

Particle size distributions of metal and non-metal elements in an urban near-highway environment

Michael D. Hays^{1,*}, Seung-Hyun Cho^{1,2,6}, Richard Baldauf^{1,5}, James J. Schauer^{3,4}, and Martin Shafer^{3,4}

¹National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, USA

²Research Participation Program, Oak Ridge Institute for Science and Education, Oak Ridge, Tennessee, USA

³Environmental Chemistry and Technology Program, University of Wisconsin–Madison, Madison, Wisconsin, USA

⁴Wisconsin State Laboratory of Hygiene, University of Wisconsin–Madison, Madison, Wisconsin, USA

⁵Office of Transportation and Air Quality, U.S. Environmental Protection Agency, Ann Arbor, MI, USA

⁶Present address: Research Triangle Institute, Research Triangle Park, North Carolina, USA

Abstract: Determination of the size-resolved elemental composition of near-highway particulate matter (PM) is important due to the health and environmental risks it poses. In the current study, twelve 24 h PM samples were collected (in July–August 2006) using a low-pressure impactor positioned 20 m from a Raleigh, North Carolina interstate. The interstate supported ~125,000 vehicles/d, the majority of which were light-duty gasoline passenger vehicles. The overall near-highway PM mass size distribution was trimodal with a major accumulation mode peak at 500–800 nm. PM mass levels reflected daily traffic activity, while mean near-highway PM₁₀ ($33 \pm 7.5 \mu\text{g}/\text{m}^3$), PM_{2.5} ($29 \pm 6.8 \mu\text{g}/\text{m}^3$), and PM_{0.1} ($1.4 \pm 0.3 \mu\text{g}/\text{m}^3$) mass levels varied less than 24% over the two week sampling period. The elemental composition of the impactor-collected PM was investigated using magnetic sector inductively coupled plasma-mass spectroscopy (SF-ICPMS). Accumulation mode sulfur ($7 \pm 4\%$ w/w) was the major inorganic constituent detected at the near-highway site followed by coarse mode group IA and IIA elements likely from re-suspension of crustal matter. As expected, elements regularly detected in asphalt, vehicle, catalyst (e.g., Pt, Rh, and Pd), brake, and tire wear (e.g., Cu and Sb) were also found in the near highway PM. Maximum concentrations of the platinum group, rare earth, and common brake and tire wear elements are observed at $d_{50} = 1\text{--}2 \mu\text{m}$, $d_{50} = 1\text{--}4 \mu\text{m}$, and $d_{50} \geq 1\text{--}4 \mu\text{m}$, respectively. Ten of the eleven metals listed as EPA air toxics (Mn, Cr, Sb, Ni, Pb, As, Co, Cd, Se, and Be) were detected in each PM size fraction but were generally enriched in PM_{0.1}. Several biologically antagonistic suites of metals (Cd, Cu, and V) were found in multiple PM size modes and may contribute to the pulmonary and cardiac effects observed and reported earlier for the different Raleigh near-highway PM size fractions. Some of these metals show erratic size distributions with daily changes in enrichment (e.g., Ni, Zn, Cd, As, and Cu) and particle size, suggesting a variety of emissions and metal exposure scenarios occurring in the near-highway environment.

*Corresponding author phone: (919)541-3984; fax: (919) 685-3346; email: hays.michael@epa.gov

Introduction

A variety of vehicle exhaust and non-exhaust air pollutants from diverse sources are emitted from roadways. Elevated health effects risks are observed in populations living near roads, and particle matter (PM) is a near-road pollutant of specific interest due to its known respiratory and cardiopulmonary effects¹. Evidence suggests that the toxicological properties of PM depend on its size and chemical composition^{2,3}. And while the mechanisms underlying PM-related health effects remain uncertain, it is hypothesized that the presence of certain organic compounds and metals (e.g., Fe, Zn, and Cu) in PM induce the formation of excess reactive oxygen species both directly and through activation of cells (e.g., macrophages), resulting in oxidative stress and ultimately in local and systemic inflammation^{4,5}.

Metal and non-metal elements emitted from traffic activity occur over a wide particle size range. Near-road aerosols may comprise combustion-derived carbonaceous nuclei or ultrafine particles (aerodynamic diameter [d_a] ≤ 100 nm) with trace amounts of vaporized S and P and metal constituents such as Ca, K, Fe, and Al from the fuel, the lubricating oils, or their additives⁶. Dilution and cooling subsequently produces accumulation mode particles ($100 \text{ nm} \leq d_a \leq 2.5 \text{ }\mu\text{m}$) via coagulation and by thermodynamically-controlled gas-to-particle conversion processes. The coarse mode ($2.5 \text{ }\mu\text{m} \leq d_a \leq 10 \text{ }\mu\text{m}$) is often linked to engine, catalyst and exhaust system deterioration, to road, brake and tire wear, and to re-suspended biological matter and soil minerals; although, through attrition these sources may also contribute metal elements to the accumulation mode and ultrafines in near-road atmospheres⁷. Large agglomerates of accumulation mode particles that build-up in the engine crankcase or exhaust system also contribute to the coarse mode following re-suspension⁸. Moreover, it is plausible that fine aerosols bound to road dust accumulate in the coarse mode. Vehicle fleet mix and technology, vehicle response to human operation (i.e., braking pressure, speed, and acceleration), distance from the road, road segment type (e.g., grade), geographic location, road, tire and vehicle materials and manufacturing practices, and even measurement techniques are additional variables that influence the near-road particle size distribution and composition. Due to the wide range of variables influencing near-road particle emissions, multiple field-based investigations are needed to develop proper risk consensus across the aerosol research community prior to regulatory or policy implementation.

Source traceability and toxicological information are enhanced by fractionated data⁹; yet complete particle size distributions of elements in near-roadway PM are relatively scant. Size bins are regularly composited to exceed the instrumental detection limits required for metals characterization. The present study uses magnetic sector (SF) inductively coupled plasma-mass spectrometry (ICP-MS) to provide elemental size distributions measured near a Southeastern U.S. highway in the summer. The application of SF-ICPMS in this study further enhances the signal-noise of the analytical technique and provides substantially improved analytical confidence for many elements present at very low concentrations and whose quantification would otherwise be compromised by spectral interferences. Lough et al.¹⁰ used a similar ICP-MS technique to

determine elemental composition in size-resolved PM collected in two Mid-Western U.S. tunnels. Their effort overcomes the limited sensitivity of the X-ray fluorescence (XRF), particle induced X-ray emission (PIXE), and instrumental neutron activation analysis (INAA) methods used in several earlier tunnel studies that may have precluded a thorough rendering of metals in fractionated PM. ICP-MS has also been utilized to determine the size-segregated metal composition in PM from a heavy-duty diesel-dominated, California freeway⁵, an arterial highway at Birmingham, UK¹¹, and urban traffic sites in Taiwan¹² and Rome, Italy¹³. The current research differs from these and other past studies in that it offers more detailed particle size distributions for metal and non-metal elements in PM emitted over 24 h periods next to a busy urban U.S. interstate dominated by gasoline vehicles. Moreover, because these measurements are obtained as part of the intensive Raleigh Near-road study, they are supported by highly time-resolved characterization of traffic activity, meteorology, gas- and particle-phase organic chemical species¹⁴, real-time inorganic gas (NO_x)¹⁵, and toxicological information¹⁶. Observations from each component of the Raleigh study will be integrated to advance our understanding of the impact of near-highway exposures on public health.

Experimental

Near-road monitoring site and sample collection. The field site, traffic activity, road grade, meteorology, monitoring equipment, and additional pertinent study details were described extensively in Baldauf et al.¹⁶. Briefly, the monitoring site was approximately 20 m north of U.S. Interstate 440 (I-440) in Raleigh, NC. Historical wind direction data from the Raleigh-Durham international airport established north of the highway as predominantly downwind. This limited-access highway supported roughly 125,000 vehicles per day, ~95% of which were light-duty, gasoline-powered vehicles. The path between the sampling site and highway was clear and at-grade with a parallel-running access road that carried fewer than 200 vehicles per day. The highway traffic was generally free-flowing with a typical weekday diurnal volume pattern of morning and afternoon rush hours. An impactor at the upwind monitoring station was not part of the sampling design.

Near-highway air was sampled over twelve, 24 h periods at ~30 L/min with a low-pressure impactor (LPI; Dekati Inc. Tampere, Finland) during July 26–31 and August 3–10, 2006; the sample inlet was positioned roughly 2 m above the ground. Substrates were typically changed in the early afternoon and thus included the morning rush hour and the afternoon rush hour of the preceding day. The LPI collected and segregated PM into 13 stages. The stage 50% cutoff diameters (d_{50}) ranged from 0.03–10 μm with $d_{50} = 29$ nm, 57 nm, and 1.6 μm at stages 1, 2, and 9, respectively. The d_{50} values assigned to each stage are thought of as approximates due to the irregular particle morphologies produced from near-road sources. In the current study, the sum of all 13 stages, stages 1–9, and stages 1–2 are referred to as PM₁₀, PM_{2.5}, and PM_{0.1}, respectively. PM at each stage was collected with pre-weighed, acid (HCl and HNO₃)-cleaned 25 mm Teflon filters (0.5 μm pore size, Zefluor, Pall Life Sciences). Lough et al.¹⁰ have provided the details of the filter cleaning procedure. All filters were handled

using established clean techniques for trace metal analysis^{10,17}. Filters were not greased owing to the nature of the chemical investigation planned.

A subset of five of the twelve daily LPI sample sets (13 stages, 7-30, 08-04, and 08-08 thru 08-10-2006) was selected for further chemical examination. These samples represent the multiple meteorological and traffic variables influencing the metal concentrations and PM size distributions at the site. Airport meteorological (Figure 1) and real-time NO data¹⁵ indicated an emissions contribution from the highway at rush hour for each sample except on 08-09-2006. The fraction of time the sampler was downwind of the highway (Table 1) and the average wind speeds during this time were estimated using hourly meteorological data.

Sample analysis. Following a 24 h equilibration period in a temperature- and humidity-controlled room (25 °C and 30-40% RH), the Teflon substrates were analyzed gravimetrically using a microbalance (Sartorius Corp., IL). Filters, including field blanks for each tests day, were then shipped to the University of Wisconsin–Madison for SF-ICPMS analysis. The five daily LPI sample sets (13 individual stages) were examined for fifty-three metal and non-metal elements using SF-ICPMS. The sample digestion and SF-ICPMS techniques used for the determination of PM elemental composition were published earlier^{10,18}. In brief, LPI substrates were placed in Teflon bombs and subjected to a microwave-assisted digestion in a mix of ultra-high purity acids (1.5 mL 16N HNO₃, 0.5 mL 12N HCl, 0.2 mL 28N HF). The microwave system (Milestone ETHOS) was ramped to 180 °C over 9 min and held fixed for 10 min prior to a 1 h cooling period. Complete solubilization of Cr, noble metals, Pt group elements, aluminosilicates and quartz are achieved with this digestion procedure. Samples were analyzed in batches consisting of roughly twenty filter samples, six standard reference materials (SRMs; recycled auto catalyst 2556, urban dust 1649a, and San Joaquin Soil 2709), four matrix blanks, two method blanks, and two matrix spikes. Uncertainty components from the SF-ICP-MS analysis (standard deviation of triplicate analyses), blank subtraction (standard deviation of multiple method blanks), and digestion recovery (standard deviation of element specific historic running average recoveries), were propagated to estimate a total uncertainty associated with each element in every sample.

Sample digests were analyzed for their elemental composition using a magnetic sector (high-resolution) inductively coupled plasma mass spectrometer (SF-ICPMS, Thermo Finnigan Element 2)^{19,20}. Fifty-two elements were quantified, of which 49 were ultimately judged to be at concentrations significantly above the blanks and therefore considered for inclusion in subsequent analyses. The SF-ICPMS (with fast scanning magnet and Pt guard electrode), was interfaced to a quartz cyclonic spray-chamber fitted with an ESI low-flow (80 µL min⁻¹) Teflon micro-concentric nebulizer. The complete analytical system is located within a trace metal clean room. Mass resolution and isotope selection were optimized for each element to ensure resolution of spectral interferences and maximize sensitivity. Quantification was performed using external standards with internal normalization (Ga, In, Bi as internal standards). A minimum of triplicate 180 s analyses on each sample was conducted following a 45 s uptake and stabilization period. Between samples the nebulizer system was

rinsed for 6 min with 2% high purity HNO₃, which eliminated carry-over and reconditioned the sampler cone. Sets of instrumental blank and calibration verification checks were run at frequent intervals during the batch sequence. Instrumental detection limits (3-sigma) were in the range of 0.01 to 2 ng L⁻¹ (equivalent to 0.01–2 pg m⁻³ of air) for most trace elements and in the range of 5 to 50 ng L⁻¹ (5–50 pg m⁻³ of air) for major elements. Sample spike recoveries were also well within our acceptance window (85–115 %). Element concentration data reported herein were corrected with the average field blank concentration calculated over the five test days. Uncertainties were propagated where appropriate using the square root of the sum of squares method. An independent one-sample *t*-test was used to confirm if the corrected concentration values were significantly different than zero. Only values indicating a statistical difference were retained for further interpretation. Comparatively high levels of Sn were observed but removed from the study due to substantial background levels in the field blanks and possible instrumental bias.

Results and Discussion

PM mass and size distributions. For the 12 test days, mean near-highway PM₁₀, PM_{2.5}, and PM_{0.1} mass concentrations show a relative standard deviation (RSD) of less than 24%, Table 1. Reductions in traffic volume and total PM mass are observed over the weekend, when PM₁₀ levels decline from as much as 41 µg/m³ to 22 µg/m³ or less. Daily PM₁₀ values measured at the site are consistently less than the 24 h U.S. ambient air quality standard (NAAQS) of 150 µg/m³ and the 2nd highest recorded levels at the regional and National scales (~50 µg/m³ ~ 60 µg/m³)²¹. On average, the PM_{2.5} fraction represents 86% w/w of the total PM₁₀ mass. The 24 h ambient PM_{2.5} standard of 35 µg/m³ is exceeded on multiple days during this study likely due to the proximity of the site to the highway. The LPI-measured PM_{2.5} mass mean value of 29 µg/m³ compares well to both the national and regional scale ambient PM_{2.5} levels (98th percentile of 24 h levels for 2005-2007, ~30 µg/m³). We checked each size fraction but observed limited if any trends among the downwind sampling time, wind speed, and PM mass data. These results clearly suggest that some of the mass in Figure 2 is from the ambient air despite sampling so close to the road. Although divergent meteorological, measurement, and site conditions worldwide complicate direct comparisons among near-road impactor studies, Table 1 values are comparable to the average PM₁₀ and PM_{2.5} values (34 µg/m³ and 17 µg/m³) determined at two traffic-impacted sites in Rome¹³. Moreover, they are within the range (PM_{7.2}) reported for a road-side (16.8 µg/m³) and tunnel (72 µg/m³) impactor study in England, where the road carried fewer cars (22,000/day) and the tunnel apparently intensified vehicle emissions²². The substantially higher coarse (191 µg/m³) and fine (140 µg/m³) PM mass near a road in urban Asia carrying 72,000 vehicles/day appears confounded by local industrial and manufacturing source contributions, as well as differences in vehicle technologies and fuels¹².

Figure 2 shows the LPI -produced size distributions of particle mass for the Raleigh near-highway study. The grey box plots are composites of the individual LPI bins over the entire test period. Daily PM mass size

distributions are provided as Supporting Information, Figure S1. Overall, the PM mass is distributed over three particle size modes. The major accumulation mode peak centered between 500-800 nm is evidence of coagulation and condensation growth of nuclei near the highway. Ultrafines account for roughly 3% w/w of the PM distribution on average. The superimposed lines in the figure exhibit the extent to which the near-highway particle mass distribution varied on a daily basis. Samples from these dates were selected for SF-ICPMS analysis; thus, further interpretation is given for these days. The 07-30 particle size distribution is influenced by low weekend traffic volume (less vehicle exhaust), higher and variable wind speeds (Figure 1), and a continuous (17 h), direct contribution from the highway. Dilution and mixing patterns likely fluctuated throughout the day, explaining the relatively wide span and unique peak positions observed for the 7-30 distribution. The 08-04 and 08-08 samples include emissions from both morning and afternoon weekday rush hour traffic. Despite the relatively limited direct highway contribution for 08-09, the enhanced fine particle mode is a likely consequence of thermal inversion which limited convection (see Table 1, wind speed) and concentrated air pollutants at the surface. These conditions appear to have resulted in coarse mode deposition as well, and likely led to the similar PM mass size distribution observed for 08-05 (see Supporting Information, Figure S1). A considerable coarse mode peak (~30% w/w) reappears for the 08-10 sample, which is strongly influenced by a morning rush hour.

Overall trends and SF-ICPMS-determined elemental compositions. Figure 3 shows the SF-ICPMS determined elemental composition in LPI-segregated coarse, fine, and ultrafine PM collected daily near the Raleigh highway. The thirty-eight elements detected are arranged in order of decreasing average concentration (ng/m^3) in PM_{10} and shown with the stage-propagated analytical error. The 5-day average concentration of each element in the fine and ultrafine aerosols is also shown. Table 2 contains both air volume-based (ng/m^3) and PM mass-normalized (mg element/kg PM) mean element concentrations in the $\text{PM}_{10-2.5}$, $\text{PM}_{2.5-0.1}$, and $\text{PM}_{0.1}$ size fractions. The sum of inorganic element concentrations accounts for 9% w/w of the near-roadway PM_{10} and $\text{PM}_{2.5}$ and 7% w/w of $\text{PM}_{0.1}$. Similar values were observed near a California freeway, which had a higher coarse component presumably due to its desert geography⁴. Figure S2 (Supporting Information) shows that the size distributions of the summed elemental concentrations resemble but do not fully coincide with those of PM mass; for example, metals appear elevated in ultrafine particles on 08-08-2006. For this case, PM mass is an unlikely surrogate for understanding near-highway exposures to metal mixtures. Paired *t*-tests comparing daily means calculated from the log-transformed elemental concentration data set indicate a significant difference between the 08-09 and the 08-10 test pair ($\alpha = 0.05$; $p = 0.04$) and a weak difference for the 07-30 and 08-10 test pair ($p = 0.06$). Total metal contributions varied more with particle size. Daily means of elemental concentration data segregated by size bin are significantly different ($\alpha = 0.05$) at stage 7 ($d_{50} = 619 \text{ nm}$) between the 07-30 and the 08-09 and 08-09 and the 08-10 test pairs and at stages 10 (08-09 and each day), 11 (08-09 and

08-04 and 08-09 and 08-10), and 13 (07-30 and 08-10 and 08-09 and 8-10) for which $d_{50} > 2.4 \mu\text{m}$. For 08-10, the substantial increase in total element mass (ng/m^3) over $d_{50} = 2.4\text{--}10.0 \mu\text{m}$ is probably due to a single source owing to the minor change seen in the overall enrichment (mg of elements/kg of PM). The decrease in the elemental mass on 07-30 due to less traffic is more subtle because in large part it occurs over a narrower size range involving smaller $d_{50} = 620 \text{ nm}$ particles.

Sulfur and crustal elements. Sulfur ($7 \pm 4\%$ w/w $\text{PM}_{2.5}$) is the major inorganic PM constituent followed by Al ($0.9 \pm 0.4\%$), Fe ($0.9 \pm 0.4\%$), Ca ($0.5 \pm 0.2\%$), K ($0.4 \pm 0.2\%$), Na ($0.3 \pm 0.2\%$) and Mg ($0.1 \pm 0.05\%$). The S particle size distribution is unimodal and centered in the accumulation mode at $d_{50} = 386\text{--}619 \text{ nm}$ (Figure 4A) typical of combustion. Sulfur is regularly in the form of SO_4^{2-} in combustion particles, and additional research conducted as part of the Raleigh study reported SO_4^{2-} levels of 57 mg/g, 370 mg/g, and 440 mg/g of PM in the coarse, fine, and ultrafine particle fractions². Trace amounts of thiophenic S and reduced metal sulfides (e.g., FeS or FeS_2) from petroleum fuels and additives are also possible in the near-road environment. The S concentration ($1.9 \pm 1.2 \mu\text{g}/\text{m}^3$, Table 2) from the current study agrees with a 2003 determination also made near a major Raleigh area highway²³. However, to better understand what caused the near-road S response, we examined XRF-measured atmospheric S in PM from eight North Carolina monitoring sites in the urban Speciation Trends Network (STN)²⁴ and from the relatively pristine Swanquarter, North Carolina monitoring site used as part of the IMPROVE Network²⁵. Respective mean S concentrations of $2.7 \pm 1.1 \mu\text{g}/\text{m}^3$ ($n = 84$) and $1.8 \pm 1.5 \mu\text{g}/\text{m}^3$ ($n = 14$) were obtained for July-August 2006. Moreover, comparisons of daily test pairs using the mean near-highway S levels show no significant difference, although 07-30 (a low-traffic day) is least alike the other test days ($0.18 \leq p \leq 0.46$). Combined, these results suggest a slight S signal from vehicles amid a potentially strong regional background component to the S measured in the Raleigh near-highway environment.

Near-road S is not correlated (Pearson product-moment correlation) with the crustal elements in the present study. The Al, Fe, and group IA and IIA metals are generally enriched in the $\text{PM}_{10-2.5}$ fraction (Table 2, Figure 4B and C). Multivariate pairwise correlations (all stages and tests) between these metals were confirmed to be higher ($r > 0.62$) for $\text{PM}_{10-2.5}$ than for $\text{PM}_{2.5-0.1}$ ($r > 0.11$), and their relative distribution in PM_{10} is within 80% of a typical soil profile. This result strongly implies a contribution of re-suspended crustal matter from the road area. The remaining fraction of mass may be from the asphalt, vehicle frame or body, engine and exhaust system deterioration, wheels, tires, or brakes, which also can contain these metals. The Ca, K, and Fe observed in the fine and ultrafine near-highway particles possibly vaporized from the lubricating oil. However, these elements correlate poorly ($r < 0.42$) in the fine fraction. For Fe and Al, one-way ANOVA test results indicate significant differences among their daily mean concentrations (log-transformed). The enrichment of Al and Fe

in PM on 08-09 is different from 08-10 and 08-04 and 08-08, respectively, suggesting meteorology controlled the near-road source contributions for these metals.

Note that Figure S3, panels A-C given in the Supporting Information shows the fraction of each element in each size bin or the relative elemental size distributions of (A) the group VB and VIB non-metals and rare earth metals (B) transition metals and (C) the alkali and alkali earth metals in the near-highway particle matter. This figure highlights the elemental size distributions while minimizing the potential impacts on the absolute concentrations due to meteorology and other factors. Generally speaking, the daily distribution for each metal tends to be more similar in these plots.

Brake and tire wear. Fe, Ba, Zn, Cu and Sb have been linked previously to brake lining emissions and may indicate tire wear to a lesser extent^{7,10,26}. A wide concentration range is possible for each of these metals in particles released as brake or tire wear. Even so, the relative distribution of Ba, Sb, Cu, and Zn levels in PM observed at the Raleigh site—despite excess Zn—closely replicates a mean brake dust profile generated using the multiple studies compiled by Thorpe and Harrison⁷. Furthermore, the highest levels of each of these metals in aerosols are observed in samples (08-04, 08-08, and 08-10) impacted by rush hour traffic when more braking is expected. And significantly different Sb concentrations are confirmed between a low (07-30) and a high traffic day (08-10). Except for Zn, these metal concentrations correlate rather well, especially in PM_{10-2.5} where $r \geq 0.8$. Also in contrast with Zn, the highest levels of airborne Fe, Sb, Ba, and Cu are primarily in particle size bins with $d_{50} > 1.6 \mu\text{m}$. For each size fraction, considerably lower pairwise correlations ($r \leq 0.37$) between Zn and the other brake wear metals are observed. The excess Zn suggests another source, possibly a combination of tire wear, fuel, or lubricating oil. Zn oxides and organic Zn complexes are used in tire manufacturing. Zn is also used in oil additives and is a major component of galvanized metals and many paints. Notably, Zn and Ca are distributed similarly in PM_{0.1}, indicating a vaporized auto oil source²⁶. The multiple plausible sources of Zn perhaps explain its multi-mode and mostly erratic size distributions; although interestingly, total near-highway Zn levels show negligible difference on a daily basis.

Platinum group elements. Deterioration of automobile catalysts releases platinum group elements (PGE) to roadside dusts and soils, airborne PM, and sediments²⁷. The PM₁₀ concentrations of the PGEs—Pt (20 pg/m³), Pd (29 pg/m³), and Rh (1 pg/m³)—in the Raleigh near-highway environment are within the limits of values reported in urban atmospheres sampled globally since 1998²⁷. Although Pd is above detection limits on 08-04 only, the Raleigh study results correspond to the investigations assembled by Rauch et al.²⁷ showing Pt/Pd and Pt/Rh ranges of 1–2.5 and 5–16 in three-way catalysts and 0.2–2.9 and 3.7–13.7 in urban air particles. The PGE size distributions are furnished in Figure 4B with Rh and Pd graphed together. The distributions vary daily over the accumulation and coarse particle size modes showing maximum peak concentrations between $d_{50} = 1\text{--}2 \mu\text{m}$.

Tests for pairwise correlation among PGE elements are inconclusive owing to limited data. Of the PGE metals, only Rh is used for further statistical inference as it has the most SF-ICPMS observations. The ANOVA model indicates no difference ($p = 0.3$) among daily mean ambient concentrations of Rh in the near-road PM. Notably, a positive correlation between Ce—which is also present in some vehicle catalysts—and Rh ($r = 0.5$), Pd ($r = 0.9$), and Pt ($r = 1$) were observed for the coarse, fine, and ultrafine [limited data ($n = 2$)] modes.

Rare earth elements. Potential sources of rare earth metals (REE) include soils and catalysts used in automobiles and petroleum refinery operations^{28,29}. The REE elements were distributed over the coarse and fine modes (concentration maxima at $d_{50} = 1\text{--}4\text{ }\mu\text{m}$) in the near-highway PM at levels observed previously in the North Carolina atmosphere²⁸. As expected, REE elements (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, and Yb) are highly correlated ($r \geq 0.85$) in $\text{PM}_{10-2.5}$. Correlation ($-0.2 \leq r \leq 0.99$) declines among REE in the fine PM owing possibly to varying source contributions and auto catalyst compositions. La/lanthanide ratios can be examined for evidence of source contributions. For the present study, $\text{La/Ce} = 0.4$, $\text{La/Pr} = 5$, $\text{La/Nd} = 1.3$, and $\text{La/Sm} = 6.7$ irrespective of the size fraction. These values are virtually identical to those in NIST SRM 2783²⁸—an airborne PM collected in Vienna, Austria—but lower than the REE ratios measured in airborne PM from Houston, TX, where zeolite catalysts are used in petroleum refineries²⁹. The La/lanthanide ratios for the Raleigh study positively correlate to those determined for an auto catalyst (SRM 2556) ($r = 0.77$) and soils ($r = 0.58$) but poorly reflect TX tunnel PM ($r = 0.22$)²⁹. ANOVA tests indicated no significant difference among daily mean concentration and PM enrichment levels of La, Ce, Nd, and Sm; thus (like the PGE) the REE in the Raleigh near-highway PM are relatively unresponsive to the trends in traffic activity and weather.

Hazardous metal air pollutants. Ten of the eleven metals listed by the U.S. EPA as air toxics are detected in the Raleigh near-highway PM. In order of decreasing concentration in PM_{10} they are Mn, Cr, Sb, Ni, Pb, Se, As, Co, Cd, and Be. These metals can be found in each size fraction— $\text{PM}_{10-2.5}$, $\text{PM}_{2.5-0.1}$ and $\text{PM}_{0.1}$. Published information about the size distributions of metals in urban atmospheres is generally limited; although, hypothetically relatively high proportions of pollutants including transition metals are found in ultrafine PM³⁰. Moreover, ultrafines can illicit a disproportionately negative toxicological response owing to vast particle surface area enhancing the delivery of reactive chemical substances to biological matter³¹. In addition to this surface reactivity, ultrafine particles can readily traverse biological membranes, thus facilitating systemic distribution in the body. Our results show on an average mass basis that the eight metal air toxics (Be, Cr, Ni, Pb, Sb, Cd, Se, and As) are enriched in $\text{PM}_{0.1}$ by as much as 23-fold; whereas, the Co and Mn are enriched in $\text{PM}_{10-2.5}$. Daily mean Mn and Pb concentrations—two potential neurotoxins—vary significantly with traffic, and the enrichment of Pb in near-roadway PM varies daily as well. We observe a mean Pb concentration of roughly 50 ppm that changes little in each size fraction. Pb can occur naturally in soils up to 50 ppm but is nearer 4 ppm

in NC soils³². The original I-440 (called U.S. 1/64) was constructed in the early 1960s; thus, a near-road Pb gradient due to past use of leaded gasoline is possible, but the correlation between Pb and the crustal elements is weak ($r \leq 0.4$). The rapid erosion of soft Pb wheel weights, which are estimated to contribute as much as 1.5×10^6 kg/yr to U.S. roadways, may explain a part of the particle-based Pb³³. Wheel weights also contain ~5% As. The Raleigh near-road PM_{10-2.5} reflects the 4 ppm of As typical in NC soils (from arsenopyrite, FeAsS)³². However, the As levels increase to 16–21 mg/kg over the fine and ultrafine size modes. This is a ~15% excess after subtracting possible soil and wheel weight contributions. Agricultural chemicals and metal alloys used in autos are additional possible sources of As in these samples. As and Pb ($r = 0.7$) and Ni and Cr ($r = 0.9$) show the highest correlation among the metal air toxics. The Ni and Cr are likely components of engine metal alloys.

There are no regulatory limits for individual metal concentrations in PM. However, mixtures containing multiple metals at low concentrations such as those found in the near-road PM can interact antagonistically and potentially carry greater toxicological risk³⁴. For example, mixtures of Zn, Ni, Cd, Cu, and V and other PM metals are increasingly being linked to respiratory and cardiac symptoms, lung injury, and in some regions human mortality³⁵⁻³⁷. Although present in all size modes, the present study shows co-constituents Zn and Cd and Cu and V are enriched in PM_{0.1} and PM_{10-2.5}, respectively. This may help explain the corresponding cardiac and pulmonary effects observed in these different Raleigh near-road PM size fractions². Note that V and Ni compare weakly here despite being commonly associated with fuel oil burning sources²⁶. Further examination of individual size bins in Figure 4B (and Figure S3 in Supporting Information) reveals Ni, Zn, Cr, and Co levels that are erratically distributed and insignificantly correlated to daily traffic activity. On the other hand, size distributions of Pb, As, Cd, Mn, Se, and more or less Sb regularly appear unimodal and normally distributed over the accumulation mode (except Mn) with site concentration changes best explained by traffic. Compared with ambient concentrations (ng/m³), enrichments (mg/kg) of Zn, Cd, Cu, Ni, Cr, and As in PM show greater daily variability irrespective of the size fraction. This result indicates that emissions contribution and particle growth variables changed daily at the Raleigh site and that near-road exposure to metals can also change on short temporal scales. Finally, taken together with the results of the present study, the relatively low concentrations of Cr, Ni, Cu, Zn, and Sb in methanol-saline extracts of the Raleigh near-road PM_{0.1} (treated with 10% nitric acid) reported by Cho et al.² suggest that the near-road PM comprises both soluble and insoluble forms of these metals possibly with multiple chemical coordination and oxidation states.

Conclusions

In the summer, the Raleigh near-highway air contained inhalable coarse, fine, and ultrafine PM mass which varied according to interstate traffic activity and prevailing meteorology at the site. Impactor data show the 24 h PM_{2.5} NAAQS standard of 35 $\mu\text{g}/\text{m}^3$ was exceeded on multiple days owing to the short 20 m distance between the monitoring site and interstate. Inorganic elements measured by SF-ICPMS accounted for 9% of the PM₁₀

and PM_{2.5} mass and 7% of PM_{0.1}. Accumulation mode S—in the form of water-soluble sulfate—was the major inorganic constituent followed by several coarse mode crustal elements likely from soil matter or asphalt wear. Sulfur was not correlated with any of the crustal elements. Elemental characterization of the PM indicates the presence of brake, tire, and catalyst wear sources. The Sb, REE, and PGE size distributions regularly associated with each of these sources were consistently different from one another opening the possibility for using size distributions of metals for source apportionment problems involving roadways. Numerous metals (e.g., Zn, Cr, Ni, and Co) showed a variety of daily enrichments and size distributions, indicating that the Raleigh near-highway PM is influenced by multiple source contributions and particle growth variables. Potentially toxic near-highway metal mixtures are observed at different levels across coarse, fine, and ultrafine size fractions, potentially explaining why equal mass doses of these different PM size fractions produced various pulmonary and cardiac responses in mice². Future near-highway research will need to glean information about the complexation state of metals with regard to their ability to undergo atmospheric transformation and modulate biological activity in the presence of organic matter.

References

- (1) Brugge, D.; Durant, J.; Rioux, C. *Environmental Health* **2007**, 6, 23.
- (2) Cho, S.-H.; Tong, H.; McGee, J. K.; Baldauf, R. W.; Krantz, Q. T.; I., G. M. *Environ. Health Perspect.* **2009**, 117, 1682.
- (3) Diociaiuti, M.; Balduzzi, M.; De Berardis, B.; Cattani, G.; Stacchini, G.; Ziemacki, G.; Marconi, A.; Paoletti, L. *Environmental Research* **2001**, 86, 254.
- (4) Ntziachristos, L.; Froines, J.; Cho, A.; Sioutas, C. *Particle and Fibre Toxicology* **2007**, 4, 5.
- (5) Ntziachristos, L.; Ning, Z.; Geller, M. D.; Sheesley, R. J.; Schauer, J. J.; Sioutas, C. *Atmos. Environ.* **2007**, 41, 5684.
- (6) Miller, A. L.; Stipe, C. B.; Habjan, M. C.; Ahlstrand, G. G. *Environ. Sci. Technol.* **2007**, 41, 6828.
- (7) Thorpe, A.; Harrison, R. M. *Science of the Total Environment* **2008**, 400, 270.
- (8) Kittelson, D. In *28th Annual Conference*; American Association of Aerosol Research: Minneapolis, MN, 2009.
- (9) Canepari, S.; Pietrodangelo, A.; Perrino, C.; Astolfi, M. L.; Marzo, M. L. *Atmos. Environ.* **2009**, 43, 4754.
- (10) Lough, G. C.; Schauer, J. J.; Park, J.-S.; Shafer, M. M.; DeMinter, J. T.; Weinstein, J. P. *Environ. Sci. Technol.* **2004**, 39, 826.
- (11) Harrison, R. M.; Tilling, R.; Callén Romero, M. S.; Harrad, S.; Jarvis, K. *Atmos. Environ.* **2003**, 37, 2391.
- (12) Lin, C.-C.; Chen, S.-J.; Huang, K.-L.; Hwang, W.-I.; Chang-Chien, G.-P.; Lin, W.-Y. *Environ. Sci. Technol.* **2005**, 39, 8113.
- (13) Canepari, S.; Perrino, C.; Olivieri, F.; Astolfi, M. L. *Atmos. Environ.* **2008**, 42, 8161.
- (14) Olson, D. A.; McDow, S. R. *Atmos. Environ.* **2009**, 43, 2862.
- (15) Thoma, E. D.; Shores, R. S.; Isakov, V.; Baldauf, R. W. *J. Air Waste Manage. Assoc.* **2008**, 58, 879.
- (16) Baldauf, R. W.; Thoma, E.; Hays, M. D.; Shores, R. S.; Kinsey, J.; Gullett, B.; Kimbrough, S.; Long, T.; Snow, R.; Khlystov, A.; Weinstein, J. P.; Chen, F.-L.; Seila, R.; Olson, D. A.; Gilmour, I.; Cho, S.-H.; Watkins, N.; Rowley, P.; Bang, J. *J. Air Waste Manage. Assoc.* **2008**, 58.

- (17) Hurley, J. P.; Shafer, M. M.; Cowell, S. E.; Overdier, J. T.; Hughes, P. E.; Armstrong, D. E. *Environ. Sci. Technol.* **1996**, *30*, 2093.
- (18) Schauer, J. J.; Lough, G. C.; Shafer, M. M.; Christensen, W. F.; Arndt, M. F.; DeMinter, J.; Park, J.-S. *Characterization of Metals Emitted from Motor Vehicles*, 2006.
- (19) Hu, S.; Herner, J. D.; Shafer, M.; Robertson, W.; Schauer, J. J.; Dwyer, H.; Collins, J.; Huai, T.; Ayala, A. *Atmos. Environ.* **2009**, *43*, 2950.
- (20) Zhang, Y.; Schauer, J. J.; Shafer, M. M.; Hannigan, M. P.; Dutton, S. J. *Environ. Sci. Technol.* **2008**, *42*, 7502.
- (21) EPA, U. S. Washington, D.C., 2009; Vol. 2009.
- (22) Birmili, W.; Allen, A. G.; Bary, F.; Harrison, R. M. *Environ. Sci. Technol.* **2006**, *40*, 1144.
- (23) Lewandowski, M.; Jaoui, M.; Kleindienst, T. E.; Offenberg, J. H.; Edney, E. O. *Atmos. Environ.* **2007**, *41*, 4073.
- (24) Page, U. E. A. E. H.
- (25) Homepage, I. M. o. P. V. E.
- (26) Dillner, A. M.; Schauer, J. J.; Christensen, W. F.; Cass, G. R. *Atmos. Environ.* **2005**, *39*, 1525.
- (27) Rauch, S.; Hemond, H. F.; Peucker-Ehrenbrink, B.; Ek, K. H.; Morrison, G. M. *Environ. Sci. Technol.* **2005**, *39*, 9464.
- (28) Kulkarni, P.; Chellam, S.; Flanagan, J. B.; Jayanty, R. K. M. *Anal. Chim. Acta* **2007**, *599*, 170.
- (29) Kulkarni, P.; Chellam, S.; Fraser, M. P. *Atmos. Environ.* **2006**, *40*, 508.
- (30) Sioutas, C.; Delfino, R. J.; Singh, M. *Environ. Health Perspect.* **2005**, *113*, 947.
- (31) Delfino, R. J.; Sioutas, C.; Malik, S. *Environ. Health Perspect.* **2005**, *113*, 934.
- (32) Hardy, D. H.; Myers, J.; Stokes, C.; Services, N. C. D. o. A. a. C., Ed. Raleigh, 2008.
- (33) Root, R. A. *Environmental Health Perspectives* **2000**, *108*, 937.
- (34) Menzie, C. A.; Ziccardi, L. M.; Lowney, Y. W.; Fairbrother, A.; Shock, S. S.; Tsuji, J. S.; Hamai, D.; Proctor, D.; Henry, E.; Su, S. H.; Kierski, M. W.; McArdle, M. E.; Yost, L. J. *Environ. Sci. Technol.* **2009**, *43*, 8478.
- (35) Gavett, S. H.; Haykal-Coates, N.; Copeland, L. B.; Heinrich, J.; Gilmour, M. I. *Environ. Health Perspect.* **2003**, *111*, 1471.
- (36) Dominici, F.; Peng, R. D.; Ebisu, K.; Zeger, S. L.; Samet, J. M.; Bell, M. L. *Environ. Health Perspect.* **2007**, *115*, 170.
- (37) Dreher, K. L.; Jaskot, R. H.; Lehmann, J. R.; Richards, J. H.; McGee, J. K.; Ghio, A. J.; Costa, D. L. *Journal of Toxicology and Environmental Health* **1997**, *50*, 285.
- (38) Dong, Y.; Hays, M. D.; Smith, N. D.; Kinsey, J. J. *Aerosol Sci.* **2004**, *35*, 1497.

Figure captions

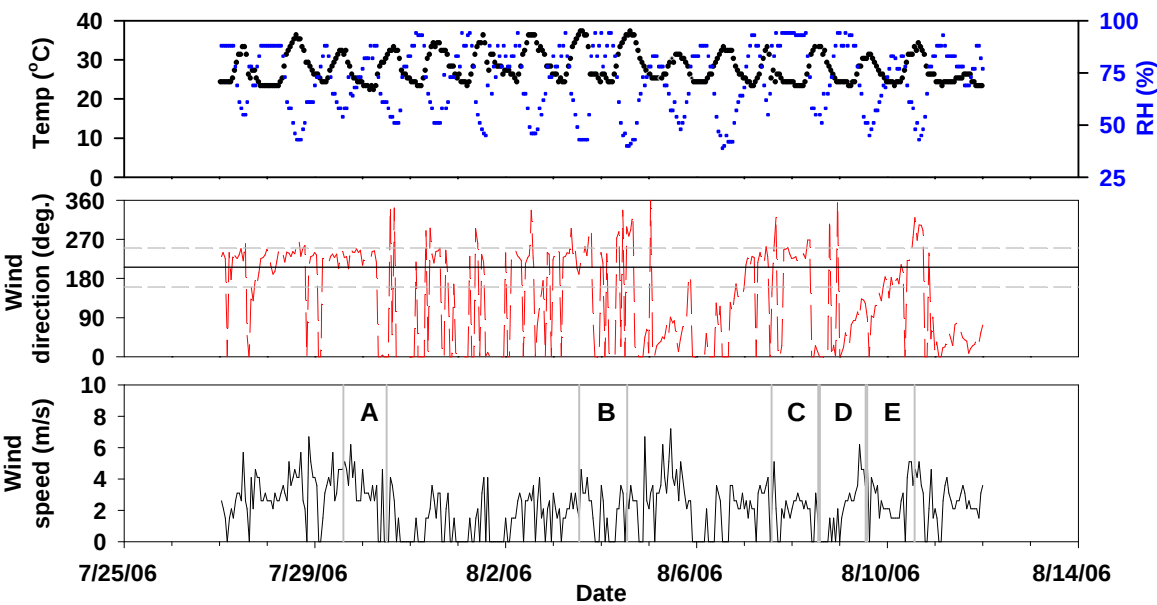
Figure 1. Meteorological data relevant to the summer 2006 near-highway study conducted at Raleigh NC. Sections A-E correspond to five 24 h sampling periods over 07-30, 08-04, 08-08, 08-09, and 08-10-2006. The solid black line in the wind direction panel indicates direct, orthogonal highway emissions impact at the monitoring site (20 m). All wind directions within the dashed gray lines are expected to impact the site.

Figure 2. Low-pressure impactor size distributions of the near-highway particle mass. Data for individual test days (A-E) are inverted using Dong et al. ³⁸ Box plots indicate the median, 10th, 25th, 75th, and 90th percentiles and consider the entire 3-week test frame. The lines indicate the representative 5-day subset selected for SF-ICPMS analysis.

Figure 3. Elemental composition of coarse, fine, and ultrafine particle matter collected over five test days near highway 440 in Raleigh, NC. Elements are shown in order of decreasing average concentration in PM₁₀. Error bars show the analytical error propagated over each 24 h, 13 impactor stage composite. The 5-day average average PM_{2.5} and PM_{0.1} concentrations are provided for comparison.

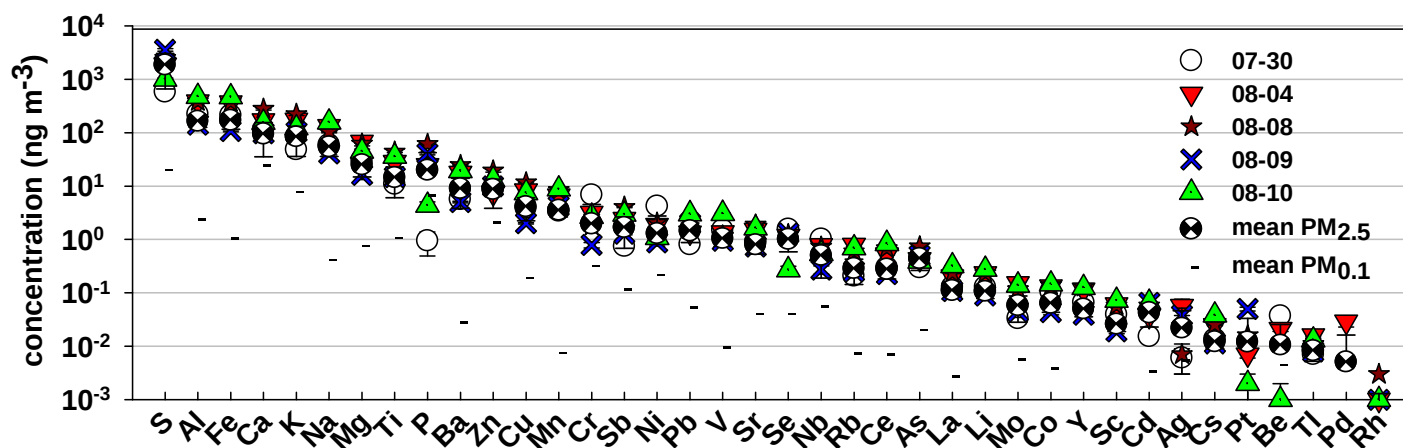
Figure 4. Size distributions of (A) the group VB and VIB non-metals and rare earth metals (B) transition metals and (C) the alkali and alkali earth metals in the near-highway particle matter.

Figure 1



460
461
462

Figure 3



463
464
465
466
467

Figure 2

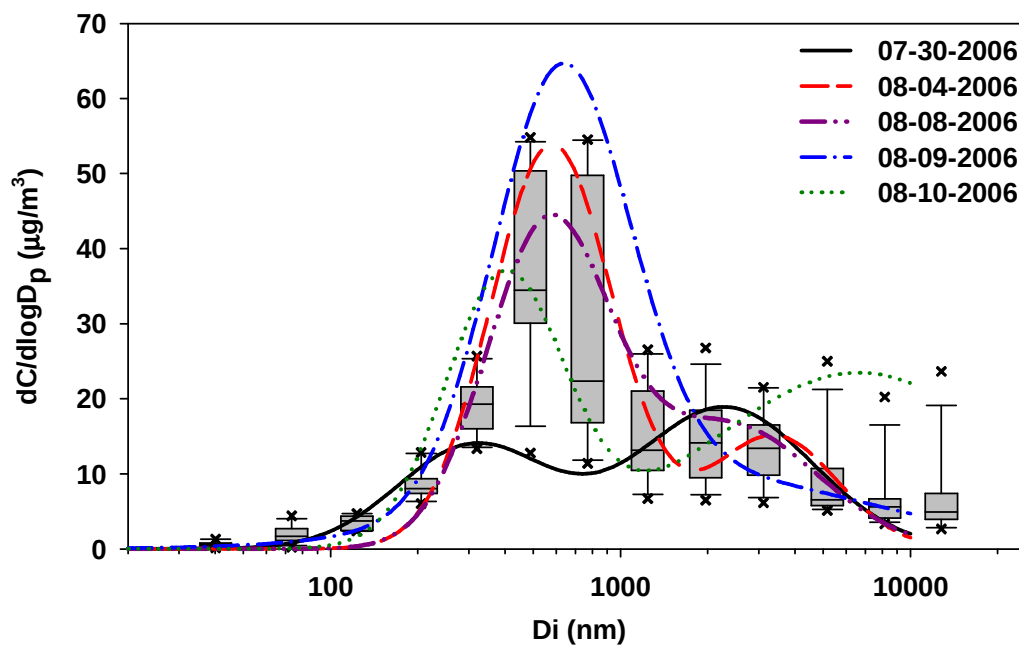


Figure 4A

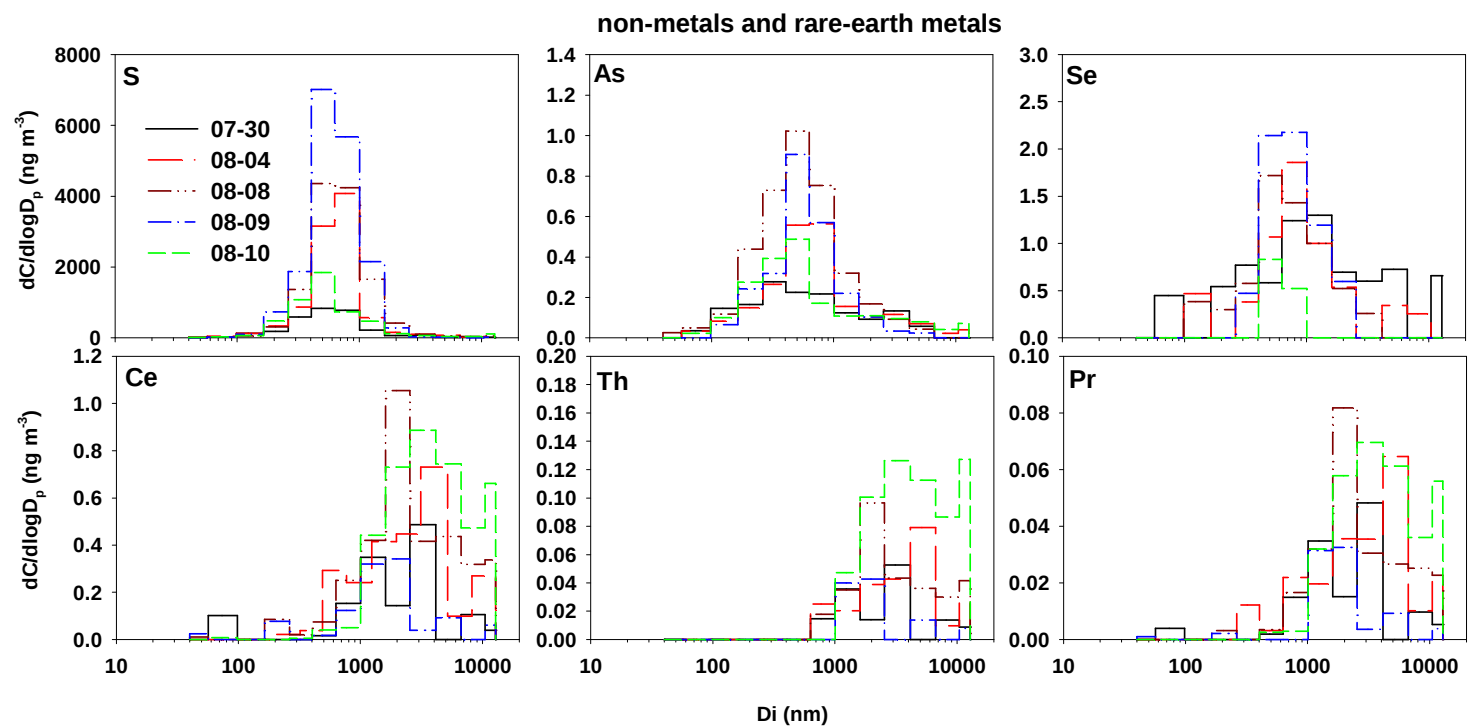


Figure 4B

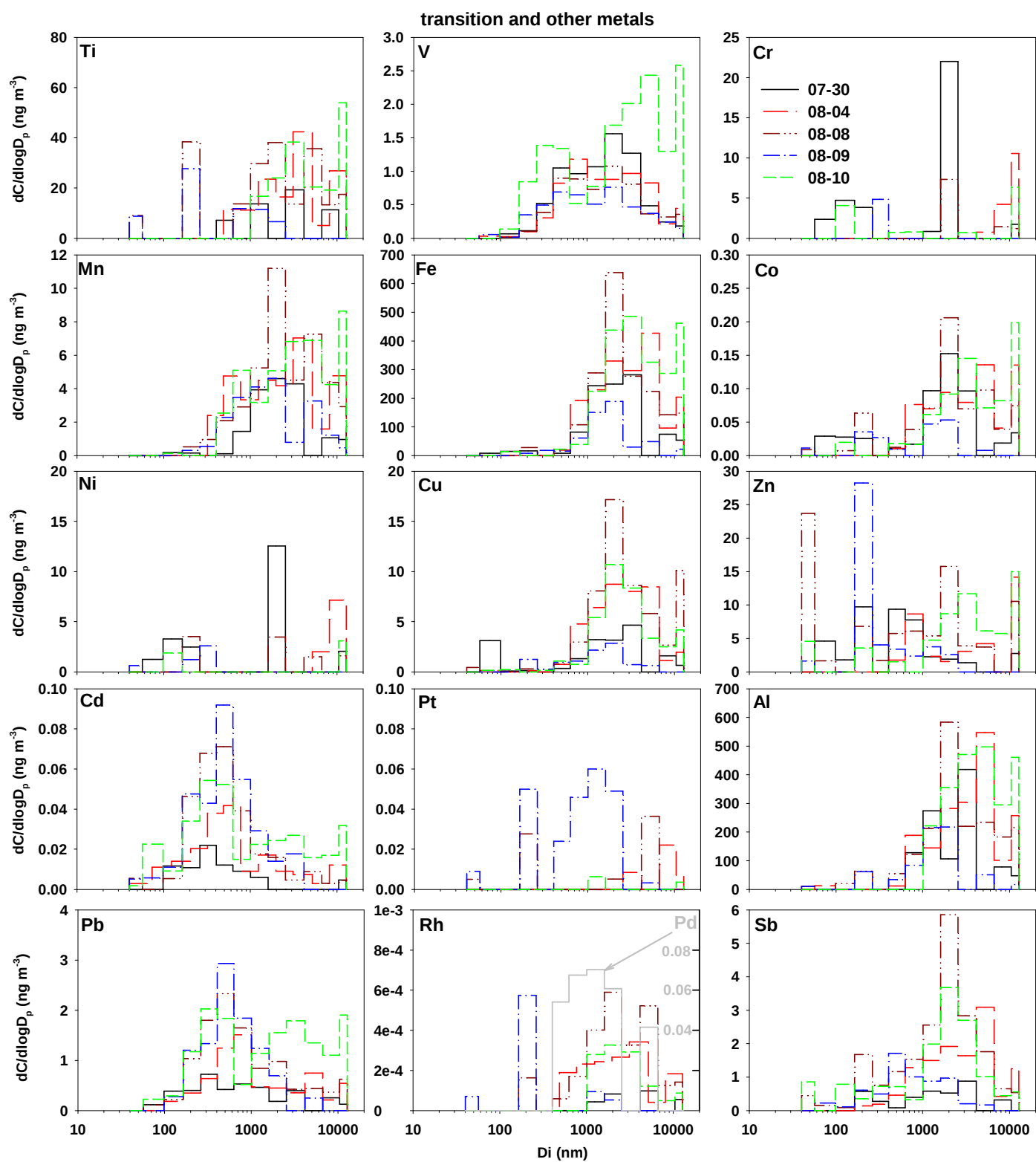


Figure 4C

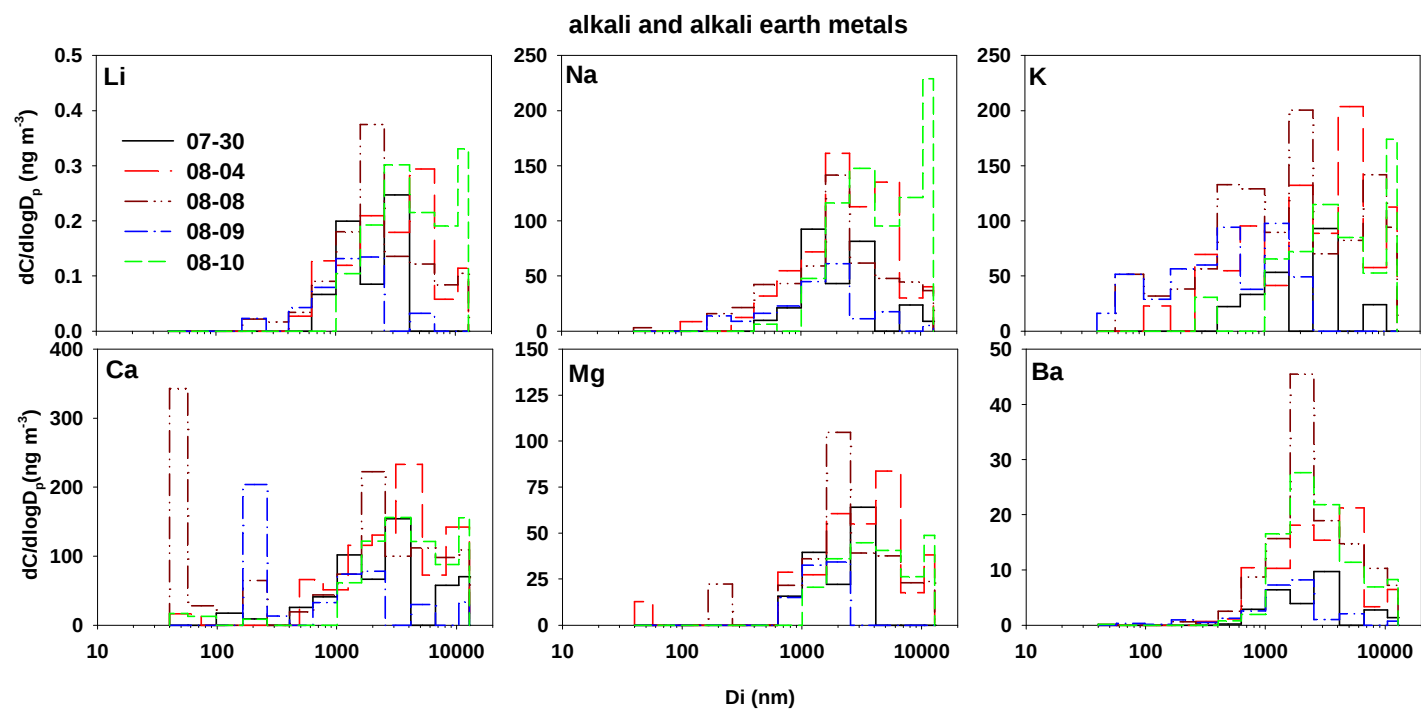


Table 1. PM mass concentrations from gravimetric analysis of LPI substrates with the fraction of time the sampler was downwind of the highway and the average wind speeds (while downwind).

Sample ID	Downwind sampling time	Wind speed	PM ₁₀	PM _{2.5}	PM _{0.1}
	(hr)	(m/s)	(µg/m ³)		
07-27	-	-	43.6	39.4	1.6
07-28	20	3.3	31.3	26.7	2.0
07-29	17	4.1	34.2	29.3	1.5
07-30 (W)	17	3.7	22.4	19.0	1.4
07-31	3	2.7	39.5	36.6	0.9
08-04	7	3.0	38.3	33.7	1.8
08-05	0	0	29.8	26.4	1.5
08-06 (W)	2	2.6	20.2	17.4	1.1
08-07	12	2.7	26.8	23.8	1.5
08-08	12	2.5	33.5	30.2	1.0
08-09	0	0	39.3	36.1	1.0
08-10	13	2.6	41.0	26.9	1.5
mean	9	2.5	33.3	28.8	1.4
std. dev.	7	1.3	7.5	6.8	0.3

Table notes: Bold face type indicates samples for which SF-ICPMS analysis was accomplished. W – indicates sampling on weekend days only. The sampling time and wind speed were estimated using hourly meteorological data.

TABLE 2. SF-ICPMS determined elemental composition in different DLPI particle size fractions collected in Raleigh, NC during the summer 2006 near-highway study.

	average conc. (ng m ⁻³)			average PM conc. (mg kg ⁻¹)		
	ΣDLPI _(PM10-2.5)	ΣDLPI _(PM2.5-0.1)	ΣDLPI _(PM0.1)	ΣDLPI _(PM10-2.5)	ΣDLPI _(PM2.5-0.1)	ΣDLPI _(0.1)
<u>alkali metals</u>						
lithium	0.09 ± 0.07	0.1 ± 0.03	—	11.5 ± 9.8	4.0 ± 1.0	—
sodium	44.3 ± 40.8	53.9 ± 17.6	0.6 ± 0.5	1268.2 ± 1168.9	1975.0 ± 632.4	422.2 ± 578.5
potassium	50.9 ± 40.3	75.9 ± 40.4	7.6 ± 9.4	6894.5 ± 5454.1	2857.7 ± 1520.7	7967.6 ± 9830.8
rubidium	0.2 ± 0.2	0.3 ± 0.1	0.01 ± 0.01	30.3 ± 25.1	10.4 ± 5.3	7.8 ± 10.7
cesium	—	0.01 ± 0.00	—	—	0.4 ± 0.1	0.5 ± 0.5
<u>alkali earth metals</u>						
beryllium	0.001 ± 0.002	0.01 ± 0.01	0.004 ± 0.01	0.2 ± 0.3	0.2 ± 0.3	4.6 ± 6.3
magnesium	18.9 ± 14.9	24.3 ± 9.8	0.8 ± 1.7	2567.4 ± 2018.8	915.9 ± 371.8	797.4 ± 1782.9
calcium	67.5 ± 38.7	70.9 ± 16.9	24.4 ± 47.0	9127.2 ± 5236.6	2670.5 ± 635.0	25391 ± 48969
strontium	0.5 ± 0.3	0.8 ± 0.2	0.04 ± 0.07	72.5 ± 46.9	28.6 ± 7.4	42.3 ± 77.1
barium	5.6 ± 3.9	8.9 ± 5.1	0.03 ± 0.03	756.6 ± 531.9	334.9 ± 190.9	29.6 ± 33.8
<u>transition metals</u>						
scandium	0.02 ± 0.02	0.03 ± 0.01	—	3.3 ± 2.3	1.0 ± 0.3	—
yttrium	0.05 ± 0.03	0.05 ± 0.01	—	6.1 ± 4.0	1.9 ± 0.5	—
lanthanum	0.1 ± 0.1	0.1 ± 0.03	0.003 ± 0.004	11.9 ± 8.9	4.1 ± 1.0	2.8 ± 4.3
titanium	12.3 ± 9.8	13.7 ± 7.3	1.1 ± 1.5	1661.8 ± 1333.9	504.6 ± 276.1	1105.9 ± 1514.6
vanadium	0.6 ± 0.6	1.0 ± 0.3	0.01 ± 0.01	76.8 ± 75.1	38.8 ± 11.2	10.1 ± 6.0
niobium	0.2 ± 0.2	0.4 ± 0.3	0.1 ± 0.1	22.5 ± 27.3	16.8 ± 9.5	57.3 ± 87.3
chromium	1.1 ± 1.3	1.6 ± 2.1	0.3 ± 0.5	147.8 ± 171.6	62.1 ± 80.4	327.8 ± 502.4
molybdenum	0.04 ± 0.04	0.1 ± 0.03	0.01 ± 0.01	5.3 ± 5.2	2.0 ± 1.2	5.9 ± 8.9
manganese	2.8 ± 1.7	3.5 ± 0.9	0.01 ± 0.01	372.5 ± 230.5	132.7 ± 33.4	7.7 ± 10.8
iron	136.5 ± 103.4	169.4 ± 54.4	1.0 ± 1.5	18460 ± 13981	6372 ± 2047	1072 ± 1622
cobalt	0.05 ± 0.04	0.1 ± 0.02	—	6.5 ± 4.9	2.3 ± 0.7	3.9 ± 3.8
nickel	0.7 ± 0.7	1.1 ± 1.2	0.2 ± 0.3	98.3 ± 94.2	40.4 ± 46.9	224.8 ± 284.9
ruthenium	—	—	—	—	—	—
rhodium	0.0004 ± 0.001	0.001 ± 0.002	—	0.1 ± 0.1	0.03 ± 0.02	0.01 ± 0.03
palladium	0.001 ± 0.002	0.01 ± 0.01	—	0.1 ± 0.3	0.2 ± 0.4	—
platinum	0.003 ± 0.004	0.01 ± 0.02	—	0.4 ± 0.5	0.4 ± 0.8	0.9 ± 1.3
silver	—	0.02 ± 0.02	0.01 ± 0.01	—	0.6 ± 0.9	5.6 ± 9.3
copper	2.5 ± 1.9	3.9 ± 2.0	0.2 ± 0.3	341.2 ± 257.5	148.4 ± 75.1	197.0 ± 313.5
zinc	3.1 ± 2.8	6.5 ± 2.6	2.1 ± 3.0	418.8 ± 379.2	245.3 ± 96.4	2188.9 ± 3148.5
cadmium	0.01 ± 0.01	0.04 ± 0.02	0.003 ± 0.002	0.8 ± 0.8	1.5 ± 0.7	3.4 ± 2.3
<u>other metals</u>						
aluminum	157.4 ± 119.4	161.4 ± 37.4	2.3 ± 2.4	21295 ± 16143	6077 ± 1407	2412 ± 2482
thallium	0.003 ± 0.002	0.01 ± 0.003	—	0.4 ± 0.3	0.3 ± 0.1	0.1 ± 0.2
lead	0.4 ± 0.4	1.4 ± 0.6	0.1 ± 0.02	53.7 ± 56.9	52.7 ± 21.6	55.1 ± 27.6
antimony	0.6 ± 0.5	1.6 ± 0.9	0.1 ± 0.1	84.6 ± 67.4	58.5 ± 33.6	123.0 ± 153.3
<u>non-metals</u>						
phosphorous	6.5 ± 7.4	13.2 ± 17.0	6.6 ± 7.2	885.3 ± 996.8	495.2 ± 641.4	6920.2 ± 7526.8
sulfur	32.8 ± 15.2	1856 ± 1198	20.3 ± 4.6	4437 ± 2051	69871 ± 45120	21147 ± 4849
arsenic	0.03 ± 0.02	0.4 ± 0.2	0.02 ± 0.01	4.1 ± 2.3	15.8 ± 6.6	20.8 ± 9.8
selenium	0.1 ± 0.2	1.0 ± 0.4	0.04 ± 0.04	14.1 ± 21.1	36.3 ± 15.2	42.2 ± 44.5
<u>rare earth metals</u>						
cerium	0.2 ± 0.2	0.3 ± 0.1	0.01 ± 0.01	31.8 ± 24.5	10.2 ± 3.7	7.4 ± 9.8
thorium	0.03 ± 0.03	0.03 ± 0.01	—	4.2 ± 4.1	1.0 ± 0.4	—
praseodymium	0.02 ± 0.01	0.02 ± 0.01	—	2.6 ± 1.9	0.8 ± 0.2	0.3 ± 0.4
neodymium	0.1 ± 0.1	0.1 ± 0.02	—	9.6 ± 7.0	3.1 ± 0.8	0.9 ± 1.0
uranium	0.02 ± 0.02	0.02 ± 0.01	—	2.2 ± 2.3	0.6 ± 0.3	0.3 ± 0.5
samarium	0.01 ± 0.01	0.02 ± 0.01	—	1.9 ± 1.4	0.6 ± 0.2	—
europium	0.003 ± 0.003	0.004 ± 0.002	—	0.4 ± 0.4	0.2 ± 0.1	—
gadolinium	0.1 ± 0.1	0.1 ± 0.04	—	9.1 ± 7.7	2.8 ± 1.6	0.7 ± 0.7
dysprosium	0.01 ± 0.01	0.01 ± 0.0	—	1.2 ± 0.9	0.4 ± 0.1	—
erbium	0.01 ± 0.0	0.01 ± 0.0	—	0.7 ± 0.5	0.2 ± 0.1	—
ytterbium	0.01 ± 0.004	0.01 ± 0.001	—	0.7 ± 0.5	0.2 ± 0.1	0.02 ± 0.1

Table notes: Reported mean and standard deviation values were derived from integrating DLPI stage data (as indicated) for each of the *n*=5 test days. The rare earth metals terbium, thulium, and lutetium were below quant limits. Compounds containing elements in bold are EPA air toxics. All values are field blank corrected.