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Gauging intraurban variability of ambient particulate matter arsenic and other air toxic metals from a network of monitoring sites

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HIGHLIGHTS

- Intraurban variability of air toxic metals characterized using a four site network.
- Scattergram of statistical metrics utilized for examining spatiotemporal variability.
- Daily concentrations apportioned to local- and larger-scale emission source impacts.
- Local emission source zones identified using apportioned local-scale contributions.
- Methodology strengths/limitations revealed by patterns observed for different metals.

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ABSTRACT

A four site monitoring network was established in the Missouri portion of Metropolitan St. Louis during 2008 to characterize spatiotemporal patterns in PM_{10} arsenic. Arsenic measured at two urban sites in the City of St. Louis was typically higher than arsenic at two suburban sites. Spatiotemporal variability in arsenic is examined by plotting the Pearson correlation coefficient (PCC) against the coefficient of divergence (COD) for each site-pair to merge the temporal tracking ability of PCC with COD's ability to gauge spatial homogeneity. Arsenic measured across the network is apportioned into a network-wide baseline and site-specific excess concentrations to semi-quantitatively differentiate local-scale emission source contributions from sources exerting influence over larger spatial scales. Comparing measured concentrations at each site against the network-wide baseline concentration using a scattergram of PCC and COD emphasizes the impact of local sources on intraurban variability. Conditional probability function (CPF) plots constructed using site-specific measured arsenic and surface winds identify a broad emission source region towards the east, but mask the bearings of local sources in the urban core. CPF plots using site-specific arsenic in excess of the baseline concentrations provide better resolution of local emission source bearings and are triangulated to identify a likely arsenic emission source zone along the industrialized Mississippi Riverfront. Additional air toxic metals measured in this study (selenium, manganese and lead) are also investigated to examine the efficacy of this methodology to characterize intraurban variability.

1. Introduction

The United States Clean Air Act Amendments of 1990 identified 187 hazardous air pollutants (HAPs, or Air Toxics) based on their potential for serious health effects. Acute exposure to air toxic metals such as arsenic can produce multiple organ toxicity, while long-term exposure can be carcinogenic (Duker et al., 2005; USEPA, 2004). The St. Louis Community Air Project (CAP), conducted over the period 2001–05, featured detailed measurements of air toxics in an urban residential neighbourhood and identified arsenic as an air toxic metal of concern due to a 1-in-100,000 increased cancer risk from a 70-year exposure sustained at the observed annual average ambient concentration (USEPA, 2005). However, these ambient particulate matter metals data were derived from Chemical Speciation Network (CSN) protocol measurements for $PM_{2.5}$ and time-average concentrations were sensitive to the method used to impute concentration values below the minimum detection limit. Annual average PM_{10} arsenic measured at Blair St., a National

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Air Toxics Trends Station (NATTS) site in the City of St. Louis, was of the same magnitude as other such sites across the United States (USEPA, 2007). However, maximum 24-h arsenic concentrations measured at Blair St. were frequently higher than those measured at the other sites. The poorly characterized influence of local sources and the need for improved arsenic detectability to estimate robust time-average concentrations motivated the examination of short-term spatiotemporal variability of arsenic to identify local sources in the St. Louis region using sampling and analytical methods with higher sensitivity than those provided by the CSN.

Ambient arsenic can originate from natural sources (e.g. soil erosion and volcanic emissions) and anthropogenic sources (e.g. smelting of metals, use of pesticides, and combustion of fuels including coal-fired power plants). However, contributions from anthropogenic sources are estimated to be almost three times more than that from natural sources (WHO, 2001). Air samples collected over a decade at 14 counties along the Texas–Mexico border indicated a rise in ambient arsenic concentrations with rapid industrialization in the region (Shields, 1991). An arsenic speciation study during 2001–02 at the highly industrialized Huelva region in southwestern Spain identified peak arsenic concentrations to occur at the urban background site for winds from the direction of a metal smelting facility (Sánchez-Rodas et al., 2007). $PM_{1.3}$ air toxic metals such as arsenic, selenium, and lead were measured at 30 min resolution in East St. Louis (USA) during 2001–02 using the Semi-continuous Elements in Aerosol System (SEAS). Wind directions during periods of high species concentration were examined to identify potential emission source regions (Wang et al., 2011).

Many air quality studies have assumed that the spatial distribution of the pollutant is homogeneous within large urban areas and that concentrations at a central site are representative of the entire study area (Burton et al., 1996; Roosli et al., 2001). However, several recent studies examining datasets on finer spatial and temporal scales often indicate greater variation within urban areas than was previously characterized (Pinto et al., 2004; Kim et al., 2005). The spatial zone of representation for observational data collected at a site depends on the spatial scale of influence exerted by emission sources and thus is species-specific. Inadequate accounting of spatial and/or temporal variability can lead to exposure misclassification in epidemiological and exposure studies used to support health-based standards (Wilson et al., 2005; Goldman et al., 2011; Mangia et al., 2013).

Summary statistics such as the mean and median are commonly used to describe variability in pollutant concentrations. Another commonly used metric is the Pearson correlation coefficient (r or PCC) which gauges the strength of association between two distributions (DeGaetano et al., 2004; Sajani et al., 2004). PCC is defined in equation (1) where,x_{ij} is the concentration for sample i at site j; $\bar{x}_j$ is the average concentration at site j; j and k are the two sampling sites; and p is the number of paired observations. PCC is the ratio of covariance between the two datasets to the product of their respective standard deviations and is bounded by $[-1, +1]$. The coefficient gauges temporal variability, i.e. association between concentrations at two sites over the entire sampling duration, with greater correlation indicated by values closer to ± 1 and low correlation expressed by values closer to zero. While being a good reference metric for tracking temporal similarity between paired sites, it can have a weak association with the actual spatial homogeneity of concentrations (Pinto et al., 2004). Spatial variability, resulting from concentration differences observed across the monitoring sites during each sampling event, is often gauged using the Coefficient of Divergence (COD) (Pinto et al., 2004; Kim et al., 2005). COD, defined in equation (2), is the root mean square of the ratio of sample-specific differences to the sum between the two datasets and is bounded by [0, 1] (Wongphatarakul et al., 1998). It utilizes daily inter-site differences to gauge the concentration variability between two sites. COD <0.20 is often associated with spatial homogeneity while higher values are associated with spatial heterogeneity (Wilson et al., 2005).

$$\mathrm{PCC}_{jk} = \frac{\sum_{i=1}^{p}(x_{ij}-\bar{x}_j)\times(x_{ik}-\bar{x}_k)}{\sqrt{\sum_{i=1}^{p}(x_{ij}-\bar{x}_j)^2\times\sum_{i=1}^{p}(x_{ik}-\bar{x}_k)^2}} \tag{1}$$

$$\mathrm{COD}_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left\{\frac{(x_{ij}-x_{ik})}{(x_{ij}+x_{ik})}\right\}^2} \tag{2}$$

PCC and COD can be interpreted either individually or together to understand temporal and spatial variations in species concentrations (Krudysz et al., 2008). A background monitoring station with ideally no contributions from local sources could provide a reference concentration time series to gauge variability across a network. In the absence of a well characterized background site, variability using PCC and COD is typically interpreted in a relative sense between site-pairs (Pinto et al., 2004). These metrics are impacted by several factors influencing the measured concentrations at a site, including the mix of source emissions occurring on one or more spatial scales (e.g. local point sources, urban-scale sources such as traffic, and regionally transported emissions). If concentration levels are dominated by regional transport, there might be only minor variations in the metrics between site-pairs. While this does capture the true concentration relationship between the sites, it also obscures the use of such metrics to gain deeper insights into the drivers for the differences that do exist.

To examine the spatial variability in arsenic and other air toxic metals across the Missouri portion of Metropolitan St. Louis, a four site monitoring network was established during the year 2008 under the United States Environmental Protection Agency (USEPA) funded Community Air Toxics program. In this study (hereafter called the Air Toxics Study), the concentration datasets were examined to identify local point sources contributing to spatiotemporal variability. Exploratory tools were investigated to take advantage of PCC's ability to track temporal similarity and COD's ability to gauge concentration homogeneity between site-pairs. Concentrations measured across the network were utilized to construct a time series for a network-wide baseline concentration to differentiate the relative contribution of local sources from larger-scale sources that impact the entire network. Site-specific peak arsenic concentrations were combined with meteorological data to estimate the local emission source zones, and were evaluated against known arsenic source locations listed in the 2008 National Emission Inventory (NEI) (USEPA, 2008). Other air toxic metals measured during the study were also examined to investigate the strengths and limitations of the proposed methodology for gauging spatiotemporal variability in species concentration and to identify emission source zones using a network of sites.

2. Method

2.1. Dataset

Fig. 1 shows the four site monitoring network where PM_{10} samples were collected at one-in-three day frequency during 2008. Two urban sites, Blair St. and Hall St., were located in the City of St. Louis at ~3 and 7 km north of the urban core, respectively, near the industrialized Mississippi Riverfront. The two suburban sites, Washington University in St. Louis (WUSTL) and Arnold, were located ~10 km west and 25 km southwest of the urban core, respectively. All sites had at least 95% data completeness for the 122