

# Characterization of PM<sub>2.5</sub> and selected gas-phase compounds at multiple indoor and outdoor sites in Mira Loma, California

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## Abstract

Fine particulate matter (PM<sub>2.5</sub>) and gas-phase carbonyls are categories of atmospheric pollutants that have components known to adversely affect human health. This work describes the chemical characterization of PM<sub>2.5</sub> and 13 carbonyl compounds measured inside 20 residences and 7 schoolrooms in Mira Loma, western Riverside County, California. Median PM<sub>2.5</sub> concentrations were 32.2 and 13.2 μg m<sup>-3</sup>, while median total carbonyl concentrations were 50.8 and 62.9 μg m<sup>-3</sup> inside the residences and schoolrooms, respectively. Organic carbon was typically the largest contributor to indoor PM<sub>2.5</sub> concentrations, while formaldehyde, acetaldehyde and acetone were the largest contributors to gas-phase carbonyl concentrations. Indoor/outdoor ratios for PM<sub>2.5</sub> were greater for residences than for schoolrooms, while the reverse was true for these ratios for gas-phase carbonyls. These results are likely due to effective PM<sub>2.5</sub> removal by filtration on the HVAC and the presence of more significant indoor carbonyl sources within the schoolrooms. Regression analysis of indoor and outdoor pollutant concentrations showed that for PM<sub>2.5</sub>, sulfate and nitrate were the best- and worst-correlated species, respectively. This suggests that nitrate is a poor tracer for outdoor-to-indoor PM<sub>2.5</sub> transfer. In addition, no significant correlations were observed for any of the carbonyl compounds measured. This further suggests the presence of indoor carbonyl sources inside the schoolrooms, and that indoor air quality especially in terms of carbonyl concentrations may be substantially poorer than outdoor air quality. © 2004 Elsevier Ltd. All rights reserved.

**Keywords:** PM<sub>2.5</sub>; Carbonyls; Indoor air quality; School; Tracer

## 1. Introduction

The effects of both gas- and particle-phase air pollution on human health have been extensively investigated over the years. It has been shown that exposure to particulate matter of aerodynamic diameter <2.5 μm (PM<sub>2.5</sub>)—both indoors and outdoors—can cause acute and chronic health effects (Quackenboss et al., 1989; Xu and Wang, 1993). Some gas-phase carbonyl compounds (aldehydes and ketones) are also

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known to have adverse effects on human health; for example, 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).

Mira Loma is a semi-rural community in western Riverside County, California, 80 km east of downtown Los Angeles. Studies have shown that the region in which Mira Loma lies has some of the highest levels of outdoor  $PM_{2.5}$  measured in the United States (Kim et al., 2000a, b). A study conducted by Gauderman et al. (2000) showed that out of 12 communities in southern California, schoolchildren in Mira Loma had amongst the lowest forced expiratory volume (FEV) levels, an indicator of lung function.

Further, studies have shown that people typically spend approximately 85–90% of their time indoors (Jenkins et al., 1992; Klepeis et al., 2001). Investigation of indoor exposure to  $PM_{2.5}$  and gas-phase toxics (such as carbonyls) is therefore of interest. Indoor and outdoor particulate matter mass concentrations in general have been investigated by various groups (Wallace, 1996; Janssen et al., 2001; Geller et al., 2002) and have been used to determine the influence of outdoor air on indoor air for both gas- and particulate-phase pollutants. Studies (primarily on the East Coast of the United States) have shown that sulfate and sulfur are suitable tracers (Sarnat et al., 2000, 2002). A recent study by Lunden et al. (2003) suggests that ammonium nitrate is not an appropriate tracer for outdoor-to-indoor  $PM_{2.5}$  transfer. This is of particular interest in California, where nitrate is typically more prevalent than sulfate (Tolocka et al., 2001).

The present study attempts to quantify and characterize indoor  $PM_{2.5}$  and gas-phase carbonyl com-

pounds found at a cross-section of sites within the Mira Loma area, including 19 residences and a local high school, and to compare indoor and outdoor concentrations for these pollutants. Fig. 1 gives the locations of these sampling sites within the Mira Loma area. It is the authors' belief that this work will be of interest to health effects researchers concerned with indoor and outdoor exposure to gas- and particle-phase compounds in polluted areas in the United States.

## 2. Experimental methods

### 2.1. Sampling methodology

A schematic of the sampling system used in this study is shown in Fig. 2. This system employed the principle for  $PM_{2.5}$  impactor design described by Biswas and Flagan (1988). The impactor was connected to a manifold with four sampling lines (A–E; Fig. 2) for measurement of total  $PM_{2.5}$  mass, organic carbon (OC) and elemental carbon (EC), ionic nitrate and sulfate, and trace elements. An additional three sampling lines (F–H) were used for measurement of gas-phase ammonia, nitric acid and carbonyl compounds, and were not connected to the  $PM_{2.5}$  impactor. Critical orifices (O'Keefe Controls, Trumbull, CT, USA) were used to control flow rates on all lines; these were calibrated before and after every sampling period using a Gilibrator 2 bubble flow meter (Sensidyne, Clearwater, FL, USA). Critical orifices were connected by means of polyethylene piping to a 0.19 kW oil-less GAST 0523 vacuum pump (GAST, Benton Harbor, MI, USA). The pump was housed in a sound-insulated weatherproof container.

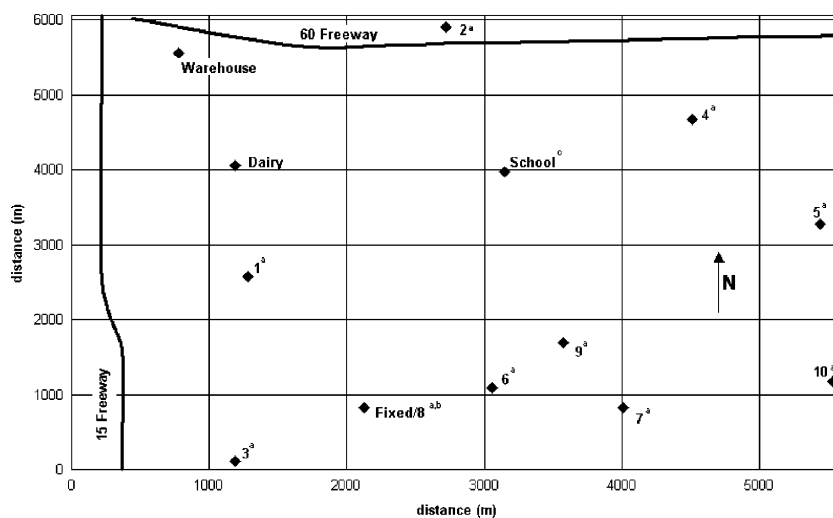


Fig. 1. Grid showing Mira Loma sampling sites: (a) each numbered location represents two residences (indoor sites) and one outdoor site; (b) the fixed outdoor site was adjacent to site 8; and (c) all the schoolroom sites were at the site marked "School".

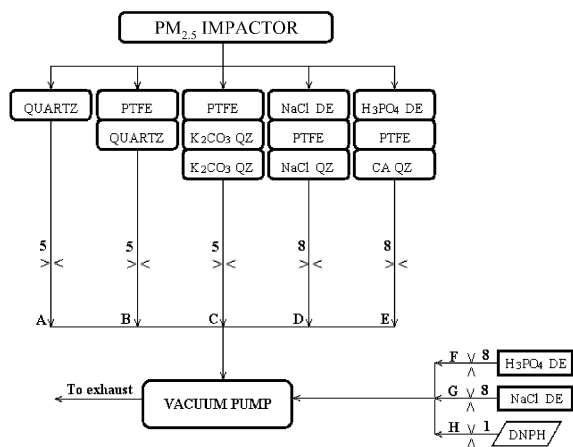


Fig. 2. Schematic of sampling system. The numbers indicate the flow rate of the sampling lines in liters per minute (LPM). Note that lines F, G, and H are for gas-phase sampling and are not connected to the  $PM_{2.5}$  particle trap.

Sampling was conducted inside twenty residences and seven schoolrooms from 17 September 2001 to 26 January 2002, except on 29 November 2001 and from 25 December 2001 to 1 January 2002 (due to holidays). Two of the seven schoolrooms were portable units with an attached air-conditioning system. Outdoor sampling was conducted at one fixed site in southwestern Mira Loma throughout the duration of the study, including the holidays. This total duration was divided into ten “sampling periods”. A “sampling period” was defined for this purpose as a period of 12 calendar days during which sampling was conducted in six alternating 24-h segments, from 8:00 PM on one calendar day up to 8:00 PM the next calendar day.

For each sampling period, residences were chosen in sets of two such that the average distance between them was  $\sim 100$  m, with a maximum of  $\sim 400$  m in one case. A sampling system was placed outside one of the two residences and assumed to reasonably approximate the outdoor gas-phase and  $PM_{2.5}$  concentrations for both residences. In order to choose sampling locations representative of both residences, efforts were made to ensure that the sampling system was not exposed to localized sources. The outdoor samples were used in the calculation of indoor/outdoor ratios for the various components sampled. Each residence was provided with a logbook to record daily activities such as cooking, cleaning, use of an air-conditioning or heating system, and smoking. Data from one residence were rejected due to obvious homeowner tampering. Details of the residences, including type and frequency of typical household activities, are given in Table 1.

Additionally, a total of seven rooms at a local high school in Mira Loma were sampled for  $PM_{2.5}$  during the

first seven sampling periods (i.e., from 17 September to 11 December 2001). These included a library, an administrative office, and five classrooms. However, a sampler in one of the classrooms had to be removed due to logistical constraints. Details of sampling within the school are given in Table 2.

## 2.2. Chemical analysis

$PM_{2.5}$  samples were collected using 47 mm diameter 2- $\mu$ m 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 (Thermo Orion, Beverly, MA, USA), both before and after sampling. The average of the two closest weights in each case (within 3  $\mu$ g) were taken to be the initial and final weights. The difference between the final and initial weights yielded the collected  $PM_{2.5}$  mass. The denuders and backup quartz filters in sampling lines D and E (Fig. 2) were used to correct for  $HNO_3$  and  $NH_3$  volatilization losses during sampling, respectively. The detection limit for this method was 0.4  $\mu$ g  $m^{-3}$ .

A thermal/optical carbon aerosol analyzer (Sunset Laboratory, Forest Grove, OR, USA) operating on the NIOSH 5040 method was used to perform analysis of OC/EC (Birch and Cary, 1996) using uncoated 47 mm diameter QAT Tissuquartz quartz fiber filters (Pall-Gelman, Ann Arbor, MI, USA). The OC values were obtained by multiplying the carbon mass by 1.9 (Turpin and Lim, 2001) to account for the hydrogen, oxygen and nitrogen atoms associated with OC. Gas-phase sorption 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 OC may be found in Na et al. (2004a). 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- $\mu$ m pore Allsep A-2 Anion column (100 mm length  $\times$  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 on sample line C.

Table 1  
Summary of residential sites sampled

Sampling period	Site ID	Smoking	Pets/livestock <sup>a</sup>		Cleaning			Cooking		Ventilation and climate control			
			Outdoors	Indoors	Vac	Dust	Solv	Type	Frequency <sup>b</sup>	Heating type	Frequency <sup>b</sup>		
											H	W	AC
9/17–9/28	1A	No	7	0	0.5	0.3	0.5	Gas	1.6	Gas	0	0.6	0.9
	1B	No	2	0	1.0	0.4	0.9	Gas	2.0	Electric	0.1	0.9	0
9/29–10/10	2A	No	0	0	0	0.3	1.0	Gas	1.8	Gas	0.1	1.0	0
	2B	No	3	0	0.5	0.5	0.7	Gas	1.7	Gas	0	0.9	0
10/11–10/22	3A	No	0	0	0.3	0.2	0.1	Gas	0.9	Gas	0	0	0.9
	3B	Yes	33	6	0.4	0.1	0.3	Electric	2.4	Electric	0	0.5	0
10/23–11/3	4A	Yes <sup>c</sup>	1	0	0.3	0.3	0.3	Gas	0.7	Gas	0	0.8	0
	4B	Yes	116	2	0.1	0.1	1.0	Gas	2.8	Gas	0.1	1.0	0
11/4–11/15	5A	Yes	0	5	0.5	0.5	0	Gas	2.5	Gas	0.5	0.9	0
	5B	Yes <sup>c</sup>	15	7	0	0.3	0.4	Gas	2.3	Gas	0.5	0.9	0
11/16–11/29	6A	No	2	0	0.5	0	0.2	Gas	1.2	Gas	0	0.4	0
	6B	No	0	4	0.2	0.3	0.1	Gas	2.0	Gas	0.9	0.3	0
11/30–12/11	7A	Yes	0	5	0	0.3	0	Gas	1.2	Gas	0.8	0	0.2
	7B	Yes	0	8	0.5	0.8	0.2	Gas	2.3	Gas	1.0	0.8	0
12/12–12/23	8A	No	2	2	0.5	0.8	0.8	Gas	2.5	Gas	1.0	0.1	0
	8B	No	1	0	0.2	0.2	0	Gas	1.3	Gas	0.6	0.1	0
1/3–1/14	9A	No	5	7	0	0.1	0.2	Gas	1.1	Gas	1.0	0.9	0
	9B	No	2	0	N/A <sup>d</sup>	N/A <sup>d</sup>	N/A <sup>d</sup>	Gas	N/A <sup>d</sup>	Gas	N/A <sup>d</sup>	N/A <sup>d</sup>	N/A <sup>d</sup>
1/15–1/26	10A	Yes <sup>c</sup>	8	0	0.3	0.1	0.1	Gas	1.0	Gas	0.9	0.4	0
	10B	No	15	0	0.3	0.2	0.2	Gas	0.6	Gas	0.8	1.0	0

Key to abbreviations: Vac: vacuuming; Dust: dusting; Solv: use of solvents; H: use of heater; W: opening of windows; AC: use of air conditioning.

<sup>a</sup>The “Pets/Livestock” field shows the actual number of animals present.

<sup>b</sup>The “Frequency” field indicates the number of times an activity was performed per day. For example, a frequency of 2.0 under the “cooking” field indicates that on average two meals were cooked per day.

<sup>c</sup>Although the residents of these homes smoked, they did not do so inside their homes.

<sup>d</sup>N/A indicates data were not available.

Table 2  
Summary of schoolroom sites sampled

Sampling period	Site ID	Site description
9/17–9/28	Room 1	Classroom
9/29–10/10	Room 2	Library
10/11–10/22	Room 3	Classroom
10/23–11/3	Room 4 <sup>a</sup>	Classroom
11/4–11/15	Room 5	Classroom
11/16–11/29	Room 6	Classroom
11/30–12/11	Room 7	Administrative office

<sup>a</sup>Sampling could not be conducted at this site due to logistical constraints.

Gas-phase nitric acid was collected on fabric denuders (Fitz, 1990) coated with 9% sodium chloride solution and quartz denuders coated with 2% sodium chloride solution (sample line D). Ammonia samples were collected on fabric denuders coated with 10% phosphoric acid and quartz denuders coated with 2% citric acid

solution (sample line E). 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). The detection limit for this method is 35 ng m<sup>-3</sup>.

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) to account for sampling breakthrough, with a nominal flow rate of 1.01 min<sup>-1</sup>. However, tests to determine the extent of breakthrough showed that the front cartridges had high collection efficiencies, typically capturing >98% of the carbonyls. Therefore, only the front cartridge was subjected to chemical analysis. 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  $\mu\text{m}$  Deltabond AK Resolution (200 cm  $\times$  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<sub>1</sub> to C<sub>8</sub> and included 11 aldehydes and 2 ketones; the detection limit was 70 ng m<sup>-3</sup>.

### 3. Results and discussion

#### 3.1. PM<sub>2.5</sub> composition

Fig. 3 shows the mass concentration of measured PM<sub>2.5</sub> components inside residences and schoolrooms for the duration of the study. The corresponding PM<sub>2.5</sub> compositions measured at the fixed outdoor site are also shown. The average PM<sub>2.5</sub> concentration inside the residences was 45.4  $\mu\text{g m}^{-3}$ , while the median concentration was 32.3  $\mu\text{g m}^{-3}$ . The substantial difference between the two values can be attributed in part to the high overall PM<sub>2.5</sub> concentrations observed at residence R5a (average: 201.4  $\mu\text{g m}^{-3}$ ). This site had an individual who smoked over 40 cigarettes per day indoors. Due to the potentially skewed distribution as a result of this activity, both average and median values have been reported for all measured gas- and particle-phase components. More information about PM<sub>2.5</sub> component values observed at R5a is given later in this section.

OC was found to be the largest contributor to PM<sub>2.5</sub> for the residences. The average and median values for OC inside the residences were 27.0 and 13.8  $\mu\text{g m}^{-3}$ , respectively, or about 40–60% of total PM<sub>2.5</sub>. This was followed by nitrate (average: 6.6  $\mu\text{g m}^{-3}$ ; median: 4.8  $\mu\text{g m}^{-3}$ ; 13–14% of total), trace elements (average: 5.0  $\mu\text{g m}^{-3}$ ; median: 4.0  $\mu\text{g m}^{-3}$ ; 11–12% of total). Ammonium, EC, and sulfate concentrations were lower, contributing approximately 8%, 6%, and 4% to total PM<sub>2.5</sub> mass respectively.

Average and median PM<sub>2.5</sub> mass concentrations at the schoolroom sites were found to be 16.3  $\mu\text{g m}^{-3}$  and 13.2  $\mu\text{g m}^{-3}$ , respectively. OC was the major contributor to PM<sub>2.5</sub> at these sites as well, contributing an average of 4.3  $\mu\text{g m}^{-3}$  (26%). The highest OC contribution (50%) was observed at S3, a portable classroom. Trace elements (average: 3.52  $\mu\text{g m}^{-3}$ ; 22%) and nitrate (average: 3.32  $\mu\text{g m}^{-3}$ ; 20%) were the next largest contributors. EC and sulfate contributed 6–7% each on average. Mass concentrations of PM<sub>2.5</sub> and its components inside the schoolrooms were typically 40–80% lower than at residential sites sampled during the same sampling period.

The residence R5a is of interest because of the chemical composition of PM<sub>2.5</sub> observed at this site. Corrections for positive OC artifact were made using backup quartz filters and application of a correction factor based on filter backups for this site. In spite of

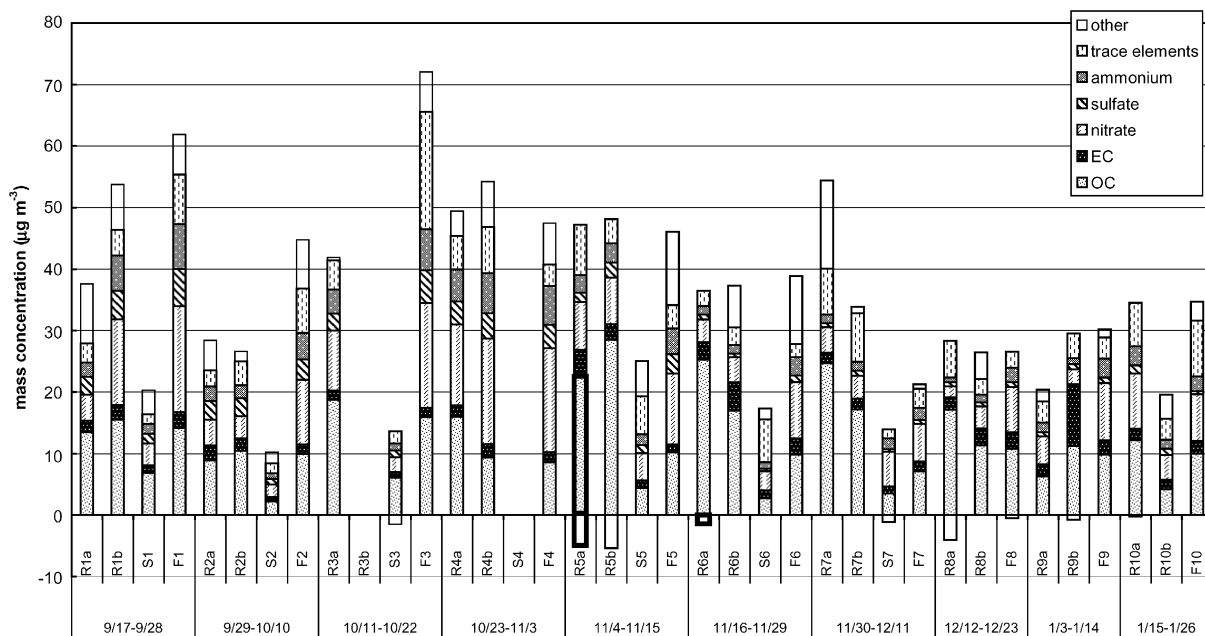


Fig. 3. Reconstituted PM<sub>2.5</sub> chemical composition inside residential (R) and schoolroom (S) sites, and at fixed outdoor (F) site. The “other” field indicates the difference between the measured PM<sub>2.5</sub> mass concentrations and the sum of the different PM<sub>2.5</sub> components and may be negative in certain cases. Heavy borders around the OC and “other” fields indicate scaling to one-tenth of actual value for convenience. No data were obtainable for sites R3b and S4 due to sampler tampering.

this, the absolute OC concentration was found to be  $229.0 \mu\text{g m}^{-3}$ , or greater than the average  $\text{PM}_{2.5}$  concentration measured at this site. This is shown to reduce to 10% of its actual value (and bounded by the thick lines) in Fig. 3, in order to preserve the visual differences between other components within the figure. The corresponding “other” field, which represents the difference between reconstituted and measured  $\text{PM}_{2.5}$  mass, is seen to be a somewhat high negative number. Visual inspection suggests that negative values for the “other” field are significant in the presence of a high OC contribution to the total  $\text{PM}_{2.5}$  mass.

In order to test this theory, the negative of the “other” field was plotted against the percentage contribution for each component of  $\text{PM}_{2.5}$ . The results showed that OC contribution was directly proportional to the extent of overestimation as represented by the “other” field. The correlation was significant ( $r = 0.83$ ). All other components showed statistically insignificant inverse relationships with the extent of overestimation. As an illustration, the next best correlated component, trace elements had  $r = 0.33$ .

Based on these results, it was determined for operational purposes that all of the observed overestimation in  $\text{PM}_{2.5}$  was due to OC alone, and that subtraction of the “other” field from the OC field for any data point would yield a reasonable estimate of the OC contribution to indoor  $\text{PM}_{2.5}$ . Using this assumption,

the OC contribution of residence R5a was found to be 88%.

### 3.2. Indoor/outdoor ratios: $\text{PM}_{2.5}$

The concentration of a given species at the corresponding outdoor fixed site in southwestern Mira Loma during the same time period as for that at a given indoor site was used as the basis for calculation of indoor/outdoor ratios in this work. The outdoor fixed site was chosen since it was statistically indistinguishable from other outdoor sites where sampling was also conducted (Sawant et al., 2004). Average outdoor  $\text{PM}_{2.5}$  concentration at this site was  $41.8 \mu\text{g m}^{-3}$  for the study duration. More information on  $\text{PM}_{2.5}$  and gas-phase carbonyl concentrations for outdoor sites in Mira Loma can be found in Sawant et al. (2004).

Fig. 4 shows the indoor/outdoor ratios for the indoor sites. The median indoor/outdoor ratio for  $\text{PM}_{2.5}$  mass for the residences was found to be 0.87. Nitrate showed the lowest median indoor/outdoor ratio among the  $\text{PM}_{2.5}$  components (0.46).

Indoor/outdoor  $\text{PM}_{2.5}$  ratios were typically lower for the schools than for the residences, with a median value of 0.38 and a range of 0.05–2.02. Trace elements showed the highest indoor/outdoor ratios, with a median of 0.62. More information on indoor/outdoor relationships

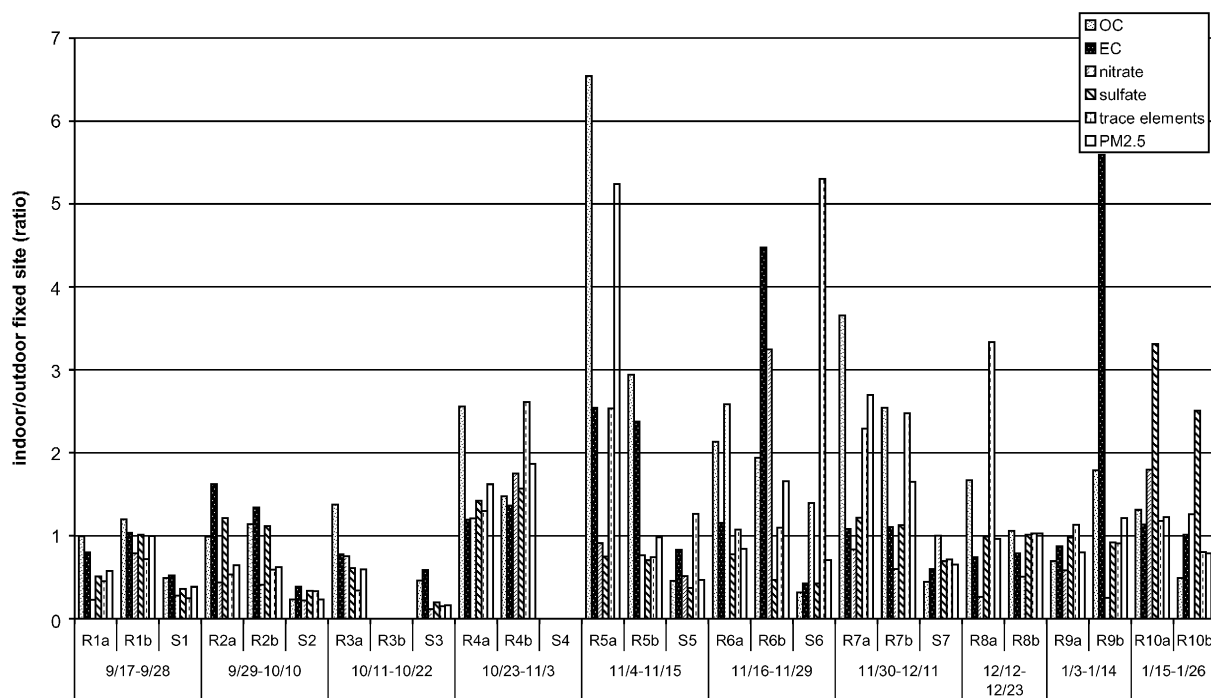


Fig. 4. Indoor/outdoor ratios of  $\text{PM}_{2.5}$  and its components for residential (R) and schoolroom (S) sites. Ratios are with respect to outdoor fixed site during same sampling period. No data were obtainable for sites R3b and S4 due to sampler tampering.



observed in this study with respect to trace elements is presented in Na et al. (2004b).

These findings suggest a more significant presence of indoor sources of  $PM_{2.5}$  for residences relative to the schools and/or a less effective  $PM_{2.5}$  removal mechanism for the residences relative to the schools. It was noted that the schoolrooms sampled all had heating, ventilation, and air-conditioning (HVAC). The HEPA filter of the air conditioning unit was cleaned regularly according to the school maintenance staff. By contrast, only three of the residences sampled used air-conditioning, and the frequency of usage was low (see Table 1). Also, the frequency of ventilation (i.e., opening the windows) averaged over  $0.6 \text{ day}^{-1}$  for the 17 homes for which data and mass concentrations were available, while it was  $0.0 \text{ day}^{-1}$  for the schoolrooms.

### 3.3. Gas-phase carbonyl concentrations

Fig. 5 shows the average concentrations of 11 aldehydes and 2 ketones measured inside the residences and schoolrooms. The corresponding carbonyl concentrations measured at the fixed outdoor site are also shown. Median total carbonyl concentrations for the residential sites were  $50.8 \mu\text{g m}^{-3}$  (range:  $8.8\text{--}99.7 \mu\text{g m}^{-3}$ ), and for the schoolroom sites were  $62.9 \mu\text{g m}^{-3}$  (range:  $38.4\text{--}105.3 \mu\text{g m}^{-3}$ ). Formaldehyde,

acetaldehyde and acetone were the main contributors to the measured carbonyl concentrations in both cases. Median contributions of these three compounds to total carbonyl concentrations were 27%, 19%, and 12%, respectively for the residences, and 24%, 17%, and 16%, respectively for the schoolrooms. In addition, concentrations of tolualdehyde were found to be roughly an order of magnitude higher at four of the schoolroom sites (median:  $3.97 \mu\text{g m}^{-3}$ ) than at the residences (median:  $0.35 \mu\text{g m}^{-3}$ ). However, an investigation into the potential contributors to tolualdehyde at the sites yielded inconclusive results.

### 3.4. Indoor/outdoor ratios: carbonyls

The median ratio of total indoor carbonyl mass concentration to that at the outdoor fixed site was 3.5 for the residences and 4.5 for the schoolrooms. The indoor/outdoor ratios for formaldehyde, acetaldehyde, acetone, and the sum of 10 other carbonyls are shown in Fig. 6. For the residences, median ratios for these four categories were 6.9, 5.4, 1.9, and 2.1, respectively. For the schoolrooms, these values were 7.8, 5.8, 2.9, and 3.8, respectively.

Typical carbonyl indoor/outdoor ratios for both residences and schoolrooms were significantly greater than 1.0, with schoolrooms having higher ratios relative

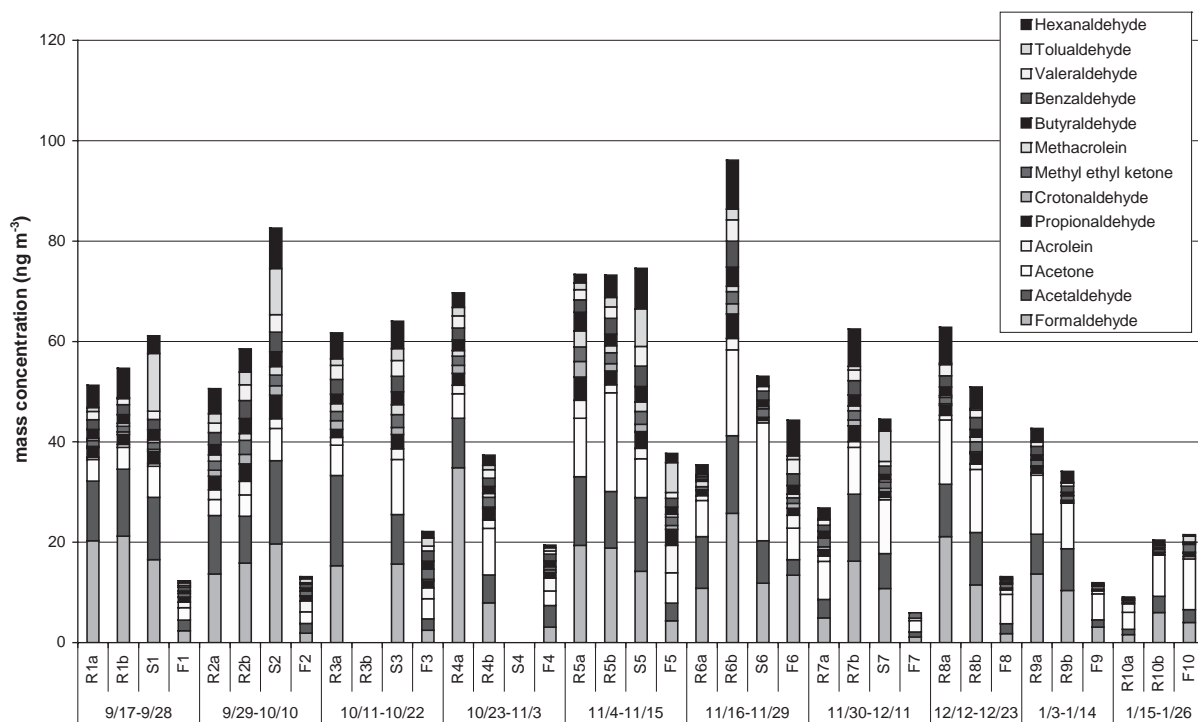


Fig. 5. Concentrations of gas-phase carbonyl compounds inside residential (R) and schoolroom (S) sites, and at fixed outdoor site (F). No data were obtainable for sites R3b and S4 due to sampler tampering.

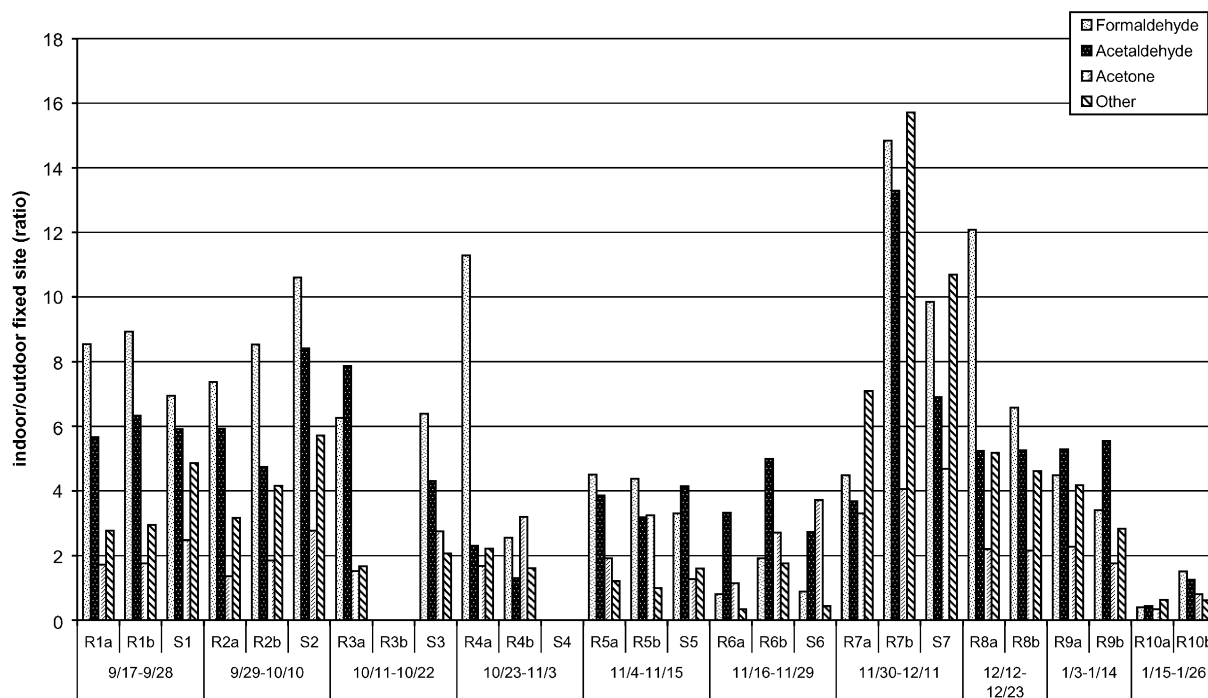


Fig. 6. Indoor/outdoor ratios for three highest carbonyls. Ratios are of three highest carbonyls and sum of remaining carbonyls ("other") measured indoors at residential (R) and schoolroom (S) sites to those measured at outdoor fixed site during the same time period. No data were obtainable for sites R3b and S4 due to sampler tampering.

to the residences. In contrast, indoor/outdoor ratios for  $PM_{2.5}$  were typically  $<1.0$ , with schoolrooms having lower ratios relative to the residences. The potential reasons for such a discrepancy between gas- and particle-phase ratios could be: potential indoor sources, preferential outdoor-to-indoor infiltration; or lack of an effective removal mechanism. Although preferential infiltration and lack of an effective removal mechanism might explain a ratio close to 1.0, the probability that these factors account for ratios as high as 3 or more appears slim. The most likely explanation, therefore, is the presence of significant indoor sources of carbonyls, although preferential infiltration and the lack of an efficient removal mechanism might contribute to the observed trends. It is known that various elements inside a building are sources of carbonyls, such as carpet, drywall, adhesives, etc. (Humfrey et al., 1996; Samfield, 1992). These are the likely sources for the high indoor/outdoor carbonyl ratios observed inside the schoolrooms and residences.

### 3.5. Regression analysis

Table 3 shows the values of correlation coefficient  $r$  for the residences and the schoolrooms for concentrations of  $PM_{2.5}$  and its components. Statistically sig-

nificant correlations are indicated in bold; this was determined using standard tables for the correlation coefficient. It is observed that sulfate was the best-correlated component, with seven sites (all residential) having a statistically significant  $r$ -value for  $p < 0.05$ . EC was the next best, showing a significant correlation for five sites (4 residences and 1 schoolroom). Nitrate was the only  $PM_{2.5}$  component not showing a statistically significant correlation for any site. This suggests that nitrate may be unsuitable as a conservative tracer for the outdoor-to-indoor transfer of  $PM_{2.5}$ , in agreement with the findings of Lunden et al. (2003). Sulfate may be more appropriate for this purpose, despite being present in significantly lower concentrations than nitrate.

## 4. Summary

This work involved the chemical characterization of  $PM_{2.5}$  and its components and gas-phase carbonyl compounds inside multiple residences and schoolrooms in the Mira Loma area. In general, OC was found to be the largest contributor to indoor  $PM_{2.5}$  concentrations. Indoor/outdoor ratios for  $PM_{2.5}$  were lower for the schoolrooms (0.38) than for the residences (0.87). Formaldehyde, acetaldehyde, and acetone were found



Table 3

Values of the correlation coefficient (*r*) for indoor versus outdoor PM<sub>2.5</sub> and its components for residences and schoolrooms

Site	OC	EC	Nitrate	Sulfate	Ammonium	Trace elements	PM <sub>2.5</sub>							
R1a	—	0.388	—	0.812	+	0.985	+	0.073	+	0.741	—	0.390	+	0.258
R1b	—	0.281	+	0.289	NS	NS	NS	NS	NS	NS	NS	NS	—	0.362
S1	—	0.659	+	0.779	—	0.990	+	0.984	—	0.949	NS	NS	—	0.912
R2a	+	<b>0.832</b>	+	0.417	+	0.322	+	0.231	+	0.226	+	<b>0.920</b>	+	<b>0.989</b>
R2b	+	<b>0.972</b>	+	0.625	—	0.327	+	0.482	—	0.058	+	<b>0.957</b>	+	<b>0.902</b>
S2	+	<b>0.888</b>	+	<b>0.957</b>	+	0.049	+	0.410	+	0.568	—	0.435	+	<b>0.970</b>
R3a	+	0.014	+	0.812	+	0.760	+	<b>0.945</b>	+	<b>0.870</b>	+	<b>0.963</b>	+	0.474
R3b	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
S3	+	0.896	+	0.839	+	0.947	+	0.834	+	0.938	—	0.634	+	0.834
R4a	+	0.343	+	0.789	+	0.671	+	<b>0.884</b>	+	0.733	+	0.818	+	0.718
R4b	+	0.544	+	0.843	+	0.545	+	0.819	+	0.612	+	0.536	+	0.599
S4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
R5a	+	0.692	+	<b>0.857</b>	+	0.483	+	<b>0.975</b>	+	0.600	—	0.942	+	0.426
R5b	+	0.821	+	0.112	+	0.935	+	<b>1.000</b>	+	0.933	+	0.892	+	0.502
S5	+	0.476	+	0.833	+	0.020	+	0.991	+	0.148	—	0.888	+	<b>0.963</b>
R6a	+	0.935	+	0.585	+	0.081	+	<b>0.998</b>	+	0.314	+	0.928	+	0.944
R6b	+	0.044	+	0.235	+	0.017	+	<b>0.989</b>	+	0.108	+	0.906	+	0.158
S6	+	0.771	+	0.697	—	0.299	—	0.141	—	0.328	NS	NS	+	0.300
R7a	+	0.154	+	<b>0.969</b>	—	0.168	—	<b>0.998</b>	—	0.331	+	0.861	+	0.585
R7b	+	0.722	+	<b>0.957</b>	+	0.253	+	0.859	+	0.170	+	0.849	+	0.702
S7	—	0.995	+	0.842	+	0.516	—	NS	+	0.595	NS	NS	—	0.864
R8a	+	0.300	+	<b>0.935</b>	+	0.385	+	0.783	+	0.159	—	0.765	+	0.796
R8b	+	0.433	+	0.994	+	0.834	—	0.044	+	0.760	—	0.215	+	0.234
R9a	—	0.417	+	0.326	—	0.005	—	0.194	—	0.089	+	0.431	—	0.205
R9b	+	0.990	+	0.917	+	0.959	+	0.904	+	0.912	NS	NS	+	0.763
R10a	+	0.391	+	0.312	—	0.212	—	0.393	—	0.384	+	0.972	+	0.689
R10b	—	0.391	+	0.755	—	0.490	—	0.066	—	0.450	—	0.426	—	0.741

*Bold* values indicate statistically significant correlations. Signs (+ or –) indicate whether a correlation was positive or negative.

“NA” stands for “not available”. Data for these fields could not be used due to sample tampering.

“NS” stands for “not significant”. Insufficient data points excluded these fields from the correlation analysis.

to be the main contributors to carbonyl concentrations for all sites. Indoor/outdoor ratios for carbonyls were greater than 1.0 for all sites, with these values being greater for the schoolrooms than for the residences. This is likely due to the presence of indoor sources of carbonyls within the schoolrooms. These findings suggest that indoor air quality can be substantially poorer than outdoor air quality even in areas regarded as highly polluted, especially with respect to carbonyl compounds. In addition, regression analysis showed that nitrate is not a conservative tracer for outdoor-to-indoor PM<sub>2.5</sub> transfer, and that sulfate is significantly better, even though it is present in much smaller quantities than nitrate.

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### Disclaimer

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## References

- Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Science and Technology* 25, 221–241.
- Biswas, P., Flagan, R.C., 1988. The particle trap impactor. *Journal of Aerosol Science* 19, 113–121.
- Bolleter, W.T., Bushman, C.J., Tidwell, P.W., 1961. Spectrophotometric determination of ammonia as indophenol. *Analytical Chemistry* 33, 592–594.
- Fitz, D.R., 1990. Reduction of the positive organic artifact on quartz filters. *Aerosol Science and Technology* 12, 142–148.
- Gauderman, W.J., McConnell, R., Gilliland, F., London, S., Thomas, D., Avol, E., Vora, H., Berhane, K., Rappaport, E.B., Lurmann, F., Margolis, H.G., Peters, J., 2000. Association between air pollution and lung function growth in southern California children. *American Journal of Respiratory and Critical Care Medicine* 162, 1383–1390.
- Geller, M.D., Chang, M., Sioutas, C., Ostro, B.D., Lipsett, M.J., 2002. Indoor/outdoor relationship and chemical composition of fine and coarse particles in the southern California deserts. *Atmospheric Environment* 36, 1099–1110.
- Humfrey, C., Shuker, L., Harrison, P., 1996. IEH Assessment on Indoor Air Quality in the Home. Leicester, Institute for Environment and Health.
- Janssen, N.A.H., van Vliet, P.H.N., Aarts, F., Harssema, H., Brunekreef, B., 2001. Assessment of exposure to traffic related air pollution of children attending schools near motorways. *Atmospheric Environment* 35, 3875–3884.
- Jenkins, P.L., Phillips, T.J., Mulberg, E.J., Hui, S.P., 1992. Activity patterns of Californians: use of and proximity to indoor pollutant sources. *Atmospheric Environment* 26A, 2141–2148.
- Kerns, W.D., Pavkov, K.L., Donofrio, D.J., Swenberg, J.A., 1983. Carcinogenicity of formaldehyde in rats and mice after long-term inhalation exposure. *Cancer Research* 43, 4382–4392.
- Kim, B.M., Teffera, S., Zeldin, M.D., 2000a. Characterization of PM<sub>2.5</sub> and PM<sub>10</sub> in the South Coast Air Basin of southern California: part 1—spatial variations. *Journal of the Air and Waste Management Association* 50, 2034–2044.
- Kim, B.M., Teffera, S., Zeldin, M.D., 2000b. Characterization of PM<sub>2.5</sub> and PM<sub>10</sub> in the South Coast Air Basin of southern California: part 2—temporal variations. *Journal of the Air and Waste Management Association* 50, 2045–2059.
- Klepeis, N.E., Nelson, W.C., Ott, W.R., Robinson, J.P., Tsang, A.M., Switzer, P., Behar, J.V., Hern, S.C., Engelmann, W.H., 2001. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. *Journal of Exposure Analysis and Environmental Epidemiology* 11, 231–252.
- Lunden, M.M., Revzan, K.L., Fischer, M.L., Thatcher, T.L., Littlejohn, D., Hering, S.V., Brown, N.J., 2003. The transformation of outdoor ammonium nitrate aerosols in the indoor environment. *Atmospheric Environment* 37, 5633–5644.
- Na, K., Sawant, A.A., Song, C., Cocker III, D.R., 2004a. Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California. *Atmospheric Environment* 38, 1345–1355.
- Na, K., Sawant, A.A., Cocker III, D.R., 2004b. Trace elements in fine particulate matter within a community in western Riverside County, CA: focus on residential sites and a local high school. *Atmospheric Environment* 38, 2867–2877.
- Nordman, H., Keskinen, H., Tuppurainen, M., 1985. Formaldehyde asthma—rare or overlooked? *Journal of Allergy and Clinical Immunology* 75, 91–99.
- Quackenboss, J.J., Lebowitz, M.D., Crutchfield, C.D., 1989. Indoor–outdoor relationships for particulate matter: exposure classifications and health effects. *Environment International* 15, 353–360.
- Samfield, M.M., 1992. Indoor air quality data base for organic compounds. United States Environmental Protection Agency: EPA-600-R-92-025.
- Sarnat, J.A., Koutrakis, P., Suh, H.H., 2000. Assessing the relationship between personal particulate and gaseous exposures of senior citizens living in Baltimore, MD. *Journal of the Air and Waste Management Association* 50, 1184–1198.
- Sarnat, J.A., Long, C.M., Koutrakis, P., Coull, B.A., Schwartz, J., Suh, H.H., 2002. Using sulfur as a tracer of outdoor fine particulate matter. *Environmental Science and Technology* 36, 5305–5314.
- Sawant, A.A., Na, K., Zhu, X., Cocker III, D.R., 2004. Chemical characterization of outdoor PM<sub>2.5</sub> and gas-phase compounds in Mira Loma, California. *Atmospheric Environment* 38, 5517–5528.
- Siegl, W.O., Richert, J.F.O., Jensen, T.E., Schuetzle, D., Swarin, S.J., Loo, J.F., Probst, A., Nagy, D., Schlenker, A.M., 1993. Improved emissions speciation methodology for phase II of the auto/oil air quality improvement research program—hydrocarbons and oxygenates. SAE Paper 930142.
- Tolocka, M.P., Solomon, P.A., Mitchell, W., Norris, G.A., Gemmill, D.B., Wiener, R.W., Vanderpool, R.W., Homolya, J.B., Rice, J., 2001. East versus West in the US: chemical characteristics of PM<sub>2.5</sub> during the winter of 1999. *Aerosol Science and Technology* 34, 88–96.
- Turpin, B.J., Lim, H.-J., 2001. Species contributions to PM<sub>2.5</sub> mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* 35, 602–610.
- US EPA, 1989. Analysis of air toxics emissions, exposures, cancer risks and controllability in five urban areas, vol. 1. Base year analysis and results, Office of Air Quality Planning and Standards, Publication No. EPA-450/2-89-012a, Research Triangle Park, NC, July.
- Wallace, L., 1996. Indoor particles: a review. *Journal of the Air and Waste Management Association* 46, 98–126.
- Xu, X., Wang, L., 1993. Association of indoor and outdoor particulate level with chronic respiratory illness. *American Review of Respiratory Disease* 148, 1516–1522.