

**Organic aerosol
during MIRAGE 2006**

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Characterization of organic ambient aerosol during MIRAGE 2006 on three platforms

S. Gilardoni^{1,*}, L. Shang¹, S. Takahama¹, L. M. Russell¹, J. D. Allan²,
R. Steinbrecher³, J. L. Jimenez⁴, P. F. Decarlo^{4,**}, E. J. Dunlea⁴, and
D. Baumgardner⁵

¹Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, USA

²National Centre for Atmospheric Science, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Manchester, UK

³Institute of Meteorology and Climate Research, Forschungszentrum, Karlsruhe GmbH (IMK-IFU), Germany

⁴Cooperative Institute for Research in the Environmental Sciences (CIRES), University of Colorado, Boulder, Colorado, USA

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⁵ Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México,
Mexico City, Mexico

* now at: Joint Research Center, Institute of Environment and Sustainability, Climate Change
Unit, Ispra, Italy

** now at: Paul Scherrer Institut, Switzerland

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Correspondence to: L. M. Russell (lrmrussell@ucsd.edu)

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Abstract

Submicron atmospheric aerosol particles were collected during the Megacity Initiative: Local and Global Research Observation (MILAGRO) in March 2006 at three platforms located in the Mexico City urban area (at the Mexico City Atmospheric Monitoring System building – SIMAT), at about 60 km south-west of the metropolitan area (Altzomoni in the Cortes Pass), and on board the NSF/NCAR aircraft C130. Organic functional group and elemental composition were measured by FTIR and XRF. The average organic mass (OM) concentration, calculated as the sum of organic functional group concentrations, was $9.9 \mu\text{g m}^{-3}$ at SIMAT, $6.6 \mu\text{g m}^{-3}$ at Altzomoni, and $5.7 \mu\text{g m}^{-3}$ on the C130. Aliphatic saturated C-C-H and carboxylic acid COOH groups dominated OM (more than 60%) at the ground sites. On the C130, a non-acid carbonyl C=O, and amine NH_2 groups were observed in concentrations above detection limit only outside the Mexico City basin. From the elemental composition of SIMAT samples, we estimated the upper bound of average contribution of biomass burning to the organic carbon (OC) as 33–39%. The average OM/OC ratio was 1.8 at SIMAT, 2.0 at Altzomoni, and 1.6–1.8 on the C130. On the aircraft, higher OM/OC ratios were measured outside of the Mexico City basin, north of the urban area, along the city outflow direction. The average carboxylic acid plus non-acid carbonyl to aliphatic saturated ratio was higher at Altzomoni relative to SIMAT, reflecting a larger average contribution of carbonyl functional groups (largely in carboxylic acids) at the mountain site.

1 Introduction

Atmospheric aerosols impact environmental quality on short time scales by affecting human health and reducing visibility (Chan et al., 1999; Pope et al., 1995). Atmospheric aerosols also affect climate by scattering and absorbing incoming solar radiation (Charlson et al., 1992; Lindberg, 1975) and by influencing cloud formation and properties (McFiggans et al., 2006). The impacts of atmospheric aerosols on the envi-

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ronment depend on particle physical properties and chemical composition.

Organic aerosols represent a large fraction of fine atmospheric aerosols, both in urban and rural locations (Hildemann et al., 1994; Putaud et al., 2004; Zhang et al., 2007). The organic fraction of fine aerosol can include saturated and unsaturated aliphatic compounds, aromatic compounds, alcohols, ketones, aldehydes, carboxylic acids, amines, sugars, polyols, and organic sulfur compounds (Seinfeld and Pandis, 1998). Organic molecules that are emitted directly into the atmosphere contribute to the Primary Organic Aerosol (POA); Secondary Organic Aerosol (SOA) is formed by oxidation of organic species in the gas phase followed by condensation of the products (homogenous oxidation) or by oxidation of precursors in the aerosol phase (cloud processing or heterogeneous oxidation). SOA is typically composed of molecules containing oxygenated functional groups, including organic hydroxyl and carbonyl groups (Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005). Aged and processed aerosols, which are dominated by SOA over POA, are expected to show a high content of oxygenated functional groups and consequently a high organic mass to organic carbon ratio (Aiken et al., 2008; Turpin and Lim, 2001).

The Mexico City metropolitan area is one of the most populated areas of the world with a population larger than 18 million in 2005. The city elevation is 2240 m above sea level, resulting in lower oxygen availability and less efficient combustion. The low combustion efficiency, older vehicle fleet, and the vehicle engine tuning (Beaton et al., 1992) release a large amount of pollutants into the atmosphere as a consequence of fossil fuel and biomass burning (Molina and Molina, 2002). In addition to anthropogenic activities, sulfate from the Popocateptl volcano (Marquez et al., 2005; Raga et al., 1999), dust (Johnson et al., 2006; Miranda et al., 2004), and forest fires (Yokelson et al., 2007) contribute to the high level of particulate matter. Mexico City is located in a basin on the central plateau of Mexico surrounded by mountain ranges on the west, south and east sides.

This paper introduces the results of aerosol samples collected at three platforms during the Megacity Initiative: Local and Global Research Observation (MILAGRO)

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in March 2006, to observe the effects of transport and aging of urban particles on the composition of the organic aerosol (Molina et al., 2008). MILAGRO is the largest of a series of international campaign in and around Mexico City, which also includes IMADA-AVER in 1997 (Edgerton et al., 1999) and MCMA-2003 (Molina et al., 2007).

This study investigates the composition of organic aerosols in Mexico City and in surrounding areas by Fourier Transform Infrared Spectrometry (FTIR). The composition of organic aerosol is still poorly characterized. Identification of individual molecules by gas-chromatographic techniques resolves only a small fraction of the organic mass (Rogge et al., 1998; Saxena and Hildemann, 1996). Fourier Transform Infrared Spectroscopy, like other techniques such as nuclear magnetic resonance (NMR) and aerosol mass spectrometry (AMS), does not identify individual molecular species but provides a functional-group based description of the physical and chemical properties of most of the organic fractions (Gilardoni et al., 2007; Maria et al., 2002, 2003). The OM/OC ratio together with the molar ratio of oxygenated functional groups relative to aliphatic C-H groups is used as an indicator of aerosol processing and aging.

2 Methods and instrumentation

2.1 Sampling

Ambient aerosol samples were collected during the MILAGRO campaign at three platforms: at the Mexico City Atmospheric Monitoring System building (SIMAT), at Altzomoni (Cortes Pass), and on board the NCAR C130 aircraft. The SIMAT building (19°25' N, 99°07' W) is located in the Mexico City urban area, south of T0 (MCMA-2006 supersite) (Molina et al., 2008). Industrialized areas, characterized by the presence of power plants and refineries, are located to the North; the dry lake bed of Texcoco Lake, a regional large source of dust, is located to the East. The Altzomoni sampling site (19°07' N, 98°38' W) is approximately 60 km southeast of Mexico City on the saddle between the Popocatepetl and the Ixtaccihuatl volcanoes at an altitude of 4010 m

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(Rappenglueck et al., 2007). During the sampling campaign the general circulation at Altzomoni was from the Northwest (Mexico City basin), the East (Puebla Valley), and the Southwest (Chalco Valley). The C130 aircraft, whose operations were based in Veracruz, performed 12 research flights over Mexico and over the coast of the Gulf of Mexico. Figure 1 reports the C130 flight tracks, and the location of SIMAT and Altzomoni. During the MILAGRO campaign several urban and rural ground platforms were operated; Fig. 1b reports the sites that were used to investigate Mexico City out-flow and that are mentioned in the present study as reference. The sampling campaign was performed during March 2006. Measurements at the three sites included a large set of online gas and particle characterization techniques.

Submicron aerosol samples were collected on 37 mm Teflon filters with a flow rate of 16.7 Lpm. At the ground platforms (Altzomoni and SIMAT) a 24-h sample was collected daily, along two 12-h samples or three 8-h samples. The 12-h Altzomoni samples were taken from approximately eleven in the morning until six in the evening and from six in the evening until eleven the next morning. The time periods were chosen to separate periods when the regional boundary layer was above and below the research site, respectively. On board the NCAR C130 samples were collected during constant altitude legs, for a sampling period that ranged in most of the cases between 20 min and 1 h. After collection, filters were put in sealed Petri dishes and stored at approximately -4°C until analysis.

2.1.1 Fourier Transform Infrared (FTIR) Spectrometry and X-Ray Fluorescence (XRF) measurements

Teflon filters were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to characterize the composition of the organic aerosols (Gilardoni et al., 2007; Maria et al., 2002, 2003). FTIR measurements were performed with a Bruker Tensor 27 FTIR Spectrometer with a DTGS detector. FTIR spectra were acquired in transmission mode in the region $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} ; for each sample spectrum 128 scans were acquired. Filters were scanned before and after sampling, and each

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aerosol spectrum was obtained by subtraction of the two absorption spectra to remove the Teflon interference. Ambient aerosol spectra were characterized by the broad signal of ammonium in the region 2800–3200 cm⁻¹, which overlaps some of the organic functional group signals. To remove the ammonium interference, the reference absorption spectra of ammonium sulfate, normalized to the ammonium signal at 3200 cm⁻¹, was subtracted from each aerosol spectrum. The FTIR spectra were integrated using an automated algorithm (Russell et al., 2009).

The organic functional groups characterized during the project are reported in Table 1 along with the corresponding absorption wavenumbers and detection limits. The identified organic functional groups included non-acid organic hydroxyl C-OH group (including sugars, anhydrosugars, and polyols, herein indicated as alcohol group), aromatic C=C-H group, aliphatic unsaturated C=C-H group, aliphatic saturated C-C-H group, non-acid carbonyl C=O group, carboxylic acid COOH group, and amine NH₂ group. The calibration coefficients of the organic groups were obtained by analysis of standard aerosol samples prepared with 1-docosanol, anthracene, sodium benzoate, 1-docosene, alanine, citric acid, and adipic acid (Gilardoni et al., 2007; Liu et al., 2009). The absorbance of the measured functional groups is proportional to the number of moles and is independent of the mixture composition (Maria et al., 2002, 2003). The organic mass (OM) concentration was calculated multiplying the molar functional group concentrations by the corresponding group molecular weights and summing the contribution from the different groups. Organic carbon (OC) concentration was obtained by summing the carbon contributions from the different functional groups, which were equal to the functional group molar concentrations multiplied by 12. The algorithm used to calculate the OM and OC concentrations assumes that saturated carbon chains were present mainly as CH₂ units. The OM contribution of organic functional groups containing sulfur (including organosulfates with C-O-S bonding) was below detection in all the samples. The uncertainty of functional group and organic mass concentration from calibration, peak integration, and sampling flow variability was between 5% and 21% (Russell, 2003; Maria et al., 2003; Gilardoni et al., 2007).

X-Ray fluorescence measurements were performed on aerosol samples collected on Teflon filters after FTIR analysis. XRF measurements (Chester LabNet, Tigard, Oregon) quantified elements heavier than Na, including S, Cl, Al, Si, K, Zn, Fe, V and Ni. The measurements uncertainties were on the order of 1–10 ng per filter for all elements except Na for which the uncertainties were 10 times higher; the relative errors were lower than 10% for all elements including Na.

2.1.2 Aerosol Mass Spectrometry AMS

Collocated Aerosol Mass Spectrometry (AMS) measurements (Canagaratna et al., 2007) were performed at Altzomoni and on the C130. At Altzomoni the quadrupole AMS (Q-AMS) instrument was operated with a time resolution of 5 min and transmission efficiency of 0.5 (Jayne et al., 2000; Jimenez et al., 2003); lower transmission efficiency for particles at the upper end of the submicron range was observed. The C130 AMS measurements were high resolution-time of flight (HR-ToF) spectra collected every 12 s (DeCarlo et al., 2008, 2006), with collection efficiency of 0.5. The AMS instruments measure the chemical composition of the non-refractory fraction of submicron aerosol (Allan et al., 2003). The organic mass was calculated using the fragmentation table approach to remove the fragments from inorganic species (Allan et al., 2004).

AMS organic mass measurements were averaged over the sampling period corresponding to each FTIR sample. Figure 2 shows the comparison between FTIR and AMS organic mass concentration at Altzomoni and on the C130. Organic mass measurements from the AMS on the C130 were available during research flights 1–3 and 9–12. The comparison included each measurement for which the AMS instrument was operated continuously during FTIR filter samples at constant altitude. The correlation coefficients (r^2) between AMS and FTIR measurements were 0.62 at Altzomoni and 0.69 on the C130. The use of separate inlets on the C130 results in a size-distribution-dependent difference which may contribute to the scatter in the airborne measurements, particularly in samples with a substantial fraction of the submicron

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mass above 500 nm. However, the small number of samples with comparable measurements for both instruments is likely to account for much of the weak correlation. The FTIR OM to AMS OM ratio was 0.87 ± 0.06 at Alzomoni. There were an insufficient number of points to obtain a reasonable line fit between the AMS and FTIR OM on the C130, but the available points typically had FTIR OM lower than AMS OM by a factor of 2, possibly reflecting both the differences between the aircraft inlets and the low filter loadings. Lower OM concentrations measured by FTIR on the C130 might result in part from the short collection times and the low concentrations of some functional groups since many of the measurements were in the free troposphere. However the magnitude of the underestimate of carboxylic acid and amine groups was calculated by estimating the upper bound of these components assuming concentrations below detection limit were equal to the detection limit. These upper bounds were smaller than the $\pm 20\%$ uncertainty expected for OM (Russell, 2003). Desorption of volatile organic compounds during legs in and out of plume might explain, for longer sampling periods, the lower concentrations from filter measurements (FTIR) compared to on-line (AMS) measurements. The uncertainty of AMS measurements is dominated by uncertainty in the collection efficiency, and was conservatively considered as $\pm 25\%$ of the measured OM.

Figure 2c shows the comparison between FTIR OM/OC ratios and AMS OM/OC ratios for the C130 sampling periods characterized by overlapping FTIR and AMS measurements. The AMS OM/OC falls in the range of variability of FTIR values, calculated taking into account the uncertainty introduced by the low filter loadings. The FTIR values were typically 1.7 ± 0.2 , which encompasses the values measured by AMS. The functional group composition, described by the pie charts, indicates that the larger variability of FTIR OM/OC is associated with samples characterized by a larger uncertainty in the amine group concentration.

3 Results and discussion

3.1 Composition of the organic mass

The organic functional groups quantified by FTIR included alcohol C-OH, aromatic C=C-H, aliphatic unsaturated C=C-H, aliphatic saturated C-C-H, non-acid carbonyl C=O, carboxylic acid COOH, and amine NH₂ groups. Organic sulfates, which can be identified by the absorption of infrared radiation associated with the bending of the carbon-oxygen-sulfur functional group, were found to be below detection limit for all samples, consistent with the lack of fragments containing C and S with high-resolution AMS at T0 (Aiken et al., 2008). This finding was verified for the C130 samples by comparing the sulfate concentration from AMS with the sulfate concentration calculated from XRF elemental sulfur. The two sets of measurements correlated with a slope of 1.07 and at a confidence level larger than 99.95% (data not shown). The 1:1 ratio indicates that the contribution of sulfur compounds other than inorganic sulfates was small compared to the total mass of sulfate, making the contribution of organic sulfur to OM negligible. This is consistent with the complete neutralization of the anions (sulfates and nitrates) by ammonium, within the error of measurements, observed with the AMS (DeCarlo et al., 2008).

The average OM concentration at standard conditions (273.15 K and 1 atm) was 9.9 $\mu\text{g m}^{-3}$ at SIMAT, 6.6 $\mu\text{g m}^{-3}$ at Altzomoni, and 5.7 $\mu\text{g m}^{-3}$ on the C130. The average OC concentration at SIMAT was 5.3 $\mu\text{g m}^{-3}$, comparable to the OC mean concentration measured by thermo-optical method at a peripheral site in Mexico City (T1) (Doran et al., 2007; Querol et al., 2008; Stone et al., 2008) but lower than the value reported by Chow et al. (2002) close to the SIMAT site during March 1997 and lower than the values reported at CENICA in 2003 and at T0 in 2006 (Aiken et al., 2008; Salcedo et al., 2006; Stone et al., 2008). Figure 3 shows the campaign average contribution of each functional group to the OM on the three platforms. For simplicity aliphatic unsaturated and aromatic groups, whose contribution was usually lower than 1% and often below detection limit, are not reported. The average composition reported for the

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C130 is obtained from the analysis of samples with collection time longer than 10 min and shorter than 2 h, to assure low noise level and reduce artifact due to loss of volatile compounds with longer sampling periods. The average compositions at the two ground platforms were similar, suggesting that when the winds are from the North or Northwest the high altitude site is affected by MCMA air masses (Rappenglueck et al., 2007). At the ground sites, the largest contribution to OM came from aliphatic saturated C-C-H and carboxylic acid COOH group, which together represented more than 60% of the OM. The average contribution of alcohol C-OH group varied, averaging 14% at SIMAT, 15–17% on the C130, and 20% at Alzomoni; amine NH₂ group represented about 10% of the organic mass both at SIMAT and Alzomoni, and 6–20% on the C130. The presence of amine at SIMAT is consistent with the results of Moffet et al. (2008) at T0 (urban site) where the nitrogen-organic carbon particles represent about 3–5% of the submicron particle number.

Figure 3d illustrates the properties of Mexico City outflow showing the percentage contribution of carboxylic acid and alcohol groups to OM, as a function of location relative to the Mexico City metropolitan area (MCMA). C130 city samples were collected at about 1000 m above ground level (a.g.l.) during the afternoon, and thus inside the mixing layer, with altitudes reaching 2000 m a.g.l. and frequently extending to 4000 m a.g.l. (Shaw et al., 2007). The C130 samples collected outside the city were often in the free troposphere. The comparison between city and outflow samples shows that the contribution of carboxylic acid COOH group outside the city basin was twice as large as the contribution over the city, but the contributions of alcohol C-OH group are similar in all sectors. The terrain structure around Mexico City is characterized by mountains to the east, south and west of the metropolitan area that reach on average 1000 m above the basin, with two volcanoes at the Southeast that reach over 5000 m a.g.l.; the terrain features, together with the prevailing meteorological conditions during the MILAGRO experiment, favored the transport of Mexico City air masses towards the North. The comparison between samples collected north and south of the urban area (Fig. 3d) shows a larger contribution of both alcohol C-OH and carboxylic acid COOH groups to

the North, where the most frequent direction of the urban outflow was located (Doran et al., 2007).

The time series of functional group composition are reported in Fig. 4, together with wind speed and relative humidity time series. For simplicity aliphatic unsaturated, aromatic groups, and non-acidic carbonyl, whose contribution was usually lower than 1%, are not reported. Meteorological data reported for the SIMAT site were recorded by the Ambient Air Monitoring Network (Red Automatica de Monitoreo Atmosferico, RAMA) at the Merced station. The organic mass concentration ranged between 3 and 35 $\mu\text{g m}^{-3}$ at SIMAT, 1 and 24 $\mu\text{g m}^{-3}$ at Altzomoni, and 2 and 22 $\mu\text{g m}^{-3}$ during the C130 flights. At Altzomoni higher OM values were observed during daytime compared to nighttime: the average OM concentrations were 9.4 $\mu\text{g m}^{-3}$ and 5.6 $\mu\text{g m}^{-3}$, respectively. Figure 4 shows similar OM temporal trends for the two ground sites. At SIMAT lower OM concentrations were observed during episodes characterized by wind speed higher than 2 m s^{-1} or relative humidity close to 100%, indicating that organic mass concentration was modulated by removal mechanisms, i.e. transport and wet deposition. The highest concentrations on 20 and 21 March are likely related to intense biomass burning plumes and smoke from nearby forest fires (Aiken et al., 2009). At Altzomoni the peaks of OM concentration observed on 14, 21, and 23 March may be related to the presence of cold surge episodes that favored the transport of air pollutants from the city basin towards the South (de Foy et al., 2008). At Altzomoni the OM concentration started decreasing on 23 March, in association with rain and snow events, to increase again after 27 March, with the reduction of wind speed and relative humidity.

Aliphatic saturated C-C-H and carboxylic acid COOH groups represented the largest fraction of the organic mass throughout the sampling campaign at the ground sites. At SIMAT the average composition of the OM was roughly constant during the entire month; at Altzomoni a larger contribution of alcohol C-OH was observed during the driest period of the campaign, before 24 March, when alcohol C-OH fraction reached peaks of 40%. The pie charts in Fig. 4b shows the average functional group composition at Altzomoni before (dry period) and after (wet period) 24 March; the average

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contribution of alcohol C-OH group to OM during the dry and wet period was 25% and 11%, respectively. Alcohol C-OH group can be found in ambient aerosol as alcohols, polyols, and sugars (Graham et al., 2002; Simoneit et al., 2004a,b). Relevant sources of sugars, anhydrosugars, and sugar alcohols are biogenic emissions and biomass burning (Graham et al., 2002; Mayol-Bracero et al., 2002). Levoglucosan, an anhydro-sugar widely used as a tracer of biomass burning, might represent more than 10% of the OC produced by wood combustion (Fine et al., 2002; Simpson et al., 2007). The importance of biomass combustion as source of alcohol C-OH group is further supported by the high correlation at SIMAT between alcohol C-OH group and K (Liu et al., 2009), an additional tracer of biomass burning. The decrease of alcohol C-OH contribution during the wet period can be linked to the lower intensity and frequency of fires in the regions, as determined by satellite measurements (Fast et al., 2007; Aiken et al., 2009). On the C130 the organic mass was on average dominated by aliphatic saturated C-C-H group; carboxylic acid COOH group was an important fraction of the organic mass in samples collected north of the city basin during research flights 5 (16 March), 7 (19 March), and 8 (22 March), when its contribution was larger than 30% of the OM.

3.2 Elemental composition of Mexico City urban aerosol

At SIMAT S, Na, K, Si and Ca were the most abundant elements measured by XRF (Table 2). The concentrations for submicron markers, including dust, were lower than reported for PM_{2.5} Mexico City aerosols (Chow et al., 2002; Miranda et al., 1996, 2004; Querol et al., 2008) but similar to particles between 0.34 and 1.15 μm during MCMA-2003 (Johnson et al., 2006), indicating that crustal elements are mainly associated with particles larger than 1 μm . As and Na were more than 4 times lower during MCMA 2003 than here.

Figure 5a shows that on 14 and 18 March during peaks in S concentration, the V and Ni time series also show two maxima suggesting that V, Ni, and S are co-emitted by a common fuel-burning source. The industrial area of Mexico City is located north of

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the SIMAT site and the highest V and Ni concentrations were observed when the wind direction was from the North. The average $[V]/[Ni]$ ratio was 5.1 ($r^2=0.86$), in accordance with emission ratios reported for fuel oil burning (Kowalczyk et al., 1982; Maenhaut and Cafmeyer, 1987). A similar episode characterized by the same $[V]/[Ni]$ ratio and transport from the North was observed during MCMA-2003, indicating a strong anthropogenic, rather than volcanic, source of sulfate (Johnson et al., 2006). We did not observe a correlation between V and the organic functional group concentrations observed in Mexico City at SIMAT (Liu et al., 2009). The temporal trend of OM and V concentrations at SIMAT, reported in Fig. 5a, indicates that fuel oil burning (associated with industrial activity) was not one of the major sources of organic mass in the urban area.

A strong correlation was observed among time series of Si, Ca and Al, commonly attributed to soil sources (Miranda et al., 2004, 1994). Si, Ca and K concentrations showed a positive correlation with Al concentrations (Fig. 6). The linear correlation coefficient r^2 was 0.95 for Si/Al and 0.80 for Ca/Al, while a poor linear correlation was observed between K and Al ($r^2=0.05$). Figure 6 also shows the range of variability for the ratios between each metal and Al observed for fugitive dust emitters in Mexico City (Vega et al., 2001). Si/Al and Ca/Al ratios measured during this study (2.3 and 1.9, respectively) were close to the ratios reported by Vega et al. (2001) for paved and unpaved roads, soil, and asphalt. K concentration was higher than the value expected for soils, indicating that road and soil dust were not the exclusive sources of this element.

A good correlation was observed for K and aliphatic saturated C-C-H (Fig. 5b), at a confidence level larger than 99.95%. Similarly a good correlation between potassium and the sum of organic and elemental carbon was observed at the urban sites (CENICA and T0) and the suburban site T1 (Querol et al., 2008), although these authors also reported a higher correlation between K and Al. The correlation between K and aliphatic C-C-H group observed at SIMAT indicates biomass burning as a possible common source for both components (Andreae and Merlet, 2001; Duan et al., 2004). Higher K concentrations were observed during the first part of the sampling campaign,

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when numerous fires were observed throughout Mexico with a large number located near the urban area (Fast et al., 2007). Figure 7 shows several fires near the SIMAT site identified by MODIS (Moderate Resolution Imaging Spectroradiometer) during the days with the highest K concentrations. In addition to forest fires (Yokelson et al., 2007), potential sources of biomass burning aerosol observed in the urban area were cooking, incineration, and refuse burning (Moffet et al., 2008).

Biomass burning aerosols are characterized by elevated OC and K content. In order to investigate the contribution of biomass burning to the organic aerosol we first estimated K from non-soil sources using:

$$[K]_{\text{non-soil}} = [K] - [Al]R_{\text{soil}}$$

where $[K]_{\text{non-soil}}$ is the non-soil K concentration, $[K]$ and $[Al]$ are K and Al concentrations, and R_{soil} is the K to Al ratio in Mexico City dust emitters (Vega et al., 2001). The minimum and maximum non-soil K concentrations were calculated using the maximum and minimum R_{soil} reported by Vega et al. (2001) (0.62 for the dry lake and 0.06 for agricultural soil). Figure 7f shows that OC co-varied with the concentration of non-soil K, with a confidence level larger than 99.9%. The average $[K]/OC$ ratio was 0.03, in agreement with the average ratio observed for $PM_{2.5}$ in T0 (0.02) by Querol et al. (2008) and with emission factors reported by Andreae and Merlet (2001) and by Watson and Chow (2001) for agricultural residue burning (0.04). The ratios here were comparable to the $[K]/OC$ ratios observed for biomass burning episodes of 0.04 for $PM_{2.5}$ in Seoul (Kang et al., 2006), 0.01–0.02 for PM_{10} in the French Alps (Aymoz et al., 2007), but lower than 0.19–0.20 for total suspended particles (TSP) in Beijing (Duan et al., 2004).

The intercepts of the linear fits reported in Fig. 7f are statistically larger than zero (2.8 ± 0.5 and $3.3 \pm 0.4 \mu\text{g m}^{-3}$ of OC), consistent with the presence of sources of OC not related to K). We estimated the contribution of biomass burning to OC as the difference between the OC concentration and the average non-biomass burning OC. On average this contribution ranged between 33% and 39% for the lowest and highest estimates of soil K, respectively. The OC associated with K calculated here includes soil and

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biomass burning emissions, in addition to urban sources that are somewhat different from more developed urban areas, namely open air grilling and cooking (Moffet et al., 2008). For this reason, the high contribution of K to the organic carbon is expected to be higher than the results of Stone et al. (2008), who reported a contribution of biomass burning ranging between 5–26% at T0 and 7–39% at T1, in particles smaller than 2.5 μm . Similarly single particle analysis of the upper end of the accumulation mode at T0 assigned 40% of particle number to biomass burning (Moffet et al., 2008) and AMS measurements apportioned 15–23% of the OM in submicron aerosol to biomass burning fires (which may not include non-traditional biomass sources) (Aiken et al., 2009).

3.3 OM/OC ratios

The organic mass to organic carbon ratio (OM/OC) is a measure of the molecular composition of the organic fraction of aerosols. Aerosols characterized by high concentrations of oxygen, nitrogen and sulfur compounds exhibit high OM/OC values; organic particles dominated by aliphatic and aromatic hydrocarbons show low OM/OC ratios (Maria et al., 2003; Russell, 2003; Turpin and Lim, 2001). Experimental measurements of OM/OC ratios are still scarce. Kiss et al. (2002) calculated an OM/OC ratio of 1.9–2 for water-soluble organic matter at a rural site in Hungary. The average OM/OC ratio for dichloromethane and acetone extracts reported for IMPROVE site aerosols was 1.92 (El-Zanan et al., 2005). FTIR measures the OM/OC ratio for polar and non-polar organic fractions without the need for solvent extraction. During the ICARTT campaign we measured OM/OC of 1.4 for recently emitted particles from coal burning power plants in Ohio, and 1.6 for or East coast outflow measured in the Gulf of Maine (Gilardoni et al., 2007).

OM/OC ratio from AMS measurements (Aiken et al., 2007) during MIRAGE ranged between 1.6–1.8 in the urban area and 1.8–2.1 on the C130 (Aiken et al., 2008). Figure 8a reports OM/OC ratios for the three MILAGRO sampling platforms; similar average OM/OC ratios were observed at SIMAT and at Alzomoni, 1.8 and 2.0, respectively.

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The lower variability observed at SIMAT compare to the other sites (5 and 95 percentile equal to 1.7 and 2.1) reflects a more uniform composition of organic aerosol during the campaign. The geographical features of the Mexico City Basin, i.e. high altitude and subtropical latitude with the consequent high solar radiation, promote the formation of photochemical pollutants leading to a highly oxidized aerosol and thus high OM/OC ratio.

Figure 8b shows the OM/OC ratio at Altzomoni, as a function of mixing-layer height (MLH) and wind direction. Mixing-layer height was determined from ceilometer data according to Emeis et al. (2007) at Tenango del Aire (19°10 N, 98°51 W), a rural background site located five kilometers to the west of Altzomoni at 2377 m a.s.l. (see Fig. 1b). Altzomoni was a high altitude site and the daily modulation of the MLH allowed air masses affected by local sources from the surrounding valleys to reach the sampling location; on the contrary, when the MLH was lower than the site altitude, free troposphere masses were sampled. The samples characterized by the highest OM/OC in Fig. 9b are located at the top corner of the panel, indicating the sampling site was inside the boundary layer. During the corresponding sampling periods, prevailing wind direction was from the North and the Northwest (i.e. Mexico City direction) as indicated by the blue/purple color of the markers. The highest OM/OC values at Altzomoni were observed on 10, 18, 20, 21, and 22 March, during the winds from the Northwest. In general, the high OM/OC indicates Altzomoni was reached by oxidized aerosol masses; the air masses reaching the site from Mexico City basin were even more oxidized than the air masses sampled when the site was outside the mixing-layer.

The average OM/OC ratio on the C130 was 1.6–1.8. Figure 8c displays the flight track segments of C130 color-coded as a function of the corresponding OM/OC ratio. An OM/OC ratio close to 2 indicates a large contribution of ketones, aldehydes, carboxylic acids and alcohols (Russell, 2003), which is consistent with the occasionally high concentration of carboxylic acid COOH group observed on the C130. Samples collected when the C130 was north or northeast of the Mexico City basin exhibited the highest OM/OC, close to the values observed at SIMAT (the urban site). The chemi-

cal properties of aerosols sampled by the aircraft confirmed North-Northeast was the most common direction of the basin outflow during the March 2006 campaign, as also indicated by basin wind transport analysis (de Foy et al., 2008; Doran et al., 2007) and gas phase analysis of aging tracers (Kleinman et al., 2008).

5 3.4 Carbonyl C=O group and aliphatic saturated C-C-H group

The molar ratio of C=O from carboxylic acid and non-acid carbonyl and groups to aliphatic C-H group is an index of concentration of secondary organic aerosol or oxygenated primary organic aerosol compared to concentration of aliphatic hydrocarbon fraction. Since physical properties of compounds with more oxidized and fewer hydrocarbon groups are expected to be associated with more water soluble compounds, C=O plus COOH to aliphatic C-H molar ratio might help to predict the CCN activity of aerosol particles.

During MIRAGE the concentration of unsaturated aliphatic C=C-H group was negligible compared to the concentration of saturated aliphatic C-C-H group, making the saturated C-C-H group representative of the aliphatic C-H fraction. Figure 9 reports the molar concentration of non-acid carbonyl plus carboxylic acid (herein indicated as C=O) versus the molar concentration of aliphatic saturated group at SIMAT and Altzomoni. The C=O to aliphatic saturated molar ratio was 0.10 at SIMAT (correlation coefficient equal to 0.83) and 0.11 at Altzomoni (correlation coefficient equal to 0.90). The slightly larger contribution of oxidized aerosol at Altzomoni might result in part from aerosol processing or rural air masses (DeCarlo et al., 2008; Maria et al., 2002; Turpin and Lim, 2001).

The C=O to C-C-H group ratio was measured with the same technique during ICARTT in summer 2004, without distinction between ketones and carboxylic acids. The C=O to C-C-H ratio measured during ICARTT was about 0.5 at the remote platforms located downwind of US continental emissions (Appledore Island in Maine, Chebogue Point in Nova Scotia, and the Ronald H. Brown cruise in New England) and 0.1 on board the CIRPAS Twin Otter in Ohio close to power plant fresh emissions. The

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Mexico City area was strongly affected by combustion processes (Salcedo et al., 2006; SMADF, 2002, 2003), as reflected in the measured high carbon monoxide concentrations (on average carbon monoxide concentration at SIMAT was 1000 ppb). Submicron particles collected at SIMAT and in Ohio, which were dominated by combustion emissions, showed similar carbonyl C=O to saturated aliphatic C-C-H ratios.

4 Conclusions

During the MILAGRO campaign, organic functional groups in the aerosol phase were investigated at an urban site, a high altitude site, and on the NCAR C130. Aliphatic saturated, aliphatic unsaturated, aromatic, alcohol (including sugars, anhydrosugars, polyols), non-acidic carbonyl, carboxylic acid, and amine groups were identified. Organic sulfur compounds were always below detection limit.

Organic aerosols at SIMAT and at Altzomoni showed that aliphatic saturated C-C-H group and carboxylic acid COOH group dominated the organic mass (OM). Similar average compositions of the OM were observed at the two sites, indicating a likely influence of the city air masses on the high altitude site. On average SIMAT showed 1.5 to 2 times higher OM compared to Altzomoni.

Compared to the ground platforms, samples collected on the NCAR C130 were characterized by higher concentration of alcohol C-OH and lower contribution of carboxylic acid COOH groups. Samples collected on the aircraft exhibit different composition as a function of location relative to the city basin: amine group was detected only outside the urban basin and the carboxylic acid group was more abundant north of the city, along the most frequent direction of Mexico City outflow.

XRF elemental analysis of samples collected at SIMAT identified some of the sources of the organic aerosol. Using non-soil K as a tracer, we estimated the upper bound of the average contribution of biomass burning to the submicron organic carbon on the order of 30 to 40%, at the upper end of results obtained by source apportionment studies and single particle measurements at T0 (Aiken et al., 2009; Moffet et al., 2008;

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Stone et al., 2008).

The average OM/OC ratio and carbonyl C=O to aliphatic C-H ratio were higher at Altzomoni compared to the urban site, as a consequence of the larger contribution of oxidized functional groups. The small variability of the OM/OC ratio in Mexico City (SIMAT) indicates a uniform composition of the organic fraction throughout the entire sampling campaign. At Altzomoni the highest OM/OC values were observed for samples collected under the likely influence of Mexico City outflow, as indicated by boundary layer height and wind direction. Although the number of samples collected when the site was outside the Mexico City mixing layer was limited, the FTIR results showed that Mexico City outflow had a higher oxidized character than the aerosol sampled outside the mixing-layer.

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Table 1. FTIR absorption signals used to identify and quantify organic functional group.

Functional Group	Frequency cm^{-1}	Quantified Peak, cm^{-1}	Absorptivity abs^{-1} ^a	Detection Limit μmol of bond	MW g mol^{-1} ^b
Aliphatic saturated C-C-H	1450, 2800–3000	1850–2920	0.6	0.079	7
Aliphatic unsaturated C=C-H	2900–3100	2980	3.8	0.4	13
Aromatic C=C-H	3000–3100	3050	8.7	1.2	13
Non-acid carbonyl C=O	1640–1850	1720	0.067	0.010	28
Carboxylic acid COOH	1640–1850	1720	10.02	0.013	45
Alcohol C-OH	3100–3500	3350	0.057	0.011	23
Organosulfate C-O-S	876				
Amine NH_2	3400, 1625	1625	0.112	0.018	11

^a Absorptivity is the micromole of functional group per unit of peak area (in absorbance). The calibration of absorptivity is instrument-specific.

^b Functional group molecular weight.

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Table 2. Mean, minimum, and maximum elemental concentrations (ng m^{-3}) at SIMAT site.

Element	Mean	Minimum	Maximum
S	950	240	3400
K	170	52	460
Si	130	16	1000
Ca	110	1	850
Na	90	10	0.49
Fe	92	2	528
Al	51	10	550
Cl	41	7.4	200
Zn	36	3.9	190
As	12	1.5	45
Sn	6.6	2.0	24
Cu	9.6	1.2	62
V	7.8	0.7	11
Br	6.3	1.3	20
Mn	4.3	0.88	25
Ti	4.5	1.1	34
P	4.8	3.4	6.2
Ni	1.6	0.49	20

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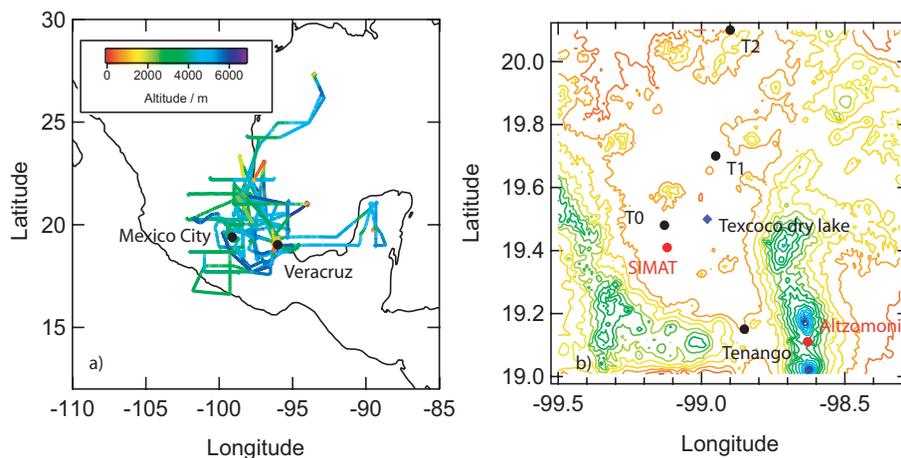


Fig. 1. NSF/NCAR C130 flight tracks colored as a function of flight altitude **(a)** and ground platform locations **(b)**. Panel (b) reports the location of SIMAT and Alzamoni (red circles), other major sampling sites of MILAGRO (black circles), and lake Texcoco (blue diamond).

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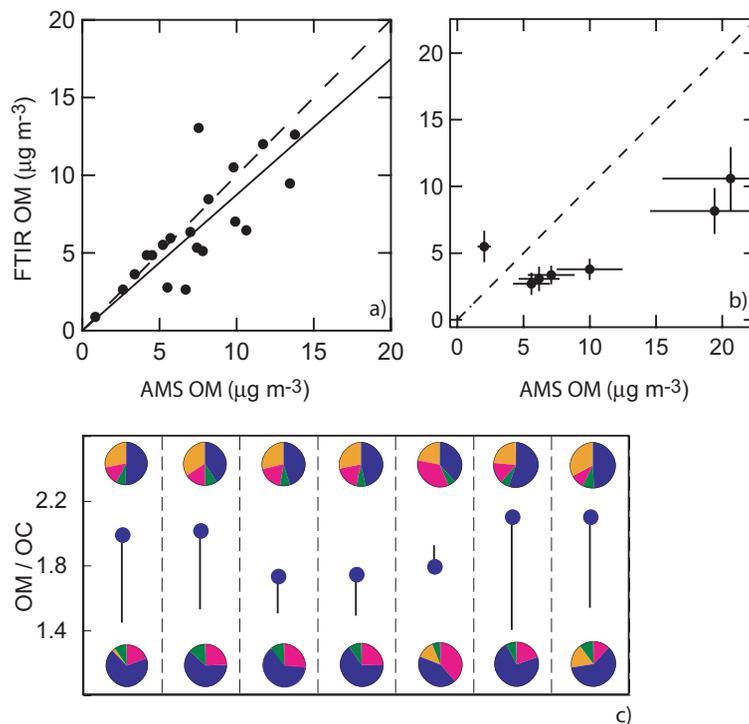


Fig. 2. Comparison of FTIR OM and AMS average OM **(a)** at Altzomoni and **(b)** on the C130; the solid line correspond to linear fit of experimental data while the dash line shows the 1:1 ratio. Panel **(c)**: comparison of FTIR OM/OC range (black lines) and AMS OM/OC (blue circles) on the C130. Pie charts indicate the organic functional group composition of the OM/OC lower and upper bounds: aliphatic saturated C-C-H in blue, amine NH_2 in yellow, carboxylic acid COOH in green, and alcohol C-OH in pink.

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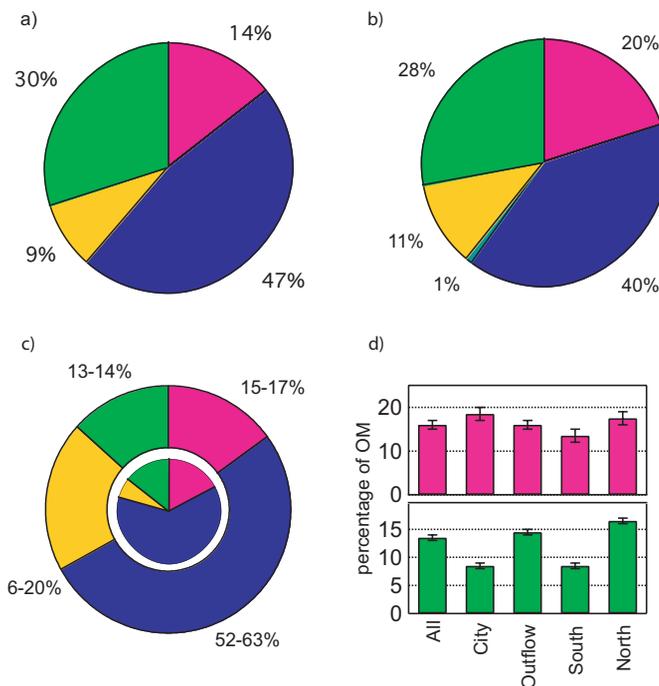



Fig. 3. Project average composition of organic mass for **(a)** Mexico City, **(b)** Altzomoni, and **(c)** C130 (the inner chart corresponds to the actual concentration and the outer chart corresponds to the assumption that concentrations below detection limit are equal to detection limit). The charts show aliphatic saturated C-C-H in blue, non-acid carbonyl C=O in cyan (below 1% in panel a and c), amine NH₂ in yellow, carboxylic acid COOH in green, and alcohol C-OH in pink. Panel **(d)** alcohol (pink) and carboxylic acid (green) contribution to OM on the C130 as a function of sampling location: over the urban area (City), outside the urban area (Outflow), North of the city (North), and South of the city (South).

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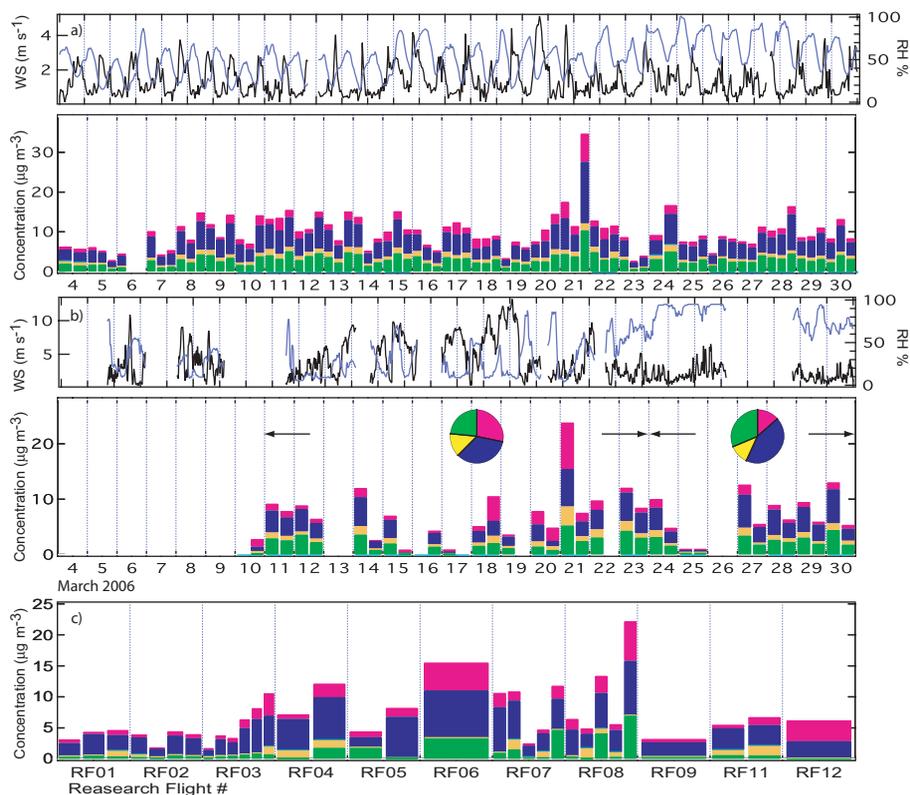


Fig. 4. Time series of the measured functional group composition with temperature (in black) and relative humidity (in blue) at **(a)** Mexico City and **(b)** Altzomoni; panel **(c)** reports functional group composition of C130 samples characterized by collection period longer than 10 min and shorter than 2 h. The charts show aliphatic saturated C-C-H in blue, amine NH_2 in yellow, carboxylic acid COOH in green, and alcohol C-OH in pink.

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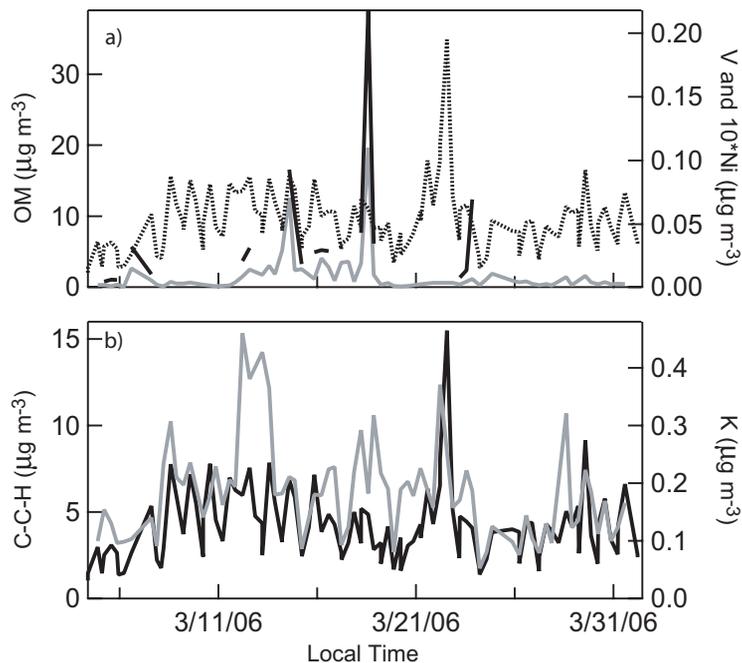


Fig. 5. Panel (a): time series for vanadium (grey), nickel (black), and organic mass OM (dotted black line) concentrations. Panel (b): time series for OM (black) and potassium (grey) concentrations.

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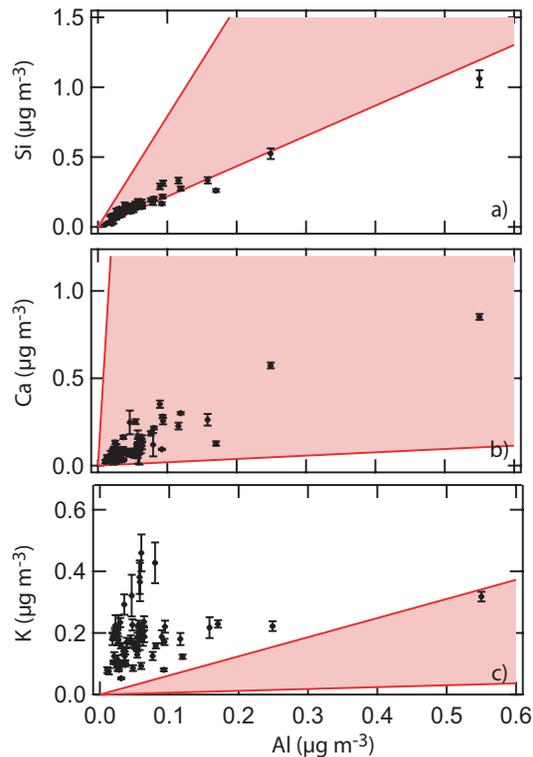


Fig. 6. Concentration of (a) silicon, (b) calcium, and (c) potassium relative to aluminum, in Mexico City; shaded areas correspond to the expected ratio according to Vega et al. (2001).

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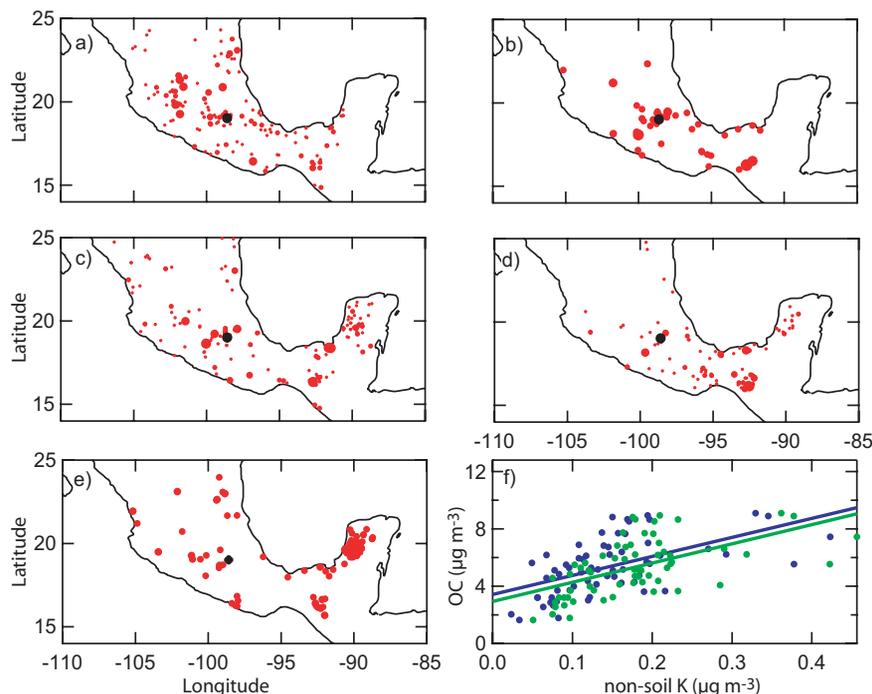


Fig. 7. Panel (a–e): SIMAT site (black) and fire locations (red) according to Terra and Aqua satellite images on days with high potassium concentration: **(a)** 8 March, **(b)** 12–13 March, **(c)** 17–18 March, **(d)** 22 March, and **(e)** 28 March; dot size is proportional to the fire size. Panel **(f)** reports OC concentration as a function of non-soil potassium concentration (lower bound in blue and upper bound in green).

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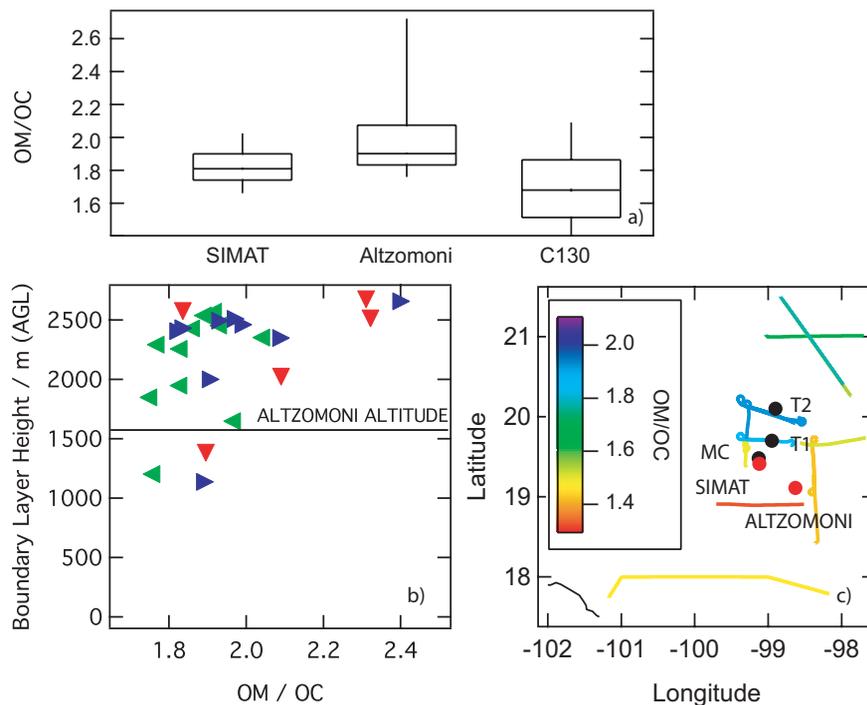


Fig. 8. OM/OC ratios at SIMAT, at Altzomoni, and on the C130 (a). Panel (b) shows OM/OC ratios at Altzomoni as a function of boundary layer height and wind direction (red from the north, blue from the west, and green from the east); panel (c) reports OM/OC on the C130 as a function of location relative to Mexico City.

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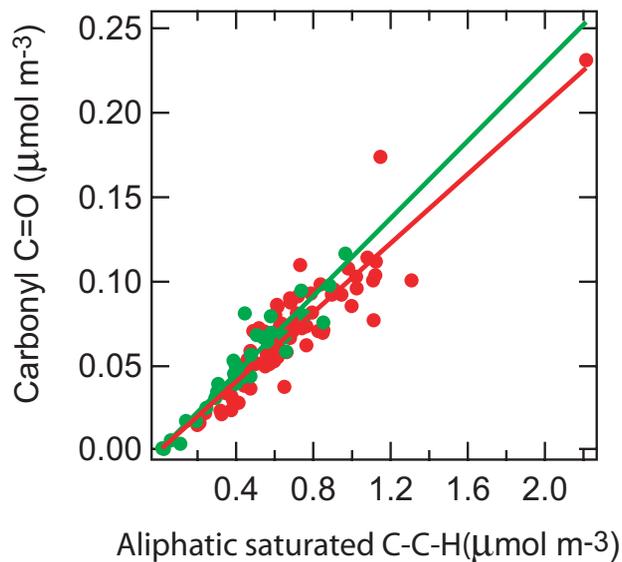


Fig. 9. Molar ratios of carbonyl C=O group (non-acid carbonyl plus carboxylic acid) to saturated aliphatic C-C-H group molar concentration in Mexico City (red) and at Altzomoni (green).

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