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Atmospheric Transport of Terrestrial Organic Matter to the Sea

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Abstract The transport of atmospheric particles with associated terrestrial organic matter to the oceans is an important process affecting various global concerns such as climate change and environmental and human health. Aerosol particulate matter over the oceans is derived from autochthonous emissions admixed with varying amounts of continental effluents. It is important to be able to assess the sources and fate (receptors) of aerosols, and both inorganic and organic tracers are of utility. The organic compounds of atmospheric particles from marine and terrestrial regions can be characterized by specific tracers for (1) natural emissions (marine lipids, vegetation waxes, terpenes), (2) fossil fuels utilization (internal combustion engine emissions, coal burning), (3) biomass burning (taxon specific, wildfires), (4) anthropogenic emissions (industry, urban activity), and (5) soil and desert sand resuspension (agriculture, wind erosion). The precursor–product chemistry can then be used to assess the secondary reactions (thermal or atmospheric) and the fate of aerosol organic matter.

Keywords Aerosols · Biomarkers · Lipids · Fossil fuels · Saccharides

1
Introduction

Organic matter can be transported to the sea by river, atmospheric, and ice rafting processes. For all these processes the continental material must first be broken down into smaller particles, i.e., eroded, before removal. This erosion is mainly by the action of flowing water, but air erodes the finer particles from areas where no moisture binds the soil or minerals together [1]. Rivers deposit large amounts of mainly mineral detritus near their deltas in the ocean. Atmospheric fallout and washout deposit lesser amounts of mineral and associated organic matter over larger areas of the oceans [2–4]. This chapter deals with the atmospheric transport of the particle-associated organic matter to the sea.

1.1
Global Dust and Wind Systems

The earliest observations on eolian dust fallout in the Atlantic Ocean were reported by Darwin [5] and Ehrenberg [6], who concluded that Africa was the most likely source of the dust on the basis of the fresh-water diatom fossil content. The identification of eolian material in marine sediments was initially reported by Radczewski [7, 8], using iron oxide coated quartz particles

(*Wüstenquarz*) as the diagnostic marker for desert dust derived from central North Africa. The presence of *Melosira granulata* in eolian dust collected at Barbados [9], and the report that this same fresh-water diatom species was present in deep-sea sediments of the tropical belt of the Atlantic Ocean [10], confirmed the wind transport of these diatoms across the sea from Africa. They originated in lakes, rivers, and swamps of central Africa, where, after the dessication during the dry season, fine dust from the bottom muds (often with plant detritus and ash) was taken up by the trade winds and blown out to sea [9]. Rex and Goldberg [11] surveyed wind-transport mechanisms and summarized three generic classes for particulate matter: (1) extraterrestrial particles, (2) solids of biological origins (including anthropogenic emissions)

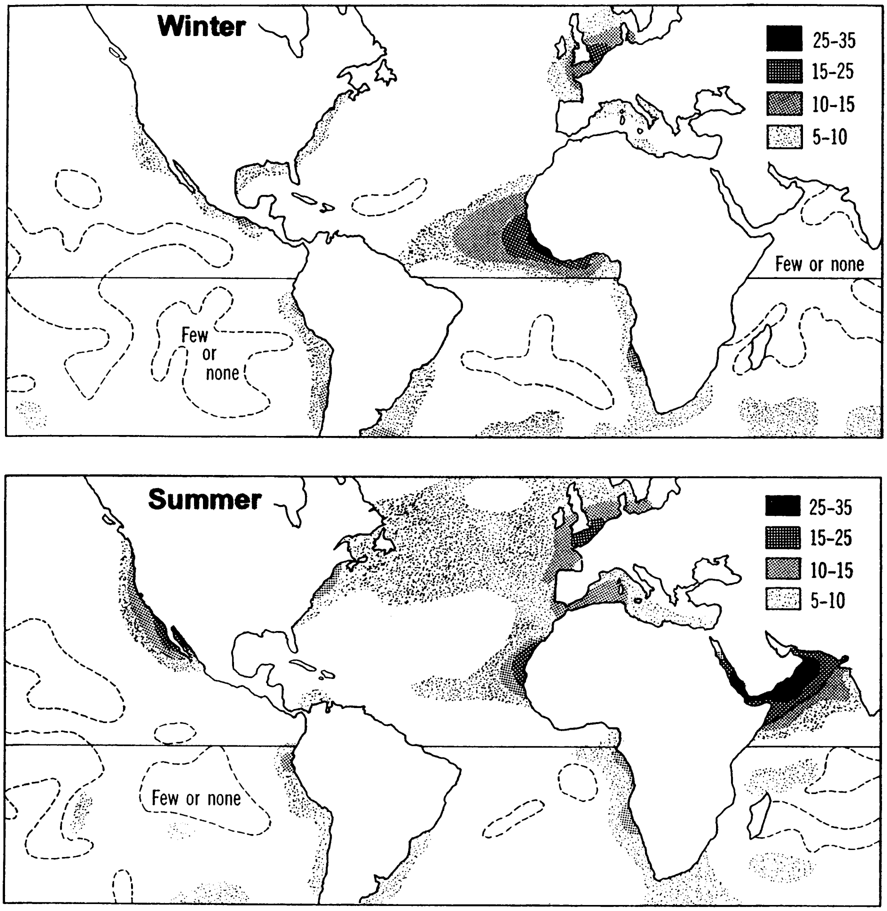

Fig. 1 Average frequency of haze over the ocean during the northern winter (*upper map*) and summer (*lower map*). Frequencies are given in percent of total number of observations. (Redrawn from Arrhenius [233]. Reproduced with permission, J. Wiley & Sons)

from the continents, and (3) solids of inorganic origins from the lithosphere, including debris from volcanic activity.

Generic class 2 is the major contributor of organic matter to eolian particulate matter and includes man's activities. Most atmospheric fallout and washout originates from the lower troposphere (altitude below 15 km [12]). The major wind patterns of the troposphere are the trade winds and westerlies. The haze observed over certain parts of the world ocean (Fig. 1) is due mainly to atmospheric particulate matter. Parts of the Atlantic Ocean (15°N–50°N, westerlies driven by the jet stream; 15°S–15°N, trade winds; 15°S–50°S, westerlies driven by the jet stream), the Indian Ocean (15°S–20°N, trade winds; 20°S–50°S, westerlies), and some areas of the Pacific Ocean (15°N–50°N, westerlies; 15°N–15°S, trade winds; 15°S–50°S, westerlies) are the major regions of the world ocean where atmospheric input to the sediments is presently significant [13].

Aerosols influence the radiative balance of the Earth through absorption and scattering of solar radiation back to space, known as the direct effect, and by increasing the amount of solar radiation that clouds reflect, the indirect effect [14]. The direct radiative effect of aerosols in strongly influenced by particle size and composition. Radiative effects of anthropogenic aerosols are relatively large compared with their mass contribution because they are in the size range which is radiatively most active [15–17]. Particles emitted from biological organic matter are a source that contributes significantly to the total particle burden in the atmosphere.

Another major concern is the potential detrimental human health effects of fine aerosol particulate matter with its associated toxic organic compounds (e.g., polycyclic aromatic hydrocarbons, PAHs [18, 19]). These health effects have been addressed mainly in urban areas; however, increasing global industrialization with concomitant urban development results in more global distributions and transport of the anthropogenic toxic emissions, even across the oceans.

1.2
Inorganic Tracers

The eolian dust veil over the North Atlantic has been investigated more extensively than any other marine area, especially in terms of inorganic chemistry [4, 20–28]. A dust fall south of the Cape Verde Islands on 17 January 1965 [25, 26], when examined under the microscope, consisted of mostly quartz and calcite in the coarse fraction (silt). Most of the remainder was phytoliths (about 5%), fresh-water diatoms (about 3%), and fungal spores (about 2%). Insect scales, plant tissue, and a few opaque spherules (urban emissions) were also observed, but pollen was not found. The phytoliths were associated with the fresh-water diatoms, indicating the same areal source, such as grasslands around intermittent lakes [25].

The major terrigenous marker minerals composing eolian dusts from various global areas are clays, quartz (usually coated with iron oxide), and feldspars [4, 29]. The clays consist of montmorillonite, illite, chlorite, and kaolinite and are all of a land-derived origin [24].

1.3

Urban–Global Mixing and Transport

The atmosphere–ocean interface is under intensive study to assess the transport and deposition of organic and inorganic chemical species from land to ocean, and ultimately to the marine sedimentary record [30, 31]. The atmospheric input of terrigenous organic carbon to the world ocean is about equivalent to the organic carbon washed out by the rivers, and is estimated to be 20 Tg per year [32]. Most of this carbon is of a contemporary biological origin, and is associated with transport of mineral dust by major wind systems that are seasonally active from the continents to the oceans [2, 3, 13, 27, 33–38]. The increasing atmospheric burden of urban particulate matter intermingles with the natural and anthropogenic emissions in the continental rural areas, and the total mixture is eventually transported to the atmosphere over the oceans [39, 40]. Major oxidative-photochemical reactions alter the organic matter composition during transport, forming derivative products with higher oxygen contents, i.e., greater polarity [41, 42]. Those secondary products form cloud condensation nuclei, complementing inorganic species such as SO_x and NO_x. Thus, molecular characterization and provision of mass balance estimates for aerosols near sources and in downwind regions will continue to be a major need.

A precautionary comment needs to be made regarding the analyses of low-level organic tracers in atmospheric particles transported over long distances. This was discussed with an example of a study from Puerto Rico which addressed organic aerosols of the trade winds in the Caribbean [43]. These authors reported primarily synthetic organic compounds found in suntan lotions and other lubricants, and proposed that those compounds were natural components of the trade wind particulate matter. All the compounds reported appear to be artifacts and contaminants from the sampling and experimental procedures, and the inferred results are not valid [44]. Successful contamination control for aerosol sampling on islands has also been extensively discussed for the SEAREX Program (Refs. [45, 166] and references therein).

1.4

Dust Input to the Ocean

The actual input of eolian dust to marine sediments occurs by two major pathways, namely, dry fallout and wet washout [45]. When the dust falls out or is washed out by rain onto the sea surface, it rapidly flocculates [46]. The floc formation appears to be aided by the presence of organic matter [47]. The settling speeds of such flocculated aggregates are many times greater that those of the constituent particles [46]. Marine filter feeders may also ingest some of the organic-rich flocs and thus aggregate the material into fecal pellets, which then also sink rapidly [9, 48, 49]

1.5
Definitions of Terms Used

Some of the terms and concepts used in this chapter need to be defined, because they are not necessarily the same as used by scientists in other disciplines. A brief selection follows:

Aerosol An atmospheric suspension of liquid and solid particles, including adsorbed water and volatile organic components on the solids.

Anthropogenic Designates derivation from human activity.

Biomarker Molecules that have definitive chemical structures, relatable either directly or indirectly through a set of diagenetic alterations to biogenic precursors (sources), and that cannot be synthesized by abiogenic processes.

Biomass Any biosynthetic matter, such as all vegetation (flora), its recent detritus (e.g., litter, humus, peat to lignite), all fauna (e.g., rendering, cooking), and all products produced by industry utilizing biomass as raw material (e.g., paper, rubber).

Bitumen The geological equivalent of lipids, consisting in the widest sense of any sedimentary hydrocarbon mixture ranging in state from tarry (asphalt), through viscous to liquid (petroleum).

Desert sand The fine fraction of wind-eroded particulate matter carried by major wind systems from continents to the sea (e.g., Kosa Asian dust, Sirocco).

Lipids A broad term that includes all oil-soluble, water-insoluble organic substances, such as fats, waxes, fatty acids, fatty alcohols, sterols, pigments, and terpenoids, all biosynthesized by contemporary biota.

Particles Can be solid or a liquid in air (gas). A mixture of such solid and liquid particles constitutes an aerosol. Typical dimensions are greater than 0.001 mm and particles can be sampled by filtration.

Smoke Small gasborne particles formed during incomplete combustion. It consists mainly of carbon and minor organic compounds and inorganic matter with typical dimensions greater than 0.01 μm.

Soil The fine particle fraction injected into the atmosphere during agricultural tilling and harvesting of fields, and by wind erosion of fallow fields.

2
Terrestrial Organic Matter in the Atmosphere

Atmospheric particulate matter contains organic tracers which are characteristic of (1) their sources (biological and geological), (2) the mode of formation, and (3) subsequent alteration during transport (secondary products) downwind. The major source categories and the production mechanisms for atmospheric particulate matter with the associated organic compound tracers are summarized in Table 1. The compound composition of urban, rural, and remote (including marine) aerosol samples will be described here briefly by using some illustrative examples. The major compound groups derived from emission sources of atmospheric particles are summarized in Table 2.

Table 1 Source categories and production mechanisms for atmospheric particulate matter (*PM*) and associated organic tracers

Source category, process	Interpretation/Application
Natural or uncontrolled processes	
1. Terrestrial	
(a) Vegetation (wind abrasion and electrostatic)	Natural-background PM (biogenic)
(b) Soil erosion/resuspension	Natural-background PM (biogenic/synthetic)
(c) Wild fires, biomass burning	Smoke/ash PM, biomarkers (biogenic)
2. Marine	
Autochthonous lipids (seaslick)	Natural-background PM (biogenic)
Anthropogenic activities	
1. Urban (industries, food preparation, home heating)	Smoke/dust, biomarkers, and synthetic compounds
2. Rural/remote (agriculture, controlled burning, soil resuspension)	Dust/smoke, biomarkers (biogenic)
3. Marine (fallout of ship emissions/ resuspension of seaslick)	Exhaust biomarkers (geologic)
Fossil fuels	
1. Petroleum (internal combustion engines)	Exhaust biomarkers (geologic)
2. Coal (burning)	Smoke biomarkers (geologic)

Table 2 Key source-specific tracers for organic components in aerosol particles

Compound or compound class		Major source [a]	Emission process [b]
n-Alkanes	C_{15}–C_{20}	Microbial (urban)	Direct/resuspension (vehicle exhaust)
	C_{20}–C_{37}	Plant waxes (urban)	Direct/biomass burning (vehicle exhaust)
n-Alkenes	C_{15}–C_{37}	Biomass (coal)	Burning
n-Alkan-2-ones	C_{15}–C_{35}	Biomass (coal)	Biodegradation (burning)
n-Alkanals	C_{15}–C_{35}	Biomass (coal)	Biodegradation (burning)
	C_3–C_{10}	Microbial (fossil fuel)	Photo-oxidation (combustion)
n-Alkanoic acids	C_{12}–C_{19}	Microbial (biomass)	Direct/resuspension (burning)
	C_{20}–C_{36}	Higher plants	Direct (burning)
n-Alkanols	C_{14}–C_{36}	Biomass	Direct (burning)
n-Alkyl amides	C_{14}–C_{32}	Biomass	Burning (cooking)
n-Alkyl nitriles	C_{14}–C_{32}	Biomass	Burning (cooking)
Alkanedioic acids	C_2–C_{28}	Various	Photo-oxidation (combustion)
Wax esters	C_{28}–C_{58}	Plant waxes	Biomass burning
Triterpenyl alkanoates		Tropical vegetation	Biomass burning
Triacylglycerides		Flora (fauna)	Biomass burning (cooking)
Methoxyphenols		Biomass with lignins	Burning
Levoglucosan (mannosan, galactosan)		Biomass with cellulose	Burning
Saccharides		Soil (sugar processing)	Direct resuspension (agricultural/industrial)
Cholesterol		Urban (algae)	Cooking (direct)
Phytosterols		Higher plants	Burning (direct)
Triterpenoids		Higher plants	Burning (direct)
Diterpenoids (resin acids)		Higher plants, i.e., conifers	Burning (direct)
Hopanes/steranes		Petroleum	Urban (vehicle exhaust, etc.)
UCM		Petroleum	Urban (vehicle exhaust, etc.)
Alkylpicenes/alkylchrysenes		Coals	Urban (burning/heating)
PAHs		Ubiquitous	All pyrogenic processes

UCM unresolved complex mixture, *PAHs* polycyclic aromatic hydrocarbons

[a] Secondary source in *parentheses*

[b] Listed in order of importance

2.1
Volatile Compounds

Volatile compounds in urban and rural airsheds are primarily hemi-, mono-, and sesquiterpenoids from vegetation and anthropogenic spillage and use of solvents, gasoline, etc. These compounds react quickly with OH, ozone, NO_x, or UV radiation, producing secondary aerosols [17, 50]; thus, the precursors and possibly the products are not expected to survive long-range transport. Volatile compounds are therefore not considered further in this review, although their secondary products may contribute to the low molecular weight polar compounds (e.g., oxalic and C_3 – C_5 dicarboxylic acids) in air parcels transported over long distances.

2.2
Organic Matter of Atmospheric Particles

The organic matter of atmospheric particles described here consists of extractable (solvent-soluble) organic compounds. It includes the fulvic and humic acid components that occur in some aerosols, but does not consider the biogenic particles such as bacteria, algae, pollen,and spores. The soluble components of biogenic particles are also extracted if they are not removed by size exclusion during sample acquisition.

2.2.1
Organic Compounds

The organic matter of atmospheric particles consists predominantly of lipids, soot, and humic and fulvic acids, and is now firmly established as a major fraction of aerosols [37, 38, 51–120]. Many of these reports present data for biological, fossil fuel, and other-source organic matter admixed in the aerosols. Furthermore, in comparison to the relatively extensive studies that have been carried out on hydrocarbons in aerosols of both natural and anthropogenic origins from urban and rural/remote regions, less molecular information is available on polar and water-soluble compounds [38–40, 45, 70, 82, 103, 105, 107, 108, 111, 121–126].

The oxidative breakdown of organic compounds in the atmosphere is another active research area. It produces, for example, short-chain-length monocarboxylic, dicarboxylic and ketocarboxylic acids (C_2–C_6), which are the secondary products (oxidation) from higher molecular weight organic compounds of both biological and fossil fuel origins, and not solely from unsaturated fatty acids [33, 34, 42, 127–129]. These carboxylic acids are found globally in the atmospheres of both urban and remote areas.

2.2.2
Urban Emissions

There have been numerous reports on organic compounds in urban atmospheric samples and most deal with the compounds related to human health effects (e.g., PAHs) and emissions from traffic. These will not be reviewed here and the reader is referred to earlier reviews[130–133], and to key summaries for the toxic PAHs [134–140]. Chemical fingerprints of emission sources have commonly been utilized to distinguish specific inputs from point sources, rather than correlation of an air parcel to its regional source [91, 141, 142]. The transport of urban emissions to remote and marine areas is an important component superimposed on the natural organic matter background and must therefore be considered in global modeling [39, 40, 143, 144].

2.2.3
Burning of Biomass

Burning of biomass is a ubiquitous process and comprises natural wildfires and numerous anthropogenic activities, such as controlled burning in agriculture and forestry, burning wood for heating or other purposes, food preparation such as grilling and frying, tobacco use, rendering industries, crematoria, and garbage disposal. Smoke, especially from wildfires, is transported globally. The fossil fuels, i.e., petroleum, coal, lignite, and peat, are derived from biological organic matter of past geological times and when burned emit compounds which are distinguishable from those derived from biomass burning. This topic and the associated organic tracers have been reviewed recently and the review also includes emissions from coal combustion [145].

Biomass burning is an important primary source of many organic compounds which are reactants in atmospheric chemistry, and of soot particulate matter that decreases visibility and absorbs incident radiation [146–148]. Thus, it is the smoke from burning processes which needs more source testing and characterization. The compound composition data of smoke particulate matter is important for understanding the contribution of organic components from biomass burning emissions to atmospheric chemistry and complements existing reports on the characterization of direct organic emissions (natural background) from biomass sources [37, 62, 81, 87, 90, 94, 99, 104, 105, 117, 125, 126, 140, 145, 149–161].

The varying temperature conditions during burning determine the molecular alteration and transformation of the organic compounds emitted from biomass fuels [125, 126]. The heat intensity, aeration, and duration of smoldering and flaming conditions determine the distributions and ratios of the natural versus altered compounds present in smoke [117, 126]. Thus, the directly emitted and the thermally altered molecular tracers in smoke provide a chemical fingerprint which is source-specific and useful for identifying contributions from single or multiple biomass fuels in samples of atmospheric particulate matter. Such data can complement the inorganic marker potassium from "potash" (water-soluble), which has been suggested as a tracer for wood smoke in receptor models [162]. However, K^+ is also emitted by other major sources in urban areas, such as meat cooking and refuse incineration [92, 163, 164], which must be taken into account in mass balance models.

2.2.4
Aliphatic Homologous Compounds

Aerosol particulate matter transported over the ocean contains mainly aliphatic lipids from terrestrial plant waxes admixed with varying amounts of urban emissions, autochthonous marine lipids, and secondary oxidation products [37, 38, 41, 45, 68, 69, 99, 100, 113, 165]. This was studied in detail during the SEAREX Program ([45, 166] and references therein) and is being confirmed under the auspices of the ACE-Asia Program [38, 40, 165, 167].

The distributions of the *n*-alkanes in ambient aerosol samples range from C_{16} to C_{40}, with a typical C_{max} at 29 or 31 and high carbon preference index (CPI) values [77, 105]. The presence of an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons in urban samples (Fig. 2a, c), the *n*-alkanes from C_{16} to C_{22}, pristane, and phytane, indicates a direct input from petroleum fuel use (Fig. 2b, d; minor *n*-alkanes are better discernable in m/z 85 key ion plots of gas chromatography–mass spectrometry, GC-MS, data) [101, 103]. The higher molecular weight constituents (above C_{23}) represent the typical petroleum components in urban atmospheric particles with a minor amount of natural plant wax alkanes superimposed [82, 101, 103, 105, 115]. In remote and marine areas, the aerosols contain predominantly natural plant wax components as illustrated in Fig. 2c and d. The plant epicuticular wax signature is evident in the key ion plot (m/z 85) showing the strong odd-carbon-number predominance and C_{max} at 29. The GC-MS data for the total extract (silylated) of aerosol particles taken in Sapporo, Hokkaido, Japan, during the Asian dust event of 2001 are summarized in Fig. 3. The major components are polar compounds with minor aliphatic lipids. Key ion plots are used to define the homologous series (e.g., m/z 85 alkanes, m/z 117 alkanoic acids). The alkanes in the Sapporo aerosol can be apportioned into plant wax and fossil fuel emissions as drawn in Fig. 3b.

The *n*-alkanoic (fatty) acids are significant components in extractable aerosol lipids (especially marine samples: Figs. 2a, c, 3a, c) and generally range from C_{10} to C_{32}, with a strong even-carbon-number predominance (CPI > 5) and bimodal distribution with C_{max} at 16 and a secondary maxium at 24 or 26. They are interpreted to be of a biogenic origin. The homologs shorter than *n*-C_{20} may be derived in part from microbial/marine sources, although these acids are ubiquitous in biota [107]. The homologs longer than *n*-C_{22} are derived primarily from vascular plant wax [37, 168]. Long-chain wax esters (LCWE) are present in aerosols and in the smoke from burning many plant species, typically with compounds from 36 up to 60 total carbon numbers and a strong even-carbon-number predominance [105, 107, 169]. The LCWE series generally comprise mainly palmitic acid esterified with fatty alcohols ranging from C_{22} to C_{34} and minor amounts of stearic (C_{18}) and arachidic (C_{20}) acids esterified with the C_{32} and C_{34} alcohols. Wax esters occur in smoke aerosols at abundances comparable to those of the *n*-alkanes,

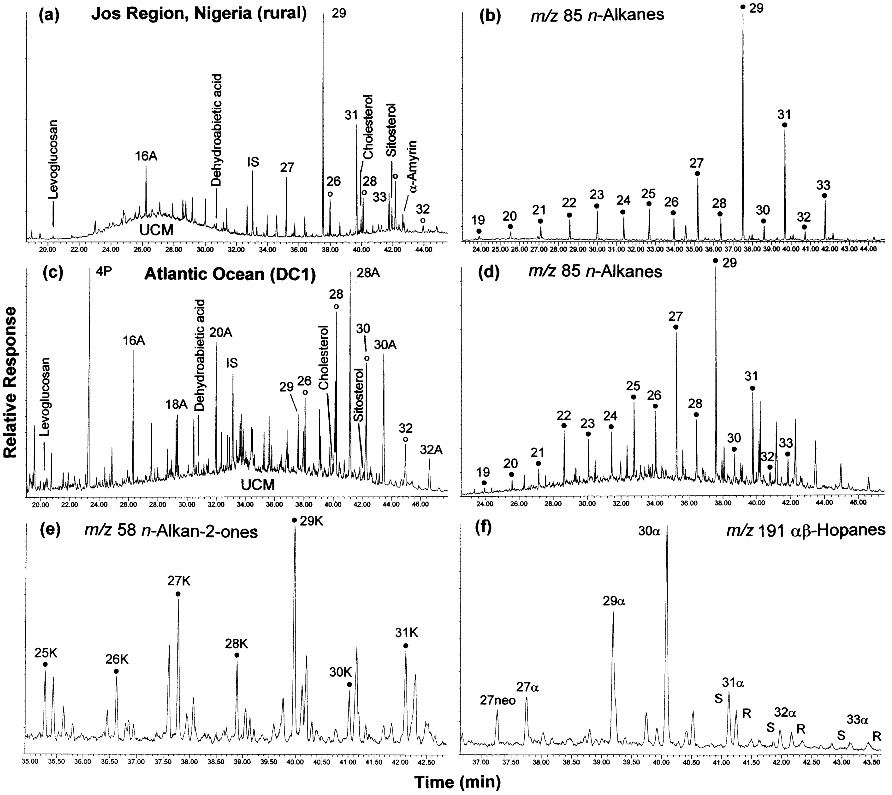

Fig. 2 Examples of gas chromatography–mass spectrometry (*GC-MS*) data for typical total extracts from aerosol particle samples (analyzed as silylated derivatives): **a** total ion current (*TIC*) trace for Jos region aerosol, Nigeria (March 1979), **b** *m*/*z* 85 fragmentogram (key ion for *n*-alkanes) for Jos aerosol showing the odd-carbon-number predominance of the wax alkanes, **c** TIC trace for Atlantic Ocean aerosol (DC2, December 1974), **d** *m*/*z* 85 fragmentogram, **e** *m*/*z* 58 fragmentogram (key ion for *n*-alkane-2-ones), and **f** *m*/*z* 191 fragmentogram (key ion for the hopane biomarkers) for DC2. The GC temperature program is different for the various samples. *UCM* unresolved complex mixture, *IS* internal standard ($C_{24}D_{50}$), *numbers* refer to carbon-chain length of *n*-alkanes, *iA* *n*-alkanoic acids, *open circles* alkanols (analyzed as trimethylsilyl ether or methyl esters)

providing further evidence for direct volatilization of very high molecular weight compounds into smoke and aerosols. They are found at trace levels in aerosols, indicating rapid and extensive alteration (hydrolysis) probably to the constituent fatty acids and alcohols.

Minor series of *n*-alkan-2-ones are often present in aerosol samples (Fig. 2e) and range from C_{25} to C_{35} with an odd-carbon-number predominance (CPI > 4). These compounds have been described for aerosols enriched in anthropogenic components [103, 104], and because they have essentially the same distribution and range as the wax alkanes indicate an origin from

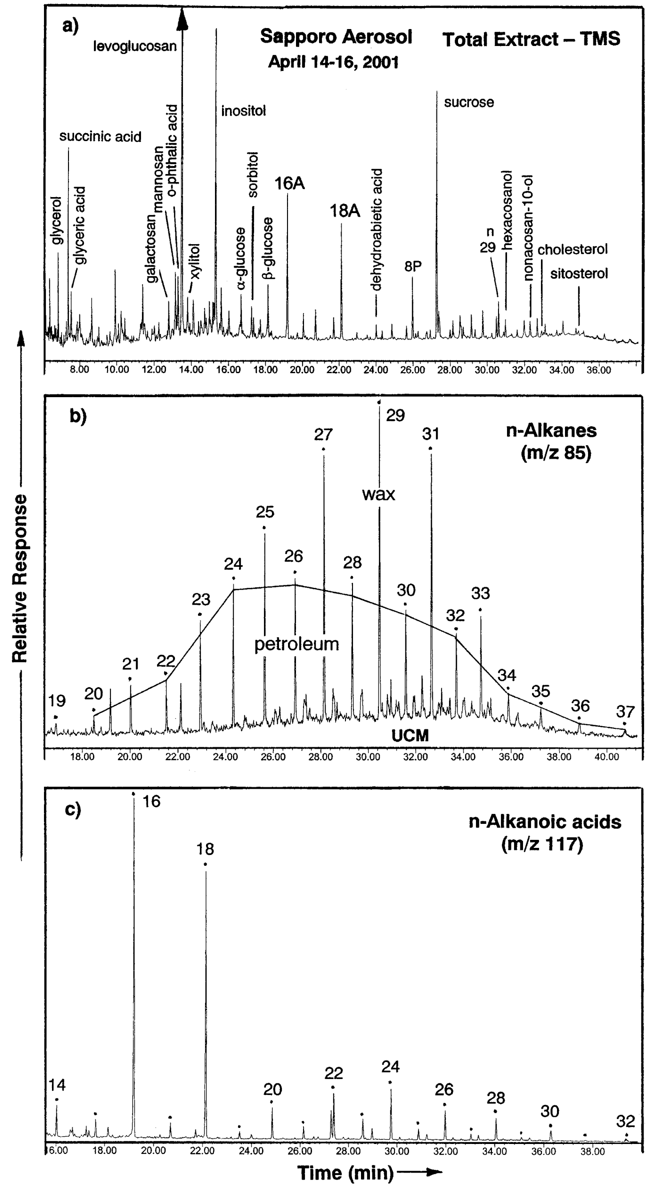

Fig. 3 GC-MS data for total extract of urban aerosol particles from Sapporo, Japan (April 2002, as silylated derivatives): **a** TIC trace, levoglucosan is shown at 0.4 of its total intensity, **b** *m/z* 85 fragmentogram (key ion for *n*-alkanes), and **c** *m/z* 117 fragmentogram (key ion for fatty acid TMS esters). Tracer compounds are labeled, *16A* and 18A are *n*-alkanoic acids, *8P* is diethylhexyl phthalate, *n29* is nonacosane, *numbers over dots* indicate carbon-chain length, *UCM* is the unresolved complex mixture, *petroleum* is the *n*-alkane contribution under the envelope drawn from fossil fuel emissions and *wax* is the amount of superimposed *n*-alkanes derived from epicuticular plant wax

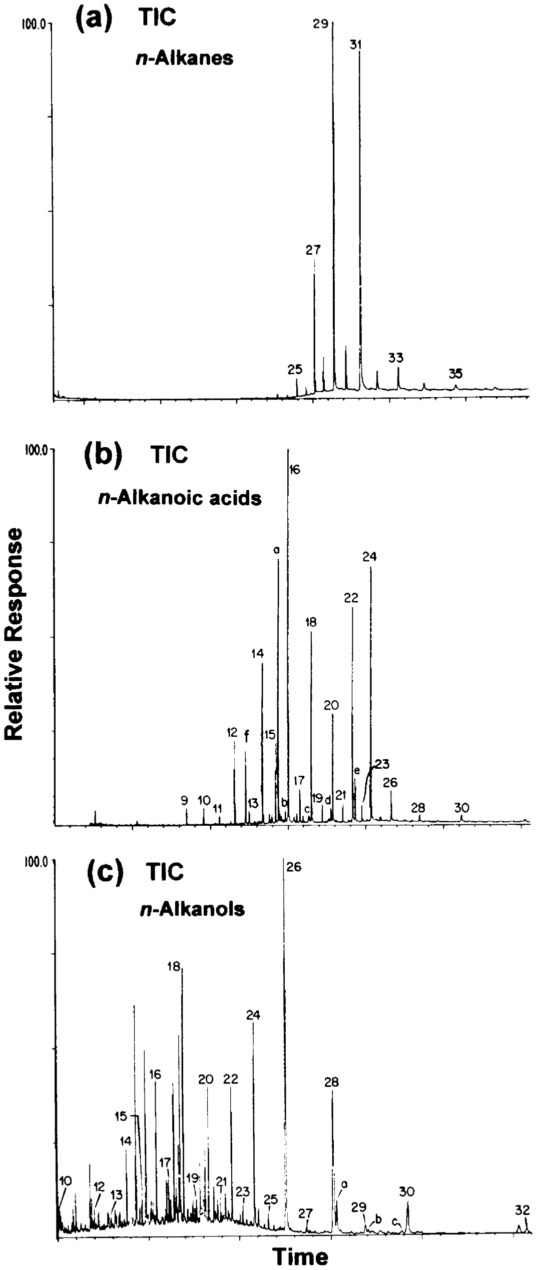

Fig. 4 TIC traces for the GC-MS analyses of extract fractions from a rural aerosol sample (Corvallis region, OR, USA): **a** total *n*-alkanes (F1), **b** alkanoic acids (analyzed as methyl esters) and *n*-alkan-2-ones (F2 and F3) (*a* phytone, *f* farnesone, *b*–*e* *n*-alkan-2-ones), and **c** alcohols (analyzed as trimethylsilyl ethers *TMS*, F4) (*a*–*e* sterols). *Numbers* refer to carbon-chain length

oxidation of vegetation wax alkanes, probably by burning [170] or microbial β-oxidation of alkanes.

Series of α,ω-alkanedioic acids are generally present, especially in marine areas, and range from C_5 to C_{29}, with C_{max} at 9 and 22 or 24 and CPI ~ 1.0. These compounds are atmospheric oxidation products from biopolymers or other lipid components (e.g., ω-hydroxyalkanoic acids) or incomplete combustion products [30, 107, 149]. The short-chain (shorter than C_{10}) dicarboxylic acids are also found and represent ubiquitous photo-oxidation products from numerous organic compounds in the atmosphere [34].

Alkanols are significant components of the extractable lipids (Figs. 2a, c, 3a, 4c) and typically range from n-C_{12} to n-C_{34}, with a strong even-carbon-number predominance (CPI > 5) and C_{max} at 26 or 28. The homologs longer than n-C_{20} are characteristic of vascular plant wax and those shorter than n-C_{20} may be derived from microbial/marine sources, because they are not major constituents of plant waxes [37, 107, 171, 172].

2.2.5
Terpenoid and Steroid Biomarkers

The major natural product (i.e., biogenic) biomarkers detected in aerosols are sterols, triterpenols, triterpenones, and diterpenoid acids (Table 2, Figs. 2, 3). The sterols (**I**, see the "Appendix" for structures cited in the text) consist primarily of cholesterol (R is =H) and minor amounts of campesterol (R is α-CH_3) and sitosterol (R is β-C_2H_5). The origin of the significant amount of cholesterol in marine areas is from algae and zooplankton. The triterpenones consist of α-amyrone and β-amyrone (**II**, **III**, R is O, respectively), which are oxidative derivatives from α-amyrin and β-amyrin (i.e., **II**, **III**, R is OH, respectively), both terrestrial natural products. The precursors are dominant constituents of higher-plant (angiosperm) epicuticular wax and gums and are converted to the ketones after direct emission and/or by combustive processes [149]. The diterpenoid acids found are generally based on the abietane skeleton and consist of dehydroabietic acid (**IV**) and 3-oxodehydroabietic (**V**) and 7-oxodehydroabietic (**VI**) acids (Figs. 2a, c, 3a). The resin acid precursors or retene are generally not detectable in aerosols which have been exposed to photoreactions. The presence of the diterpenoid compounds indicates an input from conifer wood combustion [125, 161]. Conifers are not common in tropical regions [149] and thus additional imported wood may be used as fuel in such areas (Fig. 3a). Dehydroabietic acid is detectable over the ocean off Africa (Fig. 2c), indicating its long-range transport.

Specific biomarkers that are attributable to biomass burning sources are also present and even dominant in heavily impacted airsheds. Levoglucosan (**VII**), with lesser amounts of mannosan, galactosan, and 1,6-anhydro-β-D-glucofuranose are dominant in urban areas owing to wood burning and globally from wildfires (Figs. 2a, c, 3a). They are detectable in lower amounts in remote areas and over the ocean. Levoglucosan and the other anhydrosaccharides are derived exclusively from cellulose by burning [126]. Various phenols and methoxyphenols (e.g., vanillic acid, **VIII**; catechol), derived from lignin in biomass by burning [125], are also detectable close to their source, but they are readily degraded to secondary products.

Petroleum biomarkers, mentioned here for completeness, are specific indicator compounds consisting of mainly hydrocarbons which can be utilized to define both the fossil origin and the geological source of petroleum residues [101, 103]. These compounds are relatively stable in ambient atmospheric environments. An example of such a biomarker distribution pattern is shown in Fig. 2f. The $17\alpha(H), 21\beta(H)$-hopane series (**IX**) is present as the predominant biomarker group (steranes are present at trace levels). The hopanes generally range from C_{27} to C_{35} (usually with little or no C_{28}), and minor moretanes (**X**) are sometimes detectable. The presence of hopane biomarkers in aerosols confirms an input source from fossil fuel utilization (i.e., vehicular traffic). However, it should be noted that an unusual hopane distribution pattern observed for samples may be due to some blow-off from the filters, i.e., compounds shorter than C_{29} are retained less effectively by the filter owing to their volatility. Furthermore, coal burning emits a different suite of hopanes and moretanes [173] and burning of biomass, such as tropical forest litter, has yet another hopane/moretane composition [174].

2.2.6
Compound-Specific Isotope Analysis

Organic compounds of aerosols have been analyzed by GC combustion isotope ratio MS to determine their carbon isotopic compositions [57, 98, 175–183]. This method has been applied to alkanes, fatty acids, fatty alcohols, and PAHs to differentiate the carbon fixation biochemistry of the source vegetation of the wax lipids and to distinguish the pyrogenic origin of the PAH sources. Isotope analysis of bulk aerosol organic fractions is also of utility in complementing molecular source assessments [180, 184]. For example, the carbon isotope compositions of the total hydrocarbon fractions from African aerosols support the assignment of their origin from C_4 plants typical of savannah regions [180].

2.2.7
Polar Compounds

The polar compounds documented for aerosol particles are water-soluble and consist of short-chain dicarboxylic acids, anhydrosaccharides from biomass burning (e.g., levoglucosan), saccharides from soil resuspension and microbiota, and to some extent phenolics from biomass burning [125, 126, 185].

Oxalic acid, with the other short-chain homologs of dicarboxylic, hydroxydicarboxylic, aromatic dicarboxylic, oxocarboxylic, and hydroxycarboxylic acids, as mentioned before have been reported as major water-soluble components of aerosols [34, 41, 186]. Most of these carboxylic acids are secondary oxidation products of atmospheric organic compounds and are found in remote marine as well as continental rural to urban areas [39, 40, 165].

The tracers for emissions from biomass burning, primarily levoglucosan (**VII**) from cellulose decomposition, with lesser amounts of mannosan (**XI**), galactosan (**XII**), and 1,6-anhydroglucofuranose (**XIII**), are common aerosol components [39, 40, 126, 145, 185]. These anhydrosaccharides are completely soluble in water and have been reported globally in remote-to-urban airsheds [121, 157, 187–190]. Lignin, another major biopolymer of wood, yields methoxyphenolic tracers in the smoke upon burning with distributions characteristic of the fuel type [125, 153]. These tracers (e.g., vanillic acid) are not completely water-soluble, although phenolics are polar and hygroscopic.

Major amounts of saccharides have been reported to be present in aerosols of certain geographic regions such as Amazonia, Brazil [121], northwestern Pacific with Korea and Japan [39, 40], and Santiago, Chile [191, 192]. The dominant primary saccharides consist of α- and β-glucose (**XIV**), α- and β-fructose (**XV**), sucrose (disaccharide, **XVI**) and mycose (**XVII**, trehalose), with lesser amounts of inositols, α- and β-mannose, α- and β-xylose, and α- and β-galactose. In addition, saccharide polyols (alditols, i.e., reduced sugars) are also found and include sorbitol (**XVIII**, D-glucitol), xylitol, mannitol, arabitol, erythritol, and glycerol [40, 121]. All these saccharides are emitted directly from sources and not significantly by thermal stripping during burning. They are completely soluble in water. The primary and polyol saccharides have been shown to be source-specific tracers for resuspended soils derived from agricultural tilling, harvesting, husbandry, construction, engineering, traffic on unpaved roads, and natural wind erosion [185].

2.2.8
PAH and Oxy-PAH

PAHs have been studied extensively in urban airsheds and some long-range transport data have also been published [143, 144, 193–195]. A typical PAH composition is shown in Fig. 5 for a total extract from aerosol particles collected on Gosan Island, south of Korea [165]. These aerosols were derived from Asia during the 2001 dust transit episode [40]. The PAHs range from phenanthrene (3-ring) to coronene (6-ring) and their total concentrations are significant, ranging from 0.005 to 7.8 ng m^{-3} in Gosan and from 1.7 to 19.3 ng m^{-3} in Sapporo. Their distribution patterns are similar during the dust event, indicating common sources. 1,3,5-Triphenylbenzene is present at significant concentrations, indicating a major input source of PAHs

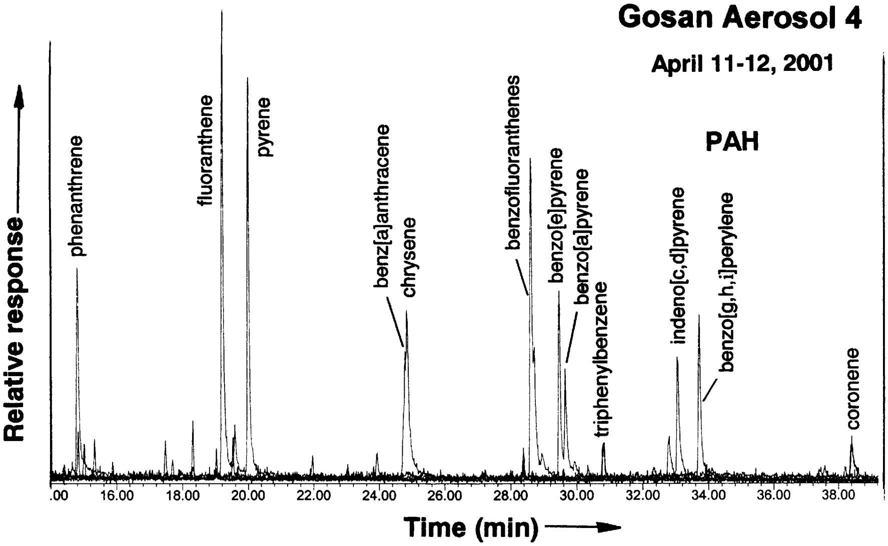

Fig. 5 Mass fragmentogram (*m*/*z* 178, 202, 228, 252, 276, 300 + 306) for typical and major polycyclic aromatic hydrocarbons (*PAHs*) in aerosol sampled during the ACE-Asia campaign on Gosan, Korea (major dust event from Asia)

from incineration and burning of refuse and plastics in urban areas [196]. This has also been reported for various cities in China [114, 197] with total PAH concentrations of 8–450 ng m^{-3}. Retene from burning conifer wood was not detectable in any of these samples. PAHs are a health concern because of their carcinogenicity, genotoxicity, and endocrine disrupting potential. Thus, the benzopyrenes are generally analyzed in environmental monitoring studies. The benzopyrenes and cyclopenta[*c*, *d*]pyrene are found at high concentrations in these aerosols and the ratio of benzo[*a*]pyrene to benzo[*e*]pyrene (Bap/Bep) ranges from 0.4 to 0.8, which is high. The Bap/Bep values for samples from urban areas of China ranged from 0.1 to 1.0 [114, 197]. Benzo[*a*]pyrene degrades more rapidly than benzo[*e*]pyrene [136]. Thus, the high concentrations of benzo[*a*]pyrene indicate that these PAHs reside in tar particulate matter of coal smoke emissions (small fire type burning) and are thus protected from secondary reactions during transport [173].

Urban aerosols of China also contained concentrations of oxy-PAHs equivalent to those of the PAHs, both primary emissions (e.g., benzo[*a*]fluoren-11-one), as well as secondary oxidation products from the PAHs (e.g., 9,10-anthraquinone) [114]. Oxy-PAHs are not significant components of the samples collected on Gosan, probably reflecting their greater reactivity toward further oxidation upon emission to, for example, the benzene dicarboxylic acids.

2.2.9
Humic and Fulvic Acids

Preliminary yields and source assessments of humic and fulvic acids isolated from marine aerosol particles were reported [100]. The aerosol particles were collected off the coast of west Africa and the fulvic and humic acids were separated, after solvent extraction, with NaOH solution by the standard method [198]. Of the two, the humic acids were the major carbonaceous fraction. The assessment of a terrigenous origin for the humic acids from soils and dried lakebeds was based on the H/C values (1.0–1.4), typical of terrestrial humates, and the $\delta^{13}C$ values of – 21 to – 23 ‰, characteristic of terrestrial and lacustrine humic organic matter [100, 198]. Soil is a major component of aerosols derived from continents and transported to the ocean. Thus, the saccharide and the humic acid contents may prove to be the characteristic tracers for soil in the atmosphere [40, 185].

2.3
Elemental Carbon

The elemental or black carbon (or soot) and the organic carbon contents are determined routinely for aerosols [16, 199, 200]. Elemental carbon and organic carbon as particulate matter components have global importance because they affect direct radiative properties by absorption and scattering of solar radiation, which is an active research topic [15, 16, 201–204]. Elemental carbon and organic carbon have multiple origins from both biological and geological carbon sources. Biological contemporary carbon has also been quantified in total aerosol carbon mixtures by ^{14}C dating [205–208]. Typical amounts of contemporary carbon in the urban atmosphere of Los Angeles vary from 19 to 36% downtown and from 25 to 81% in suburban areas, and for Denver, CO, USA 23% (mean winter) and 97% (mean summer) of the total carbon (elemental carbon + organic carbon). The elemental carbon from vehicle emissions (especially diesel engines), power plants, and numerous other combustion sources has a small average particle size and is therefore readily transported over global distances [209].

2.4
Source Signatures

The emission profiles for sources of atmospheric particles have been determined mainly for urban Los Angeles in terms of elemental carbon and organic tracer compounds. Source testing with emission rates or particle loadings have been reported for ten major urban sources. These data were then used in conjunction with inventory modeling to apportion the emissions of the airborne particulate matter in the Los Angeles air basin [82, 91, 97, 141] and elsewhere [142, 210, 211]. Additional contributing sources are numerous and minor, but may have to be tested for other global areas where they are more important. Also, some source tests for Los Angeles (e.g., vehicles) may not have the same emission factors elsewhere owing to different attributes (e.g., different fleet and fuel compositions). Additional organic compound compositions of smoke from biomass burning and coal burning have been reported (reviewed by Simoneit [145]).

2.4.1
Ambient Vegetation

Globally, the emissions from vegetation-covered areas are major contributors of organic matter to the atmosphere. The organic matter of terrestrial aerosol particles in rural regions consists primarily of vascular plant waxes. The major components are *n*-alkanes, *n*-alkanols, and *n*-alkanoic acids, with minor amounts of *n*-alkan-2-ones, *n*-alkanedioic acids, wax esters, and other lipid compounds. An example of such an end-member aerosol composition is illustrated in Fig. 4. These are the total ion current traces from the GC-MS analyses of separated lipid fractions from an aerosol sample of a rural area near Corvallis, OR, USA (number 13 in Ref. [107]). The hydrocarbon fraction consists of higher-plant-wax *n*-alkanes ranging from C_{23} to C_{35}, with a strong odd-carbon-number predominance. The total fatty acid (analyzed as methyl esters) and ketone fraction from the same sample consists of *n*-alkanoic acids derived from vascular plant wax (C_{20}–C_{30}, strong even predominance) and microbial lipid residues (part of compounds shorter than C_{20}). The major ketone is 6,10,14-trimethylpentadecan-2-one (a in Fig. 4b) with a minor amount of 6,10-dimethylundecan-2-one (f in Fig. 4b). The minor *n*-alkan-2-ones generally have an odd-carbon-number predominance (b–e). The total fatty alcohol (analyzed as trimethylsilyl ethers) fraction consists mainly of *n*-alkanols ranging from C_{10} to C_{32} with a strong even-carbon-number predominance and C_{max} at 28. The homologs longer than C_{20} are typical of higher-plant wax and those shorter than C_{20} have multiple origins. Minor sterols are also present (a–c in Fig. 4c).

2.4.2
Fossil Fuel Utilization

Fossil fuels (mainly petroleum and coal) are used in vast quantities, especially in urban regions. The major emissions are from vehicular engine exhaust and thus typical end-member organic signatures are illustrated here [83, 101–103]. Vehicular traffic with the associated fuels and lubricants emits petroleum residues comprising *n*-alkanes with no carbon number predominance, UCMs of branched/cyclic hydrocarbon components, and biomarker tracers to the ambient atmosphere as shown for examples of auto exhaust

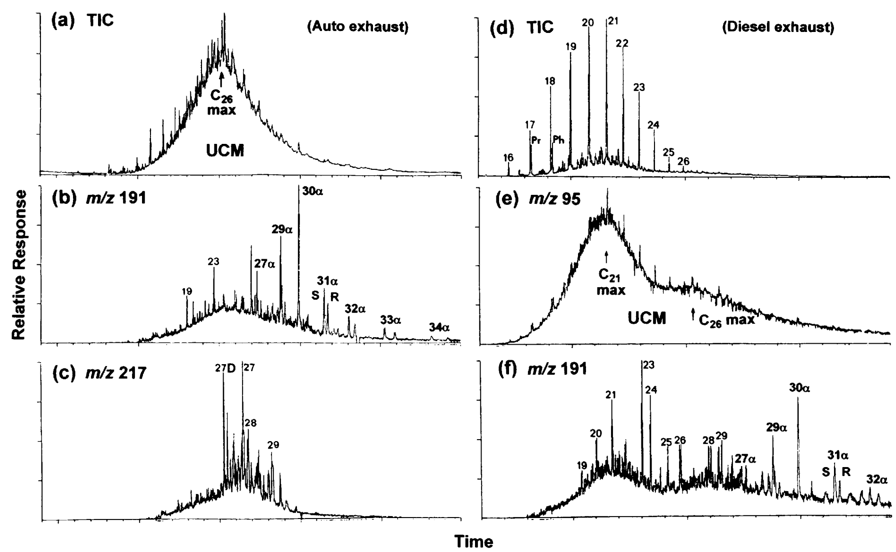

Fig. 6 Salient features of the GC-MS data for samples of automobile and diesel exhaust (total hydrocarbons). Automobile **a** TIC trace, **b** m/z 191 mass fragmentogram (key ion for hopanes and extended tricyclic terpanes), **c** m/z 217 mass fragmentogram (key ion for steranes). Diesel **d** TIC trace, **e** m/z 95 mass fragmentogram (key ion for the UCM hump), **f** m/z 191 mass fragmentogram (key ion for hopanes and extended tricyclic terpanes). *Numbers* refer to carbon-chain length or carbon number of biomarkers, *Pr* pristane, *Ph* phytane, *iα* $17\alpha(H),21\beta(H)$-hopane configuration, *S* and *R* extended hopane epimer at C-22, *D* diasterane

and diesel exhaust in Fig. 6. Auto exhaust contains relatively low concentrations of *n*-alkanes longer than C_{15}. However, diesel exhaust does contain some uncombusted fuel components (as *n*-alkanes with UCM) and reformed alkanes with a second higher weight UCM of branched and cyclic hydrocarbons.

The associated terpenoid markers are present in all engine emissions and originate from the lubricants. These compounds include the terpenoid hydrocarbons characteristic of petroleum and are the geologically mature and environmentally stable isomers of the $17\alpha(H),21\beta(H)$-hopane (IX) series (e.g., Fig. 6b, f). The identifications of these compounds are based primarily on their mass spectra and gas chromatographic retention times [101, 102]. They occur in aerosols usually at low concentrations, but their overall distribution signatures within samples can be easily determined by GC-MS and utilized for comparison purposes. This is based on the m/z 191 key ion intensity in the GC-MS data, which is the base peak of most of the hopanes as well as the extended tricyclic terpanes (XIX). The predominant analog is usually $17\alpha(H)$-hopane (IX, R is CH_3), with subordinate amounts of $17\alpha(H)$-22,29,30-trisnorhopane, $17\alpha(H)$-29-norhopane (IX, R is H), and the extended homohopanes from C_{31} to C_{35} (**IX**, R is C_2H_5–C_6H_{13}) with the C-22 diastereomers in a 22R to 22S ratio of about 0.6.

The tricyclic terpanes (**XIX**) generally range from C_{19} to C_{29} (no C_{22} or C_{27}), but the lower homologs (shorter than C_{25}) are volatile and thus not adequately collected with the aerosol particulate matter (Fig. 6b vs. f [101, 102]). These terpanes are common in diesel fuel and in part in lubricating oils and therefore are useful tracers for the volatile emissions from traffic.

Steranes (**XX**) and diasteranes (**XXI**) are additional biomarker tracers commonly found in petroleum that can be used for aerosol analyses [101–103]. These hydrocarbons are not present in contemporary biogenic materials. The distribution signature in GC-MS data of, for example, the m/z 217 fragmentogram (Fig. 6c) for steranes and diasteranes is useful supporting evidence for a petroleum component. These compounds are also introduced to the atmosphere from lubricants of vehicular engines, but at lower concentrations than the hopanes. They are not found in gasoline or diesel fuel.

The UCM from lubricants is the major organic input to the atmosphere from vehicular emissions in mainly urban regions. However, fossil fuel tracers are now recognizable in aerosols transported over longer distances [39, 40, 189]. Thus, the biomarker tracers in the lubricants are used to confirm and quantify the source strengths of these emissions.

2.4.3
Biomass Burning

Biomass burning emits numerous compounds into smoke and the compound classes include the following: homologous series of *n*-alkanes, *n*-alkenes, *n*-alkanoic acids, and *n*-alkanols; methoxyphenols from lignin; monosaccharide derivatives from cellulose; and steroid and terpenoid biomarkers [145]. The distributions and abundances of the biomass smoke constituents are strongly dependent on combustion temperature (smoldering versus flaming conditions), aeration, and burn duration. Only a few compounds are of utility as tracers owing to oxidation during transport (Table 3). A typical example of compounds in smoke from biomass burning is discussed next.

The GC-MS data of the total extract and separated fractions (by thin-layer chromatography, TLC) from smoke of a grass fire are shown in Fig. 7a–d. The total extract consists mainly of levoglucosan, *n*-alkanoic acids, and various methoxyphenolic compounds [e.g., catechol, dimethoxyphenol, syringic acid (**XXII**), vanillic acid (**VIII**)]. Grasses contain all three phenolic moieties from the lignin precursor alcohols; thus, the thermal breakdown products are not indicative tracers for this source, although they can be used as ratios with other compounds [125]. The dominant levoglucosan is derived from the thermal decomposition of cellulose, a confirming tracer for biomass burning. There are lesser contributions of the C_{16} and C_{18} *n*-alkanoic acids, C_{27}–C_{33} *n*-alkanes, and the C_{26} *n*-alkanol. The biomarkers identified in the

Table 3 Major compound groups identified in smoke particles from biomass burning

Compound group[a]	Plant source	Product
n-Alkanes (> C_{23})	Epicuticular waxes	Natural
n-Alkenes (> C_{24})	Epicuticular waxes/lipids	Altered
n-Alkanoic acids (> C_{22})	Internal lipid substances	Natural
n-Alkanols (> C_{22})	Epicuticular waxes	Natural
n-Alkan-2-ones (> C_{23})	Epicuticular waxes/lipids	Altered
Alkyl amides	Lipids	Altered
Alkyl nitriles	Lipids	Altered
n-Acyl glycerides	Lipids	Altered
Diterpenoids	Conifer resin, wax	Natural/altered
Triterpenoids	Angiosperm gum, wax	Natural/altered
Monosaccharide anhydrides	Cellulose biopolymer	Altered
Methoxyphenols	Lignin biopolymer	Altered
Steroids	Internal lipid substances	Natural/altered
Wax esters	Lipid membrane, wax	Natural
Triterpenoid esters	Internal lipid substances	Natural
PAHs	Multiple sources	Altered

[a] Includes natural product precursors and/or thermally altered derivatives

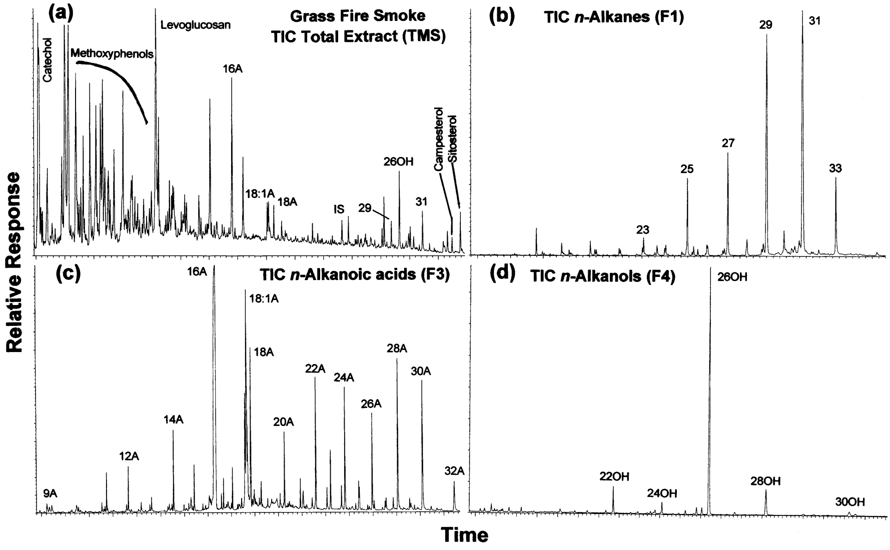

Fig. 7 Salient features of the GC-MS data (TIC traces) of grass smoke particulate matter: **a** total extract showing major compounds, **b** F1 fraction showing *n*-alkanes, **c** F3 fraction showing *n*-alkanoic acids (as methyl esters), and **d** F4 fraction showing *n*-alkanols (as TMS) (*numbers* refer to carbon-chain length of *n*-alkanes, *i*: 1 monounsaturated, *A* alkanoic acid, *OH* alkanol)

total extract include the triterpenoids oleana-2,12-diene (**XXIII**, R is CH_3), ursa-2,12-diene (**XXIV**, R is CH_3), and lupa-2,22-diene (**XXV**), and the phytosterols (sitosterol, campesterol, and stigmasterol).

The relatively high concentration of *n*-alkanes (F1), with an odd-carbon-number to even-carbon-number predominance (CPI=12), range from C_{23} to C_{33}, and C_{max} at 31, is derived from the grass wax. Alkenes are not significant components. The major PAHs (F2) are phenanthrene, fluoranthene, and pyrene, with minor contributions of anthracene, C_1- and C_2-phenanthrenes, 11*H*-benzo[*b*]fluorene, C_1-pyrenes, cyclopenta[*c*, *d*]pyrene, benz[*a*]anthracene, and chrysene. The *n*-alkanoic acids (F3) have an even-carbon-number to odd-carbon-number predominance (CPI=4) and range from C_9 to C_{30}, with C_{max} at 16. The *n*-alkanols (F4) are even-carbon-numbered (CPI=20) and range from C_{22} to C_{30}, with C_{max} at 26. All three of these homologous lipid series (full homolog ranges) are ubiquitous in biomass burning smoke and are thus are not source-specific. However, the major biomarker compound groups, including the longer-chain lipids (longer than C_{22}), identified in smoke particulate matter from burning of vegetation (e.g., wood, litter; Table 3) are source-specific. This compound list will expand as more vegetation species are tested for smoke emission profiles [153].

2.4.4
Soil/Sand Resuspension

Transport of continental dust to the ocean has been documented extensively in the Atlantic (Sect. 1), and the Asian continent has also been inferred as such a source [30, 68]. Continental dust is advected into the atmosphere from sands of desert areas and from exposed soils during tilling in agricultural regions. The organic compositions of the fine particulate matter of both types of sources are currently being characterized and their effects on atmospheric processes are under extensive study. Results from these studies should appear in the near future.

The organic compositions from some examples of sand and soil particulate matter are illustrated here and compared with an aerosol sample (also compare Fig. 3a). The dominant organic tracers of desert sands are trace amounts of plant wax components comprising primarily *n*-alkanes and *n*-alkanols, with minor amounts of nonacosan-10-ol (**XXVII**), methyl alkanoates, sterols (**I**), and triterpenols (Fig. 8a [212]). The *n*-alkanes, *n*-alkanols, and *n*-alkanoic acid esters have the typical distributions and carbon number predominances of plant waxes. The organic tracers of desert sands are low in concentration and must be used in conjunction with mineralogical and trace metal compositions for source assessments. The lipid tracer compositions of different deserts are distinguishable and reflect primarily the regional climatic conditions affecting biomass fixation, with inputs of detritus mainly from grass waxes and secondarily from algae and woody plants.

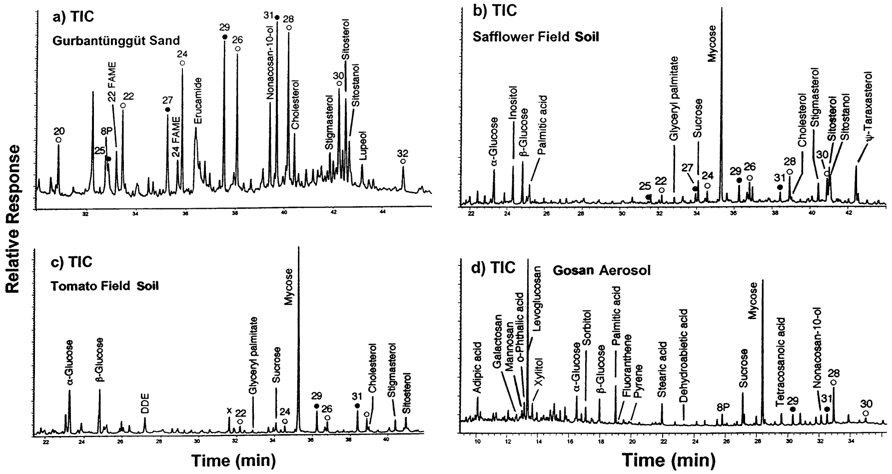

Fig. 8 Representative TIC traces from GC-MS analyses of total extracts (silylated): **a** sand (fines, Gurbantünggüt desert, Xinjiang, China), **b** soil from safflower field (San Joaquin Valley, CA, USA), **c** soil from tomato field (San Joaquin Valley, CA, USA), and **d** aerosol particulate matter (Gosan, Jeju Island, Korea, 11–12 April 2001) (compounds are labeled, *numbers* refer to carbon-chain length, see key for lipids)

Soils contain much higher concentrations of organic compounds than sands and those also comprise mainly lipids from higher vegetation. Soils contain the plant wax and biomarker compounds from the surficial or surrounding vegetation cover (e.g., resin acids, *XXVIII*–**XXXI**, from conifers in forest soil) [213]. Agricultural field soils contain the lipids from the crops, as well as the pesticide/herbicide residues remaining after use (e.g., DDE [212, 213]). The *n*-alkanols and *n*-alkanes are useful secondary tracers for fingerprinting soils, analogous to desert sands. However, these lipids have very high source concentrations in soils compared with trace levels in sands.

A novel and unique aspect is the presence of primary sugars (saccharides) in soils. The total extracts of agricultural soils from a safflower field and a tomato field are shown in Fig. 8b and c, respectively. The dominant compounds are sugars with only minor lipids and biomarkers. The most commonly encountered sugars are α- and β-glucose, inositols (**XXXII**, several isomers), sucrose (disaccharide), and mycose (fungal disaccharide metabolite) [185]. Fructose, mannose, xylose, and other monosaccharides can also occur. Another aspect of soils is their enhanced contents of sterols and triterpenoids with depleted contents of the aliphatic plant wax lipids (i.e., alkanes and alkanols). The phytosterols (sitosterol, campesterol, and stigmasterol) are dominant, but cholesterol is also present, indicating a component from algae and fauna. Some soils can contain species-specific tracers, as, for example, ψ-taraxasterol (**XXXIII**) in the safflower field (Fig. 8b). The presence of polar and water-soluble compounds in soil extracts indicates that both living and extracellular biomass was extracted. The enhanced sterol and triterpenol concentrations are probably due to their resistance toward biodegradation compared with the aliphatic plant wax lipids.

The impact of Asian dust on the northwestern Pacific region is currently under investigation and preliminary results have been reported [167]. A typical total ion current trace from the GC-MS analysis of a total extract (silylated) of aerosol particulate matter collected in Gosan (formerly Kosan) on Jeju (formerly Cheju) Island, Korea, is shown in Fig. 8d. A similar aerosol sample analysis is also shown in Fig. 3 for Sapporo. The high amounts of levoglucosan with mannosan and galactosan are tracers for smoke from biomass burning [126]. The primary sugars are α- and β-glucose, xylitol, sorbitol, sucrose, and mycose. Xylitol and sorbitol are probably microbial/fungal alteration products of primary saccharides in soil particles introduced into the atmosphere.

A minor homologous series of *n*-alkanoic acids, ranging from C_{12}–C_{30} with a strong even-to-odd carbon number predominance and a maximum at C_{16} (palmitic acid) was present, suggesting an input from terrestrial and marine biota, as well as from cooking. A trace of dehydroabietic acid further supports biomass burning. Significant amounts of dicarboxylic acids (e.g., glyceric, maleic, adipic, and benzene dicarboxylic acids) indicate secondary oxidation products [41]. The vascular plant wax components are minor and consist of the *n*-alkanes, *n*-alkanols, and nonacosan-10-ol, with traces of phytosterols. Thus, the primary inputs of organic compounds to these aerosols transported from Asia are (1) natural emissions from continental vegetation and marine lipids, (2) smoke from biomass burning, (3) soil resuspension due to agricultural activity, and (4) urban/industrial emissions from fossil fuel utilization, especially coal [39, 40, 167].

2.5
Secondary Reactions

All organic compounds in aerosols are susceptible to degradation by reaction with OH, ozone, NO_x, or ultraviolet radiation, provided that they are exposed to and accessible to the reactants [17]. Major secondary products are the short-chained dicarboxylic and keto acids, and aldehydes (carbonyls) [128, 129]. The biogenic origin can be discerned in secondary products after initial oxidation or nitration, but not in subsequent reactions where the chemical structure is lost. Then, the only possible correlatable parameter may be the stable isotope composition of the breakdown products and their ^{14}C content. Secondary products from volatile organic compounds, especially terpenes from vegetation, have an extensive literature base and constitute a separate topic on biogenic atmospheric components. Because this is not covered here, a few key references are cited [50, 214–218].

The formation of secondary reaction products in the atmosphere from source precursor compounds has been documented for the Los Angeles, CA, USA, air basin [65]. A number of nitrated and oxygenated aromatic compounds were measured during a severe photochemical smog episode and indicated secondary formation via atmospheric chemical reactions. These included 1-nitronaphthalene, 2-nitronaphthalene, 3-nitrobiphenyl, and dinitrophenol, as well as certain oxygenated aromatic compounds such as cyclopenta[*c*, *d*]phenanthrone [65, 219]. The ambient concentrations of these compounds increase progressively with transport distance inland from the coastline. Thus, oxidative alteration of organic compounds occurs during transport. Source tracers must be encapsulated in particles to survive long-range transport.

2.6
Fallout and Washout

The lower troposphere represents one compartment in the global cycling of organic matter and thus it is important to understand the transfer of organic materials to ultimate sinks. Precipitation scavenging (washout) and dry fallout are important mechanisms for the removal of atmospheric particles, including organics, with diameters between 0.1 and 10 μm [17, 220]. Few detailed reports on organic matter in fallout and washout particulate matter have appeared [68, 108, 221–223]. Those studies identified contemporary biogenic and anthropogenic organic compounds in urban, rural, and remote oceanic areas. Some made comparisons of specific organic species in the particle versus aqueous phase (e.g., PAHs, halocarbons, lipids). Washout is efficient for removing water-soluble organic compounds and coarse particles, whereas fallout removes mainly coarse and dense particles with adsorbed/included organic matter. More work should be encouraged to assess particle removal processes from the atmosphere; organic tracers can be of utility here.

2.7
Modeling

Sources and their contributions to the ambient atmosphere need to be defined so that modelers can upgrade their global modeling tasks. Such data should also aid regulatory agencies in urban areas to make decisions on how to proceed for improvement or maintenance of air quality. Additional concerns are the suspected adverse health effects of low levels of airborne fine particulate matter. The extensive source testing and ambient aerosol characterization program for the Los Angeles air basin, concentrating on the fine particle size distribution, was carried out and then summarized by modeling [82, 91, 141]. An updated study for the Los Angeles area was carried out for 1993 with comparable results [97]. This model, using the same emission sources developed for Los Angeles, was applied with a good fit in the San

Joaquin Valley during winter [142]. The major discrepancies were the vegetation and soil emission uncertainties due to the different geographic area. The apportionment of fossil fuel combustion and other sources in $PM_{2.5}$ and PM_{10} aerosols by the chemical mass balance receptor model has been reviewed as applied to urban and regional areas [224].

Tracking the origins of major global dust events and air parcels is carried out by back-trajectory modeling and/or satellite observations [166, 225]. Major dust outbreaks are easily tracked by satellites for days [36, 226]. Air mass back-trajectory analysis is well established and provides evidence for geographic source regions of aerosols or the changes and mixing of air masses during transport [65, 70, 225].

2.8
Water-Soluble Organic Matter

The water solubility of the carbonaceous organic fraction of aerosols is a major open question in climate models [227, 228]. The water-soluble saccharides comprise from 13 to 26% of the total identified compound mass (TCM) in continental aerosols with isolated, higher values over the ocean (up to 63% [40]). These saccharides are interpreted to represent viable biomass and extracellular organic matter mainly in soils, but also in lesser amounts in road dust, dried lake sediments, etc., and possibly in marine particulate matter. Saccharides have been characterized in urban aerosols that contain entrained soil dust [191], and in remote and rural areas [39, 40, 121]. They were proposed as tracers for soil resuspension with associated microbiota from agricultural tilling and harvesting, wind erosion, or traffic [185]. The secondary oxidation products of organic compounds in aerosols, especially over the oceans, are oxalic acid and the other short-chain dicarboxylic acids. They have been documented as the dominant water-soluble components of organic aerosol matter [34, 41]. The sum of all identified water-soluble compounds ranges from 14 to 89% of the TCM for typical samples and is about 40–70% of the TCM during an Asian dust episode at the ground stations [40].

3
Sampling and Analytical Methods

3.1
Sampling

Aerosol samples are typically acquired by high-volume (Hi-Vol) filtration on quartz fiber filters with or without a particle size preseparator. Hi-Vol sampling is adequate for marine studies because the coarser particles have been winnowed out during transport. However, precautions should be taken to minimize sampling the resuspended sea slick (salt haze). Sampling is carried out from 1-h to up to 24-h periods and the extraction, separation, and analysis procedures are the same as used for urban aerosols and source tests. The quartz fiber filters are annealed prior to use at 550 °C for 3 h to reduce background contamination. Filters should be stored in a freezer or sterilized by addition of some extraction solvent prior to analysis to prevent microbial and mold activity.

3.2
Extraction and Fractionation

A schematic of a suggested sample treatment, extraction, and separation procedure is given in Fig. 9, as first used by Simoneit and Mazurek [107] with some modifications. The solvent mixture of dichloromethane and methanol is excellent for extracting both lipids and water-soluble organic compounds

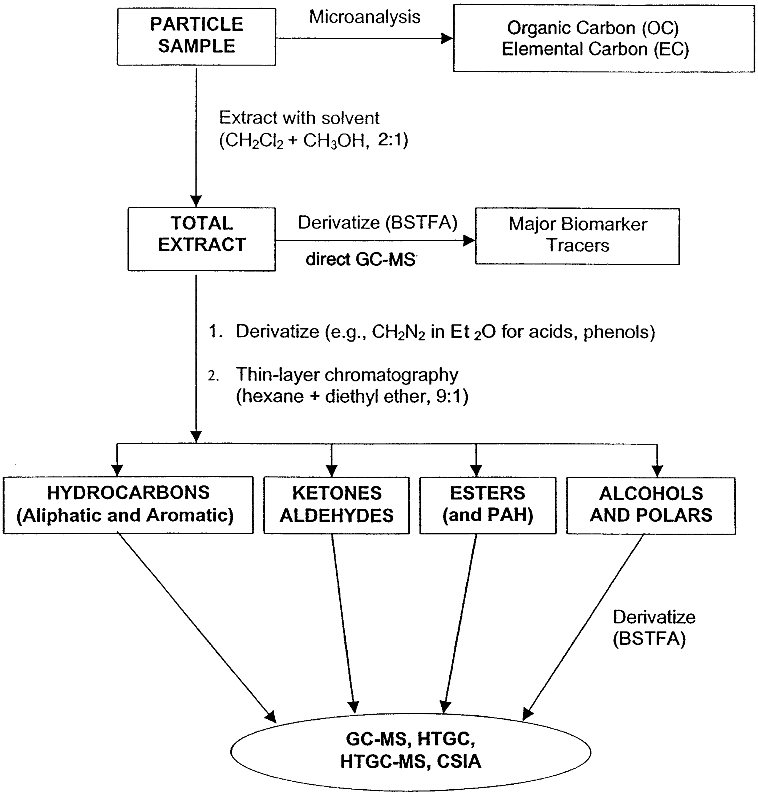

Fig. 9 Schematic of the extraction, separation, and analysis procedures for aerosol particulate matter on filters

such as sugars, levoglucosan, dicarboxylic acids, and phenols. Each filter or aliquot is extracted using ultrasonic agitation for three 20-min periods using a dichloromethane/methanol mixture (CH_2Cl_2/CH_3OH, 2 : 1, v/v). The solvent extract should be filtered to remove insoluble particles and filter fibers (Gelman Swinney filtration unit with an annealed glass-fiber filter) [107]. The filtrate is first concentrated by use of a rotary evaporator and then by a stream of filtered nitrogen gas. The final volume is adjusted exactly (e.g., 1.0 ml) by addition of CH_2Cl_2. Aliquots are then taken for derivatization or direct GC-MS analysis. Alternatively, carboxlic acid and phenolic moieties in the extracts can be methylated using diazomethane in diethyl ether prepared from the precursor *N*-methyl-*N′*-nitro-*N*-nitrosoguanidine. With current MS instrumentation, direct total extract analysis is recommended, with and without derivatization by *N*,*O*-bis(trimethylsilyl)trifluoracetamide (BSTFA) plus 1% trimethylchlorosilane, usually for 3 h at 70 °C [157, 190, 229, 230].

Methylated extracts can be separated by preparative TLC on silica gel plates with a mobile-phase eluent mixture of hexane and diethyl ether (9 : 1) or by column liquid chromatography. These procedures allow for the determination of chemical information on single molecular groups or homologous series, which may not be detected owing to the coelution in the total extract mixture. They also provide chemical information on molecular polarity or functional group constituents which further aids in structure elucidation and identification. Typically four fractions are removed from the TLC plates and contain the following classes of compounds (Fig. 9): (1) *n*-alkanes, *n*-alkenes, and saturated and unsaturated cyclic diterpenoid and triterpenoid hydrocarbons, (2) *n*-alkanones and PAHs, (3) *n*-alkanoic acids/alkenoic acids and resin acids (as methyl esters) and saturated and unsaturated diterpenoid and triterpenoid ketones, and (4) *n*-alkanols, sterols, terpenols, and polar organics. The fourth fraction is also converted to trimethylsilyl derivatives prior to analysis by reaction with BSTFA plus 1% trimethylchlorosilane.

3.3
Instrumental Analyses

The detection limits for organic compounds by GC-MS have decreased greatly since the initial studies and are currently in the 1 ng or less per compound range. The extracts or fractions can be analyzed by temperature-programmed capillary GC. However, with current instrument capabilities all samples, total extracts or fractions, can be analyzed directly by capillary GC-MS using benchtop quadrupole or ion trap mass spectrometers.

Samples that contain wax esters (plant wax) or triglycerides (e.g., beef fat from grilling) can also be analyzed by high-temperature GC and high-temperature GC-MS using custom-made or metal-covered capillary columns coated with OV-170-OH and GC oven temperatures to 400 °C [169]. All compound identifications should be based on comparisons with authentic standards whenever possible, GC retention time, literature mass spectra and interpretation of mass spectrometric fragmentation patterns. Homologous compound series should be defined with regard to carbon chain length by key ion searches on the GC-MS data and confirmed by mass spectrum and retention time comparison with standards.

The development of compound-specific stable carbon (also hydrogen and nitrogen) analysis (compound-specific isotope analysis) by GC combustion isotope ratio MS provides a secondary parameter in molecular characterization besides the chemical structure or elemental compositions [98, 179, 180, 231]. Any organic fraction that is amenable to GC analysis can be analyzed by this method. Compounds can also be measured as derivatives (e.g., methylated or trimethylsilyated), and a correction made for the isotope ratio of the derivatizing group. This is done by determining the isotope composition of suitable underivatized standards by both combustion analysis and then analyzing the standard mixture suitably derivatized versus the Pee Dee belemnite (PDB) standard for carbon, standard mean ocean water (SMOW) for hydrogen, and N_2 in air for nitrogen.

3.4
Data Modeling

A chemical mass balance approach, with specific organic compounds as tracers, is commonly used for source/receptor reconciliation [82, 91, 97, 141, 142]. In such models, the total ambient concentration of each of the organic compounds used in the mass balance model is reconstructed from the best linear combination of chemical profiles of emission sources that reproduce the composition of the ambient sample as a whole. The chemical mass balance model used in the references just cited can be expressed by the following set of linear equations:

$$c_{ik} = \sum_{j=1}^{m} a_{ij} s_{jk} , \tag{1}$$

where c_{ik}, the concentration of compound i in particles at receptor site k, equals the sum over m source types of the product of a_{ij}, the relative concentration of compound i in the particle emissions from source j, multiplied by s_{jk}, the increment to the total particulate mass concentration at receptor site k originating from source j.

The system of Eq. 1 states that the ambient concentration of each mass balance species must result only from the m sources included in the model and that no selective loss or gain of compound i occurs in transport from the source to the receptor (sampling) site. Therefore, the selection of mass balance compounds must be limited to (1) species for which all major sources are included in the model, (2) species that do not undergo selective removal by chemical reaction or other mechanisms over the time scale for transport between the source and the receptor site, and (3) compounds which do not increase in concentration owing to chemical reactions in the atmosphere. The studies summarized by Schauer et al. [91, 97] and Schauer and Cass [142] used the CMB7 receptor modeling computer program (http://www.epa.gov/scram001/tt23.htm) [232] to solve Eq. 1. This program seeks an effective variance-weighted least-squares solution for the overdetermined set of mass balance equations and takes into account the known uncertainties in the atmospheric measurements and source emission data. This model can be applied to marine aerosols to define the source inputs of anthropogenic and terrestrial components [165].

4
Overview

This section presents a brief overview of the major, persistent organic compounds and organic carbon fractions that are transported from land to sea.

4.1
Major Terrestrial Organic Tracers and Sources

The major terrestrial organic tracer compounds recognizable over the oceans are derived from vegetation (plant waxes), with varying amounts of tracers from biomass burning, soil and sediment erosion, and anthropogenic (urban) emissions [39, 40, 113, 166]. The key organic compound tracers and their sources are summarized in Table 4. Once over the oceans, the continental aerosols are admixed with marine aerosol emissions which need to be distinguished, especially if sampling is carried out on ships or islands. The input of marine-derived compounds consists mainly of lipids and sterols [40, 166]. The common marine tracers are also summarized in Table 4. The source strengths of the tracers and their ambient concentration ranges are listed if known. A distinction is also made between the water-soluble and the hydrophobic compounds.

4.2
Major Secondary Products

The dominant secondary products from organic matter oxidation in the atmosphere over the ocean are mainly oxalic acid with lesser amounts of other short-chain dicarboxylic, hydroxycarboxylic, and oxocarboxylic acids. These are all water-soluble and are thus washed out by precipitation scavenging. Secondary products from other oxidative processes such as burning

Table 4 Major tracer compounds, their sources and concentrations in aerosols over the oceans

Compound or compound group	Tracer of source	Examples of reported concentration ($ng\,m^{-3}$)	
		Near source	Marine areas
Terrestrial			
n-Alkanes ($> C_{23}$)	Higher plants	30 – 1340	0.5 – 6
n-Alkanols ($> C_{22}$)	Higher plants	15 – 1505	0.1 – 5
n-Alkanoic acids ($> C_{22}$)	Higher plants	3 – 7800	0.1 – 21
n-Alkan-2-ones	Lipids/Soils	0.4 – 124	NR
n-Alkyl amides[a]	Biomass burning	0.1 – 1070	NR
Diterpenoids[a]	Biomass burning	0.1 – 260	0.001 – 3.6
Triterpenoids[a]	Biomass burning	0.2 – 1.4	0.04 – 0.3
Monosaccharide anhydrides[a]	Biomass burning	7 – 33 400	0.2 – 27
Methoxyphenols[a]	Biomass burning	0.7 – 9	0.5 – 3.4
Phytosterols[a]	Higher plants/ biomass burning	0.5 – 10.3	0.1 – 3.2
Cholesterol	Urban/dry lakes	0.2 – 7.4	0.1 – 4.2
Wax esters	Biomass burning/ higher plants	0.2 – 15	0 – 1.2
PAH (also oxy-PAH)	Combustion processes	1 – 22	0.03 – 7
UCM ($C_{max} = 26$)	Urban (petroleum lubricants)	40 – 415	0 – 13
UCM ($C_{max} = 22$)	Dry lake beds	5 – 34	0 – 2
Saccharides[b]	Soils	14 – 574	0 – 12
Petroleum biomarkers	Urban (petroleum use)	0.3 – 4	0 – 0.1
Coal biomarkers	Coal burning	0.03 – 2	0 – 0.01
Plasticizers/antioxidants/ triphenylbenzene	Refuse burning	24 – 126	2 – 23
Marine			
n-Alkanols ($< C_{20}$)	Microbiota		0.04
n-Alkanoic acids ($< C_{20}$, with high $C_{16:1}$)	Microbiota		0.2 – 0.7
Sterols (mainly C_{27} and C_{28})	Microbiota		0.03 – 1.2
Lipids	Microbiota blooms		0.02 – 6
Squalene	Microbiota		0.1 – 2
Secondary Products			
Dicarboxylic acids (C_2–C_6)			1 – 170
Benzoic and benzenedicarboxylic acids			0.2 – 12
Oxy-PAH (mainly quinones)			0.01 – 0.03

NR not reported

[a] High values occur during wildfire seasons.

[b] High values occur during spring/summer seasons.

of biomass and fossil fuel combustion survive long-range transport, because they are in part entrapped within particles and thus protected from further oxidation. Therefore, levoglucosan in smoke from fires, and PAH in soot from urban emissions, as well as some secondary products (benzene dicarboxylic acids, phenolic acids) are detectable downwind over the ocean. The key indicator compounds for the oxidative secondary reactions in the atmosphere are also summarized in Table 4.

5
Conclusions

Organic matter of aerosol particles of both marine and continental areas is derived from two major sources and is admixed depending on environmental conditions. These particle sources are natural biogenic detritus (e.g., plant wax, terpenoids, and marine lipids) and anthropogenic emissions (e.g., soot, smoke, and oils). Combustion, both natural and anthropogenic, yields particle emissions from fossil fuel (e.g., coal and petroleum products) and biomass burning, which is superimposed on the other-source emissions. Wind erosion and resuspension of soil (agricultural activities) and desert sand (dust) advects mainly mineral components with respective major and minor organic tracers into continental atmospheres. In general, the continental aerosol mixtures are transported over the oceans by dominant weather and wind systems. Continental aerosols are diluted, oxidized, and mixed with marine aerosols during longer-range transport. These processes have been illustrated here with examples of ambient aerosols collected in urban, rural, and remote marine areas and discussed in terms of source emission profiles.

In summary, the organic compounds of atmospheric particles from marine and continental regions can be characterized as specific tracers for sources and alteration during transport from (1) natural emissions (vegetation waxes, terpenes), (2) fossil fuels' use (vehicle emissions, coal burning), (3) biomass burning (taxon-specific, wildfires, heating, etc.), (4) anthropogenic emissions (industry, cooking, etc.), and (5) soil and desert dust resuspension (agriculture, wind erosion). The precursor–product chemistry can be used to assess the secondary reactions (thermal or atmospheric) and the fate of aerosol organic matter.

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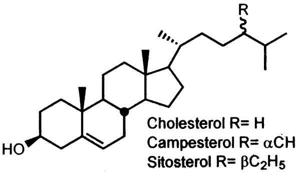
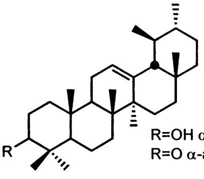
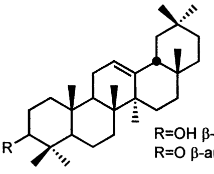
Appendix—Chemical Structures Cited in the Text


Cholesterol R= H
Campesterol R= αCH_3
Sitosterol R= βC_2H_5

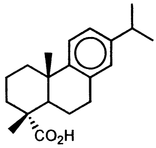
I. Sterols

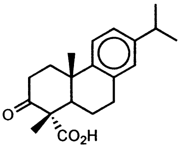

R=OH α-amyrin
R=O α-amyrone

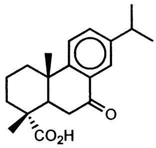
II. Ursenoids

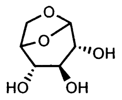

R=OH β-amyrin
R=O β-amyrone

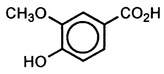
III. Oleanoids

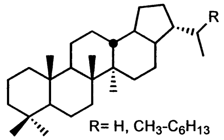

IV. Dehydroabietic acid


V. 3-Oxodehydroabietic acid

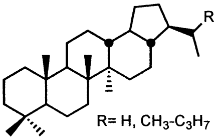

VI. 7-Oxodehydroabietic acid


VII. Levoglucosan

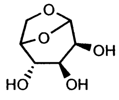

VIII. Vanillic acid

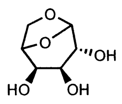

R= H, CH_3-C_6H_{13}

IX. 17α(H),21β(H)-Hopanes


R= H, CH_3-C_3H_7

X. 17β(H),21α(H)-Hopanes


XI. Mannosan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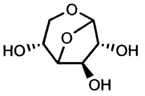
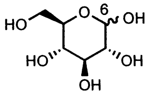
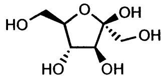
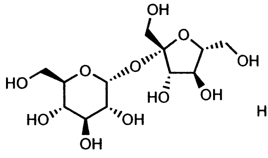

XIII. 1,6-Anhydro-β-glucofuranose


XIV. Glucose (α=6αOH, β=6βOH)


XV. Fructose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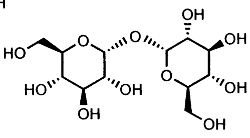
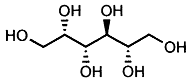
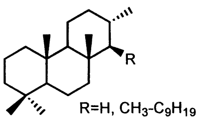
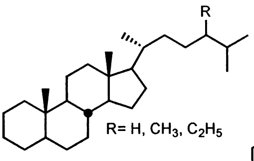

XVII. Mycose (trehalose)

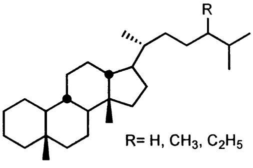

XVIII. Sorbitol (glucitol)


R=H, CH_3-C_9H_{19}

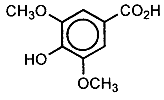
XIX. Tricyclic terpanes

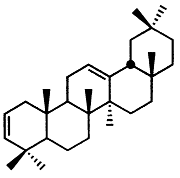

R= H, CH_3, C_2H_5

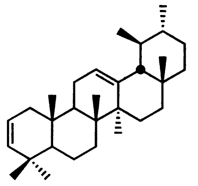
XX. 5α,14α,17α-Steranes


R= H, CH_3, C_2H_5

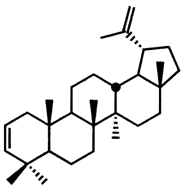
XXI. 10α,13β,17α-Diasteranes


XXII. Syringic acid

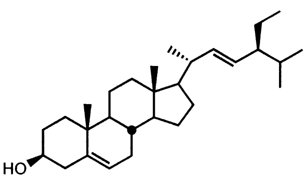

XXIII. Oleana-2,12-diene



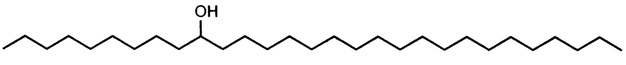
XXIV. Ursana-2,12-diene



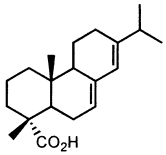
XXV. Lupa-2,22(29)-diene



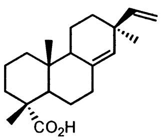
XXVI. Stigmasterol



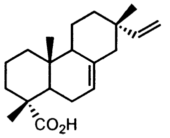
XXVII. Nonacosan-10-ol



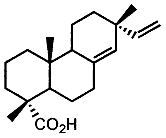
XXVIII. Abietic acid



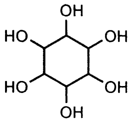
XXIX. Pimaric acid



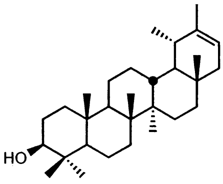
XXX. *Iso*-pimaric acid



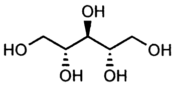
XXXI. Sandaracopimaric acid



XXXII. Inositols



XXXIII. ψ-Taraxasterol



XXXIV. Xylitol