

PMEL Organic aerosol sampling methods

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 $55 \pm 5\%$. 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. Comparisons of the total particle count ($D_p > 3 \text{ nm}$) during ACE-1 between the NCAR C-130 airplane, ground stations, and ship agreed to within 20% when sampling in the same air mass (Weber et al., 1999). A similar comparison during the Indian Ocean Experiment (INDOEX) showed agreement to within 5% (Clarke et al., 2001). These differences are on the order of the atmospheric variability over the distance between platforms and the sample flow errors implying that inlet losses in this size range are minimal. Based on the wind tunnel tests, the transmission efficiency through the sampling mast for particles with diameters less than $6.5 \text{ }\mu\text{m}$ was greater than 95% (Bates et al., submitted).

2. Sample collection

Several different combinations of impactors, filters and a denuder were used to sample organic carbon (OC) and elemental carbon (EC) on the ship. Our goal was to obtain size resolved concentrations with minimal positive (caused by the absorption of gas phase organic carbon on the filters) and negative (loss of volatile organic carbon from the particles) artifacts.

Five stainless-steel tubes extending from the base of the sampling mast supplied air at 30 l min^{-1} to each of the 5 impactors used for organic aerosol sampling. All 5 impactors contained two filters in series at the end of the sample stream. The stage 1 filter collected particles with diameters less than the 50% aerodynamic cutoff diameters, $D_{50,\text{aero}}$, of the first impactor stage. The backup filter downstream of the stage 1 filter was used to assess sampling artifacts. The two filters are referred to here as the stage 1 filter and backup filter.

Two-stage and one-stage multi-jet cascade impactors (Berner et al., 1979) sampling air at 55% 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 $10 \text{ }\mu\text{m}$. For the data reported here, submicron refers to particles with $D_{\text{aero}} < 1.1 \text{ }\mu\text{m}$ at 55% RH and supermicron, the difference between the concentrations measured with the two impactors, refers to particles with $1.1 \text{ }\mu\text{m} < D_{\text{aero}} < 10 \text{ }\mu\text{m}$ 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.

An identical submicron (two-stage) impactor was deployed with a Teflo filter (Pall Gelman Sciences, #R2PL047 PTFE membrane filter) as the stage 1 filter and a quartz filter as the backup filter.

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 ~1.8 mm. The denuder cross-sectional area was 9.6 cm².

A 7-stage multi-jet cascade impactor ($D_{50,aero}$ of 0.18, 0.31, 0.55, 1.1, 2.0, 4.1, and 10 μm) was used to determine OC and EC mass size distributions. Aluminum foils were used for the impaction substrates and 47mm quartz filters were used as the stage 1 and backup filters.

The quartz filters and Al substrates were cleaned on board ship by baking at 550°C for 12 hours. The cleaned filters and substrates 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 quartz filters from the one and two stage impactors were analyzed on board ship. The filters and Al foils from the seven stage impactor were analyzed at PMEL 3 months after the field project.

3. Sample analysis

The analysis of samples was done using a Sunset Labs thermal/optical analyzer. It heated the sample to specified temperatures for specified times, converting evolved carbon to CO₂ and then CH₄ for analysis by FID. The thermal program was the same as that used by other groups in ACE-Asia. It involved heating in 4 temperature steps to a final temperature of 870°C in a He environment to drive off OC. After cooling the sample down to 550°C, a He/O₂ mixture was introduced and the sample was heated further in 4 temperature steps to 910°C to drive off elemental carbon (EC). The instrument measures the transmission of laser light through the filter to enable the separation of EC from OC that charred during the first stages of heating. The optical OC/EC split works only on the backup filters in the impactors, not on the impactor foils.

No correction has been made for carbonate carbon in these samples so OC includes both organic carbon and carbonate carbon if it was present. Carbonate carbon evolves from the sample at the fourth temperature step in the analysis. This peak, which contains both organic carbon and carbonate carbon if present was never more than 10% of the total OC.

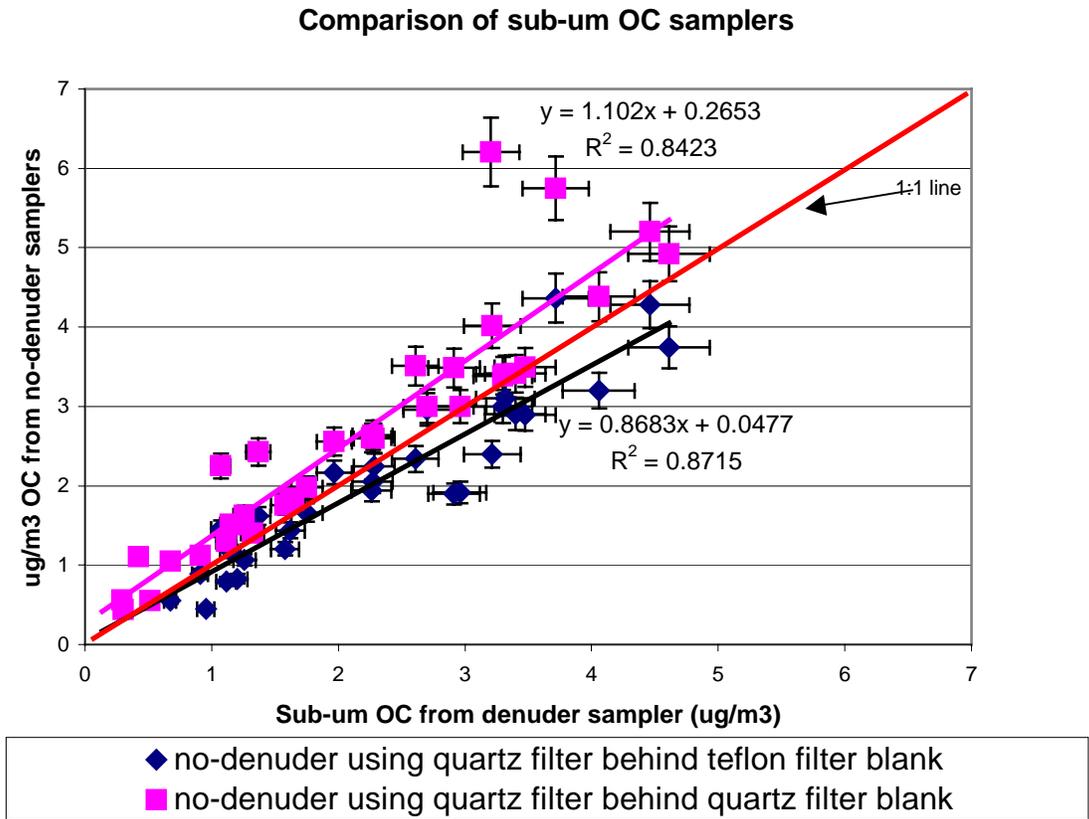
4. Data intercomparisons

To test our analytical procedure, we participated in an ACE-Asia inter-laboratory comparison organized by Jamie Schauer of the University of Wisconsin - Madison. He distributed 2 punches each from four high-volume samples and two blanks. The samples were mailed to the ship in Hawaii, stored in the freezer and analyzed at sea near the middle of the cruise (April 5, 2001). The six ACE-Asia research groups and two groups at Sunset Laboratories agreed on moderate-level OC to within 4%, low-level OC within 13%, and EC within 13%.

5. Interpretation of results from different samplers

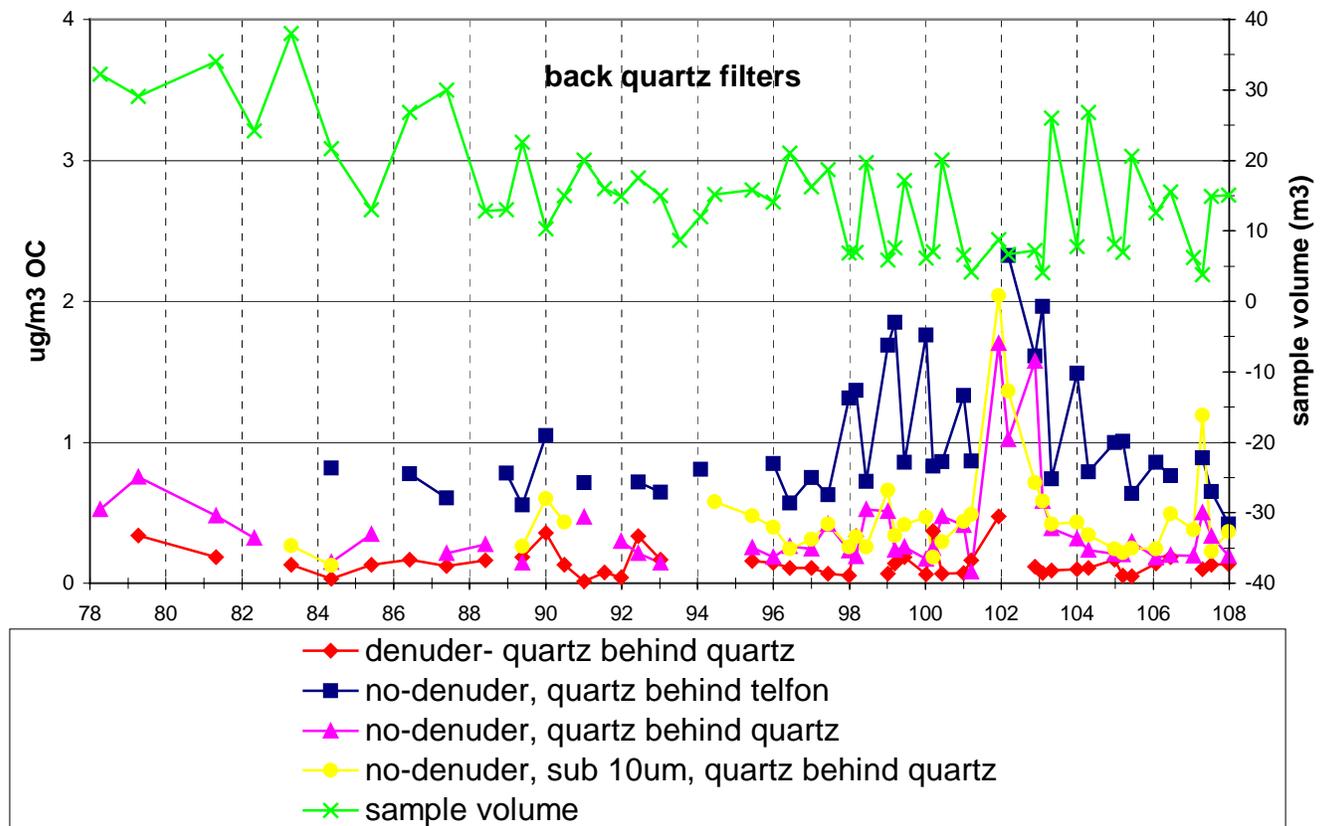
In principle, the denuder removes the gas phase organic compounds from the sample stream leaving only the particulate phase organic compounds to deposit on the quartz filter. The quartz filter behind the stage 1 filter in this sampler serves as a filter blank. In the samples without a denuder the quartz filters can absorb gas phase organic compounds. We can attempt to correct for this positive artifact by subtracting the OC measured on the quartz filter behind the quartz stage 1 filter or the quartz filter behind the teflo stage 1 filter. A comparison of the three estimates of sub-um OC is shown below (Figure 1). The error bars represent the average % difference between replicate samples from the same filter (7%).

Figure 1.



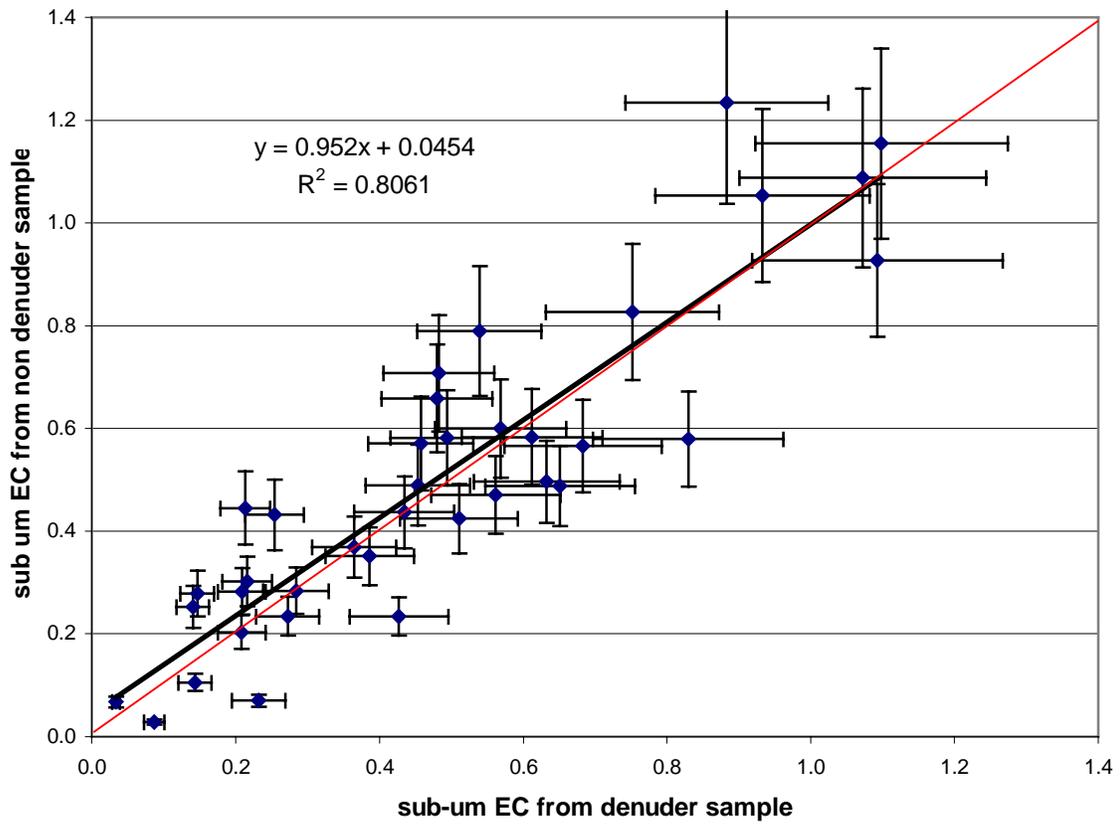
In general the concentration of OC on the backup quartz filters were as follows: denuder quartz behind quartz was < the no-denuder quartz behind quartz = no-denuder, sub 10-um quartz behind quartz which was < no-denuder quartz behind Teflon (Figure 2). The concentration of OC on the back up filter behind the Teflon filter was anti-correlated with volume (i.e. the concentration was higher when volumes were < 10 m³). There was clearly one anomalous period when the dust concentrations were high (DOY102-103) where the concentration on the no-denuder quartz behind quartz filter was much higher than normal (Figure 2). The OC concentration on the stage 1 quartz filter was also much higher than on the stage 1 quartz filter behind the denuder (note two anomalously high square points in Figure 1).

Figure 2



There was no measurable EC on the back up filters (i.e. no measurable blank). There was no consistent difference between the sub micron EC concentrations for the impactor with and without the denuder as shown below (Figure 3). The error bars represent the average % difference between replicate samples from the same filter (16%).

Figure 3.



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).
3. Super-micron OC – data are the difference between the sub-10 μm impactor and the sub-1 μm 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 μm impactor and the average of the two sub-micron impactor samplers (with and without denuders).
5. 7-Stage OC mass size distribution – The stage 1 quartz filter was corrected for blanks/artifacts using the backup quartz filter. With short sampling periods this might tend to overestimate the stage 1 OC concentration (Figure 1). However, the 7-stage impactor was run for longer time periods than the 1 and 2 stage impactors. Sample volumes ranged from 26-103 m^3 .
6. 7-Stage EC mass size distribution – an optically detected split point between OC and EC can not be used with the AI impactor foils. The split between OC and EC in the 7-stage impactors was based on a cruise average EC/TC split ratio from the two stage impactors (0.20 ± 0.06).