

Sugars—Dominant Water-Soluble Organic Compounds in Soils and Characterization as Tracers in Atmospheric Particulate Matter

BERND R. T. SIMONEIT,^{*,†,‡,§}
VLADIMIR O. ELIAS,^{†,¶}
MINORU KOBAYASHI,[§]
KIMITAKA KAWAMURA,[§]
AHMED I. RUSHDI,[†]
PATRICIA M. MEDEIROS,^{†,‡}
WOLFGANG F. ROGGE,^{||} AND
BORYS M. DIDYK[⊥]

College of Oceanic & Atmospheric Sciences,
Oregon State University, Corvallis, Oregon 97331-5503,
Environmental Sciences Graduate Program,
Oregon State University, Corvallis, Oregon 97331-2904,
Institute of Low-Temperature Science, N19W8,
Hokkaido University, Kita-ku, Sapporo 060-0819, Japan,
Department of Civil and Environmental Engineering,
Florida International University, Miami, Florida 33199, and
Refineria de Petroleo, Concon, Chile

The presence of saccharides is being reported for aerosols taken in urban, rural, and marine locales. The commonly found primary saccharides are α - and β -glucose, α - and β -fructose, sucrose, and mycose with lesser amounts of other monosaccharides. Saccharide polyols are also found in some airsheds and consist mainly of sorbitol, xylitol, mannitol, erythritol, and glycerol. In temperate climate areas these compounds increase from negligible concentrations in winter aerosols (usually dominated by levoglucosan and related anhydrosaccharides from biomass burning) to a maximum in late spring-summer, followed by a decrease to winter. The composition of the saccharide mixtures suggests soil and associated microbiota as the source. Saccharide analyses of soils confirmed these compositions. Therefore, we propose resuspension of soil (also unpaved road dust) from agricultural activities as a major component of aerosol particles and the saccharides are the source specific tracers. In addition, the saccharides as well as the anhydrosaccharide derivatives from biomass burning are completely water soluble and thus contribute significantly to the total water-soluble mass of aerosols.

Introduction

Currently there are two new research directions on particulate matter in the atmosphere. One is the organic compound

composition of the polar water-soluble fraction of atmospheric aerosols (1–3). The second is the contributions and source strengths of soil and desert dusts to the atmosphere of urban, rural, and global regions (e.g., refs 4 and 5).

Water-Soluble Organic Compounds

The water-soluble organic matter documented for aerosol particles consists of short-chain dicarboxylic acids, anhydrosaccharides from biomass burning (e.g., levoglucosan), saccharides, and to some extent phenolics. Oxalic acid, with the other short-chain homologues of dicarboxylic, hydroxydicarboxylic, aromatic dicarboxylic, oxocarboxylic, and hydroxycarboxylic acids, have been reported as major water-soluble components of aerosols (e.g., refs 6–8). 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 (e.g., ref 9).

The tracers for emissions from biomass burning, primarily levoglucosan from cellulose decomposition, with lesser amounts of mannosan, galactosan, and 1,6-anhydroglucofuranose, are also common aerosol components (10–12). These anhydrosaccharides are completely soluble in water and have been reported globally in remote to urban air sheds (e.g., Table 1 (3, 13–18)). Lignin, another major biopolymer of wood, yields phenolic tracers upon burning in the smoke characteristic of the fuel type (19–24). These tracers (e.g., vanillic acid) are not completely water soluble, although phenolics are hygroscopic.

Major amounts of saccharides (Table 1) have been reported to be present in aerosols of certain geographic regions such as Amazonia, Brazil (3), northwestern Pacific with Korea and Japan (11), and Santiago, Chile (25, 26). The dominant primary saccharides consist of α - and β -glucose, α - and β -fructose, sucrose, and mycose (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 (D-glucitol), xylitol, mannitol, arabitol, erythritol, and glycerol (3, 11). All these saccharides are emitted directly from sources, although they may also be emitted significantly by thermal stripping during burning in wildfires. These saccharides are completely soluble in water. Thus, their specific sources need to be characterized.

Soil Organic Compounds

There is a need to demonstrate potential organic tracers that are unique to soil to complement the diverse mineral and trace metal compositions of soils. Soil is a complex mixture of inorganic and organic material. Plant detritus is considered to be the major source for soil organic matter (27). Depending on the geographical location, agricultural soil may contain 5–6% of organic matter, sandy soil less than 1%, and poorly drained soils about 10%. Soil organic matter is composed of a mixture of aerial and below-ground plant litter, animal and microbial residues, lipids, carbohydrates, peptides, cellulose, lignin, and humic material (27). About 5–20% of the soil organic matter is composed of carbohydrates and up to 10% of lipids, phytosterols, and other compounds (27).

Plant detritus associated with soil is composed of “above” and “below” ground plant parts. Plant cuticles “above” and “below” ground are waterproof barriers, protecting epidermal cells of leaves, fruits, roots, and nonwoody stems with a waxlike surface layer made of lipids and biopolymers. These plant waxes consist of higher molecular weight alkanes, alkanols, wax esters, alkanolic acids, alkanals, and to a minor

* Corresponding author phone: (541)737-2155; fax: (541)737-2064; e-mail: simoneit@coas.oregonstate.edu.

[†] College of Oceanic & Atmospheric Sciences, Oregon State University.

[‡] Environmental Sciences Graduate Program, Oregon State University.

[§] Hokkaido University.

[¶] Present address: Analytical Solutions, P. Saldanha 115, Jardim Botânico 22461-220, Rio de Janeiro, Brazil.

^{||} Florida International University.

[⊥] Refineria de Petroleo.

TABLE 1. Concentrations of Major Saccharides in Aerosols

compound ^a	Santiago, Chile ^c	Kuala Lumpur, Malaysia ^c	Sapporo, Japan ^c	Ghent, Belgium ^d	Rondônia, Brazil ^e	various locales, U.S.A. ^f	Datong, P. R. China ^c
levoglucosan	12–2452 (839)	1162–33400 (14460)	6–56	121–1133 (477)	1182–6900 (2460)	500–2980 (1450)	1350
mannosan	1–233 (81)	154–4430 (1422)	0.2–15	17–153 (66)	6–371 (126)	170–322	108
galactosan	1.7–127 (45)	84–2410 (1014)	0.6–2.4	4–44 (20)	2–148 (55)	96–144	106
1,6-anhydrogluco- furanose	0.5–195 (62)	135–4005 (1520)			5–248 (82)		
glucose ^b	10–2210 (940)		1–34		14–62 (37)	10–15	102
fructose ^b			12		3–20 (9)		
galactose ^b					0.2–2.4 (0.9)		
mannose ^b		48–6800 (2053)			0.6–4 (2)	9–13	
xylose ^b					1–33 (13)	9–17	
sorbitol			3–26		0–1.7 (0.8)		
mannitol					10–50 (26)		
xylitol			2–22				
erythritol					2–39 (16)		
glycerol			3–24		0.5–9 (3)		
inositols			3–104		0.5–21 (8)		
sucrose	15–3060 (1108)		0.4–9		0.8–26 (7)	3.2–4	1148
maltose	6–2390 (622)	2–550 (130)				3–4	68
mycose	8–1660 (477)		0.2–12		5–18 (9)		54

^a Concentrations are given as ng/m³, numbers in parentheses are the mean. ^b Both α - and β -isomers are summed. ^c This work (all TSP). ^d Reference 16 – sampled during winter (PM10). ^e Reference 3 – sampled during October (PM10 and PM2.5). ^f References 14, 15, and 54 – all PM10.

extent alkanediols, aldehydes, and other biomarker compounds (28, 29). The aerial plant parts contain cutin, and the underground plant roots and tubes are comprised of suberin, both biopolyesters (30). In addition, all plants contain cellulose, and woody plants have lignin under the polyester outer sheaths. Cutin biopolyester is composed of ω -hydroxy and epoxy fatty acids, whereas suberin includes aromatics with polyesters. All lipids and biopolymers are biodegraded over time in soils.

Active soil contains a few million bacteria, up to a million actinomycetes, and several thousand fungi per gram. Therefore, microorganisms contribute lipids to the soil organic matter, including fatty acids, fatty alcohols, and hydrocarbons as well as utilize and alter the lipid pool. When compared to epicuticular plant waxes, lipids of lower molecular weight ($\leq C_{20}$) found in soil have been suggested to be mainly of a microbial origin (31–34). Over time, vascular plant material undergoes diagenic degradation caused by heterotrophic microorganisms (35) as well as heterogeneous chemical reactions on minerals contained in soil (36). Thus, the compositions of the lipid and polar fractions found in soil depend on plant growth, biochemical and physical soil properties, level of cultivation, location, and climatic conditions. It should be pointed out that ergosterol is used in soil science as the tracer for fungal biomass (37–39). It occurs in these soil extracts as a trace component among the other sterols and may be utilized as a confirming tracer for the fungal component of soils.

Therefore, stable and distinct molecular markers or an assemblage of such organic compounds are needed in order to trace the release of soil dust from the ground into the atmosphere. The half-life, i.e., chemical stability, of molecular markers required for source-receptor modeling must be adequate to exceed the particular residence time of air masses within the modeling area. Furthermore, the group of individual organic compounds or series of homologues must have a concentration pattern that is characteristic of the source under consideration.

Soil input to the atmosphere occurs by wind erosion and resuspension from anthropogenic activities in numerous ways. Natural wind erosion introduces surface fines from deserts, dried lakes and washes, denuded lands, and fallow agricultural fields. Resuspension of dirt and soil from human activities include agricultural tilling, husbandry and harvesting, construction engineering projects, and traffic on unpaved

roads. The organic and inorganic tracer compositions of soil samples from some of these input sources are being characterized (e.g., refs 40–43).

Here we demonstrate the utility of saccharides as organic tracers for soil input to the atmosphere and thus their major contribution to the water-soluble organic fraction of the particulate matter of impacted airsheds. The sources, chemistry, and quantitation of saccharide tracers will be described here in detail, so that they may be applied in source models.

Experimental Methods

Samples. Soil samples were taken by scraping the surface fines (dry) from various active and fallow agricultural fields and natural areas. The samples (~5 g) were dried in an oven at 40 °C and then sieved (<0.6 mm) to remove coarse particles. It should be noted that these soil fines do not correspond to the aerosol PM10 particle size but range to larger diameters. The samples were weighed before extraction.

Aerosol particulate matter was acquired by high-volume filtration on quartz fiber filters (Pallflex 2500 QAO) either directly without coarse particle removal or as PM10. Filters were stored in jars with Teflon-lined caps in a freezer until extraction.

Extraction and Fractionation. The samples were sonicated three times for 10 min each with dichloromethane:methanol (1:1; v/v). This solvent mixture extracts levoglucosan at 95%, β -glucose at 97%, and sucrose at 92% efficiency (44). The solvent extract was filtered and concentrated by use of a rotary evaporator and then under blow-down with dry nitrogen gas. Aliquots of the total extracts were converted to trimethylsilyl derivatives by reaction with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane and pyridine for 3 h at 70 °C. Some filter aliquots were extracted with water (double-distilled) to test extraction efficiency compared to the solvent extraction. The aqueous extracts were dried, derivatized with BSTFA, and analyzed by GC-MS. Selected total extracts were also separated by use of flash column chromatography on silica into saturated hydrocarbons, aromatic hydrocarbons, and polar compounds. The fractions were eluted with hexane, dichloromethane, and methanol, respectively, and dried under nitrogen.

Gas Chromatography–Mass Spectrometry. Gas chromatography–mass spectrometry (GC-MS) analyses of the

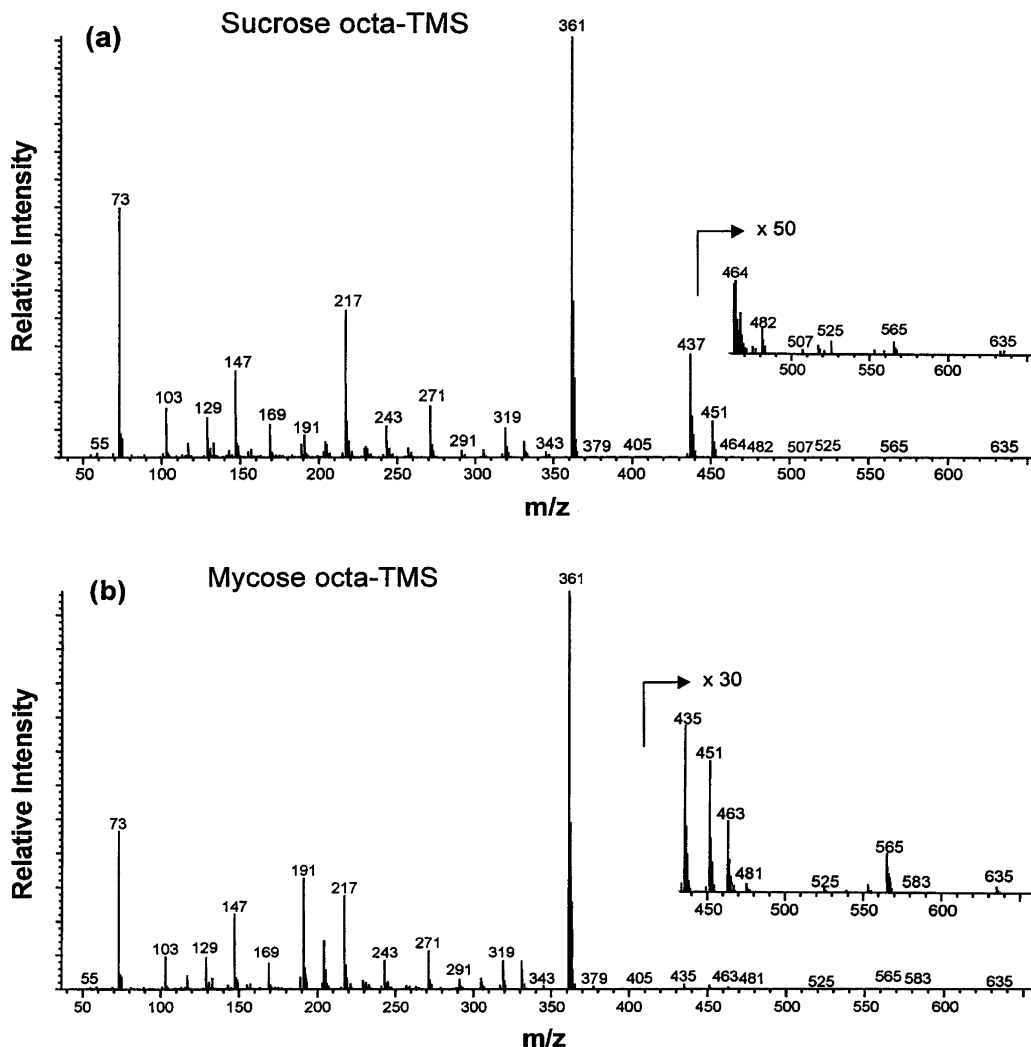


FIGURE 1. Mass spectra of silylated disaccharides: (a) sucrose octa-TMS, $C_{36}H_{86}O_{11}Si_8$ and (b) mycose octa-TMS, $C_{36}H_{86}O_{11}Si_8$.

derivatized total extracts and separated fractions were performed on a Hewlett-Packard model 6890 GC coupled to a Hewlett-Packard model 5973 MSD. Separation was achieved on a fused silica capillary column coated with DB5 (30 m \times 0.25 mm i.d., 0.25 μ m film thickness). The GC operating conditions were as follows: temperature hold at 65 $^{\circ}$ C for 2 min, increase from 65 to 300 $^{\circ}$ C at a rate of 6 $^{\circ}$ C min $^{-1}$ with final isothermal hold at 300 $^{\circ}$ C for 20 min. Helium was used as carrier gas. The sample was injected splitless with the injector temperature at 300 $^{\circ}$ C. The mass spectrometer was operated in the electron impact mode at 70 eV and scanned from 50 to 650 dalton. Data were acquired and processed with the Chemstation software. Individual compounds were identified by comparison of mass spectra with literature and library data, comparison with authentic standards, and interpretation of mass spectrometric fragmentation patterns. Relative response factors were determined using representative standards by GC-MS injection. Identifiable compounds were quantified using the MS-data system. Relative ion counts were converted to compound mass using the area counts of the external standards determined under the same instrumental operating conditions.

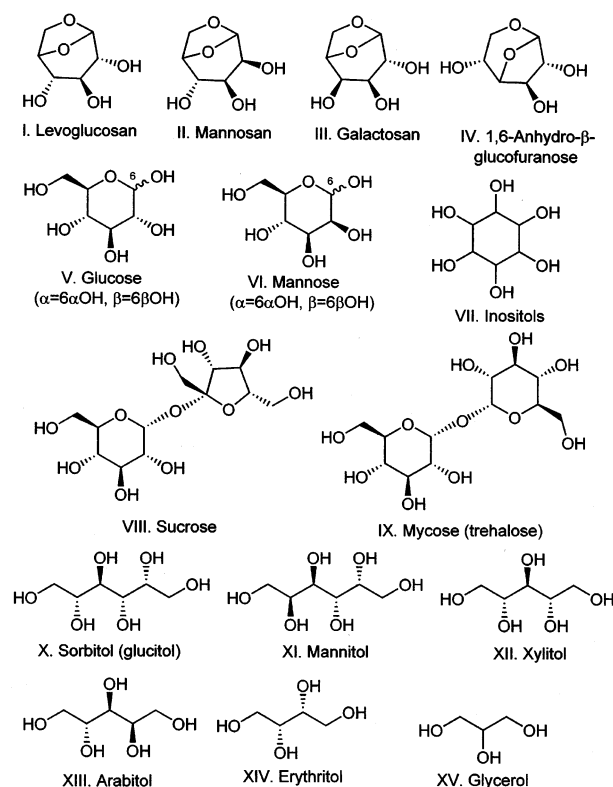
Results and Discussion

Saccharide Identification. The analysis of saccharides by GC-MS is well established and usually carried out directly on the pertrimethylsilylated (TMS) tautomeric mixtures or after initial methoximation followed by silylation (e.g., refs 45–52). The mass spectra are generally in the MS libraries but

are not necessarily specific to each compound. The key ions for pentoses, hexoses, and heptoses as TMS ethers are generally m/z 73, 147, 191, 204, and 217; disaccharides have an additional ion at m/z 361; and the reduced sugars have additional key ions at m/z 205, 217, 307, and 319. For example, the mass spectra of α - and β -glucose-perTMS are identical and exhibit no high mass nor molecular ions. Thus, the GC retention time must also be correlated with that of the standards for compound identification.

The commonly encountered disaccharides in these aerosols and source samples are sucrose, mycose (trehalose), maltose, and iso-maltose. The mass spectra of sucrose- and mycose-pertrimethylsilyl ethers are similar (Figure 1), and their presence in the soil and aerosol samples was confirmed by comparison with the authentic standards. The other common disaccharides, e.g., cellobiose, palatinose, turanose, or lactose, were not found in soils or aerosols. The mass spectrometric fragmentation patterns of sucrose and mycose octa-TMS (Figure 1) show no molecular ion at m/z 918 and have primary cleavage of the ring junction followed by double fragmentation (loss of CH_3 and trimethylsilanol) to yield the base peak at m/z 361. Minor fragments are m/z 635 (M-283), m/z 565 (M-353), m/z 463 (M-455, loss of glucose-TMS), m/z 451 (M-467, loss of fructose-TMS), and m/z 437 (M-481). The mass spectra of sucrose and mycose octa-TMS differ in the relative intensities of the fragment ions at m/z 565, 463, 217, and 191, which coupled with the GC retention index, allow the definitive identification.

CHART 1. Chemical Structures



Saccharide Recovery and Stability. The advantage of using the dichloromethane/methanol mixture (1:1 to 3:1, v/v) is its extraction efficiency for both neutral (lipids) and polar (water-soluble) compounds, without hydrolysis of organic anhydrides (e.g., phthalic anhydride). This is a well established and tested method in organic geochemistry. On the other hand, extraction with water recovers essentially 100% of the saccharides, anhydrosaccharides (e.g., levoglucosan), and other water-soluble compounds without the lipids. The anhydrosaccharides in fresh smoke from burning of biomass occur as the free compounds with varying amounts entrapped in the charcoal/soot particles (12). The free compounds are susceptible to some hydrolysis during long-range aerosol transport (weeks), but the entrapped anhydrosaccharides can be preserved in sedimentary sinks over geological times (53). Fraser and Lakshmanan (14) observed levoglucosan stability in atmospheric particulate matter and we confirm this. We have tested the hydrolysis of standard levoglucosan in water and in acid (pH ~ 2) solutions and find recoveries after 1, 3, 5, and 15 days of > 99% for both cases. Thus, the anhydrosaccharides are useful tracers for smoke from biomass burning while associated with the aerosol particle matrices. The saccharides likewise are associated with and encapsulated in particles and, therefore, are less prone to degradation.

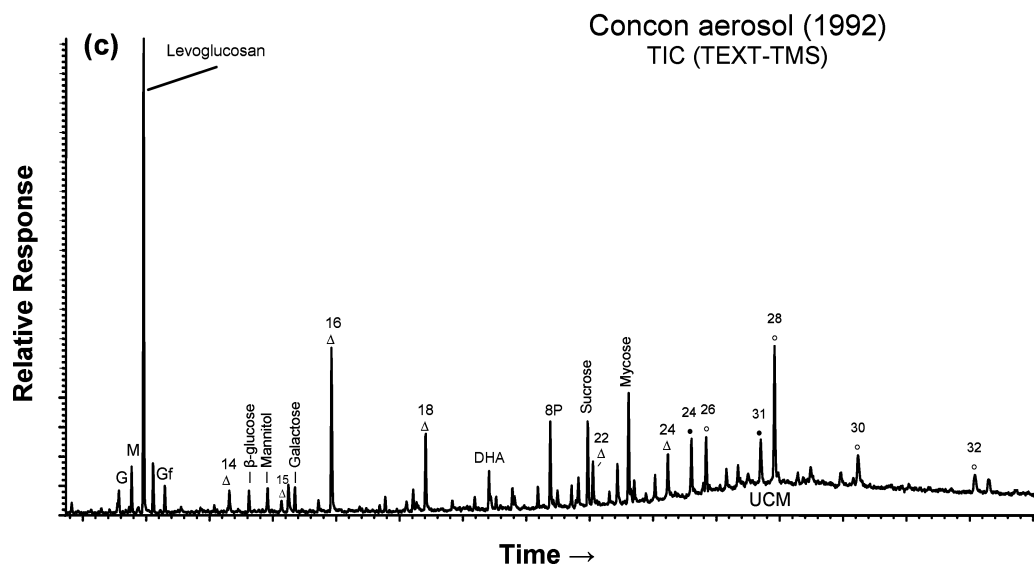
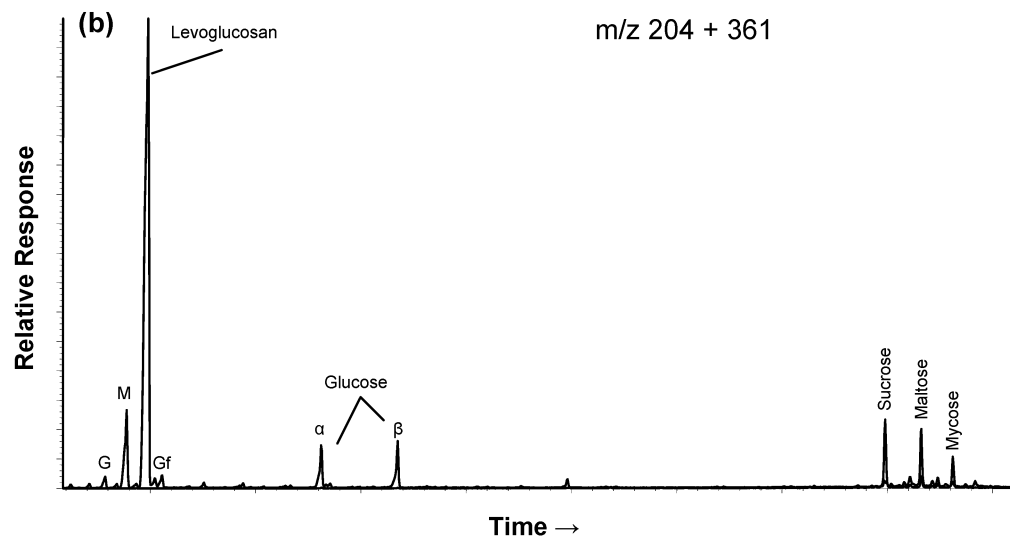
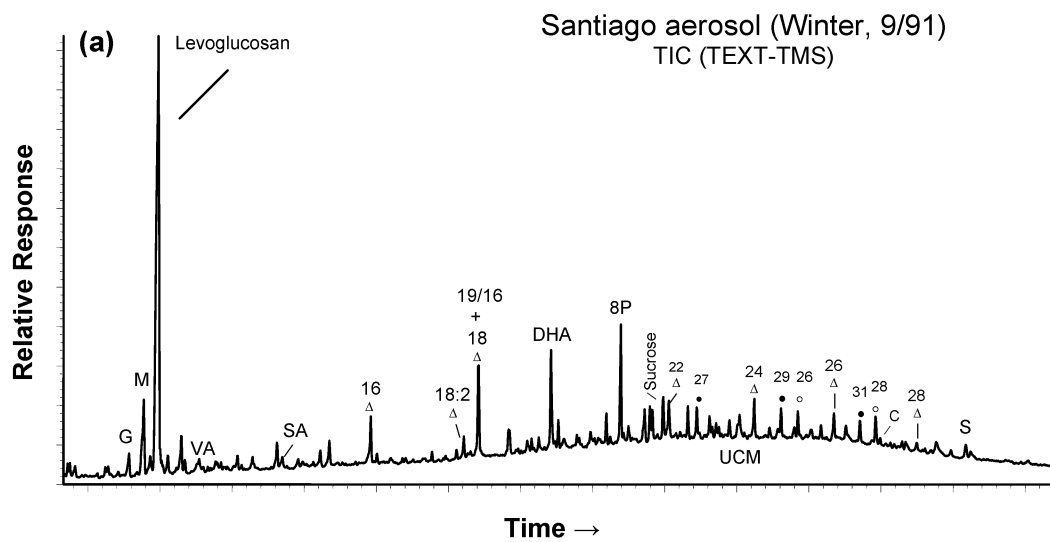
Serial dilutions of standard anhydrosaccharides, saccharides, and fatty acids were prepared and analyzed for recovery and GC-MS response factor determinations (1–200 μg mL⁻¹). Recoveries of levoglucosan, glucose, sucrose, palmitic acid, and stearic acid when spiked onto quartz filters and extracted with the dichloromethane/methanol (1:1 v/v) mixture were better than 90% (44).

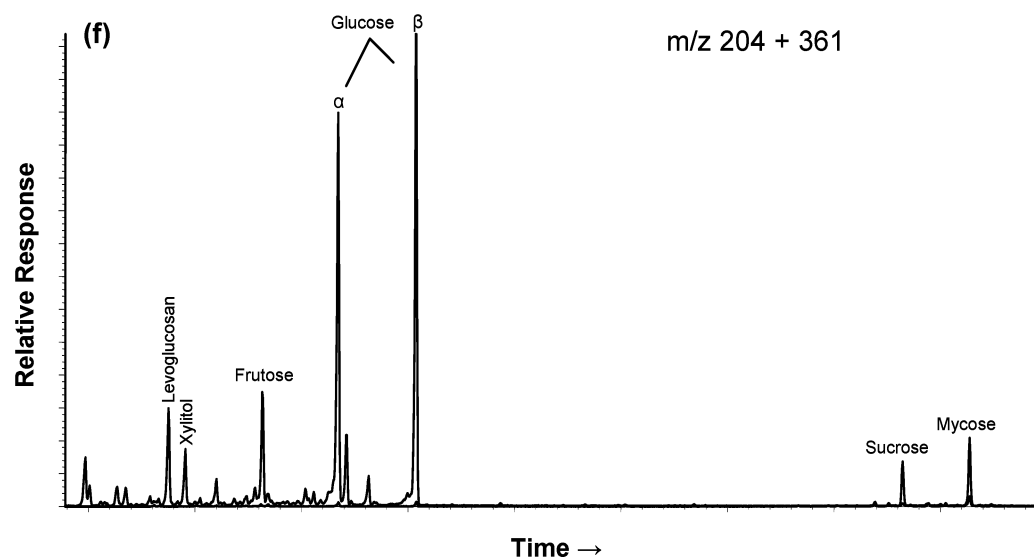
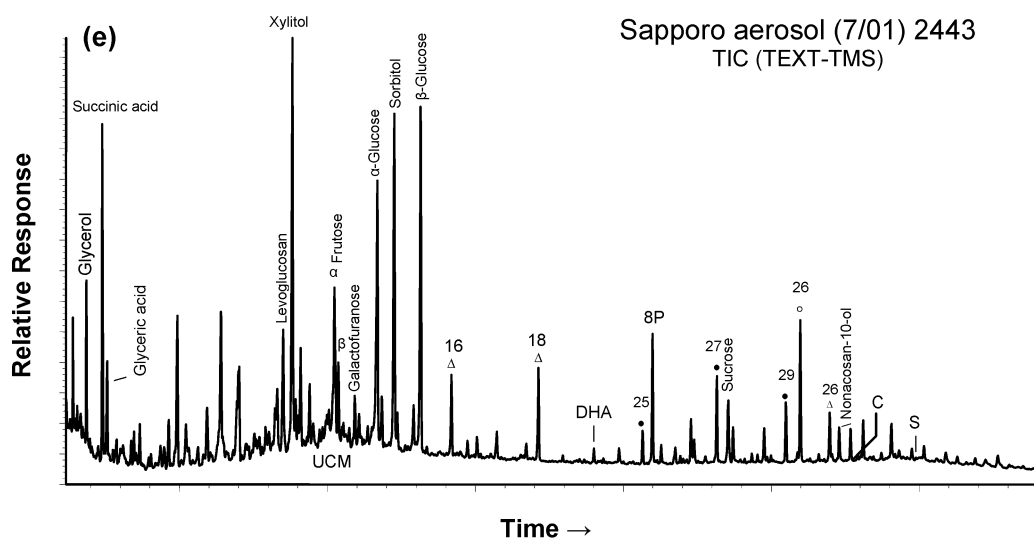
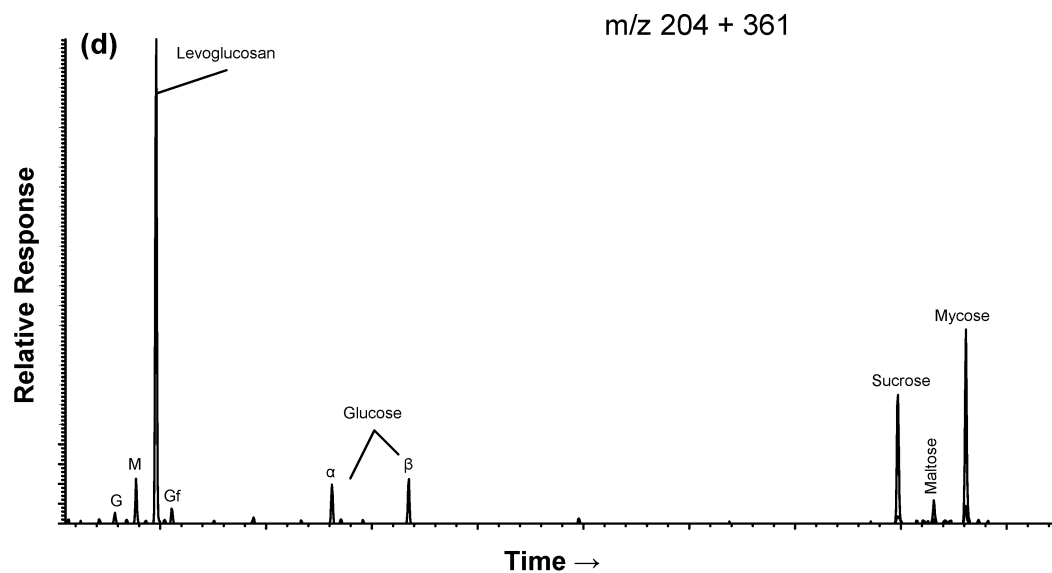
Aerosol Saccharides. The saccharides in aerosol particulate matter are comprised of three groups: (a) the anhydro derivatives comprised mainly of levoglucosan (1,6-anhydro-β-D-glucopyranose, I), chemical structures are given in Chart I), with minor mannosan (II), galactosan (III), and 1,6-anhydro-β-D-glucofuranose (levoglucosan isomer, IV); (b) the

TABLE 2. Concentrations of Major Saccharides in Soils and Unpaved Road Dusts

compound ^a	Amazonia soil (tropical)	safflower field (temperate, summer)	almond orchard (temperate, summer)	cotton field (temperate, summer)	grape orchard (temperate, summer)	tomato field (temperate, summer)	Toya, Hokkaido soil (winter)	unpaved road dust (temperate)	paved road dust (temperate)
levoglucosan	nd ^c	0.01–0.12 (0.07)	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c –0.21 (0.11)
glucose ^b	43.4	0.28–1.71 (1.10)	0.3–4.2 (2.3)	0.5–1.3 (0.6)	0.02–0.27 (0.15)	0.47–0.72 (0.6)	0.18	0.05–4.8 (0.9)	2.9–93.3 (48.1)
fructose ^b	2.0	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c –30.4 (15.2)
mannose	31.3	nd ^c	1.4–5.3 (3.4)	nd ^c	nd ^c	nd ^c	0.08	nd ^c	nd ^c –0.7 (0.3)
sorbitol	21.7	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c
xylitol	n.d.	nd ^c	3.2–3.7 (3.4)	0.02–0.28 (0.11)	0.02–0.21 (0.12)	0.23–0.30 (0.26)	nd ^c	nd ^c	nd ^c –0.43 (0.22)
glycerol	16.9	0.07–0.28 (0.18)	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c	0.06–0.19 (0.1)	0.73–1.25 (0.99)
inositol	n.d.	0.03–0.61 (0.32)	nd ^c	0.01–1.14 (0.4)	nd ^c	nd ^c	nd ^c	nd ^c	nd ^c –0.44 (0.22)
sucrose	3.9	0.84–1.78 (1.31)	0.9–2.8 (1.9)	0.37–4.9 (2.8)	0.19–0.77 (0.48)	0.3–0.6 (0.4)	0.005	0.34–10.7 (2.8)	7.6–7.7 (7.6)
mycose	48.2	5.80–6.01 (5.91)	21.7–38.7 (30.2)	0.37–4.9 (2.8)	1.03–7.52 (4.3)	3.4–6.8 (5.1)	0.01	3.3–7.2 (5.3)	6.2–19.0 (12.6)
total mean	167.4	8.9	41.2	3.91	5.05	6.36	0.275	9.1	85.34

^a Concentrations are given as μg/g (dry weight of soil fines < 0.6 mm diameter); numbers in parentheses are the mean. ^b Both α- and β-isomers are summed. ^c nd = not detected.





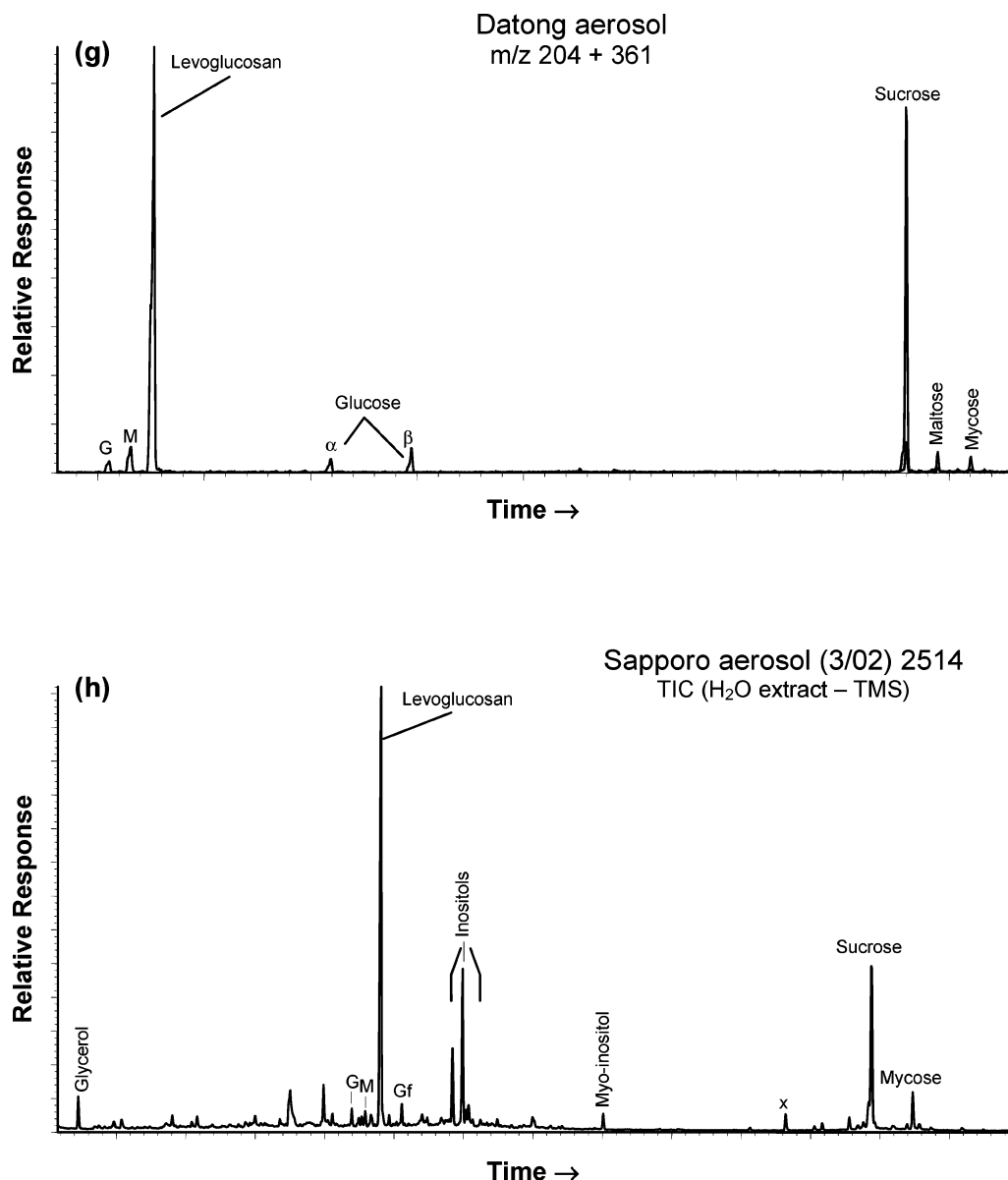


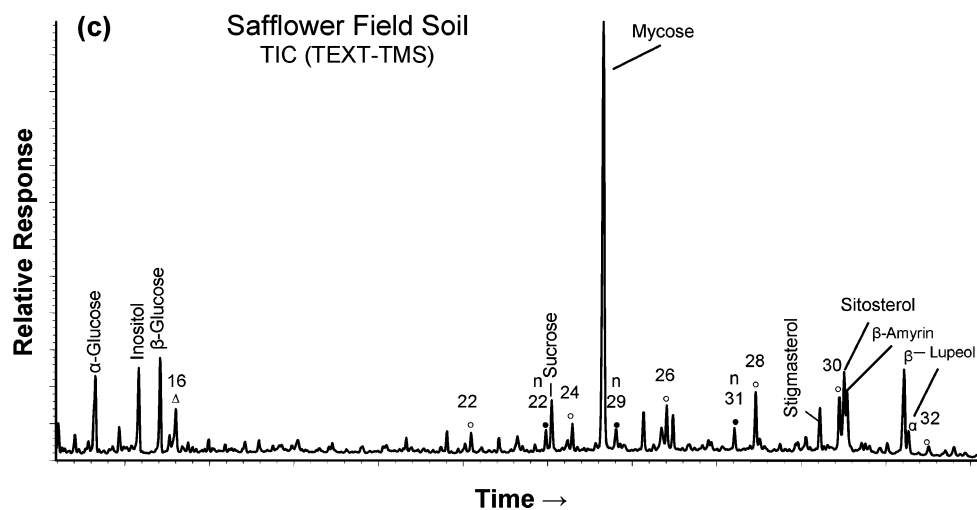
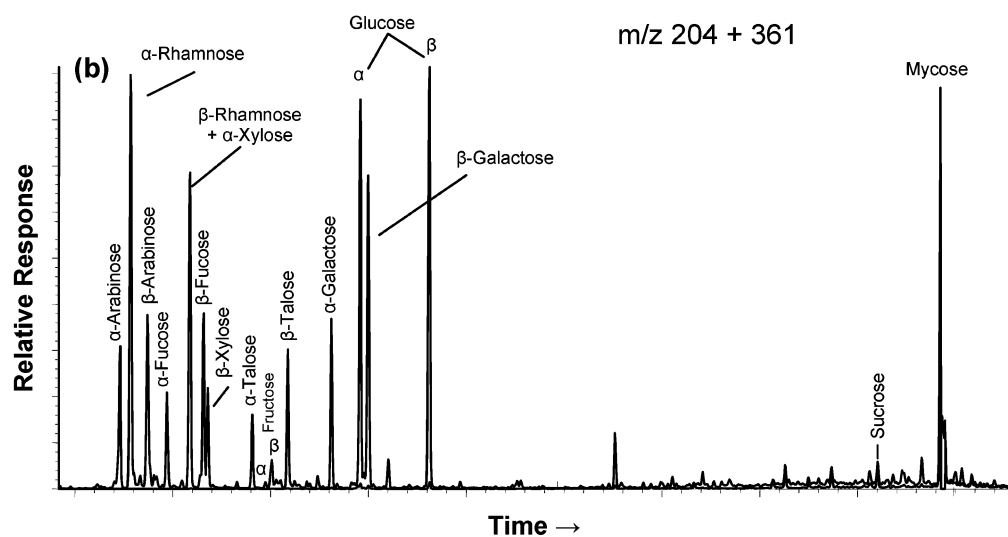
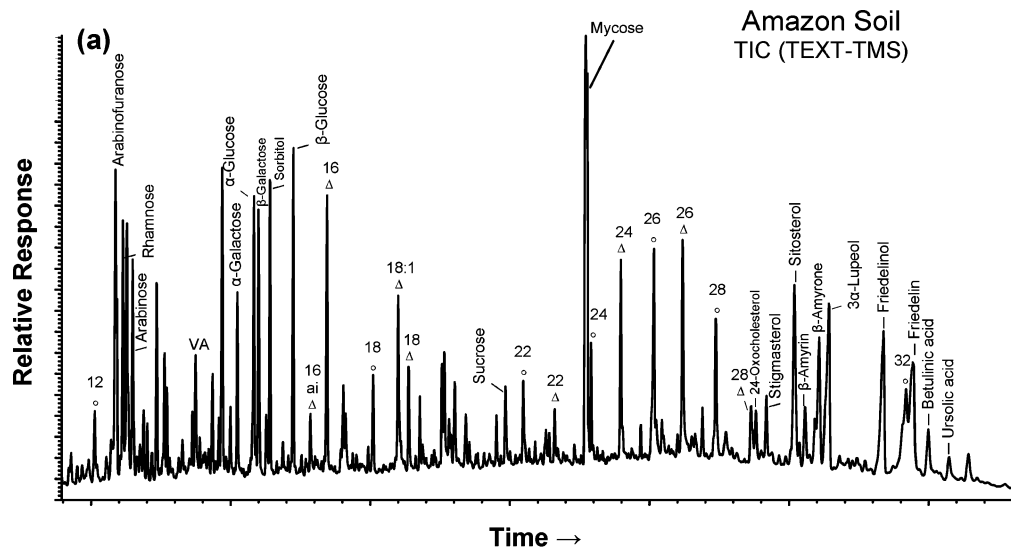
FIGURE 2. Representative examples of GC-MS data for silylated total extracts of atmospheric particulate matter: Santiago, Chile (winter 1991): (a) total ion current (TIC) trace, (b) m/z 204 and 361 key ion trace for mono- and disaccharides; Concon, Chile (suburban winter), (c) TIC trace, (d) m/z 204 and 361 key ion trace; Sapporo, Japan (June 28–July 5, 2001), (e) TIC trace, (f) m/z 204 and 361 key ion trace; (g) Datong, P. R. China (April, 1991) m/z 204 and 361 key ion trace; and (h) Sapporo, Japan (March 2002), total aqueous extract TIC trace. The saccharides and anhydrosaccharides are labeled, $i\Delta$ = n -alkanoic acids, $i\circ$ = n -alkanols, $i\bullet$ = n -alkanes, C = cholesterol, S = sitosterol, G = galactosan, Gf = 1,6-anhydro- β -D-glucofuranose, M = mannosan, VA = vanillic acid, SA = syringic acid, DHA = dehydroabietic acid, P = phthalate, X = artifact from BSTFA, UCM = unresolved complex mixture of branched and cyclic hydrocarbons.

primary saccharides consisting of α - and β -glucose (V), α - and β -mannose (VI), inositols (VII), sucrose (VIII), and mycose (trehalose, IX); and (c) the saccharide polyols (alditols, i.e., reduced sugars) ranging from sorbitol (D-glucitol, X), mannitol (XI), xylitol (XII), arabinol (XIII), erythritol (XIV), to glycerol (XV). Minor amounts of other monosaccharides (e.g., xylose, fructose, galactose) are also found in some samples.

Levoglucosan, with mannosan, galactosan, and 1,6-anhydro- β -D-glucofuranose (I–IV) are the key tracers for smoke particulate matter from burning of biomass (i.e., thermal alteration products from mainly cellulose and lesser amounts of hemicellulose (10)). These compounds have been found in aerosols over the ocean and thus are stable during long-range transport (13, 14). They are detectable at ng/m^3 levels in low-volume fine-particle aerosol samples in urban areas (e.g., refs 17 and 18) as well as in conventional aerosol particle samples taken in various global areas (e.g., refs 3, 10, 11, 15, 16, and 54).

The presence of the saccharide anhydrides (I–IV) is illustrated in Figure 2 for various aerosol samples. The dominant compound in smoke impacted air sheds is levoglucosan, as can be seen from the GC-MS data of the total silylated extracts from TSP filters (Figure 2a,c). The saccharides can also be extracted directly with water and immediately derivatized by silylation for GC-MS analysis. The saccharide anhydrides are stable to hydrolysis for brief time periods as is illustrated in Figure 2h. However, extended aqueous storage of extracts results in hydrolysis of the anhydrosaccharides. Therefore, the saccharide anhydro derivatives from biomass burning are tabulated with the corresponding data for the other carbohydrates (Table 1). The primary saccharides (e.g., glucose, sucrose, mycose, etc.) and the saccharide polyols (e.g., sorbitol, xylitol, etc.) are candidate tracers for surface soil dust and are discussed next.

The dominant primary saccharides in aerosols are comprised of α - and β -glucose (V), sucrose (VIII), and mycose



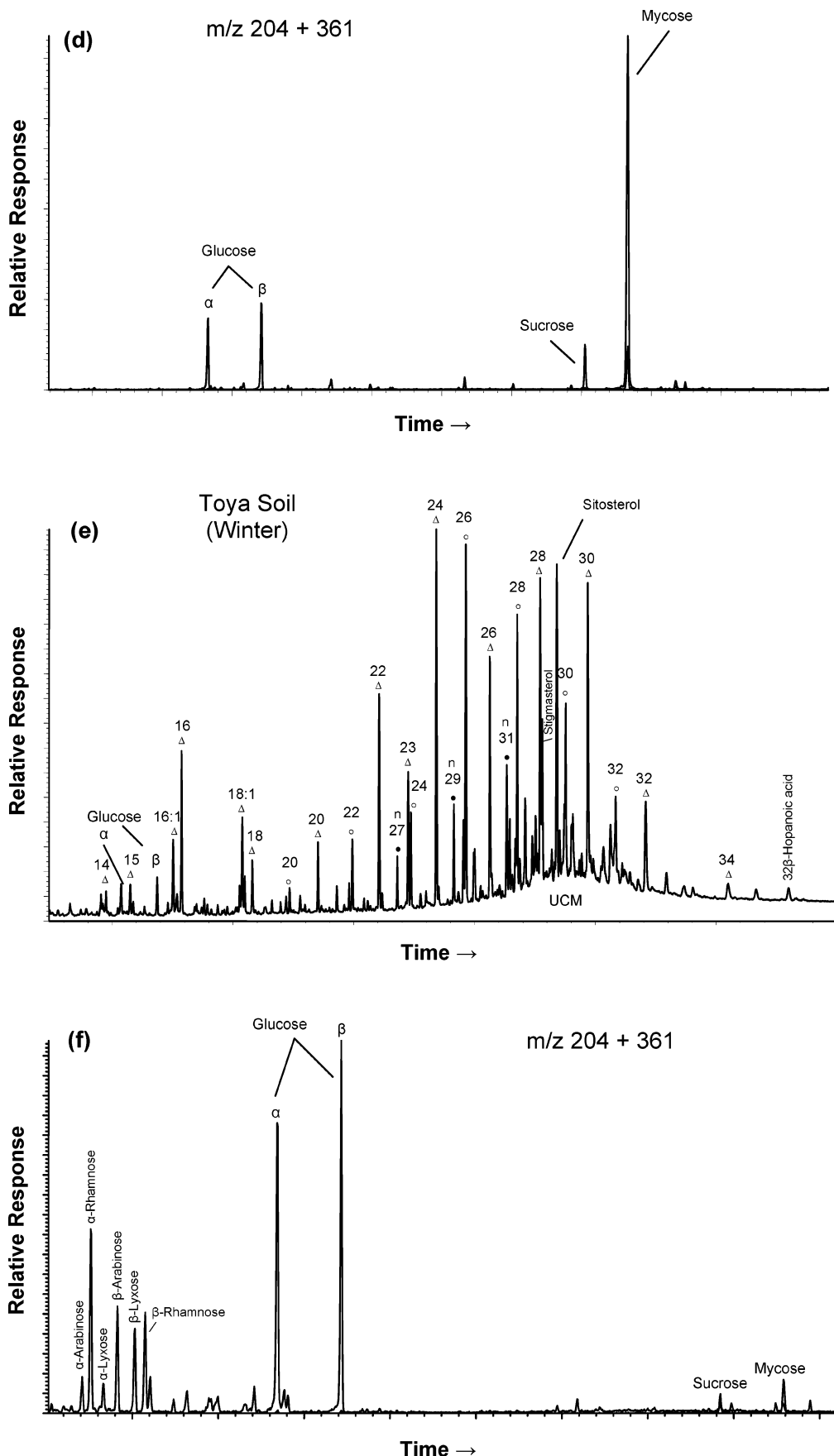


FIGURE 3. Representative examples of GC-MS data for silylated total extracts of soils: Ducke Reserve, Amazonia, Brazil (summer)—(a) TIC trace, (b) m/z 204 and 361 key ion trace; Safflower field, San Joaquin Valley, California (summer)—(c) TIC trace, (d) m/z 204 and 361 key ion trace; and Toya, Hokkaido, Japan (early spring, fallow field)—(e) TIC trace, and (f) m/z 204 and 361 key ion trace. The saccharides are labeled, ai = anteiso homolog, and numbers with symbols as in Figure 2.

(IX), with various other minor components (e.g., galactose, fructose, mannose, xylose, inositols, and maltose) at some locales (Table 1). The distributions of the silylated saccharides in aerosols are also shown in Figure 2, where the key ion plots of m/z 204 for the monosaccharides with m/z 361 for the disaccharides are given. The anhydrosaccharides also have the m/z 204 key ion. The ratio of α - to β -glucose is generally almost one, and thus the two isomers are summed for concentration reports. Sucrose (VIII) and mycose (IX) occur at varying ratios which may reflect source properties. Mycose and the reduced sugars are products of fungal metabolism (e.g., ref 33). In general, the saccharides are present at relatively low atmospheric concentrations during the early spring and become dominant into the summer season, paralleling the agricultural tilling practices which resuspend soil dust into the passing aerosols as, for example, on the Asian continent (11).

Soil Saccharides. Saccharides are a major fraction of soil organic matter (55) and have also been characterized in riverine particulate matter (56). The saccharide content of soils is summarized in Table 2 and illustrated with some examples for a tropical soil from Amazonia, Brazil and two temperate soils from the San Joaquin Valley in California and the Toya area, Hokkaido, Japan (Figure 3). The tropical soil contains a complex mixture of mono- and disaccharides (167 $\mu\text{g/g}$), whereas the temperate examples have mainly glucose, sucrose, and mycose with minor inositol, rhamnose, arabinose, and lyxose. In winter and early spring, the saccharide content of soils is low because the living biomass is dormant (Figure 3e,f), especially in frozen terrain (0.28 $\mu\text{g/g}$). The sugars represent a significant proportion of the total organic extract of soils during the growing season (Figure 3a,c vs 3e). Various representative agricultural soils have been analyzed to determine their saccharide contents for source evaluation of soil resuspension into the atmosphere (42, 43). In general, α - and β -glucose, inositols, sucrose, and mycose are the common tracers to all samples analyzed (42, 43).

Saccharide Contribution to Water-Soluble Compounds.

The saccharides comprise from 13 to 26% of the total compound mass (TCM) identified in continental aerosols and have isolated higher values over the ocean (up to 63%, e.g., ref 11). We interpret these saccharides 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 (e.g., ref 25) and in remote and rural areas (e.g., ref 3 and 11). Thus, they are proposed here as tracers for soil resuspension with associated microbiota from agricultural tilling and harvesting, wind erosion, or traffic.

The water solubility of the carbonaceous organic fraction of aerosols is a major open question in climate models (2, 57). Oxalic acid, with the other short-chain dicarboxylic acids, have been documented as the dominant water-soluble components of organic aerosol matter (e.g., refs 7 and 8). Here we propose to add the following groups of organic compounds to the list of water-soluble organic matter based on their complete aqueous solubility properties: saccharides, anhydrosaccharides, and secondary oxidation products such as methoxyphenolics and aromatic acids. The sum of these water-soluble compounds ranges from 14 to 89% of TCM for typical samples and is about 40–70% of TCM during an Asian dust episode at the ground stations (11). These water-soluble fractions are unusually high and when coupled with the oxalic and malonic acid contents determined separately (e.g., ref 9) make essentially the total compound mass water-soluble. This is quite different from the urban aerosols such as in Los Angeles, CA or Santiago, Chile, where the bulk of the identified organic compounds are hydrophobic (e.g., refs 25 and 58). It is also different when compared to the Saharan dust

aerosols from Africa over the North Atlantic which have low contents of these water-soluble compounds (13).

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Literature Cited

- (1) Saxena, P.; Hildemann, L. M. *J. Atmos. Chem.* **1996**, *24*, 57–109.
- (2) Facchini, M. C.; Mircea, M.; Fuzzi, S.; Charlson, R. J. *Nature* **1999**, *401*, 257–259.
- (3) Graham, B.; Mayol-Bracero, O. L.; Guyon, P.; Roberts, G. C.; Decesari, S.; Facchini, M. C.; Artaxo, P.; Maenhaut, W.; Köll, P.; Andreae, M. O. *J. Geophys. Res.* **2002**, *107* (D20), 8047, doi: 10.1029/2001JD000336, LBA 14/1–16.
- (4) Delany, A. C.; Zenchelsky, S. *Soil Sci.* **1976**, *121*, 146–155.
- (5) Chester, R. In *Nobel Symposium 20, The Changing Chemistry of the Oceans*; Dyrssen, D., Jagner, D., Eds.; Wiley: New York, 1972; pp 291–305.
- (6) Sempéré, R.; Kawamura, K. *Atmos. Environ.* **1994**, *28*, 449–459.
- (7) Kawamura, K.; Usukura, K. *J. Oceanogr.* **1993**, *49*, 271–283.
- (8) Kawamura, K.; Sakaguchi, F. *J. Geophys. Res.* **1999**, *104*, 3501–3509.
- (9) Mochida, M.; Umemoto, N.; Kobayashi, M.; Matsunaga, S.; Kawamura, K.; Bates, T. S.; Simoneit, B. R. T. *J. Geophys. Res.-Atmos.* **2003**, *108* (D23), 8638, doi: 10.1029/2002JD003249, ACE 6/1–12.
- (10) Simoneit, B. R. T.; Schauer, J. J.; Nolte, C. G.; Oros, D. R.; Elias, V. O.; Fraser, M. P.; Rogge, W. F.; Cass, G. R. *Atmos. Environ.* **1999**, *33*, 173–182.
- (11) Simoneit, B. R. T.; Kobayashi, M.; Mochida, M.; Kawamura, K.; Lee, M.; Lim, H.-J.; Turpin, B. J.; Komazaki, Y. *J. Geophys. Res.* In press.
- (12) Simoneit, B. R. T. *Appl. Geochem.* **2002**, *17*, 129–162.
- (13) Simoneit, B. R. T.; Elias, V. O. *Mar. Chem.* **2000**, *69*, 231–243.
- (14) Fraser, M. P.; Lakshmanan, K. *Environ. Sci. Technol.* **2000**, *34*, 4560–4564.
- (15) Nolte, C. G.; Schauer, J. J.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **2001**, *35*, 1912–1919.
- (16) Zdráhal, Z.; Oliviera, J.; Vermeylen, R.; Claeys, M.; Maenhaut, W. *Environ. Sci. Technol.* **2002**, *36*, 747–753.
- (17) Sheesley, R. J.; Schauer, J. J.; Chowdhury, Z.; Cass, G. R.; Simoneit, B. R. T. *J. Geophys. Res. (Atmos.)* **2003**, *108* (D9), 4285, doi: 10.1029/2002JD002981, AAC 8/1–15.
- (18) Simpson, C. D.; Dills, R. L.; Katz, B. S.; Kalman, D. A. *J. Air Waste Manage. Assoc.* In press.
- (19) Hawthorne, S. B.; Miller, D. J.; Barkley, R. M.; Krieger, M. S. *Environ. Sci. Technol.* **1998**, *22*, 1191–1196.
- (20) Oros, D. R.; Simoneit, B. R. T. *Appl. Geochem.* **2001a**, *16*, 1513–1544.
- (21) Oros, D. R.; Simoneit, B. R. T. *Appl. Geochem.* **2001b**, *16*, 1545–1565.
- (22) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1998**, *32*, 13–22.
- (23) Schauer, J. J.; Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **2002**, *36*, 3806–3814.
- (24) Simoneit, B. R. T.; Rogge, W. F.; Mazurek, M. A.; Standley, L. J.; Hildemann, L. M.; Cass, G. R. *Environ. Sci. Technol.* **1993**, *27*, 2533–2541.
- (25) Didyk, B. M.; Simoneit, B. R. T.; Pezoa, L. A.; Riveros, M. L.; Flores, A. A. *Atmos. Environ.* **2000**, *34*, 1167–1179.
- (26) Simoneit, B. R. T.; Rushdi, A. I.; Otto, A. Oregon State University, 2001; 86pp.
- (27) Oades, J. M. *Geoderma* **1993**, *56*, 377–400.
- (28) Kolattukudy, P. E. *Lipids* **1970**, *5*, 259–275.
- (29) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1993**, *27*, 2700–2711.
- (30) Kolattukudy, P. E. *Science* **1980**, *208*, 990–1000.
- (31) Albro, P. W. In *Chemistry and Biochemistry of Natural Waxes*; Kolattukudy, P. E., Ed.; Elsevier: Amsterdam, 1976; pp 419–445.
- (32) Lechevalier, M. F. *CRC Crit. Rev. Microbiol.* **1977**, *5*, 109–210.
- (33) Martin, F.; Ramstedt, M.; Söderhöll, K.; Canet, D. *Plant Physiol.* **1988**, *86*, 935–940.
- (34) Shaw, N. *Adv. Appl. Microbiol.* **1974**, *17*, 63–108.
- (35) Metting, F. B. In *Soil Microbial Ecology*; Metting, F. B., Ed.; Marcel Dekker: New York, 1993; pp 3–25.
- (36) Miltner, A.; Zech, W. *Org. Geochem.* **1998**, *28*, 457–463.

- (37) Newell, S. Y. In *The Fungal Community*, 2nd ed.; Carroll, G. C., Wicklow, D. T., Eds.; Marcel Dekker: New York, 1992; pp 521–561.
- (38) Djajakirana, G.; Joergensen, R. G.; Meyer, B. *Biol. Fertil. Soils* **1996**, *22*, 299–304.
- (39) Joergensen, R. G. *Soil Biol. Biochem.* **2000**, *32*, 647–652.
- (40) Ashbaugh, L. L.; Carvacho, O. F.; Brown, M. S.; Chow, J. C.; Watson, J. G.; Magliano, K. C. *Atmos. Environ.* **2003**, *37*, 1163–1173.
- (41) Rogge, W. F.; Medeiros, P. M.; Simoneit, B. R. T. *Atmos. Environ.* Manuscript in preparation.
- (42) Rogge, W. F.; Medeiros, P. M.; Simoneit, B. R. T. *Atmos. Environ.* Manuscript in preparation.
- (43) Rogge, W. F.; Medeiros, P. M.; Simoneit, B. R. T. *Atmos. Environ.* Manuscript in preparation.
- (44) Kobayashi, M. M.Sc. Thesis, Hokkaido University, Sapporo, Japan, 2002 (in Japanese).
- (45) Chizhov, O. S.; Molodtsov, N. V.; Kochetkov, N. K. *Carbohydr. Res.* **1967**, *4*, 273–276.
- (46) DeJongh, D. C.; Radford, T.; Hribar, J. D.; Hanessian, S.; Bieber, M.; Dawson, G.; Sweeley, C. C. *J. Am. Chem. Soc.* **1969**, *91*, 1728–1740.
- (47) Modzeleski, J. E.; Laurie, W. A.; Nagy, B. *Geochim. Cosmochim. Acta* **1971**, *35*, 825–838.
- (48) Páez, M.; Martínez-Castro, I.; Sanz, J.; Olano, A.; García-Raso, A.; Saura-Calixto, F. *Chromatographia* **1987**, *23*, 43–46.
- (49) Martínez-Castro, I.; Páez, M. I.; Sanz, J.; García-Raso, A. *J. Chromatogr.* **1989**, *462*, 49–60.
- (50) García-Raso, A.; Páez, M. I.; Martínez-Castro, I.; Sanz, J.; Calvo, M. M. *J. Chromatogr.* **1992**, *607*, 221–225.
- (51) Bartolozzi, F.; Bertazza, G.; Bassi, D.; Cristofori, G. *J. Chromatogr.* **1987**, *758*, 99–107.
- (52) Fiehn, O.; Kopka, J.; Trethewey, R. N.; Willmitzer, L. *Anal. Chem.* **2000**, *72*, 3573–3580.
- (53) Elias, V. O.; Simoneit, B. R. T.; Cordeiro, R. C.; Turcq, B. *Geochim. Cosmochim. Acta* **2001**, *65*, 267–272.
- (54) Nolte, C. G.; Schauer, J. J.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **2002**, *36*, 4273–4281.
- (55) Gleixner, G.; Poirier, N.; Bol, R.; Balesdent, J. *Organic Geochem.* **2002**, *33*, 357–366.
- (56) da Cunha, L. C.; Serve, L.; Blazi, J.-L. *Organic Geochem.* **2002**, *33*, 953–964.
- (57) Decesari, S.; Facchini, M. C.; Matta, E.; Lettini, F.; Mircea, M.; Fuzzi, S.; Tagliavini, E.; Putaud, J.-P. *Atmos. Environ.* **2001**, *35*, 3691–3699.
- (58) Schauer, J. J.; Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Atmos. Environ.* **1996**, *30*, 3837–3855.

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