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Seasonal variations in elemental carbon aerosol, carbon monoxide and sulfur dioxide: Implications for sources

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Abstract. As part of Maryland Aerosol Research and CHaracterization (MARCH-Atlantic) study, measurements of 24-hr average elemental carbon (EC) aerosol concentration were made at Fort Meade, Maryland, USA, a suburban site within the Baltimore-Washington corridor during July 1999, October 1999, January 2000, April 2000 and July 2000. Carbon monoxide (CO) and sulfur dioxide (SO_2) were also measured nearly continuously over the period. Tight correlation between EC and CO in every month suggests common or proximate sources, likely traffic emissions. The EC versus CO slope varies in different seasons and generally increases with ambient temperature. The temperature dependence of EC/CO ratios suggests that EC source strength peaks in summer. By using the well established emission inventory for CO, and EC/CO ratio found in this study, EC emission over North America is estimated at 0.31±0.12 Tg yr^{-1}, on the low end but in reasonable agreement with prior inventories based on emission factors and fuel consumption.

Introduction

Elemental carbon (EC), sometimes referred to as black carbon (BC) or soot, is a component of carbonaceous particles emitted into the atmosphere, predominantly during combustion. This material absorbs strongly in the visible, near UV and near IR due to its graphitic microcrystalline structure [*Rosen et al.*, 1978]. Among aerosol species, EC contributes substantially to absorption of radiation in the troposphere, causing visibility reduction and altering radiation budgets, which could impact climate [*Kaufman et al.*, 1997] and photochemistry [*Dickerson et al.*, 1997]. A source inventory calculation is crucial in estimating such influences of EC.

Globally, EC is primarily anthropogenic, coming from fossil fuel combustion and biomass burning [*Penner et al.*, 1993; *Cooke et al.*, 1999]. Atmospheric EC generally exists as submicrometer particles [*Venkataraman et al.*, 1994] and is a component of $PM_{2.5}$ (particles up to 2.5 μm in aerodynamic diameter), a proposed criteria air pollutant. In North America, fossil fuel combustion, especially vehicles with diesel engines, are believed to dominate EC production. Sulfur dioxide (SO_2) and carbon monoxide (CO) are both primary gas-phase pollutants. In the United States, ~80% of SO_2 is emitted from point sources, such as power plants, while ~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 better correlated with CO than with SO_2. Long-term and concurrent measurements of EC, CO and SO_2 at one site close to their 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, CO and SO_2 at Fort Meade (FME), MD (39.10°N 76.74°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), organic carbon (OC), nitric acid and ammonia were also measured simultaneously. These results will be published elsewhere.

Experimental Techniques

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 was 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

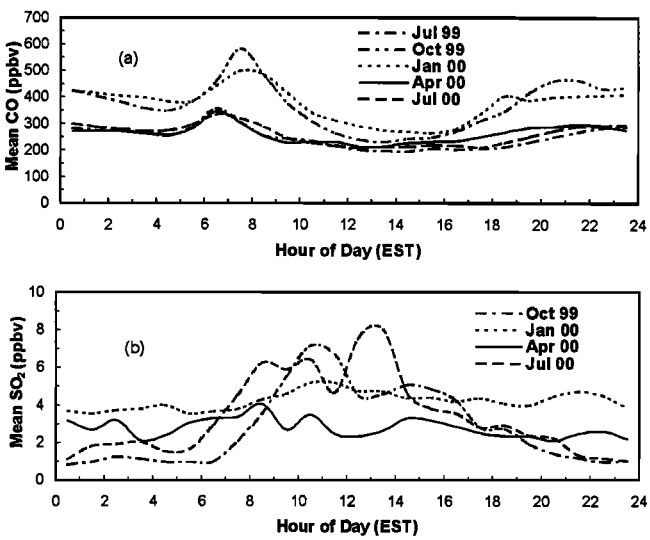

Fig. 1. Averaged diurnal variations in (a) CO and (b) SO_2 at 1-hr resolution for five intensive periods at FME, Maryland.

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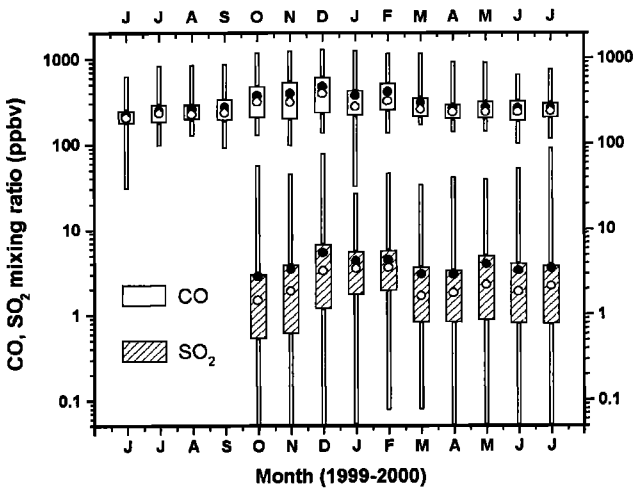

Fig. 2. Monthly variation in CO and SO_2 at FME. Box plots for each month show statistical data based on 1-hr averages. Mean values are indicated by black circles and median values by white circles. Boxes indicate the quartiles and vertical bars indicate the maximum and minimum.

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 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 and SO_2 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]. SO_2 measurements began in October 1999 via a modified commercial pulsed UV fluorescence instrument [*Luke*, 1997]. The detection limit for CO and SO_2 is 10 ppbv and 0.1 ppbv, respectively (95% confidence). Calibrations for both instruments 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% for CO and ~10% for SO_2 over the entire period.

Results & Discussion

The diurnal profiles of CO and SO_2 at FME for the five intensive periods are shown in Fig. 1. For CO, 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. There is only one, mid-day peak in the SO_2 diurnal profile. A previous study [*Stehr et al.*, 2000] suggests that long-range transport from the industrialized Midwest could be a dominant source of SO_2 observed over the Mid-Atlantic region. The highest SO_2 levels appear around noon when the boundary layer is deep and SO_2 aloft can be more effectively mixed down to the surface.

Figure 2 and Table 1 show the monthly statistics of CO and SO_2. Within the period of our study, greatest CO and SO_2 mixing ratios occurred in winter while lowest CO level 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 appears to have 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 (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%). The lifetime of SO_2 (days to weeks) is shorter and the observed winter maximum could result from lower OH and H_2O_2 [*Sakugawa et al.*, 1990], essential for oxidation of SO_2 in the gaseous or aqueous phase. This agrees with observations that the ratio of SO_2 to sulfate (a product from oxidation of SO_2) is 2-4 times larger in winter than in summer [*IMPROVE*, 2000].

Unlike sulfate, EC is generated as primary particles. At FME, EC levels show little evidence of a seasonal cycle (Table 1). The correlation between 24-hr average SO_2 and EC is generally weak (r ~ 0.1-0.3) while the correlation between 24-

Table 1. Seasonal means and standard deviations of 24-hr average CO, SO_2 and EC obtained at FME during five representative months. Linear regressions between EC and CO are also presented.

Sampling period	Mean SO_2 ±1σ (ppbv)	Mean CO ±1σ (ppbv)	Mean EC ±1σ (μg m^{-3})	Linear regression fit* and r^2
Jul. 99 (summer)	-	246±48	1.2±0.4	[EC]=0.0067[CO]-0.70 r^2=0.70
Oct. 99 (fall)	2.7±2.2	368±123	1.1±0.5	[EC]=0.0027[CO]-0.07 r^2=0.76
Jan. 00 (winter)	4.3±2.3	376±169	1.1±0.7	[EC]=0.0029[CO]-0.35 r^2=0.84
Apr. 00 (spring)	2.7±1.8	260±61	0.7±0.3	[EC]=0.0027[CO]-0.16 r^2=0.52
Jul. 00 (summer)	3.4±2.9	261±51	1.1±0.4	[EC]=0.0041[CO]-0.14 r^2=0.48

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

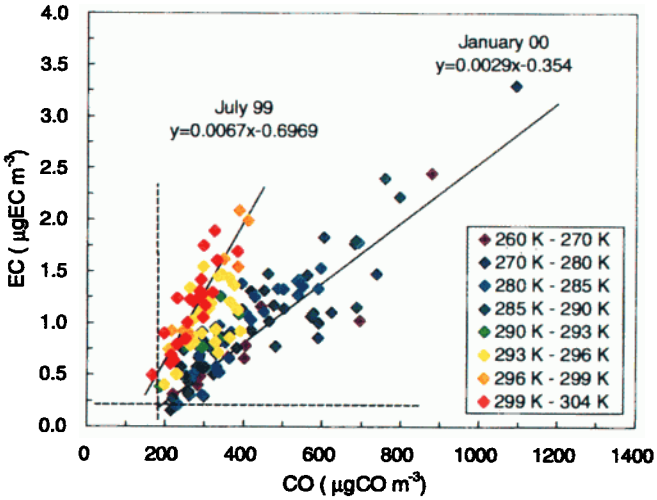

Fig. 3. Scatter plot of 24-hr average EC vs. 24-hr average CO over five intensive periods. The solid lines indicate the linear regression for July 1999 and January 2000. Selected background EC and CO levels are shown as dashed lines.

hr average CO and EC is much stronger (r ~ 0.7-0.9), especially in winter. The standard regression fits and r^2 between EC and CO are listed in 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 that 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 (Fig. 3) shows good separation of data for the highest and lowest temperatures. 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.

To further investigate the seasonal variation of EC and CO source strength, it is necessary to consider their background levels. Based on Fig. 3, values of 150 ppbv (~180 μg m^{-3}) CO and 0.2 μg m^{-3} EC are selected as backgrounds here. These values are close to the observations at Shenandoah National Park (SNP). SNP is at 1100 m elevation (MSL) in rural Virginia, generally upwind of the B-W corridor and can be considered representative of regional air quality. At SNP, CO [*Hallock-Waters et al.*, 1999] and EC [*IMPROVE*, 2000] were measured during 1994-1997. During this period, the 25th percentile of CO and EC, indicative regional background, are 154 ppbv (~185 μg m^{-3}) and 0.23 μg m^{-3}, respectively. The background levels are less sensitive to boundary layer depth, showing only minor seasonal variation and little diurnal variation in the case of CO.

ΔEC and ΔCO were then calculated by subtracting background EC and CO levels from FME data. To minimize influences caused by uncertainty in our measurements and assumed backgrounds, data points were omitted if ΔEC < 0.2 μg m^{-3} (experimental detection limit ~ 0.1 μg m^{-3}) or ΔCO < 25 μg m^{-3} (roughly the seasonal variation in regional backgrounds). Figure 4 shows ΔEC/ΔCO versus ambient temperature. ΔEC/ΔCO seems to remain relatively constant when temperature is below 290K (17°C) but increases rapidly with temperature on hotter days. This explains not only the larger EC/CO slopes but also their weaker correlations in summer. Small adjustments on backgrounds (±0.1 μg m^{-3} for EC; ±30 μg m^{-3} for CO) have limited influence on this figure.

The temperature dependence of ΔEC/ΔCO suggests that the EC emission increases with temperature once it exceeds a threshold. *Ladommatos et al.* [1998] demonstrated that increasing the temperature of air entering diesel engines generally increases particulate emission. *Human et al.* [1990] showed that a 20% decrease in air density due to the effect of high altitude could lead to a 2-4 folds increase in particulate matter released from heavy-duty diesel engines. This correlation could be highly nonlinear if it results from changes in air-fuel ratio [*Nuti*, 1998]. The ambient temperature difference between summer and winter in the B-W corridor can produce more than 10% change in intake air density and may contribute to the higher EC/CO slope observed in summer. Diesel emissions have little impact on ambient CO levels, but a fraction of EC and CO may be generated from poorly-running gasoline vehicles and the role of temperature in these processes warrants further investigation.

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 U. S. and Canada, is about 90 Tg (CO) [*USEPA*, 1997]. Therefore, EC

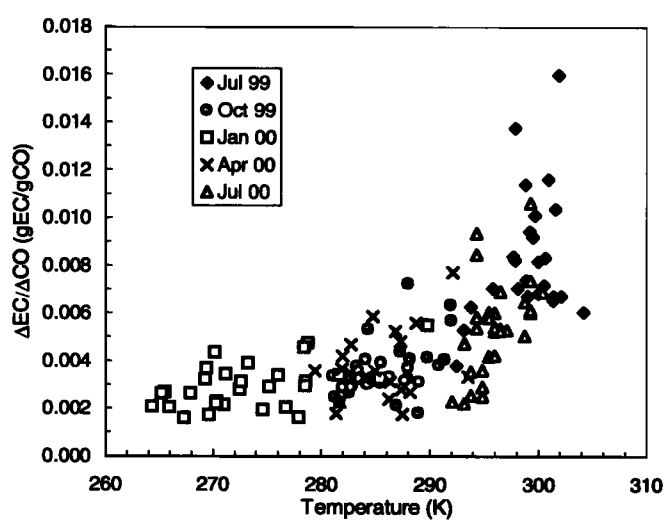

Fig. 4. Scatter plot of ΔEC/ΔCO ratio versus daily mean ambient temperature over five intensive periods, showing the apparent increase in EC emission at high temperature.

emission in North America is estimated at 90 × (0.0034 ±0.0013) = 0.31±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. Moreover, since relative source strengths of EC 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 from EC/CO ratios. Our results suggest that the temperature dependence can be an important consideration in such an effort.

Conclusion

The seasonal variation of EC, SO_2 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. After subtraction of respective background levels, the EC/CO ratio is found to increase with ambient temperature above 290K. A possible explanation is elevated diesel emissions on hot days due to low intake air density. As a first step toward evaluating the release of EC over North America, we use the measured EC to CO ratios to estimate emission of 0.31±0.12 Tg (EC) yr^{-1}, at the low end but in reasonable agreement with an existing emission inventory.

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