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Boreal forest fire emissions in fresh Canadian smoke plumes: C_1-C_{10} volatile organic compounds (VOCs), CO_2, CO, NO_2, NO, HCN and CH_3CN

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Abstract. Boreal regions comprise about 17 % of the global land area, and they both affect and are influenced by climate change. To better understand boreal forest fire emissions and plume evolution, 947 whole air samples were collected aboard the NASA DC-8 research aircraft in summer 2008 as part of the ARCTAS-B field mission, and analyzed for 79 non-methane volatile organic compounds (NMVOCs) using gas chromatography. Together with simultaneous measurements of CO_2, CO, CH_4, CH_2O, NO_2, NO, HCN and CH_3CN, these measurements represent the most comprehensive assessment of trace gas emissions from boreal forest fires to date. Based on 105 air samples collected in fresh Canadian smoke plumes, 57 of the 80 measured NMVOCs (including CH_2O) were emitted from the fires, including 45 species that were quantified from boreal forest fires for the first time. After CO_2, CO and CH_4, the largest emission factors (EFs) for individual species were formaldehyde (2.1 ± 0.2 g kg^{-1}), followed by methanol, NO_2, HCN, ethene, α-pinene, β-pinene, ethane, benzene, propene, acetone and CH_3CN. Globally, we estimate that boreal forest fires release 2.4 ± 0.6 Tg C yr^{-1} in the form of NMVOCs, with approximately 41 % of the carbon released as C_1-C_2 NMVOCs and 21 % as pinenes. These are the first reported field measurements of monoterpene emissions from boreal forest fires, and we speculate that the pinenes, which are relatively heavy molecules, were detected in the fire plumes as the result of distillation of stored terpenes as the vegetation is heated. Their inclusion in smoke chemistry models is expected to improve model predictions of secondary organic aerosol (SOA) formation. The fire-averaged EF of dichloromethane or CH_2Cl_2, $(6.9 \pm 8.6) \times 10^{-4}$ g kg^{-1}, was not significantly different from zero and supports recent findings that its global biomass burning source appears to have been overestimated. Similarly, we found no evidence for emissions of chloroform ($CHCl_3$) or methyl chloroform (CH_3CCl_3) from boreal forest fires. The speciated hydrocarbon measurements presented here show the importance of carbon released by short-chain NMVOCs, the strong contribution of pinene emissions from boreal forest fires, and the wide range of compound classes in the most abundantly emitted NMVOCs, all of which can be used to improve biomass burning inventories in local/global models and reduce uncertainties in model estimates of trace gas emissions and their impact on the atmosphere.

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1 Introduction

Boreal forests account for roughly one-third of the global forested area and include vast areas of Russia (which contains 22 % of the global forested area), Canada (7 %) and

Nordic countries (2 %) (http://www.borealforest.org). Fires in boreal regions are estimated to account for 9 % of global fire carbon emissions, primarily from forest fires with the remainder from agricultural waste fires (van der Werf et al., 2010). Boreal forest fire emissions can greatly perturb atmospheric composition and chemistry on regional and even global scales. For example, major boreal forest fires in Russia from 2002–2003 were largely responsible for anomalous global growth rates of many trace gases including carbon monoxide (CO), methane (CH_4) and ethane (C_2H_6) (Kasischke et al., 2005; Yurganov et al., 2005; Simpson et al., 2006). These short-term global trace gas anomalies have been linked to El Niño Southern Oscillation (ENSO) indices (Jones and Cox, 2005; Simpson et al., 2006), most likely via the influence of ENSO events on large-scale biomass burning activity (Baltzer et al., 2005; Carmona-Morena et al., 2005).

In addition to inter-annual influences such as ENSO, boreal forest fire activity is expected to increase on a multi-decade scale in response to global climate change (Soja et al., 2007). At high latitudes ($>55°$ N), amplification of the global warming signal may lead to increased dryness and temperature, resulting in greater fire activity (Marlon et al., 2008). The area burned in Canada has increased since 1970 (Gillett et al., 2004; Girardin, 2007) most likely due to rising temperatures and the increased frequency of large fire years (Gillett et al., 2004; Kasischke and Turtesky, 2006). In the future, fire occurrences are predicted to increase across Canada, with an estimated 30 % increase by 2030 (Wotton et al., 2010) and a 74–118 % increase in the area burned by 2100 under a tripled CO_2 scenario (Flannigan et al., 2005). The resulting increased fuel consumption is, in turn, expected to lead to a near-doubling of CO_2-equivalent greenhouse gas emissions from Canadian fires (Amiro et al., 2009).

Because of the global impact of boreal forest fire emissions and the sensitivity of high-latitude ecosystems to global climate change, boreal forest fires were the major focus of the summer phase of NASA's Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS-B) field mission (June–July, 2008). Based primarily in Cold Lake, Alberta (Canada), ARCTAS-B sought to quantify boreal forest fire emissions, assess the near-field chemical evolution of the fire plumes, and understand the implications of boreal forest fires on regional and global atmospheric composition (Jacob et al., 2010). During Flights 17–23 of ARCTAS-B, the University of California, Irvine (UC-Irvine) collected 947 whole air samples, including 105 samples collected in fresh Canadian boreal forest fire plumes and 13 in an aged Siberian plume. Each whole air sample was analyzed for 79 speciated C_1-C_{10} non-methane volatile organic compounds (NMVOCs). Here we quantify boreal forest fire emissions ratios (ERs) and emission factors (EFs) for 57 NMVOCs, including 45 species that, to our best knowledge, have not previously been characterized from boreal forest fires. The measurements are also used to clearly identify

those NMVOC species that are not emitted from boreal forest fires, and we also present simultaneous measurements of other major species that are emitted from biomass burning (CO_2, CO, CH_4, CH_2O, NO_2, NO, HCN and CH_3CN).

2 Experimental

UC-Irvine has used ground-based and airborne research platforms to measure speciated VOCs from diverse environments since the late 1970s (Simpson et al., 2010 and references therein). Our sampling and analysis technique during the ARCTAS mission has been described in Simpson et al. (2010) and is summarized here.

2.1 Airborne whole air sampling (WAS)

This work focuses on the seven northernmost flights of ARCTAS-B (Flights 17–23), which were 8-h science flights flown from 29 June–10 July 2008 over Canada, Greenland, and the Arctic Ocean from bases in Cold Lake, Alberta ($54°28'$ N, $110°11'$ W) and Thule, Greenland ($77°28'$ N, $69°14'$ W) (see Jacob et al., 2010 for flight tracks). Our sampling technique collects whole air samples (WAS) into 2-l electropolished, conditioned, evacuated stainless steel canisters each equipped with a Swagelok Nupro metal bellows valve (Solon, OH). The canisters were prepared for field use via a series of pump-and-flush procedures, after which they were evacuated to 10^{-2} Torr and injected with 17 Torr of purified water to minimize surface adsorption. During ARCTAS-B we collected up to 168 WAS per flight. The sampling was manually controlled and used a stainless steel dual head metal bellows pump to draw outside air into a window-mounted $1/4$ in. forward-facing inlet, through our air sampling manifold, and into one of the 168 canisters until it was filled to 40 psig. Samples were typically collected over a 1 min period every 3–5 min during horizontal flight legs, and every 1–2 min during ascents, descents, and plume encounters. A total of 947 whole air samples were collected during Flights 17–23.

2.2 Laboratory analysis of NMVOCs

After sampling the canisters were returned to our UC-Irvine laboratory and analyzed within 7 days. Rigorous storage tests have shown that alkene growth in the canisters is negligible over a 7 day period (<1.4 pptv), and all other compounds reported here are stable over this period to within the stated uncertainties. In particular, the more poorly constrained precision and accuracy for the oxygenated hydrocarbons (Table 1) reflects that they can increase or decrease in the canisters at a rate of few percent per day. The NMVOC analysis uses three gas chromatographs (GCs) coupled with two flame ionization detectors (FIDs), two electron capture detectors (ECDs), and a quadrupole mass spectrometer detector (MSD). For each sample a 1520 cm^3 aliquot is

Table 1. Analytical details, measurement statistics, emission ratios (ERs) and emission factors (EFs) for CO_2, CO, CH_4, NO, NO_2, HCN, CH_3CN and 57 NMVOCs that were statistically enhanced in five Canadian boreal forest fire plumes compared to background measurements during the summer 2008 ARCTAS field mission. For both long-lived and short-lived compounds, "Plume avg." is the average mixing ratio calculated from the five smoke plume averages; "Bkgd. avg." is the average of the five corresponding background air masses; and "Plume max." is the maximum mixing ratio measured in all five smoke plumes. However the ERs and EFs presented here for the short-lived compounds are based on a much smaller subset of data (see text). The CO ER uses CO_2 as its reference gas.

Compound	Formula	Lifetime[a]	LOD (pptv)	Precision[b] (%)	Accuracy (%)	Bkgd. Avg. (pptv)	Plume Avg. (pptv)	Plume max. (pptv)	ER to CO (ppbv/ppbv)	EF (g kg^{-1})	Boreal emission (Gg yr^{-1})
Long-lived											
Carbon dioxide	CO_2	> 100 yr	n/a	0.1 ppmv	0.25 ppmv	381.7 ± 1.4 ppmv	384.7 ± 1.5 ppmv	402.5 ppmv		1616 ± 180	588 ± 66 (Tg)
Carbon monoxide	CO	2 mo	n/a	1	1	160 ± 21 ppbv	674 ± 151 ppbv	1898 ppbv	0.11 ± 0.07	113 ± 72	41 ± 26 (Tg)
Methane	CH_4	9 yr	n/a	0.1	2	1848 ± 7 ppbv	1882 ± 11 ppbv	2000 ppbv	0.072 ± 0.044	4.7 ± 2.9	1.7 ± 1.1 (Tg)
Hydrogen cyanide	HCN	5 mo	15	n/a[c]	50[c]	549 ± 205	3539 ± 1053	12196	(8.2 ± 2.0) × 10^{-3}	0.89 ± 0.29	326 ± 105
Acetonitrile	CH_3CN	6 mo	20	10	30	210 ± 50	1202 ± 325	3930	(1.8 ± 0.3) × 10^{-3}	0.30 ± 0.06	109 ± 21
Ethane	C_2H_6	47 d	3	1	5	1041 ± 95	3463 ± 764	12 168	(4.6 ± 0.9) × 10^{-3}	0.56 ± 0.13	204 ± 46
Propane	C_3H_8	11 d	3	2	5	245 ± 41	932 ± 213	3586	(1.3 ± 0.3) × 10^{-3}	0.23 ± 0.05	83 ± 19
i-Butane	C_4H_{10}	5.5 d	3	3	5	16 ± 5	63 ± 14	229	(8.8 ± 1.6) × 10^{-5}	0.021 ± 0.004	7.6 ± 1.6
n-Butane	C_4H_{10}	4.9 d	3	3	5	40 ± 10	212 ± 54	776	(3.2 ± 0.5) × 10^{-4}	0.076 ± 0.015	28 ± 5
i-Pentane	C_5H_{12}	3.2 d	3	3	5	12 ± 5	46 ± 12	220	(6.5 ± 1.9) × 10^{-5}	0.019 ± 0.005	6.9 ± 1.9
n-Pentane	C_5H_{12}	3.0 d	3	3	5	16 ± 4	93 ± 24	337	(1.4 ± 0.2) × 10^{-4}	0.042 ± 0.008	15.3 ± 3.0
n-Hexane	C_6H_{14}	2.2 d	3	3	5	4.4 ± 2.1	46 ± 14	188	(7.9 ± 1.4) × 10^{-5}	0.027 ± 0.006	10.0 ± 2.1
2+3-Methylpentane	C_6H_{14}	2.2 d	3	3	5	3.5 ± 2.5	30 ± 9	141	(5.1 ± 1.1) × 10^{-5}	0.018 ± 0.004	6.4 ± 1.6
n-Heptane	C_7H_{16}	1.7 d	3	3	5	2.8 ± 1.8	34 ± 10	144	(5.9 ± 0.6) × 10^{-5}	0.024 ± 0.004	8.7 ± 1.3
Ethyne	C_2H_2	2 wk	3	3	5	205 ± 57	1244 ± 397	5904	(2.1 ± 0.9) × 10^{-3}	0.22 ± 0.09	80 ± 34
Propyne	C_3H_4	2 d	5	30	20	4.8 ± 4.0	95 ± 37	506	(1.8 ± 0.8) × 10^{-4}	0.029 ± 0.013	10.7 ± 4.7
Benzene	C_6H_6	9.5 d	3	3	5	99 ± 36	992 ± 319	4359	(1.7 ± 0.3) × 10^{-3}	0.55 ± 0.11	200 ± 40
Toluene	C_7H_8	2.1 d	3	3	5	33 ± 14	371 ± 139	1849	(6.7 ± 1.6) × 10^{-4}	0.24 ± 0.06	91 ± 23
Ethylbenzene	C_8H_{10}	1.7 d	3	3	5	2.1 ± 1.7	32 ± 14	179	(5.8 ± 2.1) × 10^{-5}	0.025 ± 0.009	9.1 ± 3.4
n-Propylbenzene	C_9H_{12}	2.0 d	3	3	5	0.7 ± 1.2	10 ± 5	58	(1.8 ± 0.8) × 10^{-5}	(8.9 ± 4.2) × 10^{-3}	3.2 ± 1.5
Methanol	CH_3OH	12 d	50	30	20	4268 ± 528	9586 ± 1785	32740	(9.6 ± 1.9) × 10^{-3}	1.2 ± 0.3	451 ± 101
Ethanol	C_2H_5OH	3.6 d	20	30	20	205 ± 26	325 ± 78	1278	(1.5 ± 1.5) × 10^{-4}	0.027 ± 0.029	9.9 ± 10.4
Acetone	C_3H_6O	15 d	100	30	30	1042 ± 109	1845 ± 245	4552	(1.6 ± 0.4) × 10^{-3}	0.37 ± 0.10	133 ± 36
Methyl ethyl ketone	C_4H_8O	9.5 d	5	30	20	94 ± 15	299 ± 69	1190	(3.8 ± 1.0) × 10^{-4}	0.11 ± 0.03	40 ± 11
Methyl nitrate	CH_3NO_3	1 mo	0.02	5	10	7.5 ± 0.5	9.8 ± 0.9	21.7	(4.6 ± 2.8) × 10^{-6}	(1.4 ± 0.9) × 10^{-3}	0.52 ± 0.32
Ethyl nitrate	$C_2H_5NO_3$	2–4 wk	0.02	5	10	4.8 ± 0.7	6.2 ± 0.5	9.8	(2.4 ± 1.2) × 10^{-6}	(8.8 ± 4.5) × 10^{-4}	0.32 ± 0.16
i-Propyl nitrate	$C_3H_7NO_3$	1–3 wk	0.02	5	10	4.0 ± 0.6	6.2 ± 0.7	13.3	(3.8 ± 2.3) × 10^{-6}	(1.6 ± 1.0) × 10^{-3}	0.58 ± 0.37
n-Propyl nitrate	$C_3H_7NO_3$	1-2 wk	0.02	5	10	0.8 ± 0.3	1.0 ± 0.1	2.1	(3.7 ± 2.8) × 10^{-7}	(1.6 ± 1.2) × 10^{-4}	0.057 ± 0.044
2-Butyl nitrate	$C_4H_9NO_3$	1–2 wk	0.02	5	10	2.3 ± 0.6	4.7 ± 0.7	13.0	(4.0 ± 2.4) × 10^{-6}	(1.9 ± 1.2) × 10^{-3}	0.70 ± 0.43
2-Pentyl nitrate	$C_5H_{11}NO_3$	4–5 d	0.02	5	10	0.6 ± 0.2	1.0 ± 0.1	2.8	(8.9 ± 5.7) × 10^{-7}	(4.8 ± 3.1) × 10^{-4}	0.17 ± 0.11
3-Pentyl nitrate	$C_5H_{11}NO_3$	4–5 d	0.02	5	10	0.6 ± 0.2	1.2 ± 0.1	3.5	(6.8 ± 3.0) × 10^{-7}	(3.6 ± 1.7) × 10^{-4}	0.13 ± 0.06
3-Methyl-2-butyl nitrate	$C_5H_{11}NO_3$	4–5 d	0.02	5	10	0.9 ± 0.3	1.5 ± 0.2	4.6	(1.1 ± 0.8) × 10^{-6}	(5.7 ± 4.6) × 10^{-4}	0.21 ± 0.17
Methyl chloride	CH_3Cl	1.0 yr	50	5	10	551 ± 8	622 ± 23	825	(1.4 ± 0.3) × 10^{-4}	0.029 ± 0.007	10.7 ± 2.7
Methyl bromide	CH_3Br	0.7 yr	0.5	5	10	8.6 ± 0.2	11.0 ± 0.8	18.9	(4.7 ± 1.1) × 10^{-6}	(1.8 ± 0.5) × 10^{-3}	0.66 ± 0.17
Methyl iodide	CH_3I	4 d	0.005	5	20	0.28 ± 0.05	0.66 ± 0.12	1.6	(6.9 ± 1.4) × 10^{-7}	(3.9 ± 0.9) × 10^{-4}	0.14 ± 0.03
Dibromomethane	CH_2Br_2	3–4 mo	0.01	5	20	0.83 ± 0.02	0.87 ± 0.03	1.07	(0.6 ± 1.1) × 10^{-7}	(4.1 ± 8.0) × 10^{-5}	0.015 ± 0.029
Ethyl chloride	C_2H_5Cl	1 mo	0.1	5	30	2.2 ± 0.2	3.2 ± 0.4	8.0	(1.4 ± 1.3) × 10^{-6}	(3.7 ± 3.5) × 10^{-4}	0.14 ± 0.13
1,2-Dichloroethane	$C_2H_4Cl_2$	1–2 mo	0.1	5	10	9.9 ± 0.3	10.6 ± 0.3	12.4	(1.6 ± 1.3) × 10^{-6}	(6.4 ± 5.1) × 10^{-4}	0.23 ± 0.19
Carbonyl sulfide	OCS	2.5 yr	10	2	10	451 ± 11	511 ± 19	706	(1.2 ± 0.2) × 10^{-4}	0.029 ± 0.007	10.5 ± 2.5
Dimethyl sulfide	C_2H_6S	1–2 d	1	10	20	4.4 ± 0.8	9.6 ± 1.9	38	(9.2 ± 4.5) × 10^{-6}	(2.3 ± 1.2) × 10^{-3}	0.84 ± 0.42

introduced to the analytical system and passed through a loop filled with glass beads maintained at liquid nitrogen temperature. A Brooks Instrument mass flow controller (Model 5850E) keeps the flow below $500\,cm^3\,min^{-1}$ to completely trap the less volatile sample components (e.g., VOCs) while the more volatile components (e.g., N_2, O_2) are pumped away. To introduce analytes into the GC columns, the less volatile species are re-volatilized by immersing the loop in hot water (80 °C) and then flushed by a helium carrier. The sample flow is split into five streams and sensed by five column/detector combinations listed in Simpson et al. (2010). The FID and ECD signals are output to a personal computer and digitally recorded using Chromeleon Software; the MSD signal uses Chemstation software. To optimize the quality of our measurements, each peak of interest on every chromatogram was individually inspected and manually integrated, for a total of more than 100 000 hand-modified peaks during ARCTAS-B.

International intercomparison experiments have demonstrated that our analytical procedures consistently yield accurate identification of a wide range of blindly selected hydrocarbons and produce excellent quantitative results (e.g., Apel et al., 1999, 2003). During ARCTAS the measurements were calibrated using both working standards collected in the Sierra Nevada mountains (analyzed every 4–8 samples) and absolute standards (analyzed once or twice daily). Our hydrocarbon standards are NIST-traceable and the halocarbon standards are either NIST-traceable or were made in-house and have been compared to standards from other groups such as NOAA/ESRL and AGAGE. It is important to note that the alkyl nitrate measurements use a new calibration scale that was implemented in June 2008, just before the ARCTAS-B

Table 1. Continued.

Compound	Formula	Lifetime[a]	LOD (pptv)	Precision[b] (%)	Accuracy (%)	Bkgd. Avg. (pptv)	Plume Avg. (pptv)	Plume max. (pptv)	ER to CO (ppbv/ppbv)	EF (g kg^{-1})	Boreal emission (Gg yr^{-1})
Short-lived											
Nitric oxide	NO	1 d	20	2	10	40 ± 36	182 ± 113	1831	$(2.4 \pm 0.1) \times 10^{-3}$	0.29 ± 0.03	n/a
Nitrogen dioxide	NO_2	1 d	30	5	10	173 ± 121	1228 ± 799	12 462	$(5.6 \pm 0.3) \times 10^{-3}$	1.03 ± 0.13	n/a
Formaldehyde	CH_2O	1 d	200	n/a[d]	200[d]	388 ± 30	4617 ± 5696	39 235	$(17.5 \pm 0.3) \times 10^{-3}$	2.1 ± 0.2	771 ± 86
Ethene	C_2H_4	1.4 d	3	3	5	378 ± 186	4084 ± 1434	18 693	$(7.3 \pm 0.1) \times 10^{-3}$	0.82 ± 0.09	300 ± 33
Propene	C_3H_6	11 h	3	3	5	89 ± 48	1095 ± 428	5465	$(2.3 \pm 0.1) \times 10^{-3}$	0.38 ± 0.04	139 ± 15
1-Butene	C_4H_8	8.8 h	3	3	5	14 ± 8	169 ± 69	867	$(3.4 \pm 0.1) \times 10^{-4}$	0.077 ± 0.009	28 ± 3
i-Butene	C_4H_8	5.4 h	3	3	5	13 ± 5	119 ± 49	604	$(2.5 \pm 0.2) \times 10^{-4}$	0.056 ± 0.007	20 ± 3
cis-2-Butene	C_4H_8	4.9 h	3	3	5	0.7 ± 1.0	14 ± 9	193	$(6.7 \pm 0.4) \times 10^{-5}$	0.015 ± 0.002	5.5 ± 0.7
$trans$-2-Butene	C_4H_8	4.3 h	3	3	5	0.6 ± 1.1	12 ± 9	184	$(8.7 \pm 0.7) \times 10^{-5}$	0.020 ± 0.003	7.1 ± 1.0
1,3-Butadiene	C_4H_6	4.2 h	3	3	5	8.4 ± 6.0	125 ± 66	802	$(3.2 \pm 0.2) \times 10^{-4}$	0.070 ± 0.008	25 ± 3
Methacrolein	C_4H_6O	9.6 h	5	30	20	75 ± 26	203 ± 45	878	$(1.5 \pm 0.1) \times 10^{-4}$	0.043 ± 0.005	16 ± 2
Methyl vinyl ketone	C_4H_6O	14 h	5	30	20	186 ± 49	443 ± 91	1906	$(3.4 \pm 0.2) \times 10^{-4}$	0.097 ± 0.012	35 ± 4
Furan	C_4H_4O	3.4 h	10	30	20	26 ± 17	471 ± 177	2344	$(1.0 \pm 0.1) \times 10^{-3}$	0.28 ± 0.03	102 ± 12
Isoprene	C_5H_8	2.8 h	3	3	5	265 ± 110	346 ± 101	1634	$(2.7 \pm 0.5) \times 10^{-4}$	0.074 ± 0.017	27 ± 6
$m + p$-Xylene	C_8H_{10}	12–19 h[e]	3	3	5	6.8 ± 4.1	82 ± 42	563	$(1.4 \pm 0.1) \times 10^{-4}$	0.060 ± 0.008	22 ± 3
o-Xylene	C_8H_{10}	20 h	3	3	5	3.0 ± 2.4	46 ± 24	328	$(6.4 \pm 0.3) \times 10^{-5}$	0.027 ± 0.003	10.0 ± 1.2
2-Ethyltoluene	C_9H_{12}	23 h	3	3	5	0.5 ± 1.0	23 ± 3.4	89	$(1.1 \pm 0.2) \times 10^{-5}$	$(5.2 \pm 0.9) \times 10^{-3}$	1.9 ± 0.3
3-Ethyltoluene	C_9H_{12}	15 h	3	3	5	0.9 ± 1.3	13.4 ± 6.3	89	$(2.4 \pm 0.3) \times 10^{-5}$	0.012 ± 0.002	4.3 ± 0.8
4-Ethyltoluene	C_9H_{12}	24 h	3	3	5	0.7 ± 1.3	7.2 ± 3.3	44	$(1.5 \pm 0.2) \times 10^{-5}$	$(7.4 \pm 1.3) \times 10^{-3}$	2.7 ± 0.5
1,2,3-Trimethylbenzene	C_9H_{12}	8.5 h	3	3	5	3.4 ± 3.7	22.0 ± 11.5	206	$(5.1 \pm 0.3) \times 10^{-5}$	0.025 ± 0.003	9.1 ± 1.1
1,2,4-Trimethylbenzene	C_9H_{12}	8.5 h	3	3	5	2.2 ± 3.0	16.0 ± 8.0	112	$(3.2 \pm 0.1) \times 10^{-5}$	0.015 ± 0.002	5.6 ± 0.6
1,3,5-Trimethylbenzene	C_9H_{12}	4.9 h	3	3	5	0.6 ± 1.3	1.9 ± 1.6	20	$(6.0 \pm 0.9) \times 10^{-6}$	$(2.9 \pm 0.5) \times 10^{-3}$	1.1 ± 0.2
α-Pinene	$C_{10}H_{16}$	5.3 h	3	3	5	48 ± 19	172 ± 82	1727	$(1.5 \pm 0.1) \times 10^{-3}$	0.81 ± 0.10	296 ± 36
β-Pinene	$C_{10}H_{16}$	3.7 h	3	3	5	154 ± 51	549 ± 210	2916	$(1.3 \pm 0.1) \times 10^{-3}$	0.72 ± 0.09	262 ± 31

[a] The lifetimes of short-lived OH-controlled species vary temporally and are shorter in the summer when the abundance of OH radicals is greater. The VOC lifetimes may be even shorter in the smoke plumes due to elevated OH levels. With the exceptions of the furan, acetone and the halocarbons, the NMVOC lifetimes are based on OH rate constants from Atkinson and Arey (2003) and assume a 12-h daytime average OH radical concentration of 2.0×10^6 molec cm^{-3}. The lifetime estimate for furan is from Atkinson et al. (2005) and also uses a 12-h daytime OH value of 2.0×10^6 molec cm^{-3}. The total tropospheric lifetime of acetone is based on Jacob et al. (2002). The total lifetimes of the long-lived halocarbons (> 1.0 yr) are based on Clerbaux et al. (2007). The global HCN lifetime is from Li et al. (2003, 2009) and Singh et al. (2003). The global CH_3CN lifetime is from Karl et al. (2003) and Singh et al. (2003). Because NO and NO_2 interchange quickly, their lifetimes are cited as a NO_x (= $NO + NO_2$) lifetime.
[b] The VOC precision deteriorates as we approach our detection limit. At low values the precision is either the stated precision or 3 pptv, whichever is larger. The NO, NO_2, NO_y and O_3 precision values are for high mixing ratios as were encountered in the smoke plumes. At low mixing ratios their precision is 20 pptv for the nitrogen species and 0.1 ppbv for O_3.
[c] The total uncertainty in the HCN measurement, a combined measure of precision and accuracy, is conservatively $\pm 50\% + 50$ pptv at 2σ.
[d] The total uncertainty in the CH_2O measurement is 200 pptv.
[e] The OH-lifetimes of m-xylene and p-xylene are 12.0 and 19.4 h, respectively.

mission. The new scale was provided to us by Prof. Elliot Atlas (University of Miami) and corrects some problems with the alkyl nitrate assignments in the primary mixture upon which the previous calibrations had been done. The correction factors that we have applied here are 2.13, 1.81, 1.24, 1.17 and 1.13 for the C_1, C_2, C_3, C_4 and C_5 alkyl nitrates, respectively.

2.3 CO$_2$, CO, CH$_4$, CH$_2$O, NO$_2$, NO, HCN and CH$_3$CN measurements

This paper also presents measurements of CO, CH_4, carbon dioxide (CO_2), formaldehyde (CH_2O), nitrogen dioxide (NO_2), nitric oxide (NO), hydrogen cyanide (HCN) and acetonitrile (CH_3CN) from ARCTAS-B. These eight gases were measured in situ aboard the DC-8 by six research teams each using fast-response, continuous real-time instruments, with analytical details given in Table 1. Briefly, CO_2 was measured using the NASA Langley Atmospheric Vertical Observations of CO_2 in the Earth's Troposphere (AVOCET) instrument (Vay et al., 2003). Methane and CO were measured by the NASA Langley Differential Absorption CO Measurement (DACOM) instrument (Sachse et al., 1987; Fried

et al., 2008). Formaldehyde was measured using a Difference Frequency Generation Absorption Spectrometer (DFGAS) (Wiebring et al., 2006, 2007). Note that even though CH_2O was measured separately, in the discussions below it is grouped together with the other 79 NMVOCs, for a total of 80 NMVOCs. The nitrogen oxides were measured using the 4-channel NCAR $NO_{xy}O_3$ chemiluminescence instrument (Weinheimer et al., 1994). Hydrogen cyanide was measured using a Chemical Ionization Mass Spectrometer (CIMS) (Crounse et al., 2006), and CH_3CN was measured using a Proton Transfer Reaction Mass Spectrometer (PTR-MS) (Sprung et al., 2001). For correlation purposes, the CO_2, CH_4, CO, CH_2O, NO_2, NO, HCN and CH_3CN data are based only on the average of those 1 s measurements (0.5 s for HCN and CH_3CN) that overlapped the VOC sampling times (i.e., the so-called hydrocarbon data merge). The complete 0.5 s and 1 s data sets for these eight compounds are available at ftp://ftp-air.larc.nasa.gov/pub/ARCTAS/DC8_AIRCRAFT/.

3 Calculations

3.1 Emission Ratios (ERs)

Trace gas emissions from biomass burning can be expressed as emission ratios or emission factors. An ER is the excess mixing ratio of trace gas X measured in a fire plume above its background value ($\Delta X = X_{plume} - X_{bkgd}$) divided by the excess mixing ratio of a simultaneously measured reference gas, usually CO or CO_2 (Andreae and Merlet, 2001). The ER occurs at $t = 0$, or in the very freshest smoke plumes (de Gouw et al., 2006). Because most of the NMVOCs that we measure are released during smoldering combustion (e.g., Blake et al., 1996; Meinardi et al., 2003), we use CO as our reference gas:

$$ER_{X/CO} = \frac{\Delta X}{\Delta CO} = \frac{X_{plume} - X_{bkgd}}{CO_{plume} - CO_{bkgd}} \qquad (1)$$

$ER_{X/CO}$ can be determined through a standard linear regression, or by first subtracting off the background average from each smoke plume sample, then calculating a slope by forcing the fit of the resulting excess values through zero (Yokelson et al., 1999). We chose the latter method because we could readily establish a background value, and because forcing the fit through zero causes higher values (i.e., those with a higher signal-to-noise ratio) to have a greater weighting in the slope determination. The difference between the two methods was found to be less than 7 %.

As soon as they are released from fires, emitted compounds begin to undergo chemical changes that can deplete or enhance their mixing ratios. This can affect the ER and EF calculations and becomes increasingly important for shorter-lived compounds. Because the compounds considered here are predominantly OH-controlled species, we defined long-lived compounds as those with $k_{OH} < 8.52 \times 10^{-12}$ cm^3 molec^{-1} s^{-1} (the rate constant for the reaction of ethene + OH), or a lifetime of more than ~1.4 d. Of the 57 emitted NMVOCs, 35 were considered to be long-lived and 22 were short-lived (Table 1). For the long-lived species, five fresh Canadian biomass burning plumes were selected for the ER calculations ($n = 105$). The plumes were encountered during three local flights departing from and returning to Cold Lake (Flights 17, 18, 19). The location and characteristics of each plume are shown in Fig. 1 and Table 2. Briefly, Plume 1 was sampled on 29 June 2008 (Flight 17) over major active fires near Lake Athabasca, Saskatchewan. Plumes 2 and 3 were sampled on 1 July 2008 (Flight 18) during a detailed characterization of fire plumes on time-scales of minutes to hours. Note that Plume 2 represents many plumes sampled in a relatively large region of hotspot activity, with detailed sampling of a fire centered at 56.5° N and 106.8° W. Plume 3 sampled this same fire again, but later in the day. Plumes 4 and 5 were sampled on 4 July 2008 (Flight 19) in northwest Ontario and near Pelican Narrows, Saskatchewan, respectively. The background measurements for each plume
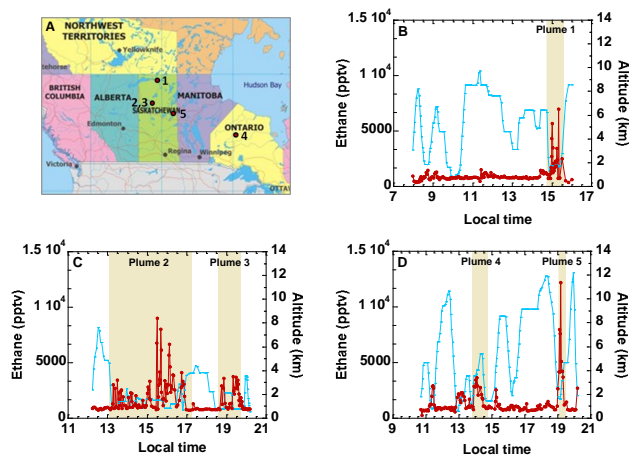

Fig. 1. (a) Approximate locations of five fire plumes that were sampled in 2008 during the summer phase of ARCTAS on 29 June (Plume 1), 1 July (Plumes 2 and 3), and 4 July (Plumes 4 and 5). The plume locations are based on the maximum 1 s CO measurement for each plume encounter, even though they were sampled over a larger area (see Table 2). **(b–d)** Time series of ethane (red circles) and altitude (blue line) for **(b)** Flight 17; **(c)** Flight 18; and **(d)** Flight 19, showing the duration of each plume encounter (shaded area).

were based on same-flight measurements made at a similar time, location and altitude to the sampled plume, typically before and after the plume encounter ($n = 86$). For each plume, the ER was calculated for each trace gas as described above (n-butane is shown as an example in Fig. 2). The five resulting ERs were averaged to give a fire-averaged ER, and its uncertainty is given as the standard deviation of the five ERs.

The plume selection was more restrictive for the short-lived compounds and included only smoke samples that were less than 17 min old, as follows. Plumes 2 and 3 included near-field perpendicular plume crossings downwind of the fire centered at 56.5° N, 106.8° W (Table 2). We defined the smoke source location based on the highest 1 s CO measurement (14 170 ppbv at 56.483° N, 106.837° W) and we selected only those samples collected within 10 km of the source, namely three smoke samples collected 3.7, 3.2 and 7.3 km from the source and two background samples collected 7.9 and 8.5 km from the source (Table 2). Although this careful analysis yielded only a small number of data points, we are confident that fresh smoke very close to the source was sampled. The measured wind speed was 8.4 m s^{-1}, 6.1 m s^{-1} and 7.0 m s^{-1} for the three smoke samples, corresponding to an estimated time since emission of 7 min, 9 min and 17 min, respectively. The ER for each trace gas was calculated as described above (isoprene is shown as an example in Fig. 3a–b), and the uncertainty in the calculated ER is given as the standard error of the slope. Note that because only one fire was used in the ER

Table 2. Characteristics of five biomass burning plumes that were used to analyze the long-lived NMVOCs (>1.4 d). A small subset of Plumes 2 and 3 were used for the analysis of short-lived NMVOCs (≤1.4 d). All times are local (UTC – 07:00 h). n = number of samples; SK = Saskatchewan.

				BKGD		PLUME						
Plume	Flight	Leg	Date	Alt (km)	n	Alt (km)	n	Time (LT)	Lat (° N)	Long (° W)	Location	Characteristics
Long-lived												
1	17	18	Jun-29	1.3–1.8	13	1.7–1.8	12	14:44–15:20	59.16–59.61	104.86–108.44	Saskatchewan	Major active fires; entered into fire plume
2	18	5–13	Jul-01	0.8–3.6	39	0.7–2.9	51	13:09–17:13	52.01–56.50	99.95–106.88	Saskatchewan	Detailed characterization of SK fire plumes
3	18	17–19	Jul-01	0.8–2.3	21	0.8	20	18:36–19:37	55.05–56.55	106.84–107.42	Saskatchewan	Detailed characterization of SK fire plumes
4	19	13–14	Jul-04	0.8–3.7	11	3.5–5.4	12	14:44–15:47	51.71–52.21	84.95–90.19	Ontario	Near-field evolution of fire plumes
5	19	22	Jul-04	2.6–4.7	2	1.6–3.5	10	19:10–19:29	55.16–55.66	102.33–102.80	Saskatchewan	Near-field evolution of fire plumes
Short-lived												
2	18	5	Jul-01	2.8	1	0.8–0.9	2	13:15–13:16	56.46–56.50	106.79–106.88	Saskatchewan	Detailed characterization of SK fire plumes
3	18	17	Jul-01	0.8	1	0.8	1	18:36	56.55	106.84	Saskatchewan	Detailed characterization of SK fire plumes
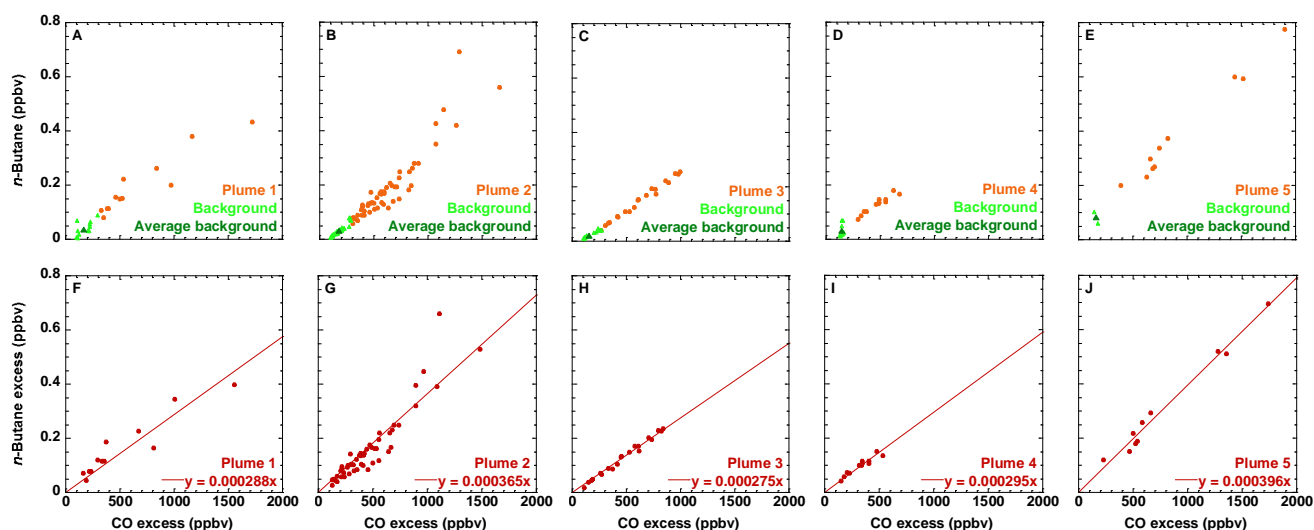
Fig. 2. Mixing ratios of n-butane versus CO in five biomass burning plumes (orange circles) and background air (light green triangles). The average background mixing ratio (dark green triangle) was subtracted from each mixing ratio measured in the biomass burning plumes to give an excess mixing ratio (red circles) for each air sample. Linear fits to the excess mixing ratios plots were forced through zero to give the emission ratio (ER) for each smoke plume. Panels **(a)** and **(f)**: Plume 1; **(b)** and **(g)**: Plume 2; **(c)** and **(h)**: Plume 3; **(d)** and **(i)**: Plume 4; **(e)** and **(j)**: Plume 5.

calculations for short-lived compounds, the uncertainty only represents sample-to-sample variability rather than plume-to-plume variability, and is likely underestimated.

3.2 Emission Factors (EFs)

An EF for compound X uses the amount of fuel burned as its reference, rather than a trace gas such as CO or CO_2. Here we calculated an EF for each species using the carbon mass balance technique described in detail by Yokelson et al. (1999):

$$EF_X \left(\frac{g}{kg} \right) = F_C \times \frac{MM_X}{MM_C} \times \frac{C_X}{C_T} \quad (2)$$

where F_C is the mass fraction of carbon in the fuel (assumed to be $500\,\mathrm{g\,C\,kg^{-1}}$ fuel; Susott et al., 1996), MM_X is the

molecular mass of compound X, MM_C is the molecular mass of carbon ($12.011\,\mathrm{g\,mol^{-1}}$), and C_X/C_T is the number of emitted moles of compound X divided by the total number of moles of carbon emitted. For long-lived species, C_X/C_T was calculated using:

$$\frac{C_X}{C_T} = \frac{\frac{\Delta C_X}{\Delta CO_2}}{\sum_{Y=1}^{n} \left(nC_Y \times \frac{\Delta C_Y}{\Delta CO_2} \right)} \quad (3)$$

where $\Delta C_X/\Delta CO_2$ is the fire-averaged ER of species X to CO_2, nC_Y is the number of carbon atoms in compound Y, and the sum is over all measured carbon-containing species including CO_2, CO and CH_4. For short-lived species, C_X/C_T was calculated as above except using the single ER calculated from the three very fresh smoke samples and the two
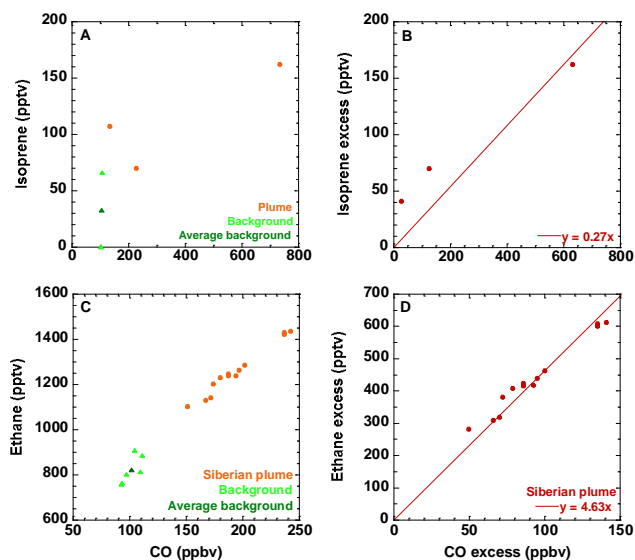
Fig. 3. As in Fig. 2 but for **(a–b)** isoprene using samples selected for the analysis of short-lived compounds, and for **(c–d)** ethane using biomass burning samples from the Siberian plume (see text).

background samples (Sect. 3.1). This method of EF determination assumes that the measured carbon-containing emissions account for all the burned carbon, which is accurate to within a few percent if CO_2, CO, and CH_4 are all measured (Yokelson et al., 1999; Akagi et al., 2011).

4 Results and discussion

4.1 General features

Biomass burning was the dominant feature of the air masses sampled during ARCTAS-B. Carbon monoxide is a general tracer of incomplete combustion, and scatter plots versus CO of many of the trace gases presented here clearly show their combustive emissions from the boreal forest fires (Figs. 4–10). In total, 57 of the 80 measured NMVOCs were considered to be emitted from boreal forest fires, based on positive correlations with CO and statistically enhanced mixing ratios in the average of the five smoke plumes compared to the corresponding background air masses (Table 1). The 57 compounds include all the measured alkanes (except 2,3-dimethylbutane); all the measured alkenes, alkynes, aromatics, sulfur species and alkyl nitrates; all the oxygenated compounds (except the gasoline additive methyl *tert*-butyl ether, or MTBE); six of the simplest halocarbons (CH_3Cl, CH_3Br, CH_3I, C_2H_5Cl, 1,2-dichloroethane, and CH_2Br_2); and CH_2O. Note that ethanol and CH_2Br_2 have been classified among the emitted species despite high plume-to-plume variability (see Sect. 4.2.3). The 23 compounds that were not emitted by the fires were primarily halocarbons and are discussed in Sect. 4.3.
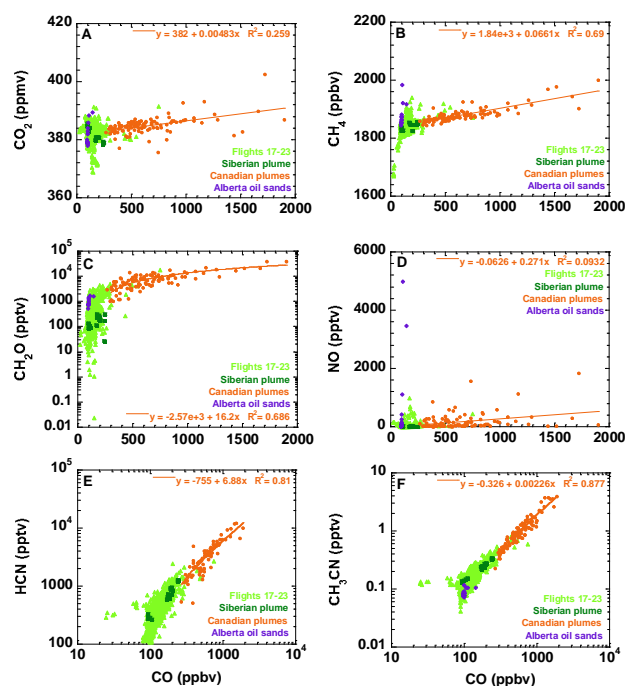
Fig. 4. Scatter plots of CO vs. **(a)** CO_2, **(b)** CH_4, **(c)** CH_2O, **(d)** NO, **(e)** HCN and **(f)** CH_3CN for all 947 whole air samples collected during ARCTAS-B (Flights 17–23). Dark green squares: Siberian boreal forest fire plume ($n = 13$); orange circles: Canadian boreal forest fire plumes ($n = 105$); purple diamonds: Alberta oil sands plume; light green triangles: rest of Flight 17–23.
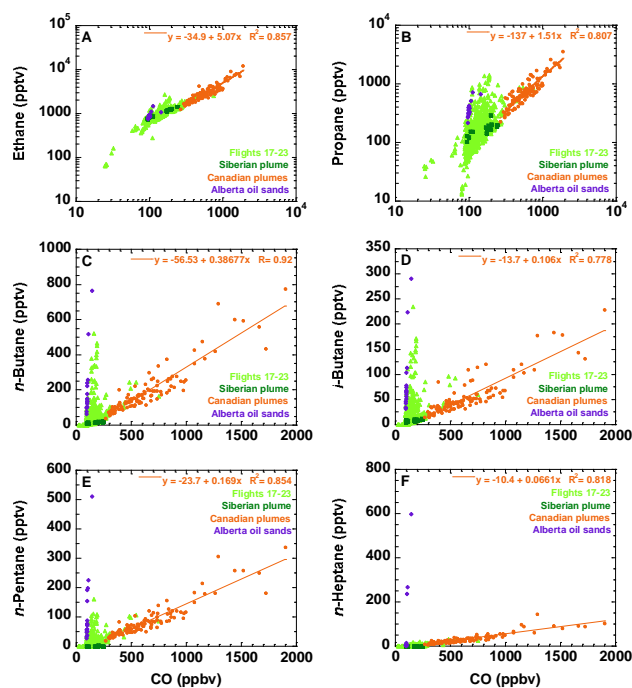

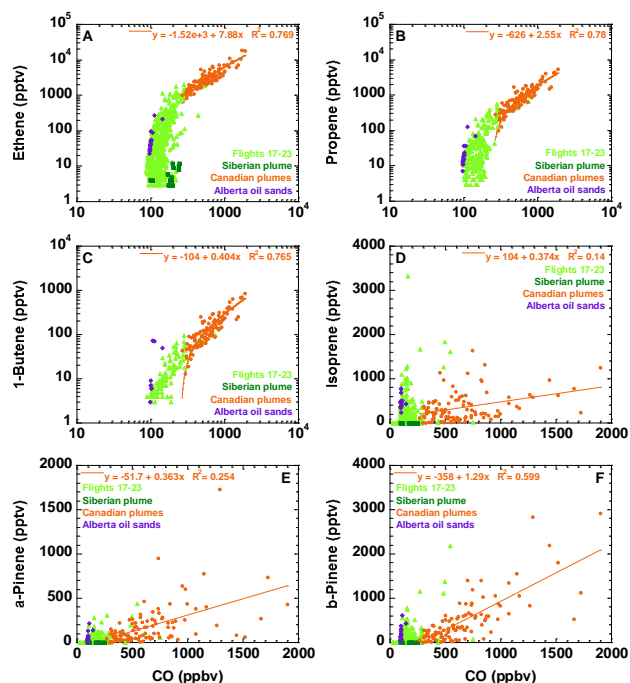**Fig. 5.** As in Fig. 4 but for selected alkanes.

Fig. 6. As in Fig. 4 but for selected alkenes.

Fig. 7. As in Fig. 4 but for ethyne and selected aromatics.

Although biomass burning was the major focus of ARCTAS-B, industrial emissions from Alberta oil sands mining operations were briefly sampled during Flight 23 and showed remarkably elevated levels of many hydrocarbons and solvents (Simpson et al., 2010). For most gases, their industrial and biomass burning influences are clearly distinguished as separate wings in Figs. 4–10, because many of the NMVOCs were released via evaporation (rather than combustion) from the oil sands and other industries, and therefore did not correlate with CO. Mixing ratios in the biomass burning wing far exceeded those in the industrial wing for most alkenes, alkynes, oxygenated compounds, methyl halides and aromatics (Figs. 6–8, 10). By contrast, the strength of the biomass burning and industrial wings varied with chain length for the alkanes. Shorter-chained alkanes (C_2-C_3) were predominantly emitted by biomass burning (Fig. 5a–b), while longer-chained alkanes ($\geq C_5$) were more strongly emitted by the oil sands industry (Fig. 5e–f). The biomass burning and industrial wings were of similar magnitude for the C_4 alkanes in these airborne samples (Fig. 5c–d). The maximum alkyl nitrate enhancements were stronger in the biomass burning wing than in the industrial wing for methyl nitrate and the C_4-C_5 alkyl nitrates, and weaker for the C_2-C_3 alkyl nitrates (Fig. 9a–e). Unlike most other combustion products reported in this paper, the maximum NO mixing ratio in the boreal smoke plumes was considerably lower than that measured over the Alberta oil sands (Fig. 4d), showing the strength of NO emissions from high-temperature combustion during oil sands upgrading operations (Simpson et al., 2010).
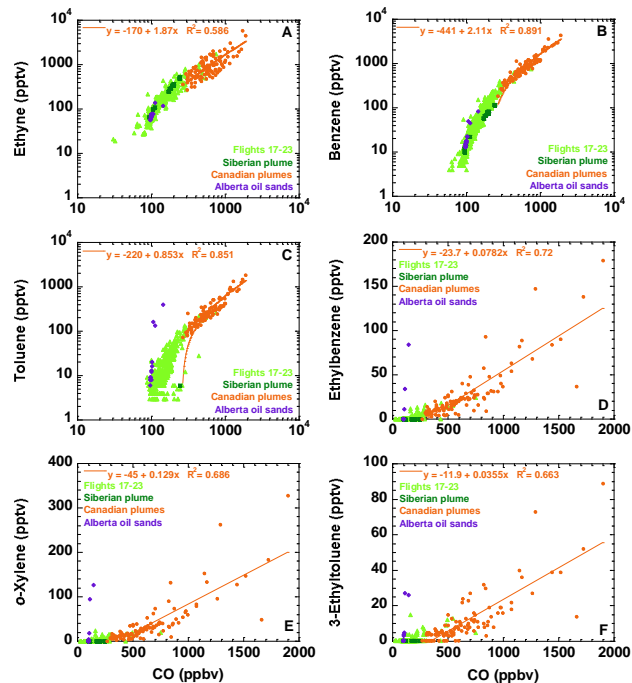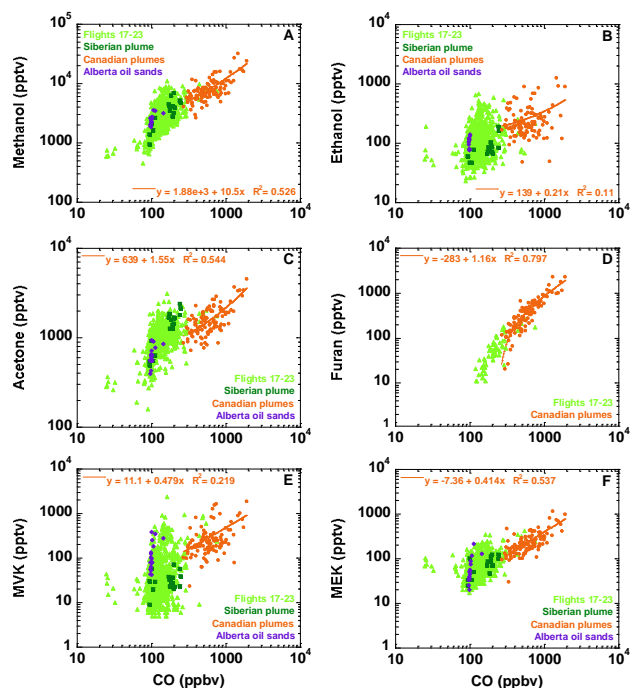

Fig. 8. As in Fig. 4 but for selected oxygenated compounds. MVK = methyl vinyl ketone; MEK = methyl ethyl ketone.

Of the 57 NMVOCs that were released from the fires, the lightest species were the most abundant in the five boreal forest fire plumes on a molar basis, similar to findings from all previous studies of biomass burning (e.g., Blake et al., 1994 – boreal forests; Sinha et al., 2003 – savanna; Yokelson et al., 2007, 2009 – tropical forests; Akagi et al., 2011 – literature survey). Maximum NMVOC mixing ratios in the smoke plumes included a range of compound classes and were (in descending order): formaldehyde (39 ppbv), methanol, ethene, ethane, ethyne, propene, acetone, benzene, propane and β-pinene (Table 1). The monoterpenes are of particular interest because they are known to react with ozone (O_3) and produce secondary organic aerosol (SOA) (e.g., Robinson et al., 2007). Monoterpenes are naturally emitted by vegetation, with stronger emissions from coniferous ecosystems than temperate deciduous forests (Fuentes et al., 2000). Here the maximum levels of α-pinene (1727 pptv) and β-pinene (2916 pptv) were respectively 36$\times$ and 19$\times$ the average background mixing ratio for the five fire plumes (48 $\pm$ 19 pptv and 154 $\pm$ 51 pptv, respectively). The strong release of the pinenes from the fires – despite that fact that they are C_{10} compounds and therefore relatively heavy – is rarely measured but expected, and likely due to heating which would distill large amounts of stored terpenes, not all of which would be oxidized in the flames. To our best knowledge this is the first time that monoterpene emissions have been reported from field measurements of boreal forest fires, though release of these species due to heating or stressing vegetation is well known (e.g., Yokelson et al., 1996; Greenberg et al., 2006; Holopainen and Gershenzon, 2010; Niinemets, 2010). Monoterpenes have been observed in smoke by mass spectrometric or infrared spectroscopy techniques, but they are difficult to speciate using those techniques due to spectral overlap of the various monoterpene features for IR techniques, and due to an indistinguishable product ion for MS techniques (Yokelson et al., 1996). By contrast, here we achieved a good separation and accurate speciation of the pinenes using MS detection coupled with gas chromatography using a DB-5ms column (Simpson et al., 2010). Inclusion of monoterpenes in a smoke chemistry model has previously been shown to improve the model agreement with observed SOA (Alvarado and Prinn, 2009), and we expect that the results presented here will help to further constrain model predictions of SOA formation. Although we did not measure limonene because it eluted after our analytical runs were stopped, its emission from boreal forest fires – as well as the emission of other major stored biogenic VOCs such as carene – should also be investigated.

4.2 Emission ratios and emission factors

4.2.1 CO$_2$, CH$_4$, CO

Emission ratios and emission factors are given in Table 1 for CO_2 (EF only), CO, CH_4, NO_2, NO, HCN, CH_3CN, and the 57 NMVOCs that were found to be emitted from boreal forest fires. The ERs for all trace gases use CO as the reference gas, except for CO which uses CO_2. As expected based on numerous previous studies of biomass burning, the highest EFs were calculated for CO_2 (1616 $\pm$ 180 g kg^{-1}), CO (113 $\pm$ 72 g kg^{-1}) and CH_4 (4.7 $\pm$ 2.9 g kg^{-1}). As shown in Table 3, the ERs and EFs reported here for CO_2, CH_4 and CO agree well with those from previous airborne studies of boreal forest fires in Alaska (Nance et al., 1993; Cofer et al., 1998; Goode et al., 2000; de Gouw et al., 2006). They also agree very closely with a literature compilation of extratropical forest fires (Andreae and Merlet, 2001), even though the compilation also includes temperate forests. Emission factors from boreal forest fires have been recently reassessed in a literature survey by Akagi et al. (2011), using an average of ground-based and airborne EFs from various boreal forest fire studies. Even though our EFs are included in the airborne EF estimates used by Akagi et al., and therefore comparing with the Akagi et al. EFs is somewhat circular, they have been included in Table 3 for completeness. Table 3 also shows the ARCTAS enhancement ratios and EFs that have been calculated for CO_2 and CH_4 using the higher resolution 1 s data set (Singh et al., 2010; Vay et al., 2011); these values agree with those reported here to within the stated uncertainties.

4.2.2 Nitrogen-containing species

Both HCN and CH_3CN are widely recognized as useful tracers for biomass burning (de Gouw et al., 2003; Li et al., 2000, 2003). Hydrogen cyanide had previously been assigned a "best guess" extratropical forest EF of 0.15 g kg^{-1} (Andreae and Merlet, 2001). Our measurements show that the HCN EF for boreal forest fires is considerably larger with a value of 0.89 $\pm$ 0.29 g kg^{-1} (Table 3). This EF is also slightly larger than those for other types of forest fires as reviewed in Yokelson et al. (2009). The CH_3CN ER and EF values reported here are generally within the range reported in the literature (Table 3). The calculated NO_x ($= NO + NO_2$) EF is also in generally good agreement with the literature. However our NO EF is significantly lower than that calculated from three black spruce fires (B280, B349 and B309) sampled by Goode et al. (2000). Goode et al. measured airborne plumes in 1997 (a drought year in Alaska), and the sampled smoke had a higher relative contribution from flaming emissions. Modified combustion efficiency (MCE), defined as $\Delta CO_2/(\Delta CO_2 + \Delta CO)$, is an indicator of a fire's combustion stage, ranging from near 0.80 for smoldering combustion to 0.99 for pure flaming combustion (Akagi et al., 2011). The MCE range for Goode et al. was 0.92–0.93 ($\sim$64 % flaming) as opposed to our average MCE of 0.89 ($\sim$47 % flaming). Because NO is a flaming compound and Goode et al. also sampled closer to the source, their higher EF for NO is expected and also identifies the naturally occurring variation in the emission of this species.

Table 3. Comparison of boreal forest fire ERs and EFs from this study with those from previous boreal forest fire studies. Note that Andreae and Merlet (2001) is a literature survey for extratropical forests that includes both boreal and temperate ecosystems. ER = emission ratio; Enh.R. = enhancement ratio; EF = emission factor; n/a = not available.

Compound	This study ER (pptv ppbv^{-1})	Goode et al. (2000)[a] ER (pptv ppbv^{-1})	de Gouw et al. (2006)[b] Enh.R. (pptv ppbv^{-1})	Singh et al. (2010)[c] Enh.R. (pptv ppbv^{-1})	This study EF (g kg^{-1})	Nance et al. (1993)[d] EF (g kg^{-1})	Cofer et al. (1998)[e] EF (g kg^{-1})	Goode et al. (2000)[a] EF (g kg^{-1})	Vay et al. (2011)[f] EF (g kg^{-1})	Andreae and Merlet (2001)[g] EF (g kg^{-1})	Akagi et al. (2011)[h] EF (g kg^{-1})
CO_2	n/a	n/a	n/a	9400 ± 3700	1616 ± 180	1640 ± 25	1515 ± 94	1667 ± 19	1698 ± 220	1569 ± 131	1485 ± 107
CO	110 ± 70	86 ± 9	n/a	n/a	113 ± 72	81 ± 12	110 ± 32	91 ± 8	n/a	107 ± 37	126 ± 45
CH_4	72 ± 44	55 ± 6	n/a	80 ± 30	4.7 ± 2.9	2.6 ± 1.0	2.3 ± 0.8	2.9 ± 0.5	n/a	4.7 ± 1.9	5.9 ± 3.1
CH_2O	17.5 ± 0.3	19 ± 2	n/a	n/a	2.1 ± 0.2	n/a	n/a	1.9 ± 0.4	n/a	2.2 ± 0.5	1.8 ± 1.2
Ethane	4.6 ± 0.9	n/a	n/a	n/a	0.56 ± 0.13	0.66 ± 0.35	n/a	n/a	n/a	0.60 ± 0.15	1.8 ± 1.1
Ethene	7.3 ± 0.1	19 ± 6	n/a	n/a	0.82 ± 0.09	n/a	n/a	1.8 ± 0.6	n/a	1.12 ± 0.55	1.4 ± 0.5
Ethyne	2.1 ± 0.9	2.7 ± 0.2	n/a	n/a	0.22 ± 0.09	0.26 ± 0.07	n/a	0.23 ± 0.05	n/a	0.27 ± 0.09	0.18 ± 0.10
Propane	1.3 ± 0.3	n/a	n/a	n/a	0.23 ± 0.05	0.23 ± 0.17	n/a	n/a	n/a	0.25 ± 0.11	0.43
Propene	2.3 ± 0.1	n/a	n/a	n/a	0.38 ± 0.04	0.51 ± 0.18	n/a	n/a	n/a	0.59 ± 0.16	1.1 ± 0.6
Benzene	1.7 ± 0.3	n/a	1.1 ± 0.4	1.6 ± 0.3	0.55 ± 0.11	n/a	n/a	n/a	n/a	0.49 ± 0.08	1.1
Toluene	0.67 ± 0.16	n/a	0.18 ± 0.52	0.7 ± 0.2	0.25 ± 0.06	n/a	n/a	n/a	n/a	0.40 ± 0.10	0.49
Methanol	9.6 ± 1.9	13.7 ± 0.5	10.8 ± 4.4	15.6 ± 9.2	1.2 ± 0.3	n/a	n/a	1.4 ± 0.2	n/a	2.0 ± 1.4	2.8 ± 1.6
Acetone	1.6 ± 0.4	n/a	6.3 ± 1.8	4.7 ± 3.3	0.37 ± 0.10	n/a	n/a	n/a	n/a	$0.52 – 0.59$	0.73
MEK	0.38 ± 0.10	n/a	0.73 ± 0.36	n/a	0.11 ± 0.03	n/a	n/a	n/a	n/a	n/a	0.22
OCS	0.12 ± 0.02	n/a	n/a	n/a	0.029 ± 0.007	n/a	n/a	n/a	n/a	$0.030 – 0.036$	0.46 ± 0.47
HCN	8.2 ± 2.0	n/a	n/a	5.6 ± 3.0	0.89 ± 0.29	n/a	n/a	n/a	n/a	(0.15)	1.5 ± 0.8
CH_3CN	1.8 ± 0.3	n/a	2.4 ± 0.4	2.0 ± 0.5	0.30 ± 0.06	n/a	n/a	n/a	n/a	0.19	0.59
NO_x (as NO)	n/a	n/a	n/a	3.5 ± 4.2	0.97 ± 0.12	1.5 ± 0.2	n/a	n/a	n/a	3.0 ± 1.4	0.90 ± 0.69
NO_2	5.6 ± 0.3	n/a	n/a	n/a	1.03 ± 0.13	n/a	n/a	n/a	n/a	n/a	n/a
NO	2.4 ± 0.1	n/a	n/a	n/a	0.29 ± 0.03	n/a	n/a	1.5 ± 0.1	n/a	n/a	n/a

[a] Goode et al. (2000) sampled fresh Alaskan fire plumes in June 1997 (airborne study).

[b] de Gouw et al. (2006) sampled aged fire plumes from Alaska and western Canada in July 2004 (airborne study).

[c] Singh et al. (2000) sampled fresh Canadian fire plumes in spring and summer, 2008 during ARCTAS-A and ARCTAS-B (airborne study).

[d] Nance et al. (1993) sampled one fresh Alaskan fire plume in June 1990 (airborne study).

[e] Cofer et al. (1998) sampled crown fires in the Northwest Territories in June and July 1997 (helicopter study).

[f] Vay et al. (2011) sampled fresh Canadian fire plumes in June and July, 2008 during ARCTAS-B between 50–60° N and 80–120° W (airborne study).

[g] Andreae and Merlet (2001) give average EFs for extratropical (temperate + boreal) forest fires based on a literature compilation.

[h] Akagi et al. (2011) give average EFs for boreal forest fires based on a literature compilation.

4.2.3 NMVOCs

Of the 57 NMVOCs that were enhanced in the smoke plumes, the greatest ERs were (in descending order): formaldehyde, methanol, ethene, ethane, propene, ethyne, benzene, α-pinene, β-pinene, and propane (Table 1). Ethanol was included among the emitted species despite strong plume-to-plume variability (Sect. 4.1). It is emitted by plants and is a solvent and chemical feedstock (Gara et al., 1993; Kesselmeier and Staudt, 1999). Although its average mixing ratio in the plumes was higher than in the background air (Table 1; Fig. 8b), it correlated poorly with CO in Plumes 1–4 ($r^2 \leq 0.22$) but showed some correlation with CO in Plume 5 ($r^2 = 0.51$) (Fig. 11a–b), which is the plume that showed maximum mixing ratios for roughly two-thirds of the emitted NMVOCs. Ethanol showed very good correlation with the biogenic tracer methanol in Plume 5 ($r^2 = 0.83$), suggesting that it could potentially be co-released with methanol from burning or heated vegetation, with high plume-to-plume variability. By contrast, Karl et al. (2007) did not observe ethanol emissions during a study of tropical biomass burning. Like ethanol, CH_2Br_2 enhancements were not detected in each plume, and in its case its fire-averaged ER was not significantly different from zero (Table 1). However, despite poor correlation between CH_2Br_2 and CO in Plumes 2, 4 and

5 ($0.06 \leq r^2 \leq 0.36$), they correlated strongly in Plume 1 ($r^2 = 0.85$) and they correlated well in Plume 3 ($r^2 = 0.63$) (Fig. 11c–d). This suggests that CH_2Br_2 is released from boreal forest fires with high plume-to-plume variability. Note that ethanol and CH_2Br_2, the two species with high plume-to-plume variability, were not emitted in the same plumes.

The sulfur-containing compounds carbonyl sulfide (OCS) and dimethyl sulfide (DMS) were clearly released from the fires (Table 1; Fig. 9f). Isoprene, the shortest-lived species that we report (2.8 h; Table 1), is known to be a major emission from various types of biomass burning (Christian et al., 2003; Yokelson et al., 2008). It has a strong terrestrial plant source from deciduous trees such as aspen (e.g., Sharkey et al., 2008; Warneke et al., 2010), which is a common species in Canadian mixedwood forests (http://www.borealforest.org). Here isoprene correlated strongly with CO in the three very fresh smoke samples that were analyzed for short-lived compounds ($r^2 = 0.92$; Fig. 3a–b), showing its emission from boreal forest fires. It is possible that some of the measured isoprene excess in this study was due to entrainment and rapid vertical transport of isoprene-rich surface air, in addition to direct emissions from the fires.
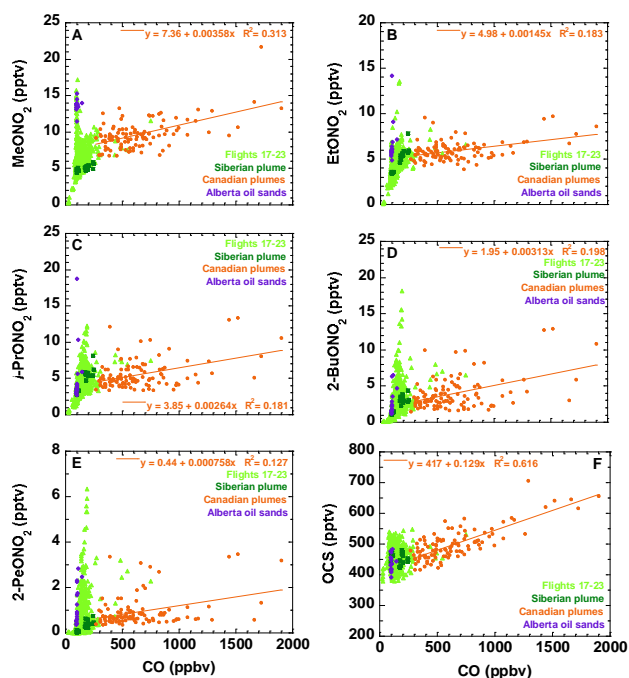
Fig. 9. As in Fig. 4 but for selected alkyl nitrates and OCS.

Fig. 10. As in Fig. 4 but for the six halocarbons that were released from the fires. Dibromomethane (CH_2Br_2) has been included despite high plume-to-plume variability (see text).

Hydrogen cyanide, CH_3CN and the 57 NMVOCs together comprised 1.4 % of the total carbon measured in the plumes, compared with 98.6 % for CO_2, CO and CH_4. The maximum NMVOC EFs in the smoke plumes were (in descending order): formaldehyde, methanol, ethene, α-pinene, β-pinene, ethane, benzene, propene, acetone and furan (Table 1; Fig. 12). Note that heavier molecules such as the pinenes have a higher ranking as EFs than as ERs, because the EF calculation takes molecular weight into account (Sect. 3.2). The top 10 NMVOCs listed above comprise 77 % of the total carbon mass released from the fires as NMVOCs (formaldehyde, 13 %; α-pinene, 11 %; ethene, 11 %; β-pinene, 10 %; benzene, 8 %; methanol, 7 %; ethane, 7 %; propene, 5 %; acetone, 3 %; and furan, 3 %). These results show the strong contribution of relatively few species to the NMVOC carbon that is released from the fires. In particular, the C_1-C_2 NMVOCs comprised 41 % of the measured NMVOC carbon, and α-pinene and β-pinene comprised 21 %. The EFs of just the two pinenes sums to approximately $1.5\,g\,kg^{-1}$, which is a significant fraction of the total mass of co-emitted fine particles for boreal forest fires ($15.3 \pm 7.0\,g\,kg^{-1}$; Akagi et al., 2011). This further illustrates the need to consider these reactive terpenes in smoke models.

The results also show the co-emission of a wide range of NMVOC compound classes from the fires. To our best knowledge, only 12 of the 57 NMVOCs have been previously quantified from boreal forest fires, and boreal forest fire emissions of 45 NMVOCs are presented here for
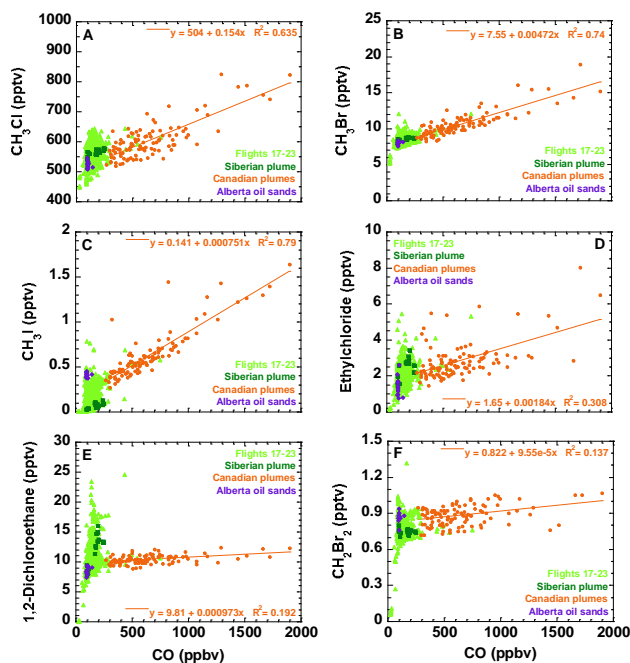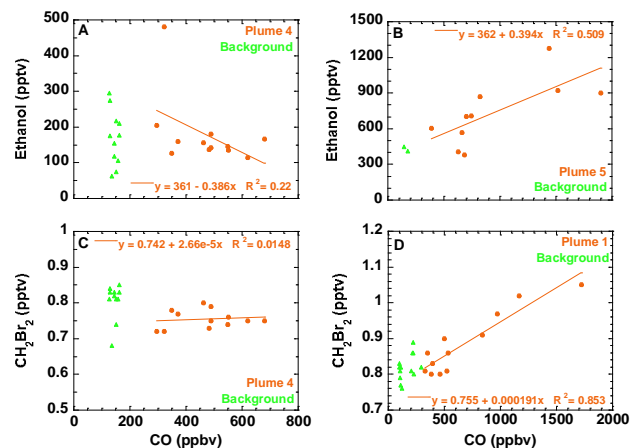

Fig. 11. Ethanol mixing ratios in **(a)** Plume 4 and **(b)** Plume 5, and CH_2Br_2 mixing ratios in **(c)** Plume 4 and **(d)** Plume 1, which shows their high plume-to-plume variability. Green triangles = background air; orange circles = smoke plumes.

the first time. Only a few NMVOCs previously measured from boreal forest fires are not included in this work, mainly formic acid and acetic acid (compiled in Akagi et al., 2011). The 12 NMVOCs quantified here and in previous work are shown in Table 3 together with values from the literature. Note that this study and Goode et al. (2000) report ERs (ΔNMVOC/ΔCO at $t = 0$), whereas de Gouw et al. (2006) and Singh et al. (2010) report enhancement ratios (Enh.R.),

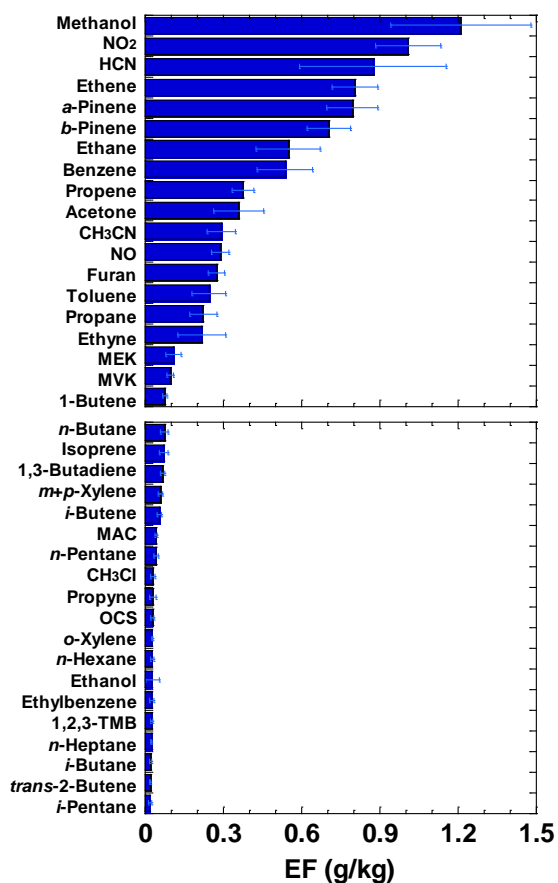**Fig. 12.** Emission factors for NO_2, NO, HCN, CH_3CN, and the top 34 NMVOCs emitted from fresh Canadian boreal forest fires, excluding CH_2O. The results show the importance of light NMVOCs and the pinenes, and the co-emission of a wide range of compound classes from the fires.

which account for aging over a transport time Δt (Lefer et al., 1994; de Gouw et al., 2006). In general the NMVOC ERs and EFs reported here show good agreement with the literature, to within the stated uncertainties. Calculated ERs can potentially be affected by biomass burning plumes mixing with non-constant background air, which can have different ratios of compounds to CO. Our method of calculating ERs – which subtracts off the background mixing ratios and forces the fit through zero – effectively weights the ERs to high values that are minimally affected by background issues. In addition, our ER and MCE values are in good agreement with measurements in very fresh boundary layer biomass burning plumes and laboratory biomass burning fires (e.g., Yokelson et al., 2008; Akagi et al., 2011), both cases in which changing background concentrations is not a complicating factor. This gives some indication that we were successful in selecting relatively fresh plumes where the original signature was still clear.

Two compounds that disagree with some literature values are acetone and ethene. The acetone ER reported here $(1.6 \pm 0.4 \, pptv \, ppbv^{-1})$ is statistically lower than the Enh.R. reported by de Gouw et al. (2006) $(6.3 \pm 1.8 \, pptv \, ppbv^{-1})$, which is an average ratio from 11 aged forest fire plumes from Alaska and western Canada sampled in July 2004. This difference lies well outside our measurement uncertainty of 30 %, which includes potential wall losses inside the canisters (Sect. 2.2). The UC-Irvine ER is also lower than other values reported for ARCTAS (Singh et al., 2010; Hornbrook et al., 2011), though the differences were not statistically significant. Singh et al. (2010) reported a mean Enh.R. of $4.7 \pm 3.3 \, pptv$ using high-frequency in situ PTR-MS measurements in fresh biomass burning plumes (0–2 km), nearly all of which were sampled during ARCTAS-B (H. Singh, personal communication, 2011). Hornbrook et al. (2011) reported $5.9 \pm 4.0 \, pptv \, ppbv^{-1}$ for Canadian biomass burning of all ages sampled during ARCTAS-B using the Total Organic Gas Analyzer (TOGA), with individual plume values ranging from 1.7 ± 0.7 to $16 \pm 1 \, pptv \, ppbv^{-1}$. Whereas Jost et al. (2003) have previously observed an increase in the acetone-to-CO ratio during plume aging by means of secondary acetone formation, the natural variability of fire plumes can obscure the aging trends in many cases, as observed by Lefer et al. (1994) and Hornbrook et al. (2011). Based on our previous experience with oxygenated species we suspect that the statistically significant difference between our results and those of de Gouw et al. (2006) is primarily related to fire-to-fire variability, but we cannot rule out a component due to aging effects. The difference in ethene ERs between this study and Goode et al. (2000) is expected to be related to emission variability since both studies used only fresh smoke.

4.3 Compounds not released by boreal forest fires

Of the 80 measured NMVOCs, 23 were not emitted by the boreal forest fires. These were primarily anthropogenic halocarbons and included short-lived solvents such as tetrachloroethene (C_2Cl_4) (Fig. 13a) and long-lived compounds such as chlorofluorocarbons or CFCs (Table 4). With the exceptions of trichloroethene (C_2HCl_3) and HCFC-141b, the fire-averaged mixing ratios of these species were not significantly different from their background average. We were unable to assess the biomass burning source of C_2HCl_3 because of a slight co-elution with an adjacent peak on the ECD that became more prominent at high mixing ratios. However, like the other heavily chlorinated industrial solvents that we measured, we do not expect C_2HCl_3 to have a biomass burning source. Similarly, even though the average HCFC-141b mixing ratio was statistically greater in the smoke plumes than in the background air (Table 4), it is included here among the non-emitted species because it seems highly improbable that this chlorofluorinated species was released from the fires. HCFC-141b was measured using GC/MS and the reason for

Table 4. Analytical details and measurement statistics for 23 NMVOCs that were not statistically enhanced in five boreal forest fire plumes as compared to background measurements made during ARCTAS-B. "Plume avg." and "Bkgd. avg." are as in Table 1.

Compound	Formula	Lifetime	LOD (pptv)	Precision (%)	Accuracy (%)	Bkgd. Avg. (pptv)	Plume Avg. (pptv)
Methyl *tert*-butyl ether	$C_5H_{12}O$	3.9 d	1	30	20	<LOD	<LOD
2,3-Dimethylbutane	C_6H_{14}	2.0 d	3	3	5	<LOD	0.7 ± 2.3
CFC-11	CCl_3F	45 yr	10	1	3	253.2 ± 0.9	254.5 ± 0.9
CFC-12	CCl_2F_2	100 yr	10	1	3	536.3 ± 1.7	536.8 ± 1.8
CFC-113	$C_2Cl_3F_3$	85 yr	5	1	3	78.9 ± 0.3	79.4 ± 0.3
CFC-114	$C_2Cl_2F_4$	300 yr	1	1	10	16.5 ± 0.1	16.6 ± 0.1
Carbon tetrachloride	CCl_4	26 yr	1	1	5	92.8 ± 0.3	92.6 ± 0.2
Methyl chloroform	CH_3CCl_3	5.0 yr	0.1	1	5	12.40 ± 0.05	12.38 ± 0.03
HCFC-22	CHF_2Cl	12 yr	2	2	5	198.0 ± 2.5	200.1 ± 2.3
HCFC-141b	$C_2H_3Cl_2F$	9.3 yr	0.5	3	10	20.9 ± 0.3	21.7 ± 0.3
HCFC-142b	$C_2H_2ClF_2$	18 yr	0.5	3	10	19.9 ± 0.4	20.1 ± 0.3
HFC-134a	$C_2H_2F_4$	14 yr	1	3	10	47.4 ± 0.9	47.9 ± 0.7
HFC-152a	$C_2H_4F_2$	1.4 yr	1	3	10	11.0 ± 2.2	11.4 ± 2.1
Halon-1211	$CBrClF_2$	16 yr	0.1	1	5	4.32 ± 0.02	4.32 ± 0.02
Halon-1301	$CBrF_3$	65 yr	0.1	10	10	3.24 ± 0.05	3.23 ± 0.05
Halon-2402	$C_2Br_2F_4$	20 yr	0.01	1	5	0.516 ± 0.003	0.518 ± 0.004
Chloroform	$CHCl_3$	3–5 mo	0.1	5	10	12.4 ± 0.6	12.6 ± 0.5
Dichloromethane	CH_2Cl_2	3–5 mo	1	5	10	35.8 ± 2.9	36.9 ± 1.3
Tetrachloroethene	C_2Cl_4	2–3 mo	0.01	5	10	3.06 ± 0.09	3.08 ± 0.07
Bromoform	$CHBr_3$	11 mo	0.01	10	20	0.64 ± 0.06	0.56 ± 0.05
Bromodichloromethane	$CHBrCl_2$	2–3 mo	0.01	10	50	0.19 ± 0.01	0.18 ± 0.01
Dibromochloromethane	$CHBr_2Cl$	2–3 mo	0.01	10	20	0.13 ± 0.02	0.13 ± 0.02

its slight enhancement in the plumes is unclear, but we found no evidence that fire-induced convection was a contributing factor.

Although many of the 23 compounds not emitted from the fires are purely anthropogenic and were not expected to have a biomass burning source (e.g., CFCs, C_2Cl_4), the ARCTAS measurements are particularly useful for compounds whose biomass burning source is currently being reassessed in the literature. Chloroform is an industrial solvent, and previous studies have suggested a minor global biomass burning source of $CHCl_3$ on the order of $2\,Gg\,Cl\,yr^{-1}$ (Keene et al., 1999; Lobert et al., 1999). During ARCTAS-B, $CHCl_3$ and CO did not correlate in the fire plumes ($r^2 < 0.01$; Fig. 13b) and its fire-averaged ER of $(-0.7 \pm 1.2) \times 10^{-6}\,ppbv\,ppbv^{-1}$ was not significantly different from zero, showing that it was not released from the fires. Likewise, previous measurements of CH_2Cl_2 in African savanna fires yielded ERs to CO of $(2.5 \pm 0.6) \times 10^{-5}\,ppbv\,ppbv^{-1}$ (Rudolph et al., 1995) from which global CH_2Cl_2 biomass burning emissions of about $58\,Gg\,yr^{-1}$ ($49\,Gg\,Cl\,yr^{-1}$) were calculated (Lobert et al., 1999). A subsequent study in Tasmanian wildfires measured much lower ERs of <1–$6 \times 10^{-7}\,ppbv\,ppbv^{-1}$ (Simmonds et al., 2006). Here CH_2Cl_2 did not correlate with CO ($r^2 < 0.01$; Fig. 13c) and its fire-averaged ER of $(2.0 \pm 2.5) \times 10^{-6}\,ppbv\,ppbv^{-1}$ was not significantly different from zero. Therefore the
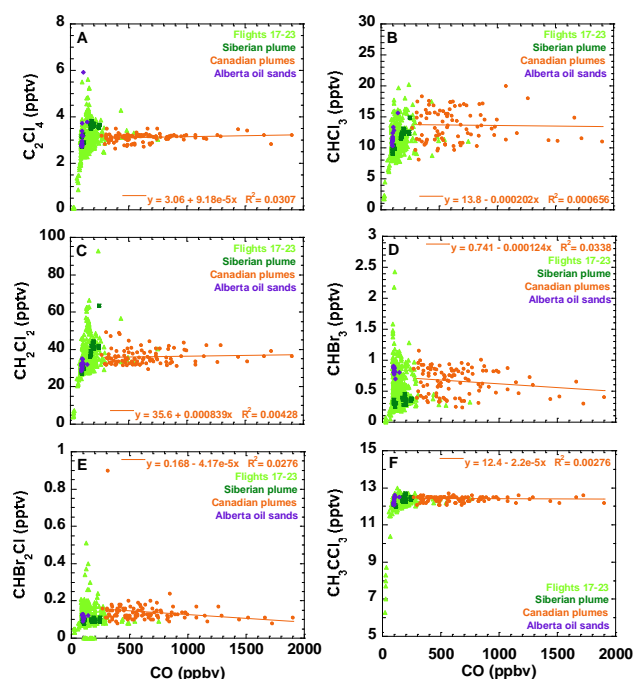
Fig. 13. As in Fig. 4 but for selected halocarbons that were not released from the fires.

overall body of evidence now suggests that global emissions of CH_2Cl_2 from biomass burning are much lower than previously estimated, most likely by more than a factor of 10.

Whereas CH_3CCl_3 was previously believed to have a minor biomass burning source of $2–10\,Gg\,yr^{-1}$ (Rudolph et al., 2000), subsequent work in very concentrated smoke plumes in the Australian savanna showed that its biomass burning source is likely negligible ($<0.014\,Gg\,yr^{-1}$; Simpson et al., 2007). Here CH_3CCl_3 did not correlate with CO ($r^2 < 0.01$; Fig. 13f) and its fire-averaged ER of $(−3.0 \pm 9.8) \times 10^{-8}\,ppbv\,ppbv^{-1}$ was not significantly different from zero, further supporting that it is not emitted from biomass burning. In fact, CH_3CCl_3 showed a small negative correlation with CO_2 in Australian flaming samples, which suggested that it could be destroyed at high temperature during biomass burning. During ARCTAS-B, the fire-averaged ER of CH_3CCl_3 to CO_2 was $(−0.1 \pm 1.1) \times 10^{-8}\,ppbv\,ppbv^{-1}$; i.e., negative but not significantly different from zero. Likewise, although some of the polybrominated species showed a negative correlation with CO during ARCTAS (e.g., Fig. 13d–e) their fire-averaged ERs were not significantly different from zero. The possibility of CH_3CCl_3 destruction at high temperature and the general idea that biomass burning can be a sink for some compounds is intriguing, but requires further investigation.

4.4 Comparison of Canadian and Siberian plumes

Although the ARCTAS-B deployments focused on emissions from Canadian boreal forest fires, a smoke plume from Siberia was intercepted on 29 June 2008 during Flight 17, just north of the border between Alberta and the Northwest Territories. Ten-day backward kinematic trajectory plots suggest that the plume was most likely emitted 3–5 days prior to sampling (not shown), which is consistent with MODIS satellite imagery of widespread fire activity in southeast Russia at the time (http://earthobservatory.nasa. gov/NaturalHazards/view.php?id=20148). Therefore short-lived gases such as toluene and ethene (1–2 d) had become depleted in the Siberian plume by the time it was sampled, whereas longer-lived species such as methanol (12 d) were still enhanced (Fig. 14).

As discussed in Sect. 3.1, meaningful ER and EF calculations should consider only the freshest smoke plumes. For the Siberian plume we calculated an ER relative to CO only for ethane, because it was clearly elevated compared to the local background for the Siberian plume (Fig. 3c–d) and because its 47 d lifetime (Table 1) is considerably greater than the Siberian plume age. The ethane ER for the Siberian plume, $(4.63 \pm 0.08) \times 10^{-3}\,ppbv\,ppbv^{-1}$, was identical to that measured in the five fresh Canadian plumes, $(4.6 \pm 0.9) \times 10^{-3}\,ppbv\,ppbv^{-1}$ (Table 1), which suggests a characteristic boreal forest fire emission signature, at least for some species. This is consistent with findings during the Arctic Boundary Layer Expedition (ABLE-3B) over eastern Canada
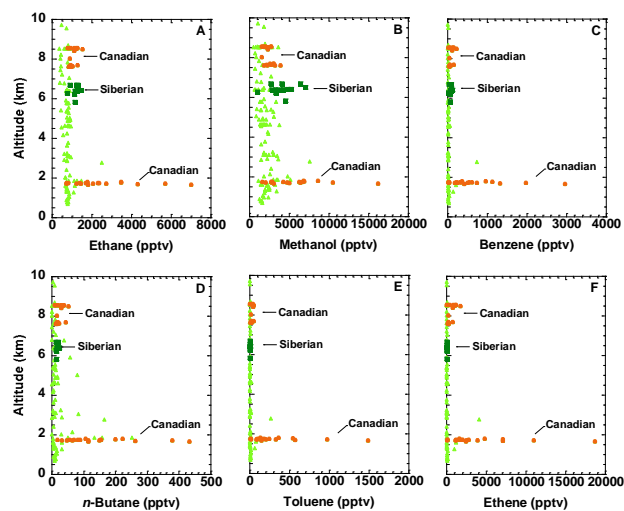

Fig. 14. Altitude profiles (lifetimes) of **(a)** ethane (47 d); **(b)** methanol (12 d); **(c)** benzene (9.5 d); **(d)** n-butane (4.9 d); **(e)** toluene (2.1 d); and **(f)** ethene (1.4 d) during Flight 17, showing encounters with Canadian (orange circles) and Siberian (dark green squares) smoke plumes.

in summer 1990, in which the NMVOC composition of fresh smoke plumes exhibited a relatively low variability, indicating the existence of a typical emission signature (Blake et al., 1994). Similarly, as part of the ARCTAS mission, emission characteristics from the boreal forest fires were compared with those from California wild fires sampled earlier during the mission (Flights 12–15; 18–24 June 2008) and were found to be broadly comparable (Singh et al., 2010).

4.5 Global emissions from boreal forest fires

This study significantly expands the amount of sampling and the range of species measured in boreal forest fire smoke plumes for both Canada and Siberia. In addition, the ER for ethane was similar for the Canadian and Siberian plumes, and the ERs and EFs from this study generally agreed well with other boreal forest fire emissions data in the literature. Therefore, we use our data to estimate global NMVOC emissions from boreal forest fires. The estimates will be a lower limit for some compounds because our EFs are based on airborne measurements, which may underestimate smoldering combustion. However, they are useful to update the approximate contribution to global budgets for numerous species.

With the exception of boreal Asia (BOAS), 2008 was a relatively low fire year with global carbon emissions from open burning of 1680 Tg C, including 49 Tg C and 165 Tg C in boreal North America (BONA) and BOAS, respectively, based on the Global Fire Emissions Database–version 3 (GFED3) (van der Werf et al., 2010). By comparison, the average annual global carbon emission from 1997–2009 was $2013\,Tg\,C\,yr^{-1}$, with $54\,Tg\,C\,yr^{-1}$ and $128\,Tg\,C\,yr^{-1}$

Table 5. Summary of global NMVOC emissions from boreal forest fires by compound class (left four columns) and by carbon number (right four columns).

Compound class	Annual Emission (Gg C yr^{-1})	Uncertainty (Gg C yr^{-1})	Percent Contribution (%)	Carbon number	Annual Emission (Gg C yr^{-1})	Uncertainty (Gg C yr^{-1})	Percent Contribution (%)
Oxygenates	699	46	29.3	C_1	482	51	20.2
Pinenes	493	42	20.7	C_2	500	56	21.0
Other alkenes	474	32	19.9	C_3	279	30	11.7
Aromatics	329	43	13.8	C_4	238	13	10.0
Alkanes	299	40	12.6	C_5	43	6	1.8
Alkynes	84	9	3.5	C_6	198	37	8.3
Halocarbons	2.7	0.6	0.12	C_7	90	21	3.8
Sulfur compounds	2.4	0.5	0.10	C_8	37	4	1.5
Alkyl nitrates	0.9	0.3	0.04	C_9	25	2	1.0
				C_{10}	493	42	20.7
Total NMVOC	2385	648	100.0	Total NMVOC	2385	648	100.0

released in BONA and BOAS, respectively. Therefore the total carbon released from boreal forest fires in 2008 (214 Tg C yr^{-1}) was about 18 % greater than in an average year (182 Tg C yr^{-1}) due to strong emissions from Asia. In Canada, Saskatchewan fires accounted for 1.1 million hectares (Mha) of the 1.5 Mha that burned in Canada in 2008 (Soja et al., 2008). For each emitted trace gas that we measured, we estimated its average global emission from boreal forest fires (Gg species yr^{-1}) using its calculated EF (Table 1), the average carbon emission from boreal forest fires from 1997–2009 (182 Tg C yr^{-1}), and a carbon mass fraction of 500 g C kg^{-1} fuel (Susott et al., 1996). The corresponding boreal emission estimates for 2008 can be calculated by multiplying the results in Table 1 by 1.18. Note that the uncertainty in the global emissions is underestimated because it does not include uncertainty in the GFED3 emissions.

In an average year, boreal forest fires account for ∼9 % of global carbon emissions from biomass burning (Sect. 1). Because our boreal forest fire EFs differ somewhat from EFs for other major ecosystems such as savanna burning (Akagi et al., 2011), we have not used our data to calculate global biomass burning emissions. However, a rough estimate of global biomass burning emissions for each trace gas can be determined by multiplying its boreal forest fire emission by a factor of 10. To more easily compare with the literature, the estimated emissions from Table 1 (Gg species yr^{-1}) have been converted to Gg C yr^{-1} below and in Table 5. Our CO emission estimate from boreal forest fires (18 ± 11 Tg C yr^{-1}) is ∼6 % of global CO emissions from biomass burning (312 Tg C yr^{-1}; Akagi et al., 2011), and the CH$_3$OH emission estimate (0.17 ± 0.04 Tg C yr^l) is ∼5 % of global CH$_3$OH emissions from biomass burning (3.3 Tg C yr^{-1}; Jacob et al., 2005). Again recall that our values are likely to be lower limits because they may underesti-

mate the contribution from smoldering emissions, which can have 2× larger EFs for some species during below-ground biomass burning. The total NMVOC emission from boreal forest fires is estimated as 2.4 ± 0.6 Tg C yr^{-1}, with 29 % of the carbon released as oxygenated hydrocarbons, 21 % as pinenes, 20 % as other alkenes, 14 % as aromatics, 13 % as alkanes, 3.5 % as alkynes, and negligible contributions from halocarbons, sulfur compounds and alkyl nitrates (Table 5). The two pinenes alone account for nearly 0.5 Tg C yr^{-1}. This is a significant fraction of the estimated total monoterpene emission from live vegetation (7.5 Tg C yr^{-1}; Guenther et al., 2000) and it represents a major previously unquantified source of carbon to the global atmosphere. The contribution of terpenes to emitted NMVOC carbon may be even larger if other stored terpenes such as limonene and carene are similarly emitted from boreal forest fires.

5 Conclusions

Based on airborne measurements from the summer 2008 ARCTAS mission, this work represents the most comprehensive characterization of trace gas emissions from boreal forest fires to date. Forty-five NMVOCs were quantified for the first time, and this work also provides new or updated emission estimates for other compounds such as HCN and CH$_3$CN. Carbon dioxide, CH$_4$ and CO comprised 98.6 % of the measured carbon released from the fires, compared to 1.4 % for 57 NMVOCs that were emitted. Apart from CO$_2$, CH$_4$ and CO, short-chained NMVOCs such as formaldehyde and methanol were released in greatest abundance from the fires, and the C$_1$-C$_2$ NMVOCs comprised 41 % of the carbon released as NMVOCs. In an average year, boreal forest fires are estimated to release 2.4 ± 0.6 Tg C yr^{-1} in the form of NMVOCs, namely as oxygenated hydrocarbons (29 %),

pinenes (21 %), other alkenes (20 %), aromatics (14 %), alkanes (13 %), alkynes (3.5 %), and halocarbons, sulfur compounds and alkyl nitrates (<0.3 %). The pinene emissions were measured for the first time, and globally we estimate that roughly $0.5\,\mathrm{Tg\,C\,yr^{-1}}$ is released from boreal forest fires in the form of pinenes. Our measurements did not include limonene or carene, two other major stored biogenic VOCs, and they may also be released from boreal forest fires in significant amounts. Acetaldehyde, formic acid, and acetic acid are other major VOCs that were not included in this work, and our estimate of the carbon released as NMVOCs is expected to represent a lower limit. 1,2-Dichloroethane was the only poly-halogenated compound to be clearly emitted from the fires, though there was evidence that CH_2Br_2 was emitted with high plume-to-plume variability. Use of these speciated emission estimates in biomass burning inventories and global models should help to reduce the uncertainty in the model estimates of their emissions and chemistry.

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