

Evolution of Nitrogen Species Air Pollutants along Trajectories Crossing the Los Angeles Area

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Ambient aerosol sampling was conducted in Diamond Bar, Mira Loma, and Riverside, CA, to observe at close range the effects of ammonia emissions on air quality. These sites are located upwind, within, and downwind, respectively, of the Chino dairy area, the largest single source of ammonia emissions in the Los Angeles area. Inertial impactors and bulk filter samplers provided 4–7-h measurements of aerosol chemical composition and size distribution. Daily average fine particle mass concentrations were in the range 22.4–143.0 $\mu\text{g m}^{-3}$. On some days the fine particulate matter concentrations were more than two times greater than the proposed 24-h Federal standard of 65 $\mu\text{g m}^{-3}$. Ammonium nitrate was the largest component of fine particle mass at all three sites; 24-h average fine particulate ammonium plus nitrate concentrations ranged from 11.7 to 75.4 $\mu\text{g m}^{-3}$. A single air mass was studied as it passed the Diamond Bar air monitoring site in the morning and stagnated near Mira Loma in the evening of the same day. Between these two sites NO was oxidized to NO₂, and the ammonia concentration increased by a factor of 5. A second air parcel trajectory, which stagnated near Mira Loma during the early morning and passed near the Riverside site approximately 24 h later, showed a decrease in ammonia concentration over time that is consistent with dilution as the air mass moved downwind from the source of ammonia in the dairy area. Particulate NH₄NO₃ concentration in that air parcel remained approximately constant over time, consistent with a continued excess of NH₃ relative to HNO₃ downwind of the dairy area.

Introduction

In the autumn of 1997 a field experiment was conducted in conjunction with the 1997 Southern California Ozone Study

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(SCOS97) (1–3) in which a network of three air monitoring stations was established, with the purpose of determining the size and chemical composition of the airborne particle population in an area having high secondary ammonium nitrate aerosol formation. Measurements were made of the particle size distribution, fine particulate matter (PM_{1.9} particulate matter with aerodynamic diameter, $D_{a} < 1.9 \mu\text{m}$) and PM₁₀ ($D_{a} < 10 \mu\text{m}$) chemical composition, and chemical composition segregated into narrow particle size intervals. Air monitoring locations were chosen along a seasonally typical wind trajectory that crosses an agricultural area located to the east of Los Angeles, CA, that has significant ammonia emissions due to livestock husbandry operations and fertilizer use (4). The intent was to first observe air parcels at the leading edge of the ammonia source area and to subsequently observe the same air parcels after they have been carried downwind through the source area. This sampling scheme was designed to provide data on the evolution over time of the ambient aerosol chemical composition at the bulk and size-segregated levels as those particles are potentially altered by gas-to-particle conversion processes and affected by continuing emissions, dilution, and dry deposition.

Several studies of nitrate-containing particle evolution using multiple observation points along a single air parcel trajectory have been conducted previously in the Los Angeles area. In a 1982 field study, gas- and particle-phase nitrogen species were sampled from a single air parcel which passed over or near three monitoring sites in succession: Long Beach, Anaheim, and Rubidoux, CA, providing insight into the process of aerosol nitrate formation and the inter-relationship between gas-phase HNO₃ and NH₃ versus particulate NH₄NO₃ (5–7). Measurements made at that time showed that the aerosol nitrate behaved as would be expected from analyses based on thermodynamic equilibrium between the gas and particle phases and verified the presence of a large ammonia source located in the agricultural and dairy area between Anaheim and Rubidoux leading to large aerosol nitrate concentrations in the Riverside (Rubidoux) area.

In 1996, a similarly designed field study was conducted using more advanced instrumentation. Aerosol sampling instruments, including samplers for fine and total suspended particulate matter chemical composition, size-segregated particulate matter chemical composition, and single particle size and composition measurements, were used to obtain information about the evolution of the aerosol as particles aged in the presence of significant aerosol nitrate formation as well as continuing emissions (8, 9). Two air parcel trajectories were identified which passed over or near three or four air monitoring stations along the Santa Catalina Island–Long Beach–Fullerton–Riverside pollutant transport corridor (9). Notable in the results of this study was the observation of large increases in particulate ammonium and nitrate concentrations between Fullerton and Riverside in air parcels which stagnated overnight in the area of large livestock and agricultural ammonia sources just west of Riverside. The data taken along air parcel trajectories was specifically designed for use in verifying a source-oriented aerosol processes trajectory model (10). The present study differs from previous work in that air monitoring stations are placed just upwind of and directly within the Chino dairy area in order to observe the effect of a major source of ammonia emissions at close range. These data will be used to examine dynamic behavior of the aerosol within the air parcels sampled during the present experiment. These data may be used to evaluate the performance of advanced air

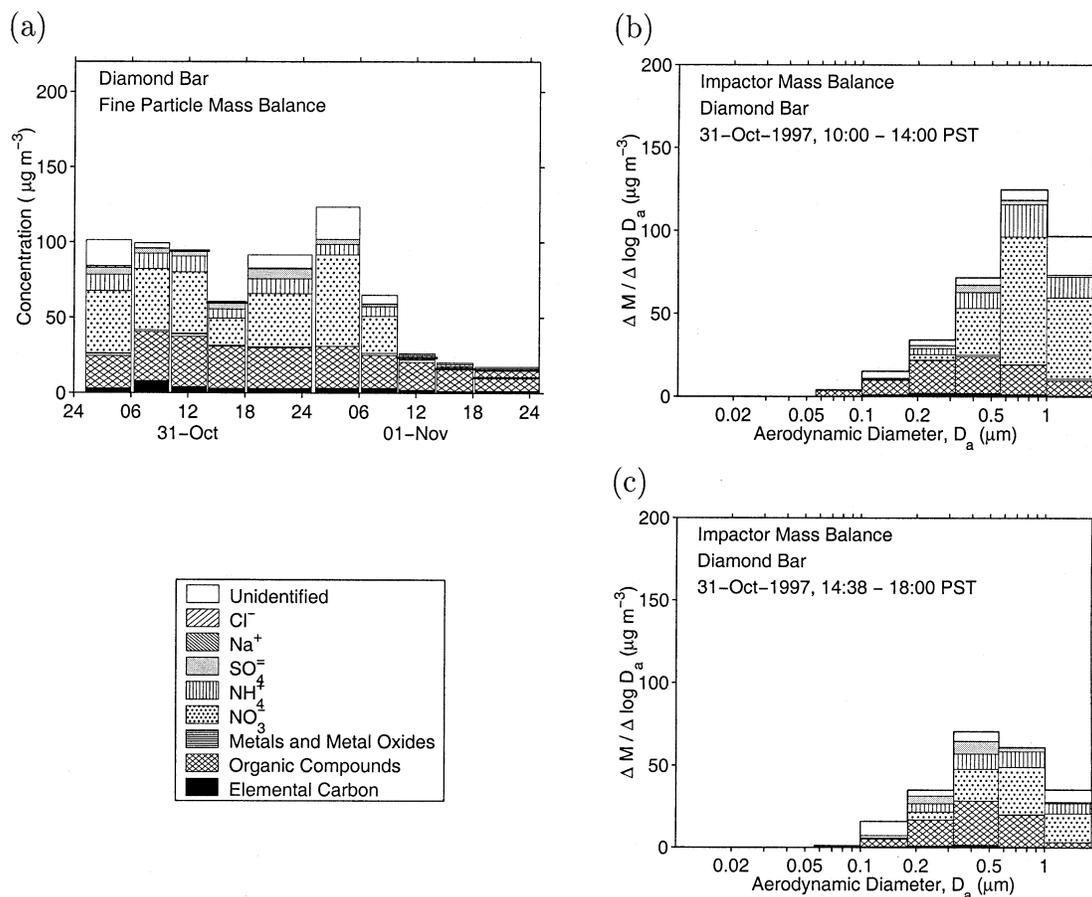


FIGURE 1. Fine particle concentration and chemical composition at Diamond Bar. (a) Bulk fine particle concentrations and chemical compositions measured during the October 31–November 1, 1997, sampling event. (b) Size-resolved fine particle mass distribution and chemical composition measured on October 31, 1997, 10:00–14:00 PST. (c) Size-resolved fine particle mass distribution and chemical composition measured on October 31, 1997, 14:38–18:00 PST.

quality models during the formation of aerosol ammonium and nitrate.

Experimental Methods

Sample Collection and Analysis. Three urban air monitoring stations were established in the Los Angeles metropolitan area to measure the effect of nitrogen species emissions on ambient particulate matter concentrations. These sites were located in Diamond Bar, Mira Loma, and Riverside, CA. The three sites were chosen because they are located along a seasonally typical wind path across the South Coast Air Basin. This allows the possibility of successive sampling of the same air parcels at multiple locations as they are transported downwind. In addition, the area traversed by an air parcel advected between two or more of these sites is exposed to substantial agricultural and livestock ammonia sources (4).

Sampling was conducted at all three sites during one 48-h period on October 31–November 1, 1997. Fine particle and PM_{10} samples for mass and chemical composition determination were collected sequentially on a 5-sample per day schedule, and a pair of micro-orifice impactors (MOIs) were operated at each site for one or two of these time periods each day.

Three filter sampling systems were used to collect particles at each air monitoring station: one to collect PM_{10} samples and two to collect fine particle samples. The PM_{10} and fine particle samplers were used to collect consecutive short time average samples for bulk and elemental analysis. Five complete sets of filter samples were collected each day on the following schedule: 0120–0600 h, 0620–1000 h, 1020–1400 h, 1420–1800 h, 1820–0100 h (the following day). All

times in the study were recorded in the local time system, Pacific Standard Time (PST). The sampling schedule provides relatively fine temporal resolution data for investigation of atmospheric processes and comparison with future air quality modeling results. In addition, a pair of MOIs (MSP Corp., Model 110) was used at each site to collect particles in the aerodynamic diameter range $0.056 < D_a < 1.8 \mu\text{m}$, in six size intervals during one or two 4-h sampling periods each day.

The impactors, filter samplers, and sample analysis methods are identical to those used in a companion study and are described in detail in Allen et al. (11, 12). Impactor substrates and filter samples were analyzed for mass gravimetrically, for Cl^- , NO_3^- , and SO_4^{2-} by ion chromatography (13), for NH_4^+ by indophenol colorimetry (14), for elemental black carbon and organic carbon by thermal evolution and combustion analysis (15, 16), and for 36 trace elements by neutron activation analysis (17). HNO_3 was measured using the denuder difference method (18). Gas-phase NH_3 was detected as NH_4^+ collected on oxalic acid-impregnated glass fiber filters used downstream of a polytetrafluoroethylene (PTFE) prefilter. Fine particulate mass, nitrate and ammonium ion measurements made using PTFE filters were corrected for volatilization losses of fine particulate NH_4NO_3 during sampling. A factor of 1.4 was applied to measured organic carbon concentrations to convert these measurements to an estimate of organic compound concentrations. This scale factor accounts for the additional mass of associated H, O, N, and S present in the organic matter of typical atmospheric organic aerosols (19).

The sum of aerosol mass measured on the impactor stages is generally about 25% lower than that collected on the fine

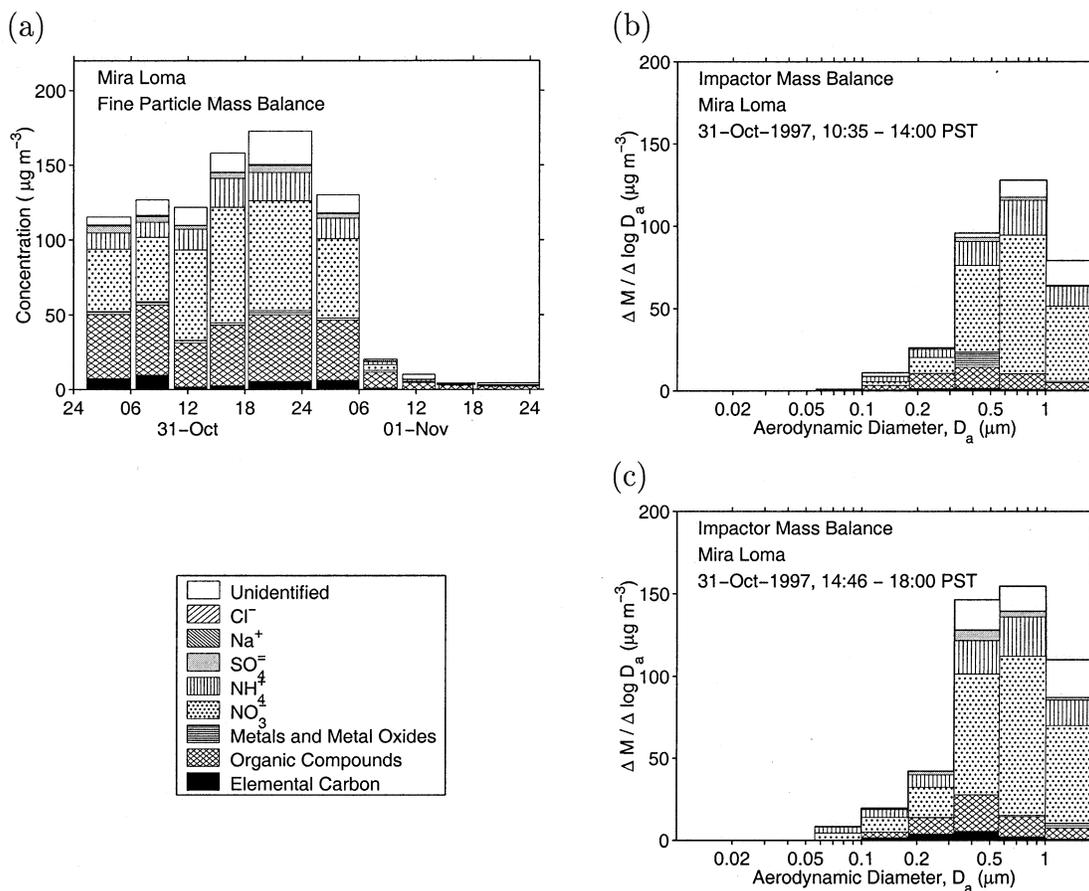


FIGURE 2. Fine particle concentration and chemical composition at Mira Loma. (a) Bulk fine particle concentrations and chemical compositions measured during the October 31–November 1, 1997, sampling event. (b) Size-resolved fine particle concentrations and chemical composition measured on October 31, 1997, 10:35–14:00 PST. (c) Size-resolved fine particle concentrations and chemical composition measured on October 31, 1997, 14:46–18:00 PST.

TABLE 1. Temperature and Relative Humidity Ranges for Sampling Sites during the October 31–November 1, 1997, Sampling Event

site	temp range °C	RH range %
Diamond Bar	11.5–34.8	12–78
Mira Loma	8.5–34.8	10–85
Riverside	12.4–33.3	26–62

particle filters. Comparisons of individual analytes demonstrated that for NH_4^+ and SO_4^{2-} , the sum of aerosol mass on the impactor stages agreed with that on the fine particle filters within the error of measurement. For NO_3^- , sum of aerosol mass on the impactor stages agreed with fine particle filter measurements within 10%. In contrast, the sum of organic matter on the impactor stages was approximately one-half of that on the fine particle filters. The filter organic matter measurement may be artificially high due to the sorption of gas-phase species on the quartz fiber filters; the impactor organic matter measurements may also be artificially low due to the volatilization of collected organics from impaction deposits during sampling. Another cause for this difference is that the quartz impactor afterfilters, which collect particles smaller than $0.056 \mu\text{m}$, could not be analyzed gravimetrically.

Meteorology. Wind fields over the South Coast Air Basin were reconstructed over a $5 \text{ km} \times 5 \text{ km}$ grid system superimposed over the airshed for each hour during the study using the method of Goodin et al. (20), based on hourly averaged wind speed and direction measurements at 28

meteorological stations maintained by the South Coast Air Quality Management District (SCAQMD). From the wind fields, back trajectories from the sampling sites were calculated, establishing the time and location history of the air parcels arriving at the sampling sites.

Temperature and relative humidity ranges for the three sampling sites during the October 31–November 1 sampling episode are presented in Table 1. Air stagnation occurred at Diamond Bar beginning at about 1700 PST in the evening each day until about 1300 PST the afternoon of the following day. Mornings were hazy, and the haze cleared in the afternoon of November 1. Air stagnation occurred at Mira Loma on the evening of October 31 at about 1700 PST, lasting until about 0600 PST the following morning. Mornings were hazy and misty; the afternoon of October 31 was hazy, but conditions cleared beginning early in the morning of November 1. Air stagnation occurred at Riverside on the evening of October 31 at about 1700 PST and lasted until about 0700 PST the following morning. October 31 was hazy, but November 1 was clear from the early morning on. None of the three sites had significant cloud cover at any time during sampling, and air quality cleared significantly at all three sites beginning on the morning or early afternoon of November 1 and lasted through the rest of that day.

Results and Discussion

October 31–November 1, 1997, Sampling Event. On Friday, October 31, all three sites had periods of relatively high pollutant concentrations. All three sites experienced drastic reductions in particle concentrations beginning in the morning of November 1 and lasting for the rest of that day.

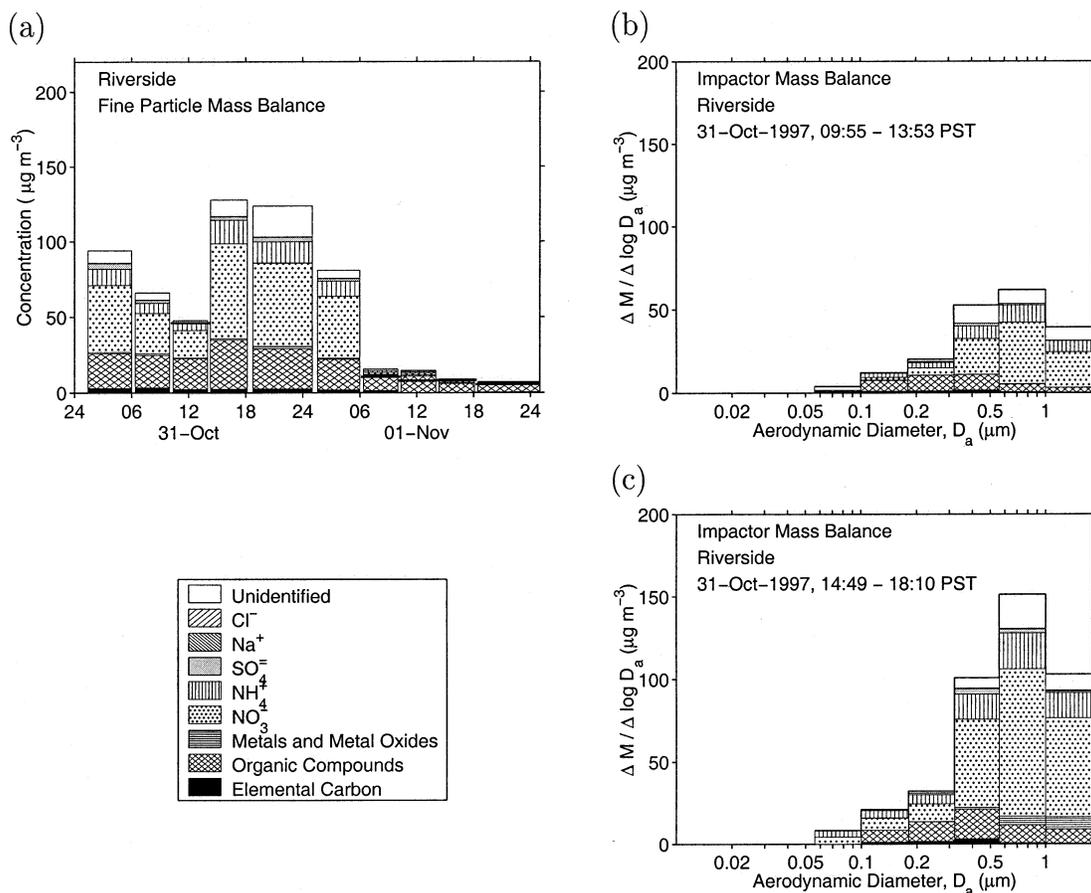


FIGURE 3. Fine particle concentration and chemical composition at Riverside. (a) Bulk fine particle concentrations and chemical compositions measured during the October 31–November 1, 1997, sampling event. (b) Size-resolved fine mass distribution and chemical composition measured on October 31, 1997, 09:55–13:53 PST. (c) Size-resolved fine mass distribution and chemical composition measured on October 31, 1997, 14:49–18:10 PST.

Changing wind patterns account for the sudden change in conditions. During the period of clean air at the end of the day on November 1, incoming air parcels at Mira Loma and Riverside approached from the mountains to the north and northeast instead of from urban and agricultural areas to the west.

Figure 1a shows the time series of fine particulate matter concentrations and chemical compositions measured at Diamond Bar over the October 31–November 1, 1997, sampling period. In this plot as well as in mass balance presentations in Figures 1, 2, 3, 5, and 6, “Metals and Metal Oxides” refers to the sum of trace elements measured by neutron activation analysis, with elemental concentrations converted to the equivalent concentrations of their most common oxides, where appropriate (11). The designation “Unidentified” applies to the difference between mass concentration determined gravimetrically and the sum of species concentrations identified by chemical analysis methods. Silicates and calcium-containing mineral matter are among the materials not detected by the methods used in the present study, and these may be included in the unidentified matter. While samples were equilibrated and weighed in an environment with low relative humidity, some water may have been retained in the samples despite desiccation.

Fine particulate mass, NO_3^- , and NH_4^+ concentrations were essentially constant for the first half of the day on October 31. These concentrations are relatively high; fine particle mass averaged $98.6 \pm 1.7 \mu\text{g m}^{-3}$, of which $40.8 \pm 0.7 \mu\text{g m}^{-3}$ was particulate NO_3^- and $10.5 \pm 0.2 \mu\text{g m}^{-3}$ was particulate NH_4^+ . By comparison, the recently proposed

Federal $\text{PM}_{2.5}$ air quality standard limits 24-h average fine particle concentrations to not more than $65 \mu\text{g m}^{-3}$ and annual average $\text{PM}_{2.5}$ concentrations to not more than $15 \mu\text{g m}^{-3}$. The air parcels reaching Diamond Bar during this night and morning period of low-to-stagnant wind speeds approached Diamond Bar from the northeast during a condition of mild off-shore wind flow after having crossed the Pacific Coast along the Santa Monica Bay 2–3 days earlier (see Figure 5a). The air mass stagnating overnight at Diamond Bar in this case already contained high particulate ammonium nitrate concentrations. In contrast, air parcels arriving during the 1400–1800 time period were transported by on-shore winds after stagnating only once overnight near Fullerton; these air parcels were over the urban area for a much shorter time, and there are minimums in the particulate NO_3^- , NH_4^+ , and fine mass concentrations accordingly. The fine particulate elemental carbon concentration increased by more than a factor of 2.5 during the 0600–1000 PST morning traffic peak period on October 31 when compared to the previous time period. This 0600–1000 PST peak in EC concentrations did not occur on Saturday, November 1, reflecting the differences between weekday and weekend traffic patterns.

Figures 1b and 1c show the size-segregated mass distribution and chemical composition of the fine particulate matter at Diamond Bar during the two sampling periods 1000–1400 PST and 1438–1800 PST on October 31, 1997. The particle size distribution data show that aerosol nitrate accumulation occurred primarily on particles larger than $0.3 \mu\text{m}$ aerodynamic diameter. The air sampled during the 1000–1400 PST time period stagnated overnight in and to the northeast of the Diamond Bar area; the air sampled in the

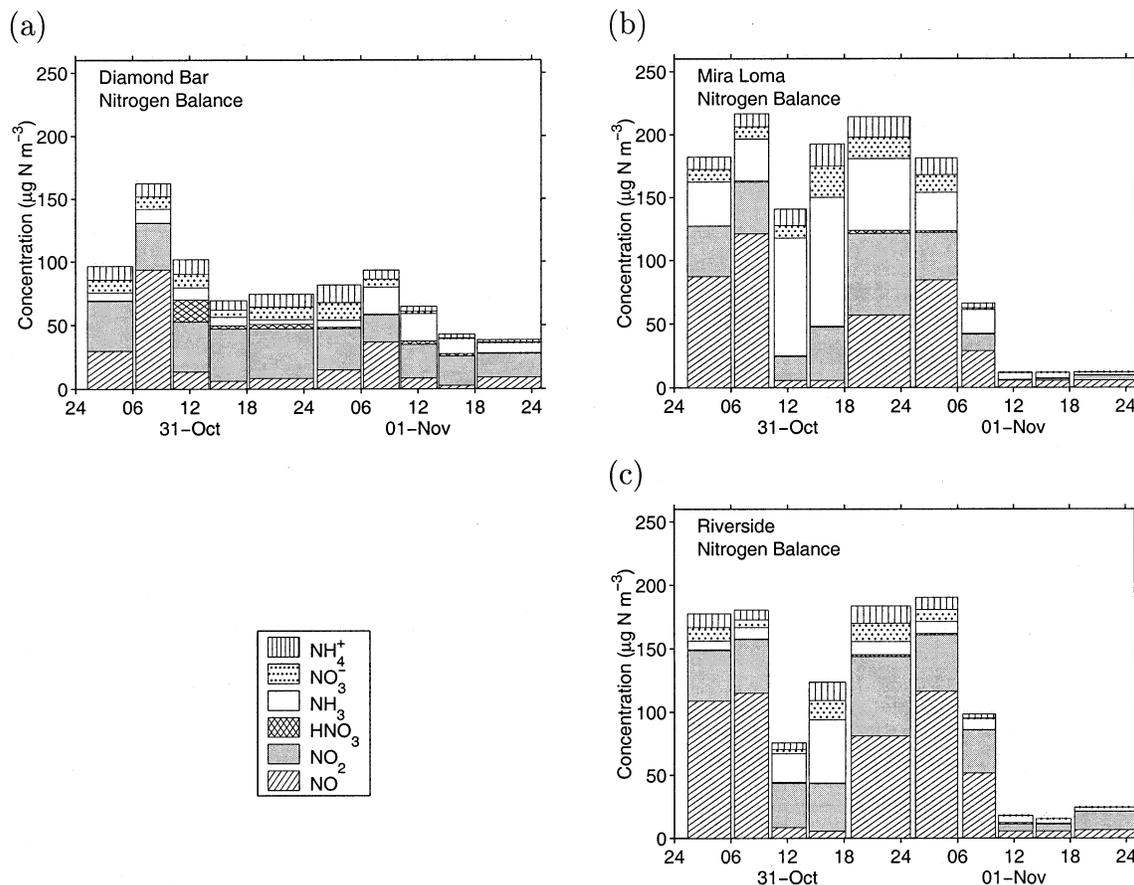


FIGURE 4. Nitrogen balances during the October 31–November 1, 1997, sampling event at (a) Diamond Bar, (b) Mira Loma, and (c) Riverside.

subsequent time period had been transported from west of Diamond Bar. The decreases in fine particulate NO_3^- , NH_4^+ , and mass, the slight decrease in fine aerosol carbon, and the slight increase in fine particle SO_4^{2-} between the two time periods apparent in Figure 1a can also be seen in the size-segregated chemical composition data.

Figure 2a shows the time series of fine particulate matter concentrations and chemical compositions measured at Mira Loma over the October 31–November 1, 1997, sampling period. Fine elemental carbon and organic compound concentrations peaked during the 0600–1000 PST peak traffic period on Friday, October 31. Other fine particulate species remained relatively constant from 0100 through 1000 h PST on October 31. Air parcel trajectories arriving at Mira Loma changed around 1100 h PST from a pattern which approached Mira Loma from the north to one which approached Mira Loma from the west. Air parcels arriving after 1100 h PST contained higher concentrations of fine particulate NO_3^- and NH_4^+ , and gas-phase NH_3 , and lower concentrations of EC. The center of the Chino dairy area is located to the west of Mira Loma, and thus it is not surprising that the highest ammonia concentrations recorded occur during periods of flow from the west. Overnight between October 31 and November 1 air parcels stagnated at Mira Loma, and the concentrations of all species remained relatively high. As mentioned previously, the wind direction shifted to produce flow from the north after 0700 PST on November 1, resulting in low fine particle concentrations for the rest of that day.

Figures 2b and 2c show the size-segregated mass distribution and chemical composition of the fine particulate matter at Mira Loma as measured by the cascade impactors during the two sampling time periods 1035–1400 PST and 1446–1800 PST on October 31, 1997. Increases in fine particle

mass, EC, organic compounds, NO_3^- , SO_4^{2-} , and NH_4^+ between the mid-day and afternoon time periods seen in Figure 2a also can be seen in the size-segregated fine particle composition data as well. Again, the greatest accumulation of nitrate occurred in particles larger than $0.3 \mu\text{m}$ aerodynamic particle diameter. There is an unusually large amount of metals and metal oxides seen in the $0.32\text{--}0.56 \mu\text{m}$ aerodynamic range; this peak consists largely of iron presumed to be in the form Fe_2O_3 , but its source is unknown.

Figure 3a shows the time series of fine particulate matter concentrations and chemical compositions measured at Riverside over the October 31–November 1, 1997, sampling event. Elemental carbon concentrations were relatively constant through October 31 and the following morning. Fine particulate mass, organic compounds, NH_4^+ , and NO_3^- peaked during the 1400–1800 PST time period on October 31; wind speeds increased at this time after the overnight stagnation period ended, thereby transporting more polluted air parcels into Riverside from the west. SO_4^{2-} concentrations peaked at $3.0 \pm 0.1 \mu\text{g m}^{-3}$ in the 1800–0100 PST period.

Figures 3b and 3c show the size-segregated mass distribution and chemical composition of the fine particulate matter at Riverside as measured from the cascade impactor samples during the two sampling time periods 0955–1353 PST and 1449–1810 PST on October 31, 1997. Again, the ammonium nitrate concentration increase between these two time periods occurs in the form of additional ammonium nitrate accumulation on particles larger than $0.3 \mu\text{m}$ aerodynamic diameter.

Another perspective on the aerosol nitrate formation problem in the South Coast Air Basin can be gained from Figure 4. This figure shows a nitrogen balance on the air masses over consecutive time periods at all three air

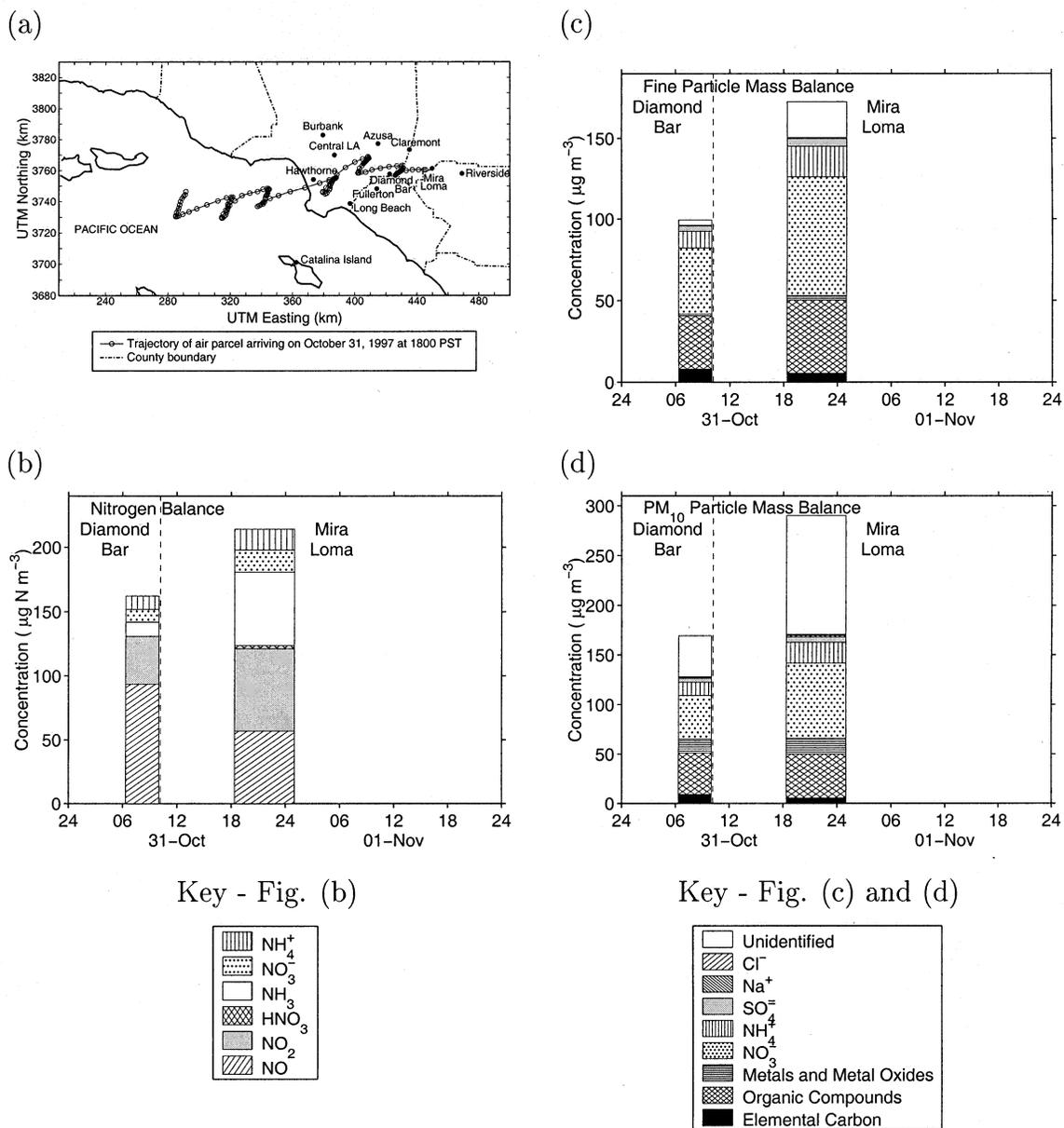


FIGURE 5. Aerosol evolution along the trajectory between Diamond Bar and Mira Loma, October 31–November 1, 1997. (a) Representative air parcel trajectory which reached Mira Loma at 1800 PST November 1, 1997. The air parcel passed within 5 km of Diamond Bar at 0830–0930 PST on October 31 before being transported to near Mira Loma during 1800–2200 PST later that day. Each circle represents an elapsed hour. (b) Nitrogen balance, (c) fine particle mass balance, and (d) PM_{10} mass balance.

monitoring sites over the October 31–November 1 sampling period. Data are presented in terms of μg of nitrogen per cubic meter. Generally, NO and NO_2 concentrations are much higher than either HNO_3 concentrations or aerosol nitrate concentrations. Thus the precursor gases needed for HNO_3 production are available in abundance. Excess ammonia is present at most times, thus any HNO_3 formed is expected to partition into the particulate phase. Although the aerosol nitrate concentrations are small relative to the total nitrogen burden in the atmosphere, the resulting NH_4NO_3 aerosol concentration is large in comparison to both other aerosol species and the fine particle air quality standards recently proposed by the US EPA.

Evolution along Air Parcel Trajectories. Two air parcel trajectories during the October 31–November 1 sampling event passed over or near two of the three air monitoring stations in succession, allowing a comparison of the pollutant concentrations and aerosol populations within single air

parcels as pollutants age in the presence of continuing emissions, transformations, and dry deposition. These air parcel trajectories are pictured in Figures 5a and 6a; each open circle along the trajectories indicates the air parcel location at successive hours during transport across the air basin.

Trajectory analysis shows that an air parcel passing within 5 km of Diamond Bar between 830 and 930 h PST on October 31 later was advected across the ammonia sources in the Chino dairy area and arrived within 5 km of the Mira Loma site between 1800 and 2200 PST later that day (see Figure 5a). The air parcel begins its travels that morning at Diamond Bar with approximately $100 \mu\text{g N m}^{-3}$ present as NO and lesser quantities of NO_2 ; nitric acid concentrations initially are close to zero, while excess NH_3 is still present in the gas phase, indicating that NH_4NO_3 present at Diamond Bar is limited by the amount of inorganic nitrate (e.g. HNO_3) available to form particulate mass (see Figure 5b). During

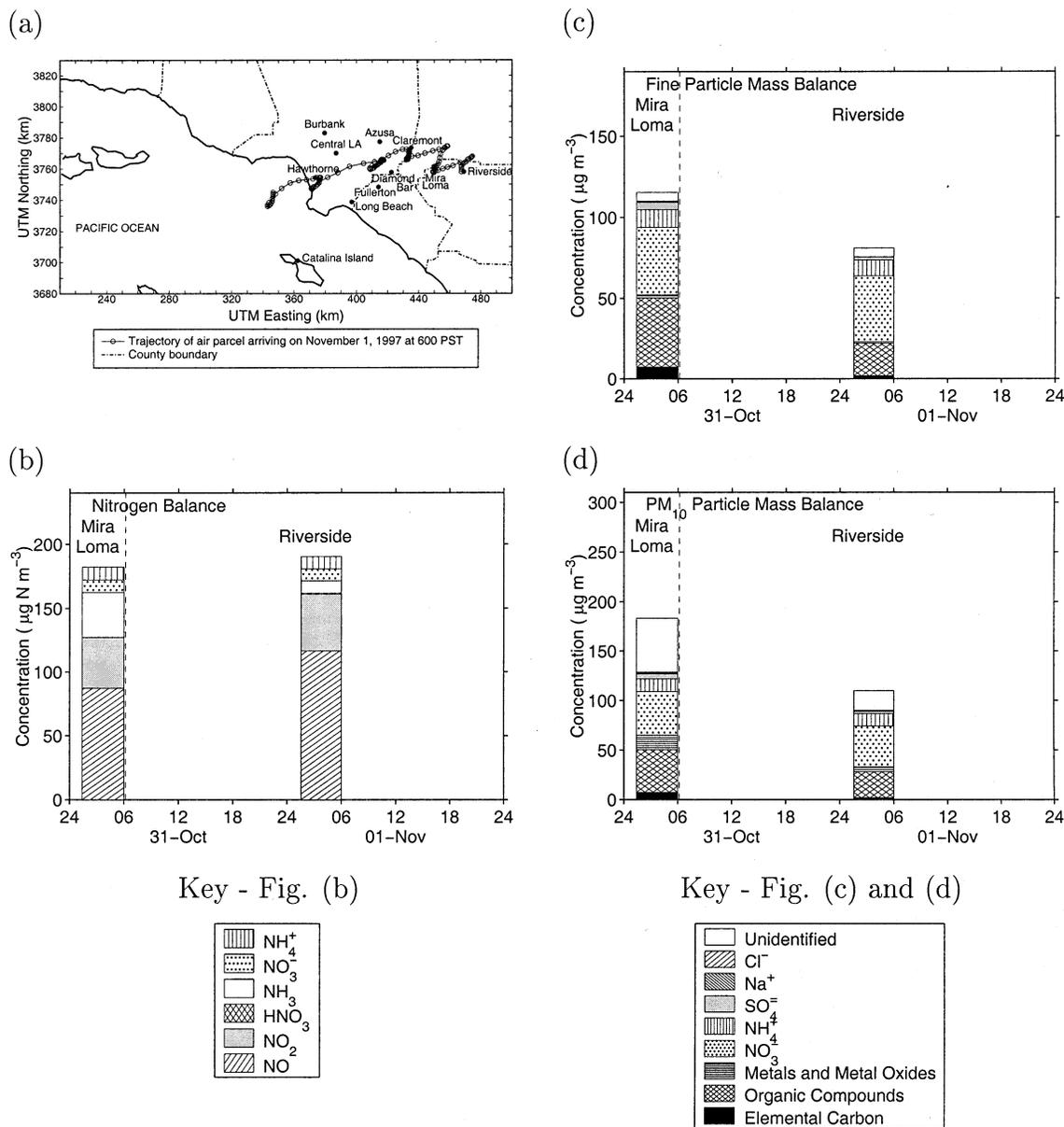


FIGURE 6. Aerosol evolution along the trajectory between Mira Loma and Riverside, October 31–November 1, 1997. (a) Representative air parcel trajectory which reached Riverside at 0600 PST November 1, 1997. The air parcel passed within 5 km of Mira Loma during 0100–0700 PST on October 31 before passing within 5 km of Riverside during 0100–0800 PST on November 1. Each circle represents an elapsed hour. (b) Nitrogen balance, (c) fine particle mass balance, and (d) PM₁₀ mass balance.

transport from Diamond Bar to Mira Loma, NO is converted to NO₂. Ammonia concentrations increase by more than a factor of 5 between Diamond Bar and Mira Loma as the air parcel passes over the local ammonia sources. The additional ammonia drives the additional HNO₃ formed into the particle phase and aerosol nitrate concentrations increase (see Figure 5c).

Trajectory analysis also shows that the air parcels stagnating near the Riverside air monitoring station in the early morning hours (0100–0800 PST) of November 1 stagnated near the monitoring station at Mira Loma approximately 24 h earlier, on October 31 from about 0100 to 0700 h PST (see Figure 6a). This air parcel was over land for approximately 3 days before arriving at Mira Loma and was over land for 4 days before arriving at Riverside. Figure 6b–d shows a material balance on the nitrogen-containing pollutants, fine particulate matter, and PM₁₀ concentrations present over time within that air parcel. NH₃ concentrations at Riverside decreased to about 25% of the concentration present at Mira

Loma. There are similar decreases in EC and organic matter concentrations. These concentration decreases are consistent with the dilution expected as one moves away from the virtual point source of ammonia in the Chino dairy area. NO₃ and NH₄⁺ concentrations are approximately the same at both Mira Loma and Riverside, reflecting a balance between NH₄NO₃ aerosol formation versus pollutant dispersion and dry deposition. PM₁₀ mass decreased proportionally more than fine particle mass; this is likely due to preferential deposition of PM₁₀ during the 24-h transit time.

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