J2.3 MEGACITIES AS SOURCES OF BLACK CARBON

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1. INTRODUCTION

Megacities are very important sources of fine aerosols and trace gases, which can be important in determining the radiative balance of the atmosphere on urban, regional, and global scales. Aerosols can be classified as primary (i.e., emitted directly from sources into the atmosphere) or secondary. Examples of primary aerosols include carbonaceous soots, wind-blown soils, volcanic ash, and sea-salt aerosols. Secondary aerosols are formed in reactions of gaseous species to form aerosol products. Examples are the reactions of monoterpenes and sesquiterpenes with ozone and other oxidants to form secondary organic aerosols, the oxidation of sulfur dioxide to form sulfuric acid aerosol, subsequent reactions of sulfuric acid aerosol with ammonia to form ammonium sulfates, and the reaction of ammonia with nitric acid to form particulate ammonium nitrate (Finlayson-Pitts and Pitts, 2000).

Aerosols have important direct and indirect effects in determining radiative balance. The direct effects involve the interactions of particles with light (shortwave radiation) and heat (longwave radiation). Radiative effects depend on how strongly the components of the aerosol absorb radiation and on the size of the particles, which determines their ability to scatter the radiation (Finlayson-Pitts and Pitts, 2000). Although most studies of aerosol effects in radiative balance have focused on sulfate aerosols, carbonaceous aerosols are beginning to gain attention because of their importance in the global radiative balance (Gaffney and Marley, 1998; Finlayson-Pitts and Pitts, 2000; Marley et al., 2001; Jacobsen, 2002). Indeed, black carbon (BC) has been found to be an important aerosol contributor to radiative effects on regional and global scales (Jacobsen, 2002). One of the biggest sources of BC is diesel engines in light- and heavy-duty vehicles.

The empirical measurement methods for characterization of carbonaceous aerosols have resulted in a number of nomenclatures for the various components of the material. The “soot” or BC fraction has traditionally been determined by measurement of the absorption of the aerosol. The other organic carbonaceous aerosol materials (OC) are typically weaker absorbers, particularly at wavelengths of 500 nm or longer, and the remaining major components of the tropospheric aerosol burden do not absorb light significantly. Therefore, the aethalometer has been developed into a tool for determining BC levels in the atmosphere (Rosen et al., 1978; Hansen et al., 1984).

“Graphitic” carbon is another term used for BC. We prefer to avoid this term, because thermal analysis of carbonaceous aerosols clearly indicates that BC is not graphitic in behavior. The extensively used term “elemental” carbon (EC) arose from thermal techniques used in attempts to separate semivolatile organic matter from the more refractory material. “Organic” carbon (OC) is another term in general use. Because EC is usually associated with the BC fraction, for this paper we will consider that results of EC determinations are generally close to or equal to the levels of BC (Hansen and McMurry, 1990).

Because the measurement methods are somewhat empirical and are meant to simplify the determinations of the complex mixtures that make up OC and BC or EC, considerable effort has been invested in attempts to resolve sampling artifacts and to distinguish thermal separation approaches from the optical methods. An approach that combines methods would appear to be the most promising for resolving the differences between measurements of BC and EC. These differences are fairly minor compared to problems in determination of the OC fraction, because much of the OC material is semivolatile, and the sampling procedures can cause considerable artifacts (Finlayson-Pitts and Pitts, 2000; Eatough et al., 2003).

2. POTENTIAL IMPACTS OF BLACK CARBON

Black carbon has been shown to be a strong absorber of both visible and infrared radiation (Gaffney and Marley, 1998; Marley et al., 2001). As Jacobsen (2002) noted, BC can have a number of effects, both direct and indirect, on radiative balance and surrounding atmospheric species. The direct effect of BC is to absorb radiation and cause heating. BC is a strong absorber of both ultraviolet and visible radiation and also has strong absorption in the infrared (Gaffney

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and Marley, 1998; Marley et al., 2001). Other effects proposed for BC are as follows (Jacobsen, 2002):

- *Self-Feedback.* The presence of BC and its heating of the air will affect the compositions of surrounding aerosols by decreasing relative humidity and therefore liquid water content of aerosols. Changes in the liquid water content can affect chemical oxidation reactions on the surfaces of aerosols — such as the reaction of hydrogen peroxide with sulfur dioxide to form sulfate aerosols — and can lead to changes in the chemical production of other aerosol species. Changes in size distributions of hygroscopic aerosols due to the effect of BC on relative humidity can alter the light scattering properties of atmospheric aerosols.

- *Photochemistry Effect*. This effect results because BC can absorb ultraviolet and visible photons that otherwise would be available for photochemical processes that produce other important infrared-absorbing species, such as ozone. Direct evidence of this effect has been reported in field observations (Gaffney et al, 2002). The heating caused by BC can also affect important thermal chemical reactions that lead to production or loss of other greenhouse gas species and/or production of aerosols.

- *Smudge Pot Effect*. This effect occurs in the presence of a nighttime inversion layer. BC can heat this layer and maintain a higher temperature, leading to changes in the stability of the boundary layer. This effect gets its name from the use of smudge pots that burned oil to produce BC layers over orange groves and other sensitive crops to heat the air and keep frost damage to a minimum. This effect can lead to feedbacks to the wind fields, and hence windblown sources can be affected as well. This feedback can then affect scattering by other aerosols (Jacobsen, 2002).

- *Daytime Stability*. Daytime BC absorption and heating of air (as in the smudge pot effect), plus light scattering, can cause cooling of the surface and increase the stability of air masses. This leads to reduced surface wind speeds and causes resuspension of aerosols (wind-blown dusts, etc.) and transport. Heating of the air where the BC is located will vent the aerosols into the free troposphere, where they will have longer lifetimes (Jacobsen, 2002).

- *Effect of Clouds on BC Absorption*. The Twomey effect predicts that higher levels of particles will lead to decreasing cloud droplet size, which in turn will cause increased scattering and cooling. The increased scattered radiation can be absorbed by BC in or above clouds, leading to enhanced direct absorption by the BC.

- *In-Cloud Effects — Cloud Lifetimes and Washout*. BC can warm the air in clouds and reduce cloud cover by decreasing relative humidity. This could result in reduced precipitation and washout.

- *Positive Feedbacks of BC on Water Vapor*. Although the heating of air decreases the relative humidity, water vapor that is released is a very strong greenhouse gas and will warm the air further. This warming ultimately increases evaporation from surfaces at the bottom of the atmosphere and increases levels of water vapor in the air. This is comparable to the anticipated effect of carbon dioxide and other greenhouse gases on water vapor content. But, whereas other aerosols scatter shortwave radiation much more than they absorb it, BC will act like a greenhouse gas in this wavelength range (Gaffney and Marley, 1998; Finlayson-Pitts and Pitts, 2000; Marley et al., 2001; Jacobsen, 2002).

- *Surface Albedo Effects*. BC in the air will reduce snowfall, which is important because snow has a high albedo. This is again similar to effects of greenhouse gases. In addition, once deposited on the surface of snow or ice, BC will act to heat that surface, causing melting and reduction in surface albedo.

Other impacts of BC on local-scale wind fields will ultimately affect large-scale meteorological processes. In summary, BC can have a number of important impacts on radiative balance and climate variables, as noted here. Thus, understanding how BC behaves in the atmosphere is important.

3. NEED TO UNDERSTAND SOURCES AND LIFETIMES

The effects of BC aerosol will depend on its concentration in the troposphere, which in turn will depend on source strengths and atmospheric lifetimes.

The main removal processes for particles are diffusion to surfaces, gravitational settling, and hygroscopic growth to form larger droplets that settle out or act as cloud condensation nuclei. Figure 1 shows the relative rates of diffusion and gravitational settling for a model particle system as a function of size. The figure clearly indicates that small particles diffuse rapidly to existing particle surfaces and that particles greater than 2-3 μm in size have settling velocities large enough to rule out long lifetimes in the troposphere. The

stable region for particles 0.1-1 μm in diameter leads to their accumulation.

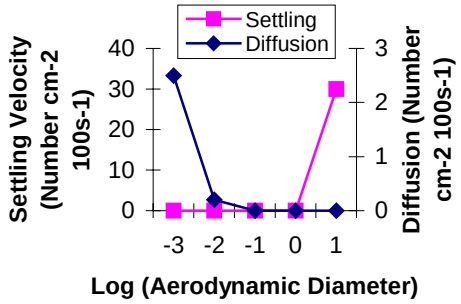

Figure 1. Settling and diffusional loss of particles as a function of aerodynamic diameter. Particles in the size range 0.1-1.0 μm tend to have long lifetimes relative to these processes.

The surface chemistry of particles in the stable region for particle removal (0.1-1.0 μm) is very important in determining their lifetimes in the atmosphere. Hygroscopic aerosols equilibrate with available water vapor in the troposphere. If the water vapor content is high enough, hygroscopic particles and aerosols actively add water and grow in size. If their growth takes them to sizes greater than 2-3 μm, they can be dry deposited or settle out on surfaces. They can also act as cloud condensation nuclei and grow large enough to rain out or be wet deposited, with shorter lifetimes. Thus, the lifetimes will be determined by the hygroscopicity of the aerosol surfaces.

Black carbon is more hydrophobic than many inorganic aerosols such as sulfates and nitrates and is thus expected to have a longer lifetime in the atmosphere with respect to wet removal. Oxidation processes on the surfaces of soots will determine how wettable they are. Wettability is expected to increase with time as the surfaces are oxidized by reactions with OH, ozone, nitrate radical, and oxygen, which may be enhanced by photochemical reactions on surface polynuclear aromatic hydrocarbons or other coatings. We must have a better understanding of the lifetimes of these key species, which currently are modeled as being subject to wet removal at rates similar to those for inorganic aerosol species.

Sources of BC need to be estimated better to determine the concentrations anticipated on regional and global scales. Many current global-scale models are underpredicting the concentrations in regional and urban areas where measurements are available for comparison (Jacobsen, 2002). This discrepancy could be due to underestimated lifetimes of BC (i.e., the lifetimes are longer than currently modeled) or to underpredicted source strengths (i.e., BC emissions from some areas are larger than modeled).

4. POTENTIAL IMPORTANCE OF MEGACITIES

Megacities are areas of urban development exceeding 10 million in population. The ten largest megacities are listed in Table 1. Many of the top ten megacities are in South America and Asia, and Los Angeles is not in the group.

Table 1. The world's top ten megacities.

	Population	
Megacity	1991	2000
Tokyo, Japan	27,245,000	29,971,000
Mexico City, Mexico	20,899,000	27,872,000
Sao Paulo, Brazil	18,701,000	25,354,000
Seoul, South Korea	16,792,000	21,976,000
New York, USA	14,625,000	14,648,000
Osaka, Japan	13,872,000	14,287,000
Bombay, India	12,101,000	15,357,000
Calcutta, India	11,898,000	14,088,000
Rio de Janeiro, Brazil	11,688,000	14,169,000
Buenos Aires, Argentina	11,657,000	12,911,000

A number of other major urban areas that are not defined as megacities can also be considered large sources of BC. For example, the Chicago area (city and suburbs) currently has a population of about 4 million. Our measurements of BC in the Chicago area (Figure 2), obtained by using a seven-channel aethalometer, clearly show significant levels of BC in this area. The BC levels shown are for a typical day at a site on Chicago's South Side, at the Hinds Laboratory at the University of Chicago. This site is not far from Lake Michigan, and the "lake effect" winds keep the BC levels low. Nevertheless, the levels are in the range of 4,000 ng m^{-3} in the early morning. The plume of this material is dispersed over Lake Michigan and results in regional levels of 300-500 nm m^{-3} (Offenberg and Baker, 2000).

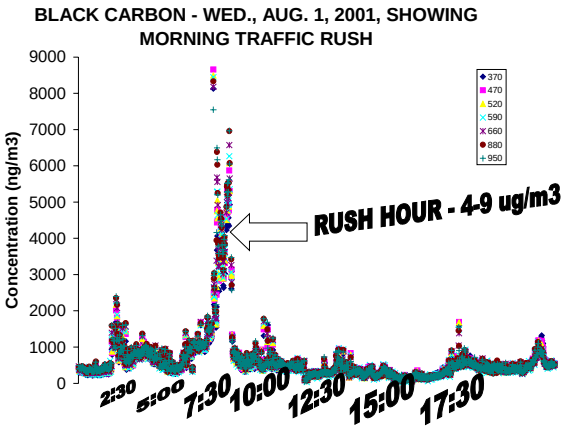

Figure 2. BC data for the Chicago area. The morning rush hour plume has levels of 4,000-9,000 ng m^{-3}. The evening rush hour concentrations reach only about 1,000 ng m^{-3}, because the boundary layer on summer evenings in Chicago rises substantially, leading to significant dilution.

In past work we have noted the potential for the second largest megacity, Mexico City, to act as a major source of both gases and aerosols in the Northern Hemisphere (Gaffney et al., 1999). We estimated that the PM-2.5 aerosol exported out of the city was on the order of 15 megatons per year, on the basis of an average concentration of 50 μg m^{-3}. If 10% of this was BC, we would estimate that BC was being transported out of Mexico City at typical levels of 5,000 ng m^{-3}, or 1.5 megatons of BC per year from one megacity alone.

In April of 2003, as part of the Mexico City Metropolitan Area (MCMA) 2003 air quality study, we obtained measurements of BC at the National Center for Environmental Research and Training (Centro Nacional de Investigación y Capacitación Ambiental, or CENICA), on the Iztapalapa campus of the Universidad Autónoma Metropolitana. Figure 3 shows BC data for a typical days.

The BC data in Figure 3 have not been corrected for atmospheric pressure in Mexico City, which is at an altitude of approximately 8,000 ft. Thus, at standard temperature and pressure the levels will be approximately 20% higher than what the figure shows. This means that BC levels during peak traffic periods are as high as 30,000 ng m^{-3}. The results also show that the levels after mixing, at about 4,000-5,000 ng m^{-3}, are consistent with our estimates from 1997. Measurements during Holy Week showed substantial drops in BC, consistent with decreased diesel vehicular sources. For other major cities, such as Beijing, levels of 6,000-11,000 ng m^{-3} have been reported, compared to modeled values of 700 ng m^{-3} (Jacobsen, 2002). Moscow has had measurements of 3,500-6,800 ng m^{-3}, compared to modeled values of 1,260 ng m^{-3} (Jacobsen, 2002), while Santiago, Chile, has had measurements of BC at levels of ranging up to 30,000 ng m^{-3}, similar to those for Mexico City, as compared to the modeled 90 ng m^{-3} (Jacobsen, 2002).

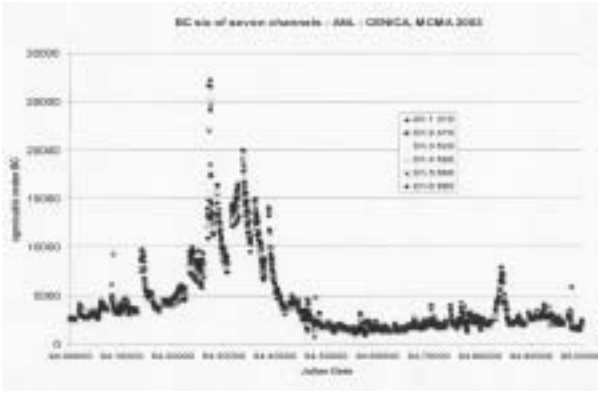

Figure. 3 Preliminary BC data from Mexico City in April of 2003.

CONCLUSIONS

Although our data for Mexico City are preliminary, they are consistent with past measurements. Megacities are clearly large sources of BC. These sources need to be characterized better to support the development of adequate modeling of the effects of BC on weather and climate. Further analyses of our data sets that are under way will be used to estimate levels of BC being exported daily out of the Mexico City area. Data of this type, along with determinations of the lifetimes of BC, will be important for modeling efforts.

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REFERENCES

Eatough, D.J., R.W. Long, W.K. Modey, and N.L. Eatough, 2003: Semi-volatile secondary organic aerosol in urban atmospheres: Meeting a measurement challenge. *Atmos. Environ.*, **37**, 1277-1292.

Finlayson-Pitts, B.J., and J.N. Pitts, Jr., 2000: *Chemistry of the Upper and Lower Atmosphere*. Academic Press.

Gaffney, J.S., and N.A. Marley, 1998: Uncertainties in climate change predictions: Aerosol effects. *Atmos. Environ.*, New Directions contribution, **32**, 2873-2874, and references therein.

Gaffney, J.S., N.A. Marley, M.M. Cunningham, and P.V. Doskey, 1999: Measurements of peroxyacyl nitrates (PANs) in Mexico City: Implications for megacity air quality impacts on regional scales. *Atmos. Environ.*, **33**, 5003-5012.

Gaffney J.S., N.A. Marley, P.J. Drayton, P.V. Doskey, V.R. Kotamarthi, M.M. Cunningham, J.C. Baird, J. Dintaman, and H.L. Hart, 2002: Field observations of regional and urban impacts on NO_2, ozone, UV-B, and nitrate radical production rates: Nocturnal urban plumes and regional smoke effects. *Atmos. Environ.*, **36**, 825-833, and references therein.

Hansen, A.D.A., and P.H. McMurry, 1990: An intercomparison of measurements of aerosol elemental carbon during the 1986 Carbonaceous Species Method Comparison Study. *J. Air Waste Man. Assn.* **40**, 894-895.

Hansen, A.D.A, H. Rosen, and T. Novakov, 1984: The aethalometer — an instrument for the real-time measurement of optical absorption by aerosol particles. *Sci. Total Environ.* **36**, 191-196.

Jacobsen, M.Z., 2002: Control of fossil-fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming. *J. Geophys. Res.*, **107**, D19, 4410-4431, and references therein.

Marley, N.A., J.S. Gaffney, J.C. Baird, C.A. Blazer, P.J. Drayton, and J.E. Frederick, 2001: The determination of scattering and absorption coefficients of size-fractionated aerosols for radiative transfer calculations. *Aerosol Sci. Technol.*, **34**, 535-549, and references therein.

Offenberg, J.H., and J.E. Baker, 2000: Aerosol size distributions of elemental and organic carbon in urban and over-water atmospheres. *Atmos. Environ.*, **34**, 1509-1517.

Rosen, H., A.D.A. Hansen, L.A. Gundel, and T. Novakov, 1978: Identification of the optically absorbing component in urban aerosols, *Appl. Opt*. **24**, 3859-3861.