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Seasonal variability of ultra-fine metals downwind of a heavily traveled secondary road

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HIGHLIGHTS

- Ultra-fine transition metals were measured downwind of a road.
- Concentrations were <10% at a suburban site 500 m upwind.
- The sources of the metals were brake wear and zinc in lubricating oil.
- Similar ultra-fine metals associate with ischemic heart disease in California.
- Concentrations decreased sharply (~×0.1) as one went from winter into spring.

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ABSTRACT

Since 2002, we have been studying the impact of a heavily traveled secondary road on an adjacent downwind school located at a stop light controlled intersection. The prior studies were all performed in winter conditions with typically strong inversions, but established significant $PM_{2.5}$ impacts on the school roughly in accord with theoretical models and the relevant literature. In this project, we have enhanced this effort by extending the study from winter to summer, and adding compositionally-resolved ultra-fine aerosol measurements. Ultra-fine aerosols, including metals derived from both brake wear and zinc in lubricating oil, were present at high concentrations in winter downwind of the roadway but absent at a residential site 500 m upwind. Their concentrations faded to minor levels in spring and early summer, while coarse roadway resuspended dust increased in that period. A comparison of ultra-fine measurements in downtown Sacramento and other California Central Valley sites indicates that these traffic derived aerosols are widely present in urban areas impacted by heavy traffic, freeways and secondary streets, especially where heavy braking is occurring. The potential for health impacts of ultra-fine metals associated with cars braking and accelerating in inversion conditions is a serious health concern based on recent epidemiological studies.

1. Introduction

There is a large body of data on the downwind impacts of aerosols from roadways, from the studies on lead in the 1970s (Cahill and Feeney, 1973; Feeney et al., 1975) to the present (including Zhu et al., 2002; Karner et al., 2010 and many others). There is also a rich history of studies investigating the health impacts of aerosols (Davidson et al., 2005) and especially toxicity of ultra-fine particles (Oberdorster et al., 2007), showing increasing concern about the impacts of ultra-fine aerosols on health. Since the Southern California studies of Peters et al. (1999a,b), abundant new data have been developed showing the increased potential for deposition into the deepest portions of the lungs (aeoli) and transmission into the circulatory system of ultra-fine particles, especially near freeways (Wilhelm and Ritz, 2003; Gauderman et al., 2004; Zhang et al., 2004; Fruin et al., 2007; Lippmann, 2009). Other studies, such as by Wallenborn et al. (2009), have chronicled the transport of isotopic ultra-fine particles through the bodies of rats demonstrating both lag times and accumulation characteristics for specific organs (i.e. heart, liver, spleen, and kidney). These data, and especially data on diesel toxicity, have been combined and used to generate predicted health impacts in models

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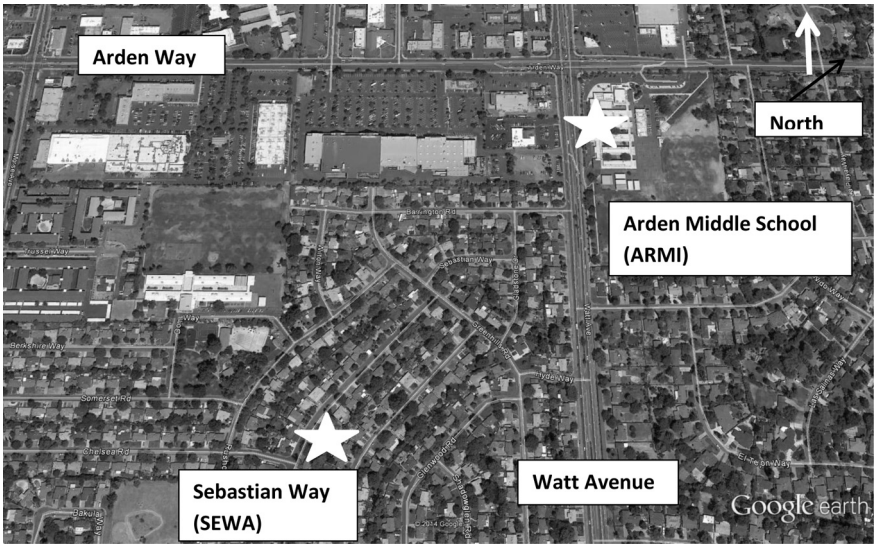

Fig. 1. Sampling sites within the Sacramento Metropolitan Area for the winter, 2007 Watt study. The distance between Sebastian Way (SEWA) and Watt Avenue, at Arden Middle School (ARMI) was 500 m. The ARB 13th and T Street aerosol monitoring site is 10 km southwest, and the Del Paso Manor site 1.2 km to the northeast.

such as Emfac2007 (ARB 2007), despite the uncertainty about exactly which roadway pollutants are responsible for specific health impacts (HEI, 2009). While an examination of the full extent of this work is beyond the scope of this paper, these studies support our efforts to document the presence of ultra-fine metals near heavily traveled roadways.

There are several problems encountered in trying to mesh the data on ambient roadway pollution to the health impacts: 1) The aerosol data rarely if ever contain information on particle size and composition, especially for very fine (<0.25 μm) and ultra-fine (<0.1 μm) metals, known to be important by medical research (HEI, 2009), 2) The aerosol data have often been taken under limited meteorological conditions, including many studies under the persistent marine inversions in the Los Angeles basin (Zhu et al., 2002; Zhang et al., 2004) and the radiation inversions in the California Central Valley in winter (Cahill et al., 2011), 3) The aerosol studies have rarely addressed the known strong effects of roadway configuration (at grade, depressed, and raised, Feeney et al., 1975), or other effects such as vegetation (Baldauf et al., 2013), 4) There are only limited data on the effects of traffic mix, traffic conditions such as speed, and traffic behavior, such as heavy braking. 5) The models routinely used do not represent the reality in several important ways. Studies show that the measured health impacts of roadways extend downwind far beyond the model predictions, up to 1600 m (Peters et al., 1999a,b), when line source dispersion models like Emfac2007 (Emfac2007) indicate little impact beyond 150 m. In addition, several studies document typical roadway pollutants, including ultra-fine aerosols, extending well upwind of the roadways (Zhu et al., 2002).

In this paper, we have attempted to address several of these concerns using a heavily traveled secondary street, Watt Avenue, in suburban Sacramento, California. Specifically, we have performed a roadway transect study under winter conditions, when inversions are strong, and into spring and summer, when inversions are weak. We have located at a site where heavy braking and acceleration are the norm, and we have focused on ultra-fine transition metals that are indicated as plausible causal factors in some of the observed health impacts in the health literature. A companion paper examined size segregated speciated organics (Cahill and Cahill, 2013) at the same sites and times.

2. Experimental methods

The University of California, Davis DELTA Group and the Health Effects Task Force of Breathe California of Sacramento-Emigrant Trails have studied a heavily traveled secondary road in suburban Sacramento, Watt Avenue (north–south, 9 traffic lanes, 65,000 v/day, 1.5% heavy trucks >5 axels) (Cahill et al., 2005, 2007; CalTrans, 2007). Watt Avenue is directly (20 m) upwind of Arden Middle School, and the studies were initiated due to potential health impacts at the school. At the north edge of the school property, Watt Avenue crosses Arden Way (east–west, 35,000 v/day, < 0.3% heavy trucks), resulting in heavy braking and acceleration upwind of the school during daylight hours. An identical site was set up in a residential neighborhood at Sebastian Way, 330 m west of Watt Ave and 500 m upwind of the school site on the prevailing southwest daytime wind direction. Regional background data were also available from the Del Paso Manor site of Sacramento Metropolitan AQMD, 1.2 km northwest of Arden Middle School, which was also a national Speciation Trends Network site (Fig. 1) (ADAM 2010).

Two earlier studies of Watt Avenue, each about 5 weeks in duration, in December 2001 to January, 2002 (Cahill et al., 2003), and January to February, 2004 (Cahill et al., 2005), looked at $PM_{2.5}$ impacts downwind of Watt Avenue. The measured $PM_{2.5}$ mass at Arden Middle School due to Watt Avenue traffic in winter, 2004, was 4.7 ± 1.0 μg/m^3, using the Sebastian Way site for background. These results were in approximate accord with roadway emission data, including the Tuscarora tunnel study (Gertler et al., 2001) which used some of the same aerosol collection and analysis protocols used later at Watt Avenue.

2.1. Collection and analysis of ultra-fine aerosols

Ultra-fine aerosols were collected using 25 mm stretched Teflon filters behind the final 0.09 μm stage of an 8 stage DRUM sampler (Cahill et al., 1985). The 0.09 μm size cut was predicted from Marple theory (Raabe et al., 1988) and validated to 0.09 ± 0.01 μm by TDMA size studies (Lawton and Cahill, 2010). Protection from coarser aerosols was provided by 6 Apiezon-coated (Wesolowski et al., 1978; Cahill, 1979) greased stages below 2.5 μm, which have been shown to essentially eliminate particle bounce from coarser stages (Cahill et al., 1985).

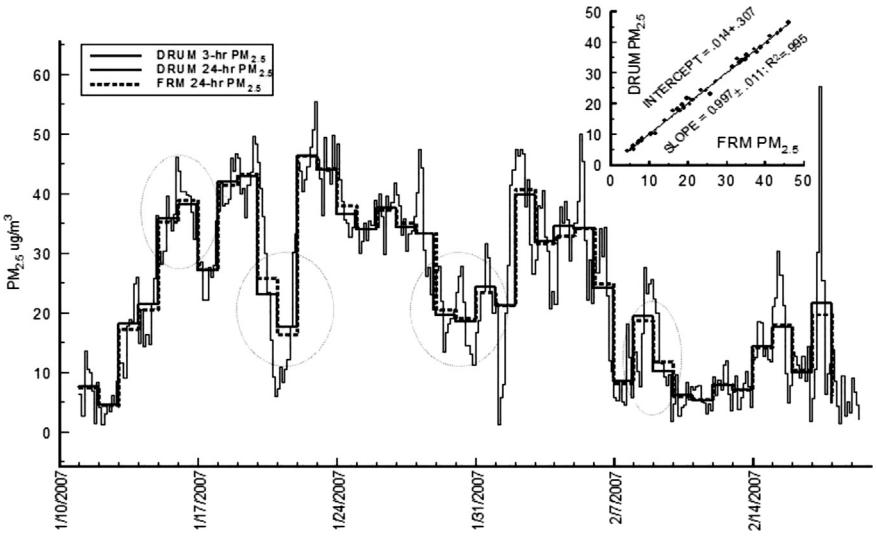

Fig. 2. Comparisons of the UC Davis 8 DRUM with ultra-fine filters, and FRM $PM_{2.5}$ data. The correlation was $R^2 = 0.995$, slope 0.997 ± 0.011, and intercept, <0.5% of mean mass.

Mass measurements for the DRUM strips deposits, necessary for the $PM_{2.5}$ Federal Reference Method (FRM) comparisons, was accomplished by soft beta ray transmission using a Ni^{63} source and NIST mass standards. Ni^{63} has a long half-life, 101 years, and decays via a β ray, with a 67 keV maximum energy and 17.4 keV average energy. The average range is such that about 1/3 of the β intensity is lost passing through the typical 250 $\mu g/cm^2$ aerosol deposit on the 480 $\mu g/cm^2$ Mylar foil used to coat the drums (DQAP, 2011).

Elemental analysis was provided by UC Davis DELTA Group elemental analysis protocol via synchrotron induced X-ray fluorescence (S-XRF) at the Advanced Light Source, Lawrence Berkeley National Laboratory. S-XRF analyses are performed using the intense beams of polarized X-rays with an energy range of 3–14 keV (Bench et al., 2002; Barberie et al., 2013). Modern high count rate Si(Li) VORTEX detectors (Barkan et al., 2003) achieved adequate sensitivity and precision for the small amounts of mass present on the drum strips and Teflon filters. The key advantage of the S-XRF analysis is the fact that the polarized beams allow rejection of >95% of all background X-rays, allowing use of the very intense multi-energy "white" beams. The X-ray beam is collimated into a 0.5 mm by 2 mm spot, yielding sensitive analysis on the limited mass available. For filters, 5 steps are made across the filter to establish spatial uniformity. For the continuous DRUM strip rotating at 4 mm/day, each 0.5 mm step is equivalent to a 3 h time bin. Typically, we recorded data on 28 elements, with sensitivities of ~0.1 ng/m^3. Numerous standards were analyzed for each sample batch, including many of the following; NIST SRMs 1832 and 1833, and ~65 thin elemental standards from Micromatter, Inc., Seattle, WA.

2.2. Validation of the sampling and analysis

Two methods were used to validate the accuracy of ultra-fine mass and elemental values on the DRUM <0.09 μm after-filter. The first involved comparisons of 6 stages of the DRUM sampler, 2.5 to 0.09 μm plus ultra-fine mass, 0.09 to 0.0 μm, with Federal Reference Method (FRM) $PM_{2.5}$ filters from an Anderson RAAS 2.5-200 dichotomous filter sampler. The second involved mass closure on ultra-fine particles by comparison of gravimetric mass to the sum of all species. These were investigated in parallel with the Watt Avenue studies for a year-long collocated study of DRUM mass versus $PM_{2.5}$ FRM samplers at the California Air Resources Board test site at 13th and T Street in downtown Sacramento. A UC Davis slotted 8 DRUM was operated in parallel with FRM samplers for a total duration of 6 months in the period from January, 2007 to December, 2007. Measurements were made in 6 size modes, 2.5 to 0.09 μm and 3 h resolution, except for the <0.09 μm integrating ultra-fine filters.

In the high mass winter periods, very good comparisons between DRUM and FRM data were achieved; 23.2 ± 1.0 $\mu g/m^3$ DRUM, 22.1 $\mu g/m^3$ ARB FRM, supporting the accuracy of ultra-fine measurements. This was despite the fact that the DRUM mass measurements required 49 separate values for the DRUM for the comparison to each single 24 h FRM mass value. For the entire study, the ratio, DRUM/FRM, was 1.01 ± 0.21.

Our data were submitted to the ARB staff, who with access to hourly mass data, made a slight change in the starting time of the DRUM (Fig. 2) and greatly improved the fit, $r^2 = 0.995$, slope $= 0.997 \pm 0.011$, intercept $= 0.014$, for January 10 to Feb 21, 2007 (Cahill and Barnes., 2009; Nichols, 2009).

For the second validation, compositional data were required, especially S-XRF data on elements. Validation of the S-XRF system has been accomplished in five multi-elemental quality assurance comparisons, including blind comparisons S-XRF to PIXE (IMPROVE) and to XRF (IMPROVE, DRI), with a mean ratio of 0.98 ± 0.15 (DQAP, 2011). A recent blind inter-comparison was performed against standard XRF and ICP/MS (Jenniskens et al., 2012), with our S-XRF values for 24 elements agreeing to a ratio of 1.005 ± 0.31 with one standard XRF and three ICP/MS laboratories (Supplemental Materials 1).

With the availability of compositional data, a second validation was performed at the end of the ARB collocated study in December 2007. The ultra-fine component of the system was validated by direct comparison of ultra-fine gravimetric mass, using the Cahn microbalance, and the reconstructed mass, the sum of all species (Malm et al., 1994). To obtain sufficient mass, the filter was exposed for a total of 30 days, following the protocol used in the Watt Avenue transects, so as to increase the mass and improve precision. In this comparison, the elemental species were compared by adding the typical oxides (Malm et al., 1994). For the organic mass, we used the IMPROVE organic-equivalent mass (OMH) via the proton–proton scattering (H(p,p)H) reaction with 4.5 MeV protons from a cyclotron (Cahill et al., 1987, 1989). This method measures organic matter by directly measuring in vacuum the hydrogen atoms bound

into non-volatile compounds after correcting for hydrogen in sulfates and nitrates. This has been validated for $PM_{2.5}$ filters by tens of thousands of inter-comparisons of OMH with organics measured from combustion from quartz filters (OMC) as part of the integral redundancy quality assurance protocols used by IMPROVE (Malm et al., 1994).

For the Watt ultra-fines study, the samplers were continuously deployed from the winter, February 7, to the late spring, June 13, 2007 (Cahill et al., 2007). Table 1 shows the schedule of aerosol collection for the DRUM used for mass and elemental analysis (3 h averages, plus 4 week averages ultra-fine filters). Another component of the study was done in parallel with the organics collected and speciated using an 8 stage and after filters DRUM (both reduced to 4 week averages) (Cahill and Cahill, 2013). As much as possible, the periods were designed to overlap each other, but some differences occurred. The most important was caused by a railroad trestle fire, of March 14, 2007, which sent a black plume of smoke from a creosote soaked railway trestle 5.8 km east towards the Watt Avenue sites (see Table 2).

3. Results

The current study was designed to monitor from winter into spring and summer conditions. However, early termination of typical winter inversions in 2007 severely limited the number of days the study operated in typical cool, hazy winter conditions. The $PM_{2.5}$ mass distributions (Fig. 3) are shown for the downtown CA Air Resources Board site at 13th and T Street, 10 km SW of Arden Middle School, and the suburban Del Paso Manor site, 1.2 km NE of the site. Thus even the "winter" conditions in the current study were less impacted by aerosols mass than are typical of the most polluted part of the year (ADAM, 2010). Note that the regional nature of the $PM_{2.5}$ mass is well illustrated, as the two sites are over 11 km apart and in very different conditions of the urban complex.

While most of the mass at both sites comes from ammonium nitrate, the excess mass at Del Paso Manor is often associated with residential wood smoke (Sharpless, 2012). Therefore, much of the current study occurred during a time of extremely good air quality with only a slight overlap with winter conditions.

The winds were overwhelmingly from the western quadrant for the entire study, and the mean velocity was relatively constant throughout the entire period – roughly 10 km/h in winter to 12 km/h in spring. From these data, it is clear that the sudden reduction of $PM_{2.5}$ aerosol mass at downtown Sacramento and Del Paso Manor (Fig. 3) was not a function of either mean wind velocity or direction. However, the masses correlated well if qualitatively with visual observations of thin (<100 m) surface based inversions common in winter.

Table 1
Mass closure for ultrafine mass, $D_p < 0.09$ μm. There is excellent agreement between the gravimetric mass and the reconstructed mass, generated by the sum of all measured species. Note the dominance of the non-soil iron, nickel, copper, and zinc in the transition metals.

Major components	μg/m^3	Minor components	ng/m^3
Mass (gravimetric)	**2.04 ± 0.2**	Phosphorus	2.4 ± 0.2
Mass (reconstructed)	**2.15 ± 0.35**	Vanadium	0.15 ± 0.01
		Chromium	0.45 ± 0.04
Major components	**ug/m^3**	**Iron (non-soil)**	**38.0 ± 6**
Organic mass (OMH)	1.72 ± 0.2	**Nickel**	**3.5 ± 0.4**
Ammonium Sulfate	0.34 ± 0.15	**Copper**	**8.3 ± 0.8**
Salt	0.04 ± 0.004	**Zinc**	**11.5 ± 1.2**
Soil (IMPROVE)	0.048 ± 0.005	Arsenic	0.6 ± 0.2
K non	0.053 ± 0.005	Selenium	0.3 ± 0.1
Metals (-iron)	0.035 ± 0.002	Bromine	3.7 ± 0.4
		Lead	4 ± 0.4

Table 2
Schedule of aerosol sampling. Data from March 15 through March 19 were excluded from the ultra-fine averages because of a large fire on a wooden train trestle could bias the data, and especially the parallel organic study. The dates are for the Watt Ave site. The May Sebastian Way organics sampler was switched on May 23.

Sampling periods	Start – elements	Stop – elements	Start – organics	Stop – organics
Winter 1	Feb 7	Mar 7	Feb 7	Mar 7
Winter 2	Mar 7	Mar 15		
Trestle Fire	*Mar 15*	*Mar 19*	*Mar 15*	*Mar 19*
Spring A	Mar 18	Apr 17	Mar 18	Apr 17
Spring B	Apr 17	May 18	Apr 17	May 23
Spring C	May 18	June 13	May 23	June 13

After mid-March, coarser soil derived aerosols increased at Watt Avenue as compared to Sebastian Way, with the inclusion of zinc data from tire wear identifying the excess as resuspended roadway soils. Strong diurnal patterns were seen in the time resolved data, correlated with daytime traffic peaks and weekday-weekend differences.

3.1. Data on ultra-fine inorganic species – 4 week averages

The primary goal of the study was the development of quantitative data on ultra-fine inorganic aerosols, especially metals. Because of the low masses involved, and to match the companion organics study (Cahill and Cahill, 2013), 4-week averages were calculated.

The seasonal pattern of ultra-fine metals was clear. During the winter period, the site downwind of Watt Avenue had much higher concentrations of almost all monitored transition metals compared to Sebastian Way (Table 3). The average ratio for all measured ultra-fine elements, expressed as downwind Watt Ave versus upwind Sebastian Way sites was 17.9 in winter. This highlights that the near roadway site had much higher concentrations of ultra-fine metals compared to the control site. Thus, with the prevailing west to east wind pattern and the lack of any industrial activity between the two sites, the time-resolved data uniquely identifies Watt Avenue roadway traffic as the key source of enhancement. It is also important to note that the dramatic difference observed in the concentrations between ultrafine metals between the two sites are not seen in the fine or coarse size fractions.

As spring and summer progressed, the differences in ultra-fine metals between the two sites decreased. By early summer, the ratio for all elements approached unity, 1.09 ± 0.09, which underscores the essentially negligible impact from Watt Avenue in ultra-fine particles during summer. The average concentrations during this period are shown below in Table 3 and selected metals in Fig. 4.

Clear enhancements downwind of Watt Avenue are seen in sulfur and calcium. Calcium is an anti-acid used in sulfur-containing diesel fuel (Zielinska et al., 2004). Potassium, chromium, manganese, iron, nickel, copper, and zinc all show enhanced levels of ultra-fine mass and high downwind/upwind ratios in winter.

It is important in these comparisons to recall that Sebastian Way was downwind of Watt Avenue only in a few hours each night, at times when Watt Avenue traffic was very low.

We regret that we were unable to get consistent ultra-fine mass measurements at Watt avenue sites because of variable field blanks. One possible difference is that the 13th and T site had the filter assembly in the DRUM shelter, where it was slightly warmed by the pump. At the Watt avenue sites the filter assembly was protected from rain by plastic bags but operated at ambient temperatures and relative humidity.

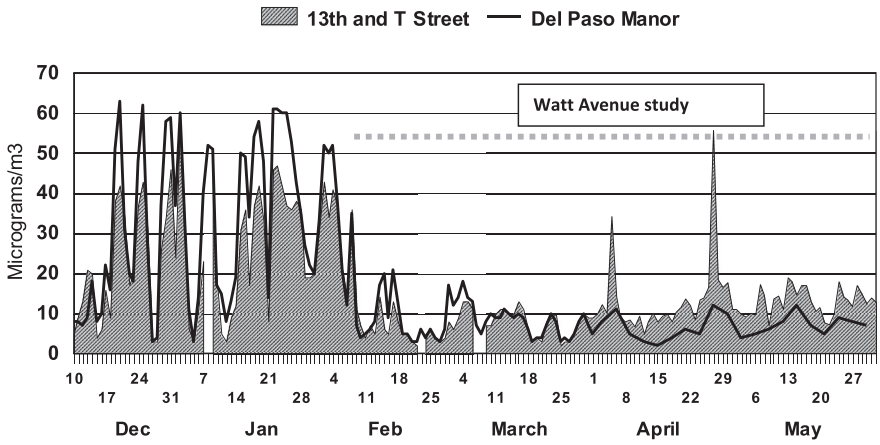

Fig. 3. $PM_{2.5}$ mass data from the ARB downtown site at 13th and T Street and Del Paso Manor sites, Dec 10, 2006 to May 31, 2007. The period of the Watt Ave study is shown in the dotted line.

An earlier companion paper has addressed size and compositionally resolved organic matter taken at the same locations and times as the present study. Size resolved organic species (PAHs, n-alkanes, sugars, and fatty acids) were measured as a function of size, including ultra-fine species, at the same time as the ultra-fine metals were analyzed (T.M. Cahill and T.A. Cahill, 2013). The data showed that most heavy PAHs were in the ultra-fine mode.

4. Analysis and interpretation

4.1. Sources of the metals

The generation of metals in the ultra-fine mode requires high temperatures and/or pressures. Thus, many sources of metals from vehicles, such as zinc from tire wear, are not candidates for sources of ultra-fine aerosols. This was confirmed in the present study by very fine and ultra-fine zinc that peaked in winter versus coarse zinc, >1.15 μm, that correlated with vehicle polluted roadway and that peaked in spring. Two potential sources of ultra-fine particles are engines, and especially diesel engines because of the high temperatures and pressures involved, and the braking systems in vehicles, as described in more detail in Cahill et al. (2011). While there is considerable information on the total particulate emissions from vehicles, the information on ultra-fine metals from vehicular exhaust is limited. In terms of vehicle exhaust, a study (Zielinska et al., 2003, 2004) involved detailed analysis of diesel aerosols, and identifies sulfur (from the fuel), phosphorus and zinc (from zinc thio-phosphate in lubricating oil), and, calcium (an antacid) in the ultrafine modes. However, negligible levels of the ultra-fine transition metals iron, nickel, and copper were observed.

A second potential source of very fine and ultra-fine metals is the braking systems of cars and trucks, since high temperatures and/or pressures are involved in this process. The brake drums have evolved from the massive iron, heat-conductive structures and asbestos-containing brake pads to “grey iron” drums, roughly 90% iron with the admixture of a few percent carbon, plus copper, silicon, and other metals in smaller amounts, making them, like brake pads, an erodible surface. Brake pads are far more complex in composition and are traditionally designed to erode. Information on brake pad composition was reviewed by Kennedy et al. (2002) and Chan and Stachowiak (2004) (Table 4).

While there is enormous variability in the data, as shown by the percentile distributions, the four main elements are usually iron, copper, zinc, and nickel. In summary, there are a wide variety of very fine and ultra-fine metals that may arise from brake drums and pads, but iron, copper, zinc, and nickel are clearly major components. Thus, in summary, the ultra-fine metals seen downwind of Watt Avenue are consistent with a mixture of zinc from lubricating oil and ultra-fine aerosols from brake drums and pads.

4.2. Spatial extent of ultra-fine particles

As seen above in Table 3, Sebastian Way has little if any impact from Watt Avenue, and routinely very low concentrations of traffic

Table 3
Ultra-fine species at Watt Avenue at Arden Middle School (ARMI) and Sebastian Way (SEWA), Winter 1 and 2 (Feb 7–March 15), and averaged spring (March 19–June 23), 2007. The values in bold have both high downwind concentrations and high downwind/upwind ratios. Potassium has many sources.

	Winter avg. 1 and 2	Winter avg. 1 and 2	ARMI/SEWA	Spring avg A, B, C	Spring avg A, B, C	ARMI/SEWA
	Downwind ARMI (ng/m^3)	Upwind SEWA (ng/m^3)	Ratio	Downwind ARMI (ng/m^3)	Upwind SEWA (ng/m^3)	Ratio
Calcium	**10.3**	**1.9**	**5.4**	**1.65**	**1.51**	**1.09**
Sulfur	**39.1**	**9.0**	**4.3**	**129**	**161**	**0.8**
Potassium	20.0	2.8	7.1	11.6	9.7	1.2
Chromium	0.83	0.04	20.7	0.05	0.045	1.1
Manganese	**1.3**	**0.09**	**14.4**	**0.16**	**0.38**	**0.42**
Iron	**29.1**	**3.9**	**7.5**	**4.8**	**2.1**	**2.3**
Nickel	**11.5**	**0.18**	**63.9**	**0.3**	**0.37**	**0.80**
Copper	**8.1**	**0.62**	**13.1**	**0.4**	**0.36**	**1.1**
Zinc	**12.8**	**0.84**	**15.2**	**2.0**	**2.0**	**1.0**
Arsenic	0.41	0.08	5.1	0.32	0.27	1.2
Selenium	0.14	0.10	1.4	0.23	0.21	1.1
Bromine	1.17	0.67	1.7	1.8	2.0	0.9
Lead	1.63	0.50	3.3	1.4	1.27	1.1

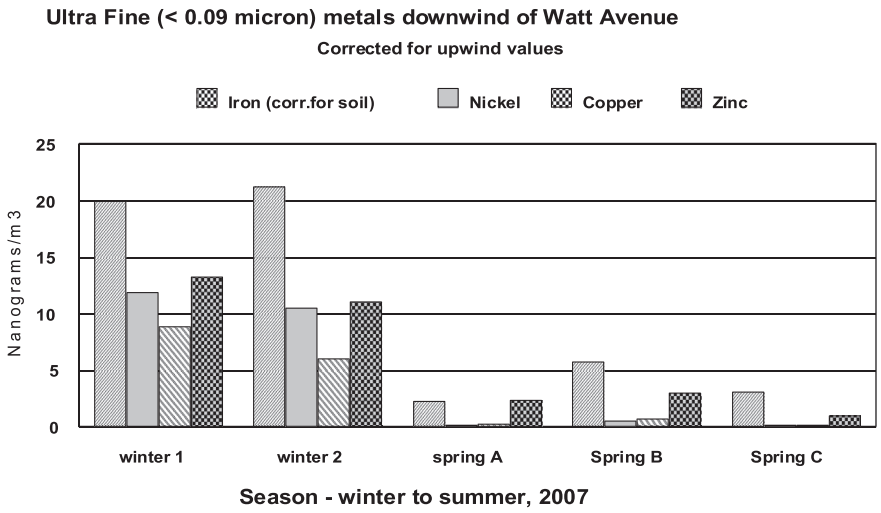

Fig. 4. Plot of selected elements from Table 3. In this plot, the winter and spring values were not averaged.

Table 4
Summary of concentrations of elements in New Zealand brake pads (Kennedy et al., 2002), from largest to smallest concentrations of transition metals plus heavier elements. The distributions are shown to emphasize the wide variability between manufacturers. The S-XRF analysis did not cover barium. Values in bold were major components of ultra-fine aerosols seen downwind of Watt Avenue in winter.

Element (ppm)	10th Percentile	Median	90th Percentile
Iron	**11,700**	**18,300**	**190,000**
Copper	**29**	**5000**	**116,000**
Zinc	**127**	**1630**	**37,400**
Nickel	**44**	**342**	**652**
Manganese	**143**	**315**	**1088**
Lead	6	50	949
Barium	558	3195	6144

derived ultra-fine metals. However, Sebastian Way is also 10.2 km downwind of Sacramento, and specifically the ARB 13th and T Street test site. The data show that the downtown site is routinely impacted by ultra-fine traffic derived aerosols (Table 1) which is not surprising considering that the area is ringed in all directions by heavily traveled freeways and secondary streets. Since the prevailing winds are southwest to northeast much of the time, the lack of ultra-fine particles at Sebastian Way indicates effective removal mechanisms, even in winter when most trees are without leaves. It is also probable that if measurements had been made earlier in winter, when the inversions were stronger and more common (Fig. 3), the concentrations downwind of Watt Ave would be higher.

A recent paper (Cahill et al., 2011) find the same very fine and ultra-fine transition metals at urban sites in the California Central valley. The relatively high levels in the southern San Joaquin Valley are associated with increases in ischemic heart disease mortality.

5. Conclusions

We have examined the impact of a heavily traveled secondary road, located at a stop light controlled intersection with traffic braking, idling, and accelerating, on an adjacent (20 m) downwind school. The study was designed to extend from winter to summer conditions, measuring aerosols from 10 to 0.09 μm equivalent diameter in 8 size modes every 3 h, and later adding time integrated ultra-fine ($D_p < 0.09$ μm) aerosol measurements from after filters. Compositional analyses were made by synchrotron-induced X-ray fluorescence for all samples, with typically 28 elements examined with sensitivities of ~0.1 ng/m^3. Ultra-fine aerosols were very low at an upwind residential site, but high downwind of Watt Avenue in winter. These ultra-fine aerosols included metals derived from both brake wear (Fe, Zn, Cu, Ni and Mn) and zinc in lubricating oil. The potential for health impacts of ultra-fine metals associated with cars braking and accelerating in winter conditions is a serious health concern based on recent epidemiological studies. These ultra-fine aerosol components faded to insignificance in spring, while coarse roadway resuspended dust increased in that period. The net result is that the roadway impact on the school was far less in spring conditions than Emfac2007 model predictions. Other examples of ultra-fine metals associated with braking and lubricating oil are in the California Central valley are discussed, showing that the presence of these ultra-fine metals is common in urban areas.

Acknowledgments

The DELTA Group (Detection and Evaluation of Long-range Transport of Aerosols) of the University of California, Davis, develops and applies high technology to aerosol sampling and analysis, primarily for studies of global atmospheric aerosols (http://delta.ucdavis.edu. The same techniques have proven useful in aerosol studies and potential health impacts.

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Appendix A. Supplementary data

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