



Sampling methods used for the collection of particle-phase organic and elemental carbon during ACE-Asia

B.T. Mader^a, J.J. Schauer^b, J.H. Seinfeld^{a,*}, R.C. Flagan^a, J.Z. Yu^c, H. Yang^c, Ho-Jin Lim^d, B.J. Turpin^d, J.T. Deminter^b, G. Heidemann^b, M.S. Bae^b, P. Quinn^e, T. Bates^e, D.J. Eatough^f, B.J. Huebert^g, T. Bertram^g, S. Howell^g

^a Department of Chemical Engineering, California Institute of Technology, MS 210-41, Pasadena, CA 91125, USA

^b University of Wisconsin-Madison, Madison, WI 53706, USA

^c Hong Kong University of Science and Technology, Hong Kong, China

^d Rutgers University, New Brunswick, NJ 08903, USA

^e Pacific Marine Environmental Laboratory, Seattle, WA 98115, USA

^f University of Hawaii-Manoa, Manoa, HI 96822, USA

^g Brigham Young University, Provo, UT 84602, USA

Received 16 August 2002; accepted 7 December 2002

Abstract

The semi-volatile nature of carbonaceous aerosols complicates their collection, and for this reason special air sampling configurations must be utilized. ACE-Asia provided a unique opportunity to compare different sampling techniques for collecting carbonaceous aerosols. In this paper detailed comparisons between filter-based carbonaceous aerosol sampling methods are made. The majority of organic carbon (OC) present on a backup quartz fiber filter (QFF) in an undenuded-filter sampler resulted from the adsorption of native gaseous OC rather than OC evaporated from collected particles. The level of OC on a backup QFF placed behind a QFF was lower than the level present on a backup QFF placed behind a Teflon membrane filter (TMF) indicating that gas/filter equilibrium may not be achieved in some QFF front and backup filter pairs. Gas adsorption artifacts can result in a 20–100% overestimation of the ambient particle-phase OC concentration. The gas collection efficiency of XAD-coated and carbon-impregnated filter-lined denuders were not always 100%, but, nonetheless, such denuders minimize gas adsorption artifacts. The median fraction of particle-phase OC that is estimated to evaporate from particles collected by denuder-filter samplers ranged from 0 to 0.2; this value depends on the sampler configuration, chemical composition of the OC, and sampling conditions. After properly correcting for sampling artifacts, the measured OC concentration may differ by 10% between undenuded- and denuder-filter samplers. Uncorrected, such differences can be as large as a factor two, illustrating the importance of sampling configurations in which gas adsorption or evaporation artifacts are reduced or can be corrected.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Carbonaceous aerosol; Organic carbon, OC; Elemental carbon, EC; Denuder; Filter sampling; Sampling artifacts; Field sampling; Aircraft sampling

1. Introduction

One of the principal goals of ACE-Asia was to determine the chemical and physical properties of atmospheric aerosol particles originating from the Asian

*Corresponding author.

E-mail address: seinfeld@caltech.edu (J.H. Seinfeld).

continent, including the levels of carbonaceous compounds. Several research groups collected carbonaceous aerosol for determination of particulate organic and elemental carbon content and sampling was conducted at different locations in Asia and from a variety of platforms.

Atmospheric carbon is often classified into three operationally defined categories: organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC). OC is carbon associated with organic compounds, either emitted directly to the atmosphere (primary emissions) or formed by the condensation of products formed via the atmospheric oxidation of volatile organic compounds (VOCs) (secondary OC). EC is formed during the combustion of hydrocarbons and is essentially non-volatile at ambient temperature. CC is present in mineral dusts but the collection and analysis of CC will not be discussed further in this manuscript.

1.1. Undenuded-filter samplers

Individual G- and P-phase semi-volatile organic compounds (SOCs) are often separated using filter/sorbent samplers. Since the level of gaseous OC (i.e. the sum of all VOC and gaseous SOCs) can be eight times greater than the level of particulate OC (Mader et al., 2001), if gaseous OC is not removed from the sample air-stream (for example by the use of a denuder) before particles are collected on a filter, the adsorption of even a relatively small amount of the total gaseous OC can result in a positive artifact in the measured P-phase OC concentration ($(\mu\text{g C m}^{-3})$) (McDow and Huntzicker, 1990; Turpin et al., 1994; Mader and Pankow, 2001a, b). A common approach to correct for positive biases involves the use of a backup filter, in which a second filter (backup filter) is placed downstream of the front filter. Since the backup filter is exposed only to particle free air, SOCs measured on this filter are presumed to originate only from the G-phase. To correct for positive gas adsorption artifacts, the mass of the given SOC measured on the backup filter is subtracted from the mass measured on the particle-loaded front filter. Thus the measured particle-phase OC concentration determined using an undenuded-filter sampler is

$$\text{OC}_{\text{meas,ud}}(\mu\text{g C m}^{-3}) = \frac{m_{\text{oc,f}} - m_{\text{oc,b}}}{V_s} \quad (1)$$

where V_s (m^3) is the volume of air sampled, and $m_{\text{oc,f}}$ and $m_{\text{oc,b}}$ are the masses ($\mu\text{g C}$) of OC measured on the front and backup filters of the undenuded-filter sampler, respectively. This correction assumes: (1) for the front and backup filters, the mass/filter area amounts of each SOC adsorbed from the gas phase onto the filters is equal; (2) the gas adsorption capacity of the front and backup filter are equal; and (3) SOC observed on the

backup filter did not result from evaporation of particles collected on the front filter.

1.2. Denuder-filter samplers

Denuders are used to first remove gaseous OC from the sample air-stream before collecting the particles on a filter. At equilibrium, semi-volatile compounds partition between the P- and G-phase governed by an equilibrium coefficient, K_p (where, $K_p = c_p/c_g$) when gas-phase SOCs are removed during flow through a denuder, $c_g \rightarrow 0$, and SOCs will evaporate from the P-phase in an attempt to re-establish P/G equilibrium. This process can occur either during transport of particles through denuders (Kamens and Coe, 1997) or when SOC-free gas is passed through a particle-loaded filter (Liang and Pankow, 1996). Mader et al. (2001) derive equations that identify parameters that influence the magnitude of the negative sampling artifact in denuder-filter samplers. Briefly, the mass of OC evaporated from filter-bound particles downstream of a denuder depends on: (1) the volume of SOC-free gas passed through the filter; (2) the P-phase concentration and K_p values of the compounds comprising the P-phase OC; (3) the temperature (values of K_p are inversely proportional to T); and (4) the mass fraction of carbon in the compounds comprising P-phase OC. For these reasons, the magnitude of evaporative losses of OC in denuder-filter samplers may vary among different sampling events and types of particles (i.e. aged vs. freshly emitted particles).

The amount of OC evaporated from particles collected downstream of a denuder is often estimated using a backup filter. Typically quartz fiber filter (QFF), carbon-impregnated cellulose (CIF), or carbon-impregnated glass filters (CIG) are used as backup filters in denuder-filter samplers. The measured particle-phase OC concentration determined using a denuder sampler is

$$\text{OC}_{\text{meas,d}}(\mu\text{g C m}^{-3}) = \frac{m_{\text{oc,f}} + m_{\text{oc,b}}}{V_s} \quad (2)$$

where $m_{\text{oc,f}}$ and $m_{\text{oc,b}}$ are the masses ($\mu\text{g C}$) of OC measured on the front and backup filters of the denuder sampler, respectively. (Note: values of $m_{\text{oc,f}}$ and $m_{\text{oc,b}}$ include field blank corrections.) This correction assumes that (1) the denuder removes native gaseous OC that can adsorb to a QFF, CIF, or CIG, so that only particle-phase OC is present on the front filter, and any OC present on the backup filter could have originated only from collected particles rather than from denuder breakthrough and (2) the gas collection efficiency of the backup filter is 100%, so that all evaporated carbon is collected by the backup filter. The validity of the first assumption can be tested by measuring the ability of the denuder to remove gaseous OC during each sampling event. Regarding the second assumption, it has been

reported that CIF collect gaseous OC with 80–100% efficiency (Eatough et al., 1993; Tang et al., 1994; Lewtas et al., 2001); the gas collection efficiency of QFF has not been determined but it is likely less than that of CIFs.

During ACE-Asia, both undenuded- and denuder-filter samplers were used to collect carbonaceous aerosols. Some participants deployed both types of samplers at the same location and all participants used the same thermo-optical method to determine the OC and EC loading on QFFs. ACE-Asia provided an opportunity to document and compare different sampling techniques for collecting carbonaceous aerosols. The specific goals of this work are to (1) provide a review of several sampling methods used for the collection of carbonaceous aerosols, (2) estimate the magnitudes of the various artifacts associated with sampling semi-volatile carbonaceous aerosols using undenuded- and denuder-filter samplers and (3) where possible compare the OC and EC values determined using these two sampling techniques after making corrections for such artifacts.

2. Air sampling methods for collection of carbonaceous aerosols

2.1. California Institute of Technology (Caltech)

Ambient air was sampled using an inlet mounted to the nose of the Twin Otter aircraft, a manifold was used to separate the sample air among the denuder-filter samplers, while maintaining isokinetic flow conditions. The compartment housing the denuder-filter samplers was neither heated nor pressurized during flights. The temperature was monitored during flights using a temperature probe located in the sampler's flow controller. The transmission efficiency of 2.3 μm particles from the inlet to the filters in samplers A and B was 80% (Mader et al., 2002).

Carbonaceous aerosol particles were collected using the denuder-filter samplers described by Mader et al. (2001). Samplers A and B operated at a flow rate of 161 min^{-1} and consisted of a XAD-coated honeycomb denuder placed upstream of a pair of either front and backup QFFs (4.7 cm diameter Tissuequartz QUO-UP 2500, Pall Gelman, Ann Arbor, MI) or a front QFF and backup carbon-impregnated glass fiber filter (CIG). The residence time of particles in the denuder portion of the sampler was 0.2 s. During air sampling, the volumetric flow, pressure, and temperature of the sample air downstream of the filters were monitored at 1-min intervals. The accuracy and precision of the volumetric flow measurement were 0.5% and 1%, respectively. Sample times ranged from 0.5 to 4.7 h.

Samplers A and B (Fig. 1a) were sometimes operated in the following configuration: Sampler A was configured with a denuder to remove gaseous OC, a filter (QFF_{f,a}) to collect P-phase OC, EC, and CC and a backup filter (QFF_{b,a} or CIG_{b,a}) to collect OC evaporated from particles collected on QFF_{f,a} (Note that if the denuder does not remove 100% of G-phase OC, it is possible that these compounds can adsorb to QFF_{b,a} or CIG_{b,a}). Sampler B was configured with a 2.0 μm Teflon membrane filter (TMF) (Zeffluor, Pall Gelman Sciences, Ann Arbor MI) to remove P-phase OC, EC and CC, a denuder to remove gaseous OC, and a filter (QFF_{b,b} or CIG_{b,b}) to adsorb gaseous semi-volatile OC not collected by the denuder. With this configuration, samplers A and B were run in parallel; it was possible to measure the OC, EC, and CC content of a sample, the amount of OC evaporated from collected particles, and the ability of the denuder to remove gaseous OC. The preparation and storage of the filters are described by Mader et al. (2001).

2.2. Hong Kong University of Science and Technology (HKUST)

A high-volume particle trap impactor/denuder-filter sampler designed by Mader et al. (2001) was deployed on the rooftop of a trailer at the Kosan, Korea surface site (33.29N, 126.16E, 70 m ASL). Samples were taken daily and the sampling time was nominally 23 h. Two pre-baked 194 mm quartz filters were loaded in the sampler. When operated at a flow of 520 l min^{-1} , the sampler had an estimated $d_{50,\text{aero}}$ of 5 μm . The denuder section of the sampler was rinsed with CH_2Cl_2 once every other day to help remove ad/absorbed organic gases, and maximize the gas collection efficiency of the XAD-coated denuder (the gas adsorptive capacity and breakthrough volume of the XAD-coated denuder has not yet been determined). Temperature and pressure readings were taken at the beginning and the end of each sample. All QFF were pre-cleaned by baking at 550°C for 16–20 h. The 194 mm QFFs were stored in aluminum pouches before and after sampling. All the aluminum foils and glass petri dishes were annealed at 550°C before they were used to store filters. The samples were stored at -4°C until analyses.

2.3. Pacific Marine Environmental Laboratory (PMEL)

Aerosol particles were sampled 18 m above the sea surface on the R/V Ron Brown 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

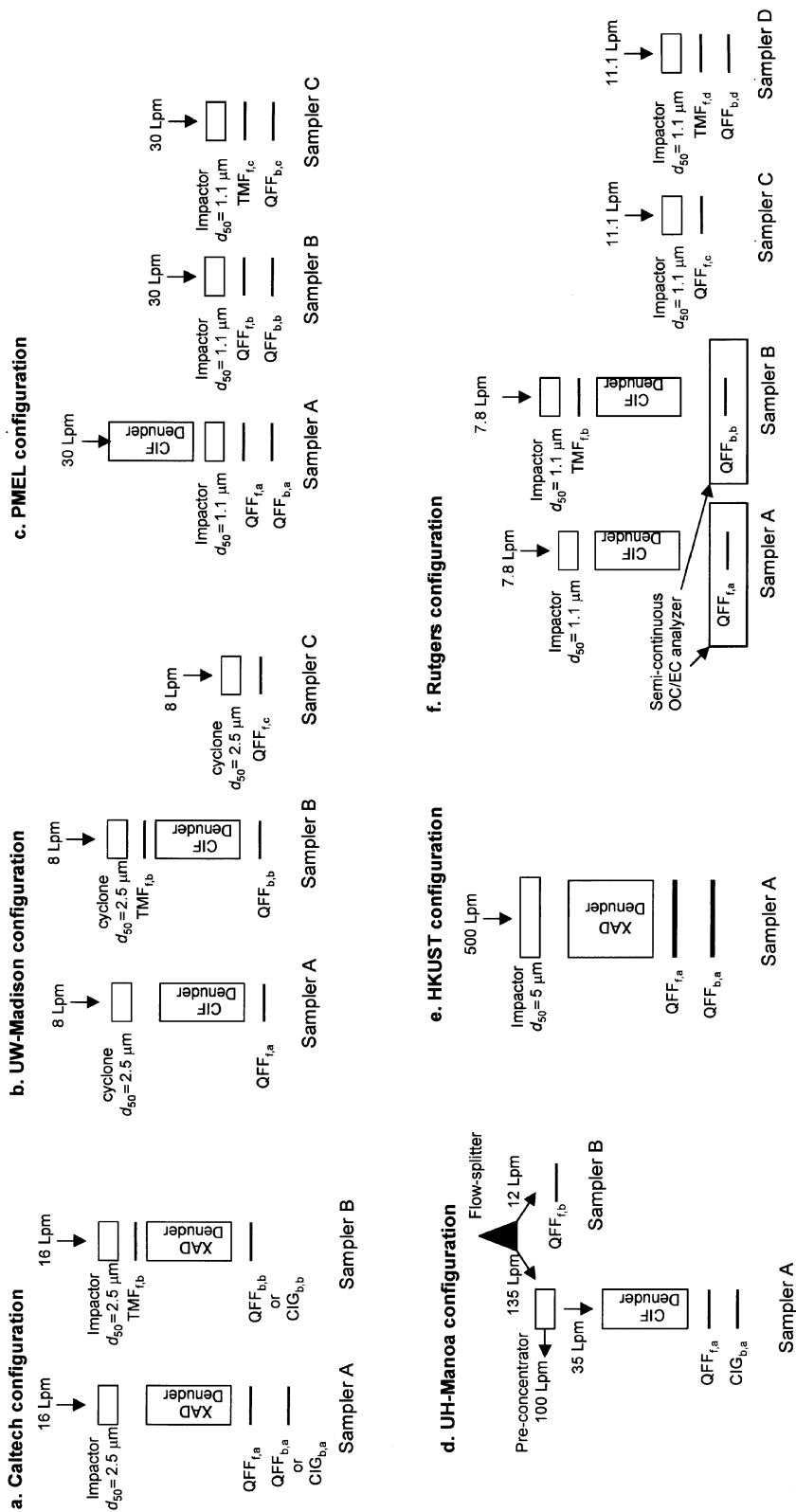


Fig. 1. Sampler configurations for the collection of organic and elemental carbon during ACE-Asia. (Note: some research groups operated more air samplers than are depicted in this figure, data from these samplers was not relevant to the focus of this manuscript.)

the 20 cm diameter mast. The lower 1.5 m of the mast was heated to dry the aerosol to a relative humidity (RH) of $55 \pm 5\%$. Based on wind tunnel tests, the transmission efficiency through the sampling mast for particles with diameters $< 6.5 \mu\text{m}$ was $> 95\%$ (Bates et al., 2002). Five stainless-steel tubes extending from the base of the sampling mast supplied air at 301min^{-1} to each of the five impactors (Bernier-type multi-jet impactors Berner et al., 1979) used for carbonaceous aerosol sampling. Sample times ranged from 2 to 20 h. A schematic of the configuration of three of the five samplers is shown in Fig. 1c (only data from three samplers is discussed in this manuscript). Sampler A consists of a front QFF (QFF_{f,a}) and backup QFF (QFF_{b,a}) filter pair downstream of an impactor having a final stage with a $d_{50,\text{aero}}$ of $1.1 \mu\text{m}$ which is downstream of a 30 cm long diffusion denuder consisting of 18 parallel strips (34 faces) of $20.3 \text{cm} \times 2.8 \text{cm}$ carbon-impregnated glass fiber (CIG) filters separated by $\sim 1.8 \text{mm}$. The denuder cross-sectional area was 9.6cm^2 . Sampler B consists of a front QFF (QFF_{f,b}) and backup QFF (QFF_{b,b}) filter pair downstream of an impactor having a final stage with $d_{50,\text{aero}}$ of $1.1 \mu\text{m}$. Sampler C consists of a front TMF (TMF_{f,c}) (Pall Gelman Sciences, #R2PL047) and backup QFF (QFF_{b,c}) filter pair downstream of an impactor having a final stage with a $d_{50,\text{aero}}$ of $1.1 \mu\text{m}$. The quartz filters were cleaned aboard the ship by baking at 550°C for 12 h. The cleaned filters and substrates were stored in aluminum 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 samplers A through C were analyzed onboard the R/V Ron Brown.

2.4. Rutgers University (Rutgers)

The ambient concentration of particulate OC and EC was measured aboard the R/V Ron Brown using two sampling systems (a schematic is shown in Fig. 1f). The first system consisted of a pair of undenuded-filter samplers and the second consisted of a denuder placed upstream of a filter present in a semi-continuous thermal-optical transmittance (TOT) carbon analyzer (Sunset Laboratory, Forest Grove, OR).

Both air sampling systems operated by the Rutgers group sampled ambient air from the same heated mast as the PMEL group (the heated mast was described in Section 2.3). From the a manifold present at the base of the heated mast air was drawn at 301min^{-1} into a plenum and then through a multi-jet impactor having a $1.0 \mu\text{m}$ aerodynamic cutoff diameter (Berner et al., 1979) In the plenum, the flow was split between the semi-continuous carbon analyzer (sampler A, Fig. 1f) and the two undenuded-filter samplers (samplers C and D, Fig. 1f).

The undenuded-filter samples were collected concurrently in two auxiliary ports. One port contained a 47 mm QFF (QFF_{f,c} in Fig. 1f) (QAT-UP, PallGelman, Ann Arbor, MI). The other contained a 47 mm Teflon membrane filter (TMF_{f,d}, Fig. 1f) followed by a 47 mm QFF (QFF_{b,d} in Fig. 1f). Prior to sampling all QFF were pre-cleaned in a muffle furnace at 550°C for more than 2 h. Sampling port flow rates were maintained at 11.1lmin^{-1} for both samplers C and D and the average sampling time was 15 h. QFF_{b,d} was exposed to particle-free ambient air and provides an estimate of OC adsorbed on the front QFF_{f,c}. Filter samples collected by the undenuded-filter samplers were stored frozen until analysis.

To substantially reduce the adsorption of gaseous OC onto the QFF present in the semi-continuous carbon analyzer, a denuder was placed upstream of the QFF present in the carbon analyzer. The flow rate of sample air through the denuder was 7.81min^{-1} . The denuder contained 15 parallel strips ($3.15 \text{cm} \times 20.3 \text{cm}$) of carbon-impregnated filter (CIF; Schleicher Schuell, Keene, NH), each strip spaced by 2 mm inside an aluminum housing. Particles passing through the denuder were collected on a QFF (1.5cm^2) present inside the semi-continuous TOT carbon analyzer (Fig. 1f). The face velocity of air through the QFF was about 70cm s^{-1} . On average, air samples were collected over a sampling period of 3 h. Immediately after sample collection, the OC and EC content of the QFF present in the semi-continuous carbon analyzer was determined automatically using a thermo-optical reflectance method. A detailed description of the semi-continuous carbon analyzer is provided by Turpin et al. (1990) and Turpin and Huntzicker (1995).

Since some vapor-phase OC may escape the denuder and can be adsorbed on a QFF downstream of the denuder, 33 dynamic blanks were measured by placing a 47 mm Teflon filter (Teflo $2 \mu\text{m}$, PallGelman, Ann Arbor, MI) upstream of the denuder to remove particles in the sample air (TMF_{f,b}, sampler B, Fig. 1f) and a QFF downstream of the denuder (QFF_{b,b}, sampler B, Fig. 1f). Thus, the denuder and QFF_{b,b} (present in the carbon analyzer) were exposed to particle-free ambient air. The amount of OC on QFF_{b,b} is an estimate of the amount of OC that would adsorb onto QFF_{f,a} resulting from the adsorption of organic gases that escaped the denuder.

Another important difference between samplers A and B and samplers C and D is that with the semi-continuous carbon analyzer (Samplers A and B) the filter sample was collected over $\approx 3 \text{h}$ period and analyzed for OC and EC content immediately after collection, whereas for samplers C and D, air was sampled over an $\approx 15 \text{h}$ period and the filter samples stored until later analysis for their OC and EC content.

2.5. University of Hawaii-Manoa (UH-Manoa)

Samples were collected aboard the C-130 using a PC-BOSS sampler (Fig. 1d) developed by the Eatough group (Brigham Young University) (Eatough et al., 1999; Lewtas et al., 2001). Once inside the fuselage, the air was conveyed through a 2.54 cm id tube to a flow splitter: a small flow of 121 min^{-1} (all rates are in actual liters per minute) went to the side filter (sampler B), while the major flow (1351 min^{-1}) passed into a particle pre-concentrator (PC) (Pang et al., 2001), the PC bypass flow was 1001 min^{-1} and the sample flow of 351 min^{-1} . The PC is a virtual impactor with a cut size around $0.1 \mu\text{m}$ that theoretically would increase the concentration of particles by a factor of about 4. The enriched flow from the PC passed into a diffusion denuder (Eatough et al., 1999) containing 15 parallel $4.5 \text{ cm} \times 58 \text{ cm}$ strips of carbon-impregnated glass fiber (CIG) filters separated by 2 mm. This denuder removed most organic vapors, some of which could have caused a positive artifact by adsorbing on the front QFF (QFF_{f,a}) (Pall Gelman 2500QAO, 47 mm). Prior to being used for sampling, the QFF had been baked for 16 h at 550°C . CIGs (Schleichert and Schuell, GF3649, Dassel, Germany, 47 mm) were used as backup filters. They were prepared prior to an experiment by baking them for 10 h at 325°C in an N_2 atmosphere.

In the PC-BOSS sampler a portion of the sample air-flow is split from the main flow and drawn through a side filter (Sampler B) present upstream of the PC. Sampler B can be used to check for particle losses in the PC and denuder. A TMF (TMF_{f,b}) was placed in this sampler B during one OC/EC sampling leg per flight. Since all gaseous SO_2 should be removed by the CIG denuder, the SO_4 concentration determined from QFF_{f,a} should equal that determined using TMF_{f,b}. During the remaining sampling legs, a single QFF (QFF_{f,b}) was placed in the sampler B and to collect EC. The amount of EC on QFF_{f,b} was compared to the sum of EC found on QFF_{f,a} collected during sampling legs in which QFF_{f,b} was present in sampler B. This enabled calculation of the concentration enhancement factor of the PC and could be used to identify any loss of EC in the PC or denuder. Thermal mass-flow controllers were used to continuously record the mass flow of air through Samplers A, B, and the PC bypass. These controllers ensured that the airflow through the various components of the PC-BOSS sampler were within the design parameters.

2.6. University of Wisconsin-Madison (UW-Madison)

A multi-channel low volume sampler was operated at the Kosan, Korea surface site (33.29N, 126.16E, 70 m ASL) to collect 24-h average total suspended particulate material (TSP), particulate matter $<2.5 \mu\text{m}$ diameter

(PM_{2.5}) and particulate matter $<1 \mu\text{m}$ diameter (PM_{1.0}) samples. Only the PM_{2.5} data will be discussed in this manuscript. PM samples from five of the 12 sampling channels were collected for OC and EC analysis. Samples for OC and EC analysis were collected on pre-baked QFFs (Pall Gelman 2500QAO, 47 mm). Two AIHL cyclone separators (John and Reischl, 1980) were operated at 241 min^{-1} to collect PM_{2.5} samples. The outlet of each cyclone was directed into a sampling manifold (Anderson Instruments, Smyrna GA) where the flow was divided into three 81 min^{-1} sample train for each cyclone. Samplers A–C (Fig. 1b) were collected at the outlet of the PM_{2.5} manifold. Sampler A consisted of a CIG denuder followed by QFF_{f,a} (Fig. 1b). The CIG denuder consisted of 15 parallel $2.5 \text{ cm} \times 10.0 \text{ cm}$ strips of carbon-impregnated GFFs separated by 2 mm. The residence time of particles in the denuder portion of the sampler was 0.5 s. Sampler B was used to evaluate the ability of the denuder to reduce the amount of gaseous OC that would adsorb to a QFF (QFF_{f,b}). A 47-mm Teflon membrane filter (Teflo, 47-mm, Pall Gelman) was placed upstream of the CIG denuder, otherwise sampler B was operated identically to sampler A. Sampler C consisted of a 47-mm anodized aluminum undenuded-filter holder loaded with QFF_{f,c}. All samples collected for OC and EC analysis were collected using a filter definer ring, which consisted of a thin stainless-steel donut-shaped plate that blinded the outer edges of the QFF to yield an even well-defined 37-mm diameter particulate matter deposit. After sampling, all samples were frozen until analysis.

3. Measurement of OC and EC levels on filters

All participants in this study measured the filter loading of OC and EC on collected samples using thermo-optical OC/EC analyzers from Sunset Laboratories (Forest Grove, OR) (Birch and Cary, 1996). In an interlaboratory comparison of the thermo-optical OC/EC analysis conducted among participants of ACE-Asia, the precision of the OC and EC filter loadings were within 4% and 13% of the consensus values, respectively (Schauer et al., 2002). The analytical method and temperature protocol of the thermo-optical method used during ACE-Asia to determine the OC and EC content of QFFs is described by Schauer et al. (2002).

CIGs were analyzed as follows: For the Caltech group OC was evolved under a stream of ultra-high-purity He while heating the sample in five temperature steps of 1 min at 250°C , 1 min at 300°C , 1 min at 350°C , 1 min at 400°C and 0.5 min at 450°C . After analysis of a CIG punch, the sample was removed and a blank QFF punch loaded into the analyzer. The analyzer was then baked to remove any EC that may have been dislodged from the CIG during analysis or the loading/unloading of a

sample. The bakeout program was as follows: Under a mixture of 2% O₂, 90% He, the blank QFF punch was heated in eight temperature steps of 0.75 min at 310°C, 0.75 min at 450°C, 0.75 min at 550°C, 0.75 min at 625°C, 0.75 min at 700°C, 0.75 min at 775°C, 0.75 min at 850°C and 5.0 min at 900°C. For the UH-Manoa group, CIG filters were heated in a He environment at 20°C min⁻¹ to a maximum front oven temperature of 300°C.

4. Results/discussion

4.1. Undenuded-filter samplers

The PMEL group used undenuded-filter samplers with front and backup QFF as one component of their sampling configuration (Fig. 1c). An estimate of the magnitude of gas adsorption artifacts is possible by comparing the amounts of OC present on the front and backup filters in these different sampler configurations. Turpin et al. (2000) suggested that OC present on backup QFF in undenuded-filter samplers results mostly from the adsorption of native gaseous OC rather than from the adsorption of OC evaporated from collected particles. This idea was confirmed by the experiments of Mader et al. (2001) who simultaneously operated denuded and undenuded-filter samplers under conditions of relatively constant temperature (ΔT approx. $\leq 5^\circ\text{C}$). In these experiments it was observed that OC present on backup QFF in undenuded-filter samplers were significantly greater than those present on backup QFF in denuder samplers. During ACE-Asia the levels of OC determined from backup filters present in the PMEL system also support this idea. For 45 samples obtained by the PMEL group, the average field blank-corrected OC levels on filters QFF_{b,c}, QFF_{b,b}, and QFF_{b,a} were 0.53 (± 0.36), 0.20 (± 0.20) and 0.02 (± 0.12) $\mu\text{g C cm}^{-2}$, respectively. Using a paired student *t*-test with ($\alpha = 0.05$) it was determined that the average OC levels on each filter were significantly different from each other. These observations indicate that the level of OC on backup QFFs in the undenuded-filter samplers was higher than the level on a backup QFF in the denuder-filter sampler. Since the denuder reduces the G-phase concentration of OC, for a given sampling time the mass of OC evaporated from collected particles would be greater in the denuder-filter sampler than the undenuded-filter sampler where the gas-phase OC concentration is not altered prior to the collection of particles onto the filter. Thus the amount of OC on QFF_{b,a} in the PMEL system is an upper estimate of the amount of OC on QFF_{b,b} and QFF_{b,c} which resulted from the adsorption of OC evaporated from particles collected on QFF_{f,b} and TMF_{f,c} in the filter samplers. This assumes that the denuder effectively removed native gaseous OC that could adsorb to QFF_{b,a}. The

PMEL group did not measure the gaseous OC collection efficiency of the denuder during ACE-Asia, but the UW-Madison group used the same type of denuder as was used by the PMEL group and they measured the level of OC on a QFF resulting from the collection of gaseous OC that escaped the CIF denuder (i.e. QFF_{b,a} in the PMEL configuration). Under field conditions during ACE-Asia, the UW-Madison denuder was found to mostly remove native gaseous OC that would adsorb to a QFF, the average field blank-corrected filter loading on filter QFF_{b,b} in the UW-Madison system was 0.11 (± 0.09) $\mu\text{g C cm}^{-2}$. The field blank-corrected UW-Madison loading was not significantly different than the average value of 0.02 (± 0.12) $\mu\text{g C cm}^{-2}$ determined on QFF_{b,a} from the PMEL group. Therefore, it is a good assumption that in the PMEL system the CIF denuder effectively removed native gaseous OC that could adsorb to QFF_{b,a} and that the majority of OC present on the backup filter in the undenuded-filter sampler is due the adsorption of native gaseous OC rather than OC evaporated from collected particles.

In the PMEL sampling configuration, the level of OC on a backup QFF placed behind a TMF was higher than the level measured on a backup QFF present behind a QFF, that is the OC level on QFF_{b,c} > QFF_{b,b}. This observation has been made in previous studies (McDow and Huntzicker, 1990; Turpin and Huntzicker, 1994; Turpin et al., 2000), and it has been suggested that it is caused by differences in the gas adsorptive capacity of TMF and QFFs. Indeed, for filters used in ambient air sampling, at RH $\approx 40\%$, the surface area normalized G/filter partition coefficients ($K_{p,s}$ ($\text{m}^{-3} \text{m}^{-2}$)) of PAHs are ≈ 3 times greater for adsorption to QFF than to TMF surfaces (Mader and Pankow, 2000, 2001a,b). The PMEL data can be used to support the assertions of Mader and Pankow (Mader and Pankow, 2001a,b) who have suggested that G/filter partitioning equilibrium may not be achieved in undenuded-filter samplers employing a pair of QFFs; the amount of OC adsorbed from the gas phase to the front QFF is likely greater than the amount adsorbed to the backup QFF, therefore the magnitude of the gas adsorption artifact underestimated in these sampling configurations. For an undenuded-filter sampler, an estimate of the fraction of OC present on the front QFF due to gas adsorption is

$$f_{\text{ads,OC}} = \frac{m_{\text{oc,b}}}{m_{\text{oc,f}}} \quad (3)$$

where $m_{\text{oc,f}}$ and $m_{\text{oc,b}}$ are the masses ($\mu\text{g C}$) of OC measured on the front and backup filters of the undenuded-filter sampler, respectively. The values of $m_{\text{oc,f}}$ and $m_{\text{oc,b}}$ are corrected using field blanks. From the PMEL data, estimates of $f_{\text{ads,OC}}$ are 0.35 (± 0.15) and 0.13 (± 0.13) for the front TMF:backup QFF filter pair, and front QFF:backup QFF filter pair configuration, respectively (samplers C and B Fig. 1c, respectively).

These data indicate that if the gas adsorption capacities of QFF_{b,b} and QFF_{b,c} are equal, gas adsorption artifacts may be underestimated by at least a factor of two when using the front and backup QFF filter pair configuration. Analysis of the PMEL data for the front TMF and backup QFF filter pair configuration indicated that the adsorption of gaseous OC to a front QFF would result on average in a 35% overestimate of the P-phase OC concentration; if G/filter equilibrium was not achieved in the TMF:QFF configuration the overestimation would be > 35%.

4.2. Denuder performance

The main purpose of the denuder section of the samplers is to remove the gaseous OC that adsorbs to QFF causing a positive bias in the measured P-phase OC concentration. During transport through a denuder, gaseous OC is adsorbed to/into the stationary phase coating the denuder. It is possible that while sampling under some conditions, such as high gaseous OC levels, long sampling times and/or high temperatures, the sorption capacity of the denuder could be exceeded. Gaseous OC levels and the P-phase OC chemical composition may vary among different locations and meteorological conditions. For this reason, the ability of the denuder to collect gaseous OC is often monitored during actual field sampling. The Caltech group tested the ability of their denuder to remove gaseous OC that would adsorb to QFF during six of the 19 airborne sampling missions. During these experiments, samplers A and B (Fig. 1a) were run simultaneously. In all such experiments an insignificant mass of OC was measured on QFF_{b,b}. (The Caltech group required the mass of OC on a filter be twice the mass present on the field blank filter to be considered significant.) A filter such as QFF_{b,b} shown in Fig. 1a is termed a dynamic blank by some authors. All samples had been field blank-corrected, and for the six sampling events in which the ability of the denuder to remove gaseous OC was tested, the mass of OC present on QFF field blanks was, on average 28%, of the mass of OC observed on a particle loaded QFF (i.e. QFF_{f,a} in Fig. 1a). The UW-Madison group operated samplers A and B (Fig. 1b) simultaneously during each of the 34 sampling events. The average OC loading on the dynamic blank of the UW-Madison system (QFF_{b,b} Fig. 1b) was $0.58 (\pm 0.24) \mu\text{g C cm}^{-2}$ which was not significantly different than the average field blank OC loading of $0.47 (\pm 0.20) \mu\text{g C cm}^{-2}$. The level of OC on field blank filters was on average 5 (± 4)% of that present on particle loaded QFFs. During 33 sampling events the Rutgers group operated the semi-continuous carbon analyzer in the configuration shown as sampler B in Fig. 1f. The average OC loading on the dynamic blank of the Rutgers system (QFF_{b,b} in Fig. 1f) was 0.33

$(\pm 0.15) \mu\text{g C cm}^{-2}$. Compared to the level of OC on their blank QFF, the level of OC on the dynamic blank was deemed significant by the Rutgers group and was subtracted from the level of OC measured on particle-loaded QFF. It must be noted that in the Rutgers semi-continuous carbon analyzer, the QFF is baked immediately prior to sampling and analyzed immediately after sampling, there is no handling or storage of the sample. For this reason the level of OC on a blank QFF in the Rutgers system was at least a factor of ten lower than the levels observed on the field blank QFFs of all the other ACE-Asia participants who handled and stored their QFF prior to the OC/EC analysis.

Since QFF may not adsorb all gaseous OC escaping a denuder, CIG were used by the Caltech group to evaluate the gaseous OC removal performance of the their XAD-coated denuders. In two experiments during ACE-Asia, the Caltech group used a CIG as a backup filter in sampler B (CIG_{b,b}, Fig. 1a) and another CIG as a field blank (CIG_{blank}). The concentration of OC ($\mu\text{g C m}^{-3}$) measured using CIG_{b,b} and CIG_{blank} was $6.59 (\pm 2.53)$ and $13.24 (\pm 1.01)$, and $28.6 (\pm 1.4)$, and $138 (\pm 7.6)$, respectively, for the two sampling events. The OC values reported for CIG_{b,b} include the subtraction of the OC levels on the field-blank filter. The relatively high levels of OC found on CIG_{b,b} suggest that some gaseous OC escapes the XAD-coated denuders; however, this OC is mostly not adsorbed by QFF (i.e. the levels of OC on QFF_{b,b} were insignificant). This phenomenon has also been observed with XAD-coated glass annular denuders. Lewtas et al. (2001) suggested this OC was gaseous VOCs. Although the XAD-coated denuders do not remove gaseous OC with 100% efficiency, as shown previously in this manuscript and by Mader et al. (2001) such denuders did minimize positive gas adsorption artifacts that occur when sampling with QFFs. (Note: XAD denuders may also be extracted and the extracts analyzed for specific organic compounds.) CIGs were baked immediately prior to sampling and the blank CIG was immediately stored in a petri dish sealed with Teflon tape and placed in a freezer. The levels of OC on blank CIGs were 15–150 times higher than the levels on QFFs, likely due to the fact that organic compounds have a higher affinity for carbon than quartz (Luo, 1996). This is a major tradeoff when selecting a CIG rather than a QFF as a backup filter in a denuder sampler, CIG offer a higher collection efficiency for gaseous OC than QFF, but have significantly higher levels of OC on filter blanks and these levels rise during storage in petri dishes sealed with Teflon tape whereas the levels of OC on QFF field blanks do not. Moreover in aircraft samples collected by the Caltech group the levels of OC on a field blank CIG were at least two times greater than the levels on particle-loaded QFF.

Overall these data indicate that during some situations denuders may not remove 100% of gaseous OC, however the level of OC that escapes a denuder and is adsorbed to QFF was small, (average filter loading of $OC \approx 0.2 \mu\text{g C cm}^{-2}$) and if unaccounted for, whether this OC results in an artifact in the measurement of the ambient particulate OC concentration will depend on the loading of particulate OC on the filter.

4.3. Evaporation of semi-volatile OC from collected particles

As discussed previously, when gas-phase, semi-volatile organic compounds (SOCs) are removed during flow through a denuder, $c_g \rightarrow 0$, SOCs will evaporate from the P-phase in an attempt to re-establish P/G equilibrium. The loss of SOCs from collected particles is frequently termed a “negative”, “evaporation”, or “volatilization” artifact. In this study some groups operating denuder-filter samplers utilized methods to estimate the magnitude of such an artifact.

Several authors have observed that QFF can adsorb gaseous OC (McDow and Huntzicker, 1990; Cotham and Bidleman, 1992; Hart and Pankow, 1994; Turpin et al., 1994; Storey et al., 1995; Mader and Pankow, 2001a, b). Moreover, Eatough et al. (1993) observed that QFF can adsorb gaseous OC evaporated from collected particles. To estimate the amount of OC evaporated from collected particles in their respective denuder-filter samplers, the Caltech, HKUST, and PMEL groups placed a backup QFF downstream of a particle-loaded QFF, and the Caltech and UH-Manoa groups utilized CIGs downstream of particle-loaded QFFs (Figs. 1a and d). If the denuders removed gaseous OC that would adsorb to QFFs, the OC found on a backup QFF in a denuder sampler would have originally been present on collected particles and evaporated from these particles during sampling. It is likely that the collection efficiency of QFFs for gaseous OC is < 100%, it has been reported that carbon impregnated cellulose filters (CIFs) collect gaseous OC with 80–100% efficiency (Eatough et al., 1993; Tang et al., 1994; Lewtas et al., 2001). (Note: CIF consist of cellulose impregnated with activated carbon and CIG consist of glass fibers impregnated with activated carbon. At a given flow rate the pressure drop through the two different filter types is similar suggesting that the packing of fibers in the two types of filters is also similar. For this reason, and since gaseous OC is removed mostly by the activated carbon rather than the cellulose or glass fibers it is likely that CIF and CIG have similar gaseous OC removal efficiencies.) The Caltech and UH-Manoa groups utilized CIGs in their denuder sampler during some, or all, sampling events.

As discussed previously if the gaseous OC collection efficiency of a denuder is < 100%, gaseous OC escaping the denuder can be adsorbed to backup QFF, CIF or

CIGs and be misinterpreted as OC evaporated from collected particles. Dynamic blanks can be used to determine the amount of OC escaping a denuder and prevent such a misinterpretation. The filters labeled QFF_{b,b} were used as a dynamic blank by the Caltech, UW-Madison and Rutgers groups and in some experiments the filter labeled CIG_{b,b} was used by the Caltech group as a dynamic blank (Fig. 1). Lewtas et al. (2001) determined that the PC-BOSS sampler had a gaseous OC removal efficiency of 98.2% and for this reason the UH-Manoa group deemed dynamic blanks unnecessary. As shown in Fig. 2a for the Caltech, HKUST and PMEL groups, the level of OC on a backup QFF in a denuder sampler was not significantly different from the level on a field or dynamic QFF blank. The Caltech and UH-Manoa groups used CIGs to determine the magnitude of evaporation artifacts. As shown in Fig. 2b the levels of OC on blank CIG was lower for the UH-Manoa group than the Caltech group.

Both groups cleaned their CIGs immediately prior to sampling. The difference in the blank levels could be due to differences in the OC analysis method used by each group. The UH-Manoa CIG filters were heated to 300°C, while the Caltech CIG filters were heated to 450°C. For CIGs used in the PC-BOSS sampler, Pang et al. (2001) observed that OC evaporated from particles collected on a filter downstream of the denuder is evolved at temperatures below 300°C. As shown in Fig. 2b for the UH-Manoa group, there was significantly more OC on the backup CIG than on a field blank CIG. For denuder-filter samplers, the fraction of the total filter-collected OC present on a backup filter is

$$f_{\text{bu,OC}} = \frac{m_{\text{oc,b}}}{m_{\text{oc,f}} + m_{\text{oc,b}}} \quad (4)$$

if (1) the gaseous OC collection efficiency of the denuder is 100% or values of $m_{\text{oc,f}}$ and $m_{\text{oc,b}}$ are corrected using dynamic blanks, and (2) the gaseous OC collection efficiency of the backup filter is 100% then

$$f_{\text{bu,OC}} = f_{\text{evp,OC}} \quad (5)$$

where $f_{\text{evp,OC}}$ is the fraction of particulate OC that evaporated during sampling with a denuder-filter sampler. In the current study, it was possible to calculate $f_{\text{bu,OC}}$, but not $f_{\text{evp,OC}}$ since assumptions (1) and (2) were not satisfied by any of the research groups. The median value of $f_{\text{bu,OC}}$ was zero for the Caltech, HKUST and PMEL groups and 0.2 for UH-Manoa group. Possible reasons for the differences in the values of $f_{\text{bu,OC}}$ among the groups is discussed in the next paragraphs.

For the Caltech, HKUST, and PMEL groups, $f_{\text{bu,OC}}$ was calculated using a value of $m_{\text{oc,b}}$ determined from a backup QFF, whereas for the UH-Manoa group $f_{\text{bu,OC}}$ was calculated using a value of $m_{\text{oc,b}}$ determined from a backup CIG. The UH-Manoa group might have observed higher $f_{\text{bu,OC}}$ values than the Caltech, HKUST,

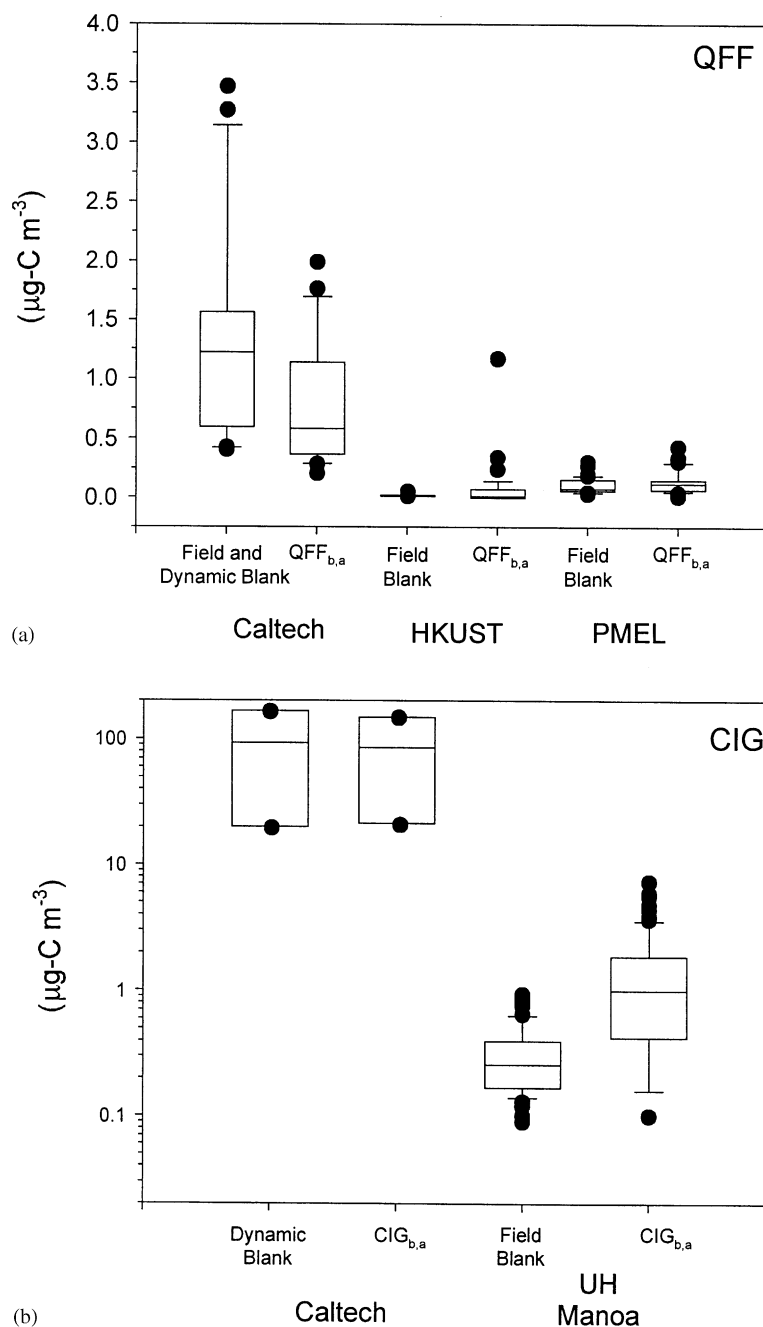


Fig. 2. Mass of OC present on field or dynamic blanks and backup filters present in denuder-filter samplers normalized by the volume of air sampled during the given sampling event: (a) QFF and (b) CIG. The boundary of the box closest to zero indicates the 25th percentile, the line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. When there are a sufficient number of data points, whiskers above and below the box indicate the 90th and 10th percentiles. The black circles indicate data that is on or outside the 90th and 10th percentiles.

and PMEL groups because that the collection efficiency of CIGs for gaseous OC is greater than that of QFFs, that is backup QFFs in the denuder-filter samplers operated by the Caltech, HKUST and PMEL groups

did not collect gaseous OC with 100% efficiency and the amount of OC evaporated from collected particles was underestimated. Therefore, the average $f_{\text{bu,OC}}$ determined by the Caltech, HKUST and PMEL groups

would be less than the value observed by the UH-Manoa group.

Since backup QFFs in denuder-filter samplers may not collect gaseous OC with 100% efficiency, on two research flights during ACE-Asia the Caltech group utilized a CIG rather than a QFF as a backup filter (CIG_{b,a}) and dynamic blank (CIG_{b,b}) (samplers A and B (Fig. 1a)), a third CIG was used as a field blank (CIG_{blank}). In these experiments the concentrations of OC ($\mu\text{g C m}^{-3}$) measured using on the backup, dynamic blank, and field blank were 8.06 (± 2.63), 6.59 (± 2.53) and 13.24 (± 1.01), and 11.70 (± 0.62), 28.6 (± 1.4), and 138 (± 7.6), respectively, for the two sampling events. (The OC values reported for backup and dynamic blank filters include subtraction of the OC levels on the field blank filter.) The amount of OC evaporated from collected particles would be estimated from the difference between the levels of OC on the backup and the dynamic blank CIGs. The OC levels on these filters was approximately half of the field blank value, and about six times the levels measured on particle-loaded QFF_{f,a}. The typical $\approx 10\%$ uncertainty in the OC levels measured for the CIGs is large relative to the OC levels found on particle-loaded QFF_{f,a}. Moreover, the field blank value for CIG in Twin Otter Research Flight 19 was a factor of 250 higher than the OC level found on QFF_{f,a}. In the Caltech system the relatively large amounts of OC present on dynamic and field blank CIGs as compared particle-loaded QFF_{f,a} makes it difficult to accurately evaluate possible evaporative losses of OC from collected particles using CIGs. For sampling under nearly constant temperatures in Pasadena, CA, (Mader et al., 2001) observed using backup and dynamic blank CIGs that $<30\%$ of particle-phase OC could have evaporated during sampling with a denuder-filter sampler.

For the Caltech configuration, the relatively high levels of OC found on the CIG dynamic blank suggests that some gaseous OC escapes the XAD-coated denuders. When a QFF is used as a dynamic blank (i.e. QFF_{b,b}) the levels of OC on the dynamic blank are low. Together these results indicate that gaseous OC not removed by the XAD-coated denuder is not significantly absorbed to a QFF, but is significantly adsorbed by a CIG. For this reason when a CIG is used as a backup filter in a denuder-filter sampler to determine the magnitude of evaporation artifacts, the level of OC measured on the backup CIG must be subtracted from the level of OC present on the dynamic blank CIG.

Another factor affecting the magnitude of evaporation artifacts is the constancy of air temperature during sampling. The K_p values of the compounds comprising the P-phase OC are an important factor governing the magnitude of the evaporation artifact, and the K_p value of a given compound is inversely proportional to

temperature (Yamasaki et al., 1982)

$$\log K_p = \frac{m}{T} + b. \quad (6)$$

For the partitioning of SOCs such as polycyclic aromatic hydrocarbons (PAHs) at temperatures between 273 and 303 K, a change of 10°C typically results in a factor of three change in K_p (Yamasaki et al., 1982; Bidleman et al., 1986). A change in K_p could cause at most a factor three increase in the mass of a given compound evaporated over a given sampling event. Thus, an increase in temperature during sampling will increase the mass of OC evaporated from collected particles. This is particularly important during aircraft sampling since sampling equipment is typically placed inside a heated cabin and the difference in air temperature inside and outside the aircraft can be quite large, especially at higher altitudes where this difference can be $\approx 60^\circ\text{C}$. In addition, if the aircraft changes altitude while sampling, the temperature will change by approximately 1°C per 100 m. If the aircraft descends while sampling such an increase in temperature would enhance the magnitude of OC evaporated from collected particles.

The Caltech denuder sampler was mounted in the unheated nose of the Twin Otter aircraft, and temperature measurements were made using probes located both outside of the aircraft and inside the flow controller of the denuder sampler (and immediately downstream of the filters). These measurements indicate that the temperature inside the samplers was typically within 4°C of the outside temperature. When sampling at a fixed altitude, the temperature varied by $<1^\circ\text{C}$. The denuder sampler operated by the UH-Manoa group was present in the heated cabin of the NCAR-C130 having the average air temperature inside the denuder sampler was 23 (± 2) $^\circ\text{C}$. The average difference between ambient outdoor and cabin air temperature was $+20$ (± 11) $^\circ\text{C}$ and ranged from $+4^\circ\text{C}$ to $+54^\circ\text{C}$. The PMEL denuder sampler was present in the heated cabin of the R/V Ron Brown where the average difference in ambient air temperature and air sampler temperature was $+4^\circ\text{C}$. To summarize, the average difference in the ambient air temperature and air temperature inside the denuder sampler was $+20^\circ\text{C}$, $+4^\circ\text{C}$, and $+4^\circ\text{C}$ for the UH-Manoa, PMEL, and Caltech samplers, respectively. This observation may also partially explain why, among these groups, the value of $f_{\text{bu,OC}}$ was in the order of UH-Manoa $>$ PMEL \approx Caltech.

4.4. Particle transmission through denuder-filter samplers

Denuder samplers are operated such that air flow through the denuder is in the laminar regime. When a denuder is oriented vertically, loss of particles occurs primarily by diffusion to the walls of the sampler. Using

an estimate of the diffusion coefficient of particles of a given diameter and the residence time of particles in the denuder, it is possible to calculate, as a function of particle diameter, the fraction of particles that are lost to the walls by diffusion. In this way, particle transmission efficiency of the denuder can be estimated. For the Caltech sampler such calculations indicate that for particles of 0.1 and 1.0 μm , approximately 2% and 0.2%, respectively, of particles entering the sampler are lost to the denuder walls. Since only particles having diameters $<0.1 \mu\text{m}$ are expected to deposit to denuder walls and since such particles do not comprise a significant fraction of the total ambient OC or EC mass, the diffusive loss of OC and EC in denuders is expected to be minimal.

At ambient temperatures EC is effectively non-volatile, residing exclusively in the particle phase. If the mass of particles lost to the denuder walls by diffusion noticeably affected the measured mass concentration of EC, the concentration of EC ($\mu\text{g C m}^{-3}$) measured using front QFF in a denuder sampler would be significantly less than that determined using a front QFF in an undenuded-filter sampler. The PMEL, Rutgers, and UW-Madison groups simultaneously operated undenuded- and denuder-samplers side by side (Fig. 1). Furthermore for a given research group, and a given sampling configuration the cyclones or impactors located upstream of the various filters had the same $d_{50,\text{aero}}$ values data, so data from these samplers can be used to assess the magnitude of the diffusive loss of EC to denuder walls. (Note: the loss of EC in the denuder portion of the Caltech sampler has previously been shown to be minimal Mader et al., 2001.) In Fig. 3 the concentration of EC ($\mu\text{g m}^{-3}$) measured using front QFF in a denuder sampler is plotted against the value determined using a front QFF in an undenuded-filter sampler (Note: the Caltech data are from experiment conducted in Pasadena, CA using the same low flow denuder-filter samplers that were used in ACE-Asia (Fig. 1a) Mader et al., 2001), the PMEL, Rutgers, and UW-Madison data are from field experiments from ACE-Asia. The slope, intercept, and r^2 values for the PMEL, UW-Madison, Caltech and Rutgers data are $0.85 (\pm 0.07)$, $0.06 (\pm 0.04)$, 0.81 ; $0.90 (\pm 0.07)$, $0.11 (\pm 0.06)$, 0.84 ; $0.98 (\pm 0.07)$, $0.01 (\pm 0.14)$, 0.99 and $1.05 (\pm 0.14)$, $0.005 (\pm 0.06)$, 0.73 . These data indicate that EC concentrations determined using the denuder sampler are nearly equal to the values determined in the undenuded-filter sampler.

Particle losses can occur in the impactor stage or in-between the impactor and denuder stages as well as in a flow splitter or pre-concentrator of denuder-filter samplers. In the case of the Caltech and UH-Manoa samplers, both employed size selective particle separators upstream of the denuder, which could also have particle losses. The Caltech group has reported particle

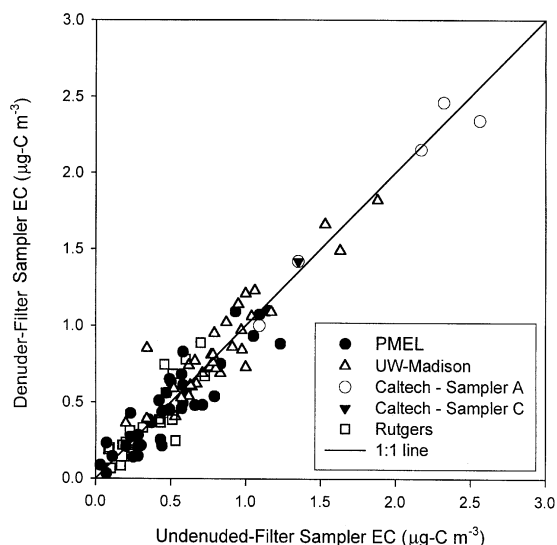


Fig. 3. Concentration of EC ($\mu\text{g C m}^{-3}$) measured using front quartz fiber filter (QFF) in a denuder sampler versus the concentration measured using a front QFF in an undenuded-filter sampler. Caltech sampler A and C are for experiments conducted in Pasadena, CA by Mader et al. (2001) using low and high flow denuder-filter samplers, respectively. The PMEL, UW-Madison, and Rutgers data are were collected during ACE-Asia.

losses in the impactor portion of the high volume denuder sampler (Fig. 1a) (Mader et al., 2001). These losses were greatest for particles having diameters close to the $d_{50,\text{aero}}$ for the impactor, but never exceeded 10% and were negligible for particles with diameters $<5 \mu\text{m}$. Particle losses occurring in the UH-Manoa sampler could be determined by comparing the EC and non-sea salt SO_4 (NSS) levels measured on front filters present in the denuder and undenuded-filter samplers ($\text{QFF}_{\text{f,a}}$ and $\text{QFF}_{\text{f,b}}$, respectively, in Fig. 1d). Such analysis indicates that $\approx 50\%$ of EC and NSS was lost in either the particle concentrator or denuder portion of the sampler. Previous studies have shown that particle losses in the denuder are expected to be $<4\%$ (Pang et al., 2001), therefore it is likely that most of the particle losses occurred in the particle concentrator. Using such side-by-side undenuded-filter sampler data the UH-Manoa group corrected for losses of particulate OC and EC.

4.5. Comparison of OC levels measured using undenuded-filter vs. denuder-filter samplers

During ACE-Asia the PMEL, Rutgers, UH-Manoa, and UW-Madison groups operated undenuded- and denuder-filter samplers side by side, and for a given group each pair of samplers had the same, or no particle size selective inlet. In Fig. 4, the concentration of P-phase OC, as determined using only the front QFF (i.e.

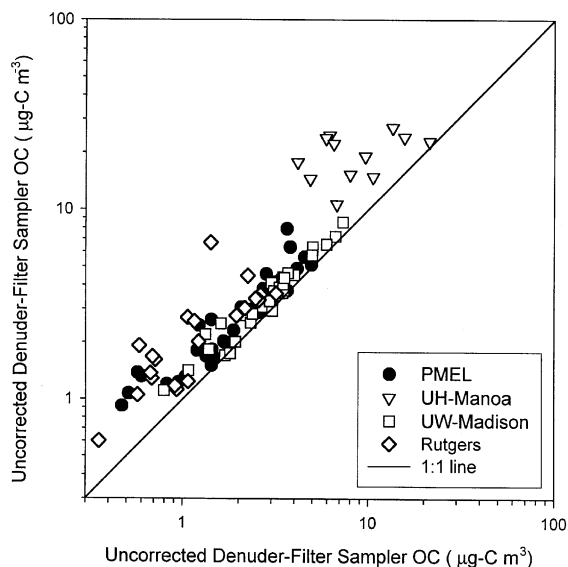


Fig. 4. Concentration of OC ($\mu\text{g C m}^{-3}$) as determined from the measured OC loading on a front quartz fiber filter (QFF) in an undeneded-filter sampler versus the concentration determined from the measured OC loading on a front QFF in a denuder-filter sampler. Data is uncorrected for gas adsorption and evaporation artifacts. (Note: data are plotted on a log scale.)

data not corrected for positive or negative artifacts) in undeneded- and denuder-filter samplers is compared. As shown in Fig. 4, for PMEL, Rutgers, UH-Manoa, and UW-Madison groups, the uncorrected OC concentration as determined using the front QFF in the undeneded-filter sampler was greater than that measured using the front QFF in the denuder-filter sampler. For the UW-Madison, PMEL, UH-Manoa, and Rutgers groups, on average the level of OC present on the front QFF of the undeneded-filter sampler was a factor 1.18, 1.33, 2.09 and 2.40 higher, respectively, than the level on the front QFF of the denuder-filter sampler. This difference could be caused by (1) primarily the adsorption of OC from the gas phase onto the front QFF in the undeneded-filter sampler, (2) primarily the evaporation of OC from particles collected on the front QFF of the denuder-filter sampler or (3) some combination of both mechanisms.

Gas adsorption artifacts in undeneded-filter samplers are corrected using Eq. (1). For denuder-filter samplers, if the gas collection efficiency of the denuder is 100%, then evaporation artifacts are corrected using Eq. (2). If the gas collection efficiency of the denuder is $<100\%$, the mass of OC on the dynamic blank ($m_{\text{oc,db}}$) must be subtracted from $m_{\text{oc,f}}$ and $m_{\text{oc,b}}$:

$$\text{OC}_{\text{meas,d}} (\mu\text{g C m}^{-3}) = \frac{(m_{\text{oc,f}} - m_{\text{oc,db}}) + (m_{\text{oc,b}} - m_{\text{oc,db}})}{V_s} \quad (7)$$

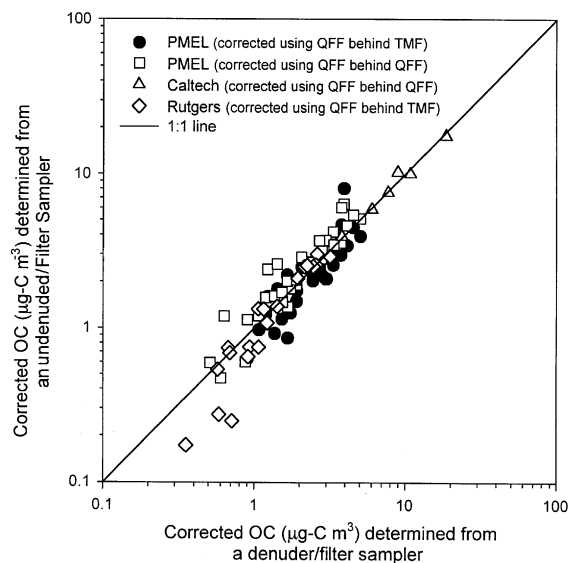


Fig. 5. Concentration of OC ($\mu\text{g C m}^{-3}$) measured using an undeneded-filter sampler versus the concentration measured using a denuder-filter sampler. Data from the undeneded-filter sampler were corrected using Eq. (1). Depending on the sampling configuration, data from the denuder-filter sampler were corrected using either Eq. (2) or Eq. (7) (Note: the Rutgers group did not utilize a backup QFF in their denuder-filter sampler, data obtained from this sampler were corrected by subtracting the amount of OC present on the dynamic blank ($\text{QFF}_{\text{b,a}}$) from the amount of OC present on $\text{QFF}_{\text{f,a}}$, essentially the second term in Eq. (7) was not used.) The legend indicates the type of backup filter used to correct the undeneded-filter data. (Note: data are plotted on a log scale.)

In Fig. 5, for a given experiment where undeneded- and denuder-filter samplers were operated side-by-side, the corrected OC concentrations (corrections based on data from backup QFF) as determined using an undeneded-filter sampler are plotted versus the corrected OC concentrations as determined using a denuder-filter sampler. For the PMEL group, the mass of OC adsorbed to the front QFF could be estimated from either (1) the mass of OC present on $\text{QFF}_{\text{b,b}}$ (Fig. 1c) or (2) the mass of OC present on the backup $\text{QFF}_{\text{b,c}}$ (Fig. 1c). As discussed previously, the level of OC on $\text{QFF}_{\text{b,c}}$ was ≈ 2.7 times greater than $\text{QFF}_{\text{b,b}}$ (Ostensibly due to the lower gas adsorption capacity of the front $\text{TMF}_{\text{f,c}}$ vs. front $\text{QFF}_{\text{f,b}}$). For the Rutgers group, the mass of OC adsorbed to the front QFF could be estimated from the mass of OC present on the backup $\text{QFF}_{\text{b,d}}$ (Fig. 1f). In Fig. 5, for the PMEL and Rutgers groups, the corrected OC concentration determined using the undeneded-filter sampler was nearly equal to the corrected OC concentration determined using the denuder-filter sampler (corrections were based on data from backup QFF). The ratio of the corrected OC concentration determined using the undeneded-filter

sampler to that determined using the denuder-filter sampler was 0.94 (± 0.29) and 0.90 (± 0.26), respectively, for the PMEL and Rutgers groups which is similar to the average value of 0.99 (± 0.08) observed by Mader et al. (2001) in Pasadena, CA (Fig. 5). Therefore in these studies the difference between the amount of OC on the front QFF of an undenuded- and denuder-filter sampler was nearly equal to the amount of OC present on the backup QFF in the undenuded-filter sampler.

For the PMEL group, the OC concentration as determined using an undenuded-filter sampler could be corrected using Eq. (1), and the mass of OC present on backup filter QFF_{b,b} (the backup QFF present behind a QFF, Fig. 1). The corrected OC concentration using this correction scheme is also shown in Fig. 5. For this correction scheme, on average the corrected OC concentration was a factor 1.18 (± 0.29) greater than the corrected OC concentration determined using the denuder-filter sampler. These results are consistent with the idea that a QFF present behind a particle-loaded QFF may not reach gas/filter equilibrium, therefore the mass of OC determined on the backup QFF is an underestimation of the amount of OC on a particle-loaded front filter that resulted from the adsorption of native gaseous OC. This analysis illustrates that depending on the sampling configuration, differences in the corrected OC concentration can exist between undenuded- and denuder-filter samplers but these differences are on average 10%.

5. Summary/suggestions

In future field experiments so as to ensure accurate comparisons across platforms, participants should utilize as similar OC/EC analysis methods as is possible. If thermal evolved gas techniques are utilized, the same temperature program and charring correction method should be used. Furthermore air sampling configurations should be used in which positive and negative gas adsorption artifacts are reduced or can be corrected. Depending on the sampling configuration, differences in the corrected OC concentration can exist between undenuded- and denuder-filter samplers, and these differences are on the order of 10%. Uncorrected for sampling artifacts, such differences can be as large as a factor of two, illustrating the importance of utilizing air sampling configurations in which gas adsorption or evaporation artifacts are reduced or can be corrected. ACE-Asia participants utilized such sampling configurations.

Acknowledgements

The Caltech group was supported by Office of Naval Research Grant N00014-96-0119 and National Science

Foundation Grant ATM-0001934. The PMEL measurements were funded by the Aerosol Project of the NOAA Climate and Global Change Program.

References

- Bates, T.S., Coffman, D.J., Covert, D.S., Quinn, P.K., 2002. Regional marine boundary layer aerosol size distributions in the Indian, Atlantic and Pacific Oceans: a comparison of INDOEX measurements with ACE-1, ACE-2, and Aerosols99. *Journal of Geophysical Research* 107, No. D19, 8026, doi: 10.1029/2001JD001174.
- Berner, A., Lurzer, C., Pohl, F., Preining, O., Wagner, P., 1979. Size distribution of the urban aerosol in Vienna. *Science of the Total Environment* 13, 245–261.
- Bidleman, T.F., Billings, W.N., Foreman, W.T., 1986. Vapor-particle partitioning of semivolatile organic compounds: estimates from field collections. *Environmental Science and Technology* 20, 1038–1043.
- Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Science and Technology* 25, 221–241.
- Cotham, W.E., Bidleman, T.F., 1992. Laboratory investigations of the partitioning of organochlorine compounds between the gas phase and atmospheric aerosols on glass fiber filters. *Environmental Science and Technology* 26, 468–478.
- Eatough, D.J., Wadsworth, A., Eatough, D.A., Crawford, J.W., Hansen, L.D., Lewis, E.A., 1993. A multiple-system, multi-channel diffusion denuder sampler for the determination of fine-particulate organic material in the atmosphere. *Atmospheric Environment* 27, 1213–1219.
- Eatough, D.J., Obeidi, F., Pang, Y., Ding, Y., Eatough, N.L., Wilson, W.E., 1999. Integrated and real-time diffusion denuder sampler for PM2.5. *Atmospheric Environment* 33, 2835–2844.
- Hart, K.M., Pankow, J.F., 1994. High volume air sampler for particle and gas sampling 2. Use of backup filters to correct the adsorption of gas phase polycyclic aromatic hydrocarbons to the front filter. *Environmental Science and Technology* 28, 655–661.
- John, W., Reischl, G., 1980. A cyclone for the size-selective sampling of ambient air. *Journal of the Air Pollution Control Association* 30, 872–876.
- Kamens, R.M., Coe, D.L., 1997. A large gas-phase stripping device to investigate rates of PAH evaporation from airborne diesel soot particles. *Environmental Science and Technology* 31, 1830–1833.
- Lewtas, J., Pang, Y., Booth, D., Reimer, S., Eatough, D.J., Gundel, L.A., 2001. Comparison of sampling methods for semi-volatile organic carbon associated with PM2.5. *Aerosol Science and Technology* 34, 9–22.
- Liang, C., Pankow, J.F., 1996. Gas/particle partitioning of organic compounds to environmental tobacco smoke: partition coefficient measurements by desorption and comparison to urban particulate material. *Environmental Science and Technology* 30, 2800–2805.
- Luo, W., 1996. Gas/Particle partitioning of semi-volatile organic compounds to two model atmospheric particulate

- materials: quartz and graphitic carbon. Ph.D. Thesis, Oregon Graduate Institute of Science and Technology, Portland.
- Mader, B.T., Pankow, J.F., 2000. Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters. 1. Gas/solid partitioning of polychlorinated dibenzodioxins, polychlorinated dibenzofurans and polycyclic aromatic hydrocarbons to teflon membrane filters. *Atmospheric Environment* 34, 4879–4887.
- Mader, B.T., Pankow, J.F., 2001a. Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters. 3. An analysis of gas adsorption artifacts in measurements of atmospheric SOCs when using Teflon membrane filters and quartz fiber filters. *Environmental Science and Technology* 35, 3422–3432.
- Mader, B.T., Pankow, J.F., 2001b. Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters. 2. Partitioning of polychlorinated dibenzodioxins polychlorinated dibenzofurans and polycyclic aromatic hydrocarbons to quartz fiber filters. *Atmospheric Environment* 35, 1217–1223.
- Mader, B.T., Flagan, R.C., Seinfeld, J.H., 2001. Sampling atmospheric carbonaceous aerosols using a particle trap impactor/denuder sampler. *Environmental Science and Technology* 35, 4857–4867.
- Mader, B.T., Flagan, R.C., Seinfeld, J.H., 2002. Airborne measurements of atmospheric carbonaceous aerosols during ACE-Asia. *Journal of Geophysical Research* 107, No. D23, 4704, doi: 10.1029/2002JD002221 for publication.
- McDow, S.R., Huntzicker, J.J., 1990. Vapor adsorption artifact in the sampling of organic aerosol: face velocity effects. *Atmospheric Environment* 24, 2563–2571.
- Pang, Y., Ren, Y., Obeidi, F., Hastings, R., Eatough, D.J., Wilson, W.E., 2001. Semi-volatile species in PM_{2.5}: comparison of integrated and continuous samplers for PM_{2.5} research or monitoring. *Journal of the American Waste Management Association* 51, 25–36.
- Schauer, J.J., Mader, B.T., Deminter, J.T., Heidemann, G., Bae, M.S., Seinfeld, J.H., Flagan, R.C., Cary, R.A., Smith, D., Huebert, B.J., Bertram, T., Howell, S., Quinn, P., Bates, T., Turpin, B., Limp, H.J., Yu, J., Yang, C.H., Keywood, M.D., 2002. ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon. Submitted for publication.
- Storey, J.M., Luo, W., Isabelle, L.M., Pankow, J.F., 1995. Gas/solid partitioning of semivolatile organic compounds to model atmospheric solid surfaces as a function of relative humidity. 1. Clean quartz. *Environmental Science and Technology* 29, 2420–2428.
- Tang, H., Lewis, E.A., Eatough, D.J., Burton, R.M., Farber, R.J., 1994. Determination of the particle size distribution and chemical composition of semi-volatile organic compounds in atmospheric fine particles with a diffusion denuder sampling system. *Atmospheric Environment* 28, 939–947.
- Turpin, B.J., Huntzicker, J.J., 1994. Investigation of organic aerosol sampling artifacts in the Los Angeles Basin. *Atmospheric Environment* 28, 3061–3071.
- Turpin, B.J., Huntzicker, J.J., 1995. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmospheric Environment* 29, 3527–3544.
- Turpin, B.J., Cary, R.A., Huntzicker, J.J., 1990. An in situ, time-resolved analyzer for aerosol organic and elemental carbon. *Aerosol Science and Technology* 12, 161–171.
- Turpin, B.J., Hering, S.V., Huntzicker, J.J., 1994. Investigations of organic aerosol sampling artifacts in the Los Angeles Basin. *Atmospheric Environment* 28, 3061–3071.
- Turpin, B.J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmospheric Environment* 34, 2983–3013.
- Yamasaki, H., Kuwata, K., Miyamoto, H., 1982. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environmental Science and Technology* 16, 180–194.