by Alvarado et al. (2010). Table 3 also shows that no changes were observed to the relationship between O_3 and CO with time. A chemical box model simulation of the plume detected on 1 July 2008 (see supplementary material) estimated an average O_3 production rate of 1 ppbv h^{-1} (in the first 3 h), which is small relative to the in-plume observed concentrations of greater than 30 ppbv, explaining the lack of O_3 NEMR increase with plume age.

Peroxyacetyl nitrate (PAN) was observed to increase relative to CO with plume age (Fig. 3i). Although the 1 July 2008 model-simulated PAN production rates are highly uncertain due to ambiguity of plume evolution time, the box model predicted an average PAN production rate of 80 pptv h^{-1} (in the first 3 h), which is of the same order as the observed PAN levels of 400 pptv and is consistent with our observed PAN NEMRs. Based on the box model results the effect of PAN on O_3 production is complex. In the first 3 h, the net production of PAN removes NO_x in the atmosphere and reduces O_3 production. As the plume ages and NO_x mixing ratios drop to ~50 pptv, PAN decom-

ACPD
11, 18589–18631, 2011

position becomes a net source of NO_x. When the plume rises to the free troposphere, lower temperatures lead to a longer lifetime of PAN (from hours to days) enabling long-range transport of reactive nitrogen from fires. Mauzerall et al. (1998) observed similar enhancements of PAN in biomass burning plumes over the tropical South Atlantic.

Inorganic aerosol components, nitrate, sulfate and ammonium (Fig. 3j, k and l) also displayed no clear trend with plume age. Nitrate relative to CO was fairly uniform after approximately 0.6 h. Sulfate was generally very low and ammonium, although more scattered, was somewhat similar to nitrate. This is expected since ammonium is likely to be associated with the aerosol nitrate and sulfate components and so should reflect the combined trends of both these species. For sulfate, high values recorded near the fires on 1 July 2008 contribute substantially to the scatter in the early stages of the plume transport. This could be due to differences in smoke emissions from different areas (locations) within the same fire, as seen from the HCN and CH_3CN data in Fig. 3a and b.

The concentrations of OA and WSOC are shown in Fig. 3m and n. Once more, no trend is observed providing no evidence for net SOA formation relative to CO. SOA formation is complex and so lack of evidence for net SOA production may be due to a number of factors in addition to the obscuring effect of variability in the very large primary organic aerosol (POA) emissions. For example, some SOA production may be compensated by POA evaporation, which may depend on a host of factors (temperature, RH, pre-existing organic aerosol mass concentrations, etc.). However, there was no evidence for secondary production of NO_3 and SO_4 suggesting that generally there was little new mass production of any secondary aerosol species, at least above what could be detected for the variability observed in these plumes and at the in-plume concentrations recorded during our measurement time period. The conditions that limited ozone production (low NO_x) may also have resulted in little secondary aerosol formation. The concentration of other oxidants, such as OH ranged from 2×10^6 molecules cm^{-3} for plumes less than an hour old to 3×10^6 molecules cm^{-3} in plumes that had a transport age between one and 16 h. Yokelson et al. (2009) observed

ACPD
11, 18589–18631, 2011

rapid formation of secondary aerosol species in fires where OH concentrations were higher than 1×10^7 molecules cm^{-3}. The observed OH values for the boreal fires are lower than that of Yokelson et al. (2009) by approximately an order of magnitude, but the transport times are an order-of-magnitude higher so differences in the extent of photochemical processing do not appear to explain the observed differences in secondary aerosol formation. On the other hand, these results are similar to those reported by Hobbs et al. (2003) from a savanna fire in South Africa ($\sim 1.8 \times 10^7$ molecules cm^{-3}). Similar results with lack of net SOA production for a subset of plumes analyzed here have been reported by Kondo et al. (2011) and Cubison et al. (2011).

It is important to note that Cubison et al. (2011) have found that organic aerosols in these plumes become more oxidized as they aged, indicated by increasing oxidation of aerosols. Thus, either heterogeneous oxidation of primary OA with little SOA production, or compensation of SOA formation (more oxidized) with POA evaporation (less so) are two possible explanations for these observations.

3.2 Overall comparisons of NEMRs between all biomass burning categories

In the following analyses, data from all fires encountered during the ARCTAS mission are compared, to contrast emission ratios in fires from a wide range of sources. This includes the boreal fires recorded in Northern Canada during ARCTAS-B discussed above, smoke plumes from springtime measurements in the Arctic (ARCTAS-A), and plumes encountered over California (ARCTAS-CARB). Although recorded in the high Arctic, practically all plumes from ARCTAS-A were associated with fires from other regions that had undergone long-range transport. For ARCTAS-CARB, most of the plumes originated from local fires; however, there were a few cases of smoke transported from other regions. ARCTAS-B plumes were exclusively from boreal fires in the region of the measurements.

During ARCTAS-A, air masses over the Arctic appeared to be broadly influenced by biomass burning emissions (Fisher et al., 2010). This was evident in the elevated HCN levels recorded throughout the ARCTAS-A study period. Biomass burning plumes

ACPD
11, 18589–18631, 2011

were frequently encountered over a wide region (Fig. 1), and generally at altitudes of ~5200 ± 800 m a.g.l. Using HYSPLIT and FLEXPART, these biomass-burning plumes were separated into five categories based on their origin of emission. Most of the emissions were from Southern Russia (Siberian), Western China (Asian) or a mixture of both (Siberian-Asian), with a few plumes traced back to European fires. European plumes were also likely influenced by some urban emissions from cities near the burning areas. The final category of plume encountered, originated from a few fires in Canada (Canadian BB, ARCTAS-A). Note that the number of plumes from each category is included on the bar graphs (Fig. 4a to o). Active fires observed in North America during this period are recorded as red circles on the map in Fig. 2.

Fire emissions directly over and in the vicinity of the Central Valley were investigated during four NASA DC-8 flights on 18, 20, 22 and 24 June 2008. Also, during the return transit flight from Cold Lake to Palmdale (13 July 2008), some California fire plumes were intercepted and are included in this analysis. The average altitude of the plumes encountered for the Californian fires studied was 1500 ± 700 m a.g.l.

The California fire plumes were further separated into plumes that were likely to have been influenced by urban emissions and ones that were not. Note that even for the plumes that are categorized as not influenced by urban emissions, there was always evidence for some urban influence (especially for the aged plumes); however, this influence was not as clear as the group defined here as urban-influenced. The correlation coefficient (r) between CO and toluene for biomass burning plumes with urban emission influence was 0.79, whereas biomass-burning plumes which were categorized as not mixed with urban emissions, had coefficients of 0.52, which is thought to be due to the higher variability of fire emissions compared to California urban areas. According to HYSPLIT back trajectories, these plumes traveled over areas that were less directly influenced by the large urban centers near the data collection area (e.g., Los Angeles, Sacramento, San Francisco and San Diego).

Analysis of variance (ANOVA) with Tukey's multiple range test was used to check the significance of the variation of each species when comparing different plume

ACPD
11, 18589–18631, 2011

categories. In this analysis, the independent variables were the categories of the plumes and the dependant variables were NEMRs of gaseous and aerosol species studied. Based on $\alpha = 0.05$, all compounds show a significant difference between the means of different categories except CH_3CN, where $p = 0.23$ and WSOC where $p = 0.42$. These differences and similarities are further discussed in the following sections. Figure 4a through o compare the NEMRs between all plumes and some results are summarized below.

3.2.1 $\Delta CH_3CN/\Delta CO$ and $\Delta HCN/\Delta CO$ (Fig. 4a and b)

Acetonitrile (CH_3CN) and hydrogen cyanide (HCN) are expected to vary little with plume age. Figure 4a shows the range of CH_3CN NEMR and Fig. 4b presents the range of NEMR for HCN in each plume category. The overall range for CH_3CN NEMR was approximately 0.1–5 ppbv ppmv^{-1}. Grieshop et al. (2009) recorded $\Delta CH_3CN/\Delta CO$ levels of 0.1–0.8 ppbv ppmv^{-1} in biomass burning simulated chamber studies. Warneke et al. (2009) reported an average of 3.1 ppbv ppmv^{-1} for agricultural fires, 2.1 ppbv ppmv^{-1} for fires from Lake Baikal and 2.4 ppbv ppmv^{-1} from Canadian boreal forest fires, while Jost et al. (2003) reported values of 3.7 and 4.1 pptv ppbv^{-1} for young Namibian biomass burning plumes. These values are consistent with the range of median values for all fires that were encountered during ARCTAS (1–2 ppbv ppmv^{-1}). Aiken et al. (2010) compare data from many studies for the observed ranges of $\Delta CH_3CN/\Delta CO$ and $\Delta HCN/\Delta CO$ in multiple laboratory and field fire studies. These values range from 0.1–4 ppbv ppmv^{-1} for CH_3CN, again consistent with the ARCTAS observations. $\Delta HCN/\Delta CO$ ratios observed here were 0.5–15 ppbv ppmv^{-1}, and were slightly more variable than $\Delta CH_3CN/\Delta CO$, with the higher values observed in fires that were transported over long distances. The observed $\Delta HCN/\Delta CO$ ratios here are also consistent with the range of 2–9.6 ppbv ppmv^{-1} summarized by Aiken et al. (2010).

ACPD
11, 18589–18631, 2011

3.2.2 $\Delta CO_2/\Delta CO$ and $\Delta CH_4/\Delta CO$ (Fig. 4c and d)

$\Delta CO_2/\Delta CO$ ratios were typically less than 50 to 60 ppmv ppmv^{-1}, but in some cases the distributions were skewed towards higher ratios, such as the CARB + urban fire plumes. The highest CO_2 NEMRs were recorded in Asian biomass burning plumes (Asian CARB). NEMRs of methane span a large range from near zero to roughly 1800 ppbv ppmv^{-1} with generally higher values in the biomass burning plumes that were influenced by urban emissions (e.g., ARCTAS-CARB-Urban, European BB and Asian BB (ARCTAS-CARB)). Modified combustion efficiency (MCE), a parameter which is often used to characterize the flaming vs. smoldering nature of the fires was calculated for each category (Yokelson et al., 2008). These values ranged from 0.79 to 0.95 for the different fire categories, with higher values found in boreal fire plumes and CARB fires and lower values for fires that were transported over long distances.

3.2.3 $\Delta BZ/\Delta CO$ and $\Delta TU/\Delta CO$ (Fig. 4e and f)

The $\Delta BZ/\Delta CO$ levels in all the plumes were very similar (means typically between 1 and 1.5 pptv ppbv^{-1}), except for the plumes that originated from Europe. These plumes contained approximately twice the $\Delta BZ/\Delta CO$. Overall, $\Delta BZ/\Delta CO$ ratios in this study were similar to those of Warneke et al. (2009), 1.1–1.3 pptv ppbv^{-1} and Jost et al. (2003), 0.72 and 1.2 pptv ppbv^{-1}.

Toluene NEMRs were generally less than 1 ppbv ppmv^{-1}. Warneke et al. (2009) reported 0.15 pptv ppbv^{-1} of $\Delta TU/\Delta CO$ for agricultural fires and 0.2 pptv ppbv^{-1} of $\Delta TU/\Delta CO$ for fires near Lake Baikal and Canada. Jost et al. (2003) report higher values observed over young Namibian biomass burning plumes (0.73 and 0.82 pptv ppbv^{-1}). The lower ratios observed by Warneke et al. (2009) may be due to the higher reactivity of toluene and the long transport times from Asia. The highest levels of $\Delta TU/\Delta CO$ were in the ARCTAS-CARB biomass burning plumes that were heavily mixed with urban emissions. Typical urban $\Delta TU/\Delta CO$ ratios vary between 0.81 and 3.07 ppbv ppmv^{-1} (de Gouw and Warneke, 2007), higher than what was recorded in the isolated fire

ACPD
11, 18589–18631, 2011

plumes. Muhle et al. (2007) also report elevated levels (~2 ppb) of toluene in ambient air masses that were influence by forest fires in California. The Asian biomass burning plumes that were intercepted near the coast of California also showed slightly higher ratios of ΔTU/ΔCO, which may reflect contributions from urban or ship emissions in this area. A number of ΔTU/ΔCO plume categories are not plotted due to lack of data.

3.2.4 $\Delta NO_x/\Delta CO$, $\Delta NO_y/\Delta CO$ and $\Delta O_3/\Delta CO$ (Fig. 4g, h and i)

$\Delta NO_x/\Delta CO$ levels were clearly highest in the California fires that were mixed with urban emissions. NO_x is expected to be depleted relative to CO as the smoke plumes age as NO_x is converted to other compounds (e.g., PAN) over time. This is reflected in the differences between NO_x NEMRs for plumes subject to long range transport vs. less aged ones. As the Siberian, European and Asian plumes were subject to long-range transport, the low levels of NO_x in these plumes are to be expected. In contrast, $\Delta NO_y/\Delta CO$ levels were fairly similar in all plumes. The ARCTAS-CARB BB mixed with urban emissions had higher NO_y NEMR values, when compared to other air-masses.

For $\Delta O_3/\Delta CO$ ratios, a number of trends were observed. In the California biomass burning plumes that were mixed with urban emissions, ozone NEMRs were often (but not always) higher than the biomass plumes not mixed with urban emissions. Some studies have reported greatly enhanced O_3 when fire and urban emissions interact (Lee et al., 2008); there was no strong evidence for that effect in this data set. Asian BB (ARCTAS-CARB) plumes encountered near the coast of California often had higher O_3 ratios, possibly due to a large Asian anthropogenic influence, and/or possibly due to mixing with nearby ship plumes, which is consistent with the toluene data discussed above. Chen et al. (2005) also reported the observation of O_3 enhancement in this area, due to ship plumes in an earlier aircraft study.

ACPD
11, 18589–18631, 2011

3.2.5 Aerosol Components: $\Delta NO_3/\Delta CO$, $\Delta SO_4/\Delta CO$, $\Delta NH_4/\Delta CO$ and $\Delta Cl/\Delta CO$ (Fig. 4j, k, l and o)

The nitrate NEMR values were generally similar in ARCTAS-CARB biomass burning plumes that were mixed with urban emissions and Siberian and Siberian-Asian plumes. Lowest levels were recorded in Asian BB along the coast of California, where the highest O_3 NEMR levels were observed. Nitrate NEMR trends were more similar to those of NO_y than NO_x for plumes that were subject to long-range transport such as the Asian and Siberian-Asian plumes.

For sulfate, lowest ratios relative to CO for all plume sources were observed in the boreal fires and California fires that were not influenced by urban sources (CARB + urban). Some studies have provided evidence for the emission of SO_2 and primary sulfate from biomass burning sources (e.g., Smith et al., 2001). The most obvious feature of the sulfate data is the much higher NEMRs in plumes subject to long-range transport. Contributions from anthropogenic SO_2 emissions in the regions of the fires may be one reason, although SO_2 emissions from the Asian fires are also thought to play a role (Kondo et al., 2011). Fine particle sulfate production in Asian anthropogenic plumes advecting to North America is well documented (Peltier et al., 2008; van Donkelaar et al., 2008; Dunlea et al., 2009) and thought to be due to the conversion of a large reservoir of SO_2 to non-volatile sulfate aerosol, which is not depleted by any precipitation scavenging on route. For this study, high sulfate NEMRs were observed in the Asian plumes intercepted near the coast of California, again possibly in part due to influence by ship emissions along the California coast.

$\Delta NH_4/\Delta CO$ levels were similar in boreal and California fire plumes and higher in the California fire plumes that were influenced by urban emissions. For the plumes subject to long-range transport, $\Delta NH_4/\Delta CO$ variability between sources followed that of $\Delta SO_4/\Delta CO$, as expected.

The Cl NEMRs (Fig. 4o) were highest in Asian biomass burning plumes and generally higher in plumes that were subject to long-range transport. The ranges of these

ACPD
11, 18589–18631, 2011

values were similar when comparing Boral and California (CARB) biomass burning plumes.

3.2.6 Aerosol components ΔOA/ΔCO, ΔWSOC/ΔCO (Fig. 4m and n)

Organic species are the largest chemical components of fine particle smoke, and secondary formation may enhance aerosol mass with plume age, although no evidence for this was observed in the ARCTAS-B boreal fire plumes. The emission data have wide and overlapping variability in each transport age group, likely due to the issues discussed in previous sections.

The boreal and California fire plumes had similar levels of OA and WSOC. Overall, the OA and WSOC NEMRs in plumes transported over larger distances were lower compared to smoke plumes encountered closer to the sources of fire (ARCTAS-B and CARB). In this regard, the behavior of these organic components is more similar to that of nitrate and not sulfate. It is also similar to the preferential loss of fine particle OA or WSOC relative to sulfate that has been observed in Asian plumes advected to North America (Peltier et al., 2008; Dunlea et al., 2009). In those cases it was proposed that SOA and sulfate formed close to the emission sources were scavenged by precipitation during ascent to the free troposphere, and that sulfate was regenerated in route as SO_2 survived wet scavenging, but SOA was not, perhaps due to the short lifetime of SOA precursors. Similar processes may apply to these smoke plumes.

4 Conclusions

A detailed study of boreal fire plume evolution for plumes that had aged up to ~16 h downwind of the fires generally showed no evidence for clear changes in most species concentration with increasing plume age. O_3 production rates in the plumes were low, with concentrations only slightly enhanced above the regional background levels (~30 ppbv). PAN was an exception and showed strong production. No evidence for

ACPD
11, 18589–18631, 2011

net secondary aerosol formation of sulfate, nitrate, organic aerosol or water-soluble organic aerosol was apparent. Highly variable emissions, low production rates compared to high primary emissions and complex mixing may have resulted in the observed data scatter and obscured any evidence for formation of secondary aerosol species. Slow oxidative processing, as indicated by low O_3 and OH levels, may have also played a role in the little secondary aerosol formation. However, some previous studies reported large secondary aerosol formation for the range of photochemical ages observed here, consistent with the variability in aerosol production in fire plumes observed when comparing previous studies. Overall, we conclude that there was no net secondary aerosol production in these boreal fires.

Apart from providing a statistical summary of NEMRs for fires from a range of sources, the analysis of all fires encountered during the ARCTAS missions showed that Asian plumes were enhanced in both ozone and sulfate. NO_x and NO_y were enhanced in California fires mixed with urban emissions.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/18589/2011/acpd-11-18589-2011-supplement.pdf.

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ACPD
11, 18589–18631, 2011

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ACPD

11, 18589–18631, 2011

Table 1. Measurements from the NASA DC-8 Aircraft Used in the Analyses Presented in This Paper.

Measurement	Abbreviation	Data Collection Rate	References
Carbon Monoxide Water Methane	CO H_2O CH_4	1 s	(Sachse et al., 1987; Diskin et al., 2002)
Carbon Dioxide	CO_2	1 s	(Vay et al., 2003)
Acetonitrile Toluene Benzene	CH_3CN $C_6H_5CH_3$ (TU) C_6H_6 (BZ)	0.5 s	(Wisthaler et al., 2002)
Hydrogen Cyanide	HCN	0.5 s	(Crounse et al., 2006; Crounse et al., 2009)
Oxides of Nitrogen Ozone	NO NO_2 NO_y O_3	10 s	(Weinheimer et al., 1994)
Non-refractory Submicron Aerosol Components (Sulfate, Nitrate, Ammonium, Chloride Organics)	Aerosol (SO_4, NO_3, NH_4, Cl, Org)*	1 s 10 s	(DeCarlo et al., 2008)
Hydroxyl Radical	OH	20 s	(Brune et al., 1999)
Peroxyacyl Nitrate	PAN	1 s	(Slusher et al., 2004; Kim et al., 2007)
Submicron Water Soluble Organic Carbon	WSOC	3 s	(Sullivan et al., 2006)

* The symbol SO_4, rather than SO_4^{2-} is used for the aerosol sulfate measured by the AMS (and similarly for other predominantly inorganic species) because these measurements may contain contributions from organic species such as organosulfates (organonitrates, etc. for the other species) (Farmer et al., 2010).

ACPD
11, 18589–18631, 2011

Table 2. Abbreviations and Description of Plumes Selected during the ARCTAS-2008 Study.

Plume Abbreviations	Plume Description
BB CARB	Biomass burning plumes that originated from California wildfires
BB CARB + Urban	Plumes of mixed California urban emissions and biomass burning plumes from California wildfires
Asian BB (CARB)	Biomass burning plumes that originated from Asian fires and were transported near the coast of California
Siberian BB (ARCTAS-A)	Plumes that were emitted from Siberian fires and encountered over the Arctic
Asian BB(ARCTAS-A)	Plumes that were originally emitted from Asian (especially Chinese) fires
European BB (ARCTAS-A)	Plumes of mixed European urban and fire emissions encountered over the Arctic
Canadian BB (ARCTAS-A)	Canadian biomass burning plumes that were encountered over the Arctic
Siberian + Asian BB (ARCTAS-A)	Mixed Asian (Chinese) and Siberian biomass burning plumes over the Arctic
Boreal Forest Fires (ARCTAS-B)	Biomass burning plumes from Canadian boreal forest wildfires

ACPD
11, 18589–18631, 2011

Table 3. In-plume Correlation Coefficients between Concentrations of Various Gaseous and Aerosol Compounds and CO Concentrations from Data Recorded within Canadian Boreal Forest Fires (ARCTAS-B). The Values Are Separated into Three Categories Based on the Transport Age of the Plumes.

Measured Compounds	Age $\leq$ 1 h r^2	Age $\leq$ 5 h r^2	Age $\leq$ 16 h r^2
CH_3CN	0.92	0.92	0.94
HCN	0.90	0.91	0.89
CO_2	0.30	0.11	0.50
Methane	0.69	0.53	0.26
Benzene	0.85	0.92	0.85
Toluene	0.69	0.92	0.80
NO_x	0.35	0.18	0.74
O_3	0.02	0.06	0.0005
PAN	0.44	0.66	0.69
NO_3	0.14	0.30	0.41
SO_4	0.053	0.21	0.31
NH_4	0.17	0.30	0.36
OA	0.52	0.83	0.69
WSOC	0.40	0.67	0.53

ACPD
11, 18589–18631, 2011

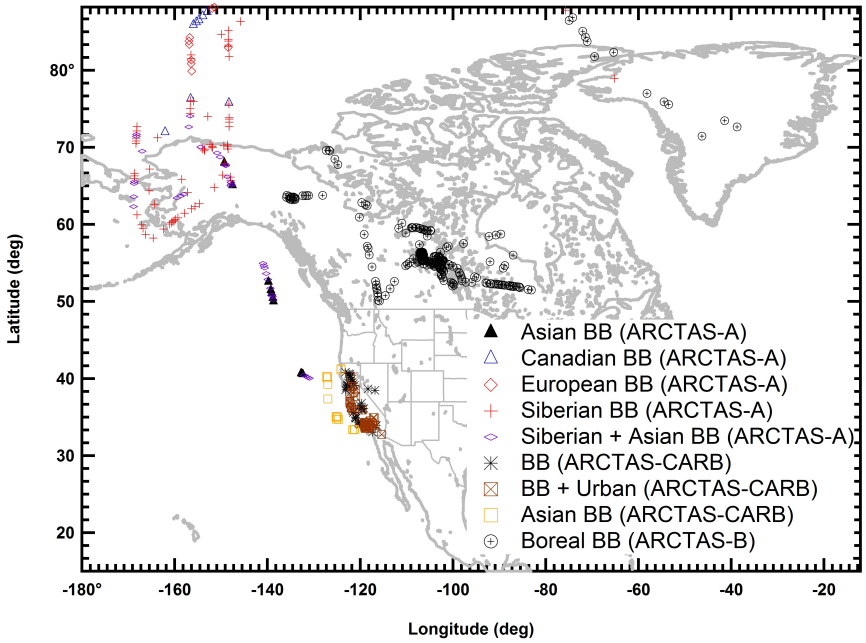

Fig. 1. Location of 495 biomass burning plumes recorded during the ARCTAS-2008 experiment aboard the DC-8 aircraft identified by fire source categories based on air mass backward trajectory analysis.

ACPD
11, 18589–18631, 2011

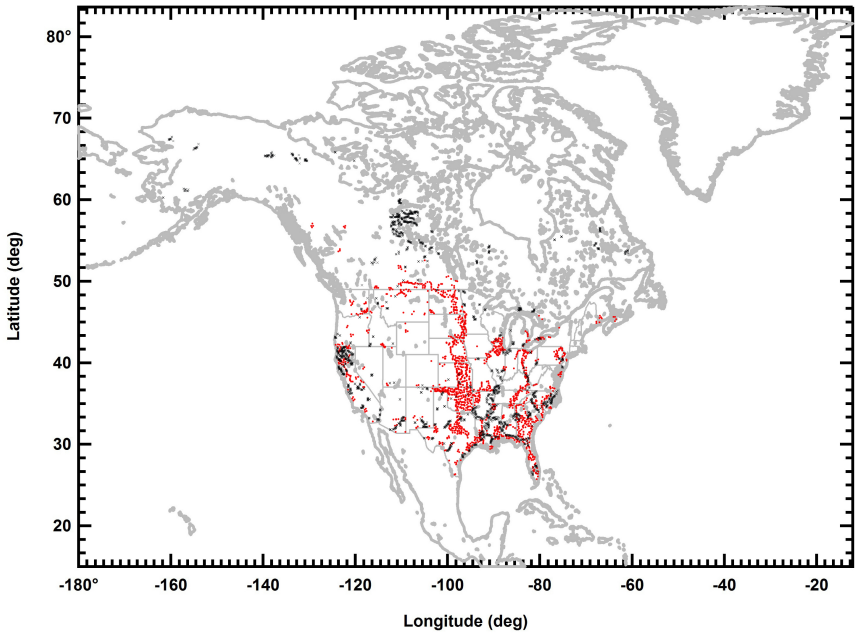

Fig. 2. Location of biomass burning events in North America during ARCTAS-2008 experiment as modified from http://firefly.geog.umd.edu/firemap/. Red circles represent observed active fires from 08 to 19 April 2008 and black squares represent fires from 17 June to 13 July 2008.

ACPD
11, 18589–18631, 2011

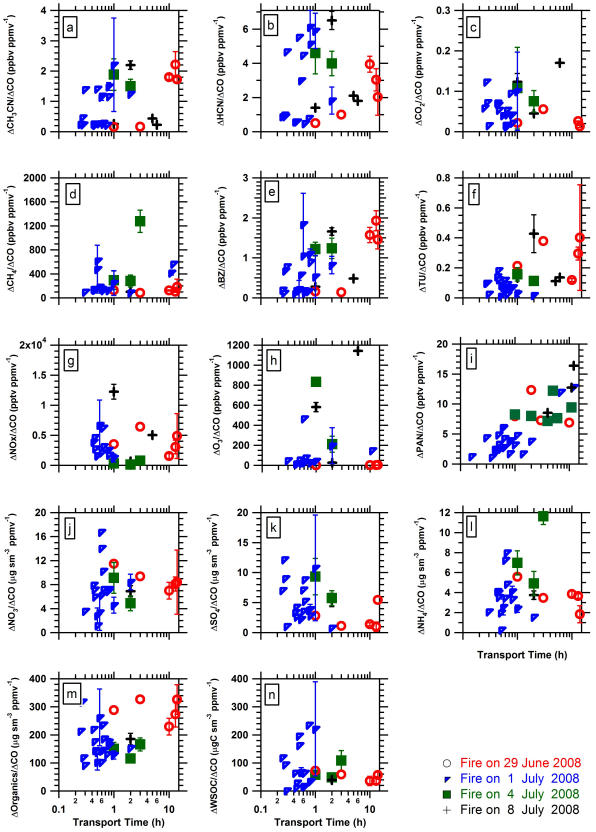

Fig. 3. Evolution of NEMRs for trace-gas and aerosol chemical components in four large boreal forest fires detected during ARCTAS-B. Specific fires are identified by date on which they were intercepted. For cases where transport times were within ±10 % for a fire measured on a given day, the mean NEMR is given and the data range shown as an error bar of ±1× standard deviation. Aerosol contributions are reported under standard conditions (STP) of 1 atm and 273 K.

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11, 18589–18631, 2011

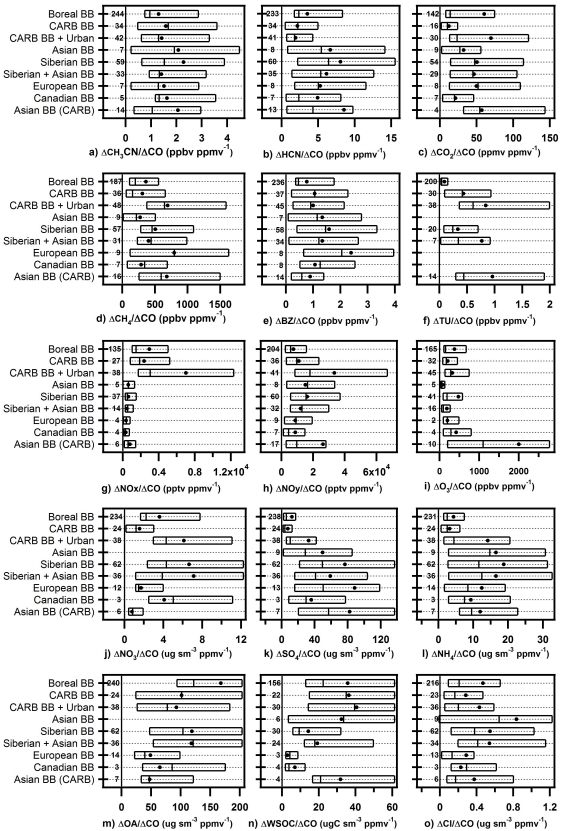

Fig. 4. Comparison of 25th and 75th percentile, mean and median NEMR values for various trace gas and aerosol components in all biomass burning plumes intercepted by the NASA DC-8 during ARCTAS-A, ARCTAS-B and ARCTAS-CARB. Numbers inside the graphs represent the number of plumes present in each category, the black dots and vertical lines in the middle are median and mean, respectively; the long black line indicates the location of zero NEMR for each compound and the sides of the rectangles are the 25th and 75th percentile values.

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11, 18589–18631, 2011