

Application of 2D-GCMS reveals many industrial chemicals in airborne particulate matter

Mohammed S. Alam^a, Charles E. West^b, Alan G. Scarlett^b, Steven J. Rowland^b, Roy M. Harrison^{a,*}

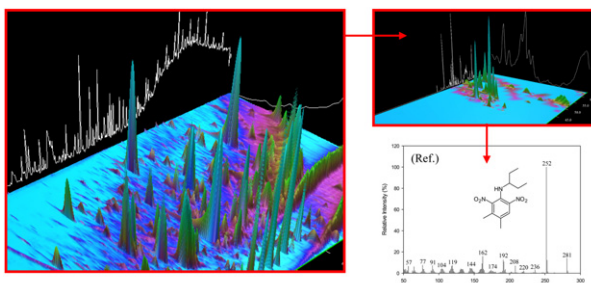
^a Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

^b School of Geography, Earth & Environmental Sciences, University of Plymouth, Plymouth, Devon PL4 8AA, United Kingdom

HIGHLIGHTS

- ▶ Daily PM_{2.5} samples were collected at an urban background site.
- ▶ Aerosol samples were analysed using GC × GC-TOFMS.
- ▶ Results reveal a remarkable range of compounds present, where 1500 peaks are detected.
- ▶ We identify natural and industrial chemicals that have not been focused on previously.
- ▶ Some of the detected compounds may contribute to the toxicity of urban particulate matter.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 July 2012

Received in revised form

5 October 2012

Accepted 8 October 2012

Keywords:

2D GCMS

Airborne chemicals

Industrial chemicals

Plasticisers

Fire retardants

ABSTRACT

Samples of airborne particulate matter (PM_{2.5}) have been collected in Birmingham, UK and extracted with dichloromethane prior to analysis by two-dimensional GC separation and TOFMS analysis. Identification of compounds using the NIST spectral library has revealed a remarkable diversity of compounds, some of which have not been previously reported in airborne analyses. Groups of compounds identified in this study include a large number of oxygenated VOC including linear and branched compounds, substituted aromatic compounds and alicyclic compounds, oxygenated polycyclic aromatic and alicyclic compounds, organic nitrogen compounds, branched chain VOC and substituted aromatic VOC, phthalates, organo-phosphates and organo-sulphate compounds. Many of the compounds identified are mass production chemicals, which due to their semi-volatility enter the atmosphere and subsequently partition onto pre-existing aerosol. Their contribution to the toxicity of airborne particulate matter is currently unknown but might be significant. The diverse industrial uses and potential sources of the identified compounds are reported.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Atmospheric aerosol particles are complex mixtures of nonvolatile and semi-volatile inorganic and organic compounds, directly released from a variety of sources, including vehicle emissions, combustion and vegetation, and may also be formed as products of gas to particle conversion through atmospheric reactions. These atmospheric aerosols affect the global radiation balance both

* Corresponding author. Present address: Department of Environmental Sciences/Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah 21589, Saudi Arabia. Tel.: +44 121 414 3494; fax: +44 121 414 3709.

E-mail address: r.m.harrison@bham.ac.uk (R.M. Harrison).

directly and indirectly, by absorbing and scattering solar radiation, and by acting as cloud condensation nuclei, respectively. The determination of aerosol particle composition is therefore of significant interest owing to the potential impacts upon climate and human health (Zhang et al., 2012; Harrison and Yin, 2000).

Since a substantial fraction of atmospheric aerosol consists of thousands of organic compounds with a broad range of solubilities, reactivities and physical properties, identification of these species remains a challenge, with many compounds remaining unidentified (Goldstein and Galbally, 2007). Added complexities to the analyses of these aerosols are the trace-level concentrations of organics and difficulties in sampling. The majority of studies have collected aerosol samples onto filters, where the compounds of interest are removed by solvent extraction or thermal desorption, followed by analysis with gas chromatography coupled to mass spectrometry (GC–MS) (Tomashuk et al., 2012; Yin et al., 2010; Harrison and Yin, 2010). However, owing to the large variety of compounds present in samples, conventional GC often proves inadequate for the separation of components, thus leading to severe peak co-elutions and poor chromatography resulting from insufficient resolving power.

Some studies have made extensive use of one-dimensional GC–MS together with selective extractions and derivatisation procedures to identify large numbers of compounds in airborne particulate matter. These include Pio et al. (2001) who identified around 400 individual organic compounds in particulate matter from a Portuguese rural area. By specifically targeting homologous series and functional groups, they were able to identify aliphatics, polycyclic aromatic hydrocarbons (PAHs), oxy-PAH, ketones, aldehydes, alcohols, *n*-alkanoic acids, *n*-alkenoic acids, aliphatic dicarboxylic acids, terpenic constituents and some VOC oxidation products. In a study of particulate matter sampled in Kuala Lumpur, Malaysia, Omar et al. (2007) reported concentrations of PAH (14 compounds), petroleum molecular markers (4), *n*-alkanols (7), triterpenols (6), *n*-alkanoic acids (7), soil and biomass burning carbohydrates (10), sterols (5), products of plastics combustion (3), *n*-alkanoic acids from cooking (4) and mono and diacylglycerols (3). In all, within samples from the urban area, the specific compounds analysed accounted for 5.3 $\mu\text{g m}^{-3}$ out of a total solvent extractable organic matter concentration of 18.1 $\mu\text{g m}^{-3}$.

Recent advances in comprehensive two-dimensional gas chromatography (GC \times GC) have led to its successful application in measuring a wide range of volatile and semi-volatile organic compounds in air (Adachchour et al., 2008; Laitinen et al., 2010; Arsene et al., 2011). For example, the unresolved complex mixture (UCM) clear from the white line in Fig. 1(A) in a traditional 1D GCMS separation typically makes up about 95% of the area of the chromatogram and is usually unresolved by analysis. 2D GCMS techniques provide an enormous advance in terms of resolving individual peaks but have yet to be exploited very fully in atmospheric analysis. Arsene et al. (2011) have recently reviewed the application of GC \times GC–MS hyphenated techniques for the analysis of volatile and semi-volatile compounds in air. They report only 12 published studies of atmospheric measurements, which are focussed largely on lower molecular mass species (less than C_{12}), oxygenates, or forest atmospheres. The studies demonstrate applicability to alkanes up to C_{30} (Laitinen et al., 2010) and roadside nanoparticles (Ochiai et al., 2007).

GC \times GC was first exploited in atmospheric analysis by Lewis et al. (2000), who isolated and classified more than 500 VOCs in urban air. This powerful technique has since been combined with flame ionisation detection (FID) and with time of flight mass spectrometry (TOFMS) in several studies (Pratt and Prather, 2012). For example, Xu et al. (2003a,b) utilised GC \times GC–TOFMS to measure C_7 – C_{11} aromatic and *n*-alkane hydrocarbons in air,

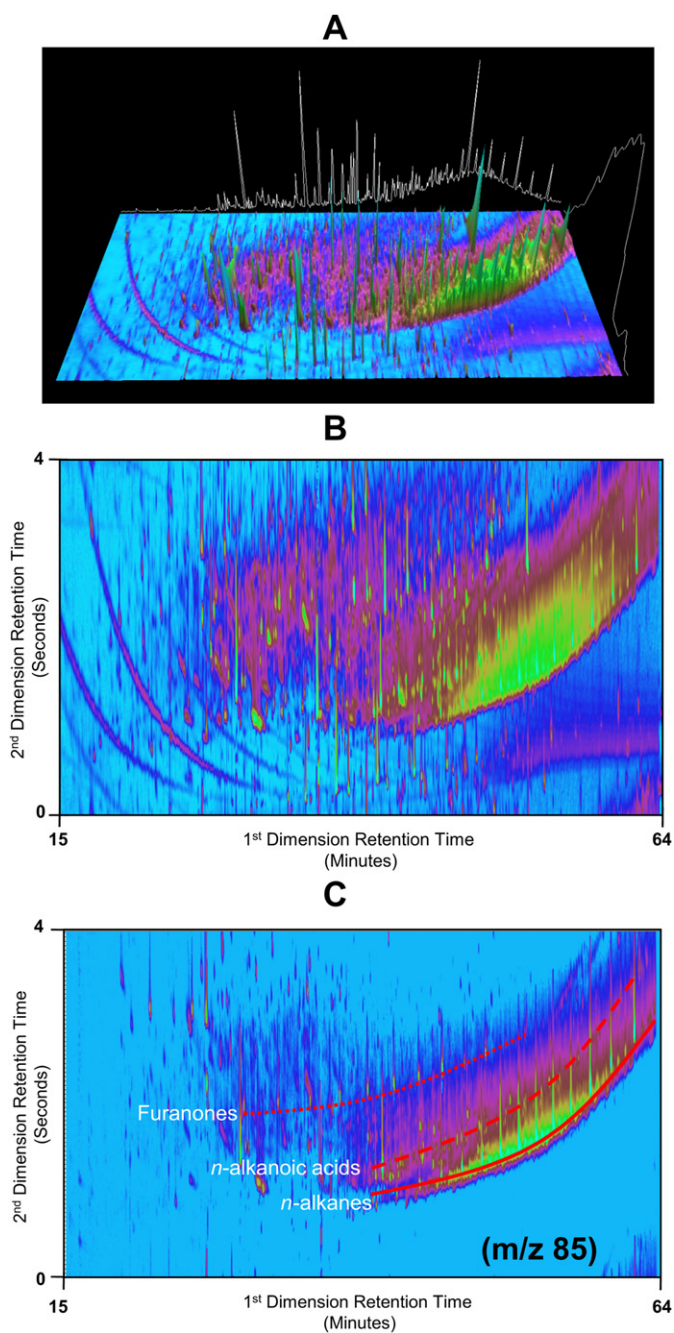


Fig. 1. (A) Total ion current chromatogram of an urban aerosol sample (Birmingham, UK) examined by GC \times GC–TOFMS illustrating improved chromatographic resolution by GC \times GC compared with GC/MS (white line on background). (B) Contour plot of total ion current chromatogram of an urban aerosol sample examined by GC \times GC–TOFMS. Colours indicate the intensities of the response (green > yellow > pink). (C) Example selected ion chromatogram (m/z 85, *n*-alkane fragment). Red lines signify the ordered appearance of compounds with similar physicochemical properties. Solid line – *n*-alkanes, dashed line – *n*-alkanoic acids, dotted line – furanones with varying alkyl chain length. Sample taken 09-02-11.

isolating approximately 650 individual peaks of which 235 were identified using published retention indices. Lee et al. (2006) exploited the use of GC \times GC–FID to study VOC ratios of high molecular mass aromatics which could not be speciated using conventional GC–MS. Welthagen et al. (2003) and Hamilton et al. (2004) used direct thermal desorption GC \times GC–TOFMS for the characterisation of semi-volatile organic compounds in $\text{PM}_{2.5}$

detecting (but not identifying) 15,000 and 10,000 peaks, respectively. Of these 10,000 peaks, Hamilton et al. (2004) report the positive identification of 130 OVOCs, where a further 100 oxygenated species were observed but not positively identified owing to the lack of mass spectral library or pure components. Williams et al. (2010) reported the first hourly in-situ measurements of speciated organic aerosol composition in an urban environment, where approximately 300 nonvolatile and semi-volatile organic compounds were identified using thermal desorption. More recently, this technique was further improved by coupling GC × GC to thermal desorption aerosol gas chromatography and has been deployed in both chamber studies investigating the photo-oxidation of diesel exhaust (Isaacman et al., 2011) and field studies (Worton et al., 2012), allowing real time measurements of a diverse range of compound classes.

2D GC–MS has extended knowledge of organic compounds present in the atmosphere particularly in the directions of organo-nitrogen compounds and oxidised compounds. However, the knowledge that thousands of VOC and SVOC compounds exist in samples that are collected from various studies and are yet to be identified and routinely measured, provides motivation for this study. GC × GC–TOFMS was applied to identify organic compounds in atmospheric aerosol collected in Birmingham, UK. In this study, we have not reported groups of compounds such as n-alkanes and PAH which have been widely reported before, but have focussed particularly on compound types which have rarely, if ever, been previously reported in the atmosphere by selecting peaks for characterisation which were not part of the main homologous series identifiable from the chromatograms.

2. Experimental

2.1. Site location

Samples of airborne fine particulate matter (PM_{2.5}) were collected at the Elms Road Observatory Site (EROS, 1.93°W; 52.45°N). EROS is an urban background site within the University of Birmingham campus. The site is approximately 3.5 km southwest of Birmingham city centre and is subject to anthropogenic emissions from a nearby railway, some moderately busy roads and surrounding activities from local residents.

2.2. Sampling

Daily PM_{2.5} samples were collected for 5 days (9–14 February 2011) using a high volume air sampler TE-6070 (Tisch Environmental, Inc). The high volume sampler involves drawing large volumes of air (800–1000 m³) through a 20 × 25 cm quartz fibre filter (QMA) substrate. Filters were pre-heated at 550 °C for 12 h and stored in a freezer prior to sampling. After exposure the filters were enclosed with clean pre-heated foil and stored in an air tight metal box under conditions of approximately –18 °C prior to analysis. No attempt was made to evaluate or correct for sampling artefacts, which can be both positive (adsorption of vapour to the filter or collected particles) or negative (loss by volatilisation).

2.3. Extraction and analysis

Whole quartz fibre filters were extracted with two 30 ml aliquots of DCM (HPLC grade) and methanol (HPLC grade) sequentially. The extracts were combined, filtered and concentrated using a turbo evaporator and then blown down under a gentle nitrogen flow to a final volume of 250 μL. Comprehensive two-dimensional gas chromatography/time of flight mass spectrometry (GC × GC–TOFMS) was utilised to analyse the sample

extracts with conditions similar to that reported by Rowland et al. (2012). Briefly, analyses were conducted using an Agilent 7890A gas chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with a Zoex ZX2 GC × GC cryogenic modulator (Houston, TX, USA) interfaced with a Almsco BenchToFdx™ time of flight mass spectrometer (Almsco International, Llantrisant, UK) operated in positive ion electron ionisation mode and calibrated with per-fluorotributylamine. The scan speed was 50 Hz. The first-dimension column was 50 m × 0.25 mm × 0.40 μm VF1-MS (Varian, Palo Alto, CA, USA). The second-dimension column was 2.5 m × 0.15 mm × 0.15 μm VF-17MS (Varian). 1 μL of sample was injected in a splitless mode at 280 °C. The initial temperature of the oven (60 °C) was held for 1 min and then increased at 5 °C min⁻¹–325 °C and held for 10 min. The modulation period was 4 s. The transfer line temperature was 280 °C and the ion source temperature was 300 °C. Helium was used as the carrier gas at a constant flow rate of 0.8 mL min⁻¹. Subsequent data processing was conducted using GC Image™ v2.1 (Zoex).

3. Results and discussion

Five high volume urban aerosol samples collected in Birmingham, on 9–14 February 2011 were analysed utilising GC × GC–TOFMS, to identify compounds within the collected samples. A typical two-dimensional separation and subsequent total ion count is presented in Fig. 1(B), where each coloured spot represents an individual compound with a corresponding full mass spectrum. The intense yellow spots are major peaks, while the magenta and dark blue spots are medium and small peaks, respectively. Compounds were separated on a volatility basis in the first dimension (X-axis) and polarity in the second (Y-axis). Approximately 1500 peaks were found in the two-dimensional chromatogram, using the blob detection routine performed by GC Image v2.1b3 (Zoex Corporation, Houston, US) software.

Peak identification was based on mass spectral data from the NIST library, where two match factors were used to assess the similarity between the library and measured mass spectra. These similarity factors were: (i) match factor (MF) – described how well the library equivalent matched the entire mass spectra of the selected chromatography peak, and (ii) reverse match factor (RMF) – described how well the explicit masses present in the library equivalent matched the masses measured for the selected peak. Positive identification was based on MF and RMF of above 750 and 800, respectively, consistent with previous studies (Dalluge et al., 2002; Ozel et al., 2009).

Although a large number of peaks were unidentifiable owing to insufficient data available in the mass spectral library, various compound groups including alkanes, alkenes, cycloalkanes, aldehydes, ketones, carboxylic acids and esters, PAHs, oxygenated-PAHs and substituted aromatics were positively identified. The ordered appearance of chemically related compounds in the GC × GC chromatogram enables further identification of species owing to the physicochemical similarities within compound classes and their steady changes with increasing chain length and/or molecular sizes. This allows the identification of unknown species without unique mass spectra, as demonstrated for the dihydro-furanone series by Hamilton et al. (2004) and amides by Ozel et al. (2009).

Further information regarding the identification of compound classes can be achieved by producing GC × GC contour plots for selected mass fragments. An example of a selected ion chromatogram is shown in Fig. 1(C), for *m/z* 85 (a branched alkane fragment), demonstrating the increased resolution and ordered appearance of chemically related compounds. Mass pattern selection rules were developed by Welthagen et al. (2003) in order to group peaks into distinct chemical classes, facilitating interpretation of the peaks

detected in PM_{2.5} samples. These selection rules provided an estimate for the identification of specific compound classes that have been extensively reported in earlier studies (see Welthagen et al. (2003) for ion abundance rules). Their retention time selection rules, however, were not absolute and therefore were not taken into consideration in this study.

Figs. 2–4 illustrate the positive identification of a range of compounds from both natural and industrial sources, based on the NIST spectral library match. The measured mass spectra demonstrate the excellent agreement between our spectra and the reference spectra contained within the NIST library. Example spectra for some naturally occurring compounds are illustrated in Fig. 2; these include three methyl esters emitted from pine resin and plants (Fig. 2A–F) and cis-pinonic acid (Fig. 2G and H), an atmospheric organic compound produced by the oxidation of terpenes (Li et al., 2010). The spectra contained within Fig. 3, demonstrate the positive identification of industrial chemicals used in PVC (Fig. 3A and B), other plastics (Fig. 3C–F) and nylon (Fig. 3G and H). Caprolactam (shown in Fig. 3G and H) was present in four out of five samples. Other industrial compounds identified are shown in Fig. 4, which include chemicals used in paper production (Fig. 4A and B), as non-ionic surfactants (Fig. 4C and D), as pesticides (Fig. 4E and F) and as flame retardants (Fig. 4G and H). All positively identified compounds were further confirmed by assessing the consistency between the two retention times measured within the five different samples.

In the ambient PM_{2.5} samples collected at Birmingham, UK, 100 out of the 1500 peaks detected were qualitatively identified, exclusive of *n*-alkanes (C₁₀–C₃₁), *n*-alkanals (C₁₈–C₂₉), *n*-alkanoic acids (C₅–C₂₅), furanones and polycyclic aromatic hydrocarbons (PAHs), all of which have been extensively reported in earlier studies. The compounds reported in this study were present in at least three of the five samples collected and have been split into five groups: (i) Oxygenated volatile organic compounds (OVOC), Table 1; (ii) Organic nitrogen compounds (ON), Table 2; (iii) Oxygenated polycyclic aromatic and alicyclic hydrocarbons, Table 3; (iv) other semi-volatile organic compounds (VOC), Table 4; and (v) Phthalates, organic phosphates and organic sulphates, Table 5. All compounds are reported with their corresponding retention times, MF, RMF and industrial use. The postulated industrial uses of the compounds listed in Tables 1–5 are not exclusive primary sources for each compound, as many of these compounds may also be products of secondary reactions in the atmosphere. For example 9,10-anthracenedione may be a primary component of vehicle emissions (Jakober et al., 2007) and is utilised in the production of dyes, paper and pesticides; but is also a product from the oxidation reaction of its parent PAH compound, anthracene, in the atmosphere. The industrial uses and potential sources of the identified compounds were gathered using internet search engines, emission databases and Wikipedia. Compounds for which little information was available in the literature were traced back to manufacturers to deduce potential industrial uses/sources.

As explained for 9,10-anthracenedione, a component of organic aerosol (OA) can have a direct source of emission and is then termed as primary organic aerosol (POA), or be formed via partitioning of oxidised gas phase species, when it is known as secondary organic aerosol (SOA). OA compounds therefore have a wide range of organic functionalities and volatilities, making it extremely difficult to distinguish between primary and secondary sources in PM samples, without the aid of source apportionment techniques such as chemical mass balance (Yin et al., 2010), principal component analysis (Mari et al., 2010) and/or positive matrix factorisation (Williams et al., 2010). Hamilton et al. (2004) identified 130 OVOC in urban aerosol using direct thermal desorption (DTD) coupled to GC × GC–TOFMS, based on retention behaviour and spectral matches. They collected their samples at both roadside

locations in London and on a rooftop close to Leeds city centre. Many of the carbonyl species observed in their study could be mechanistically linked to gas phase aromatic hydrocarbon oxidation, and hence could be secondary in nature. Many of the compounds detected by Hamilton et al. (2004) were not identified in the aerosol samples collected in this study, which may be due to differing sampling locations and local atmospheric composition. Roadside sampling sites include fresh gasoline and diesel vehicle emissions of VOCs, many of which may be oxidised rapidly, dependent upon gas-phase and heterogeneous reaction rates with respect to atmospheric oxidants (George and Abbatt, 2010). The majority of OVOCs observed in this study are widely used in industry (see Table 1), but may also be secondary in origin owing to long range transport and atmospheric processing. Of increasing interest is 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (see Fig. 3E and F), a degradation product of antioxidants used as additives for plastic materials and engine oils, which has recently been identified as a water contaminant due to leaching from water pipes. To date, however, its toxicity has not been assessed and may be of significance.

Twelve of the 16 priority PAHs, defined by the United States Environment Protection Agency (EPA), were observed in more than three of the samples. Four PAHs that were not identified in any of the samples were anthracene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and coronene. Although the absence of these PAHs may be due to them having lower emission rates relative to other PAHs, their fast conversion to PAH derivatives by atmospheric oxidants cannot be ruled out. The gas phase reaction rate constant of anthracene + OH is reported as approximately $1 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Goulay et al., 2005), which is found to be an order of magnitude slower than the more abundant PAH, phenanthrene. This relatively fast conversion of anthracene to its corresponding quinone compound may therefore partially explain the absence of anthracene and explain the presence of 9,10-anthracenedione in all samples, as well as primary emissions from vehicles and the production of dyes, paper and pesticides in the area. Recently, indeno(1,2,3-cd)pyrene, which is known as a relatively stable PAH, has been shown to undergo considerable degradation when exposed to atmospheric oxidants and was also not observed in any of the samples collected in this study (Ringuet et al., 2012). The compounds, [1R-(1 α ,4 α ,10 α)]-1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-1-phenanthrenecarboxylic acid, methyl ester (see Fig. 2A and B); 7-oxodehydroabietic acid, methyl ester (see Fig. 2C and D) and 16 β H-kauran-16-ol, however, are found naturally in the environment (see Table 2).

While there have been extensive studies of oxygenated organics in the atmosphere, relatively little attention has been given to organic nitrates, despite their environmental importance. A number of ON species have been listed by the EPA as hazardous air pollutants (e.g. nitro-PAHs), yet the lack of satisfactory methods for analysing ON compounds means that there is limited information in the literature. Although no nitro-PAHs were identified in this study, possibly owing to their low concentration in the samples, only a few ON compounds were identified in three or more samples (Table 3). Hexadecanamide was present in all samples, in agreement with the results of Ozel et al. (2009), who utilised direct thermal desorption (DTD) in combination with GC × GC–TOFMS to analyse ON compounds in urban aerosol samples from the same site. DTD permits the analysis of samples without any prior solvent extraction or sample preparation, where the samples are placed directly onto a desorption tube and subjected to controlled heating. The desorbed volatiles are then injected directly into the column. The authors reported between 17 and 57 ON compounds in any one sample, with the lowest being recorded during February. The modest number of ON compounds reported in Table 3 suggests that

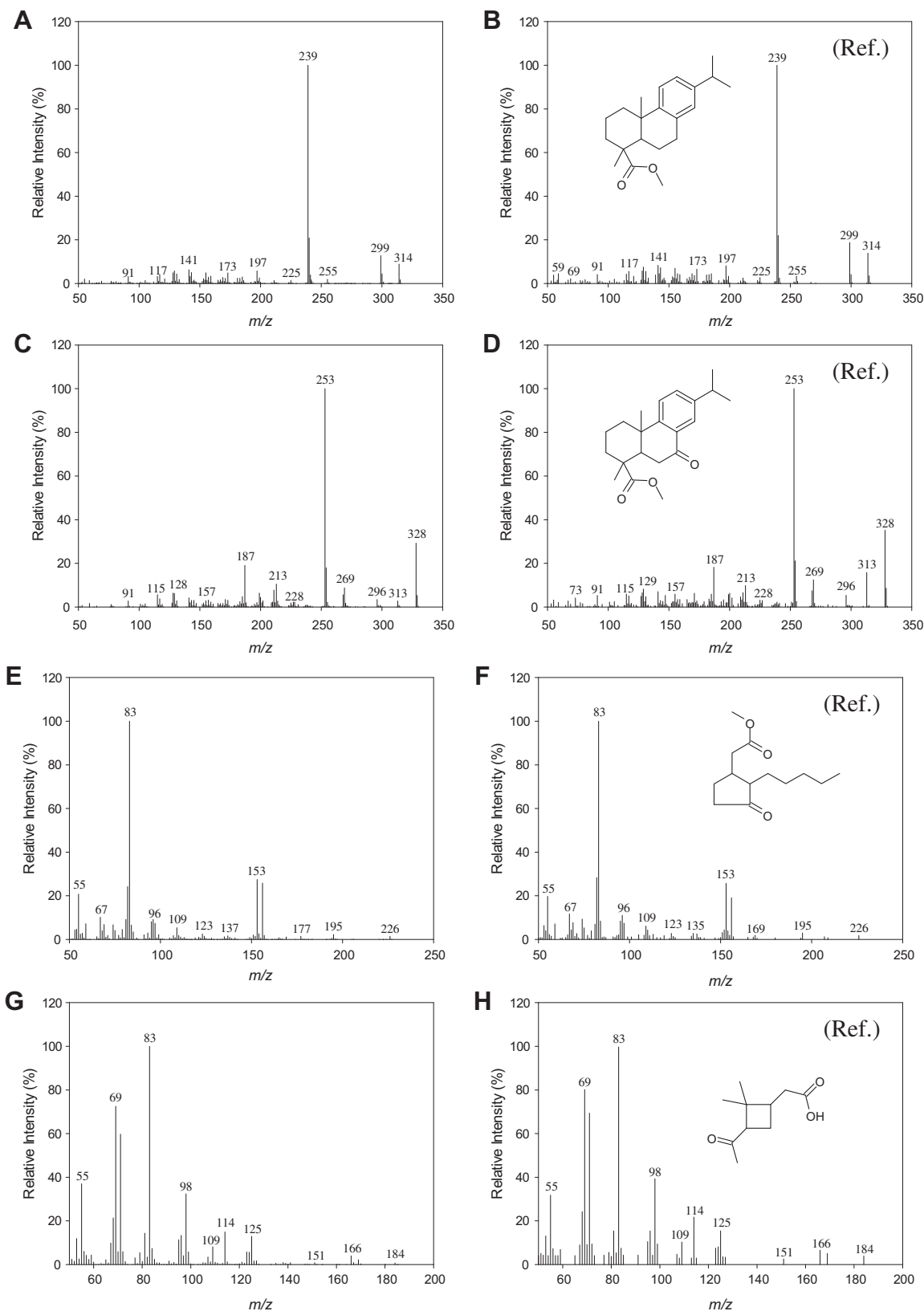


Fig. 2. Example mass spectra of naturally occurring compounds positively identified in urban aerosol samples (Birmingham, UK). Compounds (A) and (B) are compound and reference mass spectra for 1-phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1 α ,4 α β ,10 α)]); (C) and (D) are compound and reference mass spectra for 7-oxodehydroabietic acid, methyl ester; (E) and (F) are compound and reference mass spectra for cyclopentaneacetic acid, 3-oxo-2-pentyl-, methyl ester; and (G) and (H) are compound and reference mass spectra for cis-pinonic acid. (Reference spectra reproduced with permission from the National Institute of Standards & Technology spectral database ver. 2.0f Oct 8 2008).

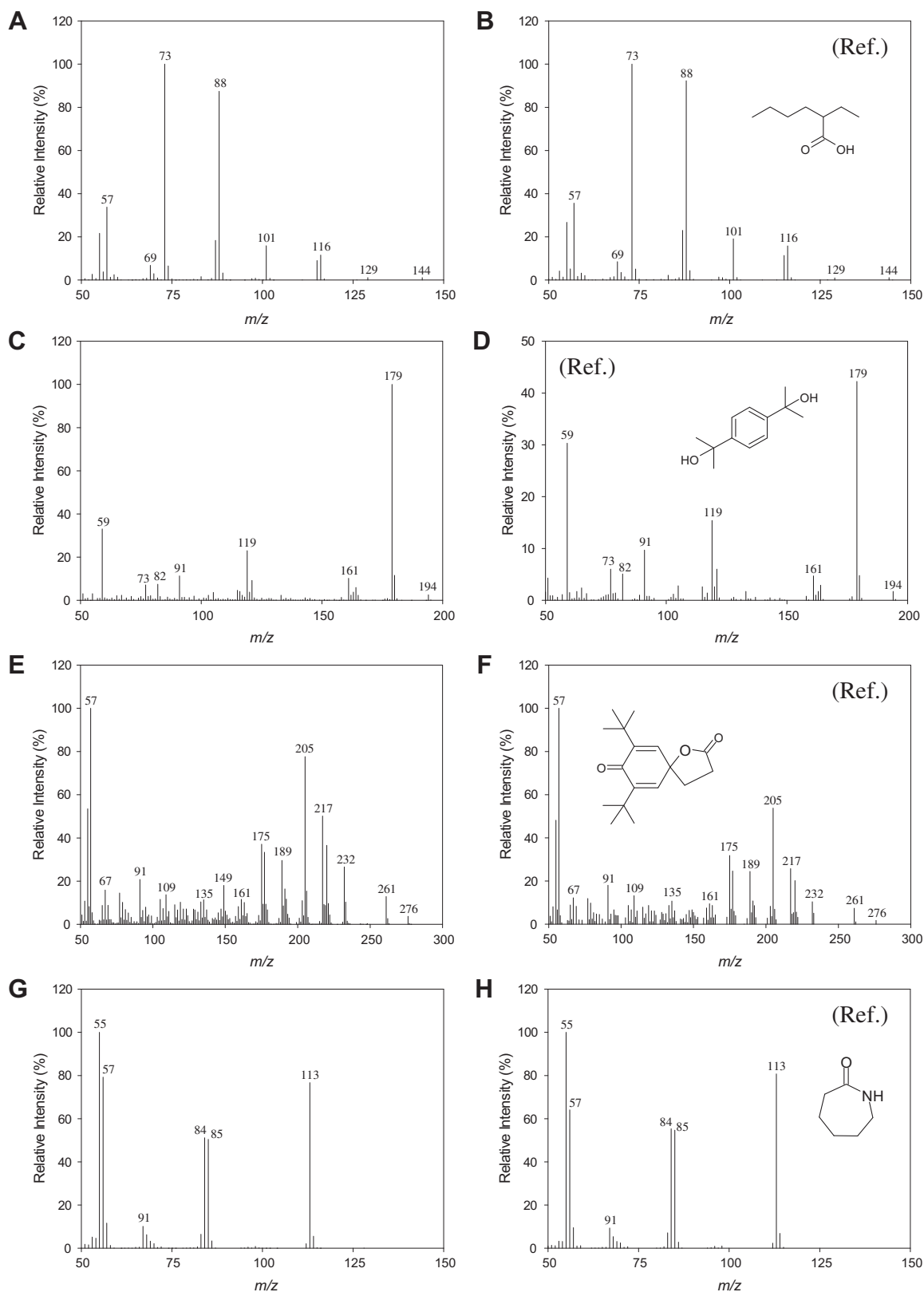


Fig. 3. Example mass spectra of industrial compounds emitted from plastics, rubber and PVC, positively identified in urban aerosol samples (Birmingham, UK). Compounds (A) and (B) are compound and reference mass spectra for hexanoic acid, 2-ethyl-; (C) and (D) are compound and reference mass spectra for $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,4-benzenedimethanol; (E) and (F) are compound and reference mass spectra for 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione; and (G) and (H) are compound and reference mass spectra for caprolactam. (Reference spectra reproduced with permission from the National Institute of Standards & Technology spectral database ver. 2.0f Oct 8 2008).

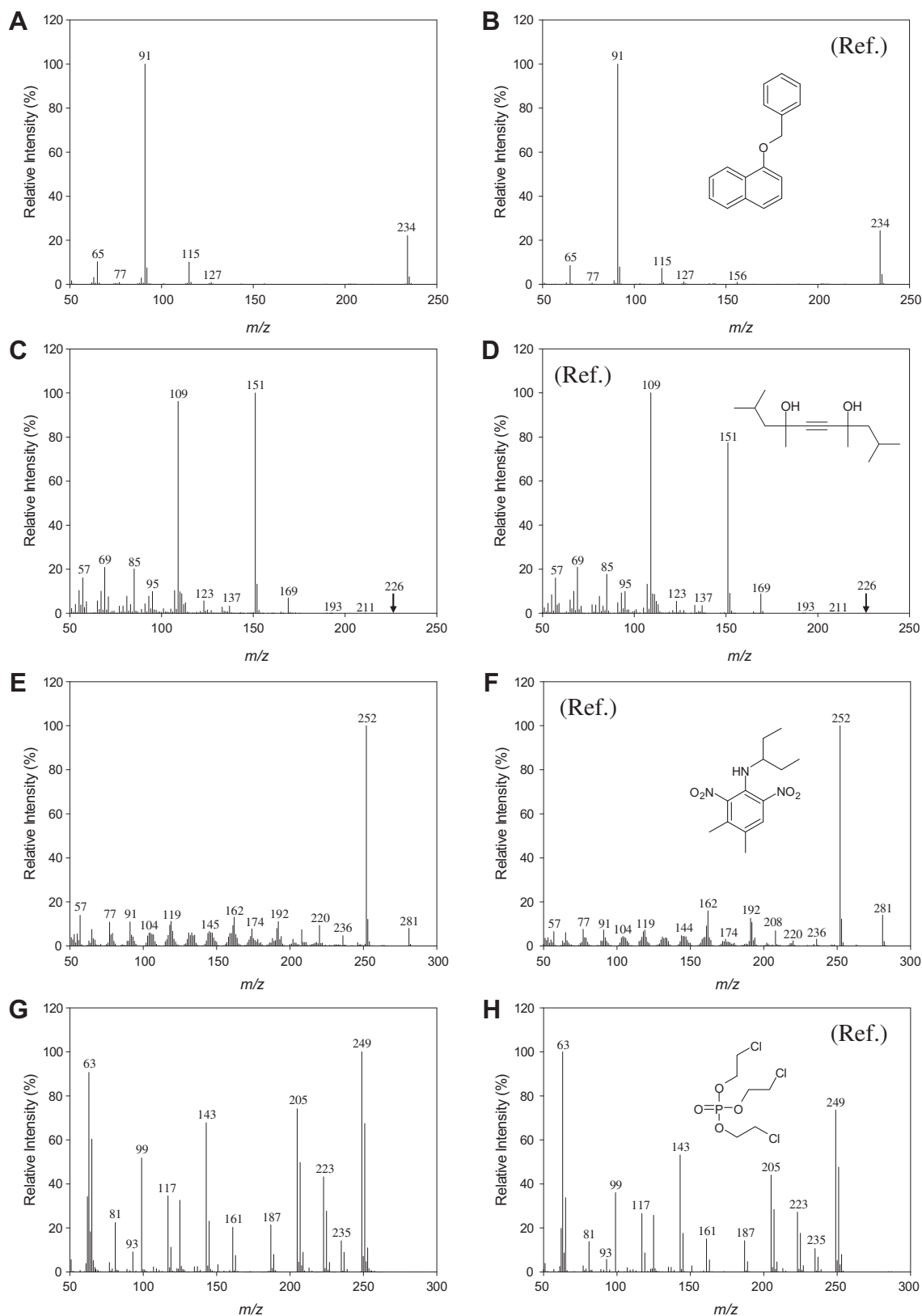


Fig. 4. Example mass spectra of pesticides, flame retardants and compounds used in paper production industries, positively identified in urban aerosol samples (Birmingham, UK). Compounds (A) and (B) are compound and reference mass spectra for naphthalene, 1-(phenylmethoxy)-; (C) and (D) are compound and reference mass spectra for 2,4,7,9-tetramethyl-5-decyn-4,7-diol; (E) and (F) are compound and reference mass spectra for penoxilane; and (G) and (H) are compound and reference mass spectra for tri(2-chloroethyl) phosphate. (Reference spectra reproduced with permission from the National Institute of Standards & Technology spectral database ver. 2.0f Oct 8 2008).

Table 1
Oxygenated volatile organic compounds detected in samples collected in Birmingham, UK, between 9 Feb and 14 Feb 2011. RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention time 2 (minutes).

Compound	CAS no	Molecular formula	MF	RMF	tR1	tR2	Industrial use/source
Linear and branched OVOCs							
Propanedioic acid, propyl–	616-62-6	C ₆ H ₁₀ O ₄	885	903	18.734	0.629	
Hexanoic acid, 2-ethyl–	149-57-5	C ₈ H ₁₆ O ₂	906	906	23.334	0.704	Stabiliser for PVC industry/preparation of metal derivatives
Ethanol, 2-(2-butoxyethoxy)–	112-34-5	C ₈ H ₁₈ O ₃	920	923	26.000	1.081	Paints, cleaning, automotive products
Dipropylene glycol monomethyl ether	34590-94-8	C ₇ H ₁₆ O ₃	813	829	29.134	1.081	Paint solvents
Ethanol, 2-(2-butoxyethoxy)–, acetate	124-17-4	C ₁₀ H ₂₀ O ₄	885	886	30.000	1.333	Buildings/furnishings/paint solvents
Vanillin	121-33-5	C ₈ H ₈ O ₃	839	885	31.600	2.639	Food industry
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	126-86-3	C ₁₄ H ₂₆ O ₂	892	894	31.934	0.955	Non-ionic surfactant
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	6846-50-0	C ₁₆ H ₃₀ O ₄	816	824	36.600	0.327	Food packaging
Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	74381-40-1	C ₁₆ H ₃₀ O ₄	840	892	36.734	1.081	Plasticizer, PVC
Octane, 1,1'-oxybis–	629-82-3	C ₁₆ H ₃₄ O	904	906	37.867	0.88	Irradiated oil emissions
Isopropyl myristate	110-27-0	C ₁₇ H ₃₄ O ₂	903	903	41.000	1.131	Cosmetic and topical medicinal preps.
2-Pentadecanone, 6,10,14-trimethyl-	502-69-2	C ₁₈ H ₃₆ O	912	915	41.534	1.181	Component of essential oil of plants
Bis(2-ethylhexyl) maleate	142-16-5	C ₂₀ H ₃₆ O ₄	786	828	46.934	1.911	Paints
Hexadecanoic acid, butyl ester	111-06-8	C ₂₀ H ₄₀ O ₂	881	881	47.534	1.634	Soaps/cosmetics/food industry/plants
2-Propenoic acid, tridecyl ester	3076-04-8	C ₁₆ H ₃₀ O ₂	857	869	49.334	1.684	Adhesives/inks
Octadecanoic acid, 2-methylpropyl ester	646-13-9	C ₂₂ H ₄₄ O ₂	841	859	50.800	1.684	Cosmetic products
Hexanedioic acid, bis(2-ethylhexyl) ester	103-23-1	C ₂₂ H ₄₂ O ₄	893	895	50.934	1.91	Plasticizer
Tetracosanoic acid, methyl ester	2442-49-1	C ₂₅ H ₅₀ O ₂	874	877	55.600	2.187	Food/beverage additives
Glycerol tricaprilate	538-23-8	C ₂₇ H ₅₀ O ₆	789	834	58.667	3.066	Pharmaceutical
Substituted aromatic OVOCs							
Ethanone, 2-(formyloxy)-1-phenyl–	55153-12-3	C ₉ H ₈ O ₃	845	960	28.334	1.935	
Terpin hydrate	2451-01-6	C ₁₀ H ₂₂ O ₃	912	914	29.400	1.534	Oil of turpentine
Ethanone, 1,1'-(1,4-phenylene)bis–	1009-61-6	C ₁₀ H ₁₀ O ₂	873	897	32.267	2.614	
cis-Pinonic acid	473-72-3	C ₁₀ H ₁₆ O ₃	884	907	32.334	1.885	Oxidation product of terpenes
Ethanone, 1-[4-(1-hydroxy-1-methylethyl)phenyl]–	54549-72-3	C ₁₁ H ₁₄ O ₂	847	855	33.400	2.362	
α,α,α',α'-Tetramethyl-1,4-benzenedimethanol	2948-46-1	C ₁₂ H ₁₈ O ₂	864	888	34.134	2.136	Rubber and plastics
2,6-Dimethoxybenzoquinone	530-55-2	C ₈ H ₈ O ₄	805	826	34.934	0.101	Plants/anti-cancer
Cyclopentaneacetic acid, 3-oxo-2-pentyl–, methyl ester	24851-98-7	C ₁₃ H ₂₂ O ₃	837	855	37.400	1.96	Plants/fragrance
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	1620-98-0	C ₁₅ H ₂₂ O ₂	848	894	40.334	2.086	Food additive
2-Propenoic acid, 3-(4-methoxyphenyl)–, 2-ethylhexyl ester	5466-77-3	C ₁₈ H ₂₆ O ₃	867	892	47.334	2.815	Cosmetics
Phenol, 4,4'-(1-methylethylidene)bis–	80-05-7	C ₁₅ H ₁₆ O ₂	771	846	48.334	0.528	Plastics
Cyclic-OVOCs							
Succinic anhydride	108-30-5	C ₄ H ₄ O ₃	880	900	18.467	3.244	Paper production
4,8,12,16-Tetramethylheptadecan-4-olide	96168-15-9	C ₂₁ H ₄₀ O ₂	853	871	50.467	2.238	Water repellent
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	C ₁₇ H ₂₄ O ₃	917	943	43.134	2.312	Plastic materials
1H-Naphtho[2,1-b]pyran, 3-ethenyldodecahydro-3,4a,7,7,10a-pentamethyl–, [3R-(3α,4aβ,6α,10aβ,10bα)]–	596-84-9	C ₂₀ H ₃₄ O	915	918	45.800	1.985	

the chemical composition of the samples collected here varies from day to day, owing to changing meteorology and complexity of emission sources, consistent with Ozel et al. (2009). A further reason for the discrepancy between the number of ON compounds

reported by Ozel et al. (2009) and those reported in this study may be due to the differing analytical procedures employed.

Table 4 reports the detection of a number of hydrocarbons, not commonly reported as present in the atmosphere. For example,

Table 2
Oxygenated polycyclic aromatic and alicyclic compounds detected in samples collected in Birmingham, UK, between 9 Feb and 14 Feb 2011. RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention time 2 (minutes).

Compound	CAS no.	Molecular formula	MF	RMF	tR1	tR2	Industrial use/source
OPAHs & alicyclic compounds							
1H-Phenalen-1-one	548-39-0	C ₁₃ H ₈ O	899	899	43.800	0.603	
9,10-Anthracenedione	84-65-1	C ₁₄ H ₈ O ₂	898	900	45.067	0.277	Dyes, paper making, pesticides
1,8-Naphthalic anhydride	81-84-5	C ₁₂ H ₆ O ₃	857	860	46.134	1.232	Dyes, pigments
9,10-Anthracenedione, methyl–	84-54-8	C ₁₅ H ₁₀ O ₂	863	877	47.467	0.327	
Naphthalene, 1-(phenylmethoxy)–	607-58-9	C ₁₇ H ₁₄ O	931	934	48.000	0.025	Heat sensitive paper
2H-Phenanthro[9,10-b]pyran	217-67-4	C ₁₇ H ₁₂ O	758	848	50.200	3.946	
8H-Naphtho[1,2-b]pyran-8-one, 3-ethyldodecahydro-3,4a,7,7,10a-pentamethyl–, [3R-(3α,4aβ,6α,10aβ,10bα)]–	55836-76-5	C ₂₀ H ₃₄ O ₂	754	807	50.467	3.091	
2-Ethyl-trans-4a,cis-4b,trans-8a,cis-10a-perhydro-trans-2,4a,8a-trimethylphenanthrene	243629 (NIST)	C ₁₉ H ₃₂ O	780	814	50.667	3.795	
1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)–, methyl ester, [1R-(1α,4aβ,10α)]–	1740-19-8	C ₂₀ H ₂₈ O ₂	891	896	50.934	3.218	Pine resin
7-Oxodehydroabietic acid, methyl ester	17751-36-9	C ₂₁ H ₂₈ O ₃	835	847	54.534	0.327	Terpenic resin
16βH-Kauran-16-ol	5354-44-9	C ₂₀ H ₃₄ O	803	813	49.934	2.791	Plants

Table 3

Organic nitrogen compounds detected in samples collected in Birmingham, UK, between 9 Feb and 14 Feb 2011. RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention time 2 (minutes).

Compound	CAS no.	Molecular formula	MF	RMF	tR1	tR2	Industrial use/source
Linear and branched ONs							
Urea, triethyl–	19006-59-8	C ₇ H ₁₆ N ₂ O	764	812	25.867	1.634	
Hexadecanamide	629-54-9	C ₁₆ H ₃₃ NO	845	845	47.400	2.438	
Substituted aromatic ONs							
Penoxaline	40487-42-1	C ₁₃ H ₁₉ N ₃ O ₄	881	885	45.867	2.966	Pesticide
Cyclic-ONs							
2,5-Pyrrolidinedione	123-56-8	C ₄ H ₅ NO ₂	864	869	22.534	2.741	Silver plating/antibacterial agent
Caprolactam	105-60-2	C ₆ H ₁₁ NO	913	913	27.267	2.967	Nylon
1,3-Diethyl-2,4,5-trioximidazolidine	10319-61-6	C ₇ H ₁₀ N ₂ O ₃	881	884	28.267	2.263	Plant metabolism
1-Ethyl-4,4-dimethyl-2,5-dioximidazolidine	37021-15-1	C ₇ H ₁₂ N ₂ O ₂	808	811	28.400	2.439	
Quinoline, 2-methyl–	91-63-4	C ₁₀ H ₉ N	798	852	29.600	2.137	Dyes, solvent for resins and terpenes

Table 4

Other semi-volatile organic compounds detected in samples collected in Birmingham, UK, between 9 Feb and 14 Feb 2011. RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention time 2 (minutes).

Compound	CAS no.	Molecular formula	MF	RMF	tR1	tR2	Industrial use/source
Linear and branched VOCs							
Nonadecane, 2-methyl-	1560-86-7	C ₂₀ H ₄₂	820	824	40.000	0.729	
Hexadecane, 2,6,10,14-tetramethyl–	638-36-8	C ₂₀ H ₄₂	892	895	41.000	0.805	Petroleum
Hexatriacontane (–C ₃₆)	630-06-8	C ₃₆ H ₇₄	800	802	61.134	2.538	Lubricating oils
Substituted aromatic VOCs							
1,1':3',1''-Terphenyl, 5'-phenyl–	612-71-5	C ₂₄ H ₁₈	887	919	60.267	3.493	
Polycyclic aromatic VOCs							
Stigmastane	601-58-1	C ₂₉ H ₅₂	791	801	62.734	0.327	

2,6,10,14-tetramethyl-hexadecane, (or phytane) has been used as a biomarker in petroleum geochemistry, where ratios of pristane and phytane have been exploited as indicators of maturity and extent of biodegradation (Hunt et al., 2002), but to our knowledge has not been routinely measured in atmospheric/environmental studies. Hexatriacontane occurs in lubricating oils manufactured within the petroleum industry; thus the presence of hexatriacontane in all five aerosol samples indicates that routine measurements may benefit future studies, serving as an oil tracer determining the unburned oil contribution to PM (Zielinska et al., 2008).

Table 5 shows some of the many compounds which are used in industry, as plasticizers, flame retardants and paint solvents. These compounds have received less attention in airborne analyses. Phthalates and organophosphates are ubiquitous chemicals in the environment and are used commercially as plasticizers and flame retardants, but are not usually measured in the atmosphere. The majority of these compounds were detected in all the samples, with abundances considerably larger than that found in the filter blank (compounds found in the filter blank are shown with an asterisk in Table 5). Some studies have evaluated the concentration of phthalates and organophosphates in indoor air (Bergh et al., 2011), but

Table 5

Phthalates, organophosphates and organosulphate compounds detected in samples collected in Birmingham, UK, between 9 Feb and 14 Feb 2011. RMF – reverse match factor; MF – match factor; tR1 – retention time 1 (minutes); tR2 – retention time 2 (minutes).

Compound	CAS no.	Molecular formula	MF	RMF	tR1	tR2	Industrial use/source
Phthalates							
Phthalic anhydride*	85-44-9	C ₈ H ₄ O ₃	947	948	29.134	2.967	Plasticizer
Diethyl phthalate	84-66-2	C ₁₂ H ₁₄ O ₄	885	905	36.000	2.414	Plasticizer, detergent bases and aerosol sprays
Phthalic acid, isobutyl octyl ester*	309045 (NIST)	C ₂₀ H ₃₀ O ₄	879	880	41.800	2.312	
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester*	84-69-5	C ₁₆ H ₂₂ O ₄	859	859	41.867	2.287	
Phthalic acid, butyl hexyl ester*		C ₁₈ H ₂₆ O ₄	917	917	43.600	2.564	
Dibutyl phthalate*	84-74-2	C ₁₆ H ₂₂ O ₄	882	886	43.667	2.538	
Benzyl butyl phthalate	85-68-7	C ₁₉ H ₂₀ O ₄	903	916	50.467	0.025	Plasticizer
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester*	4376-20-9	C ₁₆ H ₂₂ O ₄	896	898	53.200	2.69	
1,2-Benzenedicarboxylic acid, dinonyl ester	84-76-4	C ₂₆ H ₄₂ O ₄	783	800	56.734	3.317	Plasticizer
Terephthalic acid, di(2-ethylhexyl) ester	6422-86-2	C ₂₄ H ₃₈ O ₄	771	839	56.134	2.69	Plasticizer
Organophosphates							
Tributyl phosphate*	126-73-8	C ₁₂ H ₂₇ O ₄ P	759	801	33.867	1.282	Plasticizer
2-Methyl-2-propyl methylphosphonofluoridate*	13273-12-6	C ₅ H ₁₂ FO ₂ P	773	905	33.934	1.257	Plasticizer
Tri(2-chloroethyl) phosphate	115-96-8	C ₆ H ₁₂ Cl ₃ O ₄ P	900	903	39.400	2.464	Flame retardant
2-Propanol, 1-chloro–, phosphate (3:1)*	13674-84-5	C ₉ H ₁₈ Cl ₃ O ₄ P	897	902	40.467	2.413	Flame retardant
Octicizer (Diphenyl-2-ethylhexyl phosphate)	1241-94-7	C ₂₀ H ₂₇ O ₄ P	855	862	51.600	3.544	Plasticizer
Organosulphates							
Benzenesulfonamide, N-butyl–	3622-84-2	C ₁₀ H ₁₅ SO ₂ N	855	886	40.400	3.368	Plasticizer
1-Propanesulfonic acid, ethyl ester	91284-43-4	C ₅ H ₁₂ O ₃ S	817	817	51.534	1.206	

*Compounds with an asterisk were also found in the filter blank at a lower concentration.

relatively few studies have focused on levels in outdoor environments owing to suspected levels being an order of magnitude lower (Rudel and Perovich, 2009). Although volatilisation from environmental surfaces such as soil may not be a significant source to the atmosphere (Harrad and Hunter, 2006), the adsorption of these compounds by dust particles may be responsible for the widespread distribution of these chemicals. Furthermore, dependent upon volatility, phthalates, organophosphates and organosulphates may be adsorbed to airborne particulate matter and may be subject to degradation by atmospheric oxidants, such as O₃, OH and NO₃. The rate of degradation of these compounds, both in the vapour and condensed phases, by atmospheric oxidants has not been experimentally measured. However, half lives of 1–100 days have been estimated by using structure activity relationship methods for phthalates in the vapour phase with respect to OH (Atkinson, 1987; Meylan and Howard, 1992). These predicted half lives suggest that oxidation by OH radicals could be the major degradation pathway, transforming these plasticizers released into the atmosphere and could subsequently form further products of varying toxicity.

4. Conclusions

Earlier GC–MS studies of semi-volatile compounds in atmosphere aerosol have focused on specific groups of compounds and have therefore not captured the remarkable range of compounds present. This study has deliberately taken the opposite line of ignoring those groups of compounds for which there are a number of reports in the literature, but focussing on unrelated compounds in order to get a measure of the diversity of those present. As a consequence, it has revealed a quite exceptionally diverse range of compounds, many of which are in use by industry and incorporated into consumer products, for example, as plasticisers or fire retardants. Given the vapour pressures of such substances, it is not surprising that small amounts enter the atmosphere and future research on airborne particulate matter and health needs to take account of their presence. While individually they are unlikely to represent a toxic hazard, collectively, they may contribute significantly to the toxicity of airborne particulate matter. It seems far more likely that the phthalate plasticisers, for which there is evidence of endocrine disruptive potential (Sharpe and Irvine, 2004), or organo-phosphate fire retardants, present a significantly greater contribution to toxicity than the alkanes which are more commonly measured. While the polycyclic aromatic hydrocarbons probably contribute the majority of the carcinogenicity of urban particulate matter, contributions from some of the other compounds present cannot be ruled out.

Acknowledgment

Funding for part of this research was provided by an Advanced Investigators Grant (no. 228149) awarded to SJR for project OUTREACH, by the European Research Council, to whom we are extremely grateful. We also acknowledge funding from the Natural Environment Research Council (to RMH and MSA) and the assistance of Pallavi Pant and Jianxin Yin in sample collection and extraction.

References

Adahchour, M., Beens, J., Brinkman, U.A.T., 2008. Recent developments in the application of comprehensive two-dimensional gas chromatography. *Journal of Chromatography A* 1186, 67–108.

Arsene, C., Vione, D., Grinberg, N., Olariu, R.I., 2011. GC × GC–MS hyphenated techniques for the analysis of volatile organic compounds in air. *Journal of Liquid Chromatography & Related Technologies* 34, 1077–1111.

Atkinson, R., 1987. A structure–activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. *International Journal of Chemical Kinetics* 19, 799–828.

Bergh, C., Torgrip, R., Emenius, G., Ostman, C., 2011. Organophosphate and phthalate esters in air and settled dust – a multi-location indoor study. *Indoor Air* 21, 67–76.

Dalluge, J., van Rijn, M., Beens, J., Vreuls, R.J.J., Brinkman, U.A.T., 2002. Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection applied to the determination of pesticides in food extracts. *Journal of Chromatography A* 965, 207–217.

George, I.J., Abbatt, J.P.D., 2010. Heterogeneous oxidation of atmospheric aerosol particles by gas-phase radicals. *Nature Chemistry* 2, 713–722.

Goldstein, A.H., Galbally, I.E., 2007. Known and unexplored organic constituents in the earth's atmosphere. *Environmental Science & Technology* 41, 1514–1521.

Goulay, F., Rebrion-Rowe, C., Le Garrec, J.L., Le Picard, S.D., Canosa, A., Rowe, B.R., 2005. The reaction of anthracene with OH radicals: an experimental study of the kinetics between 58 and 470 K. *Journal of Chemical Physics* 122 (10), 104308.

Hamilton, J.F., Webb, P.J., Lewis, A.C., Hopkins, J.R., Smith, S., Davy, P., 2004. Partially oxidised organic components in urban aerosol using GC × GC–TOF/MS. *Atmospheric Chemistry and Physics* 4, 1279–1290.

Harrad, S., Hunter, S., 2006. Concentrations of polybrominated diphenyl ethers in air and soil on a rural–urban transect across a major UK conurbation. *Environmental Science & Technology* 40, 4548–4553.

Harrison, R.M., Yin, J.X., 2010. Chemical speciation of PM_{2.5} particles at urban background and rural sites in the UK atmosphere. *Journal of Environmental Monitoring* 12, 1404–1414.

Harrison, R.M., Yin, J., 2000. Particulate matter in the atmosphere: which particle properties are important for its effects on health? *Science of the Total Environment* 249, 85–101.

Hunt, J.M., Philp, R.P., Kvenvolden, K.A., 2002. Early developments in petroleum geochemistry. *Organic Geochemistry* 33, 1025–1052.

Isaacman, G., Worton, D.R., Kreisberg, N.M., Hennigan, C.J., Teng, A.P., Hering, S.V., Robinson, A.L., Donahue, N.M., Goldstein, A.H., 2011. Understanding evolution of product composition and volatility distribution through in-situ GC × GC analysis: a case study of longifolene ozonolysis. *Atmospheric Chemistry and Physics* 11, 5335–5346.

Jakober, C.A., Riddle, S.G., Robert, M.A., Destailats, H., Charles, M.J., Green, P.G., Kleeman, M.J., 2007. Quinone emissions from gasoline and diesel motor vehicles. *Environmental Science & Technology* 41, 4548–4554.

Laitinen, T., Martin, S.H., Parshintsev, J., Hyotylainen, T., Hartonen, K., Riekkola, M.L., Kulmala, M., Pavon, J.P.P., 2010. Determination of organic compounds from wood combustion aerosol nanoparticles by different gas chromatographic systems and by aerosols mass spectrometry. *Journal of Chromatography* 1217, 151–159.

Lee, J.D., Lewis, A.C., Monks, P.S., Jacob, M., Hamilton, J.F., Hopkins, J.R., Watson, N.M., Saxton, J.E., Ennis, C., Carpenter, L.J., Carslaw, N., Fleming, Z., Bandy, B.J., Oram, D.E., Penkett, S.A., Slemr, J., Norton, E., Rickard, A.R., Whalley, L.K., Heard, D.E., Bloss, W.J., Gravestock, T., Smith, S.C., Stanton, J., Pilling, M.J., Jenkin, M.E., 2006. Ozone photochemistry and elevated isoprene during the UK heatwave of August 2003. *Atmospheric Environment* 40, 7598–7613.

Lewis, A.C., Carslaw, N., Marriott, P.J., Kinghorn, R.M., Morrison, P., Lee, A.L., Bartle, K.D., Pilling, M.J., 2000. A larger pool of ozone-forming carbon compounds in urban atmospheres. *Nature* 405, 778–781.

Li, X., Hede, T., Tu, Y., Leck, C., Agren, H., 2010. Surface-active *cis*-pinonic acid in atmospheric droplets: a molecular dynamics study. *Journal of Physical Chemistry Letters* 4, 769–773.

Mari, M., Harrison, R.M., Schuhmacher, M., Domingo, J.L., Pongpiachan, S., 2010. Inferences over the sources and processes affecting polycyclic aromatic hydrocarbons in the atmosphere derived from measured data. *Science of the Total Environment* 408, 2387–2393.

Meylan, W., Howard, P.H., 1992. Molecular topology/fragment contribution method for predicting soil sorption coefficients. *Environmental Science & Technology* 26, 1560–1567.

Ochiai, M., Ieda, T., Sasamoto, K., Fushimi, A., Hasegawa, S., Tanabe, K., Kobayashi, S., 2007. Comprehensive two-dimensional gas chromatography coupled to high-resolution time-of-flight mass spectrometry and simultaneous nitrogen phosphorus and mass spectrometric detection for characterization of nanoparticles in roadside atmosphere. *Journal of Chromatography* 1150, 13–20.

Omar, N.Y.M.J., Abas, M.R.B., Rahman, N.A., Tahir, N.M., Rishdi, A.I., Simoneit, R.T., 2007. Levels and distributions of organic source tracers in air and roadside dust particles of Kuala Lumpur, Malaysia. *Environmental Geology* 52, 1485–1500.

Ozel, M.Z., Ward, M.W., Hamilton, J.F., Lewis, A.C., Raventos-Duran, M.T., Harrison, R.M., 2009. Analysis of organic nitrogen compounds in urban aerosol samples using GC × GC–TOF/MS. *Aerosol Science and Technology* 44, 109–116.

Pio, C.A., Alves, C.A., Duarte, A.C., 2001. Identification, abundance and origin of atmospheric organic particulate matter in a Portuguese rural area. *Atmospheric Environment* 35, 1365–1375.

Pratt, K.A., Prather, K.A., 2012. Mass spectrometry of atmospheric aerosols – recent developments & applications. Part I: off-line mass spectrometry techniques. *Mass Spectrometry Reviews* 31, 1–16.

Ringuet, J., Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., 2012. Reactivity of polycyclic aromatic compounds (PAHs, NPAHs and OPAHs) adsorbed on natural aerosol particles exposed to atmospheric oxidants. *Atmospheric Environment* 61, 15–22.

Rowland, S.J., West, C.W., Scarlett, A.G., Ho, C., Jones, D., 2012. Differentiation of two industrial oil sands process-affected waters by two-dimensional gas

- chromatography/mass spectrometry of diamondoid acid profiles. *Rapid Communications in Mass Spectrometry* 26, 572–576.
- Rudel, R.A., Perovich, L.J., 2009. Endocrine disrupting chemicals in indoor and outdoor air. *Atmospheric Environment* 43, 170–181.
- Sharpe, R.M., Irvine, D.S., 2004. How strong is the evidence of a link between environmental chemicals and adverse effects on human reproductive health? *British Medical Journal* 328, 447–451.
- Tomashuk, T.A., Truong, T.M., Mantha, M., McGowin, A.E., 2012. Atmospheric polycyclic aromatic hydrocarbon profiles and sources in pine needles and particulate matter in Dayton, Ohio, USA. *Atmospheric Environment* 51, 196–202.
- Welthagen, W., Schnelle-Kreis, J., Zimmermann, R., 2003. Search criteria and rules for comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry analysis of airborne particulate matter. *Journal of Chromatography A* 1019, 233–249.
- Williams, B.J., Goldstein, A.H., Kreisberg, N.M., Hering, S.V., Worsnop, D.R., Ulbrich, I.M., Docherty, K.S., Jimenez, J.L., 2010. Major components of atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds. *Atmospheric Chemistry and Physics* 10, 11577–11603.
- Worton, D.R., Kreisberg, N.M., Isaacman, G., Teng, A.P., McNeish, C., Gorecki, T., Hering, S.V., Goldstein, A.H., 2012. Thermal desorption comprehensive two-dimensional gas chromatography: an improved instrument for in-situ speciated measurements of organic aerosols. *Aerosol Science and Technology* 46, 380–393.
- Xu, X., van Stee, L.L.P., Williams, J., Beens, J., Adahchour, M., Vreuls, R.J.J., Brinkman, U.A.T., Lelieveld, J., 2003a. Comprehensive two-dimensional gas chromatography (GC × GC) measurements of volatile organic compounds in the atmosphere. *Atmospheric Chemistry and Physics* 3, 665–682.
- Xu, X., Williams, J., Plass-Dulmer, C., Berresheim, H., Salisbury, G., Lange, L., Lelieveld, J., 2003b. GC × GC measurements of C-7–C-11 aromatic and n-alkane hydrocarbons on Crete, in air from Eastern Europe during the MINOS campaign. *Atmospheric Chemistry and Physics* 3, 1461–1475.
- Yin, J., Harrison, R.M., Chen, Q., Rutter, A., Schauer, J.J., 2010. Source apportionment of fine particles at urban background and rural sites in the UK atmosphere. *Atmospheric Environment* 44, 841–851.
- Zielinska, B., Campbell, D., Lawson, D.R., Ireson, R.G., Weaver, C.S., Hesterberg, T.W., Larson, T., Davey, M., Liu, L.J.S., 2008. Detailed characterization and profiles of crankcase and diesel particulate matter exhaust emissions using speciated organics. *Environmental Science & Technology* 42, 5661–5666.
- Zhang, R.J., Ho, K.F., Shen, Z.X., 2012. The role of aerosol in climate change, the environment, and human health. *Atmospheric and Oceanic Science Letters* 5, 156–161.