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5 Assessing spatial and temporal variability of VOCs and PM-components in outdoor air during
6 the Detroit Exposure and Aerosol Research Study (DEARS)
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8 Sarah D. Bereznicki^{*1}, Jon R. Sobus¹, Alan F. Vette¹, Matthew A. Stiegel², and Ron W.
9 Williams¹
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15 ¹*U.S. Environmental Protection Agency, National Exposure Research Laboratory, RTP, NC*
16 *27711, USA*
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18 ²*Department of Environmental Sciences and Engineering, Gillings School of Global Public*
19 *Health, University of North Carolina, Chapel Hill, NC 27599, USA*
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31 *Corresponding author. Tel.: +1-919-541-1088; fax +1-919-541-0905
32 E-mail address: bereznicki.sarah@epa.gov (S. Bereznicki)
33
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Abstract

Exposure models for air pollutants often adjust for effects of the physical environment (e.g., season, urban vs. rural populations) in order to improve exposure and risk predictions. Yet attempts are seldom made to attribute variability in observed outdoor air measurements to specific environmental variables. This research presents a statistical strategy to identify and explain the spatial and temporal components of air pollutant measurement variance using regional predictors and large-scale (with impacts over multiple kilometers of distance) emission source effects. The emission sources considered in this investigation include major highways and industries, and were chosen based on their proximity to monitoring areas designated in the Detroit Exposure and Aerosol Research Study (DEARS). Linear mixed effects models were used to investigate 24-hr averaged outdoor residential air measurements of several pollutants, including PM_{2.5} mass, PM components (elemental carbon, organic carbon, metals, elements), nitrogen dioxide, and volatile organic compounds (VOCs). Three hierarchical statistical models were utilized to calculate and examine variance component estimates for each analyte before and after adjustment for fixed effects, which included sampling season, day of the week, air concentrations at an ambient (centralized) monitoring site, and the frequency of time a receptor was downwind of specific large-emissions sources. Results indicate that temporal variability accounted for the majority of total measurement variance (90% on average). Adjustments for ambient concentration and sampling season significantly reduced temporal variance estimates for most VOCs and for about half of the PM components (generally with reductions of 24 to 97%). Major exceptions to this trend were found with metals (Fe, Mn, and Zn), ethyltoluene, and p-dichlorobenzene, where only 4 to 30% of the temporal variance was explained after the same adjustments. Additional reductions in temporal variance (up to 37%) were observed after

adjusting for the large-emission sources and day of the week effects, with the strongest effects observed for PM components, including select metals. Thus, for the Detroit airshed, VOCs appear to have been largely affected by regional factors, whereas PM components were explained by both regional factors and localized large-emissions sources. Examination of the radial directions associated with suspected emission sources generally supported *a priori* expectations of source-analyte associations (e.g., NO₂ increases from areas of high vehicle traffic). Overall, this investigation presents a statistical multi-pollutant analysis strategy that is useful for simultaneously (1) estimating spatial and temporal variance components of outdoor air pollutant measurements, (2) estimating the effects of regional variables on pollutant levels, and (3) identifying likely emissions sources that may affect outdoor air levels of individual or co-occurring pollutants.

1. Introduction

Measurements of pollutants in outdoor air are affected by numerous natural and anthropogenic parameters. Influential parameters may be obvious and direct, such as a local emission source, or more complex and indirect, such as atmospheric photochemical reactions and turbulence. Atmospheric and exposure research strive to identify trends between influential parameters, air concentrations, and human exposures (Kousa et al., 2002; Violante, et al., 2006), but attempts are seldom made to attribute observed measurement variance to specific parameters. Such efforts may be of particular interest to modelers, risk assessors, and managers, since highly varied air concentrations, often used as model inputs, may cause large uncertainties in predicted output concentrations, population and personal exposures, health outcomes (e.g., respiratory issues, cardiovascular effects, mortality), and subsequent risk-based decisions (Zeger et al., 2000;

Calder et al., 2008; Ozkaynak et al., 2009). If air pollution measurement variance can be attributed to specific environmental parameters, then model uncertainties may be reduced. This, in turn, could promote one's confidence in model predictions and the subsequent decisions.

The research described here focuses on the measurement variability observed across residential outdoor air monitors in Detroit, MI during the Detroit Exposure and Aerosol Research Study (DEARS) (Williams et al., 2009). These monitor sites were situated with a maximum distance of 30km between any two locations. The DEARS collected a total of approximately 20,000, daily (24-hr integrated), outdoor measurements across participating households and one ambient monitoring site (Allen Park, MI MI-DEQ AIRS Site) over a three-year collection period (2004-2007). Monitored pollutants included particulate matter (PM) mass and components, volatile organic compounds (VOCs), and criteria pollutant gases. The ambient site was used as a centralized community monitor (historically used as a regulatory surrogate) for concentrations across the study domain and is assumed here to represent concentration trends induced by parameters affecting the whole DEARS area, herein deemed 'regional' effects. The monitoring scheme involved multiple seasons (3 summer, 3 winter) and repeated measures (five consecutive days per season; all samples collected at 09:00 local time $\pm$ 2.5 hr) for each sampling location. These individual locations, up to 44 per season, were designated by participant identifiers, or PIDs. The PIDs were contained within six *a priori* enumeration measurement areas (EMAs), which had different pollution impacts from regional and localized sources (Williams, 2005; Duvall et al., 2012). The specific EMAs were defined by the presence of regional-background sources (EMA7), heavy vehicle traffic (EMA6), heavy industry (EMAs 1 and 5), mixed heavy industry and vehicle traffic (EMA3), and mixed light industry and vehicle traffic (EMA4)

(Phillips et al. (2010)). EMA7 was not included in the current analysis because data were purposefully collected at only one PID, thus reducing the ability to conduct intra-EMA testing.

Initial exposure assessments associated with the DEARS, involving various PM size fractions, (George et al., 2010; Rodes et al., 2010; Thornburg et al., 2009), PM components (Baxter et al., 2008; Williams et al., 2011a), VOCs (Barzyk et al., 2009; George et al., 2011), and NO₂ (Williams et al., 2011b) have been reported. Many of these summaries have highlighted the spatial and temporal relationships between data collected in the various EMAs and at the ambient monitoring site. However, attempts have not been made to evaluate measurement variance components within each EMA before and after adjusting for regional and large-scale emissions source effects.

Using data from the DEARS, this research demonstrates an application of statistical methods for quantification and evaluation of the spatial and temporal components of air pollutant measurement variance. This work presents a first-step by which data users, modelers, and managers can begin to account for data variability in their analyses. This technique is not intended as an alternative to source apportionment or dispersion/receptor modeling efforts, but rather as an informative tool for the handling of data used as inputs to such methods. The objectives of this unique multi-pollutant analysis are to

- estimate spatial and temporal variance components of daily outdoor air pollutant measurements from the DEARS using a hierarchical statistical modeling approach.
- evaluate environmental parameters that are suspected to drive outdoor pollutant concentrations and for which data are widely available and easily accessible.

- attribute measurement variance to environmental parameters that have been, or may be considered, in deterministic air pollution or exposure models, and use estimated model coefficients to inform the direction and magnitude of these parameter effects.
- present “heat maps” to allow rapid comparisons of results between the hierarchical models and across all pollutants.

2.0 Methods and Materials

2.1 Sampling scheme and analyte selection

Table 1 provides a summary of outdoor residential data collected during the DEARS, listing the number of observations and associated PIDs across seasons and EMAs for VOCs (Table 1a) and PM-related analytes and NO₂ (Table 1b). Specific species for which data was available are also given. For ease in reporting, NO₂ is grouped with the PM components throughout this report. The number of observations differ across the tables owing to differences in sampling methodologies between VOCs (passive diffusion monitors; Mukerjee et al., 2004; McClenny et al., 2005), PM components (personal environmental monitors; Rodes et al., 2010), and NO₂ (Ogawa diffusion badges; Mukerjee et al., 2009; Varns et al., 2001). Additional information on the Detroit metropolitan area and potential source impacts can be reviewed in the DEARS project design (US. EPA, 2012a).

Measurement distributions for each pollutant were evaluated using the UNIVARIATE procedure of SAS statistical software version 9.2 (SAS Institute, Cary, NC). Normal probability plots and histograms showed the data were generally right-skewed and, therefore, measurements were log-transformed prior to further statistical analyses. Analytes were included in the statistical models when at least 75% of the total records were above an individual pollutant’s

sample-specific method detection limit (ss-MDL). These ss-MDLs were calculated as three-times the standard deviation of a set of laboratory blanks, with multiple sets of blanks over the study period resulting in several MDLs for each pollutant. Measurements falling below a ss-MDL were given an imputed value of $\text{ss-MDL} / (\sqrt{2})$ (Hornung and Reed, 1990). Specific analytes were omitted from analysis if measurements were collected in fewer than four seasons, which secured a balanced assessment of season effects in the models. These selection criteria resulted in an evaluation dataset of 20,090 outdoor residential measurements across 21 analytes.

2.2 *Data analysis and statistical model structure*

The data analysis was performed in three parts: (1) investigation of the concentration distributions across the entire study domain, (2) interpretation of statistically significant ($p \leq 0.05$) predictors of analyte levels for each EMA, and (3) evaluation of the spatial and temporal components of concentration measurement variance for each EMA. Part 1 of the data analysis included determination of the pollutant concentration percentile estimates (via Proc UNIVARIATE), geometric means (GM) and geometric standard deviations (GSD) of the ss-MDLs (via Proc MEANS), and percentage of imputed data records for individual analytes (via Proc FREQ).

Parts 2 and 3 of the data analysis were performed using linear mixed-effects models, available through Proc MIXED in SAS. First, null models containing a fixed global mean for each EMA, a random-PID effect, and a random-error effect were created for individual pollutants. Reduced and full models were then built upon the null models, with adjustments for additional fixed effects. Assumptions of the mixed models (e.g., normally-distributed random-effect estimates and residual errors) were evaluated using standard regression diagnostic

procedures, namely residuals analysis and review of the Shapiro-Wilks test statistic. Scaled residuals and Bayesian Information Criteria (BIC) output were also reviewed to ensure a proper covariance structure for the models. A compound symmetry structure was used for each model, which assumes that all random PID effects are independent and all random errors for a given PID are correlated by a constant amount. This structure was selected in part to retain model-structure homogeneity across all pollutants and simplify model output interpretation. Finally, Studentized and Pearson residuals, restricted likelihood distance, and Cook's D and Covariance Ratio outputs were evaluated to identify influential outliers. These points were compared with surrounding measurements (both in time and space) to verify that they were indeed true outliers and not the result of localized trends. From these procedures, 200 out of the total of 20,090 outdoor residential measurements (1.0%) were identified as outliers and removed from the analysis.

For all linear mixed models, let X_{hij} represent the outdoor air measurement on the j^{th} day from the i^{th} PID in the h^{th} EMA, and Y_{hij} represent the natural logarithm of X_{hij} . From Rappaport and Kupper (2004), the null model for each analyte is given in equation 1.

$$Y_{hij} = \ln(X_{hij}) = \mu_{Y_h} + b_{hi} + \varepsilon_{hij} \quad (1)$$

for $h = \text{EMA } 1, 3, 4, 5 \text{ or } 6$;

$i = 1, 2, \dots, n_h$ PIDs in the h^{th} EMA;

$j = 1, 2, \dots, n_{hi}$ measurements of a particular analyte from the i^{th} PID in the h^{th} EMA.

Here, the coefficient μ_{Y_h} represents the true (logged) mean outdoor residential air level in the h^{th} EMA, b_{hi} represents the random effect of the i^{th} PID in the h^{th} EMA, and ε_{hij} represents the random-error effect of the j^{th} measurement from the i^{th} PID in the h^{th} EMA. It is assumed that

b_{hi} and ε_{hij} are independent random variables, and that b_{hi} and ε_{hij} are normally distributed with means of 0 and variances of $\sigma_{bY_h}^2$ and $\sigma_{wY_h}^2$, representing the spatial (between-PID) and temporal (within-PID) components of total variance, respectively, for each EMA, h .

Reduced mixed models were created to evaluate regional and seasonal effects on outdoor air concentrations. Equation 2 shows the reduced models for the individual pollutants.

$$Y_{hij} = \ln(X_{hij}) = \beta_{0_h} + \beta_1 \text{AMBIENT}_{hij} + \beta_2 \text{SEASON}_{hij} + b_{hi} + \varepsilon_{hij} \quad (2)$$

Expanding from the null model (Eqn. 1), the coefficient β_{0_h} represents the intercept for the h^{th} EMA, and β_1 and β_2 are coefficients for the fixed effects of AMBIENT_{hij} and SEASON_{hij} . These represent the ambient, central-site measurement corresponding with the j^{th} outdoor residential air measurement from the i^{th} PID in the h^{th} EMA, and the climatic season during the j^{th} measurement from the i^{th} PID in the h^{th} EMA (where winter = 0 and summer = 1), respectively. An interaction between the AMBIENT_{hij} and SEASON_{hij} terms was considered, but the effect generally did not improve the model performance. Hence, the interaction was not adopted into the reduced model structure.

The reduced mixed models were expanded upon to construct the full models, which considered up to four additional source-related fixed effects, as shown in equation 3.

$$Y_{hij} = \ln(X_{hij}) = \beta_{0_h} + \beta_1 \text{AMBIENT}_{hij} + \beta_2 \text{SEASON}_{hij} + \beta_3 \text{DAY}_{hij} + \sum_{k=1}^K (\beta_{3+k} \text{ZONE}_{khj}) + b_{hi} + \varepsilon_{hij} \quad (3)$$

Here, β_3 and β_{3+k} are regression coefficients associated with the fixed effects of DAY_{hij} and ZONE_{khj} , respectively. DAY_{hij} is an indicator variable (where weekend = 0 and weekday = 1) representing the part of the week during which the j^{th} sample was collected from the i^{th} PID in

the h^{th} EMA. The ZONE_{khj} term represents up to three continuous variables reflecting the percentage of time during the j^{th} 24-hour sample period that winds traversed from a zone of large-scale emission source influence (with each individual zone identified by k , where $k = 1, 2, \dots, K$) toward the center of EMA h . Since source influences were considered with respect to the center point of each EMA, only one ZONE_{khj} value was applied to all PIDs within an EMA. A further description of the ZONE variable calculations is given in section 2.3. It is recognized that the full model presented above does not attempt to incorporate all possible model inputs, but is a compilation of variables with the highest data-completion across participants during the DEARS. Furthermore, these parameters are anticipated to be responsible for a majority of the observed measurement variability.

For the investigation of measurement variance (analysis part 3), restricted maximum likelihood (REML) estimates of $\sigma_{bY_h}^2$ and $\sigma_{wY_h}^2$, the spatial and temporal variance, were determined for each of the null, reduced, and full models. In accordance with Rappaport and Kupper (2008), the 95th-percentile spatial and temporal fold range estimates were calculated, where ${}_{bY_h}\hat{R}_{0.95} = e^{3.92\hat{\sigma}_{bY_h}}$ and ${}_{wY_h}\hat{R}_{0.95} = e^{3.92\hat{\sigma}_{wY_h}}$. Here, ${}_{bY_h}\hat{R}_{0.95}$ is the estimated fold-range containing the middle 95% of the mean pollutant levels across all PIDs within EMA h , and ${}_{wY_h}\hat{R}_{0.95}$ is the estimated fold-range containing the middle 95% of the pollutant levels for any given PID in EMA h . Fold-range estimates were compared across the three models using heat maps (available through MATLAB software version 7.8, R2009a, MathWorks, Natick, MA) to rapidly interpret (1) the amount of observed measurement variance for each pollutant (null models) and (2) the extent to which measurement variance was reduced after adjustment for regional predictors (reduced models) and localized large-emissions source effects (full models) (Pleil et al., 2011). To identify statistically significant decreases in variance estimates between

models (null vs. reduced model estimates, and reduced vs. full model estimates), one-sided Wald tests were used:

$$Z_{C, ModelA-ModelB} = \frac{\hat{\sigma}_{C, ModelA}^2 - \hat{\sigma}_{C, ModelB}^2}{\sqrt{SE(\hat{\sigma}_{C, ModelA}^2) + SE(\hat{\sigma}_{C, ModelB}^2) - 2 \text{cov}(\hat{\sigma}_{C, ModelA}^2, \hat{\sigma}_{C, ModelB}^2)}} \quad (4)$$

where Z = the standard normal distribution z-value;

C = designation of the variance component (either spatial [$\hat{\sigma}_b^2$] or temporal [$\hat{\sigma}_w^2$]);

$ModelA,B$ = designation of compared models ('Null' & 'Reduced' or 'Reduced' & 'Full');

$\hat{\sigma}^2$ = the variance estimate;

SE = the standard error of the variance estimate;

cov = the covariance between variance estimates (set to zero for a conservative test)

2.3 'ZONE' variable calculations

As part of the full models, this research tested the presence of large-emissions sources as a significant contributor to the observed variance of outdoor pollutant measurements. The 'ZONE' variable was created as a surrogate for the influence of such sources, and included facilities identified as large emitters under the US EPA National Emissions Inventory (NEI, eds. 2002 and 2005; US. EPA 2012b). To represent the wide range of analytes from the DEARS, an array of pollutants on either the NEI criteria air pollutants (CAPs) and hazardous air pollutants (HAPs) lists were assessed, specifically: carbon monoxide, ammonia, sulfur dioxide, nitrogen oxides, PM_{2.5}, PM₁₀, toluene, xylenes (combined m-, p-, and o-), benzene, ethylbenzene, styrene, butadiene, manganese, lead, and nickel. It was found that, for any given pollutant, upwards of 90% of total annual emissions were attributed to 10-15 emission points across the study domain and that many pollutants shared major sources. These NEI-identified sources were then

combined with additional suspected sources not monitored by the NEI but identified in the DEARS study plan (e.g. major freeways). Together these data established the locations of likely large-emissions sources and an evaluation dataset was established for sources within an 8-km proximity to each EMA's centroid. Next, the 360-degree geographic space around each EMA was divided into zones of source influence, identified by the physical angle-of-exposure for each suspected source or grouping of sources (Fig. 1; Lim, 2001). A 10-degree buffer distance was applied to each source zone to account for effects of low-wind-speed plume meandering. Finally, hourly wind data from the ambient monitor were used to calculate the frequency of time an EMA spent under influence from each of the different source zones; namely the individual ZONE effect parameters. To confirm that multi-collinearity was minimized in the full models, correlation analyses (Proc CORR; spearman correlations) were performed for the ZONE parameters in each EMA, and resulting r-values were less than 0.55. Similarly, correlation analyses were made between several meteorological data sites across the Detroit, MI airshed to confirm that the ambient monitor location represented wind conditions across the study domain (with correlation coefficients > 0.6).

3.0 Results and discussion

3.1 Descriptive statistics

Basic summary statistics for all VOCs and PM components measured in the DEARS are presented in Table 2 for the evaluated EMAs and the ambient site. Concentrations across the VOCs spanned no more than 1-order of magnitude at either the 50th or 95th percentile, indicating the compounds generally occurred at similar levels. Additionally, individual VOC species ranged no more than 1-order of magnitude from the lowest detected value to the 95th percentile

estimate, suggesting relatively uniform concentrations across the study domain. Fairly similar results on a per-analyte basis were observed for the PM components where, with the exception of Zn, analytes generally ranged no more than 1-order of magnitude across the lowest detected value and 95th percentile estimate. However, when examined across analytes, PM components spanned 3-orders of magnitude at both the 50th and 95th percentiles. This suggests the impact of localized emissions sources for certain PM components throughout the study area.

3.2 Mixed Model Results

3.2.1 Analysis Part 1 – Global intercept estimates (null models)

The fixed global intercepts associated with the null models (not shown) were evaluated to compare the estimated mean levels of individual pollutants across the five EMAs. The largest intercept estimates were observed in EMA 5 for 15 of the 21 analyzed species (benzene, 1,3,5-trimethylbenzene, carbon tetrachloride, ethylbenzene, m-p-xylene, o-xylene, toluene, organic carbon, PM_{2.5} mass, calcium, iron, potassium, manganese, sulfur, and zinc). Of these 15 pollutants, the second-highest estimates were observed in EMA1 for 9 species (ethylbenzene, m-p-xylene, o-xylene, toluene, calcium, iron, potassium, manganese, and zinc) and in EMA3 for another 3 species (carbon tetrachloride, organic carbon, and PM_{2.5} mass). For both nitrogen dioxide and elemental carbon, the two highest intercept estimates were observed in EMA3 and EMA1, respectively. Intercept estimates were largest for only four analytes in the remaining EMAs (EMA4 and EMA6), namely p-dichlorobenzene, tetrachloroethene (PERC), ethyltoluene, and 1,3-butadiene. Collectively, these findings highlight that the EMAs with anticipated influences from heavy industry generally presented higher concentration levels across the

majority of analytes, which is in agreement with work by Rodes et al. (2010) and Duvall et al. (2012).

3.2.2. Analysis Part 2 – AMBIENT, SEASON, DAY, and ZONE parameter effects (full models)

Results for fixed-effects parameters in the full models are presented in Table 3. Analytes are categorized as significantly affected ($p < 0.05$; either positively or negatively impacted) or as not affected by the fixed effects AMBIENT, SEASON, and DAY. A detailed review of the ZONE effect is presented in the supplemental section.

A positive AMBIENT effect indicates that as measurements at the ambient site increased/decreased, so did the corresponding measurements within an EMA. In contrast, a negative AMBIENT effect indicates a negative linear association between the two measurement sites. From Table 3, it is evident that all pollutants across the five EMAs experienced a positive AMBIENT effect except for manganese in EMA5.

A positive SEASON effect identifies an increase in summertime EMA concentrations after accounting for regional concentration trends. Conversely, a negative SEASON effect is associated with higher winter concentrations. In general, the VOCs had elevated levels across all EMAs during the summer (a trend also observed in Stocco et al., 2008), while many of the PM components did not vary seasonally. Higher summer concentrations of iron, manganese, and zinc were observed in EMA1 and may reflect a summertime increase in industrial operations around that sampling area. However, these concentration trends were not shared across the other nearby industrial areas, EMAs 3 and 5. This may reflect a reduced impact distance of the local industrial sources, thought to be the result of increased atmospheric turbulence in summertime (George et al., 2010).

During the DEARS, many factories in the study domain were suspected to be idle over weekends and to resume normal operations patterns starting on Sunday nights. Hence, the DAY term was defined as ‘weekday’ for Tuesday – Thursday samples and ‘weekend’ for Friday – Saturday samples. A positive DAY effect, therefore, indicates an increase in EMA concentrations for weekday measurements after accounting for regional and seasonal effects, and a negative effect indicates higher weekend concentrations. From Table 3, it is evident that the VOCs generally experienced no change between ‘weekday’ and ‘weekend’ scenarios. An exception to this was observed in EMA 3, where strong weekday effects were observed on several VOCs. This may be explained by changing traffic patterns along the Ambassador Bridge (see supplemental section). Similarly, nitrogen dioxide concentrations in EMA6 were found to be higher on the weekend, suggesting that nearby roadways have different traffic patterns for weekends and weekdays. Positive DAY effects were observed on iron, manganese, and zinc across EMAs 1 and 5, supporting a potential decrease in operations of the surrounding industry on weekends (US. EPA, 2012a). Additionally, a positive DAY effect was observed on PERC in EMAs 1, 3, and 5. However, when compared with the ZONE parameter effects (see supplemental section), the DAY effect could not be attributed to any large-emissions sources around these EMAs.

A positive ZONE effect indicates increased pollutant concentrations when winds came from a specific source-impact zone. A negative ZONE effect, in turn, suggests increased concentrations when winds traveled from an alternative direction. A review of the ZONE effects across the multi-pollutant suite identified suspected sources around and between the individual EMAs (results presented as supplemental material), including power generation processes, iron/steel production, automotive manufacturing, and motor vehicle operations. These results

agree with the source apportionment findings of Duvall et al. (2012), with effects noted from steel or mixed industry sources in EMAs 1, 4, and 5, and substantial evidence of motor vehicle sources around EMA3.

3.3 Analysis Part 3 – Variance component evaluation and model review

Heat maps presenting the fold-range estimates of the variance components from the null, reduced, and full models are given for VOCs (Fig. 2) and for PM components (Fig. 3). The heat maps follow a top-to-bottom layout according to increasing model complexity, with the null, reduced, and full model results in the top, middle, and bottom tier, respectfully. These plots show the temporal variance on the left half of the figure and the spatial variance on the right half. Each model section was divided into 5 distinct rows representing the unique EMAs. A white dot within an individual cell indicates a statistically significant ($p < 0.05$) decrease in the variance estimate from the previous-level model, as given by the one-sided Wald tests defined in Eqn. 4.

3.3.1 VOC Analysis

The results in Figure 2 indicate that temporal variance was predominant in the null models for nearly all VOCs. The spatial fold ranges were generally less than 4, while temporal fold ranges varied between 5 and 17. This suggests similar average concentrations across PIDs in a specific EMA, but differences for any given PID over time. An exception to the temporally-dominated fold range trend was p-dichlorobenzene (PDCL) in EMA4, which had a spatial fold range of 50 and a temporal fold range of 15. Generally, the spatial fold ranges were comparable between EMAs for any VOC, illustrating that spatial variance across the study domain was relatively uniform.

After adjusting for concentrations at the ambient monitoring site and season (reduced model), spatial fold ranges remained nearly unchanged. This result was expected, given the relatively small spatial estimates in the null models (< 4 fold). Significant reductions in temporal fold range (Fig. 2) were seen across VOCs, with many values dropping to ≤ 5 . This indicates that regional concentrations and seasonal effects explained a notable amount of the observed measurement variance. However, the introduction of these parameters did not account for the large spatial variance observed for PDCL in EMA4.

Application of the full model, adjusting for the ZONE and DAY effects, resulted in slight reductions of the variance estimates. Only the temporal fold range for toluene in EMA4 was significantly decreased from reduced model estimates. This implies that large-emissions sources and day of the week effects did not account for substantial amounts of measurement variance for VOCs across the different EMAs. The large spatial fold range observed for PDCL across EMA4 persisted through the full model results. This suggests that neither regional concentrations, seasonal effects, large-emissions sources, nor the day-of-week effects were responsible for the concentration differences among PIDs in that EMA. However, significant random-intercepts were identified for 3 of the 20 PIDs, and these locations were located within 300m of one another. This implies that PDCL levels are driven by a highly spatially-isolated event or source, such as the use of substances for tree-boring insect, moth, and mold control or wood preservation activities (US. EPA, 2000; Unger, Schniewind, and Unger, 2001).

3.3.2 PM Component Analysis

Figure 3 presents the heat map for the PM components. This figure shares features of Figure 2, with temporal fold ranges larger than spatial fold ranges (5–40 times larger). In

general, spatial fold ranges for the PM components were between 1 and 3, indicating similar average concentrations across individual PIDs within a specific EMA. Temporal fold ranges, in contrast, were often above 5–10, suggesting that day-to-day concentrations for any given PID varied considerably. The largest temporal fold ranges were associated with sulfur and the metals (iron, manganese, and zinc), implying temporally-driven associations for those species. As with the VOCs, spatial fold ranges were generally comparable between EMAs and, hence, spatial variance was relatively uniform across the study domain.

Reduced model results showed relatively no change in the spatial fold ranges; which is, again, anticipated given the small variance estimates of the null models. Significant reductions in temporal fold ranges were observed for calcium, PM_{2.5} mass, potassium, elemental carbon, organic carbon, nitrogen dioxide, and sulfur. This suggests regional concentration or seasonal drivers for these species in agreement with Thornburg et al. (2009) and Williams et al. (2009). It is noted that the organic carbon and sulfur PM components in this analysis are heavily influenced by secondary PM formations. Therefore, regional-scale, seasonal-dependant effects are expected to produce most of the trends and variability observed for these pollutants. In contrast with these analytes, zinc, manganese, and iron had temporal fold ranges of between 7 and 30, indicating little difference from the null model results. This finding coordinates well with results from Duvall et al. (2012), wherein the ambient monitor was found to not adequately represent EMAs with a close proximity to large-emissions industrial sources.

After accounting for the ZONE and DAY effects, the full models yielded several notable changes. First, the temporal fold ranges associated with manganese were reduced to under 10 across *all* five EMAs. This suggests either a common emission source type or similar day-to-day

emission patterns across the EMAs. Reductions in temporal fold range for iron and zinc across most EMAs reinforce the impact of the surrounding large-emissions sources.

3.3.3 Multipollutant Comparison and Evaluation

Comparison of the VOC and PM component results indicate that outdoor residential measurement variance was temporally-driven (agreeing with findings from Lau et al., 2009). Reduced model results demonstrate the significance of regional concentration trends and seasonal effects for nearly all pollutants, with temporal fold range estimates reduced by 24 to 97% (except for iron, manganese, zinc, ethyltoluene, and p-dichlorobenzene). Full model results suggest substantial impacts from large-emissions sources and weekday effects for a handful of PM components and for virtually none of the VOCs. This implies that VOCs are more homogeneously distributed across the Detroit airshed, while primary PM components may be influenced by localized sources.

Despite reductions in the fold range estimates, some temporal variance remained in the full model for most pollutants, with the middle 95% of observations for any PID generally occurring within an approximate 8-fold range. Exclusions to this were p-dichlorobenzene, zinc, and iron, which had temporal fold ranges of 10–20 across several EMAs. This implies that the full-model parameters explained a majority of the observed measurement variance, but did not account for all of the variance across all of the analytes. An examination of the ZONE parameter (see supplemental section) suggests impacts from additional sources not considered in this analysis.

4.0 Summary and Conclusion

The focus of this analysis was to present a statistical method by which air pollutant measurement variance could be calculated and evaluated, important predictors of pollutant concentrations could be identified, and measurement variance could be attributed to specific environmental parameters. Residential, outdoor air measurements from the DEARS were evaluated for a 21-pollutant suite including VOCs, PM components, and nitrogen dioxide. As observed with previous analyses, measurement variability was predominantly characterized by temporal variability across nearly all the analytes. Large-emissions sources and their associated operational patterns were significant in explaining the measurement variance for PM components in the Detroit urban environment. Variances in VOC data, on the other hand, were explained reasonably well by accounting for regional concentrations and season.

The presented method, utilizing mixed effect models and heat maps, has proven to be sufficient for capturing spatial and temporal data trends in agreement with other analyses. Hence, this technique is should be considered as a viable tool for the investigation of variability in outdoor air concentration measurements across complex, multi-scale, multipollutant datasets. The analysis highlights the need for more spatially-resolved, neighborhood-level monitoring to overcome the measurement variances not explained by concentration trends at an ambient, central-site monitor. By starting with more spatially and temporally refined measurement data, the parameters affecting measurement variance may be more readily identified, accounted for, and, in turn, used to reduce uncertainty in modeled outputs and subsequent decisions.

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