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

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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). Approximately 500 smoke plumes from biomass burning emissions that varied in age from minutes to days were segregated by fire source region and urban emission influences. The normalized excess mixing ratios (NEMR) of gaseous (carbon dioxide, acetonitrile, hydrogen cyanide, toluene, benzene, methane, oxides of nitrogen and ozone) and fine aerosol particulate components (nitrate, sulfate, ammonium, chloride, organic aerosols and water soluble organic carbon) of these plumes were compared. A detailed statistical analysis of the different plume categories for different gaseous and aerosol species is presented in this paper.

The comparison of NEMR values showed that CH₄ concentrations were higher in air-masses that were influenced by urban emissions. Fresh biomass burning plumes mixed with urban emissions showed a higher degree of oxidative processing in comparison with fresh biomass burning only plumes. This was evident in higher concentrations of inorganic aerosol components such as sulfate, nitrate and ammonium, but not reflected in the organic components. Lower NO_x NEMRs combined with high sulfate, nitrate and ammonium NEMRs in aerosols of plumes subject to long-range transport, when comparing all plume categories, provided evidence of advanced processing of these plumes.

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 impact biogeochemical cycles, air quality, human health, and have 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



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burning episodes 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; Turetsky et al., 2011).

Characterization of emissions from biomass combustion has been one of the more challenging areas of atmospheric research. 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; Akagi et al., 2011). Using a variety of sampling methods, both laboratory and direct studies of fires have been used to characterize 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 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), 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. A host of physical and chemical processes in the plumes can also further complicate the analysis as the plumes age.

One way to acquire a clearer picture of the fire plumes and their evolution is the study of fire emissions from mobile airborne platforms. Analysis and presentation of data on plumes emitted from different biomass burning sources, under various ambient and transport conditions is a valuable tool in both investigating plume processing mechanisms and useful in verifying regional and global emission and dispersion model results. 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). Ja-

cob 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.

The emission ratio, where the emission of a species of interest is normalized by a co-emitted, non-reactive species (typically CO or CO₂), is an 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 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 $\Delta X/\Delta \text{CO}$. 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. 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. A statistical summary of plume NEMRs is provided through contrasting various smoke emissions by broadly separating the plumes into categories according to their sources. 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 the 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. Characteristics of all the various plumes 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 (CO₂), acetonitrile (CH₃CN), hydrogen cyanide (HCN), toluene (TU), benzene (BZ), oxides of nitrogen (NO_x and NO_y), ozone (O₃), methane (CH₄), PM₁ (particulate matter with aerodynamic diameter less than 1 μm) water soluble organic carbon (WSOC), PM₁ aerosol non-refractory chemical components including sulfate (SO₄), nitrate (NO₃), ammonium (NH₄), chloride, and organic aerosol (OA). The meteorological data and aircraft position measurements (such as latitude, longitude, altitude, etc.) are also used. A list of the instruments, corresponding references to more detailed instrument descriptions and data collection rates are provided in Table 1.

To synchronize data used in the following analysis, timing of all data was checked and adjusted, if necessary, to match that of ambient water vapor (H₂O_v) concentrations. For species where measurements were performed in discrete intervals (e.g., HCN) data were interpolated over the mid-point times of the measurement for CO. Additionally, HCN and CH₃CN data were compared 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.

2.2 Plume identification and analysis

The two main trace gases emitted from biomass burning are CO and CO₂ (Crutzen et al., 1979). To identify all burning smoke plumes in the ARCTAS data set, all flights were checked for CO and CO₂ 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 CO₂ measurements were reported as 2 ppb and 0.25 ppm (Vay et al., 2011), respectively. Once the plumes were identified, CH₃CN and HCN were used as biomass burning tracers to determine if CO and CO₂ enhancements were mainly due to biomass burning or from other sources. If r^2 values for CO and CH₃CN, or CO and HCN were higher than 0.6 during the period of enhanced CO and CO₂ 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 to identify the source of the smoke. This was achieved using the 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. The details of these analyses are discussed in the following sections. The locations of the plumes are shown in Fig. 1.

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 was determined through a combination of back trajectory analysis and forward plume movement estimation (using wind direction and speed). Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLOT) analyses (<http://www.arl.noaa.gov/ready/hysplit4.html>) were conducted within 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 to up to 5 days prior to the measurement. The back trajectory analyses were repeated for 3 different altitudes (the altitude where the plume was intercepted $\pm 20\%$) for each data point. 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 HYSPLOT 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 HYSPLOT 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. Examples of typical back trajectory analysis results for the main categories of plumes are presented in Fig. 2.

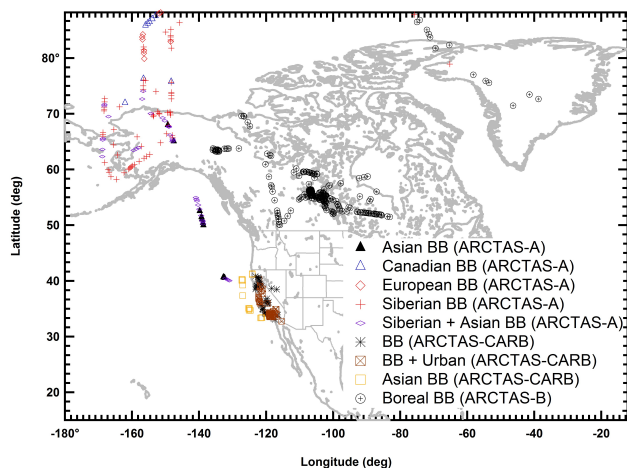
During the ARCTAS-CARB portion of the experiment, the air masses intercepted contained fire plumes emitted within or advected over somewhat rural regions with minor anthropogenic influence; on the other hand, some smoke plumes were transported over regions heavily impacted by urban emissions. These two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

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	CO	1 s	Sachse et al. (1987); Diskin et al. (2002)
Water	H ₂ O		
Methane	CH ₄		
Carbon Dioxide	CO ₂	1 s	Vay et al. (2003)
Acetonitrile	CH ₃ CN	0.5 s	Wisthaler et al. (2002)
Toluene	C ₆ H ₅ CH ₃ (TU)		
Benzene	C ₆ H ₆ (BZ)		
Hydrogen Cyanide	HCN	0.5 s	Crounse et al. (2006); Crounse et al. (2009)
Oxides of Nitrogen	NO	10 s	Weinheimer et al. (1994)
Ozone	NO ₂		
	NO _y		
	O ₃		
Non-refractory Submicron Aerosol Components (Sulfate, Nitrate, Ammonium, Chloride Organics)	Aerosol (SO ₄ , NO ₃ , NH ₄ , chloride, OA)*	1 s 10 s	DeCarlo et al. (2008)
Submicron Water Soluble Organic Carbon	WSOC	3 s	
			Sullivan et al. (2006)

* The symbol SO₄, rather than SO₄²⁻ 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).

**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.

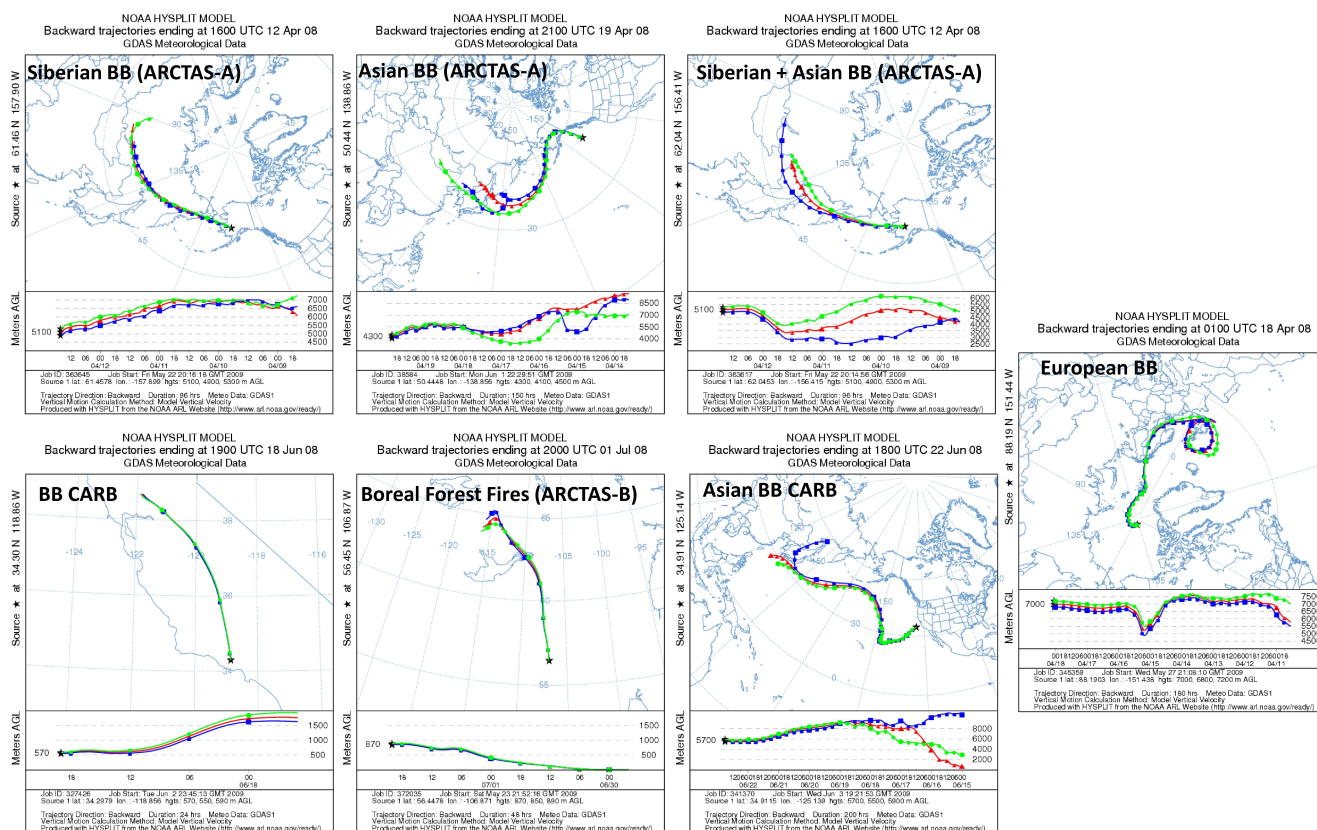
during ARCTAS-2008. The locations of the plumes are shown in Fig. 1. For some fires, there were multiple transects through what appeared to be the same smoke plume at different times and downwind distances (e.g., boreal fires). A list and description of each plume category is given in Table 2.

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 concentrations. NEMRs were determined by using the mean plume concentrations and subtraction of background values, for each plume.

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

Plume Abbreviations	Plume Description
CARB BB	Biomass burning plumes that originated from California wildfires
CARB BB + 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

**Fig. 2.** Typical HYSPLIT back trajectory analysis results for some of the major plume categories.

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 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 FIRMS data, then 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.

2.3.3 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 or uptake of gaseous species into aqueous phase. 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.

3 Results and discussion

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, there were a only few cases of smoke transported from other regions. ARCTAS-B plumes were exclusively from boreal fires in the region of the measurements. Compared to ARCTAS-A where many plumes were subject to long range transport, plumes encountered during ARCTAS-B and ARCTAS-CARB were less aged.

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 concentrations recorded throughout the ARCTAS-A study period. Biomass burning plumes were frequently encountered over a wide region, and generally at altitudes of $\sim 5200 \pm 800$ 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). The number of plumes from each category is included on the bar graphs (Fig. 3a to o).

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 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 strong as the group defined here as urban-influenced (CARB BB + Urban). The correlation coefficient (r) between CO and toluene for biomass burning plumes with urban emission influence was 0.79, compared to biomass-burning plumes which were categorized as not mixed with urban emissions ($r = 0.52$). This 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 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 $p = 0.2$ and WSOC where $p = 0.4$. These differences and similarities are further discussed in the following sections. A summary of the results from this analysis is presented in Table 3.

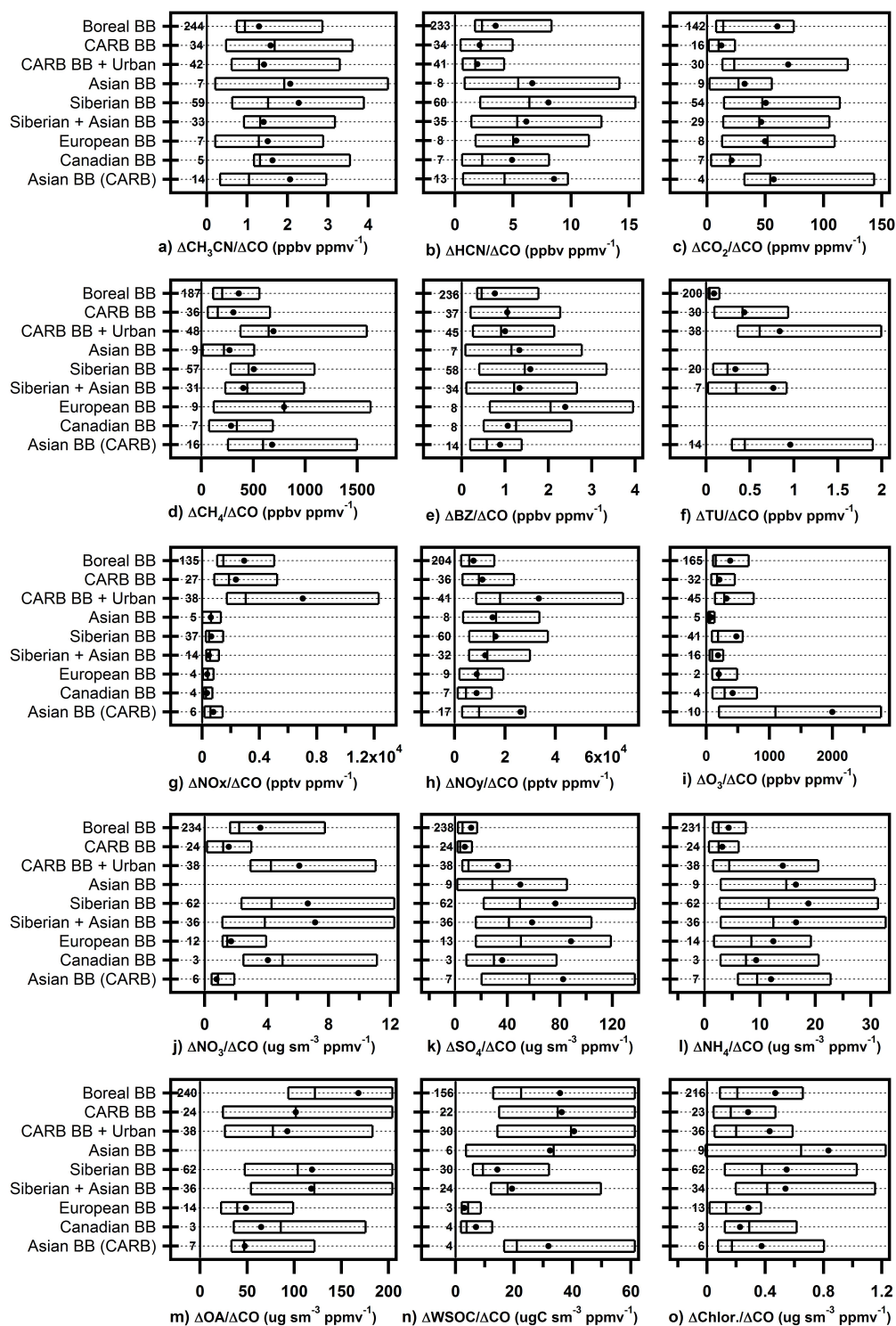


Fig. 3. Comparison of 25th and 75th percentile, mean and median NEMR values for various trace gas and aerosol components in all biomass burning plumes intercepted by the NASA DC-8 aircraft during ARCTAS-A, ARCTAS-B and ARCTAS-CARB. Numbers inside the graphs represent the number of plumes present in each 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.

Table 3. Results of the statistical comparison of NEMRs of compounds in different plumes.

	Average	Std. dev	P value
$\Delta\text{CH}_3\text{CN}/\Delta\text{CO}$ ppbv ppmv ⁻¹	1.7	0.4	0.4
$\Delta\text{HCN}/\Delta\text{CO}$ ppbv ppmv ⁻¹	5	2	0.02
$\Delta\text{CO}_2/\Delta\text{CO}$ ppmv ppmv ⁻¹	44	19	0.02
$\Delta\text{CH}_4/\Delta\text{CO}$ ppbv ppmv ⁻¹	478	199	0.03
$\Delta\text{BZ}/\Delta\text{CO}$ ppbv ppmv ⁻¹	1.3	0.5	0.002
$\Delta\text{TU}/\Delta\text{CO}$ ppbv ppmv ⁻¹	0.6	0.3	0.03
$\Delta\text{NO}_x/\Delta\text{CO}$ pptv ppmv ⁻¹	1721	2196	8×10^{-5}
$\Delta\text{NO}_y/\Delta\text{CO}$ pptv ppmv ⁻¹	15 440	8820	1×10^{-6}
$\Delta\text{O}_3/\Delta\text{CO}$ ppbv ppmv ⁻¹	472	585	9×10^{-6}
$\Delta\text{NO}_3/\Delta\text{CO}$ ppbv ppmv ⁻¹	4	2	4×10^{-5}
$\Delta\text{SO}_4/\Delta\text{CO}$ $\mu\text{g sm}^{-3}$ ppmv ⁻¹	49	30	4×10^{-7}
$\Delta\text{NH}_4/\Delta\text{CO}$ $\mu\text{g sm}^{-3}$ ppmv ⁻¹	12	5	5×10^{-11}
$\Delta\text{OA}/\Delta\text{CO}$ $\mu\text{g sm}^{-3}$ ppmv ⁻¹	95	41	0.02
$\Delta\text{WSOC}/\Delta\text{CO}$ $\mu\text{gC sm}^{-3}$ ppmv ⁻¹	24	14	0.2
$\Delta\text{chloride}/\Delta\text{CO}$ $\mu\text{g sm}^{-3}$ ppmv ⁻¹	0.4	0.2	0.0005

3.1 $\Delta\text{CH}_3\text{CN}/\Delta\text{CO}$ and $\Delta\text{HCN}/\Delta\text{CO}$ (Fig. 3a and b)

Acetonitrile (CH_3CN) and hydrogen cyanide (HCN) are expected to vary little with plume age. Figure 3a shows the range of CH_3CN NEMRs and Fig. 3b presents the range of NEMRs for HCN in each plume category. The overall range for CH_3CN NEMR was 0.1–5 ppbv ppmv⁻¹. Simpson et al. (2011) reported average emission ratios of 1.8 ± 0.3 ppbv ppmv⁻¹ from five Canadian boreal forest fire plumes encountered during ARCTAS-2008 for CH_3CN . Grieshop et al. (2009) recorded $\Delta\text{CH}_3\text{CN}/\Delta\text{CO}$ 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 $\Delta\text{CH}_3\text{CN}/\Delta\text{CO}$ and $\Delta\text{HCN}/\Delta\text{CO}$ 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. $\Delta\text{HCN}/\Delta\text{CO}$ ratios observed here were 0.5–15 ppbv ppmv⁻¹. The observed $\Delta\text{HCN}/\Delta\text{CO}$ ratios here are also consistent with 8.2 ± 2.0 ppbv ppmv⁻¹ average emission ratios reported by Simpson et al. (2011) and the range of 2–9.6 ppbv ppmv⁻¹ summarized by Aiken et al. (2010).

3.2 $\Delta\text{CO}_2/\Delta\text{CO}$ and $\Delta\text{CH}_4/\Delta\text{CO}$ (Fig. 3c and d)

$\Delta\text{CO}_2/\Delta\text{CO}$ 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 BB + 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 about 1800 ppbv ppmv⁻¹ with generally higher values in the biomass burning plumes that were influenced by urban emissions (e.g., CARB BB + Urban, European BB and Asian BB (CARB)). Simpson et al. (2011) reported average emission ratios of 72 ± 44 ppbv ppmv⁻¹ for methane, for the five Canadian boreal forest fire plumes encountered during ARCTAS-2008. 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). Kondo et al. (2011) present an analysis of the biomass burning plumes encountered during ARCTAS-2008 using MCE to categorize various plumes. In the data presented here, 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. It is important to note that the original emission ratios and MCE values may have been changed, especially for plumes that were subject to long range transport.

3.3 $\Delta\text{BZ}/\Delta\text{CO}$ and $\Delta\text{TU}/\Delta\text{CO}$ (Fig. 3e and f)

The benzene NEMRs 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 $\Delta\text{BZ}/\Delta\text{CO}$. Overall, $\Delta\text{BZ}/\Delta\text{CO}$ ratios in this study were similar to those of Simpson et al. (2011), 1.7 ± 0.3 pptv ppbv⁻¹, 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 $\Delta\text{TU}/\Delta\text{CO}$ for agricultural fires and 0.2 pptv ppbv⁻¹ of $\Delta\text{TU}/\Delta\text{CO}$ 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). Simpson et al. (2011) analyzed five boreal forest fire plumes and reported emission ratios of 0.67 ± 0.16 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 values of $\Delta\text{TU}/\Delta\text{CO}$ were in the ARCTAS-CARB biomass burning plumes that were heavily mixed with urban emissions. Typical urban $\Delta\text{TU}/\Delta\text{CO}$ 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 plumes. Muhle et al. (2007) also report elevated concentrations (~ 2 ppb) of toluene in ambient air

masses that were influenced by forest fires in California. The Asian biomass burning plumes that were intercepted near the coast of California also showed slightly higher ratios of $\Delta\text{TU}/\Delta\text{CO}$, which may reflect contributions from urban or ship emissions in this area. A number of $\Delta\text{TU}/\Delta\text{CO}$ plume categories are not plotted due to lack of data.

3.4 $\Delta\text{NO}_x/\Delta\text{CO}$, $\Delta\text{NO}_y/\Delta\text{CO}$ and $\Delta\text{O}_3/\Delta\text{CO}$ (Fig. 3g, h and i)

NO_x NEMRs 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. fresh ones. As the Siberian, European and Asian plumes were subject to long-range transport, the low concentrations of NO_x in these plumes are to be expected. In contrast, NO_y NEMRs were fairly similar in all plumes. The CARB BB + Urban plumes had higher NO_y NEMR values, when compared to other air-masses.

For $\Delta\text{O}_3/\Delta\text{CO}$ 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). 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 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.

3.5 Aerosol components: $\Delta\text{NO}_3/\Delta\text{CO}$, $\Delta\text{SO}_4/\Delta\text{CO}$, $\Delta\text{NH}_4/\Delta\text{CO}$ and $\Delta\text{chloride}/\Delta\text{CO}$ (Fig. 3j, 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 concentrations were recorded in Asian BB along the coast of California, where the highest O_3 NEMRs 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 BB + 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 (e.g., use of sulfur rich fertilizers, agricultural burning and the conversion of the released SO_2 to sulfate during long range transport) may be one reason, 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 the influence of ship emissions along the California coast or due to the use of sulfur rich compounds in crop fertilizers and the subsequent burning of the agricultural areas.

NH_4 NEMRs were similar in boreal and California fire plumes and higher in the California fire plumes that were influenced by urban emissions and possible ammonia emissions from the nearby feedlots. For the plumes subject to long-range transport, $\Delta\text{NH}_4/\Delta\text{CO}$ variability between sources followed that of $\Delta\text{SO}_4/\Delta\text{CO}$, as expected.

The chloride NEMRs (Fig. 3o) were highest in Asian biomass burning plumes and generally higher in plumes that were subject to long-range transport. The ranges of these values were similar when comparing boreal and California biomass burning plumes.

3.6 Aerosol Components $\Delta\text{OA}/\Delta\text{CO}$, $\Delta\text{WSOC}/\Delta\text{CO}$ (Fig. 4m and n)

Organic compounds comprise the largest chemical component of fine particle in smoke from biomass burning, and secondary formation may enhance aerosol mass with plume age. The emission data have wide and overlapping variability in each transport age group, likely due to the issues discussed in previous sections.

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 on 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 statistical summary of NEMRs of a wide range of gaseous and particulate species relative to CO is presented for fire plumes recorded from the NASA DC-8 aircraft as part of the ARCTAS-2008 mission. Comparisons between the wide range of fires are made with identical instrumentation and thus the observed variability is not dependent on the variations in measurement methods. This summary provides a valuable reference for comparison with previous and future studies of biomass burning emissions.

Gaseous and aerosols species emitted as primary products or produced as secondary compounds were compared. CH₃CN and HCN are considered primary biomass burning emissions and often used as tracers for such sources. HCN NEMRs showed higher variability when comparing the different plume sources. The lowest HCN concentrations were observed in boreal, CARB and CARB BB + Urban biomass burning plumes. The use of HCN as a tool to normalize and estimate other biomass burning emissions has been studied in recent years. The higher variability of HCN presented in this data may complicate such a process unless more data on the variability (dependence of burning material) and its possible change with long range transport can be collected. CO₂ and CH₄ NEMRs do not provide a clear trend; however, CH₄ concentrations are higher in biomass burning plumes that were mixed with urban emissions such as CARB BB + Urban and European BB. The benzene concentrations of European BB plumes are also higher than all the other categories, reinforcing the possible mixing of these biomass burning plumes with urban emissions. When comparing NO_x NEMRs, plumes subject to long range transport are depleted in NO_x, as is expected in well processed plumes. On the other hand, NO_y concentrations are similar in different plume categories, with some high values observed in CARB BB + Urban emissions. The highest ozone concentrations are observed in Asian BB plumes that were encountered off the coast of California. As noted before, this may be due to the transport of these plumes from regions with ship emissions.

Higher values of secondary inorganic aerosol species are observed in CARB BB + Urban air-masses, when comparing the fresh plumes (i.e. boreal BB, CARB BB and CARB BB + Urban), which may be an indication of the faster oxidation rates in these plumes. This in turn, may be a result of the high oxidative potential of the plumes in this category as evident in higher NO_x, NO_y and O₃ NEMRs. The boreal emissions have the higher organic aerosol concentrations. A similar trend is not observed in WSOC data, which may be an indication of the dominant nature of primary organic emissions from these plumes.

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