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Chemical characterization of outdoor $PM_{2.5}$ and gas-phase compounds in Mira Loma, California

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Abstract

Outdoor fine particulate matter ($PM_{2.5}$) and gas-phase compounds were investigated in Mira Loma, a semi-rural community in southern California, between September 2001 and January 2002. Outdoor $PM_{2.5}$ concentrations for the study duration averaged 41.8 μg m^{-3}, with nitrate and organic carbon being the major contributors (~26% each). Higher $PM_{2.5}$ concentrations were observed during the first half of the study relative to the second half, corresponding with actinic flux calculations. Gas-phase ammonia concentrations were 6–7 times greater than nitric acid concentrations, while formaldehyde and acetaldehyde concentrations were consistent with Air Resources Board results. Use of a back trajectory model together with $PM_{2.5}$ chemical composition data showed distinct differences in nitrate and trace element concentrations for back trajectories originating from Los Angeles and Orange counties versus those originating from Nevada. Source apportionment using a chemical mass balance model helped demonstrate that the total contribution of secondary aerosol (56%) was greater than the total primary vehicular exhaust contribution to $PM_{2.5}$ by a factor of 5. These results highlight the importance of region-wide secondary sources to the local air quality in this semi-rural area.

Keywords: Source apportionment; HYSPLIT; Southern California; Aerosol; Carbonyls; Formaldehyde; Ammonia

1. Introduction

Atmospheric particulate matter having aerodynamic diameter 2.5 μm or less ($PM_{2.5}$) has received greater attention in recent years, largely due to studies that suggest a correlation between $PM_{2.5}$ and adverse human health effects (Dockery et al., 1993; Rojas-Bracho et al., 2000; Gauderman et al., 2000). A comparison of levels of $PM_{2.5}$ in Mira Loma with those seen elsewhere in southern California and other parts of the United States indicates that Mira Loma and the surrounding areas have among the highest $PM_{2.5}$ levels in the country (Tolocka et al., 2001; Kim et al., 2000a, b).

Gas-phase carbonyl compounds in the atmosphere are also of interest because of their potentially adverse effects on human health. Formaldehyde and acetaldehyde have been classified by the United States Environmental Protection Agency (US EPA) as hazardous air pollutants (US EPA, 1991a, b). Long-term exposure to high formaldehyde concentrations is known to increase the risk for asthma and cancer (Kerns et al., 1983; Nordman et al., 1985; US EPA, 1989). Atmospheric

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carbonyl sources include primary emissions from automobiles, industrial plants, incinerators and natural vegetation, as well as secondary emissions through the atmospheric photooxidation of hydrocarbons such as methane, isoprene, and other biogenic and anthropogenic compounds (Williams et al., 1996; Zhang et al., 1994). A number of groups have conducted ambient measurements of carbonyls in urban environments (Grosjean, 1982; Grosjean et al., 1993; Williams et al., 1996; Báez et al., 2003).

The community of Mira Loma (33°59′N, 117°31′W) is located in western Riverside County, California, 80 km east of downtown Los Angeles. According to the 2000 United States census, Mira Loma has a population of 17,617 and a total area of 16.9 km^2. As seen in Fig. 1, Mira Loma is situated at the intersection of two major freeways, the CA-60 (east–west) and Interstate-15 (north–south). On the western side of Mira Loma lies an agricultural area having a large number of dairy farms. A number of warehouses/distribution centers (~70) have been constructed in Mira Loma over the past decade, particularly in the northern and western part of Mira Loma, increasing the number of heavy-duty diesel trucks that frequently pass through residential areas. In addition, Mira Loma is downwind of the Los Angeles-Long Beach-Orange County metropolitan area, which has some of the highest traffic density in the United States.

From an air quality viewpoint, the South Coast Air Basin as a whole has a number of interesting features: heavy vehicle usage (509 million daily vehicle-kilometers traveled; ARB, 2002), topographical features that restrict dispersion of the air mass, and sunlight for the major part of the year. These are all factors conducive to secondary aerosol formation, both inorganic and organic. The mechanisms for secondary organic aerosol formation are numerous and described in detail by Seinfeld and Pandis (1998). In terms of secondary inorganic aerosol, ammonium nitrate (NH_4NO_3) is an important compound for the southern California region (Hughes et al., 2002). It is formed from the photochemical transformation of primary emissions of oxides of nitrogen (NO_x) to nitric acid (HNO_3), which reacts with gas-phase ammonia (NH_3) to form particle-phase ammonium nitrate. Back trajectory analysis can be a powerful tool in determining the contribution of this and other species to local aerosol concentrations (Chen et al., 2002).

Due to the availability of both oxides of nitrogen (primary source: vehicle emissions) and ammonia (primary source: animal waste) upwind of the Mira Loma area, it may be expected that ammonium nitrate in particular and secondary aerosol in general contribute significantly to local $PM_{2.5}$ composition. On the other hand, local primary emissions sources such as diesel

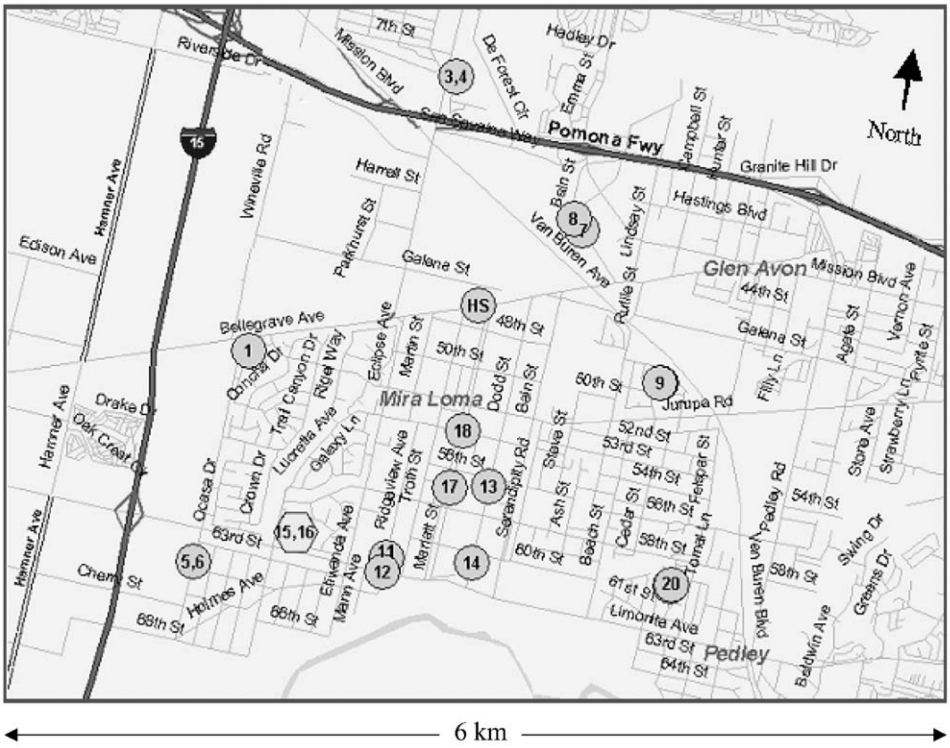

Fig. 1. The Mira Loma area with sampling sites. "HS" stands for "high school". The hexagon represents the fixed outdoor site.

trucks passing in close proximity to residential areas in Mira Loma could also be expected to have an impact on fine particulate levels both indoors and outdoors.

A study involving the chemical characterization of indoor and outdoor $PM_{2.5}$, gas-phase ammonia, nitric acid, and carbonyl mass concentrations was conducted in this area from September 2001 to January 2002. This paper details the results of this study with respect to outdoor sampling.

2. Experimental methods

2.1. Sampling methodology

The sampler systems employed the principle for $PM_{2.5}$ impactor design described by Biswas and Flagan (1988). The impactor was connected to a manifold with eight lines (A–H) as shown in Fig. 2. Critical orifices (O'Keefe Controls, Trumbull, CT, USA) were used to control flow rates; these were calibrated before every sampling period (consisting of 12 calendar days; 6 days of actual sampling) using a Gilibrator 2 bubble flow meter (Sensidyne, Clearwater, FL, USA). On each sampler, the critical orifices were connected by means of suitable piping to a $\frac{1}{4}$ horsepower oil-less GAST 0523 vacuum pump (GAST, Benton Harbor, MI, USA). The pump was housed in a sound-insulated weatherproof container.

Outdoor sampling was conducted for the entire duration of the study at a fixed residential site in southwestern Mira Loma; see Fig. 1 for details. For comparison purposes, one outdoor sampler was also set up at a location different from the fixed site, and this location changed with each sampling period. These sampling sites were chosen to provide the best possible representation of the inhabited areas of Mira Loma. Sixty effective sampling days were obtained from 17 September 2001 to 26 January 2002, after exclusion of five sampling days due to miscellaneous operational difficulties. During each sampling period, the samplers were run for 24 h at each site, from approximately 8:00 PM–8:00 PM, on alternate days. Sampling was confined to two outdoor sites only on 29 November 2001 and from 25 December 2001 to 1 January 2002, due to holidays.

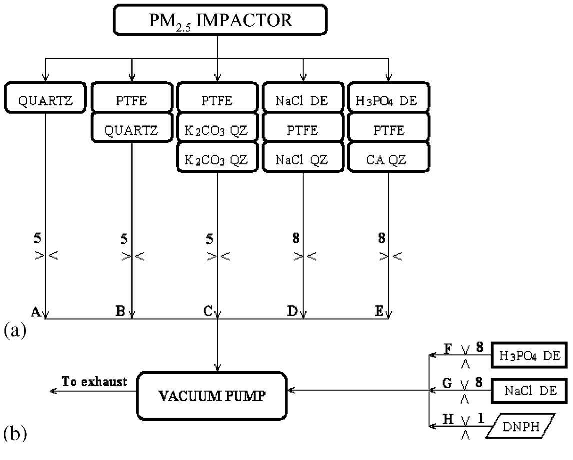

Fig. 2. Schematic of sampling system. (a) The numbers indicate the flow rate of the sampling lines in liters per minute (LPM). (b) Note that lines F, G, and H are for gas-phase sampling and are not connected to the $PM_{2.5}$ impactor.

2.2. Chemical analysis

$PM_{2.5}$ samples were collected using 47 mm diameter 2-μm pore PTFE Teflo filters (Pall-Gelman, Ann Arbor, MI, USA). The filters were weighed three times on different days in a controlled temperature/relative humidity (RH) chamber at 25 °C and 40% RH on an ATI-Cahn C-35 microbalance, both before and after sampling. The average of the two closest weights in each case (within 3 μg) were taken to be the initial and final weights. The difference between the final and initial weights yielded the collected $PM_{2.5}$ mass. In order to obtain the final $PM_{2.5}$ concentration, this mass had to be corrected for volatilization losses occurring due to the difference in temperature between the sampling location and the analytical laboratory. This was achieved by using the denuders and backup quartz filters in sampling lines D and E (Fig. 2). The detection limit for this method is $0.4\,\mu g\,m^{-3}$.

Analysis of organic carbon and elemental carbon (OC/EC) was performed using uncoated 47 mm diameter QAT Tissuquartz quartz fiber filters (Pall-Gelman, Ann Arbor, MI, USA). A thermal/optical carbon aerosol analyzer (Sunset Laboratory, Forest Grove, OR, USA) using the NIOSH 5040 method was used to perform the analyses (Birch and Cary, 1996). The OC values were obtained by multiplying the carbon mass by 1.9 to account for the hydrogen, oxygen and nitrogen atoms associated with organic carbon (Turpin and Lim, 2001). Gas-phase absorption artifact was corrected using the quartz filter in sample line B (see Fig. 2). A more detailed explanation of the measurement and calculation technique for organic carbon may be found in Na et al. (2004). The detection limit for this method is $140\,ng\,m^{-3}$.

The substrates for analysis of the ionic species sulfate (SO_4^{2-}) and nitrate (NO_3^-) were extracted with double deionized water in an ultrasonic bath. The extracts were analyzed using a Shimadzu high performance liquid chromatography (HPLC) system equipped with a CDD-6A conductivity detector (Shimadzu, Torrance, CA, USA), a 2-μm pore Allsep A-2 Anion column (100 mm length × 4.6 mm ID) and an Alltech 335 SPCS suppressor module (Alltech, Deerfield, IL, USA). The mobile phase was 2.1 mM sodium bicarbonate and 1.6 mM sodium carbonate in double deionized water. This method has a detection limit of 70 ng m^{-3}.

X-ray fluorescence (XRF) analysis of 35 trace elements was performed by the South Coast Air Quality Management District (SCAQMD, Diamond Bar, CA, USA). Samples were collected on 47 mm diameter PTFE Teflo filters.

Gas-phase nitric acid was collected on fabric denuders coated with 9% sodium chloride solution and quartz denuders coated with 2% sodium chloride solution (sample line D in Fig. 2). Ammonia samples were collected with fabric denuders coated with 10% phosphoric acid and quartz denuders coated with 2% citric acid solution (sample line E in Fig. 2). Both fabric and quartz denuders for nitric acid and ammonia were extracted and analyzed using indophenol colorimetry following the method of Bolleter et al. (1961). Briefly, a 1 mg l^{-1} standard for nitrogen was prepared by dissolving ammonium chloride in water. This was made into six standard solutions of varying concentrations to which indophenol (a solution containing sodium phosphate, sodium citrate, EDTA, phenol and sodium nitroprusside) and alkaline hypochlorite reagents were added. The solutions were set aside for 45 min, transferred to cuvettes and measured for absorbance at 635 nm on a Genesys 10 UV/visible spectrophotometer (Thermo Spectronic, Madison, WI, USA). Samples were extracted by adding 10 ml of double deionized water to a centrifuge tube containing the filter or denuder. This was followed by addition of 4 ml of indophenol and 6 ml of alkaline hypochlorite reagents, setting aside the samples for 45 min, and analyzing them in the spectrophotometer at 635 nm. The detection method for this method is 35 ng m^{-3}.

Gas-phase carbonyl compounds were collected and analyzed in accordance with the method of Siegl et al. (1993). Briefly, the sampling medium was a Sep-Pak C18 cartridge (Waters, Milford, MA, USA) coated in situ with a solution of 2,4-dinitrophenylhydrazine (DNPH). Each sampler had two cartridges serially attached to a sampling line (H in Fig. 2) with a nominal flow rate of 1 L min^{-1} to account for sampling breakthrough. The cartridges were gravity eluted using HPLC-grade acetonitrile and analyzed using a Shimadzu HPLC system equipped with an SPD-10 AV UV-Vis detector (Shimadzu, Torrance, CA, USA). The HPLC column was a 5 μm Deltabond AK Resolution (200 cm × 4.6 mm ID) with an integral guard column upstream (Thermo Hypersil-Keystone, Bellefonte, PA, USA). The analysis covered a range of carbonyl compounds from C_1 to C_8 and included 11 aldehydes and 2 ketones. The detection limit for this method is 70 ng m^{-3}.

3. Results and discussion

3.1. $PM_{2.5}$ mass concentrations at fixed and mobile sites

Fig. 3 shows the outdoor $PM_{2.5}$ mass concentrations in Mira Loma at the fixed sampling site by sampling date. The outdoor $PM_{2.5}$ in the area varied from 7.0 μg m^{-3}, seen on 27 November 2001, to 97.3 μg m^{-3}, seen on 16 October 2001. The average $PM_{2.5}$ mass concentration measured was 41.8 μg m^{-3} (represented by

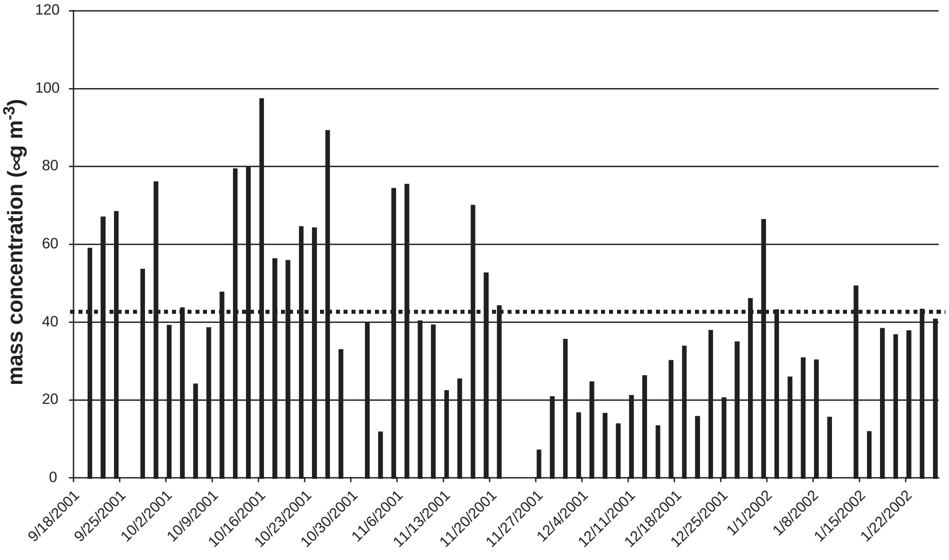

Fig. 3. $PM_{2.5}$ mass concentration at fixed outdoor site in Mira Loma by calendar day. (a) Sampling took place on alternate calendar days. Five sampling days were excluded due to operational difficulties. (b) Dashed line represents the average outdoor value (41.8 μg m^{-3}) for the duration of sampling.

the dashed line in Fig. 3). However, visual inspection of the figure suggests that the $PM_{2.5}$ concentrations are typically above the average during the first half of the sampling (9/18/01–11/21/01), and typically below the average for the second half (11/27/01–1/26/02).

An investigation of the chemical composition data provides more information on this trend. Fig. 4 shows the chemical composition of $PM_{2.5}$ at the fixed outdoor site (F) and at the mobile sites (M) measured during each 12-day sampling period. The data have been classified by sampling period to allow for comparison with data on indoor measurement sites, whose locations were changed every 12 days; these indoor/outdoor relationships are discussed in another paper (Sawant et al., 2004). The average outdoor $PM_{2.5}$ mass concentration obtained by reconstitution of the chemical components was 40.9 $\mu g\,m^{-3}$. The principal components of outdoor $PM_{2.5}$ in Mira Loma were the nitrate ion (average: 10.8 $\mu g\,m^{-3}$) and organic carbon (average: 10.7 $\mu g\,m^{-3}$), each contributing approximately 26% of the total $PM_{2.5}$ mass. This was followed by the trace elements, contributing an average of 6.4 $\mu g\,m^{-3}$, or 15% of total $PM_{2.5}$ mass; the ammonium ion (average: 3.9 $\mu g\,m^{-3}$; 9%); the sulfate ion (average: 2.4 $\mu g\,m^{-3}$; 6%); and elemental carbon (average: 2.0 $\mu g\,m^{-3}$; 5%). Other species accounted for the remaining 13%. Upon comparison of Figs. 4 and 5, the trend for higher $PM_{2.5}$ mass concentrations during the first half of sampling is seen for the mobile sites as well. An analysis of the ozone data for these days at a nearby site indicates high ozone levels and actinic flux during the first half, suggesting a higher concentration of secondary aerosol than during the second half. Na et al. (2004) have shown a significant correlation between calculated actinic flux and observed secondary organic carbon (SOC) values for the first half. Na et al. (2004) also show that SOC contributes over 50% to the total OC concentrations, implying a 12–15% contribution of SOC to total $PM_{2.5}$ alone. Nitrate is seen to be the other major contributor to elevated $PM_{2.5}$ levels. For constant ammonia and NO_x emission rates, nitrate formation is dependent on the photochemical processes leading to nitric acid and therefore dependent on actinic flux. A plot of average nitrate concentration against average actinic flux by month sampled supports this qualitative argument. The trends in nitrate concentration track the actinic flux, and the correlation coefficient for this plot is $r = 0.9$.

Table 1 compares $PM_{2.5}$ chemical composition observed in the Mira Loma area with that observed in other parts of southern California by the South Coast Air Quality Management District (SCAQMD) (Kim et al., 2000a). It is observed that the $PM_{2.5}$ mass concentration for the Mira Loma area compares favorably with the Rubidoux site in the SCAQMD study, the site closest to Mira Loma in terms of both distance and features of interest from an air quality viewpoint.

3.2. Concentrations of gas-phase ammonia, nitric acid and carbonyls

Table 2 shows the average gas-phase ammonia and nitric acid concentrations observed at the fixed and mobile sites. Average ammonia and nitric acid concentrations were 14.1 and 2.1 $\mu g\,m^{-3}$ respectively for the fixed site, and 17.6 and 2.5 $\mu g\,m^{-3}$ respectively for the

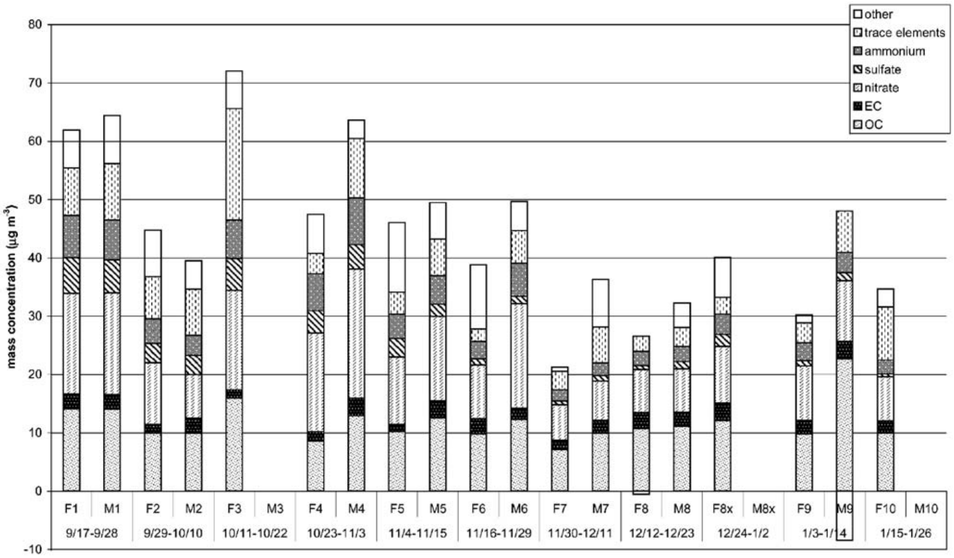

Fig. 4. Reconstituted chemical composition of $PM_{2.5}$ at fixed (F) and mobile (M) sites by sampling period. Note: "F8 × " and "M8 × " indicate the Christmas holiday season when sampling was conducted only at the fixed site.

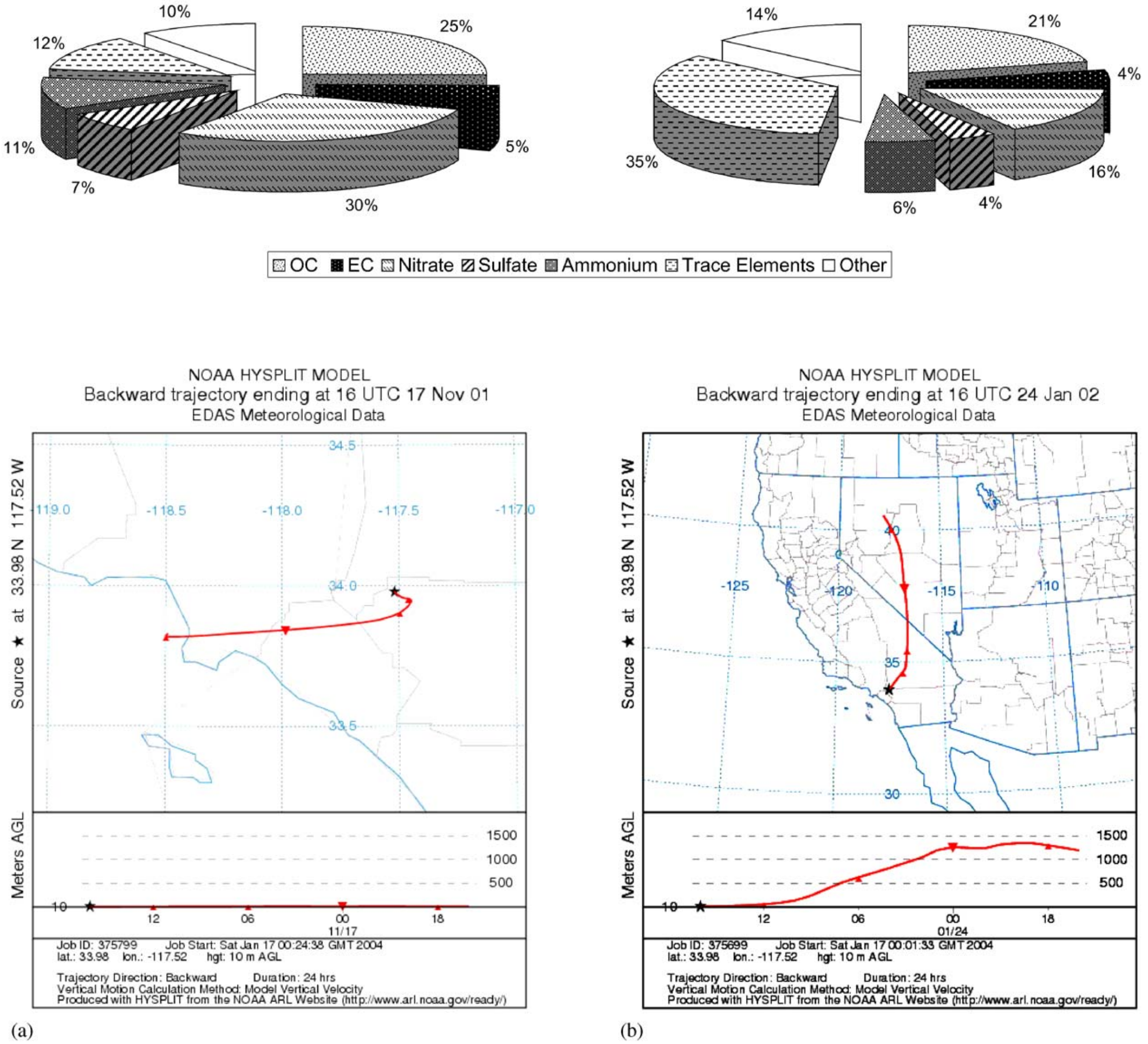

Fig. 5. Average $PM_{2.5}$ chemical composition and typical 24-h HYSPLIT back-trajectories for prevailing winds from: (a) West, i.e., Los Angeles and Orange counties. Average $PM_{2.5}$: 46.4 μg m^{-3}. (b) North by northeast, i.e., Nevada ("Santa Ana" winds). Average $PM_{2.5}$: 26.4 μg m^{-3}.

mobile sites. Ammonia concentrations were typically a factor of 6–7 higher than nitric acid concentrations, which is to be expected for a region dominated by ammonia such as this. No clear temporal trends were observed for either compound, which contrasts with the observed $PM_{2.5}$ trends discussed earlier.

Table 2 also shows the average mass concentrations for carbonyls at the two types of sites. Average 24-h concentrations for formaldehyde and acetaldehyde were 3.56 and 2.52 μg m$^{-3,}$ respectively for the fixed site, and 4.44 and 2.67 μg m^{-3} respectively for the mobile sites. These values are consistent with the mean formaldehyde and acetaldehyde concentrations observed by the California Air Resources Board (ARB) air toxics monitoring network from January 1996 to December 1996 (4.15 and 2.39 μg m^{-3}, respectively) (ARB, 1997). For comparison, average indoor formaldehyde and acetaldehyde concentrations measured concurrently with outdoor values were 15–16 and 10–12 μg m^{-3}, respectively (Sawant et al., 2004). The chronic non-cancer Reference Exposure Level (REL) for formaldehyde and acetaldehyde are 3.6 and 9.0 μg m^{-3}, respectively (ARB, 1997, and references therein).

Table 1
Comparison of chemical composition of Mira Loma outdoor $PM_{2.5}$ with other sites in southern California (Kim et al., 2000a, b)

Site	This study	Rubidoux	Fontana	Diamond Bar	Downtown LA	Anaheim	San Nicolas Island
Period	September 2001–January 2002			January 1995–February 1996			
OC	10.7	7.23	7.69	6.15	7.74	5.27	1.49
EC[a]	2.0	3.25	3.49	3.08	3.81	2.35	0.19
NH_4^+ [b]	3.9	6.77	4.98	4.20	4.55	3.34	0.58
NO_3^-	10.8	16.12	11.00	8.35	8.47	6.00	0.67
SO_4^{2-}	2.4	3.53	3.66	3.88	4.63	3.79	1.40
Trace elements	6.4	1.63	2.16	0.99	0.96	0.84	0.64
Other	5.6	2.31	3.8	−0.25	1.38	0.71	1.03
Average measured mass ($\mu g\,m^{-3}$)	41.8	39.75	35.59	25.48	30.32	21.73	6.82

[a] Kim et al. (2000a, b) used the DRI model 4000 × analyzer, which is known to give slightly lower values of EC compared with the Sunset Labs analyzer used for the Mira Loma study.

[b] The NH_4^+ mass concentration for the Mira Loma study is a stoichiometric estimate.

3.3. $PM_{2.5}$ chemical composition and wind direction

The dependence of $PM_{2.5}$ chemical composition on wind direction is useful in determining the contributions of upwind emission sources. In this study, the US National Oceanographic and Atmospheric Administration (NOAA) HYSPLIT model (Draxler and Rolph, 2003) was used to determine air parcel back trajectories (ending at Mira Loma) for each sampling day. The model was run for 24 h, ending at 8 AM on the sampling day. A mixing height of 10 m above ground level was assumed. Each back trajectory was then tagged with location of probable source (e.g., "Los Angeles and Orange counties", "Nevada", etc.). These tags were then appended to the $PM_{2.5}$ chemical composition data. Back trajectories originating from Los Angeles and Orange counties constituted more than 65% of the days for which a source could be clearly identified. Hughes et al. (2002) investigated forward trajectories in this region during the Southern California Ozone Study of 1997 (SCOS 97), focusing on one 48-h sampling period.

Investigation of the chemical composition data and tagged back trajectories showed distinct differences in $PM_{2.5}$ chemical composition between the "Los Angeles and Orange counties" and "Nevada" sources. Fig. 5 shows average $PM_{2.5}$ chemical composition for all sampling days tagged under either of these categories, as well as a typical 24-h back trajectory representative of each category. The contribution of nitrate to $PM_{2.5}$ was significantly higher for sampling days tagged "Los Angeles and Orange counties" (average: 30%) than for sampling days tagged "Nevada" (average: 16%). Conversely, the contribution of trace elements to $PM_{2.5}$ was significantly higher for sampling days tagged "Nevada" (average: 35%) than for sampling days tagged "Los Angeles and Orange counties" (average: 12%).

The high nitrate contributions are primarily because of the large quantities of NO_x transported inland from Los Angeles and Orange counties and concurrent photochemical activity leading to nitric acid, and further ammonium nitrate formation (as described in the introduction). On the other hand, the high trace element contribution can be attributed to the so-called "Santa Ana" wind events. The Santa Ana is a strong wind (with gusts of over 160 km h^{-1}) that originates in the Nevada plateau and blows southwest, occurring most commonly between October and February every year. In summary, these results underscore the influence of regional sources on local $PM_{2.5}$ in Mira Loma.

3.4. Source apportionment of outdoor $PM_{2.5}$

Daily chemical composition data for outdoor $PM_{2.5}$ in Mira Loma was used as the input to a chemical mass balance model (Miller et al., 1972; Hopke, 1985). The fundamental equation for the chemical mass balance model is

$$c_i = \sum\nolimits_j f_{i,j} c_{i,j} \tag{3}$$

where c_i is the receptor concentration of species i (from chemical composition data), $f_{i,j}$ the mass fraction of species i in emission profile j and $c_{i,j}$ the contribution of source profile j to species i.

Source profiles are selected based on expected region-specific sources as discussed in the literature and on

Table 2
Concentrations of gas-phase compounds measured at fixed and mobile sites in Mira Loma ($\mu g\,m^{-3}$)

	9/17–9/28		9/29–10/10		10/11–10/22		10/23–11/3		11/4–11/15		11/16–11/29		11/30–12/11		12/12–12/23		12/24–1/2		1/3–1/14		1/15–1/26	
	F1	M1	F2	M2	F3	M3	F4	M4	F5	M5	F6	M6	F7	M7	F8	M8	F8x	M8x	F9	M9	F10	M10
Nitrogen-containing compounds																						
NH_3	17.8	18.9	11.6	19.7	23.5		13.7	16.3	9.92	12.0	19.1	22.5	11.3	16.8	11.5	17.6			13.9	19.6	13.4	
HNO_3	1.87	2.63	1.59	2.08	1.79		1.90	2.28	2.54	2.62	1.83	2.69	1.24	1.80	3.98	3.01			2.70	3.20	1.53	
Carbonyl compounds																						
Formaldehyde	2.38	4.48	1.85	2.82	2.45		3.09	6.73	4.30	5.03	13.4	3.75	1.09	4.10	1.75	1.98			3.05	7.52	3.99	
Acetaldehyde	2.10	2.43	1.97	3.16	2.29		4.29	2.59	3.55	1.79	3.10	3.44	1.01	2.32	1.99	1.87			1.50	5.36	2.58	
Acetone	2.48	2.33	2.33	2.08	3.99		2.92	3.48	6.07	4.73	6.32	8.74	2.29	10.3	5.85	7.79			5.17	13.3	10.1	
Acrolein	1.09	0.69	2.15	2.25	2.19		2.53	2.69	5.43	4.39	2.54	2.81	0.49	1.12	0.87	1.63			0.58	1.25	0.46	
Propionaldehyde	1.00	0.61	0.98	1.68	1.37		1.19	1.94	3.19	2.37	1.42	1.65	BDL	0.97	0.41	0.75			0.30	1.52	0.61	
Crotonaldehyde	BDL	BDL	BDL	0.34	0.29		0.50	0.59	0.78	BDL	0.92	0.14	BDL	BDL	BDL	BDL			BDL	0.09	0.25	
Methyl Ethyl Ketone	0.73	0.71	0.98	0.74	2.02		0.62	1.60	1.64	1.42	1.14	1.18	1.02	1.31	0.76	1.11			0.63	2.46	1.56	
Methacrolein	BDL	BDL	BDL	BDL	BDL		BDL	0.34	0.57	BDL	0.70	0.27	BDL	BDL	0.17	0.16			BDL	BDL	BDL	
Butyraldehyde	0.49	0.49	0.59	1.06	1.61		1.14	1.42	1.51	1.24	1.74	0.71	BDL	0.87	0.27	0.29			0.18	1.06	0.31	
Benzaldehyde	0.75	0.67	0.77	1.26	2.01		1.37	2.15	1.71	1.61	2.36	0.89	BDL	BDL	0.45	0.28			0.13	0.71	0.07	
Valeraldehyde	0.36	0.71	0.30	0.90	1.03		0.58	1.40	1.14	0.33	2.86	0.69	BDL	0.95	0.14	0.12			0.02	0.40	0.10	
Tolualdehyde	0.46	0.46	0.73	1.17	1.55		0.67	1.59	5.95	0.73	0.72	0.70	BDL	0.96	0.31	0.31			0.11	2.23	1.17	
Hexanaldehyde	0.47	0.49	0.49	0.96	1.31		0.49	1.46	1.84	0.53	7.09	1.28	BDL	1.13	0.18	0.58			0.29	0.66	0.29	

[*] BDL: below detection limit.

Note: F8x and M8x indicate the christmas holiday season when no gas-phase sampling was conducted.

statistical quality of data. Selected performance criteria used in this study are R^2 (an indicator of the closeness of measured species concentrations to calculated species concentrations; >0.85 for this case), χ^2 (similar to R^2, but also considers the uncertainties in the calculated species concentrations; <4.0 for this case), and percent mass balance ($100 \pm 20\%$). The output obtained is the source contribution by mass of each of the components investigated. A comprehensive discussion of the CMB8 model and the statistical parameters used therein may be found elsewhere (Watson et al., 1998b; US EPA, 2001).

Source profiles used in the present $PM_{2.5}$ source apportionment were obtained from the literature (Watson et al., 1994, 1998a; Durbin, 2003) and are presented in Table 3. Note that a source profile for food cooking used by other researchers (e.g., Schauer et al., 1996, 2002) has not been used in the present study. For some sources, more than one source profile was used in order to obtain source contributions meeting the performance criteria stated earlier. Results are shown in Fig. 6. It is observed that secondary nitrate is by far the largest contributor to $PM_{2.5}$ in this region (~41%), with unapportioned organics and soil-related compounds contributing nearly equal amounts (~13%).

Table 3
Emission source profiles used for source apportionment of outdoor $PM_{2.5}$ in Mira Loma

Source type	Description
Gasoline exhaust	CE-CERT gasoline vehicle exhaust$^{(1)}$
Diesel exhaust	CE-CERT diesel vehicle exhaust$^{(1)}$
Biomass burning	Visalia agricultural burning$^{(2)}$
Soil-related sources	South Coast Air Basin paved road profile composite$^{(2)}$ Riverside paved road profile composite$^{(2)}$
Secondary sulfate	100% SO_4^{2-}
Secondary nitrate	100% NO_3^-
Total organics	100% organic carbon

References: $^{(1)}$Durbin (2003); $^{(2)}$Watson et al. (1994).

Table 4 compares the source apportionment results of this study with those conducted in other parts of North America (Schauer et al., 1996, 2002; Chow and Watson, 2002; Schauer and Cass, 2000; Watson et al., 1998a; Zheng et al., 2002). With the exception of the Fresno site, note the higher contribution of secondary sources to total $PM_{2.5}$ in Mira Loma compared to other areas. This type of result may be expected in any predominantly agricultural community located downwind of an urban area.

Na et al. (2004) estimate that approximately 50% of organic carbon is secondary in nature. Taking this into account, it is observed that secondary aerosol comprising secondary organic carbon, nitrate and sulfate together, account for approximately 56% of the sources of outdoor $PM_{2.5}$ in the Mira Loma area. This is significantly greater than the primary emissions from gasoline and diesel vehicles together (10%), of which only a small amount is estimated to be local. These results highlight the dominance of secondary aerosol (organic carbon and nitrate) in this area downwind of two major sources of primary pollutants and suggest that region-wide air quality strategies may be more effective than localized measures in improving the air quality of this semi-rural area.

4. Summary

Outdoor fine particulate matter ($PM_{2.5}$) and its components, and selected gas-phase compounds were investigated in Mira Loma, a semi-rural community in southern California, between September 2001 and January 2002. $PM_{2.5}$ components, namely, elemental and organic carbon, ionic species, and 35 trace elements

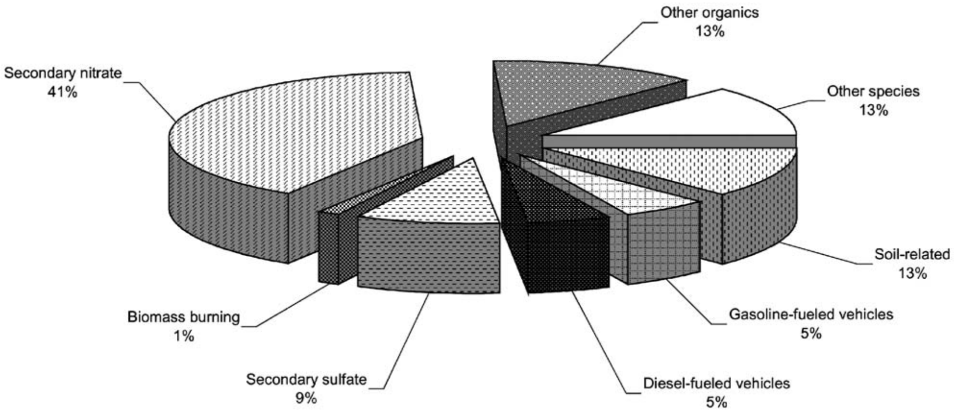

Fig. 6. Source apportionment of $PM_{2.5}$ measured at fixed outdoor site in Mira Loma.

Table 4
Comparison of source apportionment of outdoor $PM_{2.5}$ in Mira Loma to other sites in North America (%)

Site[a]	This study	Rubidoux (California)(1)	Fresno (California)(2,3)	Denver (Colorado)(2,4)	Downtown Los Angeles (California)(5)	Birmingham (Alabama)(6)
Period	September 2001 to January 2002	January–December 1982	January 1996	Summer 1996, Winter 1996, 1997	September 1993	October 1999
Gasoline exhaust	5.4	0.8	2.0	31.3	16.8	3.6
Diesel exhaust	5.4	12.7	9.3	9.0	37.4	32.1
Biomass burning[b]	1.4	1.3	26.6	6.0		10.1
Soil-related sources[b]	12.88	13.1	1.8	16.7	19.3	3.5
Primary organics[c,d]	6.4	4.6	2.7	0.8	7.3	6.5
Total primary sources	31.2	32.5	42.4	63.8	80.8	55.8
Ammonium sulfate[e]	9.0	18.8	6.7	9.6	3.8	26.8
Ammonium nitrate[e]	40.2	31.8	42.5	23.2	1.5	4.8
Secondary organics[b]	7.8	4.6	7.5		37.0	5.6
Total secondary sources	56.2	55.2	56.7	32.8	42.3	37.2
Unresolved chemical mass	12.6	12.3	0.9	3.4	—	7.0
Average measured mass ($\mu g\,m^{-3}$)[f]	41.8	42.1	55.3	14.6	47.9	22.8

[a] References: (1)Schauer et al. (1996); (2)Chow and Watson (2002); (3)Schauer and Cass (2000); (4)Watson et al. (1998a); (5)Schauer et al. (2002); (6)Zheng et al. (2002).

[b] The "biomass burning" and "soil-related sources" fields include wood smoke and paved road dust, respectively.

[c] For the Mira Loma study, the CMB calculation yielded total organics; estimates for primary and secondary organics were obtained as described in Na et al. (2004).

[d] The "primary organics" field also includes primary sources from other studies that have not been listed specifically, such as tire wear debris, vegetative detritus, natural gas combustion aerosol, cigarette smoke, and meat cooking.

[e] For the Mira Loma study, secondary nitrate and sulfate are assumed to be ammonium nitrate and ammonium sulfate.

[f] Values in this row are in $\mu g\,m^{-3}$. All other values in this table are expressed as percentages.

were measured using thermal/optical analysis, ion chromatography, and X-ray fluorescence, respectively. Gas-phase ammonia and nitric acid were measured using spectrophotometry, while carbonyl compounds were analyzed using high-performance liquid chromatography (HPLC). Average outdoor $PM_{2.5}$ concentration for the study duration was $41.8\,\mu g\,m^{-3}$, with nitrate ($10.8\,\mu g\,m^{-3}$) and organic carbon ($10.7\,\mu g\,m^{-3}$) being the major contributors (~26% each). Higher $PM_{2.5}$ concentrations were observed during the first half of the study relative to the second half, corresponding with actinic flux calculations and increased nitrate and organic carbon levels. Gas-phase ammonia concentrations were 6–7 times greater than nitric acid concentrations, while formaldehyde and acetaldehyde concentrations were consistent with ARB results.

Use of the NOAA HYSPLIT back trajectory model together with $PM_{2.5}$ chemical composition data showed that nitrate contributions to $PM_{2.5}$ were higher for back trajectories originating from Los Angeles and Orange counties (~30%) and lower for those originating from Nevada (16%). The opposite effect was seen with respect to trace element contributions (12% for Los Angeles and Orange counties; 35% for Nevada). Source apportionment using a chemical mass balance model helped to show that the total contribution of secondary aerosol (56%) was greater than the total primary vehicular exhaust contribution to $PM_{2.5}$ by a factor of 5. These results highlight the importance of region-wide secondary sources to the local air quality in this semi-rural area, and suggest that region-wide air quality improvement measures may be more effective than localized measures in improving the air quality in this semi-rural area.

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Disclaimer

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