



EXPOSURES TO VOLATILE ORGANIC COMPOUNDS IN A SOURCE IMPACTED AIRSHED

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ABSTRACT

The Detroit Exposure and Aerosol Research Study (DEARS) is a three-year monitoring study designed to assess the impacts of local industrial and mobile sources on residential areas in Wayne County, Michigan. Daily integrated (24-hr) samples are being collected of personal exposure, and residential indoor and outdoor concentrations in five neighborhoods throughout Detroit and Wayne County. Concurrent samples are being collected for comparison at a central community ambient monitoring location and a regional background site. Samples are collected over seven-week periods during summer and winter each year and analyzed for particulate matter (PM) and air toxics, including volatile organic compounds (VOCs). The fundamental objectives of the DEARS are to determine the magnitude and variability of source impacts on personal exposures and residences and to determine the relationship between exposures and a central-site community based monitor. The study is aimed at determining the factors influencing exposures to air pollutants of outdoor origin, including volatile organic compounds (VOCs) and particulate matter. Data from the first half of the DEARS (three seasons) is presented here along with preliminary statistical analyses. Personal exposures to most VOCs were higher than concentrations measured indoors, outdoors and at the central monitoring site. Seasonal differences were observed in personal exposures and residential indoor and outdoor concentrations with levels generally higher in summer than winter. Spatial differences in outdoor VOC concentrations were found between monitoring areas as compared to the central community monitoring site and a regional background site. Mobile source impacts were also observed for some compounds, which were significantly higher when the residence was downwind from a major roadway. Although personal exposures to VOCs were much higher and more variable than when measured indoors and outdoors, significant associations were found between personal exposures and indoor/outdoor concentrations. This suggests that indoor and outdoor concentrations are significantly related to personal exposures. However, the magnitude of the relationship decreased considerably between indoors and outdoors. Personal exposures were most closely related to indoor concentrations, consistent with the amount of time the DEARS participants spent indoors (> 85%).

OBJECTIVES

- Data on VOC concentrations measured during the first three seasons of the Detroit Exposure and Aerosol Research Study were used to:
- Determine mobile source impacts on outdoor concentrations
 - Assess impacts of sources on indoor concentrations and personal exposures
 - Evaluate seasonal differences in personal exposures, residential indoor and outdoor, and ambient concentrations
 - Determine the relationships between personal exposures and concurrent measurements of residential indoor and outdoor, and ambient concentrations

METHODS

Sampling Sites

- Samples were collected in six exposure monitoring areas (EMAs) throughout Detroit and Wayne County, Michigan USA and at Allen Park, a central community monitoring location (Fig. 1). The Allen Park site is used by the State of Michigan as a routine air monitoring site.
- Sample sites were chosen to investigate the impact of local industrial point and mobile sources, and regional sources on personal exposures and residential indoor and outdoor concentrations of VOCs.
- Data from EMA 5 was not included in any analyses here because samples were only collected during one season. Data from EMAs 1, 3, 4, 6 and 7 were collected over three seasons and used in the analyses presented in this poster.

Volatile Organic Compounds

- Collected onto diffusion tubes (Perkin Elmer) containing Carbo-pack-X (Supelco)
- Thermally desorbed and analyzed using GC-MS
- Results of the following VOCs are presented in this poster:

Benzene	m,p- & o-Xylenes
1,3-Butadiene	4-Ethyltoluene
1,3,5-Trimethylbenzene	Styrene
Ethylbenzene	Toluene

Statistical Analyses

- All data were used in statistical analyses including values below the detection limit to avoid bias in determining relationships among the measurement variables. Statistical analyses were conducted using SAS software (SAS Institute, Cary, NC).
- Analyses of outdoor and ambient data were conducted using non-parametric tests and mixed models to assess spatial variability. A first-order autoregressive covariance structure was used to account for repeated measures. Differences in least squares means were used to determine spatial differences.
 - Seasonal differences in personal exposures and concentrations of VOCs were determined using non-parametric tests of difference (Wilcoxon signed rank).
 - Analyses of personal exposure data were conducted using mixed models with exposures modeled as fixed-effects variables and subjects were modeled as random variables. A first-order autoregressive covariance structure was found to provide the best model fit and was used in these analyses.

RESULTS AND DISCUSSION

Relationship between personal exposures and spatial concentrations of VOCs

A comparison of VOC concentrations measured during both summer and winter of personal exposures, at residential indoor and outdoor sites, and at the Allen Park ambient monitoring site is shown in Figure 2. The box plots in Figure 2 show the expected overall trend: personal > indoor > outdoor ~ ambient, similar to results found in previous studies (1,2). For most compounds, the outdoor concentrations were more variable than those measured at the ambient site, but median concentrations were generally comparable. Not surprisingly, personal exposures and indoor concentrations of most VOCs were considerably higher and more variable than respective levels measured outdoors and at the ambient site. This is likely due to the contributions of indoor sources and other sources that are only captured in personal exposures (e.g. refueling or traveling in an automobile). Overall, the personal exposures and concentrations in the DEARS are similar to those found in EXPOLIS (2), but somewhat lower than results from the TEAM studies (1).

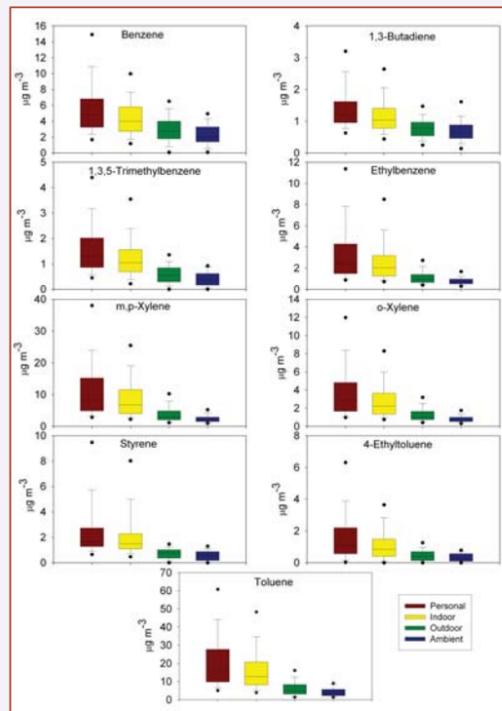


Figure 2. Boxplots of personal exposures, residential indoor and outdoor, and ambient concentrations of VOCs measured during the first three seasons of the DEARS (July-Aug, 2004; Jan-Feb, 2005; July-Aug, 2005). Boxplots indicate 5th, 25th, 50th (median), 75th and 95th percentiles.

Seasonal differences in personal exposures and spatial concentrations of VOCs

Seasonal differences were observed in VOCs concentrations and personal exposures (Table 1). Most VOCs were significantly higher during summer, as expected. However, benzene and 1,3-butadiene were notable exceptions. The Detroit area undergoes considerable differences in temperature between summer (mean T ~ 23°C) and winter (mean T ~ 0°C). Levels of 1,3-butadiene may have been higher during winter due to decreased reactivity under colder temperatures leading to higher concentrations. It is not yet clear why levels of benzene were higher outdoors during winter, but additional data collected during subsequent years may help confirm or refute this initial finding.

Table 1 – Seasonal differences in personal exposures, residential indoor and outdoor, and ambient concentrations of VOCs measured during the first three seasons of the DEARS. Shaded cells indicate significantly higher (p<0.05) levels during winter (■) and summer (■).

Pollutant	Personal	Indoor	Outdoor	Ambient
Benzene	■	■	■	■
1,3-Butadiene	■	■	■	■
1,3,5-Trimethylbenzene	■	■	■	■
Ethylbenzene	■	■	■	■
m,p-Xylene	■	■	■	■
o-Xylene	■	■	■	■
4-Ethyltoluene	■	■	■	■
Styrene	■	■	■	■
Toluene	■	■	■	■

Spatial differences in outdoor concentrations of VOCs

One of the fundamental objectives of the DEARS is to assess the spatial variability in the concentrations of air pollutants. Concentrations of VOCs measured outdoors were used to determine if differences existed between EMAs and the Allen Park ambient monitoring site. Centrally located monitoring sites are used routinely to represent exposures and concentrations in spatially diverse areas. Mixed model analyses of least square means were used to assess differences between each of the EMAs and the ambient site. The results of this analysis revealed a generally consistent pattern for all pollutants showing outdoor concentrations measured in the source impacted EMAs were significantly higher (p<0.05) than EMA 7, which represented the regional background, and the Allen Park ambient monitoring site.

Mobile source impacts on outdoor concentrations of VOCs

Mobile sources are widely regarded as significant emission sources of VOCs including BTEX, 1,3-butadiene and other aromatic hydrocarbons. Some of the EMAs used in the DEARS were chosen to assess the impacts of mobile sources on VOCs and other air pollutants. Residences within 200 m of a major roadway were selected for sampling in EMAs 3 (Ambassador Bridge), 4 (7 Mile and Gratiot Ave.) and 6 (I-96 and Southfield Freeway). This distance was believed to be within the range to detect impacts from mobile source related pollutants. Data for each residence in these EMAs were stratified according to whether or not they were upwind or downwind of the roadway each sampling day. Unfortunately, only about one third of all observations were downwind, on average, from the roadway. A Wilcoxon two-sample test was used to determine if significant differences existed in the stratified data for each compound. The results of this analysis indicated that outdoor concentrations of benzene, toluene (both at p<0.10) and 1,3,5-trimethylbenzene were significantly higher (p<0.05) when the residence was downwind of the roadway.

Associations between personal exposures and indoor, outdoor and ambient concentrations of VOCs

Personal exposures to select VOCs were significantly associated with respective concentrations measured indoors, outdoors and sometimes at the Allen Park ambient site (Figure 3). The general model term used in the mixed model analyses was Personal {VOC} = Indoor/Outdoor/Ambient {VOC} where {VOC} represents a specific compound measured in personal exposures and residential indoor, outdoor, or at the ambient site. The purpose of this type of model is to determine how personal exposures relate to concentrations measured in various locations. The slope of the mixed model illustrates the magnitude of the association between personal exposures to VOCs and concurrent measurements indoors, outdoors and at the ambient site. In general, the mixed model slopes followed the trend: indoor > outdoor > ambient. This indicates that respective indoor concentrations were generally a better estimate of personal exposures and the ambient site served as a worse predictor of personal exposures. Considering that personal exposures were much greater and more variable than ambient concentrations, it is somewhat surprising that ambient concentrations were significantly associated with personal exposures. This may be a result of the relative chemical stability of most VOCs shown here. However, it is clear that personal exposures are substantially larger than would be indicated by respective ambient measures. Nonetheless, ambient measurements of VOCs may capture some of the underlying temporal variability observed in direct measurements of personal VOC exposures.

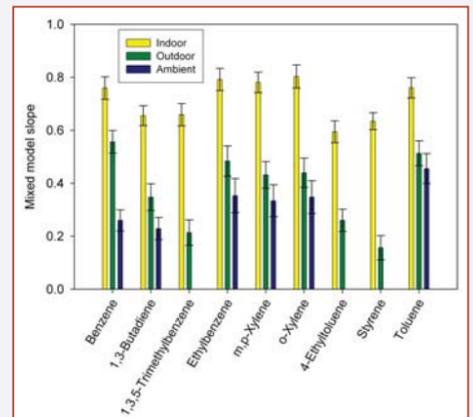


Figure 3. Relationships between personal exposures and residential indoor/outdoor and ambient concentrations of VOCs. Error bars indicate standard error in the mixed model slopes.

CONCLUSIONS

- Personal exposures to select VOCs were higher and more variable than residential indoor and outdoor, and ambient concentrations
- Seasonal differences were observed in personal exposures and concentrations of VOCs measured indoors and outdoors; in general levels were higher during summer, except for benzene and 1,3-butadiene
- Spatial differences were observed in outdoor VOC concentrations with higher levels measured in source impacted areas than at the ambient site and a regional site
- Mobile sources were found to impact downwind concentrations of benzene, toluene and 1,3,5-trimethylbenzene
- Personal exposures to VOCs were significantly associated with respective concentrations measured indoors, outdoors and at the ambient site
- Data from the remaining three monitoring seasons will provide more power to make statistical inferences and allow further insight into the factors affecting personal exposures to VOCs

REFERENCES

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DISCLAIMER

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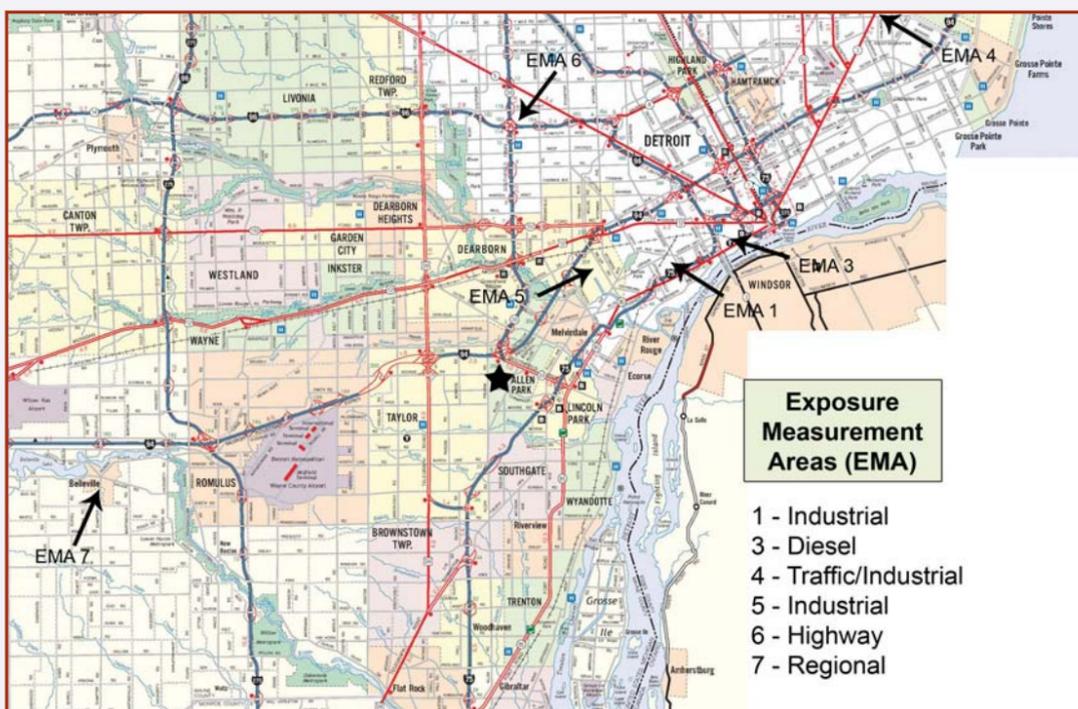


Figure 1. Map of Wayne County, Michigan showing location of sampling sites used in the Detroit Exposure and Aerosol Research Study. Allen Park (★) is the location of the community ambient monitor used by the State of Michigan as a routine air monitoring site.