

Field Method Comparison between Passive Air Samplers and Continuous Monitors for VOCs and NO₂ in El Paso, Texas

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ABSTRACT

This study evaluates the performance of Model 3300 Ogawa Passive Nitrogen Dioxide (NO₂) Samplers and 3M 3520 Organic Vapor Monitors (OVMs) by comparing integrated passive sampling concentrations to averaged

IMPLICATIONS

Comparison of passive OVMs with auto-GCs for VOCs and Ogawa badges with chemiluminescence analyzers for NO₂ are scarce. Regression analysis methods, correlation, concordance, and bias are used to evaluate collocated passive and continuous methods; the utility of duplicate sampling also is demonstrated. To account for the different number of samples collected between the reference and passive monitors, the present study employs an “adjusted *t*” statistic to better analyze the significance of the regression parameters. Finally, correction of passive sampler measurements under local ambient temperature and pressure conditions is emphasized, particularly for higher-elevation air sheds.

hourly NO₂ and volatile organic compound (VOC) measurements at two sites in El Paso, TX. Sampling periods were three time intervals (3-day weekend, 4-day weekday, and 7-day weekly) for three consecutive weeks. OVM concentrations were corrected for ambient pressure to account for higher elevation. Precise results (<5% relative standard deviation, RSD) were found for NO₂ measurements from collocated Ogawa samplers. Reproducibility was lower from duplicate OVMs for BTEX (benzene, toluene, ethylbenzene, and xylene isomers) VOCs (≥7% RSD for 2-day samples) with better precision for longer sampling periods. Comparison of Ogawa NO₂ samplers with chemiluminescence measurements averaged over the same time period suggested potential calibration problems with the chemiluminescence analyzer. For BTEX species, generally good agreement was obtained between OVMs and automated-gas chromatograph (auto-GC) measurements. The OVMs successfully tracked increasing levels of VOCs recorded by the auto-GCs. However,

except for toluene, OVM BTEX measurements generally exceeded their continuous counterparts with a mean bias of 5–10%. Although interpretation of the study results was limited due to small sample sizes, diffusion barrier influences caused by shelters that housed OVMs and differences in sampling heights between OVMs and auto-GC inlet may explain the overestimation.

INTRODUCTION

Personal passive air samplers (or badges) have been developed and used extensively for industrial hygiene and related occupational exposure purposes to measure gaseous air pollutants.^{1,2} Although a long sampling time (24 hr or longer) is usually required for passive samplers to detect ambient air pollutants, they are an attractive method for monitoring outdoor and indoor air owing to their ease of use in the field. Ogawa passive samplers have been used in air monitoring networks to monitor urban ozone (O₃),³ to assess O₃ trends at U.S. National Parks,⁴ and in determining distance of nitrogen dioxide (NO₂) emissions from highway traffic.⁵ Other species that the Ogawa passive sampler can measure include sulfur dioxide (SO₂) and other nitrogen oxide (NO_x) species, depending on the reactants used on the collection filter substrate.² In this study, Ogawa passive samplers were used solely for the collection of NO₂. Other similar studies have used Palmes tubes,⁶ filter badges, and other diffusion samplers to passively monitor NO₂.^{7–9} While Palmes tubes have been used extensively in NO₂ exposure studies (particularly in Europe^{10–14}) because of their ease of use and mitigated wind velocity effects, the length of the tube configuration of this device (7.1 cm)⁵ has been reported to result in low sampling rates,⁸ therefore requiring relatively long monitoring periods (usually 7 days depending on location).

Evaluations of the 3M Organic Vapor Monitor (OVM) for sampling of volatile organic compounds (VOCs) have been performed in other studies in controlled exposure chamber^{15–22} and indoor and outdoor settings.^{18,20,23–26} In terms of field comparisons, OVMs were found to be comparable to canister and continuous gas chromatography (GC) monitoring, with apparent over- and underestimation of concentrations.²¹ Higher humidity has been found to result in an increasing negative bias for OVM measurements,²² because water adsorbed onto the surface of the activated carbon sorbent tends to preclude adsorption of other compounds onto the charcoal active sites. Variations in wind speed and sampler orientation during sampling from calibration conditions of the OVM have been found to produce a positive bias no greater than 10%.¹⁹ Boundary layer effects (such as low face velocity and stagnant air starvation effects) also have been found to reduce OVM sampling rates.²³ Comparison of OVMs with other active (pumped) samplers using sorbent tubes

(Tenax TA, active charcoal) have revealed good agreement with apparent over- and underestimation of concentrations.^{15,17,18,25,26}

In late 1999, a pilot study was conducted by the U.S. Environmental Protection Agency (EPA) in the U.S.-Mexico border city of El Paso, TX, to measure respiratory effects in children along with NO₂, volatile organic compounds (VOCs) and ultrafine/fine particulate matter (PM) in the city's elementary schools.²⁷ El Paso and its neighboring Mexican "sister" city of Ciudad Juárez have exceeded U.S./Mexican air quality standards for O₃, particulate matter with an aerodynamic diameter <10 μm (PM₁₀), and carbon monoxide (CO).²⁸ Previous atmospheric characterization and modeling studies of O₃ episodes in this region identified urban traffic emissions of NO_x species and VOCs, along with the complex terrain and meteorological conditions (low turbulence and mixing heights), as the principal factors for these exceedances.^{29–31} Based on this understanding of air pollution conditions in the El Paso air shed and the ability to measure some of these pollutants using passive samplers, the pilot study design included use of such samplers at two continuous air monitoring stations (CAMS) operated by the State of Texas Commission on Environmental Quality (TCEQ) and at 22 El Paso schools to monitor NO₂ and VOCs. As part of the study, concentrations obtained with passive samplers were compared with NO₂ and VOC measurements obtained with continuous monitors at the two CAMS sites. It was hypothesized that if the passive samplers were comparable in performance to continuous measurements, then this could provide further validation of passive sampling networks for monitoring community exposures that could be established in El Paso and elsewhere on a cost-effective basis.

METHODS

Site Locations and Routine Monitoring

Passive monitoring was conducted at two CAMS sites operated by the TCEQ as part of routine air monitoring in El Paso. The specific sites were selected because of their influence from mobile and urban sources³⁰ and maximum O₃ precursor emissions impact. In addition, NO₂ and VOCs are monitored routinely at these locations, making them suitable for performing the method comparison. Figure 1 shows the site locations. The first site (CAMS 6) was located in a high-traffic area at 500 North Campbell Street in downtown El Paso and on a street leading to an on-ramp ingress to US Interstate Highway 10 (I-10), the major thoroughway in El Paso. The second station (CAMS 41) was located at Chamizal National Memorial in El Paso, ~1 km northwest from the Bridge of the Americas; this bridge is a principal connection between El Paso and Ciudad Juárez. As part of the routine monitoring

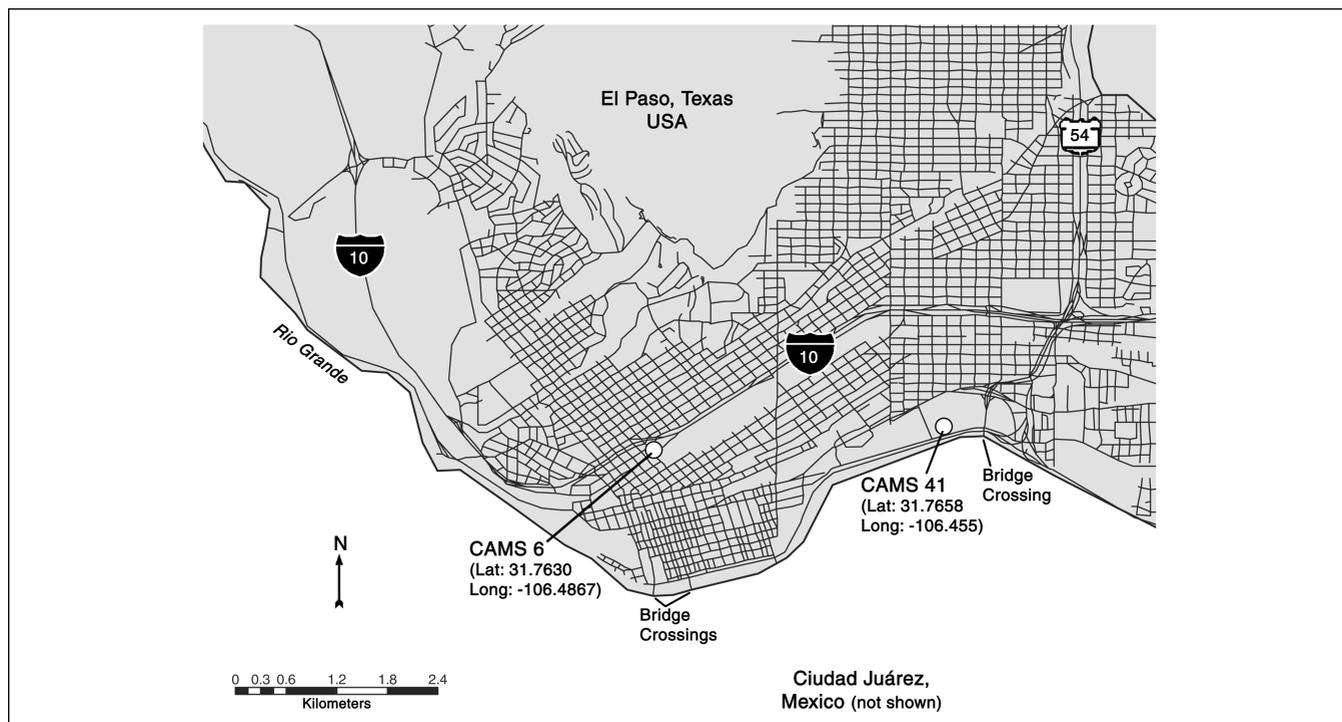


Figure 1. Map of CAMS study locations (as latitudinal and longitudinal coordinates) in relation to central El Paso region. Selected freeways are shown as numbered shields on El Paso road network.

conducted by TCEQ at these stations, both sites measured NO_x species (including NO_2) on a continuous basis using a TECO Model 42 gas-phase chemiluminescent NO_x analyzer (Thermo Environmental Instruments); these data were compared with NO_2 measurements from passive samplers. The chemiluminescent NO_x analyzers used were Federal Reference Method samplers (Designated Method RFNA-1289-074) in accordance with Title 40, Part 53 of the Code of Federal Regulations (40 CFR Part 53).^{32,33} All chemiluminescence data were above the method detection limit (MDL) and were reported in units of parts per billion by volume (ppbv).

Of the two study sites, VOCs were monitored routinely only at CAMS 41. During the study, VOCs were sampled by TCEQ on an hourly basis using a Perkin-Elmer AutoSystem Gas Chromatograph (auto-GC; Perkin-Elmer Analytical Instruments) and an ATD400 Automatic Thermal Desorption unit (Model ATD400; Perkin-Elmer) that was fitted with an air-sampling accessory. Chromatographic separation of hydrocarbons (C_2 – C_{12}) was performed with two columns, with light hydrocarbons analyzed on a 50 m \times 0.32 mm inner diameter (ID) aluminum oxide/sodium sulfate ($\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$) PLOT column (Varian) and the heavy fraction on a 50 m \times 0.22 mm ID BP1 column (SGE). Quantification was performed by flame ionization detection (FID). CAMS 41 is designated as a photochemical assessment monitoring station (PAMS) to assess trends in O_3 -related pollutants; auto-GCs are placed at the PAMS national network for this

purpose.³⁴ The auto-GC was established according to PAMS network monitoring protocol.^{33,35} Ambient samples were acquired at a flow rate of 15 mL/min for 40 min. The sample was then injected into the auto-GC and analyzed in successive temperature steps for a total data collection time of 48 min. All auto-GC measurements were above the MDL (0.01 ppbC); measurements from the auto-GC were converted to $\mu\text{g}/\text{m}^3$ to compare with VOC passive sampler measurements. In addition to the ambient measurements, both sites collected meteorological data (wind speed, wind direction, temperature, and relative humidity) with 10-m towers using Climatronics F460 Wind Sensors (Climatronics Corp.). Atmospheric pressure data were obtained from the National Weather Service station at the El Paso International Airport.

Ambient data collected by the TCEQ at the two El Paso CAMS locations were averaged on an hourly basis and reported in the EPA Aerometric Information Retrieval System (AIRS, recently renamed the Air Quality System).³⁶ Wind speed and wind direction data, discussed in the previous paragraph, were acquired directly from TCEQ.

Passive Sampling and Analysis of Measurements

Two commercially available passive air samplers were used in this study for the collection of NO_2 and VOCs. The Model 3300 Ogawa passive samplers (Ogawa & Co.) were used for collecting NO_2 . Although the cylindrical-shaped device is designed for two collection pads on either end, only one pad was employed because the

minimum integration period was 48 hr. Further details on ambient sampling of NO₂ and other gaseous species with the Ogawa sampler are presented elsewhere.^{6,37,38} All samples were blank-corrected and reported in units of ppbv. The cellulose fiber collection pads within the Ogawa sampler were coated by the manufacturer with triethanolamine (TEA); the pads were extracted and NO₂ content was determined using a TCI-NO_x 1000 automatic flow injection analyzer (Tokyo Kasei Kogyo). Final NO₂ concentrations were calculated using the appropriate concentration conversion coefficients incorporating ambient temperature, relative humidity, and the water vapor pressure coefficient as described by the manufacturer.³⁸ Vapor pressure coefficients were obtained by linear interpolation from Table 5 of Ref 38.

VOCs were sampled using the dual-charcoal pad 3M 3520 organic vapor monitor (3520 OVM; 3M Company). OVMS were ordered without identification labels, normally attached to the back of the monitor, to minimize contamination from target compounds present in the adhesive of the labels. Previous evaluations of OVMS with and without labels have revealed background contamination for certain compounds like toluene, which is probably caused by emissions from the adhesive used to attach labels to the back of the badges.²⁰ Extraction, analysis, and concentration calculations (blank-corrected in μg/m³) were performed as outlined elsewhere,^{22,39,40} but the final concentrations also were corrected for ambient pressure using the ideal gas law and diffusion principles.⁴¹ The pressure correction (not normally done in the manufacturer's sampling guide⁴⁰) was made in consideration of the elevation of the two sites, these being 1140 m above mean sea level (msl) for CAMS 6 and 1128 m above msl for CAMS 41.³¹ Briefly, the charcoal pads were placed in amber autosampler vials to which a 1-mL aliquot of a 2:1 v/v acetone/very low-benzene-grade carbon disulfide solution (Sigma-Aldrich) was added. Extraction was completed by sonication of the vials for 40 min in a water/ice bath. Analytical samples were prepared with an aliquot of this extract to which a solution of two internal standards was added, as described elsewhere.^{22,39} The extracts were analyzed by GC with mass spectrometry (MS) on a Hewlett-Packard (HP) 5890 Series II Plus GC/HP 5972 MS (Hewlett-Packard). Chromatographic separation was performed with an RTX-1 60 m × 0.25 mm ID capillary column (Restek Corp.) in SCAN or SIM mode. Samples were injected with an HP 18593B autosampler. The use of a mass spectrometer detector for the analysis of the OVM extracts allowed for quantification of halogenated and nonhalogenated compounds, while the PAMs network only reports nonhalogenated compounds because of the use of an FID detector.

Monitoring occurred for three consecutive weeks, from November 29 to December 17, 1999. Sampling periods for the Ogawa and OVM samplers were on two 3-day weekend (Friday noon through Monday afternoon; average of 75 hr), three 4-day weekday (Monday afternoon through Friday afternoon; average of 94 hr), and two 7-day week (Monday afternoon through Monday afternoon; average of 169 hr) time periods. With exception of the last 4-day period, the 3- and 4-day samples were subsets in time of the 7-day samples. At both CAMS sites, duplicate passive samples were collected during each sampling period. Passive samplers were collected and replaced with new ones at the same time. Ogawa and OVM samples were refrigerated (2–4 °C) and shipped cold (<0 °C) to the analysis laboratories on a weekly basis.

To make the comparisons described here, hourly AIRS data from the continuous samplers were averaged on the same time frames as the seven passive sampling periods. Missing hourly values were not imputed; averages were calculated only from available data. Measurements from the continuous monitors are typically quality assured before being reported in AIRS. The AIRS data were required to exhibit a data completeness level of at least 75% (i.e., 75% of valid hourly data) within each of the sampling periods. Unfortunately, this data completeness requirement did not permit use of the organic AIRS data during one of the weeks of the study, thus yielding only three sampling periods for comparison purposes. The AIRS auto-GC data were converted from ppbC to μg/m³ using the ideal gas law with ambient temperature and pressure conditions, thus placing the auto-GC and OVM sampling data on the same basis.

One or more paired passive samplers were collocated at CAMS 6 and CAMS 41. Collocated Ogawa samplers were placed in PVC shelters (15 W × 10 H cm) while collocated OVMS were placed in stainless-steel shelters (30 W × 15 H cm). Stainless-steel shelters were used to house OVMS to avoid the influence from any potential outgassing of VOCs²⁴ from the plastic material. Shelters were placed ~1 m above ground level and in well-ventilated areas. Passive samplers could not be placed at the same height as the CAMS continuous monitors, which were 3–3.5 m above ground level, owing to restricted access to the roofs of the CAMS shelters.

Statistical Methods to Evaluate Agreement

The continuous NO₂ and VOC measurements at CAMS 6 and 41 and reported in AIRS are made using standard EPA methods. Thus, the El Paso study provided an opportunity to conduct field comparisons of the performance of the passive samplers with standard EPA reference monitors. Statistical analyses for such comparisons were performed with SAS software (Release 8.2, SAS Institute).

For both NO₂ and VOCs, simple linear regressions of the passive sampling measurements on the averaged values from AIRS data were utilized to assess the performance of the passive samplers at each CAMS site. Regression analysis was chosen because it is an efficient way to compare the two methods across the range of observed values. Given that duplicate sampling was part of the study design, the regression approach allowed for lack of fit testing; this tests whether a linear model (in this case, a simple straight line) is an appropriate functional form⁴² to represent the data. Standard residual analysis and lack of fit testing were used to assess the appropriateness of the results.⁴³

The standard regression approach outlined previously assumes that for each sampling period, an independent observation was obtained for the AIRS measurement. However, this was not the case here, because there was only one AIRS value available from each sampling period. Therefore, the statistics used for testing whether the estimated slopes were equal to 1 and the estimated intercepts were equal to 0 were modified. The following formulae provide the usual standard errors for the slope (b_1) and intercept (b_0) estimates:⁴²

$$est.s.e.(b_1) = \frac{s}{\left\{ \sum_{i=1}^n (X_i - \bar{X})^2 \right\}^{1/2}}$$

$$est.s.e.(b_0) = s \left(\frac{1}{n} + \frac{\bar{X}^2}{\sum_{i=1}^n (X_i - \bar{X})^2} \right)^{1/2}$$

where s is the estimate of the standard deviation of the passive samples, n is equal to the number of passive samples collected over all sampling periods, and the X_i 's are the AIRS values.

Note, however, that these estimated standard errors underestimate the variability of the slope and intercept estimates because there are fewer than n AIRS observations. This problem was addressed in the following way. These standard errors were modified so that the mean of the AIRS values (\bar{X}) and the corrected sum of squares for the AIRS values [$\sum_{i=1}^n (X_i - \bar{X})^2$] were calculated with n set to the number of sampling periods. (Note that the n appearing alone in the formula for the standard error of b_0 was left unchanged.)

This effectively means that the tests for agreement with a slope of 1 and intercept of zero were conducted with "adjusted t " statistics. These adjusted t statistics were simple multiples of the usual t statistics generated from

the standard regression approach.⁴³ These adjusted t statistics had a probability density function (pdf) of the form

$$pdf(y) = \frac{1}{k} \frac{1}{\sqrt{\nu} B\left(\frac{1}{2}, \frac{1}{2} \nu\right)} \left(1 + \frac{y^2}{k^2 \nu}\right)^{-(1/2)(\nu+1)}$$

where k is the multiplier used to adjust the standard t statistic, B is the beta function, and ν is the error degrees of freedom from the usual regression. This is not the pdf of a t -distributed random variable. (See Rohatgi⁴⁴ for the method of obtaining pdf s of functions of random variables.) This pdf was then integrated numerically using Mathematica software (Version 4),⁴⁵ and the p values for the tests were thus obtained.

Note that an alternative approach to using adjusted t statistics would have been to simply average all the passive sampler measurements within each sampling period and then regressing these averages against the AIRS values. However, this would have some disadvantages, namely, the loss of power associated with the reduction in degrees of freedom and the poorer estimate of the variability of the passive samplers. Particularly, with a data set of this small size, these disadvantages outweighed the simplicity of this alternative approach.

In addition to the regression methodology, three other statistics also were calculated to evaluate agreement: the mean bias and Lin's bias correction factor (C_b) and concordance coefficient (ρ_c).⁴⁶ The mean bias was calculated for each sampling period by subtracting the mean reference method continuous value (already an average) from the average passive value, dividing this difference by the mean standard continuous value, and converting the result to a percentage. Mean bias indicates an overall level of difference between the continuous and passive sampling methods. It was defined as

$$\text{mean bias} = \left(\frac{\bar{X}_{\text{passive}} - \bar{X}_{\text{AIRS}}}{\bar{X}_{\text{AIRS}}} \right) 100 \quad (1)$$

The ρ_c and C_b terms are combined with the results of the specific significance tests for the slopes and intercepts to assess agreement with the 1:1 line. The formulae for these statistics are

$$\rho_c = r C_b \quad (2)$$

where r is the Pearson correlation coefficient $\sigma_{AB}/\sigma_A\sigma_B$ and C_b is the bias correction term $[1/2(\sigma_A/\sigma_B + \sigma_B/\sigma_A + (\mu_A - \mu_B)^2/\sigma_A\sigma_B)]^{-1}$. Where σ_{AB} is the covariance of samplers A and B, σ is the standard deviation of corresponding samplers (as indicated by subscript), and μ is the mean

for corresponding sampler (denoted by subscript). The C_b term indicates, generally, how well the estimated regression line agrees with the 1:1 line (unity). Values for C_b range from 0 to 1, with a value of 1 indicating no deviation from the 1:1 relationship (unity), while values approaching 0 indicate greater deviation. The ρ_c term multiplies this measure with the standard Pearson correlation coefficient (r) to provide a statistic that combines the variability of the observed data about the regression line with the line's agreement with the exact 1:1 line.⁴⁶

RESULTS

Table 1 shows summary statistics of field and laboratory blank-corrected passive sampler pollutant concentrations at each site for NO₂ and VOC species. The TCEQ continuous measurements at these sites obtained from AIRS also are summarized in Table 1. Species associated with transportation sources (NO₂ and benzene, toluene, ethylbenzene, and xylene isomers [BTEX] species) were above

corresponding MDLs for both the passive samplers and the hourly AIRS measurements. NO₂ is commonly associated with transportation, power plant, industrial combustion sources, and secondary formation from reactions between primary emissions of NO and O₃,^{47,48} while BTEX species are associated with motor vehicle tail pipe and gasoline emissions.^{29,49,50} The results presented in Table 1 suggest that, with the exception of the maximum value for toluene, these species were slightly higher in concentration at CAMS 6 than at CAMS 41. Although not shown in Table 1, average NO₂ measurements from the chemiluminescence analyzer were also higher at CAMS 6 (33 ppb) than at CAMS 41 (28 ppb). Traffic emissions from Highway I-10 were the probable reasons for these species to be higher at CAMS 6, and the fact that they were only slightly higher suggests that concentrations of these pollutants were fairly homogeneous in the central El Paso area. An exception was toluene, which showed higher variability and will be discussed later. Pearson correlation

Table 1. Passive sample descriptive statistics^a for NO₂ (ppb) from Ogawa samplers and VOC species ($\mu\text{g}/\text{m}^3$) from 3520 OVMs at CAMS 6 and 41 (Nov 29–Dec 17, 1999). Collocated NO₂ and VOC measurements from continuous samplers and reported in EPA AIRS, recently renamed the Air Quality System, in the same units as passive sampling data.

Compound	Site CAMS 6 ($n = 16$) ^b				Site CAMS 41 ($n = 18$)				AIRS Data ($n = 7$ for VOCs, Site CAMS 41)		
	MDL (max) ^c	Mean	Min	Max	MDL (max)	Mean	Min	Max	Mean	Min	Max
NO ₂	1.31	37.39	31.35	45.72	1.28	29.69 (16)	25.18	34.97	30.67(34) ^d	24.38	38.69
Butadiene	0.71	0.34	0.15	0.92	0.7	0.36	0.15	0.92	.	.	.
Methylene chloride	0.12	0.41(15) ^b	0.26	0.61	0.12	0.41	0.28	0.64	.	.	.
MTBE	0.2	1.27	0.05	2.36	0.2	1.59	0.5	2.49	.	.	.
Chloroprene	0.3	0.08	0.04	0.15	0.3	0.08	0.04	0.15	.	.	.
Chloroform	0.2	0.09	0.05	0.16	0.2	0.12	0.06	0.19	.	.	.
Carbon tetrachloride	0.29	0.57	0.34	0.68	0.29	0.54	0.48	0.6	.	.	.
Benzene	0.39	4.73	2.64	8.3	0.4	4.29	2.32	6.03	3.45	2.1	4.37
Trichloroethylene	1.44	0.51 (15)	0.30	0.72	1.43	0.53	0.3	0.71	.	.	.
Toluene	4.53	12.15	2.26	19.5	4.47	12.01	2.23	26.15	9.9	5.16	13.14
Tetrachloroethylene	0.18	0.3	0.17	0.44	0.18	0.39 (17)	0.31	0.49	.	.	.
Ethylbenzene	0.13	2.24	1.28	3.99	0.13	2.12	1.08	3.02	1.66	0.9	2.17
<i>m,p</i> -Xylene	0.39	7.47	4.40	13.13	0.38	6.9	3.55	10.08	5.59	3.14	7.26
<i>o</i> -Xylene	0.17	2.76	1.59	4.8	0.17	2.53	1.32	3.74	2.03	1.18	2.61
Naphthalene	0.11	0.03	0.02	0.06	0.11	0.03	0.02	0.06	.	.	.
Styrene	0.27	0.51	0.30	0.82	0.27	0.43	0.13	0.6	0.08	0.002	0.14
<i>a</i> -Pinene	0.26	0.12	0.03	0.24	0.25	0.1	0.03	0.16	.	.	.
<i>b</i> -Pinene	0.27	0.09	0.03	0.19	0.26	0.07	0.04	0.13	.	.	.
α -Limonene	0.41	0.28 (15)	0.11	0.67	0.41	0.19 (17)	0.11	0.59	.	.	.
<i>p</i> -Dichlorobenzene	0.39	0.39	0.10	0.71	0.38	0.4	0.1	0.63	.	.	.
Isoprene	1.22 (9)	0.48 (9)	0.29	0.61	1.23 (11)	0.51 (11)	0.29	0.61	0.14	0.08	0.18
2,3-Dimethylpentane	1.94 (9)	2.13 (9)	0.45	4.62	1.94 (11)	1.86 (11)	0.8	6.88	1.29	0.71	1.69
Nonane	0.4 (9)	0.7 (9)	0.52	1.04	0.4 (11)	0.52 (10)	0.16	1.17	.	.	.
Decane	0.34 (9)	0.94 (9)	0.56	1.44	0.34 (11)	0.58 (11)	0.14	1.86	.	.	.

^aSamples were blank-corrected with data summarized based on pollutants below detection limit assigned a value equal to half the detection limit; ^bNumbers in parentheses are the number of observations designated at the top of site column. Species with different sample sizes presented in parentheses next to mean value; ^cMaximum reported MDL [MDL (max)]. Separate detection limits were reported for each sample; ^dSample size for NO₂ from AIRS based on CAMS 6 and 41 data combined.

coefficients for other BTEX species and NO₂ between CAMS 6 and 41 were ≥ 0.9 . Lighter-molecular-weight VOCs and other organic compounds associated with industrial settings or other nonvehicular sources (such as chloroprene, chloroform, trichloroethylene, naphthalene, pinenes, and isoprene) were consistently below their MDLs at both sites; the principal exception was styrene. Possible sources of styrene include emissions from chemical/polymer manufacturing, building materials, glues and solvents, and contaminated riverian water emissions.⁵¹

Summary concentrations for selected VOCs from the passive samplers, grouped by length of sampling time, are shown for CAMS 6 (Table 2a) and CAMS 41 (Table 2b). These summary statistics were calculated within each sampling period and then pooled across periods within their sampling length category. The 3-day weekend samples in El Paso were similar in concentration to 72-hr 3520 OVM samples collected in Pasadena, TX, near Houston. In that study, mean outdoor concentrations were 2.22 $\mu\text{g}/\text{m}^3$ for benzene, 0.13 $\mu\text{g}/\text{m}^3$ for styrene, and 7.13 $\mu\text{g}/\text{m}^3$ for toluene.²¹ As shown in Tables 2a and 2b, the BTEX species had higher concentrations on weekday versus weekend time periods. This was probably because of increased traffic flows on weekdays versus weekends.

DISCUSSION

Precision

Tables 2a and 2b list the relative standard deviations [%RSD (standard deviation \div mean analyte mass as percent)] for the 3-, 4-, and 7-day duplicate OVM VOC and Ogawa NO₂ samples collected at CAMS 6 and CAMS 41. Precision error for the Ogawa samplers was determined to be less than 5%. Figures 2a and 2b show the precision of the 3-, 4-, and 7-days sampling periods for CAMS 6 and CAMS 41, respectively. Precision was lower at CAMS 6 compared with CAMS 41; however, the precision for the 7-day samples was similar for both sites. The precision error for OVM samples collected at CAMS 41 showed that the 3-day sampling precision was above 7% for the BTEX species. The 4- and 7-day samples demonstrated improved precision with the longer sampling periods with the 4-day sample having a precision error of less than 5% and the 7-day sample having a precision error generally at or lower than 5% (both 4- and 7-day assessments not inclusive of toluene). The increase in precision with longer sampling periods may be caused by the collection of larger quantities of the BTEX species, which would reduce the analytical uncertainty and the effect from variable background levels for these VOCs in the charcoal pads of the OVMs. The %RSD values for the 7-day benzene and toluene measurements in this study were lower than pre-

Table 2. (a) Sample statistics,^a pooled across sampling periods, for 3-day weekend, 4-day weekday, and 7-day weekly passive samples at CAMS 6. NO₂ data in units of ppb and VOCs in $\mu\text{g}/\text{m}^3$.

Compound	3-Day Weekend (<i>n</i> = 4) ^b					4-Day Weekday (<i>n</i> = 8)					7-Day (<i>n</i> = 4)				
	Median	Mean	% RSD	Min	Max	Median	Mean	% RSD	Min	Max	Median	Mean	% RSD	Min	Max
NO ₂	34.46	34.46	2.2	31.35	37.17	40.24	39.53	1.9	32.35	45.72	39.48	39.48	3.6	36.08	42.63
Butadiene	0.34	0.34	0	0.32	0.36	0.27	0.38	53.5	0.25	0.92	0.34	0.34	112.3	0.15	0.92
Methylene chloride	0.39 (3) ^b	0.39	9.3	0.37	0.42	0.5	0.43	16.6	0.26	0.61	0.46	0.46	14.5	0.41	0.53
Chloroform	0.1	0.1	0	0.09	0.1	0.07	0.08	51.6	0.05	0.16	0.1	0.1	6.4	0.08	0.11
Carbon tetrachloride	0.54	0.54	25.1	0.34	0.64	0.58	0.59	11.7	0.49	0.68	0.52	0.52	7.2	0.47	0.57
Benzene	3.56	3.56	41.2	2.64	5.58	5.59	5.54	14	3.54	8.3	5.15	5.15	10	3.92	6.75
Trichloroethylene	0.69 (3)	0.69	0	0.66	0.72	0.55	0.55	0.3	0.51	0.58	0.3	0.3	0	0.3	0.31
Toluene	6.59	6.59	62.5	2.26	11.71	15.01	15.23	16.4	10.81	19.50	12.97	12.97	5.9	8.92	16.37
Tetrachloroethylene	0.29	0.29	26	0.24	0.39	0.4	0.34	11.9	0.17	0.44	0.29	0.29	5.3	0.25	0.34
Ethylbenzene	1.68	1.68	40.3	1.28	2.73	2.73	2.64	12.5	1.52	3.99	2.52	2.52	4.8	1.87	3.19
<i>m,p</i> -Xylene	5.66	5.66	38.6	4.40	9.06	9.21	8.77	11.8	4.98	13.13	8.42	8.42	4.8	6.29	10.67
<i>o</i> -Xylene	2.14	2.14	33.3	1.59	3.34	3.38	3.23	12.3	1.83	4.8	3.07	3.07	6	2.24	3.97
Naphthalene	0.05	0.05	0	0.05	0.06	0.03	0.03	5.9	0.03	0.03	0.02	0.02	0	0.02	0.02
Styrene	0.4	0.4	22.9	0.30	0.58	0.62	0.59	22.4	0.37	0.82	0.55	0.55	4.3	0.4	0.68
<i>a</i> -Pinene	0.12	0.12	0	0.11	0.13	0.16	0.13	47.7	0.06	0.24	0.11	0.11	67	0.03	0.18
<i>p</i> -Dichlorobenzene	0.37	0.37	60.7	0.17	0.62	0.48	0.43	32.2	0.1	0.71	0.44	0.44	10.1	0.26	0.58
Decane	0.75 (1)	1.02 (6)	1.02	21.2	0.56	1.44	1.06(2)	1.06	34.8	0.8	1.32

Note: %RSD: relative pooled standard deviation (percentage); ^aSamples were blank-corrected with data summarized based on pollutants below detection limit assigned a value equal to half the detection limit; ^bNumbers in parentheses are the number of observations designated at the top of time integral column. Species with different sample sizes presented in parentheses next to median value.

Table 2. (b) Sample statistics,^a pooled across sampling periods, for 2-day weekend, 4-day weekday, and 7-day weekly passive samples at CAMS 41. NO₂ data in units of pbb and VOCs in µg/m³.

Compound	3-Day Weekend (n = 4) ^b					4-Day Weekday (n = 10)					7-Day (n = 4)				
	Median	Mean	%RSD	Min	Max	Median	Mean	%RSD	Min	Max	Median	Mean	%RSD	Min	Max
NO ₂	27.7	27.7	1.2	25.18	29.88	31.04 (8) ^b	31.21	3.2	27.03	34.97	30.26	30.26	1.4	27.59	32.92
Butadiene	0.34	0.34	0.1	0.33	0.35	0.27	0.32	48.6	0.26	0.73	0.5	0.5	13	0.15	0.92
Methylene chloride	0.31	0.31	15.2	0.28	0.35	0.51	0.47	11.1	0.29	0.64	0.4	0.4	4.5	0.35	0.43
Chloroform	0.1	0.1	0.1	0.09	0.1	0.1	0.11	4.1	0.06	0.19	0.13	0.13	3.4	0.09	0.17
Carbon tetrachloride	0.54	0.54	4.8	0.48	0.59	0.53	0.54	5.4	0.51	0.60	0.52	0.52	6.4	0.5	0.56
Benzene	3.56	3.56	9.5	2.32	4.99	4.27	4.56	5.7	3.23	6.03	4.55	4.55	5	3.52	5.71
Trichloroethylene	0.69	0.69	0.1	0.66	0.71	0.54	0.55	0	0.53	0.58	0.31	0.31	0	0.3	0.31
Toluene	7.28	7.28	41.3	2.23	10.3	12.64	13.64	35.7	8.7	26.15	11.73	11.73	8.2	8.96	14.92
Tetrachloroethylene	0.35 (3)	0.35	5.5	0.31	0.41	0.4	0.41	6.6	0.33	0.49	0.37	0.37	1.7	0.36	0.38
Ethylbenzene	1.78	1.78	11.7	1.08	2.43	2.12	2.25	5	1.47	3.02	2.29	2.29	1.2	1.79	2.79
<i>m,p</i> -Xylene	5.71	5.71	10.6	3.55	7.96	7	7.35	5	4.93	10.08	7.43	7.43	1.1	5.81	9.05
<i>o</i> -Xylene	2.07	2.07	7	1.32	2.96	2.55	2.7	6	1.74	3.74	2.74	2.74	1.1	2.12	3.32
Naphthalene	0.05	0.05	0.1	0.05	0.06	0.03	0.03	0	0.03	0.03	0.02	0.02	0	0.02	0.02
Styrene	0.39	0.39	38.9	0.13	0.54	0.46	0.44	14.5	0.28	0.57	0.49	0.49	0	0.38	0.60
<i>α</i> -Pinene	0.12	0.12	0.1	0.11	0.13	0.1	0.11	24.7	0.06	0.16	0.08	0.08	0	0.03	0.12
<i>p</i> -Dichlorobenzene	0.39	0.39	22.2	0.32	0.49	0.35	0.4	20.3	0.1	0.63	0.46	0.46	0.9	0.36	0.56
Decane	0.31 (2)	0.31	64.2	0.17	0.46	0.66 (8)	0.96	11.5	0.14	1.86	0.45 (1)

Note: %RSD: relative pooled standard deviation (percentage); ^aSamples were blank-corrected with data summarized based on pollutants below detection limit assigned a value equal to half the detection limit; ^bNumbers in parentheses are the number of observations designated at the top of time integral column. Species with different sample sizes presented in parentheses next to median value.

vious evaluations of the single-charcoal pad 3500 OVM measurements for these species and duration;²⁵ in that study, investigators reported %RSD for benzene at 16% and toluene at 5.8%.

Although longer sampling periods suggest an increase in precision for the OVMs, these time intervals could be an area of contention regarding loss of information related to temporal resolution. It is important also to note that the relevance of integration time for a measurement depends on the purpose for which the measurement was obtained. Thus, if the purpose is to estimate cancer-related risk (e.g., from benzene exposure), then a longer time-integrated concentration is more relevant than a short-term measurement. If the measurement is done to obtain a peak concentration for comparison with maximum concentrations estimates from a model, then the longer-duration measurement is not as useful as the short-duration one. Figure 3a shows the temporal variation of benzene from the OVMs with the hourly auto-GC measurements for the same pollutant superimposed. The OVM samples and auto-GC measurements displayed are for the study duration; duplicate passive sampler data were averaged for presentation purposes. Potential episodic or short-term influences are smoothed out by the OVMs relative to the hourly auto-GC values; the same is true for the Ogawa NO₂ measurements in comparison with hourly chemiluminescence values (see Figure 3b).

Thus, the passive samplers are valuable for integrated samples while continuous monitors are necessary to assess short-term temporal variations.

NO₂ and VOC Comparisons

Table 3 summarizes the results from regression analysis between the concentrations monitored by the passive samplers and their respective standard methods; median summaries across periods of the ratio of the mean of passive samplers to their respective standard methods also are presented. The NO₂ regression results indicated apparent discrepancies between the Ogawa passive samplers and chemiluminescence analyzers. Initial examination of the slope and intercept results indicate that they were not statistically different from their target values for measurements at both sites; the C_b and ρ_c measures suggested reasonable agreement with the 1:1 line. The passive:reference method ratios also approached 1. Both the regression results and ratios suggested overprediction by the Ogawa samplers relative to chemiluminescence analyzers. The lack of fit test and residual analysis results, however, suggested a problem at each site for the NO₂ regressions. These results were interpreted cautiously for the following reason. As mentioned earlier, only one AIRS value was available per sampling period. This meant that true repeat measurements of the AIRS observations were not obtained and, therefore, the variability utilized in the lack of fit test

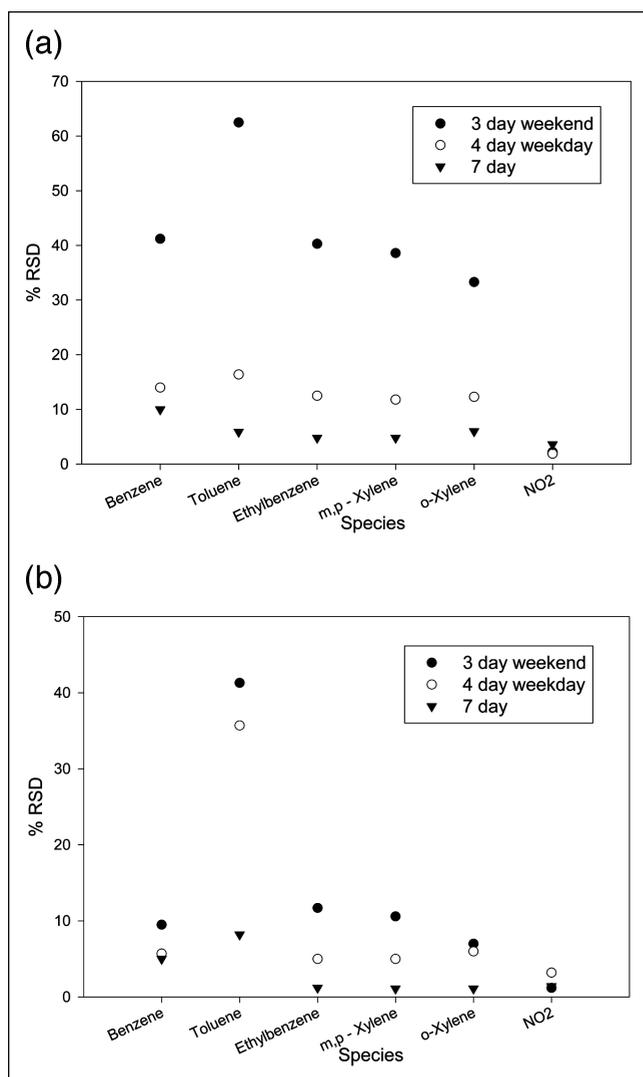


Figure 2. (a) Relative standard deviations of the 3-, 4-, and 7-day sampling periods for passive samplers at CAMS 6. (b) Relative standard deviations of the 3-, 4-, and 7-day sampling periods for passive samplers at CAMS 41.

was underestimated. Thus, the F test for lack of fit yielded a p value that was too low. Draper and Smith⁴² discuss this problem in terms of repeated versus reconfirmed measurements.

To further investigate whether a problem existed, separate regressions were done for each week at each site. This follow-up testing showed that the passive samplers and chemiluminescence analyzers compared distinctly differently during the two full weeks of the study (Figure 4a for CAMS 6 and Figure 4b for CAMS 41). While a straight line was an appropriate fit to the data for each of the two weeks separately, statistical testing showed that both the intercepts and slopes were significantly different between the two weeks. At CAMS 6 for the first week, the slope was 0.98 and the y intercept was 3.69, while the slope for the second week was 2.1 and the y intercept was -35.43 . Corresponding results for CAMS 41 were a slope

of 0.7 and intercept of 8.11 for the first week and slope of 2.5 and intercept of -41.26 during the second week. (See Kleinbaum et al.⁵² for a discussion of the comparison of regression lines.)

To further investigate this discrepancy, copies of the operator logs for the chemiluminescence analyzers were examined. A possible reason for this occurrence may have been a routine change in calibration/span gases. For CAMS 41, the span was listed as invalid twice during the first week and once during the second week; additionally, the first week of data had a warning flag. At CAMS 6, a warning status occurred in the second week and all other spans were acceptable. Other possible reasons may have been differences in emission or meteorological conditions (such as humidity spikes or wind gusts) during sampling. Based on this follow-up analysis and check of the operator logs, the comparison between the two sampling methods was inconclusive.

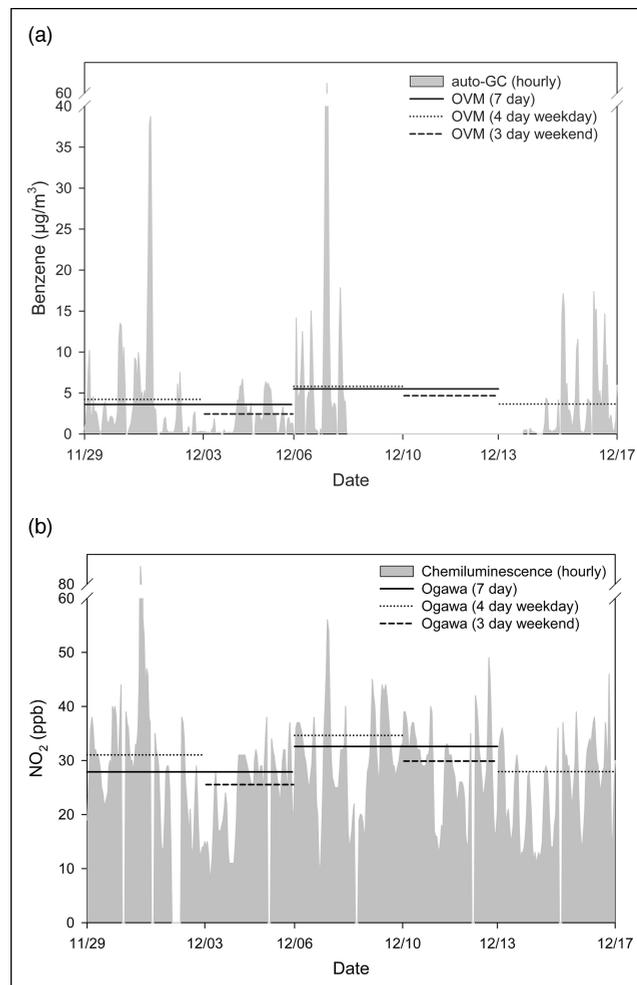


Figure 3. (a) Average benzene concentrations of duplicate OVMs (as horizontal lines) during the study period with hourly average benzene concentrations from the auto-GC. CAMS 41 measurements shown. (b) Average NO₂ concentrations of duplicate Ogawa badges (as horizontal lines) during the study period with hourly average NO₂ concentrations from a chemiluminescence analyzer. CAMS 41 measurements shown.

Table 3. Statistical comparison of passive samples and corresponding continuous monitoring data. The estimated y intercept was tested for a statistically significant difference from 0; the estimated slope was tested for a statistically significant difference from 1. Median across periods of the ratios of means of passive sampler to respective reference method monitor included.

Compound	Units	DF	y Intercept	Slope	r^2	Bias (%)	C_b	ρ_c	LOF	Ratio
NO ₂ ^a (CAMS 6) ^b	ppbV	15	-1.53	1.16	0.91	10.8	0.69	0.65	5.57 ^e	1.11
NO ₂ (CAMS 41) ^b	ppbV	15	8.63	0.76	0.57	4.8	0.82	0.62	15.88 ^d	1.05
Benzene ^c	$\mu\text{g}/\text{m}^3$	6	0.85 ^e	0.78 ^e	0.96	5.5	0.97	0.95	0.74	1.05
Toluene	$\mu\text{g}/\text{m}^3$	6	2.09	0.66	0.57	-3.8	0.91	0.69	0.38	0.96
Ethylbenzene	$\mu\text{g}/\text{m}^3$	6	0.63 ^e	0.7 ^e	0.92	10.4	0.91	0.88	0.15	1.10
<i>m,p</i> -Xylene	$\mu\text{g}/\text{m}^3$	6	1.72 ^e	0.72 ^e	0.95	6.2	0.95	0.93	0.45	1.06
<i>o</i> -Xylene	$\mu\text{g}/\text{m}^3$	6	0.38 ^e	0.84	0.97	7.1	0.98	0.97	3.19	1.07
Styrene	$\mu\text{g}/\text{m}^3$	6	0.28 ^e	1	0.28	377	0.13	0.07	0.07	4.77

Note: DF is total corrected degrees of freedom ($N - 1$); r^2 : regression r^2 (coefficient of determination); Bias is reported as the median of all sampling period mean biases; C_b : Bias correction term (see text for description); ρ_c : Concordance coefficient (see text for description); LOF: lack of fit testing; value shown is the F statistic from analysis of variance for test of LOF; Ratio: Median across periods of the ratios of means of passive sampler to AIRS monitor; ^aNO₂ comparison from Ogawa vs. chemiluminescence analyzer; ^bResidual analysis and lack of fit testing revealed problems with this straight line regression; ^cAll VOC comparisons from CAMS 41 measurements only (OVM vs. auto-GC); ^d $P < 0.001$; ^e $P < 0.05$.

Comparisons of the 3520 OVMs with the PAMS auto-GC were better than those carried out for NO₂. All of the BTEX species had high C_b values and reasonably high ρ_c and r^2 values. Residual analysis and lack of fit testing did not indicate problems with the regression for any of the BTEX species. The passive samplers performed best for the toluene and *o*-xylene species, neither slope being different from 1 and the toluene intercept not being different from 0 (see Table 3). Note that both the intercept and the slope were statistically different from their target values for benzene, ethylbenzene, and *m,p*-xylene. The r^2 for toluene was the lowest for BTEX species at 0.57 (as well as for styrene, $r^2 = 0.28$). The lower r^2 for toluene may be a reflection of the fact that toluene ambient levels were close to the OVM MDLs (max MDL = 4.47 $\mu\text{g}/\text{m}^3$), as shown in the inset of the regression plot in Figure 5a. Chung et al.²² reported that the OVM MDL for toluene was the highest among the target VOCs because of high and variable background levels found in the charcoal collection pad. This variability in background toluene levels may be responsible for some of the variability in the concentrations monitored with the OVMs as shown in Figure 5a. This was not evident for other BTEX species such as benzene (Figure 5b) and *o*-xylene (Figure 5c), which showed overall strong correlation and ambient levels well above MDLs. Low r^2 , C_b , and ρ_c for styrene (see Table 3) were expected because styrene concentrations were also low and near the limit of detection for the OVMs (see Table 1).

As indicated both by the mean biases and the y intercepts shown in Table 3, the OVMs tended to overpredict ambient BTEX concentrations (as high as 10%) when compared with the auto-GC at CAMS 41; the exception was toluene with a bias of -3.8%. (While the biases calculated from the means of all observations in Table 1 all

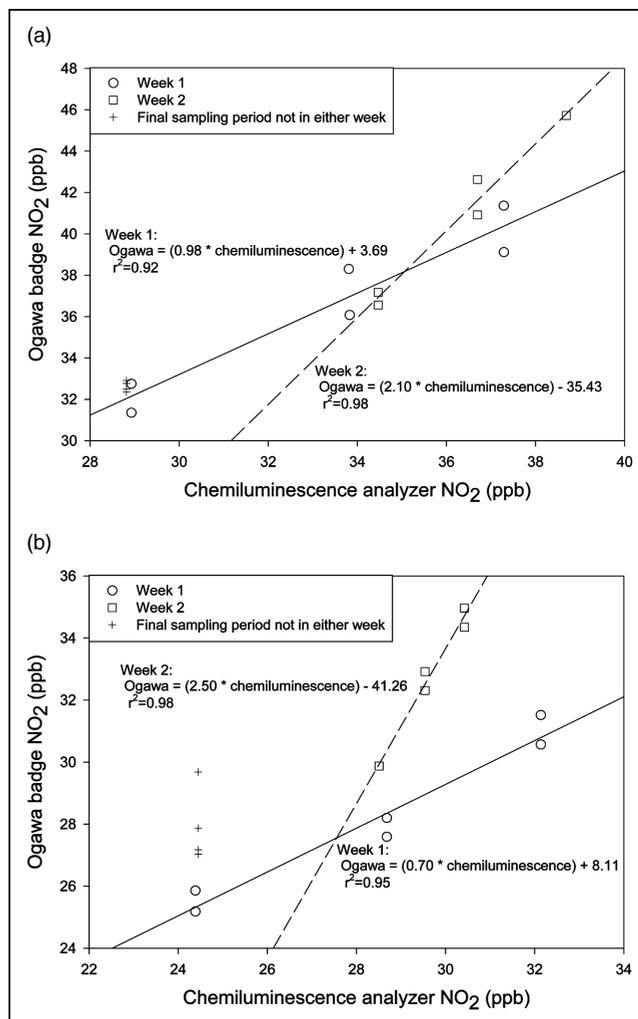


Figure 4. (a) Regression of Week 1 and Week 2 of Ogawa badges vs. chemiluminescence analyzers-NO₂ (CAMS 6). (b) Regression of Week 1 and Week 2 of Ogawa badges vs. chemiluminescence analyzers-NO₂ (CAMS 41).

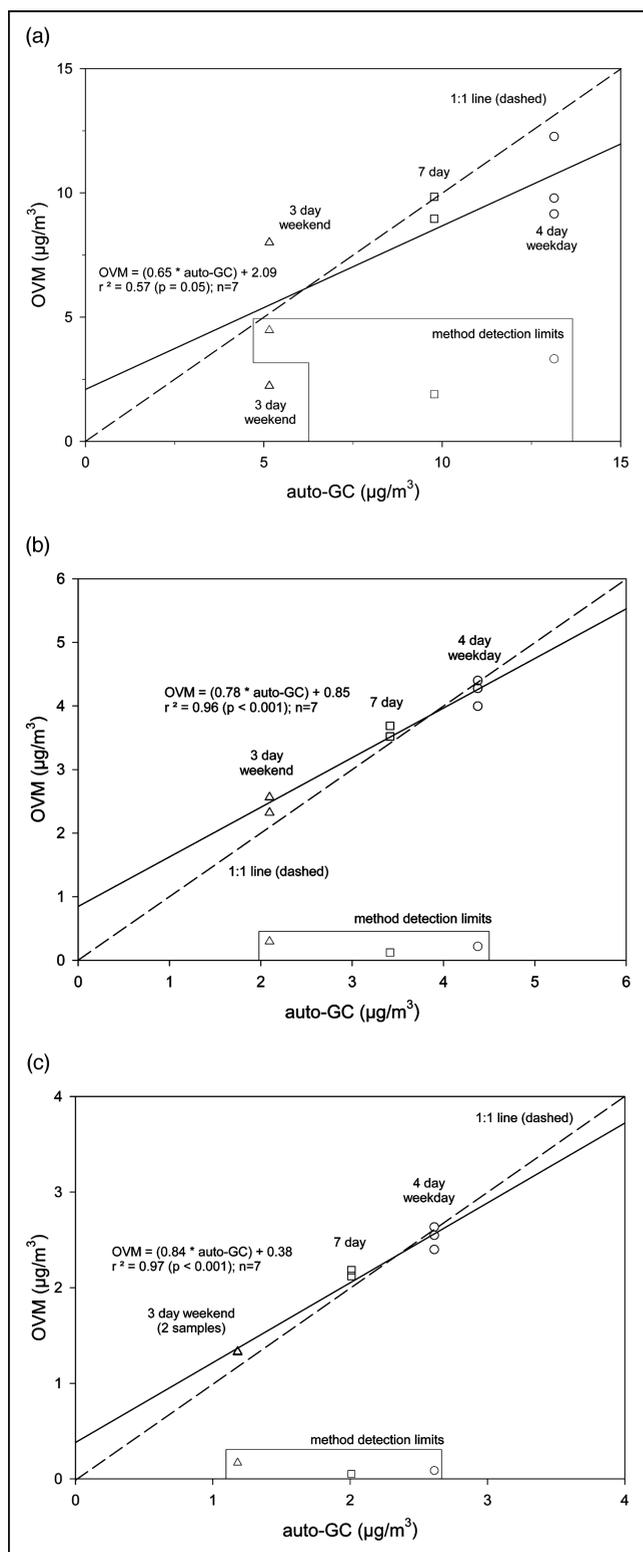


Figure 5. (a) Regression of 3520 OVM vs. auto-GC at CAMS 41–toluene. (b) Regression of 3520 OVM vs. auto-GC at CAMS 41–benzene. (c) Regression of 3520 OVM vs. auto-GC at CAMS 41–o-xylene.

exceed 20%, note that the biases and ratios reported in Table 3 are medians over the sampling periods and reduce the effect of outlying observations, thus providing better indicators of overall performance.) With the exception of

toluene, γ intercepts were significantly different from 0 ($p < 0.05$); all VOC γ intercepts were above 0. Toluene was the only VOC that the OVMs underestimated relative to their respective auto-GC measurements (see Figure 5a). The OVM:auto-GC ratios also revealed that the OVMs overpredicted concentrations relative to the auto-GC for BTEX species and styrene with the exception of toluene (see Table 3); as an aside, the bias and ratio values for styrene were much greater than the other species evaluated because its measured concentrations were close to the OVM's MDL (see Table 1). This overall overprediction by the OVM was in contrast to a previous study of 3500 OVMs (containing a single charcoal pad) that showed negative bias for BTEX species when compared with reference canister sampling methods.²⁶ The wide shelter configuration for the OVM samplers and the fact that OVM shelters had to be placed ~ 2 m lower than the auto-GC inlet may be possible reasons for the overprediction. Although CAMS 41 was situated away from immediate source influences to capture overall El Paso VOC influences, it is conceivable that the lower OVM sampling height may have been closer to ground-level emissions from traffic in nearby roads. Other investigations have observed small yet significant differences in NO_2 concentrations from passive samplers at heights of 1.5 and 3 m.⁵³

CONCLUSIONS

No firm conclusions could be made regarding comparability of NO_2 measurements between Ogawa samplers and automated methods because of potential calibration issues and underestimation of NO_2 with the chemiluminescence analyzer. While NO_2 passive sampler evaluation results were inconclusive, the utility of C_b and ρ_c along with the lack of fit test and residual analysis was demonstrated for future evaluation of similar passive/continuous methods. Note that testing for lack of fit was made possible by the collection of duplicate samples of the passive monitors. The overall conclusion for the BTEX species is that while there was a tendency for the OVMs to overpredict the auto-GC measurements (by up to 10%), they performed reasonably well as ambient levels changed; in this study, toluene and o-xylene yielded best agreement with the auto-GC. When comparing 3500 OVMs with other pumped activated charcoal tubes, the OVMs tended to underpredict these samplers.^{15,25} This study found a slight positive bias for benzene and no major bias for toluene. Although more research is needed, this may indicate that the dual-pad 3520 OVMs are more effective at capturing potential breakthrough of volatile species as opposed to the single-pad 3500 OVMs under certain circumstances and during extended sampling.

While the results obtained here may provide further encouragement to use OVMs for spatial and temporal

exposure studies, they also suggest that additional evaluation of these passive samplers be conducted with reference methods (auto-GC, canister, or actively pumped sorbent tubes) to assess potential discrepancies that also may be dependent on ambient conditions (temperature, relative humidity, etc.) unique to the airshed under study. Of particular note, the correction not only for temperature but also for barometric pressure conditions when reporting concentrations from the passive samplers is important when monitoring higher elevations such as those encountered here. Finally, the increasing trend in precision with longer sampling times for the OVMs, though not surprising, has an impact in terms of loss of information related to temporal variations; however, this limitation may or may not be relevant depending on the purpose for which the passive dosimeter measurement is obtained.

The primary caveat attached to these and the other results reported here is that this was a short-term study with collection of few samples and only one measurement available for the reference methods. Comparisons of data were, therefore, limited. Because of this, it is recommended that additional method evaluations be conducted with these passive samplers to more definitively establish their capabilities. Accordingly, methods evaluation of passive samplers should be a routine quality assurance component where such samplers are deployed in exposure assessment studies.

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