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Physical and chemical characterization of personal exposure to airborne particulate matter (PM) in the Los Angeles subways and light-rail trains

METRANS final report

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1. Abstract

An extensive sampling campaign was conducted to assess personal exposure of coarse PM ($2.5\mu m<d_p<10\mu m$) and fine PM, ($d_p<2.5\mu m$) in May - August 2010 for two lines of the Los Angeles Metro – an underground subway line (Metro red line) and a ground-level light-rail line (Metro gold line). PM_{10} is defined as the sum of coarse and fine PM. Concurrent measurements were taken at University of Southern California (USC) to represent urban ambient conditions. The major results of this study focus on measurements from: 1) real-time, continuous monitors for PM and CO_2 and 2) time-integrated instruments that collect PM based on inertial impaction.

The real-time, continuous data determined personal PM exposure of commuters of both lines, and measured PM concentrations at station platforms and inside the train. Subway commuters were exposed to PM_{10} and $PM_{2.5}$ concentrations that were 1.9 and 1.8 times greater than the light-rail commuters. The average PM_{10} concentrations for the subway line at station platforms and inside the train were 78.0 $\mu g\ m^{-3}$ and 31.5 $\mu g\ m^{-3}$, respectively; for the light-rail line, corresponding PM_{10} concentrations were 38.2 $\mu g\ m^{-3}$ and 16.2 $\mu g\ m^{-3}$. Regression analysis demonstrated that personal exposure concentrations for the light-rail line are strongly associated with ambient PM levels (R^2=0.61), while PM concentrations for the subway line are less influenced by ambient conditions (R^2=0.38) and have a background level of 21 $\mu g\ m^{-3}$. Our findings suggest that local emissions (i.e. vehicular traffic, road dust) are the main source of airborne PM for the light-rail line. The subway line, on the other hand, has an additional source of PM, most likely generated from the daily operation of trains. From a mass concentration perspective, the L.A. Metro system is relatively 'cleaner' than other worldwide subway systems.

A comprehensive chemical analysis was performed on the time-integrated data to include total and water-soluble metals, inorganic ions, and elemental and organic carbon. Mass balance showed that in coarse PM, iron makes up 27%, 6%, and 2% of gravimetric mass for red line, gold line, and USC, respectively; in fine PM, iron makes up 32%, 3%, and 1%. Ambient air is the primary source of inorganic ions for both lines. Non-crustal metals, particularly Cr, Mn, Co, Ni, Mo, Cd, and Eu were elevated for the red line and, to a lesser degree, the gold line. Mo exhibited the greatest crustal enrichment factors. The enriched species were less water-soluble on red line than corresponding species on gold line. Reactive oxygen species (ROS) activity results suggest that one unit of PM from gold line may be as toxic as one unit of PM from red line; however, PM from red line generates greater ROS activity per volume than PM from gold line and USC.

It should be noted that a more appropriate personal exposure assessment of transport microenvironments in Los Angeles should be a comparison with the predominant mode of commute—private vehicles. Passengers of the Los Angeles Metro may actually be subjected to lower levels of PM and toxic co-pollutants such as EC and transition metals. A comparison of $PM_{2.5}$ and EC concentrations measured in the proximity of the I-5 and I-710 are substantially higher than levels found on the gold line and red line. Our future work will assess "on-road" PM physical and chemical characterization of freeways and arterial roads of Los Angeles, which will offer a greater understanding of the health impacts of transportation modes to the public health.

2. Introduction

The Los Angeles air basin has the most severe ozone and particulate matter (PM) air quality problems in the United States. PM is emitted from numerous sources in the basin, although the principal source of particulate matter emissions in the Los Angeles air basin is from combustion, principally from motor vehicles (Kim et al. 2002; Westerdahl et al. 2005). Other sources such as food cooking and wood burning can also contribute as well (Schauer et al. 1999). These sources produce not only emissions of primary PM, but also the reactive gases that can act as precursors to significant secondary PM production in the atmosphere. The topography and climate of the Los Angeles air basin contribute to the area's high air pollution potential. Light winds limit ventilation during the summer and the marine layer inhibits pollutants from dispersion. Afternoon sunlight and the persistence of fog and low clouds trigger atmospheric reactions that form secondary particles. Atmospheric particulate matter is not a uniform pollutant, but ambient PM in Los Angeles is generally composed of over 50% elemental and organic carbon species by mass. The Los Angeles area is a unique environment in terms of the composition and sources of PM, local meteorology, and the potential health issues that may arise from continued population growth.

The association between elevated levels of PM concentrations, particularly fine PM or $PM_{2.5}$ (less than 2.5 micrometers in diameter), and adverse human health impacts is well-established (Pope and Dockery 2006). Determining the relationship between particle size and composition and specific health endpoints, however, remains an active area of research. Pro-inflammatory response at the cellular level as well as increased incidence of asthma, among other diseases, are linked to exposure to ultrafine particles (approximately < 0.10 micrometers in diameter) such as those emitted by motor vehicle combustion (Delfino et al. 2005). Substantial evidence suggests that it is the ability of these particles to induce oxidative stress in cells through the production of reactive oxygen species (ROS) that leads to the adverse health outcomes observed (Li et al. 2003; Nel 2005). High levels of ROS change the redox status of the cell (Schafer et al. 2003), thereby triggering a cascade of events associated with inflammation and, at higher concentrations, apoptosis (cell death) (Li et al. 2003). Although PM measurements have been made throughout the Los Angeles Basin as well as in various microenvironments, including near freeways, inside vehicles, and indoors (Singh et al. 2002; Geller et al. 2004; Pakbin et al. 2010), there have been no measurements made in its underground transportation network, the L.A. Metro. Due to the urban sprawling of Los Angeles, private vehicles remain the primary mode of transportation, but as the L.A. Metro continues to expand its coverage, ridership is expected to increase rapidly in the coming years.

Metro systems are an important transportation mode in megacities across the world that commuters take on a daily basis. However, recent measurements in cities across the world indicate that subway systems may present a unique microenvironment with particulate matter (PM) concentrations subject to different influences than ground-level sources. Studies have shown that respirable subway air can be substantially different than corresponding street-level air in terms of number and mass concentration of variable PM size ranges and chemical composition (Furuya et al. 2001; Johansson and Johansson 2003; Salma et al. 2007). Earlier studies have documented elevated PM levels in major subway systems across the world. Mean exposure levels in the London Underground rail system were 3-8 times higher than street-level

transportation modes (Adams et al. 2001; Adams et al. 2001); mean $PM_{2.5}$ and PM_{10} concentrations on station platforms in the Seoul Metropolitan Subway System were significantly higher than corresponding ambient levels (Kim et al. 2008); average daytime $PM_{2.5}$ and PM_{10} levels in a Paris railway station were approximately 5-30 times higher than levels on Paris streets (Raut et al. 2009). In addition, elevated concentrations of elements especially Fe, Mn, Cu, Ni, Cr have been observed in numerous subway systems relative to ambient urban concentrations. A personal exposure assessment of a passenger on the Helsinki subway system determined an increase of 3% for total fine PM exposure levels, but nearly 200% increase for Fe, 60% increase for Mn, and 40% increase for Cu (Aarnio et al. 2005). Another study estimated that commuters in London spending 2h in the subway per day would increase their personal daily exposure by 17 $\mu g\ m^{-3}$ (Seaton et al. 2005). High Mn, Cr and Fe concentrations of 160-350 times greater than the median for outdoors residential areas were observed for teenage commuters in the New York City subway system (Chillrud et al. 2004). Although passengers spend a relatively short amount of time in subway systems, exposures to high concentrations of PM with enriched levels of certain elements may have significant health implications. Few toxicological studies, primarily in-vitro, have been conducted on the health impacts of subway particles. Stockholm subway particles were found to be 8 times more genotoxic than ambient particles and up to 4 times more like to cause oxidative stress to cells (Karlsson et al. 2005). Furthermore, the Stockholm subway particles caused more DNA damage than particles produced from wood combustion (Karlsson et al. 2006). On the other hand, studies have reported PM levels to be lower for the Hong Kong (Chan et al. 2002) and Guangzhou (Chan et al. 2002) subway systems than compared to other transport modes. Therefore, differences between subway ventilation methods, braking systems, wheel type, air conditioning, system age, and train motive source make it impossible to directly extrapolate results from previous studies to other subway systems.

This study focuses on the personal exposure assessment and source identification of PM for two lines of the Los Angeles Metro system—a subway line (red line) and a ground-level light-rail line (gold line). Both lines cover key parts of the Los Angeles area (Hollywood, Downtown L.A., Pasadena) and are heavily trafficked especially during commute hours. Major results from this campaign are divided into two sub-campaigns – a station/train intensive campaign, results of which are from real-time monitors, and a personal exposure campaign, results of which are from time-integrated particle impaction. Portable dust monitors were used to measure real-time, $PM_{2.5}$ and PM_{10} concentrations on station platforms and inside trains, and results were used to 1) compare personal PM exposure for the Metro red and gold lines, 2) determine fine and coarse PM ($PM_{10-2.5}$) levels for both lines at station platforms and inside the train, 3) explore the relationship of PM levels of the two lines to corresponding ambient levels as measured by nearby air monitoring stations, 4) discuss possible sources that influence PM concentrations for the two lines, and 5) compare PM levels of the L.A. Metro to other subway systems worldwide. Size-fractionated PM mass were collected on personal cascade impactors to assess personal exposure for the two lines while sampling concurrently at a fixed site nearby University of Southern California (USC), which served as a basis of comparison to urban ambient conditions. Results from the personal exposure campaign were for the purpose of determining a comprehensive chemical and toxicity profiles of exposure for the two lines of the L.A. Metro.

3. Methodology

Two lines of the L.A. Metro system were sampled in this study – the red line and the gold line. The Metro red line is a fully underground subway line that spans approximately 17 km connecting downtown L.A. to North Hollywood. The first segment of the line, extending only 5 stations, began operations in 1993, with the final completion of the line in 2000. Weekly ridership for the red line is estimated to be 150,000, which is the highest of the Metro rail lines and accounts for almost 50% of system wide rail ridership. The Metro gold line, which began operation in 2003, is a ground-level light-rail line that connects Pasadena to downtown L.A. to East Los Angeles. Weekly ridership for the gold line is estimated to be 35,000 as of August 2010. The entire line consists of 21 stations, totaling a length of approximately 32 km, but only the northeast segment of the line (from Union Station to Sierra Madre) was sampled during this study. For both lines, trains pass every 8-10 minutes during rush hours and 10-12 minutes during normal hours. During weekdays, both lines operate from 4:00am to midnight and a one-way trip to and from Union Station is approximately 30 minutes (www.metro.net). Both systems employ metal wheels. Figure 1 shows a map of where the Metro red and gold lines run, two nearby air quality monitoring sites (Downtown L.A. and Burbank), and the University of Southern California (USC) urban ambient site, which was used to represent urban background concentrations. The USC site is centrally located in downtown Los Angeles and is within 130 m to the I-110. In addition, numerous studies have been conducted at this site (Moore et al. 2007; Ning et al. 2007; Pakbin et al. 2010).

3.1 Monitoring instruments and sampling campaigns

The Q-Trak Indoor Air Quality Monitor Model 7565 (TSI Inc., Shoreview, MN) was used to determine CO_2 concentrations, temperature, and relative humidity at a logging interval of 15 seconds. The DustTrak Aerosol Monitor Model 8520 (TSI Inc., Shoreview, MN) was used to measure continuous $PM_{2.5}$ and PM_{10} concentrations at a logging interval of 30 seconds. Previous studies have shown that light-scattering aerosol measuring devices are subject to error when relative humidity is greater than 60% (Lowenthal et al. 1995; Sioutas et al. 2000; Chakrabarti et al. 2004). Q-Trak reported relative humidity levels that are within the operating range of the DustTrak. Airborne PM was collected with the Sioutas™ Personal Cascade Impactor Sampler (SKC Inc., Eighty-Four, PA), also referred to as PCIS (Misra et al. 2002; Singh et al. 2003), which was operated with a Leland Legacy Pump (SKC Inc., Eighty-Four, PA) at a flow rate of 9 liters per minute (lpm) (Brinkman et al. 2008). The pumps were calibrated with Gilian Gilibrator-2 Air Flow Calibrator (Sensidyne Inc., Clearwater, FL) before and after sampling. During the sampling, the pump flows were checked regularly with flow meters. The PCIS was prepared using one impaction stage with a cutpoint of 2.5 μm and an after filter stage, collecting coarse and fine PM, respectively. For the purpose of chemical analysis, the PCIS were loaded with two types of filters. One was loaded with PTFE (Teflon) filters, with a 25mm Zefluor supported PTFE filter (Pall Life Sciences, Ann Arbor, MI) as the impaction substrate and a 37mm PTFE membrane filter with PMP ring (Pall Life Sciences, Ann Arbor, MI) as the after filter. The other unit was loaded with quartz microfiber filters (Whatman International Ltd, Maidstone, England). The Teflon filters were gravimetrically analyzed using a MT5 Microbalance (Mettler-Toledo Inc., Columbus OH), which has an uncertainty of 10μg. A total of

9 PCIS were deployed in this study, with 3 PCIS for each line and 3 PCIS at the fixed site. Figure 2b shows the set-up of the PCIS inside the carry-on suitcases that were used for PM collection on the subway.

The sampling campaign took place from May 3 – August 13, 2010. Two sub-campaigns were undertaken during this period: 1) the station/train intensive campaign, which focuses on measuring real-time $PM_{2.5}$, PM_{10}, and CO_2 concentrations simultaneously at each station and inside the train, and 2) the personal exposure campaign, focusing on airborne PM exposures for Metro commuters by sampling concurrently on the red line, gold line, and at the USC ambient fixed site. The station/train intensive sampling occurred on a weekly basis and alternated between the two lines each week (i.e. each line is sampled every other week), accruing 7 days of sampling for each line. The subject carried a suitcase equipped with two DustTraks, one with a $PM_{2.5}$ inlet and one with a PM_{10} inlet, and a Q-Trak (Figure 2a). He was directed to collect data at each station for 10-15 minutes and then ride inside the train for 1.5 round trips without stopping except at the end stations. For the personal exposure campaign, the red line, gold line, and USC fixed ambient site were sampled concurrently for 3.5 hours (9:30 am to 1:00 pm) for 4 out of the 5 weekdays. The campaign was designed to determine the personal PM exposure of riders on both lines and compare with each other and with an urban ambient site (USC). The two subjects were directed to spend approximately 75% of time in the train and 25% of time at stations, which represent a typical commute of a passenger. Each week, the subjects would stop at two different stations, so that each station along the designated line would be sampled. Two samples were collected from each site in two consecutive periods as a basis for comparison to each other. The sampling time was 90h for the first sample and 110h for the second sample. The two subjects each carried a suitcase with a DustTrak with $PM_{2.5}$ inlet and 3 PCIS that was operated individually with a battery-powered Leland Legacy pump (SKC Inc., Eighty-Four, PA) at a flow rate of 9 liters per minute (lpm) (Figure 2b). Each PCIS was installed with individual, pretested PM_{10} inlets (Pakbin et al. 2010). The USC urban ambient site was also equipped with an identical suitcase and inlets with 3 PCIS inside. At all times, the subject wore a watch that was synchronized with the time on the monitoring instruments and kept a detailed logbook of all activity such as their location and time entering and exiting a train.

3.2 Quality assurance

To determine the comparability of the two DustTraks deployed for the sampling campaign, the DustTraks were tested by collocated sampling before, in the middle, and at the end of the campaign. A correlation of the PM readings for the two DustTraks shows that they are within 10% of each other ($y = 1.10x + 0.001$) and have an R^2 of 0.99. During the campaign, the DustTrak was maintained at its working flow rate of 1.7 lpm. In addition, the DustTraks were re-zeroed and their impaction plates were cleaned on a daily basis. The Q-Trak was calibrated by zero checking and re-zeroing, if necessary, before and during the campaign. The 9 PCIS used for the campaign were also tested by collocated sampling, and gravimetric analysis revealed that the PCIS agreed within 10-15% in mass concentrations. After sampling each day, the PCIS with filter substrates were sealed with parafilm and stored in a -4°C freezer.

3.3 Chemical analysis

A comprehensive chemical analysis was performed for the time-integrated data collected. First, the Teflon filters were equilibrated for 24h and then weighed before and after sampling to determine gravimetric mass concentrations in a temperature and relative humidity-controlled room. The filters were subsequently cut into 3 equal sections. The first section was analyzed by means of magnetic-sector Inductively Coupled Plasma Mass Spectroscopy (SF-ICPMS) to determine total elemental composition using an acid extraction (Zhang et al. 2008). The second section was extracted using Milli-Q water and aliquots were dispensed for SF-ICPMS analysis to determine water-soluble elemental composition and for ion chromatography (IC) analysis to determine the PM concentrations of inorganic ions. The IC methodology is fully described in Kerr et al. (2004) (Kerr et al. 2004). For the third section, a sensitive macrophage-based in-vitro assay was used to determine the reactive oxygen species (ROS) activity of particles collected (Landreman et al. 2008). The quartz substrates were prebaked at 550°C for 12h and stored in baked aluminum foil prior to sampling. Elemental and organic carbon (EC/OC) was determined using the Thermal Evolution/Optical Transmittance (TOT) analysis (Schauer et al. 2003) and organic compounds were determined using GC/MS (Schauer et al. 1999).

4. Results and discussion

4.1 Station/train intensive campaign

4.1.1 Overview of personal exposure concentrations of Metro red line and Metro gold line

Table 1 presents the results from the personal exposure campaign, which was designed to measure the PM exposure of a typical commute of a rider (75% of time spent inside train and 25% of time spent waiting at a station platform). The average PM_{10}, $PM_{2.5}$, and $PM_{10-2.5}$, or coarse PM, mass concentrations obtained from the PCIS, and the $PM_{2.5}$ mass concentrations obtained from the DustTrak are presented. Coarse PM is a subset of PM_{10} and is calculated as the difference of the adjusted PM_{10} and $PM_{2.5}$ values. The personal exposure PM_{10} and $PM_{2.5}$ concentrations on the subway line are 1.9 and 1.8 times greater than the corresponding concentrations for the light-rail line, indicating that subway commuters are exposed to almost double the PM concentrations of light-rail commuters. In comparison to the urban ambient site (USC), PM_{10} and $PM_{2.5}$ exposure concentrations for the subway line are on average 1.4 and 1.7 times higher, respectively; for the light-rail line, the concentrations are 0.76 and 0.94 times that of corresponding USC ambient concentrations. Using a paired t-test, the personal exposure $PM_{2.5}$ levels for the subway and light-rail line reported by the DustTrak are statistically different ($p<0.001$). Interestingly, personal exposure to coarse PM levels for the subway line are almost equivalent to the urban ambient site, while light-rail levels are on average 0.43 times those of ambient levels. The lower coarse PM exposure is most likely due to the subject spending 75% of the time inside the train. This factor is further investigated in the next section.

4.1.2 PM concentrations at station platforms and inside trains

The results from the station/train intensive campaign for the subway line, light-rail line, and urban ambient site are summarized in Table 2. In general, the subway's platforms and train have PM_{10} and $PM_{2.5}$ concentrations that are approximately double those of the light-rail's platforms and train levels; however, coarse PM levels for the subway platforms and trains are 2.4 and 2.9 times greater than the light-rail platforms and train levels, likely a result of the enclosed tunnel environment of the subway line. The light-rail platform PM concentrations are comparable to the USC fixed site concentrations, while the subway stations have PM_{10}, $PM_{2.5}$, and coarse PM levels that are 2.5, 2.8, and 2.0 times greater than those at USC.

Figures 3a and 3c show the average PM_{10} and $PM_{2.5}$ concentrations from the station/train intensive campaign and the average $PM_{2.5}$ concentrations from the personal exposure campaign for the subway line and light-rail line, respectively, with error bars of one standard deviation. Note that the values presented for the station/train intensive campaign are the average of bi-weekly concentrations. For the underground subway stations, the concentrations vary (i.e. PM_{10} values range from 50 to 100 $\mu g\ m^{-3}$) while the ground-level, light-rail station PM_{10} concentrations are distributed in a narrower range (31 to 48 $\mu g\ m^{-3}$). It is possible that the ventilation system installed at some stations along the subway line may be more efficient at

removing PM than at other stations. Also, the bi-weekly variation of the light-rail line is much greater than the subway line variation; one standard deviation of the average PM values is 50% and 25% for the light-rail and subway line means, respectively. This indicates a greater temporal variation of PM levels in the light-rail line than the subway line. To further confirm this observation, a paired t-test was performed for each line between the mean $PM_{2.5}$ concentrations of the personal exposure and station/train intensive campaigns. At 95% confidence interval, the light-rail line mean data are significantly different (p=0.001), while the subway line mean data are not significantly different (p=0.64). This suggests that the light-rail line PM concentrations may vary according to seasonal and meteorological conditions, while the subway line PM concentrations are less influenced by temporal changes.

The fine fraction ($PM_{2.5}/PM_{10}$) and coarse fraction ($PM_{10-2.5}/PM_{10}$) of PM are shown for all stations and inside the train with corresponding error bars in Figures 3b and 3d for the subway line and light-rail line, respectively. The calculated PCIS fine and coarse fractions are also shown in the figures to demonstrate the agreement between the PCIS and DustTrak data. For the subway line, the station platforms and train have overall fine PM fraction averages of 0.73 and 0.79, respectively; for the light-rail line, the corresponding fine fraction averages are 0.78 and 0.86. In general, commuters are exposed to a somewhat lower fine PM fraction and thus a greater coarse fraction while they are waiting at the stations than while riding inside the train. This is consistent with a subway study conducted in Taiwan, which also found $PM_{2.5}/PM_{10}$ to be higher inside the train (0.75-0.78) than at station platforms (0.67-0.75) (Cheng et al. 2008). A possible reason for the lower coarse fraction inside the trains is that the air conditioning system of the train may be more efficient at removing larger coarse mode particles than smaller particles in the fine mode. Another subway study in Hong Kong found that a non-air-conditioned transport system had a significantly lower fine fraction (0.63-0.68) than an air-conditioned system (0.71-0.78) (Chan et al. 2002).

Figures 4a and 4b show real-time $PM_{2.5}$, PM_{10}, and CO_2 concentrations collected simultaneously for a select hour of sampling for the subway line and light-rail line, respectively. The figures demonstrate how the concentrations of these species vary while the commuter rides inside the train, steps out of the train onto a platform, and steps into a train from a platform. In general, $PM_{2.5}$ and PM_{10} concentrations follow each other consistently throughout the sampling period. One important observation is that PM concentrations are not as stable as expected inside the train, which may be due to resuspension of dust particles as passengers walk in and out of the train. A noticeable build-up of CO_2 occurs inside the train, whereas CO_2 levels drop rapidly as the commuter steps out of the train. The CO_2 measured inside the train is primarily from the exhaled breath of the riders. It is also important to note that when commuters stand right next to the train door, they are exposed to an immediate flux of particles and a reduction of CO_2 when the train door opens, which can be seen by the simultaneous peaks and dips in Figure 4a. Inside the train, CO_2 level reaches up to 1200 ppm, which is 3 to 4 times higher than the level of ambient CO_2 concentrations, but still not at a level of concern for commuters. A study in the Seoul subway system reported CO_2 levels ranging from 1153 to 3377 ppm (Park and Ha 2008). Note in Figure 4a, as the subway train departs from Union Station, CO_2 concentrations stay leveled for about 5 minutes until the train reaches 7th St/Metro Center, an extremely busy station, with a large number of passengers enter the train, thus creating a surge in CO_2 levels. As shown in Figure 4b, when the light-rail train departs from Union Station, CO_2 levels build up to ~1000

ppm as passengers stay in the car and then decrease as fewer passengers remain in the car. Although the number of passengers in the train car was not recorded during our field studies, the accumulation of CO_2 depends strongly on this factor.

4.1.3 Comparison of Metro red and gold line PM concentrations to nearby air monitoring sites

Previous studies have shown that underground transportation systems can be strongly influenced by PM from ambient air that may enter the stations through the system's ventilation system and walkways. High PM correlations (R=0.83-0.93) were found in Prague subway system between station platform concentrations and its direct ambient street concentrations (Branis 2006). A subway study in Taipei also found that PM levels of underground stations are positively correlated with outdoor concentrations (Cheng et al. 2008). In a Helsinki subway station, Aarnio et al. (2005) found that, based on particle size distribution measurements, the main source of particles with diameter <500nm inside stations was from vehicular street traffic.
To investigate the influence of ambient PM concentrations on the two Metro lines, the subway and light-rail line concentrations are plotted against ambient PM concentrations. Figures 5a-5d show the association of personal exposure $PM_{2.5}$ concentrations of the subway line (a-b) and the light-rail line (c-d) with the $PM_{2.5}$ levels recorded at the two nearest ambient air quality monitoring sites, located in Downtown L.A. and Burbank (Figure 1). PM data from the air quality monitoring sites are maintained by the South Coast Air Quality Management District (SCAQMD). Each data point represents a 3.5-hour average concentration from each day of sampling (N=54). As noted earlier, personal exposure concentrations are estimated based on spending approximately 75% of time inside the train and 25% of time at stations. The linear regression analysis reveals a moderately strong relationship between light-rail line personal exposure concentrations with ambient levels (R^2=0.62 and 0.59 for the Downtown L.A. and Burbank air quality monitoring site, respectively) and a weaker relationship between subway line personal exposure concentrations with ambient levels (R^2=0.38 and 0.38). This suggests that the light-rail line is more influenced by ambient PM levels than the subway line. Also, given the relatively small y-intercept of the regression lines (2.25 and 1.45 $\mu g\ m^{-3}$ in figures 5c and 5d, respectively), local emissions are presumably the main source of pollutants for the light-rail line. On the other hand, the subway line is less influenced by urban ambient air emissions and appears to have an almost constant background concentration of approximately 21 $\mu g\ m^{-3}$. This indicates that the trains in subway system generate a fair amount of airborne PM, which accumulates over time in the tunnel environment. The light-rail system most likely generates its own PM as well, but based on the regression analysis, it has little contribution to the personal PM exposure of its riders. In addition, the linear regression analysis also implies that on a day with high episodic ambient PM concentrations, light-rail commuters may be subjected to comparable or higher personal exposure concentrations than subway commuters.

4.1.4 Inter-correlations of PM concentrations to investigate sources

Figures 6a and 6b show the $PM_{2.5}$ and PM_{10} inter-correlation between the train and all stations for the subway and light-rail line, respectively. Regression analysis shows that PM_{10} and $PM_{2.5}$ are strongly correlated between train and station concentrations for the subway line (R^2=0.91 and 0.89) and light-rail line (R^2=0.81 and 0.78), respectively. This suggests PM inside trains and at

stations have a common source, and that the primary source of PM inside the train is PM that infiltrates the train from the station environment. The slope of the regression, or train-to-station ratio, indicates that overall, riders inside the train are exposed to 47% and 42% of the PM_{10} and $PM_{2.5}$ levels determined at station platforms for the subway line and 58% and 48% for the light-rail line. Consistent with a study on the Prague subway system, high correlation of PM_{10} was also found between station and train concentrations (R^2=0.96) (Branis 2006). However, the train-to-station ratio in that study was closer to 1.0, implying that commuters inside the train are exposed to very similar PM levels found at the stations.

As seen in Figures 4a and 4b, particles from the station infiltrate into the train when the door opens. This entrainment occurs to a greater degree for the subway line because of the relatively higher PM levels at the underground subway stations than at the ground-level light-rail stations. Dust that has accumulated over time in the trains can be resuspended as passengers walk around. To further investigate the sources of PM in the two microenvironments, station platforms and trains, correlation analysis between $PM_{2.5}$ and coarse PM was done. In Figure 7a and 7b, the data points represent the station/train intensive campaign average of the 7 days of sampling for each station and inside the train for the subway line and light-rail line, respectively. Since it was previously established that the two microenvironments have a common source of PM, a linear regression was performed for both the station and train data points. The high correlation (R^2=0.89) for the subway line scatter plot (Figure 7a) indicates that $PM_{2.5}$ and coarse PM have a common origin. Although this common PM source cannot be determined based on the data presented in this manuscript, previous studies have attributed metallic components of PM to originate from the friction of the wheels on the steel rails, the vaporization of metals due to sparking, wear of brakes (Pfeifer et al. 1999; Sitzmann et al. 1999), and particulate resuspension and dispersion from train and passenger movement (Chan et al. 2002; Raut et al. 2009). The upcoming chemical analysis of fine and coarse PM will help determine the degree to which the aforementioned sources may contribute to PM exposure in the underground environment. Figure 7b shows a weak correlation between $PM_{2.5}$ and coarse PM for the light-rail stations and train (R^2=0.21), suggesting that they do not share a common source. However, given the temporal variation of ambient air and its strong influence on the personal PM exposure levels of the light-rail line (Figure 5c and 5d), the data points presented in the figure, which represent the average of the 7 days of sampling, do not account for this significant factor. To account for the day-to-day variation of light-rail line PM concentrations, a linear regression of the daily fine and coarse PM levels was conducted for each station and the train (N=7). The correlation coefficients are presented in Table 3, which range from 0.52 to 0.92. This moderate to strong correlation suggests that fine and coarse PM for the light-rail line may indeed have a common source. It is reasonable to hypothesize that the primary source of particulate pollution for the light-rail line is from local emissions (vehicular traffic, road dust, photochemical reactions, etc). The daily operations of the light-rail trains (i.e. movement of the train) may also affect PM levels, but their impact is expected to be considerably smaller, given its exposed environment.

4.1.5 Comparison to worldwide rail systems

The Los Angeles Metro system, which began operation in 1993, is a relatively new rail system compared to other systems around the world, and is continuing to extend its operations across the L.A. Basin. Table 4 displays the average and range of PM_{10} and $PM_{2.5}$ concentrations and its fine

fraction ($PM_{2.5}/PM_{10}$) for various measurement locations at different rail systems around the world. In comparison to the PM levels of the subway systems presented, the particulate levels measured at the two rail lines of the Los Angeles Metro system fall on the relatively 'cleaner' side. On average, the underground stations of the Metro red line have PM_{10} and $PM_{2.5}$ levels that are 2.5 and 2.9 times greater than the USC urban ambient site, while an underground station in the Stockholm subway system had levels that are 4.8 and 11.2 times greater than its corresponding ambient site (Johansson and Johansson 2003). A study on the Seoul subway system reported levels of an underground station to be only 2.3 and 1.3 times greater than ambient concentrations, but the ambient PM_{10} and $PM_{2.5}$ concentrations were 155 μg m^{-3} and 102 μg m^{-3} respectively (Kim et al. 2008). The Seoul subway train PM levels are also exceptionally high because of the lack of a mechanical ventilation system inside the train (Park and Ha 2008). A study on the London subway system, the oldest rail system in the world, reported underground train $PM_{2.5}$ levels around 250 μg m^{-3} (Adams et al. 2001). A study on the New York City subway system measured $PM_{2.5}$ levels on average of 62.5 μg m^{-3}; these were determined by integrating measurements taken during 5 hours at underground subway stations and 3 hours inside trains (Chillrud et al. 2004). The PM levels of the L.A. Metro system are comparable to the Taipei, Helsinki, and Hong Kong subway systems, which are generally newer rail systems and are most likely equipped with more efficient ventilation systems and advanced braking technologies. Higher fine fractions ($PM_{2.5}/PM_{10}$) are also observed for the newer rail systems, while the older systems (London, Paris, Stockholm) exhibit considerably lower fine fractions, consistent with the fact that older ventilation systems may be less efficient at filtering larger particles. Aarnio et al. (2005) attribute the lower pollutant levels of the Helsinki subway system to be a result of the train's new electrical braking technique. The underground Metro red line utilizes electrodynamic braking from its top speed down to 8 mph, then pneumatically-operated tread braking to reach a complete stop (www.ansaldobredainc.com), which is a possible reason for its lower PM levels.

We should note that a number of additional factors may contribute to differences when comparing results from different subway systems. The time of sampling (i.e. rush hour, normal hours, weekend) and the frequency of trains in operation may influence PM levels (Birenzvige et al. 2003). Greater passenger activity may create more particulate resuspension. Also, the variation in monitoring equipment used to measure PM concentrations may also influence results to some degree.

4.2 Personal exposure campaign

4.2.1 Mass balance

To reconstruct total PM mass concentration for the red line, gold line, and USC ambient site, chemical species were grouped into six categories: organic matter (OM), elemental carbon (EC), inorganic ions, crustal metals less Fe (CM), elemental Fe, and trace metals. Organic matter was calculated using a multiplier of 1.8 to account for the oxygen, nitrogen, and hydrogen associated with organic carbon (Turpin and Lim 2001). Inorganic ions are the sum of Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Na^+, K^+, and NH_4^+. The CM category represents the sum of Al, K, Ca, Mg, Ti, and Si, each of which were multiplied by appropriate factors to convert to oxide mass (Cheung et al. 2011). Because silicon data was not acquired, Si was estimated by multiplying Al with a factor of 3.41

(Hueglin et al. 2005). For the purpose of this study, all Fe data is presented as total elemental Fe. Coarse and fine PM mass reconstructions were calculated in the same manner under the assumption that chemical species in both modes originate from the same source.

Figure 8 shows the mass reconstruction based on the six identified categories along with total gravimetric mass concentration for the gold line, red line, and USC ambient site for (a) coarse and (b) fine PM. All error bars in this study represent 1 standard deviation. In coarse PM, the gravimetric mass concentration of the gold line is approximately 40% of the USC ambient site, while mass concentration for the red line is almost equivalent to USC ambient site. Even though the gold line runs in the open atmosphere, the effect of being inside the train significantly reduces personal coarse PM exposure; however, this effect is not apparent for the red line, in which a previous study on the Los Angeles Metro has demonstrated an additional source of PM in the enclosed underground environment (Kam et al. 2011). In fine PM, the red line gravimetric mass concentration is approximately 70% greater than both the gold line and USC ambient site concentrations, while concentrations for gold line are only 5% less than USC ambient site. This suggests that the additional source of PM for the red line has a greater influence in the fine mode than in the coarse mode, and that being inside the train for the gold line does not substantially reduce fine PM exposure.

The most significant difference between the three sites is the abundance of Fe in the subway environment in both PM modes. In coarse PM, the gravimetric mass of red line, gold line, and USC ambient site contains 27%, 6%, and 2% Fe; fine PM in the corresponding sites contains 32%, 3%, and 1% Fe. This significant presence of Fe in the subway air has major implications in terms of personal exposure of subway passengers. The mass reconstruction for USC ambient site in coarse mode shows that about 48% of the gravimetric mass is unidentified. This is consistent with a coarse PM study in the Los Angeles basin that found 20-50% unidentified mass in urban sites and attributed the fraction to the uncertainty of the OC multiplier coupled with conversion factors for crustal oxides (Cheung et al. 2011). A closer look into the categories, including inorganic ions and crustal and non-crustal metals, is presented in the following sections to provide insight into the detailed PM chemical characterization and to identify their sources in the two Metro lines.

4.2.2 Inorganic ions

A total of 7 water-soluble inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Na^+, NH_4^+, and K^+) were analyzed in the coarse and fine PM samples from the three sampling sites. An investigation of the inorganic ions composition of the gold line and the red line samples reveals the extent to which ambient sources can influence PM exposure in the two microenvironments. Figure 9 shows the inorganic ions concentrations of the 5 predominant species (NO_3^-, SO_4^{2-}, Na^+, Cl^-, and NH_4^+) in (a) coarse and (b) fine mode for the gold line, red line, and USC ambient site in two sequential sampling periods, respectively. Period 1 is May 3 – June 11, 2010 and period 2 is June 14 – August 13, 2010. The gold line ions concentrations in coarse mode are presented as composites since the relatively low mass collected in each period did not meet the minimum mass requirements for reliable chemical analysis. In both modes, the ions concentrations for the red line sample consistently follow the patterns observed at the USC ambient site. This pattern is especially apparent for NO_3^- in the coarse mode and SO_4^{2-} in the fine mode, suggesting that there

are little to no sources of ions in the underground environment and that these inorganic PM species are heavily influenced by ambient air that infiltrates into the subway ventilation system. In urban environments, particulate NO_3^- and SO_4^{2-} are mainly secondary aerosol species formed by photo-oxidation of gaseous precursors (Seinfeld and Pandis 2006), while in the subway environment, these gaseous precursors are less available and thus secondary ionic aerosol formation is less favorable.
Figure 10 shows the inorganic ions composition (% of total ions) of the three sites for (a) coarse and (b) fine mode. The inorganic ions compositions are remarkably similar across all three sites, in which the coarse mode is 40-50% NO_3^-, 20-30% Na^+, 5-20% Cl^-, and 10-15% SO_4^{2-} and the fine mode comprises of 40-50% SO_4^{2-}, 15-30% NO_3^-, 15-20% NH4+, and 5-10% Na^+. This consistency further supports the influence of particle entrainment from the outdoors environment.

Previous studies have also shown that ambient air can be a major influence in underground subway air by infiltration through the ventilation system (Aarnio et al. 2005; Kam et al. 2011). The "piston effect" of a subway train is an explanation of how outdoor air can enter the underground subway environment. When the train departs the platform and enters the more enclosed subway tunnel, air in front of the train is pushed into station platforms and to the nearest ventilation shaft while drawing air from the nearest ventilation shaft behind the train. This natural ventilation mechanism simultaneously flushes subway air to the outside while bringing outdoors air into the subway environment.

4.2.3 Crustal species

Crustal species are elements that are derived from soil origins. They account for a significant portion of urban aerosols, especially in the coarse mode. Table 5 shows the average concentration of crustal species in coarse and fine PM for the gold line, red line, and USC ambient site. Except for fine mode Al and Ca, the concentrations of the latter crustal species (Mg, K, and Ti) in both modes for the red and gold lines are remarkably similar. For the red line sample, crustal species in the coarse mode also exhibit the same patterns as the inorganic ions in which the concentrations follow each other in the two sequential sampling periods (not shown), indicating the influence of ambient crustal aerosols. However, crustal species in the fine mode did not exhibit this trend. It is important to note that the average red line concentrations of fine mode Al and Ca are greater than corresponding USC concentrations, suggesting these two species may have an additional non-crustal source, which will be discussed in greater detail in the following section.

4.3.4 Non-crustal species

Selected non-crustal species concentrations (ng m^{-3}) and gold and red line to USC ambient site concentration ratios are also shown in Table 5. The species were selected based on its elevated concentrations relative to USC concentrations and results from other subway systems (Salma et al. 2007; Murruni et al. 2009). Numerous studies have determined Fe to be ubiquitous in subway environments, and are present in elevated concentrations relative to street levels by up to 50 times (Nieuwenhuijsen et al. 2007). The current study has also observed a number of non-crustal

species, particularly transition metals, to have significantly higher concentrations in the subway environment than USC ambient levels. It is important to note that the enrichment ratios of the red line relative to the gold line and USC ambient site are greater in the fine mode than in the coarse mode. For the red line, Fe concentrations (3.0 and 10.6 μg m^{-3} in the coarse and fine mode, respectively) are 12 and 45 times greater than the corresponding USC ambient site concentrations and 11 and 22 times greater than those for the gold line. A study in Budapest found Fe concentrations at station platforms to be 33.5 and 15.5 μg m^{-3} for $PM_{10-2.0}$ and $PM_{2.0}$, respectively, accounting for 40% and 46% of their corresponding total PM mass (Salma et al. 2007). Consistent with other worldwide subway studies, Mn, Cr, Co, Ni, Cu, and Ba were observed on the red line to have concentrations that are at least 2 times higher than corresponding USC ambient levels. In comparison to the gold line personal exposure, passengers on the red line are exposed to substantially higher levels of most of these trace elements. In addition, Mo, Cd, and Eu have also been identified to be significantly enriched in the subway environment, especially in the fine mode. One of the most revealing findings of this study is the substantially elevated levels of Mo in both PM modes and in both the subway and light-rail environments relative to USC ambient levels. For the red line, Mo concentrations are 113 and 146 times greater than USC levels in coarse and fine mode, respectively; for the gold line, Mo concentrations are 5 and 6 times greater than USC levels. The enriched levels of these non-crustal species observed for the red line can be attributed to its enclosed environment and a significant underground source that has resulted in the accumulation and subsequent resuspension of PM dust.

Subway dust is primarily generated by the frictional processes of the wheels, rails, and brakes of the system as well as by the mechanical wearing of these parts. Particles can also be formed by the condensation of gaseous Fe species from the sparking between the third-rail and the train (Pfeifer et al. 1999; Kang et al. 2008). Stainless steel, which is used for the rail tracks and the main body of the train for both lines, is an iron-based alloy mixed with chromium and other metallic elements. Additional elements are added to enhance the properties of the stainless steel. However, the composition of the stainless steel employed by the red and gold line could not be found as it may be proprietary information of the manufacturer.

A linear regression analysis was carried out for the crustal and non-crustal species to determine the inter-correlation in coarse and fine PM. Table 6 shows the coefficients of determination, or R^2, of these species. The regression analysis only includes total metals data from the gold line and red line samples (N=7) based on the assumption that the selected non-crustal species from the gold and red line environment are derived from a different source than corresponding species from USC ambient site. While Table 5 established the elevated concentrations of Al and Ca for the red line relative to USC ambient site, the bivariate linear regression analysis reveals that both species are strongly correlated with the majority of non-crustal species, suggesting that Al and Ca may have non-crustal sources for the gold and red line environments in addition to soil-derived sources. The strong correlation between Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Mo, Cd, Ba, and Eu suggests that these elements may share a common source, and may be components of stainless steel used by the subway and light-rail systems in this study.

Cu exhibits lower R^2 values with the other stainless steel elements, but it is still well correlated and also appears to be clustered with Zn, Ti, K, and Ca. Although Ba is strongly correlated with

the other non-crustal elements (R^2>0.96), it is not typically used as an alloy in stainless steel, but has been identified with the wear of brakes (Furuya et al. 2001). Another interesting finding for the red line environment is the enriched levels of Eu, a rare earth element that is used as an alloy. Other rare earth elements analyzed in this study include La, Ce, Pr, Nd, Sm, Dy, Ho, Yb, and Lu. Typically, rare earth elements naturally inter-correlate, however, in this case, Eu was the only rare earth element that was poorly correlated with the rest (not shown). Zn is the only non-crustal species not strongly correlated with other non-crustal species, but instead exhibits strong correlation with K and Ti. Zn is typically used as a coating on steel for corrosion protection (Marder 2000), but our regression analysis suggests its elevated concentrations may be from another source. A subway study in Buenos Aires found that the main source of Zn was from street-level vehicular emissions that penetrate through the ventilation system into the subway environment (Murruni et al. 2009).

Figure 11 shows the crustal enrichment factors (EF) for 22 elements for the gold line, red line, and USC ambient site in the (a) coarse and (b) fine mode. The crustal ratios are calculated based on Upper Continental Crust (UCC) values from Taylor and McLennan (1985) (Taylor and McLennan 1985). Total elemental concentrations are first normalized by Al and then divided by the relative abundance of the corresponding UCC ratio. A much higher crustal EF indicates anthropogenic origin for a given element, while an EF approaching 1 indicates crustal origin. The elements are sorted based on the decreasing order of the USC ambient site crustal EFs. The pattern in fine and coarse mode crustal EFs are remarkably similar to each other. Crustal EFs for Na, La, K, and Mg in both modes for the gold and red lines are lower than USC ambient site, suggesting the source is primarily from the ambient. In both modes, Mo has the highest crustal EF for the gold and red lines, followed by Fe, Mn, Ba, Cr, and Ni. It is evident that the source of these enriched elements is substantially greater on the red line than on the gold line. Table 5 showed that concentrations of Ni, Cr, and Ba for the gold line are lower or similar to corresponding concentrations at the USC ambient site, but the crustal EF analysis reveals that the EFs are actually greater than USC ambient site EFs by approximately 2-3 times. This suggests that these elements have indeed been influenced by sources other than those present at the USC ambient site.

Figure 12 shows the water-soluble concentrations (ng m^{-3}) and water-solubility (% of total) of the 11 non-crustal species that exhibited elevated concentrations on the red line relative to USC ambient site concentrations in (3a-3b) coarse and (3c-3d) fine mode. Except for Ba in coarse and fine PM and Fe in fine PM, the soluble concentrations of the latter elements exhibit much less variation across the three sites. The average red-to-gold ratios for all species are 3.4±3.1 and 2.3±1.6 for coarse and fine PM, respectively; the average fine-to-coarse ratios are 4.8±4.3, 6.7±8.1, and 2.6±1.8 for red line, gold line, and USC ambient site, respectively. In relation to total elemental enrichment ratios presented in Table 5, soluble elemental enrichment ratios are substantially lower. In terms of solubility (%), most of the select elements exhibit lower solubility on the red line than the gold line and USC ambient site. For the red line, Mn is 31% and 28% lower, Co is 30% and 21% lower, and Mo is 19% and 40% lower than USC ambient site solubility for coarse and fine PM, respectively. Our results suggest that particles generated from the subway environment are inherently different from particles generated by vehicular combustion and industrial processes, which are the predominant sources of these species in urban Los Angeles (Singh et al. 2002). Because the soluble fraction of metals is more bioavailable to

human lung cells than the insoluble fraction, there may be a greater impact in PM-induced cellular oxidative stress.

4.3.5 ROS activity

A number of transition metals that have been identified in this study to be present in elevated concentrations are known to contribute to the generation of reactive oxygen species (ROS). The last row of Table 6 shows the ROS coefficients of determination (R^2) with water-soluble crustal and non-crustal species for the red and gold lines (N=7). Non-crustal species, especially Fe, Ni, and Cr, show strong correlations with ROS activity while the crustal species show poor correlations. This is consistent with previous studies that have shown an association between certain water-soluble transition metals and ROS activity (Verma et al. 2010). Although Cd also shows a strong correlation with ROS activity, Cd is not redox active and its concentrations are below any toxicity threshold.

Figure 13 shows the ROS activity of particles for the gold line, red line, and USC ambient site in ng of Zymosan units (a) per volume (m^3) and (b) per mass (mg). The per volume basis is relevant for the personal exposure assessment of passengers, while the per mass basis is a measure of the intrinsic properties of the particles collected. On a per volume basis, fine PM accounts for 90-98% of total ROS activity. In addition, ROS activity observed on the red line is greater than USC ambient site and gold line activity by 65% and 55%, respectively. Even though total concentrations of ROS-active metals (Fe, Ni, and Cr) in both modes are 4-44 times greater on the red line than at USC ambient site (Table 5), ROS activity differs by less than 2 times. The opposite is observed when comparing the two PM modes, in which ROS activity differs by 7-29 times and total concentrations of Fe, Ni, and Cr only differ by 2-4 times. Based on these observations, it is clear that the soluble fraction of the metals plays a dominant role in ROS activity, which can be reflected in the concentrations of the soluble redox-active elements (Figure 12a and 12c). On a per mg basis, gold line ROS activity in fine mode is 13% greater than red line and USC ambient site activity, while red line and USC ambient site ROS activity are comparable. Our results suggest that one unit of PM mass on the gold line may be as intrinsically toxic as one unit of PM mass from the red line, however, from a personal exposure perspective, PM originating from the red line generates greater ROS activity on a per volume basis than PM from the gold line and at USC ambient site.

It should be noted that a more appropriate personal exposure assessment of transport microenvironments in Los Angeles should be a comparison with the predominant mode of commute—private vehicles. Passengers of the Los Angeles Metro may actually be subjected to lower levels of PM and toxic co-pollutants such as EC and transition metals. Figure 14 shows a comparison of $PM_{2.5}$ and EC concentrations measured in the immediate proximity of the I-5 and I-710 with the gold line and red line. To date, freeway commuter exposure assessments of on-road PM chemical composition measurements are limited. Our future investigation will provide a comprehensive exposure assessment of "on-road" PM physical and chemical characterization of heavily trafficked freeways and arterial roads of urban Los Angeles. In particular, EC is used by state and federal legislation in health risk assessment as a surrogate of diesel exhaust emissions. Previous studies have identified elevated levels of EC and PAHs in the immediate proximity of

freeways (Kuhn et al. 2005; Ning et al. 2008). This future study will offer a greater understanding of personal exposure to certain carcinogenic species, notably EC and polycyclic aromatic hydrocarbons (PAHs), in various transportation modes in the Los Angeles basin.

5. Conclusion

An intensive particulate sampling campaign was conducted in spring and summer of 2010 to compare two types of rail systems on the L.A. Metro, an underground subway system (Metro red line) and a ground-level light-rail system (Metro gold line). In general, commuters of the subway line are exposed to greater PM concentrations than commuters of the light-rail line by almost two-fold. Regression analysis showed that the light-rail line is heavily influenced by ambient PM levels and its particulate pollutants originate from local sources, such as vehicular emissions and road dust. The subway line is less influenced by ambient PM levels and has an additional source of airborne particulate pollution that is generated from the daily operation of trains. Strong correlations of $PM_{2.5}$ and PM_{10} between train and stations reveal that PM from stations is the main source of PM inside trains. $PM_{2.5}$ and coarse PM are also highly correlated, suggesting they are also derived from the same source. A comprehensive chemical analysis on the time-integrated data included total and water-soluble metals, inorganic ions, and elemental and organic carbon. Mass balance showed that in coarse PM, iron makes up 27%, 6%, and 2% of gravimetric mass for red line, gold line, and USC, respectively; in fine PM, iron makes up 32%, 3%, and 1%. Ambient air is the primary source of inorganic ions for both lines. Non-crustal metals, particularly Cr, Mn, Co, Ni, Mo, Cd, and Eu were elevated for the red line and, to a lesser degree, the gold line. Mo exhibited the greatest crustal enrichment factors. The enriched species were less water-soluble on red line than corresponding species on gold line. Reactive oxygen species (ROS) activity results suggest that one unit of PM from gold line may be as toxic as one unit of PM from red line; however, from a personal exposure perspective, PM from red line generates greater ROS activity per volume than PM from gold line and USC.

It should be noted that a more appropriate personal exposure assessment of transport microenvironments in Los Angeles should be a comparison with the predominant mode of commute—private vehicles. Passengers of the Los Angeles Metro may actually be subjected to lower levels of PM and toxic co-pollutants such as EC and transition metals. Previous studies have identified elevated levels of EC and PAHs in the proximity of freeways (Kuhn et al. 2005; Ning et al. 2008). In particular, a comparison of $PM_{2.5}$ and EC concentrations measured in the proximity of the I-5 and I-710 are substantially higher than levels found on the gold line and red line. Our future investigation will provide a comprehensive exposure assessment of "on-road" PM physical and chemical characterization of heavily trafficked freeways and arterial roads of urban Los Angeles as a basis of comparison to PM personal exposure for passengers on the light-rail system.

6. Publications produced from this study

1. Kam, W., Cheung, K., Daher, N., Sioutas, C. Particulate matter (PM) concentrations in underground and ground-level rail systems of the Los Angeles Metro. *Atmospheric Environment*. **2011**, 45 (8), 1506-1516.

2. Kam, W., Ning, Z., Shafer, M., Schauer, J.J., Sioutas, C. Chemical characterization of coarse and fine particulate matter (PM) in underground and ground-level rail systems of the Los Angeles Metro. Accepted for publication to *Environmental Science & Technology* in July 2011.

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9. Figures and Tables

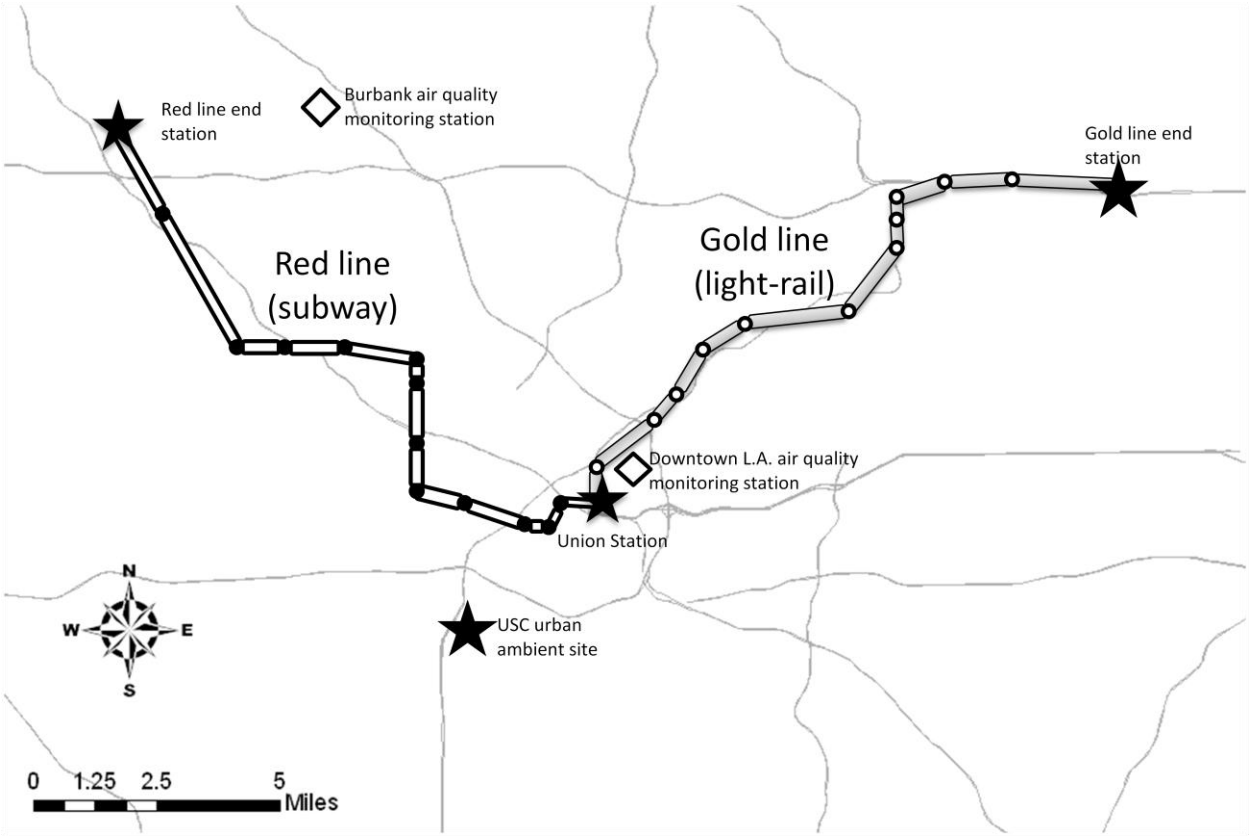


Figure 1. Map of sampling routes, the Metro red line (subway) and gold line (light-rail), two nearest air quality monitoring stations, and the University of Southern California (USC) urban ambient site.

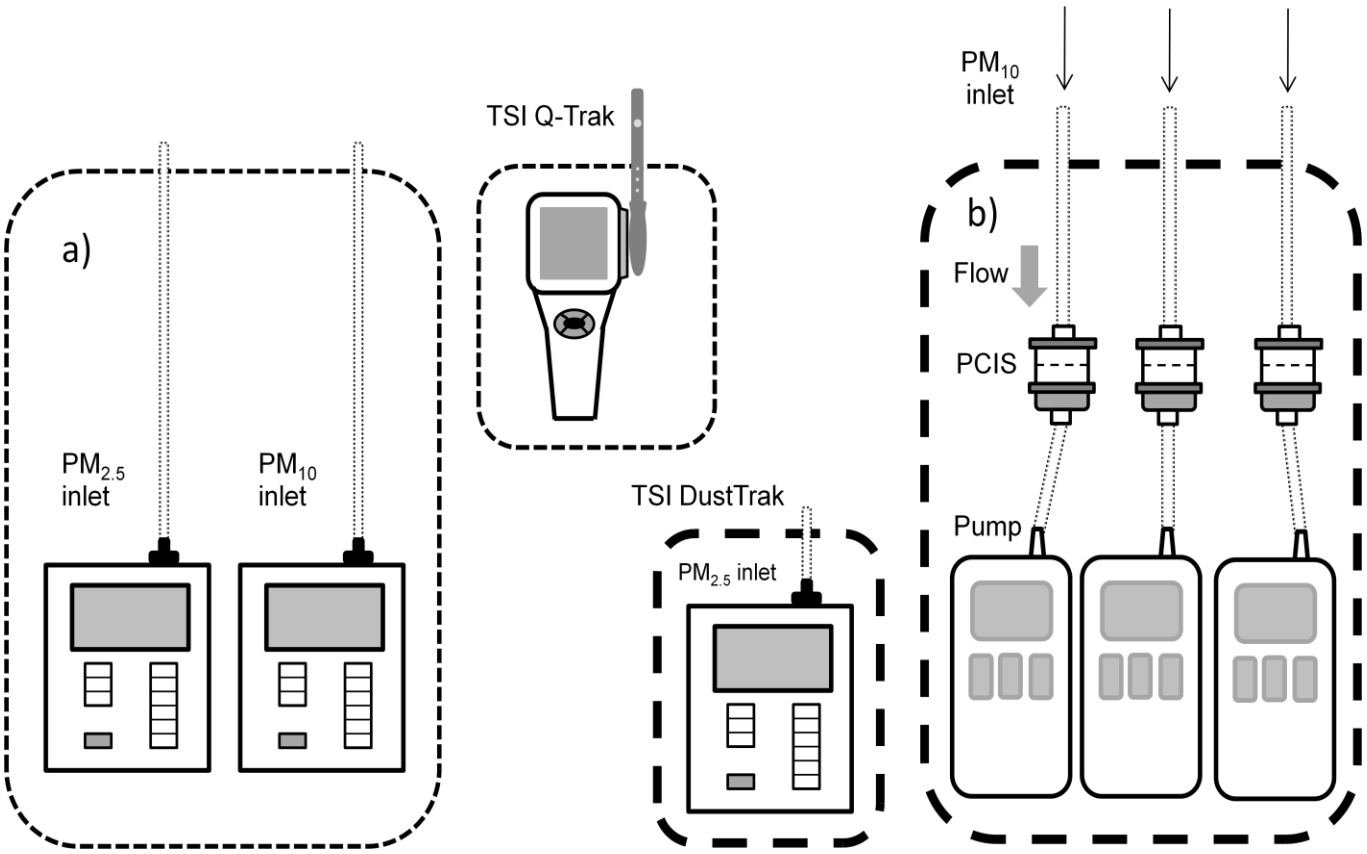


Figure 2. (a) Carry-on suitcase setup for station/train intensive campaign, two DustTraks with $PM_{2.5}$ and PM_{10} inlet. TSI Q-Trak was transported in a small bag. (b) Suitcase setup for the personal exposure campaign, three personal cascade impactor samplers (PCIS) with individual battery-powered pumps. A DustTrak with $PM_{2.5}$ inlet was transported in a small bag.

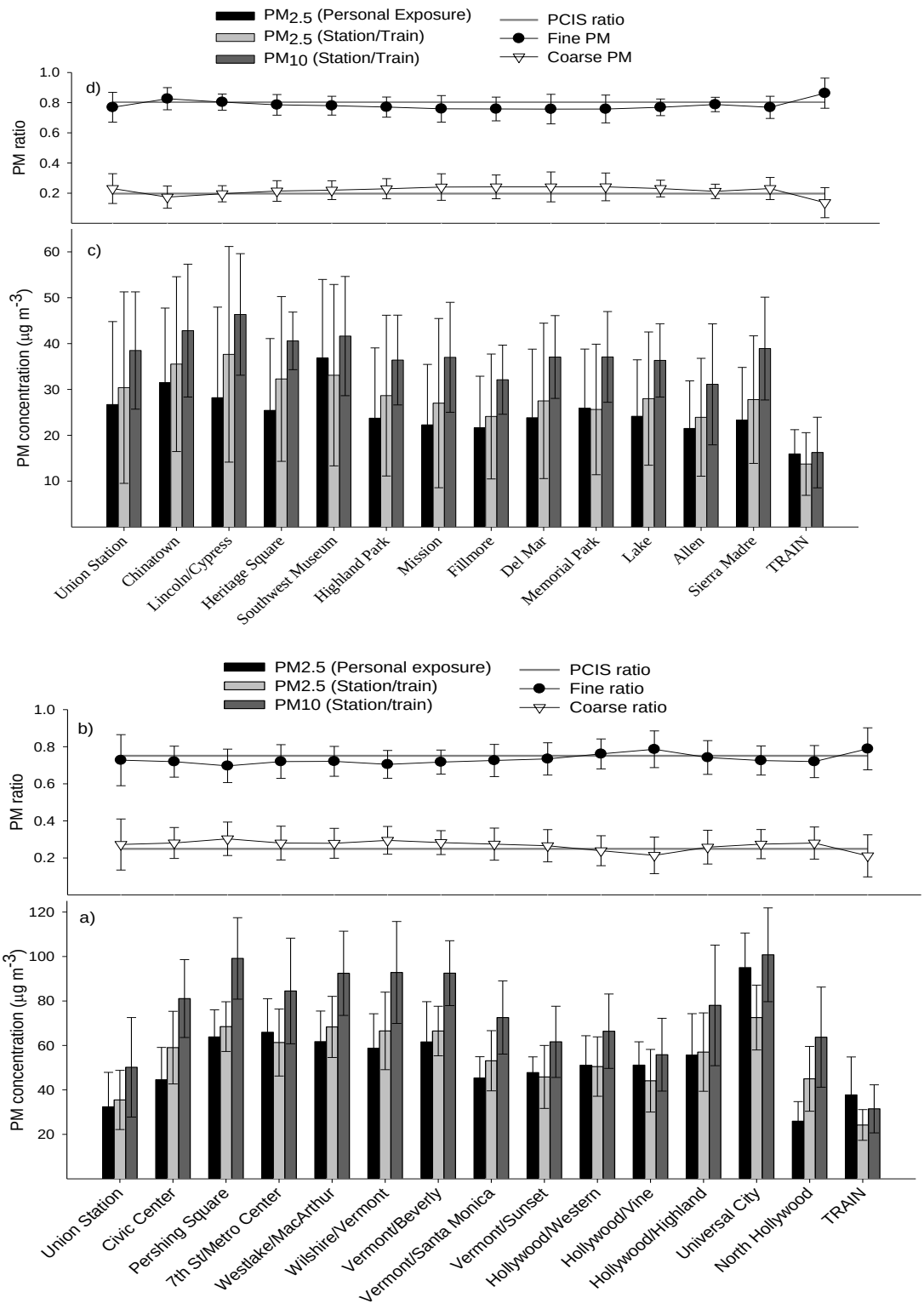


Figure 3. Particulate matter (PM) concentrations for all stations and inside the train. Mass concentrations of $PM_{2.5}$ from the personal exposure campaign and $PM_{2.5}$ and PM_{10} from the station/train intensive campaign are presented for the subway line (a) and the light-rail line (c). Fine fraction ($PM_{2.5}/PM_{10}$) and coarse fraction ($PM_{10\text{-}2.5}/PM_{10}$) data from DustTrak are presented for the subway line (b) and light-rail line (d) along with corresponding PCIS mass concentrations.

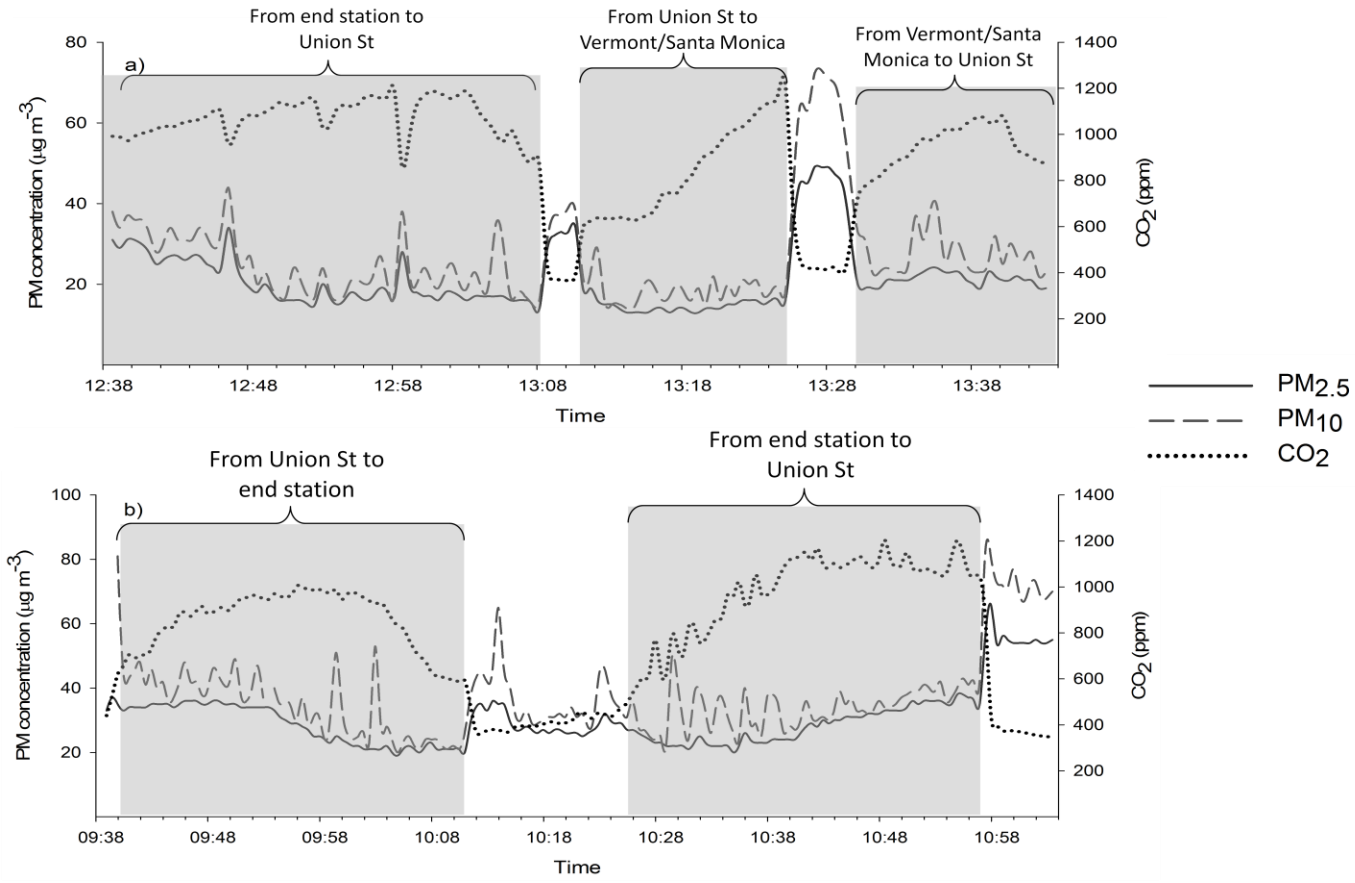


Figure 4. Continuous $PM_{2.5}$, PM_{10}, and CO_2 data for approximately one hour of sampling for the subway line (a) and the light-rail line (b). Shaded areas represent times when the subject was riding inside the train.

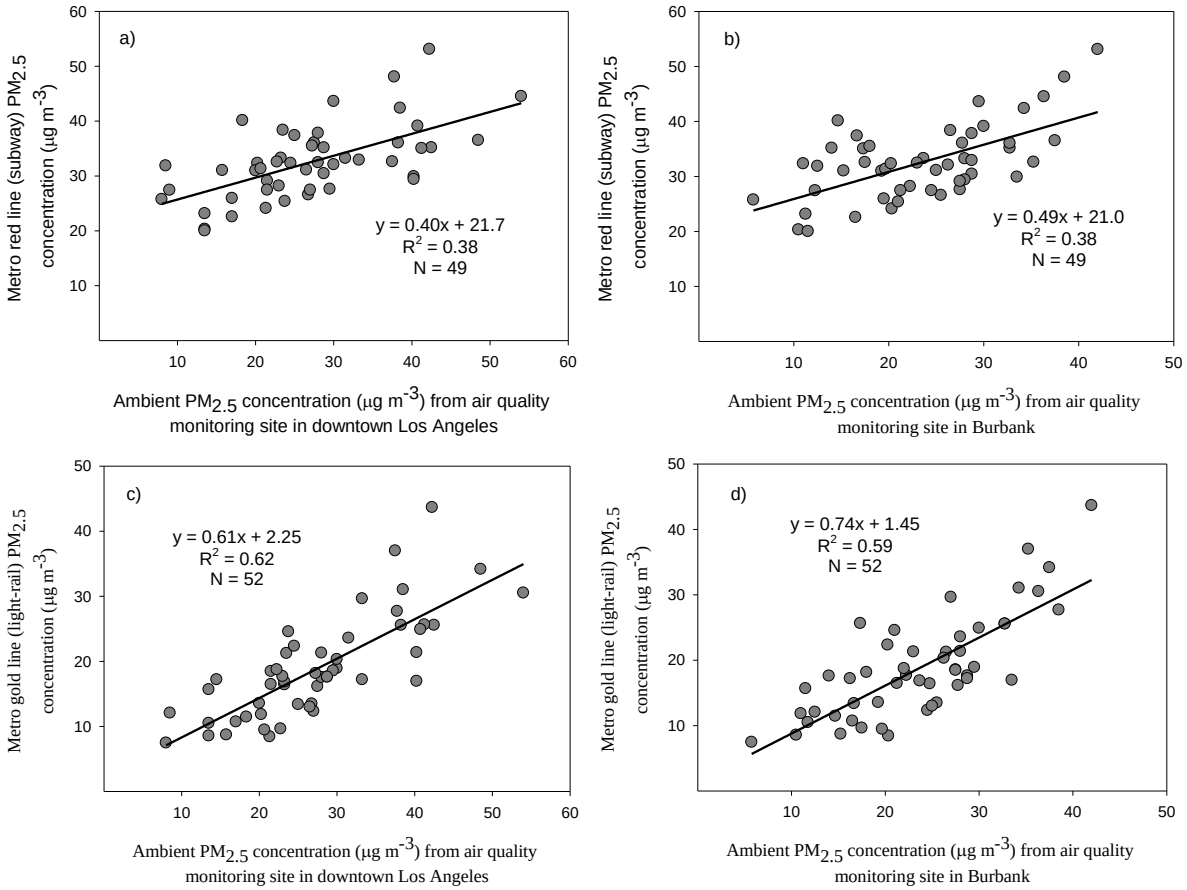


Figure 5. Comparison of $PM_{2.5}$ concentrations from personal exposure campaign with ambient $PM_{2.5}$ levels from two nearby monitoring stations (Downtown L.A. and Burbank) operated by the South Coast Air Quality Management District (SCAQMD). Each data point represents a 3.5-hour average from one day of sampling. (a) Metro red line (subway) vs Downtown L.A., (b) Metro red line (subway) vs Burbank, (c) Metro gold line (light-rail) vs Downtown L.A., and (d) Metro gold line (light-rail) vs Burbank.

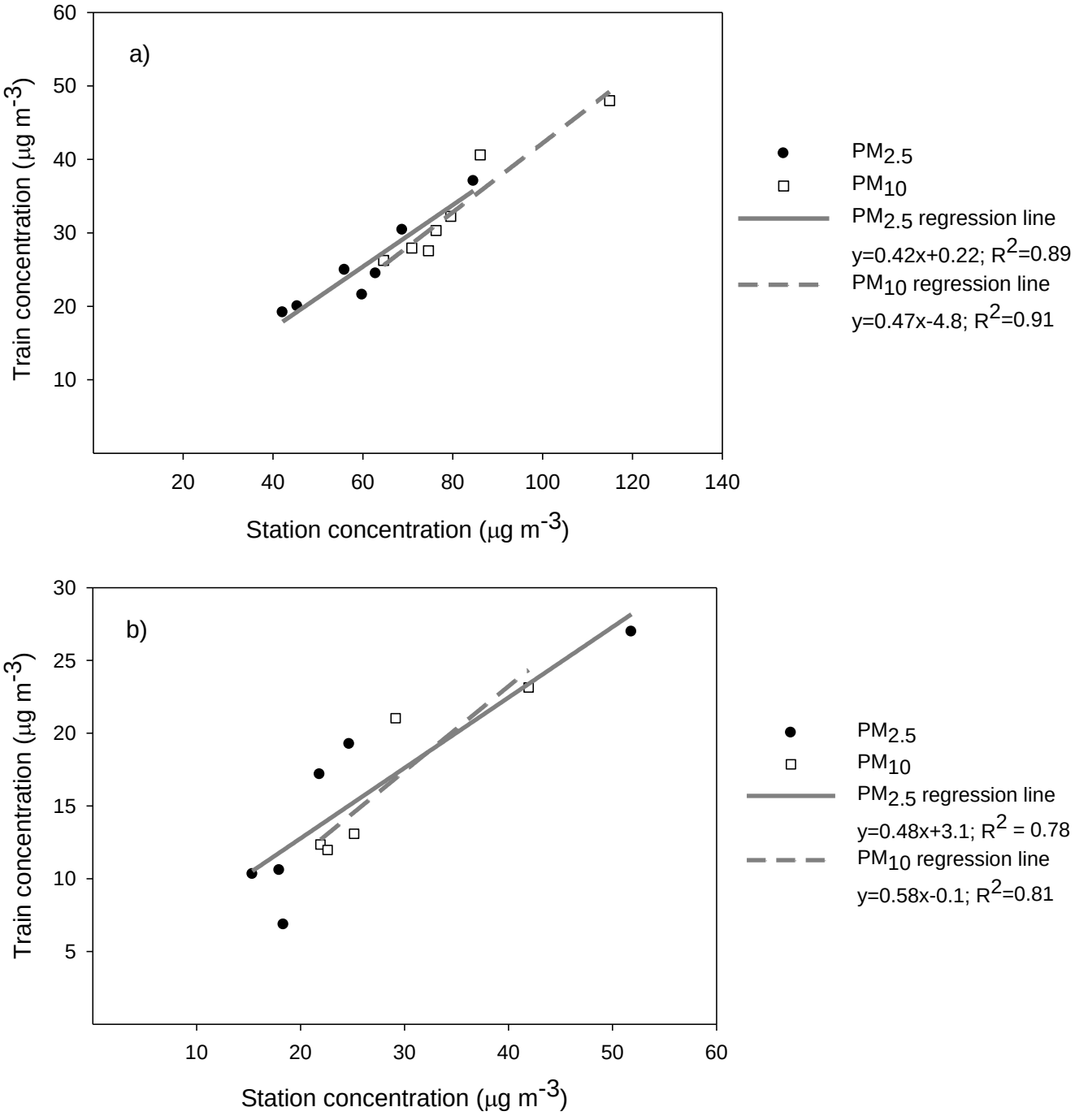


Figure 6. Correlation of $PM_{2.5}$ and PM_{10} concentrations between the train and station environments for the subway line (a) and light-rail line (b). Linear regression analysis was also conducted for PM_{10} and $PM_{2.5}$ data.

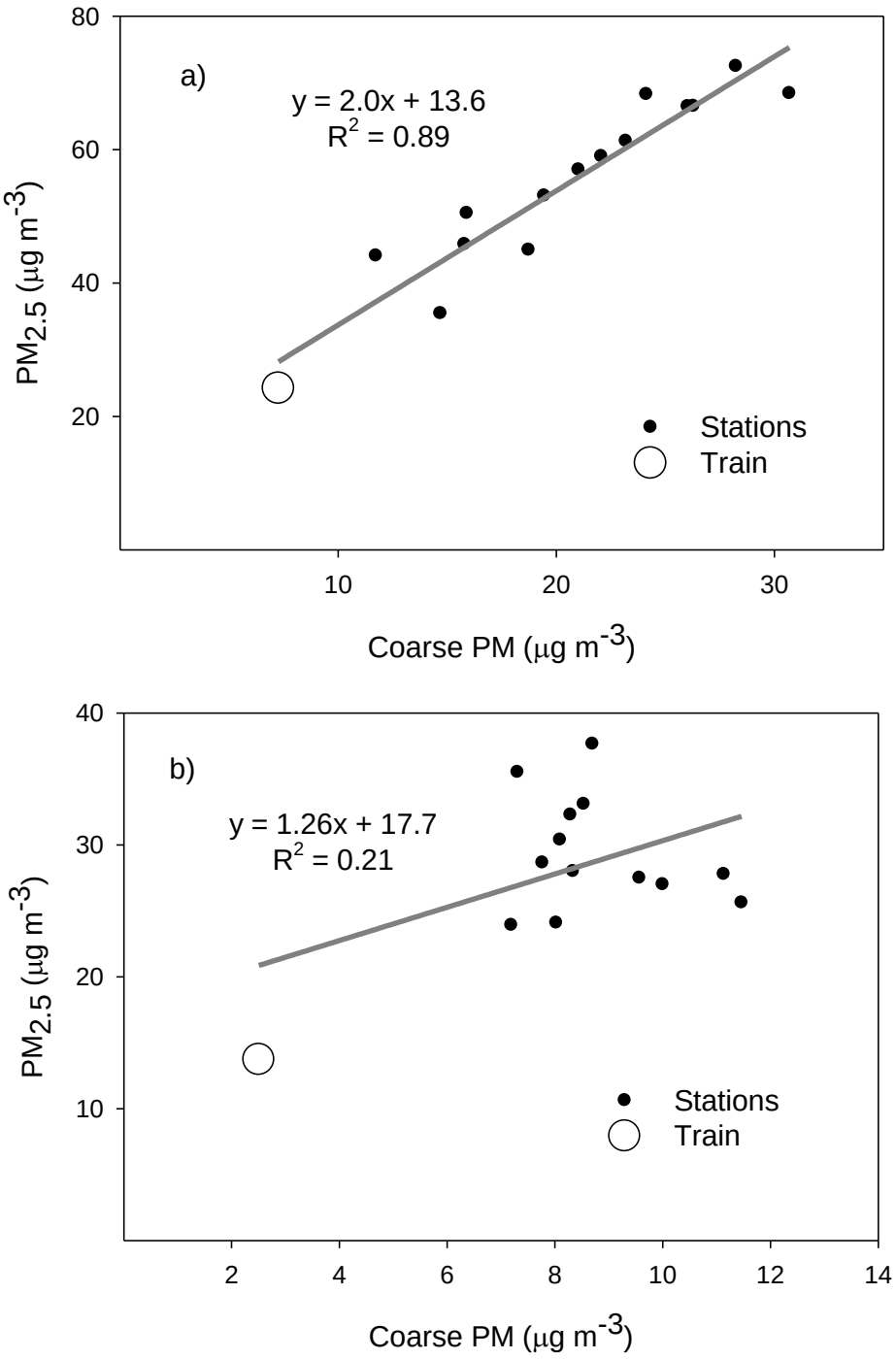


Figure 7. Correlation of $PM_{2.5}$ and coarse PM data at all stations and inside train for subway line (a) and light-rail line (b). Each data point represents an average of the 7 days of sampling from the station/train intensive campaign.

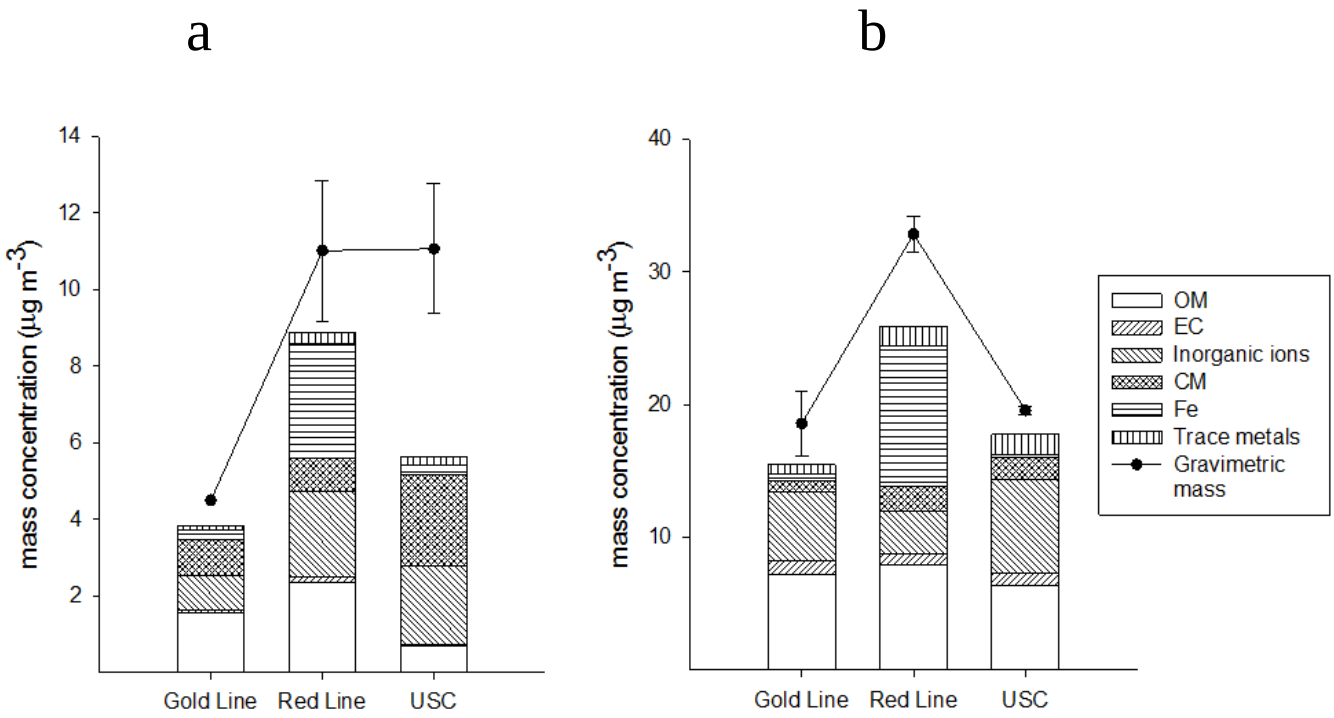
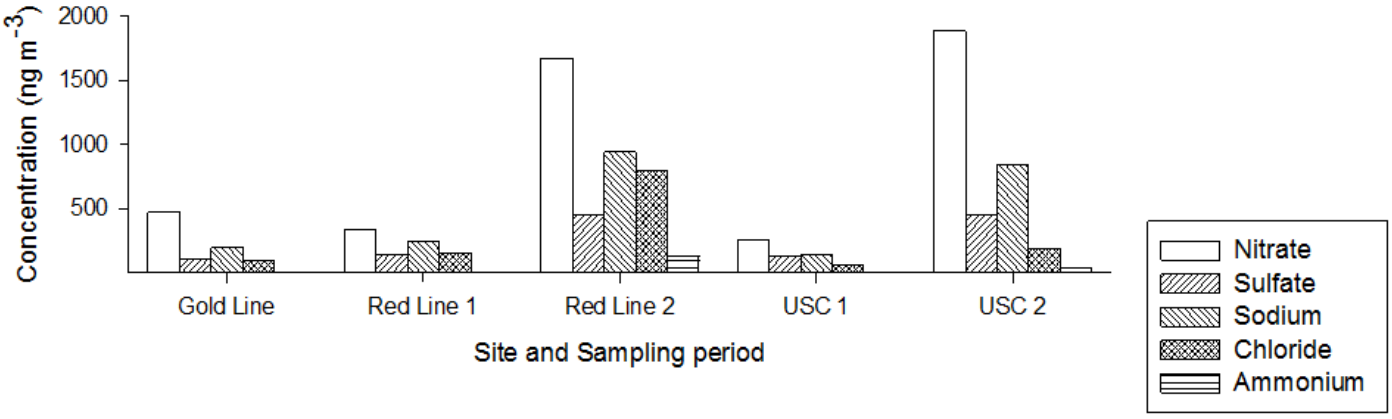


Figure 8. Mass reconstruction of the 6 identified categories for the gold line, red line, and USC ambient site in (a) coarse PM and (b) fine PM. Gravimetric mass concentrations are also presented. All error bars shown in this study represent 1 standard deviation (SD).

a



b

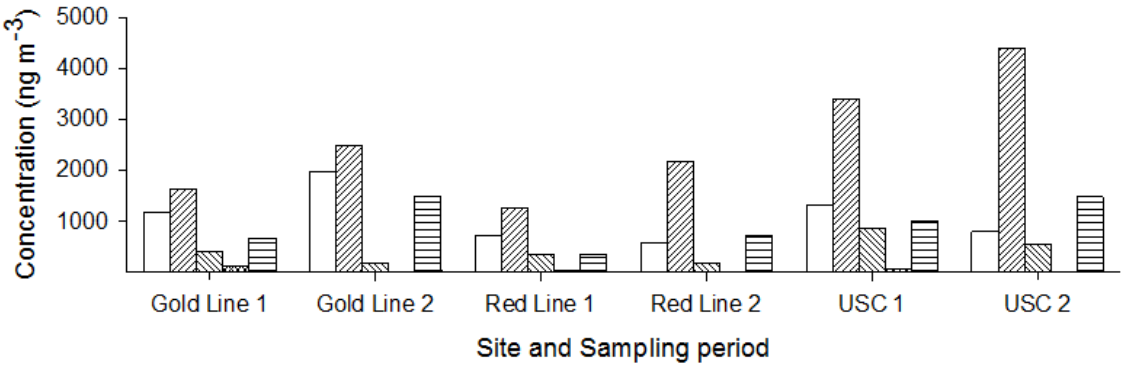


Figure 9. Inorganic ions concentrations (ng m^{-3}) of the five predominant species for (a) coarse and (b) fine PM. Two periods are displayed for all sites except for the coarse mode gold line sample, in which only composite concentrations could be determined. Period 1 is May 3 – June 11, 2010 and period 2 is June 14 – August 13, 2010.

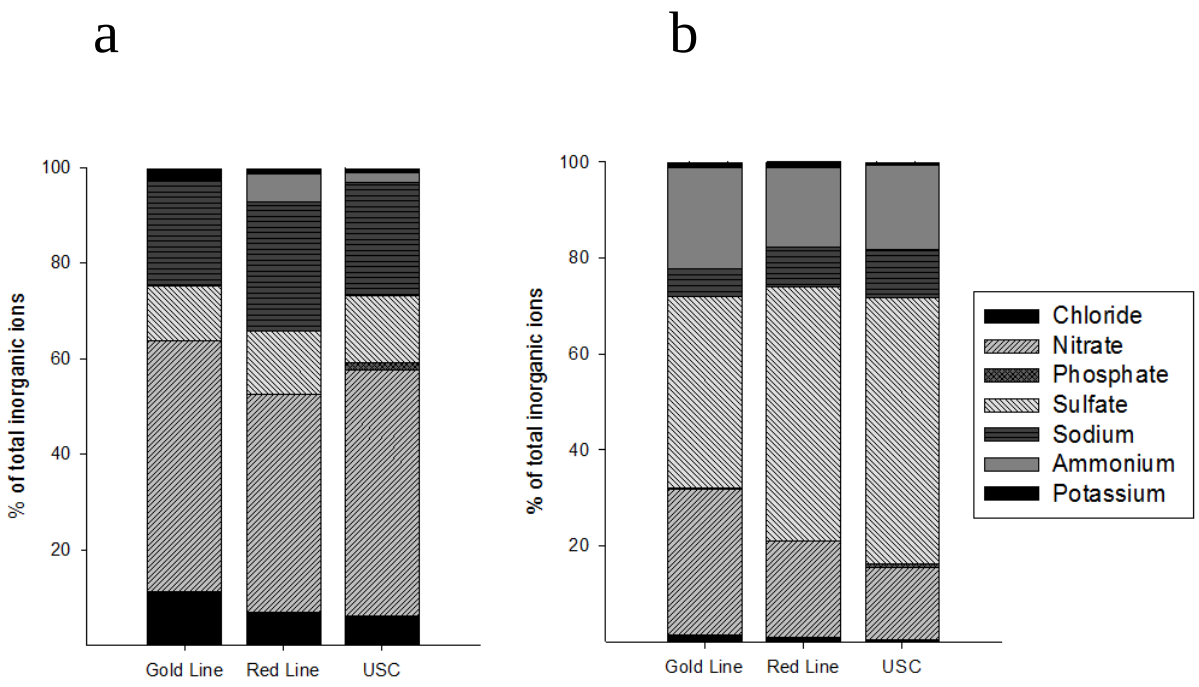
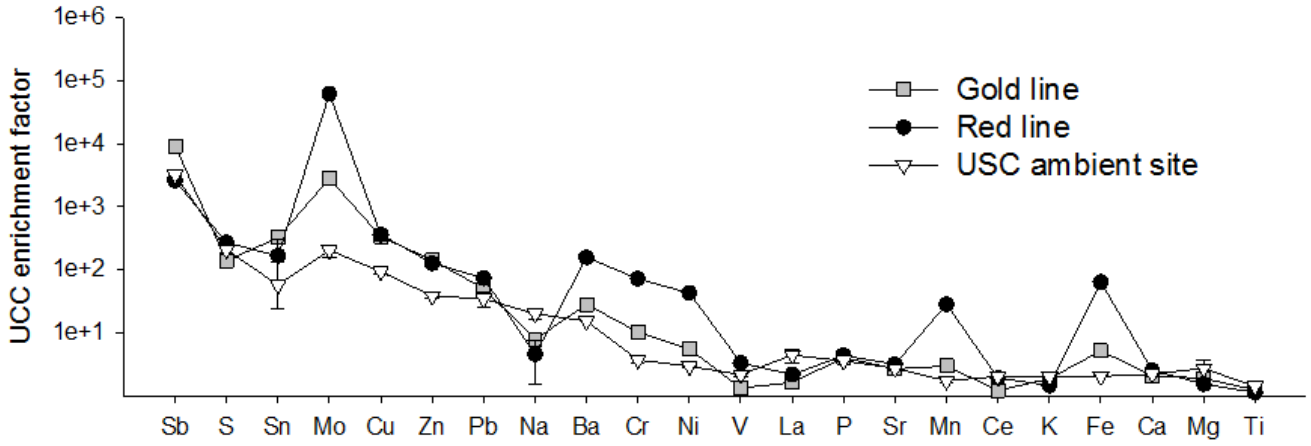


Figure 10. Average inorganic ions composition (% of total ions) of gold line, red line, and USC ambient site for (a) coarse and (b) fine PM.

a



b

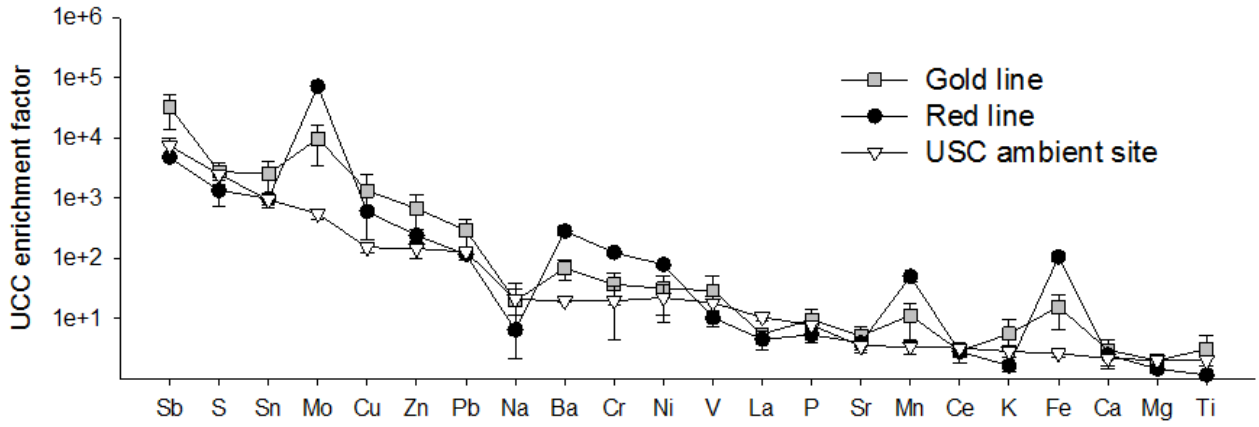


Figure 11. Upper Continental Crustal (UCC) enrichment factors (EFs) for (a) coarse and (b) fine mode in descending order of USC ambient site. Total elemental concentrations are used in the calculations. Error bars are also presented for all sites except for coarse mode gold line.

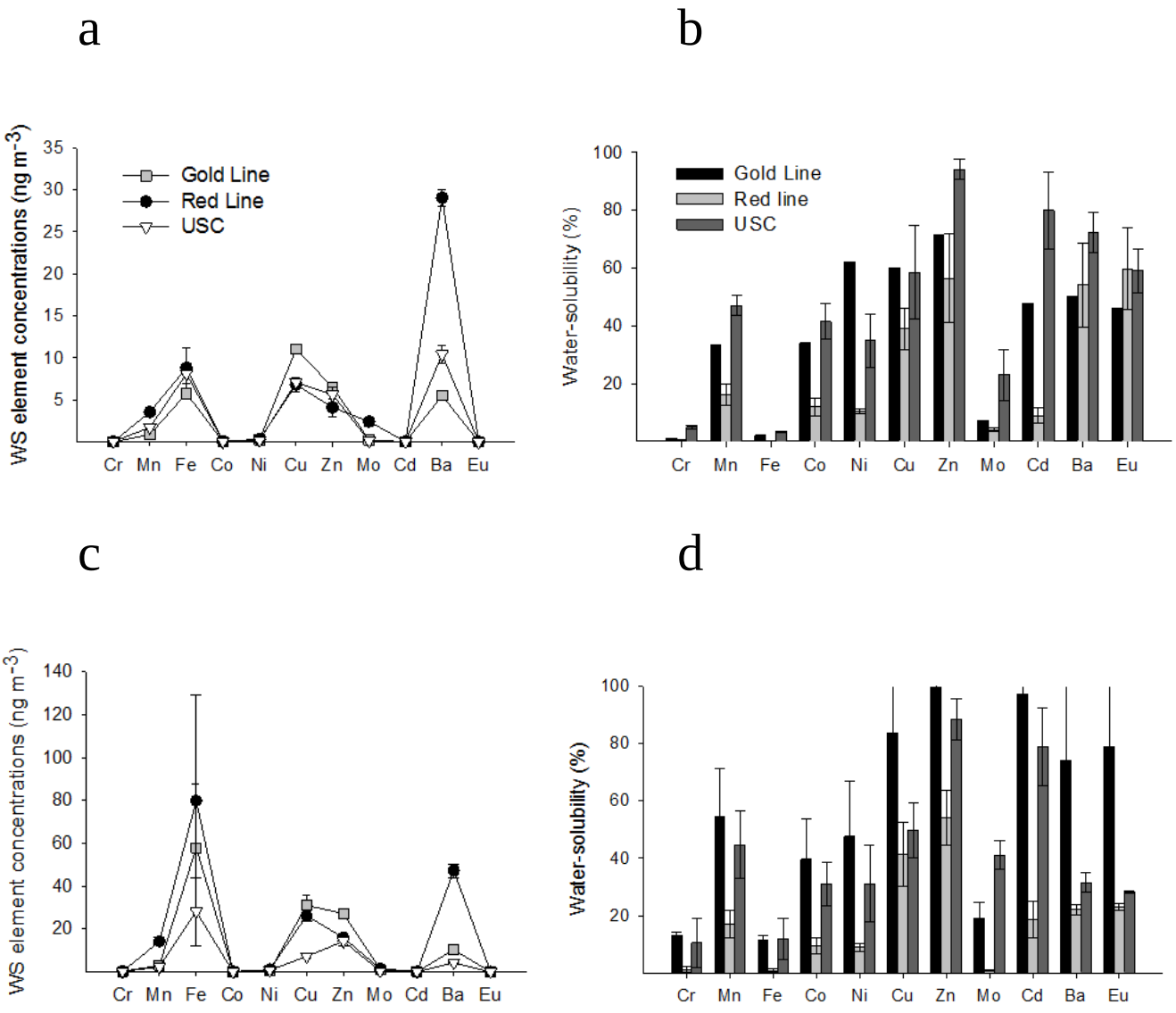


Figure 12. Water-soluble elemental concentrations (ng m^{-3}) and solubility (% of total) for (a-b) coarse mode and (c-d) fine mode.

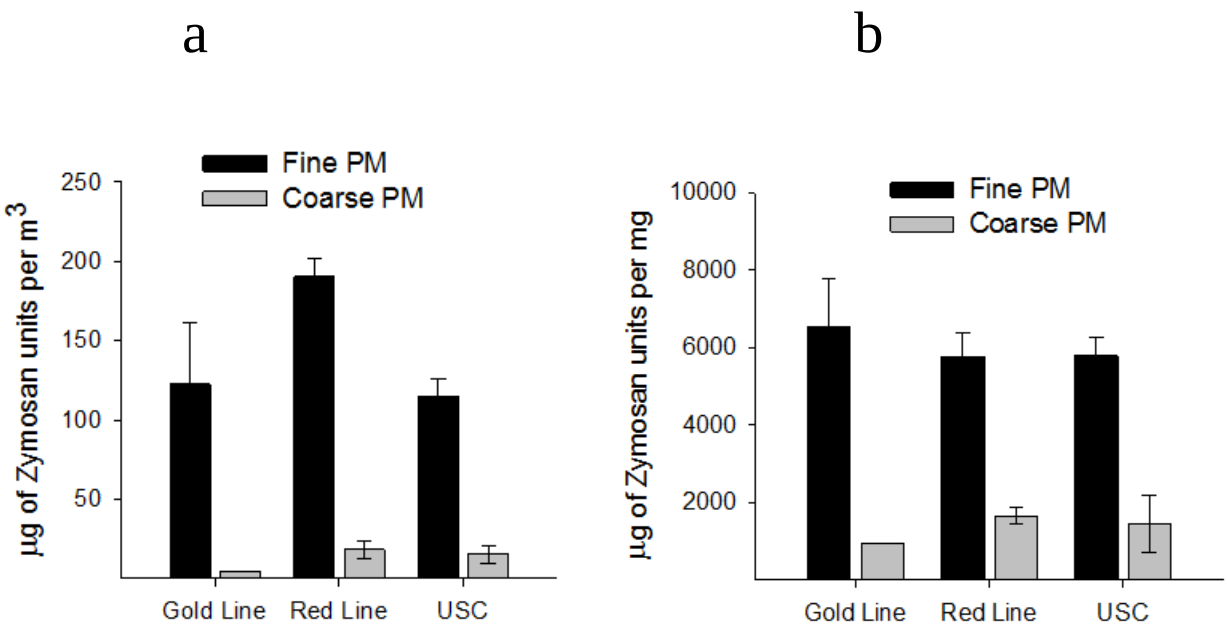


Figure 13. Reactive oxygen species (ROS) activity shown as (a) per volume (m^3) and (b) per gravimetric mass (mg).

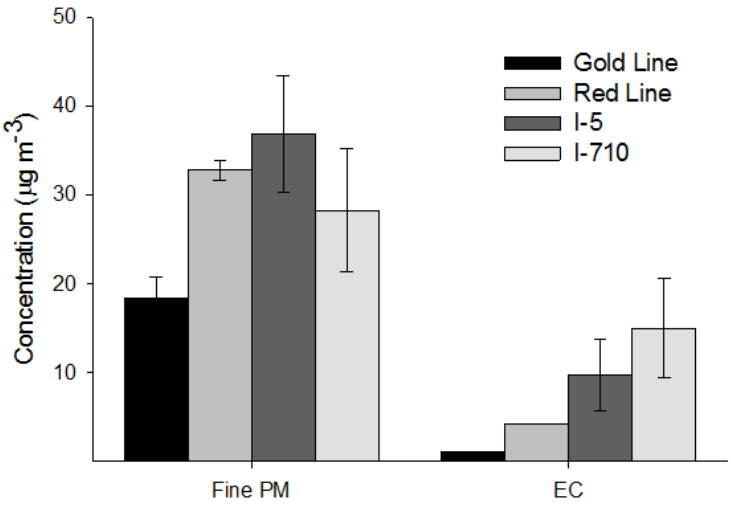


Figure 14. Comparison of average PM2.5 and elemental carbon (EC) concentrations (µg m^{-3}) for the L.A. Metro gold line, red line, I-5, and I-710.

	Period	Dates of sampling	PCIS			Dust Trak	
			PM_{10} ($\mu g\ m^{-3}$)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	Coarse PM ($\mu g\ m^{-3}$)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	Correction factor
Subway system (red line)	1	May 3 - Jun 11, 2010	45.8	33.6	12.1	28.6	0.85
	2	Jun 14 - Aug 13, 2010	41.6	32.0	9.6	35.5	1.11
Ground-level light-rail system (gold line)	1	May 3 - Jun 11, 2010	22.7	16.6	6.1	23.9	1.43
	2	Jun 14 - Aug 13, 2010	23.3	20.1	3.2	37.3	1.86
Urban ambient site (USC)	1	May 3 - Jun 11, 2010	31.0	19.0	12.1	-	-
	2	Jun 14 - Aug 13, 2010	29.5	20.0	9.5	-	-

Table 1. Summary of the personal exposure campaign. Average PCIS and DustTrak PM concentrations for the subway system (red line), light-rail system (gold line), and the USC urban ambient site are presented. DustTrak correction factors are calculated based on $PM_{2.5}$ concentrations from the PCIS.

		PM_{10} ($\mu g\ m^{-3}$)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	Coarse PM ($\mu g\ m^{-3}$)
Subway line (red)	Stations (all)	78.0 ± 16.5	56.7 ± 11.3	21.3 ± 5.6
	Train	31.5 ± 10.8	24.2 ± 6.9	7.3 ± 6.4
Light-rail line (gold)	Stations (all)	38.2 ± 4.1	29.4 ± 4.2	8.8 ± 1.4
	Train	16.2 ± 6.8	13.7 ± 5.3	2.5 ± 2.4
Urban ambient site (USC)		30.7	19.9	10.8

Table 2. Summary of the station/train intensive sampling campaign. Average PM_{10}, $PM_{2.5}$, and coarse PM concentrations for subway line, light-rail line, and USC urban ambient site are presented. Standard deviations are also shown except for USC site. The subway and light-rail data were obtained by DustTrak measurements and the urban ambient site data were obtained by PCIS analysis.

Gold line	
	R
Union Station	0.81
Chinatown	0.80
Lincoln/Cypress	0.88
Heritage Square	0.77
Southwest Museum	0.82
Highland Park	0.85
Mission	0.74
Fillmore	0.73
Del Mar	0.68
Memorial Park	0.52
Lake	0.75
Allen	0.84
Sierra Madre	0.67
TRAIN	0.92

Table 3. Correlation coefficients between $PM_{2.5}$ and coarse PM of individual stations and inside the train for the light-rail (gold) line. R values are based on the average daily concentrations (N=7).

City (study year)	Measurement location	$PM_{2.5}$ ($\mu g\ m^{-3}$)		PM_{10} ($\mu g\ m^{-3}$)		Fine fraction ($PM_{2.5}/PM_{10}$)	Reference
		average	range (min-max)	average	range (min-max)		
Los Angeles (2010)	in train (gold line - ground level)	14	3-38	16	6-53	0.88	Current study
	in train (red line - underground)	24	11-62	31	14-107	0.77	
	ground level station platforms (all stations)	29	4-77	38	8-184	0.76	
	underground station platforms (all stations)	57	9-130	78	14-197	0.73	
	urban ambient site	20	-	31	-	0.65	
Taipei (2007)	in train (underground)	31	19-51	40	22-71	0.78	*Cheng et al. (2008)*
	underground station platform	44	22-91	66	29-130	0.67	
	ground level station platform	33	7-94	44	11-131	0.75	
Paris (2006)	underground station platform (rush hours)	93	-	320	-	0.29	*Raut et al. (2009)*
	underground station platform (normal hours)	61	-	200	-	0.31	
Helsinki (2004)	in train (underground)	21	17-45	-	-	-	*Aarnio et al. (2005)*
	underground station platform	50	37-87	-	-	-	
Seoul (2004)	underground station platform	129	82-176	359	238-480	0.36	*Kim et al. (2008)*
	in train (underground)	126	115-136	312	29-356	0.40	
	urban ambient site	102	41-174	155	79-254	0.66	
Stockholm (2000)	underground station platform	258	105-388	469	212-722	0.55	*Johansson and Johansson (2003)*
	urban ambient site	23	3-89	98	6-454	0.23	
New York City (1999)	integration of 5h at station platform and 3h in train	62	-	-	-	-	*Chillrud (2004)*
Hong Kong (1999)	in train (mostly underground)	33	21-48	44	23-85	0.75	*Chan et al. (2002)*
	in train (mostly ground level)	46	29-68	60	41-89	0.77	
London (1999)	in train (underground line)	247	105-371	-	-	-	*Adams et al. (2001)*
	in train (above ground line)	29	12-42	-	-	-	

Table 4. A comparison of PM_{10} and $PM_{2.5}$ average concentrations and range for worldwide subway systems at various measurement locations. Fine fractions ($PM_{2.5}/PM_{10}$) are also presented. All reported data from the current study is obtained from DustTrak measurements except for the urban ambient site, which is obtained from PCIS analysis.

		Coarse PM (ng m^{-3})					Fine PM (ng m^{-3})				
		Gold line	Red line	USC	Gold/ USC	Red/ USC	Gold line	Red line	USC	Gold/ USC	Red/ USC
Crustal	Mg	40.6	31.9 ± 18.1	147.3 ± 78.3	0.28	0.22	30.6 ± 20.7	63.7 ± 29.5	76.3 ± 6.6	0.40	0.84
	Al	75.2	70.4 ± 28.7	183.5 ± 34.8	0.41	0.38	61.7 ± 54.6	150.8 ± 47.5	133.3 ± 14.3	0.46	1.1
	K	36.0	26.7 ± 12.7	94.6 ± 21.0	0.38	0.28	57.6 ± 10.0	62.1 ± 12.0	95.3 ± 10.4	0.60	0.65
	Ca	80.0	91.8 ± 40.7	207.2 ± 55.1	0.39	0.44	74.2 ± 39.4	189.5 ± 61.2	144.6 ± 30.8	0.51	1.3
	Ti	6.5	5.6 ± 2.5	17.6 ± 0.7	0.37	0.32	9.4 ± 3.0	11.8 ± 2.8	18.3 ± 1.3	0.51	0.64
Non-Crustal	Cr	1.0	6.1 ± 1.7	0.9 ± 0.2	1.1	7.1	2.1 ± 0.9	23.1 ± 4.7	3.1 ± 2.2	0.68	7.4
	Mn	2.6	22.6 ± 6.8	3.7 ± 0.4	0.71	6.2	5.8 ± 2.2	84.9 ± 13.1	5.2 ± 0.8	1.1	16.2
	Fe	267.1	3010.8 ± 926.2	256.1 ± 43.8	1.0	11.8	490.5 ± 195.1	10599.2 ± 1723.7	236.8 ± 8.1	2.1	44.8
	Co	0.05	0.42 ± 0.14	0.09 ± 0.01	0.55	4.6	0.10 ± 0.03	1.24 ± 0.22	0.12 ± 0.03	0.87	10.5
	Ni	0.4	3.0 ± 1.0	0.6 ± 0.1	0.77	5.5	1.4 ± 0.5	11.9 ± 2.6	2.9 ± 1.5	0.49	4.1
	Cu	18.4	18.0 ± 5.6	12.6 ± 3.2	1.5	1.4	37.5 ± 2.5	64.8 ± 11.3	14.6 ± 0.9	2.6	4.4
	Zn	9.1	7.8 ± 4.0	6.0 ± 0.7	1.5	1.3	23.9 ± 5.5	29.7 ± 2.6	16.3 ± 3.6	1.5	1.8
	Mo	3.1	62.7 ± 23.4	0.6 ± 0.2	5.5	112.5	6.3 ± 2.1	155.6 ± 26.9	1.1 ± 0.1	5.9	146.2
	Cd	0.02	0.30 ± 0.11	0.02 ± 0.003	1.3	16.2	0.13 ± 0.07	0.99 ± 0.11	0.09 ± 0.02	1.5	11.5
	Ba	11.0	55.9 ± 16.8	14.6 ± 2.8	0.75	3.8	18.4 ± 11.5	215.6 ± 33.3	13.5 ± 0.9	1.4	16.0
	Eu	0.01	0.04 ± 0.01	0.01 ± 0.003	0.63	2.9	0.013 ± 0.009	0.15 ± 0.02	0.01 ± 0.001	1.1	12.8

Table 5. Average total concentrations (ng m^{-3}) of select crustal and non-crustal species for the gold line, red line, and USC ambient site in coarse and fine PM. Except for coarse PM gold line sample (N=1), uncertainty estimates of 1 SD are shown (N=2). Average ratios are also presented.

		Crustal species					Non-crustal species										
		Mg	Al	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Mo	Cd	Ba	Eu
Crustal species	Mg	1															
	Al	0.94	1														
	K	0.43	0.42	1													
	Ca	0.90	0.96	0.40	1												
	Ti	0.68	0.68	0.92	0.64	1											
Non-crustal species	Cr	0.58	0.74	0.27	0.85	0.44	1										
	Mn	0.54	0.71	0.24	0.82	0.40	1.00	1									
	Fe	0.54	0.70	0.22	0.82	0.38	0.99	1.00	1								
	Co	0.55	0.70	0.21	0.83	0.38	0.99	0.99	1.00	1							
	Ni	0.59	0.74	0.30	0.86	0.47	1.00	0.99	0.99	0.98	1						
	Cu	0.52	0.61	0.75	0.67	0.79	0.73	0.70	0.67	0.66	0.76	1					
	Zn	0.35	0.42	0.92	0.42	0.86	0.40	0.38	0.34	0.33	0.43	0.86	1				
	Mo	0.52	0.67	0.15	0.80	0.31	0.96	0.97	0.98	0.99	0.95	0.56	0.25	1			
	Cd	0.54	0.71	0.26	0.82	0.43	0.99	0.99	0.99	0.99	0.99	0.72	0.41	0.96	1		
	Ba	0.57	0.73	0.26	0.84	0.43	1.00	1.00	1.00	0.99	0.99	0.72	0.40	0.96	0.99	1	
	Eu	0.56	0.73	0.26	0.83	0.43	1.00	1.00	0.99	0.99	0.99	0.72	0.40	0.95	0.99	1.00	1
ROS		0.21	0.67	0.04	0.10	0.00	0.79	0.66	0.78	0.58	0.91	0.66	0.43	0.13	0.96	0.36	0.34

Table 6. Coefficients of determination (R^2) of crustal species, non-crustal species, and reactive oxygen species (ROS) activity. Inter-crustal species correlations is based on total elemental concentrations. ROS is correlated with the water-soluble concentrations of the species. Results include gold and red line data only (N=7), based on the assumption that corresponding species from USC ambient site are derived from a different source.