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Original Article

Spatial analysis of volatile organic compounds using passive samplers in the Rubbertown industrial area of Louisville, Kentucky, USA

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ABSTRACT

Select volatile organic compounds (VOCs) were measured in the vicinity of chemical facilities and other operations in the Rubbertown industrial area of Louisville, Kentucky (USA) using modified EPA Methods 325A/B passive sampler tubes. Two-week, time-integrated passive samplers were deployed at ten sites which were aggregated into three site groups of varying distances from the Rubbertown area facilities. In comparison to canister data from 2001 to 2005, two of the sites suggested generally lower current VOC levels. Good precision was obtained from the duplicate tubes (≤12%) for benzene, toluene, ethylbenzene, and xylene isomers (BTEX), styrene, 1,3-butadiene, perchloroethylene, and other trace VOCs. BTEX, styrene, and 1,3-butadiene concentrations were statistically significantly higher at two site groups near Rubbertown sources than the site group farther away. As found in a similar study in South Philadelphia, BTEX concentrations were also lower for sites farther from a source, though the decline was less pronounced on a percentage basis in Rubbertown. These results suggest that EPA Methods 325A/B can be useful to assess VOC gradients for emissions from chemical facilities besides fenceline benzene levels from refineries.

1. Introduction

Volatile organic compounds (VOCs) are air pollutants known to be emitted from petroleum-related sources such as transportation, petrochemical facilities, solvent use and other anthropogenic sources. VOCs such as benzene and 1,3-butadiene are known or suspected carcinogens (National Cancer Institute, 2018).

In the United States, VOC concentrations in ambient air are typically measured with canister-based sampling using U.S. Environmental Protection Agency (EPA) Method TO-15 (EPA, 1999a). EPA has also established diffusive sorbent sampling and analysis Method 325A and 325B (325A/B) for monitoring ambient benzene at refinery fenceline locations. Method 325A/B uses passive tube samplers packed with Carbopack™ X or equivalent sorbents that are exposed for 2-week sampling intervals (U.S. Code of Federal Regulations (CFR), Title 40, Section 63.658) (EPA, 2015). Method 325A/B has potential application to measurement of other VOCs at sites other than refineries. A subset of these other VOCs includes benzene, toluene, ethylbenzene, and xylene isomers (BTEX), 1,3-butadiene, perchloroethylene, styrene, trichloroethylene, and carbon tetrachloride (Mukerjee et al., 2016; Oliver et al., 2017). In addition to EPA Methods 325A/B, the Carbopack™ X passive tube samplers have been used in personal exposure and spatial modeling studies to support air quality and health studies (Mukerjee et al., 2009a; Shin et al., 2015; Smith et al., 2011).

EPA has conducted studies using a variation of Methods 325A/B at or near fenceline and farther removed sites relative to oil and gas refineries and well pads (Thoma et al., 2011, 2016; Eisele et al., 2015; Mukerjee et al., 2016, 2018). At a refinery in Corpus Christi, Texas, elevated BTEX levels were measured downwind from the source (Thoma et al., 2011). Higher BTEX and styrene levels were found in the vicinity of a refinery in South Philadelphia, Pennsylvania, versus more distant sites (Mukerjee et al., 2016). At smaller spatial scales, no overall difference was found for VOCs at fenceline sites at a refinery in Whiting, Indiana (Mukerjee et al., 2018).

EPA and the City of Louisville Metro Air Pollution Control District (LMAPCD) conducted a project in an industrial area of Louisville, Kentucky, known as “Rubbertown” to evaluate emerging measurement approaches for select hazardous air pollutants and VOCs (Thoma et al.,

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2019). The Rubbertown area contains a variety of industrial sources. The passive sampler portion of the study deployed EPA Method 325B Carbopack™ X sorbent tubes at sites near and away from Rubbertown facilities to investigate the utility of this method over a broader spatial area with multiple sources. This paper details the VOCs collected in the Rubbertown study in terms of spatial gradients and how near versus distant gradients from the chemical facilities compare with spatial findings from the similarly-designed South Philadelphia study. Further information on these sampling methods along with the use of near-real time VOC and meteorological data to further assess the impact of Rubbertown industrial sources are described in Thoma et al. (2019).

2. Methods

2.1. Ambient air sampling

Passive sampling was performed for 26 consecutive two-week periods beginning September 12, 2017 and ending on September 12, 2018. (Method 325 stipulates a normal sampling period of two weeks (EPA, 2015); this sampling duration has been successfully evaluated and applied in other EPA studies at oil and gas facilities (Thoma et al., 2011; Eisele et al., 2015; Mukerjee et al., 2016).) The Rubbertown study area in Louisville was located generally east of the Ohio River and west of Interstate Highway 264; two school monitoring locations were east of Highway 264. Rubbertown is home to several chemical manufacturing plants, petroleum and chemical storage facilities, a municipal waste water treatment facility, and other industrial and commercial operations. As encountered in urban locations, the study area is also impacted by traffic and other VOC sources. Fig. 1 displays ten sites in the Rubbertown area where passive samplers were deployed. More extensive details on site selection are provided in Thoma et al. (2019). Based on the spatial distribution of sites in the Rubbertown area, three groups of sites were formed. Sites 1 to 3 (shown as circles) were designated as the “North” group since they were situated on the northern end of the Rubbertown area. Sites 5, 7, 8, and 10 (shown as squares) were designated as the “South” group. North and South site groups were relatively close to Rubbertown industrial facilities. Site 9 was upwind of the various Rubbertown industrial plants and Sites 4 and 6 were at schools > 1 km from any plant location; these three sites composed the “Away” group and are shown as triangles. An eleventh site is not shown since it was established near the end of the project and sampled only from June 19, 2018, until September 12, 2018 (i.e., six, two-week periods).

The Carbopack™ X passive sampling and laboratory analysis techniques used in Rubbertown are detailed elsewhere (Oliver et al., 2017; Thoma et al., 2019) and are similar to EPA Methods 325A/B. In brief, Supelco FLM Carbopack™ X Deactivated Stainless Steel thermal desorption tubes (Sigma-Aldrich Co. LLC, St. Louis, MO, USA) were fitted with diffusive sampling caps; ambient VOCs were collected for two-week sampling periods. Polyvinyl chloride shelter hoods housed each sampler and any duplicate, scheduled field blank or field control; sampling heights were approximately 1.5–4 m above ground. Field evaluations have found these samplers to be in good agreement with compliance-based canister and automated gas chromatograph methods for BTEX and other VOCs (Mukerjee et al., 2009b, 2018; Smith et al., 2011). Analysis of samples was performed at EPA using thermal desorption/GC time-of-flight (TOF) mass spectrometry (Markes International Inc., Gold River, CA, USA). Additional information on passive

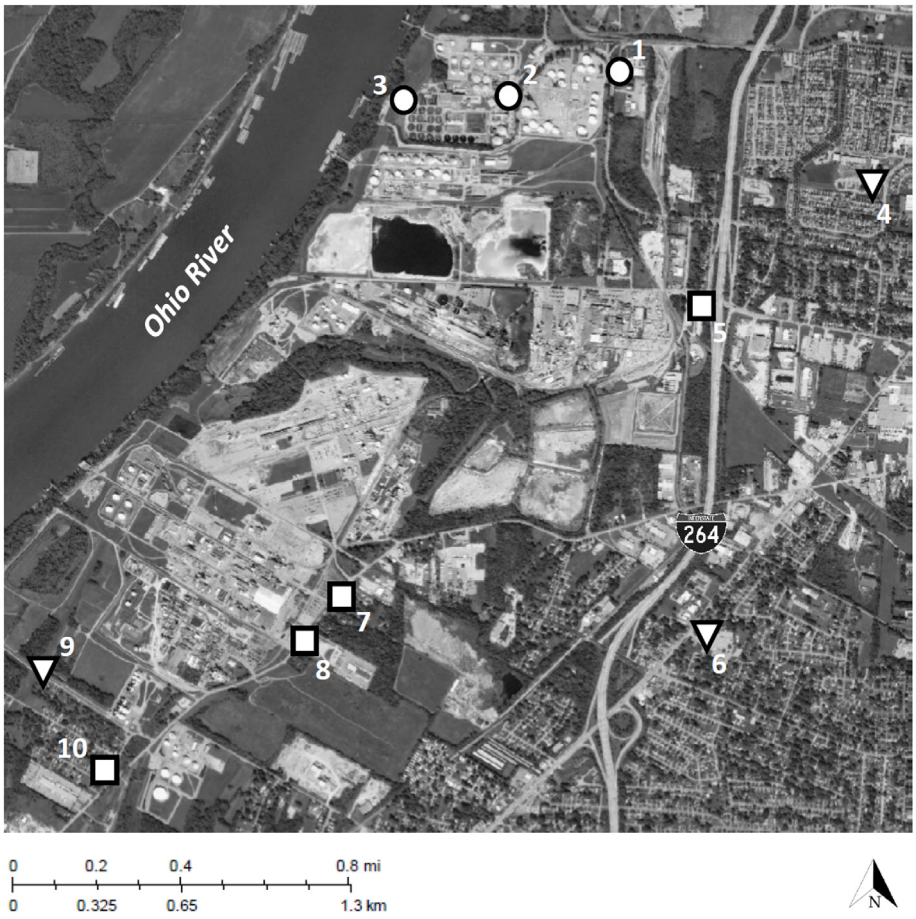

Fig. 1. Monitoring sites [a] in Rubbertown study area in west-southwest section of Louisville, Kentucky. [a] Circles are “North” sites near Rubbertown facilities. Squares are “South” sites near Rubbertown facilities. Triangles are “Away” sites.

Table 1
VOC passive sampler results for all Rubbertown sites and for each group. Median values of VOCs in ppbv for all sites and each group[a], median method detection limit (MDL, in ppbv), median percent coefficient of variation (CV) of duplicates for all sites, and average percent recovery.

VOC	MDL	CV (%)	Average Recovery (%)	All sites n: (214, 265)[b]	North n: (63, 78)	South n: (88, 104)	Near[c] n: (151, 182)	Away (Far) n: (58, 77)
Benzene	0.01	3	99	0.22 (0.09, 0.49)	0.26 (0.17, 0.49)	0.21 (0.12, 0.41)	0.23 (0.12, 0.49)	0.19 (0.09, 0.48)
Toluene	< 0.01	3	81	0.70 (0.01, 2.72)	0.87 (0.33, 1.95)	1.03 (0.01, 2.72)	0.93 (0.01, 2.72)	0.48 (0.07, 1.61)
Ethylbenzene	< 0.01	4	99	0.06 (0.01, 0.27)	0.09 (0.04, 0.17)	0.06 (0.02, 0.27)	0.07 (0.02, 0.27)	0.05 (0.01, 0.17)
m,p-Xylene	0.01	4	95	0.20 (0.03, 0.89)	0.28 (0.11, 0.59)	0.20 (0.08, 0.89)	0.23 (0.08, 0.89)	0.14 (0.03, 0.60)
Styrene	< 0.01	12	100	0.02 (< 0.01, 0.12)	0.01 (< 0.01, 0.07)	0.03 (< 0.01, 0.12)	0.02 (< 0.01, 0.12)	0.01 (< 0.01, 0.04)
o-Xylene	< 0.01	4	99	0.08 (0.01, 0.33)	0.11 (0.04, 0.22)	0.08 (0.03, 0.33)	0.09 (0.03, 0.33)	0.06 (0.01, 0.23)
Perchloroethylene	< 0.01	2	102	0.02 (0.01, 0.16)	0.01 (0.01, 0.03)	0.02 (0.01, 0.16)	0.02 (0.01, 0.16)	0.02 (0.01, 0.15)
1,3-Butadiene	< 0.01	9	95	0.10 (< 0.01, 1.40)	0.09 (< 0.01, 1.18)	0.16 (< 0.01, 1.40)	0.13 (< 0.01, 1.40)	0.05 (< 0.01, 0.47)
Freon 11	< 0.01	3	104	0.20 (< 0.01, 0.36)	0.21 (< 0.01, 0.33)	0.20 (0.01, 0.35)	0.21 (< 0.01, 0.35)	0.21 (< 0.01, 0.36)
Freon 12	0.01	2	105	0.18 (0.02, 0.50)	0.18 (0.02, 0.47)	0.19 (0.02, 0.50)	0.19 (0.02, 0.50)	0.18 (0.02, 0.49)
Freon 113	< 0.01	3	106	0.07 (< .01, .10)	0.07 (< 0.01, 0.10)	0.07 (0.03, 0.10)	0.07 (< 0.01, 0.10)	0.07 (0.05, 0.10)[d]
1,1-Dichloroethene	< 0.01	0[e]	99	< 0.01 (< 0.01, 0.01)	< 0.01 (< 0.01, 0.01)	< 0.01 (< 0.01, 0.01)	< 0.01 (< 0.01, 0.01)	< 0.01 (< 0.01, 0.01)

[a] Medians calculated over all sites for study or over all sites in each group.
[b] Sample sizes varied among chemicals; range of sample sizes, n, given in parentheses. Minimum and maximum values in parentheses. All values except CVs rounded to two decimal places. See Fig. 1 for site and group locations.
[c] Near combines North and South site groups.
[d] Reported for completeness; data capture was < 75%.
[e] 1,1 dichloroethene was frequently below the detection limit, leading to a median CV of 0.

sampler performance for compounds such as 1,3-butadiene along with an overview of comparison measurements made in this study can be found in Thoma et al. (2019).

Quality control tube samples consisting of lab spikes, field spikes, and calibration standards were used to allow evaluation of recoveries of target compounds from the Carbopack™ X sorbent tubes. Lab spikes were prepared at the same time as field spikes and refrigerated in the laboratory until analysis. Average recoveries from these check samples were calculated. Field spikes and calibration samples were diffusively loaded with nominal 2 parts per billion by volume (ppbv) concentrations at the laboratory by exposing tubes for 24 h in a chamber maintained at a constant concentration of the target analytes. Field blanks and field spikes were deployed capped in the shelters with the sampling tubes and were not exposed to ambient air. For all sampling periods, field blanks were deployed at Site 1 and field spikes at Site 8. Duplicate sampling was conducted at all sites to evaluate precision. At most sites, three of the 26 two-week periods had two samples collected. Duplicate tube sampling was conducted for 25 sampling periods at Site 8, two periods at Sites 9 and 10, and all six periods at Site 11. Corrections for temperature, pressure and humidity impacts on uptake rates were not performed for the passive samplers since the results are being investigated to assess local trends and those impacts are expected to be minimal.

2.2. Statistical analysis

Concentrations of VOCs are given in ppbv per day for the BTEX species, styrene, perchloroethylene (also known as tetrachloroethene), 1,3-butadiene, Freon 11, Freon 12, Freon 113, and 1,1-dichloroethene. These 12 VOCs had ≥75% data completeness. Thirteen other VOCs were monitored but had poor data capture.

Examination of the data by site revealed some outlying observations and a general tendency of skewness toward lower values. Therefore, nonparametric testing was used for the group comparisons and Spearman correlation coefficients were calculated for each pair of chemicals; Thoma et al. (2019) also noted outlying values for 1,3-butadiene in Rubbertown that may be associated with specific emission events. All statistical analyses were performed in SAS® Version 9.4 (SAS, 2013). Prior to statistical summarization or testing, any concentrations reported as below the method detection limit (MDL) were set to half the detection limit.

Precision from duplicate sampling was calculated for each VOC as the percentage coefficient of variation (CV). Overall recovery was calculated as the average of the lab spike, field spike, and calibration standard mean recoveries.

The comparison of the North, South, and Away groups in Rubbertown was conducted as follows. For each sampling period, the duplicate sample concentrations were averaged. Within each sampling period, concentrations were averaged over the sites within each group. Pairwise group differences were then calculated. The hypotheses that concentrations differed between the groups were examined via two-sided Wilcoxon signed rank tests applied to the pairwise differences across the sampling periods. Overall group differences were estimated with the associated Hodges-Lehmann estimator (Hollander et al., 2013).

The Rubbertown study and an earlier South Philadelphia study (2013–2015) were similar since both used EPA Method 325A/B methodology and had passive samplers near and farther away from industrial VOC sources. To explore whether similar patterns were seen in both cities as distance from sources increased, the sites in each project were divided into two groups: “Near” and “Far.” From Rubbertown, the North and South groups were combined to form the “Near” category and the Away group was re-labelled “Far” for these comparisons. From South Philadelphia, sites originally designated in Mukerjee et al. (2016) as “Near Fenceline,” “North Edge,” and “South Edge” were classified as “Near” and sites called “Removed” were re-labelled “Far” for this paper. The Near versus Far comparisons for Rubbertown and South Philadelphia were conducted in the same way as the North, South, and Away comparisons in Rubbertown. Based on the outcomes in the set of North/South/Away comparisons in Rubbertown and the earlier results reported for South Philadelphia, two-sided tests were employed for each VOC. Again, Hodges–Lehmann estimators indicated the magnitude of the differences. For both Rubbertown and South Philadelphia, the ratio of the Hodges-Lehmann estimators to the median concentrations of the Near group were formed as a percentage to give a relative measure of the change.

3. Results

3.1. Overall findings

For the VOCs statistically analyzed for this paper, Table 1 reports the median MDLs, CVs, average percent recoveries, and minimum, median, and maximum concentrations by site group and overall. Only

Table 2
Median values of 2001–2005 WLATS canister and current passive sites[a] along with site comparisons[b], all in ppbv.

VOC	Canister		Passive		Site A minus Site F[c]	Site A minus Site 1[c]	Site F minus Site 6[c]
	Site A	Site F	Site 1	Site 6			
Benzene	0.40	0.27	0.24	0.19	0.135[d]	0.17[d]	0.079[d]
Toluene	2.32	1.00	0.79	0.55	1.28[d]	1.516[d]	0.39[d]
Ethylbenzene	0.15	0	0.08	0.06	0.12[d]	0.067[d]	−0.037[d]
m,p-Xylene	0.54	0.22	0.28	0.18	0.29[d]	0.266[d]	nsd[f]
Styrene	0	0	0.01	0.01	nsd[f]	−0.013[d]	−0.011[d]
o-Xylene	0.17	0	0.11	0.07	0.12[d]	0.061[d]	−0.05[e]
1,3-Butadiene	0.68	0.32	0.10	0.05	0.18[e]	0.564[d]	0.258[d]

[a] Sites A and F from 2001 to 2005 study correspond to current, respective Sites 1 and Site 6.
[b] Wilcoxon rank sum test applied. Hodges–Lehmann estimators indicate magnitude of the differences.
[c] Estimates of the difference indicated in the column header in ppbv rounded to appropriate decimal places; negative signs indicate that the subtracted value was larger than the other one.
[d] Significant at 1% level for two-sided test.
[e] Significant at 5% level for two-sided test.
[f] nsd: no significant difference at the 10% level.

1,1-dichloroethene had a large number of measurements below the MDL (35 of 86 samples). Styrene and 1,3-butadiene each had five samples less than the MDL. None of the other nine chemicals had any sample below the MDL.

As a comparison, data from the West Louisville Air Toxics Study (WLATS) are presented. WLATS is a historical project in the area with an extensive database of air toxics (Sciences International, 2006). During WLATS, 24-h canisters were collected every twelve days from 2001 to 2005 at locations corresponding to Sites 1 and 6 in this study. Table 2 shows data from select VOCs from WLATS compared to the passive sampler data collected in this study. The median values from the two studies suggested generally lower current VOC levels.

Although not shown, the correlation structure over all sites revealed some moderate and strong relationships. Benzene, ethylbenzene, and xylene species were moderately-to-strongly correlated (Spearman correlation coefficients between 0.6 and > 0.9) with each other; toluene was moderately correlated with ethylbenzene, xylene species, and styrene. Strong correlations > 0.9 were found between Freon 11 and Freon 113; moderate correlations were observed for Freon 113 and 1,1-dichloroethene. Overall correlations of benzene with toluene and 1,3-butadiene with other VOCs were low (Spearman correlation coefficients < 0.6).

A similar correlation structure was observed for the North, South, and Away groups. However, moderate correlations were also found in the North set for the following: benzene and toluene; styrene with the three freons; Freon 12 with Freon 11, ethylbenzene, and the xylenes.

Table 1 also presents precision estimates as the median of the percent CV over all site-sampling period combinations. The precision of duplicate samples was < 10%, with the exception of styrene (12%) which had low concentrations. This was comparable to similar precision estimates found in South Philadelphia (Mukerjee et al., 2016) and at oil and gas well pads in Texas and Colorado (Eisele et al., 2015); similar precision was estimated for benzene in Corpus Christi (Thoma et al., 2011). This provided confidence that differences in VOC levels were more likely due to ambient rather than sampling method influences.

Almost all the average percentage recovery rates were near 100% (Table 1). The one exception was toluene with a recovery rate of only 81%.

Table 3
Rubbertown site group VOC comparisons.[a]

VOC	North minus Away	South minus Away	North minus South
Benzene	0.07[b]	0.62[b]	0.05[b]
Toluene	0.36[b]	0.47[b,all]	−0.14[d]
Ethylbenzene	0.03[b]	0.02[b,all]	0.01[b]
m,p-Xylene	0.11[b]	0.07[b,all]	0.05[b]
Styrene	< 0.01[b]	0.02[b,all]	−0.02[b,all]
o-Xylene	0.04[b]	0.02[b,all]	0.02[b]
Perchloroethylene	- < 0.01[b,all]	< 0.01[b,all]	−0.01[b,all]
1,3-Butadiene	0.05[b]	0.12[b,all]	−0.08[b]
Freon 11	- < 0.01[c]	< 0.01	−0.01[b]
Freon 12	−0.01[b]	- < 0.01	- < 0.01[b]
Freon 113	No test[e]	No test[e]	- < 0.01
1,1-Dichloroethene	< 0.01[c]	< 0.01[d]	- < 0.01

[all] All 26 periods were found to be greater or less, as indicated by the + or – sign.
[a] See methods section regarding how pairwise tests were conducted. Numeric entries are estimates of the difference indicated in the column header in ppbv rounded to two decimal places; negative signs indicate that the subtracted value was larger than the other one.
[b] Significant at 1% level for two-sided test.
[c] Significant at 5% level for two-sided test.
[d] Significant at 10% level for two-sided test.
[e] No test was performed as the data capture for Freon 113 in the Away group was < 75%.

3.2. Site group comparisons

Table 3 reports the outcome of pairwise tests and Hodges-Lehmann estimates of the differences between North, South, and Away site group comparisons. Statistical significance was declared at 1%, 5%, and 10% levels. Note that when compared to the Away group, higher concentrations were almost always associated with the North and South groups which were closer to Rubbertown sources, and the 1% significance level was by far the most common one in the table. Perchloroethylene, Freon 11, and Freon 12 were significantly lower for North versus Away comparisons. The only non-significant results were for Freon 11 and Freon 12 for South versus Away comparisons. Because the Away group did not meet the 75% data capture criterion, no tests were performed to compare Freon 113 levels for that group to the North or South group.

Table 3 also indicates that the North group had higher benzene, ethylbenzene, and xylene levels than the South group. On the other hand, the South group exceeded the North group levels for toluene, styrene, perchloroethylene, 1,3-butadiene, Freon 11, and Freon 12. No significant difference was found between North and South groups for either Freon 113 or 1,1-dichloroethene.

3.3. Near versus far comparisons

The Near versus Far site group comparisons for Rubbertown and South Philadelphia are given in Tables 4 and 5, respectively. Note in Table 5 that fewer VOCs were monitored in South Philadelphia. Though 1,3-butadiene was monitored in South Philadelphia, it was almost always below the MDL (Mukerjee et al., 2016). Near and Far groups for Rubbertown are summarized in Table 1.

Table 4 indicates that in the Rubbertown section of Louisville all the chemicals exhibited higher concentrations for the Near group, except for Freon 11 (with no significant difference found) and Freon 12 (for which the Far group was higher). The percentage differences relative to the Near group medians ranged from just over 70% for styrene and 1,3-butadiene (but note the low median for styrene) to almost 50% for toluene to between 35% and 40% for the xylenes and ethylbenzene to just under 20% for benzene to below 10% for the other chemicals.

For the VOCs in common, Table 5 tells a similar story from the

Table 4
Rubbertown Near versus Far site group VOC comparisons.[a]

VOC	Near minus Far difference	Near median	Difference/median (%)
Benzene	0.04[b]	0.23	18
Toluene	0.44[b,all]	0.93	48
Ethylbenzene	0.03[b,all]	0.07	38
m,p-Xylene	0.09[b,all]	0.23	38
Styrene	0.01[b]	0.02	72
o-Xylene	0.03[b,all]	0.09	36
Perchloroethylene	< 0.01[b]	0.02	8
1,3-Butadiene	0.09[b,all]	0.13	73
Freon11	- < 0.01	0.21	−0
Freon12	- < 0.01[b]	0.19	−3
Freon113	No test[e]	No test[e]	No test[e]
1,1-Dichloroethene	< 0.01[d]	< 0.01	No estimate[f]

[c] Significant at 5% level for two-sided test.
[all] All 26 periods were found to be greater.
[a] See methods section regarding how pairwise tests were conducted. Numeric entries are estimates of the difference indicated in the column header in ppbv rounded to two decimal places; negative signs indicate that the subtracted value was larger than the other one.
[b] Significant at 1% level for two-sided test.
[d] Significant at 10% level for two-sided test.
[e] No test was performed as the data capture for Freon 113 in the Away group was < 75%.
[f] An estimate would be unreliable.

Table 5
South Philadelphia Near versus Far site group VOC comparisons.[a]

VOC	Near minus Far difference	Near median	Difference/median (%)
Benzene	0.67[b,all]	0.86	78
Toluene	0.63[b,all]	0.94	68
Ethylbenzene	0.08[b,all]	0.15	58
m,p-Xylene	0.36[b,all]	0.54	66
Styrene	< 0.01[b]	0.02	30
o-Xylene	0.12[b,all]	0.20	63
Perchloroethylene	−0.02[b,all]	0.02	−94

[all] All 26 periods were found to be greater or less, as indicated by the + or – sign.
[a] See methods section regarding how pairwise tests were conducted. Numeric entries are estimates of the difference indicated in the column header in ppbv rounded to two decimal places.
[b] Significant at 1% level for two-sided test.

South Philadelphia study. Levels were higher for the sites near a source. However, it is interesting that almost all the percentage differences were notably higher in South Philadelphia. The one exception is styrene, even though the Near median is the same as Rubbertown (Tables 4 and 5).

4. Discussion and conclusion

The same passive tube sampling method used in Rubbertown was used in the refinery studies in South Philadelphia (Mukerjee et al., 2016) and Corpus Christi (Thoma et al., 2011), though study lengths were approximately a year and nine months in South Philadelphia as compared to a year in Rubbertown and Corpus Christi. During the Corpus Christi study, most monitors were placed in accordance with EPA Method 325A at fenceline locations relative to the refinery, whereas in Rubbertown and South Philadelphia the monitors were near or farther removed from sources. Placing the results obtained for Rubbertown in context, it is noted in Table 1 that overall benzene, ethylbenzene, and xylene species concentrations were lower in Rubbertown than in South Philadelphia (Mukerjee et al., 2016) with median benzene concentrations in Rubbertown being less than half of the median benzene concentrations measured in South Philadelphia. Similarly, median benzene concentrations in Rubbertown were less than one-third of median benzene concentrations (0.71 ppbv) measured at Corpus Christi. Median toluene concentrations in Rubbertown were higher than in South Philadelphia (0.70 ppbv versus 0.64 ppbv, respectively); perchloroethylene concentrations were similar between the two studies.

Differences such as seasons, length of studies, and number of different sources do not permit a definitive comparison between these three studies. While not directly comparable to EPA's New Source Performance Standards for refineries (EPA, 2015), benzene levels reported here and in the other refinery studies were below the action level of 2.8 ppbv.

Using EPA Method 325A/B methodology, passive sampling for select VOCs in Rubbertown revealed spatial differences of potential emissions from chemical operations in an urban area with other VOC sources. BTEX, styrene, 1,3-butadiene, and 1,1-dichloroethene concentrations at the groups closest to Rubbertown industrial operations were significantly higher than in the Away group which was considered to be less impacted by Rubbertown sources. For North and South group comparisons, benzene, ethylbenzene, and xylene concentrations were higher in the North than the South area, while the roles were reversed for toluene, styrene, perchloroethylene, 1,3-butadiene, Freon 11, and Freon 12. This may be indicative of different emissions due to the varying facility-specific operations at Rubbertown industrial sources.

Near versus Far comparisons in Rubbertown and the similarly-designed South Philadelphia refinery study indicate VOC concentrations closer to industrial sources were significantly higher than at site groups farther away. In fact, as shown in Table 4, the BTEX species (except benzene) and 1,3-butadiene were higher for Near versus Far sites in Rubbertown for each period. Similarly, from Table 5, BTEX were higher for each period; however, perchloroethylene was always lower in South Philadelphia. This suggests that EPA Method 325A/B can elucidate changing concentrations with distance from refinery and other industrial sources.

In comparison to WLATS canister data, it appears that VOC levels have generally decreased between the 2001–2005 timeframe and the present. WLATS was an important project that contributed to the implementation of the Strategic Toxic Air Reduction Program (STAR), aimed at reducing toxic emissions in the Louisville/Jefferson County area. The differences observed between WLATS and this study may be the result of multiple factors such as pollution control efforts, changes in facilities operations, changes in overall urban conditions, or sampling method differences. Similarly, to the current Near vs. Far comparisons, Site A was located near an emission source and Site F was further removed from emission sources. In Table 2, Site A exhibited higher levels for BTEX and 1,3-butadiene.

Limitations on these results include lack of actual source samples at Rubbertown industries and other sources to help differentiate source impacts. Also, the limited number of Rubbertown sites may have lessened the spatial representativeness of groups. Finally, passive samplers are time-integrated measurements and do not provide real-time data that may detect episodic releases.

The good precision of sample duplicates suggests that differences in VOC levels were more likely due to source impact rather than sampling method influences. As in South Philadelphia, the Rubbertown study revealed gradients of concentrations resulting from potential chemical industry emissions for BTEX, styrene, 1,3-butadiene, and 1,1-dichloroethene, notwithstanding the presence of other VOC sources. This suggests that EPA Methods 325A/B could be applicable for other chemical operations and VOCs besides refinery fenceline impacts for benzene.

Author contributions

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Writing – Review & Editing, Project administration, Funding acquisition. **Luther Smith:** Conceptualization, Formal Analysis, Writing – Original Draft, Writing – Review & Editing. **Eben Thoma:** Conceptualization, Resources, Investigation, Writing – Review & Editing, Project administration, Funding acquisition. **Donald Whitaker:** Investigation, Data Curation, Methodology. **Karen Oliver:** Conceptualization, Investigation, Methodology, Writing – Review & Editing. **Rachelle Duvall:** Conceptualization, Writing – Review & Editing. **Tamira Cousett:** Validation, Investigation.

Declaration of competing interest

The authors declare no conflict of interest.

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