

# Atmospheric Pollution Research

[www.atmospolres.com](http://www.atmospolres.com)


## 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<sub>2.5</sub>) 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<sub>2.5</sub>. 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<sub>2.5</sub> 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<sub>2.5</sub>, 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](mailto: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<sub>2.5</sub> 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<sub>2.5</sub> (particles with an aerodynamic diameter less than 2.5 μm) 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<sub>2.5</sub> 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<sup>-1</sup> collected size-resolved PM fractions in five different stages: >2.5, 2.5–1, 1–0.5, 0.5–0.25, and <0.25 μm. However, only the PM<sub>2.5</sub> 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 μm pore size 25 mm Zeffluor (Pall Life Sciences) filters, while 2.0 μm 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 °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 °C) and humidity (31–33%) environment and weighed on a microbalance (MX5, Mettler–Toledo; uncertainty ±5 μg). Field blanks were collected prior to each sampling period and measured elemental concentrations were subtracted from the elemental concentrations of the samples. The PM<sub>2.5</sub> 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<sub>2.5</sub> mass data every hour at the background location.

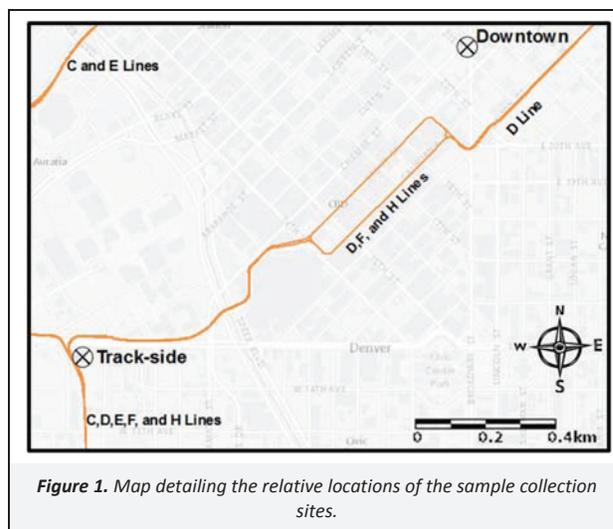


Figure 1. Map detailing the relative locations of the sample collection sites.

### 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 °C, a hold at 180 °C for 10 minutes, and a 60 minute cool-down period. Following digestion, samples were diluted to 15 mL using Milli-Q (18.2 MΩ-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<sup>-3</sup> 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.

## 2.4. Soluble metal analysis

For soluble metal analysis, the samples were extracted in 10 mL of a 0.5 mM acetate buffer (pH=4.25), to simulate cloud water, for two hours. The extracts were then filtered, acidified with HNO<sub>3</sub>, and analyzed using ICP–MS. The pH of the extract remained within 4.25±0.01 over the course of the extraction (Accumet Basic AB 15, Fisher Scientific).

## 2.5. Iron speciation analysis

Iron speciation analysis was performed using the soluble extracts and mixing 1.8 mL aliquots of extract (prior to acidification) with 0.2 mL of 5.88 μM Ferrozine reagent [(3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4',4''-disulfonic acid sodium salt), Sigma] (Stookey, 1970; Majestic et al., 2006). Using a 1 m liquid waveguide capillary cell spectrophotometer (LEDSpec, WPI, Inc.), the absorbance of the Fe(II)–Ferrozine complex was measured at 560 nm. Fe(II) concentration was determined using a calibration curve generated from stock Fe(II) solutions. Fe(III) was then determined by subtracting the Fe(II) concentration from the total Fe concentration obtained from ICP–MS analysis.

## 3. Results

Figure 2 shows the size distribution of PM<sub>2.5</sub> mass at all three sites. PM<sub>2.5</sub> mass was obtained by summing the four smallest size fractions. The highest PM<sub>2.5</sub> mass concentrations were measured at the track–side sampling site while the lowest mass concentrations were collected on board the trains. It was seen that the PM<sub>2.5</sub> concentrations collected at the downtown site were well correlated with the TEOM measurements made by the Colorado Air Monitoring Program (CAMP) at the same site (slope=1.109, R<sup>2</sup>=0.9999) indicating that the samplers were functioning properly (see the Supporting Material, SM, Figure S1). The geometric mean and standard deviation of the different size fractions were similar

at all three sampling locations as shown in Table S1 (see the SM) (Hinds, 1999).

Table 1 shows elemental concentrations and elemental ratios between sites. Na, Al, K, Ca, Fe, Cu, Zn, Sb, and Pb concentrations were higher than those measured in a recent study in Denver, CO, where PM<sub>2.5</sub> was collected at two elementary schools in residential neighborhoods (Clements et al., 2014). Of the measured elements in both studies, only As was measured at similar concentrations. In Table 1 it can also be seen that on board the train and even more so at track–side, there were higher ratios of Fe over the background site. For Fe, the ratios above the background site are 1.89 and 1.54 for the track–side and on board samples respectively. For Mn, another common element in steel, the ratios are 1.34 for the track–side but only 0.94 for the on board samples. Samples collected on board the trains also showed higher ratios over the background in Cr (1.59), Ni (1.26), and Zn (1.49), which were not as high at the track–side site.

The enrichment of the various metals was measured using the upper continental crust (UCC) enrichment factor (EF) calculated by first normalizing the data with aluminum and then dividing by the UCC ratio (Taylor and McLennan, 1995). The EF shows the extent that anthropogenic sources contribute to the metal concentrations and these are shown in Figure 3. The dashed line (EF=10) on the plot represents the level above which an element is considered to be contributed largely from anthropogenic sources. When the concentration of a particular element is normalized to Al, a predominately crustal element, the EF is calculated based on the naturally–occurring abundance of those elements. A high EF (EF>10) suggests a source of that particular metal that is not naturally occurring and a source that is most likely anthropogenic (Dasch and Wolff, 1989; Gerdol et al., 2000; Veysey et al., 2001). EF can be calculated as shown by Equation (1). The UCC ratio used in this calculation were determined by measuring the natural abundance of elements in sedimentary rocks (Taylor and McLennan, 1995).

**Table 1.** Total elemental concentrations at each site and site–to–site ratio for PM<sub>2.5</sub>. N=3 for all standard deviations

Site	Downtown (CAMP)	Track–Side (RTD)	On Board (LR)		
Element	Conc. (ng m <sup>-3</sup> )	Conc. (ng m <sup>-3</sup> )	Conc. (ng m <sup>-3</sup> )	RTD/CAMP	LR/CAMP
Na	170±110	110±50	180±120	0.65	1.06
Mg	36±16	30±9	33±21	0.83	0.91
Al	180±50	110±30	80±50	0.61	0.44
K	130±80	63±14	180±50	0.49	1.38
Ca	230±140	150±37	450±190	0.65	1.96
Sc	0.16±0.008	0.09±0.01	0.26±0.25	0.54	1.64
Ti	10.98±0.18	9.0±2.6	9.7±2.2	0.82	0.88
V	0.31±0.06	0.27±0.07	0.16±0.06	0.89	0.53
Cr	4±4	2.2±0.5	7±4	0.52	1.59
Mn	6±3	7.6±2.1	5.3±2.6	1.34 <sup>a</sup>	0.94 <sup>a</sup>
Fe	190±50	360±80	292±130	1.89 <sup>a</sup>	1.54 <sup>a</sup>
Co	0.10±0.03	0.10±0.02	0.16±0.10	1.03	1.56 <sup>a</sup>
Ni	1.8±1.3	1.12±0.07	2.2±1.7	0.63	1.26 <sup>a</sup>
Cu	90±70	30±3	41±16	0.33	0.46
Zn	38±23	30±5	57±25	0.79	1.49
As	0.20±0.17	0.19±0.10	0.15±0.08	0.97	0.72
Rb	0.23±0.10	0.19±0.06	0.17±0.04	0.85	0.72
Sr	1.2±0.5	1.5±0.4	1.4±1.0	1.25	1.18
Mo	0.08±0.03	0.09±0.03	0.11±0.04	1.07	1.34
Cd	0.9±0.5	0.65±0.15	1.3±0.7	0.68	1.36
Sn	27±18	17.1±2.6	23±13	0.63	0.85
Sb	1.4±0.4	1.39±0.23	1.7±0.6	0.96	1.17
Ba	9±3	15.1±1.9	11.8±2.9	1.67	1.30
Pb	2.1±0.4	1.58±0.20	1.4±0.4	0.75	0.64

<sup>a</sup> Represents statistical difference (p<0.05) in the enrichment factor (Figure 3)

$$Enrichment\ Factor = \frac{[M]_{sample}/[Al]_{sample}}{[M]_{UCC}/[Al]_{UCC}} \quad (1)$$

There is significant enrichment of several trace metals such as antimony (Sb) and cadmium (Cd). This is expected from an urban area as automobile brake dust is a common source of Sb, and Cd has been linked to numerous urban sources (Lough et al., 2005; Majestic et al., 2009; Saffari et al., 2013). One compelling observation made from Figure 3 is that the enrichment factor for all elements is highest for the samples collected on the train. A few exceptions are Fe, Ba, and As where the enrichment factors were similar for samples collected on board and track-side, but still greater than the urban background found at the CAMP site. The enrichment factors for copper at the downtown site and on board the trains were very similar as well. The fact that the enrichment factors are higher on board the trains is interesting because the overall PM<sub>2.5</sub> concentrations on the trains were over two times smaller than those at the other site (Figure 2).

In order to further investigate this observation, the masses of all elements measured were summed and divided by the overall

sample mass. It was determined that the measured metals, those shown in Table 1, made up (25±10)% of the sample mass, 1 400±700 ng m<sup>-3</sup>, collected on board the trains. These metals only contributed (9.6±2.4)% of the total sample mass, 1 100±400 ng m<sup>-3</sup>, at the downtown site. The track-side location had the smallest mass percent of metals in the PM (7±3)%, 900±70 ng m<sup>-3</sup>. It is possible that the higher elemental concentration in the samples collected on board the trains is a result of these samples being collected in an enclosed environment which allowed the elements to become more concentrated unlike at the other sites.

Since soluble metals are more often linked to the adverse health effects of metals in PM, soluble metal concentrations were also determined. Figure 4 shows the percent solubility of selected trace elements that exhibited noticeable solubility. In most cases, the percent solubility of the selected elements were statistically similar at all three sites. Notable exceptions are Zn, As, and Sb which exhibited lower percent solubility in the samples collected on board the trains. In these cases, the percent solubility is noticeably lower than those in the samples collected downtown or track-side.

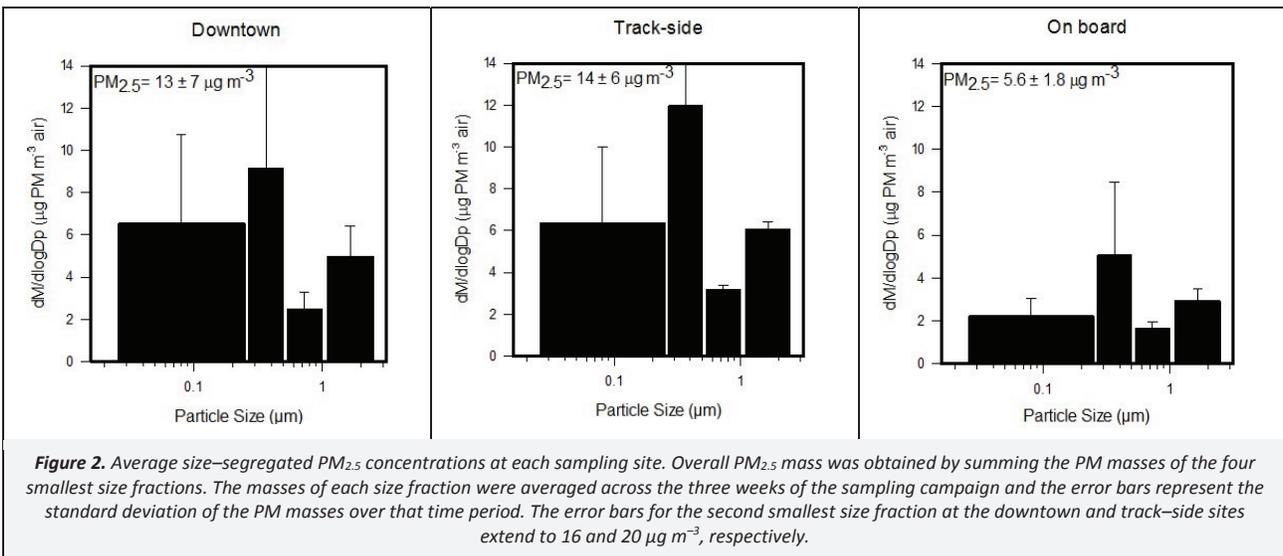


Figure 2. Average size-segregated PM<sub>2.5</sub> concentrations at each sampling site. Overall PM<sub>2.5</sub> mass was obtained by summing the PM masses of the four smallest size fractions. The masses of each size fraction were averaged across the three weeks of the sampling campaign and the error bars represent the standard deviation of the PM masses over that time period. The error bars for the second smallest size fraction at the downtown and track-side sites extend to 16 and 20 µg m<sup>-3</sup>, respectively.

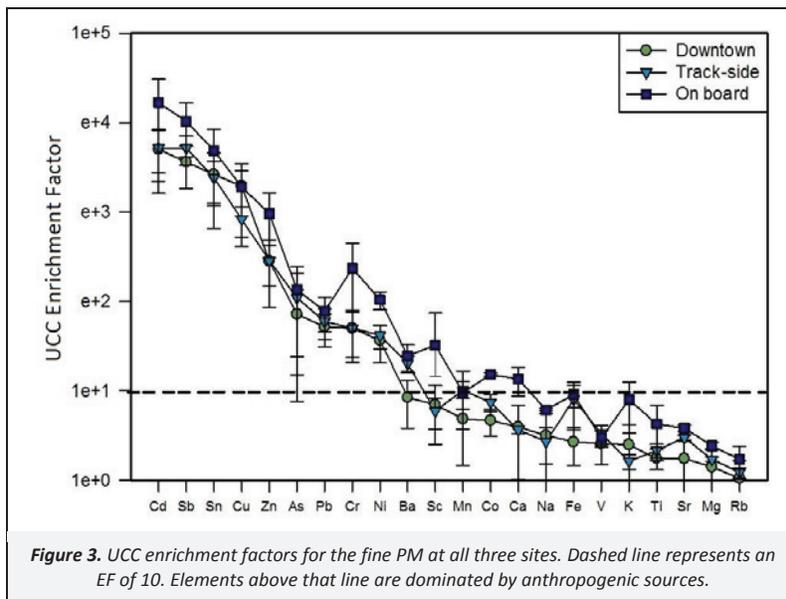
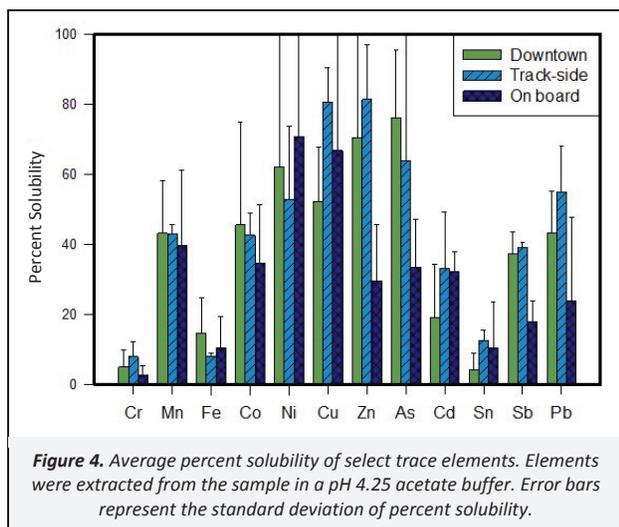


Figure 3. UCC enrichment factors for the fine PM at all three sites. Dashed line represents an EF of 10. Elements above that line are dominated by anthropogenic sources.

The speciation of the soluble Fe was also investigated and is shown in Figure 5 separated by particle size. It can be seen that Fe(II) comprised the overwhelming majority of the Fe present in the soluble fraction. Soluble Fe concentrations downtown were  $29 \pm 26 \text{ ng m}^{-3}$  or (14 $\pm$ 10)% of the Fe collected. Track-side soluble Fe concentrations were similar to that of the samples collected downtown at  $28 \pm 6 \text{ ng m}^{-3}$  but only (7.9 $\pm$ 0.9)% of the total Fe collected. The samples collected on board the trains also contained similar concentrations of soluble Fe,  $23 \pm 16 \text{ ng m}^{-3}$  or (10 $\pm$ 9)% of the total Fe in the sample. Of the soluble Fe, 87–90% of the Fe was present as Fe(II) across all three locations. The percent solubility of Fe has been studied on a global scale and has been determined to be 0.5–2% for Fe originating from crustal sources; the Fe percent solubility measured in this study is much greater than that (Sholkovitz et al., 2012), indicating a significant presence of anthropogenically produced Fe at all sites.

#### 4. Discussion

Both ground-level and underground rail systems have been previously linked to increased concentrations of metals in PM<sub>2.5</sub>. The overwhelming majority of these studies have focused on underground subway systems (Furuya et al., 2001; Chan et al., 2002; Johansson and Johansson, 2003; Chillrud et al., 2004; Aarnio et al., 2005; Chillrud et al., 2005; Karlsson et al., 2005; Seaton et al., 2005; Salma et al., 2007; Mugica-Alvarez et al., 2012; Querol et al., 2012), with only a few studies including ground-level light rail (Adams et al., 2001; Chan et al., 2002; Kam et al., 2011b; Kam et al., 2013). Also, the present study is the first to measure soluble Fe speciation in samples collected from railway sources in the Denver–Metropolitan area.



A number of researchers have presented PM<sub>2.5</sub> concentrations for samples collected inside the train cabins on both underground and ground-level rail systems (Adams et al., 2001; Chan et al., 2002; Aarnio et al., 2005; Kim et al., 2008; Cheng and Lin, 2010; Kam et al., 2011a; Querol et al., 2012; Kim et al., 2014). The average PM<sub>2.5</sub> concentrations for samples collected in the trains ranged from  $11 \mu\text{g m}^{-3}$  in Barcelona (Querol et al., 2012) to  $247 \mu\text{g m}^{-3}$  in London (Adams et al., 2001). When only considering ground level trains the range of average PM<sub>2.5</sub> concentrations is  $14 \mu\text{g m}^{-3}$  in Los Angeles (Kam et al., 2011a) to  $46 \mu\text{g m}^{-3}$  in Hong Kong (Chan et al., 2002). The PM<sub>2.5</sub> concentration in samples collected on board the trains in the present study are far less than those reported elsewhere at  $5.6 \pm 1.8 \mu\text{g m}^{-3}$  which could be explained by the RTD light rail in Denver being newer than many other rail systems as its operations began in 1994.

Comparatively, the data from this study showed similar results in trace element concentrations in PM<sub>2.5</sub> as those studies that included ground-level light rail. Also, enrichment of certain trace elements as related to train activity were similar between studies as well. Figure 6 shows a comparison of the results from this study with those published by Kam et al. (2011b) from Los Angeles. With the exception of Fe which was measured at higher concentrations in Los Angeles, the concentrations of the metals were equal to or less than the samples collected at all sites in this study. While this shows many similarities between Denver and Los Angeles, it is important to note that direct comparisons between the two cities cannot be made as the rail systems are unique to each city and not all of the measured PM is a result of light rail activity.

Previous studies have suggested that many of these elements related to steel such as Fe, Mn, and Cr are enriched in PM<sub>10</sub> and PM<sub>2.5</sub> from rail systems through frictional wearing of the rails and components of the train cars such as wheels and brakes (Chillrud et al., 2004; Chillrud et al., 2005; Kam et al., 2011b). The results from this study (Table 1) also show enrichment of Fe above the background at both the track-side site and on board the trains. Mn was shown to be enriched at the track-side site while Cr was enriched in the samples collected on board the train. Ni, another common element in steel was also enriched in the on board samples. Mo, also found in steel, was measured and shown to be enriched in the samples collected on board. While PM from frictional processes has commonly been associated with PM<sub>10</sub>, several of the previous studies regarding railway transportation systems have shown increases in PM<sub>2.5</sub> above street-level and background locations (Furuya et al., 2001; Johansson and Johansson, 2003; Aarnio et al., 2005; Kam et al., 2011b; Mugica-Alvarez et al., 2012; Kam et al., 2013). PM<sub>2.5</sub> and PM<sub>10</sub> have been found to be highly correlated in Los Angeles suggesting similar sources (Kam et al., 2011a). This is further supported by the presence of a significant ultrafine mode resulting from brake wear (Garg et al., 2000). Also, PM<sub>2.5</sub> has been shown to have a greater impact than coarse particles on the negative health effects associated with the inhalation of PM (Pope and Dockery, 2006; Hu et al., 2008).

The EF for all of the measured elements was highest in the samples collected on board the train. This can be explained by the resuspension of PM<sub>2.5</sub> by foot traffic through the train. Several studies have shown that walking will resuspend particles with the bulk of the resuspended particles being in the coarse mode. However, these studies have also shown that the coarse particles will deposit faster than the fine particles (Montoya and Hildemann, 2005; Rosati et al., 2008; Cheng et al., 2010). As a result, it can be posited that continual resuspension of PM<sub>2.5</sub> could increase enrichment of fine trace metals in the samples collected on board the train.

The cause for the observed increase in Ca in samples collected on board the trains over samples collected downtown and track-side is not fully known. As can be seen in Figure 3, Ca was shown to have a higher enrichment factor in the samples onboard the train suggesting that the Ca concentration was influenced by anthropogenic activities (EF>10). A potential source of Ca could be calcium hypochlorite, a common disinfectant that could be used in cleaning supplies used to clean the interior surfaces of the trains.

While this is the first study to measure Fe speciation and solubility in Denver, CO, Fe speciation studies in Los Angeles, CA and East St. Louis, IL have shown that Fe(III) is the predominant Fe species in atmospheric PM while Fe(II) is the predominant soluble Fe species (Majestic et al., 2007). The Fe solubility results in this study were similar to these other studies with 87–90% of the soluble Fe being Fe(II) and soluble Fe(II) also comprising 7–14% of the total Fe (Majestic et al., 2007; Oakes et al., 2012). The measured percent Fe(II) of soluble Fe in this study and the results

for Los Angeles and East St. Louis from the study by Majestic et al. (2007) are larger than results reported for Waukesha, WI where the percentage of soluble Fe(II) was found to be 50% (Majestic et al., 2007) as well as the results reported for urban Atlanta, GA where the percentage of Fe(II) in the soluble Fe ranged from 31% to 88% (Oakes et al., 2012). In both studies, Majestic et al. (2007) and Oakes et al. (2012), higher concentrations of soluble Fe(II) were measured in the winter time, a similar time period as the collection period of this study. Similarly, urban areas have been shown to have elevated soluble Fe.

This is important as soluble Fe has been directly correlated to ROS production (Kam et al., 2011b). Fe(II) has also been correlated with the reduction of hydrogen peroxide to form the hydroxyl radical (Halliwell and Gutteridge, 1986). Other soluble trace metals of note in this study that have been found to form ROS in other studies are Cr, Ni, (Kam et al., 2011b) and Cu (DiStefano et al., 2009). Cr is also known to be particularly toxic based on speciation

and has also been studied in railway transportation systems (Salma et al., 2009).

### 5. Conclusions

The results of this study provide interesting insights into the effects of light rail activity in the Denver–Metropolitan area. While the air near the tracks or on board the train may not contain more PM<sub>2.5</sub> than that of the ambient air in Denver, it is important to note that there is definite enrichment of trace metals on board the train and near the tracks. These results have also shown that the PM<sub>2.5</sub> collected on board the trains was composed of 25% (by mass) metals while the PM<sub>2.5</sub> collected at the other two sites was less than 10%. Future studies could focus on the seasonal variability of metal concentrations in the Denver–Metropolitan area as well as investigate the difference in PM<sub>2.5</sub> composition and concentration on each train line individually.

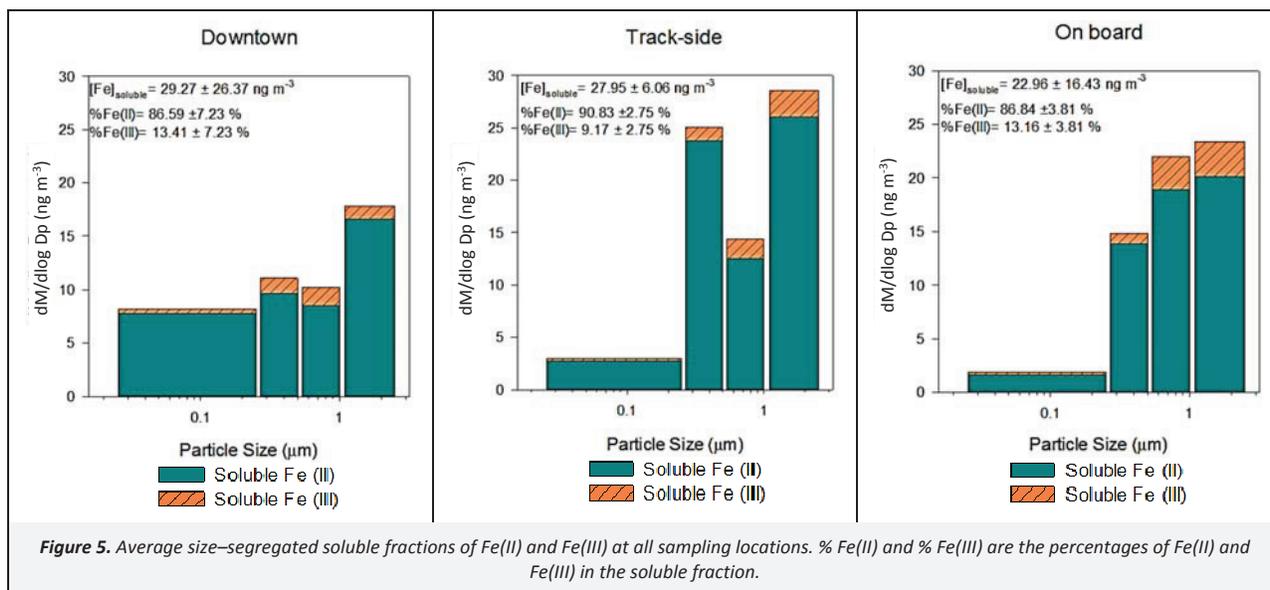


Figure 5. Average size-segregated soluble fractions of Fe(II) and Fe(III) at all sampling locations. % Fe(II) and % Fe(III) are the percentages of Fe(II) and Fe(III) in the soluble fraction.

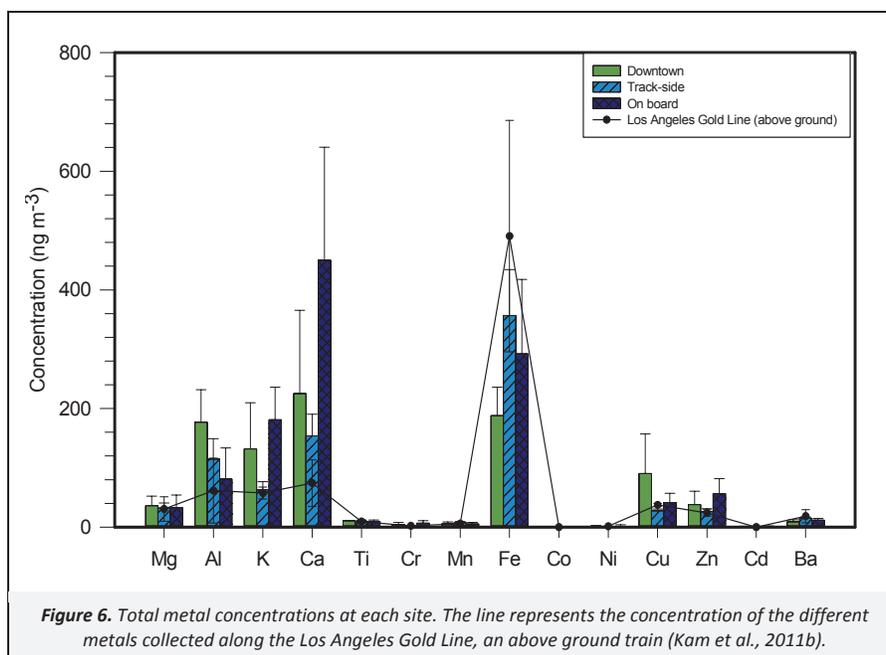


Figure 6. Total metal concentrations at each site. The line represents the concentration of the different metals collected along the Los Angeles Gold Line, an above ground train (Kam et al., 2011b).

## Acknowledgments

This study was funded by the University of Denver Faculty Research Grant and the Atmospheric Chemistry Division of the National Science Foundation grant 1206083. We thank Bradley Rink of the Colorado Air Monitoring Program, a division of the Colorado Department of Public Health and Environment, as well as the Regional Transportation District for site access, and the undergraduate volunteers at the University of Denver who helped with the sample collection.

## Supporting Material Available

PM<sub>2.5</sub> correlation plot (Figure S1), Geometric mean and standard deviation (dimensionless) of PM<sub>2.5</sub> size fractions (Table S1). This information is available free of charge via the Internet at <http://www.atmospolres.com>.

## References

- Aarnio, P., Yli-Tuomi, T., Kousa, A., Makela, T., Hirsikko, A., Hameri, K., Raisanen, M., Hillamo, R., Koskentalo, T., Jantunen, M., 2005. The concentrations and composition of and exposure to fine particles (PM<sub>2.5</sub>) in the Helsinki subway system. *Atmospheric Environment* 39, 5059–5066.
- Adams, H.S., Nieuwenhuijsen, M.J., Colvile, R.N., McMullen, M.A.S., Khandelwal, P., 2001. Fine particle (PM<sub>2.5</sub>) personal exposure levels in transport microenvironments, London, UK. *Science of the Total Environment* 279, 29–44.
- Chan, L.Y., Lau, W.L., Lee, S.C., Chan, C.Y., 2002. Commuter exposure to particulate matter in public transportation modes in Hong Kong. *Atmospheric Environment* 36, 3363–3373.
- Cheng, Y.H., Lin, Y.L., 2010. Measurement of particle mass concentrations and size distributions in an underground station. *Aerosol and Air Quality Research* 10, 22–29.
- Cheng, K.C., Goebes, M.D., Hildemann, L.M., 2010. Association of size-resolved airborne particles with foot traffic inside a carpeted hallway. *Atmospheric Environment* 44, 2062–2066.
- Chillrud, S.N., Grass, D., Ross, J.M., Coulbaly, D., Slavkovich, V., Epstein, D., Sax, S.N., Pederson, D., Johnson, D., Spengler, J.D., Kinney, P.L., Simpson, H.J., Brandt-Rauf, P., 2005. Steel dust in the New York City subway system as a source of manganese, chromium, and iron exposures for transit workers. *Journal of Urban Health-Bulletin of the New York Academy of Medicine* 82, 33–42.
- Chillrud, S.N., Epstein, D., Ross, J.M., Sax, S.N., Pederson, D., Spengler, J.D., Kinney, P.L., 2004. Elevated airborne exposures of teenagers to manganese, chromium, and iron from steel dust and New York City's subway system. *Environmental Science & Technology* 38, 732–737.
- Clements, N., Eav, J., Xie, M.J., Hannigan, M.P., Miller, S.L., Navidi, W., Peel, J.L., Schauer, J.J., Shafer, M.M., Milford, J.B., 2014. Concentrations and source insights for trace elements in fine and coarse particulate matter. *Atmospheric Environment* 89, 373–381.
- Dasch, J.M., Wolff, G.T., 1989. Trace inorganic species in precipitation and their potential use in source apportionment studies. *Water Air and Soil Pollution* 43, 401–412.
- DiStefano, E., Eiguren-Fernandez, A., Delfino, R.J., Sioutas, C., Froines, J.R., Cho, A.K., 2009. Determination of metal-based hydroxyl radical generating capacity of ambient and diesel exhaust particles. *Inhalation Toxicology* 21, 731–738.
- Faiola, C., Johansen, A.M., Rybka, S., Nieber, A., Thomas, C., Bryner, S., Johnston, J., Engelhard, M., Nachimuthu, P., Owens, K.S., 2011. Ultrafine particulate ferrous iron and anthracene associations with mitochondrial dysfunction. *Aerosol Science and Technology* 45, 1109–1122.
- Furuya, K., Kudo, Y., Okinaga, K., Yamuki, M., Takahashi, S., Araki, Y., Hisamatsu, Y., 2001. Seasonal variation and their characterization of suspended particulate matter in the air of subway stations. *Journal of Trace and Microprobe Techniques* 19, 469–485.
- Garg, B.D., Cadle, S.H., Mulawa, P.A., Groblicki, P.J., Laroo, C., Parr, G.A., 2000. Brake wear particulate matter emissions. *Environmental Science & Technology* 34, 4463–4469.
- Gerdol, R., Bragazza, L., Marchesini, R., Alber, R., Bonetti, L., Lorenzoni, G., Achilli, M., Buffoni, A., De Marco, N., Franchi, M., Pison, S., Giaquinta, S., Palmieri, F., Spezzano, P., 2000. Monitoring of heavy metal deposition in Northern Italy by moss analysis. *Environmental Pollution* 108, 201–208.
- Goldsmith, C.A.W., Imrich, A., Danaee, H., Ning, Y., Kobzik, L., 1998. Analysis of air pollution particulate-mediated oxidant stress in alveolar macrophages. *Journal of Toxicology and Environmental Health-Part A* 54, 529–545.
- Halliwell, B., Gutteridge, J.M.C., 1986. Oxygen free-radicals and iron in relation to biology and medicine—some problems and concepts. *Archives of Biochemistry and Biophysics* 246, 501–514.
- Hinds, W.C., 1999. *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, Wiley, New York.
- Hu, S., Polidori, A., Arhami, M., Shafer, M.M., Schauer, J.J., Cho, A., Sioutas, C., 2008. Redox activity and chemical speciation of size fractionated PM in the communities of the Los Angeles-Long Beach Harbor. *Atmospheric Chemistry and Physics* 8, 6439–6451.
- Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A., Kawahata, H., Kubilay, N., laRoche, J., Liss, P.S., Mahowald, N., Prospero, J.M., Ridgwell, A.J., Tegen, I., Torres, R., 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* 308, 67–71.
- Johansen, A.M., Siefert, R.L., Hoffmann, M.R., 2000. Chemical composition of aerosols collected over the tropical North Atlantic Ocean. *Journal of Geophysical Research-Atmospheres* 105, 15277–15312.
- Johansson, C., Johansson, P.A., 2003. Particulate matter in the underground of Stockholm. *Atmospheric Environment* 37, 3–9.
- Kam, W., Delfino, R.J., Schauer, J.J., Sioutas, C., 2013. A comparative assessment of PM<sub>2.5</sub> exposures in light-rail, subway, freeway, and surface street environments in Los Angeles and estimated lung cancer risk. *Environmental Science-Processes & Impacts* 15, 234–243.
- Kam, W., Cheung, K., Daher, N., Sioutas, C., 2011a. Particulate matter (PM) concentrations in underground and ground-level rail systems of the Los Angeles Metro. *Atmospheric Environment* 45, 1506–1516.
- Kam, W., Ning, Z., Shafer, M.M., Schauer, J.J., Sioutas, C., 2011b. Chemical characterization and redox potential of coarse and fine particulate matter (PM) in underground and ground-level rail systems of the Los Angeles Metro. *Environmental Science & Technology* 45, 6769–6776.
- Karlsson, H.L., Nilsson, L., Moller, L., 2005. Subway particles are more genotoxic than street particles and induce oxidative stress in cultured human lung cells. *Chemical Research in Toxicology* 18, 19–23.
- Kim, J.B., Kim, S., Lee, G.J., Bae, G.N., Cho, Y., Park, D., Lee, D.H., Kwon, S.B., 2014. Status of PM in Seoul Metropolitan Subway cabins and effectiveness of subway cabin air purifier (SCAP). *Clean Technologies and Environmental Policy* 16, 1193–1200.
- Kim, K.Y., Kim, Y.S., Roh, Y.M., Lee, C.M., Kim, C.N., 2008. Spatial distribution of particulate matter (PM<sub>10</sub> and PM<sub>2.5</sub>) in Seoul Metropolitan Subway stations. *Journal of Hazardous Materials* 154, 440–443.
- Landreman, A.P., Shafer, M.M., Hemming, J.C., Hannigan, M.P., Schauer, J.J., 2008. A macrophage-based method for the assessment of the reactive oxygen species (ROS) activity of atmospheric particulate matter (PM) and application to routine (daily–24 h) aerosol monitoring studies. *Aerosol Science and Technology* 42, 946–957.
- Lough, G.C., Schauer, J.J., Park, J.S., Shafer, M.M., Deminter, J.T., Weinstein, J.P., 2005. Emissions of metals associated with motor vehicle roadways. *Environmental Science & Technology* 39, 826–836.

- Majestic, B.J., Anbar, A.D., Herckes, P., 2009. Elemental and iron isotopic composition of aerosols collected in a parking structure. *Science of the Total Environment* 407, 5104–5109.
- Majestic, B.J., Schauer, J.J., Shafer, M.M., Fine, P.M., Singh, M., Sioutas, C., 2008. Trace metal analysis of atmospheric particulate matter: A comparison of personal and ambient samplers. *Journal of Environmental Engineering and Science* 7, 289–298.
- Majestic, B.J., Schauer, J.J., Shafer, M.M., 2007. Application of synchrotron radiation for measurement of iron red–ox speciation in atmospherically processed aerosols. *Atmospheric Chemistry and Physics* 7, 2475–2487.
- Majestic, B.J., Schauer, J.J., Shafer, M.M., Turner, J.R., Fine, P.M., Singh, M., Sioutas, C., 2006. Development of a wet–chemical method for the speciation of iron in atmospheric aerosols. *Environmental Science & Technology* 40, 2346–2351.
- Misra, C., Singh, M., Shen, S., Sioutas, C., Hall, P.A., 2002. Development and evaluation of a personal cascade impactor sampler (PCIS). *Journal of Aerosol Science* 33, 1027–1047.
- Montoya, L.D., Hildemann, L.M., 2005. Size distributions and height variations of airborne particulate matter and cat allergen indoors immediately following dust–disturbing activities. *Journal of Aerosol Science* 36, 735–749.
- Mugica–Alvarez, V., Figueroa–Lara, J., Romero–Romo, M., Sepulveda–Sanchez, J., Lopez–Moreno, T., 2012. Concentrations and properties of airborne particles in the Mexico City subway system. *Atmospheric Environment* 49, 284–293.
- Murrini, L.G., Solanes, V., Debray, M., Kreiner, A.J., Davidson, J., Davidson, M., Vazquez, M., Ozafran, M., 2009. Concentrations and elemental composition of particulate matter in the Buenos Aires underground system. *Atmospheric Environment* 43, 4577–4583.
- Oakes, M., Weber, R.J., Lai, B., Russell, A., Ingall, E.D., 2012. Characterization of iron speciation in urban and rural single particles using XANES spectroscopy and micro x–ray fluorescence measurements: Investigating the relationship between speciation and fractional iron solubility. *Atmospheric Chemistry and Physics* 12, 745–756.
- Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: Lines that connect. *Journal of the Air & Waste Management Association* 56, 709–742.
- Prophete, C., Maciejczyk, P., Salnikow, K., Gould, T., Larson, T., Koenig, J., Jaques, P., Sioutas, C., Lippmann, M., Cohen, M., 2006. Effects of select PM–associated metals on alveolar macrophage phosphorylated ERK1 and–2 and iNOS expression during ongoing alteration in iron homeostasis. *Journal of Toxicology and Environmental Health–Part A–Current Issues* 69, 935–951.
- Querol, X., Moreno, T., Karanasiou, A., Reche, C., Alastuey, A., Viana, M., Font, O., Gil, J., de Miguel, E., Capdevila, M., 2012. Variability of levels and composition of PM<sub>10</sub> and PM<sub>2.5</sub> in the Barcelona metro system. *Atmospheric Chemistry and Physics* 12, 5055–5076.
- Raut, J.C., Chazette, P., Fortain, A., 2009. Link between aerosol optical, microphysical and chemical measurements in an underground railway station in Paris. *Atmospheric Environment* 43, 860–868.
- Rosati, J.A., Thornburg, J., Rodes, C., 2008. Resuspension of particulate matter from carpet due to human activity. *Aerosol Science and Technology* 42, 472–482.
- Saffari, A., Daher, N., Shafer, M.M., Schauer, J.J., Sioutas, C., 2013. Seasonal and spatial variation of trace elements and metals in quasi–ultrafine (PM<sub>0.25</sub>) particles in the Los Angeles metropolitan area and characterization of their sources. *Environmental Pollution* 181, 14–23.
- Salma, I., Posfai, M., Kovacs, K., Kuzmann, E., Homonnay, Z., Posta, J., 2009. Properties and sources of individual particles and some chemical species in the aerosol of a metropolitan underground railway station. *Atmospheric Environment* 43, 3460–3466.
- Salma, I., Weidinger, T., Maenhaut, W., 2007. Time–resolved mass concentration, composition and sources of aerosol particles in a metropolitan underground railway station. *Atmospheric Environment* 41, 8391–8405.
- Seaton, A., Cherrie, J., Dennekamp, M., Donaldson, K., Hurley, J.F., Tran, C.L., 2005. The London underground: Dust and hazards to health. *Occupational and Environmental Medicine* 62, 355–362.
- Sholkovitz, E.R., Sedwick, P.N., Church, T.M., Baker, A.R., Powell, C.F., 2012. Fractional solubility of aerosol iron: Synthesis of a global–scale data set. *Geochimica et Cosmochimica Acta* 89, 173–189.
- Singh, M., Misra, C., Sioutas, C., 2003. Field evaluation of a personal cascade impactor sampler (PCIS). *Atmospheric Environment* 37, 4781–4793.
- Stookey, L.L., 1970. Ferrozine – A new spectrophotometric reagent for iron. *Analytical Chemistry* 42, 779–781.
- Tao, F., Gonzalez–Flecha, B., Kobzik, L., 2003. Reactive oxygen species in pulmonary inflammation by ambient particulates. *Free Radical Biology and Medicine* 35, 327–340.
- Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental–crust. *Reviews of Geophysics* 33, 241–265.
- Verma, V., Shafer, M.M., Schauer, J.J., Sioutas, C., 2010. Contribution of transition metals in the reactive oxygen species activity of PM emissions from retrofitted heavy–duty vehicles. *Atmospheric Environment* 44, 5165–5173.
- Veyseyre, A., Moutard, K., Ferrari, C., Van de Velde, K., Barbante, C., Cozzi, G., Capodaglio, G., Boutron, C., 2001. Heavy metals in fresh snow collected at different altitudes in the Chamonix and Maurienne Valleys, French Alps: Initial results. *Atmospheric Environment* 35, 415–425.