Passive sampling to capture the spatial variability of coarse particles by composition in Cleveland, OH

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HIGHLIGHTS

- Examined spatial variability of PM10-2.5 and components in Cleveland, OH.
- Used passive samplers with automated microscopy to classify particles.
- Components associated with steel and cement production highest in industrial area.
- Components associated with crustal material more uniformly distributed.
- Method may be useful to reduce exposure misclassification in epidemiological studies.

G R A P H I C A L   A B S T R A C T

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Passive samplers deployed at 25 sites for three, week-long intervals were used to characterize spatial variability in the mass and composition of coarse particulate matter (PM10-2.5) in Cleveland, OH in summer 2008. The size and composition of individual particles determined using computer-controlled scanning electron microscopy with energy-dispersive X-ray spectroscopy (CCSEM-EDS) was then used to estimate PM10-2.5 concentrations (µg m⁻³) and its components in 13 particle classes. The highest PM10-2.5 mean mass concentrations were observed at three central industrial sites (35 µg m⁻³, 43 µg m⁻³, and 48 µg m⁻³), whereas substantially lower mean concentrations were observed to the west and east of this area at suburban background sites (13 µg m⁻³ and 15 µg m⁻³). PM10-2.5 mass and components associated with steel and cement production (Fe-oxide and Ca-rich) exhibited substantial heterogeneity with elevated concentrations observed in the river valley, stretching from Lake Erie south through the central industrial area and in the case of Fe-oxide to a suburban valley site. Other components (e.g., Si/Al-rich typical of crustal material) were considerably less heterogeneous. This work shows that some species of coarse particles are considerably more spatially heterogeneous than others in an urban area with a strong industrial core. It also demonstrates that passive sampling coupled with analysis by CCSEM-EDS is a useful tool to assess the spatial variability of particulate pollutants by composition.

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1. Introduction

Exposure to fine atmospheric particulate matter (PM$_{2.5}$) has increased adverse cardiopulmonary health effects (Brook et al., 2010; Hoek et al., 2013), although effect estimates vary significantly among studies with heterogeneity in fine particle composition suspected as a factor of considerable uncertainty (Hoek et al., 2013). The evidence is less clear for adverse health effects associated with exposure to coarse particulate matter (PM$_{10-2.5}$), with recent meta-analyses reporting a lack of evidence for mortality (Hoek et al., 2013), but ‘suggestive evidence’ for increased morbidity and mortality not explained by simultaneous co-exposure to PM$_{2.5}$ (Adar et al., 2014). These meta-analyses stress the need to better characterize the heterogeneity of particulate matter exposures by composition to reduce uncertainty in effect estimates, especially for PM$_{10-2.5}$.

The combination of varying sources and short atmospheric lifetimes often leads to substantial heterogeneity in the concentration and chemical makeup of PM$_{10-2.5}$. Coarse atmospheric particles are emitted primarily by widely varying mechanical and resuspension sources, leading to a complex mixture of material from roads, soil, wear of automotive parts (e.g., tires and brakes), and biological material from vegetation (Kelly and Fussell, 2012). Particle settling velocity scales with diameter squared causing coarse particles to settle substantially faster than fine particles (Seinfeld and Pandis, 2012; Zhang and He, 2014). Consequently, the use of data from spatially sparse networks of regulatory samplers can result in substantial exposure misclassification for PM$_{10-2.5}$ that can attenuate the power of epidemiological studies (Chang et al., 2011).

Networks of active samplers—samplers that collect particles from an aspirated volume of air—have been used to measure the spatial variability of PM$_{10-2.5}$ in urban settings. Burton et al. (1996) used paired PM$_{10}$ and PM$_{2.5}$ filter samplers at eight sites to show that coarse particles (calculated by subtraction: PM$_{10}$ – PM$_{2.5}$) were heterogeneously distributed across Philadelphia, PA. This subtraction method, however, is subject to multiple measurement error from two filter samplers, introducing measurement uncertainty in gravimetric measurement that is amplified in chemical analysis (Goldman et al., 2011). Using two impactors in series, Thornburg et al. (2009) measured coarse particles separately from particles of other size. They found that PM$_{10-2.5}$ measured at five sites in Detroit, MI were temporally correlated and had low spatial heterogeneity. The spatial heterogeneity of PM$_{10-2.5}$ and its components has been studied intensively in Los Angeles, CA with networks of cascade impactors (Cheung et al., 2011; Cheung et al., 2012; Fruin et al., 2014). At 10 downtown and suburban sites, PM$_{10-2.5}$ mass was observed to be moderately heterogeneous (Pakbin et al., 2010) with greater heterogeneity observed for components of coarse particles (Cheung et al., 2011; Cheung et al., 2012; Fruin et al., 2014) identified substantial within-community heterogeneity in PM$_{10-2.5}$.

Networks of passive samplers have been used to investigate the spatial and temporal variability in PM$_{10-2.5}$. Compared to active sampling, passive samplers are relatively inexpensive, require no electricity to operate, and can be deployed at numerous locations easily and cost-effectively (Wagner and Leith, 2001). Ott et al. (2008b) used passive samplers at 30 sites with analysis by light microscopy to show that coarse PM was highly heterogeneous at a spatial scale of 4.4 km in a medium-sized Midwest city. Lagoudi et al. (2011) used a network of 25 passive samplers with light microscopy by computer-controlled scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (CCSEM-EDS) to show PM$_{10-2.5}$ mass and its components were highly heterogeneous at a spatial scale of 2 km across Rochester, NY.

Less work has been done to assess the spatial heterogeneity of PM$_{10-2.5}$ in cities with substantial industrial activity, such as Cleveland, OH. Cleveland, OH is a ‘rust belt’ city with substantial steel and cement production in a central river valley. In a previous publication, the spatial heterogeneity of iron-containing particles within the Cleveland metropolitan area was investigated using arrays of passive samplers analyzed by CCSEM-EDS (Ault et al., 2012). Results indicated that anthropogenic iron-containing coarse particles were highly heterogeneous and subject to physicochemical transformation as they moved away from their source.

The goal of the present work was to more broadly investigate the spatial heterogeneity of PM$_{10-2.5}$ mass and compositional components in Cleveland, OH using a network of passive samplers coupled with single particle analysis by CCSEM-EDS. Particles were classified into 13 compositional classes based on their X-ray spectra. The spatial variability of PM$_{10-2.5}$ and the 13 components were evaluated with visual and quantitative indicators of heterogeneity. We report that anthropogenic particles from the industrial core are more heterogeneous than crustal material. These results may be important for interpreting epidemiological data for cities with strong industrial cores. Moreover, passive sampling with single particle analysis represents an alternative exposure assessment method for the epidemiology of PM$_{10-2.5}$.

2. Methods

2.1. Study area

Sampling was conducted in the Cleveland, OH metropolitan area (Fig. 1). Included in the study area is Cleveland’s Flats District, a low-lying topography along the banks of the lower Cuyahoga River from the river’s mouth at Lake Erie stretching south approximately 8 km. The elevation of the river surface is approximately 180 m above sea level. The surrounding bluffs start at an elevation of 213 m and extend to a height of approximately 365 m above sea level. The river valley width varies from 0.8 km at its narrowest point and widens to approximately 2.4 km.

Within the Flats, large quantities of steel are produced by integrated and electric arc furnace. Steel production uses large quantities of aluminum and calcium, some of which results in slag, a waste byproduct composed mostly of alumina, lime, and trace metals (Van Oss, 2008). Slag is then used as a raw material in the manufacturing of cement, another industry common to the Flats. Other industries in this area include asphalt, gravel, petroleum, and aluminum processing, along with road salt production and storage.

2.2. Site selection

A method designed to optimize the capture of spatial variability in PM$_{10-2.5}$ was used to select sampling sites. As described by Kumar et al. (2011), a preliminary ‘demand surface’ of PM$_{10}$ with a high spatial resolution (90 m) was generated for the study area, using the empirical relationship between satellite-based aerosol optical depth and ground-based PM$_{10}$ measurements. PM$_{10}$ was used as the best available surrogate for PM$_{10-2.5}$. Sites were identified and ranked that would maximize the variability observed in the preliminary surface. This approach, unlike classical sample site selection, was adopted to minimize redundancy in sites by controlling for spatial autocorrelation. The locations of optimal sites were adjusted by moving them to the closest schools, churches, fire stations, and private homes as practical for logistic and security reasons. One sampler was damaged during the first week, and this site was dropped from the remainder of the study, leaving a total of 25 sites for the study.
2.3. Sampling and sample analysis

A UNC passive aerosol sampler (Wagner and Leith, 2001) housed in a protective shelter (Ott and Peters, 2008) was deployed for one week at each site over three consecutive weeks in August 2008. The shelter was designed to shield the passive sampler from precipitation and to minimize dependence of particle deposition on wind speed. Samplers were changed out over a period of three hours on Tuesday of each week. The weather over the study period was typical of summer in this area and fairly consistent between weeks (see Supplementary Information, Table S1). Mean temperatures (Week 1: 22°C; Week 2: 23°C; and Week 3: 21°C) and mean relative humidity (Week 1: 64%; Week 2: 59%; and Week 3: 69%) were similar between weeks. Rainfall was observed only during Week 2 (3 mm during one hour) and Week 3 (15 mm during one hour on two separate days). Winds from N and NNE were observed a portion of the time for all weeks. The highest winds were from the SW in Week 1, from the NNE in Week 2, and from the E and SE in Week 3.

The size and elemental composition of individual particles deposited on the passive sampler were determined by CCSEM-EDS. Samples were analyzed using a Personal SEM™ or PSEM (FEI Aspex, Delmont, PA) (Hopke and Casuccio, 1991). Each passive sample was coated with a thin film (~200 Å) of conductive carbon to prevent sample charging during SEM analysis. The PSEM was operated in the backscattered electron detection mode at an accelerating voltage of 20 kV. Particles were detected by rastering the electron beam across the sample surface until the backscattered electron signal exceeded a preset background threshold level. Particles with diameters between 1.5 μm and 15 μm were selected for further characterization including measuring the particle size, acquiring a digital image of the particle, and collection of an EDS spectrum to determine the particle’s composition. The process of identifying and characterizing particles was repeated until 1000 particles in the 1.5–15 μm size range were analyzed or until the entire sample area was covered (~20 mm²).

The mass of each particle was estimated by multiplying the particle volume by particle density. Following Wagner and Leith (2001), a volume shape factor (1.6) was used to convert the projected area diameter from SEM imaging to an equivalent volume diameter, which was then used to compute particle volume. The density of the particle was estimated from analysis of the x-ray spectrum assuming that the particle was in the form of an oxide. An empirical deposition velocity model was used to convert the deposited mass to ambient PM_{10-2.5} (Wagner and Leith, 2001; Ott et al., 2008a). After CCSEM-EDS analysis, the particle micro-images were manually reviewed as a quality check to reject false positive artifacts and to assist in particle classification based on morphology (e.g., pollen).

2.4. Particle classification

After analysis, particles were classified into groups with similar elemental composition using rules based on the elemental
composition of particles. Initially, pre-defined particle classification rules were used and then modified to minimize the number of particles classified as ‘Miscellaneous’. The final rules included 13 compositional classes as shown in Table 1. These rules were applied sequentially top down, beginning with Rule 1, to sort particles into distinct compositional classes: pollen, carbon-rich (C), sodium chloride (NaCl), sodium-rich (Na-rich), calcium/sulfur rich (Ca/S-rich), silica/aluminum-rich (Si/Al-rich), iron-oxide (Fe-oxide), aluminum-rich (Al-rich), silica-rich (Si-rich), metal rich (metal-rich), iron-rich (Fe-rich), calcium-rich (Ca-rich) and a “catch all” (miscellaneous) class. Table 1 also provides a listing of potential sources of particles in these classes in the Cleveland airshed. Images and EDS spectra of particles representative of several compositional classes are shown in Supplemental Information (Figure S1).

Following Leith et al. (2007), the limit of detection (LoD) by mass was calculated for PM$_{10-2.5}$ and each of its components as the mean $\mu$g/m$^3$ concentration per blank (determined from three field blanks and three trip blanks) plus three times the standard deviation. The limit of quantitation (LoQ) by mass was determined as the mean concentration per blank plus ten times the standard deviation. The percentage of sites having mean concentrations over the three week sampling period greater than the LoD and LoQ were then determined. The results are compiled by component in Table 2. The first column shows the mean number of particles with physical diameters between 1.5 $\mu$m and 15 $\mu$m (plus standard deviation) detected in blanks, which may be useful for planning future studies. Nine components including PM$_{10-2.5}$ were detected above the LoD at the majority of sites, but only PM$_{10-2.5}$, Ca-rich and Ca/Si exceeded their LoQs at more than half the sites. For Ca/S, Ca/Si, Na-rich and Pollen, it was not possible to determine LoDs and LoQs because no particles in this size range were detected in the blanks. For these components, we used the LoDs and LoQs for NaCl, which had a similar blank count in the 1.5 $\mu$m to 15 $\mu$m size range.

2.5. Spatial and temporal analysis

The Pearson correlation coefficient (r) was computed as an indicator of temporal correlation among measurements at different sites. The correlation coefficient was computed in a spreadsheet (Excel, Microsoft, Redmond, WA) from 300 site pairs. The spatial heterogeneity of observed concentrations was investigated through graphical and quantitative analyses. Normalized mean mass concentration maps were prepared to visually investigate the spatial heterogeneity of PM$_{10-2.5}$ and each of its components. For each component, the normalized mean mass concentration was calculated for each site by dividing the mean observed at that site by the mean observed for all samples (3 weeks $\times$ 25 sites = 75). These normalized mean concentrations were krigged and then plotted with mapping software (ArcMap Version 9.3, Redlands CA).

Spatial heterogeneity was also investigated for each component using two quantitative indicators: coefficient of divergence (COD) and percent spatial heterogeneity (SH%). Following Wongphatarakul et al. (1998), COD was computed from 300 site pairs as follows:

$$COD_{jk} = \frac{1}{p} \sqrt{\sum_{i=1}^{p} (x_{ij} - x_{jk})^2 / (x_{ij} + x_{jk})}$$

where $x_{ij}$ and $x_{jk}$ represent the mass concentration for week $i$ at sampling site $j$. $k$ is the number of sites, and $p$ is the number of observations. Following Li and Reynolds (1995), SH% was used as an alternative approach to quantify spatial heterogeneity. SH% was calculated as:

$$SH\% = \frac{p_{\text{nug}}}{p_{\text{sill}} + p_{\text{nug}}} \times 100\%$$

where $p_{\text{nug}}$ is the partial sill and nug is the nugget. The partial sill and the nugget were determined from the semivariogram of the natural log of concentrations using the geostatistical wizard within mapping software (ArcMap Version 9.3, Redlands CA). The nugget represents the random or stochastic component of the variability, the partial sill represents the spatial heterogeneous component, and total variance (referred to as the sill) can be expressed as ($p_{\text{nug}} + \text{nug}$). Thus, SH% represents the portion of the total variance.

### Table 1

| Class# | Component  | Rule | Potential sources in the Cleveland airshed |
|--------|------------|------|--------------------------------------------|
| 1      | Pollen     | P $\geq$ 3 and Ca $\geq$ 3 and C $\geq$ 80 | Naturally occurring plant material |
| 2      | C-rich     | C $\geq$ 50 | Material rich in carbon including plant material other than pollen, soot, tire rubber, etc. |
| 3      | NaCl       | (Na + Cl) $> 70$ and Na $> 20$ and Cl $> 30$ | Rivers and Lake Erie; Road salt (but unlikely in summer) |
| 4      | Na-rich    | Na $\geq$ 40 | Sands; Lake Erie; Na$-$S from various industrial processes |
| 5      | Ca/S-rich  | Ca $\geq$ 20 and S $\geq$ 20 | Steel making; cement production; gypsum used in construction; by-product of atmospheric reaction of Ca with S. |
| 6      | Si/Al-rich | Si $\geq$ 30 and Al $\geq$ 10 | Crustal material consistent with soil, road dust, fly ash |
| 7      | Fe-oxide   | Fe $\geq$ 75 | Spherical: combustion processes used in steel making; coal fired power plants; Non-spherical: steel making; rust |
| 8      | Al-rich    | Al $\geq$ 70 | Aluminum manufacturing; contamination from the sampler or shelter |
| 9      | Si-rich    | Si $\geq$ 60 | Crustal material consistent with soil (quartz) |
| 10     | Metal-rich | Ti $> 5$ or Cr $> 5$ or Mn $> 5$ or Ni $> 5$ or Cu $> 5$ or Zn $> 5$ or Ba $> 5$ or Pb $> 5$ | Various industrial sources including steel making or coal-fired power plants; Cu, Ba, Zn may be from brake and tire wear; Ti, Mn and Ba may also be related to crustal material |
| 11     | Fe-rich    | Fe $\geq$ 40 | Steel making (potential kish); rust |
| 12     | Ca-rich    | Ca $\geq$ 40 | Naturally occurring crustal material (calcium carbonate or calcium oxide); steel making; cement production; construction activities |
| 13     | Miscellaneous | Catch all | |
attributed to spatial heterogeneity and highlights the presence of spatial structure within a data set (Wagner and Fortin, 2005).

2.6. Concentrations in the Flats compared to valley and non-valley suburban sites

Three sites were selected to compare concentrations observed in the Flats to those observed at suburban locations. Site 20 located within the Cuyahoga River Valley was selected to represent the Flats District. Site 30 was selected as a suburban background site within the Cuyahoga River Valley, and Site 34 was selected as a suburban non-valley background site. Kruskal–Wallis one-way analysis of variance (ANOVA) was used to compare the concentration means between Sites 20, 30 and 34 for each compositional class. Median concentration 95% confidence intervals were generated (Minitab, Version 17, State College, PA) to compare the Flats industrial sites to suburban background sites. Kruskal–Wallis analysis was conducted because the assumption of normality was met for some of the components but not others and log-transformation of the data did little to improve normality.

3. Results

Normalized concentration maps are presented in Fig. 2 for: a) PM$_{10-2.5}$; b) Si/Al-rich component of PM$_{10-2.5}$; c) Ca-rich component of PM$_{10-2.5}$; and d) Fe-oxide component of PM$_{10-2.5}$. These normalized plots allow visualization of spatial heterogeneity with dark regions indicating concentrations greater than the mean and light regions indicating those less than the mean. Actual concentrations observed for PM$_{10-2.5}$ and its components are shown in Fig. 3c. PM$_{10-2.5}$ exhibited substantial heterogeneity with elevated concentrations observed in the river valley, stretching from Lake Erie south through the central industrial area (Fig. 2a). The composite mean PM$_{10-2.5}$ over all sites was 22 mg/m$^3$ with a range from 13 to 48 mg/m$^3$. The highest PM$_{10-2.5}$ means were observed in the Flats (35 mg/m$^3$ at Site 1; 43 mg/m$^3$ at Site 35; and 48 mg/m$^3$ at Site 20), whereas lower means were observed to the west and east of this area. The lowest PM$_{10-2.5}$ means were observed at the suburban background sites (13 mg/m$^3$ at Site 34; and 15 mg/m$^3$ at Site 30). A similar elongated shape of higher concentrations in the Flats area was observed for Ca-rich (Fig. 2c) and Fe-oxide components of PM$_{10-2.5}$ (Fig. 2d). In contrast, the spatial distribution of the Si/Al-rich (Fig. 2b) class was less heterogeneous compared to the other compositional classes, although the highest values were still observed at the south end of the Flats.

Table 2

| Component          | Blank Counts Mean (Std. Dev) | LOD (µg/m$^3$) | LOQ (µg/m$^3$) | %sites > LoD | %sites > LOQ |
|--------------------|------------------------------|----------------|----------------|-------------|--------------|
| PM$_{10-2.5}$      | 60 (37)                      | 1.4            | 3.4            | 100         | 100          |
| Ca-rich            | 1.2 (1.0)                    | 0.12           | 0.37           | 100         | 100          |
| Ca/Si*            | 0 (0)                        | -0.14          | -0.40          | 100         | 60           |
| Si/Al-rich         | 1.3 (1.0)                    | 0.43           | 1.28           | 96          | 44           |
| Fe-rich            | 1.3 (1.2)                    | 0.05           | 0.14           | 96          | 44           |
| Fe-oxide           | 1.5 (0.5)                    | 0.08           | 0.22           | 92          | 44           |
| Si-rich            | 8.8 (7.5)                    | 0.70           | 1.89           | 100         | 32           |
| Misc.              | 1.5 (1.5)                    | 0.07           | 0.20           | 84          | 32           |
| Ca/Si*            | 0.2 (0.4)                    | -0.14          | -0.40          | 40          | 4            |
| Al-rich            | 1.7 (2.3)                    | 0.16           | 0.50           | 36          | 0            |
| Metal-rich         | 5.7 (6.2)                    | 0.58           | 1.59           | 32          | 0            |
| C-rich             | 35.7 (30.4)                  | 0.38           | 1.05           | 20          | 0            |
| NaCl               | 0.3 (0.5)                    | 0.14           | 0.40           | 4           | 0            |
| Na-rich*           | 0.2 (0.4)                    | -0.14          | -0.40          | 0           | 0            |
| Pollen*            | 0.5 (0.5)                    | -0.14          | -0.40          | 0           | 0            |

Fig. 2. Maps of normalized concentration for: (a) PM$_{10-2.5}$; (b) Si/Al-rich; (c) Ca-rich; and (d) Fe-oxide. Normalized concentration scale bar in panel b applies to all maps. Dots with numbers represent sample locations and identification number.
A quantitative indicator of spatial heterogeneity, COD, is presented for PM$_{10-2.5}$ and components in Fig. 3a. A COD of zero indicates no difference between site concentrations (homogeneous), whereas a COD greater than 0.2 is considered to indicate substantial spatial heterogeneity (Wilson et al. 2005). COD values fell into two distinct groups (high and low), but all components had median CODs $> 0.2$. Median CODs for the highest group ranged from 0.64 to 0.76 as follows (COD values in parenthesis): metal-rich (0.64); Fe-rich (0.64); Ca/S-rich (0.65); Fe-oxide (0.66); and Al-rich (0.76). Median CODs for the lowest group ranged from 0.24 to 0.39 as follows: PM$_{10-2.5}$ (0.24); C-rich (0.26); Si/Al-rich (0.29); Si-rich (0.32); miscellaneous (0.35); and Ca-rich (0.39).

Temporal associations for concentrations observed between sites can potentially be inferred from Pearson correlation coefficient ($r$) determined from site pairs (300) over the three week study (Fig. 3b). Values of $r$ can range from negative one to positive one with greater positive values indicating a stronger temporal association in the concentrations observed at different sites. For every PM$_{10-2.5}$ component, concentrations measured at one or more site pairs were highly correlated (near 1) and highly anti-correlated (near $-1$), producing the wide range of $r$ values plotted in Fig. 3b. PM$_{10-2.5}$ had a median $r$-value of 0.09, and median correlations were within $\pm 0.4$ for all remaining components, except Ca-rich (median $r = 0.6$) and Si/Al-rich (median $r = 0.5$).

Percent spatial heterogeneity (SH%) for PM$_{10-2.5}$ and its components are presented in Fig. 4. SH% ranged from 0% for Si/Al-rich to 100% for Fe-rich. SH% was near 100% for many components (misc., pollen, Na-rich, Ca-rich, metal-rich, and Fe-rich) and for PM$_{10-2.5}$.
SH% was 34% for Si-rich, between 55% and 65% for NaCl, C-rich, and Al-rich, and 80–85% for Fe-oxide and Ca/S-rich.

In Fig. 5, median concentrations of PM$_{10-2.5}$ and components observed in the Flats are compared to valley and non-valley suburban sites. PM$_{10-2.5}$, Ca-rich, Ca/S-rich, Fe-rich, metal-rich and miscellaneous concentrations observed in the Flats were substantially and statistically higher than those observed at either suburban site. There was no statistical difference in Fe-oxide, Si/Al rich, Si-rich, Al-rich, and C-rich concentrations when compared to Site 30. Compared to background Site 34, concentrations observed at Site 20 within the Flats were significantly higher for all compositional classes except Fe-oxide, Al-rich, and C-rich. For all classes except Si/Al-rich and Al-rich, the variability in concentrations was greater within the Flats (Site 20) than at suburban background sites. For all classes except Ca-rich and miscellaneous, the variability in concentrations was also greater at Site 30 than at Site 34.

4. Discussion

This work demonstrates that some components of coarse particles are considerably more spatially heterogeneous than other components and PM$_{10-2.5}$ mass in general. The Si/Al-rich component of PM$_{10-2.5}$ was more evenly distributed throughout the airshed (Fig. 2b) than other components, such as Ca-rich (Fig. 2c) and Fe-oxide (Fig. 2d), with substantially higher concentrations in the Flats compared to outlying areas. These visual observations of heterogeneity were consistent with quantitative indicators of spatial heterogeneity. Heterogeneity indicators for the Si/Al-rich component (COD = 0.3; SH% = 0%) were substantially lower than the Ca-rich (COD = 0.4; SH% = 100%) and components (COD = 0.65; SH% = 80%). All median CODs exceeded 0.2, a level suggested by EPA to indicate substantial heterogeneity (EPA 2004). The median COD for PM$_{10-2.5}$ mass was 0.25 with greater CODs observed for all 13 components of PM$_{10-2.5}$. Median CODs for components ranged from 0.26 for C-rich to 0.82 for pollen. Percent spatial heterogeneity (SH%) ranged from 0% (low spatial heterogeneity) for Si/Al-rich to 100% (high spatial heterogeneity) for Fe-rich.

The COD results for PM$_{10-2.5}$ mass observed in this study can be compared to those observed in other cities. The median COD of 0.25 for PM$_{10-2.5}$ mass is similar to values observed in Los Angeles, CA [COD range: 0.15–0.33 (Krudysz et al., 2008); COD median: 0.24 (Pakbin et al., 2010)], Iowa City, IA [COD range: 0.21–0.36 (Ott et al., 2008b)], and Birmingham, United Kingdom (COD mean: 0.2 ± 0.1) (Lianou et al., 2007), but lower than values observed in Rochester, NY (COD$_{min}$: 0.365; COD$_{max}$: 0.7) (Lagoudi et al., 2011). Compared to the COD observed in this study, CODs for PM$_{10-2.5}$ were higher in Helsinki, Finland (COD mean: 0.5 ± 0.1) and Athens, Greece (COD mean: 0.6 ± 0.1) and lower in Amsterdam, The Netherlands (COD mean: 0.07 ± 0.01) (Lianou et al., 2007).

Pearson correlation coefficients (Fig. 3b) suggest that concentrations were not strongly temporally associated. With only 3 data points per site pair, however, any correlations must be viewed with caution. For most components, median correlations were near zero, indicating little temporal association across the region over the three, week-long sampling periods. However, median correlations for Ca-rich and Si/Al-rich classes were positively skewed with median r values greater than 0.5, indicating some positive temporal relationship. The higher median correlation for the Si/Al-rich class is consistent with a PM$_{10-2.5}$ component that is more regional in nature.

The spatial heterogeneity observed for components in this study are generally consistent with suspected sources of coarse particles in Cleveland. Substantially higher concentrations were observed in the Flats for Fe-oxide (Fig. 2d) and Ca-rich components (Fig. 2c). COD and SH% values were relatively high for Si-rich, Al-rich, Fe-oxide, Fe-rich, Ca-rich, Ca/S-rich, C-rich, and metal-rich components. These spatial patterns and higher quantitative indicators of heterogeneity are consistent with emissions from steel and cement industries common in the Flats.

Significantly higher concentrations for Ca-rich, Ca/S-rich, Fe-rich, and metal-rich components observed in the Flats (Site 20) when compared to either background site (Fig. 5) are consistent with local emissions of coarse particles that tend to settle near the source. The band of high concentrations in the map for the Ca-rich component (Fig. 2c) is restricted to the flats area suggesting limited
transport. In contrast, there is evidence that the Fe-oxide component is transported from the Flats along the Cuyahoga River Valley. The band of high concentrations for Fe-oxide stretches along the entire valley to Site 30 (Fig. 2d). As shown in Supplementary Information, Table S1, a component of winds from N and NNE were observed on all weeks, which could account for this transport. Further analysis of correlations among meteorological data from multiple stations in the Cleveland area and observed concentrations of the components of coarse particles will be the subject of a future manuscript.

Those components with low spatial heterogeneity suggest regional or ubiquitous sources. Relatively low COD and SH% values were observed for Si-rich (median COD = 0.3; SH% = 35) and Si/Al-rich (median COD = 0.3; SH% = 0). These components are associated with crustal earth material expected as a source prevalent throughout the airshed. As seen in Fig. 2b, Si/Al-rich concentrations were more evenly distributed than other components consistent with a more broadly distributed regional source. Although not statistically significant, higher median concentrations and greater variability in the Si/Al-rich component were observed at the Flats and at the valley background site (Site 30) compared to the other background site (Site 34; Fig. 5). Compared to suburban environments where vegetation acts as a natural sink for PM, there are substantially more hard paved surfaces, surface volume, and density of buildings within the Flats, which may enhance coarse particulate re-suspension. Possibly Si/Al-rich particles are re-suspended and transported along the valley.

Percent relative spatial heterogeneity may be a more meaningful quantitative indicator of heterogeneity than COD. Although COD and SH% provided consistent information in most cases, SH% values were sometimes more consistent with visual interpretation of concentrations maps. A visual rank order of the maps in Fig. 2 from least to most spatial heterogeneity of the maps is consistent with rank order by SH% but not COD: Si/Al-rich, SH% = 0, COD = 0.3 (Fig. 2b); Fe-oxide, SH% = 80, COD = 0.65 (Fig. 2d); PM10-2.5, SH% = 100, COD = 0.25 (Fig. 2a); and Ca-rich, SH% = 100, COD = 0.4 (Fig. 2b). This finding is attributed to the fact that SH% is computed from elements of the semivariogram, which by definition depicts the spatial autocorrelation in data. Thus, SH% relates directly to spatial patterns in the data, whereas COD is a statistical construct providing an indicator of measurement differences without regard to distance between sites.

However, in the limited comparison of PM10-2.5 and Ca-rich, SH% as applied in this work is not as sensitive as visual observation of the maps. For both, the SH% was 100, although visually PM10-2.5 appears less spatially heterogeneous than Ca-rich. In this case, CODs were consistent with the maps with COD = 0.25 for PM10-2.5 lower than COD = 0.4 for Ca-rich. More work is needed to investigate ways to apply information from the semivariogram to arrive at a more sensitive estimate of spatial heterogeneity.

Our results are limited to a three-week period in one season and may not be representative of coarse particle concentrations in this airshed more generally. Also, the samples collected in this study were limited to a one-week sampling duration, which for many samples resulted in particle loadings that were low for CCESEM-EDS analysis. The analysis of LoD and LoQ summarized in Table 2 provides important information for future work. These results reinforce the importance of clean blanks and adequate sampling time. LODs and LOQs would be lower had the blank substrates used in this work been cleaner, and the average particle counts for each component measured in the field samples would be greater for sampling times longer than one week. Longer sampling times, two weeks or more, may have been more appropriate from a particle loading perspective and aligned with the study of chronic health effects. Alternatively, a passive sampler with a larger collection surface would provide more particles for analysis for the study of short-term health effects.

In conclusion, a network of passive samplers analyzed by CCESEM-EDS was used to determine the spatial variability of PM10-2.5 and its components in Cleveland, OH. The concentrations of some PM10-2.5 components were substantially more spatially heterogeneous than others. PM10-2.5 and components associated with steel and cement production (Fe-oxide and Ca-rich) were higher in the industrial Flats district, whereas those components associated with crustal earth material (Si/Al-rich) were more uniformly observed throughout the airshed. There is some evidence that certain components are transported from the industrial Flats to downwind suburban valley sites. Lastly, percent spatial heterogeneity (SH%) may be a more meaningful indicator of heterogeneity than the commonly used coefficient of divergence (COD). SH% leverages the underlying spatial autocorrelation in a dataset being calculated from components of the semivariogram, whereas the COD is a statistical construct that does not account for the distances between sites.

These findings demonstrate the potential of a passive sampling network coupled with automated single particle analysis to assess the spatial and temporal variability of PM10-2.5 mass and composition. This measurement methodology could substantially reduce exposure misclassification in the epidemiological study of adverse health effects associated with exposure to PM10-2.5. The methodology may also be a valuable tool to attribute observed concentrations to specific sources.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.01.030.

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