Diagnosing black carbon trends in large urban areas using carbon monoxide measurements

Darrel Baumgardner, G. Raga, O. Peralta, I. Rosas, and T. Castro
Centro de Ciencias de la Atmósfera, Universidad Nacional Autonoma de Mexico, Mexico City, Mexico

T. Kuhlbusch and A. John
FB 9/AMT, University of Duisburg, Duisburg, Germany

A. Petzold
Deutsches Zentrum für Luft und Raumfahrt, Oberpfaffenhofen, Germany

[1]   The relationship between black carbon (BC) and carbon monoxide (CO) has been analyzed using measurements from two sites in Mexico City and five urban areas in Germany. The correlation coefficient between BC and CO is greater than 0.90 for all sites. The average slope of the linear regression line for BC versus CO is 2.2 μg mg^{-1} for German sites and 1.1 μg mg^{-1} in Mexico City. The most important factors that affect the BC to CO relationship appear to be the ratio of diesel to gasoline usage and the combustion efficiency of vehicles in a particular area. The results of this analysis suggest that CO measurements in urban areas can be used to estimate BC mass when direct measurements are not available.   *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0394 Atmospheric Composition and Structure: Instruments and techniques; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; *KEYWORDS:* black carbon, carbon monoxide, urban aerosols

1.   Introduction

[2]   Black carbon (BC) particles are an important atmospheric component because of their potential deleterious impact on health and climate. Definitive studies have yet to be conducted that conclusively link soot to health problems, but various epidemiological and toxicological studies show that BC causes tissue irritation and the release of toxic chemical intermediates from scavenger cells. Soot particles also act as carriers for the organic compounds that can be allergens, mutagens, or carcinogens [*Lighty et al.*, 2000].

[3]   Aerosols may alter climate regionally or globally as a result of their light-scattering and light-absorbing properties. Modeling studies [e.g., *Chylek et al.*, 1995] indicate that BC aerosols should not change climate on global scales where their mass concentration is less than 1% of total aerosol mass. On local and regional scales, however, where they often account for as much as 20% of the aerosol mass, they can have a significant impact on radiative forcing. For example, recent measurements with aircraft, ships, and satellites over the Indian Ocean [*Meywerk and Ramanathan*, 1999] demonstrated conclusively that urban pollution from cities in India formed a light-absorbing layer over the ocean north of the equator. Single-scattering albedos comparable to those found in Mexico City (<0.88) were measured at the surface and in the boundary layer [*Novakov et al.*, 2000]. Black carbon may also change cloud properties by increasing the optical absorption if they are inside cloud droplets [*Chylek et al.*, 1996] or by decreasing cloudiness as a result of changing the thermal structure of the atmosphere [*Ackerman et al.*, 2000].

[4]   Better estimates are needed of BC emissions to assess the potential effect of these particles on the environment. Measurements are especially lacking in urban areas as these regions are a major source of BC [*Novakov et al.*, 2000] but only a very limited set of data exists at this time from large cities, particularly those in developing countries. There are a number of reasons why such data are not currently available. The measurement of BC is nontrivial and requires the analysis of filter samples or the conversion of optical absorption measurements to BC mass with an appropriate conversion factor. The first method requires long sampling times, typically from several hours to several days to obtain sufficient mass to analyze. The analysis is time consuming if there are more than just a few samples. The conversion of optical absorption measurements to BC mass is a faster method, but the conversion factors vary over more than a factor of 10, depending upon particle composition and size distribution [*Liousse et al.*, 1993]. The conversion coeffi-

cient can be derived for a particular site but requires the use of the direct measurement technique to derive its value.

[5] An alternative methodology for diagnosing BC mass was suggested by a study at Mace Head, Ireland [*Jennings et al.*, 1996], where a good linear correlation between optical attenuation and CO measurements was found. The ratio of light attenuation to CO was seen to change depending upon the source of the air, that is, whether the air came from the European continent or from over a long stretch of the Atlantic Ocean. A study in 1997 of the properties of aerosols in Mexico City [*Baumgardner et al.*, 2000] showed a strong correlation between the aerosol absorption coefficient and CO. Most recently, a study in a suburban area of Maryland, USA, showed that BC and CO were highly correlated [*Chen et al.*, 2001].

[6] The use of CO as a surrogate for BC is appealing since CO has been measured in many urban areas for extended periods over the last 20 or more years. The measurement of CO is relatively simple and inexpensive such that CO monitors can be widely deployed in regions of developing countries where BC levels are known to be high but where few measurements exist. The response time of CO analyzers is relatively fast, of the order of several seconds, such that processes of BC formation and evolution can be studied with fine spatial and temporal resolution. This is rarely possible with the slower direct or optical measurements of BC. The use of CO as a BC surrogate hinges on the ability to understand the physical link between these two compounds.

2. Physical Basis for a BC/CO Link

[7] Combustion is the physical process that links BC and CO. Some BC is produced by abrasion of tires on pavement, and there are possibly other noncombustion sources of BC; however, the largest fraction is produced by combustion. Likewise, CO is produced almost entirely from combustion, although the types of fuel that produce BC may differ from those that produce CO. The ratio of BC to CO will vary depending upon the fuel type. BC is a component of soot that is produced by incomplete oxidation of fuel [e.g., *Goldberg*, 1985], that is, as given by *Seinfeld and Pandis* [1998],

$$C_mH_n + aO_2 \rightarrow 2aCO + 0.5nH_2 + (m - 2a)C_s \qquad (1)$$
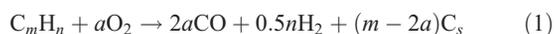
where C_mH_n is the combusting hydrocarbon and C_s is the BC that results. Thus the BC to CO relationship depends upon the composition of the fuel, amount of available oxygen, and degree of oxidation.

[8] BC particles and CO molecules are quite different in size. The thermal velocity and diffusion coefficient for CO, at 300 K, are approximately 450 and 9.9×10^{-6} m s^{-1}, respectively. A 0.1 μm BC particle (the average size of BC aerosols) has a thermal velocity and diffusion coefficient of approximately 0.15 and 1.3×10^{-10} m s^{-1}, respectively. This suggests that CO should diffuse much more rapidly than BC.

[9] Carbon monoxide is a long-lived species whose primary removal mechanism is oxidation to carbon dioxide by the hydroxyl radical, OH. This is a relatively slow process with a time constant of several days to several weeks, depending upon the other processes that compete for the available OH. BC is removed by dry or wet deposition. In the former case, local surfaces act as sinks for BC, while in the latter case, precipitation removes BC if hygroscopic compounds such as sulfates or organic acids have formed on the BC surfaces. Although the thermal velocity and diffusion coefficient are significantly larger for CO than BC, they are small enough that neither of the two species will diffuse appreciably for several hours after emission. Both compounds will decrease in concentration as they are mixed and diluted by the ambient air. Near the source the rate of this dilution should not differ appreciably between the two species.

[10] There is often confusion about the definition of BC; hence throughout the remainder of this paper we will use the definition [*Penner and Novakov*, 1996, p. 19,373], "BC is that component of soot that is insoluble in organic solvents and resistant to oxidation at temperatures below about 400°C." The term "black carbon" is used to imply that this soot component is primarily responsible for the absorption of visible light.

3. Measurement and Analysis Methodology
3.1. Instrumentation

[11] Carbon monoxide was measured in both countries with commercial, nondispersive, infrared gas filter correlation analyzers (Thermal Environmental Corporation, Franklin, Massachusetts, USA). Four of the five data sets of BC from Germany were derived with the established German reference method, VDI Part 1 [*VDI Verein Deutscher Ingenieure*, 1996]. The other German data set and the BC values from Mexico City were derived from optical absorption measurements.

[12] The VDI Part 1 reference method is a two-step technique [*Kuhlbusch*, 1995]. In the first step, organic compounds are removed from an aerosol-loaded, quartz fiber filter using a 50/50 (% volume) mixture of 2-Propanol and Toluol. Any remaining organics are removed by thermodesorption in an atmosphere of N_2. In the second step, the sample is placed in the furnace of a carbon analyzer (Ströhlein), and the remaining black carbon is oxidized at 650°C with complete oxidation occurring in a catalytic section held at 900° in the presence of CuO and platinum. The CO_2 that evolves is measured by coulometric titration while holding constant the pH of the solution that forms during a reaction between CO_2 and $Ba(ClO_4)_2$.

[13] The German BC measurements use an aethalometer [*Hansen et al.*, 1982; *Hansen*, 1984] that measures light attenuation. The absorption coefficient is converted to BC mass with a specific absorption oefficient, σ_{ae}. For these measurements, a value of $\sigma_{ae} = 19$ m^2 g^{-1}, supplied by the manufacturer (Magee Scientific, Berkeley, California, USA), was used.

[14] Black carbon in MC was derived from the absorption coefficient measured with a particle soot aerosol photometer (PSAP, Radiance Research, Inc., Seattle, Washington, USA). The absorption coefficient is converted to BC mass with an σ_{ae} derived from direct measurements of BC that use thermoseparation [*Novakov*, 1981; *Ellis et al.*, 1984]. In this technique, called evolved gas analysis (EGA), aluminum substrates from the different impactor stages of a micro-orifice uniform deposit impactor (MOUDI, MSP, Inc., Minneapolis, Minnesota, USA) are heated at a constant rate of temperature increase in the presence of oxygen. The

Table 1. Uncertainty Analysis of Evolved Gas Analysis Technique

Source	Systematic Error	Random Error
Filter collection		
Flow measurement	±5%	±1%
Particle losses	−2% + 0%	±2%
Thermal separation analysis		
Incomplete oxidation	−5% + 0%	±2%
Recuperation factor	±5%	±2%
CO_2 calibration	±5%	±1%
Organic carbon > 400 k	+20% − 0%	±20%
RSS[a]	+22% − 10%	±22%

[a]RSS denotes root-sum-square. RSS_{total} = +31% − 24%.

evolved CO_2 is measured with an infrared analyzer (Licor, Inc., Lincoln, Nebraska, USA), and the distribution of evolved carbon versus temperature is used to distinguish organic carbon (OC) from BC. Carbon mass above a temperature of 450° is assumed to be BC. The evolved mass below that temperature is designated OC.

[15] The specific absorption coefficient σ_{ae} is the ratio of the absorption coefficient to the BC derived from the EGA, where the absorption coefficient is the average value measured during the same time period as the filter impactor samples. The average σ_{ae} was 7 ± 0.5 m^2 g^{-1} for both of the Mexico City sites.

3.2. Error Analysis

[16] A number of factors affect the accuracy of CO and BC measurements. The largest sources of uncertainty in the CO analyzer are slow baseline drifts and shifts in calibration that will occur between routine calibrations. With no knowledge of the calibration frequency of the analyzers used for the measurements in this study, we estimate an accuracy of approximately 15% based upon previous experience using this type of analyzer in field studies.

[17] The coulometric titration technique has an accuracy that has been estimated as 10% [*Liousse et al.*, 1993]; however, this might be a generous estimate, based upon a report by another group [*Shah and Rou*, 1990] whose study utilized a round robin test of 10 separate analysis systems to analyze BC from the same source. Some of these systems utilized the coulometric technique, while others used the EGA technique. There was significant variability in the results, with differences sometimes exceeding factors of 10. One of the principal difficulties in determining the "best" system is in generating a representative BC sample of known mass and composition that replicates BC found in the environment. When the same sample was divided and tested by different laboratories using the same technique, there were still significant differences.

[18] There are a number of error sources in the EGA technique, as summarized in Table 1. The division between systematic and random error is used to distinguish between those uncertainties that could be removed if we had better information about the system (systematic) and fluctuations over which we have no control (random). Most of the errors are expressed as plus or minus as we cannot know for sure in which direction the uncertainty affects the results. In some cases, however, the uncertainty clearly is in one direction or the other.

[19] The first uncertainty source is associated with the collection of the particles on the filters. Particle losses that result from impaction with the inlet surfaces are expected to

be of the order of −2% or less. In order to calculate the concentration, we need to know the volumetric flow rate. The flow meters that are used to measure this flow have an uncertainty of the order of ±5%.

[20] In the thermographic analyzer the largest source of uncertainty is the separation of OC from BC. The thermographic technique used in Mexico City (MC) increases the temperature at a constant rate of 30° min^{-1} and produces a thermogram of evolved CO_2 as a function of temperature. Two, clearly separated peaks normally form, one at a temperature less than 450°, where the majority of organics volatilize, and a secondary peak above 450°, where the BC is released from the sample. The thermograms are normally symmetrical, Gaussian in shape, around each of these peaks. However, pyrolitic conversion of organic to black carbon (charring) can bias the derived BC loading above 450° [*Cadle and Groblicki*, 1982]. We minimize the influence of charring by integrating the area to the right of the peak that appears at the highest temperature. We assume that this represents 50% of the BC mass and multiply by 2 to obtain the total BC mass. The uncertainty in deriving BC with this method is estimated as approximately +20%, as some of the carbon derived in this fashion may still be a result of charred organics. Using the method of propagating errors, the uncertainties are summed in quadrature to obtain a root-sum-square (RSS) error of +31%−24% for BC derived from this method.

[21] *Bond et al.* [1999] evaluated the uncertainty in light absorption measurements by the PSAP. The uncertainties are expected to be very similar with the aethalometer as it utilizes the same principles of operation and collects aerosols on filters of the same material. The primary difference is the wavelength of light used.

[22] The PSAP derives the absorption coefficient, σ_{ap}, from Beer's law of light attenuation, that is,

$$\sigma_{ap} = [A/V]\ln[I_0/I] \qquad (2)$$

where I is the intensity of light transmitted through an aerosol-loaded quarts filter and I_0 is the reference signal, that is, light transmitted through a clean filter. The area of the filter and the volumetric flow rate are given by A and V, respectively. Corrections are needed to the flow rate and area. The calibration of the flow meter used in the instrument may be as much as ±20% in error, and the actual diameter of the aerosol area varies as much as ±30%, depending upon the flow rate and quality of the O-ring seal [*Bond et al.*, 1999]. The corrected σ_{ap} becomes

$$\sigma_{adj} = \sigma_{PSAP} F_{flow} F_{spot} \qquad (3)$$

where

$$F_{flow} = Q_{indicated}/Q_{flow} \qquad (4)$$

$$F_{spot} = (D_{measured})^2/(5)^2 \qquad (5)$$

$Q_{indicated}$ and Q_{flow} are the flows indicated by the flow meter and the flow measured with an independent flow meter, respectively. $D_{measured}$ is the diameter in millimeters of the aerosol area that is measured independently from the manufacturer-specified area of 5 mm.

Table 2. Uncertainty Analysis of Particle Soot Aerosol Photometer Measurements

Source	Systematic Error	Random Error
Absorption Measurements		
Reference intensity (I_0)	±2%	±2%
Absorption intensity (I)	±2%	±2%
Volumetric flow rate		
Flow measurement	±5%	±1%
Correction factor (F_{flow})	±2%	±2%
Area of Filter		
Area measurement	±2%	±2%
Correction factor (F_A)	±2%	±2%
Scattering coefficient correction		
Scatter coefficient measurement	±5%	±1%
Correction factor (K_1)	±5%	±1%
Absorption correction factor (K_2)	±10%	±1%
RSS[a]	±15%	±5%

[a]RSS denotes root-sum-square. RSS_{total} = ±16%.

[23] Light transmission depends upon light scattered and absorbed by particles on the filter [*Petzold et al.*, 1997; *Bond et al.*, 1999]. The absorption coefficient is derived after removing the effect of scattering. The PSAP has an internal correction factor to account for this factor, but *Bond et al.* [1999] found that an additional correction was needed to decrease the indicated absorption coefficient, that is,

$$\sigma_{corrected} = \sigma_{adj} - K_1\sigma_{sp} \qquad (6)$$

where $K_1 = 0.02$ and σ_{sp} is the scattering coefficient. This same study found that the corrected absorption coefficients, indicated by the instrument, were 22% too high and require an additional correction, that is,

$$\sigma_{apcorrected} = (\sigma_{adj} - K_1\sigma_{sp})/K_2 \qquad (7)$$

where $K_2 = 1.22$. Table 2 summarizes the estimated uncertainties associated with the absorption measurements, where the total RSS of uncertainties is of the order of ±16%.

[24] The specific absorption coefficient σ_{ae} is the ratio of $\sigma_{apcorrected}$ to BC, derived from the EGA technique. The uncertainty in σ_{ae}, using error propagation, is +35%−30%. The BC mass is derived from the PSAP measurements by dividing $\sigma_{apcorrected}$ by σ_{ae}. The RSS of these uncertainties is +38%−34%.

[25] The MC measurements of BC were derived using the combination of absorption measurements and derived σ_{ae}. In order to correct for the aerosol scattering (7), the scattering coefficient was measured at the same time as the absorption coefficient, using a Radiance Research nephelometer that used the same wavelength as the PSAP (550 nm). The largest source of error is the truncation of light scattered in the forward direction, due to the optical configuration of the instrument [*Anderson et al.*, 1996]. This study estimated measurement errors of the order of ±10%. These uncertainties have been factored into the total uncertainty in deriving BC mass from the PSAP.

[26] The importance of using a site-appropriate specific absorption coefficient has been documented in numerous studies [*Liousse et al.*, 1993; *Petzold and Niessner*, 1995; *Petzold et al.*, 1997; *Fuller et al.*, 1999]. The σ_{ae} has been measured over a range of values as small as 2 m^2 g^{-1} and as large as 25 m^2 g^{-1}. The value depends upon the composition of the particles and their size distribution. The BC

values derived in two of the data sets from Germany used in this study are from aethalometer measurements and used a fixed σ_{ae} value of 19 m^2 g^{-1}. We assume that a lower bound on the error in BC derived from the aethalometer is given by the uncertainty analysis for the BC values derived from the PSAP.
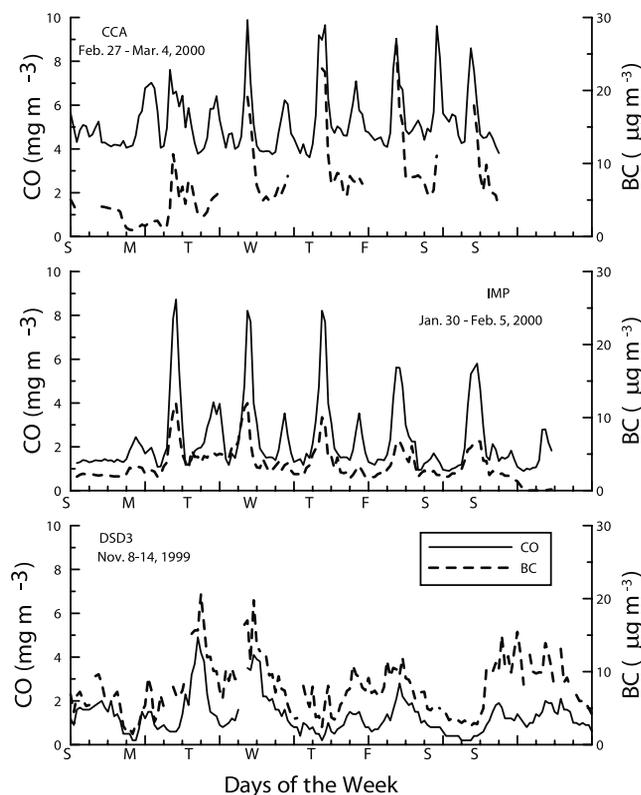
4. Results

[27] There are eight data sets that are used for the BC versus CO comparisons. Table 3 lists the locations, sampling periods, sampling frequency, and method of BC determination. The two data sets from MC are from different locations and time periods. Mexico City (19°15′N, 99°11′W) covers an area of approximately 1300 km^2 and is situated in the southeastern portion of a basin at an average altitude of 2240 m above sea level. Mountains surround the basin on the east, south, and west. A measurement program, intended to investigate the link between BC and CO, was conducted in MC in February and March 2000. The measurement sites are separated by approximately 20 km, one in the north central quadrant of the city, the other in the far southwest. The northern measurements were made from the roof of an office building at the research institute of the national petroleum company, PEMEX (Instituto Mexicano del Petróleo, IMP). The roof is approximately 30 m above the ground, 500 m to the southwest of a six-lane highway that carries heavy car, truck, and bus traffic. The second measurement site was the roof of the Centro de Ciencias de la Atmósfera (CCA) at the Mexican National University (Universidad Nacional Autónoma de México, UNAM) in the southwest sector of the city. The measurements were made in air brought down a 9 m chimney. The combined height of roof and chimney was approximately 30 m, 500 m west of a six-lane highway that also carries heavy traffic of all modes of transportation. In addition, the university subway station is 500 m to the east. This is a location where buses load and unload their passengers throughout most of the workday (approximately 0600–2200 local standard time (LST)). The city government has estimated that more than 50,000 vehicle pass these sites daily [*PROAIRE*, 1997].

[28] The measurements from Germany were taken in Munich, Düsseldorf, Essen, and Duisburg. The latter three cities are in the Ruhr area, a heavily populated and industrialized region in the central western part of Germany. These sites are all situated within 1600 km^2 and apart from the Duisburg station are directly situated next to major highways. Duisburg Buchholz (51.38°N, 6.77°E; altitude, 30 m) is located between a major street and a highway, 350 m and 600 m away, respectively. Düsseldorf Mörsenbroich (51.25°N, 6.80°E; altitude, 38 m) is situated on a traffic island with approximately 35,000 vehicles passing per weekday. Düsseldorf Corneliusstrasse (51.21°N 6.79°E; altitude, 37 m) is located directly next to a busy street and in the middle of two major highways, a kilometer to the NE and SW, respectively. The Essen Ost site (51.45°N, 7.04°E; altitude, 100 m) is on a traffic island in the middle of busy streets, 100 m south of a highway. The equipment for determining BC and CO was placed in a measurement container with the aerosol inlet 3.50 m above the ground for all of these stations.
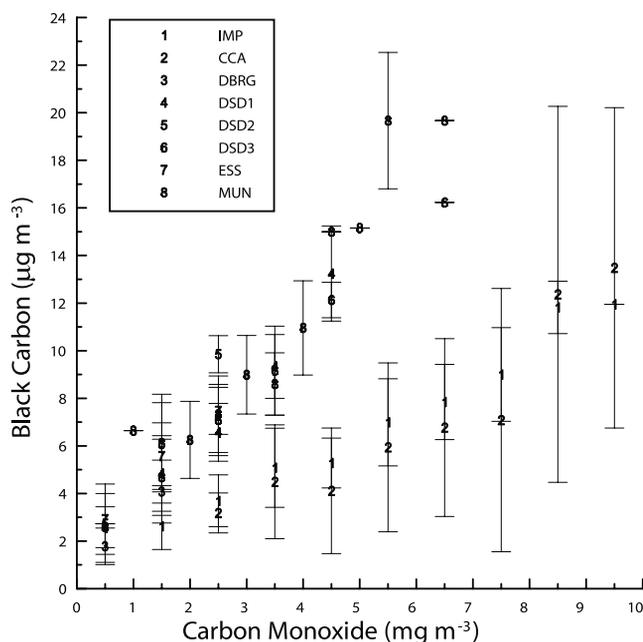
Table 3. Measurement Sites

Name	Location	Sampling Period	Sampling Frequency	Method of Black Carbon Determination
IMP	Instituto Mexicano del Petróleo, north central Mexico City	30 Jan. to 5 Feb. 2000	10 min averages, 24 hours per day	Derivation from σ_{ap}
CCA	Centro de Ciencias de la Atmósfera, UNAM, SW Mexico City	22 Feb. to 10 March 2000	10 min averages, 24 hours per day	Derivation from σ_{ap}
DBRG	Bucholz Station, Duisburg, Germany	11 Jan. to 15 Dec. 1996	124 averages of 24 hours	VDI method
DSD1	Cornelius Strasse, Düsseldorf, Germany	6 Jan. 1997 to 30 Oct. 2000	214 averages of 24 hours	VDI method
DSD2	Mörsenbroich, Düsseldorf, Germany	8–30 Nov. 1999	30 min averages, 24 hours per day	Derivation from σ_{ap}
DSD3	Mörsenbroich, Düsseldorf, Germany	4 Jan. to 13 Aug. 2000	73 averages of 24 hours	VDI method
ESS	Essen, Germany	8 March 1997 to 30 June 2000	275 averages of 24 hours	VDI method
MUN	Munich, Germany	11 Nov. 1992 to 30 April 1993	24 hour averages	Derivation from σ_{ap}

[29] Figure 1 illustrates daily trends in CO and BC at the two MC sites and from the Düsseldorf-Mörsenbroich site (DSD3) where all measurements are averaged in 30 min intervals. All measurements have been adjusted to a standard atmosphere. In general, the daily trends in CO and BC follow one another closely; however, it is interesting to note that the daily, secondary peak in CO seen in the IMP measurements is generally not as pronounced in the BC data. The CO at the German site generally reaches a maximum once a day, but not always at the same time. The CO in MC has an initial peak during the morning rush hour, around 0700 LST, and then a secondary peak during the evening rush hour of 2000 LST. Occasionally, a third peak occurs in CO around 1400 LST that is associated with traffic during the lunch hour. Another feature seen in the BC measurements from both MC and Germany is that the BC always seems to have an elevated "background" level; that is, during periods of minimum CO the BC values are still

Figure 1. The carbon monoxide (CO) and black carbon (BC) values, averaged in 30 min intervals, are shown over representative 7 day periods for (top) Mexico City Centro de Ciencias de la Atmósfera (CCA) site, (middle) Instituto Mexicano del Petróleo (IMP) site, and (bottom) the Germany Mörsenboicher site.

Figure 2. The relation between BC and CO is shown by average values of BC in fixed, 0.5 μg m^{-3} intervals of CO, for the two Mexico City measurement sites and six sites in Germany. The vertical error bars are the standard deviation about the averages.

Table 4. Statistics of Black Carbon Versus CO Regression Analysis

Name	Least Squares Regression Slope	Least Squares Regression Intercept	Coefficient of Determination	N	χ^2
IMP	1.0	1.5	0.97	19	0.75
CCA	1.1	0.5	0.88	16	1.00
DBRG	2.2	1.2	0.95	4	0.06
DSD1	2.4	1.5	0.97	10	0.74
DSD2	2.5	2.2	0.96	6	0.23
DSD3	2.2	2.0	0.99	11	0.11
ESS	2.3	2.4	0.92	6	0.47
MUN	1.8	3.4	0.93	12	0.66

relatively high. DSD3, IMP, and CCA have background levels of about 5, 2, and 5 μg m^{-3}, respectively. The minimum CO levels at IMP and CCA are also higher than at DSD3.

[30] The BC measurements from all the sites were partitioned into CO intervals of 0.5 ppm by calculating the average and standard deviation values of BC found in each of these intervals. Figure 2 shows the average BC values as a function of CO for each of the eight data sets. The values of BC follow approximately the same linear trend with respect to CO at all the German sites. The relation between BC and CO at the MC sites is also linear, but with a different slope than for the German data. The vertical bars at each data point show the standard deviation about the mean BC values within each CO interval.

[31] Table 4 summarizes the statistics of the variance-weighted, regression analysis of each of the data sets, where the slope and intercept define the relation between BC and CO. The coefficient of determination (the square of the correlation coefficient) is a measure of the linearity between the two parameters. The goodness of fit, given by the chi-square parameter, χ^2, is the average of the squared residuals between the best fit line and observations. The coefficients

of determination are all quite high, significant at the $P = 0.01$ level.

[32] The average slope for BC versus CO is 2.2 μg mg^{-1} with an intercept of 2.0 μg mg^{-1} at the German sites. The average slope and intercept from the IMP and CCA measurements are 1.1 and 1.0 μg mg^{-1}, respectively.

[33] Table 5 lists the averages and standard deviations for all the measurement stations. This table, along with Figure 2, shows that the MC measurements vary more than the German data. The average standard deviation for all of the data sets is tabulated in the last row of Table 5. With the exception of the standard deviation of the CCA measurements (60%), the average standard deviations are well within the expected uncertainty in BC measurements, that is, +38%−34%.

5. Discussion

[34] The relationships of BC to CO, from the eight data sets, are well described by first-order linear equations. The slope of the BC to CO regression line found in the German data sets is about twice that from the MC measurements. A number of factors influence the relation between BC and CO, for example, the composition of combusted fuel, the source of combustion, the proximity of the measurement site to the emissions' source, and the local meteorological conditions. The latter two possibilities can probably be discounted as they impact the amount of mixing and dilution during the transit between emission source and measurement site. All the measurements were made in close proximity to the source of emissions with little time for dilution and removal of either CO or BC. For example, on the basis of the average local winds, the both the German and MC measurements were made in air that would have taken less than 5 min to come from the point of BC and CO emission.

[35] Meteorology alters the height of the boundary layer, creates thermal inversions, generates turbulence, and pro-

Table 5. Averages and Standard Deviations of Black Carbon Versus CO[a]

CO	IMP avg	IMP std	CCA avg	CCA std	DBRG avg	DBRG std	DSD1 avg	DSD1 std	DSD2 avg	DSD2 std	DSD3 avg	DSD3 std	ESS avg	ESS std	MUN avg	MUN std
0.5	–	–	–	–	1.78	0.77	2.55	1.45	2.73	0	2.58	0.86	2.92	1.48	–	–
1.0	2.38	0.44	–	–	2.61	1.13	3.41	1.30	4.01	0.54	3.69	1.33	3.93	1.63	6.64	0
1.5	2.62	0.98	–	–	4.08	1.32	4.84	1.59	6.07	1.74	4.68	1.60	5.57	1.40	6.12	2.05
2.0	3.33	1.25	–	–	6.48	0	5.57	1.49	6.34	1.31	5.63	1.41	7.56	1.70	6.25	1.62
2.5	3.69	1.09	3.18	0.84	–	–	6.57	1.22	9.85	0.78	7.09	1.50	7.47	0.99	7.33	1.61
3.0	4.28	1.48	3.51	1.23	–	–	8.19	1.55	11.57	0	7.83	1.27	7.99	0.29	8.99	1.65
3.5	5.08	1.66	4.49	2.39	–	–	9.34	1.34	–	–	9.16	1.87	–	–	8.60	1.31
4.0	4.77	1.46	5.57	3.10	–	–	10.57	1.33	–	–	10.54	1.37	–	–	10.96	1.98
4.5	5.28	1.05	4.11	2.64	–	–	13.24	2.00	–	–	12.13	0.74	–	–	15.00	0
5.0	6.93	2.39	5.82	4.58	–	–	12.01	2.66	–	–	13.52	1.89	–	–	15.16	0
5.5	6.99	1.83	5.94	3.55	–	–	–	–	–	–	–	–	–	–	19.67	2.87
6.0	7.03	1.54	6.51	4.14	–	–	–	–	–	–	–	–	–	–	–	–
6.5	7.84	1.58	6.77	3.74	–	–	–	–	–	–	16.23	0	–	–	19.67	0
7.0	7.81	0.19	7.76	6.02	–	–	–	–	–	–	–	–	–	–	–	–
7.5	9.00	1.97	7.08	5.53	–	–	–	–	–	–	–	–	–	–	–	–
8.0	9.41	2.11	8.66	6.80	–	–	–	–	–	–	–	–	–	–	28.93	0
8.5	11.82	1.10	12.37	7.90	–	–	–	–	–	–	–	–	–	–	–	–
9.0	10.79	1.84	12.37	6.36	–	–	–	–	–	–	–	–	–	–	–	–
9.5	11.95	0	13.48	6.73	–	–	–	–	–	–	–	–	–	–	–	–
10.0	11.79	1.70	15.67	10.23	–	–	–	–	–	–	–	–	–	–	–	–
Avg. std (% of avg)	24%		60%		30%		26%		14%		22%		26%		16%	

[a] Here avg denotes average and std denotes standard deviation.

duces clouds and precipitation. Only the latter condition would possibly impact the BC to CO relationship. The first three meteorological conditions impact mixing rates, but as in the prior argument, this should have little impact on the two species. The presence of clouds and rain could impact BC more than CO if hygroscopic material has coated the BC particles; however, such wet removal processes typically require more time to be effective than would have been possible in the short period between emissions and measurements.

[36] The factor that has the greatest impact on the relative mixture of BC and CO is the composition of the fuel and the type of combustion. From equation (1),we see that the ratio of C_s to CO is given by their relative coefficients, $(m-2a)/2a$. The more carbon atoms in the fuel, the larger the ratio.

[37] Related to the fuel composition is the type of combustion. Studies of different BC sources show that motor vehicles contribute more than 80% of BC to the urban atmosphere [*Muhlbaier and Williams*, 1982; *Muhlbaier and Cadle*, 1989; *Watson et al.*, 1990]. Diesel-powered vehicles may contribute more than 70% to the total BC [*Schauer et al.*, 1999]. According to *Hamilton and Mansfield* [1999], diesel emissions produce 70% to 90% of the BC in western Europe. Similar estimates are not available for MC; however, according to the city government [*PRO-AIRE*, 1997], diesel-burning vehicles consume 12% of the energy used for transportation in MC. The majority of diesel vehicles are buses and large trucks, as very few private cars use diesel. In Germany, however, according to a recent business report [*Alexander's Gas and Oil*, 2000], diesel fuel in 1999 represented 27% of all fuel consumed.

[38] Fuel composition varies somewhat, depending upon the particular refining process; in general, diesel fuel consists of hydrocarbons with $m = 15-30$, whereas gasoline has m values in the range of $8-15$. This is consistent with the fact that larger values of m produce a larger ratio of C_s to CO, where by definition, C_s is directly proportional to the amount of BC. Thus the difference in diesel fuel consumption in MC and Germany likely accounts for the differences in BC to CO ratios. This is substantiated by a recent study of CO and BC emissions from vehicles in two tunnels [*Kirchstetter et al.*, 1999] near San Francisco, California. The ratio of BC to CO in this study was approximately 3 in the tunnel where heavy, diesel truck traffic was 4% of the traffic volume. In the tunnel where heavy trucks were 0.4% of the traffic this ratio was 0.5, supporting the hypothesis that the BC to CO relationship is sensitive to the amount of diesel vehicle emissions relative to gasoline emissions.

[39] It may not be possible to use the relative difference in diesel traffic in different regions to directly scale the BC to CO relationships between sites, as other factors also contribute to BC production. Engine efficiency and load will alter this ratio; that is, more efficient engines produce less CO and BC, and higher engine loading produces more of each of these components. The average atmospheric pressure of MC is 741 mbar compared to 1000 mbar in Germany. This means the average level of oxygen is 25% less in MC than in Germany. The lower oxygen levels imply decreased combustion efficiency and a subsequent increase in BC. Poorly maintained engines, more often found in Mexico than in Germany, will also increase both CO and BC production. The maximum CO values in DSD3, seen in
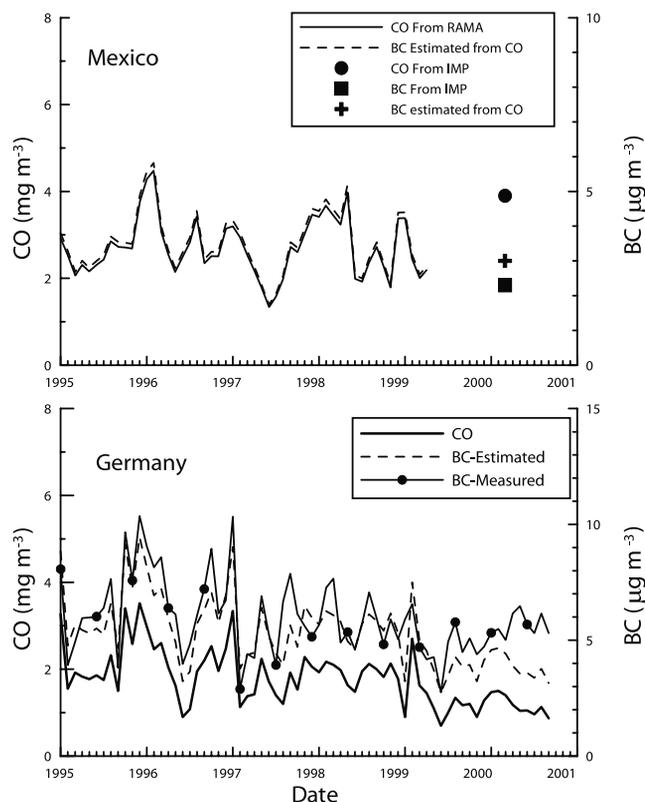
Figure 3. Monthly averages of CO (solid line) and CO-estimated BC (dashed line) are shown over a 6 year period (top) for a site in the SW of Mexico City and (bottom) for the Düsseldorf-Cornelius Street site in Germany. The direct measurements of BC for the site in Germany are plotted as solid circles. Average values of CO, BC, and CO-estimated BC, from the Mexico City CCA site, are shown in the top panel as a solid circle, square, and cross, respectively.

Figure 1, are half the maximum values in MC. Figure 2 also shows that the range of CO values in MC is twice that of Germany. Thus it is the combination of diesel consumption and combustion efficiency that has the largest effect on the BC to CO relationship.

[40] Figure 3 illustrates the utility of CO as a surrogate for BC. Monthly averages over a period of 6 and 5 years are shown for CO (solid lines) and the BC estimated from the CO (dashed line) for measurement sites in MC and Germany. The top panel of Figure 3 shows CO and estimated BC measurements from Pedregal (PED), a city government, air quality monitoring site in the SW of the city. The CO, measured BC, and estimated BC from the winter 2000 field project are plotted in this panel, as well. The bottom panel of Figure 3 is a 6-year record from the Düsseldorf-Cornelius site (DSD1). The solid circles are the measured values of BC.

[41] The CO and BC levels at the German site show a gradual decrease with time, while the average MC level shows little change. In general, the CO and BC reach their maximum values in the winter, when the strongest temperature inversions occur. In summer, with deeper mixed layers and more frequent precipitation, the CO and BC levels are the lowest. The monthly fluctuations in CO and BC for both

measurement sites are of the same order of magnitude, but the average CO value in MC is almost twice that of the German site. The BC levels in MC are about two thirds those in Germany.

[42] The CO-estimated BC values at the German site are generally in good agreement with the measured values. After the middle of 1999, however, the measured values are systematically higher than the estimated ones. This could reflect the increasing use of diesel in private vehicles in Germany. According to the German agency responsible for issuing license tags for vehicles (Kraftfahrt-Bundesamt-Flensburg; http://www.kba.de), the number of diesel cars had increased by 28% from 1999 to 2000. This would change the overall fraction of diesel consumption and the subsequent relationship between BC and CO.

6. Summary and Conclusions

[43] Measurements of BC and CO from urban areas in Germany and Mexico have been evaluated to determine the relationship between these two primary pollutants from motor vehicles. All the data sets show significant BC and CO correlations, and the relationship can be expressed with first-order linear equations. The slope of the regression line between BC and CO, for the six data sets from Germany, is approximately twice the slope found from two measurement sites in Mexico City. Previous studies have shown that diesel combustion produces the majority of BC from vehicle emissions. Diesel consumption is almost 30% of the total fuel consumption in Germany, while it is 12% of fuel consumption in MC. This is indirect evidence that the BC to CO relationship will be most sensitive to the relative fractions of diesel fuel used in an urban area compared to other types of fuel. An offsetting factor in the ratio of BC to CO is the effect of decreased combustion efficiency related to geographical or socioeconomic factors that will increase the emissions of both CO and BC, but not necessarily in the same proportions.

[44] The present study suggests that CO can be used to estimate BC values if information is available about the fraction of diesel fuel used relative to total fuel consumption. If such information is not available, the results from the current data sets imply that an average value of 2 μg mg^{-1} could be used for a rough estimate of BC from CO in urban areas, with an estimated uncertainty of ±50%. This method of estimating BC will be useful for studying the physical processes that lead to the formation and evolution of BC. Emission rates of BC in urban areas can also be estimated from the CO emission rates; for example, in MC the estimated CO emission rate for 1994 was 2.4 megatons (Mt) yr^{-1}. The associated emission rate of BC would be about 2.4 kt yr^{-1}, on the basis of the average CO to BC relation tabulated in Table 4. The BC to CO relationship can be further refined once data sets from other urban areas are acquired, along with additional demographic information that describes patterns of fuel consumption.

References

Ackerman, A. S., O. B. Toon, D. E. Stevens, A. J. Heymsfield, V. Ramanathan, and E. J. Welton, Reduction of tropical cloudiness by soot, *Science*, 288, 1042–1047, 2000.

Alexander's Gas and Oil, 5(4), Germany's oil and energy use in 1999, 2000.

Anderson, T., et al., Performance characteristics of a high-sensitivity, three-wavelength, total scatter/backscatter nephelometer, *J. Atmos. Oceanic Technol.*, 13, 967–986, 1996.

Baumgardner, D., G. B. Raga, G. Kok, J. Ogren, I. Rosas, A. Baez, and T. Novakov, On the evolution of aerosol properties at a mountain site above Mexico City, *J. Geophys. Res.*, 105, 22,443–22,455, 2000.

Bond, T. C., T. L. Anderson, and D. Cambell, Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols, *Aerosol Sci. Technol.*, 30, 582–600, 1999.

Cadle, S. H., and P. J. Groblicki, An evaluation of methods for the determination of organic and elemental carbin in particulate samples, in *Particulate Carbon: Atmospheric Life Cycles*, edited by G. T. Wolf and R. L. Klimisch, pp. 89–108, Plenum, New York, 1982.

Chen, L. W. A., B. G. Doddridge, R. R. Dickerson, J. C. Chow, P. K. Mueller, J. Quinn, and W. A. Butler, Seasonal variations in elemental carbon aerosol, carbon monoxide and sulfur dioxide: Implications for sources, *Geophys. Res. Lett.*, 28, 1711–1714, 2001.

Chylek, P., G. Videen, D. Ngo, R. G. Pinnick, and J. D. Klett, Effect of black carbon on the optical properties and climate forcing of sulfate aerosols, *J. Geophys. Res.*, 100, 16,325–16,332, 1995.

Chylek, P., G. B. Lesins, G. Videen, J. G. D. Wong, R. G. Pinnick, D. Ngo, and J. D. Klett, Black carbon and absorption of solar radiation by clouds, *J. Geophy. Res.*, 101, 23,365–23,371, 1996.

Ellis, E. C., T. Novakov, and M. D. Zeldin, Thermal characterization of organic aerosols, *Sci. Total Environ.*, 36, 261–270, 1984.

Fuller, K. A., W. C. Malm, and S. M. Kreidenweis, Effects of mixing on extinction by carbonaceous particles, *J. Geophys. Res.*, 104, 15,941–15,954, 1999.

Goldberg, E. D., *Black Carbon in the Environment*, John Wiley, New York, 1985.

Hamilton, R. S., and T. A. Mansfield, Airborne particulate elemental carbon, its sources, transport, contribution to dark smoke and soiling, *Atmos. Environ.*, 25, 715–723, 1991.

Hansen, A. D. A., The aethalometer—An instrument for real-time measurement of optical absorption by aerosol particles, *Sci. Total Environ.*, 36, 191–196, 1984.

Hansen, A. D. A., H. Rosen, and T. Novakov, Real-time measurement of the absorption coefficient of aerosol particles, *Appl. Opt.*, 21, 3060–3062, 1982.

Jennings, S. G., T. G. Spain, B. G. Doddridge, H. Maring, B. P. Kelly, and A. D. A. Hansen, Concurrent measurements of black carbon aerosol and carbon monoxide at Mace Head, *J. Geophys. Res.*, 101, 19,447–19,454, 1996.

Kirchstetter, T. W., R. A. Harley, N. M. Kreisberg, M. R. Stolzenburg, and S. V. Hering, On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles, *Atmos. Environ.*, 33, 2955–2968, 1999.

Kuhlbusch, T., A method for determining black carbon in residues of vegetation fires, *Environ. Sci. Technol.*, 29, 2695–2702, 1995.

Lighty, J. S., J. M. Veranth, and A. F. Sarofim, Combustion aerosols: Factors governing their size and composition and implications to human health, *J. Air Waste Manage. Assoc.*, 50, 1565–1618, 2000.

Liousse, C., H. Cachier, and S. G. Jennings, Optical and thermal measurements of black carbon aerosol content in different environments: Variation of the specific attenuation cross-section, sigma (σ), *Atmos. Environ.*, 27A, 1203–1211, 1993.

Meywerk, J., and V. Ramanathan, Observations of the spectral clear-sky aerosol forcing over the tropical Indian Ocean, *J. Geophys. Res.*, 104, 24,359–24,370, 1999.

Muhlbaier, P. K., and S. H. Cadle, Atmospheric carbon particles in Detroit urban area: Wintertime sources and sinks, *Aerosol Sci. Technol.*, 10, 237–248, 1989.

Muhlbaier, P. K., and R. L. Williams, Fireplaces, furnaces and vehicles as emission sources of particulate carbons, in *Particulate Carbon: Atmospheric Life Cycle*, edited by G. T. Wolff and R. Klimsch, pp. 185–205, Plenum, New York, 1982.

Novakov, T., Microchemical characterization of aerosols, in *Nature, Aim and Methods of Microchemistry: Proceedings 8th International Micro-*

chemical Symposium, edited by R. Belcher, M. Grassenbaum, and H. Malissa, pp. 141–165, Springer-Verlag, New York, 1981.

Novakov, T., M. O. Andreae, R. Gabriel, T. W. Kirchstetter, O. L. Mayol-Bracero, and V. Ramanathan, Origin of carbonaceous aerosols over the tropical Indian Ocean: Biomass burning or fossil fuels?, *Geophys. Res. Lett.*, 27, 4061–4064, 2000.

Penner, J. E., and T. Novakov, Carbonaceous particles in the atmosphere: A historical perspective to the Fifth International Conference on Carbonaceous Particles in the Atmosphere, *J. Geophys. Res.*, 101, 19,373–19,378, 1996.

Petzold, A., and R. Niessner, Method comparison study on soot-selective techniques, *Mikrochim. Acta*, 117, 215–237, 1995.

Petzold, A., C. Kopp, and R. Niessner, The dependence of the specific attenuation cross-section on black carbon mass fraction and particle size, *Atmos. Environ.*, 31, 661–672, 1997.

PROAIRE, Programa para mejorar la calidad del air en el valle de México: 1995–2000, 244 pp., Dep. del Distrito Fed. Gobierno del Estado México, Secret. de Medio Ambiente, Recursos Nat. y Pesca y Secret. de Salud, Mexico City, 1997.

Schauer, J. J., M. J. Kleenam, G. R. Cass, and B. R. T. Simoneit, Measurement of emission from air pollution source, 2, C1 through C30 organic compounds from medium duty diesel trucks, *Environ. Sci. Technol.*, 33, 1578–1587, 1999.

Seinfeld, J. H., and S. N. Pandis, *Atmospheric Chemistry and Physics*, 1326 pp., John Wiley, New York, 1998.

Shah, J. J., and J. A. Rou, Carbonaceous species methods comparison study: Interlaboratory round robin interpretation of results, final report to research division, contract A832-154, Calif. Air Resour. Board, Sacramento, 1990.

VDI Verein Deutscher Ingenieure, Number 2465, Part 1, Measurement of soot — Chemical analysis of elemental carbon by extraction and thermal desorption of organic carbon, Beuth, Berlin, 1996.

Watson, J. G., J. C. Chow, L. C. Pritchett, J. Houck, R. A. Ragassi, and S. Burns, Chemical source profiles for particulate motor vehicle exhaust under cold and high altitude operating conditions, *Sci. Total Environ.*, 93, 183–190, 1990.

————————

D. Baumgardner, T. Castro, O. Peralta, G. Raga, and I. Rosas, Centro de Ciencias de la Atmósfera, Universidad Nacional Autonoma de Mexico, Circuito Exterior, Ciudad Universitaria, O4510 Mexico D. F., Mexico. (darrel@servidor.unam.mx)

A. John and T. Kuhlbusch, FB 9/AMT, University of Duisburg, Bismarckstrasse 81, 47057 Duisburg, Germany. (tky@uni-duisburg.de)

A. Petzold, Deutsches Zentrum für Luft und Raumfahrt, Institut für Physik der Atmosphare, Deutsches Zentrum für Luft- und Raumfahrt, 82234 Wessling, Germany.