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

Received 13 March 2001; revised 13 August 2001; accepted 31 August 2001; published 17 September 2002.

[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 $2.2 \, \mu g \, g^{-1}$ for German sites and $1.1 \, \mu g \, g^{-1}$ 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 Ramathan, 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 [Liousses 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.

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 depend-
ing 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 coeffi-
cient 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
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,
and there are possibly other noncombustion sources of
BC; however, the largest fraction of CO that is produced CO
diffuses 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 absorp-
tion of visible light.

3. Measurement and Analysis Methodology

3.1. Instrumentation

[11] Carbon monoxide was measured in both countries
with commercial, non-dispersive, infrared gas filter correla-
tion analyzers (Thermal Environmental Corporation, Frank-
lin, 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 absorp-
tion measurements.

[12] The VDI Part 1 reference method is a two-step
method [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 ther-
mosorption in an atmosphere of N2. 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 CO2 that evolves is measured by coulometric titration
while holding constant the pH of the solution that forms
during a reaction between CO2 and BaClO42-.

[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 coefficient, σae. For these
measurements, a value of σae = 19 m2 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 σae derived from direct measurements of BC that
use thermoseparation [Novakov, 1981; Ellis et al., 1984]. In
this technique, 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
evolved CO₂ 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°C is assumed to be BC. The evolved mass below that temperature is designated OC.

The specific absorption coefficient σ<sub>ae</sub> 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<sub>ae</sub> is 7 ± 0.5 m<sup>2</sup> g<sup>−1</sup> for both of the Mexico City sites.

### 3.2. Error Analysis

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.

The EGA technique used in Mexico City (MC) increases the uncertainty is the separation of OC from BC. The thermograms of evolved CO₂ as a function of temperature. Two, clearly separated peaks normally form, one at a temperature less than 450°C, where the majority of organics volatilize, and a secondary peak above 450°C, where the BC is released from the sample. The thermograms are normally symmetrical, Gaussian in shape, around each of these peaks. However, pyrolytic conversion of organic to black carbon (charring) can bias the derived BC loading above 450°C [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.

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.

The PSAP derives the absorption coefficient, σ<sub>ap</sub>, from Beer’s law of light attenuation, that is,

\[
σ_{ap} = \frac{A}{V} \ln[I_0/I]
\]

where \( I \) is the intensity of light transmitted through an aerosol-loaded quartz 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<sub>ap</sub> becomes

\[
σ_{adj} = σ_{PSAP} F_{flow} F_{spot}
\]

where

\[
F_{flow} = \frac{Q_{indicated}}{Q_{flow}}
\]

\[
F_{spot} = \frac{(D_{measured})^2}{5^2}
\]

\( Q_{indicated} \) 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

<table>
<thead>
<tr>
<th>Source</th>
<th>Systematic Error</th>
<th>Random Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Measurements</td>
<td>±2%</td>
<td>±2%</td>
</tr>
<tr>
<td>Reference intensity (I₀)</td>
<td>±2%</td>
<td>±2%</td>
</tr>
<tr>
<td>Absorption intensity (I)</td>
<td>±2%</td>
<td>±2%</td>
</tr>
<tr>
<td>Volumetric flow rate</td>
<td>±5%</td>
<td>±1%</td>
</tr>
<tr>
<td>Flow measurement</td>
<td>±2%</td>
<td>±2%</td>
</tr>
<tr>
<td>Correction factor (F_C)</td>
<td>±2%</td>
<td>±2%</td>
</tr>
<tr>
<td>Area of Filter</td>
<td>±2%</td>
<td>±2%</td>
</tr>
<tr>
<td>Scattering correction</td>
<td>±5%</td>
<td>±1%</td>
</tr>
<tr>
<td>Correction factor (K_s)</td>
<td>±5%</td>
<td>±1%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>±10%</td>
<td>±1%</td>
</tr>
<tr>
<td>RSS</td>
<td>±15%</td>
<td>±5%</td>
</tr>
<tr>
<td>*RSS denotes root-sum-square. RSS_total = ±16%.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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,

$$\sigma_{corrected} = \sigma_{adj} - K_1 \sigma_{sp}$$

(6)

where $K_1 = 0.02$ and $\sigma_{sp}$ 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,

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

(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%.

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

The MC measurements of BC were derived using the combination of absorption measurements and derived $\sigma_{se}$. 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.

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 $\sigma_{se}$ 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 $\sigma_{se}$ 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 km² 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 Atmosfera (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 busses 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 km² 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 Mörenbroich (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

<table>
<thead>
<tr>
<th>Name</th>
<th>Location</th>
<th>Sampling Period</th>
<th>Sampling Frequency</th>
<th>Method of Black Carbon Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMP</td>
<td>Instituto Mexicano del Petróleo, north central Mexico City</td>
<td>30 Jan. to 5 Feb. 2000</td>
<td>10 min averages, 24 hours per day</td>
<td>Derivation from σ_ap</td>
</tr>
<tr>
<td>CCA</td>
<td>Centro de Ciencias de la Atmósfera, UNAM, SW Mexico City</td>
<td>22 Feb. to 10 March 2000</td>
<td>10 min averages, 24 hours per day</td>
<td>Derivation from σ_ap</td>
</tr>
<tr>
<td>DBRG</td>
<td>Buchholz Station, Duisburg, Germany</td>
<td>11 Jan. to 15 Dec. 1996</td>
<td>124 averages of 24 hours</td>
<td>VDI method</td>
</tr>
<tr>
<td>DSD2</td>
<td>Mörsenbroich, Düsseldorf, Germany</td>
<td>8 – 30 Nov. 1999</td>
<td>30 min averages, 24 hours per day</td>
<td>Derivation from σ_ap</td>
</tr>
<tr>
<td>DSD3</td>
<td>Mörsenbroich, Düsseldorf, Germany</td>
<td>4 Jan. to 13 Aug. 2000</td>
<td>73 averages of 24 hours</td>
<td>VDI method</td>
</tr>
<tr>
<td>ESS</td>
<td>Essen, Germany</td>
<td>8 March 1997 to 30 June 2000</td>
<td>275 averages of 24 hours</td>
<td>VDI method</td>
</tr>
<tr>
<td>MUN</td>
<td>Munich, Germany</td>
<td>11 Nov. 1992 to 30 April 1993</td>
<td>24 hour averages</td>
<td>Derivation from σ_ap</td>
</tr>
</tbody>
</table>

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

[32] The average slope for BC versus CO is 2.2 $\mu g$ mg$^{-1}$ with an intercept of 2.0 $\mu g$ mg$^{-1}$ at the German sites. The average slope and intercept from the IMP and CCA measurements are 1.1 and 1.0 $\mu g$ 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 4. Statistics of Black Carbon Versus CO Regression Analysis

<table>
<thead>
<tr>
<th>Name</th>
<th>Least Squares Regression Slope</th>
<th>Least Squares Regression Intercept</th>
<th>Coefficient of Determination</th>
<th>N</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMP</td>
<td>1.0</td>
<td>1.5</td>
<td>0.97</td>
<td>19</td>
<td>0.75</td>
</tr>
<tr>
<td>CCA</td>
<td>1.1</td>
<td>0.5</td>
<td>0.88</td>
<td>16</td>
<td>1.00</td>
</tr>
<tr>
<td>DDBG</td>
<td>2.2</td>
<td>1.2</td>
<td>0.95</td>
<td>4</td>
<td>0.06</td>
</tr>
<tr>
<td>DSD1</td>
<td>2.4</td>
<td>1.5</td>
<td>0.97</td>
<td>10</td>
<td>0.74</td>
</tr>
<tr>
<td>DSD2</td>
<td>2.5</td>
<td>2.2</td>
<td>0.96</td>
<td>6</td>
<td>0.23</td>
</tr>
<tr>
<td>DSD3</td>
<td>2.2</td>
<td>2.0</td>
<td>0.99</td>
<td>11</td>
<td>0.11</td>
</tr>
<tr>
<td>ESS</td>
<td>2.3</td>
<td>2.4</td>
<td>0.92</td>
<td>6</td>
<td>0.47</td>
</tr>
<tr>
<td>MUN</td>
<td>1.8</td>
<td>3.4</td>
<td>0.93</td>
<td>12</td>
<td>0.06</td>
</tr>
</tbody>
</table>

### Table 5. Averages and Standard Deviations of Black Carbon Versus CO

<table>
<thead>
<tr>
<th>CO</th>
<th>IMP ave</th>
<th>IMP std</th>
<th>CCA ave</th>
<th>CCA std</th>
<th>DBRG ave</th>
<th>DBRG std</th>
<th>DSD1 ave</th>
<th>DSD1 std</th>
<th>DSD2 ave</th>
<th>DSD2 std</th>
<th>DSD3 ave</th>
<th>DSD3 std</th>
<th>ESS ave</th>
<th>ESS std</th>
<th>MUN ave</th>
<th>MUN std</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.38</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
<td>1.78</td>
<td>0.77</td>
<td>2.55</td>
<td>1.45</td>
<td>2.73</td>
<td>1.23</td>
<td>0</td>
<td>2.58</td>
<td>0.86</td>
<td>2.92</td>
<td>1.48</td>
<td>1.0</td>
</tr>
<tr>
<td>1.0</td>
<td>2.62</td>
<td>0.98</td>
<td>-</td>
<td>-</td>
<td>4.08</td>
<td>1.32</td>
<td>4.84</td>
<td>1.59</td>
<td>6.07</td>
<td>1.74</td>
<td>4.68</td>
<td>1.60</td>
<td>5.57</td>
<td>1.40</td>
<td>6.12</td>
<td>2.05</td>
</tr>
<tr>
<td>2.0</td>
<td>3.33</td>
<td>1.25</td>
<td>-</td>
<td>-</td>
<td>6.48</td>
<td>0</td>
<td>5.57</td>
<td>1.49</td>
<td>6.34</td>
<td>1.31</td>
<td>5.63</td>
<td>1.41</td>
<td>7.56</td>
<td>1.70</td>
<td>6.25</td>
<td>1.62</td>
</tr>
<tr>
<td>2.5</td>
<td>3.69</td>
<td>1.09</td>
<td>3.18</td>
<td>0.84</td>
<td>6.57</td>
<td>1.22</td>
<td>9.85</td>
<td>0.78</td>
<td>7.09</td>
<td>1.50</td>
<td>7.47</td>
<td>0.99</td>
<td>7.33</td>
<td>1.61</td>
<td>6.94</td>
<td>1.36</td>
</tr>
<tr>
<td>3.0</td>
<td>4.28</td>
<td>1.48</td>
<td>3.51</td>
<td>1.23</td>
<td>8.19</td>
<td>1.55</td>
<td>11.57</td>
<td>0</td>
<td>7.83</td>
<td>1.27</td>
<td>7.99</td>
<td>0.29</td>
<td>8.99</td>
<td>1.65</td>
<td>10.96</td>
<td>1.98</td>
</tr>
<tr>
<td>3.5</td>
<td>5.08</td>
<td>1.66</td>
<td>4.49</td>
<td>2.39</td>
<td>9.34</td>
<td>1.34</td>
<td>-</td>
<td>-</td>
<td>9.16</td>
<td>1.87</td>
<td>-</td>
<td>-</td>
<td>8.60</td>
<td>1.31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.0</td>
<td>4.77</td>
<td>1.46</td>
<td>5.57</td>
<td>3.10</td>
<td>10.57</td>
<td>1.33</td>
<td>-</td>
<td>-</td>
<td>10.54</td>
<td>1.37</td>
<td>-</td>
<td>-</td>
<td>10.96</td>
<td>1.98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.5</td>
<td>5.28</td>
<td>1.05</td>
<td>4.11</td>
<td>2.64</td>
<td>13.24</td>
<td>2.00</td>
<td>-</td>
<td>-</td>
<td>12.13</td>
<td>0.74</td>
<td>-</td>
<td>-</td>
<td>15.00</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.0</td>
<td>6.93</td>
<td>2.39</td>
<td>5.82</td>
<td>4.58</td>
<td>12.01</td>
<td>2.66</td>
<td>-</td>
<td>-</td>
<td>13.52</td>
<td>1.89</td>
<td>-</td>
<td>-</td>
<td>15.16</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.5</td>
<td>6.99</td>
<td>1.83</td>
<td>5.94</td>
<td>3.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>19.67</td>
<td>2.87</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6.0</td>
<td>7.03</td>
<td>1.54</td>
<td>6.51</td>
<td>4.14</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6.5</td>
<td>7.84</td>
<td>1.58</td>
<td>6.77</td>
<td>3.74</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7.0</td>
<td>7.81</td>
<td>0.19</td>
<td>7.76</td>
<td>6.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7.5</td>
<td>9.00</td>
<td>1.97</td>
<td>7.08</td>
<td>5.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8.0</td>
<td>9.41</td>
<td>2.11</td>
<td>8.66</td>
<td>6.80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8.5</td>
<td>11.82</td>
<td>1.10</td>
<td>12.37</td>
<td>7.90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9.0</td>
<td>10.79</td>
<td>1.84</td>
<td>12.37</td>
<td>6.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9.5</td>
<td>11.95</td>
<td>0</td>
<td>13.48</td>
<td>6.73</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10.0</td>
<td>11.79</td>
<td>1.70</td>
<td>15.67</td>
<td>10.23</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(Here avg denotes average and std denotes standard deviation.)
duce 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.

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 \( \frac{C_m}{s} \) to CO is given by their relative coefficients, \( \frac{m-2a}{2a} \). The more carbon atoms in the fuel, the larger the ratio.

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 [Muhlbaiier and Williams, 1982; Muhlbaiier 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.

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 \( C_m \) to CO, where by definition, \( C_m \) 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 0.5, supporting the hypothesis that the BC to CO relationship is sensitive to the amount of diesel vehicle emissions relative to gasoline emissions.

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 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.

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.
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.

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

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.

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 mg m$^{-1}$ 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.

Acknowledgments. The authors would like to thank the Federal State Environmental Agency of Northrhine-Westfalia for providing the data from Essen, Duisburg, and Düsseldorf-Corneliusstrasse, the Instituto Mexicano del Petróleo for the CO and meteorological data from the IMP measurement site, and Ing. Pedroza and his team at the Red Automática de Monitoreo Atmosférico (RAMA), who provided data from the monitoring network sites. We would also like to offer our thanks to Tica Novakov and Craig Corrigan of the Berkeley National Laboratory for their assistance in building the carbon analyzer used in the analysis of Mexico City filter samples. The comments of one of the anonymous reviewers were very helpful in correcting some errors in the interpretation of the measurements.

References


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

ICC 4 - 8 BAUMGARDNER ET AL.: RELATIONSHIP BETWEEN CO AND BC IN URBAN AREAS


