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An enhanced procedure for measuring organic acids and methyl esters in $PM_{2.5}$

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Abstract

We have developed an enhanced analytical procedure to measure organic acids and methyl esters in fine aerosol with much greater specificity and sensitivity than previously available. This capability is important because of these species and their low concentrations, even in highly polluted atmospheres like Beijing, China. The procedure first separates the acids and esters from the other organic compounds with anion-exchange solid- phase extraction (SPE), then, quantifies them by gas chromatography coupled with mass spectrometry. This allows us to accurately quantify the C4-C11 dicarboxylic and the C8-C30 monocarboxylic acids. Then the acids are separated from the esters on an aminopropyl SPE cartridge, whose weak retention isolates and enriches the acids from esters prevents the fatty acids and dimethyl phthalate from being overestimated. The resulting correlations between the aliphatic acids and fatty acid methyl esters (FAMEs) suggest that FAMEs had sources similar to those of the carboxylic acids, or were formed by esterifying carboxylic acids, or that aliphatic acids were formed by hydrolyzing FAMEs. In all, 17 aromatic acids were identified and quantified using this procedure coupled with gas chromatography-tandem mass spectrometry, including the five polycyclic aromatic hydrocarbon (PAH) acids 2-naphthoic, biphenyl-4-carboxylic, 9-oxo-9H-fluorene-1-carboxylic, biphenyl-4,4′-dicarboxylic, and phenanthrene-1-carboxylic acid, plus 1,8-naphthalic anhydride. Correlations between the PAH-acids and the dicarboxylic and aromatic acids indicated that the first three acids and 1,8-naphthalic anhydride were mainly secondary, the last two mainly primary.

1 Introduction

Organic matter can account for 20–50 % of the mass of fine aerosol ($PM_{2.5}$) (Turpin et al., 2000; Kanakidou et al., 2005; Cheng et al., 2011). Organic acids, including C6–C32 monocarboxylic acids, C2–C12 dicarboxylic acids (DCAs), ketocarboxylic acids, and 1-, 2-, and 3-substituted aromatic acids (AMAs), are ubiquitous in aerosols (Kawamura, 1993; Sempére and Kawamura et al., 1994; Fraser et al., 2003; Kawamura and Yasui, 2005; Wang et al., 2006; Li and Yu, 2005; Jung et al., 2010), and can account for 20–80 % of the organic matter (Satsumabayashi et al., 1989; Barbara and Ho, 2001; Huang et al., 2006; Duan et al., 2009).

Organic acids can be primary or secondary. The C20–C30 monocarboxylic and terephthalic acids are primary, mainly from the combustion of fossil fuels and biomass, vehicular exhausts, and cooking (Kawamura and Kaplan, 1987a; Sempére and Kawamura, 1994; Reid et al., 1998, 2005; Graham et al., 2002; Gao et al., 2003; Pio et al., 2008; Yu et al., 2008; Kundu et al., 2010; Tan et al., 2013). C2-C6 DCAs are mainly secondary, formed in the atmosphere as their anthropogenic and biogenic precursors are oxidized (Kawamura et al., 1996; Claeys et al., 2004; Ervens et al., 2004; Gelencser, 2004; Kanakidou et al., 2005; Kawamura and Yasui, 2005). Phthalic acids are oxidation products of naphthalene and alkyl naphthalenes (Wang et al., 2007). OH radicals can initiate the aerobic degradation of phenanthrene (Tan et al., 2007), but only limited products were detected for explaining the degradation mechanism of three-ring PAHs. So it is necessary to develop more-sensitive analytical methods that can be used to identify possible tracers to help understand the formation mechanisms of secondary organic aerosol.

Organic acids are commonly extracted from aerosol samples along with other organics by sequential solvents, then converted to esters with BF_3–methanol, BF_3–butanol, or N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) before they are measured by gas chromatography (Kawamura, 1985, 1993; Fu et al., 2009). The butyl- and trimethylsilyl- (TMS) derivatives have been used more often than methyl esters for low-molecular-weight organic acids, including C2-C10 DCAs, C2-C9 ketocarboxylic acids (Boucharat et al., 1998; Limbeck and Puxbaum, 1999; Nolte et al., 2002; Wang et al., 2006; Oliveira et al., 2007). Yet the methyl esters of C8–C32 monocarboxylic acids and AMAs are more volatile and convenient for GC analysis than butyl- and TMS-esters (Kawamura and Gagosian, 1987c; Plewka et al., 2003; Fraser et al., 2003).

GC-MS methods have been used to identify organic compounds (mainly organic acids, alkanes, cycloalkanes, PAHs, oxy-PAHs, and steranes) in atmospheric aerosols (Kawamura, 1993; Jaoui et al., 2004; Simoneit et al., 2004; Medeiros and Simoneit, 2007). However, it is difficult to use GC-MS to identify the trace oxygenated PAHs in raw extracts because other compounds interfere (Walgraeve et al., 2010). To deal with problem, advanced pretreatment methods have been coupled with high-resolution analytical instruments. For example, solid phase extraction (SPE) is a fast and simple method for separating, purifying, and concentrating organic compounds, and it offers clean extracts with very good recoveries and good enrichment (Rosenfeld, 1999; Liska, 2000; Sochor, 2000; Wells and Yu, 2000; Anastassiades et al., 2003; Ericsson and Colmsjo, 2003). Organic acids have been purified and concentrated through ion exchange with OH groups on anion exchange SPE cartridges and then eluted with eluents that contain a stronger acid (Wang et al., 2014). Gas chromatography-tandem mass spectrometry (GC-MS-MS) has been used to measure oxygenated polycyclic aromatic compounds in aerosol. The MS-MS technique allows multiple reaction monitoring (MRM) to exclude extraneous chromatographic peaks. The first MS detector is used in selected-ion monitoring (SIM) mode, and excludes all of the ions produced except for precursor ions that are used for qualitative analysis. The selected ions enter the collision cell, where ions are produced under specific collision energy. The second MS detector is also used in SIM mode. It monitors the daughter ions (the selected fragments of the precursor ions), and generates a unique product-ion mass spectrum for quantification.

We applied our enhanced analytical procedure to organic aerosol in Beijing. Extracts of $PM_{2.5}$ were fist cleaned with a selective SPE cartridge, then analyzed with GC and a triple quadrupole mass analyzer. The organic material was sampled in January 2013, when the haze was particularly heavy and had spread over much of eastern China. The air quality index in Beijing (Beijing Environment Protection Bureau, http://www.zhb.gov.cn/) reached nearly 500, and visibility was sometimes below 100 m.

2 Experiment and methodology

2.1 $PM_{2.5}$ sample collection

Samples of $PM_{2.5}$ were collected between 1 June 2012 and 30 April 2013. The samples discussed here came from 1–30 January, which contained the periods of heaviest haze. The samples were collected on quartz-fiber filters (20 cm × 25 cm Pallflex; Pall Corporation, Port Washington, NY, USA) with a high-volume sampler (VFC-PM10; Thermo Fisher Scientific Inc., Waltham, MA, USA) at 1.13 $m^3\,min^{-1}$ from 9.00 p.m. local time for 24 h). The sampler was installed on the roof of a building at Tsinghua University (40°00′ N, 116°32′ E, 52 m a.s.l.). Before sampling, unexposed filters and foils were baked at 560 °C for 6 h to remove organic contaminants. Each sample was wrapped in aluminum foil and stored in a freezer (at −25 °C) until it was extracted.

2.2 Sample pretreatment

An area of 40 cm^2 was punched from the sample and extracted successively with 20 mL dichloromethane, 20 mL hexane, and 20 mL acetonitrile (all chromatographically pure; Sigma-Aldrich, St Louis, MO, USA). Acetonitrile was used as a polar organic extraction solvent (rather than methanol) because it gives better recoveries of fatty acids and avoids the risk of esterification between organic acids and methanol (Polidori et al., 2008). Each extraction lasted for 10 min in an ultrasonic instrument. The three extracts were combined and filtered through a 0.45 µm nylon syringe filter (Millex, Billerica, MA, USA) to remove quartz fiber filter particles and insoluble suspended particles.

The extracts were cleaned by passing them through one of two commercial reverse-phase SPE cartridges, an LC-NH_2 cartridge (3 mL, containing 500 mg of a silica-based matrix with bonded aminopropyl active groups; Supelco, Bellefonte, PA, USA) or an LC-SAX cartridge (3 mL, containing 500 mg of a silica-based matrix with quaternary amine active groups and Cl^- counterions; Supelco). The 60 mL extract was percolated through a preconditioned cartridge at a flow rate of 1–1.5 $mL\,min^{-1}$ (controlled

throughout the SPE procedure by adjusting the vacuum). After the extract had been passed through the cartridge, the cartridge was washed with 8 mL hexane and then 4 mL dichloromethane, and air was passed through the cartridge to dry it. The retained organic acids were eluted with 2 mL of 5 % HCl in MeOH, which was collected in a conical flask. The cleaned extract was concentrated under vacuum and then mixed with 500 µL of 14 % BF_3 in MeOH (Sigma-Aldrich) to allow the analytes to be derivatized following the Kawamura method, and the mixture was placed in a water bath at 55 °C for 40 min (Kawamura and Gagosian, 1987c). The reaction mixture was washed with 3 mL of hexane and then 1 mL of a saturated Na_2SO_4 (aq) solution. The hexane layer (containing the derivatized analytes) was transferred to a clean 2-mL vial and (Millex, Billerica, MA, USA).

The NH_2 SPE cartridge extracted the acids more efficiently than the SAX cartridge did. The sample from 1 January 2013 provides an example. The numbers of each class of analyte (DCAs, AMAs, monocarboxylic acids, and FAMEs) and the concentration of each analyte that was found when the NH_2 and SAX SPE cartridges were used to concentrate a $PM_{2.5}$ extract are shown in Fig. 1. The total concentrations with the NH_2 SPE cartridge were 430 $ng\,m^{-3}$ for nine DCAs, 250 $ng\,m^{-3}$ for 17 AMAs, and 6020 $ng\,m^{-3}$ for 34 MCAs. They contrasted with 320 $ng\,m^{-3}$ for eight DCAs, 160 $ng\,m^{-3}$, for 13 AMAs, and 3950 $ng\,m^{-3}$ for 27 MCAs with the SAX cartridge. The numbers and concentrations of the FAMEs were similar for the two cartridges, however: (17 FAMEs for each, and total concentrations of 251 and 256 $ng\,m^{-3}$ with NH_2 and SAX, respectively).

These results indicate that the active group bonded to the silica-based matrix in the SPE cartridge had a marked influence on the effectiveness of the cartridge for extracting the analytes from the $PM_{2.5}$ extract. This was probably explained by the ability of nonpolar groups to become detached from the silica surface and leave behind strong anionic groups that could interact with the bonded amine groups. The extraction efficiency with the SAX cartridge was relatively low because of the relatively strong alkaline nature of the active quaternary amine groups. The SAX cartridges have exclusively anion exchange interactions with weak acids, which will lead some of each analyte to be retained by the cartridge rather than eluted. The aminopropyl active groups in the NH_2 cartridges offer only weakly selective retention. These results showed that the NH_2 cartridges were the most suitable for isolating organic acids, but that the SAX cartridges were most suitable for purifying nonpolar groups.

The uncleaned extracts and the solutions that had been passed through the cartridges were concentrated under vacuum, and then dried under a stream of nitrogen, washed with 2 mL of dichloromethane, and evaporated to 1 mL under a steam of nitrogen before being analyzed. A solution of 1 $\mu g\,mL^{-1}$ of hexamethylbenzene in hexane (Sigma-Aldrich) was added to each sample and calibration standard just before instrumental analysis to serve as an internal standard (to account for variations in the injected volume). The recoveries of the overall procedure were tested by extracting and analyzing blank filters that had been spiked with known quantities (at five different concentrations) of about 55 organic acid standards. The adipic acid standard was used to determine the recoveries and to quantify adipic acid and 3-methylpentanedioic acid; the pentadecanoic acid standard was used for 13-methyltetradecanoic acid, 12-methyltetradecanoic acid, and pentadecanoic acid; the palmitoleic acid standard was used for 14-methylpentadecanoic acid and palmitoleic acid; the heptadecanoic acid standard was used for 15-methylhexadecanoic acid, 14-methylhexadecanoic acid, and heptadecanoic acid; the fatty acid methyl ester (FAME) standards were used for the appropriate fatty acids and FAMEs 9-hydroxy-9-fluorene carboxylic acid methyl ester was used for 9-oxo-9H-fluorene-1-carboxylic acid. We used separate phthalic acid and dimethyl phthalate standards. The whole extraction and analytical procedure had a reproducibility of 96.8 %. Those values were high enough that no correction factors were applied to the analyte concentrations.

2.3 GC-MS and GC-MS-MS analysis

The organic compounds in the extracts were identified by comparing the spectra with spectra from the National Institute of Standards and Technology NIST08 mass spectral reference library, and the identities were confirmed by comparing the spectra with

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spectra for authentic standards. An Agilent 6890 N GC system (Agilent Technologies, Santa Clara, CA, USA) equipped with an Agilent 7683 autosampler was coupled to a Quattro Micro GC triple quadrupole mass spectrometer (Waters, Milford, MA, USA). The GC separation was achieved using an SPB^{TM}-1 fused silica capillary column (30 m long, 0.25 mm i.d., 0.25 µm film thickness; Supelco). A 1 µL aliquot of each sample was injected into the GC instrument in splitless injection mode. The MS system was operated in MS-MS (MRM) mode using the parameters shown in the targeted analysis section. The collision gas was argon (99.995 %), at 2.8×10^{-3} mbar. The GC carrier gas was high-purity helium, at a flow rate of 1 $mL\,min^{-1}$.

The column oven was programmed as follows: the temperature was initially set at 60 °C, held for 1 min, increased at 9 °C min^{-1} to 160 °C, held for 1 min, increased at 3 °C min^{-1} to 250 °C, held for 1 min, increased at 15 °C min^{-1} to 280 °C, and held for 1 min. The injector, ion source and interface transfer line temperature were 260, 230 and 270 °C, respectively. The analytes were ionized by electron impact (70 eV), and the emission current was 800 µA. the trap current was 200 mA, the repeller was set at 7.2 V and the Multiplier was set at 650.

3 Results and discussion

3.1 Identification of organic acids and FAMEs

Chromatograms of the organic acids in a sample that had been pretreated with an NH_2 SPE cartridge are shown in Fig. 2. The GC-MS chromatogram (Fig. 2a) shows that only the organic acids were isolated and concentrated from the extract and that polar and weakly polar compounds had been removed (meaning that the background noise level was low). However, the peaks of the trace multi-substituted AMAs and PAH-acids were so low that even their SIM signals were masked by the baselines. The selectivity and sensitivity of the assay was improved by using GC-MS-MS in MRM mode, because

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only the daughter ions of the selected precursors were detected (Fig. 2b), decreasing the disturbances in the signals and improving the signal strengths.

3.2 Ambient concentrations of acids in January

Table 1 presents the ambient concentrations of the aliphatic acids in $PM_{2.5}$ during January 2013, along with the GC-MS validation parameters. Table 2 presents the ambient concentrations of the aromatic acids and GC-MS-MS validation parameters. The results suggest that the method could also be used on samples from other seasons. Nonanedioic acid and succinic acid were the most abundant of the DCAs that were measured, with concentrations of 21–398 $ng\,m^{-3}$ (mean 124 $ng\,m^{-3}$) and 6–225 $ng\,m^{-3}$ (mean 78 $ng\,m^{-3}$), respectively. The aromatic DCAs were dominated by 1,2-benzenedicarboxylic (phthalic) acid and 1,4-benzenedicarboxylic (terephthalic) acid, with concentrations of 31–286 $ng\,m^{-3}$ (mean 131 $ng\,m^{-3}$) and 13–187 $ng\,m^{-3}$ (mean 54 $ng\,m^{-3}$), respectively.

The mean concentrations of the n-alkanoic acids, n-alkenoic acids, and FAMEs in the samples from January 2013 are shown in Fig. 3. The alkanoic acids were strongly dominated by those with even numbers of carbon atoms, and the pattern reached a maximum at stearic acid (C18 : 0), with a concentration of 270–3268 $ng\,m^{-3}$ (mean of 1491 $ng\,m^{-3}$). The acid with the next highest concentration was palmitic acid (C16 : 0), which was found at concentrations of 124–1487 $ng\,m^{-3}$ (mean of 743 $ng\,m^{-3}$). The C18 : 0 and C16 : 0 acids contributed 20–65 % (mean of 43 %) by mass to the organic acids that were quantified, consistent with previous measurements of a similar suite of organic acids in various ambient environments (Hou et al., 2006; Huang et al., 2006; Guo et al., 2007; Duan et al., 2009, 2013).

The polarity of the residual solutions (from which the acids had been removed by passing them through the SPE cartridges) had been decreased enough to make them suitable for direct GC analysis (Fig. 2c), and the concentrations of 17 FAMEs were measured. Of those, methyl stearate had the highest concentrations, 19–332 $ng\,m^{-3}$ (mean of 65 $ng\,m^{-3}$), contributed 2–23 % (mean of 6 %) to the total FAME concentrations. Next highest were the concentrations of methyl palmitate, at 18–278 $ng\,m^{-3}$ (mean of 63 $ng\,m^{-3}$), contributed 2–28 % (mean of 10 %) of the total FAME concentrations. The integrated area of the palmitic acid peak in the initial extract of the $PM_{2.5}$ sample from 22 January and the area of the methyl palmitate peak in the solution that had been passed through the NH_2 SPE cartridge are shown in Fig. 2d. It is clear that there is a complex suite of organic compounds in $PM_{2.5}$ extracts, but the selective separation of organic acids improves our ability to detect species that are otherwise difficult to determine and increases the sensitivity of the method.

From the SPE-GC-MS-MS data, we measured the concentrations of 1,8-naphthalic anhydride and five PAH-acids (2-naphthoic, biphenyl-4-carboxylic, 9-oxo-9H-fluorene-1-carboxylic, biphenyl-4,4′-dicarboxylic, and phenanthrene-1-carboxylic acids) in the. Phenanthrene-1-carboxylic acid and 9-oxo-9H-fluorene-1-carboxylic acid were the most abundant of the PAH-acids that were measured, and had concentrations of 10–32 $ng\,m^{-3}$ (mean of 16 $ng\,m^{-3}$) and 9–19 $ng\,m^{-3}$ (mean 12 $ng\,m^{-3}$), respectively. PAH-acids can be primary or derived from parent PAHs. Phenanthrene-1-carboxylic acid can be derived from phenanthrene, and 9-oxo-9H-fluorene-1-carboxylic acid can be derived from 9-fluorenone, and this suggests that they have similar sources or formation mechanisms.

3.3 Correlations between FAME and n-alkanoic acid concentrations

The correlation coefficients between the C16 : 0, C14 : 0, and C18 : 0 acids, and between the C13–C30 n-alkanoic acids except for C14, C16, and C18 were significant ($R^2 > 0.88$, $p < 0.01$), but those between C14, C16, and C18 and the other fatty acids were lower ($R^2 < 0.80$). The scatter plots and best-fit curves for C14 : 0 and C18 : 0 vs. C16 : 0, for C15: and C26 : 0 vs. C24 : 0, for C14: and C18: vs. FAME16, and for C17 : 0, and C24 : 0 vs. FAME24 are shown in Fig. 4. Their high correlations implied that these acids had common sources (Ho et al., 2011; Hyder et al., 2012). The C14–C18 fatty acids are considered to have mainly primary sources, with dominant contributions from direct emission sources, such as biomass burning, vehicular exhausts, and cooking (Pietrogrande et al., 2014; Zhao et al., 2014). The n-alkanoic acids (C14 : 0, C16 : 0, and C18 acids) are mainly primary, with dominant contributions from sources such as cooking, biomass burning, fossil fuels (including in motor vehicles), and vegetation detritus (Simoneit, 1986; Rogge et al., 1991, 1993; Schauer et al., 1999, 2001; Fraser et al., 2003).

The C18 : 0/C16 : 0 ratio has been used as a qualitative tool for assessing organic acid sources (Ho et al., 2010), and we found C18 : 0/C16 : 0 > 1 during our sampling period. Taking into account a recent study of organic acids (Zhao et al., 2014), we suggest that there was a strong input of organic acids to $PM_{2.5}$ from cooking emissions (as well as contributions from vehicular emissions) in Beijing in January 2013. Concentrations of high molecular-weight n-alkanoic acids (≥C20) in aerosols are generally higher in the winter because of the release of plant waxes from dead leaves and wind abrasion of other sources (Simoneit and Mazurek, 1982; Rogge et al., 1993; Guo et al., 2003; Simoneit et al., 2004; Kawamura et al., 2005; Feng et al., 2006).

The methyl esters of the C20–C30 waxy acids were strongly dominated by those with even numbers of carbon atoms (as found for the n-alkanoic acids). The pattern had a maximum at methyl lignocerate (C24), at concentrations of 26–148 $ng\,m^{-3}$ (mean of 70 $ng\,m^{-3}$). The next-highest ester was methyl hexacosanoate (C26). The methyl esters of the C13 and C19 acids were lower than the GC-MS (in SIM mode) detection limits, and they could not be measured by GC-MS-MS-MRM because of their low molecular-ion signal strengths. The correlation coefficients for the relationships between the methyl esters of the C12–C30 fatty acids were similar to those for the fatty acids. The correlations between C14, C16, and C18 methyl esters, and between the C13–C30 methyl esters (except for the C14, C16, and C18 methyl esters) were high ($R^2 > 0.85$). Those between the C14, C16, and C18 methyl acids and the other fatty acid methyl esters were lower ($R^2 < 0.70$).

From the information described above and the molecular structures, we suggest that FAMEs could either have similar sources to carboxylic acids, be formed by esterifying carboxylic acids, or that a fraction of the fatty acids were formed by hydrolyzing FAMEs. Also, the uncertainty in the measurements of phthalic acid and dimethyl phthalate would have been 20 % during the sampling period if they had not been separated. The abundances of dimethyl phthalate and FAMEs justify the use of the NH_2 SPE technique to avoid overestimating the corresponding fatty acids in the extracts. The measurements of fatty acids and esters were more accurate when the NH_2 SPE technique was used.

3.4 Correlations between DCA and AMA concentrations

The correlation coefficients between the C4–C11 DCAs and AMAs are shown in Table 3. The DCAs were strongly correlated ($r^2 > 0.85$, $p < 0.01$). They could be divided into two groups, low molecular weight DCAs (di-C4–C5) and high molecular weight DCAs (di-C7–C11). The di-C4–C5 DCAs (succinic, glutaric, and 3-methylpentanedioic acids) were strongly correlated with three of the AMAs (phthalic, 4-methylphthalic, and benzene-1,2,4-tricarboxylic acids), two of the PAH-acids (9-oxo-9H-fluorene-1-carboxylic and 2-naphthoic acids), and 1,8-naphthalic anhydride. Previous studies have suggested that C4–C5 DCAs are mainly secondary products of a range of volatile organic compound precursors (Kawamura and Gagosian, 1987a; Kawamura et al., 1996; Graham et al., 2002; Claeys, 2004; Ervens et al., 2004; Gelencser, 2004; Kanakidou et al., 2005; Kawamura and Yasu, 2005; Oliveira et al., 2007). Phthalic acid is derived from incomplete combustion of PAHs (e.g., naphthalene) in vehicular exhausts (Kawamura and Gagosian, 1987a), or produced by atmospheric oxidation of PAHs (Guillard, 1993; Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005). Phthalic acids are widely used as plasticizer substrates (Fraser et al., 2003; Fine et al., 2004), indicators of photochemical activity, and surrogates for the contributions of secondary organic aerosols to particular ambient environments (Fine et al., 2002; Ho et al., 2010). In view of this, we suggest that 9-oxo-9H-fluorene-1-carboxylic acid, 2-naphthoic acid, and 1,8-naphthalic anhydride, together with the di-C4–C5 acids, are mainly secondary.

The di-C7–C11 acids correlated strongly with five of the AMAs (terephthalic, isophthalic, 2-hydroxy-5-methylbenzoic, 4-(ethoxycarbonyl) benzoic, and phenanthrene-1-carboxylic acids). Correlations between adipic acid (di-C6) and the di-C4–C5 acids were higher ($r^2 > 0.85$) than those between adipic acid and the di-C7–C11 acids. However, the correlation between adipic acid and terephthalic acid (0.61) and isophthalic acid (0.68) acid, which are used as tracers of primary emissions from motor vehicles and domestic heating with fossil fuels (Kawamura and Kasukabe, 1996; Fine et al., 2002; Fraser et al., 2003; Wang et al., 2006), were higher than for adipic acid and phthalic acid (0.34) and 4-methylphthalic acid (0.45), which are tracers of secondary sources. Adipic acid (di-C6) is produced by oxidizing anthropogenic cyclic hexane (Grosjean et al., 1978; Kawamura and Ikushima, 1993), and may also be emitted directly by motor vehicles (Fraser et al., 2003). Azelaic acid (di-C9) has been found to be a product of biogenic unsaturated fatty acids containing double bonds predominantly at the C9 position, such as C18 : 1 (Kawamura and Kaplan, 1987), so the di-C6/di-C9 ratio has been used to indicate the relative strengths of anthropogenic and biogenic sources of precursors to the diacids (Kawamura and Ikushima, 1993). We found low di-C6/di-C9 ratios (0.18–0.62, mean 0.33) which seem to mean that phenanthrene-1-carboxylic acid and di-C6 acid were primary during January.

The correlation between biphenyl-4-carboxylic acid and benzoic acid, 0.73, is higher than those between the other acids. Benzoic acid may be primary from vehicular exhausts (Kawamura and Gagosian, 1987a; Rogge et al., 1993) and secondary from photochemical degradation of aromatic hydrocarbons such as toluene, emitted by automobiles (Ho et al., 2006; Sun et al., 2006; Li et al., 2009). The aromatic biphenyl is a widely distributed pollutant (Selesi and Meckenstock, 2009), and it is found in coal tar at concentrations of 0.2 to 0.4 %. The oxidation of toluene in the atmosphere is more complicated than the breaking of the single bond that is found in biphenyl, so we suggest that biphenyl-4-carboxylic acid is mainly a secondary product of the photochemical degradation of biphenyl. The biphenyl-4,4′-dicarboxylic acid correlated relatively strongly with di-C8 acids (0.80), di-C10 acids (0.82), and terephthalic acid

(0.81), which are all mainly primary, as noted above. In view of this, we suggest that biphenyl-4,4′-dicarboxylic acid in $PM_{2.5}$ is mainly primary.

4 Conclusions

Organic acids (alkanoic acids, alkenoic acids, and AMAs) and FAMEs were identified and measured with NH_2 SPE pretreatment and GC-MS and GC-MS-MS. They contributed strongly $PM_{2.5}$ in January 2013 at Beijing. The NH_2-SPE method is easy to perform and combines high preconcentration with satisfactory precision and selectivity. Five PAH-acids and 1,8-naphthalic anhydride were identified and measured in $PM_{2.5}$. Seventeen FAMEs were separated from their corresponding n-alkanoic acids, and, taking into account the large amounts of FAMEs that are emitted, were found to be of potential use determining the relative importance of primary emissions and secondary processes to the concentrations of organic acid esters that are found in typical winter haze episodes in Beijing.

The interference of FAMEs on the corresponding fatty acids was eliminated by using the NH_2 SPE cartridge cleanup, so the overestimation of the fatty acid concentrations was avoided using the selective SPE extraction technique. The correlations between the FAMEs and the aliphatic acids were statistically significant, indicating that FAMEs could come from the same sources as the waxy acids. The correlations between tracer and DCA and AMA suggested that 9-oxo-9H-fluorene-1-carboxylic acid, 2-naphthoic acid, C3–C5 DCAs, and AMAs (including phthalic acids) were mainly secondary during January 2013. We found that phenanthrene-1-carboxylic acid, the C6–C10 DCAs, biphenyl-4-carboxylic acid and benzoic acid were mainly secondary products of photochemical degradation, and that biphenyl-4,4′-dicarboxylic acid could primarily have been produced by burning coal. The C18 : 0/C16 : 0 ratio was > 1, which indicated that, apart from the contribution of vehicular emissions, there were significant inputs from cooking emissions in January 2013 in Beijing.

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Table 1. Parameters used to determine organic acids and the concentrations found in samples collected in January 2013, Beijing.

Acids	MW[a]	RT[b] (min)	SIM (derivatization m/z)	Recovery (%)	MDL[c] ng µL^{-1}	Air concentration (ng m^{-3})	
						mean	range
Dicarboxylic acids (DCAs)							
Succinic	118	5.52	115/87/59/55	86.4 ± 4.2	0.14	78.5	6.4–225.5
Glutaric	132	7.22	129/100/59/55	93.1 ± 3.9	0.26	38.3	6.3–108.6
3-Methylpentanedioic	146	7.76	143/114/101/69	89.6 ± 0.7	0.27	20.7	6.0–62.6
Adipic	146	8.90	143/101/111/59	89.6 ± 0.7	0.27	35.6	7.7–71.5
Heptanedioic	160	10.44	157/128/115/74	83.7 ± 1.4	0.16	10.6	6.4–21.5
Octanedioic	174	11.95	171/138/129/125/74/55	93.5 ± 6.2	0.18	24.2	10.9–64.3
Nonanedioic	188	13.52	185/152/143/111/74/55	92.3 ± 5.4	0.12	123.7	20.9–398.1
Decanedioic	202	15.37	199/166/138/125/77/55	88.4 ± 4.1	0.10	30.6	17.0–80.3
Undecanedioic	216	17.61	213/171/152/139/98/74	80.3 ± 2.1	0.19	17.4	10.9–41.2
Monocarboxylic acids (MCAs)							
Octanoic (C8 : 0)	144	7.03	144/115/127/87/74	114.2 ± 9.7	0.08	24.2	6.1–58.5
Nonanoic (C9 : 0)	158	8.60	143/141/129/87/74	88.4 ± 3.6	0.26	17.6	6.0–45.8
Decanoic (C10 : 0)	172	10.14	186/155/143/87/74	112.6 ± 4.7	0.06	12.8	6.8–22.7
Undecanoic (C11 : 0)	186	11.60	200/169/157/143/87/74	88.5 ± 4.2	0.17	12.6	7.1–23.5
11-Dodecenoic (C12 : 1)	198	11.79	212/196/166/124/77/55	72.5 ± 2.6	0.07	16.3	6.6–41.0
Dodecanoic (C12 : 0)	200	13.10	214/183/171/143/87/74	96.9 ± 4.5	0.10	41.4	9.4–99.6
Tridecanoic (C13 : 0)	214	14.93	228/197/185/143/87/74	97.7 ± 5.8	0.24	22.9	8.1–53.3
Tetradecanoic (C14 : 0)	228	17.00	242/211/199/143/87/74	109.4 ± 5.4	0.38	182.1	15.0–937.1
13-Methyltetradecanoic	242	18.49	256/225/213/143/87/74	96.7 ± 3.8	0.60	12.0	7.56–22.3
12-Methyltetradecanoic	242	18.69	256/225/213/143/87/74	96.7 ± 3.8	0.60	13.5	7.7–25.2
Pentadecanoic (C15 : 0)	242	19.32	256/225/213/143/87/74	96.7 ± 3.8	0.60	59.7	8.2–154.2
Palmitic (C16 : 1)	254	20.39	268/236/194/152/87/74	83.4 ± 5.1	0.56	22.8	8.8–54.3
14-Methylpentadecanoic	256	20.99	270/239/227/143/87/74	111.3 ± 9.2	0.25	12.7	8.9–22.1
Palmitoleic (C16 : 0)	256	22.02	270/239/227/143/87/74	111.3 ± 9.2	0.25	742.6	123.7–1487.4
15-Methylhexadecanoic	270	23.66	284/253/241/143/87/74	95.9 ± 2.7	0.16	15.5	10.3–28.0
14-Methylhexadecanoic	270	23.88	284/253/241/143/87/74	95.9 ± 2.7	0.27	22.8	10.9–46.5
Heptadecanoic (C17 : 0)	270	24.70	284/253/241/143/87/74	95.9 ± 2.7	0.16	86.4	17.9–236.3
Linoleic (C18 : 2)	294	26.51	294/263/95/81/67/55	78.7 ± 3.1	0.18	118.4	12.7–328.0
Oleic (C18 : 1)	296	26.68	296/264/222/191/69/55	93.8 ± 2.1	0.22	74.7	10.7–208.6
Stearic (C18 : 0)	284	27.43	298/255/199/143/87/74	97.9 ± 2.9	0.14	1490.5	269.8–3268.3
Nonadecanoic (C19 : 0)	298	30.13	312/281/269/143/87/74	94.8 ± 2.3	0.29	34.9	10.8–90.3
11-Eicosenoic (C20 : 1)	324	32.06	324/292/250/67/55	83.9 ± 3.9	0.37	22.5	10.6–142.1
10-Oxooctadecanoic	312	32.13	281/214/156/55	78.9 ± 2.7	0.18	24.5	16.8–49.5
Eicosanoic (C20 : 0)	312	32.82	326/295/283/143/87/74	95.2 ± 2.2	0.26	130.9	24.6–370.1

[a] Molecular weight.

[b] Retention time.

[c] Method detection limit.

Table 1. Continued.

Acids	MW[a]	RT[b] (min)	SIM (derivatization m/z)	Recovery (%)	MDL[c] $ng\,\mu L^{-1}$	Air concentration ($ng\,m^{-3}$)	
						mean	range
Henicosanoic (C21 : 0)	326	35.44	340/297/241/143/87/74	96.7 ± 3.8	0.36	80.9	14.2–239.3
Docosanoic (C22 : 0)	340	37.99	354/311/255/143/87/74	96.5 ± 2.6	0.17	196.2	17.2–626.3
Tricosanoic (C23 : 0)	354	40.43	368/325/269/143/87/74	93.5 ± 2.9	0.27	114.6	16.1–380.6
Tetracosanoic (C24 : 0)	368	42.86	382/339/199/143/87/74	94.8 ± 7.3	0.19	322.5	19.2–1080.3
Pentacosanoic (C25 : 0)	382	45.10	396/353/297/143/87/74	97.2 ± 6.5	0.34	74.7	15.6–244.2
Hexacosanoic (C26 : 0)	396	46.51	410/367/311/143/87/74	89.5 ± 5.6	0.34	252.4	17.5–858.5
Heptacosanoic (C27 : 0)	410	47.92	424/381/355/143/87/74	91.6 ± 6.4	0.41	46.6	22.4–129.3
Octacosanoic (C28 : 0)	424	49.50	438/395/199/143/87/74	84.9 ± 3.8	0.46	143.2	15.1–538.2
Nonacosanoic (C29 : 0)	438	51.47	452/423/199/143/87/74	79.4 ± 3.7	0.51	23.0	13.5–56.2
Triacontanoic (C30 : 0)	452	53.74	466/437/199/143/87/74	73.6 ± 2.7	0.64	45.9	13.3–161.0
Fatty acid methyl esters (FAMEs)							
Methyl dodecanoate	172	13.10	214/183/171/143/87/74	96.9 ± 4.5	0.10	10.3	7.2–16.8
Methyl myristate	242	17.00	242/211/199/143/87/74	109.4 ± 5.4	0.38	13.6	8.1–33.8
Methyl pentadecanoate	256	19.32	256/225/213/143/87/74	96.7 ± 3.8	0.64	12.7	8.4–18.6
Methyl palmitate	270	22.00	270/239/227/143/87/74	111.3 ± 9.2	0.25	62.9	17.8–279.6
Methyl heptadecanoate	284	24.70	284/253/241/143/87/74	95.9 ± 2.7	0.14	15.4	10.8–27.8
Methyl stearate	298	27.42	298/255/199/143/87/74	97.9 ± 2.9	0.26	85.3	18.8–654.0
Methyl arachidate	326	32.82	326/295/283/143/87/74	95.2 ± 2.2	0.32	30.7	20.1–50.7
Methyl heneicosanoate	340	35.44	340/297/241/143/87/74	96.7 ± 3.8	0.36	12.9	12.3–13.9
Methyl behenate	354	37.99	354/311/255/143/87/74	96.5 ± 2.6	0.17	25.2	14.6–47.6
Methyl tricosanoate	368	40.43	368/325/269/143/87/74	93.5 ± 2.9	0.27	11.6	8.3–24.4
Methyl lignocerate	382	42.86	382/339/199/143/87/74	94.8 ± 7.3	0.19	69.9	26.4–148.3
Methyl pentacosanoate	396	45.10	396/353/297/143/87/74	97.2 ± 6.5	0.34	17.1	14.6–23.5
Methyl hexacosanoate	410	46.51	410/367/311/143/87/74	89.5 ± 5.6	0.34	32.6	17.7–60.2
Methyl heptacosanoate	424	47.92	424/381/355/143/87/74	91.6 ± 6.4	0.41	20.9	18.4–35.0
Methyl octacosanoate	438	49.50	438/395/199/143/87/74	84.9 ± 3.8	0.46	22.3	14.3–36.8
Methyl nonacosanoate	452	51.47	452/423/199/143/87/74	79.4 ± 3.7	0.51	13.4	12.0–18.3
Methyl triacontanoate	466	53.74	466/437/199/143/87/74	73.6 ± 2.7	0.64	12.7	12.2–13.9

[a] Molecular weight.

[b] Retention time.

[c] Method detection limit.

Table 2. Parameters used to determine aromatic acids (AMAs), dimethyl phthalate and the concentrations found in samples collected in Jan 2013, Beijing.

Compounds	MW	RT (min)	MRM Quantitative ion pairs (collision energy ev)	Recovery (%)	MDL $ng\,\mu L^{-1}$	Air concentration ($ng\,m^{-3}$)	
						mean	range
Benzoic	122	6.61	136 > 105(10); 136 > 77(15)	86.4 ± 4.3	0.24	23.3	6.5–40.8
2-Hydroxybenzoic	136	8.21	152 > 1120(10); 152 > 92(15)	81.4 ± 5.1	0.16	15.0	6.1–36.5
2-Hydroxy-5-methylbenzoic	152	10.00	166 > 134(10); 166 > 77(15)	79.6 ± 2.7	0.37	8.5	5.6–12.0
3,5-Dimethylbenzoic	150	10.59	164 > 133(10); 166 > 105(15)	83.2 ± 4.4	0.46	16.6	7.3–22.4
Phthalic	166	12.12	194 > 163(15); 163 > 135(20)	91.5 ± 5.2	0.38	54.1	13.3–187.2
Terephthalic	166	12.74	194 > 163(15); 163 > 135(20)	92.3 ± 4.6	0.22	130.6	31.3–286.4
Isophthalic	166	12.98	194 > 163(15); 163 > 135(20)	88.4 ± 4.3	0.40	12.8	7.6–23.5
4-Methylphthalic	180	14.00	208 > 163(10); 193 > 149(20)	80.8 ± 5.1	0.39	15.2	6.8–48.5
4-(ethoxycarbonyl)benzoic	180	14.07	208 > 163(15); 179 > 149(25)	67.5 ± 3.2	0.57	7.8	7.0–10.5
2-Naphthoic	172	15.38	186 > 155(20); 155 > 127(25)	84.2 ± 7.4	0.49	2.5	2.8–8.1
Benzene-1,2,4-tricarboxylic	210	19.81	252 > 221(20); 221 > 193(25)	80.4 ± 3.6	0.46	3.4	2.6–10.8
Biphenyl-4-carboxylic	198	19.99	212 > 181(10); 181 > 152(20)	92.6 ± 5.8	0.36	11.5	4.5–22.2
1,8-Naphthalic anhydride	198	24.67	198 > 154(15); 154 > 126(25)	82.5 ± 4.2	0.58	11.0	4.8–26.9
9-Oxo-9H-fluorene-1-carboxylic	224	27.76	238 > 207(10); 180 > 151(25)	68.5 ± 3.4	0.37	11.6	3.7–19.0
Biphenyl-4,4′-dicarboxylic	242	29.37	270 > 239(15); 270 > 152(25)	76.9 ± 4.5	0.49	10.3	2.7–15.8
Phenanthrene-1-carboxylic	222	30.87	236 > 205(20); 205 > 177(25)	87.3 ± 5.8	0.44	16.4	3.5–32.2
Dehydroabietic	300	32.97	314 > 299(20); 299 > 239(25)	79.4 ± 5.7	0.68	25.4	16.7–40.2
Dimethyl phthalate	194	12.12	194 > 163(15); 163 > 135(20)	87.5 ± 2.7	0.54	11.4	8.1–18.8

Table 3. Correlation matrix of C4-C11 DCAs and aromatic acids concentrations measured in Jan 2013, Beijing.

	C5[b]	C5[c]	C6[d]	C7[e]	C8[f]	C9[g]	C10[h]	C11[i]	AMA[j]	AMA[k]	AMA[l]	AMA[m]	AMA[n]	AMA[o]	AMA[p]	AMA[q]	AMA[r]	AMA[s]	AMA[t]	AMA[u]	AMA[v]	AMA[w]	AMA[x]	AMA[y]	AMA[z]
C4[a]	0.97	0.87	0.75	0.74	0.62	0.50	0.80	0.77	0.42	0.23	0.67	0.26	0.79	0.68	0.78	0.77	0.43	0.54	0.63	0.31	0.70	0.68	0.63	0.46	0.31
C5[b]		0.93	0.86	0.91	0.90	0.85	0.92	0.88	0.40	0.21	0.61	0.21	0.76	0.61	0.78	0.73	0.36	0.50	0.71	0.31	0.68	0.68	0.63	0.39	0.27
C5[c]			0.91	0.61	0.59	0.76	0.64	0.82	0.27	0.20	0.61	0.20	0.93	0.66	0.87	0.90	0.37	0.46	0.75	0.28	0.76	0.70	0.62	0.44	0.20
C6[d]				0.82	0.76	0.66	0.77	0.77	0.76	0.35	0.71	0.34	0.45	0.61	0.68	0.44	0.45	0.28	0.43	0.56	0.59	0.49	0.68	0.55	0.47
C7[e]					0.96	0.85	0.95	0.93	0.54	0.25	0.74	0.34	0.55	0.69	0.82	0.53	0.46	0.34	0.66	0.58	0.74	0.61	0.78	0.64	0.62
C8[f]						0.94	0.95	0.97	0.51	0.25	0.68	0.29	0.54	0.70	0.82	0.50	0.41	0.25	0.64	0.59	0.77	0.54	0.80	0.66	0.56
C9[g]							0.86	0.90	0.46	0.20	0.59	0.30	0.59	0.59	0.73	0.58	0.37	0.16	0.50	0.64	0.66	0.45	0.77	0.66	0.56
C10[h]								0.91	0.55	0.30	0.75	0.29	0.58	0.78	0.87	0.65	0.46	0.26	0.61	0.61	0.81	0.57	0.82	0.74	0.60
C11[i]									0.55	0.20	0.62	0.26	0.42	0.79	0.74	0.78	0.34	0.21	0.51	0.60	0.81	0.46	0.73	0.55	0.56
AMA[j]										0.72	0.67	0.43	0.21	0.50	0.49	0.26	0.43	0.18	0.22	0.73	0.43	0.28	0.57	0.69	0.55
AMA[k]											0.63	0.54	0.19	0.45	0.52	0.45	0.30	0.56	0.12	0.13	0.52	0.36	0.43	0.46	0.57
AMA[l]												0.55	0.57	0.80	0.79	0.62	0.83	0.57	0.51	0.64	0.75	0.72	0.66	0.83	0.77
AMA[m]													0.20	0.25	0.42	0.23	0.41	0.25	0.18	0.36	0.22	0.44	0.46	0.36	0.50
AMA[n]														0.84	0.90	0.97	0.34	0.45	0.72	0.30	0.93	0.70	0.66	0.44	0.18
AMA[o]															0.93	0.89	0.60	0.34	0.53	0.46	0.91	0.62	0.78	0.84	0.57
AMA[p]																0.40	0.73	0.65	0.81	0.56	0.87	0.84	0.81	0.83	0.60
AMA[q]																	0.38	0.53	0.65	0.34	0.95	0.74	0.62	0.93	0.21
AMA[r]																		0.48	0.29	0.39	0.52	0.75	0.61	0.71	0.60
AMA[s]																			0.86	0.13	0.90	0.78	0.41	0.31	0.39
AMA[t]																				0.32	0.86	0.70	0.64	0.37	0.29
AMA[u]																					0.37	0.84	0.62	0.37	0.61
AMA[v]																						0.66	0.69	0.86	0.48
AMA[w]																							0.67	0.61	0.58
AMA[x]																								0.83	0.63
AMA[y]																									0.79

[a] Succinic acid. [b] Glutaric acid. [c] 3-methylpentanedioic acid. [d] Adipic acid. [e] Heptanedioic acid. [f] Octanedioic acid.[g] Nonanedioic acid. [h] Decanedioic acid. [i] Undecanedioic acid. [j] Benzoic acid. [k] 2-hydrobenzoic acid. [l] 2-hydroxy-5-methylbenzoic acid. [m] 3,5-dimethylbenzoic acid. [n] Phthalic acid. [o] Terephthalic acid. [p] Isophthalic acid. [q] 4-methylphthalic acid. [r] 4-(ethoxycarbonyl)benzoic acid. [s] 2-naphthoic acid. [t] Benzene-1,2,4-tricarboxylic acid. [u] Biphenyl-4-carboxylic acid. [v] 1,8-naphthalic anhydride. [w] 9-oxo-9H-fluorene-1-carboxylic acid. [x] Biphenyl-4,4′-dicarboxylic acid. [y] Phenanthrene-1-carboxylic acid. [z] Dehydroabietic acid.

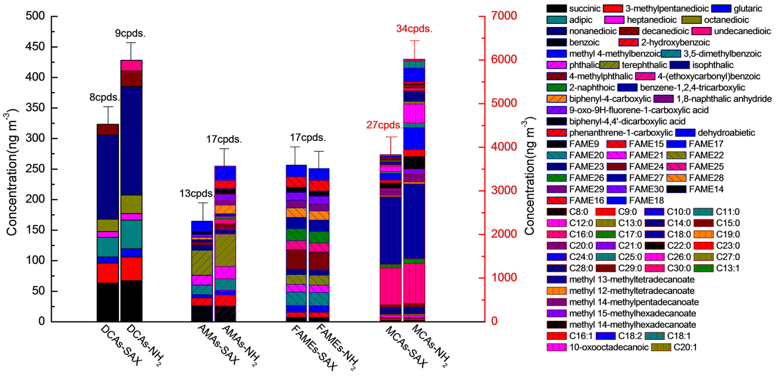

Figure 1. Concentrations of analytes found when an extract of $PM_{2.5}$ collected on 1 January 2013 in Beijing was analyzed using the SAX and NH_2 solid phase extraction cartridges. The left-hand *y* axis (in black) is for the dicarboxylic acids (DCAs), aromatic acids (AMAs), and fatty acid methyl esters. The right-hand *y* axis (in red) is for the monocarboxylic acids. The T-shaped marks indicate the numbers of compounds (cpds.) that were found.

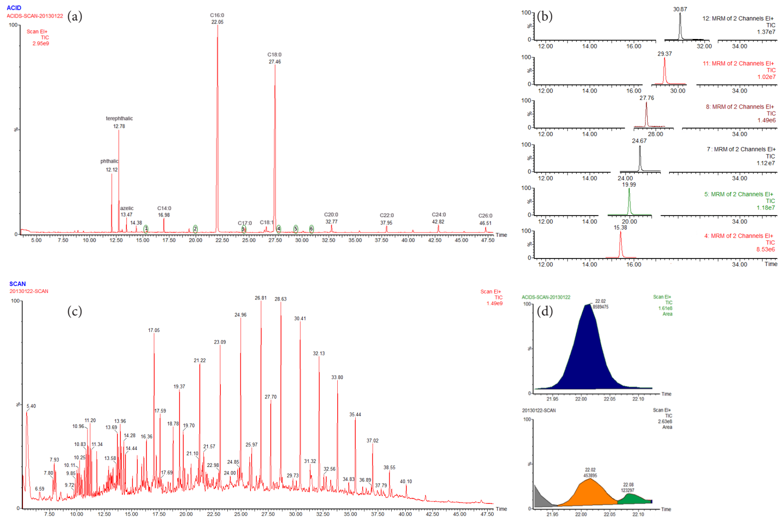

Figure 2. Chromatograms of the organic compounds in an extract of a $PM_{2.5}$ sample that was collected on 22 January 2013 in Beijing after the extract had been pretreated using an NH_2 solid phase extraction (SPE) cartridge. **(a)** GC-MS chromatograms of organic acids. **(b)** GC-MS-MS chromatograms of PAH-acid. **(c)** GC-MS chromatogram of compounds in the extract solution that had been passed through the SPE cartridge (i.e, from which the analytes had been removed). **(d)** The integrated areas of palmitoleic acid in the uncleaned solution and methylhexadecanoate in the eluted (cleaned) extract.

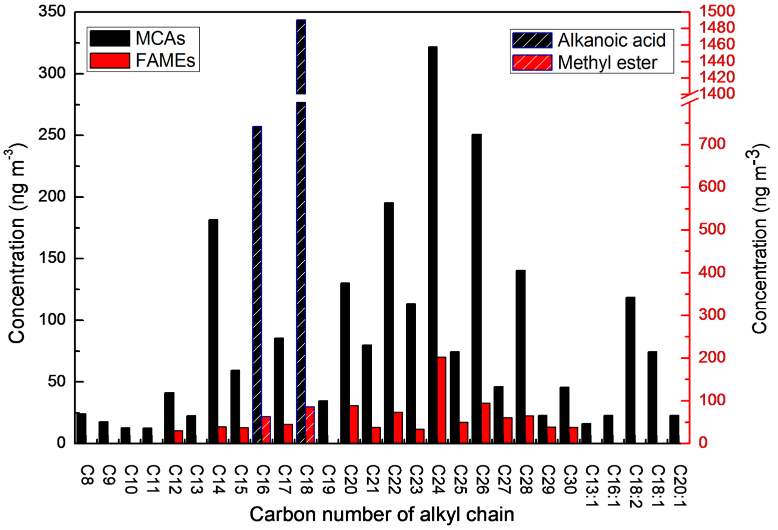

Figure 3. Mean monocarboxylic acid (MCA) and fatty acid methyl ester (FAME) concentrations in $PM_{2.5}$ samples collected in January 2013 in Beijing.

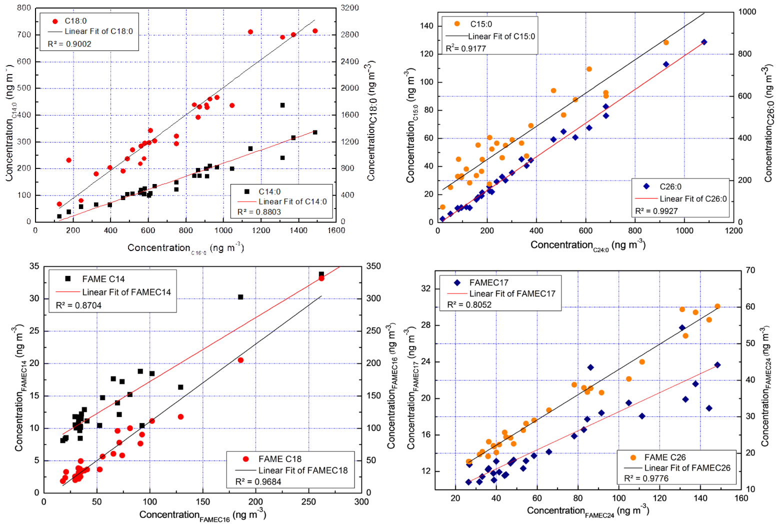

Figure 4. Correlations between selected pairs of carboxylic acids and fatty acid methyl esters (FAMEs).