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The Relationship between Real-Time and Time-Integrated Coarse (2.5–10 μm), Intermodal (1–2.5 μm), and Fine (<2.5 μm) Particulate Matter in the Los Angeles Basin

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ABSTRACT

A periodic review of the National Ambient Air Quality Standards for Particulate Matter by the U.S. Environmental Protection Agency (EPA) will assess the standards with respect to levels, particle size, and averaging times. Some members of the scientific community in the United States and Europe have suggested the use of PM_1 instead of $PM_{2.5}$ as the fine particle measurement standard. This proposed standard is intended to reduce the influence of coarse particle sources on $PM_{2.5}$, because some evidence suggests that $PM_{1–2.5}$ is dominated by coarse particulate matter (PM) sources.

In this study, coarse ($PM_{2.5–10}$), intermodal ($PM_{1–2.5}$), and fine ($PM_{2.5}$) mass concentrations at four different sites are measured with continuous and time-integrated sampling devices. The main objective is to compare variations in these three size ranges while considering the effects of location, sources, weather, wind speed, and wind direction. Results show strong correlations between PM_1 and intermodal PM in receptor sites. The contribution of $PM_{1–2.5}$ to $PM_{2.5}$ is highest in the summer months, most likely due to enhanced long-range transport. Coarse PM is poorly correlated with intermodal PM. Continuous data suggest that PM_1 is growing into $PM_{1–2.5}$ via complex processes involving stagnation of the aerosol during high relative humidity conditions, followed by advection during daytime hours

IMPLICATIONS

Members of the regulatory community have recently discussed the establishment of a PM_1 standard that would eventually replace the current $PM_{2.5}$ standard. The new standard is predicated on the assumption that the PM_1 component of $PM_{2.5}$ may be more reflective of the health effects associated with fine PM, based on the fact that PM_1 is mainly composed of combustion and atmospheric reaction byproducts, whereas $PM_{1–2.5}$ is often dominated by crustal materials associated with the coarse PM mode. Although a few studies have been conducted with results that support the change to a new standard, the study locations were not representative of heavily populated areas because they were surrounded by desert or rural areas and were not downwind of metropolitan areas. This study presents the relationship between $PM_{1–2.5}$ and both fine and coarse PM in source and receptor sites in an urban region.

INTRODUCTION

Ambient particulate matter (PM) has been traditionally divided into three modes by both the regulatory and scientific communities. These modes are based on the aerodynamic diameter of the particles and were typically based on size distribution profiles and, to some extent, chemical composition. Coarse mode PM consists of particles with diameters greater than 2.5 μm and contains crustal metals (Al, Si, CA, Fe, Ti), road dust (brake linings, tire residue), and bioaerosols (e.g., pollen, mold spores). Accumulation mode PM includes particles from 0.1 to 2.5 μm in diameter and is comprised of combustion aerosols and particles that grow from photochemical and physical processes that occur in the atmosphere. The remainder of the particles (with diameters less than 0.1 μm) comprises the ultrafine PM mode, which consists of combustion-formed particles and nucleation of vapors in the atmosphere.[1]

Because the focus of PM regulation has extended beyond PM_{10} (PM with aerodynamic diameters less than 10 μm) to $PM_{2.5}$ (PM with aerodynamic diameters less than 2.5 μm), both scientific and regulatory communities have pondered whether an alternate PM standard might provide a better indicator for fine particles. For example, PM_1 has been considered to presumably reflect an unambiguous separation of the coarse and fine PM modes. One prevailing theory is that 1–2.5 μm particles primarily originate from the "tail" of the coarse mode PM mass distribution; thus, these particles have the same sources as coarse particles, and consequently their potential contribution to health effects should not be considered part of the fine ($PM_{2.5}$) PM mode.[2] Evidence supporting this

argument has been provided by studies in Spokane, WA, and Phoenix, AZ, where coarse and intermodal PM ($PM_{1-2.5}$) are highly correlated.[3,4] Proponents of the PM_1 standard argue that recent research demonstrates that PM_1 has greater health implications because of its sources, size, chemical composition, and observed health effects. If the standard is approved and PM_1 originates from the same sources as $PM_{1-2.5}$ and/or grows to particles in the 1–2.5 μm range, $PM_{2.5}$ could essentially be studied in two halves. Dividing a mode in this fashion only complicates regulations and may ignore an important fraction of PM that may be toxic. On the other hand, if the intermodal mass has a different chemical composition and different biological properties, it would be appropriate to exclude it from the fine particle indicator.

The goal of this paper is to demonstrate the extent of correlation between intermodal PM and PM_1 in various areas of the Los Angeles Basin. The existence of this correlation has great significance for regulators because intermodal PM cannot be discounted if it is both correlated with PM_1 and comprises a substantial fraction of $PM_{2.5}$. Furthermore, a PM_1 standard, if adopted, should reflect studies in multiple cities that have both urban and rural characteristics.

METHODS

Sampling Locations

The instruments described below were operated inside a mobile particle laboratory developed by the Southern California Particle Center and Supersite (SCPCS) measurement and monitoring program funded by the U.S. Environmental Protection Agency (EPA). During the period of this study, measurements were conducted at four sites for about 5–12 months each and across separate seasons (Figure 1). From October 2000 through February 2001, sampling was done in Downey, a typical urban site in south central Los Angeles impacted mostly by primary vehicular emissions. From mid-February through August 2001, sampling was conducted in Riverside; from September through August 2002, sampling was conducted in Claremont. Riverside and Claremont are both considered receptor areas in the eastern inland valleys of the basin because they lie downwind of the aerosol plume generated by the millions of vehicles in the western portion of the Los Angeles Basin. This plume is advected by the predominantly westerly winds after aging for several hours to a day.[5] Riverside (unlike Claremont) also lies downwind of significant ammonia emissions from nearby farming and livestock operations, resulting in high concentrations of ammonium nitrate after atmospheric chemical reactions.[6] From October 2002 through February 2003, sampling occurred near the University of Southern California (USC) at an urban site impacted by freeway emissions, local vehicle emissions, and construction site emissions from a local sewer replacement project.

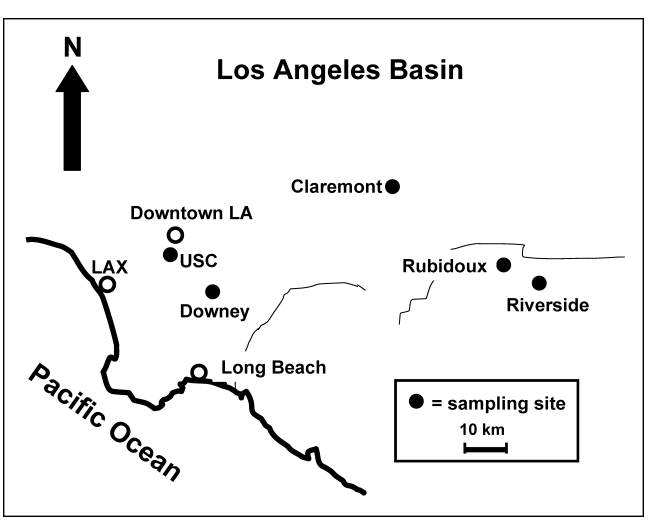

Figure 1. Map of the sampling locations.

Instrumentation

Both continuous and time-integrated data were collected for coarse, fine, and intermodal PM. The sampling devices employed included the Aerodynamic Particle Sizer (APS, TSI Model 3320, Shoreview, MN), which was used to measure hourly concentrations of particles in the size range of 0.5–10 μm, the β-Attenuation Monitor (BAM, Met-One Instruments, Grants Pass, OR), which provided hourly $PM_{2.5}$ mass concentrations, the Micro-Orifice Uniform Deposit Impactor (MOUDI, MSP Corp., Minneapolis, MN), the Dichotomous Partisol-Plus (Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co. Inc., Albany, NY) for time-integrated coarse and $PM_{2.5}$ mass concentrations, and the Harvard/EPA Annular Denuder System[7] (HEADS) for 24-hr averaged $PM_{2.5}$ mass and inorganic ion (sulfate and nitrate) concentrations. Additionally, intensive studies were conducted for short time intervals in which the USC Continuous Coarse Monitor[8] and Cascaded ADI Continuous Nitrate Monitor[9] were collocated with the above instruments for a short time. All samples were drawn through conductive stainless-steel pipes with diameters proportional to sample air velocities for each instrument.

Both the MOUDI and Partisol sampled approximately once per week and over time periods varying from 4 to 24 hr, depending on location and observed pollution levels. Particles were classified by the MOUDI in the following aerodynamic particle diameter ranges: <0.10, 0.10–0.32, 0.32–0.56, 0.56–1.0, 1.0–2.5, and 2.5–10 μm. Teflon filters with diameters of 4.7 and 3.7 cm (2-μm pore size; Gelman Science, Ann Arbor, MI) were used to collect particles in the MOUDI stages and after-filter, respectively.

The Partisol uses a PM_{10} inlet operating at 16.7 L/min to remove particles larger than 10 μm in aerodynamic diameter. The remaining PM_{10} aerosol is drawn through a virtual impactor, or "dichotomous splitter," located after the inlet. Two separate flow controllers maintain coarse aerosol flow at 1.67 L/min and that of the fine aerosol stream at 15 L/min. Coarse and fine particles are collected on two 4.7-cm Teflon filters, which are housed in reusable cassettes placed in the minor and major flows of the Partisol virtual impactor. The Teflon filters of both the MOUDI and Partisol samplers were pre- and postweighed with a Mettler Microbalance (MT5, Mettler–Toledo, Inc., Hightstown, NJ) after 24-hr equilibration under controlled humidity (40 ± 5%) and temperature (24 ± 3 °C) to determine particle mass concentrations.

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 a second MOUDI configured identically to the first. After weighing, filters were analyzed by X-ray fluorescence for metals and other trace elements. Samples to determine the size-fractionated concentrations of elemental carbon (EC) and organic carbon (OC) were obtained by simultaneous sampling with a third MOUDI. Aluminum substrates of 47 mm were used for the impaction stages and a 37-mm quartz fiber filter (Pallflex Corp., Putnam, CT) was used as the after-filter (ultrafine stage). EC and OC values were determined with the Thermal Evolution/Optical Transmittance (TOT) analysis of Birch and Cary.[10] Concurrent to the 24-hr MOUDI sampling, fine and coarse mass measurements were performed with 47-mm Teflon filters in a dichotomous sampler (Partisol-Plus, Model 2025 Sequential Air Sampler, Rupprecht and Patashnick). Mass and elemental concentrations of coarse and fine size fractions were determined by the same methods as described previously for MOUDI sampling. Partisol results were compared with MOUDI data to check for consistency and, in a few cases, used in the analysis when MOUDI results were not available.

In addition to time-integrated chemical composition data, the USC Continuous Coarse Monitor[8] operated during a winter intensive study at the USC site. The operating principle of the monitor is based on enriching coarse particle concentrations by a factor of about 25 by means of a 2.5-μm cut-point round-nozzle virtual impactor, while maintaining a mass of $PM_{2.5}$ at ambient concentrations. The aerosol mixture is subsequently drawn through a Tapered Element Oscillating Microbalance (TEOM 1400A, Rupprecht and Patashnick), the response of which may be dominated by the contributions of coarse PM caused by concentration enrichment.

Another intensive study was conducted during September 2001 in Claremont, in which the newly developed ADI Continuous Nitrate Monitor was located at the Claremont site for an intensive study. This monitor yields hourly nitrate concentrations of $PM_{2.5}$ classified in the following three aerodynamic size ranges: <0.4; 0.4–1.0; and 1.0–2.5 μm. The operation and characterization of this device is described by Stolzenburg et al.[9] and Fine et al.[11]

RESULTS AND DISCUSSION

$PM_{1-2.5}$ and $PM_{2.5}$ mass concentrations are very highly correlated ($R^2 = 0.76$) for all sites (Figure 2). Figure 2 also indicates that, contrary to the prevailing perception, the 1–2.5 μm range accounts for a substantial fraction of the total $PM_{2.5}$ mass, ranging from 20% to 45%, depending on location and season, as discussed in the following sections. The chemical characteristics of intermodal PM are displayed by site in Figure 3. These results are similar to those discovered by Hughes et al.,[12] in which they determined the chemical composition of the fine mode PM at four locations in Southern California. In contrast, the coarse size mode does not demonstrate as high of a positive correlation with intermodal PM. Intermodal PM tracks much better with PM_1 than the coarse mode in receptor sites, whereas the correlations between coarse and intermodal PM as well as between PM_1 and intermodal PM become closer in source sites. The following section will describe this in detail.

Site-by-Site Comparison

University of Southern California. Figure 4a shows the relationship between intermodal PM and coarse mode PM at the USC sampling site 1 mi south of downtown Los Angeles. The correlation coefficient (R^2) of 0.11 reflects the divergence of these two modes in the ambient air near this site. Because the site is urban and crustal particles are not locally emitted, this result is not unusual. The site is

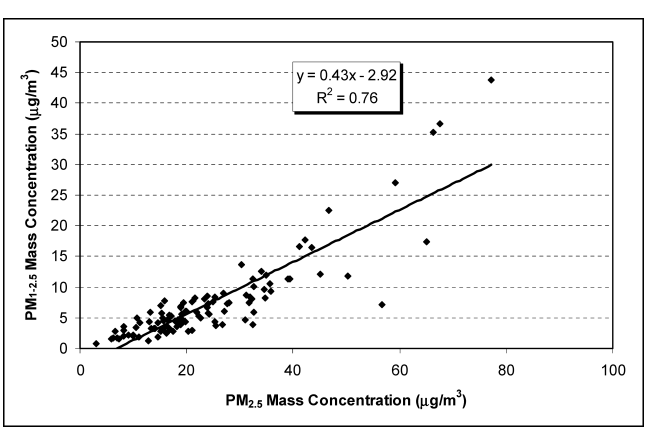

Figure 2. $PM_{1-2.5}$ vs. $PM_{2.5}$ at all sites.

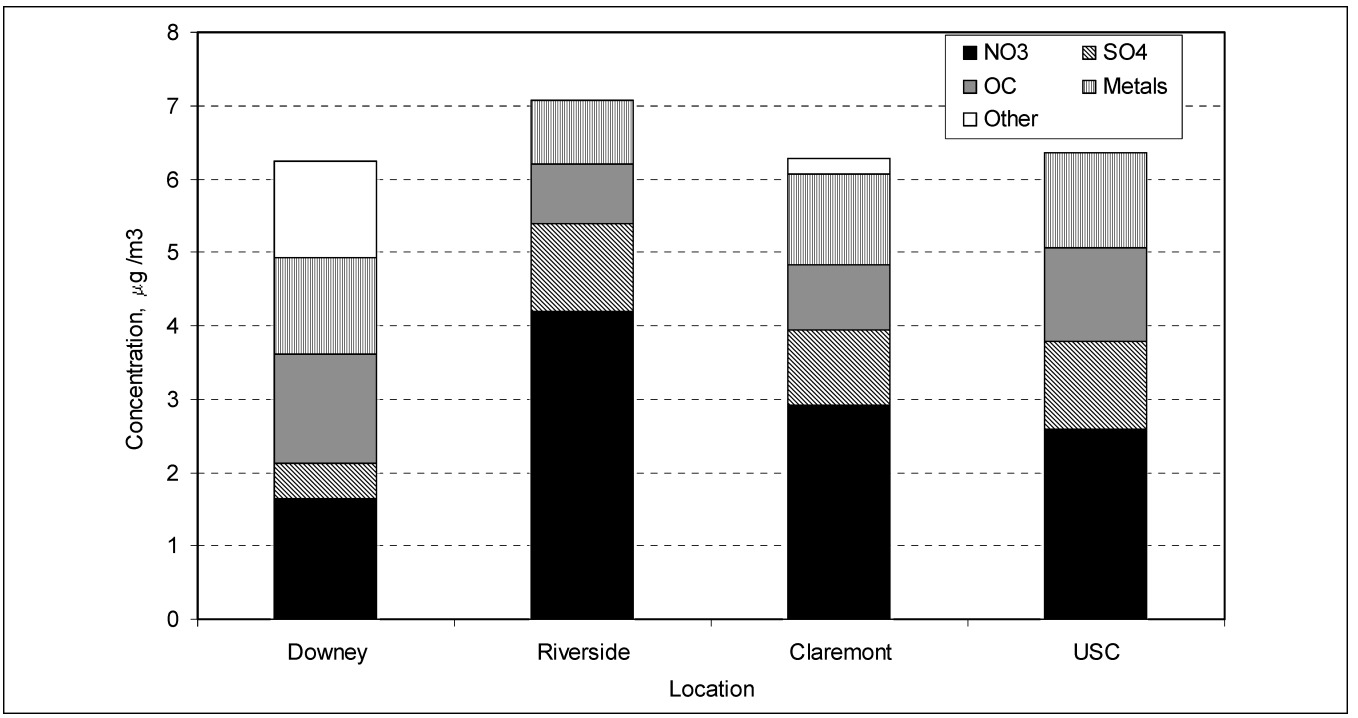

Figure 3. Chemical composition of intermodal PM averaged by location.

also not directly impacted by a freeway (unlike the Downey site), which would emit coarse particles in the form of road dust. Intermodal PM correlates moderately with PM_1, however, with an R^2 of 0.53 (Figure 4b). At a source site such as USC, this correlation is most likely driven by direct emission of both PM_1 and intermodal particles from the same automobile sources.

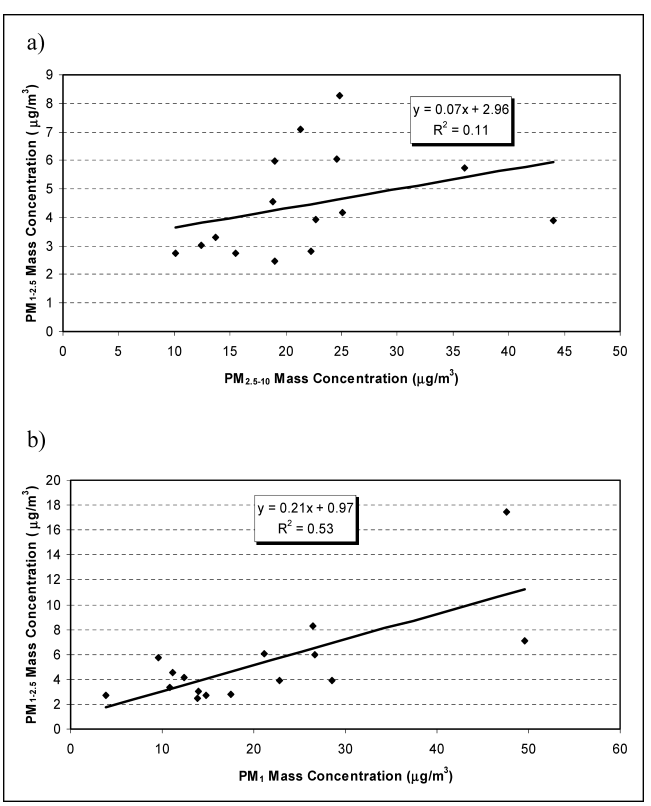

Figure 4. (a) Intermodal vs. coarse PM; (b) intermodal vs. PM_1 at USC.

The continuous data displayed in Figure 5a and b represent 2 weeks of intensive sampling at USC. Winter days are normally cool (~10 °C) and humid (>70%) in the mornings and dry (<40%) and temperate (~19 °C) in the afternoons. Figure 5a illustrates a week during early winter in which a Santa Ana wind event occurred from November 25 to November 29 and a rain event occurred from November 29 to December 1. From the graph, it is apparent that coarse mode concentrations increase and wind becomes erratic at the beginning of the week. Intermodal PM tracks the coarse mode during this time because Santa Ana winds blow crustal particles from the California deserts while creating hot and dry conditions that do not favor particulate growth. The drastic mass concentration drop in all size modes marks the arrival of the rainstorm. Figure 5b presents a more typical winter week in December 2002. Intermodal PM concentration tracks with both $PM_{2.5}$ and coarse concentrations. The continuous data do not show whether intermodal PM is more closely associated with coarse or fine PM during this week; all modes appear interrelated. For the week of December 2 to December 9, 2002, a correlation was performed between the continuous intermodal mass data and both the coarse and fine PM data. The resulting Pearson correlation coefficients (R values) were 0.35 and 0.64, respectively. This demonstrates the obvious correlation between

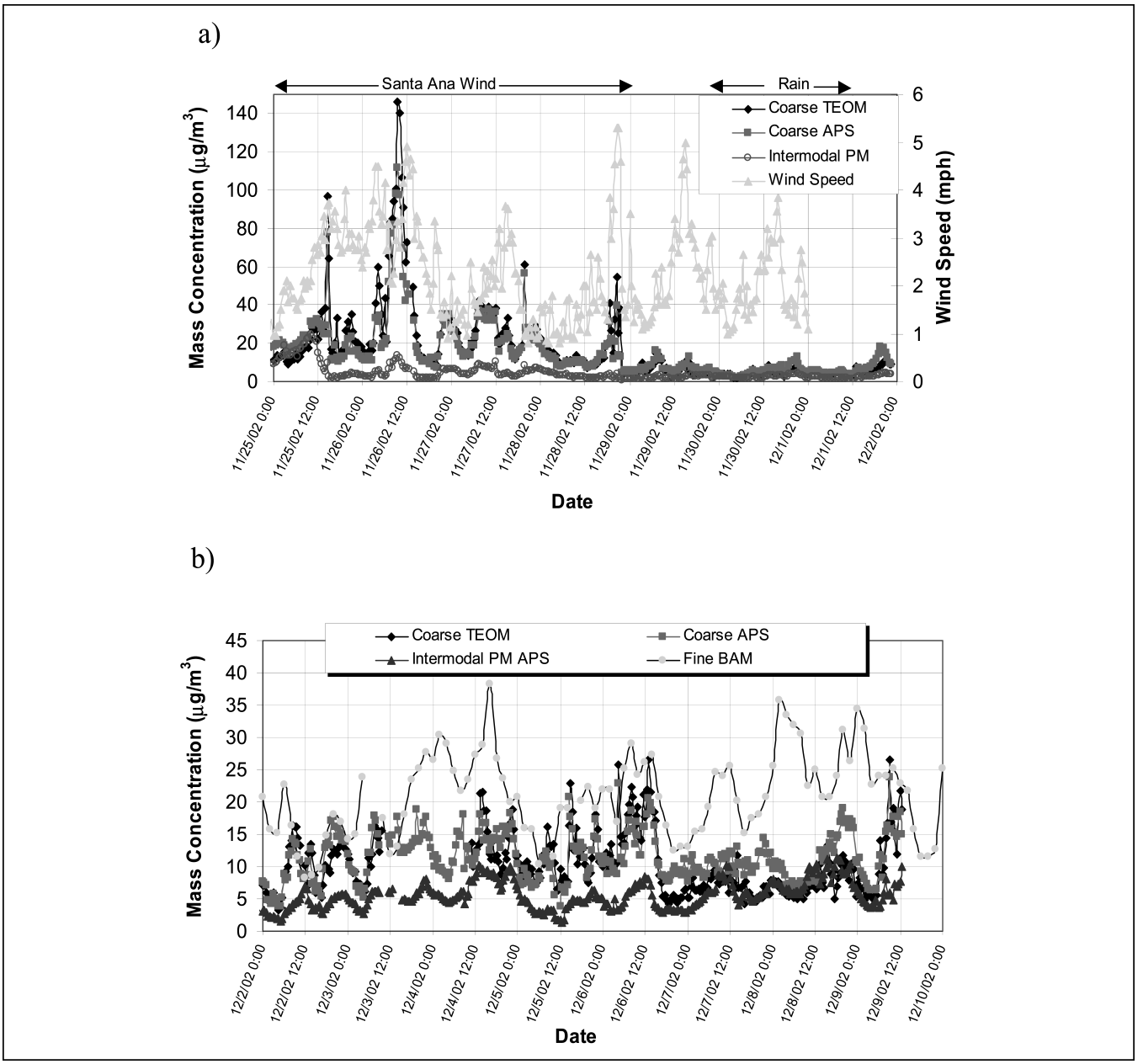

Figure 5. Coarse, intermodal, and fine PM mass concentrations at USC from (a) November 25 through December 1, 2002 and (b) December 5 through December 9, 2002.

intermodal and fine PM, whereas a much weaker one exists between the intermodal and coarse PM.

Downey. Figure 6a and b demonstrate the correlations between intermodal PM and both coarse and PM_1 mass concentrations, respectively. The correlations between intermodal PM and the other two modes are similar, with $R^2 = 0.49$ for intermodal coarse PM and $R^2 = 0.47$ for intermodal PM_1. A possible explanation for this finding is that the site is located downwind of a high-capacity freeway (I-710) with a large number of trucks and automobiles, which may be the dominant particle source at that site for particles of all ranges. Coarse particles in Downey are dominated by resuspended road and tire dust, whereas fine particles are a mixture of about 40% combustion emissions and 30% resuspended road and tire dust.[13] Moreover, this site is not near any source of crustal particles (i.e., all nearby surfaces are paved), so intermodal PM correlation with coarse PM is most likely driven by road dust, which is known to contain toxic compounds.[14]

Riverside. Intermodal PM is graphed versus coarse PM in Figure 7a. The R^2 of 0.14 is very surprising in this location because it is a rural site with local dust emissions. This result indicates that the tail of the coarse PM distribution is not significantly affecting intermodal concentrations

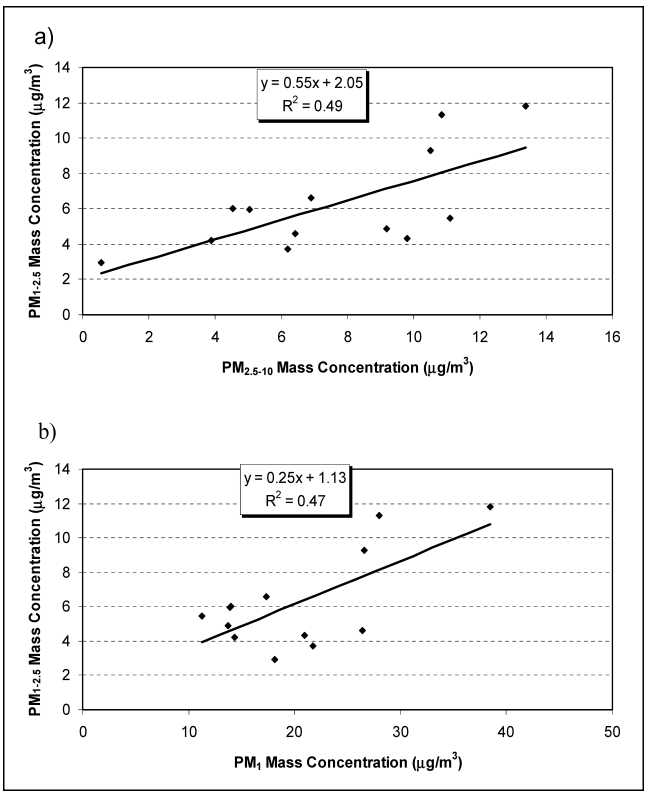

Figure 6. (a) Intermodal vs. coarse PM; (b) intermodal vs. PM_1 at Downey.

and thus fine PM concentrations. The relationship between intermodal PM and PM_1 is strong at this site (Figure 7b). The R^2 of 0.74 is significant and may be explained by condensational growth of particles less than 1 μm in diameter to particles between 1 and 2.5 μm in diameter. The submicrometer particles are emitted west of Riverside in the Los Angeles area and grow while advection transports them to Riverside. This process often occurs over hr time intervals of 6–12 hr.[15]

Although a linear correlation does provide a good fit, the data in Figure 7b appear to have an exponential trend. To explore this further, the data points for which chemical data were known were split into two regions. Group 1 (n = 5) included $PM_{1–2.5}$ concentrations less than 5 μg/m^3 and group 2 (n = 4) included those points in which $PM_{1–2.5}$ was greater than 5 μg/m^3. These groups were then statistically tested to determine whether their chemical compositions are significantly different based on the following three parameters: nitrate fraction, OC fraction, and sulfate fraction. The nonparametric Wilcoxon Rank Sum test was employed because of small sample size and assumed non-normality of the distribution. The results of this test showed that the median nitrate fraction of intermodal concentrations less than 5 μg/m^3 in Riverside is significantly lower than the median nitrate fraction of intermodal concentrations greater than 5 μg/m^3 (p < 0.01). This test also confirmed that median OC fraction of intermodal concentrations less than 5 μg/m^3 in Riverside is significantly higher than the median OC carbon fraction of intermodal concentrations greater than 5 μg/m^3 (p = 0.026). Median sulfate fraction was nearly significantly lower in group 1 than in group 2 (p = 0.111). These results reinforce our hypothesis that higher $PM_{1–2.5}$ concentrations are caused by increases in hygroscopic compounds such as nitrate and sulfate instead of the more hygrophobic OC.

Claremont. At first glance, an R^2 of 0.1 indicates that intermodal PM are not correlated with coarse mode PM (Figure 8a). However, the correlation increases to R^2 = 0.43 when all points with intermodal PM mass concentrations greater than 8 μg/m^3 are excluded, suggesting that there is some association between coarse and intermodal PM in that location, but the highest concentrations in the range of 1–2.5 μm are not associated with days during which coarse PM concentrations were high. This is counterintuitive to the argument that the tail of the coarse mode contributes to fine PM during times when high coarse concentrations are measured. Because Claremont is also a rural site, coarse PM would be expected to correlate with intermodal PM, but this is only true for relatively low coarse PM mass concentrations. Intermodal PM correlates well (R^2 = 0.65) with PM_1 without excluding high mass concentrations (Figure 8b).

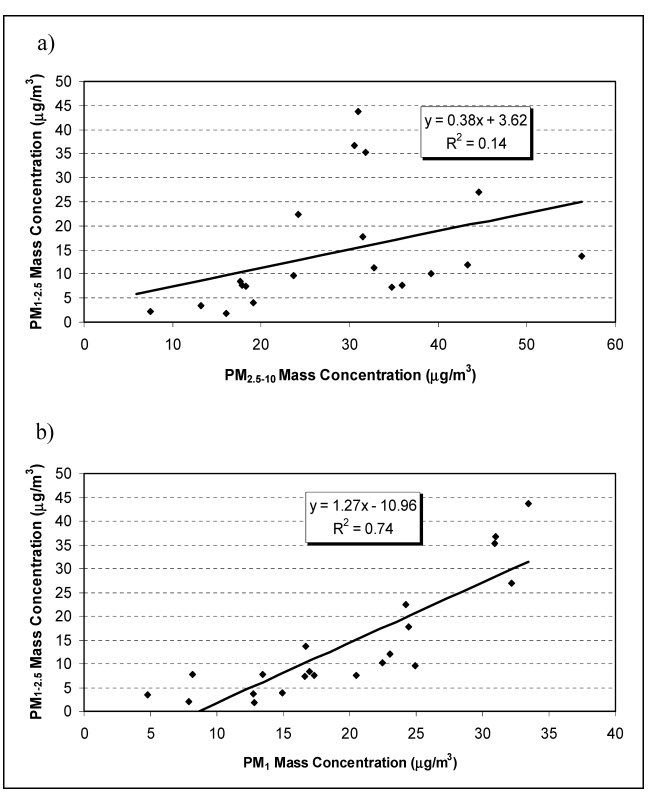

Figure 7. (a) Intermodal vs. coarse PM; (b) intermodal vs. PM_1 at Riverside/Rubidoux.

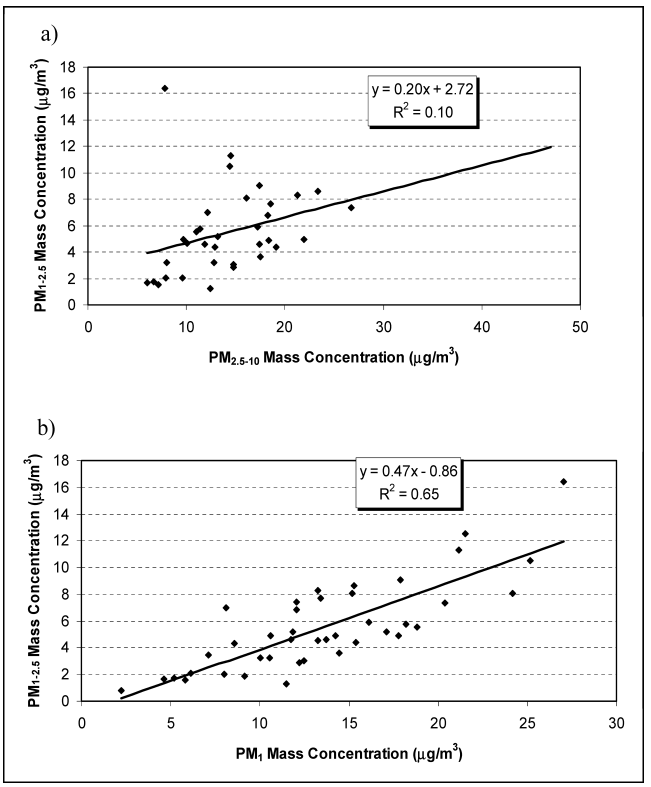

Figure 8. (a) Intermodal vs. coarse PM; (b) Intermodal vs. PM_1 at Claremont.

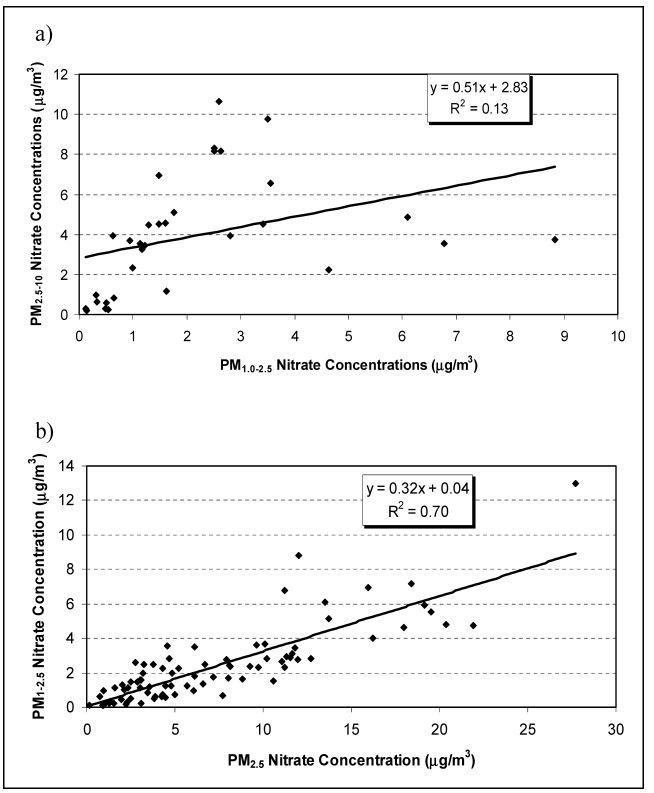

Figure 9. Nitrate mass concentrations at all sites. (a) $PM_{2.5-10}$ vs. $PM_{1-2.5}$; (b) $PM_{1-2.5}$ vs. $PM_{2.5}$.

Thus, at the receptor site Claremont, advection of fine PM outweighs the local coarse emissions with respect to contributions to intermodal PM.

Comparisons between PM Modes Based on Chemical Composition

Particulate nitrate is the predominant chemical constituent of the 1–2.5 μm range, accounting (with the exception of the Downey site) for about 40–65% of the total mass in that range (Figure 3). The relationship between coarse, intermodal, and fine PM was also investigated for this species. The correlation between coarse and intermodal nitrate is weak (R^2 = 0.13), which demonstrates the divergence of the sources of these particles (Figure 9a). Previous studies in Southern California indicated that coarse mode nitrate is a mixture of sodium and ammonium nitrate, whereas nitrate in the fine mode is mostly ammonium nitrate.[16] Figure 9b shows that intermodal nitrate is well correlated with $PM_{2.5}$ nitrate, with R^2 = 0.70, and it also comprises a substantial fraction of $PM_{2.5}$ nitrate (indicated by the regression line slope of 0.32). A similarly high degree of correlation between continuously measured intermodal nitrate and PM_1 nitrate (R^2 = 0.80) is shown in Figure 10, using the data generated by the Cascaded ADI Continuous Nitrate Monitor.[9] These two figures confirm that $PM_{1-2.5}$ nitrate is a significant portion of total $PM_{2.5}$ bound nitrate, probably originating from the submicrometer range by condensational growth. The exact mechanism through which accumulation mode PM grows to the micrometer range—including aqueous phase reactions[17] as well as activation of sub-0.5-μm particles to form fog or cloud droplets, followed by aqueous phase chemistry and fog evaporation[18]—has been debated in several previous publications. Growth of hygroscopic ambient PM beyond the 1-μm range has been observed in several other studies,[19,20] when relative humidities reached greater than 90%.

The period between April and August in the Los Angeles Basin is characterized by frequent fog-like conditions with high relative humidities in the overnight and

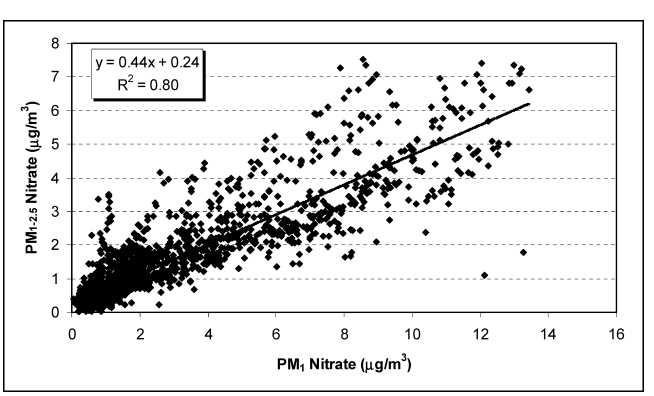

Figure 10. Continuous $PM_{1-2.5}$ vs. PM_1 nitrate at Claremont, CA, in September 2001.

early morning hours. Particles emitted mostly to the west travel by advection eastwards towards the inland valleys of the basin, such as Claremont. While in transit, these particles experience condensational growth and participate in photochemical reactions. Some particles remain in the submicrometer range after growth, whereas others become intermodal particles. This process takes place over multihour time spans, whereby PM_1 particles may grow into $PM_{1-2.5}$ after several hours of advection and stagnation. Growth of submicrometer nitrate into the supermicrometer range is also supported by previous studies showing very similar chemical composition between PM_1 and $PM_{1-2.5}$.[11,16,21]

A previous study identified sea salt and sea salt reaction products as a major component of the intermodal (1–2.5 μm size) mass in Riverside.[27] That study was conducted from April through May 1995. To investigate the possibility that a portion of the intermodal mass may be mostly sea salt (which should be excluded from the indicator for a fine particle standard), the 24 hr averaged concentrations of nitrate and sodium in the 1–2.5 μm range were correlated for the receptor sites of Riverside and Claremont, for which the conversion of sea salt to sodium nitrate would be more pronounced. The resulting coefficients of statistical determination (R^2) between sodium and nitrate concentrations were 0 and 0.16 for Riverside and Claremont, respectively, thereby confirming that the majority of nitrate in the size range of 1–2.5 μm is not associated with sodium nitrate. Moreover, the average nitrate-to-sodium concentrations ratio was 87.3 (± 26.1) and 60.7 (± 25.7) for Riverside and Claremont, respectively, and hence much higher than the stoichiometric concentration ratio of 2.82 for these species. Our results are also consistent with previous intensive sampling campaigns in the areas of Claremont and Riverside,[12,17] which showed that the concentrations of particle-bound ammonium were at least 1 order of magnitude higher than those of sodium for PM in the 1–2.5 μm range, thereby supporting the argument that nitrate in this size range is mostly ammonium and not sodium nitrate.

The data plotted in Figure 11 further support the argument that intermodal nitrate originates from fine and not coarse PM. Whereas wind speed peaks at 3 PM, the ratio of intermodal to PM_1 nitrate peaks at 6 PM. The Claremont site is surrounded by many large unpaved areas and gravel pits. If the wind were creating resuspension of local coarse particles that were in turn affecting intermodal nitrate PM concentrations, wind speed would peak concurrently with PM nitrate concentration. Advection, however, would be represented by the time lag seen here. After wind speed peaks, intermodal PM nitrate particles that have been undergoing photochemistry and growth

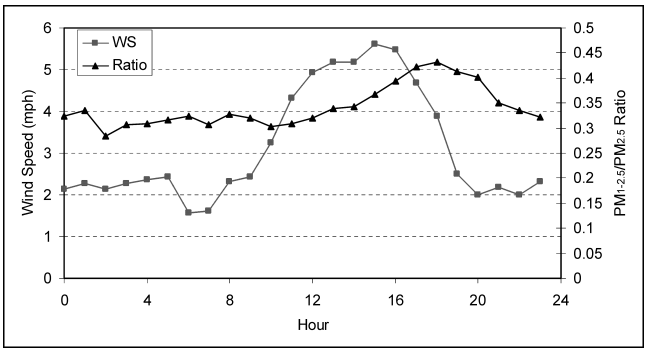

Figure 11. Daily wind speed and $PM_{1-2.5}/PM_{2.5}$ nitrate at Claremont, CA, in September 2001.

blow toward Claremont and peak shortly thereafter. Figure 12 also illustrates the photochemical growth and advection of intermodal PM in the Los Angeles Basin. The mass concentration ratio of intermodal to fine mode PM in all sites (based on time-integrated data) increases during the summer months because of increased solar radiation and enhanced advection.

Figure 13a and b shows the OC and sulfate concentrations versus nitrate concentrations for the PM range of 1–2.5 μm in source and receptors sites, respectively. Nitrate and sulfate are correlated for this size range in source sites (R^2 = 0.63), whereas OC concentrations are poorly correlated with nitrate concentrations (R^2 = 0.14). This suggest that even in the source sites, nitrate and sulfate in the intermodal PM range share a common origin, that is, secondary formation and growth by condensation into the supermicrometer range, whereas OC in that range most likely originates from traffic road dust (the correlation between OC concentrations in the size ranges of 1–2.5 μm and 2.5–10 μm yielded R^2 = 0.61. A similar correlation between these two OC modes in receptor sites yielded R^2 = 0.21, suggesting that the presence of OC in that range is not caused by road dust in receptor areas). The sulfate and nitrate concentrations of the PM range of 1–2.5 μm in receptor sites are very well correlated (R^2 = 0.77), whereas moderate correlations (R^2 = 0.51) were also observed between the nitrate and OC concentrations. These results are consistent with the findings of John et al.[22] that nitrate and sulfate are uniformly mixed in the so-called "droplet" mode, defined as one containing accumulation mode PM exceeding about 0.5–0.7 μm in diameter. Whether organics are externally or internally mixed is not clear from our data. However, Pandis et al.[23] showed that organics in the larger size range of the accumulation mode can result only if there exist sufficient primary particles in the >0.5-μm range and/or if the condensable organic species have a strong affinity for that size range. The former condition is consistent with our field data of several years in the Los Angeles Basin, showing that the aerosol size distribution in receptor areas of

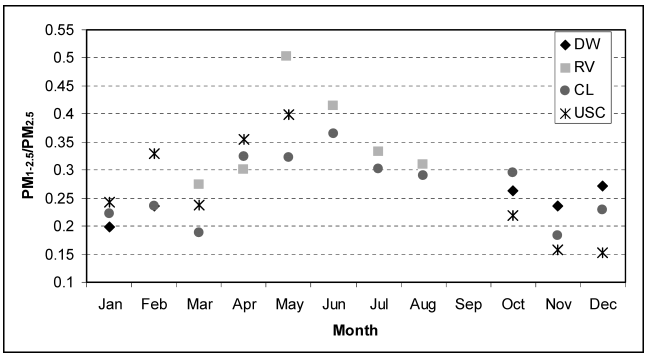

Figure 12. Monthly average of the ratio of intermodal PM to total $PM_{2.5}$.

this basin contains a much larger number of particles in the larger size range of the accumulation mode compared with source sites,[24,25] as a result of aerosol aging in the atmosphere caused by advection and long-range transport. The existence of a pronounced inorganic "droplet" mode, which possibly extends beyond the 1-μm range, will likely influence the presence of organics in that range through condensation, given that at least some portion of OC is soluble.[18]

Figure 14 displays the relationship between coarse and intermodal crustal metal concentrations. The crustal metal concentrations were obtained by analyzing MOUDI Teflon substrates via X-ray fluorescence (XRF) and using the following formula:[26]

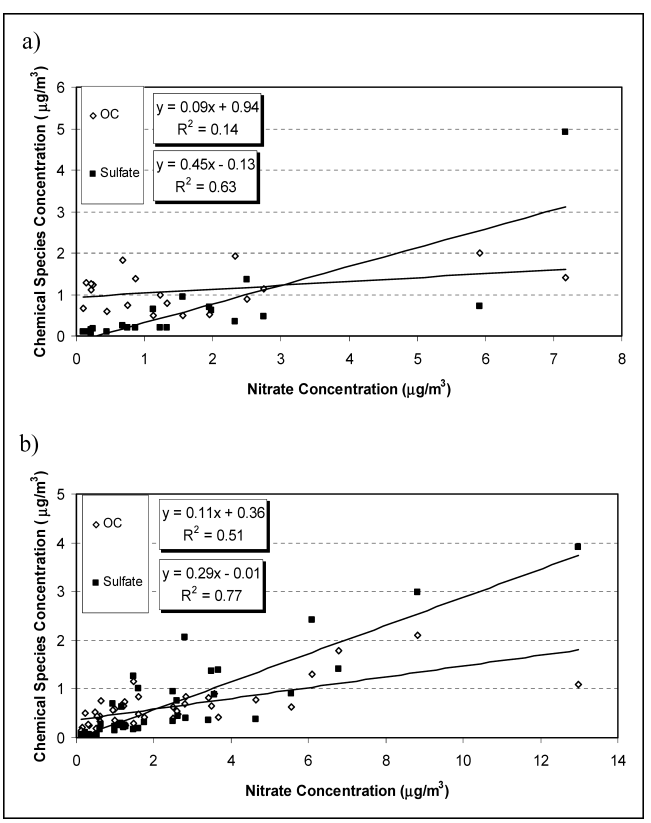

Figure 13. OC and sulfate vs. nitrate concentration in the range of 1–2.5 μm at (a) source sites and (b) receptor sites.

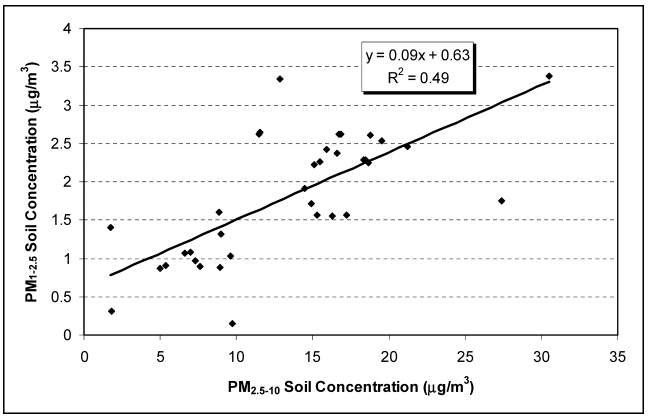

Figure 14. Intermodal vs. coarse PM crustal elements for Claremont, CA.

$$PM_{\text{soil}} = 2.2 * Al + 2.49 * Si + 1.63 * Ca + 2.42 * Fe + 1.94 * Ti \quad (1)$$

The moderate correlation ($R^2 = 0.49$) between intermodal and coarse crustal metals is expected because the tail of the coarse mode crustals infiltrates $PM_{2.5}$ to a limited extent, which is indicated by the rather low concentrations of crustal metals found in intermodal PM. The relationship between intermodal PM mass to its soil (crustal) component is shown in Figure 15. As evident by the slope of 3.42, the soil component of $PM_{1-2.5}$ is less than 25% of the total mass and has a moderate correlation with total mass ($R^2 = 0.54$). This result differs from the study of Kegler et al.[4] in which they found a similar correlation between intermodal mass and soil concentrations, but with a much higher slope. The crustal component in Spokane, WA, is closer to 50% of the total intermodal mass, which is to be expected in a city that is surrounded by rural areas. Although the contribution of crustal metals to the intermodal PM mass is not negligible, it is far lower than that of nitrate, as illustrated in Figure 3. This may also explain the overall low correlation between the intermodal and coarse PM concentrations obtained in our study.

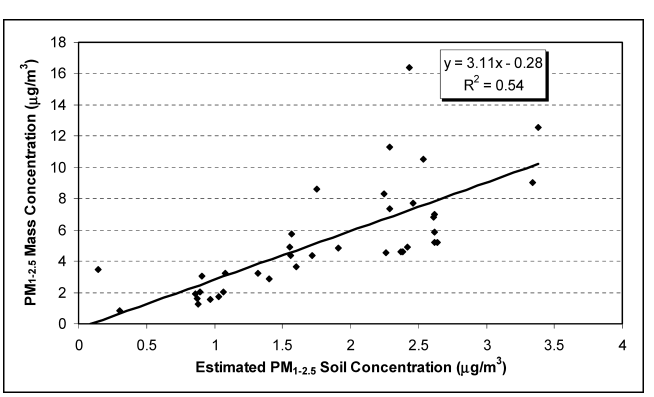

Figure 15. $PM_{1-2.5}$ vs. estimated $PM_{1-2.5}$ soil concentration.

Figure 16 displays the lack of correlation between the most prominent chemical species that comprise intermodal PM and the crustal metals found in that mode. Whereas nitrate, sulfatem, and (at least in receptor sites) OC correlate well with one another, none correlate with the crustal component. Although the crustal component of intermodal PM is moderately correlated with the intermodal mass (Figure 15), the majority of the mass, consisting of nitrate, sulfate, and OC, does not correlate with the crustal component and is chemically more similar to particles in the PM_1 range.

CONCLUSIONS

Although previous research does suggest a relationship between coarse mode and intermodal PM, the sites in which these studies were conducted are not representative of all locations. Similar data for coarse, intermodal, and fine PM were collected across four sites in the Los Angeles Basin. This study included a large database of time-integrated samples spanning nearly 3 years and complementary continuous measurements during intensive campaigns.

Although some similarities exist between these results and those of comparable studies, the main finding established here is that intermodal PM consists of a significant portion of particles that are similar in chemical composition to smaller particles that are thought to cause the greatest health effects. In general, some fraction of intermodal PM originates from the lower size range "tail" of the coarse PM size distribution. In Los Angeles, however, that correlation is not as strong as the one between PM_1 and intermodal PM. Even the rural locations in this study demonstrated high correlations between PM_1 and intermodal PM, which validates the strength of the $PM_{2.5}$ standard for locations that have both a crustal source and advected aerosol from an urban area upwind.

The receptor sites in this study showed a peak in the ratio between intermodal nitrate and fine nitrate in the early evening, which was 3 hr after the peak wind speed, indicating advection of particulate nitrate from upwind sources and growth into the intermodal size range. Overall, intermodal nitrate correlated very well with both PM_1 and $PM_{2.5}$ nitrate, signifying its strong relationship to the fine mode. Intermodal sulfate and nitrate demonstrated similar correlations and were also correlated with each other and OC in receptor sites. Intermodal crustal material did not correlate with any other chemical constituent.

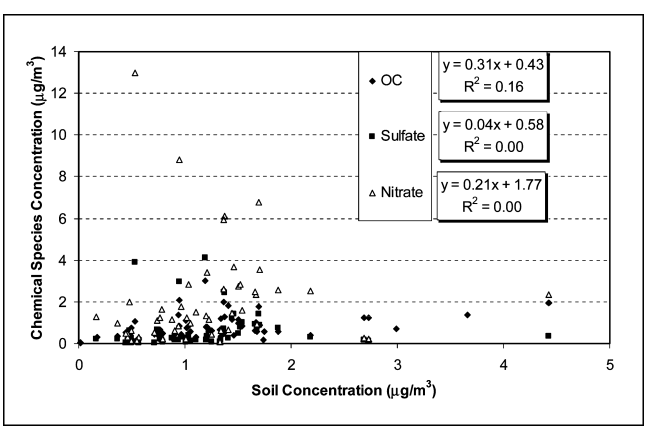

Figure 16. OC, nitrate, and sulfate concentrations vs. soil concentration in intermodal PM.

This study was performed to shed light on the origin and chemical composition of intermodal particles between the coarse and fine PM modes in Los Angeles, a unique city where crustal, oceanic, anthropogenic primary, and secondary sources are responsible for the high observed PM levels. Our results indicate that a PM_1 standard would not constitute an unambiguous separation of coarse and fine mode PM in this urban air shed. Further studies at various locations are warranted, especially at sites in areas of the eastern United States where air parcels are advected across much larger distances than those in Los Angeles, to determine the degree to which the promulgation of a PM_1 standard would be justifiable.

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