

Emissions from forest fires near Mexico City

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Abstract. The emissions of NO_x (defined as NO (nitric oxide) + NO₂ (nitrogen dioxide)) and hydrogen cyanide (HCN), per unit amount of fuel burned, from fires in the pine forests that dominate the mountains surrounding Mexico City (MC) are about 2 times higher than normally observed for forest burning. The ammonia (NH₃) emissions are about average for forest burning. The upper limit for the mass ratio of NO_x to volatile organic compounds (VOC) for these MC-area mountain fires was ~0.38, which is similar to the NO_x/VOC ratio in the MC urban area emissions inventory of 0.34, but much larger than the NO_x/VOC ratio for tropical forest fires in Brazil (~0.068). The nitrogen enrichment in the fire emissions may be due to deposition of nitrogen-containing pollutants in the outflow from the MC urban area. This effect may occur worldwide wherever biomass burning coexists with large urban areas (e.g. the tropics, southeastern US, Los Angeles Basin). The molar emission ratio of HCN to carbon monoxide (CO) for the mountain fires was 0.012±0.007, which is 2–9 times higher than widely used literature values for biomass burning. The ambient molar ratio HCN/CO in the MC-area outflow is about 0.003±0.0003. Thus, if only mountain fires emit significant amounts of HCN, these fires may be contributing about 25% of the CO production in the MC-area (~98–100 W and 19–20 N). Comparing the PM₁₀/CO and PM_{2.5}/CO mass ratios in the MC Metropolitan Area emission inventory (0.0115 and 0.0037)

to the PM₁/CO mass ratio for the mountain fires (0.133) then suggests that these fires could produce as much as ~79–92% of the primary fine particle mass generated in the MC-area. Considering both the uncertainty in the HCN/CO ratios and secondary aerosol formation in the urban and fire emissions implies that about 50±30% of the “aged” fine particle mass in the March 2006 MC-area outflow could be from these fires.

1 Introduction

The MILAGRO (Megacity Initiative Local and Global Research Observations) project is sponsored by the US National Science Foundation (NSF), Department of Energy, National Aeronautics and Space Administration (NASA), and the Molina Center for Energy and the Environment. MILAGRO was designed to study the local to global atmospheric impacts of pollutants generated in megacities (<http://www.eol.ucar.edu/projects/milagro>). The first field campaigns under this initiative occurred in March 2006 and focused on Mexico City (MC), which is North America's largest metropolitan area (Fast et al., 2007). A main objective was to understand the chemical evolution and influence of the MC-area plume on the regional to global scale. In the MC area, a typical long-range transport event begins when the boundary layer over MC increases to a depth sufficient for pollutants to escape the confines of the mountains that

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surround MC – usually between the hours of 10 a.m. and 6 p.m. During the January through June dry season, readily visible biomass burning in the surrounding mountains also occurs mainly during the afternoon. Thus, an air mass may mix with: fire emissions upwind of MC, then the MC pollutants (which may contain some urban biomass burning emissions), and then fire emissions immediately downwind of MC. The resulting plume then further evolves chemically downwind during regional transport. A key goal of MILAGRO is to develop photochemical models that accurately reproduce the actual evolution of the MC plume measured during March 2006 research flights. For these dry season measurements, entrained fire emissions could affect the observed photochemical transformations. Since HCN is likely emitted mostly or exclusively by fires (Li et al., 2000), measurements of HCN emissions by fires and of HCN in the downwind plume could help quantify the biomass-burning contribution to the downwind plume.

As part of MILAGRO, an instrumented US Forest Service Twin Otter aircraft measured the emissions from 63 fires throughout south-central Mexico. This paper focuses on a “study area” ranging from 19–20°N and 98–100°W that includes the MC metropolitan area and the adjacent mountains. This “box” approximates the source region relevant for airborne measurements several hours to several days downwind of MC. The Twin Otter sampled 8 fires in this study area, of which 7 were sampled with instrumentation capable of measuring reactive nitrogen species. All the fires were located in the pine-dominated forests that dominate the mountains near MC. One plume from a similar MC-area fire was profiled by the NCAR C-130 while measuring HCN and CO and both these species were also measured regionally on board the C-130. The purpose of this paper is to present emission factor and emission ratio measurements for the pine-dominated forest fires in the MC-area mountains and a few preliminary implications of those measurements. In addition, we propose that the emissions from these fires were probably impacted by the deposition of urban pollutants in the MC plume. This is likely relevant to understanding atmospheric chemistry wherever biomass burning coexists with urban areas globally. Future papers will present other atmospheric chemistry measurements made on the MILAGRO research aircraft and the emission factors for the other fires sampled throughout south-central Mexico. The latter included tropical deforestation fires, other forest fires, shrub and grassland fires, and agricultural waste burning.

2 Experimental details

2.1 Data acquisition

2.1.1 Airborne Fourier transform infrared spectrometer (AFTIR)

The AFTIR on the Twin Otter provided measurements of several nitrogen species and other reactive and stable trace gases present above ~5–20 ppbv. The AFTIR had a dedicated, halocarbon-wax, coated inlet that directed ram air through a Pyrex, multipass cell. The AFTIR was used for continuous measurements of water vapor (H₂O), carbon dioxide (CO₂), carbon monoxide (CO), and methane (CH₄); or to grab samples for signal averaging and measurement of H₂O, CO₂, CO, nitric oxide (NO), nitrogen dioxide (NO₂), ammonia (NH₃), hydrogen cyanide (HCN), CH₄, ethene (C₂H₄), acetylene (C₂H₂), formaldehyde (HCHO), methanol (CH₃OH), acetic acid (CH₃COOH), formic acid (HCOOH), and ozone (O₃). The details and the accuracy of the AFTIR technique are described by Yokelson et al. (1999, 2003a, b).

2.1.2 Whole air sampling (WAS)

A forward facing, 25 mm i.d. stainless steel elbow sampled ram air into stainless steel canisters on board the Twin Otter. Two-liter canisters were shipped to the University of Miami and analyzed by gas chromatography (GC) with a flame ionization detector (FID) for CH₄, and the following non-methane hydrocarbons: ethane, C₂H₄, C₂H₂, propane, propene, isobutane, n-butane, t-2 butene, 1-butene, isobutene, c-2-butene, 1,3 butadiene, cyclopentane, isopentane, and n-pentane, with detection limits in the low pptv. CO was measured in parallel with the CH₄ measurement, but utilized GC with a Trace Analytical Reduction Gas Detector (RGD). Starting 18 March, 800-ml canisters were also filled with the same sampling system and analyzed later at the United States Forest Service (USFS) Fire Sciences Laboratory by GC/FID/RGD for CO₂, CO, CH₄, H₂, and several C₂-C₃ hydrocarbons. Details of the canister analysis are given by Weinheimer et al. (1998), Flocke et al. (1999), and Hao et al. (1996). GC with mass-selective detection (MSD) measurements of higher molecular weight hydrocarbons and halocarbons will be reported elsewhere. CO and CH₄ were measured with high accuracy by both the AFTIR and the cans, which facilitated coupling the data from these instruments.

2.1.3 Nephelometry

The large-diameter, fast-flow, WAS inlet also supplied sample air for a Radiance Research Model 903 integrating nephelometer that measured b_{scat} at 530 nm at 0.5 Hz; synchronized with a Garmin GPS. Both were available and logged by USFS starting 18 March. Immediately after the field

campaign, the measurements of b_{scat} by the nephelometer were compared to gravimetric (filter-based) measurements of the mass of particles with aerodynamic diameter <2.5 microns ($\text{PM}_{2.5}$) for 14 fires in pine forest fuels burned in the US Forest Service Missoula biomass fire simulation facility. We obtained (and applied) a linear relationship between b_{scat} and $\text{PM}_{2.5}$ in $\mu\text{g}/\text{m}^3$ of standard temperature and pressure air.

$$b_{\text{scat}} \times 228\,000(\pm 11\,000(2\sigma)) = \text{PM}_{2.5}(\mu\text{g}/\text{m}^3) \quad (1)$$

The conversion factor is similar to the 250 000 measured by Nance et al. (1993) for smoke from Alaskan wildfires in coniferous fuels, which they showed was within $\pm 20\%$ of the factors determined in other studies of biomass burning smoke. In addition, an earlier study in the Missoula fire lab, with fires in a larger variety of wildland fuels, found that the conversion factor of 250 000 reproduced gravimetric particle mass measurements within $\pm 12\%$ (Trent et al., 2000). We note that these conversion factors were measured in fresh smoke and are used only for fresh smoke in this work.

2.1.4 TEM analysis and co-located, fast, isokinetic particle and CO_2 measurements

An isokinetic particle inlet (Jonsson et al., 1995) was used on the Twin Otter to sample fine particles with a diameter cut-off of a few microns. Both the measured and previously published particle size distributions show that particles of diameter below 1 micron account for nearly all the fine-particle ($\text{PM}_{2.5}$) mass emitted by biomass fires (Radke et al., 1991). This inlet supplied sample air for two MPS-3 particle samplers (California Measurements, Inc.) that were used to collect 182 samples over time intervals of ~ 1 to 10 min for analyses using transmission electron microscopy (TEM). Each sampler consists of a three-stage impactor, which collects particles with aerodynamic diameters of >2 , 2 – 0.3 , $<0.3 \mu\text{m}$. A CM 200 (FEI) microscope was used for subsequent TEM analysis at Arizona State University, which revealed details of the chemistry and structure of individual particles.

The same inlet also supplied a LiCor (Model #7000) measuring CO_2 and H_2O at 5 Hz and the UHSAS (Ultra High Sensitivity Aerosol Spectrometer, Droplet Measurement Technologies) (both deployed by U. Colorado). The UHSAS provided the number of particles in each of 99 user-selectable bins for diameters between 55 and 1000 nm at 1 Hz. All three inlets were located near each other as can be seen in the photo at (<https://www.umd.edu/chemistry/faculty/yokelson/galleries/Mexico/Airborne/Aircraft/index.html>). Use of a single inlet for both the UHSAS and fast CO_2 enabled coupling the particle and trace gas data.

2.1.5 HCN and CO measurements on the C-130

The California Institute of Technology chemical ionization mass spectrometer (CIMS) measured selected product ions

on the C-130 via reaction of the reagent ion CF_3O^- with analytes directly in air. HCN is measured by monitoring the product ion with $m/z=112$, which is the cluster of CF_3O^- with HCN. The sensitivity is dependent on the water vapor mixing ratio. Sensitivity changes due to water vapor changes are corrected for using the dewpoint hygrometer water measurement from the C-130 aircraft, and a water calibration curve which has been generated through laboratory measurements. Non-water sensitivity changes are corrected for using in-flight standard addition calibrations of H_2O_2 and HNO_3 (other species measured by the CIMS) and proxied to laboratory calibrations of HCN. The detection limit ($S/N=1$) for HCN for a 0.5 second integration period is better than 15 pptv for moderate to low water vapor levels (H_2O mixing ratio ≤ 0.004) (Crouse et al., 2006).

A CO vacuum ultraviolet (UV) resonance fluorescence instrument, similar to that of Gerbig et al. (1999), was operated on the C-130 through the National Center for Atmospheric Research and NSF. The MILAGRO data have a 3 ppbv precision, 1-s resolution, and a typical accuracy of $\pm 10\%$ for a 100 ppbv ambient mixing ratio.

2.1.6 Airborne sampling protocol

The Twin Otter and C-130 were based in Veracruz with the 4 other MILAGRO research aircraft (<http://mirage-mex.acd.ucar.edu/>). The Twin Otter flew 67 research hours from 4–29 March in the approximate range 16–23 N and 88–102 W. Background air was thoroughly characterized while searching for fires. The nephelometer, LiCor, UHSAS, and the AFTIR were usually operated continuously in background air with similar time resolutions from 0.5 to 5 Hz. At many key locations, the MPS-3 obtained integrated samples and WAS and AFTIR acquired “grab” samples of background air. To measure the initial emissions from the fires, we sampled smoke less than several minutes old by penetrating the column of smoke 150–500 m above the flame front. The LiCor, UHSAS, and nephelometer profiled their species while penetrating the plume. The AFTIR, MPS-3, and WAS were used to acquire “grab” samples in the smoke plumes. More than a few kilometers downwind from the source, smoke samples are usually already “photochemically aged” and better for probing post-emission chemistry than estimating initial emissions (Goode et al., 2000; Hobbs et al., 2003). To determine excess concentrations in the smoke-plume grab-samples, paired background grab-samples were acquired just outside the plume.

The C-130 concentrated on sampling regional background air and the MC outflow up to several days old. However, one smoke plume was profiled near MC, while making pseudo-continuous measurements of HCN, CO, and other species. HCN and CO were also measured extensively throughout the region.

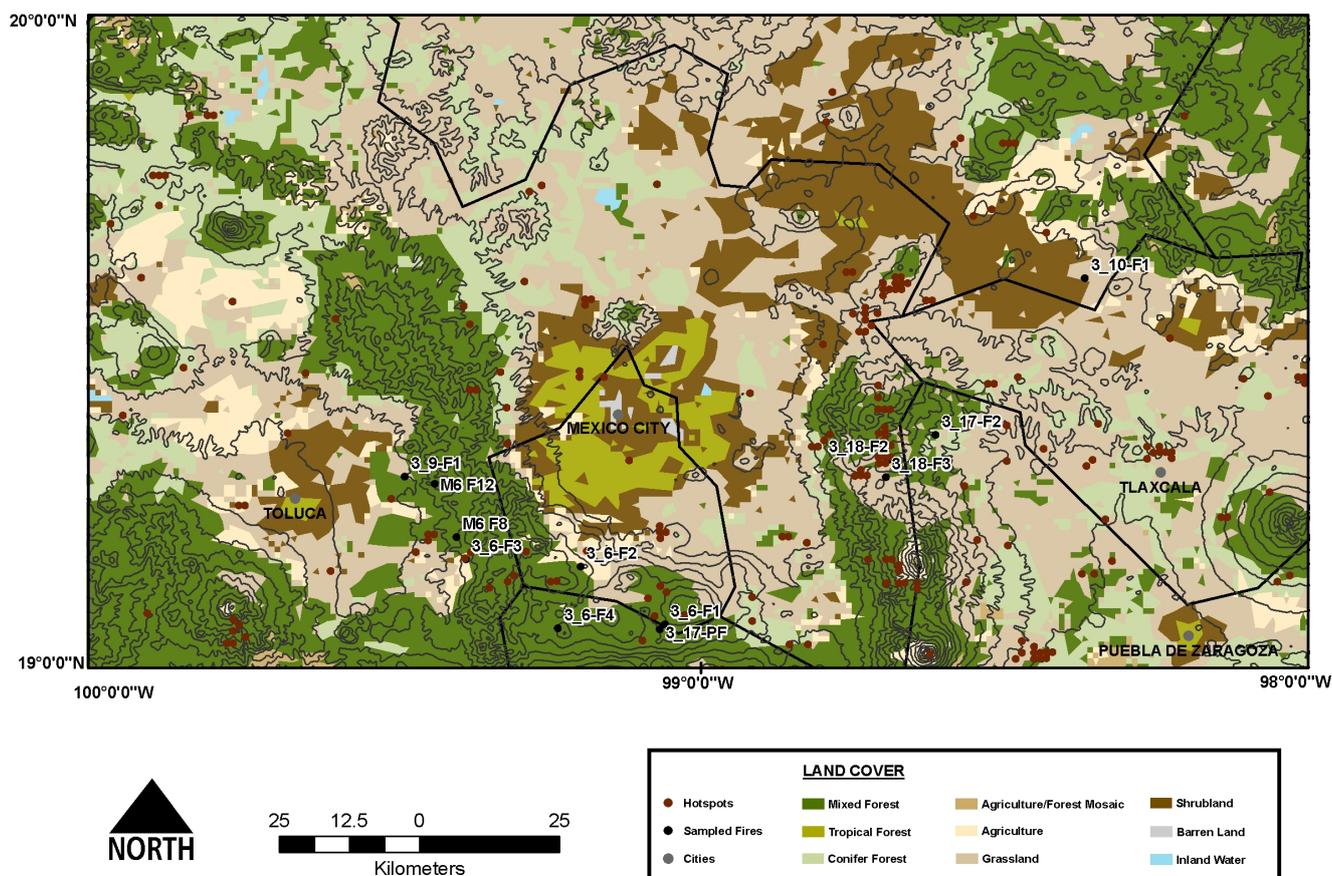


Fig. 1. The location of the MODIS hotspots and the fires sampled by MILAGRO aircraft in the study area. The land cover map in Fig. 1 is based on the 1 km² resolution North American Seasonal Land Cover Database Version 2.0 (SLCV2.0) from the USGS Land Cover Characterization Database (<http://edcns17.cr.usgs.gov/glcc/glcc.html>; Loveland et al., 2000). The original land cover categories of SLCV2.0 were aggregated to produce the simplified land cover classification used in Fig. 1. The mixed forest category consists mostly of pine mixed with other conifers or oak.

2.1.7 Ground-based fire and fuel consumption measurements

All but a few of the many fires observed from the MILAGRO aircraft in our MC study area were understory fires in forests dominated by pine that were located in the mountains. However, overlapping the March 2006 MODIS hotspots (<http://maps.geog.umd.edu>; Justice et al., 2002) with a vegetation map (Loveland et al., 2000) indicates that a sizeable fraction of the fires occurred in grassland or shrubland (Fig. 1). This may be partly due to the fact that fires under a forest canopy can be difficult to detect from space (Brown et al., 2006). In addition, at least two of the forest fires we actually sampled (and photographed) are in non-forest areas according to multiple vegetation maps (INEGI and INE, 1998; CONABIO, 1999; Loveland et al., 2000). In any case, to ensure both airborne and ground-based sampling of a representative, well-characterized fire; a planned fire was carried out by CONAFOR (Mexican Federal Forest Service) and the Department of Ecology of the state of Morelos. Prescribed

fires are conducted every year before the fire season to reduce fuels and the wildfire hazard in the region. However, CONAFOR agreed to burn an area in March to allow us to measure fire behavior, fuel consumption, and smoke emissions representative of the fire season. The fire included adjacent units of grassland and pine forest and was located within the Cumbres de Ajusco, Zempoala and Tepozteco National Parks; an area which has one of the highest incidences of forest fires in central Mexico. The planned fire was ignited around noon local time on 17 March and burned for about one hour. The fuel consumption was measured by the difference between pre- and post-fire fuel loading as determined by the linear intersect method (Brown, 1974). In the grassland areas the fuel consumption was 5.36 Mg/ha. In the forested section, the fuel was mainly grass plus some litter, shrubs, and woody debris and the fuel consumption was 7.9 Mg/ha. The area burned by the fire and the total fuel consumption are shown in Table 1.

Table 1. Locations, times, and fuel consumption for the pine-dominated forest fires sampled by the MILAGRO aircraft or ground crew in the mountains surrounding Mexico City.

Fire Name	Sampled by	Burn Date(s) dd/mm/yyyy	Lat (N) dd.dddd	Long (W) dd.dddd	time of airborne sampling		Coverage by cloud-free MODIS OP		UMD hotspot? Y or N	Fuel Consumption Mg total	Burned Area hectares	
					start hh:mm (LT)	finish hh:mm (LT)	Terra hhmm (LT)	Aqua hhmm (LT)				
3.6-F1	TO ^a	06/03/2006	19.0763	99.0537		13:27		11:15	14:20	N	nm	nm
3.6-F2	TO, G ^b	06/03/2006	19.1739	99.1903		13:32		11:15	14:20	N	61	7.7
3.6-F3	TO	06/03/2006	19.1881	99.3783	17:05	17:09		11:15	14:20	N	nm	nm
3.6-F4	TO	06/03/2006	19.0711	99.2283		17:14		11:15	14:20	N	nm	nm
M6 F12	G	06/03/2006	19.3142	99.4290		none		11:15	14:20	N	85	3.7
3.9-F1	TO	09/03/2006	19.3269	99.4775		13:20		11:41	none	N	nm	nm
3.10-F1	C-130	10/03/2006	19.6431	98.3578		17:16		10:55	13:55	N	nm	nm
3.17-PF	TO, G	17/03/2006	19.0681	99.0616	11:58	12:42		10:55	14:00	N	145	22.2
3.17-F2	TO	17/03/2006	19.3862	98.6066	13:06	13:18		10:55	14:00	N	nm	nm
3.18-F2	TO, G	18/03/2006	19.3456	98.6851	15:46	16:39		11:34	none	N	873	27.2
3.18-F3	G	~17–19/03/2006	19.3174	98.6888		none		Hotspot at 19.32, -98.72 (3/17 AQUA at 14:00)			~3100	~300
M6 F8	G	unknown	19.2252	99.3934		none				N	nm	6.9
Approximate Mexico City Center			19.411	99.131								

^a TO indicates USFS Twin Otter (see text).

^b G indicates ground-based fire characterization crew (see text).

Some of the other pine-understory fires sampled by the Twin Otter were later located by the ground-based crew. The burned area was measured and the fuel consumption was measured by comparing adjacent burned and unburned areas that had similar vegetation and terrain (Table 1). In addition, forest fires that were not sampled by the MILAGRO aircraft were also located by the ground-based crew and the burned area and fuel consumption measurements obtained are also shown in Table 1.

2.2 Data processing and synthesis

Grab samples or profiles of an emission source provide excess mixing ratios (ΔX , the mixing ratio of species “X” in the plume minus the mixing ratio of “X” in the background air). ΔX reflect the instantaneous dilution of the plume and the instrument response time. Thus, a useful, derived quantity is the normalized excess mixing ratio where ΔX is compared to a simultaneously measured plume tracer such as ΔCO or ΔCO_2 . A measurement of $\Delta X/\Delta \text{CO}$ or $\Delta X/\Delta \text{CO}_2$ made in a nascent plume (seconds to a few minutes old) is an emission ratio (ER). For any carbonaceous fuel, a set of ER to CO_2 for the other major carbon emissions (i.e. CO , CH_4 , a suite of non-methane organic compounds (NMOC), particulate carbon, etc.) can be used to calculate emission factors (EF, g compound emitted/kg dry fuel burned) for all the emissions quantified from the source using the carbon mass-balance method (Yokelson et al., 1996). In this project, the carbon data needed to calculate EF was provided mostly by AFTIR measurements of CO_2 , CO , CH_4 , and NMOC and also canister sampling of CO_2 , CO , CH_4 , and non-methane hydrocarbons (NMHC). The particle data allowed inclusion of particle carbon in the carbon mass balance. Next we summarize a few details of the methods we used to synthesize the data from the various instruments on the aircraft and to calculate ER and EF.

2.2.1 Estimation of fire-average, initial emission ratios (ER) for trace gases

First we describe the computation of ER on a molar basis to CO and/or CO_2 for each species detected in the AFTIR and canister grab samples. This is done for each individual fire or each group of co-located, similar fires. If there is only one grab sample of a fire (as for the 9 March fire) then the calculation is trivial and equivalent to the definition of ΔX given above. For multiple grab samples of a fire (or group of similar fires) then the fire-average, initial ER were obtained from the slope of the least-squares line (with the intercept forced to zero) in a plot of one set of excess mixing ratios versus another. This method is justified in detail by Yokelson et al. (1999).

The molar ER to CO_2 for the NMHC measured in the U-Miami cans was derived for each fire as follows. The molar ER to CO measured in the cans from a fire was multiplied by the molar CO/CO_2 ER measured on that same fire by AFTIR. All the molar ER we obtained for each fire can be retrieved from the EF in Table 2 (calculated as described next) after accounting for any difference in molecular mass. The modified combustion efficiency (MCE, $\Delta \text{CO}_2/(\Delta \text{CO}_2 + \Delta \text{CO})$) for each fire is also shown in Table 2. The MCE indicates the relative amount of flaming and smoldering combustion for biomass burning. Lower MCE indicates more smoldering (Ward and Radke, 1993).

The molar HCN/CO ratio for the MC-area outflow is the average ratio of all the C-130 measurements in the outflow that were not in distinct local plumes. The molar $\Delta \text{HCN}/\Delta \text{CO}$ emission ratio for the fire plume sampled by the C-130 was the integrated excess HCN divided by the integrated excess CO .

Table 2. Emission factors for the pine-dominated forest fires sampled in the mountains surrounding Mexico City in March 2006.

Species	6 March	9 March	17 March	17 March	18 March	All Fires	All Fires
	Fires 1–4 EF (g/kg)	Fire 1 EF (g/kg)	Planned Fire EF (g/kg)	Fire 2 EF (g/kg)	Fire 2 EF (g/kg)	Average	Standard Deviation
CO ₂	1655	1652	1747	1611	1646	1662	51
CO	83.2	88.6	30.9	112.5	99.2	82.9	31.1
MCE	0.927	0.922	0.973	0.901	0.914	0.927	0.027
NO	6.14	5.88	1.95	2.68		4.16	2.16
NO ₂	5.51	6.70	3.37	4.54		5.03	1.42
NO _x as NO	9.73	10.25	4.15	5.64		7.44	3.01
H ₂	nm ^a	nm	nm	nm	1.51	1.51	nm
CH ₄	6.92	5.00	2.81	4.69	5.39	4.96	1.48
C ₂ H ₄	0.90	0.36	1.38	1.17	0.88	0.94	0.38
C ₂ H ₂	0.24	nm	0.20	0.12	nm	0.19	0.06
C ₂ H ₆	0.34	nm	0.35	0.55	1.09	0.58	0.35
C ₃ H ₆	0.19	nm	0.42	0.48	0.92	0.50	0.30
HCHO	2.37	3.32	3.73	2.55		2.99	0.64
CH ₃ OH	1.48	2.56	1.45	2.77		2.06	0.70
CH ₃ COOH	3.18	6.65	3.61	2.40		3.96	1.86
HCOOH	1.66	4.34	1.83	nm		2.61	1.50
NH ₃	1.81	0.65	0.30	0.89		0.91	0.65
HCN	1.50	0.32	1.67	0.60		1.02	0.66
propane	0.948	nm	0.141	0.069		0.386	0.488
isobutane	0.119	nm	0.015	nm		0.067	0.074
n-butane	0.326	nm	0.040	nm		0.183	0.202
t-2 butene	0.013	nm	0.030	0.044		0.029	0.016
1-butene	0.042	nm	0.086	0.105		0.078	0.032
isobutene	0.053	nm	0.072	0.118		0.081	0.033
c-2-butene	0.010	nm	0.021	0.031		0.021	0.011
cyclopentane	0.004	nm	0.002	nm		0.003	0.001
isopentane	0.032	nm	0.011	nm		0.022	0.015
n-pentane	0.051	nm	0.018	0.008		0.026	0.023
1,3 butadiene	0.042	nm	0.090	0.069		0.067	0.024
PM1	7.08	7.40	6.83	21.0	13.0 ^b	11.05	6.10

^a nm indicates “not measured”

^b The 18 March particle measurement was of PM_{2.5}.

2.2.2 Estimation of fire-average, initial emission factors (EF)

We estimated fire-average, initial EF (g/kg) for PM1 and each observed trace gas from our fire-average, initial ERs using the carbon mass balance method (Yokelson et al., 1999). In brief, we assume that all the volatilized carbon is detected and that the fuel carbon content is known. By ignoring unmeasured gases, we may inflate the emission factors by 1–2% (Andreae and Merlet, 2001). We assumed that all the fires burned in fuels containing 50% carbon by mass (Susott et al., 1996), but the actual fuel carbon percentage may vary by $\pm 10\%$ (2σ) of our nominal value. (EF scale linearly with assumed fuel carbon percentage.) The fire-average, initial EF for each compound and fire are listed in Table 2. Because NO is quickly converted to NO₂ after emission, we also report a single EF for “NO_x as NO.”

2.2.3 Determination of particle mass

The nephelometer was used to profile PM_{2.5} per unit volume of air ($\mu\text{g}/\text{m}^3$) during plume penetrations of the 18 March fire. The LiCor simultaneously measured the mass of CO₂ per unit volume of air during each pass through the plume. The ER (on a mass basis) for PM_{2.5} to CO₂ for each fire (or group of similar fires) was obtained by linear regression as above, except that the integrated excess mass values for each profile through the plume were used in lieu of grab sample excess mixing ratios. Assuming the particles were 60% carbon by mass (Ferek et al., 1998) gave the contribution of PM_{2.5} to the total carbon emitted for the emission factor calculations. The PM_{2.5}/CO₂ mass ratio times EFCO₂ (g/kg) gave EFPM_{2.5} (g/kg). The EFPM_{2.5} for 18 March is likely accurate to within $\pm 10\%$.

Because, the nephelometer was not available before 18 March, the UHSAS particle size data which was collected at a sample rate similar to that of the nephelometer (and from a nearby inlet that was also used for fast CO₂ measurements) was used to determine particle mass as described next.

We assumed spherical particles and integrated over the size distribution measured by the UHSAS, to obtain an estimate of the volume of particles at 1 Hz. For each of the 8 plume penetrations on 18 March that featured both the UHSAS and nephelometer sampling pine-forest fires in the MC-area mountains, the integrated particle mass was ratioed to the integrated particle volume. For the densest plumes, only data from the more dilute parts of the plume ($<100 \mu\text{g}/\text{m}^3$) were used to avoid effects of saturation in the UHSAS. The mass to volume ratio was $1.858 \pm 0.183 \text{ g}/\text{cc}$. It is tempting to interpret this mass/volume ratio as an estimate of particle density, but the real density should be lower since: the particles are not perfectly spherical, there is a small amount of particle mass in the diameter range 1–2.5 microns, and the particles are also $\sim 8\%$ black carbon by mass (Ferek et al., 1998; Reid et al., 2005), which would partially absorb the UHSAS laser. In any case, we used the above “empirical” m/v ratio to convert the integrated UHSAS particle volume to integrated particle mass for the pine forest fire, plume-penetration samples obtained 6–17 March. The simultaneous co-located CO₂ measurements again provided the comparable integrated mass of CO₂ for each plume penetration. The ER (on a mass basis) for PM₁ to CO₂ were used as described above for the emission factor calculations. The EFPM₁ values obtained as described above, may only be accurate to $\pm 25\%$, but are not large enough to introduce significant error in the trace gas EF. Because of the size distribution mentioned above, EFPM₁ should be essentially equivalent to EFPM_{2.5}.

3 Results and discussion

3.1 Description and relevance of fires sampled

Detailed information about the MODIS and AVHRR hotspots detected in the entire country of Mexico since 2003 is conveniently tabulated at (http://www.conabio.gob.mx/conocimiento/puntos_calor/doctos/puntos_calor.html). The data shows that fire activity increases gradually and then sharply from November to May before dropping to low levels by August. The months of March, April, and May accounted for about 12, 31, and 43% of the total MODIS hotspots from 2003–2006, respectively. Nationwide, March 2006 showed average activity for March not counting the 2003 El Niño year. However, Mexican Forestry personnel (personal communication to E. Alvarado) and casual inspection of MODIS hotspot maps produced by the University of Maryland (UMD) Web Fire Mapper (<http://maps.geog.umd.edu>) (Justice et al., 2002) indicate that the level of fire activity in



Fig. 2. Photo taken a few km northwest of the site of fire 3.6-F4 on 6 March at 5:13 p.m. local time. A large number of pine-forest fires are burning in, and mixing with, the MC outflow on a mountain pass to the south of the city.

March 2006 in the mountains around MC was above normal for March in that area and similar to levels that normally occur in that area in April.

Table 1 shows location, time, and any fuel consumption and burned area information we have for the pine-forest fires that we were able to sample in the study area. Figure 1 shows all the MODIS UMD hotspots detected during March 2006 from 98–100 W and 19–20 N – the geographic limits of our MC-area study. Fire detections were made in the study area on 19 of the 31 days in March and totaled 218. The true number of fires is much larger as discussed below. Clouds or lack of coverage likely impacted the hotspot count on at least 14 of 31 days and that combined with a possible lack of sufficiently large fires at overpass time likely explain the days without detections. None of the fires that we sampled from the air in the study area registered as UMD-MODIS hotspots, because they were mostly short-lived (~ 1 h) and occurred >1 h before or after the Terra or Aqua overpass. However our fires were located in the precise areas showing the most hotspot activity. Thus, we conclude that (1) the number of hotspots provides a lower limit on the number of fires, (2) the hotspots are concentrated in the areas with the most burning, and (3) the fires we sampled were in the areas with the most burning.

Figure 2 is a photo, taken a few km NW of the site of fire 3.6-F4, at 5:13 p.m. LT on 6 March. Well after the last day-time satellite overpass at 2:20 p.m., a large number of pine-forest fires were burning in, and mixing with, the MC outflow on a mountain pass to the south of the city.

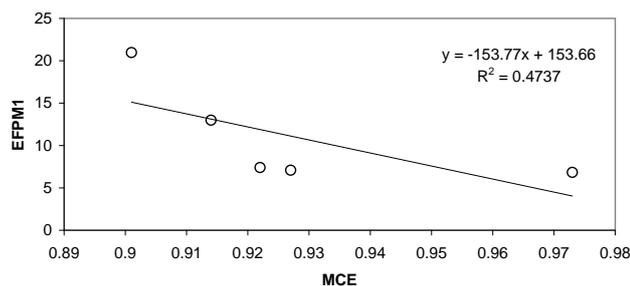


Fig. 3. Fire-average emission factors (EF) plotted versus fire-average modified combustion efficiency (MCE) for PM₁ (data from Table 2). A range of EF occurs, which correlates with the relative amount of flaming and smoldering.

3.2 Initial emissions from pine-forest fires in MC-area mountains

Table 2 gives the EF for every species we detected for each fire (or group of similar fires) and the average and standard deviation for all the species measured. The standard deviation is a fairly large percentage of the average value for many species. Figure 3 shows EFPM₁ vs MCE (index of the relative amount of flaming and smoldering). Figure 3 suggests that much of the variability in EFPM₁ is correlated with the different relative amounts of flaming and smoldering that occur naturally on biomass fires. For nitrogen species there is also a contribution to variability from the differing fuel nitrogen content (Yokelson et al., 1996, 2003a). The sum of the EF for VOC in Table 2 is 18.85 g/kg. However, oxygenated VOC (OVOC) normally dominate the NMOC emitted by biomass fires and, in this study, we did not have the capability to detect several OVOC common in biomass smoke (Christian et al., 2003). Therefore, we use 20 g/kg as a conservative estimate of the real sum of VOC, which may be as high as 25 g/kg.

3.3 Comparison to other biomass burning emission factors and the influence of urban pollution on fire emissions

Most of the average EF shown in Table 2 are similar to previously measured average values for forest burning. For instance, our study average EFPM₁ (11±6 g/kg) agrees well with the recommended EFPM_{2.5} for extratropical forest burning (13±7 g/kg) in Andreae and Merlet (2001). However, large differences with previous forest fire measurements occur for NO_x and HCN. In Fig. 4 we compare our EF for NO_x, HCN, and NH₃, to those from other types of biomass burning. In Fig. 4 the data for MC-area pine forest is from the present study. The data for US pine forest is from several published sources (Yokelson et al., 1996; Goode et al., 1999; Radke et al., 1991) and also includes some very similar unpublished lab-fire values obtained during the fol-

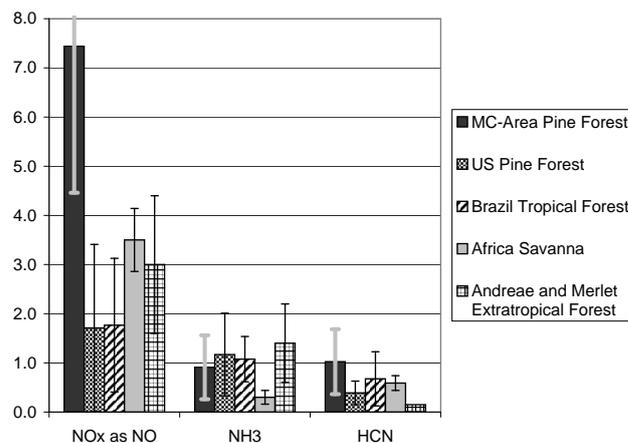


Fig. 4. Comparison of EF for selected nitrogen containing species between the MC-Area pine forest (affected by deposition), US Pine forest (in pristine area), tropical forest in Brazil, and savanna in Africa.

lowing studies (Christian et al., 2003¹). The Brazil tropical forest values are from a 2004 field campaign in the Amazon (Yokelson et al., 2007) and the African savanna data are from Yokelson et al. (2003a). The EF for extratropical forest from the widely-used recommendations of Andreae and Merlet (2001) are also shown.

For NH₃ the MC-area pine-dominated forest EF is close to what has been measured for other forest burning and the recommendation of Andreae and Merlet. However for NO_x the MC-area pine forest EF is about 4 times typical measurements for other forests and more than twice the recommendation of Andreae and Merlet. For HCN the MC-area pine forest fire EF is about 3 times that measured for US pine forests and about twice that for tropical forests and savannas. Our EFHCN is almost 7 times higher than the recommendation of Andreae and Merlet. Our higher values for HCN could also indicate that a larger EF for acetonitrile (CH₃CN) is appropriate, but we did not measure the latter.

It is interesting that our average EF for NO_x and HCN are 3–4 times the average measured for US pine forests. The difference in the mean is statistically significant for NO_x (7.44±3.0 MC-area, 1.71±1.7 US), whereas for HCN the variability in the MC-area EF overlaps the US mean (1.023±0.66 MC-area, 0.39±0.24 US). Nevertheless, the indication is that the true HCN mean is also higher for the MC-area. We note that the MC-area forests are heavily impacted by deposition of MC pollutants (Fenn et al., 1999), whereas the US pine forest data is from pristine pine forest ecosystems. Thus we speculate that the high NO_x and HCN emissions in the MC-area pine forests may be due to enrichment

¹Christian, T. J., Karl, T. G., Yokelson, R. J., Guenther, A., and Hao, W. M.: The tropical forest and fire emissions experiment: Laboratory fire measurements and synthesis of campaign data, Atmos. Chem. Phys. Discuss., in preparation, 2007.

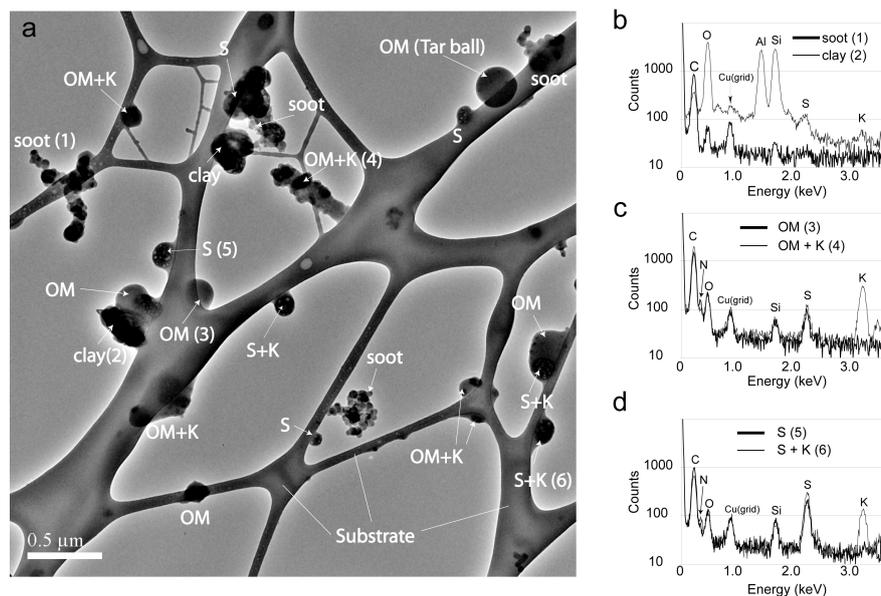


Fig. 5. Bright-field TEM image and EDS spectra of particles collected approximately 40 km south of the center of MC (sample 3.17-PF in Table 1 and Fig. 1a; collected 17 March 2006; start time 11:57:50, stop time 11:58:30 – local time.). They are the products of biomass burning (forest fire). **(a)** Image of various kinds of particles on a substrate of lacey carbon. OM – organic material, OM+K – organic material with inclusions of K compounds, S – sulfate, and S+K – ammonium and K sulfate. **(b)** EDS spectra for the particles in (a). The particle types were identified by their compositions and morphological properties. Numbers (1) to (6) in the inserts in (b) to (d) correspond to particles in the TEM image (a). The Cu peaks in the spectra are from the TEM grids.

of fuel nitrogen components that contribute to the emissions of these species via deposition of nitrogen-containing pollutants to the vegetation. The near-normal NH_3 emissions may indicate that they arise from other more ubiquitous fuel nitrogen components. These assumptions could be further tested in the future after we analyze the IR spectra from the pine forest fires sampled in less-polluted Mexican environments.

The observations of larger-than-normal NO_x and HCN emissions from the MC-area fires may also be relevant to understanding the local-regional atmospheric chemistry in other fire-impacted urban areas such as the Los Angeles basin where Radke et al. (1991) observed fire-induced resuspension of CFC-12. In addition, Hegg et al. (1987) measured higher emissions of NO_x , SO_2 , and particle nitrate from burning chaparral near Los Angeles than in the Pacific Northwest. In the latter study, the fuel types were different and the higher emissions of flaming compounds from chaparral were very likely partly due to the higher MCE of the chaparral fires, but deposition/resuspension probably also contributed to the difference as they suggested. In our study, we seem to support their hypothesis in a comparison of more similar fuel types. If industrial deposition does impact fire emissions, this could also be important in the southeastern US where widespread prescribed burning occurs near urban areas and in most urban areas in “developing countries” since they usually coexist with biomass burning.

3.4 Overview of particle chemistry

TEM studies show that many of the aerosol particles consist of internally mixed aggregates of several distinct particle types. For example, Fig. 5 shows a range of such particles ($<0.3 \mu\text{m}$ aerodynamic diameter) together with their compositions, measured using energy dispersive X-ray spectrometry (EDS). This sample was collected when the Twin Otter passed through the plume of the planned fire on 17 March. Identified particle types include soot, clay (probably kaolinite), tar balls, other organic material (OM), and a variety of sulfates and nitrates with and without K. The ammonium sulfates as well as KNO_3 and, to a lesser extent, K_2SO_4 tend to decompose in the electron beam and are thus difficult to analyze using TEM. Some OM particles have inclusions of K compounds like the products of biomass burning from other areas, although we did not observe discrete crystals of KCl like those found during SAFARI-2000 (Pósfai et al., 2003; Li et al., 2003). The inclusions of K compounds appear darker than their host OM (Fig. 5a) (Pósfai et al., 2003). The tar balls are round, amorphous OM particles that occur as a result of biomass burning (Pósfai et al., 2004; Hand et al., 2005). Although EDS analysis is not sensitive for detecting light elements such as N, most OM particles clearly showed a N peak (Fig. 5c and d). The OM particles without identifiable inclusions of K compounds and ammonium sulfate such as particle OM (3) (Fig. 5a and c) also contained N. As burning of pine forests in the MC area emits large amounts of

NO_x (see Sect. 3.3), the gaseous nitrogen may also contribute to the N in OM particles and, conversely, particles may host an appreciable fraction of the emitted N.

3.5 Preliminary assessment of the contribution of fires to the MC-area plume

Fire emission factors (g/kg) can be multiplied by fuel consumption data (kg) to estimate total emissions at various scales. However, it is difficult to measure the amount of fuel burned for a large fire-prone geographic area. Consideration of the fires we sampled, combined with the MODIS hotspots, allows a crude estimate of the total fuel burned by mountain fires in the study area during March 2006. We base our rough estimate on the assumption that the planned fire had a size (22.2 ha), duration (~1 h) and fuel consumption (6.54 Mg/ha) that is approximately average for the study area mountain fires. These assumptions seem conservative since the total fuel consumption of 145 Mg was about one-half the average total fuel consumption of 295 Mg for the 5 fires sampled by the ground crew in the area. We approximate the time period during which “average fires” burn as noon to five p.m. local time. (We choose noon as the beginning of the burning period because during one flight to southern Mexico we actually observed numerous fires being simultaneously ignited over a large, previously-clean area a few minutes after noon.) We note that cloud-free MODIS coverage of the study area (98–100 W and 19–20 N) during this “burning period” occurred on 2 of the 4 days (or one-half of the days) that the Twin Otter sampled fires there. If the average fire lasts for one hour, then an overpass during the burning period could detect up to one-fifth of the average fires if they were evenly distributed throughout the burning period. Coupling the above factors suggests that the actual number of mountain fires could be about 10 times larger than the 218 detected from space. Thus, 2180 fires times the total fuel consumption for the planned fire (145 Mg) estimates the total fuel consumption by these fires for the study area for March 2006, which is ~317 000 000 kg.

If the average fire duration is actually longer than the 1 h duration of the planned fire or if the number of fires peaks sharply at overpass time, then we have overestimated the number of fires, but this error could tend to be cancelled by the larger total fuel consumption expected for longer-lasting or more intense (mid-afternoon) fires. (The key assumption is the fuel consumption rate.) The study-area fuel consumption estimated this way may well be a lower limit since it does not account for fires that are obscured by the canopy, too small to register as hot spots (but potentially numerous), or large multi-day fires that would consume fuel for more than 5 h per day (several were observed from the Twin Otter in restricted airspace and one was measured at ~300 ha by the ground crew). A good, satellite-based, burned area measurement for this region would reduce the uncertainties associated with our assumptions above, but is not available to

our knowledge. This estimate also explicitly leaves out any small-scale urban burning for cooking, garbage disposal etc.

In any case, our estimated March 2006 study-area fuel consumption (317 000 000 kg) can be multiplied by any EF (g compound emitted per kg fuel burned) in Table 2 to estimate the total study-area emissions of that compound for the month produced by the mountain, pine-forest fires (hereinafter “mountain fires”). Our March 2006 mountain-fire CO emissions can be compared to 1/12 of the annual CO in the 2004 MC metropolitan area emissions inventory (MCMAEI, <http://www.sma.df.gob.mx/sma/index.php?opcion=26&id=392>) and they represent about 18% of that value. Thus this analysis implies that these fires were responsible for about 15% of the CO exported in the March 2006 MC-area plume, although West et al. (2004) argued that the CO and VOC emissions may be underestimated in the MCMAEI. Our preliminary, bottom-up estimate suggests similar fire contributions to the total for NO_x (14%), NH₃ (16%), and VOC (12%) and coincidentally the upper limit for the NO_x/VOC mass ratio from fires (~0.38) is similar to that in the MCMAEI (~0.34). In contrast to the similar contributions calculated for the trace gases above, the fire contribution to the primary PM₁₀ is estimated to be much larger at 67%. The true contribution could be higher since PM₁/PM₁₀ from fires is about 0.7 (Andreae and Merlet, 2001). Comparing to the MCMAEI PM_{2.5} suggests that 86% of the primary PM_{2.5} produced in the study area is from the mountain fires. The above estimates also do not include the fire emissions due to any other biomass burning not sampled by our aircraft (Bertschi et al., 2003a; Yevich and Logan, 2003). Another relevant insight is derived by noting that the primary PM₁₀/CO and PM_{2.5}/CO mass ratios in the MCMAEI are ~0.0115 and 0.0037, respectively; whereas the primary PM₁/CO ratio from mountain fires was ~0.133. Thus, regardless of the fire fraction of CO in the MC-area plume, the fire fraction of primary fine PM should be much greater.

The contribution of fire emissions to the MC-area plume can be estimated by another approach since HCN and CH₃CN are both thought to be emitted primarily by biomass burning (Li et al., 2000; de Gouw et al., 2006). This hypothesis can be largely verified for HCN for MILAGRO by considering other potential sources. Coupling our EFHCN and biomass fuel consumption estimate with the MCMAEI, and data from Arai et al. (1993) suggests that HCN from diesel use is <0.3% of the HCN from mountain fires. Coal combustion is a potential source of HCN, but the MCMAEI suggests that coal use is only about 1/5 of diesel use. Biogenic emissions of HCN should be low during MILAGRO since it was not during the growing season (Shim et al., 2007; A. Guenther, personal communication). Thus, our fire ER HCN/CO can be coupled with measurements of HCN/CO in the MC-area outflow to estimate the biomass burning contribution to the outflow CO. This analysis rests on several assumptions: (1) that the study-average mix of fire emissions we sampled resembled the real, average fire-emissions mix – on

the days of the downwind measurements, (2) that other types of biomass burning in the study area may be ignored, and (3) that our airborne measurements of the fire ER HCN/CO are also valid for any initially-unlofted smoldering fire emissions (Bertschi et al., 2003b). The third assumption is supported by the fact that EFHCN are not strongly dependent on MCE in this work (or in Africa (Yokelson et al., 2003a) or Brazil (Yokelson et al., 2007)).

Explicitly, the average MC-area mountain-fire molar ER for HCN/CO measured during MILAGRO is 0.012 ± 0.007 (combining 0.0128 ± 0.0096 from the Twin Otter and 0.011 from the single MC-area fire measurement of HCN/CO on the C-130, which is in good agreement with the Twin Otter mean). The average outflow HCN/CO molar ratio measured on the C-130 was about 0.003 ± 0.0003 implying that about 25% of the study area CO was from the mountain fires we sampled. This is actually fairly consistent with our crude bottom-up estimate above. Note, that use of fire HCN/CO ER from the other sources shown in Fig. 4 would have increased the estimate of the biomass burning contribution by a factor of 2–9. Given the large uncertainty in both the urban and fire emissions mentioned above, it would be useful to develop estimates based on additional biomass burning indicators if possible (e.g. CH_3CN , CH_3Cl , particle ^{14}C , etc.).

We can go a step further with the “tracer-based analysis” since according to the fire and urban primary PM/CO ratios quoted above; a 25% fire contribution to study-area CO implies fire contributions to study-area primary PM_{10} and $\text{PM}_{2.5}$ of 79% and 92%, respectively. We again emphasize that these fractional values depend strongly on the accuracy of our fuel consumption estimate and the MCMAEI (e.g. if the MCMAEI primary $\text{PM}_{2.5}$ was higher, then our estimate of the fire fraction of primary $\text{PM}_{2.5}$ produced in the study area would be lower). However, it is interesting that this second, partially-independent approach also suggests that fires are the main source of primary, fine-particle mass in our study area in March 2006. Finally we note that in both the bottom-up estimate and the HCN-based analysis we have so far ignored how other types of biomass burning in the study area (e.g. cooking, garbage burning, etc.) would affect an estimate of the fire contribution to the MC-area outflow. In the case of the bottom up estimate, adding more types of burning increases the overall fire contribution. We can also deduce the likely affect on the tracer-based estimates as follows. Bertschi et al. (2003a) found that HCN was below their detection limits for cooking fires. Thus, most likely, the HCN/CO ratio for the other types of burning is lower than for the mountain fires and the same HCN/CO ratio in the outflow would then imply that biomass burning as a whole makes a larger contribution to the outflow CO and particulate.

In addition to the near-source mixing of fire and urban emissions in the MC-area plume, we note that the more aged MC-area plume also likely interacts with biomass burning emissions from other regions of Mexico. For example, on 12 March and 29 March the Twin Otter sampled (mostly)

widespread agricultural waste burning (also characterized by relatively high N emissions) on the western Yucatan peninsula. On both of these days, HYSPLIT forward trajectories from the western Yucatan fires trend to the NW and pass close to the NE-trending forward trajectories from MCMA over the Gulf of Mexico (Draxler and Rolph, 2003). The projected mixing would be after emissions from both sources had aged 1–3 days. To aid in modeling this potential interaction, the Twin Otter sampled approximately 20 fires on the Yucatan and the C-130 also sampled 3 fires there. The results for those fires will be presented in a separate paper.

Even if the MC plume does not mix with additional downwind fire or urban emissions, the particles observed hours to days downwind from MC will reflect both the primary emissions from our study area and secondary processes such as oxidation, coagulation, and secondary organic and inorganic aerosol formation. Secondary processes make a strict source apportionment less rigorous. For instance gases from fossil fuel sources can condense on biomass burning particles and vice versa. Biogenic emissions can condense on both types of particles. A biomass burning particle can coagulate with a particle generated from fossil fuel combustion making a larger particle with an ambiguous source. Particle constituents could evaporate and then recondense (with or without oxidation) onto other particles (Robinson et al., 2007). A full analysis of these issues would require a modeling study similar to that of Olcese et al. (2007).

However, it is of interest to consider secondary processes (ignoring mixing of the two particle sources considered in this paper) and then roughly re-estimate the mass contribution of the two sources to the downwind plume. The secondary process with the most potential to alter source PM/CO ratios is secondary aerosol formation. Secondary aerosol formation is promoted by the presence of large amounts of condensable gases or high levels of O_3 , which can convert volatile NMOC to condensable gases (Reid et al., 1998; Olcese et al., 2007; Kang et al., 2007). Both of these factors are present in abundance for both sources in our study area.

The mass ratio for primary particles to CO in the MCMA EI is 0.0115. According to DeCarlo (attributed comment²) and references therein (e.g. Salcedo et al., 2006) a mass ratio for PM/CO that realistically includes secondary aerosol formation in the fossil-fuel aerosol from the MC area would range from 0.04 to 0.08. This represents an increase over the MCMA EI PM_{10} by a factor of 3.5–7. PM/CO is also likely to increase in the biomass burning aerosol. Moffet et al. (2007) measured a factor of 1.6 increase in the volume of biomass burning particles aged for several hours in the MC-urban area during MILAGRO. A review article on biomass

²DeCarlo, P.: Interactive comment on “Emissions from forest fires near Mexico City” by R. Yokelson et al., *Atmos. Chem. Phys. Discuss.*, 7, S2685–S2688, <http://www.atmos-chem-phys-discuss.net/7/S2685/2007/>, 2007.

burning particles by Reid et al. (2005) gives many examples of biomass burning aerosol mass (ratioed to CO) increasing by factors from 1.7 to 2.0 over 1–3 days in the absence of significant contributions from other sources (see also Reid et al., 1998). Growth factors as low as 1.2 have not been measured for biomass burning aerosol, but we adopt that factor as our lower limit for fires. This is justified by using the 2004 MCMAEI and our Table 2 and then assuming that the same percentage of co-emitted gas-phase precursors condense onto the biomass burning particles as is implied by our lower limit of 0.04 PM/CO for the urban aerosol. This could be reasonable because it essentially assumes that similar chemistry and physics affect the two types of combustion particles. We do not consider evaporation of gases from the particles for either source because strong evidence exists that on real fires significant growth in PM accompanies large \sim 50-fold dilution of the emissions (Ward et al., 1992; Babbitt et al., 1996). The range of growth factors we consider for biomass burning aerosol is much smaller than that for fossil fuel aerosol, but corresponds to the addition of similar mass. In fact, more mass could add to the biomass burning particles since the fire particles are produced at higher elevation, which implies that more O₃ and UV and lower temperatures (favoring condensation) are relevant. In addition, the forest fire particles are produced in an environment likely to have higher concentrations of biogenic emissions and the NMOC gases co-emitted by fires are much more reactive than for fossil fuel combustion (Reid et al., 1998; Christian et al., 2004).

We now re-estimate a range of mass fractions in the MC-area outflow under the approximation of just two sources (mountain pine forest fires and MCMA). A lower estimate for the fire, fine-particle mass contribution in the outflow is 40% (60% from MCMA). This is obtained by starting with our HCN-based estimate of the fire contribution to study-area CO and then assuming that the PM/CO mass ratio in the aged MCMA aerosol should be 0.08 and that our fire PM/CO should be multiplied by 1.2 to account for secondary aerosol formation. A higher fire contribution is estimated by assuming a mass-growth factor of 2 for biomass burning and a PM/CO mass ratio of 0.04 for the MCMA aerosol. In this case the fire contribution is estimated as 69% (31% MCMA contribution). The midpoint of this range corresponds to 55% of the fine particle mass in the MC-area outflow being due to the mountain fires. Of course, different assumptions, additional downwind data, or a detailed modeling exercise could lead to adjustments in these estimates.

3.6 Possible nature of fire impacts on the MC-area plume photochemistry

The main purpose of this paper is to present the study area EF and a preliminary assessment of their significance. Having established that fires will likely produce a visible signal in the MC-area plume measurements we now list some fairly obvious potential influences of fires on the plume pho-

tochemistry. Introductory material about these effects can be found in atmospheric chemistry textbooks (Finlayson-Pitts and Pitts, 1986). For example, the injection of fresh “fire-NO_x” into the MC plume immediately downwind of MC could contribute to the measured change in the NO_x/NO_y ratio between downtown MC and further downwind. Both NO_x and VOC from fires could alter the downwind O₃ production (which could also be impacted by the high dust levels observed (Moffet et al., 2007)). NO_x from fires could also contribute to aerosol nitrate (Fig. 5). Ammonia is another reactive fire emission that could contribute to aerosol particles such as ammonium sulfate or ammonium bisulfate and affect secondary aerosol formation in general. The particles emitted by fires are enriched in organic carbon (Fig. 5a) compared to particles from industrial sources and this could affect observed downwind heterogeneous chemistry. Also, the addition of organic rich particles to the MC plume by fires should not be confused with secondary aerosol formation. Confirmation of any of these impacts may be found in the MILAGRO airborne data.

3.7 Relevance to ground-based measurements in the Mexico City basin

Previous atmospheric chemistry measurements in the MC-area were nearly all ground-level measurements in the heart of the MC urban area. An influence of biomass burning was recognized in some of these reports. Bravo et al. (2002) analyzed the particulate data for the MC urban area from 1992 to 1999. They observed some large increases in urban PM₁₀ and total suspended particulate (TSP) during March-May of 1998, which they attributed to greatly increased biomass burning in Mexico at that time (Galindo et al., 2003). Moya et al. (2003) analyzed urban MC particulate from December 2000 to October 2001. There was a marked peak in total loading during April of 2001, which coincides with the usual annual peak of fire activity in the area.

A number of researchers in the MCMA-2003 campaign noted a biomass burning influence on the April 2003 urban particle data as reported by Molina et al. (2007). In particular, Johnson et al. (2006) estimated that on average, for April 2003, biomass burning contributed about 12% of the particle mass (their Fig. 1). However, there are some intriguing aspects of their data worth noting. For instance, K, H, and Cl, which are said to be elemental markers of biomass burning, increased strongly in the 0.07–0.34 and 1.15–2.5 micron size ranges late in the month when fire activity increased (their Fig. 4). However, in the 0.34–1.15 micron size range, which accounts for most of the mass of biomass burning particles, the increase was much smaller. In any case, we note that a 12% contribution of fires to ground-level downtown MC PM is not a-priori incompatible with our estimate of fires producing 70–90% of the primary fine PM in our study area. For any given wind direction, the emissions from the fires in at least half our study area (downwind and parallel) would

not be expected to find their way to downtown MC. Even for directly upwind mountain fires, much of the emissions could pass above ground-level monitors.

As part of the March 2006 MILAGRO campaign, at least two ground-based studies focused on source apportionment for particles, in the MC basin, during roughly the same time period as our airborne measurements. Stone et al. (2007) estimated that biomass burning accounted for 5–50% of the organic carbon in particles collected on filters in the Mexico City basin. At a downtown MC site during MILAGRO, Moffet et al. (2007) found that particles with a biomass-burning core accounted for the largest number fraction (41%) of sub-micron, ambient particles. The results of both of these studies would have been partially affected by types of biomass burning other than the mountain fires that we directly sampled from the air and discuss in this paper. Nevertheless, as explained above, both of these estimates are consistent with our preliminary source apportionment for the outflow.

4 Conclusions

The MILAGRO experiment was conducted to further the understanding of the outflow from the Mexico City (MC) area. This paper presents data that is useful for modeling the biomass burning contribution to the outflow photochemistry that arises due to fires in the pine-dominated forests located in the mountains around MC. The average forest fire emissions of HCN were ~ 2 times higher than normally observed for forest fires, which should be taken into account in source apportionment. The average forest fire emissions of NO_x were 2–4 times higher than would be assumed based on literature values. This is important in modeling plume photochemistry. The high N emissions from MC-area forest fires may be relevant to understanding atmospheric chemistry throughout the world in the many urban areas that coexist with biomass burning.

For source apportionment purposes, we designate the region from 19–20° N and 98–100° W (which includes MC and the adjacent mountains) as the “Mexico City area.” Preliminary “bottom-up” or “tracer-based” analysis then suggests that mountain fires produced about 15 or 25%, respectively, of the CO, and similar percentages of VOC, NH_3 , and NO_x in the MC area in March 2006; but a much larger percentage (67–92%) of the primary fine particles. Assuming the mountain fire contribution to the CO in the March 2006 MC-area outflow is 25% (based on the HCN/CO ratios) and coupling with a range of values for secondary aerosol formation in the urban and forest fire emissions suggests that about 40–69% (55% midpoint) of the fine particle mass in the outflow was from the mountain fires. Coupling the uncertainty in the HCN/CO ratios with the above analysis suggests that the March 2006 mountain fire contribution to the MC-area outflow fine particle mass was approximately $50 \pm 30\%$ (i.e. 20–80%). The large range highlights the need for more work.

However, it is interesting that our “bottom-up” and “tracer-based” approaches to these estimates agreed well. Taken together they suggest that biomass burning is a significant component of the MC-area outflow during the biomass burning season in Mexico (March–May). There are likely days of higher and lower fire influence on the outflow, but fires are probably a significant influence, on average, during these three months. Further, we do not claim that Mexico City’s air quality problems could be solved by eliminating regional biomass burning, but there is a strong possibility that the application of smoke management techniques (Hardy et al., 2001) to regional biomass burning could improve the March–May Mexico City air quality.

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