



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

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Abstract. A solid-phase extraction (SPE) pretreatment procedure allowing organic acids to be separated from methyl esters in fine aerosol has been developed. The procedure first separates the organic acids from fatty acid methyl esters (FAMES) and other nonacid organic compounds by aminopropyl-based SPE cartridge and then quantifies them by gas chromatography/mass spectrometry. The procedure prevents the fatty acids and dimethyl phthalate from being overestimated, and so allows us to accurately quantify the C₄–C₁₁ dicarboxylic acids (DCAs) and the C₈–C₃₀ monocarboxylic acids (MCAs). Results for the extraction of DCAs, MCAs, and AMAs in eluate and FAMES in effluate by SAX and NH₂ SPE cartridges exhibited that the NH₂ SPE cartridge gave higher extraction efficiency than the SAX cartridge. The recoveries of analytes ranged from 67.5 to 111.3%, and the RSD ranged from 0.7 to 10.9%. The resulting correlations between the aliphatic acids and FAMES suggest that the 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. Through extraction and cleanup using this procedure, 17 aromatic acids in eluate were identified and quantified by gas chromatography/tandem mass spectrometry, including 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 suggested that the first three acids and 1,8-naphthalic anhydride were secondary atmospheric photochemistry products and the last two mainly primary.

1 Introduction

Organic acids, including C₆–C₃₂ monocarboxylic acids (MCAs), C₂–C₁₂ dicarboxylic acids (DCAs), ketocarboxylic acids, and 1-, 2-, and 3-substituted aromatic acids (AMAs), are ubiquitous in aerosols (Kawamura, 1993; Sempère and Kawamura, 1994; Fraser et al., 2003; Kawamura and Yasui, 2005; Wang et al., 2006; Li, 2008; Jung et al., 2010), and they can contribute major part of the organic matter in city atmosphere (Satsumabayashi et al., 1989; 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 Gagation, 1987a, b; Sempère and Kawamura, 1994; Reid and Hobbs, 1998; Graham et al., 2002; Gao et al., 2003; Reid et al., 2005; Pio 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; Gelencsér, 2004; Kanakidou et al., 2005; Kawamura

and Yasui, 2005). Although some aromatic acids formed from oxidation reactions of volatile and/or semivolatile polycyclic aromatic hydrocarbons (PAHs) have been studied extensively, such as phthalic acid, which is an oxidation product of naphthalene analogues with OH, nitrate radicals, and ozone (Wang et al., 2007), their mechanistic features and other oxidation products (e.g., 2-hydroxybenzoic acid and phthalic anhydride) of PAHs were still poorly characterized (Lee and Lane, 2009; Kautzman et al., 2010). Thus, it is necessary to develop novel analytical methods that can be used to identify possible tracers and help understand the formation mechanisms of secondary organic acid aerosol.

Generally, organic acids are extracted from aerosol samples along with other organics by liquid–liquid or solid-phase extraction (SPE). SPE is the most widely used preconcentration technique which mainly depends on the sort of the packing and properties of the solvent. Due to the difference of selectivity, affinity, and capacity of packing, efficient enrichment of target compounds is provided through adsorption or ion-exchange separation mechanism. Adsorption-type SPE, such as a polyurethane foam, silica, and silica-alumina mixture, has been used to concentrate organic analytes from organic extraction in fine aerosol (Fraser et al., 1997; Hou et al., 2006; Duan et al., 2006).

SPE also can separate target analytes and clean up interference with good recoveries and enrichment (Rosenfeld, 1999; Ericsson and Colmsjö, 2003; Hou et al., 2006; Zhao et al., 2014). Adler and Siren studied the enrichment of α , ω -dicarboxylic acids (C₂–C₁₀) by revised-phase polymeric Oasis HLB, Strata X, strong nonpolar Isolute 101 and strong anion-exchange SAX, and J. T. Baker NH₂ and Quaternary Amine SPE materials in the water-soluble fraction of fine aerosols (Adler and Siren, 2014). Results showed that the nonpolar sorbents possessed higher selectivity than ion-exchange SPE for C₄–C₁₀ DCAs under inorganic matrix. However, an aminopropyl imidazole-modified silica sorbent exhibited high extraction efficiency towards carboxylic acids and PAHs in river water samples based on electrostatic, π – π , and hydrophobic interactions (Wang et al., 2014). The anion-exchange SPE cartridges have also been used to cleanup and/or concentrate organic acids in organic matrices. Wang et al. (2013) demonstrated a novel NH₂/Carb SPE procedure to separate organic acids from indoxacarb/acetonitrile solution based on ion-exchange interaction and electrostatic (Wang et al., 2013). Although the interactions between organic compounds and silica bonded ion-exchange SPE have been investigated, application of anion-exchange SPE to separate polar compounds from complex organic matrices was relative few. Hence, the silica anion-exchanged SPE shows potential for the separation and enrichment of organic acid in fine aerosol.

Gas chromatography/mass spectrometry (GC-MS) as a specific ion detection method has been widely used to study the detailed composition of atmospheric aerosols. For GC-MS, organic acids need to be derivatized to more volatile esters with BF₃-methanol, BF₃-butanol, or N,O-bis-

(trimethylsilyl)trifluoroacetamide (Kawamura and Kaplan, 1987; Kawamura, 1993; Fu et al., 2009). The butyl and trimethylsilyl (TMS) derivatives are often used 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). 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, 1987a, b; Plewka et al., 2003; Fraser et al., 2003). However, quantification of trace amounts of oxygenated PAHs (O-PAHs), including aromatic acids, identified in urban or diesel particles is still difficult because of the low levels and interference of the complex background compounds (Walgraeve et al., 2010). Moreover, during purification or fractionation which involves evaporation, volatile and/or semivolatile compounds can be lost. To deal with this problem, an advanced pretreatment technique which is capable of enriching and separating target analytes from others and high-resolution analytical methods deserve to be developed.

Tandem mass spectrometry (MS-MS) is an approach which reduces the background caused by the complex matrix by excluding all ions except the parent ion, which can then be fragmented under specific collision energy and generate a unique product ion mass spectrum. GC-MS-MS has been applied to detect and quantify O-PAHs in airborne particulate (Nicol et al., 2001). For this work, we developed a pretreatment technique to aerosol sampled in Beijing during January 2013, when 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/>) had reached nearly 500, and visibility was sometimes below 100 m. The objective of this technique was to separate organic acids from methyl esters with anion-SPE cartridge in the raw extract of fine aerosol and to quantify them by GC-MS and GC-MS-MS.

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 30 samples discussed here came from 1 to 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), which were placed into a high-volume sampler (VFC-PM₁₀; Thermo Fisher Scientific Inc., Waltham, MA, USA) at 1.13 m³ min⁻¹ from 21:00 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

For sample extraction, an area of 40 cm^2 was punched out of the quartz-fiber filter and extracted successively with 20 mL hexane, dichloromethane (DCM), and acetonitrile in turn (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 extracts were combined and filtered through a $0.45\text{ }\mu\text{m}$ nylon syringe filter (Millex, Billerica, MA, USA) to remove quartz fiber filter particles and insoluble suspended particles.

For SPE, separation of organic acid from other species in solvent extract is conducted by use of two anion-exchange SPE materials: NH_2 cartridge (3 mL, containing 500 mg of a silica-based matrix with bonded aminopropyl active groups; Supelco, Bellefonte, PA, USA) and SAX cartridge (3 mL, containing 500 mg of a silica-based matrix with quaternary amine active groups and Cl^- counterions; Supelco) after filtration. Before sample application, the cartridges were preconditioned with 3.0 mL hexane, dichloromethane, and acetonitrile in turn. The 60 mL extract was percolated through the preconditioned cartridge at a flow rate of $1\text{--}1.5\text{ mL min}^{-1}$ (controlled throughout the SPE procedure by adjusting the vacuum). After sample application, the cartridge was washed with 8 mL hexane and then 4 mL dichloromethane, and air was passed through the cartridge to dry it. After washing in this way, the GC-MS chromatogram of the eluate exhibited no noise at all (flat baseline). The retained organic acids were eluted with 2 mL of 5% HCl–methanol into conical flasks. For enrichment, the eluate was evaporated using a rotary evaporator at reduced pressure then under ultra-pure nitrogen gas to about $100\text{ }\mu\text{L}$, and then the organic acids in the eluate were derivatized with 14% BF_3 –methanol ($500\text{ }\mu\text{L}$, Sigma-Aldrich) to obtain the corresponding methyl esters. The mixture was placed in a water bath at 55°C for 40 min. 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 methyl derivatives) was transferred to a clean 2 mL vial (Millex, Billerica, MA, USA) and then reduced in volume to 1 mL under ultra-pure nitrogen gas flow before analysis. The effluente and wash solutions were merged and concentrated by rotary evaporation under reduced pressure until nearly dry, then washed with 2 mL of dichloromethane, and then reduced to 1 mL under ultra-pure nitrogen before being analyzed.

2.3 GC-MS and GC-MS-MS analysis

The concentrated organic extracts were analyzed with an Agilent 6890N GC system (Agilent Technologies, Santa Clara, CA, USA) equipped with an Agilent 7683 autosampler, a Quattro Micro GC triple quadrupole mass spectrometer (Waters, Milford, MA, USA), and a SPBTM-1 fused silica capillary column (30 m long, 0.25 mm i.d., $0.25\text{ }\mu\text{m}$ film thickness; Supelco). Individual analytes were identified by comparing the mass spectra to the standard or searched by the National Institute of Standards and Technology (NIST08) reference library. A $1\text{ }\mu\text{L}$ sample was injected in splitless injection mode at 260°C . The GC-MS-MS system was operated in multiple reaction monitoring (MRM) mode using the parameters shown in Table 1. The collision gas was argon (99.995%), at 2.8×10^{-3} mbar. High-purity helium was used as the GC carrier gas at a flow rate of 1 mL min^{-1} . The column oven was programmed as follows: the initial temperature of the oven was set at 60°C , held for 1 min, increased at $9^{\circ}\text{C min}^{-1}$ to 160°C , held for 1 min, increased at $3^{\circ}\text{C min}^{-1}$ to 250°C , held for 1 min, increased at $15^{\circ}\text{C min}^{-1}$ to 280°C , and held for 1 min. The ion source and interface transfer line temperature were 230 and 270°C , respectively. The analytes were ionized by electron ionization (70 eV), and the emission current was $800\text{ }\mu\text{A}$. The trap current was 200 mA, the repeller was set at 7.2 V, and the multiplier was set at 650.

2.4 Method validation

To investigate the recoveries of analytes and the repeatabilities, 240 cm^2 quartz fibers were punched from one real fiber filter sample and divided into six equal pieces. The quantitative standard mixture was spiked into five of the six pieces, and then the samples were analyzed following the above-mentioned procedures. The methyl esters of n-alkanoic acid standard were used to determine the recoveries and to quantify both the n-alkanoic and branched-chain isomer acid and corresponding methyl esters. For 9-oxo-9H-fluorene-1-carboxylic acid, 9-Hydroxy-9-fluorene carboxylic acid methyl ester was used. Hexamethylbenzene/hexane ($50\text{ }\mu\text{L}$, $1.0\text{ ng }\mu\text{L}^{-1}$; Sigma-Aldrich) was used as an internal standard to correct losses due to evaporation and variations in injection volume before each GC injection. The recoveries of organic acids were determined by comparing the whole peak areas of the eluate (after derivatized) with the peak areas from corresponding standard mixtures, and the recoveries of fatty acid methyl esters (FAMES) were determined by comparing the peak areas of the combined effluente and washing solvent (without derivatization) with the corresponding standard mixtures. The recoveries and relative standard deviations (RSD) of analytes are given in Table 1 and 2.

The limits of detection (LODs) were calculated based on a signal-to-noise ratio of 3 ($S/N = 3$) by analyzing a series of

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

| Acids | MW ^a | RT ^b (min) | SIM (derivatization <i>m/z</i>) | Recovery (%) | RSD % (<i>n</i> = 5) | 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 | 97.2 | 3.7 | 0.61 | 24.2 | 6.1–58.5 |
| Nonanoic (C9 : 0) | 158 | 8.60 | 143/141/129/87/74 | 88.4 | 8.4 | 1.96 | 17.6 | 6.0–45.8 |
| Decanoic (C10 : 0) | 172 | 10.14 | 186/155/143/87/74 | 96.6 | 3.9 | 0.46 | 12.8 | 6.8–22.7 |
| Undecanoic (C11 : 0) | 186 | 11.60 | 200/169/157/143/87/74 | 88.5 | 7.2 | 1.27 | 12.6 | 7.1–23.5 |
| 11-Dodecanoic (C12 : 1) | 198 | 11.79 | 212/196/166/124/77/55 | 72.5 | 9.1 | 0.54 | 16.3 | 6.6–41.0 |
| Dodecanoic (C12 : 0) | 200 | 13.10 | 214/183/171/143/87/74 | 92.4 | 6.4 | 0.77 | 41.4 | 9.4–99.6 |
| Tridecanoic (C13 : 0) | 214 | 14.93 | 228/197/185/143/87/74 | 91.2 | 8.7 | 0.24 | 22.9 | 8.1–53.3 |
| Tetradecanoic (C14 : 0) | 228 | 17.00 | 242/211/199/143/87/74 | 101.3 | 4.2 | 0.38 | 182.1 | 15.0–937.1 |
| 13-Methyltetradecanoic | 242 | 18.49 | 256/225/213/143/87/74 | 89.6 | 9.2 | 0.60 | 12.0 | 7.56–22.3 |
| 12-Methyltetradecanoic | 242 | 18.69 | 256/225/213/143/87/74 | 89.6 | 9.2 | 0.60 | 13.5 | 7.7–25.2 |
| Pentadecanoic (C15 : 0) | 242 | 19.32 | 256/225/213/143/87/74 | 89.6 | 9.2 | 0.60 | 59.7 | 8.2–154.2 |
| Palmitoleic (C16 : 1) | 254 | 20.39 | 268/236/194/152/87/74 | 78.4 | 10.4 | 0.56 | 22.8 | 8.8–54.3 |
| 14-Methylpentadecanoic | 256 | 20.99 | 270/239/227/143/87/74 | 102.4 | 4.2 | 0.25 | 12.7 | 8.9–22.1 |
| Palmitic (C16 : 0) | 256 | 22.02 | 270/239/227/143/87/74 | 102.4 | 4.2 | 0.25 | 742.6 | 123.7–1487.4 |
| 15-Methylhexadecanoic | 270 | 23.66 | 284/253/241/143/87/74 | 88.4 | 6.5 | 0.16 | 15.5 | 10.3–28.0 |
| 14-Methylhexadecanoic | 270 | 23.88 | 284/253/241/143/87/74 | 88.4 | 6.5 | 0.16 | 22.8 | 10.9–46.5 |
| Heptadecanoic (C17 : 0) | 270 | 24.70 | 284/253/241/143/87/74 | 88.4 | 6.5 | 0.16 | 86.4 | 17.9–236.3 |
| Linoleic (C18 : 2) | 294 | 26.51 | 294/263/95/81/67/55 | 77.1 | 7.6 | 0.18 | 118.4 | 12.7–328.0 |
| Oleic (C18 : 1) | 296 | 26.68 | 296/264/222/191/69/55 | 90.2 | 7.1 | 0.22 | 74.7 | 10.7–208.6 |
| Stearic (C18 : 0) | 284 | 27.43 | 298/255/199/143/87/74 | 94.9 | 4.9 | 0.14 | 1490.5 | 269.8–3268.3 |
| Nonadecanoic (C19 : 0) | 298 | 30.13 | 312/281/269/143/87/74 | 87.7 | 7.3 | 0.29 | 34.9 | 10.8–90.3 |
| 11-Eicosenoic (C20 : 1) | 324 | 32.06 | 324/292/250/67/55 | 79.9 | 9.2 | 0.37 | 22.5 | 10.6–142.1 |
| 10-Oxo-octadecanoic | 312 | 32.13 | 281/214/156/55 | 78.9 | 7.7 | 0.18 | 24.5 | 16.8–49.5 |
| Eicosanoic (C20 : 0) | 312 | 32.82 | 326/295/283/143/87/74 | 94.2 | 5.3 | 0.26 | 130.9 | 24.6–370.1 |
| Henicosanoic (C21 : 0) | 326 | 35.44 | 340/297/241/143/87/74 | 90.7 | 8.1 | 0.36 | 80.9 | 14.2–239.3 |
| Docosanoic (C22 : 0) | 340 | 37.99 | 354/311/255/143/87/74 | 93.5 | 4.6 | 0.17 | 196.2 | 17.2–626.3 |
| Tricosanoic (C23 : 0) | 354 | 40.43 | 368/325/269/143/87/74 | 90.4 | 5.9 | 0.27 | 114.6 | 16.1–380.6 |
| Tetracosanoic (C24 : 0) | 368 | 42.86 | 382/339/199/143/87/74 | 92.7 | 3.3 | 0.19 | 322.5 | 19.2–1080.3 |
| Pentadecanoic (C25 : 0) | 382 | 45.10 | 396/353/297/143/87/74 | 91.4 | 9.0 | 0.34 | 74.7 | 15.6–244.2 |
| Hexacosanoic (C26 : 0) | 396 | 46.51 | 410/367/311/143/87/74 | 87.6 | 8.1 | 0.34 | 252.4 | 17.5–858.5 |
| Heptacosanoic (C27 : 0) | 410 | 47.92 | 424/381/355/143/87/74 | 88.4 | 8.3 | 0.41 | 46.6 | 22.4–129.3 |
| Octacosanoic (C28 : 0) | 424 | 49.50 | 438/395/199/143/87/74 | 84.0 | 9.1 | 0.46 | 143.2 | 15.1–538.2 |
| Nonacosanoic (C29 : 0) | 438 | 51.47 | 452/423/199/143/87/74 | 76.5 | 10.2 | 0.51 | 23.0 | 13.5–56.2 |
| Triacosanoic (C30 : 0) | 452 | 53.74 | 466/437/199/143/87/74 | 72.4 | 10.9 | 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 | 0.77 | 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 triacosanoate | 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 AMAs, dimethyl phthalate, and the concentrations found in samples collected in January 2013, Beijing.

| Acids | MW ^a | RT ^b (min) | SIM (derivatization <i>m/z</i>) | Recovery (%) | RSD % (<i>n</i> = 5) | MDL ^c ng μL ⁻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 | 7.6 | 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 |

standard mixtures. The liquid-phase LODs were transformed into the corresponding atmospheric method detection limit (MDL) of the compounds. The MDL as atmospheric concentration furthermore depends on the sampling rate of the filter sampler (1.13 m³ min⁻¹), the sampling time (24 h), the extracted filter area (40 cm²), and the solvent volume for filter extraction (60 mL), for elution (2 mL), and for injection (1 mL). These sampling and sample preparation conditions result in a theoretical sampled air volume of 130.17 m³ being enriched, and the enrichment factor was 30 in each concentrated SPE extract. The LODs (ng μL⁻¹) in solvent were translated to MDL in air concentrations by multiplying 7.68 [= (LOD × concentrated sample solution volume)/sampled air volume]. Seven blank filters were spiked, extracted, and analyzed to monitor the extraction procedures and detect possible contamination. The few significant contaminants identified via GC-MS as solvent byproducts were excluded from the data set.

3 Results and discussion

3.1 Efficiency of SPE

The extraction efficiency of SPE, expressed as percentage recovery, was calculated as ratio of the concentration obtained by subtracting the measured quantity before adding standard from after adding standard to the theoretical adding standard. The results are shown in Table 1 for DCAs, MCAs, and FAMES and in Table 2 for AMAs. Extraction efficiencies for DCAs ranged from 80.3 to 93.5 %, for MCAs ranged from 72.4 to 102.4 %, and for FAMES ranged from 73.6 to

111.3 %. The results were similar with the DCM/menthol extract of organic acids (70–110 %) by ultrasonic without SPE (Huang et al., 2006; He et al., 2006) and hexane/DCM extract of organic acids (75–96 %) by ultrasonic and silica-based or silica mixed alumina SPE (Duan, 2006; Hou et al., 2006), which suggested the adsorption properties were suitable for the extract of organic acids from methyl esters. Method precisions, expressed as the RSD, were calculated across replicate measurements (*n* = 5). As can be seen from Tables 1 and 2, the RSD of DCAs ranged from 0.7 to 6.2 %, MCAs ranged from 3.3 to 10.9 %, FAMES ranged from 2.2 to 9.2 %, and AMAs ranged from 2.7 to 7.6 %, the repeatability values of which we considered to be acceptable.

Adsorption-type SPE, such as silica-based materials, should be preferred for concentration of organic acids in organic matrices but provides little cleanup efficiency of polar functionalized acids, which are likely to be produced in oxidation reactions in the atmosphere. One advantage capacity of anion-exchange SPE was the cleanup efficiency of organic acids from acetonitrile matrices. Although the fatty acids could be separated from their corresponding methyl esters through butyl and TMS derivatization instead of methylation, the low volatility makes the detection by GC of long-chain products difficult. To improve the sensitivities, the extraction efficiency of the SAX and NH₂ SPE cartridges for organic acids were investigated with 1 January 2013 provided as an example. Results for the extraction of analytes (DCAs, MCAs, and AMAs in eluate and FAMES in effluete) are shown in Fig. 1. The total concentrations with the NH₂ 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 con-

trasted with 320 ng m⁻³ for eight DCAs, 160 ng m⁻³ for 13 AMAs, and 3950 ng m⁻³ for 32 MCAs with the SAX cartridge, which indicated that the NH₂ SPE cartridge gave higher extraction efficiency than the SAX cartridge.

Nevertheless, of the two silica-based anion-exchange materials, NH₂ SPE gave higher extraction efficiencies to organic acids with long hydrophobic alkyl chain and polycyclic compounds, especially the C₁₄–C₃₀ MCAs, 1,8-naphthalic anhydride, 4-(ethoxycarbonyl)benzoic, 2-naphthoic, phenanthrene-1-carboxylic, and undecanedioic acid. In addition, NH₂ and SAX extracted equal amount of 17 FAMES (251 and 256 ng m⁻³, respectively), which indicated that π – π interactions make an important contribution to the extraction. These results indicate that the active group bonded to the silica-based matrix in the SPE cartridge had a marked influence on the extraction efficiency of the analytes from the PM_{2.5}. The active quaternary amine groups based on the SAX cartridges might have exclusively electrostatic interactions with weak acids, which will lead some analytes to be retained by the cartridge rather than eluted. The aminopropyl active groups in the NH₂ cartridges offer only weakly selective retention. The results showed that the NH₂ cartridges were the most suitable for isolating organic acids but that the SAX cartridges were most suitable for purifying nonpolar compounds.

3.2 Identification of organic acids and FAMES

Chromatograms of the organic acids in a sample that had been pretreated with an NH₂ SPE cartridge are shown in Fig. 2. The GC-MS chromatogram (Fig. 2a) shows that the organic acids were isolated and concentrated from the extract and the polar and weakly polar compounds had been cleaned (meaning that the background noise level was low). 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 difficult to determine and increases the sensitivity of the method.

Even separated from the extracts, the signals of the trace multi-substituted AMAs and PAH acids were still under the LODs of GC-MS in SIM mode. The selectivity and sensitivity of the assay was improved by using GC-MS-MS in MRM mode, because only the daughter ions of the selected precursors were detected (Fig. 2b), decreasing the disturbances in the signals and improving the signal strengths.

3.3 Ambient concentrations of organic 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. Nonane-

dioic 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 alkanolic acids were strongly dominated by those with even numbers of carbon atoms, and the pattern reached a maximum at stearic acid (C_{18:0}), concentration ranged from 270 to 3268 ng m⁻³ (mean of 1491 ng m⁻³), followed by palmitic acid (C_{16:0}), ranged from 124 to 1487 ng m⁻³ (mean of 743 ng m⁻³). The C_{18:0} and C_{16:0} acids contributed 20–65 % (mean of 43 %) by mass of the quantified organic acids.

Seventeen FAMES in the combined effluate and washing solvent were measured, from which the acids had been removed by passing them through the SPE cartridges. Of those, methyl stearate had the highest concentrations, 19–332 ng m⁻³ (mean of 65 ng m⁻³), and contributed 2–23 % (mean of 6 %) of the total FAME. The next higher one was methyl palmitate, which ranged from 18 to 278 ng m⁻³ (mean of 63 ng m⁻³) and contributed 2–28 % (mean of 10 %) of the total FAME. 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 combined solution (effluate and washing solvent) are shown in Fig. 2d, the methyl palmitate represented 6 % of the palmitic acid, but the highest result can account for 13 % in this period.

Through SPE-GC-MS-MS method, we quantified 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 tested fine aerosol samples. Phenanthrene-1-carboxylic acid and 9-oxo-9H-fluorene-1-carboxylic acid were the most abundant of the PAH acids 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.

3.4 Correlations between FAME and n-alkanoic acid

The correlation coefficients between the C_{16:0}, C_{14:0}, and C_{18:0} acids, and the other C₁₃–C₃₀ n-alkanoic acids were significant ($R^2 > 0.88$, $p < 0.01$), which implied common primary sources from biomass burning, vehicular exhausts, cooking, and vegetation detritus (Simoneit, 1986; Rogge et al., 1991, 1993a, b; Schauer et al., 1999, 2001; Fraser et al., 2003; Hyder et al., 2012; Pietrogrande et al., 2014). The C_{18:0}/C_{16:0} ratio has been used as a qualitative tool for assessing organic acid sources (Ho et al., 2010), and we found C_{18:0}/C_{16:0} > 1 during our sampling period. Taking into

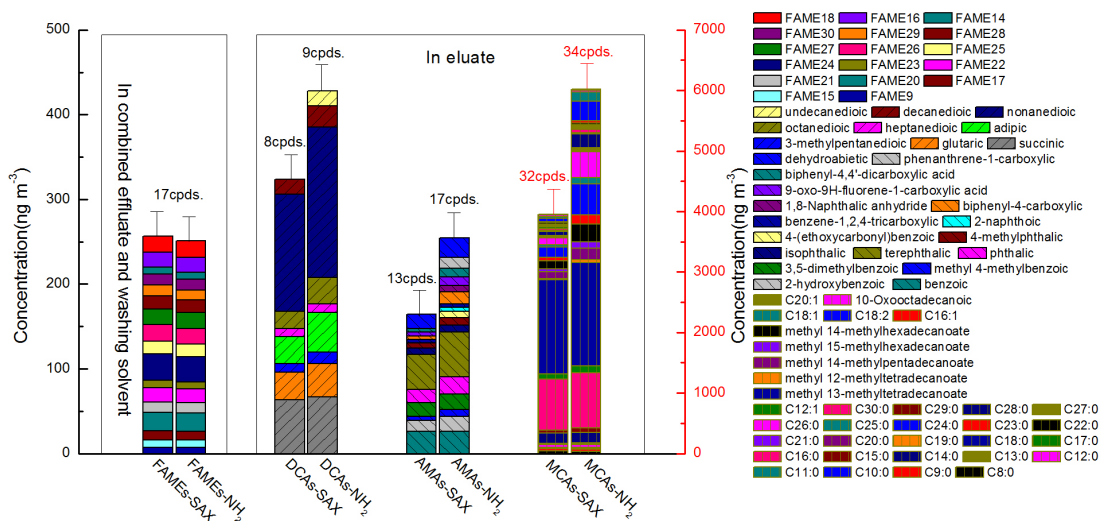


Figure 1. Concentrations of analytes found when an extract of PM_{2.5} collected on 1 January 2013 in Beijing was analyzed using the SAX and NH₂ SPE cartridges. The left-hand y axis (in black) is for the DCAs, AMAs, and fatty acid methyl esters. The right-hand y axis (in red) is for the MCAs. The T-shaped marks indicate the numbers of compounds (cpds.) that were found.

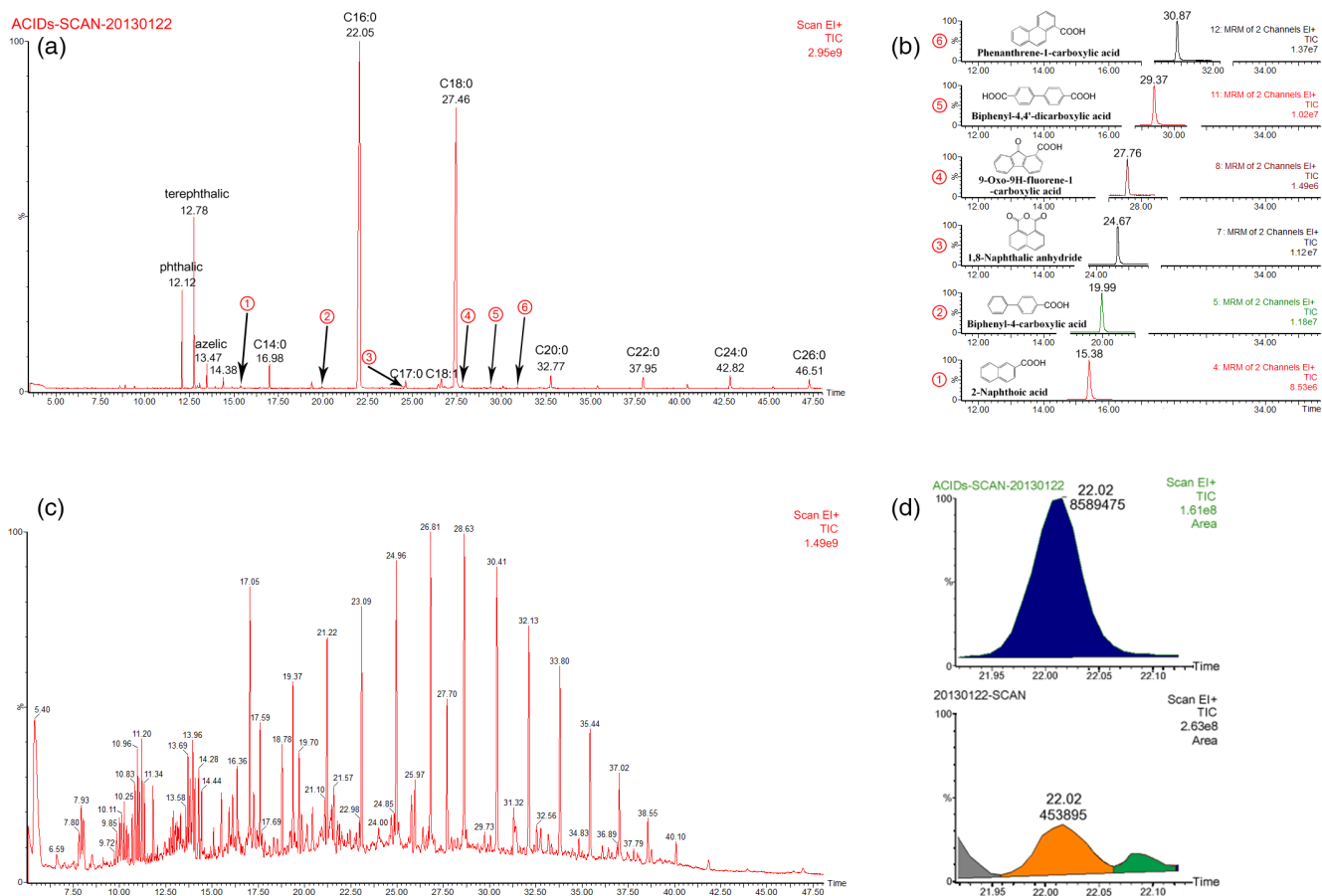


Figure 2. Chromatograms of the organic compounds of the PM_{2.5} sample collected on 22 January 2013 in Beijing after pretreatment using an NH₂-SPE cartridge. (a) GC-MS chromatograms of organic acids in SPE eluate. (b) GC-MS-MS chromatograms of PAH acids in SPE eluate. (c) GC-MS chromatogram of compounds from combined effluate and washing solution. (d) The integrated areas of palmitic acid in the eluate (top) and methyl hexadecanoate in the combined solution (bottom).

Table 3. Correlation matrix of C₄–C₁₁ DCAs and AMAs concentrations measured in January 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 | 0.57 | 0.42 | 0.23 | 0.41 | 0.25 | 0.18 | 0.36 | 0.22 | 0.44 | 0.46 | 0.36 | 0.50 | |
| AMA ⁿ | | | | | | | | | | | | | | 0.20 | 0.42 | 0.23 | 0.41 | 0.25 | 0.18 | 0.36 | 0.22 | 0.44 | 0.46 | 0.36 | 0.50 | |
| AMA ^o | | | | | | | | | | | | | | | 0.93 | 0.90 | 0.90 | 0.34 | 0.45 | 0.72 | 0.70 | 0.66 | 0.44 | 0.18 | | |
| 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 | | | | | | | | | | | | | | | | | | | | | | | | 0.61 | 0.63 | |
| AMA ^y | | | | | | | | | | | | | | | | | | | | | | | | | 0.79 | |
| AMA ^z | | | | | | | | | | | | | | | | | | | | | | | | | | 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-hydroxybenzoic 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 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.

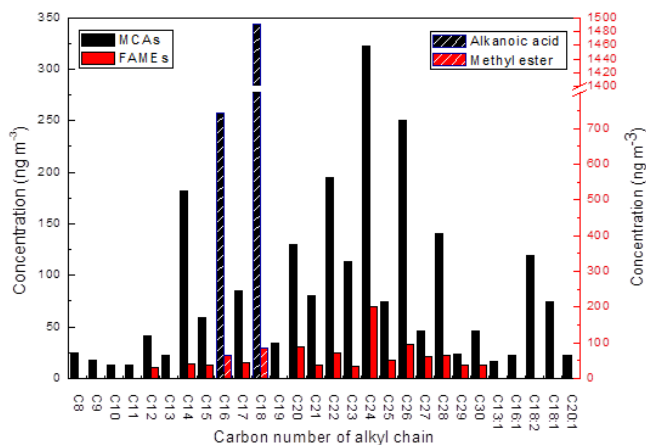


Figure 3. Mean monocarboxylic acids (MCAs) and fatty acid methyl esters (FAMEs) concentrations in PM_{2.5} samples collected in January 2013 in Beijing.

account a recent study of organic acids (Zhao et al., 2014), we suggest the strong contribution from cooking and vehicular emissions in Beijing in January 2013. Concentrations of high molecular-weight n-alkanoic acids ($\geq C_{20}$) are high in this period, which suggested the release of plant waxes from dead leaves and wind abrasion of other sources (Simoneit et al., 1981, 2004; Rogge et al., 1993b; Guo et al., 2003; Kawamura and Yasui, 2005; Feng et al., 2006).

Like n-alkanoic acids, the methyl esters of the C₂₀–C₃₀ waxy acids also have even carbon preference. The pattern had a maximum at methyl lignocerate (C₂₄), with concentrations ranging from 26 to 148 ng m⁻³ (mean of 70 ng m⁻³), followed by 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 also could not be measured by GC-MS-MS-MRM because of their low molecular-ion signal strengths. The correlations between C₁₄, C₁₆, and C₁₈ methyl esters and among the other C₁₃–C₃₀ methyl esters were high ($R^2 > 0.85$), which was quite similar to the fatty acids. From the above information and the molecular structures, we suggest that FAMEs could 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 have been avoided by the use of the NH₂ SPE technique, like fatty acids separated from their corresponding methyl esters.

3.5 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 ($r^2 > 0.85$, $p < 0.01$). The di-C₄–C₅ DCAs (succinic, glutaric, and 3-methylpentanedioic acids) were strongly

correlated with phthalic, 4-methylphthalic, benzene-1,2,4-tricarboxylic acids, and 1,8-naphthalic anhydride, and the newly identified 9-oxo-9H-fluorene-1-carboxylic and 2-naphthoic acids. Previous studies have suggested that C₄–C₅ DCAs are mainly secondary products of volatile organic compound precursors (Kawamura and Kaplan, 1987; Kawamura and Kasukabe, 1996; Graham et al., 2002; Claeys, et al., 2004; Ervens et al., 2004; Gelencsér, 2004; Kanakidou et al., 2005; Kawamura and Yasui, 2005; Oliveira et al., 2007). Phthalic acid has been proposed as a surrogate for the contribution of secondary organic aerosols (Fine et al., 2002; Ho et al., 2010), since it mainly derives from the oxidation of PAHs (e.g., naphthalene) or phthalates in vehicular exhaust and biomass burning (Guillard et al., 1993; Kawamura and Ikushima, 1993; Kawamura and Kaplan, 1987; Kawamura and Yasui, 2005). In light of the above-mentioned facts, we suggest that 9-oxo-9H-fluorene-1-carboxylic acid, 2-naphthoic acid, and 1,8-naphthalic anhydride are mainly secondary.

Phenanthrene-1-carboxylic acid correlated strongly with the di-C₇–C₁₁ acids terephthalic, isophthalic, 2-hydroxy-5-methylbenzoic, and 4-(ethoxycarbonyl) benzoic. Among these acids, terephthalic acid and isophthalic acid 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), which indicated phenanthrene-1-carboxylic acid was primary during January.

The correlation between biphenyl-4-carboxylic acid and benzoic acid (0.73) is higher than for other acids. Benzoic acid may be primary from vehicular exhausts (Kawamura and Kaplan, 1987; Rogge et al., 1993a) 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 (Slesi 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 is mainly primary.

4 Summary (for January 2013, Beijing)

Organic acids (alkanoic acids, alkenoic acids, and AMAs) and FAMEs were identified and measured with NH₂-SPE pretreatment and GC-MS and GC-MS-MS, they contributed strongly PM_{2.5} in January 2013 at Beijing. Seventeen FAMEs were separated from their corresponding n-alkanoic

acids and the interference of FAMES on the corresponding fatty acids was eliminated by using the NH₂-SPE cartridge. Taking into account the large amounts and possible formation mechanism of FAMES, this procedure is of potential use for determining the relative importance of primary emissions and secondary processes of organic acid esters that are found in typical winter haze episodes in Beijing.

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. Five PAH acids and 1,8-naphthalic anhydride were identified and measured in PM_{2.5}. The correlations between DCA and AMA tracers suggested that 2-naphthoic, biphenyl-4-carboxylic, and 9-oxo-9H-fluorene-1-carboxylic acid plus 1,8-naphthalic anhydride were mainly secondary products of photochemical degradation during January 2013. Phenanthrene-1-carboxylic acid could be primary from fossil fuel emission. Biphenyl-4,4'-dicarboxylic could be primary from coal burning. The C_{18:0}/C_{16:0} 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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