Observation of carbonaceous aerosols and carbon monoxide at a suburban site: Implication for an emission inventory

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ABSTRACT

Carbonaceous aerosols consist of elemental carbon (EC) and organic carbon (OC), accounting for a significant fraction of fine particulate matter ($PM_{2.5}$) in the atmosphere. Recent studies strongly suggest the link between carbonaceous aerosols and many health effects of $PM_{2.5}$. As part of Maryland Aerosol Research and Characterization (MARCH-Atlantic) study, 24-hour EC and OC concentration measurements were made at Fort Meade, MD (39.10°N 76.74°W; elevation 46 m MSL), a suburban site in the Baltimore-Washington corridor, during July 1999, October 1999, January 2000, April 2000 and July 2000. Carbon monoxide (CO) was also measured nearly continuously over the period. The strong correlation between EC and CO in every month suggests common or proximate sources, likely traffic emissions. The EC versus CO slope, however, varies in different seasons and is found to increase with ambient temperature. EC source strength may peak in summer. OC shows strong correlation with EC only in winter, suggesting that OC is also of the same primary sources during wintertime. Our findings offer a test of emission inventories of EC and primary OC for North America. By using the well established emission inventory for CO as well as EC/CO and OC/EC ratios found in this study, EC and primary OC emission over North America are estimated at 0.31±0.12 Tg yr^{-1} and 0.74±0.29 Tg yr^{-1}, respectively, in reasonable agreement with prior inventories based on emission factors and fuel consumption.

INTRODUCTION

In recent years, there is an increasing concern that carbonaceous aerosols, including elemental and organic carbon (EC and OC) may play an important role in climate and health effect of fine particulate matter ($PM_{2.5}$). In many continental areas, carbonaceous aerosols are found to be the second major fraction of ambient fine PM after sulfate. EC and OC could contribute substantially to the absorption and scattering of radiation in the troposphere and cause direct forcing to the climate system. Additionally, carbonaceous aerosols contain many toxic compounds that could risk the health of susceptible and elderly individuals. A source inventory calculation is crucial in estimating such influences of carbonaceous aerosols.

EC, sometimes referred to as soot or black carbon (BC), is only emitted directly from combustion process. Fossil fuel and biomass burning dominate EC emission but their relative contributions vary spatially and temporarily. In North America, fossil fuel combustion, especially vehicles with diesel engines, are believed to dominate EC production. Carbon

monoxide (CO) is primary gas-phase pollutant subjected to long-term monitoring. In the United States, ~80% of CO emission can be attributed to on-road and non-road engines and vehicles [*USEPA*, 1997]. Assuming that vehicles equipped with diesel engines generally account for a fixed fraction of total traffic, one would expect that ambient EC is well correlated with CO. Primary OC originates from biogenic sources and anthropogenic sources, usually along with EC. There is also secondary OC coming from oxidation of hydrocarbons in the atmosphere. Long-term and concurrent measurements of EC, OC and CO at one site close to sources can help understand the emission features and provide tests to current emission inventories.

One of the goals of the MARCH-Atlantic study is to determine the characteristics and possible origins of regional aerosols. In this paper, we present the measurements of EC, OC, and CO at Fort Meade (FME), MD (39.16°N 76.51°W; elevation 46 m MSL) from June 1999 to July 2000 and investigate their seasonal variations. FME is in the middle of the Baltimore-Washington (B-W) corridor, a highly populated and industrialized area of the United States. Total $PM_{2.5}$ mass, key anions/cations (nitrate, sulfate and ammonium), sulfur dioxide, nitric acid and ammonia were also measured simultaneously. These results will be published elsewhere.

METHODS

The sampling site is within a broad open field, about 100 m from the closest minor road. Two major highways (MD-295 and I-95) run 2 km and 4 km to its west, respectively. EC and OC were measured by a sequential filter sampler (SFS) on a platform 2.5 m above the surface. The SFS was equipped with a $PM_{2.5}$ inlet that excluded particles larger than 2.5 μm in diameter and was programmed to sample air for 24 hours through sets of filter packs replaced manually every third day. Each filter pack contains two quartz filters in series [*Chow et al.*, 1996]. The exposed filters, well sheltered, remained on site for 0.5 to 2.5 d before being collected, refrigerated, and then shipped to Desert Research Institute, Reno, NV, for analysis. The two filters in each pack were analyzed by thermal optical reflectance method [*Chow et al.*, 1993] to determine EC and OC. EC and OC data presented here are exclusively from the front filters. Analytical uncertainty of each single measurement is ~ 10%. The measurements were made in five intensive periods, July 1999 (7/1-8/3), October 1999 (9/30-11/2), January 2000 (12/30-2/1), April 2000 (3/31-4/30) and July 2000 (6/30-7/31), chosen to represent different seasons.

CO instruments at FME were kept in a climate-controlled shelter with a glass/Teflon sample tubing running from the instruments to an air inlet 4 m above the surface. CO has been measured continuously since June 1999 by a commercial nondispersive infrared monitor, modified to improve sensitivity and selectivity [*Dickerson and Delany*, 1988]. The detection limit for this instrument is ~ 10 ppbv CO (95% confidence). Calibrations were made before and after each intensive period in the laboratory with bottled standards traceable to National Institute of Standards and Technology. The calibration factors were found to vary by ~1% over the entire period.

RESULTS & DISCUSSIONS

The diurnal profiles of CO at FME for the five intensive periods are shown in Figure 1. A distinct AM peak clearly corresponds to morning rush hour, while the PM rush hour signal though somewhat less distinct is still present. This is consistent with the assumption that on-road vehicles dominate CO emission. Figure 2 and Table 1 show the monthly statistics of CO. Within

the period of our study, the greatest CO mixing ratio occurred in winter while the lowest appeared in summer. Since the lifetime of CO is relatively long (~1 to 3 mo or longer [*Holloway et al.*, 2000]) with respect to synoptic time scale (~4 d), the seasonal change in lifetime has little impact on ambient CO level near source regions. At FME, with no obvious variation regarding CO source strength, day-to-day variation of CO could be mostly influenced by meteorological conditions, especially boundary layer depth [*Glen et al.*, 1996]. The boundary layer usually becomes deeper in summer because of greater solar insolation and stronger turbulent eddies. This dilutes pollutants released at the surface and results in lower ambient concentrations. The relatively low CO in January 2000 (compared to those in December and February), however, is believed due to more frequent strong winds that enhanced the dispersion of pollutants. Hourly-averaged surface wind speeds were recorded at Baltimore-Washington International (BWI) airport, about 15 km northeast of FME, and strong winds (wind speed > 5 m/s) were nearly twice as probable in Jan. 2000 as in Dec. 1999 and Feb. 2000 (30% versus ~15%).

At FME, EC levels show little evidence of a seasonal cycle; the correlation between 24-hr average CO and EC is strong ($r \sim 0.7$-0.9), especially in winter (Table 1). An orthogonal fit was also calculated but showed no significant difference. In such a source-dominated environment, the tight correlations suggest that EC and CO have proximate sources, likely traffic emissions. The change in EC versus CO slope may be due to seasonal variation of EC source/sink strength. EC is removed from atmosphere primarily through precipitation scavenging after it is internally mixed with salts (such as sulfate) and becomes soluble. Wet removal is usually faster in summer when sulfate concentration and the rate of precipitation are greater in this region. Boundary layer development, which causes seasonal variation of CO, also influences the distribution of fine particles. EC concentration should also have a distinguishable minimum in summer if its sources remain constant. The observations, however, suggest greater emissions of EC in summer, and this produces higher EC versus CO slopes in summer.

Ambient temperature may play a role on EC production. A scatter plot of EC versus CO categorized according to daily mean temperatures (Figure 3) shows good separation of data for the highest and lowest temperatures. The EC/CO slope seems to increase with ambient temperature. July 1999 was unusually hot in the Mid-Atlantic region. The daily mean temperature in 25 out of 34 sampling days was at or above 25°C (the recent 30 year climate norm) at BWI. July 2000 was cooler with only 7 out of 32 sampling days at or above 25°C. Both the seasonal variation in EC/CO slope and the difference between the two summers could be linked to temperature.

OC shows a seasonal cycle opposite to that of CO, with maximum concentration of OC in the summer. OC is positively correlated with EC, and the correlation coefficient reaches a maximum ($r^2 = 0.91$) in winter (Table 1). This suggests that, in cooler months, the major fraction of OC is generated as primary particles along with EC. *Liousse et al.*, [1996] suggests that fossil fuel combustion is a major source of OC, and our observations support this contention, at least in winter. In summer, due to higher temperatures and greater levels of solar isolation, oxidants and biogenic hydrocarbons reach maximum concentrations. The higher OC level and weak correlation of OC with EC and CO suggest that gas to particle conversion produces substantial amounts of secondary OC in the warmer months. There is a significant difference in monthly mean OC levels between July 1999 and July 2000 while EC levels stay close. Again, this could be linked to a much cooler weather pattern in July 2000.

The tight correlation between EC and CO observed at FME offers a test of the EC emission inventory for North America. The annual average and standard deviation of EC versus CO slopes

found from the five intensive periods is 0.0034±0.0013. Annual CO emission in North America, including United States and Canada, is about 90 Tg (CO) [*USEPA*, 1997]. Therefore, EC emission in North America is estimated at $90 \times (0.0034 \pm 0.0013) = 0.31 \pm 0.12$ Tg (EC) yr^{-1}. This value is smaller than a previous estimate, 0.55 Tg (BC) yr^{-1} [*Cooke et. al.*, 1999], but that estimate was for 1984, and controls have become stricter since then. Assuming that OC/EC ratio of their sources remains close throughout the year, ambient OC/EC ratio in winter can be used to estimate primary OC emission in North America. This is approximately $2.4 \times (0.31 \pm 0.12) = 0.74 \pm 0.29$ Tg (OC) yr^{-1}, comparing to an estimate of 0.48 Tg (OC) yr^{-1} from fossil fuel combustion [*Cooke et. al.*, 1999]. Since relative source strengths of EC, OC and CO as well as controlling meteorology could vary over North America, multi-location monitoring of EC and CO is essential to examine emission inventories of EC or OC from EC/CO and OC/EC ratios. Our results suggest that the temperature dependence can be an important consideration in such an effort.

CONCLUSIONS

The seasonal variation of EC, OC and CO has been observed at a suburban site within the B-W corridor during 1999-2000. The strong correlation between 24-hr average CO and EC implies proximate sources, most likely traffic emissions. A relatively uniform EC concentration throughout the year suggests stronger source strength in the summer. The EC/CO slope is found to increase with ambient temperature. Strong correlation between OC and EC is only observed in winter, suggesting OC is of the same primary sources during wintertime. As a first step toward evaluating the release of EC and primary OC over North America, we use the measured EC/CO and OC/EC ratios to estimate emissions of 0.31 ± 0.12 Tg (EC) yr^{-1} and 0.74 ± 0.29 Tg (OC) yr^{-1}, in reasonable agreement with an existing emission inventory.

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KEYWORD

Carbonaceous aerosols
Emission Inventories
$PM_{2.5}$

Table 1. Seasonal means and standard deviations of 24-hr average CO, EC and OC obtained at FME during five representative months. Linear regressions between EC and CO are also presented.

Sampling period	Mean CO ±1σ (ppbv)	Mean EC ±1σ (μg m^{-3})	Linear regression fit* and r^2 (EC vs. CO)	Mean OC ±1σ (μg m^{-3})	r^2 (OC vs. EC)
Jul. 99 (summer)	246±48	1.2±0.4	[EC]=0.0067[CO]-0.70 r^2=0.70	4.2±1.2	r^2=0.29
Oct. 99 (fall)	368±123	1.1±0.5	[EC]=0.0027[CO]-0.07 r^2=0.76	2.7±1.3	r^2=0.57
Jan. 00 (winter)	376±169	1.1±0.7	[EC]=0.0029[CO]-0.35 r^2=0.84	2.8±1.7	r^2=0.91
Apr. 00 (spring)	260±61	0.7±0.3	[EC]=0.0027[CO]-0.16 r^2=0.52	2.3±1.1	r^2=0.53
Jul. 00 (summer)	261±51	1.1±0.4	[EC]=0.0041[CO]-0.14 r^2=0.48	3.2±0.9	r^2=0.34

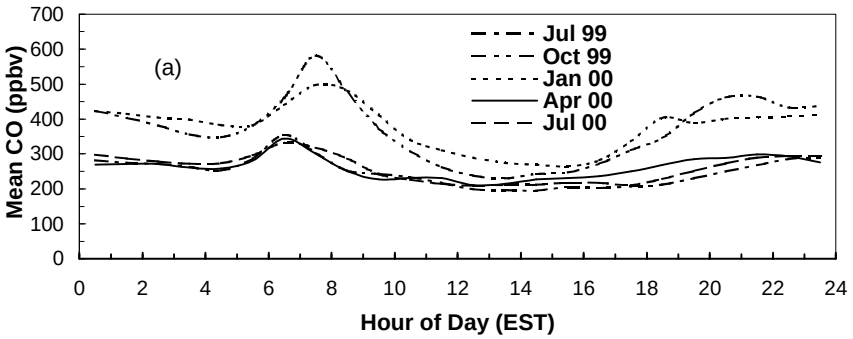

Figure 1. Averaged diurnal variations in CO at 1-hr resolution for five intensive periods at FME, Maryland.

* CO concentrations are converted to μg m^{-3} based on daily mean temperature before regression.

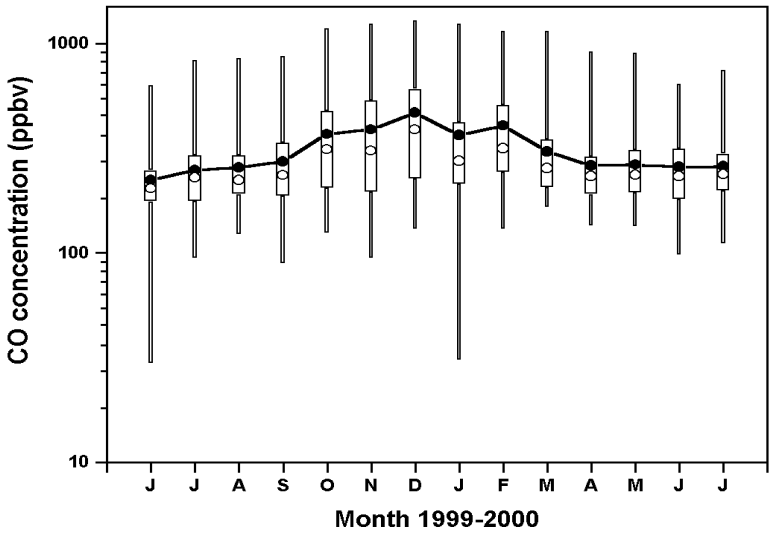

Figure 2. Monthly variation in CO and SO_2 at FME. Box plots for each month show statistical data based on 1-hr averages. Mean values are indicated by black circles and median values by white circles. Boxes indicate the quartiles and vertical bars indicate the maximum and minimum.

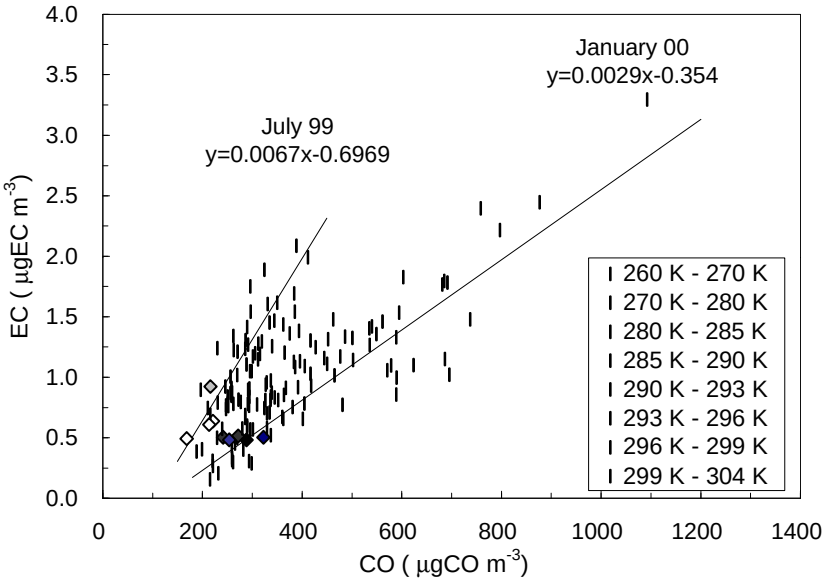

Figure 3. Scatter plot of 24-hr average EC vs. 24-hr average CO over five intensive periods. The solid lines indicate the linear regression for July 1999 and January 2000.

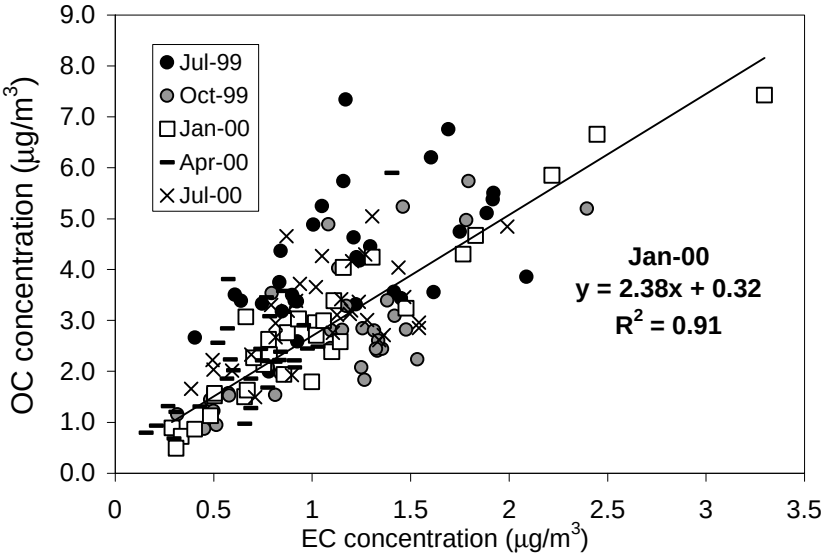

Figure 4. Scatter plot of 24-hr average OC versus EC at FME. The solid line indicates the linear regression fit of data during January 2000.