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Mapping and modeling airborne urban phenanthrene distribution using vegetation biomonitoring

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HIGHLIGHTS

- We examine the spatial distribution of phenanthrene using vegetation biomonitoring.
- Phenanthrene concentrations in Fresno show significant spatial clustering.
- The major sources of phenanthrene in our data in Fresno are highways and railroads.

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ABSTRACT

To capture the spatial distribution of phenanthrene in an urban setting we used vegetation biomonitoring with Jeffrey pine trees (*Pinus jeffreyi*). The major challenge in characterizing spatial variation in polycyclic aromatic hydrocarbon (PAH) concentrations within a metropolitan area has been sampling at a fine enough resolution to observe the underlying spatial pattern. However, field and chamber studies show that the primary pathway through which PAHs enter plants is from air into leaves, making vegetation biomonitoring a feasible way to examine the spatial distribution of these compounds. Previous research has shown that phenanthrene has adverse health effects and that it is one of the most abundant PAHs in urban air. We collected 99 pine needle samples from 91 locations in Fresno in the morning on a winter day, and analyzed them for PAHs in the inner needle. All 99 pine needle samples had detectable levels of phenanthrene, with mean concentration of 41.0 ng g^{-1}, median 36.9 ng g^{-1}, and standard deviation of 28.5 ng g^{-1} fresh weight. The ratio of the 90th:10th percentile concentrations by location was 3.3. The phenanthrene distribution had a statistically significant Moran's *I* of 0.035, indicating a high degree of spatial clustering. We implemented land use regression to fit a model to our data. Our model was able to explain a moderate amount of the variability in the data ($R^2 = 0.56$), likely reflecting the major sources of phenanthrene in Fresno. The spatial distribution of modeled airborne phenanthrene shows the influences of highways, railroads, and industrial and commercial zones.

1. Introduction

In order to capture the short-term spatial distribution of airborne polycyclic aromatic hydrocarbons (PAHs) in an urban setting we employed a vegetation biomonitoring approach using Jeffrey pine trees (*Pinus jeffreyi*) in Fresno, California. Other researchers have used vegetation biomonitoring for examining local source–receptor relationships (Hwang and Wade, 2008; Lehndorff and Schwark, 2004; Meharg et al., 1998), whereas our primary interest is to establish the magnitude and shape of the PAH spatial distribution to inform future air monitoring studies and exposure assessment in epidemiology studies. Because PAH concentrations vary widely within most urban areas and because air sampling for PAHs is a labor-, equipment-, and time-intensive task, urban air monitoring has been limited to relatively few simultaneous sampling locations (Guo et al., 2003; Manoli et al., 2004; Noth et al., 2011; Thornhill et al., 2008). We elected to use a vegetation biomonitor because it potentially offers a convenient, available, and reliable passive monitor for characterizing PAHs.

We have focused our research on vapor-phase phenanthrene, the second most abundant airborne PAH in the environment and the PAH implicated in multiple adverse health outcomes (Gale et al., 2012; Miller et al., 2004; Nadeau et al., 2010; Tsien et al., 1997). PAHs are ubiquitous toxic air pollutants with complex

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spatial distributions. Major sources for ambient PAHs are open biomass burning, residential heating, power generation, trains, ships, motor vehicles, and industrial processes (EPA, 1998; Jenkins et al., 1996). Multiple studies in urban and suburban settings have shown phenanthrene to have the highest airborne concentrations of the 16 EPA PAHs, excepting naphthalene (Rogge et al., 2011; Zhu and Jia, 2012). Additionally, in personal exposures to PAHs the concentration of phenanthrene is the highest for PAH with three or more rings when compared either for total (vapor- and particle-phase), or vapor-phase (Li et al., 2010; Nethery et al., 2012).

PAHs are well-known to be carcinogenic individually and in mixtures (International Agency for Research on Cancer, 1987), but there is an extensive literature developing that implicates phenanthrene as a toxic agent in adverse health outcomes from subclinical immunological changes through asthma and wheeze. Phenanthrene exposure in *ex vivo* human studies caused the conversion of regulatory T-cells to pro-allergic Th-2 effector T-cell phenotype, which is associated with allergic asthma (Liu et al., 2013). *In vitro* studies by Schober et al. (2006, 2007) demonstrated that phenanthrene enhanced the allergic reaction to birch pollen by strongly inducing basophils taken from birch pollen allergic patients, significantly enhancing cytokine secretion (IL-4 and IL-8), and significantly enhancing histamine release (Schober et al., 2006, 2007). Furthermore, phenanthrene exerts these same pro-allergic effects on sensitized basophils from allergic individuals even in absence of the allergen itself (Lubitz et al., 2010). Phenanthrene has also been shown to enhance the allergic response to ragweed in ragweed-sensitive subjects by increasing IgE synthesis following *in vivo* human nasal challenge (Saxon and Diaz-Sanchez, 2000). Nadeau et al. (2010) have demonstrated an association between airborne PAH exposure and decreased FEV_1, increased asthma severity, and suppression of regulatory T-cell function through methylation of the FoxP3 gene (Nadeau et al., 2010). Gale et al. (2012) found significant associations with ambient phenanthrene exposure and wheeze in a cohort of 315 asthmatic children (Gale et al., 2012). In conclusion, evidence is accumulating that respiratory health can be seriously impacted by phenanthrene exposure.

The literature on vegetation biomonitoring for PAHs is well-developed. Chamber studies and field studies, controlled and observational, have been used to examine distributions of PAHs and other persistent organic pollutants (POPs) in vegetation and dependencies of vegetation concentrations on local sources. Controlled field and physico-chemical studies show that the primary pathway through which phenanthrene enters plants is from air into the leaves, and uptake from soil is negligible (Barber et al., 2004; Kipopoulou et al., 1999; Ryan et al., 1988; Simonich and Hites, 1995; Welsch-Pausch et al., 1995). For the purposes of using pine needles as passive samplers for vapor-phase phenanthrene, the inner needle concentrations provide the most stable and least variable concentrations. Minimizing the non-spatial variability is especially important because we wanted to focus on spatial variability. Vapor-phase phenanthrene can penetrate into the inner needle directly through the stomata or by diffusing through the outer waxy layer (Paterson et al., 1991; Schönherr and Riederer, 1989). Photolysis and photodegredation of PAHs contribute to the higher variability of the outer wax layer, relative to the inner needle (Niu et al., 2003; Simonich and Hites, 1995; Wang et al., 2005; Wild et al., 2005). Controlled experiments found that the half-life of PAHs in the outer needle surface of conifers was shorter by at least 50% than the half-life in the inner needle (Wild et al., 2005). The half-life for phenanthrene in the whole needle was found by Wang et al. (2005) to be 34.5 h Wenzel et al. (1998) show that analysis of the inner needle results in good precision, with relative standard deviations under 20% (Wenzel et al., 1998), and that most of the total phenanthrene measured in the needle is present in the inner needle compartment. Experiments show that the majority of phenanthrene is present in the inner needle portion of 2-year old *Pinus sylvestris* L. needles collected in urban environments in Argentina and Germany (mean = 73% of total needle phenanthrene concentration is from the inner needle) (Wenzel et al., 1998) and in Germany and Russia (mean = 73% of total needle phenanthrene concentration is from the inner needle) (Wenzel et al., 1998).

Field studies show that accumulation of PAHs in leaves is sensitive to variations and changes in air concentration (Alfani et al., 2001, 2005; Hwang et al., 2003; Hwang and Wade, 2008; Lehndorff and Schwark, 2004; Wagrowski and Hites, 1997). Wagrowski and Hites (1997), Hwang et al. (2003), Hwang and Wade (2008), Alfani et al. (2001, 2005) and Lehndorff and Schwark (2004) each collected and analyzed vegetation for PAH concentrations and found an increasing concentration gradient along the rural-urban gradient. Additionally, Hwang and Wade (2008) and Meharg et al. (1998) show that point sources can be detected in vegetation concentrations (Hwang and Wade, 2008; Meharg et al., 1998). Hwang and Wade (2008) found that two sites located in Houston, Texas, USA near the "largest petrochemical complex in the United States," had very high concentrations of PAH in pine needles (*Pinus taeda*) when compared to samples collected in other parts of the Houston metropolis. Meharg et al. (1998) showed that phenanthrene concentrations in grasses downwind from a large chemical fire were up to 67 times the concentrations in grasses upwind.

The goal of this research was to use Jeffrey pines (*P. jeffreyi*) to characterize the spatial distribution of one of the more volatile PAHs, phenanthrene, in Fresno, California, USA. We selected phenanthrene because of the research showing a relationship between exposure and health outcomes and because it is one of the most abundant of the PAHs in ambient air. The general approach was to obtain a cross-sectional dataset of PAHs at approximately 100 locations and use regression modeling with land use, traffic data, and other neighborhood characteristics to build a spatial model of phenanthrene concentrations for Fresno, CA.

2. Methods

2.1. Field collection

Two methods informed the choice of locations for pine needle sampling. In the first method, systematic sampling of the grid of 1-square mile United States Public Land Survey System (PLSS) blocks was used to capture the spatial range of ambient PAH concentrations throughout Fresno. Fresno contains approximately 150 PLSS blocks. This number was reduced to 42 blocks by selection of alternating blocks within each row of blocks. Each selected 1-square mile block was visited and the locations of Jeffrey pine trees were recorded on a paper map and electronically with a Garmin eTrex GPS device (Olathe, KS, USA).

In the second method, a "demand" surface was created that indicated areas of Fresno with high density of participants in the Fresno Asthmatic Children's Environment Study (FACES) and where PAH concentrations were likely to be very high or very low (Noth et al., 2011). FACES is an epidemiology study that examines the relationship between asthma attacks and air pollutant concentrations. Our results will inform future collection of air monitoring data for epidemiology studies such as FACES, therefore the population density of participants is of particular interest. The demand surface used traffic density as a proxy for PAH concentrations. The traffic count data used roadway locations from the TeleAtlas MultiNet™ USA (TAMN) roadway database and the annual average daily traffic (AADT) count from the California Department of Transportation for vehicle activity data (Margolis et al., 2009). The