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## Near-road enhancement and solubility of fine and coarse particulate matter trace elements near a major interstate in Detroit, Michigan



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## HIGHLIGHTS

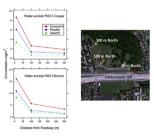
- $\bullet$  Compared near-road spatial gradients and solubility for  $PM_{2.5}$  and  $PM_{10\text{-}2.5}$  elements.
- PM<sub>2.5</sub> and PM<sub>10-2.5</sub> metals were elevated within 100 m of major roadway when downwind.
- Traffic, industrial, and regional sources impacted roadside PM<sub>2.5</sub> and PM<sub>10-2.5</sub>
- Metals indicative of brake wear (Ba, Cu) had largest increases near roadway.
- Water-soluble PM<sub>2.5</sub> and PM<sub>10-2.5</sub> metals were enhanced in the near-road environment.

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



## ABSTRACT

Communities near major roadways are disproportionately affected by traffic-related air pollution which can contribute to adverse health outcomes. The specific role of particulate matter (PM) from traffic sources is not fully understood due to complex emissions processes and physical/chemical properties of PM in the near-road environment. To investigate the spatial profile and water solubility of elemental PM species near a major roadway, filter-based measurements of fine (PM<sub>2.5</sub>) and coarse (PM<sub>10-2.5</sub>) PM were simultaneously collected at multiple distances (10 m, 100 m, and 300 m) from Interstate I-96 in Detroit, Michigan during September–November 2010. Filters were extracted in water, followed by a hot acid extraction, and analyzed by magnetic sector field high resolution inductively coupled plasma mass spectrometry (HR-ICPMS) to quantify water-soluble and acid-soluble trace elements for each PM size fraction. PM<sub>2.5</sub> and PM<sub>10-2.5</sub> species measured in the near-road samples included elements associated with traffic activity, local industrial sources, and regional pollution. Metals indicative of brake wear (Ba, Cu) were dramatically enriched near the roadway during downwind conditions (factor of 5 concentration increase), with the largest increase within 100 m of the roadway. Moderate near-roadway increases observed for regional PM species (S). Water solubility varied by PM species and size, and for PM<sub>2.5</sub> included highly (S,

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K, Ca, Mg, Zn, Ba), moderately (Cu, Mn, Sb, Pb), and minimally (Fe, Ti) water-soluble species, with lower water solubility for most species in  $PM_{10-2.5}$ . Results from this study indicate that water-soluble  $PM_{2.5}$  and  $PM_{10-2.5}$  metals, particularly from brake/tire wear, were enhanced in the near-roadway environment which may have human health implications.

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## 1. Introduction

Traffic-related air pollution consists of a complex mixture of gaseous and particulate species, including nitrogen oxides, carbon monoxide, carbonaceous particles, ionic species, and trace metals. Due to potentially prolonged exposure to these pollutants, living near a roadway has been linked to an elevated risk of asthma exacerbations, pulmonary decrements, cardiovascular events, diabetes, mortality and adverse birth outcomes (Health Effects Institute, 2010). In addition to public health concerns, medical expenses associated with near-road pollution impose a large financial burden on affected households (Brandt et al., 2014). Given that a large fraction of the U.S. population (up to 20% based on 2010 US Census) lives within 100 m of a busy roadway (Rowangould, 2013; Tian et al., 2013), there has been increased public health interest in understanding the properties of traffic-related air pollution and the extent to which this pollution affects the welfare of near-road communities.

Of the pollutants within the traffic mixture, determining the health effects of particulate matter (PM) has been challenging because it originates from a number of processes including combustion, vehicle wear and resuspension of road dust, which emit different chemical species with varying physical properties and toxicities. Fuel and lubricating oil combustion generally emit ultrafine PM ( $<0.1 \mu m$  mass median aerodynamic diameter) or PM<sub>2.5</sub>  $(<2.5 \,\mu m)$  as carbonaceous particles along with trace elements such as Zn and S (Pant and Harrison, 2013). Resuspension of road dust as well as mechanical abrasion of brakes and tires emit particles in multiple size ranges including  $\text{PM}_{2.5}$  and  $\text{PM}_{10\text{-}2.5}$  (between 2.5 and 10 µm) comprised of metals (Harrison et al., 2012). The complex physicochemical nature of near-road PM may contribute to its toxicity (Cho et al., 2009; McGee et al., 2015). For example, redoxactive metals (Fe, Cu) or organic PM species present in the traffic mixture can participate in mechanisms forming toxic byproducts, such as reactive oxygen species (ROS) which have been linked to oxidative damage in biological systems (Pardo et al., 2016; Valavanidis et al., 2013; Ghio et al., 2012). The ROS-forming capacity of these components may be influenced by particle size or the degree to which these species are soluble in water, thereby bioavailable to humans (Saffari et al., 2014; Boogaard et al., 2012). While many factors (e.g., water solubility, chemical composition) are hypothesized to influence PM toxicity, limited information exists on the physicochemical properties inherent to PM near the roadway. Characterizing the unique properties of traffic-related PM is essential to understanding the connection between PM exposure and health effects among individuals living close to the roadway (Cassee et al., 2013).

Previous research demonstrate pollutant concentration gradients near roadways, however, only a small subset of these studies have characterized spatial profiles of PM species, particularly the elemental portion of PM which may have unique impacts on human health. Studies examining dispersion of PM species near the roadway indicate a general enrichment closer to the roadway often comparing roadside concentrations to levels far downwind of the roadway (Pant and Harrison, 2013). While these studies provide insight to urban-scale variability of PM traffic pollution, they offer less information on concentration changes over small spatial scales near the roadway (within 10-100 m of the roadway). Pollutant concentrations within this microscale spatial buffer can vary substantially (Karner et al., 2010), which in turn affect the extent to which nearby communities are exposed to traffic-related pollution. In addition, near-road PM characterization research has largely focused on carbon-containing components emitted by combustion processes such as tailpipe exhaust. Fewer studies have reported measurements of PM constituents from non-exhaust emissions such as mechanical wear and resuspension of road dust which are generally comprised of metals. Furthermore, quantifying the contribution of non-exhaust (brake/tire wear) to total mobile source emissions near the roadway is becoming increasingly important as exhaust emissions continue to decline as a result of existing and emerging control technologies (Grigoratos and Martini, 2015; Denier van der Gon et al., 2013) and the increasing adoption of hybrid and electric vehicles (IEA, 2013).

In this study, our goal was to quantify PM<sub>2.5</sub> and PM<sub>10-2.5</sub> trace element composition and water solubility near a heavily trafficked interstate highway in Detroit, Michigan, USA. The study location is representative of a typical busy interstate in the U.S. We characterized fine-scale spatial profiles of individual PM species within 300 m of the roadway by size fraction and solubility to determine whether elemental PM species have different solubility and spatial gradients near the roadway that are related to PM size fraction and emission source. This study provides novel information about impacts from traffic-related PM that can be used to evaluate the role of elemental PM species in eliciting near-road health effects which continues to draw significant scientific concern due to health effect disparities among near-road communities.

## 2. Methods

### 2.1. Near-road PM sample collection

PM samples and meteorological measurements were collected at three air pollutant monitoring sites located in the Eliza Howell Park adjacent to Interstate-96 in Detroit, MI. The monitoring sites were established as part of a collaborative research study conducted by the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Transportation Federal Highway Administration (FHWA) (US EPA, 2013), and concurrently used as part of EPA's Near-road Exposures and Effects of Urban Air Pollutants Study (NEXUS) (Vette et al., 2013). This specific link of Interstate-96 is characterized by high traffic volume (~160,000 Annual Average Daily Traffic, AADT), with generally level to gently down-sloping terrain and no roadside barriers present. The monitoring sites were located within a large grassy area of the park to the north of Interstate-96 at approximately 10 m, 100 m, and 300 m from the center lane of traffic as shown in Fig. 1. Identical trailers were used at each site for the monitoring equipment, with sample inlets approximately 3 m from the ground. Measurements from the 10 m N monitoring site were considered most representative of roadside concentrations; thus, the 10 m N monitor is referred to as

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