

Seasonal and spatial variability of the size-resolved chemical composition of particulate matter (PM₁₀) in the Los Angeles Basin

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[1] For a period of almost 3 years, sampling of size-fractionated ambient particulate matter with diameter below 10 μm (PM₁₀) was performed at urban source sites (Downey and University of Southern California) and inland receptor sites (Claremont and Riverside) in the Los Angeles Basin as part of the Southern California Particle Center and Supersite. Results for size-resolved PM₁₀ mass, inorganic ions (sulfate and nitrate), metals, elemental carbon, and organic carbon were obtained. Three collocated micro-orifice uniform deposit impactors (MOUDIs) were deployed to collect 24-hour samples roughly once a week. Ultrafine particle concentrations (particle diameter $d_p < 0.1 \mu\text{m}$) were found to be the highest at the source sites resulting from fresh vehicular emissions. Mass concentrations in the accumulation mode ($0.1 < d_p < 2.5 \mu\text{m}$) were lower in winter than in summer, especially at the receptor sites. PM concentrations in the coarse mode ($2.5 < d_p < 10 \mu\text{m}$) were lower in winter and were composed mostly of nitrate and crustal elements (iron, calcium, potassium, silicon, and aluminum). Consistent relative levels of these elements indicate a common source of soil and/or road dust. In the accumulation mode, nitrate and organic carbon were predominant with higher nitrate levels found at the receptor sites. The ultrafine mode PM consisted of mostly organic carbon, with higher wintertime levels at the source sites due to increased organic vapor condensation from vehicles at lower temperatures. Conversely, higher ultrafine organic carbon levels at the receptor areas are due to secondary organic aerosol formation by photochemical reactions as well as increased advection of polluted air masses from upwind.

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1. Introduction

[2] Atmospheric particulate matter (PM) has been associated with adverse health effects. Epidemiological studies have shown significant relationships between ambient PM and respiratory related mortality and morbidity [Adler *et al.*, 1994; Dockery *et al.*, 1993; Gordian *et al.*, 1996; Schwartz and Dockery, 1992]. The observed effects are even more significant in susceptible populations, such as the elderly, with preexisting respiratory and cardiovascular diseases [Saldiva *et al.*, 2002]. PM material has also been shown to have toxic properties such as the ability to produce oxidative stress and cell damage [Li *et al.*, 2003].

[3] Particle size has been shown to be an important factor in the impact that airborne particles have on human health. Epidemiological results have demonstrated higher associations with particulate matter with diameter below 2.5 μm (PM_{2.5}) than PM₁₀ [Anderson, 2000], and fine particles have been shown to have more toxic properties [Brown *et al.*, 2000; Ferin *et al.*, 1990]. Recent toxicological studies have shown that ultrafine particles (smaller than 100 nm) have higher oxidative stress potential and can penetrate and

destroy mitochondria within epithelial cells [Li *et al.*, 2003]. Furthermore, particles of different sizes differ greatly in terms of the extent and the location of deposition in the lung [Phalen *et al.*, 1991].

[4] In addition to particle mass and particle size, particle bound chemical species have also been associated with various adverse health effects. Elemental carbon rich diesel vehicle emissions particles are suspected of being carcinogenic to animals and humans [Guillemin *et al.*, 1997]. Studies by Batalha *et al.* [2002] have found associations between particle-bound sulfate and silicon levels and the vasoconstriction of small pulmonary arteries in rats. Carter *et al.* [1997] showed that respiratory tract epithelial cells respond to elevated metal concentrations by production and release of inflammatory mediators. A study by Clarke *et al.* [2000] found bronchial changes to be associated with concentrations of vanadium and nickel. Saldiva *et al.* [2002] have demonstrated significant inflammatory reactions in rat lungs exposed to concentrated air particles with significant statistical associations between particulate vanadium and bromine and the observed health outcomes.

[5] Numerous previous studies have demonstrated that the chemical composition of atmospheric particles can vary with season, size, and sampling location. Neusüß *et al.* [2002] observed that the mass percent particulate carbon

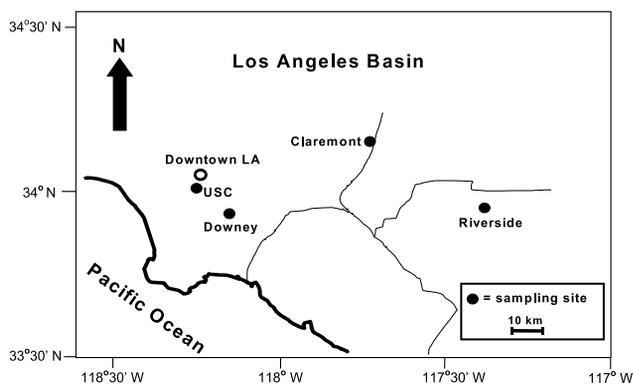


Figure 1. Locations of source sites (Downey and USC) and receptor sites (Claremont and Riverside) in the Los Angeles Basin.

increases with decreasing size, and that carbon content is higher in winter than in summer. In the Los Angeles Basin, previous work has found that fine particle ammonium nitrate can contribute more than half of the fine aerosol mass at some locations on some of the most polluted days of the year [Christoforou *et al.*, 2000]. Another study by Cass *et al.* [2000] measured ultrafine particle mass and chemistry at seven Southern California locations and found that 50% or more of ultrafine particle mass consisted of organic compounds. Differences in ambient temperature, relative humidity, photochemical activity, and source contributions are important parameters contributing to the differences in concentrations and size distributions of a particular chemical species. Since particle chemistry and particle size most likely affect the toxicological potential of PM, knowledge of the seasonal and spatial variability of the size-resolved PM chemical composition is vital in understanding PM effects on health. This knowledge can also be utilized in the design of health studies that take advantage of this variability to examine the relative effects of different particle characteristics.

[6] Because of relatively consistent and repeatable weather patterns, and generally high pollutant levels, the Los Angeles Basin is an ideal site for air pollution studies. Studies in Los Angeles Basin examining atmospheric aerosols at multiple locations across the basin have been conducted since the early 1970s [Cass *et al.*, 2000; Christoforou *et al.*, 2000; Hidy *et al.*, 1980; Hughes *et al.*, 1999; Russell and Cass, 1986]. However, all the previous size-resolved PM chemistry studies in Los Angeles have included only a few days or weeks of sampling. In the current work, size-resolved PM chemical data are presented from a long-term sampling campaign operated by the Southern California Particle Center and Supersite (SCPCS). The result is a more comprehensive representation of Los Angeles Basin aerosol characteristics from over two and half years of weekly data at four different monitoring sites throughout the Los Angeles Basin.

2. Methods

[7] Measurements of size-fractionated mass, inorganic ions (sulfate and nitrate), elemental and organic carbon, and trace elements and metals were conducted as part of the

routine sampling protocol of the SCPCS. Sampling occurred sequentially at four different sites in the Los Angeles Basin (Figure 1). At the first site, Downey, sampling was conducted between December 2000 and January 2001. Downey, located in central Los Angeles, is downwind of the “Alameda corridor,” a narrow industrial zone and transportation route between the Ports of Los Angeles/Long Beach and Downtown Los Angeles. The area is characterized by an extremely high density of diesel trucks, which serves to transfer overseas cargo from the Port to industrial sites, warehouses, and the rail yards near downtown Los Angeles. The Downey site is approximately 10 km downwind of some oil refineries, 3 km downwind of two major freeways, and is heavily impacted by vehicular sources.

[8] Sampling at the second site, Riverside, was conducted between February and September of 2001. The sampling location at the Citrus Research Center and Agricultural Experiment Station (CRS-AES), a part of the University of California, Riverside, is about 90 km east of downtown Los Angeles. The site is also about 25 km downwind of the Chino area dairy farms, a strong ammonia source leading to high concentrations of ammonium nitrate [Hughes *et al.*, 2000]. The area is upwind of surrounding freeways and major roads. The predominantly westerly wind transports particles generated near central Los Angeles toward Riverside [Allen *et al.*, 2000], resulting in an aged and often photochemically processed aerosol. Riverside is also characterized by some of the highest PM levels in the Basin. The next site was located in Claremont, where sampling was conducted from September 2001 through August 2002. Like Riverside, Claremont is situated on the eastern side of the Basin about 60 km east of downtown Los Angeles. It is located at the foot of the San Gabriel Mountains and is located north, and thus not downwind, of the dairy farms in Chino. The final site was at the University of Southern California near downtown Los Angeles. Sampling there was performed from September 2002 to September 2003. The sampling location was approximately 150 m downwind of a major freeway, and represents an urban mix of industrial, vehicular and construction sources.

[9] Although samples were not collected concurrently at the different sites, the consistent meteorology in Southern California allows for seasonal comparisons between sites, even though samples may have been collected in different years. To confirm this, monthly average levels of PM₁₀ measured by a local monitoring network were compiled at one of the sampling sites, Claremont, for a period of three consecutive years (2000–2002) corresponding to the period of sampling. The PM₁₀ data showed low interyear variability with relative standard deviations no more than 25%, indicating consistent meteorological and ambient particulate matter parameters in the Los Angeles basin from year to year.

[10] Because of their relatively western locations and urban environments, Downey and University of Southern California (USC) are considered “source” sites where fresh particles are emitted primarily from vehicular and industrial sources. The other two sites, Riverside and Claremont are designated “receptor” sites where the aerosol is composed of advected, aged and photochemically processed particles from the central Los Angeles area, as well as some local emissions [Pandis *et al.*, 1992]. The transport time of air

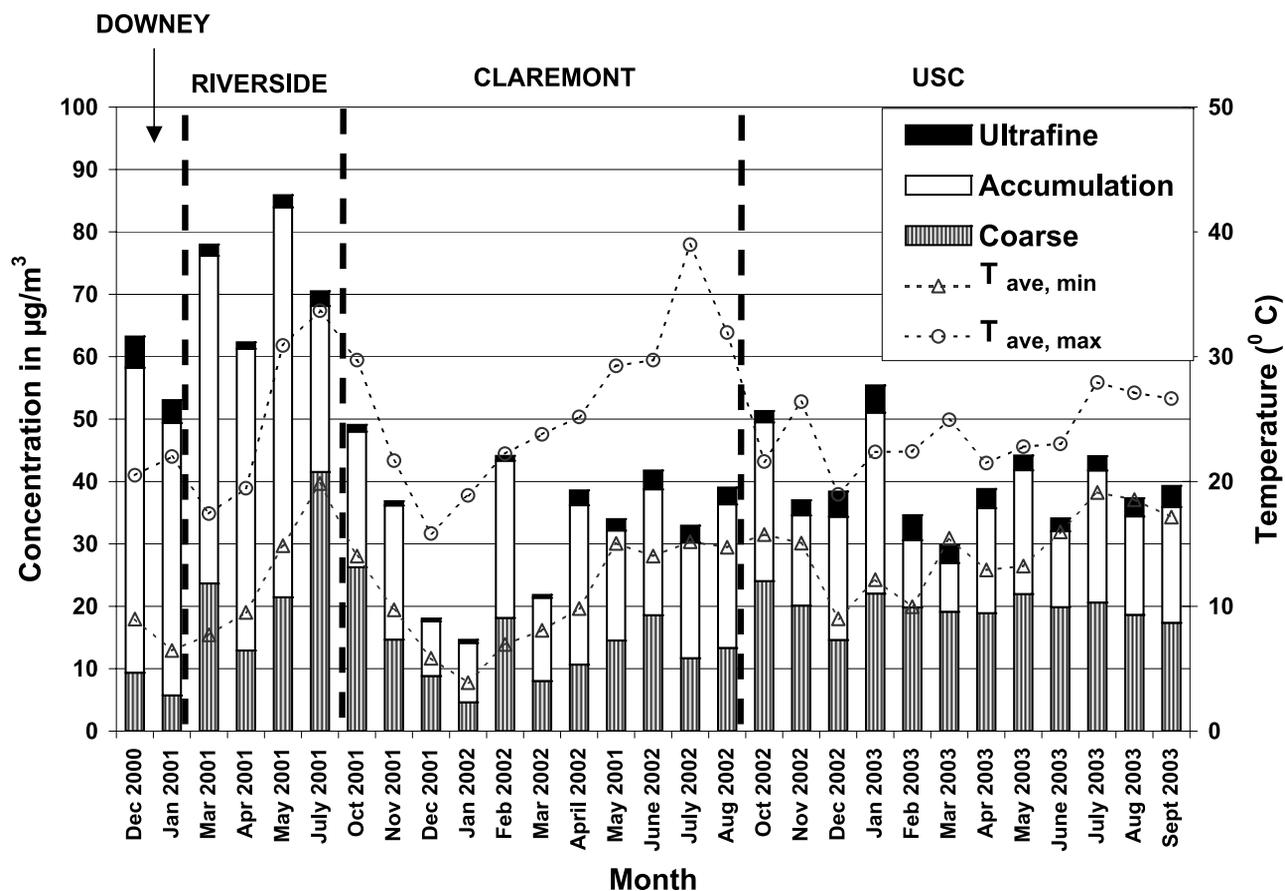


Figure 2. Monthly average PM mass in the coarse, accumulation, and ultrafine size modes.

masses from source to receptor sites can vary from a few hours to more than a day.

[11] Sampling was conducted once a week, by three, collocated micro-orifice uniform deposit impactors (MOUDIs) (Model 110, MSP Corporation, Minneapolis, Minnesota) for 24 hours (midnight to midnight). The sampling day was restricted to a rotation of Tuesdays, Wednesdays and Thursdays. The MOUDIs were run at the manufacturer-specified flow rate of 30 liters per minute (LPM), and configured for collecting particles in the following size bins: 0–0.1, 0.1–0.32, 0.32–0.56, 0.56–1.0, 1.0–2.5, and 2.5–10 μm . The size range of 2.5–10 μm is considered the “coarse” mode and the 0–0.1 μm size range constitutes the “ultrafine” mode. The analysis presented here combines the other four size bins between 0.1 and 2.5 μm and designates these sizes as the “accumulation” mode [Hering *et al.*, 1997]. Monthly average values for mass and chemical species were calculated only for months encompassing a minimum of three valid sampling days. Therefore, because of some missing data due to trailer moves, power outages, and malfunctioning instrumentation, some monthly averages are missing from the following tables and figures.

[12] Forty-seven millimeter Teflon filters (PTFE, Gelman, 2 μm pore, Ann Arbor, Michigan) were used as the substrate in the first MOUDI. Particles with diameters less than 0.1 μm (ultrafine) were collected on a 37 mm Teflon after-filter. The substrates were weighed before and after sampling with a Mettler 5 Microbalance (MT 5, Mettler Toledo Inc., Highstown, New Jersey), after at least 24 hours of equilibration at a

temperature of 22°–24°C and a relative humidity of 40–45%. The Teflon filters were then used to determine sulfate and nitrate concentrations by ion chromatography. For measurement of metals and trace elements, a second set of Teflon filters was collected in the second MOUDI configured identically to the first. After weighing, filters were analyzed by X-ray fluorescence (XRF) for metals and other trace elements. Elemental measurements less than three times the detection limit of XRF analysis were discarded.

[13] Size-fractionated PM concentrations of elemental carbon (EC) and organic carbon (OC) were obtained by simultaneous sampling with a third MOUDI. 47 mm aluminum substrates were used for the impaction stages and a 37 mm quartz fiber filter (Pallflex Corp., Putnam, Connecticut) was used as the after-filter (ultrafine stage). EC and OC values were determined using the Thermal Evolution/Optical Transmittance (TOT) analysis of Birch and Cary [1996], modified slightly for aluminum foil substrates. EC/OC analysis on aluminum MOUDI substrates has been performed for both ambient [Hughes *et al.*, 1999] and source [Kleeman *et al.*, 1999, 2000] samples. As described by Kleeman *et al.* [1999], the analysis includes an assumption of a split point between EC and pyrolyzed OC, which may contribute to some uncertainty in the results. The split point used for the current analysis was based on numerous PM_{2.5} quartz filter samples collected in Los Angeles previously.

[14] In our analysis and data presentation, the inorganic ions and organic carbon were represented in their measured

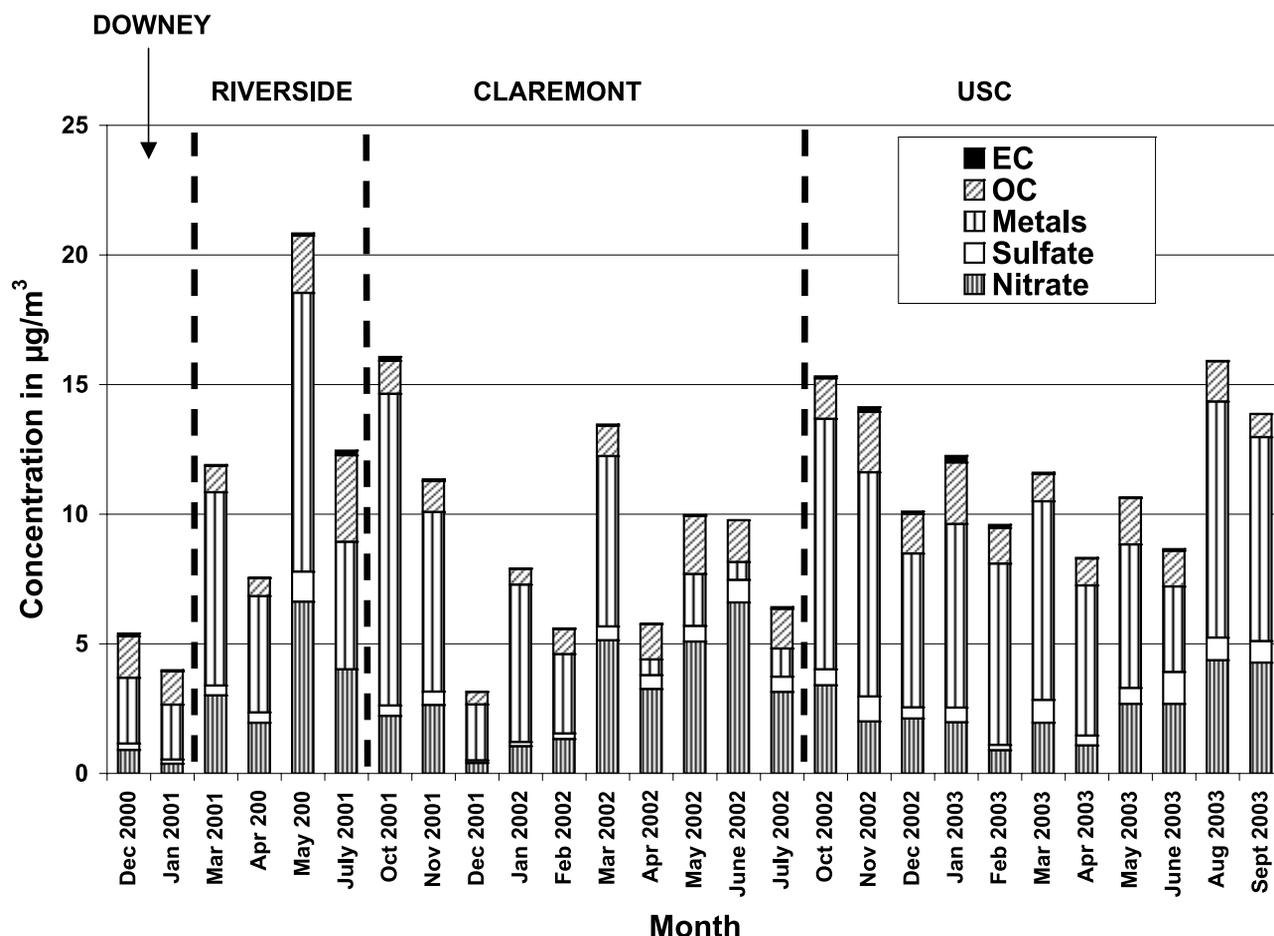


Figure 3. Monthly average PM chemical composition in the coarse mode.

form (not converted to mass accounting for associated atoms). Nevertheless while attempting a mass balance, inorganic nitrate and sulfate concentrations were assumed to be solely associated with their ammonium salts, and thus were multiplied by 1.29 and 1.38, to be converted to ammonium nitrate and sulfate, respectively. The assumption of nitrate and sulfate being associated largely to ammonium has been supported by previous studies [Hughes *et al.*, 2000, 2002]. Furthermore, for the same purpose of mass balance organic compound concentrations were estimated by multiplying organic carbon concentrations by a factor of 1.4 to account for the mass of H, O, N, and S in the organic compounds [Hughes *et al.*, 2002]. However, the more oxygenated organic compounds will generally have a mass-to-organic carbon ratio of greater than 1.4. As it will be discussed later, the sum of chemical species for at least the coarse and accumulation mode PM agreed well with the measured mass concentrations, which implies that the use of the 1.4 conversion factor is certainly reasonable. Metals and trace element concentrations were presented as the equivalent mass concentrations of their common oxides, using the conversion factors recommended by Cass *et al.* [2000].

3. Results and Discussion

[15] The monthly average PM mass distribution in the three size modes (ultrafine, accumulation, and coarse) is

presented for all four sampling sites in Figure 2. Also shown are the monthly averaged high and low temperatures on the days of sampling. The average monthly PM₁₀ mass ranged from 14.6 $\mu\text{g}/\text{m}^3$ in winter (January, 2002) at Claremont to 85.9 $\mu\text{g}/\text{m}^3$ during the summer (May 2001) at Riverside. The highest PM levels are observed at one source site, Downey, and the receptor site of Riverside. The highest ultrafine concentrations occurred at the source sites of Downey (December and January) and USC (December, January and February), with ultrafine mass concentrations of 4.34 ± 0.96 and 4.15 ± 0.19 $\mu\text{g}/\text{m}^3$ over the winter months of sampling, respectively. Both sites are influenced by nearby high traffic density and industrial areas, thus fresh primary emissions contribute to the high observed ultrafine concentrations. Furthermore, the wintertime steady atmospheric conditions with low wind speed and low mixing height contributes to higher PM concentrations at these sites during winter months. In the receptor areas, the mass concentrations in the accumulation and ultrafine modes are higher in the summer than in the winter, a possible result of increased secondary PM formation with higher photochemical activity. For example, the concentrations in the accumulation mode at Claremont during winter (December and January) and summer (June and July) are 9.15 ± 0.52 and 19.36 ± 1.16 $\mu\text{g}/\text{m}^3$, respectively. Summer in the Los Angeles Basin is also characterized by increased southwesterly winds in the afternoon that transport air

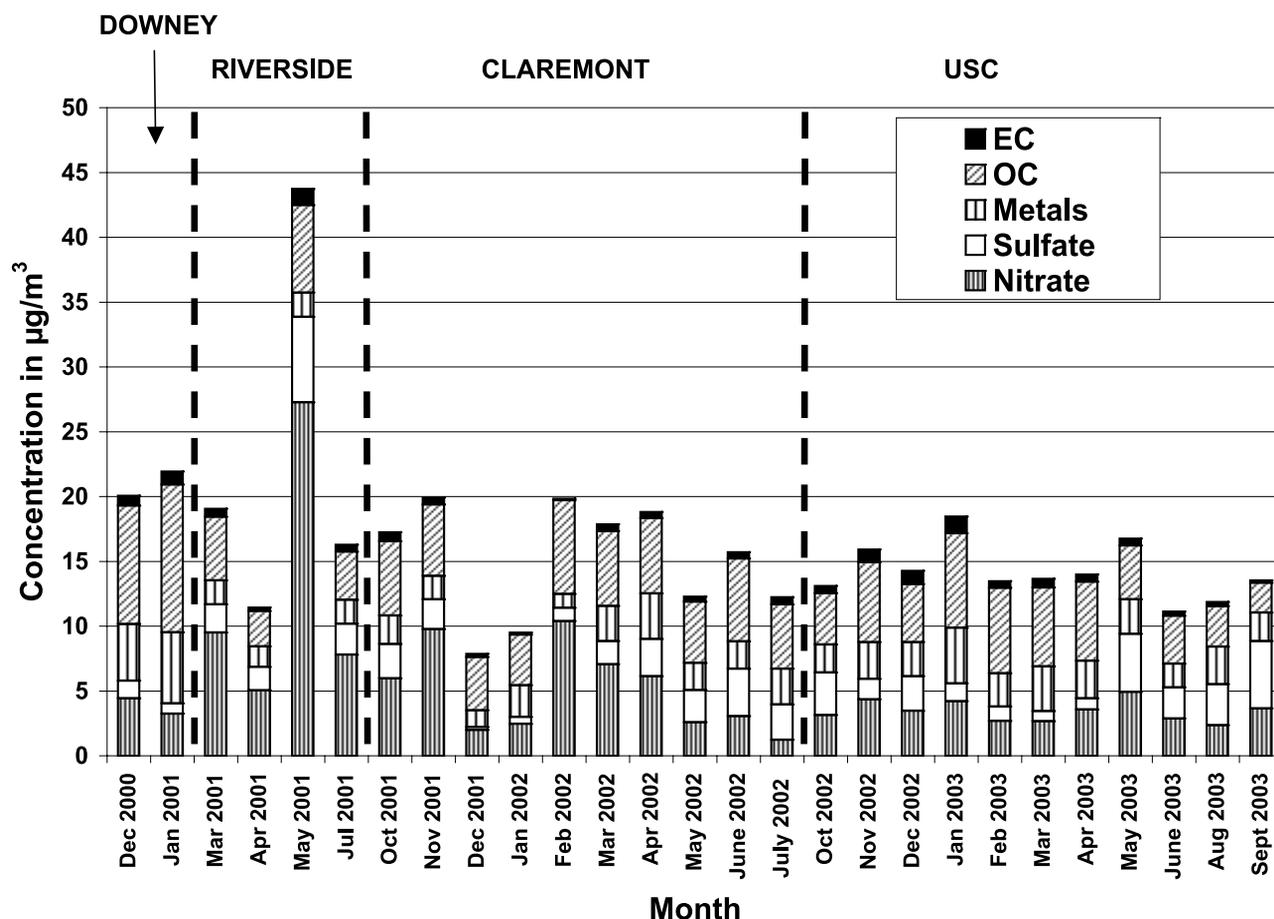


Figure 4. Monthly average PM chemical composition in the accumulation mode.

masses from the source areas to the receptor areas. Thus the combination of secondary photochemical reactions and increased advection result in the higher concentrations in the accumulation and ultrafine modes at the inland sites [Pandis *et al.*, 1992]. The coarse mode PM mass is also seen to generally increase in the summer, presumably because of higher contributions from windblown dust. The only exception appears to be USC, where coarse PM concentrations seem to be relatively consistent (between 14.6 and 24.0 $\mu\text{g}/\text{m}^3$) throughout the sampling period.

[16] Figure 3 illustrates the monthly average chemical composition of the coarse mode at all four sites. The sum of chemical species explained on average $78 \pm 7.4\%$ of the total mass concentrations for all sites, indicating that a reasonable mass balance was obtained between measured mass and the sum of the chemical species. The major chemical species of PM are shown, namely nitrate, sulfate, elemental carbon, organic carbon and the sum of the metals and trace elements. In general, metals and nitrate dominate the coarse mode across all sites. As mentioned earlier, the overall levels of coarse PM mass are observed to be generally lower in the winter compared to the summer. The wintertime stable conditions, low wind speeds, and higher soil moisture results in less resuspension of road and soil dust, the main contributors to coarse mode aerosol. The high observed metal and elemental content confirms that crustal materials are one of the major sources of coarse PM.

[17] Coarse PM nitrate levels are also higher in the summer in all sites. The period between April and July in the Los Angeles basin is characterized by frequent fog-like conditions with high relative humidity in the overnight and early morning hours. Particles emitted mostly to the west travel by advection eastward toward the inland valleys of the basin. It is conceivable that under these conditions, sub- $0.5 \mu\text{m}$ particles are activated to form fog or cloud droplets, followed by aqueous phase chemistry and then fog evaporation [Meng and Seinfeld, 1994]. Growth of hygroscopic ambient PM species, including nitrate, beyond the $1 \mu\text{m}$ range has been observed in several other studies [Hughes *et al.*, 1999; Geller *et al.*, 2004], when relative humidity reach greater than ninety percent. It is also possible that a small fraction of the nitrate in the coarse mode may be in the form of sodium nitrate, as suggested by a previous study conducted in Riverside [Noble and Prather, 1996]. We believe that sodium nitrate may be only a small fraction of the total nitrate because the 24-hour averaged concentrations of nitrate and sodium in the coarse mode were not correlated ($R^2 = 0.04$), so conversion of sea salt to sodium nitrate does not explain the majority of nitrate found in the coarse PM in this study. Similarly the correlation (R^2) of nitrate with calcium in the coarse fraction was only 0.09, indicating that calcium is also not the predominant nitrate cation. The monthly average PM chemistry in the accumulation mode is shown in Figure 4. An excellent overall agreement was obtained between the sums of the chemical species and

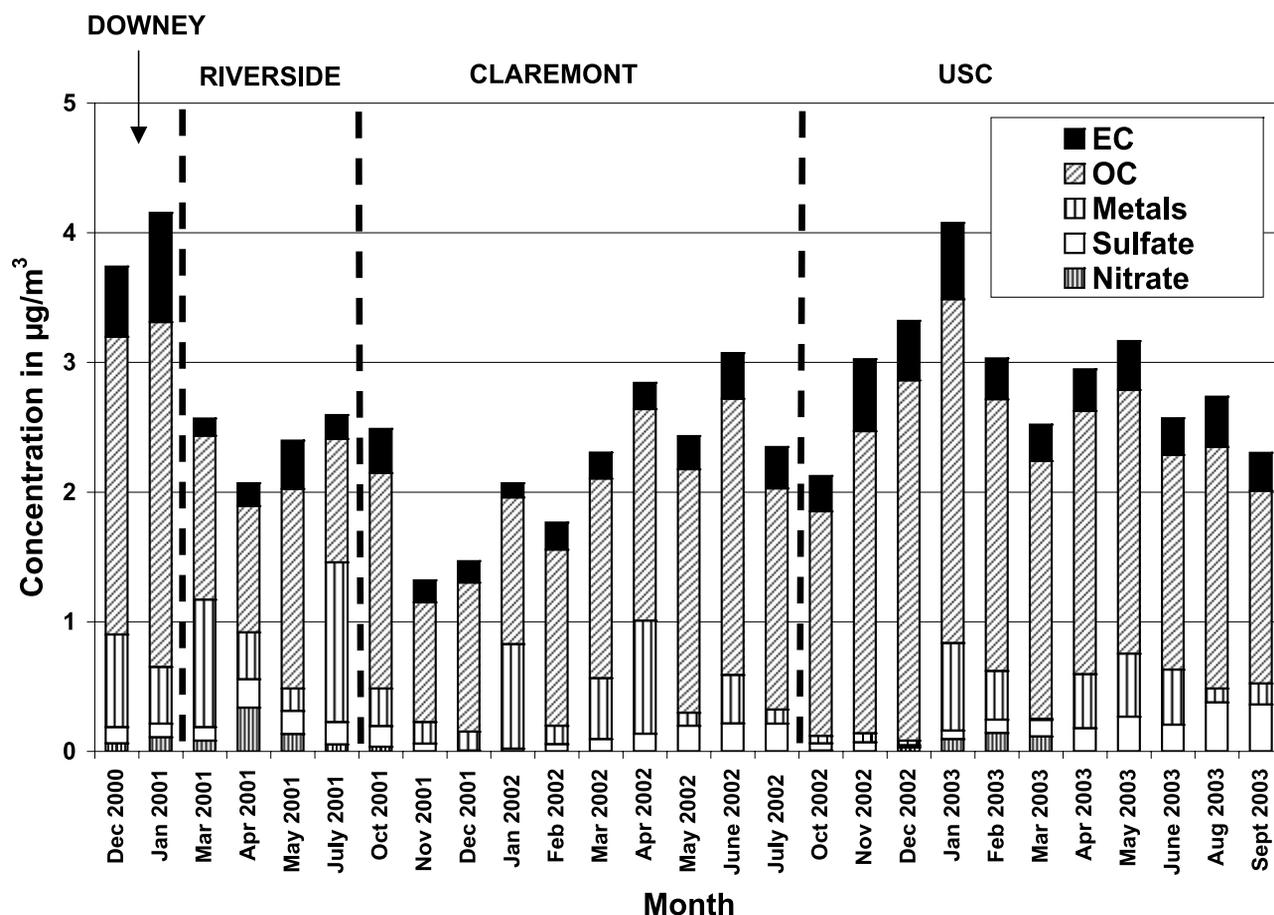


Figure 5. Monthly average PM chemical composition in the ultrafine mode.

measured mass concentrations (despite the assumptions made about conversion factors for organics, metals and inorganic ions) with the sum of species accounting for, on average, $102 \pm 8.2\%$ of the total mass. Nitrate and organic carbon are the two most prevalent species in this PM size range. The particulate nitrate concentrations are generally higher at the receptor sites, especially in Riverside. This site is downwind of the intense ammonia sources at the Chino area dairy farms [Singh *et al.*, 2002; Chow *et al.*, 1994]. Fugitive ammonia reacts with nitric acid in the air to form particle phase ammonium nitrate. Although not as high as Riverside, the nitrate concentrations at Claremont, another receptor site, are also higher than source sites. Although Claremont is not directly downwind of the dairy farms, it has been shown that vehicular sources can emit large quantities of ammonia as well [Fraser and Cass, 1998]. This and other ammonia sources may be sufficient to cause the high particulate nitrate concentrations observed at Claremont. It is of particular interest to note that the nitrate levels in the accumulation mode do not follow a pattern corresponding to seasonal photochemical activity levels. Other factors, such as the lower inversion height in the winter and the lower winter temperatures favoring ammonium nitrate in the particle phase, also influence the nitrate concentrations. The generally higher organic carbon composition at the source sites can be explained by primary emissions from nearby vehicle sources. The highest sulfate concentrations in the accumulation mode occur at the

receptor sites in summer, with high levels observed at USC in the warmer months as well. The average accumulation mode sulfate concentration at Claremont, a receptor site was $0.59 \mu\text{g}/\text{m}^3$ in the winter (December, January and February) compared to $3.17 \mu\text{g}/\text{m}^3$ in the summer (June and July). Higher summer sulfate concentrations may be due to increased photochemical formation and/or increased advection of background aerosol from over the Pacific Ocean with the higher wind speeds [Mysliwiec and Kleeman, 2002].

[18] The average monthly PM chemical composition in the ultrafine mode is given in Figure 5. The data plotted in Figure 5 should be prefaced by the cautionary statement that the OC concentrations shown may be subjected to positive artifacts, which are well known when collecting PM for organic analysis using quartz filters [Mader *et al.*, 2003; Schauer *et al.*, 2003]. Indeed, the ratio of the sum of chemical species to total mass concentrations for the ultrafine mode was $1.97 (\pm 1.22)$. Note that the organic carbon, nitrate and sulfate concentrations were converted to equivalent masses in estimating the reconstructed mass in Figure 6. Methods and justifications for these conversions are discussed in section 2. While assumptions converting OC, nitrate, sulfate and metal concentrations to their organic mass, ammonium nitrate, ammonium sulfate and oxide states, respectively, may be responsible for some of this discrepancy, adsorption of gaseous organic vapors on the quartz MOUDI after-filter, and thus higher measured OC

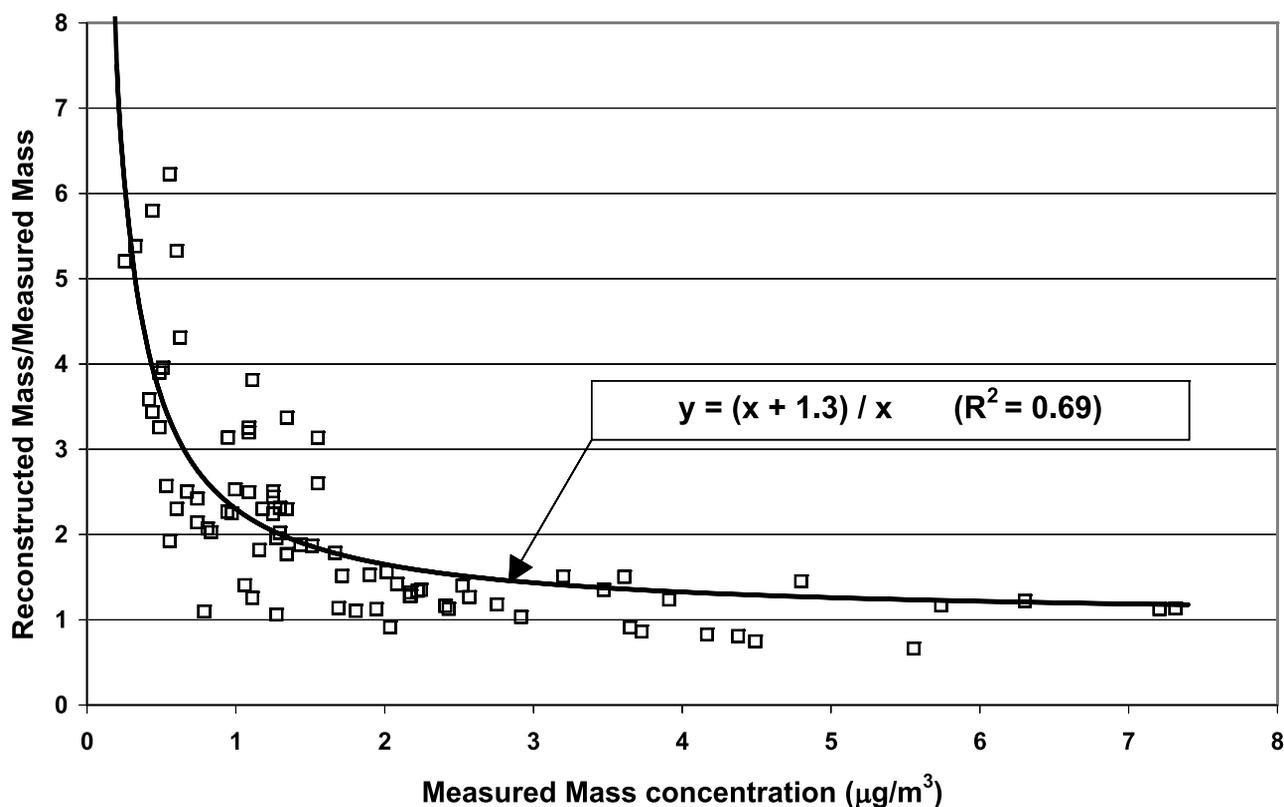


Figure 6. Plot of the ratio of reconstructed-to-measured ultrafine PM mass concentration as a function of measured ultrafine mass concentration.

concentrations, is the most likely reason for the overbalance. In a previous study conducted in the Los Angeles Basin, *Kim et al.* [2001] conducted measurements to quantify positive organic carbon artifacts in $PM_{2.5}$ measurements. Annual average concentrations in the basin were $7.20 \mu\text{g}/\text{m}^3$ for organic carbon, and $2.17 \mu\text{g}/\text{m}^3$ for the positive organic artifact, equivalent to 18.1% and 5.5% of the total $PM_{2.5}$ mass, respectively. This study indicated that the positive organic artifacts approached a nearly constant saturation value of approximately $2 \mu\text{g}/\text{m}^3$, regardless of the PM mass level, a finding that suggests that these artifacts may be more important at lower mass concentrations. This argument is further supported by the data shown in Figure 6, in which the ratio of the reconstructed mass (by adding chemical species) to the measured mass concentration for the ultrafine mode is plotted against the mass concentration. It can be seen that at mass concentrations lower than about $1.7 \mu\text{g}/\text{m}^3$, positive artifacts may be quite significant. For mass concentrations exceeding approximately $2 \mu\text{g}/\text{m}^3$, the reconstructed and measured mass concentrations are in very good agreement with their ratio very close to 1, suggesting that these data (roughly 30% of the total) are less prone to positive artifact errors. Further, the average positive adsorption artifact was determined to be approximately $1.3 \mu\text{g}/\text{m}^3$ by the best fit line shown in Figure 6. It is important to note that the positive artifact value of $1.3 \mu\text{g}/\text{m}^3$ in our study is slightly lower than the $2.17 \mu\text{g}/\text{m}^3$ determined by the *Kim et al.* [2001] study, which may be due to the fact that their group determined the artifact for filter sampling under quasiambient pressure. In our study, the MOUDI after-filter collects particles under a lower pressure (about 0.8 atm due

to the pressure drop across the last MOUDI stage) and this is likely to cause losses of some volatile OC. This acts to compensate for some of the adsorption artifact thereby lowering the value to $1.3 \mu\text{g}/\text{m}^3$. Hence the resulting estimate for the adsorption artifact is essentially MOUDI specific. Note, however, that given the high degree of variability of the adsorption seen in Figure 6, the organic data in our analysis is not corrected by subtracting the positive artifact. Given the unquestionable occurrence of these positive artifacts, however, the statements made in following paragraphs regarding ultrafine OC concentrations need to be qualified and put into perspective. The concentrations of the rest of ultrafine PM constituents (i.e., mass, EC, metals, inorganic ions) are not affected by this problem. Finally, it should be noted that the development of instrumentation for reliable measurement of ultrafine PM properties remains to this day, a developing field, and that at the time of this study, the MOUDI sampler, despite its potential problems, was one of the very few technologies available to us for collecting ultrafine PM.

[19] Figure 5 indicates that organic carbon dominates the ultrafine mode across all the sites ranging from 37% of the total mass in July 2001 at Riverside to 84% in December 2002 at USC. The predominance of OC is more extreme at the source sites during winter (for which the corresponding mass concentration data are highest and thus more reliable), possibly because of the lower temperatures favoring particle formation by condensable organics freshly emitted from vehicles. At the receptor sites, OC is higher in the ultrafine mode in the summer, during which secondary organic aerosol formation is favored and new ultrafine particle

Table 1. Relative Standard Deviations of Measured PM Components for Each Month of Sampling^a

	Mass			EC			OC			Sulfate			Nitrate		
	UF	Acc	C	UF	Acc	C	UF	Acc	C	UF	Acc	C	UF	Acc	C
<i>Downey</i>															
Dec. 2000	0.26	0.19	0.10	0.09	0.23	0.28	0.14	0.34	0.24	0.03	0.29	0.26	0.21	0.32	0.21
Jan. 2001	0.29	0.13	0.09	0.12	0.10	0.15	0.01	0.14	0.01	0.21	0.22	0.15	0.19	0.32	0.24
<i>Riverside</i>															
March 2001	0.26	0.24	0.18	0.01	0.08	0.26	0.09	0.15	0.30	0.27	0.23	0.20	0.19	0.34	0.18
April 2001	0.06	0.20	0.21	0.31	0.41	0.24	0.21	0.15	0.30	0.11	0.33	0.23	0.08	0.31	0.28
May 2001	0.14	0.09	0.07	0.09	0.08	0.14	0.11	0.08	0.09	0.21	0.11	0.19	0.21	0.16	0.08
July 2001	0.40	0.06	0.12	0.25	0.08	0.26	0.20	0.16	0.14	0.28	0.15	0.12	0.01	0.06	0.02
<i>Claremont</i>															
Oct. 2001	0.33	0.15	0.21	0.11	0.17	0.14	0.22	0.19	0.10	0.30	0.23	0.12	0.35	0.26	0.21
Nov. 2001	0.21	0.34	0.22	0.15	0.18	0.09	0.21	0.39	0.39	0.27	0.42	0.12	0.19	0.38	0.32
Dec. 2001	0.21	0.23	0.10	0.13	0.27	0.15	0.09	0.24	0.15	ND	0.15	0.12	0.19	0.23	0.31
Jan. 2002	0.16	0.17	0.25	0.11	0.27	0.16	0.03	0.17	0.11	0.39	0.36	0.27	ND	0.28	0.03
Feb. 2002	0.03	0.17	0.16	0.14	0.03	0.02	0.18	0.12	0.02	0.08	0.08	0.12	ND	0.22	0.24
March 2002	0.13	0.15	0.21	0.14	0.29	0.09	0.05	0.09	0.23	0.08	0.09	0.18	ND	0.13	0.16
April 2002	0.47	0.30	0.16	0.23	0.32	0.18	0.16	0.32	0.21	0.16	0.26	0.12	ND	0.45	0.11
May 2002	0.05	0.19	0.09	0.17	0.36	0.01	0.05	0.07	0.10	0.26	0.26	0.16	ND	0.22	0.16
June 2002	0.21	0.04	0.06	0.07	0.23	0.19	0.10	0.43	0.10	0.21	0.13	0.12	0.12	0.11	0.19
July 2002	0.19	0.11	0.12	0.16	0.34	0.05	0.12	0.24	0.31	0.03	0.23	0.15	0.10	0.02	0.06
<i>USC</i>															
Oct. 2002	0.22	0.26	0.02	0.10	0.27	0.21	0.02	0.21	0.12	0.36	0.03	0.10	0.06	0.07	0.20
Nov. 2002	0.30	0.29	0.25	0.19	0.12	0.19	0.12	0.03	0.11	0.10	0.40	0.19	0.01	0.14	0.05
Dec. 2002	0.23	0.31	0.29	0.18	0.18	0.29	0.16	0.21	0.23	0.12	0.31	0.22	0.22	0.19	0.03
Jan. 2003	0.21	0.37	0.31	0.14	0.34	0.25	0.11	0.22	0.21	0.28	0.39	0.29	0.09	0.18	0.11
Feb. 2003	0.20	0.31	0.12	0.14	0.03	0.12	0.39	0.06	0.07	0.06	0.09	0.43	0.29	0.43	0.49
March 2003	0.32	0.31	0.16	0.22	0.15	0.12	0.25	0.44	0.33	0.13	0.09	0.21	0.12	0.17	0.19
April 2003	0.22	0.19	0.18	0.07	0.20	0.32	0.21	0.28	0.18	0.36	0.48	0.46	0.16	0.34	0.24
May 2003	0.29	0.36	0.22	0.35	0.43	0.08	0.14	0.43	0.30	0.41	0.32	0.29	ND	0.09	0.29
June 2003	0.27	0.32	0.30	0.31	0.27	0.06	0.06	0.24	0.08	0.38	0.49	0.14	ND	0.20	0.05
July 2003	0.13	0.13	0.33	0.20	0.29	0.35	0.16	0.15	0.29	0.40	0.36	0.19	ND	0.16	0.32
Aug. 2003	0.15	0.18	0.23	0.24	0.21	0.17	0.19	0.33	0.27	0.18	0.31	0.18	ND	0.22	0.18
Sept. 2003	0.35	0.44	0.19	0.15	0.09	0.12	0.07	0.20	0.02	0.06	0.25	0.29	ND	0.30	0.27

^aUF, ultrafine mode; Acc, accumulation mode; C, coarse mode; ND, not detected.

organic mass may be formed via photochemical processes [Kim *et al.*, 2002]. The large contribution of organic carbon to ultrafine mass was also observed by Hughes *et al.* [1998]. The general trend of higher elemental carbon (a tracer of vehicular emissions) in the western, source areas of the Los Angeles basin results from the decreasing density of heavy-duty diesel traffic as one moves toward the east.

[20] A limited number of sampling days (a minimum of three per month) were used to compute the monthly average values for the measured chemical species. Table 1 presents the relative standard deviations, a measure of the intramonthly variability, of the measurements that were combined to form monthly averages. The table shows that in the majority of cases, the relative standard deviations were less than 30%, which corroborates the consistency of the data within a given month for any location, species and size mode. The previous discussions of seasonal and spatial trends do not rely on the few cases where the variability was higher.

[21] In addition to the chemical species presented above, analysis for specific elements and metals was also performed for all three size modes. The monthly average metal and element distribution in the coarse mode is given in Figure 7. Only the most abundant elements, e.g., iron, calcium, potassium, silicon and aluminum, are shown individually and are all primarily of crustal origin in the coarse mode. The less abundant metals (zinc, copper,

barium, titanium, chromium, manganese, nickel and lead) are summed together and shown as “other metals” in this and subsequent figures. Crustal metals dominate the monthly average metal content in the coarse mode. A closer look reveals very consistent relative levels of these components with respect to one another. For instance the average silicon to aluminum ratio is 2.43 with a standard deviation of only 13%. The consistency of this silicon to aluminum ratio across all sites is an indication of a common source, namely soil and/or road dust [Hildemann *et al.*, 1991; Schauer and Cass, 2000; Schauer *et al.*, 1996].

[22] Monthly average metal and element concentrations in the accumulation mode are presented in Figure 8. The iron levels at Downey and USC in this size range are found to be higher relative to other metals and other sites, indicating possible contributions from vehicular sources. Iron may be emitted directly from tailpipes but is also a component of resuspended road dust [Hildemann *et al.*, 1991]. The ratio of iron to silicon at Downey and USC for the coarse mode was found to be 0.71 ± 0.02 and 0.58 ± 0.24 , respectively. For the same months in the accumulation mode, the ratios were 1.05 ± 0.02 and 0.77 ± 0.32 for Downey and USC, respectively. A two-tailed paired *t*-test showed that a significant difference exists between the ratios of Fe to Si in the two modes at both the sites ($p = 0.004$ and 0.02 for Downey and USC, respectively). Since the accumulation mode ratio is statistically higher than the

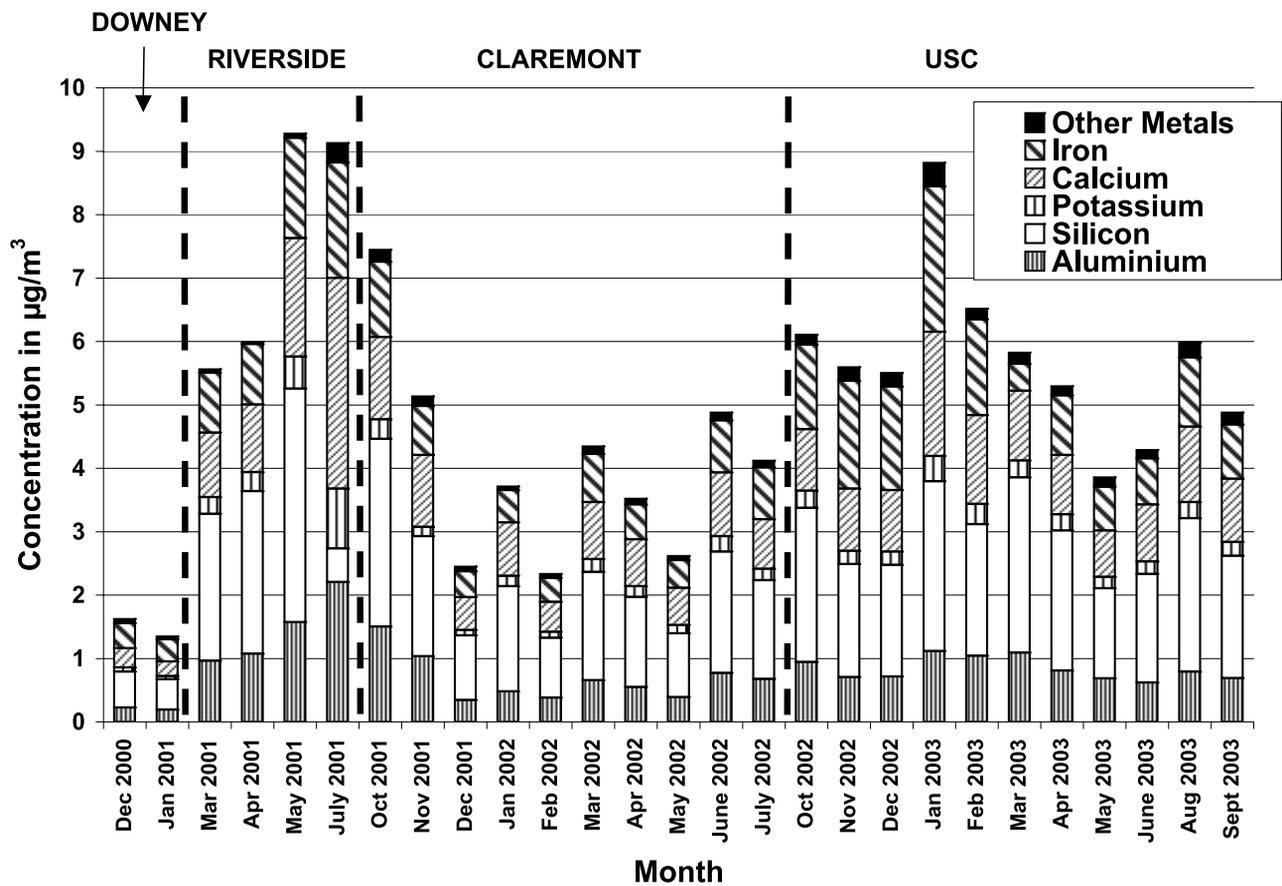


Figure 7. Monthly average metals and elements in the coarse mode.

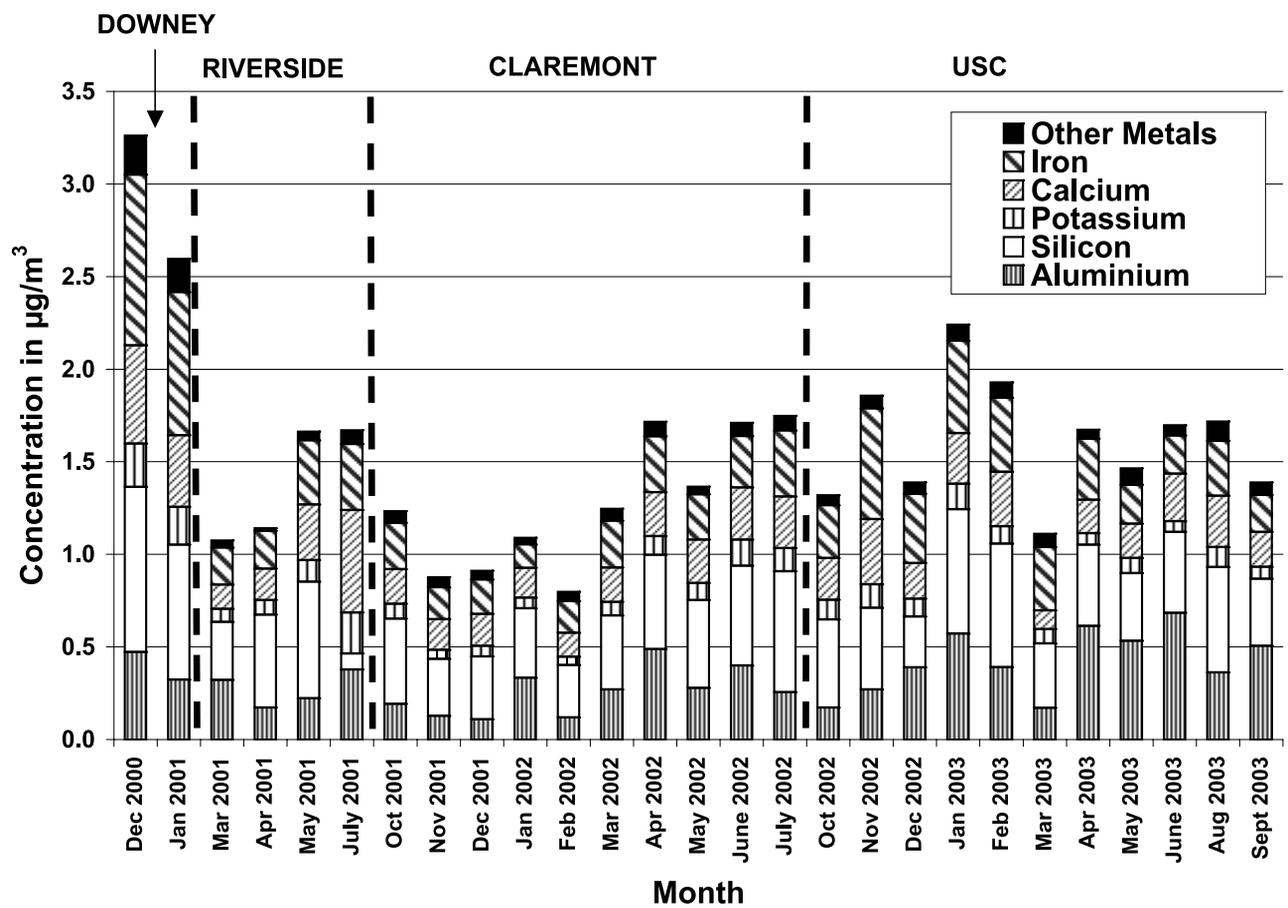


Figure 8. Monthly average metals and elements in the accumulation mode.

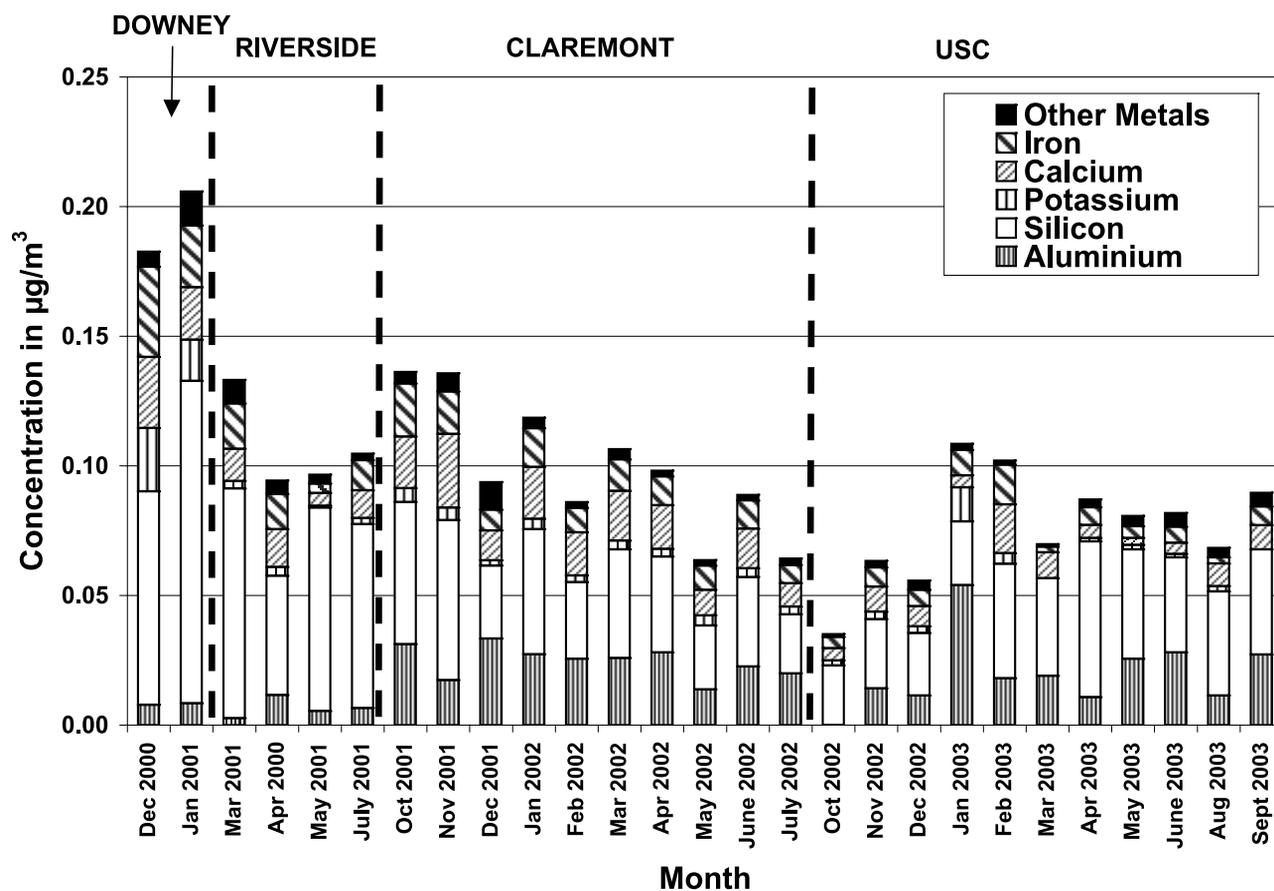


Figure 9. Monthly average metals and elements in the ultrafine mode.

crustal ratio found in the coarse mode, and relatively less crustal material is expected in the smaller size range, tailpipe emissions are a possible additional source of iron in the accumulation mode.

[23] Figure 9 shows the monthly average of the metals and elements found in the ultrafine mode. The mass of metals and elements are extremely low in the ultrafine mode compared to the other two size ranges. The highest observed concentration across all sites was only $0.21 \mu\text{g}/\text{m}^3$ at Downey in January 2001. High silicon levels relative to Al and the other elements suggest an additional source of silicon (other than crustal) in the ultrafine mode. One possible source may be the small amount of silicon previously observed in the particulate emissions from vehicles [Hildemann *et al.*, 1991].

[24] The monthly average elemental carbon distribution in the three modes is given in Figure 10. It was observed that the elemental carbon concentration in the ultrafine mode is higher at the source sites because of fresh emissions from diesel vehicles. At the receptor sites, higher elemental carbon concentrations occur during the summer in the ultrafine and accumulation modes. At Claremont, the concentration in the accumulation mode is $0.52 \pm 0.05 \mu\text{g}/\text{m}^3$ in the summer (June and July) and $0.17 \pm 0.06 \mu\text{g}/\text{m}^3$ in the winter (December through February). The concentration in the ultrafine mode also shows a similar trend, with a summer and winter concentration of $0.34 \pm 0.2 \mu\text{g}/\text{m}^3$ and $0.16 \pm 0.06 \mu\text{g}/\text{m}^3$, respectively. Since particulate elemental carbon only comes from primary sources, high concentra-

tions of elemental carbon at receptor sites is most likely due to advection of PM from the upwind source areas. Local EC sources, including wood burning and local diesel trucks, may also play a role, but this would not explain the low winter EC concentrations. Thus it appears that increased summer wind speeds and the advection of polluted air masses overwhelm local sources and any dilution effect due to the higher mixing height in the summer months.

[25] The ratio of organic carbon to elemental carbon has been proposed as a method for distinguishing between the primary and secondary carbon content of PM [Lim and Turpin, 2002]. Table 2 shows the average ratio of OC to EC at all the sites for $\text{PM}_{2.5}$ (the sum of the ultrafine and accumulation modes). The weekly EC and OC data are averaged to calculate the overall average for each site. The source sites have a lower OC/EC ratio and higher levels of correlation between EC and OC relative to the receptor sites, both of which are indicative of primary emissions from vehicular sources. The receptor sites have a generally higher organic to elemental carbon ratio above the primary emissions ratios of the source sites. The formation of secondary organic compounds in the atmosphere, which condense onto the particle phase, can cause the higher OC content relative to EC. The higher organic to elemental carbon ratios observed in Claremont may also be driven by a lack of concentrated diesel sources upwind. Claremont has an average elemental carbon concentration of $0.6 \pm 0.36 \mu\text{g}/\text{m}^3$, while Riverside has an average concentration of $0.94 \pm 0.5 \mu\text{g}/\text{m}^3$. The more southerly location of Riverside

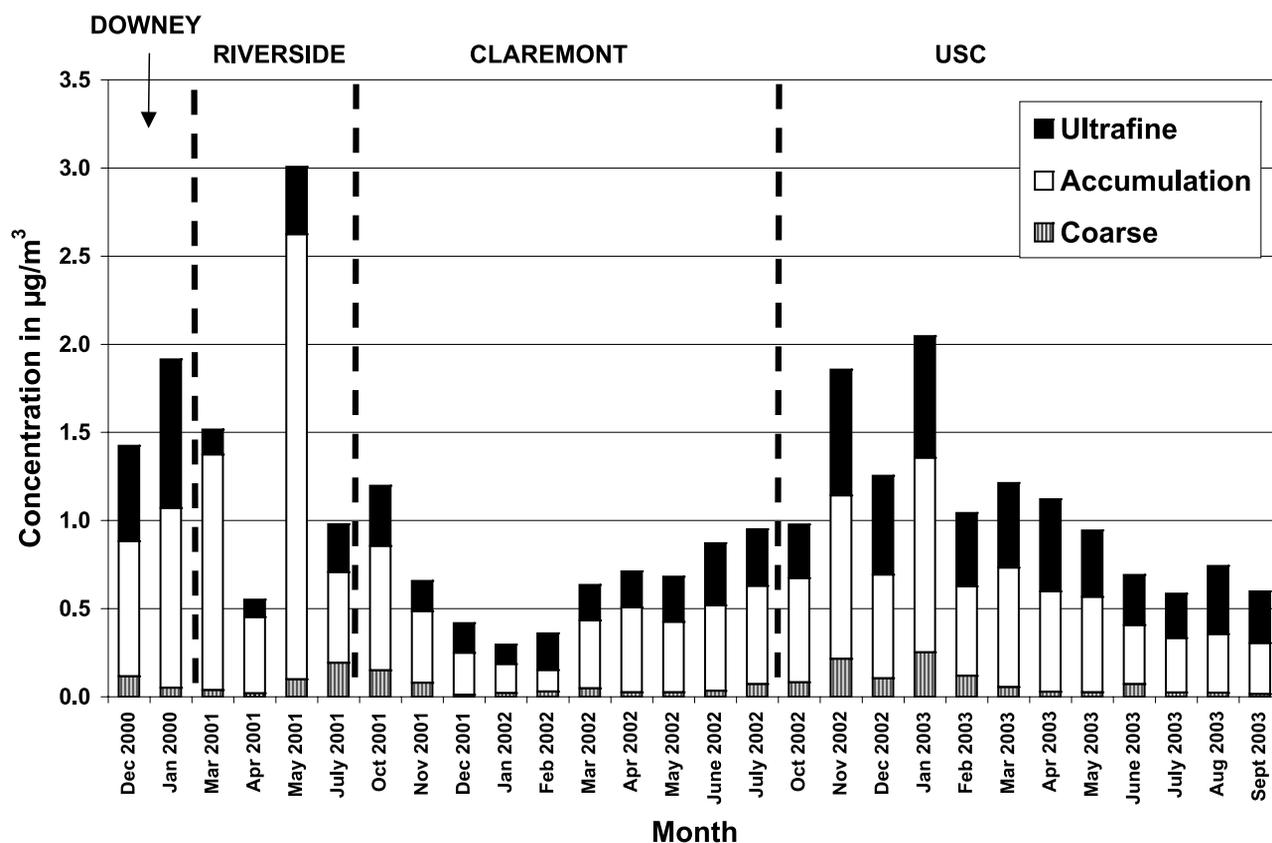


Figure 10. Monthly average elemental carbon distribution in the coarse, accumulation, and ultrafine modes.

lies on a more direct wind trajectory from the port and industrial areas of Los Angeles and Long Beach, and may be influenced more by upwind diesel emissions than Claremont to the north.

[26] The correlation coefficients between measured daily metal concentrations in the coarse and fine (accumulation plus ultrafine) modes at receptor and source sites are given in Table 3. Only the most significant correlations are included ($R^2 > 0.6$). In the coarse mode at the source sites, high correlations are observed for many of the elements. The highest correlations suggest a common source of Al and Si, and a related source of Fe, V, Ti, Mn, Zn, and Cu. The major source of coarse particles is soil and road dust, with the former being the likely origin of Al and Si and the latter being the most likely source of Fe, Ti, Mn, Zn, and Cu [Harrison *et al.*, 2003]. Cu has been recently shown to be a marker of car break lining [Espinosa *et al.*, 2004], which is consistent with its high correlation with elements originating from road dust. In the fine mode at the source sites, the degree of correlation among elements drops significantly. Fine particles have more varied sources than coarse particles, and thus interelement correlations are reduced by varying contributions by multiple sources of the same element. The results show moderately high correlations among some metals (Fe, Si, Mn, Zn), which may originate from crustal, vehicular, or industrial sources. Additional high correlation coefficients were observed in the coarse mode at the receptor sites between Al and Si and some other crustal metals indicating a soil/road dust source. Unlike the coarse mode, no significant correlations were

observed in the fine mode at the receptor sites. In general, less correlation is expected at the downwind receptor sites because of the potential influence of a greater variety of sources upwind.

4. Summary and Conclusions

[27] The results presented in this paper indicate that location and season significantly influence the size resolved chemical composition of PM in the Los Angeles Basin. Summer months at the receptor sites show higher concentrations, which are influenced both by increased advection and secondary formation by photochemical reactions. These two effects overwhelm the effect of a higher summertime inversion height promoting a greater degree of mixing. Crustal material and nitrate dominate the coarse mode, while nitrate and organic carbon dominate the accumulation mode. Organic carbon is by far the most abundant species in the ultrafine mode, and the source sites have a high

Table 2. Averaged $PM_{2.5}$ OC/EC Ratios and Correlation Coefficients at Source and Receptor Sites

Source Site	Average and SD	Range	R^2
Downey	3.63 ± 1.6	1.93–6.84	0.81
USC	5.07 ± 1.14	3.26–7.35	0.86
Receptor Site	Average and SD	Range	R^2
Riverside	7.49 ± 3.01	2.64–15.92	0.56
Claremont	10.60 ± 5.6	3.14–25.50	0.38

Table 3. Correlations Between 24-Hour Averaged Mass Concentrations of Selected Metals and Elements at Source and Receptor Sites^a

Element 1	Element 2	n	R ²	Slope	Intercept, $\mu\text{g}/\text{m}^3$
<i>Source Sites (Downey/USC): Coarse Mode</i>					
Al	Si	36	0.98	2.16	-0.0029
Al	Fe	36	0.81	2.04	0.0146
Al	Ti	36	0.76	0.13	0.0008
Al	Mn	36	0.79	0.13	-0.0003
Al	Zn	36	0.6	0.03	0.0020
Si	Fe	36	0.84	1.09	0.0201
Si	Ti	35	0.77	0.03	0.0010
Si	Mn	35	0.69	0.07	0.0001
Si	Zn	35	0.73	0.04	0.0015
Fe	Ti	35	0.83	0.10	-0.0019
Fe	V	35	0.85	0.00	-0.0017
Fe	Mn	35	0.88	0.02	-0.0003
Fe	Cu	35	0.95	0.06	-0.0028
Fe	Zn	35	0.86	0.03	0.0008
Ti	V	35	0.81	0.06	-0.0019
Ti	Mn	35	0.91	0.27	0.0014
Ti	Cu	35	0.88	0.56	-0.0017
Ti	Zn	35	0.88	0.39	0.0013
V	Mn	35	0.79	1.22	0.0022
V	Cu	35	0.92	4.79	0.0036
V	Zn	35	0.78	2.86	0.0077
<i>Source Sites (Downey/USC): Fine Mode</i>					
Si	Fe	36	0.88	1.37	0.0400
Si	Mn	35	0.79	0.09	0.0011
Si	Zn	35	0.76	0.06	0.0169
Fe	Ti	35	0.88	0.04	0.0154
Fe	Mn	35	0.77	0.027	0.0063
Fe	Cu	35	0.72	0.033	0.0034
Fe	Zn	35	0.79	0.062	0.0241
Mn	Zn	36	0.81	2.85	0.0133
<i>Receptor Sites (Claremont/Riverside): Coarse Mode</i>					
Al	Si	55	0.92	0.94	0.0200
Al	Fe	55	0.64	0.88	0.1800
Al	Mn	55	0.81	0.02	0.0013
Al	Cu	55	0.66	0.01	0.0031
Mn	Cu	55	0.71	0.44	0.0026

^aOnly cases when $R^2 > 0.6$ are given.

elemental carbon content because of diesel traffic. The metals are found primarily in the coarse mode with only trace amounts in the ultrafine mode. Metals in the coarse mode indicate a common source of soil and road dust and are higher in summer because of higher summertime wind speeds causing resuspension. Metals measured in the accumulation and ultrafine modes also have other non-fugitive dust sources.

[28] The variation in the PM chemical constituents with site, season and size fraction needs to be considered in the design of future epidemiological and particle toxicity studies. The observed differences in particle characteristics can also be utilized to test hypotheses on the associations between health outcomes and size-resolved particle chemistry. Finally, similar data currently being generated by the other supersites will allow interesting comparisons between particle characteristics in different areas of the country.

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