

PMEL OC/EC aerosol sampling methods for NEAQS 2004

December 30, 2004

1. Inlet

Aerosol particles were sampled 18m above the sea surface through a heated mast that extended 5 m above the aerosol measurement container. The mast was capped with a cone-shaped inlet nozzle that was rotated into the relative wind to maintain nominally isokinetic flow and minimize the loss of supermicron particles. Air was drawn through the 5 cm diameter inlet nozzle at $1 \text{ m}^3 \text{ min}^{-1}$ and down the 20 cm diameter mast. The lower 1.5 m of the mast were heated to dry the aerosol to a relative humidity (RH) of $60 \pm 5\%$. This allowed for constant instrumental size cuts through variations in ambient RH. Twenty three 1.9 cm diameter electrically conductive polyethylene or stainless-steel tubes extend into this heated zone to direct the air stream at flows of 30 l min^{-1} to the various aerosol sizing/counting instruments and impactors. The efficiency of the mast inlet is discussed in Bates et al. (JGR 2002).

2. Sample collection

Stainless-steel tubes extending from the base of the sampling mast supplied air at 30 l min^{-1} to each of the impactors used for organic aerosol sampling. Two-stage and one-stage multi-jet cascade impactors (Berner et al., 1979) sampling air at 60% RH were used to determine the submicron and sub 10 micron concentrations of organic carbon (OC) and elemental carbon (EC). The 50% aerodynamic cutoff diameters, $D_{50,\text{aero}}$, were 1.1 and 10 μm . For the data reported here, submicron refers to particles with $D_{\text{aero}} < 1.1 \mu\text{m}$ at 60% RH and supermicron, the difference between the concentrations measured with the two impactors, refers to particles with $1.1 \mu\text{m} < D_{\text{aero}} < 10 \mu\text{m}$ at 55% RH. A 47mm quartz filter (Pall Gelman Sciences, #7202, 9.62 cm^2 effective sample area) was used as the stage 1 filter in these impactors. An additional quartz filter was used as the backup filter to assess sampling artifacts.

A third submicron impactor with two quartz filters was deployed downstream of a 30 cm long diffusion denuder that contained 18 parallel strips (34 faces) of 20.3 cm x 2.8 cm carbon-impregnated glass fiber (CIG) filters separated by $\sim 1.8 \text{ mm}$. The denuder cross-sectional area was 9.6 cm^2 .

The quartz filters were cleaned on board ship by baking at 550°C for 12 hours. The cleaned filters were stored in Al foil lined (press-fitted) petri dishes, sealed with Teflon tape, in a freezer dedicated solely to these filters. After sample collection the filters and substrates were returned to their petri dishes and stored in the freezer until analysis. All samples were analyzed on board ship.

3. Filter sample analysis

The analysis of the filter samples was done using a Sunset Laboratory thermal/optical analyzer. The instrument heated the sample converting evolved carbon to CO_2 and then CH_4 for analysis by a FID. The thermal program was the same as that used during ACE-Asia (Schauer et al. 2003, Mader et al., 2003). Four temperature steps were used to achieve a final temperature of 870°C in He to drive off OC. After cooling the sample down to 550°C , a He/ O_2 mixture was introduced and the sample was heated in

four temperature steps to 890°C to drive off elemental carbon (EC). The instrument measured the transmission of laser light through the filter to enable the separation of EC from OC that charred during the first stages of heating.

No correction has been made for carbonate carbon in these samples so OC includes both organic carbon and carbonate carbon if it was present.

4. On-line, semicontinuous sample analysis

A fourth submicron impactor (maintained at 60% RH) was deployed without filters upstream of a 30 cm long diffusion denuder and a real-time, semi-continuous Sunset Laboratory OC/EC instrument. The flow was split downstream of the denuder with a 20 l min⁻¹ bypass flow and 10 l min⁻¹ going to the OC/EC instrument. The instrument sampled air for 45 or 105 minutes depending on the OC concentrations. At the end of the sampling time the instrument analyzed the filter (15 minutes) using the same temperature program as the laboratory instrument described above. The concentration of evolved CO₂ was measured with an NDIR detector. The sampling times were not sufficient to measure EC above the instrument detection limit (0.35 ug/m³ based on a 45 min sample time).

5. Uncertainties

The uncertainties associated with positive and negative artifacts in the sampling of semi-volatile organic species can be substantial [Turpin *et al.*, 1994; Turpin *et al.*, 2000]. An effort was made to minimize and assess positive (adsorption of gas phase species) and negative (volatilization of aerosol organic species which may have resulted from the pressure drop across the impactor and filter) artifacts by using a denuder upstream of the impactor and by comparing undenuded and denuder-filter samplers. Results from these comparisons have shown that after correcting for sampling artifacts, measured OC concentrations can vary by 10% between samplers [Mader *et al.*, 2003]. Other sources of uncertainty in the OC mass include the air volume sampled (5%), the area of the filter (5%), 2 times the standard deviation of the blanks measured over the course of the experiment (0.44 µg/cm²) which was on average 10% of the sample, and the precision of the method (5%) based on the results of Schauer *et al.* [2003]. The total uncertainty, calculated as the sum of the squares was 13%. Sub-micron OC values were always above the detection limit of 0.1 to 0.8 ug/m³ which varied with volume (the one impactor sample with no value is a missing sample). The supermicron OC values are the difference between generally similar numbers. Blank values indicate the difference was insignificant (<0.1 ug/m³).

Sources of uncertainty in the EC mass include the air volume sampled (5%), the area of the filter (5%), and the precision of the method (5%) based on the results of Schauer *et al.* [2003]. The total uncertainty, calculated as the sum of the squares was 9%. The limit of detection varied from 0.015 to 0.12 ug/m³ based on the volume sampled. Blank values indicate the value was below the detection limit.

Sources of uncertainty for the real-time semicontinuous OC measurement include the air volume sampled (5%) and the precision of the method (3%) based on injection of a CH₄ standard with each run. The total uncertainty, calculated as the sum of the squares was 6%. EC concentrations were below the detection limit of this instrument (0.35 ug/m³ based on a 45 min sample time).

6. Data reported in archive

The following OC/EC data sets are reported in the data archive:

1. Sub-micron OC – data are from the denuder/impactor sampler. The back up quartz filter behind the stage 1 quartz filter was used as the blank.
2. Sub-micron EC – data are the average of the two sub-micron impactor samplers (with and without denuders). Missing data were below the limit of detection.
3. Super-micron OC – data are the difference between the sub-10 um impactor and the sub-1 um impactor. Both impactors were run without denuders. Both impactors were corrected for blanks/artifacts using the backup quartz filter behind the stage 1 quartz filter.
4. Super-micron EC – data are the difference between the sub-10 um impactor and the average of the two sub-micron impactor samplers (with and without denuders).
5. Sub-micron RTOC – data are from the Sunset Laboratory Real-time, Semi-continuous Field Instrument.
v1 data have been scaled to sub-micron OC (data set 1 above) – higher face velocity in RT instrument has resulted in blow off of volatile organics. (See Eatough et al.)

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