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Characterisation of solvent extractable organic constituents in atmospheric particulate matter: an overview

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ABSTRACT

In spite of accounting for 10-70% of the atmospheric aerosol mass, particulate-phase organic compounds are not well characterised, and many aspects of aerosol formation and evolution are still unknown. The growing awareness of the impact of particulate aerosols on climate, and the incompletely recognised but serious effects of anthropogenic constituents on air quality and human health, have conducted to several scientific studies. These investigations have provided information about the behaviour of atmospheric particulate matter and the description of the character of its carbonaceous content. The compilation of such results is important as they append to the emergent global-wide dataset of the organic composition of atmospheric aerosols. The contribution of the major emission sources to regional particulate pollution can be diagnosed by using specific molecular markers. This overview is mainly focused on results obtained with gas chromatography coupled with mass spectrometry, since it is the analytical method of choice in elucidating the solvent-extractable organic compounds in atmospheric particulate matter. A synopsis of the selection of organic tracers and the application of geochemical parameters to the analysis of organic constituents as a tool for source apportionment is shown here. Besides the assessment of current knowledge, this paper also presents the identification of further areas of concern.

Key words: atmospheric aerosol, gas chromatography-mass spectrometry, organic compounds, source apportionment, tracers.

INTRODUCTION

Aerosols are mixtures of solid and liquid droplets of material that vary in size and origin. Airborne suspended particulate matter can be either primary or secondary in nature. Primary particles are emitted directly into the atmosphere both by natural or anthropogenic sources, while secondary particles are produced in the atmosphere from the oxidation and subsequent reactions of sulphur dioxide, nitrogen oxides and volatile organic compounds. Primary biogenic aerosols are particles that are produced by the crumbling and dispersion of plant and animal material, and the spreading of microbes from a variety of surfaces into the atmosphere. Industrialisation, human activities and the growing levels of traffic result in an anthropogenic sources prevalence, particularly in urban areas (Alves et al. 2007). Mass and composition tend to be divided into two main groups: coarse particles and fine particles. The barrier between coarse and fine particulate matter is sometimes fixed by convention at 2.5μm in aerodynamic diameter for measurement purposes. Thus, two categories of particle pollution may be addressed: (i) fine particles ($PM_{2.5}$), which are 2.5μm in diameter and smaller; and (ii) inhalable coarse particles ($PM_{10-2.5}$), which are smaller than 10μm in diameter, but larger than $PM_{2.5}$. The smaller particles contain the secondarily formed aerosols (gas-to-particle conversion), combustion particles and recondensed organic and metal vapours. The larger particles generally include

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earth crust materials and fugitive dust from roads and industries. The fine fraction encompasses most of the acidity (hydrogen ion) and mutagenic activity of particulate matter, although in fog some coarse acid droplets are also present. The major aerosol components include inorganic substances such as sulphates and carbonaceous species. The carbonaceous aerosol is formed by a complex mixture of organic compounds, normally referred as organic carbon (OC), and a mass of carbon atoms with a graphitic-like structure that is black in colour and is normally named as soot, black carbon or elemental carbon (BC or EC). Organic matter is an important fraction of the atmospheric aerosols, contributing with 10-70% of their mass (Turpin et al. 2000).

Atmospheric PM is an environmental concern, above all because it can dramatically reduce visual range (Hobbs 2002), and have a profound effect on climate (Penner et al. 1998). The direct and indirect radiative forcing of climate by anthropogenic aerosols is believed to be similar in magnitude but opposite in sign to the global warming caused by the emissions of greenhouse gases (Farquhar 1997, Mahlman 1997). Fine particles and the associated organic compounds are also of current concern because of their putative health effects (Abelson 1998, Pope et al. 2004, Poschl 2005). There is a general consensus that the organic composition of atmospheric aerosol should be understood to correctly describe the chemical mechanisms and models concerning the multiphase atmospheric system and to evaluate its environmental and health effects. Despite the progress made in elucidating the source types, their relative importance and contribution to certain particulate components, the organic composition of aerosols and particle formation processes are still scarcely known. This is probably due to analytical difficulties, complexity of phenomena and huge number of compounds that are present (Alves et al. 2006).

The objective of this paper is to contribute to clarifying the role and importance of the carbonaceous aerosol in the environment by answering to questions such as: Which are the sources of the carbonaceous aerosol? Which are the best tracers to track the contributions of the main sources? Is the organic aerosol of primary or secondary origin? How much of the organic carbon is extractable and identifiable by common laboratory equipments used for organic speciation (e.g. gas chromatograph/mass spectrometer)? Is it possible to close the material balance of the organic aerosol? Which are the organic constituents that we haven't been able to quantify? What problems are ripe for further investigation? The discussion of these points constitutes the main goal of the present review study. A comparison of recent results obtained in different researches throughout the world and the limitations that still persist are presented.

METHODOLOGIES FOR THE DETERMINATION OF ORGANIC AEROSOL COMPOSITION

A variety of methods have been used to typify the organic composition of atmospheric aerosols. These methods may be separated into integral methods that characterise only some properties of organic particulate matter, such as OC content, functional groups, isotope ratios, etc., and molecular-level methods that allow the speciation of individual organic compounds. Organic compound speciation affords the most helpful information about organic aerosol composition, sources, and atmospheric transformation processes. At present it is not possible to entirely resolve all OC mass into concentrations of specific organic compounds and no sole analytical technique is proficient of analysing the whole organic composition. The molecular level methods typically have need of extraction of a sample with organic solvents, followed by analysis by gas chromatography/mass spectrometry (GC / MS), gas chromatography / Fourier transform infrared spectroscopy/mass spectrometry (GC/FTIR/MS), high performance liquid chromatography/mass spectrometry (HPLC/MS) and other techniques. Traditionally, chemical characterisation of particulate OC has been performed using single or multiple solvent extractions of samples followed by GC/MS (Facchini et al. 1999, Gogou et al. 1998, Plewka et al. 2003, Rissanen et al. 2006, Sin et al. 2002, Zappoli et al. 1999). However, in these experimental works a significant portion of polar oxygenated organic compounds remains unknown. Identified organic compounds in aerosol typically account for 10% or less of the mass of total OC measured by thermal analysis, although this percentage could reach values above 60%, when more complex extraction methodologies and detection techniques are used (Alves et al. 2002, 2006, Carvalho et al. 2003, Decesari et al. 2000, Feng et al. 2007). This is because universal solvents for both polar and non-polar OC do not exist, high-molecular organics ($>C_{40}$) and highly polar compounds (particularly multifunctional) do not elute through a GC column and identified compounds are embedded in an unresolved complex mixture. Polar organic compounds need derivatisation prior to analysis, to convert them into less polar and more volatile derivatives that will elute chromatographically. However, the derivatisation techniques are compound-class specific and thus several different methods may be required for a wide-ranging analysis. On the other hand, since derivatisation procedures are compound-class specific, require *a priori* knowledge about the particulate matter composition. The derivatisation reagent by-products, the complexity of derivatisation procedures, lack of standards, and limited mass spectral libraries makes these analyses difficult and time consuming. The combined GC/FTIR/MS technique offers the advantage of additional information from the FTIR spectrum, complementary to mass spectrum information, and is helpful in identification of individual components, especially isomers; often these compounds have very similar mass spectra, but unique IR spectra (Zielinska 2002).

HPLC coupled with a mass spectrometer or a photodiode array detector seems to be especially suitable for the analysis of polar organic compounds. Aqueous solutions can be injected into reverse-phase columns, and polar compounds do not need a derivatisation step in order to elute from most of the LC columns (Zielinska 2002). However, compared with GC and GC/MS, HPLC has infrequently been used for the study of organic aerosol (Jacobson et al. 2000). This is perhaps because LC columns present less resolving power than GC columns and are habitually intended for restrict organic classes. Moreover, even though that numerous commercial LC/MS systems are available, they are not properly developed for atmospheric investigation. From the two types of interfaces available between LC and MS, electrospray and particle beam, the last one seems to be more promising (Kiss et al. 2003). Additional progress of separation methods and mass spectral libraries is also essential.

Sierau et al. (2003) developed a method for rapid measurement of particle size and chemical composition. The method uses a saturator/condenser system and an impactor; the saturator/condenser system grows submicrometer particles to a size where they can be easily collected by the impactor. This system was called condensation-growth and impaction system, or C-GIS. To do size-segregated analysis, an optional differential mobility analyser (DMA) can be added upstream of the C-GIS to select the particle size that is introduced into the condenser. The C-GIS converts the sampled aerosol into a hydrosol, and provides liquid samples sufficiently concentrated for the liquid-phase analytical instruments used for chemical analysis without on-line pre-concentration of the sample. The results indicate that the C-GIS can be used for size-segregated particle sampling with subsequent off-line chemical particle analysis with a sampling time of at least 20 min under typical atmospheric conditions. For atmospheric applications, however, its capability to rapidly measure size-segregated chemical composition is limited by the particle concentration present downstream of the DMA, and therefore, such measurements typically can only be made in heavily polluted areas or within the scope of source-characterisation studies.

Several novel methods have lately been proposed for a molecular-level organic aerosol speciation. Neusüss and co-workers (2000) employed flash evaporation by Curie point pyrolysis coupled with GC/MS (CPP-GC/MS) for direct analysis of atmospheric semi-volatile organic constituents. The benefit of this method is that only a few micrograms of sample are required, permitting its utilisation with size-segregated sampling without posterior sample preparation. The inconvenience is that very polar organic compounds may either not elute from a GC column, or be shattered during the flash evaporation process. To overcome this difficulty, the same investigators recommend using complementarily capillary electrophoresis (CE) for analysis of dicarboxylic and hydroxy dicarboxylic acids. The system also enables the analysis of common inorganic ions and methanesulfonate. Because of their different electrophoretic mobilities, in CE, ions are separated in a strong electric field. The possibility of analysing both inorganic and organic ions in a single run represents an advantage of this method in comparison with ion chromatography and GC or HPLC. In addition, the separation efficiency is higher than in LC and the required sample amount is very low (Zielinska 2002). Thermal desorption particle beam mass spectrometry has been lately developed and employed for identification of secondary organic aerosol constituents produced in environmental chambers (Tobias and Ziemann 2000). In this method, a number of particles are trapped on a cold step and gradually heated, to separate compounds depending on their volatility. This analytical equipment presents a large capability for identification of organic compounds formed in controlled laboratory experiments. However, its resolving power to identify and quantify single compounds within a complex organic mixture, as observed in atmospheric aerosols, is very limited. Recently, several researchers have developed instruments for real-time *in situ* analysis of single particles, including carbon analysers and single particle instruments to fragment each particle into ions using either a high-power laser or a heated surface and to then use a time-of-flight mass spectrometer for measuring the ion fragments in a vacuum (Guyon et al. 2004, Johnston and Wexler 1995, Silva and Prather 1997, Thompson and Murphy 1994, Turpin and Huntzicker 1995). Direct thermal desorption – gas chromatography – time-of-flight mass spectrometry (DTD-GC-TOFMS) and comprehensive two-dimensional (2D) gas chromatography – time-of-flight mass spectrometry (GC×GC-TOFMS) was applied by Welthagen et al. (2003) for characterisation of semi-volatile organic compounds in $PM_{2.5}$. These investigators concluded that GC×GC-TOFMS is a suited technique to study the nature of the yet unidentified compounds forming the unresolved complex mixtures (UCM). The considerably increased chromatographic resolution in GC×GC allows separation of many UCM compounds while the TOFMS supplies mass spectral data of all separated compounds. However, the data sets were considered enormously complex. In the near future *in situ* single-particle TOFMS analysis methods are unlikely to quantify, compound by compound, the concentration of a large (50-100%) fraction of organic material in atmospheric PM (Turpin et al. 2000). Generally these instruments are more appropriate for inorganic than organic species, but the future technical development could surmount this panorama.

One important objective of detailed chemical analysis of the organic aerosol is the mass closure of the aerosol mass. Until now it has been impossible to identify and quantify all the organic mass present in the atmospheric aerosol. Little is known about the type and abundance of water-soluble organic compounds (WSOC) in atmospheric particulate matter. The limited results available to date indicate that WSOC could account for 20-90% of total carbon in aerosols (Alves et al. 2002, Decesari et al. 2000, 2001, Facchini et al. 1999, Graham et al. 2002, Saxena and Hildemann 1996). Yang et al. (2003) compared two methods for the determination of WSOC in ambient aerosols, one based on a total organic carbon analyser (TOC) and the other based on an aerosol carbon analyser (ACA). Investigators concluded that, although the sample treatment procedures and the detection limits of these two methods are different to some extent, both are suitable for the determination of WSOC in aerosol samples. Recently, some studies have attempted the most abundant WSOC in fog water and aerosols. Decesari et al. (2000, 2001) and Fuzzi et al. (2001) used ion exchange chromatography and proton nuclear magnetic resonance spectroscopy (HNMR) to characterise the WSOC in atmospheric aerosols, fog and cloud droplets. Zappoli et al. (1999) have shown that a substantial part of the organic aerosol is not soluble in water and organic solvents, indicating that insoluble compounds are of larger molecular sizes. The organic aerosol according to current knowledge are the "Humic Like Substances" (HULIS), occurring in the aerosol as water soluble as well as water insoluble fractions. Different extraction procedures and detection methods were presented in the literature. Spectroscopic methods such as ultraviolet, fluorescence, or infrared spectroscopy were most often used to characterise this organic mass fraction, but electrospray ionisation mass spectroscopy and laser desorption/ionisation mass spectrometry (LDI/MS) were used as well (Havers et al. 1998, Kalberer et al. 2004, 2006, Kiss et al. 2003, Krivácsy et al. 2001, Samburova et al. 2005, Varga et al. 2001, Zappoli et al. 1999). Because of the large number of compounds detected with mass spectrometric methods (Kiss et al. 2003, Samburova et al. 2005), and because the chemical properties of these compounds are mostly unknown, it is difficult to determine their concentration or their molecular weight distribution (Kalberer et al. 2006).

GC/MS CHARACTERISATION STUDIES

GC/MS has by far been the most common means of identifying organic compounds in atmospheric aerosol. The motive is that GC can be used to separate a very ample range of compounds on a single column, and the simple on-line coupling to mass spectrometry (usually electron-impact quadrupole) makes compound identification rather easy. The preliminary GC/MS results on atmospheric organic particulate matter were obtained at the end of the seventies and beginning of the eighties. However, the content of these works were focused mainly on practical details, such as the evaluation of the analytical methodologies of solvent extraction, and did not attempt to present an exhaustive description of the aerosol composition (Barkenbus et al. 1983a, b, Cautreels and Cauwenberghe 1977, Hill et al. 1977, Karasek et al. 1978, Ketseridis et al. 1976, Wauters et al. 1979). If chemical analysis is performed using a chromatographic method, aerosols collected on filters or impactor plates are subjected to an extraction procedure (ultrasonication, Soxhlet, supercritical fluid CO_2 extraction, etc.). An example illustrating the entire procedure is provided in Figure 1. Thermal/optical carbon analysis (TOC) is a technique for separating and measuring the total amount of organic and elemental carbon, commonly from quartz filter samples. This determination is essential in any study that involves extraction of material from filters because it permits measurement of the extraction efficiency. The filter sample is placed into a chamber and heated in the presence of one or more purge gases through a succession of temperature steps. A catalyst converts the evolved gases to either CO_2 or CH_4, which are quantified using infrared or flame ionisation detection, respectively. In most of the thermal evolution techniques, the division between organic and elemental carbon is based on the temperature and/or the type of purge gas used for analysis (Birch 1998, Birch and Cary 1996, Cadle and Mulawa 1990, Carvalho et al. 2006, Chow et al. 1993, 2001, 2004, 2005, Conny et al. 2003, Venkatachari et al. 2006, Watson and Chow 2002). OC is generally defined as the non-carbonate carbon that evolves under a heating cycle in the presence of either He or N_2, and EC is defined as that which evolves in a succeeding heating step in the presence of a gas mixture including oxygen, such as 98%He + 2%O_2 (Birch and Cary 1996, Chow et al. 1993, 2001, Schauer et al. 2003a). It should be noted that some organic compounds pyrolyse or "char" before they are evolved under the He/O_2 part of the analysis. The char that is produced in the analysis, if not accurately accounted for, would be erroneously reported as EC present in the original sample (Schauer et al. 2003a). Usually, a laser absorbance procedure is used to correct for charring in thermo-optical methods.

The knowledge gained through testing experimental procedures began to be applied to the detailed characterisation of aerosols emitted by specific sources or activities, such as volcanic eruptions (Pereira et al. 1982), meat cooking operations (Hildemann et al. 1991, Kleeman et al. 1999, Nolte et al. 1999, Rogge et al. 1991, Schauer et al. 1999a), road dust and tire debris (Rogge et al. 1993a), particulate abrasion products from leaf surfaces of urban plants (Chen and Simoneit 1994, Rogge et al. 1993b), home boilers (Hildemann et al. 1991, Rogge et al. 1993c, 1997a), hot asphalt roofing tar plot plumes (Rogge et al. 1997b), biomass burning (Abas et al. 1995, 2004a, Duan et al. 2004, Elias et al. 1997, 1998, Fang et al. 1999, Fine et al. 2001, 2002a, b, 2004a, Jayaratne and Verna 2001, Jordan et al. 2006, Kleeman et al 1999, Oros and Simoneit 2001a, b, Rogge et al. 1998, Schauer et al. 2001, Simoneit 2002, Simoneit and Elias 2001, Simoneit et al. 1993, 1996, 1999, 2000, Standley and Simoneit 1994), motorised vehicles (Fraser et al. 1999, Hildemann et al. 1991, Rogge et al. 1993d, Schauer et al. 1999b, Simoneit 1984), tobacco smoke (Kavouras et al. 1998a, Kleeman et al. 1999, Morrical and Zenobi 2002, Rogge et al. 1994), coal-fired power station (Santos et al. 2004), waste landfill (Yassaa et al. 2001a) and eolian transport of vegetal detritus (Boon et al. 1998, Simoneit 1997, Simoneit et al. 1988). Some of the researches have also focused upon the assessment of natural *versus* anthropogenic contributions to the carbonaceous aerosol by searching molecular markers or tracers (Abas et al. 1995, 2004a, b, Alves and Pio, in press, Cass 1998, Elias et al. 1999, Fraser et al. 1999, Gogou et al. 1996, 1998, Hawthorne et al. 1988, Kavouras et al. 2001a, Khalil and Rasmussen 2003, Lau et al. 2006, Li and Kamens 1993, Nolte et al. 2001, 2002, Oros et al. 1999, Oros and Simoneit 2001a, b, Rinehart et al. 2006, Rogge et al. 2006, Rushdi et al.

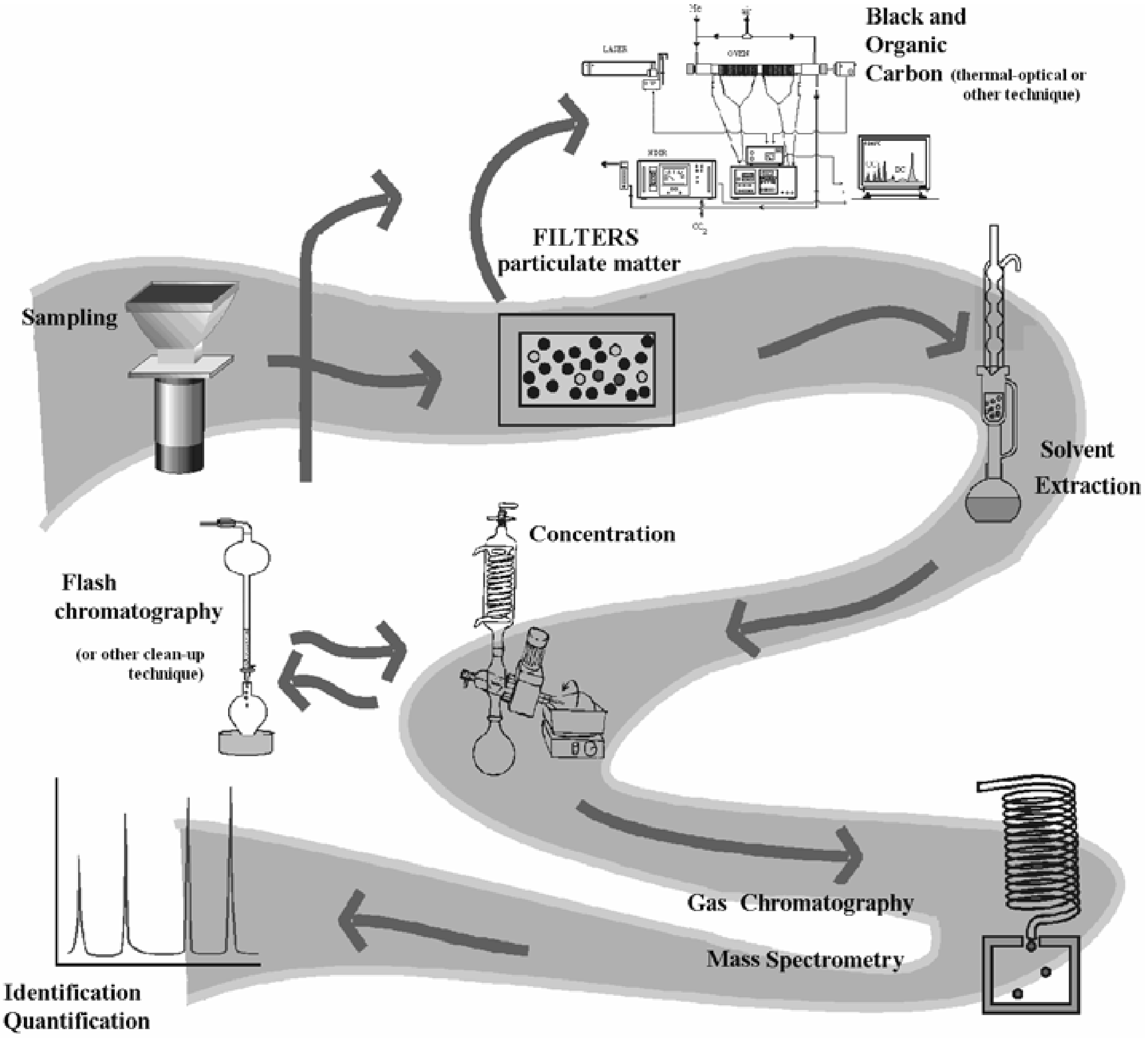


Fig. 1 – Scheme representing a common sampling, extraction and GC/MS procedure for organic speciation of atmospheric aerosols.

2003, Schauer et al. 1996, Sheesley et al. 2003, Simoneit 1989, 1999, 2002, Simoneit and Elias 2001, Simoneit and Mazurek 1989, Simoneit et al. 1990, 1993, 1996, 1999, 2003a, b, 2004a, b, Standley and Simoneit 1994, Zheng et al. 2002). Source-receptor reconciliation by chemical mass balance (CMB) has been used to characterise the composite sources of organic compounds that includes gasoline vehicle exhaust, meat cooking, cigarette smoke, wood burning, etc. (Calhoun et al. 2003, Chow and Watson 2002, Feng et al. 2006, Khalil and Rasmussen 2003, Li and Kamens 1993, Mazurek 2002, Robinson et al. 2006a, b, Schauer et al. 2002a, Watson et al. 2002, Zheng et al. 2002, 2005).

Such as it happens with the OC and EC determinations, most of the investigations to date on the characterisation of organic aerosols deal almost exclusively with urban samples. The scientific literature of the last two decades comprehends several works which report the particulate matter analyses for different metropolis: Heraclion, Crete (Gogou et al. 1996, Stephanou and Stratigakis 1993), Hong Kong (Zheng et al. 1997, 2000, Lee et al. 2001, Yu et al 2004), cities in the Pan-Japan Sea countries (Kawamura and Yasui 2005, Tang et al. 2005), Algiers city area (Yassaa et al. 2001b), Chinese urban areas (Bi et al. 2002, 2003, Cao et al. 2003, 2004, Duan et al. 2004, Guo et al. 2003, 2004, Hou et al. 2006, Simoneit et al. 1991a, Yang et al. 2005a, Wang et al. 2002, 2006a, b, 2007, Wang and Kawamura 2005, Zheng et al. 2005), Barcelone (Aceves and Grimalt 1992, 1993), London (Kendall et al. 2001), Houston, Texas (Fraser et al. 2002, Laurent and Allen 2004, Yue and Fraser 2004), Miami, Florida (Lang et al. 2002), Kuala Lumpur, Malaysia (Abas et al. 2004b, Abas and Simoneit 1996), Toronto (Blanchard et al. 2002), Prato, Italy (Cincinelli et al. 2003), Launceston, Australia (Keywood et al. 2000), Santiago, Chile (Didyk et al. 2000, Kavouras et al. 1999a, 2001a, Romero et al. 2002, Tsapakis et al. 2002), Temuco, Chile (Tsapakis et al. 2002), Oporto, Portugal (Oliveira et al. 2007a), Gent, Belgium (Kubátová et al. 2002), Birminghan, UK (Harrad et al. 2003), Helsinki, Finland (Kallio et al. 2003), Copenhagen (Oliveira et al. 2007a), the Brazilian cities of Rio de Janeiro (Azevedo et al. 1999), Campo Grande (Ré-Poppi and Santiago-Silva 2002), São Paulo (Vasconcellos et al. 2003) and Campos dos Goytacazes (Azevedo et al. 2002), Philadelphia (Li et al. 2006), Seattle (Kim et al. 2004) and Tel Aviv, Israel (Graham et al. 2004). However, the Los Angeles metropolitan area represents, incontestably, the one that is favoured by a higher number of studies on organic composition of atmospheric aerosols (Fine et al. 2004b, Fraser et al. 1997, 1999, Hildemann et al. 1994, 1996, Lough et al. 2006, Manchester-Neesvig et al. 2003, Rinehart et al. 2006, Rogge et al. 1993e, 1996, Schauer et al. 2002a, Simoneit 1984, Simoneit and Mazurek 1989, Zhu et al. 2004). Comparatively, few studies have investigated remote, rural and semi-rural environments (Alves et al. 2000, 2001, 2007, Cheng et al. 2006, Feng et al. 2007, Oliveira et al. 2007b, Pio et al. 2001a, b, Rissanen et al. 2006, Shimmo et al. 2004a, Simoneit et al. 1990) or have been performed above ocean areas. These investigations include the Mediterranean (Gogou et al. 1996, 1998, Grimalt et al. 1988, Sicre et al. 1987, Simó et al. 1991), the North Pacific (Gagosian et al. 1981, 1982, Kawamura 1995, Kawamura et al. 2003), the South Pacific (Gagosian et al. 1987, Sicre and Peltzer 2004), the Caribbean (Mayol-Bracero et al. 2001) and the Atlantic (Conte and Weber 2002, Simoneit and Elias 2000, Simoneit et al. 1977, 1991b).

SPECIATION OF ORGANIC AEROSOLS

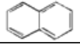
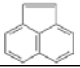
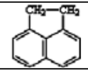
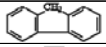
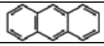
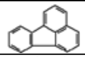
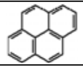
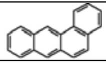
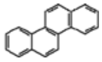
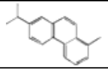
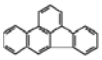
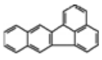
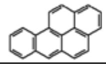
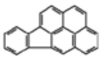
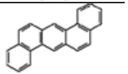
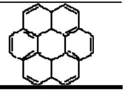
POLYCYCLIC AROMATIC HYDROCARBONS

The polycyclic aromatic hydrocarbons (PAH) represent an organic class more investigated than any other, because they are believed to be carcinogenic and/or mutagenic (Baek et al. 1991, Brown et al. 1996, Crimmins and Baker 2006, Dyremark et al. 1995, Li et al. 2003). The carcinogenicity of PAH is about $1/10^3$–$1/10^4$ of that of 2,3,7,8-TCDD. The PAH concentration in the atmosphere is about 10^4–10^6 times higher than that of TCDD. Therefore, the carcinogenic risk of PAH in the atmosphere is so high that it must be monitored as we would monitor dioxins (Okuda et al. 2006). Fossil fuel combustion is the main anthropogenic activity responsible for the introduction of PAH into the urban atmospheres. Stationary sources such as domestic heating, various industrial processes, incineration and energetic production systems are also responsible for the imprint of polyaromatics (Baek et al. 1991, Cincinelli et al. 2007, Lee et al. 2002, Liu et al. 2006, Sklorz et al. 2007). The natural sources responsible for the release of PAH comprise forest fires, microbiological processing of detritus (e.g. fossil fuel) and mechanisms of biosynthesis carried out by algae, plants and bacteria (Cincinelli et al. 2007, Smith and Harrison 1998).

Atmospheric PAH in the air (Table I) are associated both with the vapour phase and the particulate matter, being incorporated onto aerosols via condensation and adsorption processes (Lewis et al. 1995, Shimmo et al. 2002). The temporal resolution of these compounds in ambient air is limited by the detection limits of current analytical techniques. Either collecting more sample or increasing the analytical sensitivity is required to increase the detectability of PAH and nitro-PAH in ambient air. Greater sampling flow rates and the corresponding larger pressure drops may increase volatilisation losses from the sampling substrate. In addition, the higher sample volumes and longer sampling times may increase the exposure of PAH and nitro-PAH to oxidants. Increasing collection surface area to increase sampler flow rates without additional pressure drops may increase both gas ab/adsorption and the potential for greater matrix contamination (Crimmins and Baker 2006). In most cases, PAH have been collected as

TABLE I

Properties and structures of select PAH (Sources: http://chemfinder.cambridgesoft.com/; http://www.europa.eu.int/comm/environment/air/pdf/annex_pah.pdf).

PAH	Formula	Molecular weight (g mol^{-1})	Boiling point (ºC)	Melting point (ºC)	Vapour pressure (at 25ºC) (Pa)	Water solubility (at 25ºC) (μg L^{-1})	Structure
Naphtalene	$C_{10}H_8$	128	217.9	81	10.4	3.17E4	
Acenaphtilene	$C_{12}H_8$	152	295	92-93	8.9E-1	3.93E3	
Acenaphthene	$C_{12}H_{10}$	154	279	95	2.9E-1	3.93E3	
Fluorene	$C_{13}H_{10}$	166	295	115-116	8.0E-2	1.98E3	
Phenanthrene	$C_{14}H_{10}$	178	340	100.5	1.6E-2	1.29E3	
Anthracene	$C_{14}H_{10}$	178	342	216.4	8.9E-4	73	
Fluoranthene	$C_{16}H_{10}$	202	375	108.8	1.2E-3	260	
Pyrene	$C_{16}H_{10}$	202	393	150.4	6.0E-4	135	
Benzo[a]anthracene	$C_{18}H_{12}$	228	400	160.7	2.8E-5	14	
Chrysene	$C_{18}H_{12}$	228	448	253.8	8.4E-5 (20ºC)	2.0	
Retene	$C_{18}H_{18}$	234	390- 394	99		< 1g L^{-1} (18ºC)	
Benzo[b]fluoranthene	$C_{20}H_{12}$	252	481	168.3	6.7E-5 (20ºC)	1.2	
Benzo[k]fluoranthene	$C_{20}H_{12}$	252	480	215.7	1.3E-8 (20ºC)	0.76	
Benzo[a]pyrene	$C_{20}H_{12}$	252	496	178.1	7.3E-7 (20ºC)	3.8	
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276	536	163.6	1.3E-8 (20ºC)	62	
Benzo[ghi]perylene	$C_{22}H_{12}$	276	545	278.3	1.4E-8	0.26	
Dibenzo[a,h]anthracene	$C_{24}H_{14}$	278	266.6	524	1.3E-8 (20ºC)	0.5 (27ºC)	
Coronene	$C_{24}H_{12}$	300	525	>350	2E-10	0.122	

particulate compounds on glass- or quartz-fibre filters by using air conventional high-volume samplers. However, as pointed out in several articles, 3- to 5-ring PAH, which have relatively high vapour pressures, are also found in the gas phase at ambient temperatures and their retention on the filter media is not complete. Thus, it has been recommended the simultaneous utilisation of trapping materials such polyurethane foam plugs or resins for sampling the gaseous fraction (Conde et al. 2004, Dimashki et al. 2000, Kavouras et al. 1999a, Knecht and Woitowitz 1988, Ligocki and Pankow 1989, Lim et al. 1999, Shimmo et al. 2002, 2004b, Zielinska et al. 2004).

It is known that PAH undergo chemical and photochemical degradation in the atmosphere, especially in the presence of atmospheric oxidants such as ozone, hydroxyl radical and nitrate radical. These reactions continue during sampling. As a result, the PAH concentration profiles will be changed during sampling and their potential adverse health effects will be over- or underestimated (Liu et al. 2006). A possible way to reduce ozonisation reaction during sampling is the use of a denuder to remove ozone from the air stream prior to the collection of aerosol particles on the filter. Recently, some researchers have applied ozone denuders to high- and low-volume sampling to inspect their influence on the sampling of ambient PAH. Schauer et al. (2003b) made use of an activated carbon denuder in a low-volume sampler. It was found that the degradation of 5- and 6-ring PAH on filter had a near-linear dependence on ozone volume mixing ratio. According to this investigation, filter reaction artefact can lead up to a 2-fold underestimation of real atmospheric PAH levels. Tsapakis and Stephanou (2003) employed a high-volume oxidant denuder, consisting of tubes coated with water/glycerol KNO_2 solution. Most of the gas and particulate phase PAH were vulnerable to ozone degradation under long sampling times with high O_3 levels. Creutznacher et al. (2003) studied the ozone cross-sensitivity of particle accumulated PAH, using a manganese oxide ozone denuder. In disagreement with the previous studies, the authors concluded that, for an average ozone level of 60 μg m^{-3}, only benzo[a]pyrene had a perceptible degradation of approximately 15% in the non-denuded samples by comparing their average yearly concentrations. Liu et al. (2006) used a MnO_2 ozone denuder and found that levels of 5- to 7-ring PAH were underestimated in non-denuded samples, while the 4- to 5-ring oxygenated PAH were overestimated. The highest losses due to reaction with atmospheric oxidants were observed for benzo[a]pyrene and perylene.

Extraction of PAH from their sampling media has been traditionally performed using Soxhlet or ultrasonic agitation. A more recent alternative to these two methods is the use of supercritical fluid extraction (SFE) [Friedrich and Kleiböhmer 1997, Hawthorne and Miller 1987, Lewis et al. 1995, Shimmo et al. 2002, 2004b]. Quantitative analysis is generally performed by GC or high HPLC coupled with fluorescence, UV, FID and MS detectors (Becker et al. 1999, Brown et al. 1996, Dimashi et al. 2000, Lewis et al. 1995). Some authors reported also direct analysis of PAH by thermal desorption GC/MS applied mostly to urban dust reference materials (Crimmins and Baker 2006, Falkovich and Rudich 2001, Waterman et al. 2000). Ochsenkühn-Petropoulou et al. (2003) presented the development of an on-line technique, the pyrolysis/GC-MS for the identification and the quantification of PAH in airborne particulate matter collected on cellulose filters. By this technique a pre-treatment of the samples is not necessary, avoiding the time consuming and expensive extraction step (Fabbri et al. 2002).

Since traffic, a prominent source of polynuclear hydrocarbons, present large emissions and have dramatic effects on air quality, attention has been focused on urban areas, especially in busy roads, tunnels and city centres (Tables II and III). Background concentrations of PAH reported at remote sites are 1-2 of magnitude lower (Halsall et al. 1997). Some other studies have been devoted to the identification of PAH in particular combustion sources or in the proximity of specific emissions sources: wildfires (Masclet et al. 1995, Okuda et al. 2002), charcoal grilling (Dyremark et al. 1995), biomass burning (Fine et al. 2001, 2002a, b, 2004a, Freeman and Cattell 1990, Hays et al. 2005, Keshtkar and Ashbaugh 2007, Lee et al. 2005, Oros and Simoneit 2001a, b, Rogge et al. 1998, Santos et al. 2002, Schauer et al. 2001, Sheesley et al. 2003), ferries (Cooper et al. 1996), diesel exhausts (Cho et al. 2004, Jiao and Lafleur 1997, McDonald et al. 2004, Reilly et al. 1998. Schauer et al. 1999b, Zielinska et al 2004), burning of sugar plantations (Godoi et al. 2004, Santos et al. 2002), near power plants (Kalaitzoglou et al. 2004), vegetable oil processing plant (Kavouras et al. 2001b), cooking with seed oils (Schauer et al. 2002b), incinerators (Besombes et al. 2001, Lee et al. 2002, Mao et al. 2007), burning of foliar fuels (Hays et al. 2002), roadside (Harrison et al. 2003) and vehicle exhausts for different fuels, lubricants and engine operating conditions (Brandenberger et al. 2005, Lim et al. 2005, 2007, Pedersen et al. 1980, Schauer et al. 2002c, Westerholm et al. 1988, 1992, Yang et al. 2005b, 2007, Zielinska et al. 2004).

The discovery in the 1970s of potent mutagenic nitro-PAH in the organic extracts of atmospheric particu-

TABLE II
Comparison of PAH concentrations obtained at road tunnels throughout the world (ng m^{-3}).

Compound	Baltimore USA Gordon et al. (1989)	Santa Barbara Brazil Miguel and Pereira (1989)	Chicago USA Khalili et al. (1995)	Queensway Birmingham, UK Smith and Harrison (1996)
Fluorene	18.0	96.9	300	25.6
Acenaphthene	2.9	4.19	177	9.41
Anthracene	20.0	69.6	117	21.1
Fluoranthene	27.0	76.3	193	29.9
Pyrene	7.6	51.3	90.2	11.6
Benz[a]anthracene		69.5	77.9	18.5
Chrysene		88.2	43.6	5.4
Benzo[b]fluoranthene		36.7	41.2	12.7
Benzo[k]fluoranthene	5.8	90.7	62.6	35.2
Benzo[a]pyrene	8.0	162.0	17.0	35.2
Benzo[ghi]perylene	4.6	84.2	20.0	21.5
Indeno[1,2,3-cd]pyrene	4.7			11.8

Compound	Kurashiki, Japan (north entrance) Oda et al. (2001)	Kurashiki, Japan (south entrance) Oda et al. (2001)	Kurashiki, Japan (centre of the tunnel) Oda et al. (2001)	Rio de Janeiro Azevedo et al. (1999)
Fluorene				
Acenaphthene				2.2
Anthracene				
Fluoranthene	12	13	25	12.1
Pyrene	18	20	25	18.2
Benz[a]anthracene	5.4	6.6	11	2.1
Chrysene				
Benzo[b]fluoranthene	5.5	7.0	11	
Benzo[k]fluoranthene	2.5	2.6	4.4	
Benzo[a]pyrene	4.2	6.2	11	0.6
Benzo[ghi]perylene	3.8	5.3	9.8	0.5
Indeno[1,2,3-cd]pyrene	1.5	2.2	3.1	

late matter and later in the extracts of diesel exhausts has led to a sharp increase in interest in the environmental occurrence of these compounds and in the improvement of analytical procedures for their quantification (Bamford and Baker 2003, Bamford et al. 2003, Dimashki et al. 2000). Nitro-PAH can be 100,000 times more mutagenic and 10 times more carcinogenic compared to the unsubstituted-PAH (Bamford and Baker 2003). Concentrations of the different compounds vary with the extent of urbanisation (Table IV). For example, 1-nitropyrene is normally the most abundant nitro-PAH measured in urban/industrial cities; however, in suburban and rural locations, the concentration of nitro-PAH produced from gas-phase reactions, such as 2-nitrofluoranthene, are typically higher (Bamford and Baker 2003). The nitroaromatic constituents seem to derive from a wide range of emitter sources, including combustion processes, vehicle exhausts, stationary sources, kerosene heaters, cigarette smoke and atmospheric photo-chemical reactions (Bamford and Baker 2003, Ciccioli et al. 1996, Dimashki et

TABLE III

Comparison of PAH concentrations obtained at urban areas throughout the world (ng m^{-3}). I – Santiago of Chile (Kavouras et al. 1999a); II – Birmingham, UK (Smith and Harrison 1996); III – Munich, Germany (Schnelle–Kreis et al. 2001); IV – Hong Kong, China (Zheng et al. 1997); V – Pavia, Italy (Minoia et al. 1997); VI – London, UK (Brown et al. 1996); VII – Portland, USA (Ligocki and Pankow 1989); VIII – Moe, Australia (Lyall et al. 1988); IX – Tokyo, Japan (Okuda et al. 2000); X – Temuco, Chile (Tsapakis et al. 2002); XI – Kuala Lumpur, Malaysia (Omar et al. 2002); XII – Fuji, Japan (Ohura et al. 2004); XIII – Shimizu, Japan (Ohura et al. 2004); XIV – Lahore, Pakistan (Smith et al. 1996); XV – São Paulo, Brazil (Martinis et al. 2002); XVI – Bravo Murillo, Las Palmas de Gran Canaria, Spain (Cancio et al. 2004); XVI –industrial park in Taichung, Taiwan (Fang et al. 2004); XVII – roadside, Hong Kong (Ho et al. 2002); XVIII – Seoul, Korea (Park et al. 2002); XIX – Athens, Greece (Mandalakis et al. 2002).

	Phenanthr.	Anthrac.	Fluoranth.	Pyrene	MPhen.	B[a]ant.	Crysene	B[b]fl.
I	0.00-1.54	0.00-0.04	0.00-0.23	0.00-0.07		0.01-0.14	0.03-0.50	0.06-1.73
II	1.08/0.25	0.39/0.16	1.17/0.55	2.36/0.55		1.48/0.13	2.21/0.21	1.87/0.34
III			0.02-2.12	0.02-2.16			0.01-2.01	
IV	1.06		0.23	0.58			1.00	
V						0.19/0.08		0.38/0.25
VI	24.0/19.5	2.0/1.8	8.0/19.8	12.0/17.5			6.4/4.5	
VII	0.28				0.16-0.19	1.2		
VIII				0.072				
IX	27.0*	27.0*	5.2	3.1	13.3			
X	50.6	6.7	18.9	15.5	12.3	115.7	163.2	98.5**
XI	0.32	<0.03		0.18	0.06	0.06	0.09	0.05
XII	26.27/12.57	0.42/0.93	9.84/12.57	3.00/2.86	2.22/1.35	0.12/0.98	0.41/1.60	0.06/0.15
XIII	17.25/10.10	0.32/0.34	5.56/4.74	1.51/1.19	0.81/1.69	0.04/0.39	0.11/0.93	0.02/0.06
XIV	0.97	4.99	2.81	2.93		5.39	8.64	9.87
XV	10.9	1.8	6.9	12.2		3.2	3.5	
XVI	145.7	184.7	86.6	124.7		16.9	37.3	9.1
XVII	30.9		7.1	6.7				
XVIII	16.46	2.7	8.1	12.56		2.62	3.62	4.89#
XIX	0.46	0.14	0.15	0.19	0.43	0.11	0.45	0.86

	B[j+k]fl.	B[e]pyr.	B[a]pyr.	I[1,2,3-cd]P	B[ghi])Per	D[a,h]A	Coron.
I	0.07-1.34	0.03-0.86	0.03-0.68	0.01-0.32	0.10-1.32		0.05-0.66
II	1.12/0.14		0.73/0.23	1.95/0.42	1.91/0.76	0.78/0.07	1.03/0.27
III	0.06-4.51		0.02-1.66		0.02-2.75		
IV		0.65	0.08	0.32	0.33		0.28
V	0.18/0.02		0.370.03	0.13/b.d.l.		0.09	
VI	6.1/2.5	7.0/3.2	2.7/1.1	3.6/1.8	4.1/2.0	0.2/0.1	2.0/1.1
VII	3.6						
VIII	0.104	0.26	0.2		0.46		0.17
IX	1.0	0.4	0.1	0.4	0.4		0.20
X	98.5**	73	98.5	68.8	75.8		
XI	0.05	0.03	0.05	0.18	0.47	0.05	0.41
XII	0.38/1.69	0.32/1.18	0.18/1.08	0.18/1.14	0.29/1.29	0.04/0.11	0.07/0.46
XIII	0.12/0.90	0.26/0.70	0.07/0.53	0.10/0.61	1.22/0.63	0.01/0.06	0.05/0.27
XIV	4.61		9.32	12.31	14.64	3.85	5.40
XV		0.4	0.7	0.1	0.2		
XVI	12.6	29.1	9.7	5.2	6.5	5.6	22.2
XVII			0.5	0.5	0.7	0.1	
XVIII	4.89#		2.55	3.59	3.21	0.55	
XIX	**	0.35	0.17	0.45	0.44	0.08	4.94

Note: MPhen = Methylphenanthrenes; B[a]ant. = Benzo[a]anthracene; B[b]fl. = Benzo[b]fluoranthene; B[j+k]fl. = Benzo[j+k]fluoranthene; B[e]pyr. = B[e]pyrene; B[a]pyr. = B[a]pyrene; I[1,2,3-cd)P = Indeno[1,2,3-cd)pyrene; B[ghi])Per. = Benzo[ghi])perylene; D[a,h]A = Dibenzo[a,h]anthracene, Coron. = Coronene; cells in white represent concentrations not determined; / = summer/winter concentrations; b.d.l. = bellow detection limit; *Phenanthrene+Anthracene; **Benzo[b+j+k]fluoranthene; # Benzo[b+k]fluoranthene.

al. 2000, Korfmacker et al. 1987, Perrini et al. 2005). The specific isomers of the nitro-PAH observed in ambient air suggest that they are formed in the atmosphere through the gas-phase reactions of the 2- to 4-ring PAH (Schneider et al. 1990). Thus, ambient air contains nitro-PAH isomers distinct from the PAH electrophilic nitration products reported in direct emissions. The nitro-PAH isomers not formed from electrophilic nitrations were observed, however, in laboratory simulations of the atmospheric reactions of the PAH, providing strong evidence for atmospheric formation of nitro-PAH (Atkinson and Arey 1994). The apprehension committed to mono- and dinitro-derivates of PAH is due to their ability to provoke direct mutagenic activity and to contribute for 10% to the total mutagenicity of inhalable suspended particles in polluted areas (Atkinson and Arey 1994, Marino et al. 2000). Though numerous nitro-PAH have been detected in atmospheric as well as emission particulates, nitrated pyrenes and fluoranthenes seem to be responsible of the main effect on health of humans (Marino et al. 2000).

The occurrence of 2-nitrofluoranthene and 2-nitropyrene in particulate matter collected in urban, suburban, forest and remote areas located in Europe, America, Asia and Antarctica was investigated by Ciccioli et al. (1996). The results that were obtained confirm the photochemical origin of these components by gas-phase reactions with OH radicals and their ubiquitous occurrence in the troposphere. In addition, it was verified that to disperse photochemically produced nitro-PAH in areas where their occurrence is somehow prevented, carbon particles can contribute to their formation by providing a suitable surface for converting NO_2 into nitrous and nitric acid by reaction with water. Bamford and Baker (2003) measured 26 nitro-PAH in an urban and suburban area of Baltimore. Concentrations of nitrated compounds produced from gas-phase reactions were significantly correlated with levels of NO_x. The only nitro-PAH negatively correlated with NO_x and correlated with O_3 were 3-nitro- and 4-nitrophenanthrenes, suggesting a different formation mechanism. The relative contribution of gas-phase reactions and primary emission sources of nitrated aromatics were evaluated using source specific concentration ratios of nitrofluoranthene and nitropyrene: 2-NF/1-NP and 2-NF/2-NP. It was concluded that the daytime OH-initiated reaction was the dominant gas-phase formation pathway of 2-nitrofluoranthene, especially in the summer. Laser desorption ionisation time-of-flight (LDI-TOF) mass spectrometry has been used by Bezabeh et al. (1999) for the selective screening of PAH and nitro-PAH in trapped airborne particles. In addition to PAH, the investigators selectively detected nitro-PAH, which are known to be 1–2 orders of magnitude less abundant than their analogous PAH, in a complex environmental matrix by employing low laser powers and negative ion detection. The three detected nitro-PAH, at estimated concentration of <100 pg m^{-3} of air (<300 ng g^{-1} of particulate matter), were tentatively identified as nitropyrene, nitroperylene, and nitrodibenz[a,h]anthracene. PAH with molecular masses of 300–450 Da were observed in positive ion spectra, illustrating the capability of the LDI mass spectrometry technique to examine a mass range beyond that accessible by GC/MS. The ability to examine aerosols from small air volumes (0.32–0.98 m^3) is essential to the understanding of factors that affect aerosol composition and may be useful for identifying individual vehicles that emit greater quantities of mutagenic combustion by-products. LDI-TOF mass spectrometry has proven to be a powerful analytical method for the screening of PAH and nitro-PAH from aerosol particulate matter and promises to support more extensive studies of toxic constituents of combustion aerosols. Hayakawa et al. (2002) measured four nitro-PAH, pyrene and benzo[a]pyrene in the downtown and in a suburban area of Kanazawa, Japan, in each season for seven years. Concentrations of these PAH and nitro-PAH were higher at the downtown sites than at the suburban site, suggesting the dilution of these compounds during the transportation from the downtown to the suburban area. The concentration ratios of nitro-PAH to PAH were larger at the downtown sites than at the suburban site. Studies using UV light and sunlight showed that degradation of nitro-PAH was faster than that of PAH. Thus, the lower concentrations of nitro-PAH in the suburban sites may be due to their being photodegraded faster than PAH during the atmospheric transportation from the downtown area to the suburban area.

The partitioning of the PAH between the gaseous and particulate phase is an important factor in estimating the rate of removal processes. PAH are removed from the atmosphere by transformation, wet and dry depo-

TABLE IV
Comparison of atmospheric concentrations of selected nitro-PAH (pg m^{-3}) measured in several locations around the world. 1-NNap (1-nitronaphthalene); 9-NAnth (9-nitroanthracene); 2-NFluor (2-nitrofluoranthene); 3-NFluor (3-nitrofluoranthene); 1-Npy (1-nitropyrene); 2-Npy (2-nitropyrene); 7-NB[a]A (7-nitrobenzo[a]anthracene); 6-NCh (6-nitrochrysene).

Location	Reference	1-NNap	9-NAnth	2-NFluor	3-NFluor	1-Npy	2-Npy	7-NB[a]A	6-NCh
Baltimore, MD	Bamford and Baker (2003)								
Winter		59	64	60	0.5	27	6.5	23	0.4
Summer			53	99	0.3	8.1	2.7	3.4	0.1
Fort Meade, MD	Bamford and Baker (2003)								
Winter		23	46	49	0.3	21	4.0	12	0.4
Summer			15	28	0.3	1.4	0.8	0.7	0.3
Birmingham, UK (a)	Dimashki et al. (2000)	89	187	221	90		33		
Copenhagen, Denmark (b)	Feilberg et al. (2001)		63	91	39	127	20		
Riso, Denmark (c)	Feilberg et al. (2001)		30	60	32	30	8		
Torrance, CA (d)	Arey et al. (1987)								
Night-time		2300	100	400		30	30		
Day-time		3000	50	300		40	40		
Houston, TX (e)	Wilson et al. (1995)	354	29	39		9.3			2.3
Columbus, OH (f)	Chuang et al. (1991)		50	60	20				
Claremont, CA (g)	Zielinska et al. (1989)			400	1.0	16	3		
Athens, Greece (h)	Marino et al. (2000)			90	60	40			
Rome, Italy (i)	Ciccioli et al. (1996)			470		70	70		
Madrid, Spain (j)	Ciccioli et al. (1996)			70	10	20			
Montelibretti, Italy (k)	Ciccioli et al. (1996)			91		13	16		

(a) Mean of 25 samples, Nov. 1995-Feb. 1996; (b) Mean of 20 winter-spring samples, 1996; (c) Mean of 14 samples, Feb. 1998-1999; (d) Mean of 6 samples collected 20 km south of Los Angeles, Jan.-Feb. 1985; (e) Mean of 19 samples measured between Aug. 1990-1991; (f) winter 1986/97; (g) Mean of 6 samples collected 30 km northeast of central Los Angeles; Sept. 1995; (h) Mean of 32 samples, Jan.-Dec. 1996; (i) Mean of 10 samples, Sept. 1991; (j) Mean of 14 samples, Oct. 1990; (k) Mean of 22 samples, Feb. 1988-Dec. 1994.

sition, and air–water exchange. The concentration and deposition levels of a PAH compound are influenced by the composition and strength of the emissions, the turbulence and the removal process type. There are two main removal mechanisms, including dry and wet deposition, in the atmosphere. Dry deposition refers to the transfer of both gaseous and particulate to a surface including soil, water, and vegetation when there is no precipitation (Tasdemir and Esen 2007). Wet deposition of airborne PAH occurs with the scavenging of particles by, and partitioning of organic vapour into, rain and snow (Sahu et al. 2004). A comparison of different methods for measuring deposition fluxes of particulate matter and PAH in the ambient air can be found in Shannigrahi et al. (2005). Besides the atmospheric loss/removal processes, the PAH air concentrations are controlled by a complex array of variables, some of which may also influence the seasonality in ambient levels. These variables include secondary sources of PAH into the atmosphere (i.e. possible volatilisation from soil, water, vegetation or/and urban surfaces), photochemical reactions, scavenging by vegetation, dilution/advection factors that are influenced by wind speed and direction, and mixed boundary layer height. Finally, seasonal temperature changes drive the gas to particle distribution and atmospheric reaction rates of PAH (Prevedouros et al. 2004).

The particulate phase PAH tend to distribute in combustion aerosols (such as soot particles) that dominantly distribute in the fine particle size range. On the other hand, considerable amounts of PAHs are also found in coarser particles, which consist mostly of geologic materials such as mineral particles. Thus, a sizeable amount of the PAH in the atmosphere is apparently associated with mineral particles. (Tamamura et al. 2007). PAH may be sorbed on dust particles, and transported over long distances (Fang et al. 2005). Long-range transport of PAH over hundreds to thousands of km has also been of concern in various locations in the world

(Hou et al. 2006, Hung et al. 2005, Tamamura et al. 2007).

HOMOLOGOUS COMPOUND SERIES

Aliphatic hydrocarbons, particularly normal alkanes, represent ubiquitous organics which are released into the atmosphere by many sources, rendering difficult the association between the levels of different compounds and their origin. Selected mass fragmentograms for *n*-alkanes can be obtained by searching m/z 85 or 99. Usually, the homologous compound distributions of *n*-alkanes in atmospheric aerosols range from C_{12} to C_{40}. The higher molecular weights with an odd carbon number represent typical *n*-alkanes attributable to natural plant waxes (Abas and Simoneit 1996, 1997). It should be referred that the layer of the plant cuticles comprises long-chain, usually saturated aliphatic molecules with even-carbon called epicuticular waxes. The wax layer could be composed of up to 100 normal saturated hydrocarbons, grouped into at least 12 substituent classes having different functional groups (Günthardt-Goerg 1994). Epicuticular waxes form a bloom on the surface consisting of wax protrusions that are characteristic of each plant species (Rogge et al. 1993e). The epicuticular wax layer ranges from only a few nanometres to a few microns in thickness. Due to its position at the leaf surface, composition can certainly be altered by environmental factors, such as rain, wind, high temperatures and air pollutants, such as ozone (Percy et al. 1994). Plant wax lipids could be released, for example, by both a dust blasting effect on plant surfaces and wind abrasion causing sloughing of wax directly (Percy et al. 1994). The dominance of the n-C_{27}, n-C_{29} and n-C_{31} homologs generally observed during summer shifted towards lower carbon numbers in the range n-C_{21}-n-C_{25} during the colder season. Changes in the modal chain-length of *n*-alkane distributions have been attributed to differences in growing-season temperatures of the source regions (Simoneit et al. 1991a). However, Schefuß et al. (2003) suggest a large influence of the regional precipitation regime on the chain-length distributions of leaf-wax lipids, in agreement with their biologic functionality as regulators of the plant moisture balance.

Linear alkanones and alkanals are a group of oxygenated compounds identified in aerosols. The distribution diagrams are given by the m/z 58 and 82 of the GC/MS analysis, respectively. The *n*-alkan-2-ones $<C_{20}$ may in part be derived from anthropogenic activity (Seinfield and Pandis 1998, Simoneit et al. 1988) or from atmospheric oxidative processes (Simoneit et al. 1988). In some cases, the possible absence of alkanals of higher masses ($>C_{20}$) may reflect their reactivity to oxidation yielding alkanoic acids. Long chain *n*-alkan-2-ones are typically found in the waxy portion of the plant materials. The homologous series may range from C_8 to C_{38}. The *n*-alkanals with odd carbon number higher than 20 are of biogenic origin, whereas the lower compounds indicate oxidation of alkanes as possible precursors (Gogou et al. 1996). Aldehydes may occur in the epicuticular waxes as a result of the reaction of O_3 on unsaturated hydrocarbons (Garrec 1994).

Typical distributions of *n*-alkanols range from C_{10} to C_{36}. The selected mass fragmentograms for the corresponding trimethylsilyl ethers that result from the derivatisation process is plotted by searching the m/z 75. Even-to-odd carbon number predominance is found in aerosols with a major biogenic contribution. The homologs $<C_{20}$ are not found in fresh vascular plant waxes and may have a microbial origin. The homologs $>C_{20}$ may derive from epicuticular vegetation (Abas and Simoneit 1996, 1997).

Fatty acids constitute another chief group of solvent-extractable compounds present in aerosol samples. They are majorly represented by *n*-alkanoic, *n*-alkenoic, dicarboxylic and oxo-carboxylic acids. The distribution patterns of the*n*-alkanoic acids, which present m/z 74 and 87 key fragments (as methyl esters), range usually from n-C_7 to n-C_{35}. A pattern where the n-C_{22}-n-C_{28} mode is predominant is characteristic of contributions from higher plant waxes. The homologs $< n$-C_{20} are probably derived from microbial sources, although these acids are ubiquitous in biota (Abas and Simoneit 1996, Simoneit et al. 1990). Other sources are cooking, grilling and food preparation, where these compounds are directly volatilised into the fumes (Rogge et al. 1991). These substances could also be attributed to microbial reworking during storage of vials that can occur even when sample conservation is done at –20°C (Aceves and Grimalt 1993). In addition, the microbial lipids could also arise by the remobilisation of soil (Simoneit et al. 1988). Other biogenic contributors are fungi, bacteria, spores, pollen and algae (Rogge et al. 1993e). Lower molecular weights for *n*-alkanoic acids ($<C_{18}$) were found in emissions from petroleum-based sources such as gasoline- and diesel-powered vehicle exhaust or from distillate fuel oil, tire wear debris and road dust (Rogge et al. 1993a). The synthesis of *n*-fatty acids in plant leaves is practically identical to the synthesis of *n*-alkanes. These compounds proceed via elongation and descarboxylation reactions involving C_{16} and C_{18} *n*-fatty acids (Rogge et al. 1993e). Contrary to plant epicuticular wax, seeds (and seed oils, e.g. cooking oil), plant organelles, leaf cells, chloroplast and pollen contain predominantly *n*-C_{16}, *n*-C_{18}, mono-unsaturated ($C_{n:1}$), di-unsaturated ($C_{n:2}$) and poly-unsaturated fatty acids (Rogge et al. 1993b). It should be noted that the unsaturated fatty acids are indicators of recent biogenesis (Simoneit et al. 1988, Abas and Simoneit 1996).

Unsaturated *n*-fatty acids (alkenoic acids) are emitted to the atmosphere from microbial sources and from the processing, degradation and combustion of plant and animal constituents (Rogge et al. 1993e). Meat cooking is an important source of *n*-alkenoic acids, mainly oleic ($C_{18:1}$) and palmitoleic acid ($C_{16:1}$) (Rogge et al. 1991). Phytoplankton and bacteria also contain a number of unsaturated fatty acids (Rogge et al. 1993e, Simoneit et al. 2004a). Biomass burning presents, in general, as primary components palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids (e.g. Oros and Simoneit 1999). Once emitted into the atmosphere, unsaturated fatty acids, which are indicators of recent biogenesis (Simoneit et al. 1991a), are likely to be attacked by free radicals, ozone and other oxidants, producing aldehydes, lower weight carboxylic acids and dicarboxylic acids (Rogge et al. 1993e). One method that has been used to gauge the age of aerosol is to take the ratio between the concentrations of the saturated C_{18} alkanoic acid ($C_{18:0}$) and the mono-unsaturated C_{18} acid ($C_{18:1}$). This ratio is used as an aerosol age indicator since the mono-unsaturated acid breaks down much faster by atmospheric oxidation than the saturated analogue. The abundance of the saturated acid compared to the mono-unsaturated homologue can, therefore, indicate a relative decomposition rate (Brown et al. 2002). Values between 5 and 11, with an average of 6.6, for the $C_{18:0}/C_{18:1}$ ratio were reported for rural samples collected in remote Big Bend National Park, Texas. These high, rural-like ratios were ascribed to a combination of local rural biogenic emissions and aged aerosol advected from urban areas (Brown et al. 2002). While stearic and palmitic acids are, as individual compounds, not source specific, the $C_{18:0}/C_{16:0}$ fatty acid ratio is unique and can be used in source apportionment studies. The major contributors for particulate matter have $C_{18:0}/C_{16:0}$ ratios ranging from 0.17 to 0.71, depending on source type. In countries where dried cattle dung is used for cooking purposes, fine particulate smoke presents the characteristically elevated ratio around 2, whereas for foliar vegetation or wood smoke and car exhaust, values below 0.5 are typical. The surface soil and dusts from feedlots and open lot dairy farms showed an average $C_{18:0}/C_{16:0}$ ratio of 3.0. Values between 0.5 and 1 were also found in agricultural fields, dust from paved and unpaved roads and in $PM_{2.5}$ of rural and urban sources, such as hamburger charbroiling (Rogge et al. 2006 and references therein).

A series of alkanedioic acids is frequently present in atmospheric aerosol samples. These compounds could be oxidation products from biopolymers or other lipid components (e.g. hydroxyalkanoic acids), or incomplete combustion products (Abas and Simoneit 1996). Thus, they could represent secondary organic compounds formed by photochemical reactions. Oxo-carboxylic acids are likely photo-oxidation products from cyclic olefins and unsaturated fatty acids also detected in aerosol samples. As examples, we have the C_5 and C_6 homologs, produced by oxidation of anthropogenic cyclic olefins, and the C_8 and C_9 compounds which are formed by photo-oxidation of unsaturated carboxylic acids such as the oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids (Gogou et al. 1996). Products like 9-oxononanoic acid and nonanoic acid, both detected in the aerosol samples, form the final reaction products of the oleic acid with ozone (Rogge et al. 1993e). Aliphatic dicarboxylic, acids found in the particulate matter are an important compound class due to their possible formation by chemical reaction in the atmosphere (Grosjean and Seinfeld 1989, Rogge et al. 1993e). Kawamura and Kaplan (1987) found that butenedioic related acids (methyl maleic, succinic, and malic acid) are the most frequent particulate dicarboxylic acids with origin in combustion engines. Rogge et al. (1991) reported meat cooking as an emission source of C_4-C_8 dicarboxylic acids, pointing out the importance of adipic acid (hexanedioic). Pereira et al. (1982) identified dicarboxylic acids ranging from C_4 to C_9 in airborne ash resulting from pyrolysis of organic soil constituents, plants and trees. Acids in the range C_{10}-C_{24} have been stressed by Simoneit and Mazurek (1982) as possible oxidation products of hydroxy acids from vegetation.

Table V presents the levels of the homologous compound series in atmospheric aerosols from different environments all over the world. Fatty acids and *n*-alkanes, followed by *n*-, are the dominant organic classes. The homologous compounds associated with fossil fuel and biomass burning may be up to 30 times more abundant in winter that in summer due to stronger emissions during the cold season (Wang et al. 2006b). The increase in concentrations during winter could also be related to the fact that lower winter temperatures promote the decrease of mixing heights and the existence of inversion layers, leading to poorer dispersion and diminishing the dilution factors and, therefore, conducting to an increase of atmospheric pollutant concentrations. On the other hand, as some compounds have a highly temperature dependent gas/particle partitioning coefficient, the high summer temperature could promote their displacement from particulate to gas phase, decreasing their aerosol phase concentrations (Oliveira et al. 2007a). In China, concentrations of the homologous organic classes are generally 1-3 orders of magnitude higher than in developed countries (Wang et al. 2006b). The levels measured in the background marine atmosphere over the north Atlantic are lower than those measured in the Mediterranean and of the same order as those reported for the remote Chichi-Jima Island in the western Pacific. In contrast, the concentrations are higher than those registered in the aerosol of Enewetak Atoll, north Pacific. Hydrocarbon concentrations ranging from 30 to 2800 ng m^{-3} were found by Simoneit et al. (1991b) over the south Atlantic. The highest values were observed when approaching part of Tierra del Fuego, where extensive petroleum production occurred. The high *n*-alkane concentrations (0.3–680 ng m^{-3}) found by Simoneit and Elias (2000) in samples of particulate matter from the atmosphere over the Atlantic along the South American and African continents were associated to epicuticular wax components of continental vegetation, which are introduced into the aerosols mainly by direct emission due to abrasive and related processes. However, long-range transport of smoke from biomass burning off the continents was also found an important factor influencing the composition of marine aerosols (Alves et al. 2007).

Molecular Markers

The assessment of natural *versus* anthropogenic contributions to the carbonaceous aerosol is often done by searching molecular markers or tracers, which include organic compounds that are source specific, react slowly in the atmosphere and do not change to gas-phase during the transport. Numerous compounds were identified and quantified in the atmospheric samples, including cigarette smoke components, vehicle exhaust markers, meat smoke tracers, combustion products of plastics, coal burning emissions, phytosterols of higher photosynthetic plants and wood smoke constituents (Table VI).

Tobacco smoke

It has been pointed out that the major tracers for tobacco smoke in the urban atmosphere are 2-methyl- (*iso*-) and 3-methylalkanes (*anteiso*-alkanes) ranging from C_{29} to C_{34} (Kavouras et al. 1998a, Morrical and Zenobi 2002, Rogge et al. 1994). Their mass spectra contain the typical fragmentation pattern ($M^{\bullet +} - [C_3H_7^{\bullet}]$, *m*/*z* 393) for the branched alkanes. Results from the analysis of environmental tobacco smoke showed that several unique peaks are present in the mass spectrum when compared to other combustion sources, such as automobiles and diesel trucks (Table VII). In particular, ions at *m*/*z* 118, 132, 146, and 160 are consistently present and are not found in other combustion sources (Morrical and Zenobi 2002). Other researchers have chosen compounds such as nicotine (LaKind et al. 1999, Leaderer and Hammond 1991) and solanesol (LaKind et al. 1999, Tang et al. 1990) as markers for tobacco smoke. Nicotine and solanesol are both specific to environmental tobacco smoke and may be appropriate for the indoor environment where their reactivity may be slower, but have been shown not to be very suitable for the outdoor environment due to a high rate of reaction (Morrical and Zenobi 2002). Using *iso*- and *anteiso*-alkanes, with nicotine as a confirming tracer, ambient fine cigarette smoke particles were estimated

TABLE V

Concentrations (ng m^{-3}) of homologous compound series in atmospheric aerosols from different environments all over the world.

Sampling area	Organic classes						References
	n-alkanes	*n*-alkanals	*n*-alkanones	*n*-alkanols	Fatty acids (saturated)	Fatty acids (unsaturated)	
Rural coastal area of Eastern Mediterranean	5.09-35.24	0.9-16.85	0.4-5.12	2.74-94.50	22.06-112.63	2.12-6.14	Gogou et al. (1998)
Melbourne, Western Mediterranean	7.3-13						Simó et al. (1991)
Cruise in the Western Mediterranean	7.1-14						Sicre et al. (1987)
Minety Mile Beach, New Zealand, South Pacific	0.022-0.270			0.048-0.488	0.431-0.722		Gagosian et al. (1987)
Enewetak Atoll, Marshall Islands, North Pacific	0.023-0.160			0.072-0.245	0.040-0.381		Gagosian et al. (1981)
South Atlantic from about 30-70°S	30-2800			1-1200	7.0-26.0		Simoneit et al. (1991b)
Chichi-Jima, Western North Pacific	0.11-14.1 (1.8)			0.18-19.7 (2.2)	2.4-60.2 (13.8)		Kawamura et al. (2003)
Atlantic Ocean, along the South American and African Continents	0.3-680	0.1-780					Simoneit and Elias (2000)
Kosan, Sapporo, Chichi-Jima, Western North Pacific	0.3-150.3			0.80-134.2	3.2-143.0		Simoneit et al. (2004a)
Ninety Mile Beach, West coast of the North Island, New Zealand	0.022-0.539	0.010-0.26		0.048-0.766			Sicre and Peltzer (2004)
Terceira Island, North-Eastern Atlantic	0.30-6.18 (1.11)	0.11-3.27 (1.01)	0.05-1.69 (0.18)	0.75-18.61 (3.47)	0.42-86.56 (7.09)		Alves et al. (2007)

TABLE V (continuation)

Sampling area	Organic classes						References
	n-alkanes	*n*-alkanals	*n*-alkanones	*n*-alkanols	Fatty acids (saturated)	Fatty acids (unsaturated)	
15 Chinese cities	516 (winter) 138 (summer)			91 (winter) 21 (summer)	1020 (winter) 457 (summer)		Wang et al. (2006b)
Two urban areas of Chile	258-282				756-843	111-604	Tsapakis et al. (2002)
Hong Kong	8.7-41.1			6.0-18.7	31.1-157.9		Zheng et al. (2000)
Shanghai	12.2-341.9			4.4-170.9	93.6-668.0		Feng et al. (2006)
Philadelphia, USA	7.06-124.6				6.1-486.9		Li et al. (2006)
Rubidoux, California	49				258	20	Rogge et al. (1993e)
Miami, USA	11.38 ± 3.64				6.63 ± 4.86 $\leq C_{20}$ 3.40 ± 2.79 $>C_{20}$	0.01-0.82	Lang et al. (2002)
Kuala Lumpur, Malaysia	335-1009	10-563	37-166	9-122	2.87	7400	Abas et al. (2004b)
Lisbon, Portugal	245	273		518	618		Alves et al. (2002)
Campo dos Goytacazes (downtown), Brazil	20.3-148.9			3.05-6.15	6.89-27.6		Azevedo et al. (2002)
Algiers city, influence of fat manufacture plant	914	123			14000		Yassaa et al. (2001c)
Giesta, rural area, Portugal	456	87		130	782		Pio et al. (2001b)
Moitinhos, coastal rural area. Portugal	20.0 (winter) 14.3 (summer)	8.0 (winter) 3.1 (summer)	0.2 (winter) 0.6 (summer)	25.2 (winter) 19.9 (summer)	41.6 (winter) 25.2 (summer)		Oliveira et al. (2007b)
Amazonia, Brazil	300-810			10-110	200-620		Simoneit et al. (1990)
Melpitz, grassland, Germany	16-262			2.2-262	72-366		Alves et al. (2006)
Hyytiälä, boreal forest, Finland	7.2-95.2			1.0-17.4	39-192		Alves et al. (2006)
Pertouli, Abies forest, Greece	349-3486	38.6-625.5		30.7-179.4	124-3851		Pio et al. (2001a)

Average concentrations in parentheses.

TABLE VI
Specific tracers for organic components in atmospheric aerosols.

Compounds	Major source	Emission process
n-Alkanes, C_{15}-C_{20} (odd/even)	Microbial	Direct/resuspension
C_{20}-C_{37} (odd/even)	Plant waxes	Direct/biomass burning
C_{15}-C_{37} (CPI=1)	Vehicles	Exhaust
C_{16}-C_{40+} (even predomin.)	Plastics	Directly volatilised during open burning
n-Alkenes, C_{15}-C_{37}	Biomass/coal	Combustion
Isoprenoid hydrocarbons (pristane, phytane)	Ubiquitous/ not in gasoline	Exhaust
Triterpenoid hydrocarbons (steranes and diasteranes), C_{27}-C_{35}	Ubiquitous/ not in gasoline and diesel fuels	Lubricants of vehicular engines exhaust
Alkylcyclohexanes, C_{16}-C_{29}	Urban aerosols	Auto exhaust
n-Alkanones, C_{15}-C_{35}	Biomass/coal	Biodegradation/combustion
n-Alkanals, C_{15}-C_{35}	Biomass/coal	Biodegration/combustion
n-Alkanoic acids, C_{15}-C_{37}	Microbial/biomass	Direct/resuspension/combustion
C_{20}-C_{36}	Higher plants	Direct/combustion
n-Alkanoic acid salts, C_{15}-C_{20}	Marine biomass	Sea slick resuspension
n-Alkanols, C_{14}-C_{36}	Biomass	Direct
n-Alkanedioic acids, C_6-C_{28}	Various	Photo-oxidation/combustion
Wax esters	Plant waxes	Biomass combustion/direct
Triterpenyl alkanoates	Vegetation	Biomass combustion
Triacylglycerides	Flora/fauna	Biomass combustion/cooking
Methoxyphenols	Biomass with lignins	Combustion
Levoglucosan	Biomass with cellulose	Combustion
Galactosan	Biomass with cellulose	Combustion
Mannosan	Biomass with cellulose	Combustion
Cholesterol	Meat/algae	Cooking/direct
Mono- and diglycerides	Meat	Cooking/direct
Phytosterols	Higher plants	Combustion/direct
Triterpenoids	Higher plants	Combustion/direct
Diterpenoids (resin acids)	Higher plants (gymnosperms)	Combustion/direct
Hopanes/steranes	Petroleum	Vehicle exhaust and others
UCM	Petroleum	Vehicle exhaust and others
Alkylpicenes/alkylchrysenes	Coal	Combustion/heating
Plasticisers/Antioxidants	Plastics	Volatilised by steam stripping during open burning

to be present at a concentration of 0.28–0.36μg m^{-3} in the Los Angeles outdoor air, accounting for 1.0-1.3% of the fine particle mass concentration (Rogge et al. 1994).

Vehicle emission markers

Petroleum molecular markers are specific indicator compounds mainly present in the hydrocarbon fractions. These kind of tracers may include the 17α(H), 21β(H)-hopane series, the 5α(H), 14α(H), 17α(H) and 5α(H),-14β(H), 17β(H)-sterane series, alkylcycloalkanes, the isoprenoids pristane and phytane, as well as the chromatographic unresolved complex mixture (Gogou et al. 1996, Simoneit 1984, 1999, Simoneit et al. 1991a).

The presence of steranes (m/z 217), diasteranes (m/z 218) and hopane triterpenoids (m/z 191) indicates

TABLE VII
Cigarette specif tracers.

Mass/Charge (m/z)	Possible identities of ions at given m/z
118	indazole, benzimidazole, myosmine M-$C_2H_4^+$ fragment, indane
132	C_1-alkylindazole, C_1-alkylbenzimidazole, mysomine M-CH_2^+ fragment, C_1-alkylindane
146	C_2-alkylindazole, C_2-alkylbenzimidazole, mysomine, C_2-alkylindane
160	C_3-alkylindazole, C_3-alkylbenzimidazole, C_3-alkylindane

petroleum residue contamination (Simoneit 1984, Simoneit et al. 1991a). Generally, the distribution patterns of petroleum biomarkers show that the 17α(H),21β(H)-hopane series is the predominant group, ranging from C_{27} to C_{35} with the homologs $>C_{29}$ present as the typically mature C-22 R/S pairs (Simoneit et al. 1990). Distributions showing concentrations of the 22S hopanes higher than those for the corresponding 22R pairs are commonly found in aerosols emitted by gasoline and diesel engines. Biogenic precursors contain only the 22R configuration (Zheng et al. 1997). Steranes are introduced into the atmosphere from lubricants of vehicular engines, but they are not found in gasoline or diesel fuel (Abas and Simoneit 1996).

Paraffinic components of petroleum, alkylcycloalkanes, could be identified in the particulate matter, by searching m/z 82 and m/z 68-69 typical masses, respectively, for alkylcyclohexanes and alkylcyclopentanes. Vehicular traffic with the associated fuels and lubricants emit these compounds into the ambient atmosphere. The presence of unsaturated hydrocarbons like pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,-10,14-tetramethylhexadecane) is consistent with fossil fuel sources of carbon in the range of C_{16}-C_{20}, which is approximately the distillation range of diesel fuels (Abas and Simoneit 1996, Aceves and Grimalt 1992, Azevedo et al. 2002, Fraser et al. 1997, Rogge et al. 1997a, Zheng et al. 1997). Pristane and phytane result from the diagenesis of phytol and are not primary components of the majority of terrestrial living organisms (Simoneit 1984). Biogenic inputs are often dominated by a predominance of the odd carbon alkanes and the C_{17} isoprenoid (pristane). Since phytane is rarely found in biological material (except some bacteria), most biological hydrocarbons have a Pr/Ph ratio $>>1.0$. Low Pr/Ph ratios indicate a hydrocarbon signature derived from petrochemical use. It should be noted, however, that the identification of compounds such as pristane and phytane in atmospheric samples are dependent on the sampling period. Simoneit et al. (2004a) referred to the volatile compound blow-off from the filters over a 1–2-day acquisition time and the consequent depletion of aliphatics $<C_{21}$, and therefore of the petroleum tracers.

Generally, chromatograms from the aliphatic fraction show a hump that is constituted by branched and cyclic unresolved hydrocarbons, expressing the existence of microbial or petroleum derived contaminants, especially naphthenes (Bi et al. 2002, Simoneit 1984). This UCM (unresolved complex mixture) may be plotted by searching the m/z 95 fragmentogram. In general, samples show a bimodal pattern, with a minor maximum at $<C_{20}$ and a major one at the C_{26} or C_{28} naphthene. The first mode may indicate a source input typical of biodegraded detritus from algae and other microorganisms, which could arise by remobilisation of soil dust or from a recycled component of hydrocarbons eroded from sedimentary outcrops (Simoneit et al. 1991a). The hump observed in contaminated aerosols correlate with vehicular emissions. Auto exhaust exhibits a narrow hump maximising at C_{26} or at the neighbour naphthenic hydrocarbons (Simoneit 1984). The ratio of unresolved to resolved hydrocarbon components (U:R) is a parameter used to assess the magnitude of petroleum contributions to atmospheric aerosols (Tang et al. 2006). The hump: n-alkane ratios are determined from the gas chromatogram by the area of unresolved material above the background (measured by planimetry or integration) divided by the sum of the GC area of resolved n-alkanes

and other major components (Azevedo et al. 1999). U:R values for rural, mixed and urban samples are 0.2–4, 1.4–3.4 and 0.9–25, respectively (Azevedo et al. 2002). An U:R value >>1 indicates considerable contributions from petroleum combustion sources; pure hydrocarbon mixtures from plant waxes have U:R < 0.1, i.e. they have no UCM. Generally, urban aerosols contain the largest component of petroleum-derived compounds, while rural and mixed rural/urban environments show variable contributions of anthropogenic pollutants. The average U:R ratio for conifer smoke (1.0) suggests that the UCM of rural aerosol particles from the western United States consists mainly of recent (immature) organic matter derived from conifer and perhaps other biomass combustion source emissions, such as grass smoke released from agricultural field burning, and less pronounced fossil fuel combustion emissions (Oros and Simoneit 2001a). Several U:R ratios have been determined from more mature fossil fuel derived combustion emission sources which include the following: lignite coal = 3.2 and bituminous coal = 3.3 (Oros and Simoneit 2000); catalyst-equipped automobile engine exhaust = 5.5 and heavy-duty diesel truck engine exhaust = 9.3 (Rogge et al. 1993d). Thus, the lower U:R ratio of conifer smoke shows that this parameter is useful for distinguishing between conifer biomass burning and fossil fuel derived combustion source emissions. Ultimately, the U:R ratio may be used as an indicator for identifying atmospheric transport trajectories from regional biomass burning and fossil fuel combustion emission containing air parcels. This is especially useful for determining the contributions of organic matter derived from rural *versus* urban emission sources (Oros and Simoneit 2001a).

Meat smoke

During the cooking process, triglycerides from the fat can be hydrolysed or thermally oxidised, producing free glycerol, mono- and diglycerides and free fatty acids (Nolte et al. 1999). The emission rates of these compounds can be found in Schauer et al. (1999a) and Nolte et al. (1999). Meat cooking operations were considered to be a major source of organic aerosol emissions to the urban atmosphere, comprising up to 21% of the primary fine organic carbon particle emissions in the Los Angeles area (Rogge et al. 1991). Prominent among the compounds emitted are *n*-hexadecanoic acid (i.e., palmitic acid), *n*-octadecanoic acid (i.e., stearic acid), *cis*-9-octadecenoic acid (i.e., oleic acid), nonanal, 2-octadecanal, 2-octadecanol, saturated monoglycerides and cholesterol. However, the majority of these compounds, and especially fatty acids, are emitted from so many sources in addition to meat smoke that data on their concentration alone is insufficient to determine the quantity of meat smoke aerosol in ambient air (Nolte et al. 1999). The presence of cholesterol in oceanic aerosols more likely indicates an input from marine sources such as algae, which also can contribute to continental cholesterol sources in environments downwind from lacustrine areas (Simoneit and Elias 2001). The presence of cholesterol in particles has been associated with sea spray deriving from secretions of aquatic organisms (Alves et al. 2007, Fine et al. 2004b). The sea spray explanation is supported by the occurrence of cholesterol predominantly in the larger particles (Fine et al. 2004b).

The C_{16} monoglycerides, 1-palmitin and 2-palmitin, dominate in meat smoke aerosols, but there are also significant emissions of C_{18} (1-stearin) and $C_{18:1}$ (1-olein) monoglycerides (Nolte et al. 1999). Although cholesterol can be emitted from other sources, concentrations measured in the West Los Angeles atmospheric aerosol were consistent with the cholesterol mass emission rates calculated from meat cooking source tests. Thus, a group of compounds (Fig. 2), instead a single tracer, was considered to be more useful as an indicator of the quantity of meat smoke in the atmosphere. Of this assemblage, cholesterol seems to be most suitable, complemented by monoglycerides and perhaps oleic acid in the exact proportionalities (Nolte et al. 1999, Robinson et al. 2006b).

Tracers for the open burning of plastics

One way in which waste plastics impact the environment is through combustion, whether on purpose or not. Some discarding practices comprise intentional burning of waste, including plastics and plastic bags. In other occasions, wind-blown plastic litter collects in clumps and is burnt in wildfires. Anyway, smoke particles and combustion products, some of which are noxious to humans, are released into the atmosphere. In a recent investigation specific tracer compounds generated during

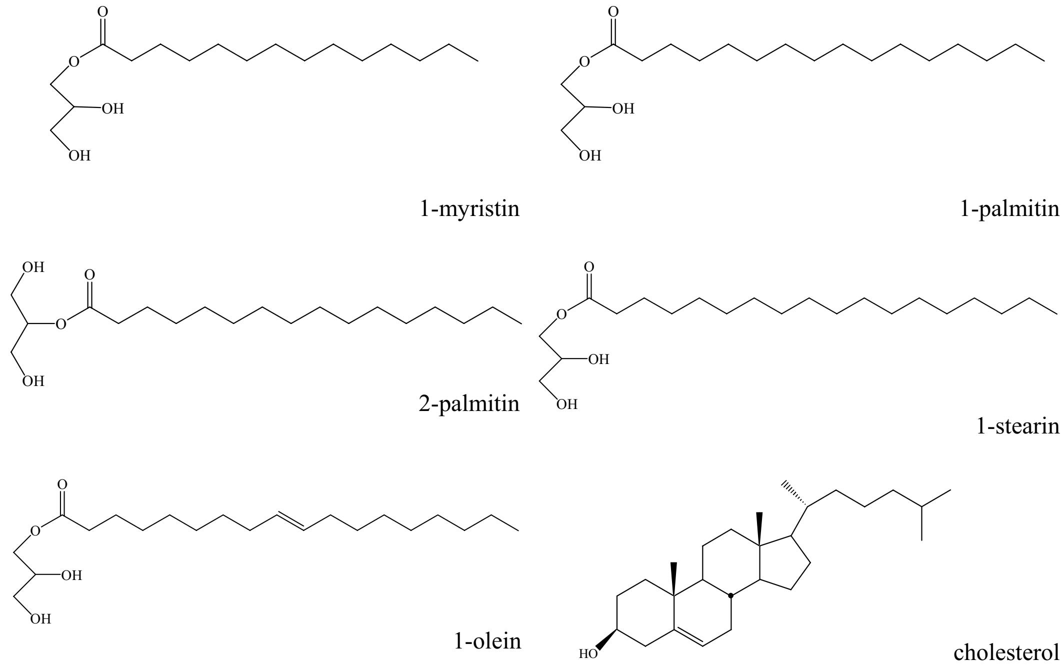
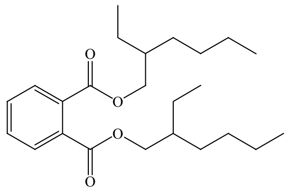


Fig. 2 – Chemical structures of constituents detected in meat smoke.

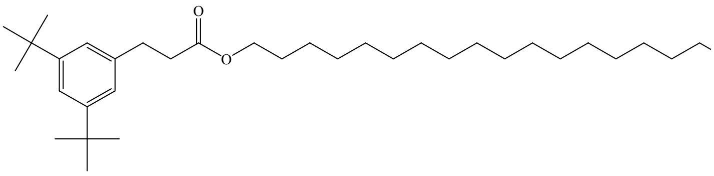
the open-fire combustion of plastics that can be used to detect episodes of plastic refuse burning were studied (Simoneit et al. 2005). Plastics consisting above all, but not entirely, of polyethylene plastic bags, were handpicked from the roadside and landfills, and analysed in two ways. The amounts of extractable compounds in the hexane extracts and smoke particles were 29-43 and 5.4-17.5 mg g^{-1} of plastic, respectively. The most important compounds extracted from the plastics were plasticisers, antioxidants and *n*-alkanes with an even carbon number (C_{16}-C_{40}), derived from the polymerisation of ethylene. Dialkyl esters of benzene-dicarboxylic acids (phthalates) are representative of plasticisers, which are widespread in the environment. The principal plasticiser was bis(2-ethylhexyl) phthalate (DEHP), a probable human carcinogen, with minor amounts of other phthalates, which are also suspected health risks (Fig. 3). In the smoke particles, the main compounds found were terephthalic acid, 4-hydroxybenzoic acid, and the phthalates. *n*-Alkanes were found once more, but with no carbon number predominance, indicating incomplete combustion and thermal cracking of polyethylene. The researchers proposed the minor components 1,3,5-triphenylbenzene (TPB) and tris(2,4-di-*tert*-butylphenyl) phosphate (TDPP) as candidate marker compounds because it was considered that they are not usually detected in the atmosphere. This hypothesis was confirmed by matching up to aerosol particulate matter from regions where plastic and refuse are burnt in open fires (Santiago, Chile; Saporo, Japan; Gosan Island, Korea) with that from areas supposed to be clean (Los Angeles, CA; Corvallis, OR). Both TPB and TDPP were found in the locations where open-fire burning of plastics is frequent, but were lacking from the areas apparently uncontaminated. Santiago presented the highest plastic marker content (613-6920 ng m^{-3} of DEHP; 7-132 ng m^{-3} of Irganox 1076), which is in agreement with the greater occurrence of garbage, litter and plastic-related combustion compared with the other cities. The plastic tracers were undetectable or present at much lower levels than those of Chile in the particulate matter from the other places.

Very high levels of phthalates (up to 2200 ng m^{-3}) dominated by DEHP, dibutyl and diisobutyl phthalates were also detected in the aerosol from 15 Chinese cities, especially in summer, possibly due to an enhanced evap-



Diethylhexyl phthalate ($C_{24}H_{38}O_4$)

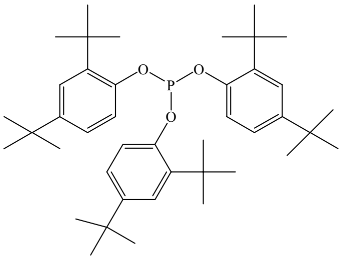
$M^{\bullet+}$ 390 (0.5), *m/z* 279 (17), 167 (39), 150 (12), 149 (100), 113 (9), 71 (17), 57 (24)



Octadecyl 3-(3 ,5 -di-*tert*-butyl-4 -hydroxyphenyl)propionate

Irganox 1076 ($C_{35}H_{62}O_3$)

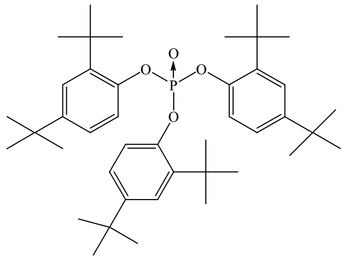
$M^{\bullet+}$ 530, *m/z* 515, 219, 57



tris(2,4-di-*tert*-butylphenyl)phosphite

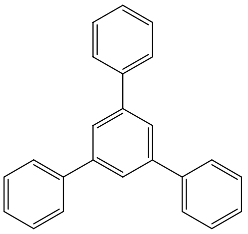
Irgafos 168 ($C_{42}H_{63}O_3P$)

$M^{\bullet+}$ 646, *m/z* 441, 308, 191, 147, 57



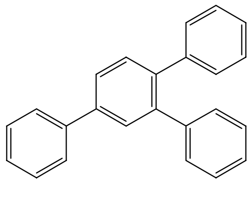
tris(2,4-di-*tert*-butylphenyl)phosphate ($C_{42}H_{63}O_4P$)

$M^{\bullet+}$ 662, *m/z* 647, 308, 316, 191, 57



1,3,5-Triphenylbenzene ($C_{24}H_{18}$)

$M^{\bullet+}$ 306, *m/z* 289



1,2,4-Triphenylbenzene ($C_{24}H_{18}$)

$M^{\bullet+}$ 306, *m/z* 289

Fig. 3 – Chemical structures of organic tracers in smoke from burning plastics and characteristic mass spectra. For the dominant plasticiser, ions are listed as m/z with relative intensities following in parentheses.

orative realise from plastics, followed by adsorptive deposition on pre-existing particles (Wang et al. 2006b). Phthalate levels in China are 1-3 orders of magnitude higher than those in the Swedish (Thuren and Larsson 1990), Belgian (Kubátová et al. 2002) and French (Teil et al. 2006) atmospheres. Taking into account their ubiquitous and abundant occurrences, as well their carcinogenic and endocrine-disrupting characteristics, the determination of plasticiser markers in atmospheric environments will be helpful in measuring the degree of plastic burning and will assist in establishing air pollution control programs.

Tracers in coal smoke

The burning of coal to produce electricity contributes significantly to the emission of fine particulate matter into the atmosphere. The sort and loads of organic components in coal smoke particulate matter depend on combustion temperature, aeration, burn time and geologic maturity, i.e. coal rank (Oros and Simoneit 2000). The maturity of the fuel may be evaluated indirectly by determining some indicators in smoke. It is registered a decrease in carbon preference index values (see section 6) of *n*-alkanoic acids, UCM and phenolic compounds and an increase in the homohopane index [S/(S+R)] with increasing rank. In general, the U/R and the 17α(H),-21β(H)-hopane to 22R-17α(H),21β(H)-homohopane ratios characteristic of coal smoke are in the range 2.9–3.3 and 0.05–0.35, respectively. The generic markers for coal smoke emissions comprise a series of C_{27} to C_{31} hopanes (no C_{28}), phenolics, C_2-picenes and C_2-hydropicenes (Oros and Simoneit 2000). The source specific markers are listed in Table VIII.

Tracers for wood burning, vegetation and other natural inputs

Most of the tracer molecules from vegetation are phytosterols and terpenoids, including sesquiterpenoids, diterpenoids and triterpenoids with 3, 4 and 5 isoprene units, respectively. Phytosterols are sterols of higher photosynthetic plants originated by a biosynthetic pathway of cyclisation, where squalene is the precursor (Kozlowski and Pallardy 1997, Simoneit et al. 1991a), which can be selected by searching m/z 129. Besides the precursor, the most common phytosterols that have been found in the solvent-extractable fraction of organic aerosols, derived from vegetation waxes and plant lipid membranes (Oros and Simoneit 2001a, b), consist of ergosterol (C_{27}), campesterol (C_{28}), sitosterol (C_{29}) and stigmasterol (C_{29}). Whereas sitosterol and stigmasterol are indicators for vegetation in general, campesterol has been pointed out as a specific molecular tracer for gramineae (Simoneit 2002). Different carbon number distributions have been obtained in distinct experiments, suggesting that the phytosterol patterns may be related to geographical characteristics, particularly, the specific plant communities and the climatic conditions. For example, aerosol samples from both rural and urban western United States compare with $C_{27} > C_{29} > C_{28}$ distribution of the wax from the Sierra Nevada vegetation or Oregon coastal forest (Simoneit 1989). For aerosol samples from Nigeria, an inverted ordering was encountered, where the pattern $C_{29} > C_{27} > C_{28}$ was evident. This distribution correlated with the predominance of wax components from the Nigerian and desert vegetation and also from grass (Simoneit et al. 1988). The Nigerian phytosterol pattern coincides with that of aerosol samples and composites from the Amazon region (Simoneit et al. 1990). In aerosols from a Portuguese semi-rural area and from a Greek *Abies* forest, the C_{28} phytosterol was not present at detectable levels and a $C_{27} > C_{29}$ distribution was observed (Alves and Pio, in press).

Sesquiterpenoid compounds possess in their structures the cadinane skeleton, an important constituent of resin plants (Simoneit and Mazurek 1982). Some sesquiterpenoids of lower volatility have been detected in aerosols from rural locations, including bicyclic (e.g. caryophyllene, cadalene and calamenene) and tricyclic (e.g. longifolene, copaene and patchoulol) constituents (Alves and Pio, in press, Pio et al. 2001b).

Diterpenoid components derive from the steroid skeletons of abietane and pimarane, which are the major constituents produced by higher plants, especially conifers (Standley and Simoneit 1994). Oxidation, polymerisation, disproportionation and aromatisation reactions of these unstable diterpenoids produce secondary compounds, such as resin acids (Pio et al. 2001a, Simoneit and Mazurek 1982). Retene (1-methyl-7-isopropyl-phenanthrene), a completely dehydrogenated resin diterpenoid, is a pyrolysis end product from diterpenoids that have the abietane or pimarane skeletons and has been proposed as molecular tracer for coniferous wood combustion (Ré-Poppi and Santiago-Silva 2002, Rogge et al. 1998, Simoneit and Mazurek 1982, Standley and Simoneit 1994).

Resin acids are protectants and wood preservatives that are produced by parenchymatous epithelial cells that surround the resin ducts in trees from temperate coniferous forests. The resin acids are formed when two- and three-carbon molecules couple with isoprene building units to form mono-, sesqui-, and diterpene structures. Resin acids have two functional groups, carboxyl group and double bonds. Nearly all have the same basic skeleton: a 3-ring fused system with the empirical formula $C_{19}H_{29}COOH$. Resin acids, which are biosynthesised mainly by gymnosperms (e.g. pine and spruce) in temperate regions (Oros and Simoneit 1999, Rogge et al. 1998, Simoneit et al. 1993), are generally found in aerosols in significant concentrations. They include unaltered (levopimaric, pimaric, isopimaric and sandaracopimaric acids) and thermal degradation products (neoabietic, palustric, dehydroabietic and 7-oxodehydroabietic acids). Dehydroabietic acid has been used as a biogenic source indicator for conifer resin, either directly

TABLE VIII
Dominant source-specific molecular markers for smoke from each coal type.

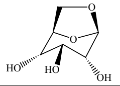
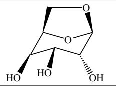
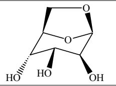
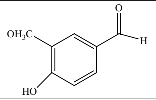
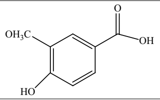
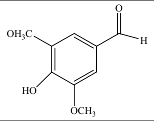
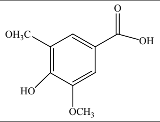
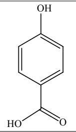
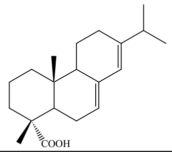
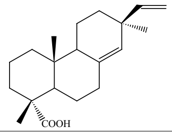
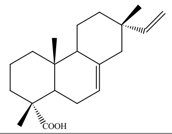
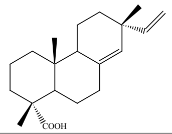
Coal type	Markers
Lignite	Dominant C_{31}-hopanes, divanillyl and 1,2-divanillylethane lignans, diterpenoids and dehydrogenated and 3-oxo triterpenoid derivatives
Brown coal	Allobetul-2-ene, 3,4,7-trimethyl-1,2,3,4-tetrahydrochrysene and 1,2-(5'-isopropylcyclopenteno)-7-methylchrysene
Sub-bituminous coal	17β(H),21β(H)-hopane, C_{28} triterpenoids and 2,2-dimethyl-1,2,3,4-tetrahydropicene
Bituminous coal	Picene and methylpicenes

to the aerosol, or from combustion of wood (Graham et al. 2004, Standley and Simoneit 1994). This compound was not identified in aerosols from Nigeria and Amazonia, in accordance with the absence of conifer vegetation in those regions (Simoneit et al. 1988, 1999). In cities where wood is used for heating, ambient dehydroabietic acid concentrations ranged from 48 to 440 ng m^{-3} (Standley and Simoneit 1994). The compound was also detectable in oceanic samples at concentrations ranging from 0.0001 to 0.4 ng m^{-3}, whereas in terrestrial aerosol particulate matter, it was present at much higher levels (0.23-440 ng m^{-3}). The presence of this tracer in atmospheric matter over the ocean confirmed the long-range transport of smoke from biomass burning of the continents (Simoneit and Elias 2001).

In smoke samples from biomass combustion (Table IX), triterpenoids are used as organic tracers for the contribution of directly volatilised natural constituents from vegetation (Elias et al. 1997). The most encountered triterpenoids in plants are α-amyrin, β-amyrin and their derivatives. These pentacyclic triterpenes have been considered tracers for angiosperm waxes, especially in their gums and mucilages (Oros and Simoneit 2001a, b). Their biosynthesis proceeds from squalene-2,3-epoxide to the basic ursane and oleanane skeletons and further oxidative steps lead to triterpenic acids and other pentacyclic oxygenated compounds (Simoneit 1989). Simoneit et al. (1991c) found various triterpenoids in aerosols from mountainous regions and from the southeast coast of Australia. Global yields ranged from 0.4 to 6 ng m^{-3}. The same investigators detected amyrinols, at trace levels, in aerosol samples taken from Amazonia (Simoneit et al. 1990). Alves and Pio (in press) detected triterpenic oxygenated compounds such as amyrinol and derivatives in aerosols from Portuguese and Greek rural areas. In smoke aerosol from Amazonia, high molecular weight components consisting of a series of wax esters (long chain alcohols esterified with long chain fatty acids) with up to 58 carbon numbers, triglycerides and triterpenyl esters (e.g. α- and β-amyryl stearate) were detected (Elias et al. 1997, 1998). Some of the structures are represented in Figure 4.

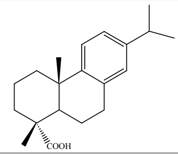
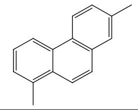
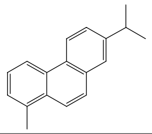
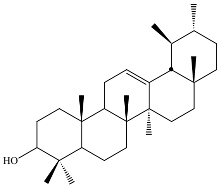
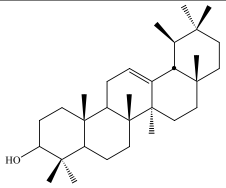
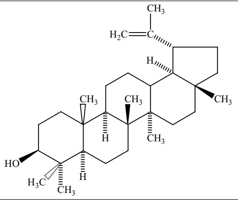
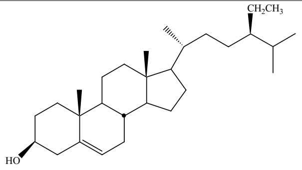
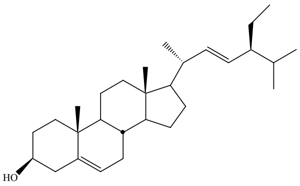
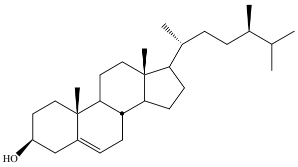
Lignin is a biopolymer that represents a substantial portion of wood, deriving primarily from *p*-coumaryl, coniferyl and sinapyl alcohols. Breakdown products are emitted upon combustion of wood, including aromatic phenols, aldehydes, ketonic acids and alcohols. In the smoke emissions, some volatilised thermal combustion products condense on pre-existing smoke particles. Because the monomers in the lignin are linked via the substituent *para* to the –OH group to the polymer, the lignin breakdown products disagree only in that substituent (Rogge et al. 1998). Both hard and softwoods produce guaiacol (2-methoxyphenol) derivatives in the smoke, whereas hardwood originates high levels of syringeol (1,3-dimethoxy-phenol) derivatives in addition (Hawthorne et al. 1988, Simoneit 2002). Vanillin and vanillic acid are detected in pine wood smoke. Minor amounts of syringaldehyde, syringic acid and *p*-anisic acid are also present. Hardwood smoke (e.g. oak) is enriched in syringaldehyde and syringic acid, showing minor amounts of other sinapyl- and vanillyl-type constituents. Grass smoke consists of *p*-anisaldehyde, *p*-anisic acid and, in less extent, *p*-coumaryl, vanillyl- and syringyl-type lignin pyrolysis products (Simoneit 2002). Other lignin products such as veratrol (dimethoxy-benzene) and veratric acid (3,4-dimethoxy-benzoic acid) are examples of compounds that have been detected in the par-

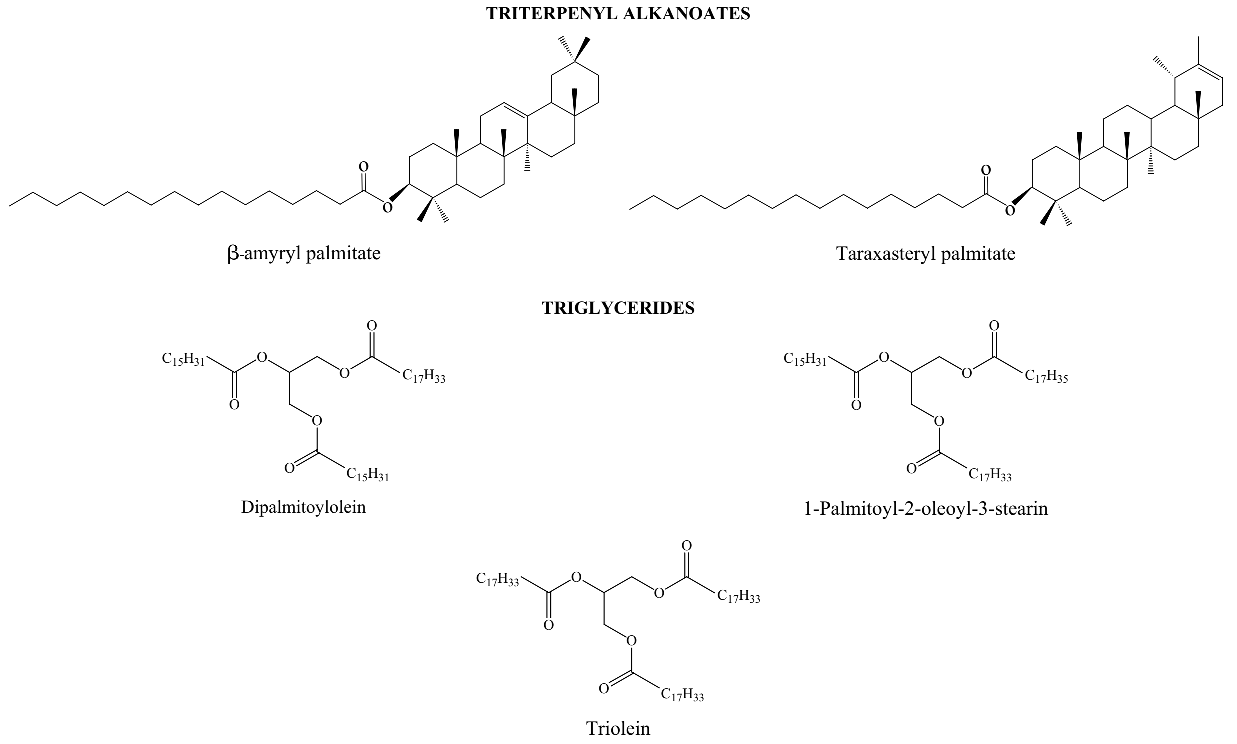
TABLE IX
Molecular tracers for biomass burning aerosols.

Chemical group	Molecular markers	Molecular structures	MS key ions and M$^+$	Source
Monosaccharide derivatives	Levuglocosan		*73*, 204, 217, 333, 378 (as TMS)	Biomass with cellulose
	Galactosan		*73*, 204, 217, 333, 378 (as TMS)	Biomass with cellulose
	Mannosan		*73*, 204, 217, 333, 378 (as TMS)	Biomass with cellulose
Methoxyphenols	Vanillin		123, 137, *151*	Conifers
	Vanillic acid		*73*, 267, 297, 312 (as TMS)	Conifers
	Syringaldehyde		*182*	Angiosperms
	Syringic acid		*73*, 312, 327, 342 (as TMS)	Angiosperms
	p-Hydroxybenzoic acid		77, 82, 105, 111, *136*, 142 (as methyl ester)	Gramineae
Diterpenoids	Abietic acid		73, 241, *256*, 359, 374 (as TMS)	Conifers
	Pimaric acid		73, *121*, 257, 359, 374 (as TMS)	Conifers
	Iso-pimaric acid		73, *241*, 256, 359, 374 (as TMS)	Conifers
	Sandaracopimaric acid		73, *121*, 241, 257, 359 (as TMS)	Conifers

ticulate matter (Alves and Pio, in press). Furan derivatives (e.g. 2-acetylfuran, 2-furanmethanol) have been described as minor constituents of smoke and attributed to cellulose combustion/decomposition process (Edye and Richards 1991, Simoneit 2002). Lignans are present as noteworthy components in the smoke from softwood

TABLE IX (Continuation)

Chemical group	Molecular markers	Molecular structures	MS key ions and M^+	Source
Diterpenoids	Dehydroabietic acid		73, *239*, 357, 372, (as TMS)	Conifers
	Pimanthrene		191, *206*	Conifers
	Retene		*219*, 239	Conifers
Triterpenoids	α–Amyrin		73, 189, 203, *218*, 393, 483, 488 (as TMS)	Angiosperms
	β–Amyrin		73, 189, 203, *218*, 393, 483, 498 (as TMS)	Angiosperms
	Lupeol		189, 203, 218, 231, 279, 369, 408, 483, *498* (as TMS)	Angiosperms
Phytosterols	β–Sitosterol		137, 151, 167, *181*, 402	All biomass sources
	Stigmasterol		*83*, 129, 255, 394, 469, 484	All biomass sources
	Campesterol		73, *129*, 343, 367, 382, 457, 472 (as TMS)	Gramineae



TRITERPENYL ALKANOATES

β-amyryl palmitate

Taraxasteryl palmitate

TRIGLYCERIDES

Dipalmitoylolein

1-Palmitoyl-2-oleoyl-3-stearin

Triolein

Fig. 4 – Structures of some compounds representative of the homologous series of triterpenols esterified to long chain fatty acids and of triglycerides in smoke extract from Amazonia.

(e.g. pine), are less significant in the hardwood smoke (e.g. oak) and are not measurable in grass smoke (Simoneit et al. 1993). The leading lignans of softwood smoke are matairesinol and shonanin (tetrahydro-3,4-divanillyfuran). Minor quantities of methylated derivative are detectable. The hardwood smoke encompasses a variety of highly oxygenated isomers of dihydrovanillylsyringyl-2(3H)-furanone, dihydro-3(2', 3', 4'-trimethoxybenzyl) - 4 - veratryl - 2(3H) - furanone and tetrahydro-3-vanillyl-4-veratrylfuran, which are released unaltered from the combustion sources and may be considered tracers of biomass burning. In addition, softwood smoke includes derivatives from coniferyl-type precursors, such as divanillyl, divanillylmethane, bis(3,4-dimethoxyphenyl)methane and diveratryl. Hardwood smoke comprises components originated from sinapyl-type precursors, including bisguaiacylsyringyl, disyringyl and bis(3,4,5-trimethoxyphenyl)ethane. Dianisyl, a derivative from a *p*-coumaryl-type precursor, is the only tracer in the grass smoke (Simoneit 2002).

The pyrolysis derivatives from the thermal breakdown of cellulose and hemicellulose during burning are the dominant smoke tracers in continental air sheds. The major tracer compound is levoglucosan, with lesser amounts of galactosan and mannosan. These are the tracers utilised for the assessment of particulate matter from biomass burning in the atmosphere because they cannot be generated by non-combustive processes. They are characterised by the base peak at m/z 204 and by m/z 217 and 333 in mass fragmentograms. The mass spectrum of levoglucosan tritrimethylsilyl ether exhibits only a small molecular ion (m/z 378) with fragments due to loss of CH_3 (m/z 363), CH_5Si (m/z 333), $C_6H_{17}OSi_2$ (m/z 217) and $C_7H_{18}OSi_2$ (m/z 204, base peak). The mass spectra of the other monosaccharide dehydration derivatives (galactosan and mannosan) are similar (Abas et al. 2004a, Pashynska et al. 2002). Levoglucosan is emitted in relatively high concentrations, 40 mg kg^{-1} to 1200 mg kg^{-1} of wood burned, and shows no decay over an eight-hour exposure to ambient atmospheric conditions (Larsen et al. 2006). Potential acid-catalysed hydrolysis of levoglucosan in atmospheric droplets was

TABLE X
Elemental carbon, organic carbon and levoglucosan in fine particulate matter from different categories of biomass burning measured recently in different investigatios (adapted from Puxbaum et al. 2007).

Sampling site	Fuel category	EC mg/g of $PM_{2.5}$	OC mg/g of $PM_{2.5}$	Levoglucosan (mg/g OC)	Factor OC/Levogl.	Reference
Fireplace NE-US	Hardwood		866	129	6.7	Fine et al. 2001
	Softwood		911	76.4	11.9	
Fireplace South-US	Hardwood		787	136	5.8	Fine et al. 2002a, b
	Softwood		1000	42.6	23.5	
Fireplace Mid-W and W-US	Hardwood	20	767	183	4.2	Fine et al. 2004c
	Softwood		890	123	7.2	
Wood stove US	Hardwood		553	164	3.4	Fine et al. 2004a
	Softwood		620	353	1.8	
Asian biomass fuel	Leaves, straw, dung, etc.	32.4	525	79	6.6	Sheesley et al. 2003
Rhondonia Pasture Site		1.4	29.2	2.46	11.9	Graham et al. 2003
Rhondonia Forest Site		0.7	14.5	1.18	12.3	
Southern United States	Fresno Rural-urban		32.7	7.6	4.3	Schauer and Cass 2000
Southeast Asia	Kuala Lumpur Urban-haze		115	40.24	2.9	Abas et al. 2004a
Recommended average US					7.35	Fine et al. 2002a, b
Recommended for small stoves Austria					7.1*	Schmidl 2005

investigated as one potential loss mechanism. Results using simulated rainwater indicate no degradation over a 10-day period (Fraser and Lakshmanan 2000). Thus, it is a good candidate for tracing biomass burning emissions. Levoglucosan has been detected in atmospheric aerosols from U.S. urban areas, e.g. Seattle, 13-750 ng m^{-3} (Simpson et al. 2004), Fresno and Bakersfield, 23-7590 ng m^{-3} (Schauer and Cass 2000), and about 120 ng m^{-3} in Los Angeles (Fine et al. 2004b). In a Portuguese semi-rural coastal area, during the 2003 summer intense forest fire period, levoglucosan presented levels between a minimum of 17 ng m^{-3} and an upper limit of 105 ng m^{-3} (Pio et al. 2007), which was achieved during a vast wildfire period. Much higher average levels of 1200 and 2500 ng m^{-3} have been reported for forest and pasture sites, respectively, in 1999, during the burning season in Rhondonia, southwest Amazonia (Graham et al. 2002). However, these values are far lower than concentrations that have been reported during severe episodes of biomass smoke in Southeast Asia, 1400-40240 ng m^{-3} (Abas et al. 2004a). Table X presents the contribution of levoglucosan to OC in fine particles from different fuel types and distict burning conditions. Based on the average value between the OC/levoglucosan ratio of 12.3 measured for the fine dry season aerosol in Rhondonia (Graham et al. 2002) and the ratio of 10.5 obtained for a pine forest fire in southeast USA (Lee et al. 2005), it was found a smaller than expected contribution (11-36%) of wood combustion to the amount of OC throughout the summer of 2003, which was characterised by an intense heat wave and forest fires in Portugal (Pio et al. 2007). Thus, unrealistically, its seems that the major fraction of OC measured in both fine and coarse aerosols during the Portuguese study was chiefly related to other primary anthropogenic and biogenic sources, as well secondary formation processes. In spite of a noteworthy raise in OC levels during the two weeks with strongest impact from the forest fire smoke plumes, the levoglucosan concentrations and the estimated contribution of wood burning to OC did not increase as expected. However, if the average levels of OC and levoglucosan measured during the 3 weeks less affected by wildfires were taken as baseline values and if these values were subtracted from the corresponding concentrations during the intense forest fire periods, then an OC/levoglucosan ratio of 80 was obtained. The investigation of Pio et al. (2007) made evident that the OC/levoglucosan relationships proposed in the literature for deriving the amount of OC from wood or biomass combustion in ambient aerosols should be taken with precaution. Since the ratios are quite variable for different burning conditions and wood types, it has yet to be estimated more specific factors with application to wildfires under extreme weather conditions (dryness and high temperatures), such as those in the Mediterranean countries. This conclusion was consistent with the results presented by Jordan et al. (2006), who obtained a smaller than expected levoglucosan mass fraction in aerosols generated by bushfires after using factors determined for wood burning. The different fuel and combustion conditions encountered during bushfires gave rise to lower mass fractions.

Besides anhydrosugars, recent studies indicate that sugar polyols and sugars are relatively abundant water-soluble organic constituents of atmospheric aerosols (Table XI). Saccharide alcohols (reduced sugars) are known components of bacteria, fungi, lichens, invertebrates and lower plants, acting as osmoregulators, stress inhibitors or carbohydrate suppliers (Graham et al. 2003, Medeiros et al. 2006). There are several sources of monosaccharides including microorganisms, vascular plants and animals (Medeiros et al. 2006). Simoneit et al. (2004b) suggested soil and associated microbiota as the main source of sugars to the atmosphere. According to these researchers, all these compounds derive mainly from soil resuspension into the atmosphere, though emissions of considerable amounts may occur by thermal stripping during biomass burning events. The dominant primary saccharides in aerosols include α- and β-glucose, sucrose and mycose (trehalose) with various minor constituents.

OXIDATION PRODUCTS OF VOC

The fraction of particulate organics resulting from the conversion of volatile compounds is of particular interest for the understanding of the chemistry of rural atmospheres, because of the large VOC emissions from vegetation in these areas. These compounds have an exceptional ability to produce condensable products as result of rapid oxidation into less volatile oxygenated organics. Among biogenic emissions from vegetation, 50 Tg of α-pinene are emitted per year, which is almost 45% of the estimated global annual emission of monoterpenes (Bhat and Fraser 2007). Terpene and isoprene oxidation products have been observed in aerosols in smog chamber studies and in the ambient atmosphere (Alves and Pio 2005, Alves et al. 2000, 2001, 2002, 2006, Bhat and Fraser 2007, Böge et al. 2006, Cahill et al. 2006, Claeys et al. 2004a, b, 2007, Clements and Seinfeld 2007, Edney et al. 2003, 2005, Engling et al. 2006, Herckes et al. 2006, Jaoui and Kamens 2003, Jaoui et al. 2005, Kavouras et al. 1998b, 1999b, c, Kavouras and Stephanou 2002a, b, Lewandowski et al. 2007, Oliveira et al. 2007b, Pio et al. 2001a, b, Sheesley et al. 2004, Spanke et al. 2001, Yu et al. 1999).

Pinic acid, pinonic, pinonaldehyde and nopinone are common pinene oxidation products detected both in smog chamber and field experiments (Table XII). The ozonolysis of α-pinene is a known source of pinic acid (e.g. Christoffersen et al. 1998). Another pathway for the formation of this compound is the reaction of β-pinene with O_3/NO_x (Jaoui and Kamens 2003). In laboratory experiments with α-pinene and OH radicals or ozone, the formation of pinonaldehyde and pinonic acid was observed (Hakola et al. 1994, Kamens and Jaoui 2001, Larsen et al. 2001). Pinonaldehyde may also take place in the particulate phase by oxidation of α-pinene through reaction with other oxidising species such as NO_3 and N_2O_5 (Wängberg et al. 1997). The major product from β-pinene oxidation identified in the particulate matter is nopinone. This compound has been detected in laboratory studies as a product of the precursor through reaction with O_3 or OH (e.g. Hakola et al. 1994, Jaoui and Kamens 2003, Larsen et al. 2001). The formation of nopinone may also take place after oxidation of β-pinene by NO_x (Grosjean et al. 1992, Paulson et al. 1990), O_3/NO_x (Palen et al. 1992) or NO_x/SO_2 (Kotzias et al. 1990).

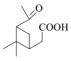
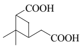
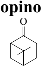
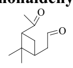
TABLE XI

Concentrations (ng m^{-3}) of major saccharides in aerosols (mean levels in parenthesis).

Saccharides	Santiago, Chile Simoneit et al. (2004b)	Kuala Lumpur, Malaysia Simoneit et al. (2004b)	Sapporo, Japan Simoneit et al. (2004b)	Datong, China Simoneit et al. (2004b)	Rhondonia, Brazil Graham et al. (2002)	Ghent, Belgium Zdráhal et al. (2002), Pashynska et al. (2002)	Diverse locations, Fraser and Lakshmanan (2000), Nolte et al. (2001, 2002)	Howland Forest, Maine, USA Medeiros et al. (2006)	Sierra Nevada Mountains, California Cahil et al. (2006)
Levoglucosan	12-2452 (839)	1162-33400 (14460)	6-56	1350	1182-6900 (2460)	121-1133 (477) 9.1-1900	500-2980 (1450)	1-54	16 ± 2.6
Mannosan	1-233 (81)	154-4430 (1422)	0.2-15	108	6-371 (126)	17-153 (66); 2.0-290	170-322	1.8-10.4	
Galactosan	1.7-127 (45)	84-2410 (1014)	0.6-2.4	106	2-148 (55)	4-44 (20); 0.67-115	96-144	1.0-2.6	
1,6-anhydro-glucofuranose	0.5-195 (62)	135-4005 (1520)			5-248 (82)	— ; 0.90-140			
Glucose	10-2210 (940)		1-34	102	14-62 (37)	— ; 30-610	10-15	3.1-45.7	13± 5.2
Fructose			12		3-20 (9)	— ; 10-440		0.1-5.3	4.9± 2.5
Galactose					0.2-2.4 (0.9)			1.1-22.2	
Mannose		48-6800 (2053)			0.6-4 (2)		9-13	0.8-14.1	
Xylose					1-33 (13)		9-17		
Sorbitol			3-26		0-1.7 (0.8)				
Mannitol					10-50 (26)	— ; 7.8-220		0.9-10.2	8.8± 3.4
Xylitol			2-22						
Erythritol					2-39 (16)				
Glycerol			3-24		0.5-9 (3)				
Inositols			3-104		0.5-21 (8)	— ; 1.3-97			
Sucrose	15-3060 (1108)		0.4-9	1148	0.8-26 (7)	— ; 7.2-200	3.2-4	0.7-5.6	
Maltose	6-2390 (622)	2-550 (130)		68			3-4	1.3-5.3	
Mycose	8-1660 (477)		0.2-12	54	5-18 (9)			1.5-18.3	

TABLE XII

Concentrations (ng m^{-3}) of some terpene photo-oxidation products detected in aerosols from field experiments.

Sampling site	Reference	Pinonic acid 	Pinic acid 	Nopinone 	Pinonaldehyde 
Two Japanese mountains	Satsumabayashi et al. (1990)				30-100
Near Ispra, Italy	Calogirou et al. (1997)				90
Kejimkujik National Park (Nova Scotia) and San Bernardino National Forest (California)	Yu et al. (1999)	0.1-0.8	0.5-0.6		0.2-1.0
Eucalyptus forest, Portugal	Kavouras et al. (1998b)	7.1-60.1 (isomer *cis*); 1.5-42.9 (isomer *trans*)		0.0-13.2	0.2-32.1
Boreal forest	Spanke et al. (2001)	0.8-4.0 (pinonic+pinic acids)			
Greek conifer forest	Kavouras et al. (1999b) Pio et al. (2001a)	< 25.7	< 4.4	< 0.6	< 1.2
Giesta, rural, Portugal	Pio et al. (2001b)		6.8	1.4	
Aveiro, coastal city, Portugal	Alves et al. (2002)	25.3	15.8	2.4	13.7
Lisbon, Portugal	Alves et al. (2002)	1.0	< 0.5	< 0.1	< 0.5
Lower Fraser Valley, Vancouver	Cheng et al. (2004)	5.9			
Sierra Nevada Mountain, CA	Cahill et al. (2006)	2.6-37	1.7-10	1.5-5.1	16-320
Yosemite National Park, CA	Engling et al. (2006)	21	12	0.9	21
Hyytiälä, boreal forest, Finland	Alves et al. (2006)	2.6	5.0	0.2	5.5
Melpitz, German meadow	Alves et al. (2006)	7.8	7.2	0.1	14
Coniferous forest, Germany	Plewka et al. (2006)	2.5 (night); 3.5 (day)	3.2 (night); 9.5 (day)		13.7 (night); 2.7 (day)
Duke Forest (pine), North Carolina	Bhat and Fraser (2007)	0.11-20.8	1.5-25.1		
Oporto, Portugal	Oliveira et al. (2007a)	2.9-3.6 (winter); 2.9-5.2 (summer)			
Copenhagen, Denmark	Oliveira et al. (2007a)	2.0-3.8 (winter); 2.8-3.6 (summer)			

Although monoterpenes are an important source of biogenic organic aerosols (Kavouras et al. 1999c, Hoppel et al. 2001), we still have missing sources that contributes to secondary organic aerosols of biological origin. Matsunaga et al. (2003) measured, in both gas and particle phases, glycolaldehyde and hydroxyacetone which are known as the oxidation products of isoprene (Atkinson 1990), together with biogenic semi-volatile aldehydes (n-nonanal and n-decanal; Kesselmeier and Staudt 1999). These investigators discovered a strong diurnal variation of these carbonyls with their particulate concentrations being comparative to the oxidation product of monoterpenes (pinonic acid). They are most likely produced in and/or emitted to the atmosphere as gases, and later converted to the particles. This study demonstrated that the semi-volatile carbonyls largely contribute to the formation and growth of aerosols in the forest and potentially play a significant role in the global budget of organic aerosols. Matsunaga et al. (2004) measured particulate concentrations of 4-oxopentanal (4-OPA) up to 207 ng m^{-3} in a Japonese forest, which was found to be comparable to those of pinonic acid, indicating that 4-OPA is also an important constituent of organic aerosols in the forestal atmosphere. This carbonyl is produced by the oxidation of 6-methyl-5-hepten-2-one, which is heterogeneous oxidation product of squalene and similar terpenoids present on the surface of plant leaves and other parts.

The organic analysis of $PM_{2.5}$ rural aerosol collected during summer at K-puszta, Hungary, from a mixed deciduous/coniferous forest showed the presence of polar oxygenated compounds that are also formed in laboratory irradiated α-pinene/NO_x/air mixtures (Claeys et al. 2007). The unknown photo-oxidation products were structurally identified as 3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid and 2-hydroxy-4-isopropyladipic acid. The detection of 3-hydroxyglutaric acid and 2-hydroxy-4-isopropyladipic acid at appreciable levels during daytime (avg. 16.8 and 14.9 ng m^{-3}, respectively), provided an explanation for the relatively low atmospheric concentrations of pinic acid in forest environments, since these two acids correspond to a further reaction product of pinic acid involving addition of a molecule of water and opening of the dimethylcyclobutane ring. The same three oxygenated products were detected in samples collected from Research Triangle Park, NC, USA, during the summer of 2003 (Lewandowski et al. 2007). Methyltetrols, along with 2-methylglyceric acid, were also observed. It has been suggested that these compounds may be the products of isoprene oxidation (Böge et al. 2006, Claeys et al. 2004b, Edney et al. 2005). The concentrations of 2-methylthreitol and 2-methylerythritol ranged from 18 to 365 ng m^{-3} (0.9% of the total organic matter), suggesting that isoprene SOA may be a significant component of ambient PM$_{2.5}$ in the southeastern US during the summer (Lewandowski et al. 2007). Other studies have reported methyltetrol levels of up to 29.4 ng m^{-3} in the Southeast during June of 2004 (Clements and Seinfeld 2007) and 131 ng m^{-3} in the northeastern US during the summer of 2005 (Xia and Hopke 2006). The discrepancies in the reported concentrations are due, in part, to the absence of authentic standards for the methyltetrols and, consequently, to variations in the quantification methods employed. However, a more important aspect contributing to the high methyltetrol levels detected in aerosols from the Research Triangle Park may be the deliberate choice of stagnant, highly polluted days for sample collection (Lewandowski et al. 2007). During the July 2001 LBA-CLAIRE wet season campaign in the Amazonian rainforest in Balbina, Brazil, Claeys et al. (2004a) detected 2-methylthreitol and 2-methylerythritol, in ambient PM$_{2.5}$ samples, at total concentrations of 49 ng m^{-3} during the day and 65 ng m^{-3} at night. These two tetrols were also observed in ambient PM$_{2.5}$ in a mixed deciduous/coniferous forest at K-puszta, Hungary, ranging from 1 to 34 ng m^{-3} and from 1 to 85 ng m^{-3}, respectively, during the summer of 2003 (Ion et al. 2005). In the Hungarian study, the polar oxygenated compound 2-methylglyceric acid was observed at ambient levels ranging between 2 ng m^{-3} and 18 ng m^{-3}. Two diastereoisomeric 2-methyltetrols were detected in aerosol samples collected in the Sierra Nevada Mountains of California (Cahill et al. 2006), with 2-methylthreitol (32 ± 9.6 ng m^{-3}) being about 2.5 fold more abundant than 2-methylthreitol (13 ± 3.8 ng m^{-3}), which is a similar ratio as determined for the Amazon (Claeys et al. 2004a), and boreal Finnish forests (Kourtchev et al. 2005). The concentrations (05–1.7 ng m^{-3}) measured at Melpitz, Germany (Böge et al. 2006) are by far lower than in the other places, especially in Amazonia. However, the isoprene mixing ratio in the Amazonian rainforest was between 4 and 10 ppb (Claeys et al. 2004a, b), whereas those in Melpitz were usually between 10 and 200 ppt. According to Cahill et al. (2006) this substantiates the ubiquitous nature of the 2-methyltetrols in SOA from very much different geographic regions. Althought the 2-methyltetrols have been considered photochemical products, their concentrations in ambient samples do not always show a clear diurnal cycle, like some of the monoterpene oxidation products (e.g. pinonic acid and pinonaldehyde). An unclear pattern was observed by Cahill et al. (2006), which contrasts with the concentration maxima occurring during the day measured by Ion et al. (2005). These disagreements were attributable to differential meteorological conditions at the sites. Due to the fact that 2-methyltetrols may be linearly correlated with glucose and fructose, it has been suggested that the polyols may derive from a similar biological source as the sugars, in addition to the well accepted photochemical pathway (Cahill et al. 2006).

One of the predominant ketones found in the atmospheric aerosol samples is phytone (6,10,14-trimethylpentadecan-2-one). It is produced by thermal alteration and oxidation of phytol emitted from plants, or has a marine origin, and has been proposed as a marker for secondary biogenic aerosol (Abas et al. 1995, Brown et al. 2002, Gogou et al. 1996, Simoneit et al. 1988). This isoprenoid compound has been previously detected in an *Abies* forest of central Greece (Pio et al. 2001a), rural aerosols from Crete (Gogou et al. 1996), forest and rural locations of Portugal (Alves et al. 2001, 2007; Pio et al. 2001b), a German urban/industrial influenced grassland location (Alves et al. 2006), a coniferous forest in Germany (Plewka et al. 2006), a Finnish boreal forest (Alves et al. 2006, Shimmo et al. 2004a), western United States (Simoneit and Mazurek 1982), Canada (Brown et al. 2002, Cheng et al. 2006), Amazonia (Abas et al. 1995), Nigeria (Simoneit et al. 1988) and Yosemite National Park (Engling et al. 2006) at levels of dozens of ng m^{-3}.

In addition to previously reported biogenic oxidation products (pinic acid, pinonic acid, norpinic acid, nopinone, and pinonaldehyde), seven multifunctional organic compounds were found by Jaoui et al. (2005) in both field and laboratory samples. These compounds, which were proposed as possible atmospheric tracers for secondary organic aerosol from monoterpenes, were consistent with the following identifications: 3-isopropyl pentanedioic acid, 3-acetyl pentanedioic acid, 3-carboxy heptanedioic acid, 3-acetyl hexanedioic acid, 2-isopropyl-1 , 2-dihydroxybutanol, 4-isopropyl-2 , 4-dihydroxyhexanol and 3-(2-hydroxy-ethyl)-2,2-dimethyl-cyclobutane carboxylic acid. The occurrence of these compounds suggests that SOA originating from biogenic hydrocarbons are contributing to the regional aerosol burden in the southeastern United States. Several of these compounds also appear to contribute to the global aerosol burden in that they have also been identified in Europe and Brazil (Jaoui et al. 2005).

Kubátová et al. (2000) employed GC/MS after various types of derivatisations for the quantification of dichloromethane extractable compounds in aerosols samples collected in the Amazon basin. Four unkowns were identified: two derivatives of glutaric acid (3-isopropyl pentanedioic acid and 3-acetyl pentanedioic acid), 3-acetyl hexanedioic acid and 3-carboxy heptanedioic acid. The biogenic precursors of the novel identified compounds could not be pinpointed, but most likely include monoterpenes and fatty acids. In addition, two tricarboxylic acids (propane-1,2,3-tricarboxylic acid and 3-carboxy heptanedioic acid) could be characterised. The oxidative degradation products represented 0.5% of OC.

Aliphatic diacids and aromatic di-, tri-, and tetra-acids have also been reported as indicators of SOA in urban atmospheres, as they can be quantified readily using standard GC/MS techniques (Fine et al. 2004d, Schauer et al. 2002a, Zheng et al. 2002). Nevertheless, in aerosol samples enclosing a mixture of both SOA and primary source emissions, the origins of these compounds have not yet been definitively identified (Sheesley et al. 2004). Aromatic acids, particularly phthalic acid, have been thought to be secondary products of the oxidation of PAH, including naphthalene (Fraser et al. 2003, Jang and McDow 1997), while origins proposed for aliphatic dicarboxylic acids comprise the formation by photochemical oxidation of anthropogenic hydrocarbons and biogenic compounds, direct emission from combustion engines, or biomass combustion (Kubátová et al. 2000 and references therein). Although dicarboxylic acids can be of primary or secondary origin, several studies have revealed contributions to SOA by dicarboxylic acids formed *in situ* during atmospheric aerosol processing (Glassius et al. 2000, Kavouras et al. 1998b, 1999c, Kawamura et al. 1996). The dicarboxylic acids measured by Engling et al. (2006) during the summer of 2002 in Yosemite National Park (CA, USA) showed a relatively large variability in concentrations throughout the study based on the weekly composite samples (1.3–11 ng m^{-3} for the sum of C_4 through C_{14} dicarboxylic acids). It has been verified that they accumulate in aerosols and account for 1–15% of the total aerosol carbon and display their highest concentrations during periods of increased solar radiation. In addition to ω-dicarboxylic acids, keto mono- and dicarboxylic acids and α-dicarbonyls have also been reported to be atmospheric oxidation products (Kubátová et al. 2000 and references therein).

Jang et al. (2002) showed that some of the highly volatile carbonylic oxidation products can significantly contribute to the increase of SOA mass if mixed with acidic inorganic seed particles. A possible explanation for this is that condensation and polimerisation reactions of carbonyls in the acidic particles contribute to SOA mass increase. Reaction chamber experiments have showed that about 50% of SOA from aromatic oxidation is composed of polymers with a molecular mass up to 1000 daltons. The formation and ageing processes of these polymeric subtances take more than 20 hours (Kalberer et al. 2004). Because aromatics are the main anthropogenic SOA precursors, these polymers are supposed to be found at appreciable concentrations in urban environments. On the other hand, aldehydes are abundant products of biogenic terpenic compounds and, probably, acetal polymers are formed in large quantities in rural atmospheres. It can be expected that all these polymerisation reactions influence aerosol properties (e.g. optical parameters, hygroscopic growth and cloud condensation nuclei potential) affecting the role in the global climate system (Kalberer et al. 2004, Tolocka et al. 2004). The parametrisation of these reactions is an important and novel issue, which should be addressed in modern aerosol models.

The measurement of SOA comprises inumerous difficulties. They not only are polar but their levels seem to be only a few nanograms per cubic meter. Another difficulty is the partitioning of these compounds between the gas and particulate phases. As most of them are semi-volatile their aerosol fingerprint alters constantly. In addition, some of the most volatile ones (e.g. pinonaldehyde and nopinone) have been shown to have atmospheric lifetimes of the order of a few hours and their reactivity has not been investigated in any detail. Further research of the stability of these compounds will be needed to better assess their capability as tracers for SOA. Although quantitative collection of both semivolatile and particulate-phase constituents is wanted for tracing SOA, it should be noted that the existing sampling networks are not prepared for the challenge. Thus, it will be necessary to exploit advanced sampling and analytical techniques in order to take advantage of both non-volatile and semi-volatile tracers in source apportionment studies.

MATERIAL BALANCE

Material balances describing the chemical composition of aerosols collected at a forest site and in cities that face some air pollution problems are shown in Figure 5. The unexpected high levels of particulate matter observed in the Greek wood were attributable to dust contamination from the passage of trucks in nearby unpaved forest roads (Pio et al. 2001a). Background annual average concentrations for continental Europe are 7.0 ± 4.1 μg m^{-3} and 4.8 ± 2.4 μg m^{-3} for PM$_{10}$ and PM$_{2.5}$, respectively (Dingenen et al. 2004). Querol et al. (2004) reported PM$_{10}$ levels varying from 28 to 42 μg m^{-3} at urban background and from 37 to 53 μg m^{-3} at kerbside sites in seven selected cities throughout Europe. Annual average levels of 24, 52, 157 and 54 μg m^{-3} were measured in New York, São Paulo, Tegucigalpa and Hong Kong, respectively (Baldasano et al. 2003). In Santiago, the average concentrations of OC (52 μg m^{-3}) and EC (31 μg m^{-3}) represent 21% and 13% of the PM$_{10}$ particulate matter. These levels are notably higher (factor of 4–10 times) than those described for Los Angeles, New York or the average for 46 USA urban areas (Didyk et al. 2000 and references therein). In the case of the forest samples, the total extractable material contained approximately 2 times more mass than the corresponding OC fraction. Two possible explanations were considered for this difference. Either the solvent extract contained other compounds besides organic matter, and/or the organic matter had an important contribution of other atomic species, such as oxygen, nitrogen and sulphur. The expression “Non C organics?” represents solvent extractable matter, such as oxygen, nitrogen, etc., that is not determined on the black/organic carbon analysis by the thermal/optical method (Pio et al. 2001a). It should be referred that a significant portion of the more polar oxygenated organic compounds are not extractable by common solvents, such as dichoromethane. The organic matter that is extractable and that elutes from the chromatographic columns represents a small fraction (usually less than 10%) of the total organic extract. The mass of chromatographically elutable organics can be subdivided into resolved (identifiable peaks) and unresolved complex mixture, consisting above all of cyclic and branched chain hydrocarbons from the incomplete combustion of fossil fuels (Tang et al. 2006). The extractable organic fractions able to separate chromatographically into identifiable compounds are limited to molecules with carbon atoms, in general, less than 40. Thus, macromolecular and other complex components, resulting from oligomerisation and polimerisation processes, which are expected to exist in the aged aerosol particles as result of either direct emission or from secondary atmospheric particulate transformation processes, constitute an analytically non-accessible fraction. The bulk of organic carbon representing more hydrophilic compounds (e.g. dicarboxylic acids, sugar polyols, anhydrosugars, cellulose and humic like substances) are not quantifiable by classic solvent extraction followed by GC/MS. The chromatographically identifiable organic material consists mainly of fatty acids and aliphatic constituents, with minor amounts of alcohols, aldehydes, ketones and aromatic compounds. This characterisation of organic aerosol samples shows that in rural and forested areas oxygenated species and products from terpenes emitted by vegetation constitute the major particulate fraction. Petroleum residues and pyrogenic constituents predominate in urban samples, standing out the aliphatic hydrocarbons and cyclic components derived from vehicular emissions.

GEOCHEMICAL PARAMETERS, DIAGNOSTIC RATIOS AND LIPID SOURCE ASSIGNMENT

The identification and quantification of homologous compound series (e.g. *n*-alkanes, *n*-alkanols and *n*-alkanoic acids) present in the lipid extract, associated with the application of diagnostic parameters, provides supportive data that can be used in the characterisation of emission sources. The carbon preference index (CPI)

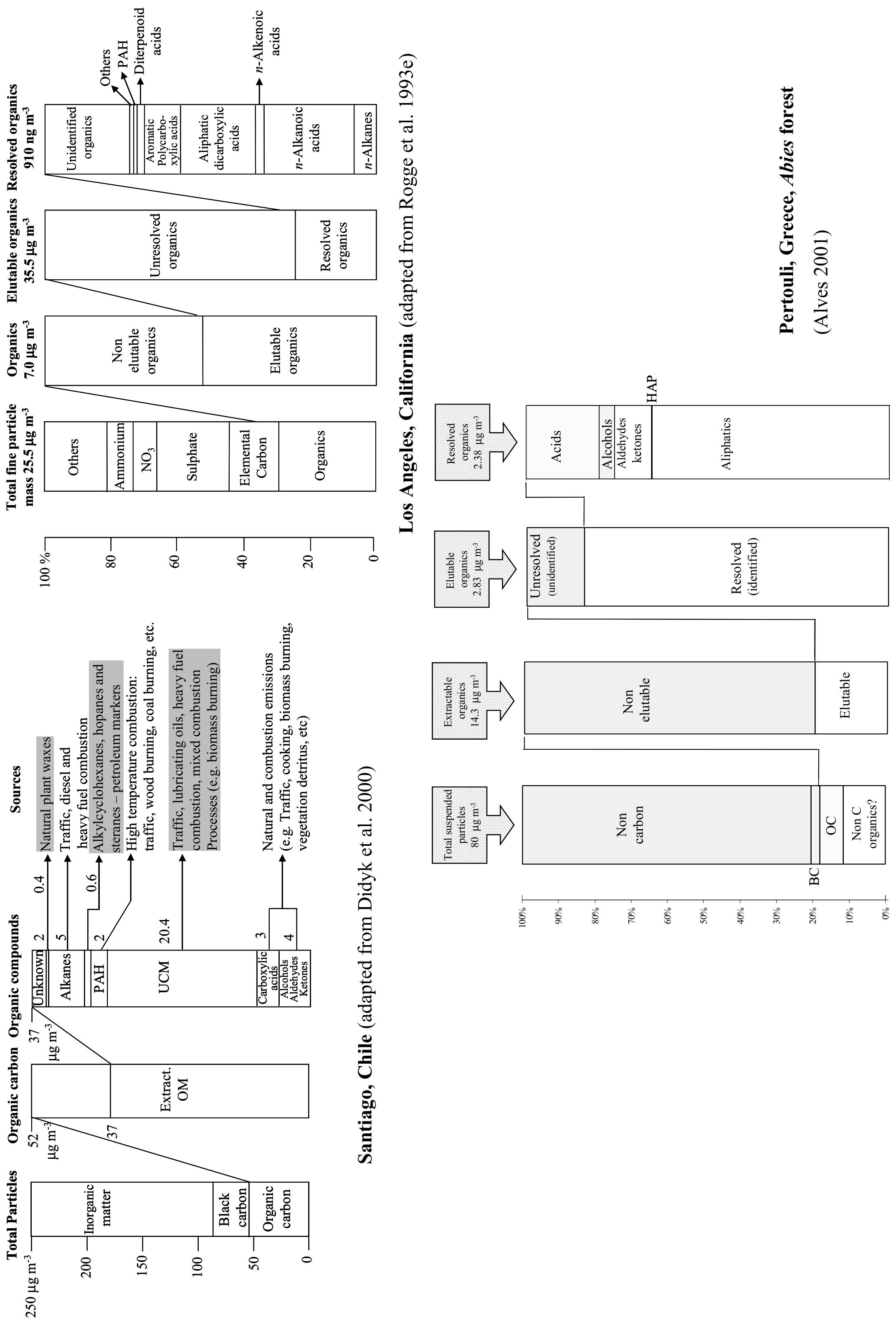


Fig. 5 – Material balances with the chemical composition of aerosols from different atmospheric environments.

has been suggested as a qualitative tool to assess the influence of biogenic and anthropogenic inputs (Simoneit 1989). For n-alkanes, n-alkanals and n-alkanones this empirical parameter is expressed as a sum of the odd carbon number homologs, over a range, divided by a sum of even carbon homologs, over the same range. For n-alkanols and n-alkanoic acids CPI is calculated in a similar way, only inverting the ratio to have even-to-odd homologs. Splitting the CPI range we can distinguish microbial contributions (n-C_{10}–n-C_{24}) and higher plant wax inputs (n-C_{22}–n-C_{34}). Thus, for n-alkanes, n-alkanals and n-alkanones:

$$\text{CPI whole range (petroleum)} = \frac{\sum C_{13} - C_{35}}{\sum C_{12} - C_{34}}$$

$$\text{CPI split range (bacterial, algal)} = \frac{\sum C_{11} - C_{25}}{\sum C_{10} - C_{24}}$$

$$\text{CPI split range (higher plant wax)} = \frac{\sum C_{27} - C_{35}}{\sum C_{26} - C_{34}}$$

For n-alkanols and n-alkanoic acids, CPI is calculated as follows:

$$\text{CPI whole range (biogenic, also pyrogenic)} = \frac{\sum C_{12} - C_{34}}{\sum C_{13} - C_{35}}$$

$$\text{CPI split range (bacterial, some algal)} = \frac{\sum C_{13} - C_{35}}{\sum C_{12} - C_{34}}$$

$$\text{CPI split range (higher plant wax)} = \frac{\sum C_{13} - C_{35}}{\sum C_{12} - C_{34}}$$

For biologically synthesised n-alkanes, an odd-to-even carbon number predominance is observed over a given carbon number range, while for n-alkanoic acids and n-alkanols an even-to-odd bias is evident. CPI values close to unity express a significant input of compounds with anthropogenic origin. A high value (CPI >3) indicates a major incorporation of recent biological components into the aerosol sample. Table XIII presents some results of the application of this parameter obtained for different atmospheric environments.

Since it is known that petroleum-derived n-alkanes have CPI$\approx$1, it is possible to subtract this contribution to determine the residual plant wax alkanes (Simoneit et al. 1991a). The concentrations of the wax n-alkanes are calculated by subtraction of the average of the next higher and lower even carbon numbered homologs, taking as zero the negative values of C_n:

$$\text{Wax } C_n = [C_n] - \left[\frac{C_{n+1} + C_{n-1}}{2}\right]$$

As stated before, C_{max} can also give an indication of relative source inputs. It represents the carbon number of the compound with maximum concentration in the homologous series (Abas and Simoneit 1996, Simoneit 1989). The average chain length (ACL) is another parameter that may be used as an additional indicator of source composition, particularly for the lipid components present in the plant waxes. It is calculated as an average number of carbon atoms per molecule based on the abundance of the odd or even high homologs (Oros et al. 1999):

$$\text{ACL } (n\text{-alkanes}) = \frac{23 \times [C_{23}] + 25 \times [C_{25}] + 27 \times [C_{27}] + \cdots + 35 \times [C_{35}]}{[C_{23}] + [C_{25}] + [C_{27}] + \cdots + [C_{35}]}$$

$$\text{ACL } (n\text{-alkanols; } n\text{-carboxylic acids}) = \frac{22 \times [C_{22}] + 24 \times [C_{24}] + 26 \times [C_{26}] + \cdots + 34 \times [C_{34}]}{[C_{22}] + [C_{24}] + [C_{26}] + \cdots + [C_{32}]}$$

It has been assumed that in warmer tropical climates longer-chain compounds are biosynthesised as wax lipids, whereas in cooler temperate regions predominantly shorter chain compounds are produced. However, certain environmental conditions, such as fog exposure, precipitation regime, aridity and growing-season temperature, may influence the plant or microbial enzymatic mechanisms, shifting the wax composition and, consequently, the aerosol constitution (Schefuß et al. 2003). The induced changes may include the cleavage and loss of one or two carbons of the long chain homologues. On the other hand, transport of air masses influenced by inputs of different taxonomic species may also play an important role (Alves et al. 2007). ACL values from 22 and 29 were found in aerosols from rural Portuguese areas, showing a significant augment by two carbon numbers with increased distance away from the coast (Alves et al. 2001). This observation may be due to taxonomic and aging differences among the emitter vegetation from place to place.

Further assessment of processes affecting the composition of hydrocarbons, such as type of vehicular emissions, wood burning, coal combustion, etc., can be obtained from concentration ratios between PAH (Bi et al. 2002, Gogou et al. 1996, Tsapakis et al. 2002). Table XIV gathers bibliographic information on distintict

TABLE XIII

Carbon Preference Index of *n*-alkanes for various aerosol sources.

Aerosol type/location	CPI	Reference
Rural Western US	1.6–8.4	Simoneit (1989)
Urban Western US	1.2–2.8	Simoneit (1989)
Oceanic aerosol: Pacific	2–4	Simoneit (1989)
Vascular Plant Wax	6–10	Simoneit (1989)
Oceanic aerosol: Atlantic	5–10	Simoneit (1989)
Natural fire smoke	1.2–10	Simoneit (1989)
Vehicular exhaust: cars	0.93	Simoneit (1989)
Vehicular exhaust: diesel	1.02	Simoneit (1989)
Biomass combustion, Amazonia	3.6	Abas et al. (1995)
Santiago, Chile	1.11–1.28	Didyk et al. (2000)
Hong Kong	1.2–1.9	Zheng et al. (2000)
Eastern Mediterranean, urban	1.3–1.6	Gogou et al. (1996)
Eastern Mediterranean, rural	1.6–3.3	Gogou et al. (1996)
Big Bend Nacional Park, Texas	1.2–4	Brown et al (2002)
Miami, Florida, urban	1.9 ± 0.3	Lang et al. (2002)
Guangzhou, China, urban	1.03–1.16	Bi et al. (2003)
Qinddao, China, coastal city	1.17–5.20	Guo et al. (2003)
Athens, urban	2.70 ± 0.30	Mandalakis et al. (2002)
Campos de Goytacares, Brazil (downtown, suburbs and lagoon 28 km from downtown)	0.94–3.74	Azevedo et al. (2002)
Birmingham, UK, urban	1.05–1.48	Harrad et al. (2003)
Prato, Italy, urban under influence of a sewage plant and textile industrial activity	1.20 ± 0.21	Cincinelli et al. (2003)
Shanghai, urban	1.0–1.6	Feng et al. (2006)
Shanghai, rural	1.0–2.8	Feng et al. (2006)
14 Chinese cities	1.17 ± 0.14 (winter) 1.16 ± 0.12 (summer)	Wang et al. (2006a)
Petrana, rural site, western Greece	2.41 ± 0.58	Kalaitzoglou et al. (2004)
Central California	1.7 ± 0.3	Rinehart et al. (2006)
Hyytiälä, Finland, boreal forest	2.69 ± 1.05	Alves et al. (2006)
Melpitz, Germany, grassland	3.09 ± 1.38	Alves et al. (2006)
Lower Fraser Valley, Canada, forest	2.39 ± 0.47	Cheng et al. (2006)
Island of Terceira, north-eastern Atlantic	1.61–11.34	Alves et al. (2007)

diagnostic ratios between PAH, typical values and their interpretation.

The apportionment of various solvent extractable compounds to sources may be roughly estimated by taking into consideration different contributions (Alves and Pio, in press, Simoneit et al. 1988, Tsapakis et al. 2002):

(a) *Plant wax* – sum of the Wax C_n concentrations for *n*-alkanes; *n*-alkanoic acids, C_{22}–C_{34}; *n*-alkanols, C_{22}–C_{34}; *n*-alkan-2-ones, C_{22}–C_{35}; *n*-alkanals, C_{22}–C_{35}; and biogenic molecular markers such as phytosterols.

(b) *Microbial components* – sum of the concentrations of *n*-alkanoic acids, C_{10}–C_{18} with CPI >2; *n*-alkan-2-ones, C_{15}–C_{21}; and *n*-alkanols C_{12}–C_{20}.

TABLE XIV

Diagnostic ratios between PAH reported in the literature.

Ratio or Index	Value	Interpretation/Emission source	Reference
IcdP/(BghiP+IcdP)	0.18	Emissions from cars	Grimmer et al. (1983)
	0.37	Diesel emissions	Grimmer et al. (1983)
	0.56	Coal emissions	Grimmer et al. (1983)
BaA/(BaA+CT)	0.16 ± 0.12	Crude oil emission	Sicre et al. (1987)
	0.38–0.64	Diesel cars	Sicre et al. (1987)
	0.22–0.55	Gasoline cars	Simcik et al. (1999)
	0.43	Wood combustion	Li and Kamens (1993)
	0.28	Cement plant	Yang et al. (1998)
	0.08	Vehicle construction	Manoli et al. (2004)
BeP/(BeP+BaP)	0.50	Freshy emitted PAH. This ratio is affected by the strong reactivity in the atmosphere since BaP is easily decomposed by light and oxidants. Most of the fresh exhausts have similar contents of BeP and BaP, thus the increasing of the ratio can be regarded as an index of the aging of particles.	Grimmer et al. (1983)
	0.70	Diesel cars	Rogge et al. (1993d)
	0.60–0.80	Gasoline cars	Rogge et al. (1993d)
	0.34	Wood	Li and Kamens (1993)
	0.54	Road dust	Rogge et al. (1993a)
	0.45	Roadway soil	Oda et al. (2001)
	0.85–0.94	Vehicle construction	Manoli et al. (2004)
	0.90–0.99	Fertilizer production	Manoli et al. (2004)
Flu/(Flu+Pyr)	0.44	Catalytic automobiles	Rogge et al. (1993d)
	< 0.40	Car emissions and used motor or lubricating oils	Azevedo et al. (1999)
	0.60–0.70	Diesel cars	Sicre et al. (1987)
	0.40	Gasoline cars	Rogge et al. (1993d)
	0.42	Road dust	Rogge et al. (1993a)
	0.54	Roadway soil	Oda et al. (2001)
	0.21–0.26	Industrial	Yang et al. (1998)
	0.25	Cement plant	Yang et al. (1998)
	0.45	Metal scrap burn	Tsai et al. (1995)
IcdP/(BghiP+IcdP)	0.21-0.22	Gasoline cars	Khalili et al. (1995)
	0.35–0.70	Diesel emissions	Rogge et al. (1993d)
	0.56	Coal emissions	Grimmer et al. 1983
	0.62	Wood burning	Gogou et al. (1996), Sicre et al. (1987)
	0.36	Road dust	Rogge et al. (1993a)
	0.42	Roadway soil	Oda et al. (2001)
	0.36–0.57	Industrial	Yang et al. (1998)
	0.65	Cement plant	Yang et al. (1998)
BghiP/BeP		Indicator for traffic, with higher ratios indicating a higher traffic contribution	Nielson et al. (1996)
BghiP/BaP	1.2-2.2	Diesel cars	Rogge et al. (1993d)
	2.5–3.3	Gasoline cars	Rogge et al. (1993d)
	< 0.5	Oil burning	Simcik et al. (1999)
	0.91	Road dust	Rogge et al. (1993a)
	0.86	Roadway soil	Oda et al. (2001)
	0.02–0.06	Industrial	Yang et al (1998)
	0.06	Cement plant	Yang et al (1998)
	0.09	Metal scrap burn	Tsai et al. (1995)

TABLE XIV (continuation)

Ratio or Index	Value	Interpretation/Emission source	Reference
CPAH/ΣPAH	0.41	Emissions from non-catalyst-equipped automobiles	Rogge et al. (1993d)
	0.51	Emissions from catalyst-equipped automobiles	Rogge et al. (1993d)
	0.30	Emissions from heavy-duty diesel trucks	Rogge et al. (1993d)
	> 0.50	Ferrous metal electroplating, steel manufacture, fertilizer production, and asphalt emissions	Monoli et al. (2004)
	0.48	Metal scrap burn	Tsai et al. (1995)
MPh/Ph	1–8	Represent evidence for enhanced mobile sources or unburned fossil organic material contribution	Gogou et al. (1996)
	< 1	Typical of emissions from stationary sources where fuel is burning at higher temperatures	Gogou et al. (1996)
	0.5	Atmospheric fallout	Takada et al. (1991)
	0.5–1.0	Combustion sources	Prahl and Carpenter (1983)
	1.0	Street and urban dusts	Takada et al. (1990, 1991)
	2.0–6.0	Fossil fuel	Prahl and Carpenter (1983)
	4.0	Crankcase oil	Pruel and Quinn (1988)
BFs/BghiP	1.60	Diesel cars	Li and Kamens (1993)
	0.33	Gasoline cars	Li and Kamens (1993)
	2.18	Wood	Li and Kamens (1993)
	4.7	Road dust	Rogge et al. (1993a)
	1.8	Roadway soil	Oda et al. (2001)
	7.1–11.2	Industrial	Yang et al. (1998)
	7.8	Cement plant	Yang et al. (1998)
	4.0	Metal scrap burn	Tsai et al. (1995)
α	3×10^{-4}–40×10^{-4}	Common emission sources for PAH and BC	Blanchard et al. (1994)
BaPE		Index that has been introduced instead of the sole BaP since the later is easily decomposed in reactive air. It tries to parameterise the health risk for humans related to ambient PAH exposition and is calculated by multiplying the concentrations of each carcinogenic congener. Exposition to a significant cancer risk if values exceed 1.0 ng m^{-3}.	Cecinato et al. (1998), Marino et al. (2000), Yassaa et al. (2001b)

BaA – Benzo[a]anthracene; CT – Crysene and Tryphenylene; BeP – Benzo[e]pyrene; BaP – Benzo[a]pyrene; Flu – Fluoranthene; Pyr – Pyrene; IcdP – Indeno[1,2,3-cd]pyrene; BghiP – Benzo[ghi]perylene; CPAH – nine combustion PAH (Fluoranthene, Pyrene, Benzo[a]anthracene, Crysene, Benzofluoranthenes, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene] and Benzo[ghi]perylene); ΣPAH – total concentration of PAH; MPh – Methylphenanthrenes; Ph- Phenanthrene; BFs = Benzofluoranthenes; $\alpha = \Sigma\text{PAH/BC}$; BaPE – Benzo[a]pyrene-equivalent carcinogenic power = BaPE = $\text{BaA} \times 0.06 + \text{BFs} \times 0.07 + \text{BaP} + \text{DBA} \times 0.6 + \text{IcdP} \times 0.08$; DBA = Dibenzo[a,h]anthracene.

(c) *Thermally maturated and pyrogenic components* – sum of the concentrations of anthropogenic n-alkanes (Total C_n – Wax C_n) and the corresponding unresolved complex mixture; n-alkanoic acids, C_{10}–C_{18}, with CPI$<$1.5; alkylcyclohexanes; alkylcylopentanes; hopanes; steranes; diasteranes; pristane; phytane; ketones and aldehydes with CPI < 1.5; biomass burning tracers and PAH.

To exemplify the application of this methodology, the different source groups contributing to the aerosol constitution in different locations are plotted in Figure 6. Surprisingly, high relative concentrations of biomass smoke and petrogenic constituents in organic matter were observed for wintry conditions at European continental low level sites (Moitinhos and K-Puszta). This indicates the transport from urban emissions in the vicinities and a sizable impact of domestic biomass burning on air quality. The contribution of petroleum residues and other thermally produced constituents at these non-urban European sites is comparable to those reported for Asiatic urban and suburban aerosols. The lipid wax components ranged from a minimum of 17% in Hong Kong to a maximum of 83% in rural Nigeria of the apportioned organic mass. The fractions of microbial components for European sites are of the same order than those of the Nigerian rural aerosol, but one-half lower than the one estimated for the Amazon particulate matter.

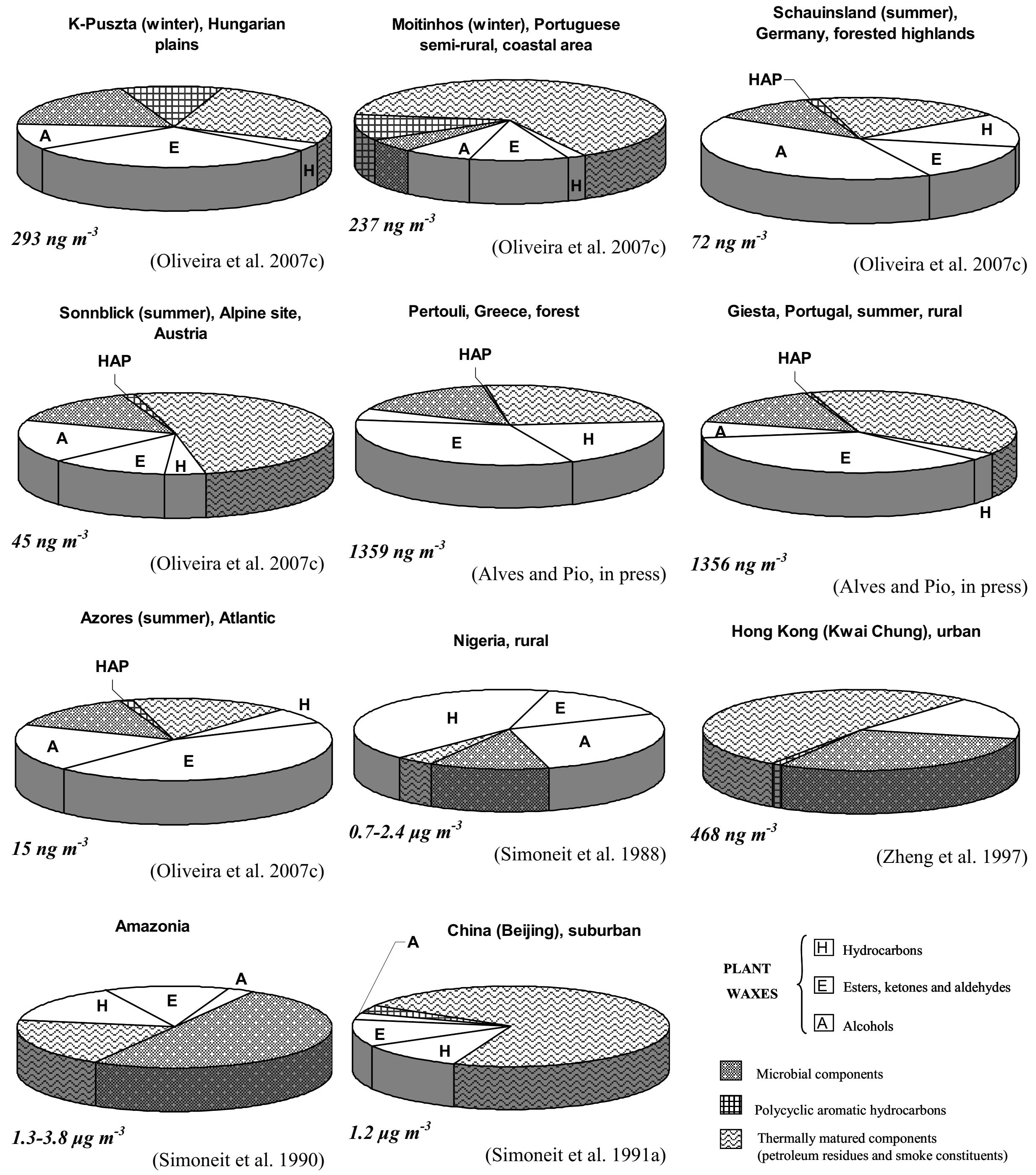
CONCLUSIONS AND RECOMMENDATIONS

Various studies on the composition of atmospheric particulate matter revealed that a significant fraction of the total mass could be attributed to organic constituents. Despite its abundance, the role of the organic aerosol as a substrate for chemical reactions is not well understood. Due to the large variety of organic functional groups at the particle surface they are possible reactants for many chemical processes with gaseous molecules in the troposphere. The difficulties in characterising the large variety of compounds present are still aggravated, because this study represents a complicated, time-consuming and expensive process. Much of the research to date has focused upon urban areas, where organic emissions are large and have dramatic effects on air quality and particulate mass concentrations. More pristine environments, especially forests where VOC emissions are large and potential contributors to SOA, remain poorly characterised. Assessment of natural *versus* anthropogenic and of primary *versus* secondary organic contributions to aerosol in non-urban regions represents an important research area, since very little is known about these environments.

Usually, *n*-alkanes and aliphatic acids constitute the dominant solvent-extractable components of the atmospheric particulate matter. Smaller quantities of alcohols, aldehydes, ketones, terpenoids and PAH are also observed. These constituents are emitted directly from biogenic sources (vascular plant wax, microorganisms, pollen, etc.) or derive from anthropogenic activities (vehicular emissions, wood combustion, etc.). The aerosol compounds that are formed by direct oxidation from volatile organic precursors are also detected in the particulate matter, representing a fraction of the total chromatographycally resolved organic mass. Molecular marker techniques can be used to identify contributions of sources such as combustion and biogenic emissions. However, source apportionment strategies will still need the challenge of truthfully determining the concentration of SOA in the particulate phase. Additional field studies are required in locations that are impacted by SOA deriving from both biogenic and anthropogenic sources. Although quantitative collection of both semi-volatile and particulate phase organic compounds is enviable, the existing sampling equipment is not capable of efficiently collect compounds with lower vapour pressures. Also, further smog chamber experiments will be usefull in providing information on stability of potential tracers for SOA and atmospheric reactions. Moreover, these experiments will constitute an opportunity to test more advanced analytical techniques, to model the fate of the secondary aerosol from precursor to sink, and to perform an integration of experimental procedures among field campaigns, primary source measurements and laboratory studies. It seems important to evaluate the methods in use for measuring secondary aerosol components.

One of the most important goals associated with the detailed chemical analysis of organic aerosols consists of mass balances relating gravimetric measures, carbonaceous content and organic compound classes. Until now the scientific investigation did not allow to close these mass balances because of the difficulties in extracting and measure some complex constituents by conventional methods. Recent results on water-soluble organic carbon supplement data of previous studies, but the overall understanding of the organic aerosol remains relatively obscure. New approaches for the chemical analysis of the organic aerosol based on a combination of solvent and water extractions, preparatory separations into different functional groups and efficient instrumental determination will give a more clear insight into the origin and formation processes of primary and secondary carbonaceous particles. Once more, it should be recognised the necessity of future work to assess the overall organic composition of atmospheric aerosols, including their hydrophilic constituents, and to develop more efficient analytical equipments able to discriminate the carbonaceous content.

Accurate quantification of the amounts of trace gases and particulate matter emitted from forest fires and other sources of biomass burning on a regional and global basis is required by a number of users, including scientists studying a wide range of atmospheric pro-



K-Puszta (winter), Hungarian plains

293 ng m⁻³ (Oliveira et al. 2007c)

Moitinhos (winter), Portuguese semi-rural, coastal area

237 ng m⁻³ (Oliveira et al. 2007c)

Schauinsland (summer), Germany, forested highlands

72 ng m⁻³ (Oliveira et al. 2007c)

Sonnblick (summer), Alpine site, Austria

45 ng m⁻³ (Oliveira et al. 2007c)

Pertouli, Greece, forest

1359 ng m⁻³ (Alves and Pio, in press)

Giesta, Portugal, summer, rural

1356 ng m⁻³ (Alves and Pio, in press)

Azores (summer), Atlantic

15 ng m⁻³ (Oliveira et al. 2007c)

Nigeria, rural

0.7-2.4 µg m⁻³ (Simoneit et al. 1988)

Hong Kong (Kwai Chung), urban

468 ng m⁻³ (Zheng et al. 1997)

Amazonia

1.3-3.8 µg m⁻³ (Simoneit et al. 1990)

China (Beijing), suburban

1.2 µg m⁻³ (Simoneit et al. 1991a)

Fig. 6 – Pie diagrams showing the apportionment of various lipid fractions to sources in various regions of the word.

cesses, national governments who are required to report greenhouse gas emissions, and those interested quantifying the sources of air pollution that affect human health at regional scales. In Europe and other parts of the world, data on detailed emission factors from biomass burning are rather inexistent. Emission inventories and source apportionment, photochemistry and climate change models use default values obtained for US biofuels, uncommon in other countries. Thus, it is desirable to use more specific locally available data.

In spite of comparisons between sites being difficult due to the lack of harmonisation in sampling and analytical techniques, it would be advantageous the compilation of existing results in a freely accessible scientific database. The assessment of the variability of aerosol in space and time would permit a better understanding of their sources, properties, atmospheric behaviour and effects. Also, it would help evaluate the representation of aerosols in chemical transport and climate models.

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RESUMO

Apesar de constituirem 10-70% da massa do aerosol atmosférico, a caracterização dos compostos orgânicos particulados permanece ainda deficitária e vários aspectos relativos à formação e evolução do aerossol são ainda desconhecidos. A crescente preocupação com o impacto do aerosol particulado no clima e os reconhecidos efeitos dos constituintes antropogênicos na qualidade do ar e na saúde humana têm motivado a realização de numerosos estudos. Estas investigações têm fornecido informações relevantes sobre o comportamento da matéria particulada na atmosfera e sobre o seu conteúdo carbonáceo. A compilação de tais resultados reveste-se da maior importância, dado que possibilitará coligí-los numa ainda emergente base de dados global sobre a composição orgânica dos aerossóis. A contribuição das principais fontes de emissão para a poluição particulada a nível regional pode ser diagnosticada através da utilização de marcadores moleculares específicos. Esta revisão foca sobretudo os resultados obtidos por cromatografia gasosa acoplada a espectrometria de massa, dado que é o método analítico de eleição para a clarificação dos compostos orgânicos extratíveis por solventes presentes na matéria particulada atmosférica. Uma sinópse da selecção de compostos traçadores e da aplicação de parâmetros geoquímicos à análise dos constituintes orgânicos como ferramenta para estimar a contribuição das diversas fontes é aqui apresentada. Além de uma avaliação do conhecimento atual, o artigo identifica também as necessidades de investigações futuras.

Palavras-chave: aerossol atmosférico, cromatografia gasosa-espectrometria de massa, compostos orgânicos, fontes contributivas, traçadores.

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