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Emissions of Metals Associated with Motor Vehicle Roadways

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Emissions of metals and other particle-phase species from on-road motor vehicles were measured in two tunnels in Milwaukee, WI during the summer of 2000 and winter of 2001. Emission factors were calculated from measurements of fine (PM_{2.5}) and coarse (PM₁₀) particulate matter at tunnel entrances and exits, and effects of fleet composition and season were investigated. Cascade impactors (MOUDI) were used to obtain size-resolved metal emission rates. Metals were quantified with inductively-coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF). PM₁₀ emission rates ranged from 38.7 to 201 mg km⁻¹ and were composed mainly of organic carbon (OC, 30%), inorganic ions (sulfate, chloride, nitrate, ammonium, 20%), metals (19%), and elemental carbon (EC, 9.3%). PM₁₀ metal emissions were dominated by crustal elements Si, Fe, Ca, Na, Mg, Al, and K, and elements associated with tailpipe emissions and brake and tire wear, including Cu, Zn, Sb, Ba, Pb, and S. Metals emitted in PM_{2.5} were lower (11.6% of mass). Resuspension of roadway dust was dependent on weather and road surface conditions, and increased emissions were related to higher traffic volumes and fractions of heavy trucks. Emission of noble metals from catalytic converters appeared to be impacted by the presence of older vehicles. Elements related to brake wear were impacted by enriched road dust resuspension, but correlations between these elements in PM_{2.5} indicate that direct brake wear emissions are also important. A submicrometer particle mode was observed in the emissions of Pb, Ca, Fe, and Cu.

Introduction

Exposure to inhalable PM_{2.5} and PM₁₀ particulate matter emissions from roadways has been implicated as detrimental to human health and increased risk of respiratory illnesses (1, 2). The regulatory framework for controlling emissions

from on-road motor vehicles, in almost all locations of the world, is predominantly focused on tailpipe emissions. Due to the regulatory focus on tailpipe emissions, studies that have shown adverse health effects associated with proximity to roadways have largely been interpreted as evidence that exposure to tailpipe emissions is the source of observed health effects. However, the emissions of brake wear, tire wear, and resuspended road dust from roadways are also associated with motor vehicle activity. Although these nontailpipe emissions are not regulated in a manner similar to tailpipe emissions, all of these emissions need to be considered in assessing the impact of motor vehicles on human health and the environment. Additionally, observed associations of health effects with roadway exposure may be more closely related to specific chemical components (3–5) than to total mass concentrations of inhalable particles. As metals are suspected to be linked to health impacts and exacerbation of asthma (5–7), there is a great need to better characterize the metal emissions from motor vehicle roadways.

Human exposure to particulate matter emitted from motor vehicle roadways includes simultaneous exposure to PM₁₀ and PM_{2.5} emissions from tailpipes (8, 9), brake and tire debris (10, 11), and resuspension of road dust by passing vehicles (11–14). Vehicle tunnels can be used to measure these total roadway emissions of particulate matter from in-use fleets (15). Several studies have shown that particulate matter emissions measured in vehicle tunnels are larger than tailpipe emissions measured with vehicle dynamometers. Tunnels also typically have very different driving cycles than controlled dynamometer tests. Due to these disparities, tunnel emission rates should not be directly compared to dynamometer results.

The purposes of the tunnel tests pursued in the study were to characterize roadway particulate matter and metal emissions from a mixed, on-road fleet, and to investigate the impacts of roadway conditions on total emissions of metals. Previous studies of in-use vehicle emissions have primarily focused on gaseous, semivolatile, and particulate organic compounds (16–19), with minimal emphasis on characterization of trace metals. Several studies have reported elemental emission rates for tailpipe exhaust of vehicles on dynamometers (8, 16, 20–22), and others have reported concentrations near roadways (23). Gillies et al. (24) reported PM₁₀ and PM_{2.5} emission rates for 40 elements, measured by XRF, in the Sepulveda Tunnel. However, the analytical techniques employed yielded statistically significant emission rates for only five elements in each size fraction. Gertler et al. (25) reported roadway tunnel emission rates for light-duty and heavy-duty vehicles. That study used PIXE and XRF to quantify emission rates of 20 elements in PM_{2.5}, but measured statistically significant emission rates for only six. Allen et al. quantified fine and coarse emissions of 36 elements, with instrumental neutron activation analysis, for light-duty and heavy-duty fleets in the Caldecott tunnel (26), but only 13 elements were found to be emitted in statistically significant amounts in any sample. Pierson and Brachaczek (27) completed the most comprehensive analysis of metals emitted from motor vehicle roadways, but the results are for TSP only and were conducted more than 20 years ago. In the present study, both ICP-MS and XRF were used for metals analysis to ensure low detection limits for a wide range of elements. Combination of the two analytical techniques allowed quantification of a total of 42 elements, 32 of which were emitted in statistically significant amounts in individual tests (greater than twice the total measurement uncertainty). Multiple tunnel tests were conducted in two tunnels with

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TABLE 1. Tunnel Studies Conducted in Milwaukee, WI

test	location	date	day	sampling hours	vehicles total no.	trucks %	SF ₆ release
A	Kilborn	31-Jul-00	Monday	4	2310	1.6	
B	Kilborn	3-Aug-00	Thursday	4	2792	2.5	
C	Kilborn	8-Aug-00	Tuesday	4	3665	1.7	yes
D	Kilborn	9-Aug-00	Wednesday	4	2403	2.3	yes
E	Kilborn	10-Aug-00	Thursday	4	2364	3.0	
F	Howell	23-Aug-00	Wednesday	4	4486	6.1	yes
G	Howell	27-Aug-00	Sunday	4	2336	1.5	yes
H	Howell	27-Aug-00	Sunday	4	2621	2.4	
I	Howell	28-Aug-00	Monday	4	3112	9.4	
J	Howell	28-Aug-00	Monday	4	4822	6.5	
K	Howell	13-Dec-00	Wednesday	7	6720	7.0	yes
L	Howell	14-Dec-00	Thursday	8	7579	7.2	
M	Howell	10-Jan-01	Wednesday	8	7062	7.7	
N	Howell	11-Jan-01	Thursday	8	7860	7.7	yes
O	Howell	16-Jan-01	Tuesday	8	7964	7.2	yes
P	Howell	17-Jan-01	Wednesday	8	7977	6.6	

different fleet characteristics to illuminate the effects of traffic volume and heavy-duty vehicle fraction. In one tunnel, variation between emissions from a weekday rush hour fleet and a weekend fleet was explored. Tunnel measurements were also performed in both summer (25 °C) and winter (0 °C) conditions to examine seasonal differences in emissions. The low detection limits achieved through application of both XRF and ICP-MS allowed observation of differences among total roadway emissions of individual elements under these roadway conditions.

In addition to the roadway conditions of fleet composition, traffic volume, and season studied here, the emissions of metals from roadway traffic will clearly vary with other factors such as geographic area and varying inputs from specific emission sources. The quantification of total roadway emissions of a broad range of elements in this study is important to efforts to obtain comprehensive information about elemental composition of emissions from roadways under many conditions. Such information will provide important information for health effects studies and source reconciliation modeling efforts.

Methods

Sample Collection. Particulate matter emission rates were measured in two tunnels in Milwaukee, WI. The first tunnel, referred to as the Kilborn tunnel, is an entrance ramp for a major highway, Interstate 43, in downtown Milwaukee. In the tunnel, traffic merges from two lanes to one lane, and then accelerates through an approximately 45° curve and 1% upgrade onto the interstate. Vehicles brake in the tunnel while merging lanes and are forced to turn slightly while accelerating. Vehicle speeds recorded at the tunnel inlet and exit averaged 32 and 39 mph (51 and 62 kph), respectively. The tunnel was periodically swept, and there was minimal dirt on the roadway during these tests. The road surface was concrete and in good repair. The tunnel had a forced exhaust in the middle of the tunnel for ventilation. Only the first half of the tunnel was used for sampling, between the vehicle entrance and the forced ventilation outlet. Samplers were located on the sidewalk next to the tunnel roadway, several feet from the wall. Upwind samplers were placed 5 m inside the tunnel entrance, and tunnel exit samplers were 15 m upwind of the exhaust outlet. The total length between samplers was 200 m. In the Kilborn tunnel, five 4-h summertime tests were conducted during weekday rush hours (tests A–E, Table 1), averaging 700 vehicles per hour and 2.2% heavy-duty trucks.

The second tunnel, referred to as the Howell tunnel, is on Howell Avenue and is very similar to the Van Nuys Tunnel

in California, where several previous tunnel tests have been conducted (15, 28). This tunnel has two opposing, completely separate, three-lane bores, and sampling was conducted in the southbound bore. The tunnel has no grade, no curve, and no mechanical ventilation. Traffic cruised in the tunnel with very little braking, and average vehicle speeds at both the entrance and the exit during the tests were around 31 mph (50 kph). The Howell tunnel was not swept, and noticeable amounts of dirt were present on the roadway and roadside. The road surface in this tunnel was concrete in good repair. As in the Kilborn tunnel, samplers were located on the sidewalk in the tunnel. Samples were collected 5 m inside the tunnel entrance, and 15 m upwind of the tunnel exit, for a total length between samplers of 215 m. As listed in Table 1, three 4-h tests over summer weekday rush hours (F, I, J), two 4-h summer weekend traffic tests (G, H), and six 8-h winter tests (K–P) were conducted in the Howell tunnel. Both summer and winter weekday tests at the Howell had approximately 1000 vehicles per hour and 7.2% heavy-duty trucks, while summer weekend tests had 600 vehicles per hour and 2.0% heavy-duty trucks. One summer test in each tunnel was determined to be invalid because of equipment problems, and the results are not included in Table 1 nor are the data reported in this manuscript.

Vehicles were counted and classified using loop counts and two sets of video recording. Loop counts, provided by the Wisconsin Department of Transportation (DOT), were available only in the summertime and provided basic vehicle counts. Videotaping of the passing vehicles corroborated the loop counts and allowed classification of vehicle types and actual heavy- and light-duty vehicle counts.

Particulate matter was collected with samplers built at UW-Madison. As shown in Figure 1, the sampler separates particle sizes with a PM₁₀ inlet (URG Corp.) and PM_{2.5} cyclones (Thermo-Andersen Instruments). Both size fractions were collected on multiple collocated filters for mass and chemical analyses. Five PM₁₀ and six PM_{2.5} filters were collected by each sampler; each PM₁₀ filter was operated with a flow rate of 6.4 LPM, and each PM_{2.5} filter was operated with a flow rate of 8.0 LPM. Flow rates through each filter holder were calibrated in the laboratory, and flow rates were rechecked in the field before and after each test. A separate series of experiments in which the samplers were operated in a sealed chamber verified that contamination with metals possibly emitted from the vacuum pump, such as Zn and Cu, did not occur. During two winter tests, 11-stage Micro-Orifice Uniform Deposit Impactors (MOUDI, MSP Corp.) were operated alongside the inlet and outlet samplers to investigate the size distribution of emissions in the tunnel. One set of

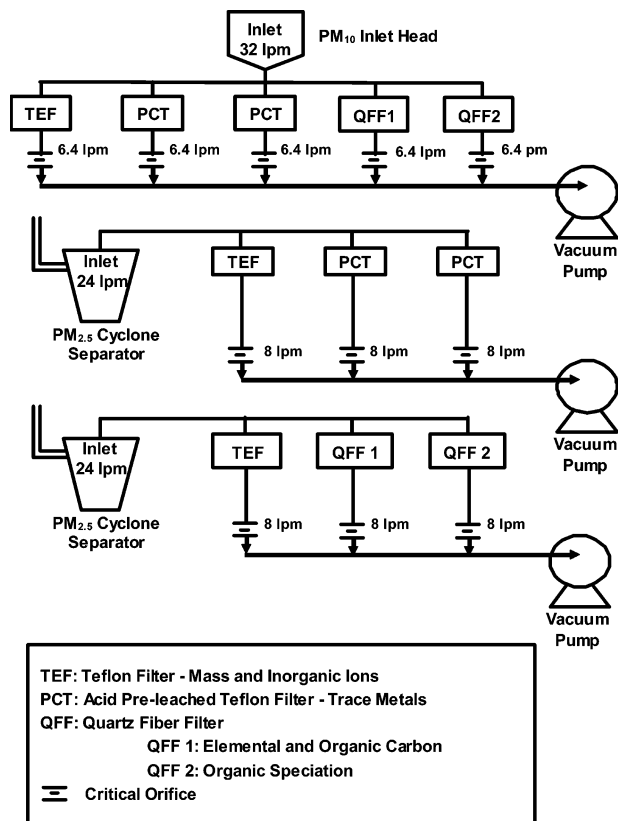


FIGURE 1. Sampler schematic diagram.

MOUDI substrates was used over two consecutive tests to obtain sufficient mass for analysis on each stage.

Analytical Methods. All substrates were prepared in the laboratory before sampling. Teflon substrates (Teflo, 2 μm , Pall Life Sciences, 47 mm) used to collect trace metals samples were preleached in a trace metals clean room. High-purity 2 N HCl and 2 N HNO₃ were drawn sequentially through each filter, in a flow-through filter holder, and each was flushed with 18 M Ω (Milli-Q) water. After cleaning, the filters were air-dried in a HEPA-filtered hood. Polystyrene Petri dishes for trace metals substrates were cleaned by soaking 12 h in 10% HCl, 12 h in 10% HNO₃, and rinsing with Milli-Q water. Trace metals substrates were triple bagged in plastic zip bags and treated with clean handling techniques in the field. Preleached filters were not available for one test and for some samples for XRF analysis, and the greater variability of field blanks similar to sample filters was applied for uncertainty analysis. For mass measurements, additional Teflon filters were equilibrated in a temperature- and humidity-controlled room for 24 h. Acid pre-cleaned, uncoated Teflon filters for MOUDI sampling were also preweighed to allow quantification of mass and trace metals with the same substrate. Quartz fiber filters (Pall Life Sciences, 47 mm), used for measurement of elemental and organic carbon, were prepared by heating to 550 $^{\circ}\text{C}$ for 12 h and were stored in Petri dishes lined with baked aluminum foil.

Volumetric flow rates of air through the tunnels were calculated using inert sulfur hexafluoride (SF₆) gas as a tracer, together with measurements of wind speed at the entrances and exits of the tunnels (29, 30). Small known amounts (1.5–3.0 g min⁻¹) of inert SF₆ were released downwind of the tunnel inlet samplers at a constant flow rate over the entire test period. Stainless steel canisters with passivated internal surfaces (SUMMA cans) were filled slowly with a constant flow rate over the course of the tests, positioned near the aerosol samplers at the tunnel entrance and exit. Concentrations of SF₆ in the SUMMA cans were measured with gas

chromatography-electron capture detection (GC-ECD). Using the concentration increase of SF₆ at the tunnel outlet and air velocity measurements, an empirical relationship between volumetric flow rate through the tunnel and air velocity was determined. This factor was then applied to air velocities measured in all tests to determine specific volumetric dilution rates. Sulfur hexafluoride is very accurately measured by GC-ECD, and the uncertainty associated with these measurements was dominated by the ability to accurately measure air velocities and SF₆ release rates. Through comparison of SF₆ results and airflow measurements, the total impact of these uncertainties on tunnel air dilution rate measurements was estimated to be 5% in tests with SF₆ release. Based on variation in the measured factors for airflow, uncertainty of airflow measurements in tests with no SF₆ release was approximately 15%. Dilution rates were combined with vehicle counts and CO and CO₂ measurements, also made with the SUMMA cans, to calculate average vehicle miles traveled per gallon fuel consumed in the tunnels. Average fleet fuel mileage was determined to be in the range of 20–30 miles per gallon (8.5–13 km per liter).

In addition to the SF₆ release to determine tunnel ventilation rates, one test in the Kilborn tunnel was performed to check for back-mixing across the central exhaust vent. SUMMA cans were placed with the aerosol samplers as usual, but SF₆ was released 50 feet beyond the exhaust vent, in the second half of the tunnel. No SF₆ was detected in the test canisters; thus back-mixing of air and emissions from the second half of the tunnel to the tested tunnel section was found to be negligible.

Elemental composition of the particulate matter samples was measured using inductively coupled plasma mass spectrometry (ICP-MS) techniques, which allowed quantification of 35 elements. Sample dissolution was achieved by microwave-assisted acid digestion, using techniques that were specifically developed for the analysis of the low levels of metals in airborne particulate matter samples. These techniques achieve effective sample solubilization along with minimization of contamination. The polymethylpentene support rings were removed from the Teflon filters, and the filter membranes were placed in a digestion bomb with a mixture of 1.5 mL of 16 N HNO₃ (Ultrex grade, Fisher Scientific), 0.2 mL of 28 N HF (Optima grade, J. T. Baker), and 0.5 mL of 12 N HCl (Optima/trace metal grade, J. T. Baker). The samples were digested in closed Teflon digestion vessels using a programmable microwave digestion unit (ETHOS, Milestone). The digestion protocol was comprised of a 9 min ramp to 180 $^{\circ}\text{C}$ followed by a 10 min hold at 180 $^{\circ}\text{C}$ and 1 h of ventilation/cooling. Digestates were diluted to 30 mL with high purity water (18 M Ω cm⁻¹) generated by a Milli-Q system (Millipore, Bedford, MA), and were stored in low-density polyethylene (LDPE) bottles. To minimize contamination, all Teflon tubes and vessels were cleaned before use by soaking in an 8 N hot nitric acid bath for at least 24 h, followed by a Milli-Q rinse. LDPE digestate storage bottles were soaked in 4 N HCl for 48 h, 3 N HNO₃ for 48 h, and rinsed with Milli-Q.

Digestates were analyzed for 35 trace metals using ICP-MS (PQ Excell, ThermoElemental). Most elements were quantified using standard plasma conditions (1350 W forward power) and a desolvating microconcentric nebulizer (MCN6000, CETAC Technologies Inc.), which significantly reduced oxide- and chloride-based interferences. Lighter elements (Na, K, Ca, Al, Mg, and Fe), which are impacted by polyatomic interferences in standard plasma mode, were quantified using Cool Plasma/Shielded Torch conditions. With this method, a significantly lower plasma temperature is used to reduce ionization and polyatomic formation within the annular channel of the plasma, improving detection limits

for elements with such polyatomic interferences by at least an order of magnitude.

When coupled with microwave-assisted acid digestion, ICP-MS techniques provide the accuracy and sensitivity to analyze atmospheric particulate matter samples for a wide range of elements. Propagated uncertainties were calculated from the standard deviation of field blank measurements and the standard deviation of replicate analyses of Standard Reference Materials (SRMs, NIST). A minimum of six solid samples of three SRMs were digested and analyzed with every batch of 25 samples. The relative uncertainties in each measurement were represented by the uncertainties in the extraction and analysis of replicate SRM samples plus the absolute uncertainty of the field blanks, assuming that these errors are normally distributed and independent. Supporting Information Table S1 lists the instrument and method detection limits for species quantified with ICP-MS.

The concentrations of 13 reported elements (Al, Si, P, S, Cl, K, Ca, Sc, Ge, Se, Br, I, and Ce) were obtained by X-ray fluorescence spectrometry (XRF). Analysis with XRF has strengths in quantification of these elements as compared to ICP-MS methods, and the two methods were used to expand the menu of quantifiable elements. XRF elemental analysis was conducted by the US EPA (Research Triangle Park, NC) using an energy-dispersive XRF instrument (Kevex EDX-771). Calibration checks were performed using an SRM (Thin Glass Film on Polycarbonate, NIST1833). Details of XRF analysis and quantification are described elsewhere (31).

Samples on tared filters were equilibrated for 24 h in a temperature- and humidity-controlled room before weighing using a microbalance (Mettler MX-5). Elemental and organic carbon (EC/OC) were quantified with a thermal-optical analyzer (Sunset Laboratory Inc., Forest Grove, OR) with the NIOSH 5040 method (32). Inorganic ions sulfate, nitrate, chloride, and ammonium were analyzed with water extraction and ion chromatography (IC). All of these measurements, and all ICP-MS analyses, were conducted at the Wisconsin State Laboratory of Hygiene, Madison, WI.

Increases in concentrations ($\mu\text{g m}^{-3}$) of particulate matter and chemical species between the tunnel inlet and outlet were converted to emission rates. Total increase was multiplied by the calculated tunnel dilution rate ($\text{m}^3 \text{h}^{-1}$) and divided by the number of vehicles that passed through the tunnel during the time of the sampling period and the distance between samplers to obtain an emission rate on a per-kilometer basis ($\text{mg km}^{-1} \text{vehicle}^{-1}$). These calculations are parallel to those performed in other tunnel studies (30). Analytical and measurement uncertainties, incorporating the uncertainty of repeated field blank measurements, were propagated through the calculation of emission rates for individual species as the square root of the sum of the squared uncertainties. Emission rates for individual species in tests of the same type (summer weekday Kilborn, summer weekday Howell, summer weekend Howell, winter weekday Howell) were averaged. The uncertainty associated with each average is presented as the standard error (SE) of the averaged measurements, equal to the standard deviation of the n individual measurements, divided by the square root of n . Results were considered to be statistically significant if different from zero with a 95% confidence interval using Student's t -test.

Results

Summer tunnel tests were divided into three categories: weekday Kilborn tunnel tests (A, B, C, D, E), weekend Howell tunnel tests (G, H), and weekday Howell tunnel tests (F, I, J). Winter Howell tunnel tests (K, L, M, N, O, P) were a fourth category. One winter test (Test P) is treated as a separate case, as it had a unique distribution, heavily impacted by road salt application. Test P will be discussed separately and

not included in the discussion of averages and the statistical summary of all tests. A summary of emission rates ($\text{mg km}^{-1} \text{vehicle}^{-1}$) of trace elements and other chemical species in PM_{10} and $\text{PM}_{2.5}$ from the four different categories of tunnel tests and test P is presented in the Supporting Information tables (Tables S2 and S3).

Bulk Emission Rates. Tunnel tests were 4 or 8 h long to obtain sample filter loadings in the optimal range for ICP-MS analysis, but gravimetric mass measurements of the low loadings had relatively high uncertainties. Masses of $\text{PM}_{2.5}$ and PM_{10} were therefore also obtained by summing chemical measurements which had less measurement uncertainty for low filter loadings, including organic carbon (OC), elemental carbon (EC), inorganic ions (sulfate, nitrate, ammonium, and chloride), and elemental oxides. Organic carbon mass was multiplied by 1.4 to estimate mass of organic compounds, and element masses were added as the mass of the most common oxide (21, 26), which are more relevant for mass comparisons than individual element masses. The gravimetric measurements showed excellent agreement with the reconstructed mass values, but reconstructed masses had much lower total uncertainties, and therefore were used as the best estimate of the mass emission rates. The average $\text{PM}_{2.5}$ reconstructed mass was $102 \pm 24\%$ of the gravimetric value, and PM_{10} was $106 \pm 12\%$.

Emission rates of PM_{10} varied from 38.7 to 201 $\text{mg km}^{-1} \text{vehicle}^{-1}$, with an average rate of $91.9 \pm 14.7 \text{ mg km}^{-1} \text{vehicle}^{-1}$. $\text{PM}_{2.5}$ emission rates ranged from 9.14 to 87.2 $\text{mg km}^{-1} \text{vehicle}^{-1}$, averaging $33.4 \pm 5.3 \text{ mg km}^{-1} \text{vehicle}^{-1}$. These PM_{10} emissions fall between the rates reported for light-duty (9 $\text{mg km}^{-1} \text{vehicle}^{-1}$) and heavy-duty vehicles (420 $\text{mg km}^{-1} \text{vehicle}^{-1}$) in the Fort McHenry Tunnel (33). Tests in the Sepulveda Tunnel, with traffic volumes and fleet composition similar to that of the present study, reported comparable emission rates of $69 \pm 30 \text{ mg km}^{-1} \text{vehicle}^{-1}$ for PM_{10} and $52 \pm 27 \text{ mg km}^{-1} \text{vehicle}^{-1}$ for $\text{PM}_{2.5}$ (24).

Average OC and EC emission rates in PM_{10} were 26.5 ± 4.4 and $8.4 \pm 1.7 \text{ mg km}^{-1} \text{vehicle}^{-1}$, respectively, which accounted for $29 \pm 3\%$ and $9.3 \pm 1.5\%$ of PM_{10} roadway mass emissions. Emission rates of OC in $\text{PM}_{2.5}$ ranged from 1.5 to 23.6 $\text{mg km}^{-1} \text{vehicle}^{-1}$, average $9.2 \pm 1.8 \text{ mg km}^{-1} \text{vehicle}^{-1}$, and EC from 1.6 to 17.2 $\text{mg km}^{-1} \text{vehicle}^{-1}$, average $6.0 \pm 1.2 \text{ mg km}^{-1} \text{vehicle}^{-1}$. PM_{10} emissions are shown in Figure 2. The OC measurements in both size fractions are similar in magnitude and mass fraction to measurements in the Sepulveda Tunnel (24), Caldecott Tunnel (26), and Van Nuys Tunnel (28). In Milwaukee, this study observed more OC than EC in both size fractions, opposite of the Sepulveda and Caldecott studies, which may be due to the differences between the analytical methods for EC and OC (32, 34). The Van Nuys study, which applied the NIOSH 5040 method also used in the present study, had very similar ratios of carbon species in the fine particle fraction. Ratios of EC to OC averaged 0.31 ± 0.04 in PM_{10} emissions for the mixed fleet in this study, but the average ratio in $\text{PM}_{2.5}$ was higher (0.44 ± 0.06). This follows from enrichment of PM_{10} with OC from sources such as road dust and wear of organometallic brake pads (11). Also, it is important to note that under the low speed, low engine load operating conditions in these tunnels, emissions of EC from heavy trucks are expected to be relatively low (35–37), consistent with the measured $\text{PM}_{2.5}$ EC/OC ratio. However, the impact of small increases in heavy trucks on EC emissions was observed in the Howell tunnel. Summer weekday and weekend tests at the Howell tunnel had similar ratios of EC to OC in PM_{10} (weekday 0.31 ± 0.04 , weekend 0.21 ± 0.09), but the contribution of EC in $\text{PM}_{2.5}$ was much more distinct. Weekend tests, with 2% heavy-duty truck traffic, had a $\text{PM}_{2.5}$ EC/OC ratio of 0.18 ± 0.01 , while that in weekday tests, which had 7% heavy-duty vehicles, was 0.74 ± 0.01 .

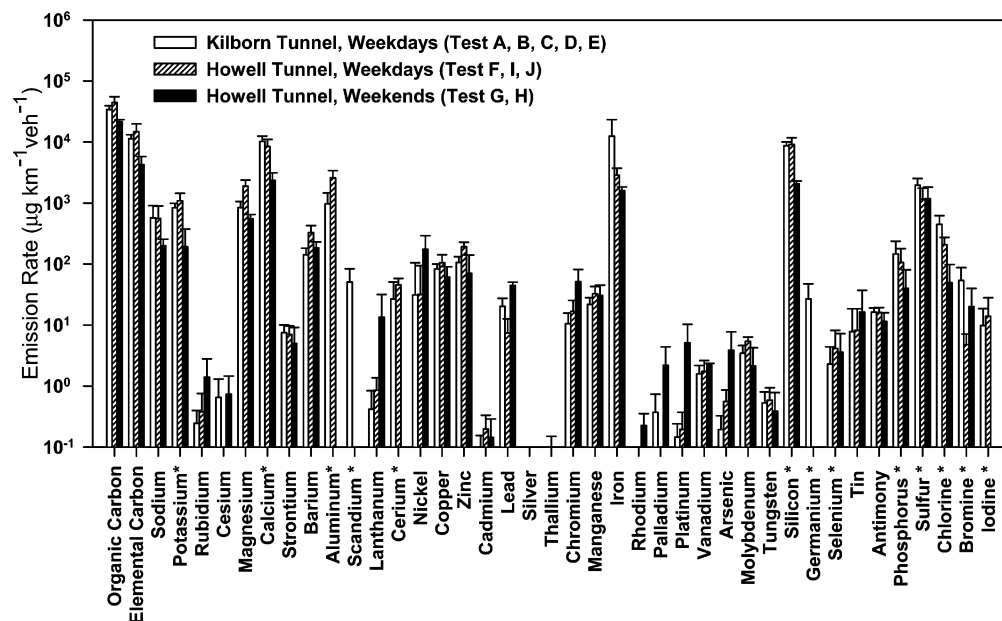


FIGURE 2. Average emission rates of chemical species in PM₁₀ from vehicle fleets measured in two tunnels in Milwaukee, WI. Error bars indicate standard errors. Elements with "*" indicate XRF analysis.

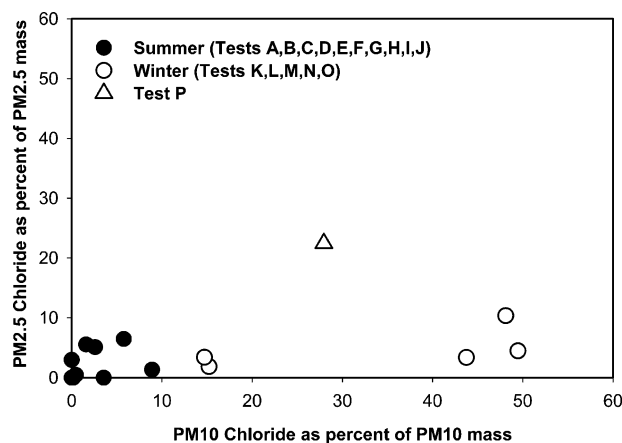


FIGURE 3. Chloride as percent of PM_{2.5} and PM₁₀ mass in tests in two tunnels: summer tests, winter tests, and test P.

The sum of inorganic ions sulfate, nitrate, ammonium, and chloride composed, on average, $20 \pm 4.8\%$ of PM₁₀ emissions, and $20 \pm 3.4\%$ of PM_{2.5} emissions. Emissions of three of the species, sulfate, nitrate, and ammonium, were similar across all test types. As shown in Figure 3, chloride varied distinctly with seasons, averaging $2.5 \pm 0.9\%$ of PM₁₀ mass in summer tests, and $34 \pm 7.9\%$ in winter tests, due to application of salt to melt ice on roadways in the winter. The impact of salt on average winter chloride emissions was not seen in PM_{2.5}, with average summer and winter emission rates very similar, averaging overall $1.0 \pm 0.2 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ and $4.1 \pm 1.5\%$ of mass. Test P had a much higher PM₁₀ chloride emission rate than any other test, $125 \pm 1.1 \text{ mg km}^{-1} \text{ vehicle}^{-1}$, but it contributed $28 \pm 1.0\%$ of PM₁₀ mass, similar to other winter tests. Also, distinct weather conditions during test P resulted in much higher emissions of chloride in PM_{2.5}, $10 \pm 0.8 \text{ mg km}^{-1} \text{ vehicle}^{-1}$, $23 \pm 2.3\%$ of mass (Figure 3). Although the weather in all tunnel tests was dry, a significant amount of snow was present outside of the tunnel during the winter tests, causing the roadway to be wetted by snow and slush carried in with the vehicles. Because the wet roadway attenuated resuspension of road dust, average winter mass emission rates of PM₁₀ were less

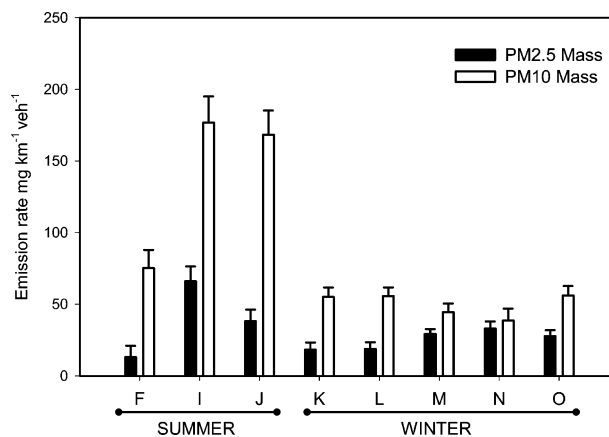


FIGURE 4. PM_{2.5} and PM₁₀ mass emission rates in comparable summer and winter weekday tests in the Howell Tunnel.

than half those in similar summer weekday tests, while PM_{2.5} mass emissions were similar in both seasons (Figure 4). According to the local climatological record, the average daily temperatures during winter tests K, L, M, N, and O were fairly constant ($0\text{--}2^\circ\text{C}$, $32\text{--}35^\circ\text{F}$), warm enough to continue melting snow and keep the roadway wet. However, the day before test P was slightly warmer, and a significant amount of snow melted, thoroughly wetting the roadway. The nighttime low before test P was -5°C (23°F), which may have prompted road crews to apply extra salt to prevent freezing. After a warm day and a very cold night, the daytime temperature during test P did not get above 0°C (32°F), conditions which promoted drying of the wet, salted roadway. Therefore, the road became relatively drier throughout the test, and resuspension of dried salts and drying of salty spray became a huge source of emissions for both PM₁₀ and PM_{2.5}. The impact of the drying conditions in test P on emissions of elements from resuspension of soil and salts was also apparent, as discussed below. Rock salt (halite, sodium chloride) is the most commonly used road de-icer in Wisconsin. The mass ratio of pure sodium and chloride in the de-icer can be approximated as 0.65 (mole ratio 1:1). That chloride and sodium in PM₁₀ in winter tests were correlated with a slope of 0.43 ± 0.03 ($r^2 = 0.99$) is likely due

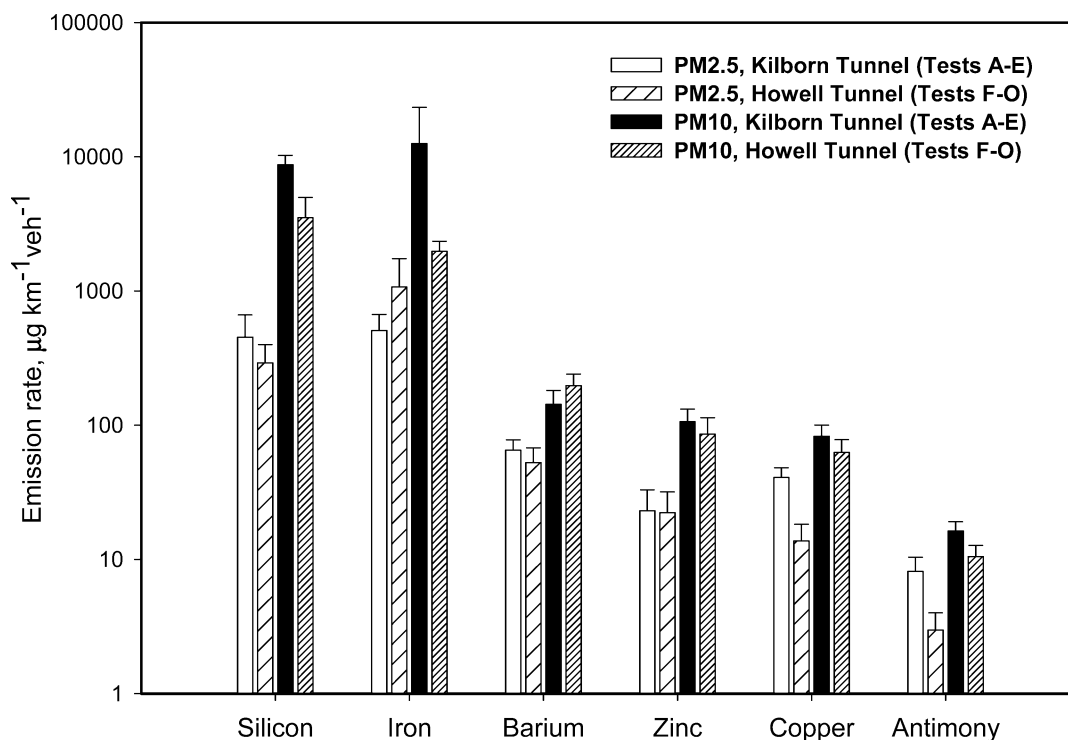


FIGURE 5. Emissions of elements associated with brake wear. PM_{10} and $PM_{2.5}$ in weekday summer tests, Kilborn and Howell Tunnels.

to the fact that the de-icer also contains other chloride salts and impurities.

Metal Emission Rates. Several of the elements for which roadway emission rates were quantified are classified by the U.S. EPA as air toxics, including antimony (Sb), lead (Pb), manganese (Mn), nickel (Ni), arsenic (As), cadmium (Cd), and chromium (Cr). This further emphasizes the importance to health studies of understanding total roadway emissions of metals. Emission rates of total elements in PM_{10} measured by XRF and ICP-MS varied from 1.8 ± 1.6 to 78.5 ± 56.6 $mg\ km^{-1}\ vehicle^{-1}$, and the average emission rate accounted for $18.9 \pm 2.4\%$ of PM_{10} mass. The most abundant elements emitted in PM_{10} in the tunnel were iron (Fe, average $4.5 \pm 1.7\%$ of PM_{10} mass), calcium (Ca, $4.2 \pm 0.9\%$), silicon (Si, $3.9 \pm 0.8\%$), sodium (Na, $2.2 \pm 0.8\%$), magnesium (Mg, $1.1 \pm 0.2\%$), sulfur (S, $0.84 \pm 0.26\%$), aluminum (Al, $0.69 \pm 0.24\%$), and potassium (K, $0.41 \pm 0.10\%$). The sum of these eight elements accounted for an average $94 \pm 1\%$ of the total PM_{10} emission of 42 measured elements. They were also present in $PM_{2.5}$ in much lower amounts and were significantly different from zero in $PM_{2.5}$ in only a few tests. These elements are major components of crustal materials and soil and are predominantly attributed to resuspension of road dust due to the large amounts present in PM_{10} . Many studies have previously shown that the dust resuspended from roadways is enriched in many elements that are emitted from anthropogenic sources (38–41). The elemental distribution of the measured PM_{10} emissions in the present study further supports this observation. The average Si and Al content of the PM_{10} tunnel emissions were much lower than typically found in uncontaminated crustal material. The tunnel PM_{10} emissions averaged 3.9% Si and 0.69% Al by mass, whereas crustal materials typically contain about 28% Si and 8.1% Al (42). In contrast, the Fe, Ca, Na, and Mg content of the PM_{10} emissions were similar to average crustal materials, which contain about 5.0% Fe, 3.6% Ca, 2.8% Na, and 2.1% Mg (42). The relative shift in composition can be attributed to the contributions of other roadway sources and enrichment of roadway soil with previously deposited PM from motor vehicles. That fact that Fe, Ca, Na, and Mg are present in the

PM_{10} emissions in similar ratios to those found in crustal materials, while Si and Al are present in much lower levels in the emissions, indicates that these four elements have important roadway sources and are enriched in roadway soil. Some important roadway sources for these elements include combustion of motor oil additives for Ca, Mg, and S, and wearing of engines, tires, and brakes for Fe (10, 20). Sulfur is emitted primarily from emissions of fuel, motor oil, and additives such as zinc dithiophosphate (20). Very poor correlations observed between the emissions of Zn, P, and S from the roadway support the notion that zinc dithiophosphate is not the only source of Zn, P, or S from the roadway. For measurements in the Sepulveda tunnel, Gillies et al. reported emission rates of S in PM_{10} 1.05 ± 11.94 $mg\ km^{-1}\ vehicle^{-1}$, and $PM_{2.5}$ 0.32 ± 0.56 $mg\ km^{-1}\ vehicle^{-1}$, similar to average measurements in the present Milwaukee tests (PM_{10} 1.0 ± 0.27 $mg\ km^{-1}\ vehicle^{-1}$, $PM_{2.5}$ 0.51 ± 0.14 $mg\ km^{-1}\ vehicle^{-1}$). Sulfur was somewhat correlated with crustal elements in PM_{10} (r^2 with Si = 0.49, Ca = 0.42, K = 0.35, Fe = 0.22), but showed no correlation in $PM_{2.5}$ ($r^2 < 0.02$) or with other elements in either size fraction. The regression of mass emission rates of sulfate to sulfur was found to have a slope of 0.42 ± 0.11 for the PM_{10} and 0.40 ± 0.09 for the $PM_{2.5}$, which demonstrates that the sulfur emissions were predominantly in the form of sulfate because sulfate is 33% sulfur by mass.

Significant emissions of barium (Ba), zinc (Zn), copper (Cu), antimony (Sb), and lead (Pb) were also detected in PM_{10} in all tests (Figure 2), which is consistent with the results of other tunnel studies (13, 43). Although the sum of these five elements did not exceed 1% of PM_{10} mass, they may be important for health effects and can provide some indications of the sources of particulate matter emissions, such as brake wear. Brake wear emissions contain significant amounts of Ba, Zn, Cu, Sb, Fe, and crustal elements (10). Antimony, which has been suggested as a tracer for brake wear (44), was correlated in PM_{10} with Cu ($r^2 = 0.72$) and Ba ($r^2 = 0.52$). Antimony was correlated to a lesser extent with Zn, Ca, and Si ($r^2 = 0.30, 0.28, 0.26$), suggesting that additional sources exist for these elements, such as road dust. Because resus-

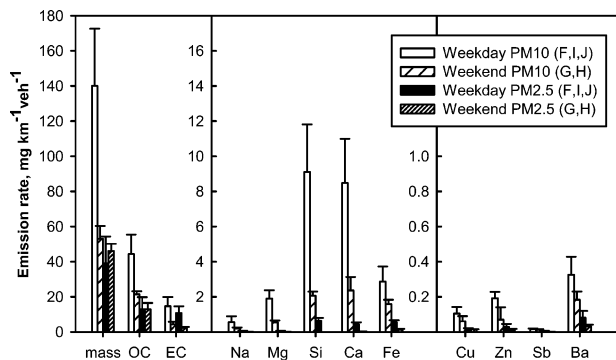


FIGURE 6. Howell tunnel weekday and weekend emissions of selected elements in PM₁₀ and PM_{2.5}.

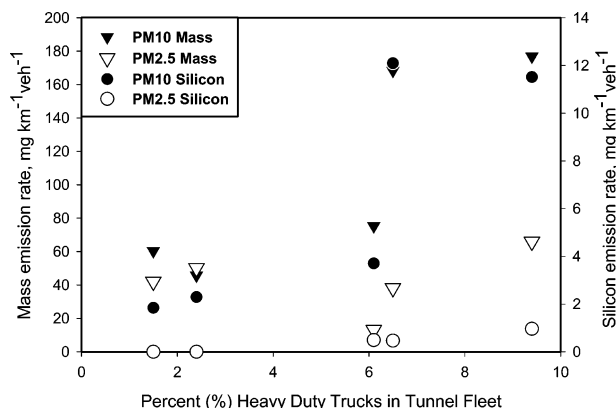


FIGURE 7. Emission rates of mass and silicon in PM₁₀ and PM_{2.5} versus the percentage of heavy-duty trucks present in the Howell Tunnel fleet, summer tests.

pension of road dust will not dominate in the fine fraction, correlations between these elements in the PM_{2.5} fraction indicates that brake wear may be an important source. In PM_{2.5} in these tests, Sb had higher correlations with Cu ($r^2 = 0.77$), Ba (0.64), Ca (0.45), and Si (0.58). Correlation between Sb and Zn was not improved in the fine fraction, indicating that other sources are also very important for Zn in this size range, including tailpipe emissions of motor oil (20, 45) and tire wear (46). Fe, one of the most abundant measured

elements, shows no correlations with other brake wear elements due to its presence in many potential sources such as crustal materials and tailpipe emissions. It is interesting to note that, although vehicles tend to brake in the Kilborn tunnel, but not in the straight Howell tunnel, emissions of brake wear elements were not distinctly increased in the Kilborn tunnel. No differences were seen in PM₁₀ emission rates, and the slight increases in Cu and Sb emissions in PM_{2.5} apparent at the Kilborn tunnel were not statistically significant (Figure 5). Sternbeck et al. (13) suggested that wear particles can accumulate on the wheelrims during braking and later be emitted by resuspension from the wheelrims, resulting in similar per-kilometer emission rates in both tunnels in this study. Although more vehicles in the Kilborn tunnel braked, vehicles in both tunnels were traveling at similar speeds, and emissions of brake wear elements due to resuspension from wheelrims were similar in both tunnels.

Lead (Pb) may be emitted from several sources, including fuel and motor oil combustion, brake wear, and resuspension of enriched road dust (10, 20, 47). In tests with significant emissions of Pb, the fraction in PM_{2.5} accounted for only up to 17% of PM₁₀ levels, indicating that resuspension of road dust is likely the predominant source of the emissions. Tailpipe emissions prior to the phaseout of leaded gasoline and industrial sources have been proposed as the causes of lead enrichment in roadway dirt. However, a more likely source of the persistent lead enrichment of roadway soil is lead wheel weights which are dropped from vehicle wheels and pulverized by traffic (48). A number of older, pre-1980 cars, which used leaded fuel before it was phased out, were noted and videotaped on the weekend, but Pb in PM_{2.5} was an order of magnitude lower than PM₁₀, and not statistically significant, indicating that tailpipe emissions from older cars were not an important source of emissions.

Although the impact of the older vehicles was not seen on Pb, it was observed in emissions of platinum group metals platinum (Pt), rhodium (Rh), and palladium (Pd). These elements are components of catalytic converters and have been detected in automobile emissions and roadway dust in many studies (38, 41, 49, 50). Zereini et al. (2001) cite one study in Germany that estimated roadway emissions of Pt from catalytic converters, using measurements in soil and traffic volume, to be 270 ng km⁻¹ vehicle⁻¹ and a second laboratory experiment that determined average Pt emission

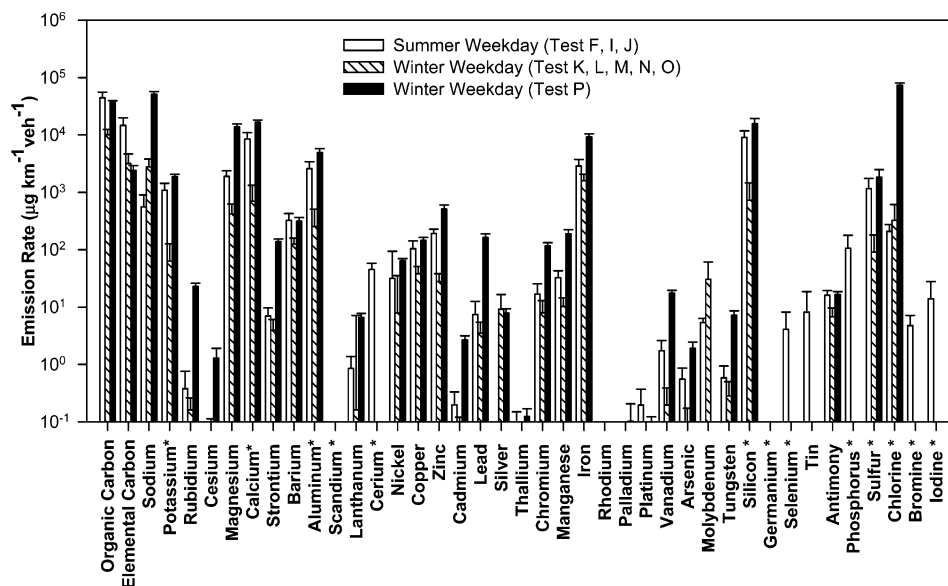


FIGURE 8. Temporal variability in the emissions of chemical species in PM₁₀ in the Howell tunnel in summer tests, winter tests, and test P. Elements with "*" indicate XRF analysis.

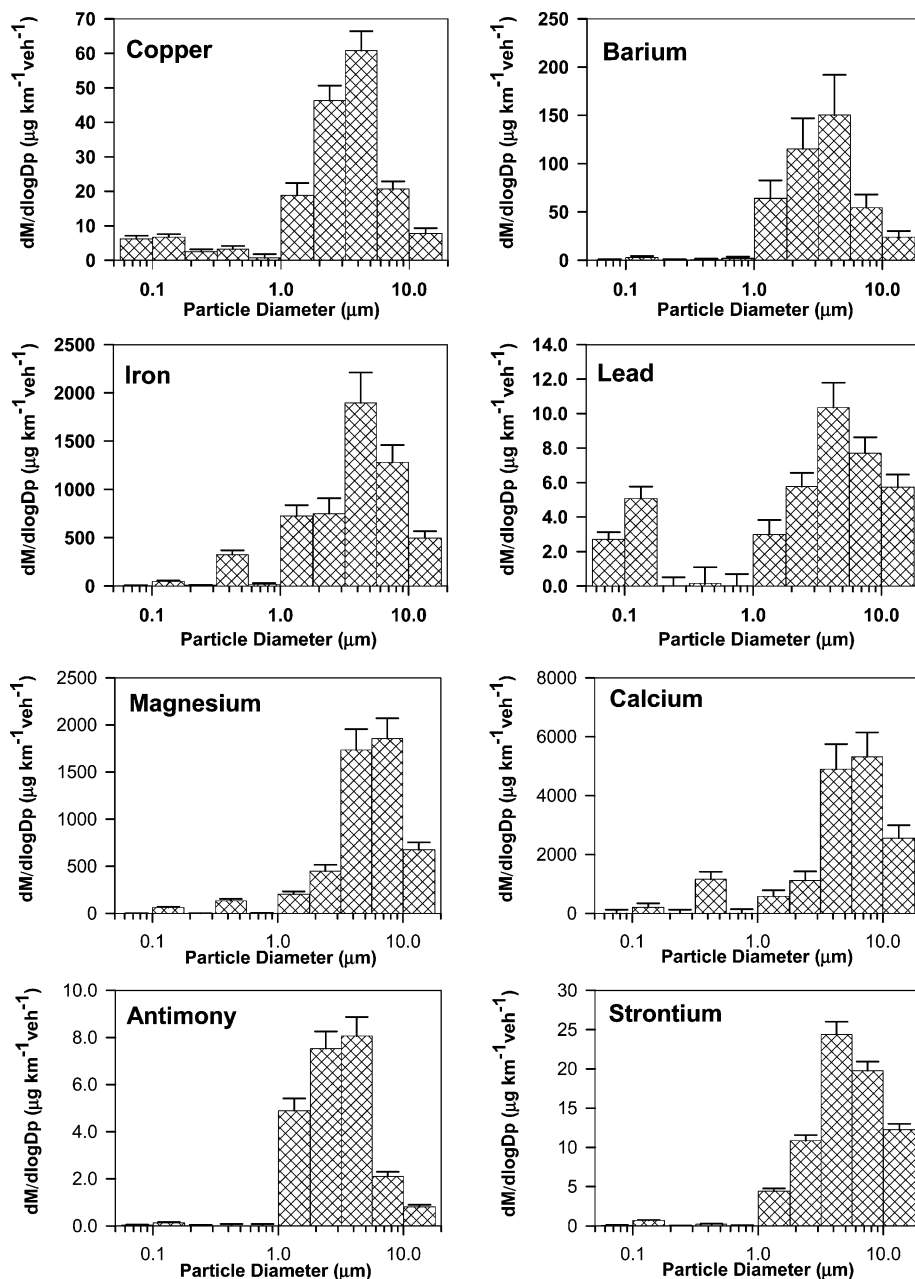


FIGURE 9. Size-resolved metals emissions from motor vehicle roadway tests, analyzed by ICP-MS. Samples were collected with 11-stage MOUDI impactors during winter tunnel tests (tests O and P).

rates of $9\text{--}124\text{ ng km}^{-1}\text{ vehicle}^{-1}$ (51). Zereini et al. also noted that noble metal emissions will vary with the age of the catalytic converter. Pt was detected in the tunnel tests (Figure 2), in quantities similar to those studies, and Rh and Pd were also measured. Average PM_{10} emission rates in all weekday tests were $100 \pm 49\text{ ng Pt km}^{-1}\text{ vehicle}^{-1}$, $17 \pm 11\text{ ng Rh km}^{-1}\text{ vehicle}^{-1}$, and $150 \pm 130\text{ ng Pd km}^{-1}\text{ vehicle}^{-1}$. However, in one of the tests conducted in the Howell tunnel on a summer weekend, emission rates were at least an order of magnitude higher than any other test, $10\,200 \pm 2500\text{ ng Pt km}^{-1}\text{ vehicle}^{-1}$, $350 \pm 85\text{ ng Rh km}^{-1}\text{ vehicle}^{-1}$, and $4400 \pm 2800\text{ ng Pd km}^{-1}\text{ vehicle}^{-1}$. This test was conducted in the afternoon on the weekend and included several older, classic 1970s vehicles that were not as common in the other tests. Significant emissions of these catalyst elements were probably due to the older cars with early generation catalytic converters that are likely to have different emissions of metals.

To investigate the contribution of heavy-duty vehicles in the fleet to overall roadway metal emissions, weekday and

weekend tests conducted at the Howell tunnel during the summer were compared. These tests had similar temperature and road surface conditions, but much different traffic composition. Weekday tests had higher traffic volume and a higher proportion of trucks (7%) than the weekend tests (2%) (Table 1). Although light-duty vehicles comprise the vast majority of the vehicle fleets, a small fraction of heavy-duty trucks can significantly affect PM emissions, through tailpipe emissions as well as increased resuspension of soil. Corresponding with increased traffic and fraction of heavy trucks, weekday PM_{10} emissions ($140 \pm 33\text{ mg km}^{-1}\text{ vehicle}^{-1}$) were much larger than weekend emissions ($54 \pm 8\text{ mg km}^{-1}\text{ vehicle}^{-1}$). As compared to weekend tests, weekday PM_{10} emissions of EC and total metals were larger by factors of approximately 3, while OC was doubled. The large differences in emission rates of PM_{10} elements between weekday and weekend tests here were generally attributed to the contribution of crustal elements (Na, Mg, Al, Si, Ca, Fe) from

resuspended road dust (Figure 6). Increased resuspension of dirt was due to the greater number of large trucks, which has also been observed in other studies (52). Greater traffic volume may also have contributed, with more constant flow of traffic and fewer gaps between groups of vehicles. Higher weekday PM_{10} emissions of some wear elements (Cu, Zn, Sb, and Ba) were also observed (Figure 6) due to increased resuspension of enriched road dust, and possibly also due to the larger scale of tire and brake wear from heavy-duty trucks. As stated previously, the impact of heavy-duty trucks was apparent in a higher weekday ratio of EC to OC in $PM_{2.5}$, but the very low levels of metals in $PM_{2.5}$ were not statistically differentiable between tests. Sulfur, which is expected to be emitted in much higher amounts from heavy-duty vehicles due to higher levels of sulfur in diesel fuel (53), was not statistically significant in either size fraction in weekend or weekday tests. The average ratio of $PM_{2.5}$ to PM_{10} emissions for weekday tests was 0.26 ± 0.06 , much smaller than the 0.84 ± 0.39 ratio for the weekend tests, showing greater weekday contribution of coarse particles from resuspension. Figure 7 compares emission rates of mass and silicon in fine and coarse particulate matter with the fraction of heavy-duty trucks in the vehicle fleet during the test. An increased fraction of heavy trucks results in a relatively low increase in $PM_{2.5}$ emission rates, and a much larger increase in PM_{10} emissions.

Winter tests (K, L, M, N, O, P), conducted at the Howell tunnel during weekdays, had a traffic volume and composition similar to that of the Howell tunnel summer weekday tests (F, I, J). Again, the unique profile of test P is treated separately from the five average winter tests. As discussed earlier, emission rates in winter tests were lower than summer tests by a factor of approximately 2, largely attributed to the wetting of the road surface by melting snow, limiting road dust resuspension. Elemental emission rates measured from summer and winter Howell tunnel tests are compared in Figure 8. Very few elements were statistically significant in PM_{10} in winter tests. However, test P showed a unique distribution of elements and had the highest PM_{10} mass emission rate ($446 \pm 14 \text{ mg km}^{-1} \text{ vehicle}^{-1}$) of any summer or winter test. The measured mass and chemically reconstructed mass for test P agreed well. The contribution of elements measured by ICP-MS and XRF in test P was $192 \pm 10 \text{ mg km}^{-1} \text{ vehicle}^{-1}$, or $43 \pm 2.7\%$ of the mass. Metal emissions were predominantly ($57 \pm 5\%$) comprised of elements that are components of road salts and crustal materials (Si, Na, Mg, Fe, K, Ca). Increased emissions of enriched road dust also impacted emissions of less abundant elements, including Cu, Zn, Sb, Ba, and Pb. Na and Mg show size distributions similar to that of chloride discussed above, with both elements contributing a much larger fraction of $PM_{2.5}$ mass in test P than in other tests. In summer tests at the same tunnel, Na and Mg each account for significantly less than 1% of $PM_{2.5}$ mass, but in test P Na contributes $9.2 \pm 1.4\%$, and Mg $4.9 \pm 0.68\%$. For other elements, ratios in $PM_{2.5}$ and PM_{10} are very similar between test P and other tests, indicating that their high emissions in test P are primarily due to weather conditions that promoted enormous resuspension of enriched road dust. Huge emissions in test P could also be due to brake and tire wear particles being more freely emitted under dry roadway and wheel conditions than in other winter tests, although no significant differences in ratios of brake wear elements are seen between winter tests and test P. These results show that the resuspension of road dust, which plays an important role in emissions of metals from roadways, is very dependent on weather and road surface conditions, including wetness and the presence of excess dirt. Thus, simply averaging the contribution of road dust under various roadway conditions could easily over- or underestimate direct vehicle emission rates.

Size-Resolved Metals Emissions. To investigate size distributions of particulate matter emissions in the Howell tunnel, MOUDIs were collocated and operated in parallel with the other aerosol samplers in selected tests. To obtain enough mass for analysis, the impactors were operated with one set of substrates over two similar tests on consecutive days, for 16 h in tests O and P. Figure 9 shows size distributions of roadway emissions for eight elements (Mg, Fe, Ca, Cu, Sr, Sb, Ba, and Pb) measured in statistically significant amounts during the combined test. It is important to note that these samples include emissions in test P, the winter test that involved a road dust resuspension event. Elemental size distributions showed primary modes in the coarser range of particles ($1.0\text{--}18 \mu\text{m}$), consistent with resuspension of road dust and tire and brake wear. Emissions of wear elements (Zn, Sb, and Ba) showed size distributions similar to those of the crustal elements, consistent with their emission from enriched roadway dust. Submicrometer modes, indicative of combustion or high temperatures, were also seen for some elements (Pb, Ca, Fe, Cu). Lead and copper had bimodal distributions, with modes in the $0.1 \mu\text{m}$ size range from nonmechanical processes, such as combustion of fuel and lube oil or vaporization from hot brake surfaces. Calcium and iron were also emitted to a lesser extent in the submicrometer range, which can be attributed to tailpipe emissions of lubricating oil and is consistent with previous studies (25).

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Supporting Information Available

Three tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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