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## Black carbon over Mexico

R. Subramanian et al.

# Black carbon over Mexico: the effect of atmospheric transport on mixing state, mass absorption cross-section, and BC/CO ratios

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## Abstract

A single particle soot photometer (SP2) was operated on the NCAR C-130 during the MIRAGE campaign (part of MILAGRO), sampling black carbon (BC) over Mexico. The highest BC concentrations were measured over Mexico City (sometimes as much as  $2 \mu\text{g}/\text{m}^3$ ) and over hill-fires to the south of the city. As expected, older, diluted air masses had lower BC concentrations. A comparison of carbon monoxide (CO) and BC suggests a CO background of around 65 ppbv, and a background-corrected  $\text{BC}/\text{CO}_{\text{net}}$  ratio of  $3.1 (\text{ng}/\text{m}^3 \text{ STP})/\text{ppbv}$  ( $\pm 25\%$ ). This ratio is similar for fresh emissions over Mexico City, as well as for aged air masses. Comparison of light absorption measured with a particle soot absorption photometer (PSAP) and the SP2 BC suggests a BC mass-normalized absorption cross-section (MAC) of  $10.3 \text{ m}^2 \text{ g}^{-1}$  ( $\pm 30\%$ ) at 660 nm (or  $12.4 \text{ m}^2 \text{ g}^{-1}$  @ 550 nm, assuming MAC is inversely dependent on wavelength). This appears independent of aging and similar to the expected absorption cross-section for aged BC, but values, particularly in fresh emissions, could be biased high due to instrument artifacts. SP2-derived BC coating indicators show a prominent thinly-coated BC mode over the Mexico City Metropolitan Area (MCMA), while older air masses show both thinly-coated and thickly-coated BC. BC mass per particle of the thinly-coated mode appears to increase as the air mass ages, possibly due to coagulation and/or increased coating of the particles containing smaller BC masses. Differences in the coating indicator patterns for similarly-aged air masses may be due to differences in atmospheric processing on each day, including mixing with non-MCMA air masses.

## 1 Introduction

Strongly-light absorbing carbon (LAC) particles play a major role in climate change (Jacobson, 2002; Bond, 2007; Levy et al., 2008) by absorbing solar radiation and re-radiating the energy as heat, warming the local atmosphere. LAC is emitted by combustion processes, particularly in diesel engine exhaust and biomass smoke. Hence,

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LAC is used as a marker of these anthropogenic processes for air quality monitoring (Subramanian et al., 2006a). The mixing state of LAC is also important from a climate change perspective, as LAC coated with non-absorbing matter such as ammonium sulfate or organic compounds can absorb up to 50% more light than uncoated LAC (Bond et al., 2006).

Conventional filter-based techniques to measure LAC have been the subject of numerous intercomparisons (Schmid et al., 2001; Schauer et al., 2003), showing that these methods suffer from an operational definition. The term used to describe the substance is tied to the measurement technique (Bond and Bergstrom, 2006); with thermal/optical techniques, the measured quantity is called elemental carbon (EC); light-absorption measurements produce BC. Hence, to avoid a method-based nomenclature, Bond and Bergstrom proposed the term LAC. Subramanian et al. (2006b) examined the biases that can cause up to a factor-of-two difference between thermal-optical analysis protocols (Chow et al., 2001), and suggest that biases are unavoidable in any thermal protocol used to measure EC. Filter-based techniques for BC or particle light absorption that depend on optical observations of the filter deposit can experience problems with particulate emissions from smoldering biomass burning or other sources of liquid organic matter (Subramanian et al., 2007).

The single particle soot photometer (SP2, Droplet Measurement Technologies, Boulder, Colorado, USA) is a laser-induced incandescence instrument that detects particles which absorb light (at the laser wavelength of 1064 nm), are refractory, and incandesce (Stephens et al., 2003). Certain metals can also meet these criteria, but such non-LAC particles can be filtered by monitoring their incandescence temperature (Schwarz et al., 2006), which is different from that of LAC. Since the incandescent signal is proportional to the incandescing mass, the SP2 is a true-mass detector without the problem of operationally-defined measurements experienced with conventional filter-based absorption (BC) or thermal (EC) techniques. Further, given the properties of this measured quantity – refractory, strongly-light absorbing (absorbs light even in the infra-red, unlike organic carbon, Sun et al., 2007), but independent of assumptions about the

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absorption per unit mass and wavelength dependence of the absorption – the SP2 measurements are closer to LAC than the previously-discussed thermal or optical techniques. However, we continue to refer to the SP2 data as BC in this paper, in keeping with the convention established by earlier SP2 studies (Schwarz et al., 2006; Moteki et al., 2007).

Other issues with conventional filter-based approaches to measuring BC include an inability to determine the mixing state of BC, and relatively high detection limits that increase sampling times. The latter is particularly important for aircraft measurements that require fast time resolution. Since the SP2 measures individual particles, it has a much lower detection limit than conventional filter-based measurements, allowing for highly time-resolved data collection. An added advantage is the ability to evaluate the mixing state of BC using a light scattering detector also included in the SP2 (Moteki and Kondo, 2007).

During the recent Megacity Impacts on Regional and Global Environment (MIRAGE) study, part of the larger Megacity Initiative: Local and Global Research Observations (MILAGRO) campaign (Molina et al., 2009), the SP2 was deployed on the NSF/NCAR C-130 aircraft. Black carbon measurements were made on ten C-130 flights over the Mexico City basin and other regions of Mexico including the Yucatan peninsula, and offshore locations. Events sampled included fresh city emissions, biomass fires, as well as 1- and 2-day-old air masses transported from Mexico City. The flights usually included passes over three ground sites called T0, T1 and T2. A comprehensive description and the rationale for selecting these ground sites is summarized by Fast et al. (2007). Briefly, prior to the study, the MILAGRO modeling working group determined that during March, Mexico City pollutants are transported northeastward 20–30% of the time, with no preferred direction for the remaining period. Fresh pollutants emitted in the Mexico City metropolitan area were sampled over and at the T0 ground site (19.489° N/99.148° W), located at the northern edge of the city. T1 (19.703° N/98.982° W) is 29 km northeast of T0, and experiences a mixture of fresh and aged pollutants. When winds are from the southwest, the MCMA air mass is

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transported over T2 (20.011° N/98.906° W), which is 63 km northeast of T0, after aging for a few hours depending on the wind speed. Thus, we can look at aerosol aging within a few hours of emission by sources in and around Mexico City.

This paper focuses on measurements in significant pollution layers encountered during the flights on 18, 19, 22 and 23 March (research flight numbers 6, 7, 8 and 9, respectively; see <http://catalog.eol.ucar.edu/milagro/missions/missions.html>). Fresh emissions and a 1-day-old air mass sampled on 18 March were measured again on 19 March as 1-day-old and 2-day-old air masses, respectively, as shown in Fig. 1. Similarly, fresh outflow and 1-day-old emissions sampled on 22 March were measured a day later on 23 March. The age of the air mass and its source (typically the Mexico City area) is based on the modeling predictions used to determine the flight path during the field campaign (Fast et al., 2007). These air masses will be used to study the effects of aging during atmospheric transport on the physical characteristics of BC. The BC to carbon monoxide ratio (BC/CO) and BC light absorption cross-section, determined using absorption data from a particle soot absorption photometer (PSAP), are also examined for effects of atmospheric aging on these quantities.

## 2 Methodology and instrument characterization

### 2.1 Instrument description

The DMT single particle soot photometer (SP2) uses a patented technique based on excitation by a 1064 nm Nd:YAG intracavity laser to detect particles by scattering and/or incandescence. Scattering (1064 nm) and broadband (350 nm to 800 nm) and narrow-band incandescence (630 to 800 nm) signals are recorded at 5 MHz, with the data from each particle spanning 36  $\mu$ s in 180 intervals of 0.2  $\mu$ s each. Stephens et al. (2003) showed that a variety of materials, including pure metals, absorb light and incandesce. However, the dominant absorbing component of atmospheric particulate matter is BC (Rosen et al., 1978). Furthermore, the ratio of the incandescence signals from the

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broadband and narrowband detectors, proportional to the vaporization temperature, can be used to identify the type of the incandescing particle, as metals and BC have different incandescence temperatures (Schwarz et al., 2006). More details, a schematic and further characterization of the SP2 are provided by Schwarz et al. (2006), Moteki and Kondo (2007), and Baumgardner et al. (2007). An intercomparison of the SP2 with other methods of BC measurement is reported by Slowik et al. (2007).

For the MIRAGE campaign, the sample flow recorded during ascents and descents was not the actual flow, an issue with the flow measurement system used in the 2006 version of the SP2. While a discussion of vertical profiles is not included in this manuscript, BC concentrations for a descent through the 2-day-old air mass sampled on 19 March and into a biomass burning plume on 23 March (described later) are presented in Table 1, but are an overestimate and reported for reference purposes only. *Relative* abundances of thinly-coated and thickly-coated BC in the 19 March 2-day-old air mass (shown in Fig. 8) are unaffected as the flow error cancels out when comparing two modes from the same air mass. All other data are for level flight segments.

Uncertainties in BC mass concentrations are about  $\pm 20\%$  (Baumgardner et al., 2007), but this does not include the scaling factor uncertainty described in a later section. Including the scaling factor uncertainty of  $\pm 10\%$  increases the overall uncertainty on BC mass during level legs to  $\pm 22\%$ .

## 2.2 Specificity of the SP2 for BC

For a black body, the incandescence temperature is linearly proportional to the ratio of the broadband and narrowband incandescence signals (Moteki and Kondo, 2007). The exact relationship between these two quantities depends on the optical set-up as well as the electronic gains in the detectors. For this study, we used empirically-derived limits for the BC incandescent temperature ratio, based on the glassy carbon material used to calibrate the SP2. However, the incandescent temperature ratio could not be determined for small BC masses, where the narrowband signal was noisy. In these cases, the shape of the broadband signal was used as a filter, based on visual

inspection of over 400 particles.

The incandescent temperature ratio (IR) filter, without the shape-based filter, excludes 22% of the incandescent mass detected during the 18 March flight. The peak shape-based criteria adds back 18% of the BC mass; these particles were excluded by the IR filter as the ratio either could not be determined or was calculated as higher than the allowed upper limit. Hence, we caution that the BC data reported here may be biased high by as much as 18%, depending on the accuracy of the shape-based filter.

### 2.3 Scaling factors

The incandescence signal is proportional to the BC mass, with the incandescence peak height calibrated to BC mass. In the following discussions, the BC mass is converted to a mass-equivalent diameter (MED), assuming the density of BC as  $1.9 \text{ g/cm}^3$  based on the recommendations of Bond and Bergstrom (2006). In case of detector saturation (which for MIRAGE occurred at  $\sim 36 \text{ fg BC}$  or  $330 \text{ nm BC MED}$ ), the particle mass is not calculated, though the particle is counted as part of the BC number concentration. Though the SP2 can detect a BC mass of  $1 \text{ fg}$  or lower, calibrations for the MIRAGE experiment were made only down to about  $3 \text{ fg BC}$ , or about  $145 \text{ nm MED}$ . The mass limitation at the upper end and the mass and count limitations at the lower end mean that the SP2 does not measure the full range of atmospheric BC. Schwarz et al. (2006) estimate that their SP2 detected about 60% of the BC mass and 5% of the BC number for the BC mass range from  $3\text{--}300 \text{ fg/particle}$ .

Following the approach of Schwarz et al. (2006), we fit a log-normal curve to the BC mass size distribution between BC mass-equivalent diameters of  $145\text{--}325 \text{ nm}$  ( $3.0$  to  $34 \text{ fg BC}$ ), extrapolated over the  $10\text{--}1000 \text{ nm BC MED}$  range, and obtain a BC mass scaling factor that is then used to determine the number scaling factor as well (Fig. 2). Changing the diameter range over which the log-normal curve is fitted, from  $130 \text{ nm}$  to  $170 \text{ nm}$  at the lower end and from  $300$  to  $325 \text{ nm}$  at the upper end changes the mass scaling factor by less than  $\pm 10\%$ . Fitting portions of the flight, such as the fresh outflow over T2 and the 1-day-old air mass sampled on 18 March does not produce

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scaling factors outside of the  $\pm 10\%$  uncertainty for these individual legs. For the entire 18 March flight, the SP2 appears to detect 75% of BC mass and 44% of the BC-containing particle number.

Johnson et al. (2005) observed soot aggregates larger than 1000 nm in Mexico City in fresh emissions; however, this refers to overall size and not to the BC mass (or BC MED) in these aggregates. The particles they observed, at sites a little farther away from the main downtown area and that could have undergone some atmospheric processing, were mostly submicron in size. Hence, our log-normal fit-based scaling factor should account for any BC particles that saturate the SP2 incandescence detector.

## 2.4 Optical particle diameter

The scattering signal is collected over two cones of scattered light, from  $30^\circ$ – $60^\circ$  and from  $120^\circ$ – $150^\circ$ . The scattering signal in combination with Mie theory and an assumed particle composition can be used to estimate the overall particle diameter. The optical diameter calculations here assume a homogeneously-mixed BC volume fraction of 25%, 50%, 75% or 100%, whichever is closest to the estimated particle composition; a core-shell model does not appear to make an appreciable difference in this calculation. The truncated collection cone and lower gain employed on the scattering detector used in the SP2 means non-incandescent particles smaller than 200 nm diameter (assuming a 1:1 organosulfate mixture) are not detected efficiently (if at all) in the scattering channel. Another issue with the scattering signal is that as an incandescent particle absorbs light, its temperature increases, volatilizing any non-refractory coating. Hence, the peak scattering signal measured by the photodetector may not be representative of the original size of incandescent particles. Gao et al. (2007) employed an additional, two-element avalanche photodetector to construct a Gaussian peak based on the leading edge of the actual scattering signal to avoid this problem (called Leading Edge Optimization, LEO); however, this technique was developed after the MIRAGE campaign and cannot be used in the present analysis. Due to particle volatilization effects on the scattering signal, the scattering-based optical diameters used here are

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biased low.

## 2.5 Mixing state of BC

We can determine the mixing state of BC by using the separation between the scattering and incandescent peaks, which we call the incandescent lag, similar to the method employed by Moteki and coworkers (Moteki and Kondo, 2007; Moteki et al., 2007). Figure 3 shows that for thinly-coated or pure BC particles, the scattering and incandescent peaks occur at almost the same time (incandescent lag  $\sim 0$ ). Wider separations (3–4  $\mu\text{s}$ ) indicate a thicker non-BC coating.

As the LEO correction could not be applied to the scattering signal in this data set, we use the scattering-based optical particle diameter only to show the relevance of the incandescent signal-based coating thickness classification. Figure 3 also shows a comparison of scattering-based coating thickness estimates (determined as described in the previous section) with the incandescent lag. Since the two parameters are reasonably correlated, we use the incandescent lag-based classification of BC particles as a mixing state indicator by stratifying the data as either “thinly-coated” or “thickly-coated” BC. In keeping with the definition by Moteki et al., we use 2  $\mu\text{s}$  as the limiting gap distinguishing a thinly-coated particle from a thickly-coated particle.

## 2.6 Complementary measurements

The aircraft carried an extensive suite of gas and particle instruments during the project; among them were sensors to measure CO and particle light absorption. The NCAR/NSF C-130 CO vacuum UV resonance fluorescence instrument is similar to that of Gerbig et al. (1999). The MIRAGE CO data have a 3 ppbv precision, 1 s resolution, and a typical accuracy better than  $\pm 10\%$  for a 100 ppbv ambient mixing ratio. The aerosol light absorption coefficient was measured using a 3-wavelength Radiance Research PSAP operated by the University of Hawaii, and is expected to be accurate to within  $\pm 20\%$  (excluding any bias due to liquid organic matter, dis-

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cussed later). Both datasets are available as part of the MILAGRO data archives (<http://www-air.larc.nasa.gov/cgi-bin/arcstat-b>).

### 3 Results

#### 3.1 BC concentrations

5 The MIRAGE field campaign was conducted between 3–31 March 2006, and used the NSF/NCAR Hercules C-130 based at Veracruz International Airport. The analysis for the study presented here is from four of the 10 flights that were flown. The time histories of BC mass concentrations measured during these flights are presented in Fig. 4 (normalized to STP, 1 bar and 273.15 K); spatial distributions (BC concentrations along the flight paths) were shown in Fig. 1.

10 On 18 March, the aircraft did an east-west transect at 22.2° N, sampling 1-day-old emissions from Mexico City at multiple altitudes between 3.5–5.4 km above sea level (ASL). BC mass concentrations were higher at the western ends of these transects, averaging  $\sim 200 \text{ ng/m}^3$ , while BC mass at the eastern ends averaged  $\sim 60 \text{ ng/m}^3$  or less. The aircraft rendezvoused with the Department of Energy (DOE) Gulfstream-1 (G1) aircraft for a parallel east-west intercomparison flight near the T2 sampling site. During this period BC concentrations were high, occasionally over  $1000 \text{ ng/m}^3$ . Following the intercomparison, the aircraft flew over Mexico City. South of the city, the air was relatively clean with BC often below  $50 \text{ ng/m}^3$ . Emissions from a small mountain fire were sampled southeast of Mexico City, with BC as high as  $1041 \text{ ng/m}^3$ . The plane then flew back over T0, where BC averaged  $375 \pm 77 \text{ ng/m}^3$ , before flying back to Veracruz. These and similar events encountered during the four flights are summarized in Table 1.

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### 3.2 Carbon monoxide and BC

Carbon monoxide (CO) and BC are both products of incomplete combustion, and thus indicators of combustion emissions. The BC/CO ratio has been suggested as dependent on the source mix, for example, the fraction of heavy-duty diesels in the fleet (Kirchstetter et al., 1999), though other factors like fleet age and condition may also affect the ratio (Baumgardner et al., 2002). BC/CO ratios have also been used to estimate BC emissions based on CO emission inventories (Dickerson et al., 2002). This assumes that both BC and CO are conserved, so that the BC/CO ratio is constant despite atmospheric dilution, and changes in the BC/CO ratio are due to other effects.

Figure 5 shows the BC/CO ratios measured during the 18 and 22 March 2006 flights. Figure 5a shows a substantial CO concentration apparently not associated with BC. This is likely the background concentration of CO due to the longer atmospheric lifetime of CO relative to BC – about a month in tropical regions for CO (Khalili and Rasmussen, 1990) and about a week for BC (in the absence of rain) (Ogren and Charlson, 1983). Hence, BC/CO ratios should be considered after correcting for this background. For the March 18 and 22 flights, this value is estimated at 62 and 67 ppbv CO, respectively, determined rather simplistically by plotting a frequency distribution of the CO data, and picking the lowest frequency peak as the background CO concentration. Figures 5b,c present background CO-corrected BC/CO<sub>net</sub> ratios as time-series plots, and a histogram of BC/CO<sub>net</sub> ratios is plotted in Fig. 5(d). Despite the differently-aged air masses sampled during these flights, relatively little variation is seen in the BC/CO<sub>net</sub> ratios; the mean BC/CO<sub>net</sub> ratio for both flights is around 3.1 (ng/m<sup>3</sup> STP)/ppbv, or ~2.5 ng BC/μg CO, with an uncertainty of about ±25%.

Dickerson et al. (2002) find a BC/CO ratio of 12.5 ng BC/μg CO measured on board the R/V Ronald H. Brown and a BC/CO ratio of 27 ng BC/μg CO in the free troposphere as measured on board the C-130 aircraft in 1999 during INDOEX (these values are the slopes, which effectively removes background CO as the intercept), which are both higher than our measurements on the MIRAGE flights. Kondo et al. (2006) measured

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$\Delta EC/\Delta CO$  ratios of  $\sim 6$  ( $\text{ng}/\text{m}^3$ )/ppbv (reported at ambient conditions) in Japan, and found this to be at the higher end compared to previously-reported surface measurements, which ranged from 0.88 in Mexico City (Baumgardner et al., 2002) to 4.1 in Fort Meade, USA (Chen et al., 2001). Though the data presented and tabulated by Kondo et al. involve either light absorption or thermal-optical techniques for measuring BC/EC, a comparison with data based on SP2 measurements is probably acceptable to within a factor-of-two. A more recent study by Baumgardner et al. (2007) using an SP2 at a ground site in Mexico City, close to vehicular traffic, suggests the BC/CO ratio is approximately  $1 \text{ ng}/\mu\text{g}$ . Thus, our airborne BC/CO<sub>net</sub> ratios of  $3.1$  ( $\text{ng}/\text{m}^3$  STP)/ppbv or  $2.5 \text{ ng}/\mu\text{g}$ , corrected to near-surface STP conditions, are similar to these surface measurements.

The background CO measured on the MIRAGE flights (62–67 ppbv or 76–83  $\mu\text{g}/\text{m}^3$  STP) is almost a factor-of-two lower than Dickerson et al.'s aircraft-measured background CO ( $138 \mu\text{g}/\text{m}^3$ ) over the Indian Ocean. Our background CO values are similar to Kondo et al.'s data for Tokyo (71 ppbv in July and 20 ppbv in January), though lower than Chen et al.'s estimate of  $180 \mu\text{g CO}/\text{m}^3$  for Fort Meade. A more appropriate comparison is the MOPITT (<http://web.eos.ucar.edu/mopitt/>) monthly averaged data at 850 mbar for the Pacific Ocean just west of Mexico, which suggests a CO background of about 80 ppbv in March/April 2006 (after correcting for a 20% bias, Emmons et al., 2008). Our estimates compare favorably with the MOPITT data.

### 3.3 Particle light absorption and BC

We compare BC concentrations measured with the SP2 to the PSAP absorption measurements at 660 nm, where interference from non-BC species is expected to be minimal. Figure 6 shows time-series plots and histograms (for BC  $> 30 \text{ ng}/\text{m}^3$ ) of the BC mass-normalized absorption cross-section (MAC) on a 1-minute-average basis (both the PSAP data and BC concentrations are at ambient conditions). The absorption cross-sections are shown in Table 2 as the average and standard deviation for each

event/over the location.

The 1-day-old air masses appear to have a higher MAC than the fresh outflow over T2, but the measurements over T0 on 22 March seem similar to the older air masses (there is no PSAP data over T0 for the 18 March flight). However, the average MAC values for the different air masses are not significantly different, particularly given the large standard deviations for the 1-day-old air masses and the measurements over T0. This is surprising, as one might expect that with age, as the non-BC coating thickness increases, the absorption cross-section would also increase by as much as 50% (Bond et al., 2006), and so MAC would be lower over T0 compared to that in 1-day-old aerosol. The fire-influenced air mass sampled on 22 March has an absorption cross-section similar to the samples not directly influenced by biomass burning. The biomass burning-influenced aerosol measured on 18 March has a somewhat higher, though more variable, MAC of  $12.2 \pm 5.5 \text{ m}^2/\text{g}$ . Ensemble frequency distributions (Fig. 6c) of the BC MAC suggest a mean of  $10.3 \text{ m}^2/\text{g}$  BC at 660 nm, with an uncertainty of  $\pm 30\%$  (propagating the uncertainties associated with the SP2 mass and PSAP absorption measurements). In comparison, the MAC for fresh combustion soot is expected to be around  $7.5 \pm 1.2 \text{ m}^2/\text{g}$  at 550 nm, or  $6.25 \text{ m}^2/\text{g}$  at 660 nm assuming an inverse-wavelength ( $\lambda^{-1}$ ) dependence (Bond and Bergstrom, 2006). Thus, our measurements of the BC MAC are about 65% higher than that expected for fresh soot, but within the uncertainty bounds ( $\pm 30\%$ ) of the 50% increase in MAC expected for aged soot compared to fresh soot. Other possibilities are discussed in a later section.

Baumgardner et al. (2007) used an SP2 to measure BC at the ground-level in Mexico City, close to vehicular traffic including a bus terminal. Based on the BC mixing state and particle optical diameter detected by the SP2 (a similar procedure as described in the methods section here), the MAC (using Mie theory) was estimated to be between  $4.5 \pm 0.2$  and  $5.0 \pm 0.2 \text{ m}^2/\text{g}$  at 550 nm. Assuming that MAC varies inversely with wavelength, this translates to around  $4 \text{ m}^2/\text{g}$  BC at 660 nm. While the MIRAGE data does include a few MAC values below  $5 \text{ m}^2/\text{g}$ , the mean MAC from the C-130 measurements is  $\sim 2.5$  times the Baumgardner et al. estimates.

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### 3.4 Evolution of BC mixing state

Moteki et al. (2007) looked at the evolution of BC mixing state using an SP2. They presented results in terms of the fraction of BC-containing particles that is thickly-coated. Their results were focused on particles with a BC content of 5.4 fg/particle (180 nm MED with a BC density of 1.77 g/cm<sup>3</sup>, or 176 nm MED at the BC density we use, 1.9 g/cm<sup>3</sup>). Figure 7 shows a similar analysis for the 18 March MIRAGE flight, when the aircraft sampled fresh Mexico City emissions as well as 1-day-old outflow at 22.2° N. Though the comparison is between 18 March emissions and aged aerosol emitted the previous day, similar aging processes are expected to affect emissions from either day. In contrast to Moteki et al., however, we do not see a significant change in the number fraction of thickly-coated BC particles even after a day of aging.

As an alternative, we compare results from corresponding air masses sampled on 18 and 19 March and on 22 and 23 March (Fig. 1). As described earlier, the air masses sampled on the first day of each pair of flights were again sampled on the second day based on model predictions, so sampling of the same air mass on consecutive days should provide better insight into the evolution of BC during atmospheric transport. Further, instead of focusing on just one narrow BC mass range, we look at the entire range of BC masses (as the mass-equivalent diameter, MED) measured by the SP2. Figure 8 shows the BC mixing state for different air masses sampled on the 18 and 19 March flights, with incandescence lag on the *y*-axis and BC MED on the *x*-axis; the color corresponds to BC number concentration. As explained earlier, zero incandescence lag (or close to zero) indicates thinly-coated BC, while thickly-coated BC show an incandescence lag greater than 2 μs.

The top left and middle panels in Fig. 8 show fresh emissions sampled over Mexico City (T0) and over T2, while the top right panel shows the same air mass sampled a day later at 24.25° N. Two interesting features are seen in these plots. First, the fresh emissions over T0 appear to be unimodal, with most BC particles showing almost-zero incandescent lag, i.e. the BC is thinly-coated. The MED peaks around 150 nm

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for this mode. As the air mass moves toward T2, we see more particles at larger incandescent lags closer to  $4 \mu\text{s}$  – thickly-coated BC. One day later, the MED seems to have increased for the thinly-coated mode, and the thickly-coated BC mode is clearly seen.

5 The bottom panels in Fig. 8 start with 1-day-old aerosol sampled on 18 March between 3.5 km–4.1 km (above sea level), ending with the aerosol sampled one day later off the Texas coast on 19 March. The 1-day-old aerosol sampled on 18 March shows similar characteristics as the fresh emissions emitted on March 18 and sampled a day later on 19 March (top row, third panel), with similar MED size distributions and the presence of both thinly-coated and thickly-coated BC, though the thickly-coated BC is relatively more prominent at 4.1 km than at 3.5–3.8 km. The two-day-old air mass shows a more dispersed distribution. Thus, apart from the usual dilution process that reduces BC concentrations as the air mass ages, we see an increase in the fraction of thickly-coated BC at least for the 1-day-old air masses, as well as an apparent increase in the modal BC MED (BC mass/particle) of the thinly-coated BC mode.

15 Figure 9 compares the 22 and 23 March data. Fresh emissions sampled over T0 on 22 March (top left) show a prominent BC mode centered around 170 nm MED with incandescence lag close to zero, i.e. thinly-coated BC. The same aerosol sampled a day later (top right) shows a second mode in the same diameter range but with an incandescence lag between 3–4  $\mu\text{s}$ , i.e. thickly-coated BC. The 1-day-old aerosol sampled on 22 March off Veracruz (bottom left) is dominated by thickly-coated BC. When the air mass was sampled again on 23 March (bottom right), the thickly-coated BC mode appears less prominent than the thinly-coated mode (compared to the 22 March sample). However, this 2-day-old air mass appears similar to the 2-day-old air mass sampled on March 19 off the Texas coast (Fig. 8).

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## 4 Discussions and conclusion

Two important factors have to be considered when discussing the data presented here. The first is that mountain fires influence the aerosol and gas-phase pollutants measured over Mexico City (Yokelson et al., 2007). The second is that the MCMA outflow is not transported in isolation over Mexico, but likely interacts with other pollution sources along the way, including other populated areas and biomass burning events.

The BC/CO and background CO measurements over Mexico during this study are lower than similar measurements made over the Indian Ocean (Dickerson et al., 2002), but comparable to corrected MOPPITT data over the Pacific Ocean off the Mexican coast for March/April 2006. The lower CO background over Mexico may be due to lower gross emissions of CO from Mexico compared to emissions from the Indian subcontinent. Dickerson et al. estimate that in 1999, CO emissions from India were 67 Tg CO/yr, including 15 Tg CO/yr from fossil fuel combustion and 40 Tg CO/yr from biomass burning. Jiang et al. (2005) estimate that vehicular CO emissions (almost all of CO) from Mexico City in 2002 were 1.2 Tg CO/yr in 2003. A 1999 Mexico National Emissions Inventory (SEMARNAT, 2006) suggests total CO emissions of 7.5 Tg CO/yr. Though neither of these studies is for the 2006 period (when MIRAGE was conducted), it is clear that CO emissions from Mexico are almost an order of magnitude lower than those from India. However, the background CO depends not just on the gross emissions, but also the flux at the point of measurement; such calculations are beyond the scope of this study. One explanation for the lower BC/CO ratios is that the source mix may be different between the Indian subcontinent and Mexico. Baumgardner et al. (2002) suggest that operating conditions including the altitude can also affect the BC/CO ratio.

Jiang et al.'s results suggest that BC and CO measured in Mexico City should be proportional; this was seen by Baumgardner et al. (2007) for a ground site close to vehicular traffic in Mexico City. We do see a certain amount of background CO (not associated with BC) in our airborne measurements over Mexico City. This could be

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explained by mixing of the MCMA outflow with CO-containing background air flowing in to the city, including CO from mountain fires to the southeast/southwest of MC, which contribute about one-fifth of the MCMA CO (Yokelson et al., 2007). This theory depends on the contribution of the incoming background air to ambient BC in Mexico City, which needs further investigation.

Our measurements of the BC absorption cross-section, about  $10.3 \text{ m}^2/\text{g}$  @ 660 nm, translate to  $12.4 \text{ m}^2/\text{g}$  @ 550 nm assuming a  $\lambda^{-1}$  dependence. This is higher than the median values of  $\sim 9 \text{ m}^2/\text{g}$  @ 550 nm reported by Doran (2007) and 2.5 times the MAC values reported by Baumgardner et al. (2007) for measurements at T1 and in Mexico City, respectively. The Baumgardner et al. data may be biased low as the optical particle diameter used to estimate MAC of coated BC in their Mie calculations did not account for volatilization of the non-refractory coating described by Gao et al. (2007). However, our SP2/PSAP-based MAC is less than  $13 \text{ m}^2/\text{g}$  @ 550 nm, the *upper limit* of the range suggested by Bond and Bergstrom (2006) ( $7.5 \pm 1.2 \text{ m}^2/\text{g}$  @ 550 nm), after accounting for the 50% enhancement suggested due to aging (Bond et al., 2006).

The SP2 data show that BC over Mexico City is dominated by the thinly-coated mode, which means that the BC MAC we measured over Mexico City (as similar to that measured in older air masses) is likely biased high. This could occur if the SP2 collection efficiency for BC masses below 3 fg BC (which might be more prominent in fresh emissions rather than coagulated older aerosol) is overestimated by our BC mass scaling factor, or if the PSAP absorption is biased high.

The PSAP data was corrected using the results of Virkkula et al. (2005); using the Bond et al. (1999) corrections would further increase the absorption and the derived MAC. A positive bias in the as-presented data can be caused by liquid organic matter coating the PSAP filter (Subramanian et al., 2007; Cappa et al., 2008; Lack et al., 2008), which would result in our MAC values being higher than actual. This potential bias in the PSAP absorption measurements onboard the C-130 depends on the relative amounts of non-absorbing organic matter and BC (Lack et al., 2008). From DeCarlo et al. (2008), the average organic aerosol concentration over Mexico City during MIRAGE

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was  $\sim 16 \mu\text{g}/\text{m}^3$ . The empirical studies by Lack et al. (2008) suggest that in such conditions, the PSAP could measure as much as 40–70% higher absorption.

One possible explanation is that liquid-phase biomass smoke aerosol creates an artifact in the PSAP absorption measurements while mixed externally with the city emissions over MCMA; but as the air masses mix further during transport away from MCMA, the liquid organic matter coagulates with more-refractory BC to form a coating on the aerosol that enhances the inherent particulate light absorption (separate from artifacts in absorption measurement). The initial PSAP artifact is similar in magnitude to the enhancement due to coating during aging, at  $\sim 50\%$ ; finer differences are likely masked by the  $\pm 30\%$  uncertainty on our MAC values. However, both the SP2 measurement efficiency at smaller BC masses, particularly for fresh emissions, as well as PSAP response to organic matter of different ages and in different mixing states, need further research to resolve these discrepancies.

The SP2 data, Figs. 8 and 9, shows that as the aerosol mass ages, the BC becomes thickly coated. When comparing just one narrow mass range of BC ( $\sim 180 \text{ nm MED}$ ) as Moteki et al. (2007) did, we did not see a significant change in the fraction of BC that is thickly-coated. Broadening our perspective to the entire range of BC mass measured by the SP2, we see distinct patterns in the coating thickness and mass size distribution of BC particles as indicated by the incandescent lag measurements. Fresh emissions show mostly thinly-coated BC particles. As the air mass ages, we find a greater fraction of thickly-coated BC particularly in the 1-day-old air masses.

The BC mass/particle (BC MED) of the thinly-coated BC appears to increase with age. This could mean either a preferential coating of smaller BC particles during aging (i.e. these smaller particles are lost from the thinly-coated mode), or due to coalescence of particles, or both. For instance, a review by Reid et al. (2005) suggests that during long range transport of a fire plume, coagulation is the dominant particle growth mechanism. A modeling study of soot aging timescales by Riemer et al. (2004) suggests that while condensation is the dominant growth mechanism during the day, coagulation is more important at night. The concurrent appearance of the thickly-coated

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mode suggests that both coagulation and coating deplete the thinly-coated, lower-MED mode of fresh emissions.

The comparisons between 1-day-old and 2-day-old air masses show that while the 1-day-old air mass has a distinct thickly-coated BC mode, what appears to be the same aerosol mass measured the next day does not. Further, on the March 19 flight, the thickly-coated BC mode is more prominent in the measurements at 4.1 km than at the lower altitudes (3.5–3.8 km). There are at least two possible explanations for these observations. First is the mixing of the MCMA air mass with fresher aerosol from other sources, which can change the ensemble characteristics. For example, there are many local villages as well as a major highway going to the northeast out of Mexico City that could be producing significant concentrations of fresh particulate matter.

Second, while aging increases the non-BC coating thickness, wet removal processes would preferentially wash out the (likely more hydrophilic) thickly-coated BC. Depending on which processes are more dominant over the life of the aerosol, BC concentrations and coating thicknesses may differ during atmospheric transport even if the sources are the same. Further, the concentrations and coating characteristics may end up looking similar during later stages of the aerosol lifetime. This means that the overall lifetime effect of BC on radiative forcing may not be the same for emissions from the same source even for emissions just a few days apart. However, it could be argued that such variations average out over time, but this needs more study.

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**Table 1.** Summary of major episodes encountered during the four MIRAGE flights.

Flight date (all 2006)	Pollution event	Altitude (km above sea level)	BC (ng/m <sup>3</sup> STP) Average±SD (low-high)
18 Mar	Fresh emissions over T0 22:41–22:47 UTC	2.7	375±77 (240-526)
	Fresh outflow over T2 20:50–21:36	3.8	457±162 (68-1259)
	1-day-old emissions @ 22.2° N 18:28–18:48 UTC	3.5	193±66 (81-317)
	18:13–18:24 UTC	3.8	204±67 (71-328)
	16:36–17:12 UTC	4.1	220±103 (24-445)
	Hill fires southeast of MC 22:10–22:13 UTC	4.1	527±357 (89-1041)
19 Mar	Fresh outflow over T2 01:05–01:16 UTC	3.5	301±63 (177-537)
	01:18–01:31 UTC	3.8	273±64 (161-408)
	1-day-old @ 24.25° N 23:10–23:37 UTC	3.2	176±41 (58-288)
	2-day-old off Texas coast (27.3° N, 93.5° W) 21:32–21:37 UTC	Profile <sup>a</sup> 5.3–4.2	152±90 (11-327)
22 Mar	Fresh emissions over T0 20:11–20:20 UTC	2.6–3.2	1070±242 (717-1859)
	Fresh outflow over T2 18:46–18:56 UTC	3.45	439±130 (221-992)
	18:59–19:11 UTC	3.15	461±143 (0-734)
	1-day-old emissions off Nautla 17:32–17:49 UTC	4.15	382±100 (159-591)
	17:52–18:12 UTC	4.46	227±119 (12-551)
	21:25–21:37 UTC	4.1	393±121 (80-562)
	Hill fires/South of MC 19:32–19:42 UTC	4.1	697±294 (283-2004)
	19:46–20:03 UTC	3.8	657±219 (366-1407)
20:05–20:09 UTC	3.5	607±101 (467-901)	
23 Mar	1-day-old emissions over Gulf 17:45–17:59 UTC	4.6	157±41 (11-221)
	2-day-old emissions (northern tip of Yucatan) 18:57–19:03 UTC	4.9	120±23 (76-160)
	20:34–20:48 UTC	4.8	117±30 (18-181)
	Biomass burning plume 19:56–20:12 UTC	Profile <sup>a</sup> 5.4–0.3	413±1107 (0.8-8047)

<sup>a</sup> During ascents/descents, the sample flow recorded is not the actual flow, a deficiency of the flow measurement system used in the 2006 version of the SP2. Concentrations reported here are for the descents only, are an overestimate, and are reported for reference purposes only. All other data are for level segments of the flight.

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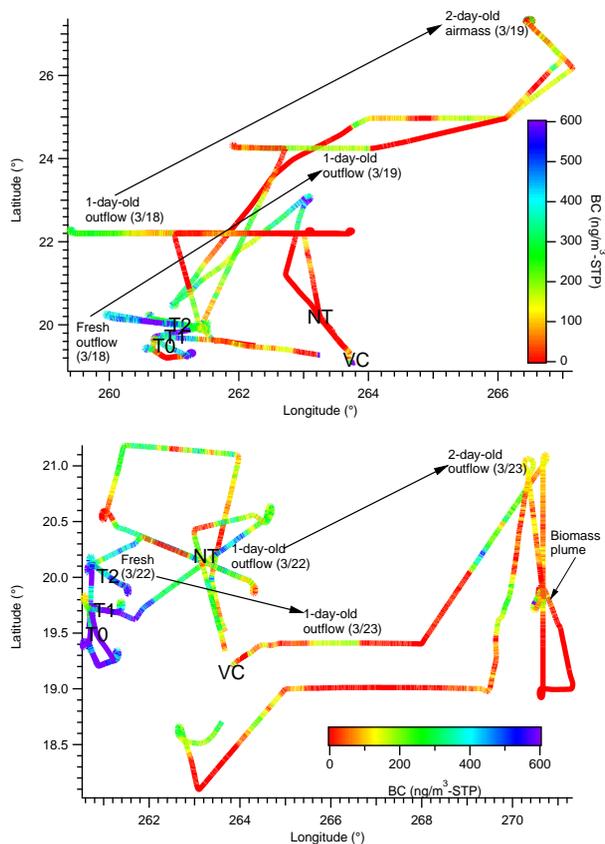
**Table 2.** BC mass absorption cross-section (MAC) at 660 nm (based on BC and PSAP data at ambient conditions).

Event/location	18 Mar	22 Mar
Over T0	N/A	$11.6 \pm 3.9 \text{ m}^2/\text{g}$
Fresh outflow over T2	$10.6 \pm 1.9 \text{ m}^2/\text{g}$	$10.3 \pm 1.5 \text{ m}^2/\text{g}$
One-day-old air mass	$11.2 \pm 3.6 \text{ m}^2/\text{g}$	$11.1 \pm 3.8 \text{ m}^2/\text{g}$
Hill fires	$12.2 \pm 5.5 \text{ m}^2/\text{g}$ (SW of MC)	$11.6 \pm 2.5 \text{ m}^2/\text{g}$ (SE/SW of MC)

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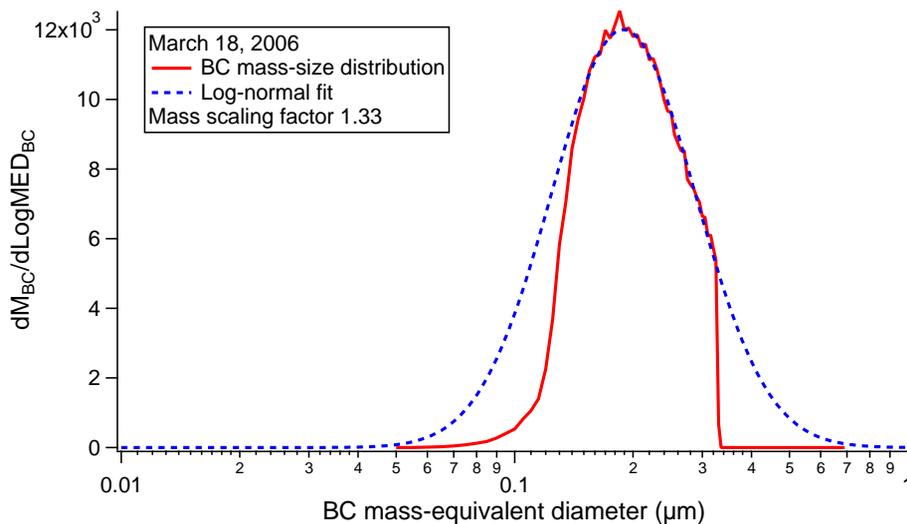


**Fig. 1.** Flight paths, colored by the BC mass concentration (at STP), for the four MIRAGE flights discussed in this paper. Top: 18 and 19 March; bottom: 22 and 23 March. T0, T1, T2 are ground sites described in the text (T0 is in Mexico City); VC is Veracruz, where the C130 took off and landed; NT is Nautla. The color scales are truncated at a BC concentration of  $600 \text{ ng/m}^3$  for visual clarity.

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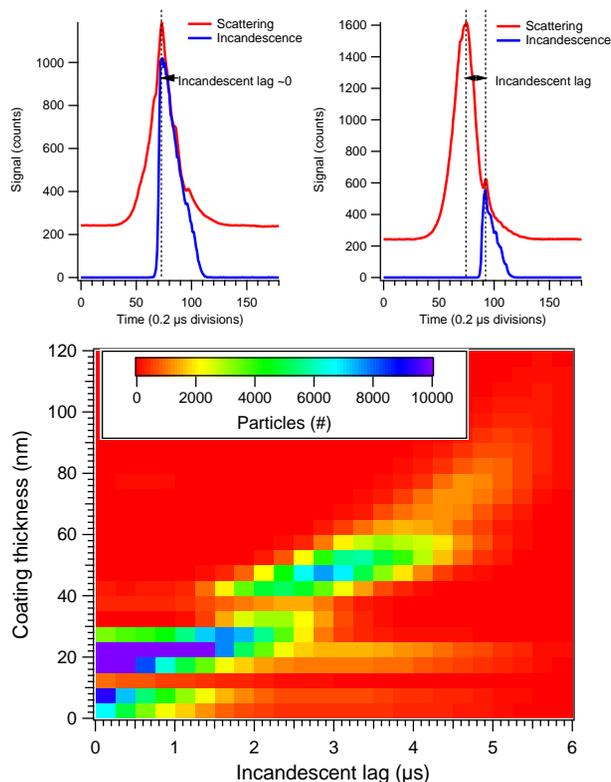


**Fig. 2.** To account for BC masses outside the SP2 detection limits (3–36 fg), a log-normal distribution is fitted to the measured BC mass between 145–325 nm MED (3–34 fg BC). Scaling factors are calculated from the ensemble BC mass distribution for each flight.

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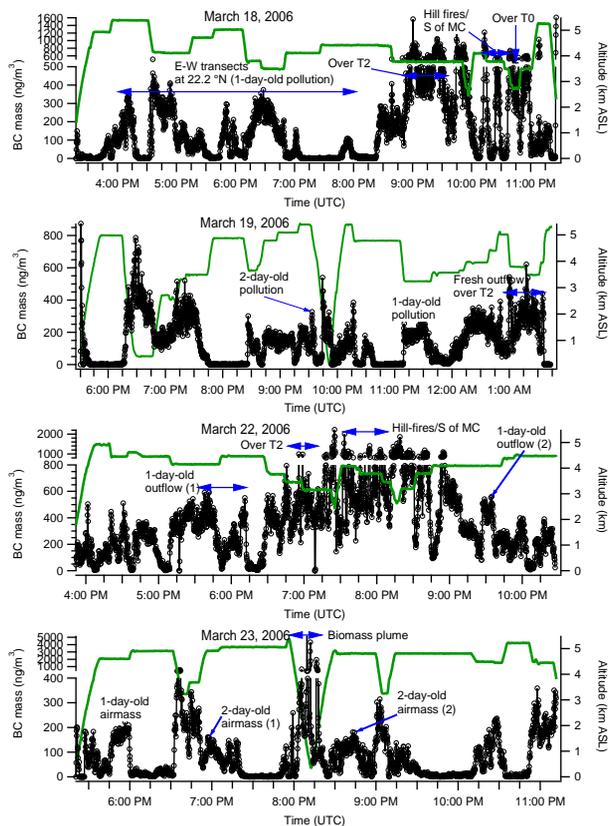


**Fig. 3.** The mixing state of BC can be determined using the separation between the incandescent and scattering peaks, or incandescent lag. An incandescent lag close to zero (top left) indicates thinly-coated BC, while larger values ( $\sim 4 \mu\text{s}$ , top right) indicate thickly-coated BC. A comparison of the incandescent lag with coating thicknesses based on the scattering signal (bottom) shows a reasonably positive correlation between the two quantities. Data from the 18 March 2006 flight.

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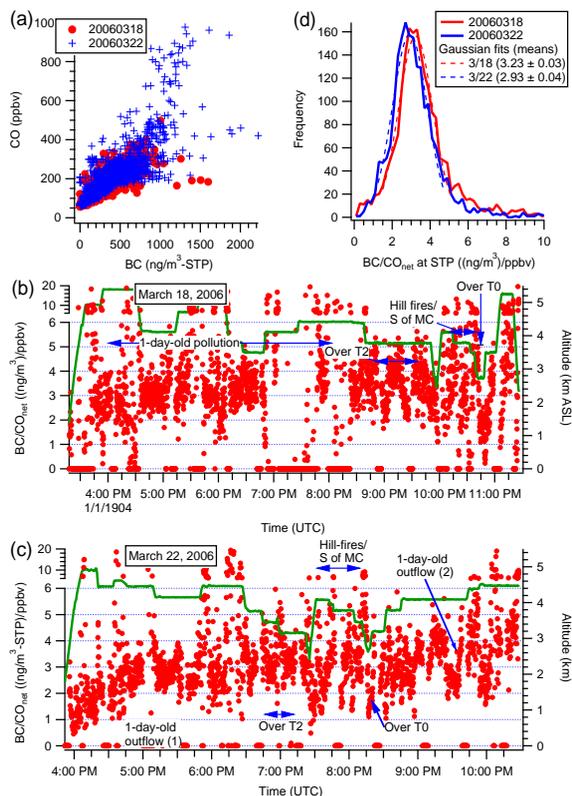


**Fig. 4.** BC concentrations measured by the SP2 during four flights of MIRAGE. Data are presented at standard temperature and pressure (273.15K, 1 bar). Green lines show flight altitude.

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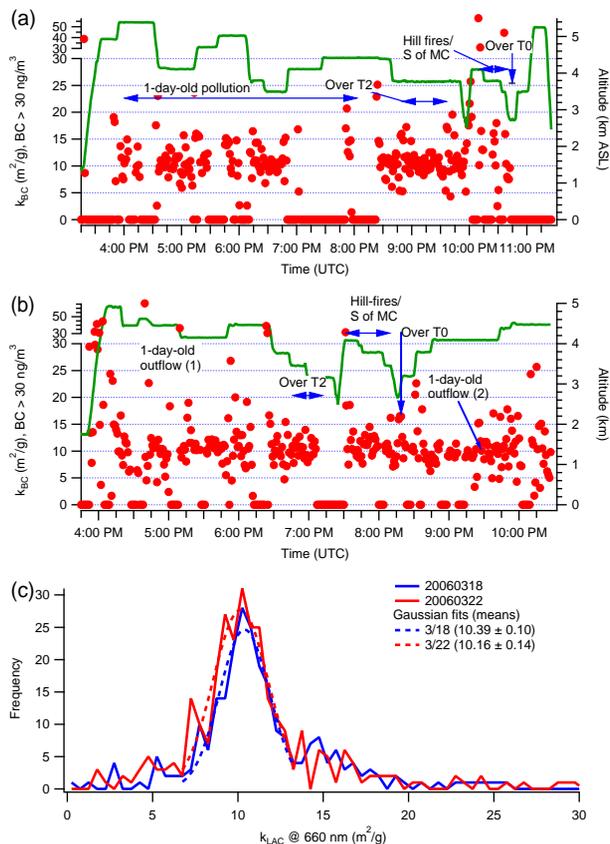


**Fig. 5.** BC/CO ratios during the 18 and 22 March 2006 flights, with BC corrected to STP (1 bar, 273.15K). Plot (a) shows a substantial background concentration of CO, probably due to the longer lifetime of CO compared to BC. Plots (b), (c) and (d) show BC/CO<sub>net</sub> ratios after correcting CO for an approximate background value. No significant change is seen in the BC/CO<sub>net</sub> ratio for fresh or aged air masses (b, c), with the mean BC/CO<sub>net</sub> ~3.1 (ng/m<sup>3</sup> STP)/ppbv for both flights (d).

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**Fig. 6.** Absorption cross-section of BC at 660 nm, assuming that all light absorption at this wavelength is due to BC. 1-minute-averaged data, limited to BC concentrations over  $30 \text{ ng/m}^3$ . The absorption cross-section does not vary appreciably with air mass age (a, b). Gaussian fits to the absorption cross-section distribution (c) suggest a mean BC absorption cross-section of  $\sim 10.3 \text{ m}^2/\text{g}$  BC at 660 nm.

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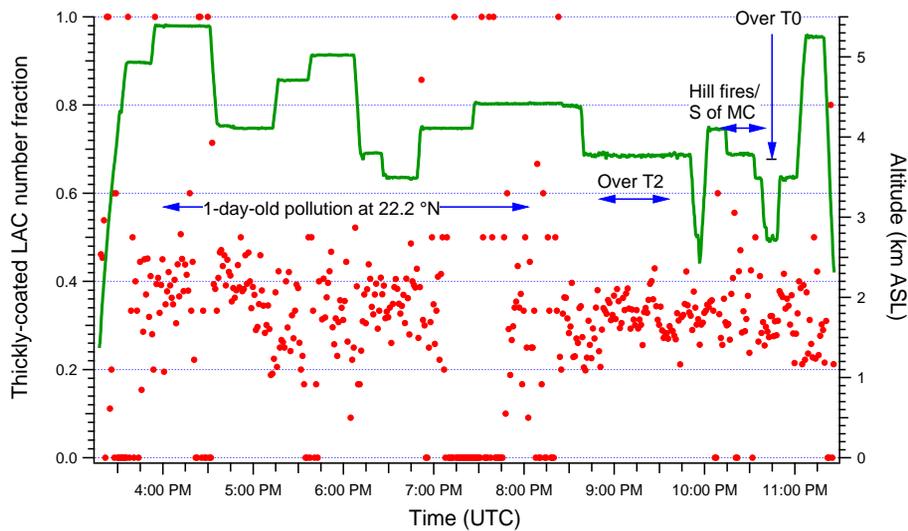
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**Fig. 7.** Thickly-coated BC number fraction for particles containing 5.3–6.3 fg BC/particle (175–185 nm MED) for the 18 March 2006 flight.

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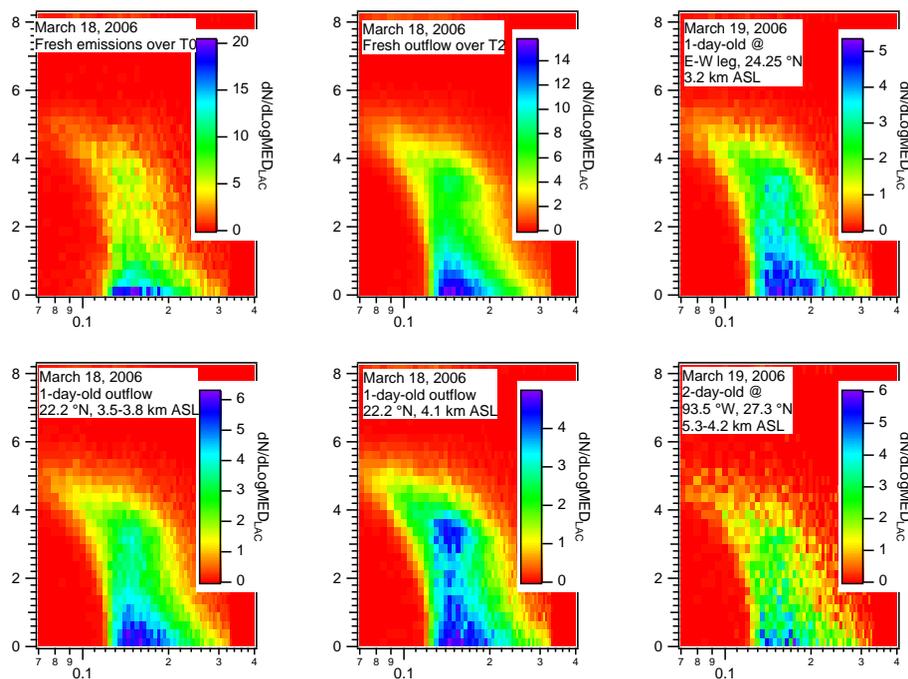
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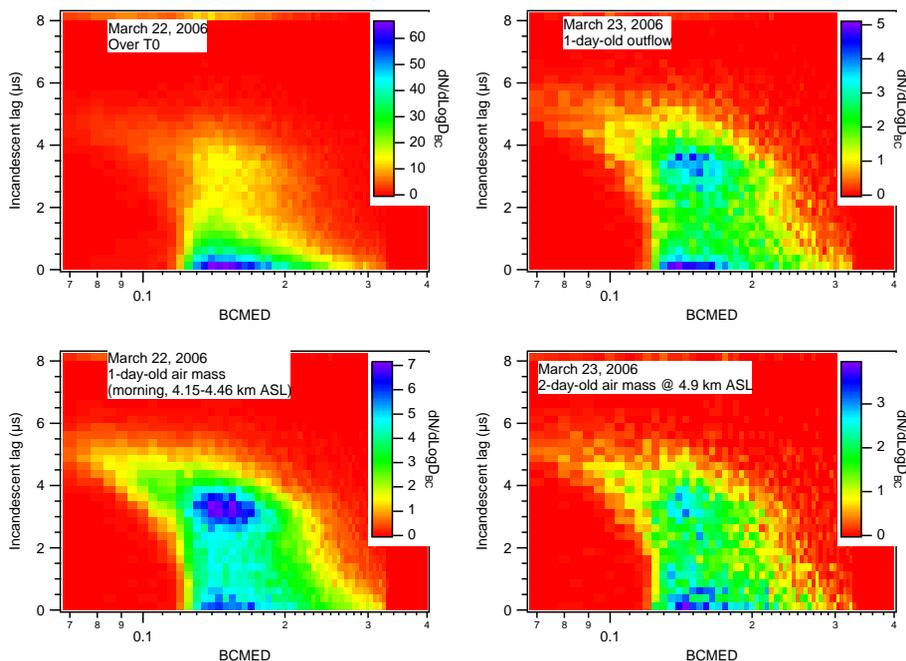
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**Fig. 8.** Evolution of BC mixing state during transport north/northeast between 18 and 19 March 2006. The top panels show fresh emissions from Mexico City transported over T0 and further north to about  $24.25^\circ$  N a day later; a thickly-coated mode is seen to develop during the transport process. Bottom panels show a 1-day-old air mass measured on March 18 at two different altitudes, and the same air mass measured on March 19 a day later off the Texas coast. Incandescent lag ( $\mu$ s) plotted on the  $y$ -axis, and BC mass/particle (MED,  $\mu$ m) on the  $x$ -axis.

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**Fig. 9.** BC mixing state spectra for the air masses sampled on 22 and 23 March. The top panels show fresh emissions measured over T0 on March 22 (left), and then measured one day later over the Gulf of Mexico off Veracruz (right). The bottom panels show 1-day-old air mass sampled on 22 March (left), sampled again as 2-day-old aerosol on 23 March (right).

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