Evaluation of a Passive Sampling Method for Long-Term Continuous Monitoring of Volatile Organic Compounds in Urban Environments

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ABSTRACT: Environmental Protection Agency Method 325 was developed for continuous passive monitoring of volatile organic compounds (VOCs), particularly benzene, at petroleum refinery fencelines. In this work, a modified version of the method was evaluated at an Ontario near-road research station in winter to assess its suitability for urban air quality monitoring. Samples were collected at 24 h and 14 day resolution to investigate accuracy for different exposure times. Tubes were analyzed by thermal desorption—gas chromatography—mass spectrometry, and 11 VOCs were quantified, including aromatic air toxics. The same VOCs were simultaneously monitored using traditional canister sampling for comparison, and a subset of four were also monitored using a novel miniature gas chromatograph. Good agreement (within 10%) was observed between the 14 day passive tube samples and the canister samples for benzene. However, field-calibrated uptake rates were required to correct passive tube concentrations for less volatile aromatics. Passive tube deployment and analysis is inexpensive; sampling does not require power, and accurate measurements of benzene are demonstrated here for an urban environment. The method is expected to be advantageous for the generation of long-term continuous benzene data sets suitable for epidemiological research with greater spatial coverage than is currently available using traditional monitoring techniques.

INTRODUCTION

The measurement of volatile organic compounds (VOCs) in ambient air through passive sampling is becoming more prevalent,1−4 and applications include indoor air quality,5−7 outdoor air quality,8−12 and soil vapor intrusion assessments.13 Passive sampling approaches include permeation devices,14,15 polycarbonate foam disks,16,17 solid phase microextraction fibers,18−20 and thermal desorption (TD) tubes packed with sorbent materials.21−23 Environmental Protection Agency (EPA) Method 325, involving passive sampling of VOCs on low-cost stainless steel TD tubes containing Carbopack X, is currently used to assess VOC concentrations at petroleum refineries in the United States under the Code of Federal Regulations (CFR), title 40.24 The method has also recently been introduced by refineries in Ontario, Canada, to meet the province’s Petroleum Refining Industry Standard.25 EPA Method 325 was developed to enable continuous monitoring of VOCs associated with fugitive emissions from refineries with an emphasis on benzene, a known carcinogen.26,27 Fugitive VOC emissions are difficult to predict through modeling,28 and thus, continuous year-round VOC monitoring offers the advantage of capturing any unexpected or intermittent emission events, irrespective of their duration.

In EPA Method 325 applications, each TD tube is housed in a shelter, fitted with a diffusion end cap, and exposed to ambient air for a period of ≤2 weeks during which ambient VOCs diffuse to the sorbent and are retained.24 While laboratory-based testing has demonstrated good agreement between EPA Method 325 and traditional evacuated canister sampling for a range of VOCs under controlled conditions,29 field studies assessing accuracy and potential biases of the method have been uncommon and focused on petrochemical facility fenceline sampling locations.22,23,30−32 A previous side-by-side comparison of 24 h passive Carbopack X tube samples and evacuated canister samples in indoor environments demonstrated good agreement between the two approaches in the range of 0.1−28 ppbv, although some low-concentration tube samples (<0.3 ppbv) were biased low by approximately 50% for xylenes. A low bias has also previously been observed for aromatic VOC samples using passive tubes in a summertime study in Wisconsin; however, a different sorbent was used in these studies.

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The concentration calculation steps to the following equation:

$$C_c = \frac{m_{\text{meas}} \times 10^6}{U_{\text{NTP}} \left( \frac{T_{\text{SS}}}{298} \right) t}$$

where $C_c$ is the ambient concentration of the VOC at standard temperature and pressure (micrograms per cubic meter), $m_{\text{meas}}$ is the mass of the VOC measured on the passive tube (micrograms), $U_{\text{NTP}}$ is the literature $U_{\text{eff}}$ of the VOC at standard temperature and pressure (milliliters per minute), $T_{\text{SS}}$ is the mean ambient temperature (kelvin) during sampling, and $t$ is the sampling duration (minutes). This formula adjusts the VOC effective uptake rate by accounting for the decrease in diffusion rates of VOCs with a decrease in temperature and is applied in this study.

All passive sampling was performed using Supelco Carbopack X TD Tubes for Fenceline Monitoring supplied by Sigma-Aldrich. Prior to sampling, each tube was conditioned using a Markes International TC-20 multitube conditioner. Tubes were continuously purged with nitrogen (purity of 5.0) at a rate of 100 mL min$^{-1}$, heated to 350 °C, held at 350 °C for 30 min, and cooled to room temperature. This thermal cycle was then repeated to minimize VOC contamination. Laboratory and field blanks were conditioned in the same way. All tubes were sealed at both ends using Swagelok nut and ferrule sets, stored in individual metal cans in a refrigerator at 4 °C prior to use, and used within 14 days of being conditioned.

Calibration tubes were prepared using a 1 ppmv cylinder of 1,3-butadiene, trichloroethylene (TCE), benzene, toluene, tetrachloroethylene (PCE), chlorobenzene, ethylbenzene, m-, xyylene, styrene, 1,3,5-trimethylbenzene, and naphthalene in nitrogen prepared by Praxair. Tubes were doped by diluting the standard cylinder flow with nitrogen (purity of 5.0) using an Environics Series 2014 Computerized VOC Gas Dilution System and passing the diluted gas through each tube at a rate of 100 mL min$^{-1}$ for 6 min. This equivalent sample volume of 600 mL provides masses of each VOC on the sorbent that are similar to what is expected to be collected through passive sampling for a 24 h deployment. Calibration tubes were prepared using concentrations of 0.1−20 ppbv. A wide concentration range was chosen because the same method was used to quantify tubes with sampling durations of 1 and 14 days. Tubes were analyzed using a PerkinElmer TurboMatrix 650 automated thermal desorption (TD) unit coupled with a PerkinElmer Clarus 680 gas chromatograph (GC) interfaced with a PerkinElmer Clarus SQ29C single quadrupole mass spectrometer (MS). Detailed descriptions of the TD method, the GC method, MS settings, and blank signal subtraction are provided in the Supporting Information.

Separate low- and high-concentration range calibration curves were generated for quantification, and nonlinearity is apparent in the high-concentration range (1.6−20 ppbv) TD−GC−MS response for the least volatile VOCs (ethylbenzene, m-xylene, styrene, 1,3,5-trimethylbenzene, and naphthalene). The concentration−response profile for these species is better.
Field sampling was performed by placing the tubes in shelters designed to meet EPA Method 325 shelter requirements located on the roof of the near-road station 4 m above ground level. Tubes were fitted with diffusion end caps and placed in the shelter for periods of 24 h and 14 days for a six-week period (January 16 – February 27, 2018). One 24 h duplicate and one 24 h field blank were performed every 7 days. All 14 day samples were performed in triplicate, and a 14 day field blank was included during each deployment. Upon collection, tubes were sealed using a Swagelok nut and ferrule. Each sampling set, stored in individual metal cans, and refrigerated at 4 °C until analysis could be performed. All tubes were analyzed within 1 week of collection and were dry purged for 2 min at room temperature using a 50 mL min⁻¹ flow of nitrogen (purity of 5.0) prior to analysis to minimize the introduction of water into the TD–GC–MS instrument. One laboratory blank and one calibration check were included in each TD–GC–MS sequence. Calibration checks involved doping tubes with 600 mL of 0.5 ppbv of the standard VOC mixture described above.

The mass of benzene on these calibration check tubes was within 50% of the values determined on the ambient passive tubes for 14 day deployments. All field data were blank corrected by subtracting the average field blank response for each species.

The main differences between the method described here and EPA Method 325 are the inclusion of naphthalene as an analyte and the absence of internal standards during analysis. We have used the URₐ values for the most similar compound tested instead, 1,3,5-trimethylbenzene (0.41 mL min⁻¹). Despite the absence of internal standards, the precision was found to be good (<10%) for field duplicates and triplicates for the species quantitated above their MDLs as discussed below. The collection efficiency of the tubes for the VOCs quantitated was also assessed by using two tubes in series and is described in Table S1. The desorption efficiency was assessed by analyzing tubes spiked with standards twice in a row and is also described in Table S2.

Evacuated Canister Sampling and GC–MS Methodology. Passivated 6 L Summa canisters (BRC Rasmussen/ Hillsboro/Scientific Instrument Specialist) were cleaned, evacuated, and used to collect VOCs in air at the near-road station for 24 h periods. Samples were analyzed using a cryogenic preconcentration technique followed by GC–MS. The same species quantitated for the passive tube samples were quantitated in the canister samples. An EnTech model 7200 preconcentrator with an EnTech model 7016D autosampler was used for sample preconcentration; 500 mL of air was drawn from each canister through a multistage purge and trap concentration system that separates water and CO₂ from the VOC analytes. An Agilent 7890 gas chromatograph coupled to an Agilent 5975C mass spectrometer was used for analysis. The GC–MS method has been described in detail previously and is also provided in the Supporting Information.

Field sampling using evacuated canisters was performed using an RM Environmental Systems model 910C automated canister sampler, which enables sequential sampling of multiple evacuated canisters. The flow rate of air sampled by the canisters was set to 10 mL min⁻¹, and ambient air was drawn from the roof of the near-road station using a 1/4 in. Teflon sampling line at a height of 4 m above ground level. Forty 24 h canisters were collected over the six-week study period, with 2 days missed due to a power failure at the site.

Online GC-PID System. An Airpointer mini-gas chromatograph BTEX analyzer (Multi-recordum Environmental Monitoring Solutions GmBH, Mödling, Austria), housed in an air-conditioned shelter located adjacent to the near-road research station, was used to monitor benzene, toluene, ethylbenzene, and m/p-xylene (BTEX) at 15 min resolution. The system collects BTEX on a preconcentrator and performs separation using a microelectronic mechanical systems (MEMS) GC column with air as the carrier gas. Eluting VOCs are quantitated using a photoionization detector (PID, 10.6 eV). The method is described in detail in the Supporting Information. The manufacturer lower detection limit is 0.1 ppbv for the collection volumes used in this work, although performance below this limit was also investigated here. The instrument operated continuously for the six-week study, with the exception of 2 days due to the power failure mentioned above. The inlet for the mini-gas chromatograph sampled air from a height of 2 m above ground level and was located 4 m below the near-road station inlets. An assessment of the performance of the mini-gas chromatograph and a comparison with the evacuated canister data is provided in the Supporting Information, with linear regressions shown in Figure S3. The mini-gas chromatograph was found to be accurate for the measurement of BTEX, and differences between the mini-gas chromatograph and the canister data sets were not statistically significant as discussed in the Supporting Information. The dependence of BTEX ambient concentration data upon wind speed and direction is also shown in Figure S4, confirming the highway as the major local source of these four VOCs.

Meteorology. The air temperature, pressure, relative humidity, wind speed, and wind direction were measured at a height of 10 m above ground level at the near-road station using a model WXT520 Vaisala weather transmitter. A wide range of meteorological conditions were observed. Clear skies, heavy rain, fog, and heavy snow were all observed during the six-week study. Twenty-four hour mean ambient temperatures and relative humidities were in the ranges of −10 to 12 °C and 54−90%, respectively, providing a wide range of conditions for testing the suitability of the method for continuous monitoring.

RESULTS AND DISCUSSION

Method Detection Limits, Data Completeness, and Precision. The method detection limits (MDLs) for the 24 h passive tube samples and the 24 h evacuated canisters are provided in Table S3. TCE and chlorobenzene were found to be below their respective MDLs for all 24 h canister and tube samples, and PCE was below its MDL for almost all canister and tube samples. Thus, the performance of the passive tubes
for chlorinated VOCs could not be assessed. Only benzene, toluene, ethylbenzene, and m/p-xylene were measured above their MDLs for both methods for >75% of the study period. A minimum of 75% data coverage is required for continuous MOECC data sets to be considered valid.40 These four VOCs were also simultaneously measured using the online mini-gas chromatograph for additional verification, and thus the discussion of passive tube performance will focus on these species. The average precision values for 24 h passive tube field duplicates were 5, 6, 6, and 8% (calculated as the difference between the two reported concentrations divided by their mean24) for benzene, toluene, ethylbenzene, and m/p-xylene, respectively. For 14 day passive tube field triplicates, these values were 2, 3, 7, and 9% (coefficient of variation), respectively. Three canister field samples were analyzed twice, and the average duplicate injection concentration precision values for BTEX were 2, 2, 2, and 1%, respectively.

**Evaluation of the Passive Tube Method Performance for 14 Day Deployments.** A comparison of the mean concentrations observed for the 14 day resolution (the most typical deployment duration in EPA Method 325 fenceline applications) passive tube samples and the canister data for the entire study period, and for each of the three separate 14 day periods, is shown in Figure 1. Concentration data from the mini-gas chromatograph are also included here for reference. Good agreement is observed between the 14 day passive tube samples and the canisters for benzene and toluene for the entire study period (within 1 and 10%, respectively) and also for each individual two-week period (within 3−10 and 3−27%, respectively). Differences between the data sets for these two species are not statistically significant as discussed in the Supporting Information and shown in Table S4. However, the passive tube concentrations for ethylbenzene and m/p-xylene are higher than the canister concentrations by 75 and 90%, respectively, for the entire study period and by 64−137%, respectively, for the individual 14 day periods. The results indicate that the passive tube sampling approach is well suited to accurate quantification of benzene and toluene in the winter months in Ontario, but that positive bias may be an issue for ethylbenzene and m/p-xylene. The accuracy observed here for benzene, however, is encouraging for existing applications of EPA Method 325 at refineries in locations with colder climates where the impacts of winter meteorology have not been assessed in the field. Ambient temperatures down to −10 °C do not appear to affect the performance of the method for benzene when 14 day sampling durations are employed.

**Evaluation of the Passive Tube Method Performance for 24 h Deployments.** A more pronounced difference is observed between the 24 h passive tube concentrations and the 24 h canister concentrations as shown in Figure 2. In theory, 24 h passive tube deployments should be appropriate for passive monitoring of VOCs using EPA Method 325, although the mass of each analyte collected on the tube sorbent will be more than an order of magnitude lower than that of the 14 day tube samples, which may reduce the accuracy for the former considering the relatively low concentrations measured here (<1 ppbv).

It is apparent in Figure 2 that the 24 h concentrations determined from the passive tubes are higher than those determined using canisters. The positive biases of the mean concentrations of the 24 h tubes for the entire study period

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**Figure 1.** Comparison of the mean VOC concentrations determined for the entire six-week study and for each 14 day period for the 14 day passive TD tubes, the canisters, and the mini-gas chromatograph. Error bars in the first panel represent the 95% confidence interval.
relative to the canisters are 47, 50, 185, and 272% for BTEX,
respectively, and differences between the two methods are
statistically significant for all four VOCs as shown in Table S5.
Linear regressions are also shown in Figure S5, and the
temporal agreement observed between the 24 h passive tubes
and the canisters is much poorer than that observed between
the mini-gas chromatograph and the canisters in Figure S3.
The magnitude of the difference between the 24 h tube and
canister concentrations increases for the four VOCs in the
following order: benzene < toluene < ethylbenzene < m/p-
xylene. The difference between the two methods also varies as
a function of time, resulting in poorer correlations for the latter
two compounds in particular. To explore this finding further,
the ratio of the 24 h passive tube concentrations and canister
concentrations for each species is shown as a function of time
in Figure 3. Data points are colored as a function of ambient
temperature during sampling, and the largest differences
between the tube and canister concentrations, for ethylbenzene
and m/p-xylene in particular, are observed in the first week of
February, when mean 24 h temperatures were below 0 °C.
When the same tube/canister ratios are plotted as a function
of ambient temperature, the relative severity of the temper-

Figure 2. Comparison of the mean VOC concentrations determined for the entire six-week study for the 24 h passive TD tubes, the canisters, and the mini-gas chromatograph. The error bars represent the 95% confidence interval.

Figure 3. Ratio of 24 h resolution passive tube concentrations and 24 h canister concentrations for each day of the measurement period. Data points are colored as a function of the mean ambient temperature at the time of sampling. The gray lines indicate a ratio of 1.
dependent upon the vapor pressure and, therefore, the volatility of the VOCs investigated as shown in Figure 5. Analogous relationships are observed when octanol/air partition coefficient and boiling point data are used in place of vapor pressure as shown in the Supporting Information, with the strongest positive biases observed for the least volatile VOCs (Figure S6). The 14 day samples are affected to a much lesser extent by this positive bias, as shown in Figure 1, and thus, longer sampling times are found to be much more appropriate for ambient air quality monitoring for the VOCs investigated here, in particular under low-temperature conditions.

The relative humidity was not found to have a strong influence upon the positive bias observed, as shown in Figure S7, in line with the minimal impact of relative humidity upon passive tube uptake rates demonstrated previously through laboratory testing. The mean wind speed was stable for the three 14 day periods investigated (2.2, 2.3, and 2.4 m s$^{-1}$), and therefore, the impact of wind speed upon positive bias could not be assessed for the 14 day samples. However, a wide range of wind speed values were observed for the 24 h deployment periods (0.8–4.5 m s$^{-1}$), enabling the impact of this variable upon positive bias to be investigated for the 24 h tube data. A reasonably strong linear relationship is observed between 24 h tube data positive bias and wind speed for benzene ($R^2 = 0.53$), with higher wind speeds leading to higher positive biases for the 24 h tube sample data as shown in Figure S8. To the best of our knowledge, this is the first time this effect has been reported for EPA Method 325 and highlights another limitation of 24 h sampling durations. The linearity of the relationship between positive bias and wind speed is less strong

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**Figure 4.** Ratio of 24 h resolution passive tube concentrations and 24 h canister concentrations as a function of ambient temperature. The red lines are linear regressions of the ratios and ambient temperature. The gray lines indicate a ratio of 1.

**Figure 5.** Relationship between the slope of the tube/canister ratio vs temperature relationships shown in Figure 4 and the subcooled vapor pressure of the VOCs at 298 K.
for toluene ($R^2 = 0.18$), ethylbenzene ($R^2 = 0.25$), and $m/p$-xylene ($R^2 = 0.31$). If wind speed were the only source of positive bias, then all VOCs would be expected to exhibit similar positive biases, and this was not the case in our work. Instead, the least volatile VOCs exhibit more severe positive biases at lower temperatures, likely because of enhanced deposition on the passive tube interior.

**Comparison of the Passive Tube Performance to Those of Previous Studies.** Recently, a side-by-side comparison of one-week passive Carbopack X tube samples (modified EPA Method 325) and simultaneous one-week evacuated canister samples (EPA Method TO-15) was performed at a refinery fenceline in Whiting, Indiana. The mean ambient temperature was 14 °C, much warmer than the mean temperature in this work (~1 °C), and reasonably good agreement was observed between the two methods, although the tube samples (median values) were higher by approximately 15% for benzene and toluene, 43% for ethylbenzene, and 25% for $m/p$-xylene relative to the canister samples. The relatively long sampling times did not allow for an examination of the relationship between ambient temperature and any potential biases in that case. The same modified EPA Method 325 approach has been applied to assess VOC concentration spatial variability in the vicinity of refineries in Philadelphia, Colorado, and Texas, and the precision for duplicate tube samples has been shown to be excellent for the compounds quantified (<11%), in agreement with the precision observed in this work and in previous laboratory assessments.

A detailed laboratory exposure chamber evaluation of the performance of Carbopack X passive tubes for 1,3-butadiene and benzene at concentrations of approximately 5–25 ppbv and exposure times of 24 h relative to evacuated canisters (EPA Method TO-15) has also recently been undertaken, showing agreement within 25% for both species after applying a blank correction step. In that study, a separate chamber experiment involving tubes exposed to an expanded compound list (1,3-butadiene, benzene, toluene, styrene, ethylbenzene, $m/p$-xylene, $o$-xylene, and styrene) yielded good agreement (within ~30%) between independent laboratory results and expected concentrations based on EPA Method 325 diffusive uptake rates; however, only room-temperature conditions were explored. The impact of temperature on effective uptake rates was evaluated separately in a third chamber experiment, with 24 h passive tube concentrations found to agree well for benzene (within ~30%) but less so for 1,3-butadiene (within ~70%) when compared to those of EPA Method TO-15 in the temperature range of ~14 to 47 °C. However, no other VOCs were investigated in that case, and thus, the impact of low ambient temperatures upon the accuracy of EPA Method 325 for compounds less volatile than benzene has not been established prior to this work to the best of our knowledge.

Our findings indicate that low ambient temperatures introduce a significant positive temperature-dependent bias for ethylbenzene and $m/p$-xylene when commonly used literature uptake rates are applied and that shorter sampling durations result in more severe positive biases. Critically, however, benzene concentrations remain accurate for 14 day deployments.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Relationship between field-calibrated uptake rates ($U_{\text{field}}$) and ambient temperature (red line) for 14 day passive tube deployments. Ideal uptake rates ($U_{\text{ideal}}$) based on diffusion theory (solid gray line) and effective uptake rates ($U_{\text{eff}}$) based on literature laboratory data are also included for reference.
passive tube samples even under sub-zero ambient temperatures, and the accuracy of the method for benzene is not influenced by the occurrence of rain, snow, or fog. This result provides evidence to support the suitability of EPA Method 325 for accurate refinery fenceline monitoring of benzene in the northern United States and Canada in the winter months. Furthermore, accurate low-temperature data for less volatile VOCs may also be obtained by applying more representative uptake rates as described below.

**Calculation of Field-Calibrated Uptake Rates for Low-Temperature Conditions.** While positive bias is observed in this study when the literature uptake rates from McClenny et al. are applied in the calculations, the data set collected also provides the opportunity to develop “field-calibrated” uptake rates as a function of temperature that users can employ to avoid reporting similar positive biases in future studies. The mass collected on the passive tubes for each VOC can be compared directly with the concentrations observed in the evacuated canisters to calculate field-calibrated uptake rates as follows:

$$U_{\text{field}} = \frac{m_{\text{meas}} \times 10^6}{C_{\text{can}} t}$$

where $U_{\text{field}}$ is the uptake rate determined for each passive tube sample (milliliters per minute), $m_{\text{meas}}$ is the mass of the VOC measured on the passive tube (micrograms), $C_{\text{can}}$ is the accurate VOC concentration measured using the canister (micrograms per cubic meter), and $t$ is the sample duration (minutes). This calculation was performed for each passive tube sample, and regressions against ambient temperature were performed to determine $U_{\text{field}}$ as a function of temperature for both 14 day and 24 h deployments, as shown in Figures 6 and 7, respectively.

As shown in Figure 6, for 14 day passive tube deployments, the field-calibrated uptake rates ($U_{\text{field}}$) for benzene and toluene agree quite well with those determined by McClenny et al. However, the $U_{\text{field}}$ values for ethylbenzene and $m$/$p$-xylene are much higher than the McClenny $U_{\text{eff}}$ values and are also much higher than the maximum uptake rates predicted by diffusion theory ($U_{\text{ideal}}$) using literature diffusion coefficients for each VOC in air as listed in Table S6. Deposition of the less volatile VOCs on the tube surface represents an explanation for this deviation from diffusion theory. We propose that future users apply the $U_{\text{field}}$ values shown in Figure 6 to ethylbenzene and $m$/$p$-xylene field data, but only for samples collected at <280 K. At >280 K, it is apparent that the linear fits in Figure 6 predict $U_{\text{field}}$ values that are lower than the $U_{\text{eff}}$ values of McClenny et al., and previous work has demonstrated that those $U_{\text{eff}}$ values are representative at warmer temperatures. A full list of $U_{\text{field}}$ values for all four compounds as a function of temperature is provided for reference in Table S7.

It can be seen in Figure 7 that the 24 h deployment $U_{\text{field}}$ values for toluene, ethylbenzene, and $m$/$p$-xylene deviate to a much greater extent from their respective $U_{\text{eff}}$ and $U_{\text{ideal}}$ values than is observed for the 14 day deployment data. While modeled diffusive uptake rates for sorbent-packed TD tubes have been found to be higher for 24 h exposures than for 14 day exposures, diffusive uptake alone cannot account for the
high $U_{\text{field}}$ values observed in this work. Uptake by direct deposition appears to dominate over uptake through diffusion at temperatures below approximately 280 K for toluene, ethylbenzene, and $m$/$p$-xylene when tubes are deployed for 24 h periods. The curves shown in Figure 7 can be applied to correct 24 h deployment field data at low temperatures, and $U_{\text{field}}$ values as a function of temperature are listed in Table S8. However, the low sensitivity, low blank/sample signal ratios, and the apparent dominance of deposition at lower temperatures observed for the 24 h deployment data suggest that 14 day deployments should instead be favored for accurate ambient monitoring of aromatic VOCs.

Implications for Urban Air Quality Monitoring. Benzene is a carcinogenic air pollutant associated with a variety of sources, including not only industrial and petrochemical processes but also vehicle exhaust and residential combustion. Continuous benzene monitoring at high spatial resolution will be of great benefit for the assessment of chronic exposure in near-road, urban, and industrial environments and will help to generate the long-term ambient data sets needed to support effective epidemiological research. Widely used traditional evacuated canister samples typically provide only one-in-six day data coverage and are often limited to deployment at established air quality stations. Online automated GC instruments are accurate but expensive, require power, and are also limited to air quality stations. Although EPA Method 325 was originally developed to provide continuous monitoring of VOCs exclusively at refinery and petrochemical facility fencelines, the results here support the wider applicability of the method to urban air quality monitoring. The thermal desorption tubes are housed in basic shelters during sampling, require no power, and can be reused multiple times. Laboratory analysis is also reasonably straightforward and inexpensive, with achievable detection limits for benzene of <10 pptv for 14 day tube deployments. While lower temperatures introduce the need to apply corrections for benzene at low temperatures provided that tubes are deployed for 14 day periods.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b02792.

Description of sampling site, calibration curves, method descriptions, method detection limits, method comparisons (with linear regressions and statistical analysis), dependence of ambient VOC concentrations on wind speed and direction, dependence of TD tube positive bias on relative humidity, wind speed and physicochemical properties, diffusion coefficients of VOCs in air, and TD tube uptake rates modeled as a function of ambient temperature (PDF)

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Notes

The authors declare no competing financial interest.

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