Near-Road Multi-Pollutant Profiles: Associations between Volatile Organic Compounds and a Tracer Gas Surrogate Near a Busy Highway

Timothy M. Barzyk<sup>a</sup>, Anna Ciesielski<sup>b</sup>, Richard C. Shores<sup>c</sup>, Eben D. Thoma<sup>c</sup>, Robert L. Seila<sup>a</sup>, Vlad Isakov<sup>a</sup>, Richard W. Baldauf<sup>e,d</sup>

<sup>a</sup> U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Research Triangle Park, NC, U.S.
<sup>b</sup> U.S. Environmental Protection Agency Contractor, National Exposure Research Laboratory, Research Triangle Park, NC, U.S.
<sup>c</sup> U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC, U.S.
<sup>d</sup> U.S. Environmental Protection Agency, Office of Air and Radiation, Office of Transportation and Air Quality, Ann Arbor, MI, U.S.

# **INTRODUCTION**

Volatile organic compounds (VOCs) are a primary chemical subset in motor fuels and motor vehicle exhaust. They represent a varied range of compounds associated with human health effects that include asthma, respiratory symptoms, birth and developmental effects, premature mortality, cardiovascular effects and cancer.<sup>1-4</sup>

One of the most common groups of VOCs associated with vehicle emissions is comprised of benzene, toluene, ethylbenzene and m,p- and o-xylene, commonly known as *BTEX*. BTEX component concentrations are strongly correlated to each other in the near-road environment due to their common source.<sup>5</sup> Lane reductions have been shown to increase BTEX concentrations due to the increased traffic congestion.<sup>6</sup> Pankow et al. (2003) examined correlations between 88 VOCs in 13 locations and found significant associations between BTEX components; their research represented area-wide, not near-road, ambient air conditions of various locations ranging categorized as having "Low", "Moderate", or "High" degrees of urbanization.<sup>7</sup> BTEX represents only the small fraction of compounds emitted by motor vehicles.<sup>8</sup>

In America, 35 to 45 million people live within 100 m of a highway or major road, with 90 to 135 million within the near-road "exposure zone" of 300 to 500 m.<sup>4,9,10</sup> Low-income and minority populations are particularly vulnerable because large sections of low-rent or low-property-value residential structures are located near these types of roadways.<sup>11,12</sup>

Environmental Justice (EJ) advocates have called for the use of scientific methods that are transferable and informative to characterize local hazards in order to decrease the risk of exposure and health effects.<sup>13</sup> Near-roadway exposure-reduction methods have been emplaced with reasonable predictions of success, such as with residential filtration measures in a subsidized housing complex near Boston, Massachusetts.<sup>14</sup>

Characterizing near-roadway exposures and health effects has typically involved methods such as proximity, land use regression, or surrogate measurements (e.g. of ultrafine particles or NO<sub>2</sub>) to estimate the magnitude of exposure.<sup>15-20</sup> While these methods have demonstrated the impacts of near-roadway exposures and highlight the importance of examining mobile-source pollutants, they are often site-specific and difficult to apply or transfer to other locations without significant technical resources. They also tend to focus on a few compounds instead of the broader mobile source mixture, and correlation of these surrogates with actual pollutant levels is not well understood.

This research quantifies associations between various individual VOCs, and between them and a tracer gas. Results include the ratios and probabilities in which these pollutants co-occur, thus reducing uncertainty in the type of mixture produced within this particular near-road environment. Near-road health effect studies often focus on geographic indicators, such as proximity to roadway or lengths of roadways within a given buffer, or on specific pollutants, such as particulate matter or black carbon. This research attempts to broaden the suite of near-road pollutants to which people are exposed, in order to help reduce uncertainty about etiological agents of human health effects.

#### METHODS

This section describes the site, tracer release, measurement methods for the VOCs and  $SF_6$ , wind conditions for the sampling periods and procedures for statistical analysis. Baldauf et al. (2008) provides a more comprehensive overview of site characteristics and pollutant assessment methods.<sup>21</sup>

The highway in this study is similar to many other U.S. highways, supporting a moderate traffic volume (125,000 vehicles per day) with distinguishing activity patterns that affect atmospheric concentrations, like rush hour and weekend differences in traffic volumes. Venkatram et al. (2009) found strong similarities between the emissions and concentration patterns of this highway compared to national default estimates.<sup>22</sup>

### **Field Site and Tracer Release**

A full description of the study area is provided by Baldauf et al. (2008).<sup>21</sup> In summary, an open, at-grade field extends for approximately 120 m to the north of Interstate 440 (I-440), a limited access highway in Raleigh, North Carolina. The only structures between the field and travel lanes were a guardrail and shrubbery, approximately 1 m in height and width. Apart from the highway, there were no other major air pollution sources within several kilometers. The monitors and collection canisters were aligned perpendicular to the roadway (Figure 1). Incoming winds from the southwest at 206° are directly normal to the roadway (sensors would be directly downwind).

Two releases of sulfur hexafluoride (SF<sub>6</sub>), an inert tracer gas, occurred on the 7<sup>th</sup> and 8<sup>th</sup> of August, 2006, corresponding to Day 2 and 3 of the overall sampling campaign. One was performed before, during and after morning rush hour (long duration), and another during the peak of morning rush hour (short duration). Mass flow rates were consistent between releases. The August release was 6 hrs 27 min in duration and occurred between 4:47 a.m. and 11:14 a.m.; the August 8 release was 1 hr 27 min between 8:14 a.m. and 9:41a.m. During each release, real-time measurements and 35 min canister samples were collected (Table 1).

A tank (52.2 kg) of 99.8% pure  $SF_6$ , was connected via mass flow controller to fourteen 3 m lengths of ID conduit 1.7 cm diameter. The conduit had holes drilled in it at 1.5 m intervals. The 28 holes each had a diameter of 0.7 mm in an effort to produce constant flow from each one. The conduit sections were connected by 0.9 m sections of garden hose fastened with screw clamps. The tube was placed 7 m from and parallel to the nearest travel lane of the highway. Figure 1 shows the release tube relative to the roadway and monitors.

#### **Measurement Methods**

The chemicals included in this analysis were SF<sub>6</sub> and 102 VOCs. Air samples were collected in SUMMA canisters at seven distances ranging from 13 to 74 m from the highway edge (Figure 1) and subsequently analyzed at an off-site laboratory approximately 15 km from the study area. SF<sub>6</sub> was also measured from all the canisters. There were five intensive sampling periods during the research study, as shown in Table 1, two in the afternoon of August 3 (Days 1.1 and 1.2) and one on the mornings of August 7, 8, and 10 (sampling Days 2, 3, and 4, respectively).<sup>21</sup> During each sample period a set of ten SUMMA canisters were suspended ~1.5 m above the ground from metal stakes and located 13, 19, 25, 31, 43, 58, and 74 m along a transect normal to I-440. When the canister valve was opened, ambient air flowed through a filter and critical orifice (Entech Instruments, Inc., Simi Valley, CA) into the evacuated canister (evacuated pressure was initially ~0.5 atm) over a 35 min period. Sample pumps, which can be sources of contamination, were not used. Canisters were pressurized to approximately 1.3 atm with zero-grade air before analysis. Prior to sampling, the canisters were cleaned in the laboratory by filling and evacuating humidified zero-grade air three times in an oven at 120 °C.

In addition to canister measurements, real-time SF<sub>6</sub> measurements were also recorded at 4minute intervals with electron capture gas chromatographs optimized for SF<sub>6</sub> detection (Autotrac® Model 101, Lagus Applied Technology, Inc., San Diego, CA). Four Autotracs were placed at increasing distances from the SF<sub>6</sub> release at 20, 50, 100 and 275 m. An optical path Fourier transform infrared spectrometer (OP-FTIR) also recorded SF<sub>6</sub> at 30 sec intervals 10 m from the source.<sup>23,24</sup> The beam length was 149 m, and the beam path was 2 m above ground level. More details on the OP-FTIR are provided in previous publications.<sup>21,25</sup>

VOC concentrations were measured using a capillary gas chromatograph (GC) coupled to a flame ionization detector (FID). C-2 to C-14 compounds were separated on a 60 m, 0.3 mm internal diameter fused silica column coated with 1 mm DB-1 (J&WScientific, Folsom, CA) non-polar liquid phase. The GC oven and column were cooled by liquid nitrogen and subsequently programmed from -50 °C, held for 2 min, to 280 °C for 1.75 min at 8 °C per minute. A Dewar containing liquid argon at -185.9 °C cryogenically concentrated 450 ml of air in a stainless steel, U-shaped, one-eighth inch outer diameter tube containing glass beads. The

trap containing condensed VOCs was immersed in a Dewar of near boiling water to volatilize and inject the VOCs onto the GC column. Further details on this method and its detection limits are provided in Seila et al. (1989).<sup>26</sup> A propane-in-air standard reference material (National Institutes of Science and Technology) was employed to determine the FID per carbon calibration factor. o-Xylene was measured as the azeotrope o-xylene 1,1,2,2-tetrachloroethane, but is referred to here simply as o-xylene.

Wind speed and direction were measured with a sonic anemometer at 1 min time intervals (Model 81000, R.M. Young Company, Traverse City, MI). It was placed 5 m from the roadway edge and 2 m above the ground.

Table 1 summarizes the sampling dates, collection times, analytes, measurement methods, time intervals and distance-from-source for the VOC and  $SF_6$  measurements. Baldauf et al. (2008) includes additional details on monitor types and placements.<sup>21</sup>

Of the 102 VOCs measured in this study, 59 were measured on all five samplings days and at all distances from the highway. These 59 VOCs were used for the correlation analysis. In cases where duplicate measurements were recorded from the same canister for a certain VOC, the average of the two measurements was used. Based on findings from previous studies, Pearson correlation coefficients were calculated to determine associations between the VOCs and between each VOC and  $SF_6$ ; these correlations were calculated for each sampling period individually and also for whole sets of measurements spanning all five sampling periods.<sup>2, 27-32</sup>

## **RESULTS AND DISCUSSION**

### **BTEX and Tracer Concentration Profiles**

BTEX comprises a signature mixture of pollutants related to mobile source emissions. However, VOC concentrations measured here (including BTEX) include the direct contribution of road emissions and background concentration that cannot be attributed to road emissions. These "background" contributions, defined as concentrations attributable to long-range pollutant transport, unidentified emission sources, and natural emission sources, can be significant for some air toxics and should be taken into account in near-road air quality assessments.<sup>22</sup>

BTEX concentrations are plotted against distance-from-roadway in Figure 2. Tracer concentrations, plotted against distance from the tracer release (7 m from the roadway edge), are also plotted for sample Days 2 and 3 when the releases occurred.

Over the five sampling periods, toluene was found to have the highest concentrations, followed by benzene, m&p-xylenes, o-xylene, and ethylbenzene. The contribution of the compounds to total BTEX concentrations over distance was relatively consistent, with ranges of 36-39%, 24-26%, 19-22%, 8-9%, and 8-9%, respectively. Similar trends were found by Pérez-Rial et al. (2009).<sup>33</sup>

Dispersion of the  $SF_6$  was similar between the two releases, as shown in Figure 2. The concentration profiles most closely resemble power trends, with  $R^2$  of 0.9496 for Day 2 and 0.9863 for Day 3. This exponential decay of pollutant concentrations has been found in other studies as well.

## **VOC and Tracer Gas Associations**

Table 2 lists the correlation coefficients between the BTEX components for each sampling period. Caselli et al. (2010) found that significant high correlations between compounds are suggestive of a common source.<sup>30</sup> Relationships between BTEX components further substantiate them as a marker for traffic-related emissions.

Of the 102 VOCs available for analysis, Pearson correlation coefficients were calculated for the 59 that had measurements available for every sampling day and distance. A subset of twenty-six chemicals that had correlation coefficients greater than 0.8 are listed in Table 3 (additional results are presented in supplemental materials). These 26 chemicals are listed by the EPA (2006) as mobile source emissions, though some may be emitted at very low levels.

 $SF_6$  was used as a tracer gas to try to assess near-roadway dispersion patterns. Correlations of  $SF_6$  and VOC concentrations were calculated for Days 2 and 3 (when the tracer was released) to determine similarities between the VOC and tracer dispersion profiles. These associations,

shown in Table 4, suggest that the tracer may be a reliable tool for estimating mobile source VOC dispersion profiles with a reasonable level of certainty. However, the sharp decline in  $SF_6$  indicates that factors other than atmospheric dispersion may have played a role in its concentration profile; for example, since the  $SF_6$ -release tubing was finite and winds were variable, the tracer may have missed the canisters farthest from the source, thus causing a sharp decrease in concentrations with distance. This lateral miss could possibly be corrected if a longer line source were used. In contrast, the VOCs had a near-constant source from the laterally extensive highway, such that VOC contributions from more oblique wind directions would still be collected at the more distant canisters.

As in Parra et al. (2006), the VOCs were categorized by chemical class and are noted as such in Table 4.<sup>31</sup> Correlation coefficients between each class and SF<sub>6</sub> are presented in Table 5, with cycloalkanes having the highest correlation of the chemical classes (0.59). The average correlation coefficient is 0.25 between SF<sub>6</sub> and VOCs listed in EPA (2006) as "emitted by mobile sources," compared to -0.02 for VOCs not on this list.<sup>8</sup> As a group, BTEX was found to be the most correlated with the tracer (0.78). These results support the use of SF<sub>6</sub> to predict dispersion of mobile source pollutants from the roadway, especially for BTEX and other highly-correlated VOCs; especially if lateral miss or other experimental design factors are accounted for. Not surprisingly, VOCs that have similar correlations to SF<sub>6</sub> here also have similar correlations with each other, as shown in Table 3.

## **VOC Consistency with Distance**

Hansen et al. (1996) found a strong linear correlation between toluene and benzene, with  $R^2=0.96$  and a slope of 2.2.<sup>34</sup> In our study, similar correlations were seen on Days 1.1 ( $R^2=0.96$ ) and 4 ( $R^2=0.96$ ), with correlations from all Days ranging 0.77-0.96. Slopes were not similar to those found by Hansen et al., however, having a range of 0.76-1.61. Thus, our results indicate that though the concentrations vary together, benzene concentrations are consistently lower than toluene.

Overall, for the chemicals listed in Table 3, the strong correlation coefficients suggest that associations between chemicals remain consistent through time and with distance, at least under

these sampling conditions. This further suggests that this multi-pollutant mixture is common to this roadway and potentially others like it. Our results indicate the degree to which multiple mobile source pollutants are related based on a real-world example of a near-road environment.

In a near-roadway pollutant profile, chemical concentrations are generally expected to be highest near the roadway and then decrease with distance from the roadway. In this set of measurements, chemicals measured at several 10s of meters from the highway occasionally exceeded the measurements taken nearest the roadway; however, most of the compounds measured decreased monotonically as distance from the roadway increased. Figure 3 is a histogram that shows the frequency (number of chemicals) where maximum concentrations (based on distance) occurred for each sampling period. As discussed in Hahn, et al. (2009) it is important to consider these peaks along with mean concentrations because both chronic and acute health effects may be associated with exposure concentrations.<sup>35</sup>

On Day 1.2, for example, more VOCs had peak concentrations at 58.3 m than at the nearroadway distance of 13 m. A potential explanation is that another source existed in addition to traffic. However, sampling occurred in an open field area with no other known VOC sources that would preferentially impact just one of the monitoring sites. A similar pattern is observed during the other sampling periods; however, the distances at which unexpected peaks occur are not consistent. For example, on Day 1.1 there were peaks at 42.9 m and on Day 2 there were peaks at 31 m. Unknown contaminant sources (such as from the access roadway) or other effects may account for this, but we were unable to ascertain the exact cause of the discrepancies.<sup>25</sup>

## **Meteorological Effects**

At an incoming wind direction of 206°, instruments were directly downwind from the highway source. As seen from the wind roses in Figure 1, the instruments were not generally downwind during the sampling periods. Examination of the association between real-time tracer measurements and wind direction deviations reveals that the less-than-favorable wind conditions may not have had a significant effect on the chemical concentrations measured in the study. For each distance, the tracer concentration did not vary significantly even though wind direction may have deviated from between  $5^{\circ}$  and  $100^{\circ}$ . Within this directional range, SF<sub>6</sub> concentrations at

each distance and for each time period are correlated at p < 0.05. Indeed, previous studies indicate that receptors do not need to be perfectly downwind of a roadway for mobile sources to contribute to near-road concentration levels.<sup>36,37</sup> The consistently high concentrations observed nearest to the roadway (5m) suggest that wind patterns adjacent to the road are likely altered by the local-scale effects of vehicle-induced turbulence.<sup>21</sup>

## CONCLUSIONS

Associations were calculated for 59 mobile source related VOCs, with a subset of results reported here (based on degree of statistical correlation; further results available in supplemental materials). The tracer gas, SF<sub>6</sub>, showed strong associations with mobile source pollutants, some more than others. The VOCs that showed strong correlations to each other also had strong correlations with the tracer. This work demonstrates that the VOC multi-pollutant mixture can be well characterized based on a subset of measurements, and that SF<sub>6</sub> could potentially be used to estimate a broader set of mobile source chemicals.

This work characterizes a multi-pollutant profile for a moderately traveled highway with typical rush hour characteristics. The mobile source pollutant mix presented here, and the correlations between pollutant components provide insight into potential exposures to multiple chemicals occurring in the near-road environment. Additional research is needed to characterize multi-pollutant profiles under a range of conditions, including meteorological variations, traffic volumes, fleet mix, fuel types, or chemical transformative processes.

Previous studies have often addressed one or a limited number of pollutants instead of a complete mixture. This research characterizes the relative concentrations of nearly sixty VOCs, and quantifies the mixture profile through correlation coefficients; therefore, it offers a degree of predictability if some pollutants are known while others are not. In terms of exposure assessments, a mixture is a better representation of pollutants that could account for near-road health impacts, and could provide insight into the contribution of individual components or the mixture as a whole.

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### **ABOUT THE AUTHORS**

Timothy M. Barzyk is a research physical scientist at the U.S. Environmental Protection Agency. He can be contacted at barzyk.timothy@epa.gov, or (919) 541-1520. Anna Ciesielski is a graduate-level researcher on contract to the U.S. EPA. Richard Shores, Eben Thoma, Vlad Isakov and Richard Baldauf are all scientists at the U.S. EPA.

# **TABLES**

Table 1. Date and sample number, canister-based sample collection times, analyte, measurement method, time interval of measurement, measurement methods, distances from source, sampling time intervals, and sampling dates and times for SF<sub>6</sub> and VOCs.

Date [Day] in 2006	Collection Times	Avg. Wind Speed (km/hr)	Avg. Wind Direction	Approx. Vehicles/ 5 min	Analyte	Methods	Collection Time	Distance from Highway (m) <sup>a</sup>
8/3 [1.1] 8/3 [1.2] 8/7 [2] 8/8 [3] 8/10 [4]	3:12 p.m. – 3:47 p.m. 5:05 p.m. – 5:40 p.m. 10:18 a.m. – 10:53 a.m. 8:32 a.m. – 9:07 a.m. 10:16 a.m. – 10:51 a.m.	8-16 8-16 8-16 ~8 8-16	SW WSW-SW SW-SSW SW-W SW	700 800 550 700 550	Whole Air: SF <sub>6</sub> <sup>b</sup> and 59 VOCs	SUMMA canister; Electron capture gas chromatograph	35 min	13, 19, 25, 31, 43, 58, 74
8/7 [2] 8/8 [3]	4:47 a.m11:14 a.m. 8:14 a.m9:41 a.m.	0-16 ~8	SSW-WSW W	Variable 600-800	$SF_6$	Electron capture gas chromatograph	4 min	13, 43, 93, 268
8/7 [2] 8/8 [3]	4:47 a.m11:14 a.m. 8:14 a.m 9:41 a.m.	0-16 ~8	SSW-WSW W	Variable 600-800	$SF_6$	Optical path Fourier transform infrared spectrometer	30 sec	10

<sup>a</sup> SF<sub>6</sub> source was released 7 m from the highway, so distances shown in this column should be subtracted by 7 to obtain the distance from the SF<sub>6</sub> release. <sup>b</sup> SF<sub>6</sub> collection occurred on 8/7 and 8/8.

**Table 2.** Pearson correlation coefficients for benzene, toluene, ethylbenzene, m,p- and o-xylene (BTEX) for each sample period. The Day 4 m,p-Xylene correlations in parentheses indicate the resulting values when anomalous concentration measurements nearest to the roadway are removed.

	В	Т	Е	m&p-X	o-X
Day 1.1					
В	1				
Т	0.98	1			
Е	0.59	0.51	1		
m&p-X	0.81	0.84	0.19	1	
o-X	0.88	0.91	0.31	0.98	1
Day 1.2					
В	1				
Т	0.88	1			
E	0.92	0.90	1		
m&p-X	0.81	0.74	0.66	1	
o-X	0.86	0.70	0.74	0.94	1
Day 2					
В	1				
Т	0.91	1			
Е	0.81	0.89	1		
m&p-X	0.56	0.85	0.75	1	
o-X	0.60	0.87	0.72	0.99	1
Day 3					
В	1				
Т	0.95	1			
Е	0.83	0.91	1		
m&p-X	0.91	0.98	0.92	1	
o-X	0.92	0.97	0.89	0.99	1
Day 4					
В	1				
Т	0.98	1			
Е	0.83	0.87	1		
m&p-X	-0.37	-0.30	-0.36	1	
	(0.96)	(0.95)	(0.72)		
o-X	0.64	0.66	0.47	0.43	1

VOC	1-butene	2,3,4-trimethylpentane	2,3-dimethylbutane	2,3-dimethylpentane	2,4-dimethylpentane	2-methylhexane	2-methylpentane	3-methylpentane	benzene	cyclopentane	ethylbenzene	isobutane	isopentane	m&p-xylene	m-ethyltoluene	n-butane	n-heptane	n-hexane	n-pentane	o-ethyltoluene	o-xylene	propylene
2,3-dimethylpentane	e		0.85																			
2-methylhexane			0.96	0.87																		
2-methylpentane			0.96	0.84		0.95																
3-methylpentane			0.98	0.84		0.96	0.98															
a-pinene	0.83																					
benzene			0.91			0.85	0.85	0.87														
cyclopentane			0.88	0.80		0.85	0.86	0.86														
isobutane			0.92		0.80	0.89	0.91	0.90	0.90		0.82											
isopentane			0.98	0.81		0.97	0.96	0.98	0.93	0.85	0.80	0.93										
n-butane			0.83				0.81	0.80	0.82			0.91	0.82									
n-heptane		0.80	0.86		0.80	0.83	0.84	0.84	0.89			0.92	0.87			0.81						
n-hexane			0.97	0.83	0.80	0.95	0.93	0.96	0.90	0.83		0.92	0.97				0.88					
n-pentane			0.97			0.93	0.94	0.96	0.91	0.82		0.94	0.97			0.84	0.88	0.94				
o-xylene														0.86			0.80	0.84		0.83		
propylene		0.83													0.82		0.82	0.84			0.85	
toluene		0.81	0.97	0.81		0.95	0.94	0.96	0.94	0.83	0.82	0.92	0.98			0.81	0.89	0.98	0.95		0.82	0.81

**Table 3.** VOC-VOC correlations averaged across all sampling periods. Only those correlations with  $R^2 \ge 0.8$  are shown. A table with average correlation coefficients for all VOCs measured in this study is included in supplemental materials.

Chemical Classification <sup>a</sup>	Tracer / VOC	Day 2	Day 3	Average
_	SF <sub>6</sub>	1.00	1.00	1.00
М	i-propylbenzene		0.98	0.98
А	isopentane	0.95	0.81	0.88
А	n-pentane	0.94	0.81	0.88
А	2,3-dimethylbutane	0.91	0.84	0.87
А	isobutane	0.91	0.79	0.85
А	3-methylpentane	0.89	0.81	0.85
М	benzene	0.91	0.79	0.85
С	cyclohexane	0.82	0.87	0.85
А	2-methylpentane	0.84	0.84	0.84
М	toluene	0.89	0.76	0.83
А	n-butane	0.85	0.80	0.82
М	p-ethyltoluene		0.81	0.81
А	n-hexane	0.81	0.82	0.81
С	methylcyclopentane	0.77	0.84	0.81
А	2,3,4-trimethylpentane	0.77	0.83	0.80
С	cyclopentane	0.73	0.86	0.80
Е	1,3-butadiene		0.76	0.76
А	3-ethylpentane		0.76	0.76
А	2-methylhexane	0.79	0.74	0.76
М	o-xylene	0.64	0.87	0.76
М	1,2,4-trimethylbenzene	0.79	0.72	0.76
М	ethylbenzene	0.92	0.59	0.75
М	o-ethyltoluene	0.65	0.84	0.74
А	2,3-dimethylpentane	0.76	0.72	0.74
С	1-c-3-dimethylcyclopentane		0.72	0.72
М	m&p-xylene	0.61	0.80	0.70
А	n-heptane	0.67	0.69	0.68
М	m-ethyltoluene	0.41	0.86	0.64
Е	olefin		0.64	0.64
А	2,2-dimethylbutane	0.62	0.66	0.64
Е	propylene	0.52	0.73	0.62
А	2,4-dimethylpentane	0.72	0.50	0.61
А	3-methylheptane	0.47	0.74	0.60
А	2-methylheptane	0.28	0.90	0.59
L	a-terpineol		0.51	0.51

**Table 4.** Correlations with an average 0.5 or greater between  $SF_6$  and each of the VOCs that had complete data for Days 2, 3 or both. Correlations between  $SF_6$  and all 102 VOCs are available in supplemental material.

<sup>\a</sup>A: alkane; C:cycloalkane; E: alkene; L: alcohol; M: monocyclic arene

**Table 5.** Average correlations between  $SF_6$  and the 102 distinct VOCs measured on the tracer release days. Day 2 includes 68 distinct VOCs listed as mobile sources, and Day 3 includes 73 mobile source VOCs according to the EPA Master List of Compounds Emitted by Mobile Sources (2006).

	Day 2	Day 3	Days 2 and 3 Combined
All VOCs	0.16	0.33	0.23
BTEX	0.79	0.76	0.78
Mobile source	0.26 (68 VOCs)		```
Not listed as mobile source	-0.22 (3 VOCs)	-0.23 (6 VOCs)	-0.02 (7 VOCs)
Chemical Class			
Cycloalkane	0.58	0.59	0.59
Alcohol		0.51	0.51
Monocyclic arene	0.27	0.59	0.44
Alkane	0.31	0.37	0.34
Terpene	-0.01	0.40	0.22
Ketone		0.16	0.16
Alkene	-0.08	0.13	0.03
Halogen containing compounds	-0.19	0.04	-0.06
Alkyne	-0.44	0.22	-0.11
Bicyclic arene	-0.49	0.04	-0.23
C10-C13 aromatics	-0.33	-0.34	-0.34
Ester	-0.44		-0.44

## FIGURE CAPTIONS

**Figure 1.** Aerial view of site. Includes locations of tracer release, SUMMA canisters for whole air sample collection, Autotrac @ gas chromatograph monitors (for continuous SF<sub>6</sub> measurements), and the open path Fourier transform infrared spectrometer (OP-FTIR). Inset (a) shows a ground-level view of the site. Incoming wind directions are shown for the time periods of (b) the first tracer release (on Day 2) and (c) the second tracer release (on Day 3).

**Figure 2.** SUMMA canister BTEX and sulfur hexafluoride tracer gas concentrations as a function of distance from their respective sources for the canister sample collection periods (distance to I-440 for BTEX, and distance to hose for  $SF_6$ ).

**Figure 3.** Number of VOCs having their maximum concentrations at the indicated distances during each sampling period (out of the 59 total VOCs that had complete results for all distances and all sampling periods).