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## Spatial variation of volatile organic compounds in a “Hot Spot” for air pollution

Xianlei Zhu<sup>a,b,1</sup>, Zihua (Tina) Fan<sup>a,b,\*</sup>, Xiangmei Wu<sup>a,b</sup>, Qingyu Meng<sup>a,b,2</sup>, Sheng-wei Wang<sup>a,b</sup>, Xiaogang Tang<sup>a,b</sup>, Pamela Ohman-Strickland<sup>a,c</sup>, Panos Georgopoulos<sup>a,b</sup>, Junfeng Zhang<sup>a,d</sup>, Linda Bonanno<sup>d</sup>, Joann Held<sup>e</sup>, and Paul Lioy<sup>a,b</sup>

<sup>a</sup> University of Medicine and Dentistry of NJ (UMDNJ), USA

<sup>b</sup> UMDNJ – Robert Wood Johnson Medical School, USA

<sup>c</sup> UMDNJ, School of Public Health, USA

<sup>d</sup> The New Jersey Department of Environmental Protection, USA

<sup>e</sup> Air Toxics Analysis Services, Pennington, NJ, USA

### Abstract

The spatial variations of volatile organic compounds (VOCs) were characterized in the Village of Waterfront South neighborhood (WFS), a “hot spot” for air toxics in Camden, NJ. This was accomplished by conducting “spatial saturation sampling” for 11 VOCs using 3500 OVM passive samplers at 22 sites in WFS and 16 sites in Copewood/Davis Streets (CDS) neighborhood, an urban reference area located ~1000 m east of the WFS. Sampling durations were 24 and 48 h. For all 3 sampling campaigns (2 in summer and 1 in winter), the spatial variations and median concentrations of toluene, ethylbenzene, and xylenes (TEX) were found significantly higher ( $p < 0.05$ ) in WFS than in CDS, where the spatial distributions of these compounds were relatively uniform. The highest concentrations of methyl *tert*-butyl ether (MTBE) (maximum of  $159 \mu\text{g m}^{-3}$ ) were always found at one site close to a car scrapping facility in WFS during each sampling campaign. The spatial variation of benzene in WFS was found to be marginally higher ( $p = 0.057$ ) than in CDS during one sampling campaign, but similar in the other two sampling periods. The results obtained from the analyses of correlation among all species and the proximity of sampling site to source indicated that local stationary sources in WFS have significant impact on MTBE and BTEX air pollution in WFS, and both mobile sources and some of the stationary sources in WFS contributed to the ambient levels of these species measured in CDS. The homogenous spatial distributions (%RSD < 24%) and low concentrations of chloroform ( $0.02\text{--}0.23 \mu\text{g m}^{-3}$ ) and carbon tetrachloride ( $0.45\text{--}0.51 \mu\text{g m}^{-3}$ ) indicated no significant local sources in the study areas. Further, results showed that the sampling at the fixed monitoring site may under- or over-estimate air pollutant levels in a “hot spot” area, suggesting that the “spatial saturation sampling” is necessary for conducting accurate assessment of air pollution and personal exposure in a community with a high density of sources.

### Keywords

Spatial variation; VOCs; Hot spot; Air toxics; Proximity; Personal exposure; New Jersey

\*Corresponding author. EOHSI, 170 Frelinghuysen Road, Piscataway, NJ 08854, USA. Tel.: +1 732 445 3194; fax: +1 732 445 0116. zfan@eohsi.rutgers.edu (Z.(Tina) Fan).

<sup>1</sup>Present address: China University of Petroleum, Beijing, China.

<sup>2</sup>Present address: US Environmental Protection Agency, Research Triangle Park, NC.

## 1. Introduction

A “hot spot” of air pollution is an area where the average concentrations of air pollutants are higher than those in surrounding areas and individuals living or working in the area have the potential to be exposed to elevated levels of air toxics (adapted from CA ARB, 1987). In a “hot spot”, localized concentrations of air toxics can occur due to large or small emission sources (Sweet and Vermette, 1992; Spicer et al., 1996; Hung et al., 2005; Vardoulakis et al., 2005; Smith et al., 2007). Thus, an understanding of the spatial distribution of air toxics in a “hot spot” is important for conducting accurate assessment of ambient air pollution and personal exposure (Burnett et al., 2001; Leikauf, 2002; Jerrett et al., 2005; McCarthy et al., 2005; Weis et al., 2005).

Spatial variability of air pollutants has been reported in urban and regional scales (Harkov et al., 1983; Sweet and Vermette, 1992; Spicer et al., 1996; Lee et al., 2002; Zhu et al., 2002; Hung et al., 2005; McCarthy et al., 2005; Vardoulakis et al., 2005; Ohura et al., 2006; Smith et al., 2007). It was found that pollutant concentrations were normally high around areas with industrial facilities and heavy traffic. The concentrations decreased with increasing distance from emission sources. Recently, Touma et al. (2006) reported a wide range of the spatial variability in air toxics between and within cities in US, and the spatial variability is compound and location specific. Thus, they suggested a detailed characterization of spatial distribution of air toxics in “hot spots” with additional monitors (or mobile monitors) so that personal exposure to air pollution and potential health risks can be better estimated.

The Village of Waterfront South (WFS) in Camden, New Jersey (NJ) has been considered as a suspected “hot spot” because of many local stationary and mobile sources of air toxics (NJDEP, 2005). We conducted a study to characterize ambient and personal concentrations of a suite of air toxics in WFS and the Copewood/Davis Streets (CDS) neighborhood, an urban reference area located ~1000 m east of the WFS (Fig. 1). For the measurement of neighborhood ambient air toxics, one fixed sampling site was selected in each neighborhood. Considering the measurements obtained at the fixed site cannot adequately capture the spatial variability of air toxics resulting from the intensive local sources in WFS, a “Spatial Saturation Sampling” (SSS) was designed to better understand the impact of local sources on neighborhood air quality and personal exposure. The approach of SSS is to place a number of samplers in a small area, i.e. to “saturate” a study area with samplers. This manuscript reports spatial variation of volatile organic compounds (VOCs) in WFS and CDS obtained from the SSS and identified the major local sources contributing to the VOC air pollution in the study areas.

## 2. Experimental method

### 2.1. Study areas

The WFS neighborhood is located in south Camden and can be characterized as a rectangular area measuring 1200 m North to South and 800 m West to East (Fig. 1). It is affected by numerous local sources of air toxics and urban plume transported from Philadelphia (NJDEP, 2005). The local sources include 26 industrial and manufacturing facilities (NJDEP, 2005, Fig. 1), such as a sewage treatment facility (S1), recycling plants (S6 and S22), metal processing companies (e.g. S8, S12), food processing companies (e.g. S13), industrial paint shops (e.g. S14), a chemical company (S16), and a car scrapping facility (S23). Emissions from local truck traffic and automobiles on Interstate 676 (I-676) may also contribute to the air pollution in WFS. There are 275–825 trucks day<sup>-1</sup> traveling and idling within WFS to service local industry (NJDEP, 2005). I-676 is located at the ~100 m eastern boundary of the WFS. It is one of the major commuting routes between NJ and

Philadelphia, with a traffic volume of  $\sim 80,000$  vehicles  $\text{day}^{-1}$  (NJDOT, 2006). Almost all WFS residences live within 200 m of stationary sources of air toxics or mobile sources.

The CDS neighborhood is a residential area (Fig. 1). The area of CDS is similar to WFS, measuring 1000 m North to South and 600 m West to East. There are no identified industrial facilities in or near ( $<1000$  m) CDS. The major local roads, State highway 168 (NJ-168,  $\sim 25,000$  vehicles  $\text{day}^{-1}$ ) and Haddon Ave. ( $\sim 8000$  vehicles  $\text{day}^{-1}$ ), are located  $<100$  m to the western and eastern boundary of the CDS, respectively. Most residents in the CDS live within 3 blocks ( $<500$  m) from either NJ-168 or Haddon Ave.

## 2.2. Sampling approach

Based upon the locations of stationary sources, main roads, and residences, the SSS approach with a grid-based sampling design was used to monitor spatial variation of VOCs, i.e. 22 sampling sites were selected in WFS, which only measures  $\sim 0.96$   $\text{km}^2$ , and 16 sampling sites were chosen in CDS, which measures only  $\sim 0.60$   $\text{km}^2$  (Fig. 1). The number of samplers per unit of area was similar in WFS (23 sites/ $\text{km}^2$ ) and CDS (27 sites/ $\text{km}^2$ ), which allowed direct comparison of the spatial variation between the two neighborhoods. Sampling sites were placed in the main residential areas to enhance the utility of the collected data for evaluating personal exposure. Most sampling sites were located at street intersections, and the distance between sampling sites was approximately 150–250 m. In WFS, some sampling sites were located within  $\sim 50$  m of stationary sources, e.g. sites W3 and W19 (Fig. 1), to investigate the impact of emissions from those industrial facilities on ambient air pollution in the adjacent areas. Sites W8 and C13 were the fixed monitoring sites used in the main exposure study (Lioy et al., 2008). C13 is also the NJDEP air toxics monitoring location.

## 2.3. Spatial saturation sampling campaigns

Three SSS campaigns were conducted in 2005, two during the summer ( $\sim 48$ -h samples from 7/20 to 7/22 and  $\sim 24$ -h samples from 8/17 to 8/18) and one during the winter ( $\sim 48$ -h samples from 12/20 to 12/22). The proposed sampling period was 72 h in order to collect sufficient mass for the determination and to smooth out temporal variability. However, the sampling had to be ended earlier due to unexpected strong thunderstorm or snow during each sampling period, as the samplers, which were covered by aluminum foil to protect from sunshine, were not protected from the heavy rain/snow.

Hourly meteorological data were obtained from the Philadelphia International Airport weather station located about 8 miles southwest of centroid of the Camden sampling sites. The data were then extracted to match each sampling period. Except for temperature ( $T$ ) and wind speed (WS), the meteorological conditions were similar among the 3 sampling campaigns. The dominant wind directions were from the west or the southwest/northwest during each sampling period (78%, 43% and 81% for the July, August and December sampling campaigns, respectively) and 36% was from the east during the August campaign. The average WS was  $3.22$   $\text{m s}^{-1}$  and  $3.58$   $\text{m s}^{-1}$  for the July and August samplings, respectively, and both were lower than that in the December campaign ( $4.41$   $\text{m s}^{-1}$ ). Particularly, the high WS ( $5.7$ – $8.23$   $\text{m s}^{-1}$ ) occurred during 24.5% of the sampling period on 12/20–22/05 while only occurred during 3.6% of the sampling period in the both summer campaigns.

VOCs were collected by the passive Organic Vapor Monitors (OVM 3500) (3 M Company, St Paul, MN). The samplers were deployed by 4 field team members within one hour to ensure simultaneous sampling at all the 38 sampling sites. Most samplers were hung on street signs (34 sites), 2 were placed outside of residents' houses (road houses), 1 was placed

on a street fence, and 1 was hung on a sampling rack at the NJDEP site (open field). The sampling height was 4–7 ft. Two field blanks were deployed in each area during each sampling campaign.

#### 2.4. Analytical method and QA/QC

Eleven VOCs were initially targeted based on the emission sources identified in WFS by the NJDEP (2005), e.g. diesel emissions, a municipal sewage plant, several metal processing companies and automobile repair shops. Styrene and 1,3-butadiene are not reported in this paper because blank-subtracted concentrations of more than half of the samples were below the method detection limits (MDLs). Hexane was not included due to the high lab blank levels during the July and August sampling campaigns, which may bias the measured concentrations and spatial variability. The remaining eight target compounds are listed in Table 1. After sample collection, the charcoal pad in each badge was extracted with 1 mL of acetone/carbon disulfide mixture by sonication for 45 min in an ice-water bath. After sonication, a 200- $\mu\text{L}$  aliquot of the extract was pipetted into a 2-mL amber glass vial containing 10  $\mu\text{L}$  of deuterated toluene solution (200 ng  $\mu\text{L}^{-1}$ , internal standard). One  $\mu\text{L}$  sample extract was then analyzed by an HP 6890 GC/5973 MSD for determination of the target VOCs. The detailed analytical conditions and QA/QC information can be found in Liroy et al. (2008). The MDL of each target compound, which was defined as 3 times of the standard deviation of the field blanks collected, ranged from 0.06 to 1.08  $\mu\text{g m}^{-3}$  for a sampling duration of 24 h (Liroy et al., 2008). The 48-h MDLs were not determined in this study since no replicate field blanks were collected for a 48-h sampling duration. Regardless, the MDLs for a 48-h sampling duration are generally expected to be lower than those for 24 h because the sampling volume for a 48-h sampling duration doubled. The method precision (%cv, Table 1) was evaluated by a total of 6 duplicate samples (6 pairs) collected from sites W8 and C13. The %cv is given by the pooled standard deviation

( $\sigma_{\text{pooled}}$ ) divided by the mean value of the pairs. For the paired data,  $\sigma_{\text{pooled}} = [\sum d_i^2 / 2n]^{1/2}$ , where  $d$  is the difference between pair  $i$  values and  $n$  is the number of pairs.

#### 2.5. Data analysis method

The sample concentrations were corrected by the average of the field blanks collected from each sampling trip. After blank subtraction, any values lower than the MDLs (<10% of the total number of samples collected) were substituted with one half of the MDL for data analysis. Given the non-normal distribution, geometric means (GMs) and geometric standard deviations (GSDs) of the VOC concentrations measured at all sampling sites during each sampling period were calculated. A non-parametric test, Wilcoxon rank sum test (Smith et al., 2001), was used to compare the median and the spatial variability of VOCs between WFS and CDS. For spatial variation comparison, the absolute deviation of each measurement from the medians during each sampling period and location was used. Spearman correlation analysis was also performed among all species to identify potential sources of VOCs in WFS and CDS.

To understand the impact of proximity to the known VOCs emission sources on VOC air pollution in WFS and CDS, multiple regression models were developed using the VOCs concentrations and the distance of each site to both stationary and line sources (Kwon et al., 2006). Only the 5 major roads (I-676, S. Broadway, NJ-168, Haddon Ave., and Atlantic Ave.) were selected for analysis because the traffic volume on other small roads was very low based on our site observation. Samplers placed in the parking lot of the Ferry Ave. Train Station in CDS (C16) were lost during two sampling campaigns, and therefore the parking lot was not included in the proximity regression analysis.

Distance of each sampling site to a road or stationary emission source was calculated by GIS processing, similar to the approach reported by Kwon et al. (2006). The positional error using the software vs. direct measurement with GPS devices was estimated to be less than 5 m. The output distance was exported to SAS (version 9.0, SAS Institute Inc., Cary, NC) for statistical analysis.

To determine the effect of proximity to the emission source on the variation of VOCs, the stepwise regression analyses were performed on the log transformed ambient VOC concentrations and the distance of each site to each source (Kwon et al., 2006). Although the meteorological parameters, i.e.  $T$ , WS, and relative humidity (RH), can influence the VOC air concentrations significantly, the data were not sufficient to examine the effects of each individual meteorological parameter on spatial variation of VOCs due to the limited sampling campaigns ( $n = 3$ ) conducted in this study. Therefore, a two-step set of regressions was conducted to examine the effect of proximity to each source on the measured VOC concentrations by excluding the effects of WS,  $T$  and RH. First, a regression with only the mean WS,  $T$  and RH during each sampling period in the model was performed to obtain the raw residuals. Subsequently, the residuals were used in a regression model with only the distance of each sampling site to each emission source as predictors to obtain the partial  $R^2$  value, which explained the amount of variation in the response that was solely due to the proximity to the emission source. The significant predictors ( $p < 0.05$ ) are summarized in Table 4.

### 3. Results and discussion

Forty-two VOCs samplers were deployed in each sampling campaign, and more than 90% of them were retrieved. The GMs, GSDs, and concentration range for each compound measured at the 22 WFS sites and the 16 CDS sites during each sampling campaign are presented in Table 1. The  $p$  values obtained from Wilcoxon rank sum test applied to the median comparison ( $p_1$ ) and variability comparison ( $p_2$ ) between WFS and CDS are also presented in Table 1.

#### 3.1. VOCs concentrations and spatial variability

As shown in Table 1 and Fig. 2, spatial variations and concentrations of MTBE, benzene, toluene, ethylbenzene, and xylenes (BTEX) in WFS were found to be higher than or similar to CDS. In WFS, the greatest variability was observed for toluene and MTBE during all three sampling campaigns, with relative standard deviation (%RSD)  $> 70\%$  among the measurements obtained from the 22 sampling sites, followed by ethylbenzene (%RSD, 36–176%), *m/p*-xylenes (40–175%), *o*-xylene (39–134%) and benzene (21–54%). In contrast, spatial variations of above compounds were small in CDS. The %RSD was less than 29% for BEX and MTBE, and 22–49% for toluene (Table 1). During the July and August sampling campaigns, the variability of TEX concentrations measured in WFS was significantly or marginally greater than that in CDS ( $p_2 = 0.057$  for toluene in the July sampling campaign and  $< 0.05$  for the rest of the measurements, Table 1). During the August period, besides the above species, the variability of benzene concentrations was also found to be marginally higher ( $p_2 = 0.057$ ) in WFS than in CDS. During the December sampling period, similar trends were observed, but only toluene was found to be significantly ( $p_2 = 0.007$ ) higher, and ethylbenzene was marginally higher ( $p_2 = 0.064$ ) in WFS. The smaller difference in spatial variability between the two neighborhoods was probably partially due to the higher wind speed in December than the other two sampling campaigns. For MTBE, there were no significant differences in variability ( $p_2 > 0.164$ ) between the two locations, although the %RSD was found to be large in WFS (76–196%). This is because the large %RSD of MTBE was primarily driven by one high value measured at site W3. If the highest



MTBE concentration was excluded, the %RSD dropped from 76–196% to 17–35% during the 3 spatial sampling campaigns.

In WFS, multiple “hot spots” were observed for TEX (Fig. 2) but the highest concentration of MTBE was always observed at site W3 close to a car scrapping facility, i.e.  $29 \mu\text{g m}^{-3}$ ,  $159 \mu\text{g m}^{-3}$  and  $5.7 \mu\text{g m}^{-3}$  during the July, August, and December sampling campaigns, respectively. The concentrations at W3 were 3–9 times higher than the mean concentration of MTBE calculated for each sampling period. A large concentration gradient was also observed for toluene. For instance, during 8/17–18/2005, the highest concentration of toluene ( $60 \mu\text{g m}^{-3}$ ) occurred at site W19 which was located  $\sim 50$  m west of a recycling company (S28). The toluene concentration exponentially decayed at sites away from the facility (Fig. 3).

In CDS, the highest concentrations of MTBE and BTEX were observed at sites located along NJ-168 (Fig. 2), particularly at site C6 where stopping and idling traffic occurred frequently. However, all concentrations, except for  $18 \mu\text{g m}^{-3}$  of MTBE observed on 8/17–18/2005, were below  $10 \mu\text{g m}^{-3}$ . The comparison of medians showed that the median concentrations of TEX were significantly lower in CDS than in WFS ( $p_1 < 0.05$ ) during the summer sampling campaigns. No significant differences were found in the median concentrations of either benzene or MTBE between WFS and CDS.

The spatial distribution of chloroform and carbon tetrachloride were close to homogenous in both WFS and CDS, with %RSD less than 24% for chloroform and less than 16% for carbon tetrachloride. In addition, the concentrations of chloroform and carbon tetrachloride remained relatively stable, ranging from  $0.03$  to  $0.29 \mu\text{g m}^{-3}$  and  $0.19$  to  $0.60 \mu\text{g m}^{-3}$  respectively during the 3 sampling campaigns in both neighborhoods. No significant differences ( $p > 0.078$ ) were detected either in the median concentrations or spatial variability of these two compounds between WFS and CDS.

### 3.2. Major sources of VOCs in WFS and CDS

Sharp gradients of air toxics reflect point sources, while area and regional source emissions lead to relatively homogeneous concentrations of species (Sweet and Vermette, 1992; Spicer et al., 1996; Hung et al., 2005; McCarthy et al., 2005; Ohura et al., 2006; Touma et al., 2006; Smith et al., 2007). The steep concentration gradient of MTBE around site W3 ( $>3$  times of the mean concentrations in WFS) indicated that there were one or more stationary sources of MTBE nearby. In fact, an automobile recycling company (S23) is located 50 m from W3. Heavy duty trucks carrying recyclable cars and gasoline leaking from scrapped cars was observed at the site during the sampling periods. Since MTBE may still be used as a fuel additive in NJ, evaporation from gasoline leaking from the scrapped cars could have resulted in the high level of MTBE. In fact, this was confirmed by the proximity analysis presented in Section 3.4. However, the results suggested that the impact of this facility on MTBE concentrations was in a limited area ( $<300$  m) because the concentrations of MTBE measured at the sites located  $>300$  m from the facility were similar to the average concentrations of MTBE observed in WFS.

The occurrence of elevated concentrations of TEX compounds indicated significant impacts from local industrial sources in WFS. These observations are consistent with the emission inventory information reported by the NJDEP (2005). According to the inventory data, TEX are associated with some industries/business operations, such as industrial paint shops, a sewage treatment facility, metal processing companies and recycling plants. Emissions from these facilities could have resulted in considerable concentration gradients of these compounds observed in WFS. These arguments are also supported by the correlation and proximity analysis results in Tables 2 and 4. A better correlation was found among TEX

(correlation coefficient ( $R$ ) of 0.32–0.99) and poorer correlation between TEX and traffic-related compound MTBE ( $R$  of 0.02–0.67). Moreover, the BTEX ratios at sites adjacent to industrial facilities, e.g. 1:6:1:5 at W3 on 7/20–22/2005, 1:5:10:30 at W15 and 3:370:10:30 at W19 on 8/17–18/2005, were different from those measured in areas dominated by mobile sources, e.g. 3:14:1:4 in Newark (Harkov et al., 1983) and 1.0:6.9:1.3:2.1 in one of the areas with high volumes of traffic in Hong Kong (Lee et al., 2002), suggesting considerable impacts of industrial facilities in WFS. Benzene was found to be highly correlated with MTBE in the three spatial sampling campaigns ( $R$  of 0.37, 0.79 and 0.92). Based on the source information in WFS and the proximity analysis results (Table 4), the evaporative emission from the gas tanks at the scrapping facility was a major contributor to the benzene air pollution in WFS besides emissions from the local traffic.

The air pollution in CDS is significantly affected by automobile exhausts from local traffic, and thus, low spatial variations of VOCs were observed. These arguments were supported by the correlation analysis results, i.e. many correlation coefficients for BTEX and between MTBE and BTEX were found to be  $>0.8$  (Table 2). Further, the BTEX ratios were within a range of 2:5:1:4 to 2:9:1:4, comparable to those measured in areas with dominated mobile sources (Harkov et al., 1983; Lee et al., 2002). These results reinforced that automobile exhausts are one of the major sources for MTBE and BTEX in CDS. Some local stationary sources in WFS also contributed to the air pollution of these species in CDS, which is discussed in Section 3.4.

The concentrations of chloroform/carbon tetrachloride measured in both WFS and CDS were close to regional background levels in North America (McCarthy et al., 2005; Touma et al., 2006). Given the uniform spatial distribution and poor correlations between chloroform/carbon tetrachloride and MTBE/BTEX (most  $R$ s  $< 0.3$ , Table 2), it could be concluded that there are no significant sources of these two compounds in the study areas.

### 3.3. Comparison between spatial variation sampling and fixed site monitoring

In the main exposure study (Lioy et al., 2008), measurements were obtained from one fixed sampling site in WFS (W8) and one in CDS (C13) to represent the neighborhood VOC concentrations. To evaluate whether the measurements from the fixed site were representative of the VOC concentrations in the whole neighborhood, the concentrations measured at W8 and C13 during each SSS campaign were compared to the median concentrations over all sampling sites in each neighborhood (Table 3). During the summer sampling campaigns, the measurements obtained from W8 and C13 were similar to the median concentrations of VOCs measured in each neighborhood, with a difference of 10% for TEX in WFS and less than 20% for BTEX and MTBE in CDS, but the concentrations of MTBE and benzene were over-estimated by 20–50% at W8. In contrast, the concentrations of BTEX and MTBE measured at W8 and C13 were found to be 10–30% lower than the medians obtained from the SSS sites in both WFS and CDS during the winter sampling campaign. For chloroform and carbon tetrachloride, no difference was found between the measurements obtained from the fixed monitoring sites and the median concentrations over the spatial sampling sites (Table 3). These observations indicated that the fixed site monitoring is appropriate for compounds without significant local sources (e.g.  $\text{CCl}_3$  and  $\text{CCl}_4$ ), but may under- or over-estimate the concentrations of the species with strong local sources (e.g. TEX), depending on the strength of each individual source and wind direction during each sampling period.

### 3.4. Proximity effects and major sources of VOCs

The partial  $R^2$  of the significant predictors ( $p < 0.05$ ), i.e. the inverse distances of the sampling sites to emission sources, are presented in Table 4. In WFS, the inverse distances

to industrial or commercial facilities were found to be the significant predictors in the best-fitting model for BTEX and MTBE. It could explain about 17–75% of the variances of concentrations of these compounds. For example, the inverse distance to a car scrapping facility (S23) was a significant predictor for BTEX and MTBE ( $p < 0.0001$  for BEX and MTBE,  $p = 0.0196$  for toluene, Table 4). It is speculated that this could be due to evaporation of these compounds from an un-removed gas tank in the junk cars. The inverse distances to an industrial paint shop (S14) and a welding and soldering equipment manufacturer (S12) were also significant predictors ( $p < 0.05$ , Table 4) for benzene, ethylbenzene, and xylenes. The operations in these facilities involve solvent use and application of paints which contain aromatic VOCs (NJDEP, 2005). The Camden sewage treatment and sludge recycling facility (S1) was found to be significantly associated with *o*-xylene concentrations ( $p = 0.050$ ) in WFS. None of the target compounds (except for benzene) were significantly associated with any of the major roads located in or near WFS. These observations confirmed that local industrial sources dominant VOC air pollution in WFS.

In CDS, both roadways and some of the local stationary sources in WFS were found to be significant contributors to some of the target pollutants (Table 4). For example, the inverse distances to Haddon Ave. accounted for 51% ( $p < 0.0001$ ) of the variability observed for toluene, 25% ( $p = 0.001$ ) for benzene, and 6.1% ( $p = 0.0386$ ) for MTBE. The inverse distances to each of the NJ-168 and S. Broadway accounted for ~5–8% ( $p < 0.05$ ) of the variability observed for xylenes and ethylbenzene. None of the target compounds were associated with the interstate I-676 located upwind of CDS during most of the year. This is probably due to the farther distance (~900 m) between I-676 and CDS than Haddon Ave. and NJ-168 and less emissions resulted from the vehicles traveling at a fast speed on the I-676 than those at a slow speed on S. Broadway. The scrapping facility (S23) was found to be a significant source ( $p < 0.0001$ , partial  $R^2 = \sim 45\%$ ) for ethylbenzene and xylenes in CDS. Surprisingly, this source was not selected for MTBE but the sewage treatment facility (S1) and a food processing factory (S13) were. The underlying reasons for these observations are not clear and require further investigation.

### 3.5. Limitation of the study

The major limitation of this study is the limited number of sampling campaigns, which would not allow for analysis of seasonal or meteorological effects on spatial variability. In addition, some sampling sites were at intersections, which may tend to overemphasize the traffic sources. Further, a risk assessment study would be necessary to further evaluate the potential for harmful health effects based on the findings of the spatial variation study.

## 4. Conclusions

Spatial variation and concentrations of pollutants were observed significantly higher in our hot spot – WFS with significant local sources than CDS, where there are no identified local industrial sources. Because of the uneven distribution of air toxics in WFS, measurements collected from the fixed monitoring site may underestimate the concentrations of VOCs in the areas adjacent to emission sources (<300 m), and therefore may underestimate exposure and potential health risks associated with air pollution for the residents living in those areas. This study demonstrated that spatial variation study is cost effective, timely and a valuable approach for future air pollution and exposure research in a “hot spot” area. It can provide spatial distribution of air toxics for conducting accurate assessment of air pollution and personal exposure. The robust information obtained by spatial saturation sampling can be used for identifying significant emission sources and designing air monitoring programs and exposure studies in a “hot spot”, such as the optimum number and placement of monitoring sites and target analytes. Ultimately, the information obtained from spatial variation study



can aid in developing effective strategies to control the major air toxics sources of concern and therefore to reduce local exposures in communities.

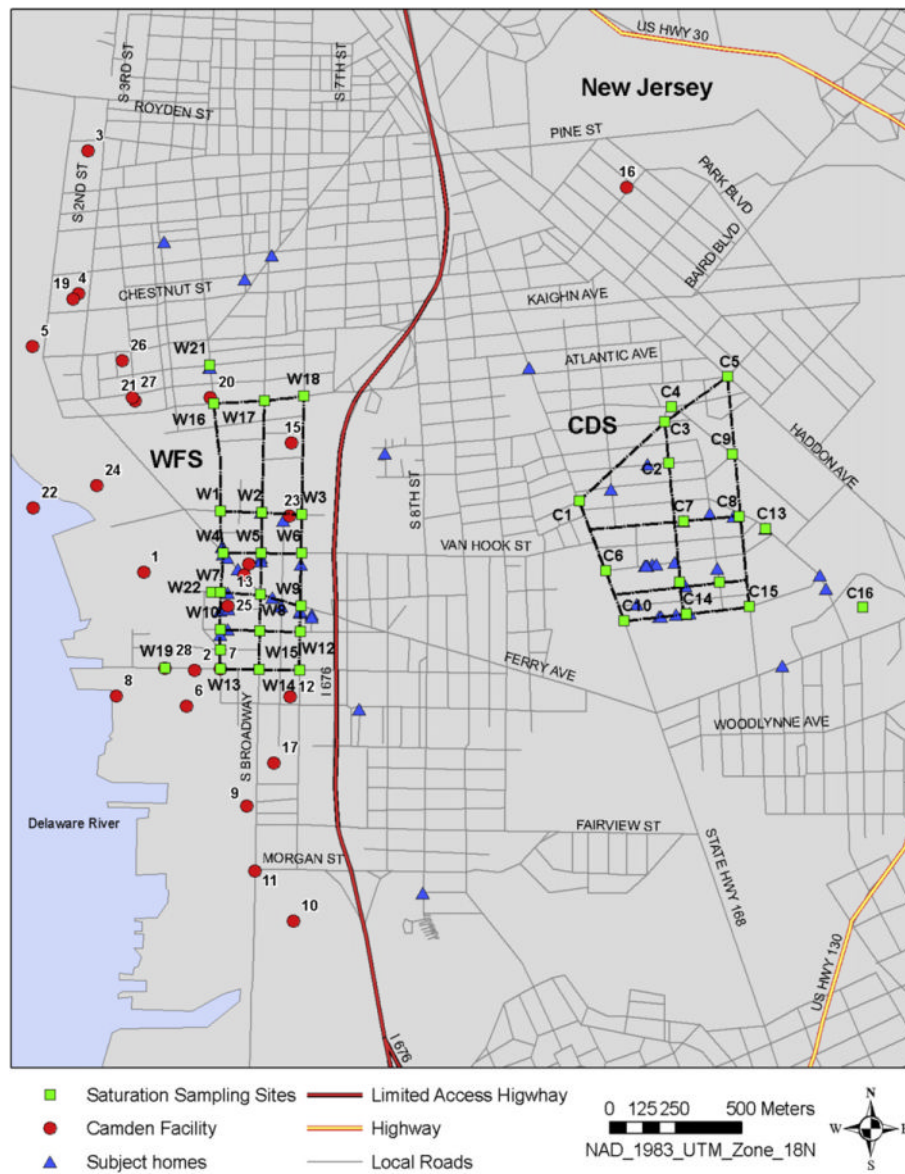
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**Fig. 1.** Spatial saturation sampling sites in WFS (left) and CDS (right) areas. The facility number (e.g. 1, 6 in the map) is equivalent to the source number (e.g. S1, S6, etc.) in the text and Table 4.

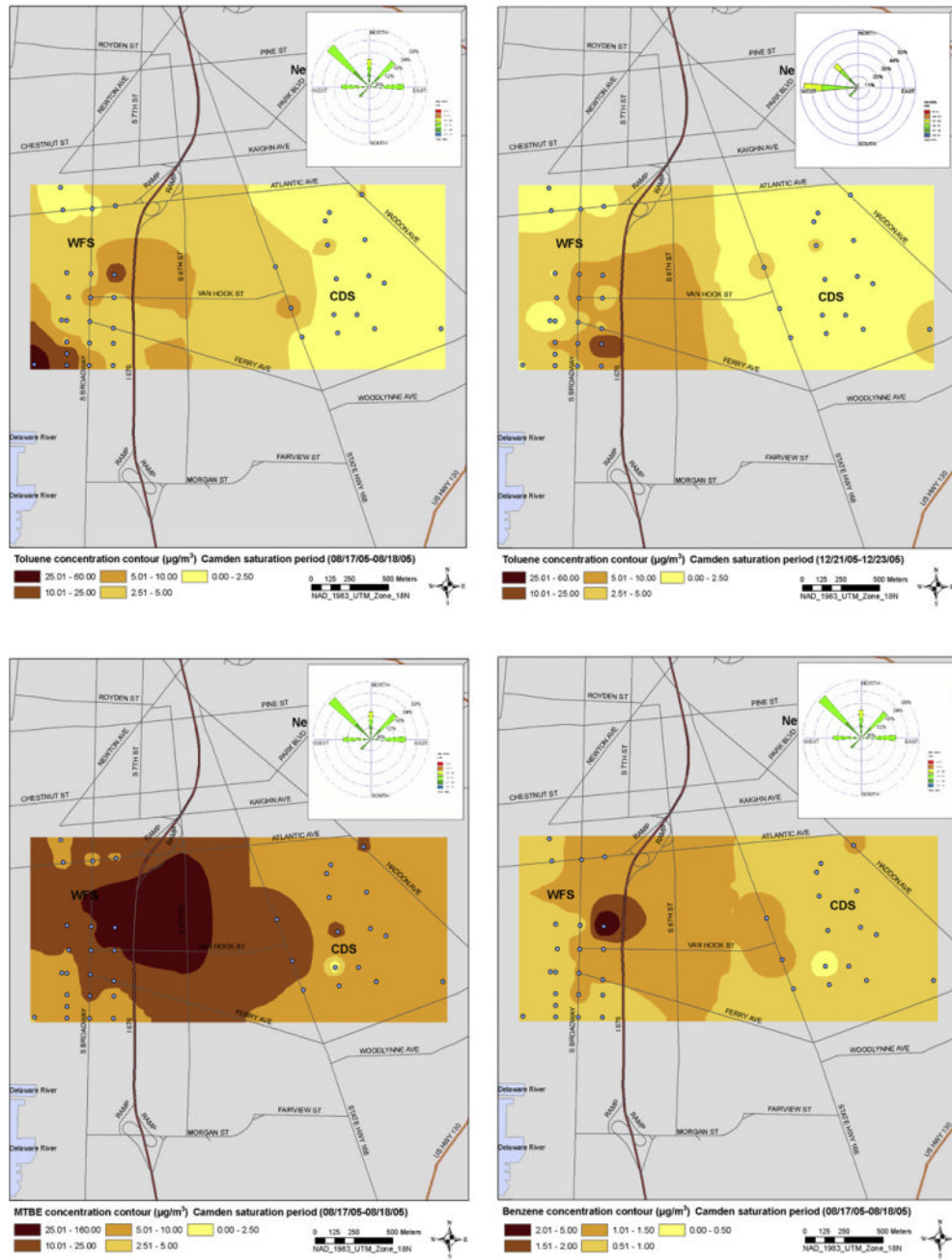
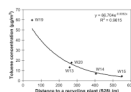


Fig. 2. Spatial distribution of toluene (August and December, 2005, top), MTBE and benzene (August, 2005, bottom left and right, respectively).



**Fig. 3.**  
Toluene concentration downwind of a recycling facility (S28) (August 17–18, 2005).



**Table 1**  
**The concentration ( $\mu\text{g m}^{-3}$ , GM, GSD, %RSD, and range) of VOCs measured at the 22 sites in WFS and the 16 sites in CDS<sup>a</sup>**

	MDL ( $\mu\text{g m}^{-3}$ )			WFS			CDS			cv%	$P_1$	$P_2$
	GM	GSD	%RSD	Range	GM	GSD	%RSD	Range				
<i>7/20-22/2005</i>												
MTBE	0.28	5.1	1.6	92	3.0-29	5.4	1.2	19	4.3-7.8	5.1	0.13	0.37
Chloroform	0.05	0.23	1.1	9	0.21-0.29	0.22	1.1	8	0.20-0.26	45	0.09	0.59
Carbon tetrachloride	0.06	0.57	1.0	3	0.54-0.60	0.56	1.1	5	0.51-0.60	7.5	0.31	0.42
Benzene	0.45	1.2	1.3	28	0.79-2.6	1.4	1.2	22	1.1-2.2	5.4	0.13	0.98
Toluene	0.81	6.4	1.7	83	3.7-32	3.9	1.3	36	3.1-8.2	33	0.0003	0.05
Ethylbenzene	0.44	0.86	1.5	50	0.44-2.5	0.63	1.2	25	0.48-1.1	25	0.002	0.03
<i>m/p</i> -Xylene	1.08	2.5	1.5	60	1.2-8.9	1.8	1.3	26	1.4-3.1	24	0.002	0.02
<i>o</i> -Xylene	0.60	0.79	1.5	60	0.41-2.9	0.60	1.3	26	0.45-1.0	20	0.002	0.05
<i>8/17-18/2005</i>												
MTBE	0.28	10	2.0	196	4.9-159	9.1	1.3	29	6.4-18	5.1	0.91	0.16
Chloroform	0.05	0.14	1.1	13	0.11-0.19	0.15	1.2	16	0.13-0.23	45	0.65	0.61
Carbon tetrachloride	0.06	0.45	1.0	4	0.42-0.51	0.46	1.1	5	0.41-0.49	7.5	0.09	0.69
Benzene	0.45	0.89	1.5	54	0.50-3.1	0.84	1.2	24	0.67-1.4	5.4	0.94	0.06
Toluene	0.81	4.5	2.4	164	1.9-60	2.3	1.4	49	1.9-6.8	33	0.0004	0.008
Ethylbenzene	0.44	0.66	2.2	176	0.30-9.2	0.41	1.2	26	0.32-0.74	25	0.002	0.05
<i>m/p</i> -Xylene	1.08	1.8	2.2	175	0.81-25	1.1	1.3	29	0.85-2.1	24	0.002	0.006
<i>o</i> -Xylene	0.60	0.61	2.0	134	0.29-4.9	0.41	1.3	27	0.31-0.73	20	0.003	0.01
<i>12/20-22/2005</i>												
MTBE	0.28	1.2	1.6	76	0.49-5.7	1.4	1.3	24	0.90-1.9	5.1	0.34	1.00
Chloroform	0.05	0.09	1.3	24	0.03-0.15	0.08	1.0	4	0.07-0.09	45	0.005	0.07
Carbon Tetrachloride	0.06	0.50	1.3	16	0.19-0.56	0.51	1.0	3	0.49-0.55	7.5	0.03	0.11
Benzene	0.45	1.2	1.3	21	0.54-1.8	1.2	1.1	12	1.0-1.6	5.4	0.19	0.49
Toluene	0.81	4.1	1.9	94	1.9-23	2.2	1.2	22	1.7-3.5	33	0.001	0.007
Ethylbenzene	0.44	0.51	1.4	36	0.32-0.99	0.45	1.2	17	0.33-0.62	25	0.42	0.06
<i>m/p</i> -Xylene	1.08	1.4	1.4	40	0.87-3.2	1.2	1.2	21	0.88-1.9	24	0.40	0.16
<i>o</i> -Xylene	0.60	0.44	1.4	39	0.24-1.1	0.41	1.2	20	0.30-0.62	20	0.62	0.15

$\sigma_{cv}$  is for the 6 sets of duplicate samples collected from site W8 and C13;  $p_1$  is the p value applied to the concentration comparison between WFS and CDS by Wilcoxon rank sum test, and  $p_2$  is for the variability comparison by Wilcoxon rank sum test.

Table 2

## Correlation coefficients among all VOCs

	MTBE	Chloroform	Carbon tetrachloride	Benzene	Toluene	Ethylbenzene	<i>m,p</i> -Xylene	<i>o</i> -Xylene
<i>CDS</i>								
<i>7/20-22/2005</i>								
MTBE	1.00							
Chloroform	-0.37	1.00						
Carbon tetrachloride	0.27	-0.09	1.00					
Benzene	0.64	-0.08	0.73	1.00				
Toluene	0.58	-0.14	0.69	0.74	1.00			
Ethylbenzene	0.34	0.11	0.69	0.88	0.66	1.00		
<i>m,p</i> -Xylene	0.43	0.07	0.64	0.91	0.62	0.98	1.00	
<i>o</i> -Xylene	0.52	-0.04	0.62	0.90	0.72	0.90	0.93	1.00
<i>8/17-18/2005</i>								
MTBE	1.00							
Chloroform	0.33	1.00						
Carbon Tetrachloride	0.04	0.01	1.00					
Benzene	0.45	0.23	0.64	1.00				
Toluene	0.69	0.36	0.31	0.59	1.00			
Ethylbenzene	0.78	0.13	0.18	0.68	0.74	1.00		
<i>m,p</i> -Xylene	0.82	0.18	0.15	0.67	0.80	0.97	1.00	
<i>o</i> -Xylene	0.79	0.20	0.16	0.75	0.78	0.92	0.96	1.00
<i>12/20-22/2005</i>								
MTBE	1.00							
Chloroform	-0.38	1.00						
Carbon Tetrachloride	0.29	0.30	1.00					
Benzene	0.87	-0.03	0.50	1.00				
Toluene	0.87	-0.20	0.13	0.77	1.00			
Ethylbenzene	0.89	-0.18	0.39	0.92	0.88	1.00		
<i>m,p</i> -Xylene	0.80	0.01	0.35	0.89	0.92	0.95	1.00	
<i>o</i> -Xylene	0.79	0.06	0.36	0.90	0.88	0.92	0.97	1.00
<i>WFS</i>								

	MTBE	Chloroform	Carbon tetrachloride	Benzene	Toluene	Ethylbenzene	<i>m,p</i> -Xylene	<i>o</i> -Xylene
<i>7/20-22/2005</i>								
MTBE	1.00							
Chloroform	-0.44	1.00						
Carbon Tetrachloride	0.04	0.58	1.00					
Benzene	0.92	-0.37	0.06	1.00				
Toluene	0.06	-0.06	0.25	-0.06	1.00			
Ethylbenzene	0.25	0.04	0.03	0.19	0.39	1.00		
<i>m,p</i> -Xylene	0.26	0.03	0.04	0.20	0.40	0.99	1.00	
<i>o</i> -Xylene	0.43	0.03	0.11	0.38	0.32	0.94	0.95	1.00
<i>8/17-18/2005</i>								
MTBE	1.00							
Chloroform	-0.70	1.00						
Carbon tetrachloride	0.03	0.24	1.00					
Benzene	0.79	-0.61	-0.06	1.00				
Toluene	-0.09	0.11	-0.16	-0.19	1.00			
Ethylbenzene	0.02	0.17	-0.03	0.05	0.77	1.00		
<i>m,p</i> -Xylene	0.04	0.17	-0.01	0.02	0.76	0.99	1.00	
<i>o</i> -Xylene	0.13	0.09	-0.06	0.11	0.67	0.96	0.97	1.00
<i>12/20-22/2005</i>								
MTBE	1.00							
Chloroform	-0.08	1.00						
Carbon Tetrachloride	0.01	0.57	1.00					
Benzene	0.37	0.30	0.54	1.00				
Toluene	0.12	0.27	0.32	0.31	1.00			
Ethylbenzene	0.52	0.23	0.38	0.58	0.68	1.00		
<i>m,p</i> -Xylene	0.63	0.22	0.34	0.57	0.66	0.98	1.00	
<i>o</i> -Xylene	0.67	0.23	0.33	0.53	0.56	0.95	0.98	1.00

**Table 3**  
**Ratio of the concentrations measured at each fixed monitoring site to median of each area**

Compound	WFS				CDS			
	7/20-22/05	8/17-18/05	12/20-22/05	12/20-22/05	7/20-22/05	8/17-18/05	12/20-22/05	12/20-22/05
MTBE	1.2	1.5	0.9	0.9	0.9	1.0	0.7	0.7
Chloroform	1.0	0.9	1.1	1.0	1.0	0.9	1.0	1.0
Carbon tetrachloride	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzene	1.2	1.4	1.0	0.9	0.9	0.9	0.8	0.8
Toluene	1.0	1.1	0.9	0.9	0.9	0.9	0.8	0.8
Ethylbenzene	1.0	1.0	0.7	0.8	0.8	0.9	0.7	0.7
<i>m/p</i> -Xylene	1.0	1.1	0.7	0.8	0.8	0.9	0.7	0.7
<i>o</i> -Xylene	1.0	1.1	0.8	0.8	0.8	0.9	0.7	0.7



**Table 4**  
**Summary of proximity analysis results for selected VOCs (lg-transformed concentrations)**

<b>CDS (n = 40)</b>		<b>Partial R<sup>2</sup> of the inverse distances of sampling sites to emission sources (p &lt; 0.05)<sup>a</sup></b>							
Compound	Total R <sup>2</sup>	NJ-168 <sup>-1</sup>	HaddonAve <sup>-1</sup>	S1 <sup>-1</sup>	S13 <sup>-1</sup>	S22 <sup>-1</sup>	S23 <sup>-1</sup>	S. Broadway <sup>-1</sup>	
MTBE	0.526		0.061	0.076	0.340				
Benzene	0.557		0.514*						
Toluene	0.253		0.253						
Ethylbenzene	0.573	0.059			0.069		0.445*		
<i>m,p</i> -Xylenes	0.577	0.067					0.454*	0.056	
<i>o</i> -Xylene	0.591	0.082					0.442*	0.067	

<b>WFS (n = 61)</b>		<b>Partial R<sup>2</sup> of the inverse distances of sampling sites to emission sources (p &lt; 0.05)</b>							
Compound	Total R <sup>2</sup>	NJ-168 <sup>-1</sup>	S1 <sup>-1</sup>	S6 <sup>-1</sup>	S8 <sup>-1</sup>	S12 <sup>-1</sup>	S14 <sup>-1</sup>	S16 <sup>-1</sup>	S23 <sup>-1</sup>
MTBE	0.748				0.029				0.720*
Chloroform	0.079						0.079		
Benzene	0.438	0.120							0.318*
Toluene	0.168			0.093					0.075*
Ethylbenzene	0.509					0.193	0.059		0.256*
<i>m,p</i> -Xylenes	0.323					0.079	0.055		0.189*
<i>o</i> -Xylene	0.564		0.050			0.209*			0.305*

\* p Value < 0.0001.

<sup>a</sup> Emission source type: S1: a sewage treatment facility; S6 and S22: recycling plants; S8 and S12: metal processing companies; S13: a food processing factory; S14: an industrial paint shop; S16: a chemical company; S23: a car scrapping facility.