

Particulate carbon measurements in California's San Joaquin Valley

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Abstract

Aerosol carbon sampling methods and biases were evaluated during the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) and Fresno Supersite programs. PM_{2.5} sampling was conducted using Desert Research Institute (DRI) sequential filter samplers (SFS) from December 1999 through February 2001 at two urban sites (Fresno and Bakersfield), one regional transport site (Angiola), and two boundary sites (Bethel Island and Sierra Nevada Foothills) during CRPAQS in the San Joaquin Valley (SJV). Additional filter-based sampling was done in Fresno as part of the US Environmental Protection Agency (EPA) Supersites program. Organic carbon (OC) and elemental carbon (EC) concentrations were higher during winter (December–February) than summer (June–August) and this trend was most pronounced at Fresno and Bakersfield. OC and EC displayed similar diurnal trends during winter and summer at Fresno and during winter at Angiola. The diurnal pattern at Angiola reflected the transport of secondary pollutants to the site. Collocated measurements of OC and EC on undenuded quartz-fiber filters were made at Fresno with the DRI SFS and the Andersen FRM and RAAS samplers. All average differences in OC between samplers were less than their respective measurement uncertainties. Positive and negative OC biases were evaluated at Fresno using the Andersen RAAS sampler with carbon-denuded and undenuded channels with Teflon-membrane and quartz-fiber filter pairs. Differences between the denuded particle OC and that obtained by subtracting the quartz-behind-Teflon or quartz-behind-quartz OC from the undenuded quartz-fiber front filter were less than twice their measurement uncertainties in most cases. Particulate OC in the denuded channel agreed most closely with the difference between undenuded front and backup quartz-fiber OC.

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1. Introduction

The California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) was conducted in central California over 14 months, from December 1999 through January 2001, to determine the causes of elevated levels of PM_{2.5} and PM₁₀ (particles with diameters less than 2.5

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and 10 micrometers [μm], respectively) and to evaluate the means of reducing them with respect to Federal and state air quality regulations (Watson et al., 1998). For compliance with $\text{PM}_{2.5}$ National Ambient Air Quality Standards (NAAQS), the US Environmental Protection Agency (EPA) requires the use of a Federal Reference Method (FRM) sampler for collecting $\text{PM}_{2.5}$ on a Teflon-membrane filter and determining its mass gravimetrically (US EPA, 1997).

Organic carbon (OC) is a large fraction of the $\text{PM}_{2.5}$ in urban and remote locations (Chow et al., 1994, 1998; Malm et al., 1994; Andrews et al., 2000; Watson and Chow, 2002a). Bulk OC is typically determined with thermal techniques on quartz-fiber filters that can be heated to up to 1000 °C (Chow et al., 1993). Quartz-fiber filters adsorb volatile organic compounds (VOC) from the atmosphere. Adsorption results in a positive bias in the measurement of particulate organic carbon (POC) on a quartz-fiber filter, while the loss of semi-volatile organic compounds (SVOC) from particles on the filter leads to a negative bias (Eatough et al., 1990; McDow and Huntzicker, 1990; Turpin et al., 1994). Eatough et al. (1990) and Tang et al. (1994) found that volatilized POC exceeded adsorbed OC, while Turpin et al. (1994) came to the opposite conclusion at a different time and location, using a different measurement method. Several sampling strategies have been devised to quantify these biases. Turpin et al. (1994) recommended that in an undenuded carbon sample stream, a quartz-fiber filter could be placed behind a Teflon-membrane filter to estimate the positive artifact. The OC concentration on this backup filter is subtracted from the OC concentration on a front quartz-fiber filter in a parallel channel. Similarly, a quartz-fiber filter behind an undenuded quartz-fiber filter has been used for the same purpose. Carbon denuders have also been used in an attempt to remove organic gases to minimize filter adsorption (Eatough et al., 1993; Gundel et al., 1995; Ding et al., 2002; Subramanian et al., 2004). However, these denuders also reduce the equilibrium vapor pressures over the particulate organic matter (POM), thereby enhancing volatilization.

To evaluate carbon sampling artifacts at the Pittsburgh Supersite, Subramanian et al. (2004) tested OC on two denuded and two undenuded channels. One of the two carbon-denuded sample streams was preceded by a Teflon-membrane filter to remove particles. Both denuders were followed by quartz-fiber filters with carbon-impregnated glass-fiber filter backups. Two additional sampling channels consisted of quartz-fiber backups to Teflon-membrane and quartz-fiber front filters, respectively. This experimental setup is similar to the one used in Fresno, and comparisons are made between the two.

In this paper, carbon measurements during the CRPAQS and Fresno Supersite programs are examined.

Several samplers are compared and their differences quantified. Sampling artifacts for OC on quartz-fiber filters are evaluated at the Fresno Supersite and the results are compared with those from previous studies.

2. Methods

Aerosol sampling during CRPAQS was conducted at two urban sites (Fresno and Bakersfield), one regional transport site (Angiola), and two boundary sites (Bethel Island, located east of the San Francisco Bay area, and Sierra Nevada Foothills, located on the west slope of the Sierra Nevada) (Fig. 1). The samplers were: (1) an Andersen Instruments multi-channel reference ambient air sampling (RAAS) speciation sampler (Smyrna, GA); (2) an Andersen single-channel FRM sampler; and (3) Desert Research Institute (DRI, Reno, NV) sequential filter samplers (SFS). OC and elemental carbon (EC) were sampled on 47 mm quartz-fiber filters (Pall Gelman, Putnam, CT, #2500) and analyzed by the IMPROVE thermal/optical reflectance (TOR) protocol (Chow et al., 1993, 2001, 2004). Sampling system configurations are illustrated in Fig. 2 (Watson and Chow, 2002a,b). All samplers were preceded by $\text{PM}_{2.5}$ size-selective inlets: an AIHL cyclone for the RAAS, an EPA WINS impactor for the FRM, and a Sensidyne Bendix 240 cyclone for the SFS (Watson and Chow, 2001).

Undenuded single quartz-fiber filter channels from the FRM and SFS were used for comparison with multi-channel RAAS carbon. The RAAS was configured with three channels: (1) a double-stage Teflon-membrane/quartz-fiber filter pack (TQ), (2) a double-stage quartz-



Fig. 1. Locations of California Regional $\text{PM}_{10}/\text{PM}_{2.5}$ Air Quality Study (CRPAQS) anchor sites, including boundary Sierra Nevada Foothills and Bethel Island, urban Fresno and Bakersfield, and regional transport Angiola sites.

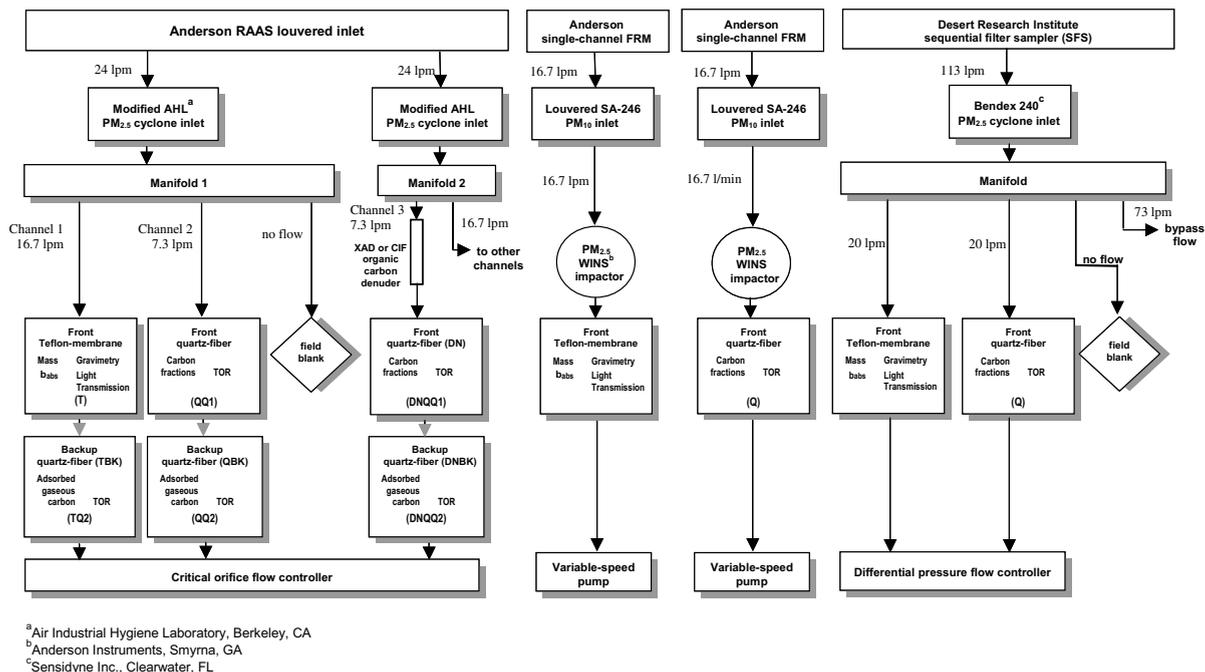


Fig. 2. Collocated sampling configurations: (1) Andersen RAAS sampler with parallel undenuded tandem Teflon–quartz and quartz–quartz filters, (2) Andersen FRM single-channel sampler, and (3) DRI (Reno, NV) SFS sampler with undenuded single quartz channel.

fiber/quartz-fiber filter pack (QQ), and (3) an organic gas denuder followed by a double-stage quartz-fiber/quartz-fiber filter pack (DNQQ). An XAD-coated glass denuder (URG Corporation, Chapel Hill, NC) was used from January 1, 2000 to June 30, 2000, and a charcoal-impregnated cellulose-fiber filter (CIF) parallel-plate denuder (Brigham Young University [BYU], Provo, UT) was used after July 11, 2000. The XAD denuder (27 cm long \times 2.8 cm outside diameter) consisted of four 0.2 cm thick \times 20 cm long concentric tubes spaced 0.2 cm apart and coated with washed XAD-4 resin (Alltech Associates Inc., Deerfield, IL) following the procedure developed by Gundel et al. (1995). The CIF denuder followed the design of Eatough (1999) (46.4 cm long \times 4 cm wide \times 4 cm high) with 13 rectangular filter strips (24.5 cm long 3.7 cm wide \times 0.41 mm thick) (Schleicher & Schuell, Keene, NH) separated by 2 mm diameter aluminum rods. Denuders were cleaned, recoated, or replaced with unexposed CIF strips every one to two months. Twenty-four-hour Andersen FRM and RAAS samples were collected in Fresno on the EPA six-day schedule from July 5, 1999 through December 29, 2003.

During CRPAQS, 24-h samples were collected on the EPA six-day schedule starting on December 2, 1999 through February 3, 2001 at the Fresno, Bakersfield, and Angiola sites. Sampling at Bethel Island and Sierra Nevada Foothills began on December 2, 2000. Daily SFS samples were collected at Fresno and Angiola

during the fall 2000 intensive sampling campaign on October 14, October 16–20, October 22–24, and November 2–9. A winter intensive study was conducted at all five sites on December 15–18 and December 26–28, 2000, and January 4–7 and January 31–February 3, 2001, when daily SFS samples were collected from 0000–0005, 0005–1000, 1000–1300, 1300–1600, and 1600–2400 Pacific Standard Time (PST). In addition, 30-min averaged total particle carbon (TC) and OC were acquired in Fresno and Angiola using R&P 5400 Ambient Carbon Particulate Monitors (Rupprecht & Patashnick, Albany, NY). EC was obtained by difference.

3. Results and discussion

3.1. Spatial and temporal trends during CRPAQS

PM_{2.5} OC and EC concentrations at Angiola ranged from 0.12 ± 0.21 and $0.0 \pm 0.1 \mu\text{g}/\text{m}^3$ on October 21, 2000 to 15.4 ± 0.21 and $4.2 \pm 0.6 \mu\text{g}/\text{m}^3$ on November 8, 2000. The corresponding PM_{2.5} mass concentrations were 0.04 ± 0.45 (below minimum detection limits) and $98 \pm 5 \mu\text{g}/\text{m}^3$, respectively. At Bakersfield, OC and EC concentrations ranged from 2.2 ± 0.3 and $0.70 \pm 0.16 \mu\text{g}/\text{m}^3$ on October 27, 2000 to 24 ± 3 and $8.3 \pm 1.6 \mu\text{g}/\text{m}^3$ on January 1, 2001. The corresponding PM_{2.5} mass concentrations were 6.1 ± 0.5 and $133 \pm 7 \mu\text{g}/\text{m}^3$, respectively. At Fresno, OC and EC concentrations

ranged from 2.3 ± 0.3 and $0.30 \pm 0.10 \mu\text{g}/\text{m}^3$ on September 3, 2000 to 37 ± 5 and $10.3 \pm 1.7 \mu\text{g}/\text{m}^3$ on January 6, 2001. The corresponding $\text{PM}_{2.5}$ mass concentrations were 4.1 ± 0.4 and $129 \pm 7 \mu\text{g}/\text{m}^3$, respectively.

Fig. 3 presents time series of monthly average TC, OC, and EC concentrations measured with the SFS sampler at the five sites during CRPAQS. Carbon concentrations were 2–5 times higher during winter, compared to summer, with the seasonal differences most pronounced at the two urban sites (Fresno and Bakersfield). Increased residential wood combustion (RWC) during cold winter periods coupled with enhanced surface radiation inversions result in elevated carbon concentrations (Schauer and Cass, 2000; Watson et al., 2000). OC and EC concentrations at Bethel Island and Sierra Nevada Foothills during the final three months

of the CRPAQS study were similar to those found at Angiola (Fig. 3).

Diurnal trends for TC, OC, and EC—measured continuously with the R&P 5400 analyzer at Fresno during summer (June–August) and winter (December–February), and at Angiola during winter—are presented in Fig. 4. In Fresno, there were morning and late afternoon rush hour peaks during summer. During winter, OC, and EC concentrations peaked at night and carried over to the early morning period, probably due to RWC and the development of a nighttime inversion. There was also evidence of a morning rush-hour effect around 0700 PST. The pattern at Angiola during winter was different, with lower carbon concentrations and less-pronounced diurnal variations compared to the urban Fresno site. The afternoon OC increase at Angiola corresponded to increases of secondary atmospheric constituents, such as ozone and particulate nitrate. These were attributed to a combination of photochemical con-

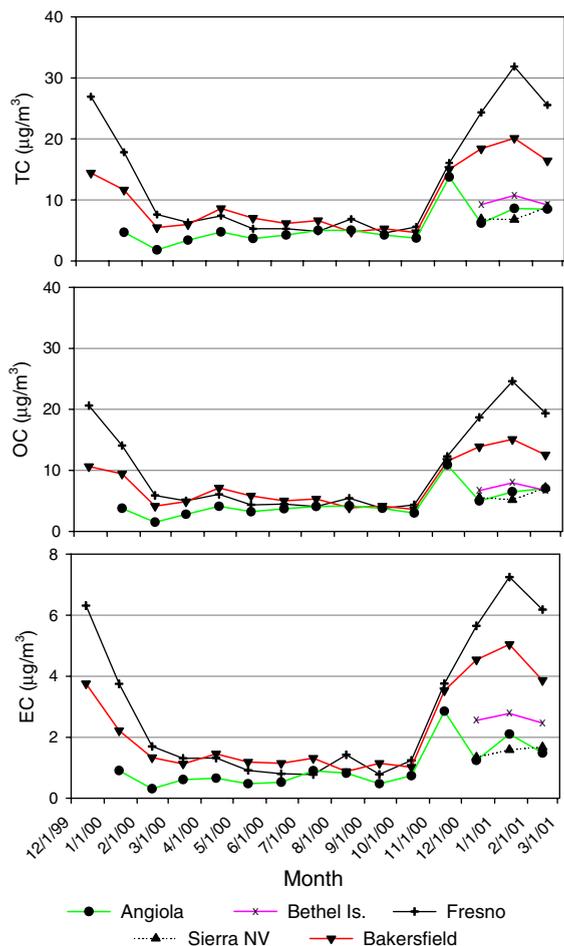


Fig. 3. Monthly average total carbon (TC) (sum of OC and EC), organic carbon (OC), and elemental carbon (EC) at the Bethel Island, Sierra Nevada Foothills, Fresno, Bakersfield, and Angiola sites during CRPAQS.

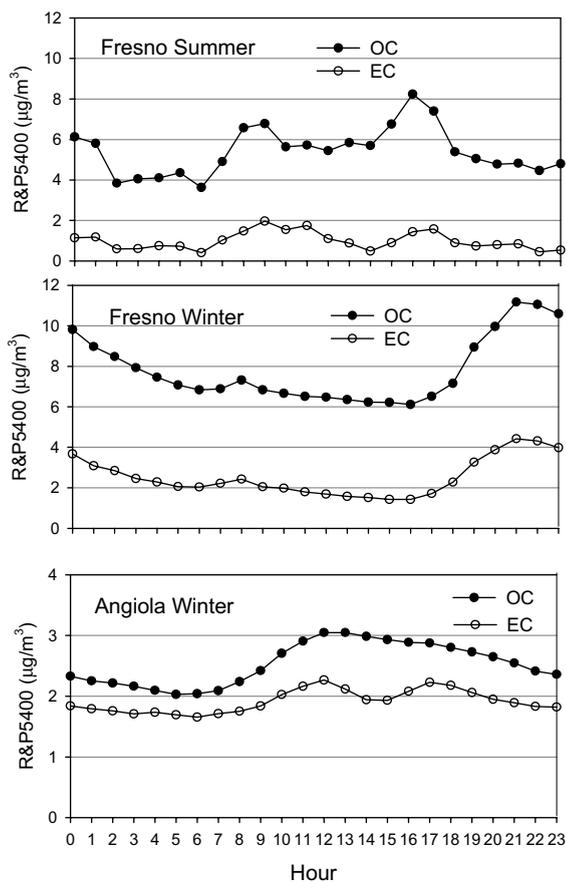


Fig. 4. Diurnal (hourly) trends for OC and EC measured with the R&P 5400 at Fresno during winter (December–February) and summer (June–August) and at Angiola during winter. Hours in Pacific Standard Time (PST).

version of urban pollutants and boundary layer convection, followed by vertical and horizontal transport to non-urban locations (Watson and Chow, 2002b).

3.2. Sampler inter-comparisons

Figs. 5 and 6 compare 24-h average TC, OC, and EC measured with the SFS and R&P 5400 samplers at the Angiola and Fresno sites, respectively. Methods and metrics used for method or sampler inter-comparisons (e.g., Y versus X) are described by Watson and Chow (2002a). Table 1 summarizes the respective comparison statistics. Uncertainties are not reported for the R&P 5400 data. Fig. 5 shows that SFS TC and OC were 26–37% higher than the corresponding R&P 5400

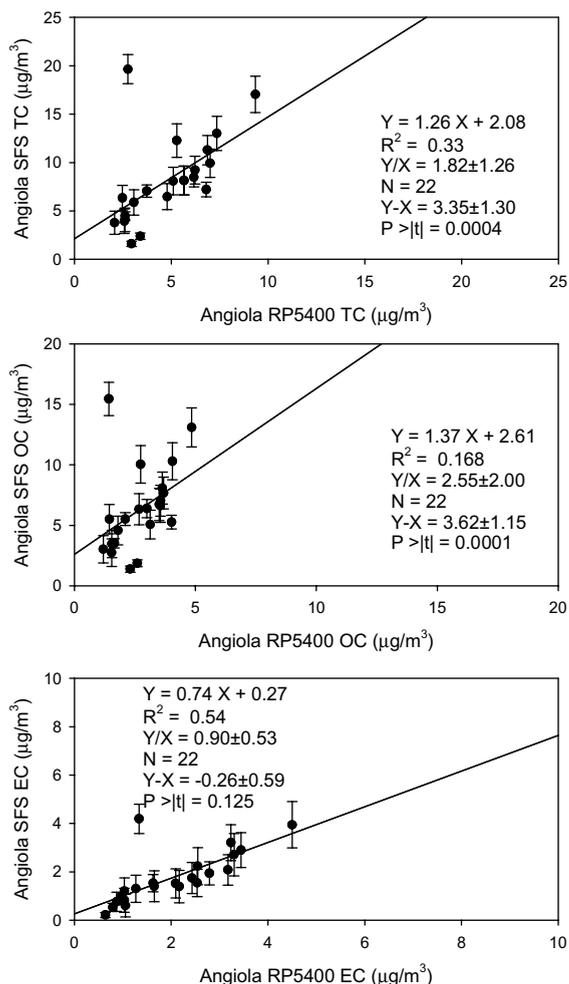


Fig. 5. Comparison between SFS and R&P 5400 24-h average total, organic, and elemental carbon (TC, OC, and EC) at the Angiola site from November 2000 through January 2001.

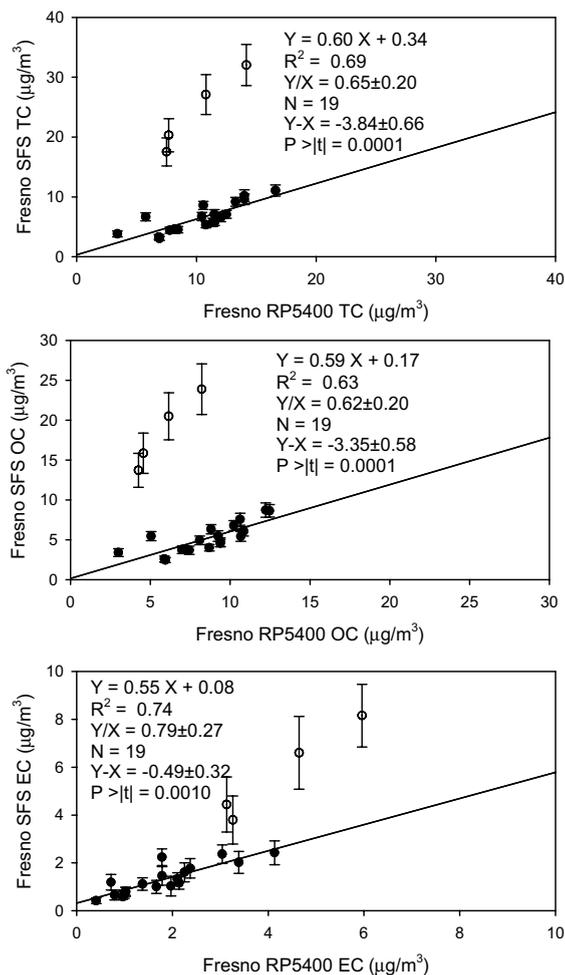


Fig. 6. Comparison between SFS and R&P 5400 24-h average TC, OC, and EC at Fresno from January 2000 through January 2001. Open circles represent samples collected after May 2000, when the R&P 5400 instrument malfunctioned, as described in the text.

concentrations at Angiola, with significant (2–2.6 $\mu\text{g}/\text{m}^3$) intercept and low correlations. The average difference ($Y - X$) of 3.4 to 3.6 $\mu\text{g}/\text{m}^3$ was larger than the propagated uncertainty of the SFS measurements. However, the average difference for EC was not significant, either statistically ($P > 0.05$) or with respect to the measurement uncertainty, which was larger. In Fresno, the R&P 5400 instrument malfunctioned after May 2000. Before this time, SFS TC, OC, and EC concentrations were 40–45% lower than the corresponding R&P 5400 concentrations (Fig. 6).

Figs. 7 and 8 compare 24-h average OC and EC concentrations, respectively, measured on undened quartz-fiber filters in RAAS, FRM, and SFS samplers at the Fresno Supersite (Watson and Chow, 2001).

Table 1
Inter-comparison statistics for R&P 5400, SFS, FRM, and RAAS samplers during CRPAQS and at the Fresno Supersite

Y	X	EV slope	EV unc.	EV int.	EV unc.	OL slope	OL unc.	OL int.	OL unc.	Corr.	N	Y/X	Std.	del < 1 s	1–2 s	2–3 s	>3 s	Y – X	Std. (y – x)	Unc. (y – x)	P > t
<i>Angiola 24-hour average CRPAQS (11/8/00–2/3/01)</i>																					
SFS_TC	RP_TC	1.61	0.12	–1.59	0.44	1.26	0.40	2.12	2.08	0.57	22	1.82	1.26	1	7	6	8	3.35	3.72	1.30	0.0004
SFS_OC	RP_OC	1.24	0.20	0.37	0.51	1.37	0.68	2.61	1.98	0.41	22	2.55	2.00	0	4	7	11	3.62	3.21	1.15	0.0001
SFS_EC	RP_EC	0.91	0.10	–0.19	0.12	0.74	0.15	0.27	0.34	0.74	22	0.90	0.53	14	6	0	2	–0.26	0.78	0.59	0.1248
<i>Fresno 24-hour average CRPAQS (11/9/00–2/3/01)</i>																					
SFS_TC	RP_TC	0.57	0.05	0.17	0.43	0.60	0.10	0.34	1.05	0.83	19	0.65	0.20	1	1	1	16	–3.84	1.87	0.66	0.0001
SFS_OC	RP_OC	0.56	0.05	0.08	0.42	0.59	0.11	0.17	0.97	0.79	19	0.62	0.20	2	0	0	17	–3.35	1.51	0.58	0.0001
SFS_EC	RP_EC	0.60	0.07	0.15	0.10	0.55	0.08	0.32	0.16	0.86	19	0.79	0.27	3	9	4	3	–0.49	0.55	0.32	0.0010
<i>Fresno Supersite Filter Samplers (12/2/99–1/31/01)</i>																					
RAAS_OC	SFS_OC	1.06	0.05	–0.04	0.26	1.08	0.03	–0.10	0.31	0.98	55	1.06	0.18	33	18	3	1	0.55	1.59	1.64	0.0127
FRM_OC	SFS_OC	0.98	0.04	–0.05	0.20	1.05	0.02	–0.38	0.27	0.99	55	0.99	0.13	40	13	1	1	0.02	1.34	1.56	0.9354
RAAS_OC	FRM_OC	1.02	0.04	0.18	0.21	1.02	0.02	0.32	0.25	0.99	56	1.07	0.17	40	9	5	2	0.51	1.25	1.40	0.0037
RAAS_EC	SFS_EC	0.93	0.05	0.05	0.07	1.04	0.03	–0.09	0.08	0.98	55	1.01	0.3	40	13	1	1	0.01	0.43	0.65	0.9165
FRM_EC	SFS_EC	0.99	0.05	0.10	0.06	1.01	0.03	0.12	0.10	0.98	55	1.11	0.25	42	10	2	1	0.14	0.50	0.62	0.0405
RAAS_EC	FRM_EC	0.88	0.04	0.00	0.06	0.99	0.04	–0.12	0.11	0.97	56	0.92	0.24	26	24	4	2	–0.14	0.58	0.49	0.0846
RAAS_TC	SFS_TC	1.05	0.04	–0.05	0.27	1.08	0.02	–0.24	0.33	0.99	55	1.04	0.17	34	16	4	1	0.59	1.79	1.75	0.0176
FRM_TC	SFS_TC	1.00	0.03	–0.04	0.22	1.04	0.02	–0.32	0.28	0.99	55	1.01	0.13	39	14	1	1	0.15	1.40	1.73	0.4214
RAAS_TC	FRM_TC	1.01	0.03	0.09	0.24	1.03	0.02	0.10	0.27	0.99	56	1.04	0.16	37	14	4	1	0.40	1.36	1.52	0.0304
<i>Fresno Supersite RAAS Sampler (7/5/99–12/29/03)</i>																					
RAASDN_EC	RAAS_EC	0.79	0.02	0.03	0.02	1.03	0.02	–0.08	0.06	0.96	247	1.04	0.59	129	61	34	23	–0.02	0.62	0.48	0.6433
QP_OC	DNP_OC	0.80	0.02	1.00	0.09	0.87	0.02	0.78	0.15	0.97	193	1.13	0.39	93	70	16	14	–0.02	1.65	0.96	0.8765
TP_OC	DNP_OC	0.80	0.02	0.03	0.08	0.91	0.02	–0.30	0.16	0.97	193	0.87	0.31	99	46	19	29	–0.87	1.62	0.89	0.0001
TP_OC	QP_OC	0.99	0.02	–0.84	0.08	1.04	0.01	–1.08	0.07	0.99	193	0.78	0.19	72	80	32	9	–0.85	0.63	0.89	0.0001

Statistics include: (1) linear regression ($Y = aX + b$) using effective variance-weighted least squares (EV), where weighting is based on the uncertainties of the dependent and independent variables, and ordinary (un-weighted) least squares (OL); (2) linear correlation; (3) the average ratio of Y/X and its standard deviation; (4) the frequency with which $Y - X$ is less than or greater than one, two, and three times its propagated measurement uncertainty; (5) the average of $Y - X$, its standard deviation, and RMS (root mean squared) measurement uncertainty; and (6) the paired-difference t -test for $Y - X$, which is significantly greater than zero when $P < 0.05$.

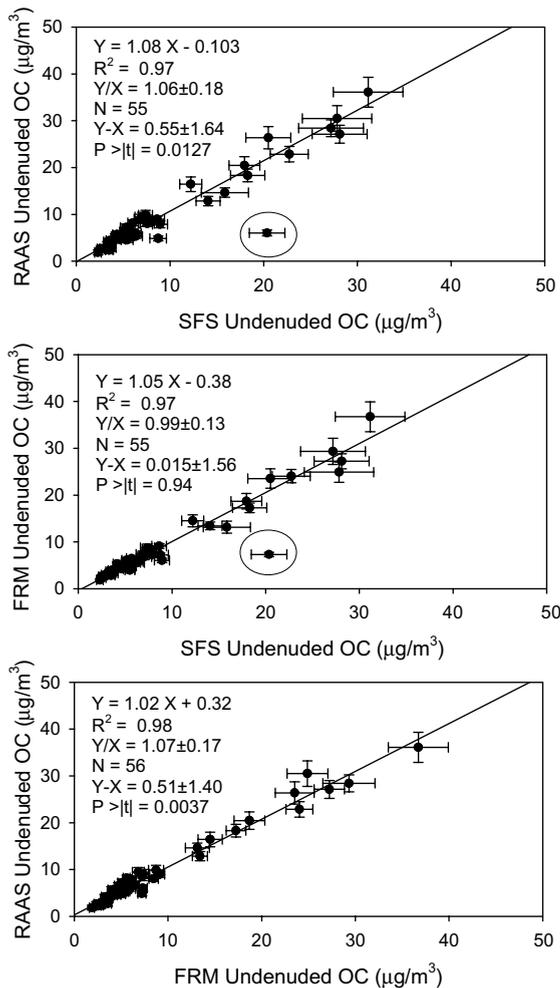


Fig. 7. Comparison between RAAS, FRM, and SFS front quartz-fiber filter OC at the Fresno Supersite during CRPAQS. (Circled data points excluded from statistics.)

Excluding one outlier, it is apparent that there were no significant differences between any of these measurements. Table 1 shows that in a few cases (e.g., RAAS versus SFS and RAAS versus FRM undenuded OC) the differences were significant according to the paired-difference *t*-test ($P < 0.05$). However, in each of these cases, the average difference was smaller than its measurement uncertainty (Figs. 7 and 8) and the majority of differences for all comparisons were less than twice their measurement uncertainties. Table 1 also shows comparison statistics for RAAS undenuded and denuded front quartz-fiber filter EC concentrations in Fresno from July 1999 through December 2003. Again, there was no significant difference between these measurements. This demonstrates that the carbon denuder had no effect on the EC measurement and that particle loss in the denuder was not significant. Subramanian

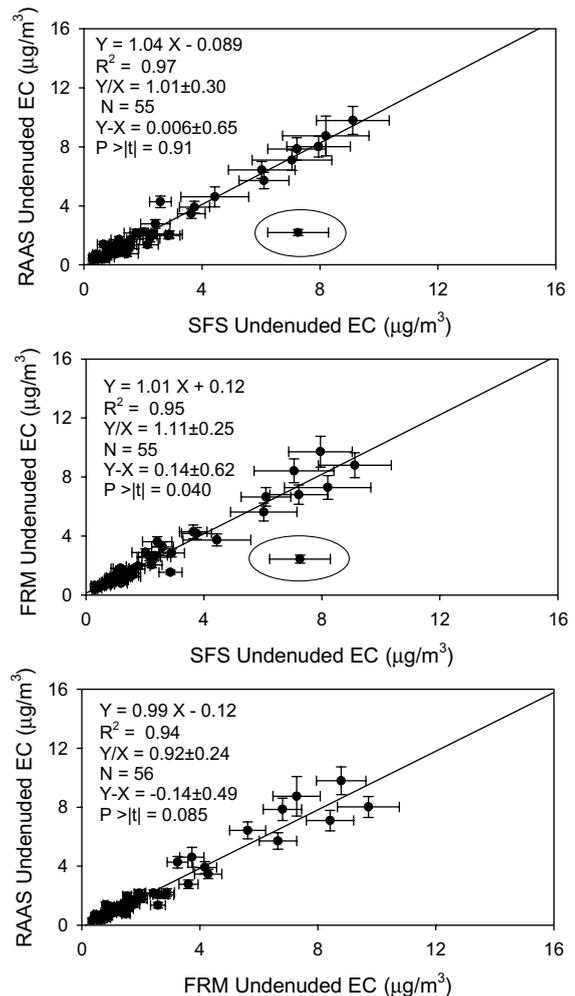


Fig. 8. Comparison between RAAS, FRM, and SFS front quartz-fiber filter EC at the Fresno Supersite during CRPAQS. (Circled data points excluded from statistics.)

et al. (2004) reported similar results for undenuded and denuded front quartz-fiber filter EC at the Pittsburgh Supersite.

3.3. Organic carbon sampling artifacts

The terminology reported by McDow and Huntzicker (1990) is used here to describe OC on the various RAAS filters shown in Fig. 2. Teflon-membrane and quartz-fiber filters are referred to as “T” and “Q”, respectively. A number is used to identify the position of a filter in a sequence. For example, DNQQ2 refers to OC on the quartz-fiber backup filter in the carbon-denuded (DN) channel. Watson and Chow (2002a) concluded that there were no systematic variations of RAAS denuded backup quartz-fiber (DNQQ2) filters between changes of either the XAD or CIF denuder in

Table 2
Average RAAS organic carbon concentrations with measurement uncertainties ($\mu\text{g}/\text{m}^3$)

OC concentration ^a	Winter ^b ($N = 44$)	Summer ^c ($N = 90$)	All ($N = 193$)
QQ1	11.76 ± 1.21	4.8 ± 0.6	7.2 ± 0.8
QQ2	1.28 ± 0.45	0.91 ± 0.46	0.91 ± 0.45
TQ2	2.1 ± 0.3	1.84 ± 0.28	1.75 ± 0.27
TPOC	9.7 ± 1.2	2.9 ± 0.6	5.4 ± 0.9
QPOC	10.4 ± 1.3	4.0 ± 0.7	6.3 ± 1.0
DNQQ1	10.8 ± 1.1	3.9 ± 0.5	6.0 ± 0.8
DNQQ2	0.25 ± 0.41	0.50 ± 0.42	0.31 ± 0.41
DNPOC	11.0 ± 1.2	4.4 ± 0.7	6.3 ± 0.9
TQ2/QQ1 (%)	24	44	34
QQ2/QQ1 (%)	10.9	24	17.5
DNQQ2/DNQQ1 (%)	1.88	12.0	7.8

^a QQ1: undenuded quartz front filter from the quartz–quartz channel; QQ2: undenuded quartz backup filter from the quartz–quartz channel; TQ2: undenuded quartz backup filter for Teflon–quartz channel; TPOC: particulate OC estimated as QQ1 minus TQ2; QPOC: particulate OC estimated as QQ1 minus QQ2; DNQQ1: denuded quartz front filter from the quartz–quartz channel; DNQQ2: denuded quartz backup filter from the quartz–quartz channel; DNPOC: DNQQ1 + DNQQ2.

^b Winter (December–February).

^c Summer (June–August).

Fresno prior to January 1, 2001. The efficiency of the BYU CIF denuder was claimed to be 97% at a flow rate of 38 liters per minute (lpm) (Ding et al., 2002). At this flow rate, denuder breakthrough in the BYU PC-BOSS sampler was only $0.1 \pm 0.4 \mu\text{g}/\text{m}^3$ (Ding et al., 2002). This value was consistently less than the uncertainty of the data and was uncorrelated with particulate organic carbon concentration (Ding et al., 2002). Gundel et al. (1995) reported XAD efficiencies greater than 90% for polycyclic aromatic hydrocarbons (PAH) at flow rates comparable to those used in the RAAS denuded channel (7.3 lpm). However, it is difficult to extrapolate this result because PAHs are not necessarily representative of the bulk of ambient VOC.

Average DNQQ2 concentrations and root-mean squared (RMS) measurement uncertainties for the XAD and CIF periods were 0.82 ± 0.45 and $0.31 \pm 0.41 \mu\text{g}/\text{m}^3$, respectively. The relative difference was even larger during winter periods ($0.80 \pm 0.46 \mu\text{g}/\text{m}^3$ for the XAD denuder versus $0.25 \pm 0.41 \mu\text{g}/\text{m}^3$ for the CIF denuder). The ratios of DNQQ2 to DNQQ1 were 13.9% and 7.8% during the XAD and CIF periods, respectively. The difference was larger during winter periods (7.8% versus 1.9%). DNQQ2 was larger than its measurement uncertainty in 73% of samples with complete data (36/49) during the XAD period compared with 28% of the time (54/193) when the CIF denuder was in use. These differences imply that the CIF denuder was more efficient than the XAD denuder at the low (7.3 lpm) flow rate. The following analysis is therefore limited to the 193 samples with complete data collected between July 11, 2000 and December 29, 2003.

McDow and Huntzicker (1990) and Turpin et al. (1994) found that OC on TQQ3 (the second quartz-fiber

filter behind a Teflon-membrane filter) was similar to that of QQ2 at the same face velocity. This implies that particles on the Teflon-membrane filter do not alter the amount of organic vapors adsorbed on TQ2. Therefore, TQ2 represents adsorption on QQ1 and should be subtracted from QQ1 to estimate particulate OC. McDow and Huntzicker (1990) concluded that the inequality between TQQ2 and TQQ3 or QQ2 resulted from non-equilibrium conditions between VOC in the sample stream and the quartz-fiber filters. Hart and Pankow (1994) found that PAH concentrations were similar on quartz-fiber filters behind either the undenuded quartz-fiber or Teflon-membrane filters. They collected samples for 6 h at a flow rate of 1400 lpm.

Table 2 summarizes the RAAS OC concentrations for winter (December–February), summer (June–August), and for all samples with complete data. Average particle OC (TPOC = QQ1 – TQ2 or QPOC = QQ1 – QQ2) concentrations were 2.5–3.3 times higher in winter than in summer. Seasonal differences for the backup filters were smaller: 1.1 for TQ2 and 1.4 for QQ2. The average ratio of TQ2/QQ1 was 34%, the same as that reported by Subramanian et al. (2004) and similar to the 30% reported by Kim et al. (2001). On average, the denuded backup filter OC (DNQQ2) was 7.8% of the denuded front quartz-fiber filter (DNQQ1). During winter, this ratio was 1.88%, about one-tenth of the corresponding ratio of TQ2 to QQ1. McDow and Huntzicker (1990) and Turpin et al. (1994) found that gaseous adsorption by TQ2 or QQ2 (a quartz-fiber backup to a Teflon-membrane or quartz-fiber front filter) varied inversely with face velocity. It is therefore likely that TQ2, with a flow rate of 16.7 lpm (Fig. 2), under-represents the positive

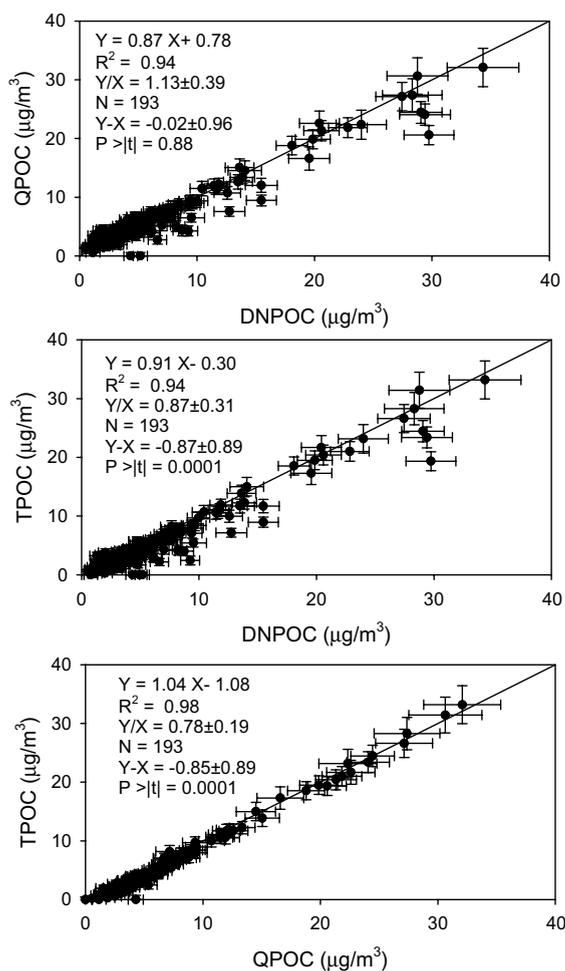


Fig. 9. Comparisons among RAAS DNPOC (DNQQ1 + DNQQ2), QPOC (QQ1 – QQ2), and TPOC (QQ1 – TQ2), where DNQQ1: Denuded quartz-fiber front filter from the quartz–quartz channel, DNQQ2: Denuded quartz-fiber backup filter from the quartz–quartz channel, TPOC: Particulate OC estimated as QQ1 minus TQ2, QPOC: Particulate OC estimated as QQ1 minus QQ2, QQ1: undenuded quartz-fiber front filter from the quartz–quartz channel, QQ2: undenuded quartz-fiber backup filter from the quartz–quartz channel, TQ2: undenuded quartz-fiber backup filter for Teflon–quartz channel.

adsorption on QQ1, with a flow rate of 7.3 lpm. The three estimates of particulate OC are compared in Fig. 9. The corresponding comparison statistics are presented in Table 1. Average differences among QPOC (QQ1 – QQ2), TPOC (QQ1 – TQ2), and DNPOC (DNQQ1 + DNQQ2) were all smaller than their measurement uncertainties.

The Fresno comparisons show that OC on TQ2 was consistently larger than that on QQ2, consistent with McDow and Huntzicker (1990), Turpin et al. (1994),

Kirchstetter et al. (2001), and Subramanian et al. (2004). Table 2 shows that TQ2 and QQ2 displayed much less seasonal variation than denuded OC (DNPOC) and undenuded OC (TPOC or QPOC), but were 14–40% higher in winter, when particle OC was higher. This is similar to trends observed in Pittsburgh, except that the seasonality was reversed, with higher OC concentrations during summer (Subramanian et al., 2004). Fig. 10 displays relationships among undenuded front quartz-fiber OC (QQ1), backup Teflon-membrane (TQ2), backup quartz-fiber (QQ2) OC, and their ratios to QQ1. There was a direct relationship between QQ1 and both TQ2 and QQ2 as seen by Kim et al. (2001). There was also a clear inverse relationship between the ratio of TQ2/QQ1 and QQ1, as seen by McDow and Huntzicker (1990) and Subramanian et al. (2004). However, the relationship between QQ2/QQ1 and QQ1 was less distinct, as was also seen by Subramanian et al. (2004).

Subramanian et al. (2004) suggested that OC on the undenuded quartz-fiber behind the Teflon-membrane filter (TQ2) was systematically higher than OC on the quartz-behind-quartz (QQ2) because of self-adsorption by the undenuded front quartz-fiber filter (QQ1) of SVOC lost from particles on QQ1 (i.e., part of the OC volatilized from the particles was adsorbed in the bottom part of QQ1). They concluded that subtraction of TQ2 from QQ1 overcorrects for the adsorbed OC. This is consistent with the results presented in Table 2, where DNPOC (DNQQ1 + DNQQ2) agrees most closely with undenuded QPOC (QQ1 – QQ2). However, the accuracy of QQ2 as a correction for the adsorbed OC depends on whether equilibrium is reached between VOC in the sample stream and both filters in the QQ pair. Mader and Pankow (2001) noted that equilibrium occurs only after a temperature-, relative humidity-, and compound-specific sample volume has been exceeded for a given filter area. Ideally, the front quartz-fiber filter should adsorb VOC until equilibrium is reached, after which time VOC passes through the front filter to be adsorbed by the backup quartz-fiber filter until it, too, equilibrates. Subramanian et al. (2004) stated that equilibrium was not reached in short-duration samples (4–6 h), but it was reached for 24-h samples collected at a flow rate of 16.7 lpm. Since VOC concentrations vary over the course of a 24-h sample, the relevance of equilibrium theory to the amount of VOC that ends up on front and backup quartz-fiber filters is questionable. Additional experiments are needed to resolve these issues, especially the specific characterization of compounds responsible for the adsorbed positive and volatilized negative biases and the conditions under which equilibrium is reached under different sampling conditions.

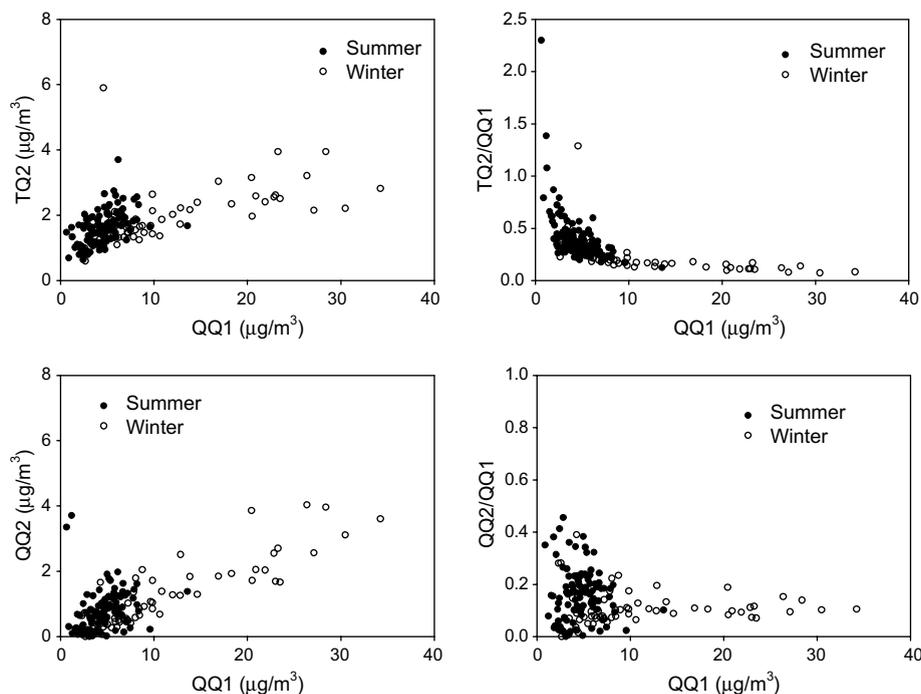


Fig. 10. Undenuded OC on front quartz-fiber filter (QQ1) versus quartz-fiber backup to Teflon (TQ2) and quartz-fiber backup to quartz-fiber (QQ2) as concentrations and ratios of TQ2 and QQ2 to QQ1 by season (summer = June–August; winter = December–February).

4. Conclusions

PM_{2.5} aerosol sampling was conducted during the CRPAQS and Fresno Supersite programs. Carbon sampling methods and artifacts were evaluated using DRI sequential filter samplers (SFS) at CRPAQS urban Fresno and Bakersfield sites, regional Angiola site, and boundary Bethel Island and Sierra Nevada Foothills sites in the San Joaquin Valley, and with SFS, Andersen FRM, and multi-channel RAAS samplers at the Fresno Supersite.

OC and EC concentrations were higher during the colder months and the trend was most pronounced at Fresno and Bakersfield, where OC and EC concentrations reached 37 ± 5 and $10.3 \pm 1.7 \mu\text{g}/\text{m}^3$ on January 6, 2001, at Fresno and 24 ± 3 and $8.3 \pm 1.6 \mu\text{g}/\text{m}^3$ on January 1, 2001 at Bakersfield, respectively. OC and EC displayed similar diurnal trends at the urban Fresno site during winter (December–February) and summer (June–August) and at the regional Angiola site during winter. In Fresno during winter, OC and EC concentrations peaked at night due to residential wood combustion and the development of a nighttime inversion. During summer, there were distinct morning and late-afternoon rush hour peaks. The winter diurnal pattern at Angiola reflected transport of secondary pollutants to this site.

Collocated measurements of OC and EC on undenuded quartz-fiber filters were made in Fresno with the RAAS, FRM, and SFS samplers. Average ratios of RAAS/SFS, FRM/SFS, and RAAS/FRM OC were 1.06 ± 0.18 , 0.99 ± 0.13 , and 1.07 ± 0.17 , respectively. Average ratios of RAAS/SFS, FRM/SFS, and RAAS/FRM EC were 1.01 ± 0.30 , 1.11 ± 0.25 , and 0.92 ± 0.24 , respectively. All average differences between samplers were less than their respective measurement uncertainties. Further, the average ratio of RAAS denuded to undenuded front quartz-fiber filter EC was 1.04 ± 0.59 and the average difference was less than its measurement uncertainty.

On average, POC measured behind a BYU charcoal-impregnated cellulose-fiber filter (CFF) denuder agreed most closely with the difference between OC sampled on an undenuded quartz-fiber front filter (QQ1) and OC measured on a quartz-fiber filter directly behind it (QQ2). However, differences between POC measured behind the denuder and undenuded POC obtained by subtracting quartz-behind-Teflon (TQ2) or quartz-behind-quartz (QQ2) OC from the front quartz-fiber filter OC as a correction for adsorbed organic vapors were negligible (i.e., less than their measurement uncertainties). OC on the quartz-fiber backup filter in the denuded channel (DNQQ2), presumably reflecting desorption of volatile compounds from particles on the front quartz-

fiber filter, ranged from 1.88% to 12% of the denuded front quartz-fiber filter OC (DNQQ1) concentration in winter and summer, respectively. Undenuded quartz-behind-Teflon OC (TQ2) was consistently larger than quartz-behind-quartz OC (QQ2), in agreement with other studies. However, results for the Fresno Supersite support the conclusion of Subramanian et al. (2004) that TQ2 overestimates the positive vapor adsorption because it includes organic vapors desorbed from particles on the Teflon filter, and that subtracting the quartz-fiber backup from the front quartz-fiber OC on an undenuded sample stream was the most appropriate correction for the organic vapor adsorption.

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