

A functional group characterization of organic PM_{2.5} exposure: Results from the RIOPA study

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Received 16 August 2006; received in revised form 26 March 2007; accepted 26 March 2007

Abstract

The functional group (FG) composition of urban residential outdoor, indoor, and personal fine particle (PM_{2.5}) samples is presented and used to provide insights relevant to organic PM_{2.5} exposure. PM_{2.5} samples (48 h) were collected during the Relationship of Indoor, Outdoor, and Personal Air (RIOPA) study at 219 non-smoking homes (once or twice) in Los Angeles County, CA, Elizabeth, NJ, and Houston, TX. Fourier transform infrared (FTIR) spectra of PM_{2.5} samples were collected, and FG absorbances were quantified by partial least squares (PLS) regression, a multivariate calibration method.

There is growing evidence in the literature that a large majority of indoor-generated PM_{2.5} is organic. The current research suggests that indoor-generated PM_{2.5} is enriched in aliphatic carbon–hydrogen (CH) FGs relative to ambient outdoor PM_{2.5}. Indoor-generated CH exceeded outdoor-generated CH in 144 of the 167 homes for which indoor or outdoor CH was measurable; estimated indoor emission rates are provided. The strong presence of aliphatic CH FGs in indoor PM_{2.5} makes particulate organic matter substantially less polar indoors and in personal exposures than outdoors. This is a substantial new finding. Based on the quantified FGs, the average organic molecular weight (OM) per carbon weight (OC), a measure of the degree of oxygenation of organic PM, is in the range of 1.7–2.6 for outdoor samples and 1.3–1.7 for indoor and personal samples. Polarity or degree of oxygenation effects particle deposition in exposure environments and in the respiratory system.

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Keywords: Organic aerosol; OM/OC; FTIR; Indoor air; Exposure assessment

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1. Introduction

Airborne fine particulate matter (PM_{2.5}) is a ubiquitous presence in the urban environment and is known to exert deleterious effects on human health (USEPA, 2004). Identification of the chemical compounds or properties responsible for these effects is an area of active research. Anywhere from 10% to 70% of ambient (outdoor) PM_{2.5} mass is organic matter (Turpin et al., 2000); ambient organic PM_{2.5} is composed of potentially thousands of different compounds that remain largely uncharacterized despite substantial effort (Schauer and Cass, 2000). Ambient organic PM_{2.5} includes alkanes, aldehydes, carboxylic acids, ketones, and aromatics (Seinfeld and Pandis, 1998).

Although sources of indoor PM_{2.5} such as cooking (Olson and Burke, 2006; Wallace, 2006), dust resuspension (Ferro et al., 2004), indoor gas-to-particle chemical reactions (Wainman et al., 2000), and the infiltration of ambient PM_{2.5} (Meng et al., 2005b) have been identified, the chemical composition of indoor residential organic PM_{2.5} concentrations and exposures has not been characterized to the same degree as outdoor PM_{2.5}. Phthalate esters, phosphor-organics, and poly brominated di-phenyl ethers have been identified in residential indoor dusts (e.g., Wensing et al., 2005; Fromme et al., 2004; Rudel et al., 2003). Alkanes, aliphatic alcohols, acids, esters and ester phosphates have been found in airborne office building particles and are hypothesized to originate from indoor sources including floor polish, sealants and lubricants (Weschler, 1980, 1984; Walker and Weschler, 1980; Weschler and Fong, 1986). A more complete characterization of the PM_{2.5} mixture in outdoor, indoor, and personal air will aid in the development of hypotheses regarding the mechanisms responsible for observed health effects and in the development of strategies for exposure mitigation.

Fourier transform infrared (FTIR) spectroscopy has been used to characterize the functional group (FG) composition of ambient PM_{2.5} samples without extraction (e.g., Garnes and Allen, 2002; Maria et al., 2002; Blando et al., 1998; Krost and McClenny, 1994; Mylonas et al., 1991). It chemically characterizes both polar and non-polar compounds at the FG level, albeit with larger uncertainties than those enjoyed by established molecular level techniques. Thus, it is a useful complement to gas chromatography–mass spectroscopy (GC–MS), which provides individual com-

pound concentrations for selected low to moderate polarity compounds comprising roughly 10–20% of ambient organic PM_{2.5} (Schauer and Cass, 2000; Rogge et al., 1993b). By treating PM_{2.5} as a collection of FGs, several properties important to particle behavior and fate can be predicted, including aerosol hygroscopicity, water solubility (Ming and Russell, 2001; Peng et al., 2001; Koo et al., 2003), and gas-particle partitioning (Jang et al., 1997). Hygroscopicity and phase (gas or particle) have a large influence on the fate of compounds in the environment (Seinfeld and Pandis, 1998) and in the human respiratory system (Broday and Georgopoulos, 2001).

In this work, FG concentrations from PM_{2.5} samples collected during the Relationship of Indoor, Outdoor, and Personal Air (RIOPA) study were quantified using partial least squares (PLS) regression, a multivariate calibration method new to the study of PM_{2.5}. Quantities of sulfate (SO₄²⁻), aliphatic carbon–hydrogen (CH), and carbonyl C=O FGs from PM_{2.5} FTIR spectra are reported and used to better understand human exposure to organic PM_{2.5}. Compositional differences between outdoor, indoor, and personal organic PM_{2.5} are discussed and organic molecular weight to carbon weight ratios (OM/OC) are estimated. The merits of multivariate calibration are also noted.

2. Experimental

2.1. RIOPA field study

Forty-eight hour outdoor, indoor, and personal PM_{2.5} samples were collected at 219 non-smoking homes (169 of which were sampled twice) in Los Angeles County, CA, Elizabeth, NJ, and Houston, TX between summer 1999 and spring 2001 and analyzed for PM_{2.5} mass and species. Some homes were in very close proximity to primary PM sources (i.e., highways, refineries, truck loading), while others were further and impacted by the mix of urban and regional sources (Weisel et al., 2005). Outdoor and indoor samples were collected on 37 mm Teflon filters at 10 L m⁻¹ using a PM_{2.5} Harvard Impactor. Personal samples were collected on 25 mm Teflon filters using a PM_{2.5} BGI personal sampler modified to operate at 3.2 L min⁻¹. A second sampler (MSP Corp., 10 L m⁻¹; 37 mm quartz fiber filter and polyurethane foam adsorbant) collected outdoor and indoor samples for organic (OC) and elemental carbon (EC) and trace organic

species. A backup filter was used to correct for OC sampling artifacts. A blank filter was transported with each day's field samples, and collocated samples (duplicates) were collected at several homes. Filter samples were transported cold and stored frozen until analysis. Further study details and PM_{2.5} results are provided elsewhere (Weisel et al., 2005; Meng et al., 2005a; Reff et al., 2005; Meng et al., 2005b; Polidori et al., 2006; Naumova et al., 2002, 2003; Offenbergl et al., 2004). An examination of coupled indoor and outdoor PM_{2.5} species concentrations suggested that indoor-generated PM_{2.5} was predominately organic (Polidori et al., 2006).

2.2. FTIR spectroscopy

The absorbance spectra of 968 Teflon filter samples were collected using a Mattson 100 Research Series Spectrometer containing a deuterated triglycine sulfate (DTGS) detector. Two hundred scans were performed at 4 cm⁻¹ resolution from 450 to 4000 cm⁻¹ both before and after field sampling with the filter in the same orientation. Each pre-sampling spectrum was subtracted from its post-sampling spectrum to remove the infrared spectrum of the Teflon filter (Krost and McClenny, 1994). The spectrum of a polystyrene film standard was collected on each analysis day to monitor for wavenumber drift and variations in instrument sensitivity.

A qualitative assessment of these FTIR spectra and additional analytical details are provided elsewhere (Reff et al., 2005). The mean of the spectra obtained from outdoor, indoor, and personal Los Angeles County samples (Fig. 1) is typical of individual spectra.

2.3. Calibration standards

Aerosol calibration standards of known composition were generated, collected and analyzed by FTIR spectroscopy and used to build calibration models that predict FG quantities directly from FTIR sample spectra without peak integration (Table 1). Aerosol calibration standards were generated by atomizing solutions containing one or more compound dissolved in water or an organic solvent in a Collison nebulizer operated at 35 psi (May, 1973). For aqueous solutions, resulting particles were dried in a 1.2 m (48 in) long Nafion annular diffusion drier (Perma Pure Inc, MD-110-

48S) with an annular counter-flow of 4 L min⁻¹ dry air. For organic solutions, resulting particles were dried using a 43 cm long activated carbon annular diffusion drier. These particles were then collected for 0–10 min on a 47 mm Teflon filter (2 μm pore; Gelman, R2PJ047). Solvent blanks were also collected. FTIR spectra were taken on calibration filter samples and blanks before and after sample collection using the same procedures as for RIOPA field samples. Loadings of FG quantities on calibration filter samples (μg of FG mm⁻² of filter) were calculated by taking the difference between the gravimetric mass of the filter after and before sampling, subtracting solvent blank mass, multiplying by the FG mass/compound mass ratio for the calibration compound, and dividing by the exposed filter area. (Note: calibration standard filter samples were weighed twice after 24 h equilibration at 44 ± 7% RH and 27 ± 4 °C. Water contributes approximately 25% to the measured mass of ammonium sulfate at 44% RH (Chan et al., 1992), a smaller quantity to organic acid, and a negligible quantity to the measured mass of aliphatic CH.) Loadings spanned the range of loadings observed on RIOPA samples.

2.4. Quantitation by PLS regression

Previous PM_{2.5} FG quantitation efforts have employed univariate calibration procedures to obtain peak areas (Maria et al., 2002; Garnes and Allen, 2002; Blando et al., 2001; Holes et al., 1997; Allen et al., 1994). The typical procedure is to use calibration standards to relate peak area to FG quantity, yielding an extinction coefficient (ϵ ; absorbance/mole) for each FG of interest, and to multiply the sample peak area by ϵ to calculate the FG loading (moles) in the sample. Curve fitting procedures are sometimes used to resolve overlapping peaks and obtain peak areas.

If a peak exhibits no overlap with other peaks and has a level baseline, an effective area can be computed simply by summing the absorbances (minus the baseline) at each wavelength that the peak encompasses. When overlap exists, curve fitting procedures can provide peak areas if (1) the number of spectral peaks in the region of interest is known, (2) peak overlap is below a certain threshold, and (3) the baseline is resolvable (Vandeginste and Galan, 1975). FTIR spectra of ambient aerosol samples frequently do not meet these requirements (Blando et al., 2001). Multivariate spectroscopic

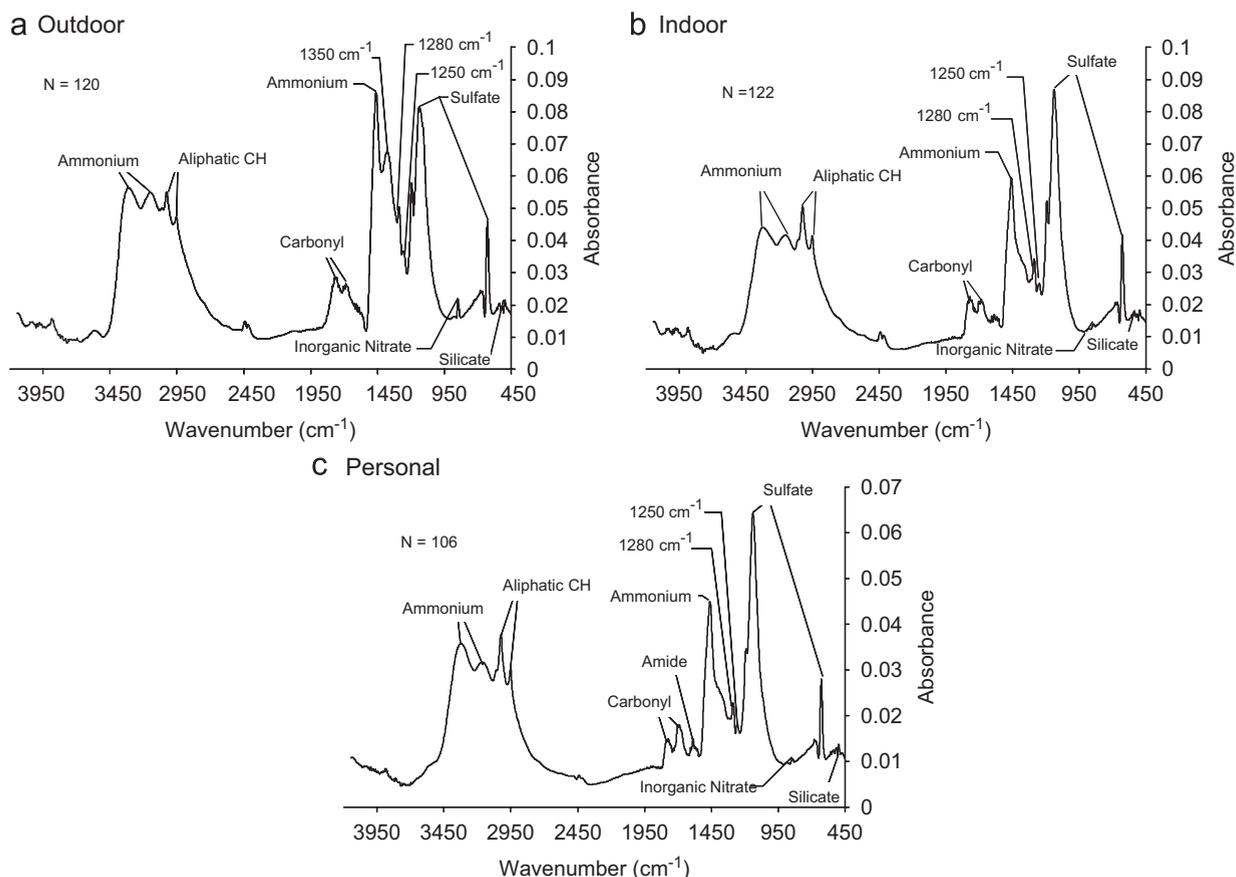


Fig. 1. Means of RIOPA (a) outdoor, (b) indoor and (c) personal $PM_{2.5}$ FTIR spectra for Los Angeles County, CA study homes. N is sample size. Note sharp aliphatic CH absorbances protrude out of or sit on top of large broad ammonium absorbances. Note amide is present in the mean personal and perhaps in the mean indoor spectra. Mean indoor and personal spectra are also enhanced in CH relative to the mean outdoor spectrum. Nitrate is much larger in the mean outdoor than indoor and personal spectra. Carbonyl and sulfate are present in all three spectra. Individual spectra are discussed elsewhere (Reff et al., 2005).

quantitation methods have the potential to yield more effective results for aerosol samples than univariate methods since they use the spectral data directly rather than fitted curves and allow for mixture effects (compound interactions) to be taken into consideration. These calibration procedures also can reduce data processing time substantially, since peak integration is not needed.

In this work, a multivariate method called PLS regression (SAS V8.2, Cary, NC) was used to construct calibration models to predict FG loadings from FTIR spectra. PLS models have the form:

$$y_j = x_k \cdot b_{kj} + e_j, \quad (1)$$

where y_j is the j th independent variable (FG loading), x_k is the spectral absorbance of the k th wavenumber, b_{kj} is matrix of regression coefficients, and e_j is the model error. The PLS algorithm

optimizes the relationship between loadings and spectral features relevant to making predictions in unknown samples. The algorithm was designed to generate more accurate predictions of complex mixtures than other multivariate calibration models such as multiple linear regression (MLR) and principal components regression (PCR) (Brereton, 2003; Malinowski, 2002; Martens and Naes, 1989). It has been used extensively in fields such as food science (Tojo and Prado, 2003; Gomis et al., 2003; Brenna and Pagliarini, 2001), soil science (Rumpel et al., 2001), and industrial process monitoring (Andrade et al., 1997). It has also been applied to ambient $PM_{2.5}$ source apportionment (Song et al., 2001).

The FG loadings (μgmm^{-2} of filter) and FTIR spectra (absorbance vs. wavenumber) for the calibration standards and solvent blanks

Table 1
Functional group (FG) data for partial least squares (PLS) calibration, filter loadings, and detection limits (DL)

FG	Range (<i>N</i>) of FG loadings in standards ($\mu\text{g filter}^{-1}$)	Absorbances used in PLS model (cm^{-1})	Median FG quantity in RIOPA samples ($\mu\text{g filter}^{-1}$)	Filter DL ^a ($\mu\text{g cm}^{-2}$) Sample DL ^b ($\mu\text{g m}^{-3}$)		% Field samples >DL	
				37 mm filters	25 mm filters	25 mm filters	37 mm filters (out/in)
SO ₄ ²⁻	0–159 (6)	608–646	26.5	3.76 1.43	2.67 1.46	38	74/51
C=O	0–64 (6)	1682–1760	9.90	2.96 1.12	1.91 1.04	13	27/20
CH (mix) ^c	0–398 (36)	2700–3500	79.8	1.60 0.61	1.28 0.70	69	10/57
NH ₄ ⁺ (mix) ^d	0–34 (36)	2700–3500	NA	1.31 0.50	0.72 0.39	86	76/74
CH (sc) ^e	0–25 (13)	2700–3500	NA	7.69 2.92	3.60 1.96	NA	NA
NH ₄ ⁺ (sc) ^e	0–64 (6)	2700–3500	NA	0.75 0.29	0.22 0.12	NA	NA

sc, single component model; mix, mixture model; FG, functional group; DL, detection limit; *N*, number of samples.

^aFilter detection limit was calculated as 3σ of RIOPA field blank samples.

^bSample detection limit is equal to filter DL times filter area divided by mean sample volume.

^cMixture model was used for CH quantitation.

^dNH₄⁺ concentrations were not reported because no effort was made to prevent NH₄NO₃ loss during sampling.

^eSingle component CH and NH₄⁺ results were only used for model comparison.

(loading = 0) were used in PLS to create a best fit b_{kj} calibration matrix. Each b_{kj} calibration matrix was then multiplied by the FTIR spectral absorbances (x_k) in field samples to yield field sample FG quantities. FG loadings were multiplied by filter area and divided by sample volume to calculate FG concentrations ($\mu\text{g FG m}^{-3}$ air). A separate calibration matrix was generated for each FG. Additionally, a calibration matrix was generated using an orthogonal series of calibration mixtures (Breerton, 2003) containing ammonium (NH₄⁺) and CH FGs. Previously, quantitation of these FGs in aerosol samples has been particularly problematic because of severe peak overlap (i.e., sharp CH absorbances protrude out of or sit on a large, broad NH₄⁺ absorbance; see Fig. 1).

3. Quality control and assurance

3.1. FTIR spectroscopy

Analyses of the polystyrene film standard indicate that instrument drift and changes in absorptivity were small over the course of sample analysis. Specifically, the wavenumber assignment precision (1σ) was 0.93 cm^{-1} (0.03%) based on the wavenumber variability of the large polystyrene film

absorbance at 2923.3 cm^{-1} . The absorbance of this peak was 1.77 ± 0.099 absorbance units ($N = 97$). Thus, the uncertainty due to variations in instrument sensitivity over the course of the study is 5.6%.

3.2. PLS model fit

PLS models constructed using data from single component calibration standards accounted for over 99% of the variation in sulfate and carbonyl FG loadings and spectral absorbances. The PLS model built using loadings and absorbances of the calibration mixtures of NH₄⁺ and CH also accounted for 99% of the variance in both loadings and absorbances.

3.3. Uncertainties

Detection limits (DLs), calculated as 3 times the standard deviation (σ) of the concentrations predicted from the spectra of field blanks, are reported in Table 1. DLs are higher than those reported by Maria et al. (2002) for FG concentrations by FTIR peak integration. However, it should be noted that in Maria et al. (2002) DLs were defined differently, as 2σ of the peak areas of blanks or the smallest

loading at which a peak could be seen, whichever was smaller. In the data analyses that follow, all data below DLs were assigned a value of DL/2. We expect that future PLS method optimization will lead to further reductions in DLs.

Analytical precision, expressed as the pooled coefficient of variation (CV) of concentrations obtained by replicate sample analysis, was 6% for SO_4^{2-} ($N = 10$ pairs) and 5% for CH ($N = 5$ pairs). Measurement precision, expressed as the pooled CV of measurements from collocated samples, was 28% ($N = 9$ pairs) and 15% ($N = 12$ pairs) for SO_4^{2-} and CH, respectively. Carbonyl measurements were within 10% for the one pair of collocated samples with carbonyl concentrations above DL. (Unfortunately, carbonyl FG concentrations were below DLs in most samples/homes selected for replicate analysis and collocated sampling.)

3.4. Comparison with independent measurements

Reasonable agreement was seen between sulfate (as S) by FTIR-PLS and total sulfur by XRF measured on the same filters (Fig. 2a). The comparison of total particulate OC (as C) measured by thermal-optical-transmittance (TOT) on collocated filters (Polidori et al., 2006) and carbon in aliphatic CH plus carbonyl FGs quantified by FTIR-PLS (Fig. 2b) is reasonable when the mixture model (solid dots) rather than the single component model (open squares) was used to quantify CH. Carbon in aliphatic CH and carbonyl FGs was calculated as follows:

$$\text{OC}_{\text{FTIR}} = \left(\frac{120}{141}\right) \cdot [\text{CH}] + \left(\frac{12}{28}\right) \cdot [\text{C}=\text{O}], \quad (2)$$

where [CH] and [C=O] are the aliphatic CH and carbonyl concentrations, respectively, the value $\left(\frac{120}{141}\right)$ is the C:CH mass ratio calculated using a CH_3 : CH_2 ratio of 1:9 (i.e. for undecanal), and $\left(\frac{12}{28}\right)$ is the C:C=O mass ratio. The fact that total particulate carbon should exceed the sum of these two FG concentrations and the much higher R^2 between TOT and FTIR carbon for the mixture model ($R^2 = 0.66$) compared to the single component model ($R^2 = 0.26$) provide evidence that quantitation of CH via a mixture model is more accurate than single component calibration. Single component calibration does not explicitly account for ammonium absorbances in the 2700–3500 cm^{-1} region of the infrared spectrum. (The circled outlier

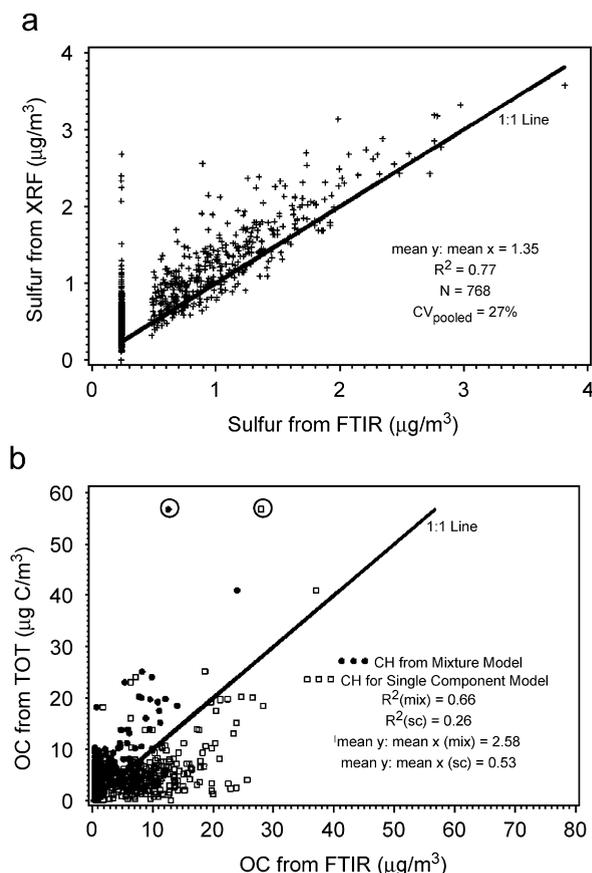


Fig. 2. Comparison of FTIR-PLS and independent measurements: (a) $\text{PM}_{2.5}$ sulfur by XRF and sulfate (as S) by FTIR; (b) OC (as C) by TOT and OC in measured functional groups (as C) by FTIR. OC from FTIR was calculated as the sum of carbon from C=O and aliphatic CH from the mixture (mix) model (solid dots) and from the single component (s.c.) model (open squares). Coefficients of determination (R^2) given in parentheses were calculated without circled outliers.

in Fig. 2b contains a unique absorbance (727 cm^{-1}) that was not quantified.)

3.5. Comparison with peak integration

A small subset of samples ($N = 22$) were quantified using the more traditional and more time consuming approach of peak integration and univariate calibration, in which calibration standards convert integrated peak areas to their mass loadings (Maria et al., 2002; Blando et al., 2001; McClenny et al., 1985). Specifically, GRAMS (Thermo Galactic, Salem NH) peak analysis software was used to integrate the carbonyl peaks near 1720 cm^{-1} , and the aliphatic CH peaks near 2900 cm^{-1} in 22 samples and all calibration spectra.

Baselines were assigned to each region of interest, Gaussian–Lorentzian curves were fit to the spectral region by the software, and peak areas were integrated. For CH peaks, an ammonium sulfate standard spectrum was subtracted from the sample to minimize the interference of the ammonium absorbance, as done by Maria et al. (2002). Linear calibration curves ($R^2 = 0.99$ – 0.998) relating FG loading and peak area for standards were used to quantify aliphatic CH and carbonyl. Carbonyl carbon predicted by PLS and by peak integration agreed quite well ($R^2 = 0.92$, mean peak integration/mean PLS = 1.00). Agreement for CH was within a factor of five ($R^2 = 0.38$, mean peak integration/mean PLS = 0.21). For the reasons stated above, we expect that CH quantified by PLS is more accurate.

3.6. Uncertainties in quantitation

As is typically done by those using FTIR spectroscopy to quantify complex mixtures of unknowns, each organic FG was quantified based on the absorptivity of a single compound. In this work, the reported carbonyl FG concentrations are the concentrations that would result if all carbonyl FGs in the mixture had the absorptivity of glutaric acid. Likewise, aliphatic CH was quantified as if it was undecanal. In the case of carbonyl, this assumption introduces substantial uncertainty since the strength of the carbonyl bond (and thus its absorptivity) can be strongly affected by the other FGs in a molecule. Molecular-level analyses of $PM_{2.5}$ (e.g., Rogge et al., 1993b) have shown that multiple types of carbonyl-containing compound classes exist, and so considerable variation in carbonyl FG absorptivity is expected. Even within a compound class the infrared absorptivity of C=O bonds can vary by factors of 2–4 (Cetina and Mateos, 1960; Pratt, 1953; Marion et al., 1951; Hampton and Newell, 1949). The peaks that are present in the C=O region of the $PM_{2.5}$ spectra (between ~ 1650 and $\sim 1750\text{ cm}^{-1}$) are the combined result of the infrared absorbances of many types of C=O groups. Although glutaric acid is one of the more dominant organic acids in ambient $PM_{2.5}$, its use as a surrogate for the carbonyl carbon in hundreds of individual $PM_{2.5}$ compounds and oligomers (Gao et al., 2004) introduces uncertainties of at least 200–400%. Despite this limitation, quantitation of carbonyl carbon as if it is glutaric acid is a reasonable and practical approach.

In contrast to C=O, little variation in CH molar extinction coefficients is expected due to the relative stability of the inductance of the bonds, i.e. other electron withdrawing or donating FGs in the same molecule are not expected to affect the bond strength and thus the extinction coefficient of the CH FG (Vollhardt and Schore, 1994).

4. Results

4.1. $PM_{2.5}$ organic FG composition

Fig. 3 shows the mean contributions of CH and carbonyl FGs to $PM_{2.5}$ organic carbon (as C) for each RIOPA location and environment. “Other carbon” is the difference between total particulate OC (as C) measured by TOT (Polidori et al., 2006) and carbon quantified by FTIR (i.e., C in CH and C=O by Eq. (2)). Personal samples were not collected for thermal–optical carbon analysis and therefore “other carbon” was not calculated for personal samples. For comparison, aliphatic CH and carbonyl FG quantities in 83 organic compounds measured by GC–MS (Rogge et al., 1993b; Gray et al., 1986) in downtown and west Los Angeles samples (outdoors) are also shown. The

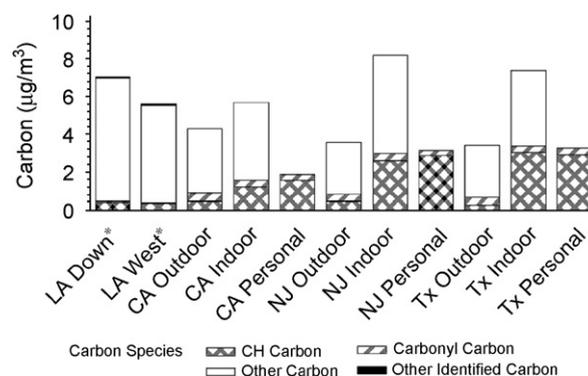


Fig. 3. Mean indoor, outdoor, and personal organic carbon (as C) at Los Angeles County (CA), Elizabeth (NJ), and Houston (TX) RIOPA study homes and from a previous Los Angeles study (downtown Los Angeles: LA Down*; West Los Angeles: LA West*; Rogge et al., 1993b). Shown are aliphatic CH and carbonyl functional groups and “other carbon” (i.e., the difference between particulate OC measured by TOT and the sum of quantified functional groups). “Other carbon” was not calculated for personal samples because personal samples for particulate OC analysis were not collected. Functional group concentrations reported for the Rogge study were calculated from compound concentrations measured by GC–MS. Also shown is the contribution of carbon in other functional groups for compounds identified by Rogge et al. (other identified carbon).

mean PM_{2.5} aliphatic CH concentration measured by FTIR-PLS in RIOPA outdoor Los Angeles County samples (CA Outdoor) was similar to aliphatic CH quantified previously in outdoor Los Angeles samples by GC–MS (LA Down*; LA West*). In contrast, carbonyl carbon measured by FTIR-PLS was greater (~ factor of 10) than carbonyl carbon in the 83 organic compounds quantified by GC–MS. These findings are not surprising because (1) a large majority of CH is expected to be found in low polarity organics that GC–MS characterizes well, e.g., alkenes, (2) unlike CH, carbonyl FGs are predominantly contained in polar compounds, (3) FTIR spectroscopy “sees” all carbonyl carbon regardless of compound polarity, and (4) GC–MS only quantifies a small portion of polar organic compounds and those only through the use of species-specific derivitization methods.

A substantial portion of PM_{2.5} OC in indoor and outdoor samples remains uncharacterized. It is recognized that variations in absorptivity between compound classes is a large source of uncertainty in carbonyl FG concentrations (see Quality Control section). Also, not all organic FGs were quantified. Aromatic CH, alcohol groups, and some functionalities in organic-nitrogen compounds, for example, were not quantified and are likely to contribute to PM_{2.5} OC, at least in some of the sampled environments.

4.2. Sources of FG exposure

Indoor concentrations of PM_{2.5} FGs (C_i) can be described by a single component mass balance model as the sum of the indoor concentration of ambient (outdoor) generated FG (C_{ag}) and indoor generated FG (C_{ig}), as follows (Wilson et al., 2000; Meng et al., 2005b):

$$C_i = \frac{PaC_a}{a+k} + \frac{Q_i/V}{a+k} = C_{ag} + C_{ig}, \quad (3)$$

where C_a is the ambient (outdoor) PM_{2.5} FG concentration, P is the dimensionless penetration coefficient, a is the air exchange rate (h^{-1}), k is the particle loss rate (h^{-1}), Q_i is the indoor FG source strength ($\mu g h^{-1}$), and V is the house volume (m^3). All parameters vary from home-to-home, day-to-day and species-to-species. Personal exposure concentrations (C_p) can be described similarly as the sum of FG contributions generated outdoors (C_{ag}), generated indoors (C_{ig}) and enhanced by personal

activities (C_{pg}):

$$C_p = tC_a + (1-t) \left[\frac{PaC_a}{a+k} + \frac{Q_i/V}{a+k} \right] + C_{pg} \\ = C_{ag} + C_{ig} + C_{pg}, \quad (4)$$

where t is the fraction of time the participant spent outdoors.

Below, the relative importance of ambient and non-ambient FG sources to indoor concentrations and personal exposures are described using site-specific FG concentration distributions and correlations (Fig. 4; Table 2), outdoor–indoor–personal FG scatter plots pooled over the three sampling sites (Fig. 5), and Eqs. (3) and (4), assuming $P = 1$ and $k = 0$. This provides lower bounds estimates of the non-ambient contribution to C_i (i.e., C_{ig}) and to C_p (i.e., $C_{ig} + C_{pg}$). Using the lower bound estimates of C_{ig} , $k = 0$, and measured a and V , lower-bound estimates of indoor emissions rates (Q) were also calculated from Eq. (3).

4.2.1. Sulfate

As has been observed in other studies (Wallace and Williams, 2005), PM_{2.5} sulfate concentrations were highest outdoors (median = $2.62 \mu g m^{-3}$) and lowest in personal exposure samples (median < DL). Outdoor–indoor, outdoor–personal, and indoor–personal correlation coefficients were moderate to strong ($R = 0.54–0.90$). These observations support the current understanding that the ambient (outdoor) environment is the predominant source of personal sulfate exposure and indoor sulfate concentrations. Sulfate is formed in the atmosphere from photooxidation of sulfur dioxide (Seinfeld and Pandis, 1998). The indoor/outdoor ratio and the correlation coefficient between indoor and outdoor sulfur were smaller for Houston (TX) than for Los Angeles Co. (CA) and Elizabeth (NJ) study homes, suggesting that the infiltration of sulfate (penetration and persistence indoors) was lower for Houston homes. This is likely due to the greater air conditioning use and lower air exchange rates observed in the Houston study homes (Weisel et al., 2005; Meng et al., 2005a).

4.2.2. Aliphatic CH

Indoor and personal concentrations of PM_{2.5} aliphatic CH (medians = 1.07 and $1.51 \mu g m^{-3}$) were substantially greater and more variable than outdoor concentrations (median < DL). Indoor–personal concentrations were also more highly

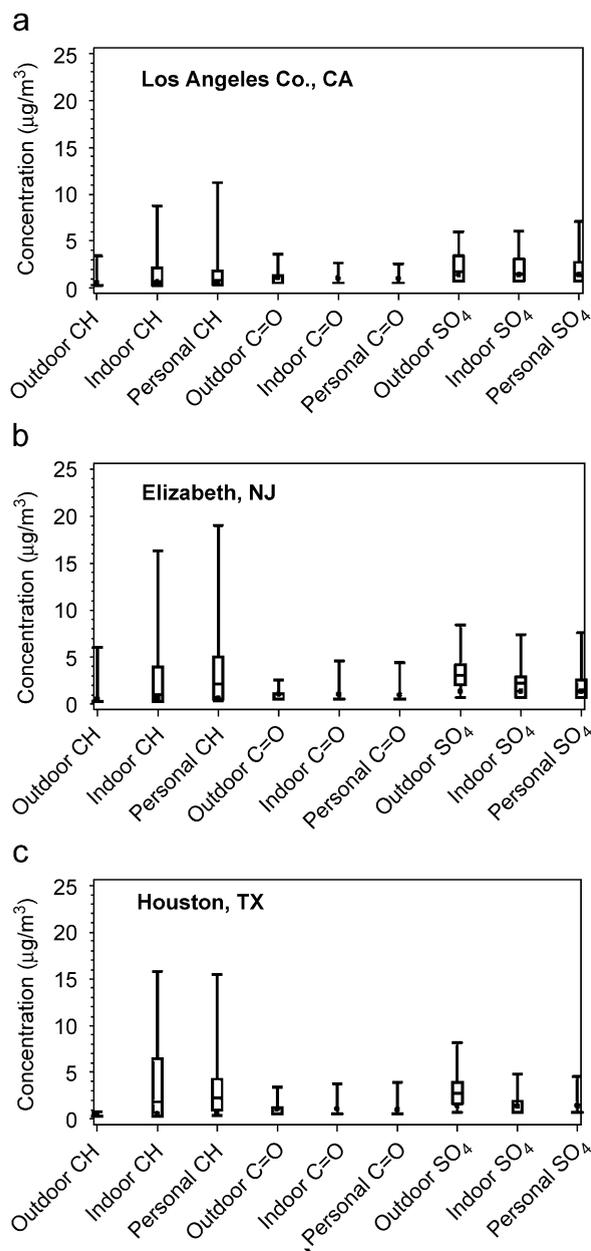


Fig. 4. $PM_{2.5}$ aliphatic CH, carbonyl (C=O), and sulfate (SO_4) functional group (FG) concentrations in outdoor, indoor and personal samples at (a) Los Angeles Co., CA, (b) Elizabeth, NJ, and (c) Houston, TX study homes. Bars in the boxes are medians, boxes extend from the 25th to 75th percentiles, and whiskers extend to the 1st and 99th percentiles. The dots overlaid on the boxes are the detection limits.

correlated ($R = 0.41$ – 0.85) than outdoor–indoor and outdoor–personal concentrations ($R = -0.07$ to 0.35). These observations strongly suggest that indoor and/or personal activity sources of CH exist and are substantial enough to impact exposure.

Inside 146 of the 167 homes with indoor or outdoor CH concentrations $>DL$, the contribution of indoor-generated CH (C_{ig}) exceeded the contribution of ambient-generated CH (C_{ag}). Similarly, for 163 of 175 participants, the non-ambient contribution to C_p (i.e., $C_{ig} + C_{pg}$) exceeded the ambient contribution (C_{ag}). Non-ambient contributions to C_i ($>DL$) ranged from 0.62 to $25.4 \mu g m^{-3}$ and to C_p ranged from 0.73 to $23.3 \mu g m^{-3}$. The 75th and 95th percentile non-ambient contributions to C_i were 2.8 and $10.3 \mu g m^{-3}$ and to C_p were 2.8 and $10.4 \mu g m^{-3}$. Lower-bound indoor emission rates (Q) ranged from 0.033 to $22.5 mg h^{-1}$, with a median of $0.64 mg h^{-1}$ ($N = 93$). Cooking, combustion, and floor polishes are some possible indoor sources of CH-rich compounds such as alkanes and phthalate esters (Schauer et al., 1999, 2002; Rogge et al., 1998, 1993a). These findings are consistent with earlier research (Weschler, 1984; Weschler and Fong, 1986), where concentrations of several non-polar organic compounds were found to be considerably higher inside than outside office buildings.

4.2.3. Carbonyl

Differences between outdoor, indoor and personal $PM_{2.5}$ carbonyl FG concentrations (medians $<DL$) were small. Outdoor concentrations (95th percentile = $2.45 \mu g m^{-3}$) typically exceeded indoor and personal concentrations (95th percentiles = 1.99 and $1.77 \mu g m^{-3}$, respectively), suggesting that indoor sources of carbonyl-containing compounds were small in most homes. However, personal–indoor correlations were in some cases higher than outdoor–indoor and outdoor–personal correlations (Table 2), and indoor and personal carbonyl FG concentrations in several homes were greater than outdoor concentrations, suggesting that both indoor and outdoor sources can be important contributors to indoor and personal carbonyl FG concentrations. The non-ambient contribution exceeded the ambient contribution inside 27 of 105 homes and for 14 of 87 participants with indoor or outdoor concentrations above DL. Non-ambient contributions to C_i ($>DL$) ranged from 1.28 to $4.49 \mu g m^{-3}$. Non-ambient contributions to C_p ranged from 1.42 to $20.7 \mu g m^{-3}$. Lower-bound indoor emission rates (Q) were above DL in eight homes; these values ranged from 0.249 to $0.96 mg h^{-1}$, with a median of $0.45 mg h^{-1}$. Particulate carbonyl-containing compounds are formed in the atmosphere through photochemistry (Seinfeld and Pandis, 1998), and constitute a ubiquitous

Table 2

Correlation coefficients between sulfate (SO₄), carbonyl (C=O), and aliphatic CH functional group (FG) concentrations for Los Angeles County (CA), Elizabeth (NJ), and Houston (TX) RIOPA study homes

Location	Sample type	FG	Outdoor			Indoor			Personal		
			SO ₄	C=O	CH	SO ₄	C=O	CH	SO ₄	C=O	CH
CA	Outdoor	SO ₄	1.00								
		C=O	0.42	1.00							
		CH	-0.28	-0.20	1.00						
	Indoor	SO ₄	0.76	0.67	-0.29	1.00					
		C=O	0.17	0.61	-0.15	0.51	1.00				
		CH	-0.42	-0.11	0.35	-0.34	0.03	1.00			
	Personal	SO ₄	0.64	0.73	-0.25	0.90	0.57	-0.26	1.00		
		C=O	0.21	0.69	-0.12	0.45	0.67	0.04	0.59	1.00	
		CH	-0.24	-0.04	0.17	-0.22	-0.02	0.41	-0.15	0.07	1.00
NJ	Outdoor	SO ₄	1.00								
		C=O	0.35	1.00							
		CH	-0.15	0.00	1.00						
	Indoor	SO ₄	0.76	0.42	-0.05	1.00					
		C=O	0.06	0.12	0.08	0.05	1.00				
		CH	-0.19	-0.04	-0.08	-0.21	0.63	1.00			
	Personal	SO ₄	0.73	0.42	-0.15	0.90	0.04	-0.24	1.00		
		C=O	0.10	-0.13	-0.02	-0.04	0.77	0.48	-0.02	1.00	
		CH	-0.26	-0.09	0.19	-0.30	0.67	0.76	-0.29	0.61	1.00
TX	Outdoor	SO ₄	1.00								
		C=O	0.45	1.00							
		CH	-0.15	0.28	1.00						
	Indoor	SO ₄	0.54	0.38	-0.10	1.00					
		C=O	0.21	0.57	-0.06	0.24	1.00				
		CH	0.11	0.22	-0.05	0.04	0.58	1.00			
	Personal	SO ₄	0.54	0.51	-0.07	0.84	0.26	0.09	1.00		
		C=O	-0.06	0.05	-0.03	-0.05	0.07	0.11	0.00	1.00	
		CH	0.08	0.26	-0.07	-0.03	0.49	0.85	0.07	0.11	1.00

component of aged outdoor aerosol (Kerminen et al., 2000; Yu et al., 1998; Saxena and Hildemann, 1996; Stephanou and Stratigakis, 1993). Indoor sources include heating and cooking (Rogge et al., 1993a; Schauer et al., 1999), and secondary indoor chemistry such as ozone reactions with terpenes (Wainman et al., 2000; Weschler and Shields, 1999).

4.3. OM/OC ratios

An important tool in air quality management planning is the PM_{2.5} species mass balance, where measured species are used to reconstruct measured PM_{2.5} mass. In such work, organic matter (OM; mass of organic compounds) is calculated by multiplying the carbon contained in particulate organic compounds (measured OC) by a value representing the average organic molecular weight per carbon weight (OM/OC) (Turpin and Lim,

2001). Measurements of OM/OC are needed for this reason, and are useful as an indicator of the polarity or hygroscopicity of an organic aerosol. To our knowledge, measurements of OM/OC have not previously been made for indoor and personal PM_{2.5}.

OM/OC for outdoor PM was initially estimated from the modest fraction of organic mass identified by GC-MS. The focus of GC-MS analyses on low polarity compounds led to underestimates of OM/OC in areas dominated by aged aerosol (Turpin and Lim, 2001). While the unidentified carbon in this study is still substantial, a larger fraction of PM_{2.5} OC was identified. More importantly, FTIR spectroscopy characterizes both more and less oxygenated (polar) compounds. This, and the reasonable agreement with more recent estimates of outdoor OM/OC (below), provides confidence in the indoor and personal OM/OC estimates provided below.

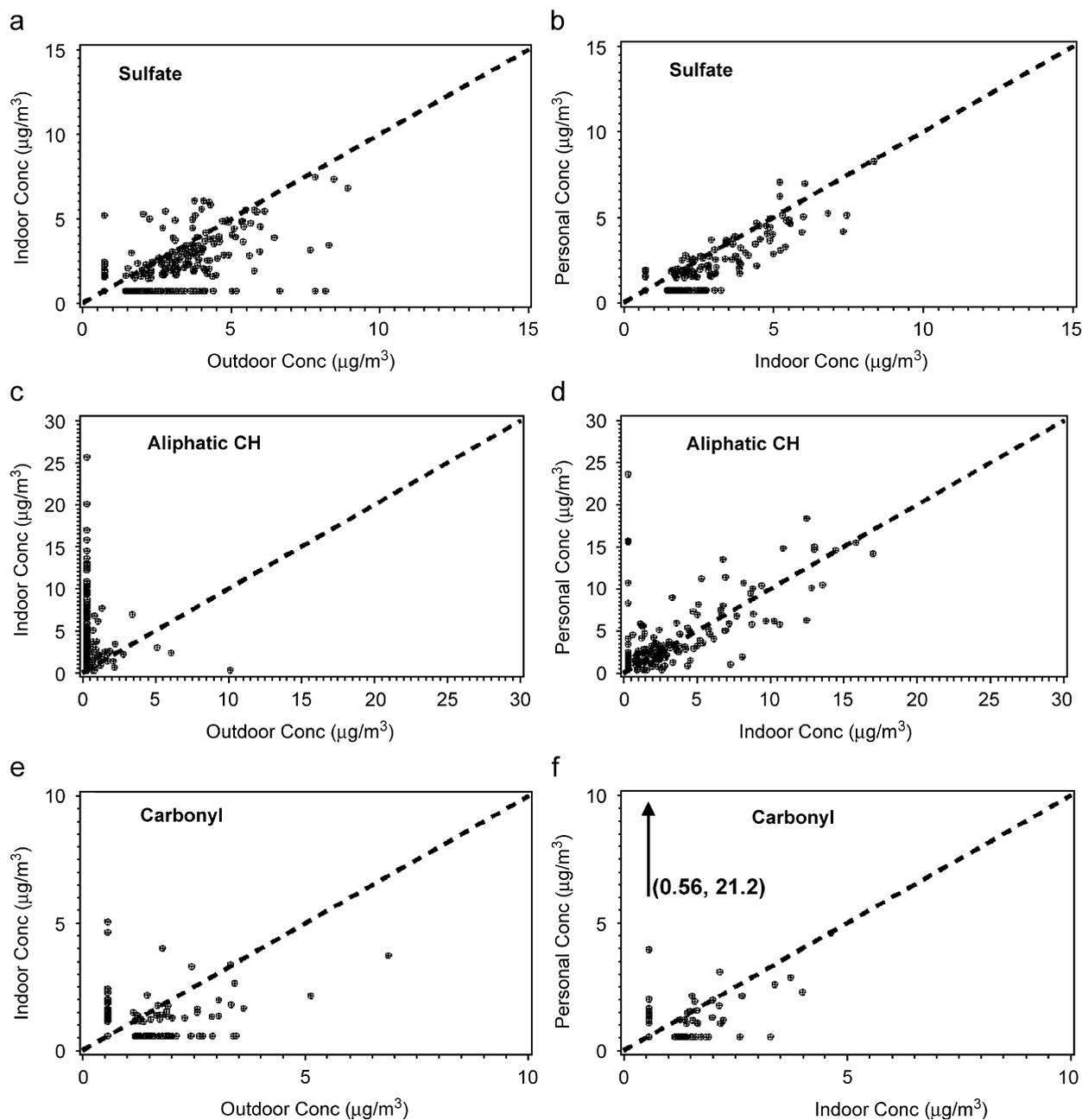


Fig. 5. Outdoor, indoor, and personal concentrations of sulfate (a, b), aliphatic CH (c, d), and carbonyl (e, f) functional groups from all RIOPA homes. The dashed lines are the 1:1 lines. A data point located at (0.56, 21.2) in (f) is indicated on the graph, but not shown (off scale).

In this work OM concentrations were calculated as the sum of aliphatic CH and carbonyl, expressed either as C=O or as carboxylic acid [i.e., (C=O)–OH], and OC concentrations were calculated using Eq. (2). Results are provided in Table 3. Outdoor OM/OC was 1.7–2.6, similar to the range of the values estimated by others (i.e., 1.6

for fresh urban aerosol to 2.1 for aged aerosol; Turpin and Lim, 2001). Indoor and personal OM/OC were 1.3–1.7 and 1.3–1.6, respectively. These OM/OC ratios suggest that indoor and personal OC is relatively non-polar due to the presence of compounds rich in aliphatic CH, such as alkanes and phthalate esters from

Table 3
Outdoor, indoor and personal mean PM_{2.5} organic matter (OM) to mean organic carbon (OC) ratios for Los Angeles County (CA), Elizabeth (NJ), and Houston (TX) RIOPA study homes

Sample type	Location	OM/OC	
		Using C=O	Converting C=O to (C=O)-OH
Outdoor	CA	1.74	2.42
	NJ	1.70	2.35
	TX	1.86	2.69
Indoor	CA	1.43	1.74
	NJ	1.31	1.49
	TX	1.29	1.44
Personal	CA	1.37	1.59
	NJ	1.28	1.42
	TX	1.31	1.47

sources such as cooking, combustion, and floor polishes.

5. Conclusions

This study demonstrates the application of multivariate calibration (PLS) to FG quantitation in aerosol samples. PLS quantitation reduces data processing time considerably by eliminating the need for peak integration. More importantly, it accounts for compound interactions and peak overlap, which hamper quantitation of complex mixtures of aerosol species.

This work provides strong evidence that indoor-generated PM_{2.5} is enriched in aliphatic CH FGs relative to outdoor-generated PM_{2.5}. This is important because indoor-generated PM_{2.5} is predominantly organic (Polidori et al., 2006), and the introduction of CH carbon alters the properties, behavior and effects of organic PM_{2.5} indoors and in personal air (i.e., the breathing zone). This work suggests an OM/OC ratio for indoor and personal samples of 1.45 ± 0.17 and 1.40 ± 0.11 (Table 3), respectively. Certainly, it would be of value to extend FTIR-PLS quantitation to additional FGs in PM_{2.5} and to further improve data handling to reduce DLs.

Acknowledgments

This research was supported by the Health Effects Institute, the Mickey Leland National Urban Air

Toxics Center, the NIEHS Center of Excellence, the NJ Agricultural Experiment Station. We gratefully acknowledge the hard work of all the students and technicians in the field and laboratories of RIOPA investigators and the hospitality of the RIOPA participants. Additionally, we thank Annmarie Carlton, Robert Giovannetti, Andrea Polidori, Jong Hoon Lee, Robert Porcja, Qing Yu Meng, Robert Harrington, Jay Min Kwon, Shahnaz Alimokhtari, Silvia Maberti, Derek Shendell, Jennifer Jones, Corice Farrar, Charles Weschler, and Paul Lioy for their invaluable assistance.

Research described in this article was conducted, in part, under contract to the Health Effects Institute (HEI), an organization jointly funded by the United States Environmental Protection Agency (EPA: Assistance Agreement R828112) and automotive manufacturers. The contents of this article do not necessarily reflect the views of HEI, nor do they necessarily reflect the views and policies of EPA or of motor vehicle and engine manufacturers. This article has been subjected to EPA review and approved for publication.

References

- Allen, D.T., Pallen, E.J., Haimov, M.I., Hering, S.V., Young, J.R., 1994. Fourier transform infrared spectroscopy of aerosol collected in a low pressure impactor (LPI/FTIR): method development and field calibration. *Aerosol Science Technology* 21, 325–342.
- Andrade, J.M., Garcia, M.V., Lopez-Mahia, P., Prada, D., 1997. A review of the main factors influencing the FT-IR-PLS abilities exemplified with petrochemical qualimetric applications. *Talanta* 44, 2167–2184.
- Blando, J.D., Porcja, R.J., Li, T.-H., Bowman, D., Lioy, P.J., Turpin, B.J., 1998. Secondary formation and the Smoky Mountain organic aerosol: an examination of aerosol polarity and functional group composition during SEAVS. *Environmental Science and Technology* 32, 604–613.
- Blando, J.D., Porcja, R.J., Turpin, B.J., 2001. Issues in the quantitation of functional groups by FTIR spectroscopic analysis of impactor-collected aerosol samples. *Aerosol Science and Technology* 35, 899–908.
- Brenna, O.V., Pagliarini, E., 2001. Multivariate analysis of antioxidant power and polyphenolic composition in red wines. *Journal of Agricultural and Food Chemistry* 49, 4841–4844.
- Brereton, R.G., 2003. *Chemometrics: Data Analysis for the Laboratory and Chemical Plant*. Wiley, West Sussex, England.
- Brodsky, D.M., Georgopoulos, P.G., 2001. Growth and deposition of hygroscopic particulate matter in the human lungs. *Aerosol Science and Technology* 34, 144–159.

- Cetina, R., Mateos, J.L., 1960. Intensities of carbonyl bands in the infrared spectra of substituted cycloalkanones. *Journal of Organic Chemistry* 25, 704–708.
- Chan, C.K., Flagan, R.C., Seinfeld, J.H., 1992. Water activities of $\text{NH}_4\text{NO}_3/(\text{NH}_4)_2\text{SO}_4$ solutions. *Atmospheric Environment* 26A, 1661–1673.
- Ferro, A.R., Kopperus, R.J., Hildemann, L.M., 2004. Source strengths for indoor human activities that resuspend particulate matter. *Environmental Science and Technology* 38, 1759–1764.
- Fromme, H., Lahrz, T., Piloty, M., Gebhart, H., Oddoy, A., Ruden, H., 2004. Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin. *Indoor Air* 14, 188–195.
- Gao, S., Ng, N.L., Keywood, M., Varutbangkul, V., Bahareini, R., Nenes, A., He, J., Yoo, K.Y., Beauchamp, J.L., Hodys, R.P., Flagan, R.C., Seinfeld, J.H., 2004. Particle phase acidity and oligomer formation in secondary organic aerosol. *Environmental Science and Technology* 38, 6582–6589.
- Garnes, L.A., Allen, D.T., 2002. Size distributions of organonitrates in ambient aerosol collected in Houston, Texas. *Aerosol Science and Technology* 36, 983–992.
- Gomis, D.B., Tamayo, D.M., Alonso, J.J.M., 2003. Evolution of sugars in cider brandy aged in oak barrels: a contribution to its characterization. *Journal of Agricultural and Food Chemistry* 51, 923–926.
- Gray, H.A., Cass, G.R., Huntzicker, J.J., Heyerdahl, E.K., Rau, J.A., 1986. Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles. *Environmental Science and Technology* 20, 580–582.
- Hampton, R.R., Newell, J.E., 1949. Infrared spectroscopic determination of ester carbonyl. *Analytical Chemistry* 21, 914–916.
- Holes, A., Eusebi, A., Grosjean, D., Allen, D.T., 1997. FTIR analysis of aerosol formed in the photooxidation of 1,3,5-trimethylbenzene. *Aerosol Science and Technology* 26, 516–526.
- Jang, M., Kamens, R.M., Leach, K.B., Strommen, M.R., 1997. A thermodynamic approach using group contribution methods to model the partitioning of semivolatile organic compounds on atmospheric particulate matter. *Environmental Science and Technology* 31, 2805–2811.
- Kerminen, V.-M., Ojanen, C., Pakkanen, T., Hillamo, R., Aurela, M., Merilainen, J., 2000. Low-molecular-weight dicarboxylic acids in an urban and rural atmosphere. *Journal of Aerosol Science* 31, 349–362.
- Koo, B., Ansari, A.S., Pandis, S.N., 2003. Integrated approaches to modeling the organic and inorganic atmospheric aerosol components. *Atmospheric Environment* 37, 4757–4768.
- Krost, K.J., McClenny, W.A., 1994. FT-IR transmission spectroscopy for quantitation of ammonium bisulfate in fine particulate matter collected on Teflon filters. *Applied Spectroscopy* 48, 702–705.
- Malinowski, E.R., 2002. *Factor Analysis in Chemistry*. Wiley, New York.
- Maria, S.F., Russell, L.M., Turpin, B.J., Porcja, R.J., 2002. FTIR measurements of functional groups and organic mass in aerosol samples over the Caribbean. *Atmospheric Environment* 36, 5185–5196.
- Marion, L., Ramsay, D.A., Jones, R.N., 1951. The infrared absorption spectra of alkaloids. *Journal of the American Chemical Society* 73, 305–308.
- Martens, H., Naes, T., 1989. *Multivariate Calibration*. Wiley, New York.
- May, K.R., 1973. The collision nebulizer: description, performance, and application. *Aerosol Science* 4, 235–243.
- McClenny, W., Childers, J., Rohl, R., Palmer, R., 1985. FTIR transmission spectrometry for the non-destructive determination of ammonium and sulfate in ambient aerosols collected on Teflon filters. *Atmospheric Environment* 19, 1891–1898.
- Meng, Q.Y., Turpin, B.J., Korn, L., Weisel, C.P., Morandi, M., Colome, S., Zhang, J., Stock, T., Spektor, D., Winer, A., Zhang, L., Lee, J.H., Cui, W., Giovanetti, R., Kwon, J.M., Alimokhtari, S., Shendell, D., Jones, J., Maberti, S., 2005a. Influence of outdoor sources of indoor and personal fine particle concentrations: analyses of RIOPA data. *Journal of Exposure Analysis and Environmental Epidemiology* 15, 17–28.
- Meng, Q.Y., Turpin, B.J., Polidori, A., Lee, J.H., Weisel, C., Morandi, M., Colome, S., Stock, T., Winer, A., Zhang, J., 2005b. $\text{PM}_{2.5}$ of ambient origin: estimates, exposure errors, and epidemiological implications. *Environmental Science and Technology* 39, 5105–5112.
- Ming, Y., Russell, L.M., 2001. Predicted hygroscopic growth of sea salt aerosol. *Journal of Geophysical Research* 106, 28259–28274.
- Mylonas, D.T., Allen, D.T., Ehrman, S.H., Pratsinis, S.E., 1991. The sources and size distributions of organonitrates in Los Angeles aerosol. *Atmospheric Environment* 25A, 2855–2861.
- Naumova, Y.Y., Totten, L.A., Eisenreich, S.J., Turpin, B.J., Colome, S.D., Morandi, M.T., Weisel, C.P., Stock, T.H., Winer, A.M., Alimokhtari, S., Kwon, J., Maberti, S., Shendell, D., Wall, S.J., 2002. Polycyclic aromatic hydrocarbons in the indoor and outdoor air of three cities in the US: results from the RIOPA study. *Environmental Science and Technology* 36, 2552–2559.
- Naumova, Y.Y., Offenberg, J.H., Eisenreich, S.J., Polidori, A., Meng, Q.Y., Turpin, B.J., Weisel, C.P., Morandi, M.T., Colome, S.D., Stock, T.H., Winer, A.M., Alimokhtari, S., Kwon, J., Maberti, S., Shendell, D., Jones, J., Farrar, C., 2003. Gas/particle distribution of polycyclic aromatic hydrocarbons in coupled outdoor/indoor atmospheres. *Atmospheric Environment* 37, 703–719.
- Offenberg, J., Naumova, Y., Turpin, B., Eisenreich, S., Morandi, M., Stock, T., Colome, S., Winer, A., Spektor, D., Zhang, J., Weisel, C., 2004. Chlordanes in the indoor and outdoor air of three US cities. *Environmental Science and Technology* 38, 2760–2768.
- Olson, D.A., Burke, J.M., 2006. Distributions of $\text{PM}_{2.5}$ source strengths for cooking from the Research Triangle Park particulate matter panel study. *Environmental Science and Technology* 40, 163–169.
- Peng, C., Chan, M.N., Chan, C.K., 2001. The hygroscopic properties of dicarboxylic and multifunctional acids: measurements and UNIFAC predictions. *Environmental Science and Technology* 35, 4495–4501.
- Polidori, A., Turpin, B., Meng, Q.-Y., Lee, J.H., Weisel, C., Morandi, M., Colome, S., Stock, T., Winer, A., Zhang, J., Kwon, J., Alimokhtari, S., Shendell, D., Jones, J., Farrar, C., Maberti, S., 2006. Indoor and outdoor organic $\text{PM}_{2.5}$: analysis of the RIOPA study data. *Journal of Exposure Analysis and Environmental Epidemiology*, doi:10.1038/sj.jea.7500476.

- Pratt, E.L., 1953. Quantitative estimation of the carbonyl groups in saturated ketocholeonic acids. *Analytical Chemistry* 25, 175–177.
- Reff, A., Turpin, B.J., Porcja, R.J., Giovenetti, R., Cui, W., Weisel, C.P., Zhang, J., Kwon, J., Alimokhtari, S., Morandi, M., Stock, T., Maberti, S., Colome, S., Winer, A., Shendell, D., Jones, J., Farrar, C., 2005. Functional group characterization of indoor, outdoor, and personal PM_{2.5}: results from RIOPA. *Indoor Air* 15, 53–61.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993a. Sources of fine organic aerosol. 5. natural gas home appliances. *Environmental Science and Technology* 27, 2736–2744.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., 1993b. Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. *Atmospheric Environment* 27, 1309–1330.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1998. Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces. *Environmental Science and Technology* 32, 13–22.
- Rudel, R.A., Camann, D.E., Spengler, J.D., Korn, L.R., Brody, J.G., 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust. *Environmental Science and Technology* 37, 4543–4553.
- Rumpel, C., Janik, L.J., Skjemstad, J.O., Kogel-Knabner, I., 2001. Quantification of carbon derived from lignite in soils using mid-infrared spectroscopy and partial least squares. *Organic Geochemistry* 32, 831–839.
- Saxena, P., Hildemann, L.M., 1996. Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds. *Journal of Atmospheric Chemistry* 24, 57–109.
- Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environmental Science and Technology* 34, 1821–1832.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources 1. C1 through C29 organic Compounds from meat charbroiling. *Environmental Science and Technology* 33, 1566–1577.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of emissions from air pollution sources 4 C1–C27 organic compounds from cooking with seed oils. *Environmental Science and Technology* 36, 567–575.
- Seinfeld, J.H., Pandis, S.N., 1998. *Atmospheric Chemistry and Physics*. Wiley, New York.
- Song, X.H., Faber, N.M., Hopke, P.K., Seuss, D.T., Prather, K.A., Schauer, J.J., Cass, G.R., 2001. Source apportionment of gasoline and diesel by multivariate calibration based on single particle mass spectral data. *Analytica Chimica Acta* 446, 327–343.
- Stephanou, E.G., Stratigakis, N., 1993. Oxocarboxylic and α -dicarboxylic acids: photooxidation products of biogenic unsaturated fatty acids present in urban aerosols. *Environmental Science and Technology* 27, 1403–1407.
- Tojo, E., Prado, J., 2003. Chemical composition of carrageenan blends determined by IR spectroscopy combined with a PLS multivariate calibration method. *Carbohydrate Research* 338, 1309–1312.
- Turpin, B.J., Lim, H.J., 2001. Species contributions to PM_{2.5}: mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* 35, 602–610.
- Turpin, B.J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmospheric Environment* 34, 2983–3013.
- USEPA, 2004. *Air Quality Criteria for Particulate Matter*, US Environmental Protection Agency, Research Triangle Park, NC.
- Vandeginste, G.M., Galan, L.D., 1975. Critical evaluation of curve fitting in infrared spectroscopy. *Analytical Chemistry* 47, 2124–2132.
- Vollhardt, K.P.C., Schore, N.E., 1994. *Organic Chemistry*, Second ed. W.H. Freeman and Company, New York.
- Wainman, T., Zhang, J., Weschler, C., Liyo, P., 2000. Ozone and limonene in indoor air: a source of submicron particle exposure. *Environmental Health Perspectives* 108, 1139–1145.
- Walker, M.V., Weschler, C.J., 1980. Water-soluble components of size-fractionated aerosols collected after hours in a modern office building. *Environmental Science and Technology* 14, 594–597.
- Wallace, L., 2006. Indoor sources of ultrafine and accumulation mode particles: size distributions, size-resolved concentrations, and source strengths. *Aerosol Science and Technology* 40, 348–360.
- Wallace, L., Williams, R., 2005. Use of personal–indoor–outdoor sulfur concentrations to estimate the infiltration factor and outdoor exposure factor for individual homes and persons. *Environmental Science and Technology* 39, 1707–1714.
- Weisel, C.P., Zhang, J., Turpin, B.J., Morandi, M.T., Colome, S., Stock, T.H., Spektor, D.M., Korn, L., Winer, A., Alimokhtari, S., Kwon, J., Mohan, K., Harrington, R., Giovanetti, R., Cui, W., Afshar, M., Maberti, S., Shendell, D., 2005. The relationships of indoor, outdoor and personal air (RIOPA) study: study design, methods, and quality assurance/control results. *Journal of Exposure Analysis and Environmental Epidemiology* 15, 123–137.
- Wensing, M., Uhde, E., Salthammer, T., 2005. Plastics additives in the indoor environment—flame retardants and plasticizers. *Science of the Total Environment* 339, 19–40.
- Weschler, C.J., 1980. Characterization of selected organics in size-fractionated indoor aerosols. *Environmental Science and Technology* 14, 428–431.
- Weschler, C.J., 1984. Indoor–outdoor relationships for nonpolar organic constituents of aerosol particles. *Environmental Science and Technology* 18, 648–652.
- Weschler, C.J., Fong, K.L., 1986. Characterization of organic species associated with indoor aerosol particles. *Environment International* 12, 93–97.
- Weschler, C.J., Shields, H.C., 1999. Indoor ozone/terpene reactions as a source of indoor particles. *Atmospheric Environment* 33, 2301–2312.
- Wilson, W.E., Mage, D.T., Grant, L.D., 2000. Estimating separately personal exposure to ambient and nonambient particulate matter for epidemiology and risk assessment: why and how. *Journal of the Air and Waste Management Association* 50, 1167–1183.
- Yu, J., Flagan, R.C., Seinfeld, J.H., 1998. Identification of products containing, –COOH, –OH, and –C=O in atmospheric oxidation of hydrocarbons. *Environmental Science and Technology* 32, 2357–2370.