



Metal concentrations and soluble iron speciation in fine particulate matter from light rail activity in the Denver–Metropolitan area

Benton T. Cartledge, Brian J. Majestic

Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado 80208-9020, United States

ABSTRACT

Fine particulate matter samples (PM_{2.5}) were collected from three locations around the Denver–Metropolitan area to study the impacts of the ground–level light rail on airborne metal concentrations. Size–segregated PM was collected on board the trains, at the side of the tracks, and at a background location in downtown Denver. Results from this study showed highest crustal enrichment factors of metals in samples collected on board the train, despite lower concentrations of total PM_{2.5}. Metals commonly found in steel such as Fe, Cr, Mn, and Ni, all exhibited elevated concentrations relating to train activity over the background site. Iron in the PM_{2.5} at track–side and on board the trains was above the background by a factor of 1.89 and 1.54, respectively. For Mn, the ratios were 1.34 for the track–side and 0.94 for the on board samples. Cr and Ni exhibited higher ratios over the background only in samples collected on board the trains at 1.59 (Cr) and 1.26 (Ni). Soluble metals were measured with Ni (53–71%), Cu (52–81%), and Zn (30–81%) exhibiting the highest solubilities across the different sites. Soluble Fe ranged from 8–15% for the total measured Fe, indicating a non–crustal source of Fe. Soluble Fe was also characterized as Fe(II) and Fe(III) with 87–90% of the soluble Fe being Fe(II), similar to results from studies in Los Angeles, CA and East St. Louis, IL but higher than in Atlanta, GA and Waukesha, WI.

Keywords: PM_{2.5}, elemental concentration, soluble elements, iron speciation, ICP–MS



Corresponding Author:

Brian J. Majestic

☎ : +1-303-871-2986

📠 : +1-303-871-2254

✉ : brian.majestic@du.edu

Article History:

Received: 31 August 2014

Revised: 04 December 2014

Accepted: 05 December 2014

doi: 10.5094/APR.2015.055

1. Introduction

Railway based transportation systems are becoming a more widely used method of mass transportation as cities continue to grow and become less centralized. The long–term exposure to particulate matter (PM) from subway and light rail transit systems has been of special interest as more of these types of transportation systems are developed. Railway studies in New York City (Chillrud et al., 2004; Chillrud et al., 2005), Los Angeles (Kam et al., 2011a; Kam et al., 2011b; Kam et al., 2013), Barcelona (Querol et al., 2012), Mexico City (Mugica–Alvarez et al., 2012), Helsinki (Aarnio et al., 2005), Tokyo (Furuya et al., 2001), Budapest (Salma et al., 2007), Stockholm (Johansson and Johansson, 2003; Karlsson et al., 2005), Hong Kong (Chan et al., 2002), Buenos Aires (Murrini et al., 2009), Seoul (Kim et al., 2008; Kim et al., 2014), Taipei (Cheng and Lin, 2010), Paris (Raut et al., 2009), and London (Adams et al., 2001; Seaton et al., 2005) have shown elevated levels of PM_{2.5} as a result of train activities relative to urban ambient conditions. In many cases, increased concentrations over the background of chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), and copper (Cu) have been observed in PM collected from these systems (Furuya et al., 2001; Chillrud et al., 2004; Aarnio et al., 2005; Chillrud et al., 2005; Salma et al., 2007; Kam et al., 2011b; Mugica–Alvarez et al., 2012; Kam et al., 2013). PM from these rail systems is generated by the frictional processes and wearing between the wheels, rails and brakes. Since all rail–based transit systems vary greatly from each other, results from one system do not always apply to another system (Kam et al., 2011b).

Large amounts of research have linked chronic exposure to PM and certain metals to a wide array of diseases and cancers

through the formation of reactive oxygen species (ROS) and oxidative stress on the respiratory system (Goldsmith et al., 1998; Tao et al., 2003; Prophete et al., 2006; Landreman et al., 2008; Verma et al., 2010). The studies performed in Los Angeles (Kam et al., 2011b) and Stockholm (Karlsson et al., 2005) have studied the effects of PM samples collected from rail systems on oxidative stress and ROS activity in alveolar macrophage cells. Per unit mass, Kam et al. (2011b) showed that ROS activity increased by 13% from the samples collected on the ground–level light rail. However on a per volume of air basis, which was used to represent personal exposure, the subway samples exhibited higher ROS activity by 55–65% (Kam et al., 2011b). The study in Stockholm found that the PM collected from the subway was eight times more genotoxic than other PM and more likely to cause oxidative stress to lung cells (Karlsson et al., 2005). Studies have also shown links to ROS activity from the soluble fraction of PM (Verma et al., 2010) as well as the particle size (Hu et al., 2008).

Iron (Fe) is of particular interest as it is the most abundant transition metal in the atmosphere and the fourth most abundant element in the Earth's crust (Johansen et al., 2000; Jickells et al., 2005). Fe has also been identified as a component of PM that leads to the formation of ROS through Fenton chemistry (Goldsmith et al., 1998; Prophete et al., 2006). The study performed in the Stockholm subway showed that the mass of the particle was dominated by Fe and related this finding to the genotoxicity of the subway samples (Karlsson et al., 2005). The redox activity of Fe and the ability of intracellular formation of ROS has also been related to the amount of Fe in the soluble fraction (Kam et al., 2011b) as well as the Fe speciation [soluble Fe(II) or Fe(III)] (Halliwell and Gutteridge, 1986; Faiola et al., 2011).

This study focuses on the measurement of metals and soluble Fe speciation in $PM_{2.5}$ (particles with an aerodynamic diameter less than $2.5\ \mu m$) across all five lines of the Regional Transportation District (RTD) light rail system in the Denver–Metropolitan area, CO, USA. Due to the complex nature in which PM can affect the respiratory system and the wide array of differences in railway systems, it is important to study transit systems individually; especially in the pretenses of this study as Denver's light rail is completely at ground level and most previous studies have focused on underground systems. Samples were collected on board the trains, track-side, and at a downtown location 0.28 km from the tracks. In all three locations, $PM_{2.5}$ mass, size-fractionated total metals, soluble metals, soluble Fe(II), and soluble Fe(III) are reported. This is the first study to report soluble Fe redox speciation potentially originating from a light rail system. In addition, this is the first manuscript to report soluble Fe speciation in the city of Denver, CO. As mentioned previously, soluble Fe speciation has implications on ROS production in the lungs, and the understanding of Fe speciation in PM is extremely limited in all but a few urban areas around the USA.

2. Experimental Section

2.1. Sampling methods

Samples were collected at three locations: first, on board trains running on each line and second, at two stationary sites, one northeast and one southwest of downtown Denver, CO, USA. The track-side stationary site southwest of downtown was located at ground-level 1 m from the tracks where all five lines entered and exited downtown Denver. Figure 1 shows a map of the relative location of the sample collection sites. At this site, all trains passing through this area were braking to pass through curves leading into the downtown area. Also, southbound trains (leaving downtown) were frequently stopped here to let northbound trains pass due to the track alignment that forced them to cross the northbound tracks. On average, 31 trains pass through this area per hour during the time frame used for sample collection. The site located to the northeast of downtown Denver was located at a Colorado Department of Public Health and Environment air monitoring station, which represents urban ambient conditions. This site is 0.28 km from the nearest light rail tracks. The samples collected on board the trains were collected on each of the five train lines every day of the sample collection periods. A sampler was attached to a backpack and placed in a seat away from the doors. Samples were only collected while on the train and not on the platform.

At all sites, PM samples were collected three times a week from January 24 to February 16, 2012 using 5 Sioutas Personal Cascade Impactor Samplers (PCIS, SKC Inc.) (Misra et al., 2002; Singh et al., 2003). Two samplers were co-located at each stationary site (downtown and track-side) and one was carried onboard the trains. The PCIS, operating at $9\ L\ min^{-1}$ collected size-resolved PM fractions in five different stages: >2.5 , $2.5-1$, $1-0.5$, $0.5-0.25$, and $<0.25\ \mu m$. However, only the $PM_{2.5}$ fraction, the four smallest size fractions, was analyzed in this study. Samples at the two stationary sites were collected for 14 hours a day, while on-train samples were collected simultaneously for 12 hours a day. This time scale allowed for the collection of samples before, during, and after both the morning and evening rush hours (6–9 am and 3–7 pm).

Acid-washed Teflon collection substrates for the largest four size fractions were $0.5\ \mu m$ pore size 25 mm Zefluor (Pall Life Sciences) filters, while $2.0\ \mu m$ pore size 37 mm Teflon (Pall Life Sciences) filters were used for the smallest size fraction. After each sampling period, substrates were removed, placed into acid-washed Petri dishes, and into a freezer at $-18\ ^\circ C$. Field blanks were also collected at each site at the beginning of each sampling period.

2.2. Gravimetric analysis

Prior to and following sampling, all four sets of filters (112 filters in all) were equilibrated for 24 h in a constant temperature ($23-24\ ^\circ C$) and humidity (31–33%) environment and weighed on a microbalance (MX5, Mettler-Toledo; uncertainty $\pm 5\ \mu g$). Field blanks were collected prior to each sampling period and measured elemental concentrations were subtracted from the elemental concentrations of the samples. The $PM_{2.5}$ mass was determined by summing the masses of the four smallest size fractions. The gravimetric measurements were compared to an on-site tapered element oscillating microbalance (TEOM) collecting $PM_{2.5}$ mass data every hour at the background location.

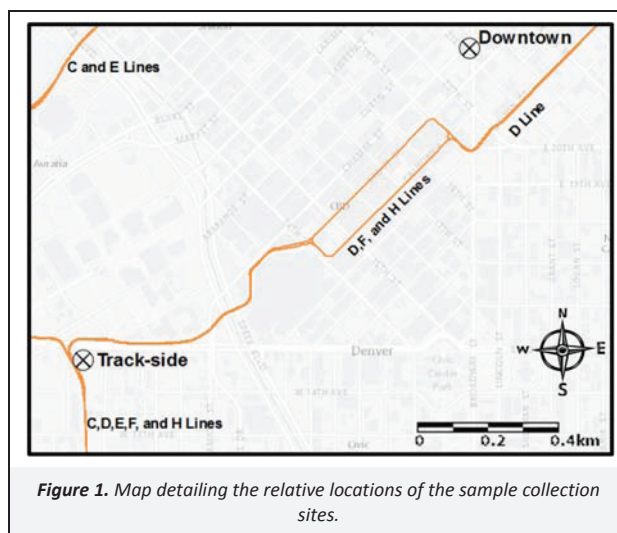


Figure 1. Map detailing the relative locations of the sample collection sites.

2.3. Total metal analysis

With two sets of samples from each stationary site, one set was used for total metals analysis while the other set was used to assess soluble metal concentrations. The filters for the samples collected on board the trains were cut in half in order to perform both total and soluble metals analyses. Solubilization of the metals was achieved using a microwave digestion system (Ethos EZ, Milestone, Inc). Samples were digested in a Teflon vial using 750 μL nitric acid (Fisher), 250 μL hydrochloric acid (Fisher), 100 μL HF (Fisher), and 100 μL hydrogen peroxide (Fisher). All acids and the hydrogen peroxide were trace-metal grade purity. Samples were digested in Teflon vessels following a temperature program of a 9 minute ramp to $180\ ^\circ C$, a hold at $180\ ^\circ C$ for 10 minutes, and a 60 minute cool-down period. Following digestion, samples were diluted to 15 mL using Milli-Q ($18.2\ M\Omega\text{-cm}$) water and analyzed via quadrupole inductively-coupled plasma mass spectrometry (ICP-MS, Agilent 7700) using indium as internal standard and a He collision cell to remove polyatomic interferences. Detection limits via PCIS collection and ICP-MS analysis have been previously studied and are near $1\ ng\ m^{-3}$ for most metals (Majestic et al., 2008).

Standard reference materials (SRMs) were also digested by this same process. The two SRMs used were Urban Particulate Matter (1648a, NIST), to represent the anthropogenic portion of the sample, and San Joaquin Soil (2709a, NIST), to represent the crustal portion of the sample. The acceptable percent recovery of elements from these SRMs was set at 80–120%. One of each SRM was digested per 21 samples as well as one method blank which consisted solely of the digestion matrix. Field blanks were also digested as samples using the method described above.

Download English Version:

<https://daneshyari.com/en/article/4434573>

Download Persian Version:

<https://daneshyari.com/article/4434573>

[Daneshyari.com](https://daneshyari.com)