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Application of passive sorbent tube and canister samplers for volatile organic compounds at refinery fenceline locations in Whiting, Indiana

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Abstract

Select volatile organic compounds (VOCs) in ambient air were measured at four fenceline sites at a petroleum refinery in Whiting, IN, using modified EPA Method 325 A/B with passive tubes and EPA Compendium Method TO-15 with canister samplers. One-week, time-integrated samplers were deployed for 8 weeks with tubes and canister samplers deployed in duplicate. Good precision was obtained from the duplicate tubes (<7%) and duplicate canisters (≤10%) for BTEX, perchloroethylene, and styrene. The tubes yielded statistically significantly higher concentrations than canisters for benzene, toluene, ethylbenzene, and *m,p*-xylene. However, all differences were estimated to be <0.1 ppbv. No concentration differences among the four Whiting sites were found for any of the VOCs.

Implications: Recently enacted EPA Methods 325A/B use passive-diffusive tube samplers to measure benzene at refinery fenceline locations. This pilot study presents VOC data applying a modified version of EPA Method 325 A/B and its comparison to EPA Compendium Method TO-15 canister samplers at four refinery fenceline sites. The findings from this study provide additional confidence in application of the tube method at refineries to ascertain VOC source influence since tube and canister samplers were comparable and good precision was obtained from duplicate sampling for both methods. No overall difference in these reported VOC concentrations was found between Whiting sites for tubes or canisters.

Introduction

Volatile organic compounds (VOCs) are air pollutants encountered in urban and industrial areas and are usually associated with emissions from transportation, solvent use, petrochemical facilities, and other anthropogenic sources. Many VOCs are also hazardous air pollutants; for example, benzene is a known carcinogen. Fugitive and other emissions from oil and gas facilities such as refineries are potential sources of VOCs (Thoma et al. 2016). These pollutants are typically measured with U.S. Environmental Protection Agency (EPA) approved methods such as time-integrated canister samples (U.S. EPA 1999a).

The EPA recently established Methods 325A and 325B as a screening-based compliance method to monitor fenceline benzene levels that may originate from fugitive and area sources within petroleum refineries (U.S. Code of Federal Regulations [CFR], title 40, sec. 63.658) (U.S. EPA 2015). These methods include use of passive tube samplers with Carbopack™ X or equivalent sorbents, which are deployed for 2-week sampling intervals to measure pollutants. While both canister and tube samplers are reusable and do not require a power source, the tube samplers are less expensive and more easily portable than standard 6-L canisters. Air samples collected in canisters may be analyzed for more than 60 VOC species in EPA Compendium Method TO-15, whereas Carbopack X passive tubes have been demonstrated to perform well for a subset of these species including benzene, toluene, ethylbenzene, and xylene isomers (BTEX), 1,3-butadiene, perchloroethylene, styrene, trichloroethylene, and carbon tetrachloride (U.S. EPA 1999a; 2015; McClenny et al. 2005).

EPA has conducted demonstration studies using a variation of Methods 325A/B at or near fenceline and farther removed sites relative to petroleum refineries and natural gas production well pads (Eisele et al. 2016; Mukerjee et al. 2016; Thoma et al. 2011). For refinery applications, elevated BTEX levels were encountered downwind of a refinery in Corpus Christi, TX (Thoma et al. 2011). Higher BTEX and styrene levels were found in the vicinity of a refinery in South Philadelphia, PA, versus more distant sites (Mukerjee et al. 2016). The pilot study reported here sought to establish the utility of Method 325 A/B in comparison with EPA Method TO-15 at refinery fenceline sites in Whiting, IN.

Methods

Sampling and laboratory analytical techniques for the Carbopack X passive tube samplers used in Whiting and the other refinery studies in South Philadelphia and Corpus Christi are presented in Thoma et al. (2016) and Oliver et al. (2017) and are similar to those referenced in Methods 325 A/B. Supelco FLM Carbopack X Deactivated Stainless Steel TD tubes (part 28686-U, Sigma-Aldrich Co. LLC, St. Louis, MO) were fitted with diffusive sampling caps for collection of VOCs in ambient air and deployed for 7-day sampling periods. A protective shelter hood housed each sampler, its duplicate, and any scheduled field blank or field control; shelters were positioned at a height of approximately 5 m above ground. Concentrations of VOCs were reported in parts per billion by volume (ppbv) for BTEX species, perchloroethylene, styrene, carbon tetrachloride, and 1,3-butadiene. Because carbon tetrachloride did not meet quality assurance (QA)/quality control (QC) criteria and 1,3-butadiene was always below detection limit (BDL), these two VOCs were not part of this statistical analysis for the samples. All statistical analyses were performed in SAS® Version 9.3 (SAS).

Canister sampling and analysis of VOCs were based on EPA Compendium Method TO-15 (U.S. EPA 1999a). Samples were collected in either 15-L or “12-L” (two 6-L canisters connected in parallel) Silonite passivated canisters attached to an Entech model CS 1200E passive canister sampler (Entech Instruments, Simi Valley, CA). The passive canister sampler restricted flow so that when the evacuated canister was opened it would fill with a linear flow over a 1-week period; flow rates were 1.3 mL/min for the 15-L canister and 1.0

mL/min for 12-L samples. Each canister sampler was deployed concurrently with the passive tube sampler.

Sampling occurred in eight consecutive 1-week periods beginning September 4, 2014, and ending on October 30, 2014. Figure 1 displays the four refinery fenceline locations in the city of Whiting, IN, in the Chicago Metropolitan Area on the shore of Lake Michigan. The air sampling sites were established by the refinery to assess VOC impacts in the Whiting community. Three of the study sites were situated on the western fenceline perimeter in a north to south direction; the fourth site was on the southeastern fenceline perimeter. Other industrial facilities, traffic, and other urban sources of VOCs also impacted the area. Further description of these refinery fenceline sites are provided elsewhere (http://raqis.radian.com/pls/raqis/bpw.whiting). The inset in Figure 1 shows the mean wind frequencies by direction and speed during the study from a local compliance site in neighboring Hammond, IN. For 1-week sampling times, meteorological conditions were typically very variable. For the study, the most frequent wind directions were from the south and west. The mean wind speed was 2.9 m/sec. Temperatures ranged from 2 to 31°C. The 25th percentile for temperature was 11ºC and the 75th percentile was 18ºC. The average and median temperatures were the same, 14°C.

Duplicate tube sampling was conducted for all sampling periods to evaluate precision. Duplicate canister samples were collected during seven of the eight sampling periods. Quality control tube samples consisting of field blanks and field spikes were also included in all sampling periods to allow evaluation of tube background contributions and recoveries of target compounds from the Carbopack X sorbent tubes. Field blanks consisted of tubes randomly selected by the field operator from the stock of tubes prepared for sample collection. Field spikes were diffusively loaded with nominal 2-ppbv concentrations at the laboratory by exposing tubes for 24 hr in a chamber maintained at a constant concentration of the target analytes. One field blank tube and one field spike tube were deployed at each of the four sites during two different sampling periods. The site having the field blank and field spike tubes rotated from sampling period to sampling period. Field blanks and field spikes were deployed capped in the shelters with the sampling tubes and were not exposed to ambient air.

Results

All field blanks were reported as BDL for each of the VOC species. The average percent recovery from the field spikes for 1,3-butadiene was 80%, suggesting a loss of the chemical; a similar result was obtained by Oliver et al. (2017). All other species had an average percent recovery near 100%. These results from the tube field blanks and spikes suggest that with the exception of 1,3-butadiene, field deployment, per se, did not affect concentration.

Table 1 reports the minimum, median, and maximum concentrations from Whiting fenceline tube and canister sampling and from tubes collected near the fenceline of the refinery in South Philadelphia detailed in Mukerjee et al. (2016). Thoma et al. (2011) also measured benzene at Corpus Christi refinery sites. The same tube method was used in South Philadelphia and Corpus Christi, though with 2-week sampling intervals and for a study length of approximately 1 year and 9 months in South Philadelphia and 1 year in Corpus Christi. Placing the results obtained here in context, it is noted that overall VOC concentrations were lower in Whiting than in South Philadelphia, with median benzene concentrations in Whiting being less than one-third of the median benzene concentrations measured in South Philadelphia. Similarly, median benzene concentrations in Whiting were less than half of median benzene concentrations (0.71 ppbv) measured at Corpus Christi. (Differences in sampling period, seasons, and length of studies preclude a definitive comparison between these three studies.) While the sampling strategies used in these studies are not directly comparable to those of EPA's New Source Performance Standards for refineries (U.S. EPA 2015), benzene levels reported here and in the other refinery studies were below action levels of 2.8 ppbv.

Table 1 also presents the median relative percent differences for VOCs from duplicate tube samples at Whiting, all of which were <7%. Analysis of duplicate canister samples also indicated good precision: the median relative percent difference was 3% for benzene and ranged from 1 to 10% for the other compounds (see Table 1). These results were well within the ±20% duplicate precision criterion specified in EPA Compendium Method TO-17 for sorbent tubes (U.S. EPA 1999b) and ±25% replicate precision in Method TO-15 for canisters (U.S. EPA 1999a), indicating good precision. Similar precision for the tubes was also estimated for benzene in Corpus Christi (Thoma et al. 2011). The precision value of 0% (styrene from tubes and canisters; perchloroethylene for canisters) was assigned (as opposed to calculated) because of the large number of duplicate sample pairs that were reported as BDL.

For tube sampling, styrene was BDL (DL = 0.02 ppbv) in 75% of the samples. Besides 1,3-butadiene, as noted earlier, no other species was BDL. For canister sampling, the BDL occurrences were ethylbenzene in one sample (DL = 0.125 ppbv); styrene in 74% of the samples (DL range of 0.025 to 0.125); and perchloroethylene 80% of the time (DL range of 0.025 to 0.125). These counts reflect all samples, including duplicates. For calculations reported here, a value of half the detection limit was used for the BDL sample.

Potential differences in concentration between the tubes and canisters were assessed with the Wilcoxon signed rank test, except for styrene and perchloroethylene. For these latter two species, the large number of BDL samples made use of either the Wilcoxon signed rank or the Fisher sign test problematic at best, so no formal test was done. For these VOCs, the conclusion is that they were not measurably different. Table 2 presents the results of this testing. Statistically significant concentration differences were found at least at the 10% level for benzene, toluene, ethylbenzene, and *m,p*-xylene. The tube samples were higher in concentration than the canisters. Note that while statistically significant differences were found, the magnitudes of the median concentration differences were <0.1 ppbv.

Figure 2 presents Whiting benzene concentrations from tubes and canisters by site. Potential differences in VOC concentration between sites were examined with the Kruskal–Wallis test. No statistically significant (10% level) differences were found among the Whiting sites for either the tubes or canisters; *p* values for tubes ranged from 0.11 to 0.79 and for canisters from 0.18 to 0.64. Since Kruskal–Wallis testing found no difference, pairwise comparisons between sites were not done.

Discussion and conclusion

Results of the collection and determination of selected VOCs in ambient air with Carbopack X diffusive tube samplers using a modified version of EPA Method 325 A/B were compared to results obtained for collocated canister samples collected and analyzed using EPA Method TO-15. This pilot study at refinery fenceline sites in Whiting, IN, showed that similar VOC concentrations were obtained with the two methods for samples collected over 1-week periods. While statistically significant differences were found between concentrations for tubes and canisters, the concentration differences were <0.1 ppbv. This is very good agreement, given the differences in sampling methodologies, laboratories, and chemical analysis methods for tubes and canisters.

Good precision estimates were obtained with duplicate sampling for tubes and canisters. This echoes precision estimates found in earlier studies using the same tube sampler in South Philadelphia and for benzene in Corpus Christi. The good precision of tube sample duplicates here and in the other refinery studies suggest that duplicate sampling can be reduced to a representative number of sites, such as at 1 in 10 sites, indicated in Method 325 A.

Median BTEX levels at Whiting refinery fenceline sites were less than those measured with the tubes near the refinery fenceline in South Philadelphia; median benzene levels at Whiting were also lower than refinery fenceline sites in Corpus Christi. However, sampling at Whiting was limited to 8 weeks in fall 2014, whereas sampling in South Philadelphia was over 1.5 years in duration in 2013–2015 and Corpus Christi was yearlong in 2008–2009. Nationwide data studies have shown that ambient BTEX concentrations tend to be higher in the wintertime (McCarthy et al. 2007). Thus, it is possible that the September to October sampling period may not have captured the peak season for the Whiting location. Seasonal influences not captured in Whiting, as well as monitoring in different years with varying refinery production levels, might explain the differences between studies. Again, differences between these three studies do not allow a definitive comparison.

Finally, Methods 325 A/B require that multiple sampling sites be established at a refinery to assess fugitive benzene impacts. Though limited in this case, no overall difference in VOC concentrations was observed between Whiting sites for tubes or canisters.

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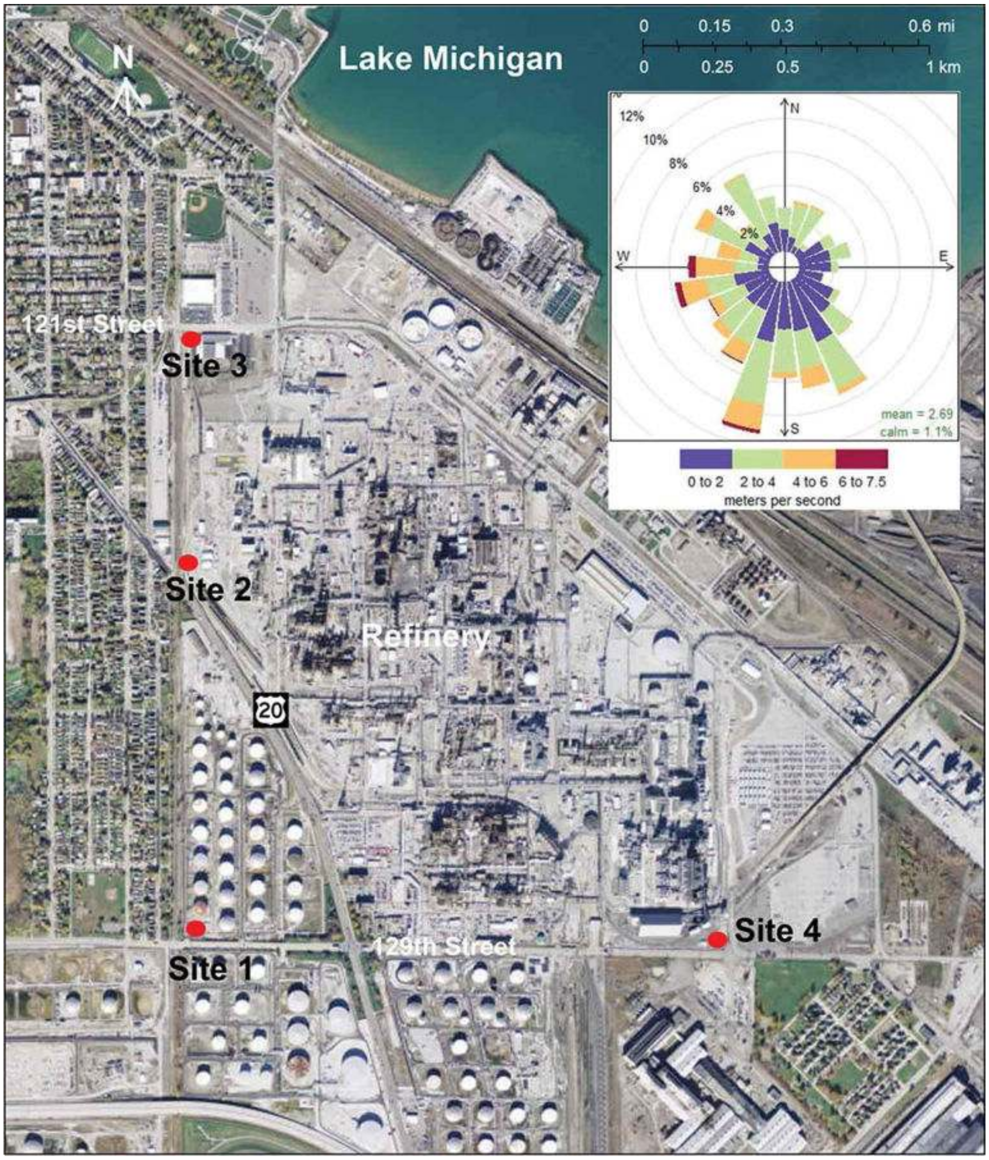

Figure 1.

Refinery fenceline monitoring sites in Whiting, IN. Inset shows mean frequencies of wind direction and speed at a compliance site in neighboring Hammond, IN, during the study. Frequencies in percent indicate direction from which the wind is blowing. Wind speed in m/sec.

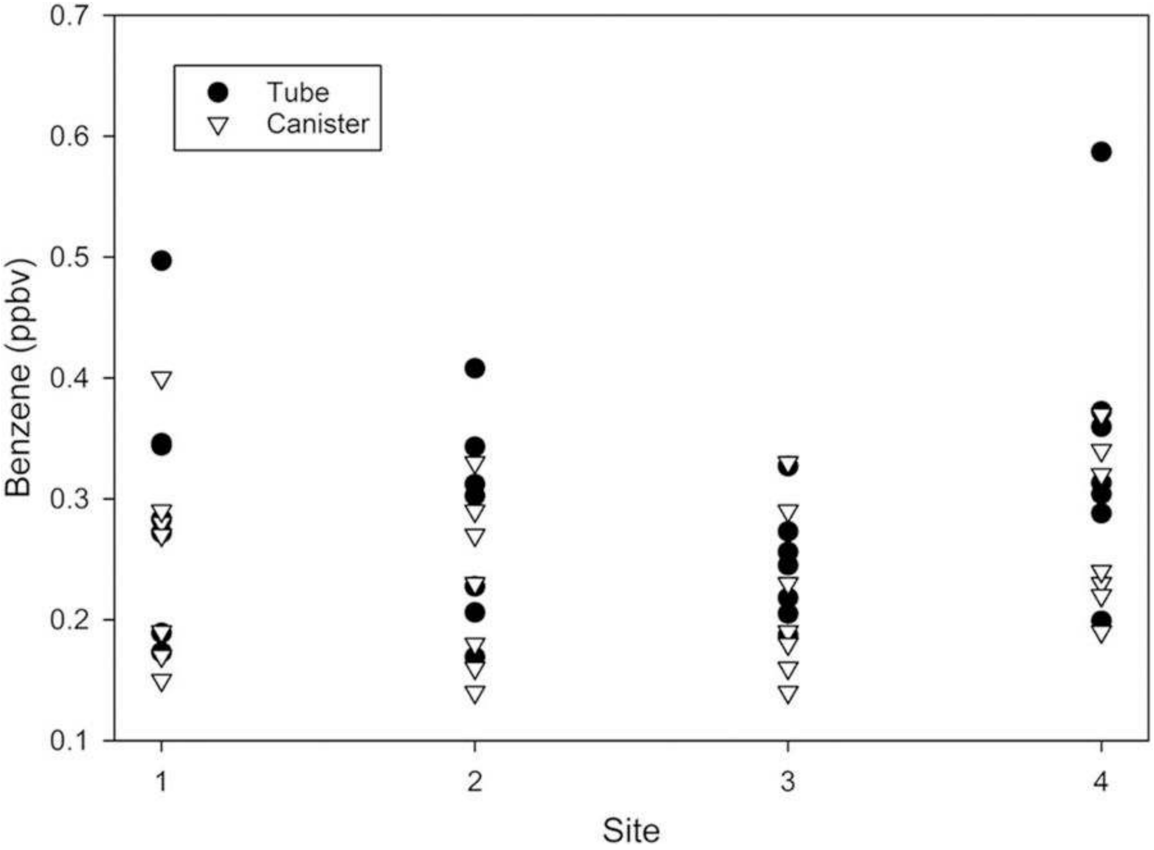

Figure 2.

Whiting benzene concentrations from tube and canister samples by site. Site numbers correspond to site number locations in Figure 1.

Table 1.

Median values of VOCs in ppbv and median relative percent differences for tubes and canisters from duplicate sampling for all Whiting fenceline sites and median concentrations of tube data from sites near the fenceline of a refinery in South Philadelphia.

VOC	Relative percent difference (canister, *n* = 7)	Relative percent difference (tube, *n* = 8)	Whiting (canister)	Whiting (tube)	South Philadelphia (tube)[a]
Benzene	3	5	0.24 (0.14, 0.40)[b]	0.28 (0.17, 0.59)	1.06 (0.19, 5.02)
Toluene	2	3	0.52 (0.26, 1.04)	0.60 (0.27,1.02)	1.05 (0.14, 4.61)
Ethylbenzene	2	6	0.07 (0.04, 0.20)	0.10 (0.03, 0.29)	0.15 (0.03, 1.06)
m,p-Xylene	1	7	0.24 (0.11, 0.61)	0.30 (0.08, 0.94)	0.60 (0.12, 4.76)
o-Xylene	10	6	0.09 (0.04, 0.22)	0.10 (0.03, 0.32)	0.20 (0.04, 1.64)
Perchloroethylene	0[c]	5	< 0.03 (< 0.02, 0.04)	0.02 (0.01, 0.04)	0.02 (0.01, 0.04)
Styrene	0[c]	0[c]	< 0.04 (< 0.02, 0.07)	0.01 (<0.02, 0.04)	0.01 (<0.01, 0.06)

Notes:

[a] From Mukerjee and others (2016); detection limits reported there.

[b] Minimum and maximum values in parentheses. All values except median relative percent differences rounded to two decimal places. See Figure 1 for Whiting site locations.

[c] Zero value assigned because of the large number of duplicate BDL sample pairs.

Table 2.

Concentration differences between tube and canister sampling at the Whiting fenceline sites.

Chemical	Sample size	p-value	Tube minus canister median difference (ppbv)
Benzene	28	0.0005[a]	0.06
Toluene	28	0.0656[c]	0.10
Ethylbenzene	28	0.0656[c]	0.01
m,p-Xylene	28	0.0286[b]	0.06
o-Xylene	28	0.1323	0.02
Perchloroethylene	28	NT[d]	NT[d]
Styrene	28	NT[d]	NT[d]

Notes:

[a] Statistically significant at the 1% level.

[b] Statistically significant at the 5% level.

[c] Statistically significant at the 10% level.

[d] Though no formal test (NT) was done, no significant difference between tubes and canisters is concluded for either perchloroethylene or styrene because of the large number of BDLs.