

## Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign

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[1] The organic compound tracers of atmospheric particulate matter, as well as organic carbon (OC) and elemental carbon (EC), have been characterized for samples acquired during the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) from Gosan, Jeju Island, Korea, from Sapporo, Japan, and from Chichi-jima Island in the western North Pacific, as well as on the National Oceanic and Atmospheric Administration R/V *Ronald H. Brown*. Total extracts were analyzed by gas chromatography–mass spectrometry to determine both polar and aliphatic compounds. Total particles, organic matter, and lipid and saccharide compounds were high during the Asian dust episode (early April 2001) compared to levels at other times. The organic matter can be apportioned to seven emission sources and to significant oxidation-producing secondary products during long-range transport. Terrestrial natural background compounds are vascular plant wax lipids derived from direct emission and as part of desert sand dust. Fossil fuel utilization is obvious and derives from petroleum product and coal combustion emissions. Saccharides are a major polar (water-soluble) carbonaceous fraction derived from soil resuspension (agricultural activities). Biomass-burning smoke is evident in all samples and seasons. It contributes up to 13% of the total compound mass as water-soluble constituents. Burning of refuse is another source of organic particles. Varying levels of marine-derived lipids are superimposed during aerosol transport over the ocean. Secondary oxidation products increase with increasing transport distance and time. The ACE-Asia aerosols are composed not only of desert dust but also of soil dust, smoke from biomass and refuse burning, and emissions from fossil fuel use in urban areas.

**INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1055 Geochemistry: Organic geochemistry; 3339 Meteorology and Atmospheric Dynamics: Ocean/atmosphere interactions (0312, 4504); **KEYWORDS:** levoglucosan, glucose, organic aerosols, OC/EC, carboxylic acids, *n*-alkanes

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### 1. Introduction

[2] Long-range atmospheric transport of continentally derived particulate matter is an active area of research [e.g., Andreae, 1996; Griffin *et al.*, 2002; Prospero,

1996a, 1996b]. Aerosol particles have relevance for radiative forcing of climate and pollution transport [Wilkening *et al.*, 2000]. The direct radiative effect of aerosols is strongly influenced by particle size and composition. Radiative effects of anthropogenic aerosols are relatively large compared to their mass contribution because they are in the size range that is radiatively most active [Seinfeld and Pandis, 1998]. Particles of source emissions from biological organic matter also contribute significantly to the total particle burden in the atmosphere, either directly [e.g., Arpino *et al.*, 1972; Cox *et al.*, 1982; Gagosian *et al.*, 1981, 1982, 1987; Mazurek and Simoneit, 1997; Simoneit and Mazurek, 1982] or indirectly by burning of biomass [e.g., Abas *et al.*, 1995; Crutzen and Andreae, 1990; Levine, 1991, 1996; Simoneit, 2002].

[3] Dust fallout and haze were first described for the North Atlantic Ocean off West Africa [Darwin, 1846; Ehrenberg, 1847] and has been studied most extensively

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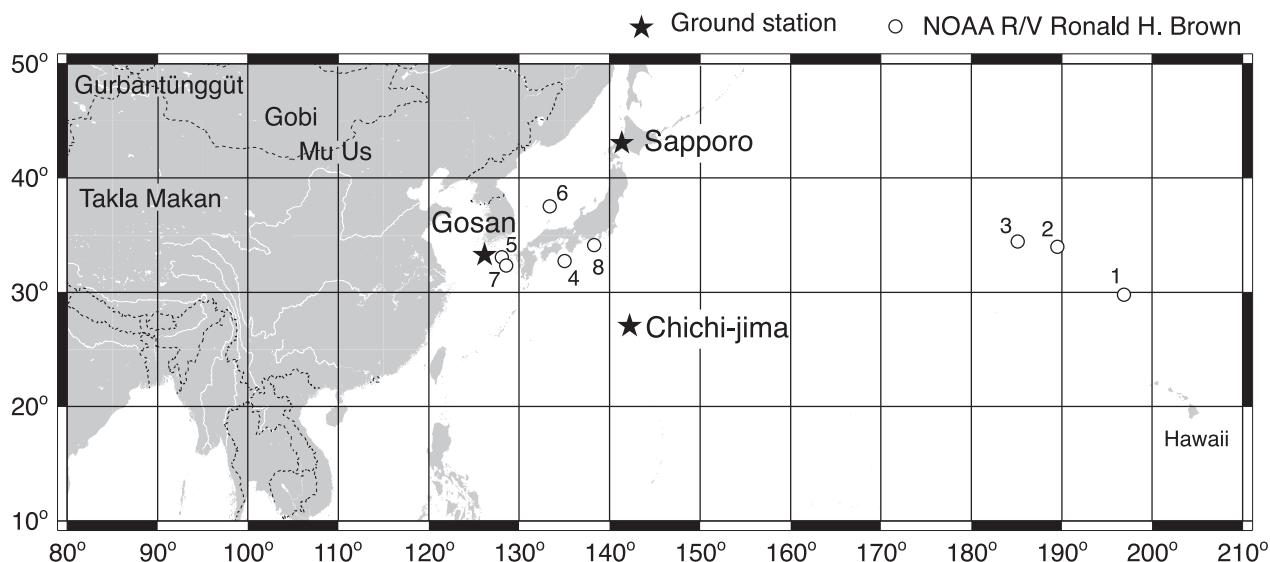
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**Figure 1.** Map showing the sampling locations and major deserts of China. See Table 1 for the sampling dates.

in terms of long-range transport. Initial research was concerned primarily with the inorganic chemical composition and mineralogy of the atmospheric particles [e.g., *Aston et al.*, 1973; *Chester et al.*, 1972; *Delany et al.*, 1967; *Glaccum and Prospero*, 1980; *Parkin et al.*, 1972; *Prospero et al.*, 1970]. The effects of long-range transport of aerosol particles on direct radiative forcing, on ultimate receptor areas, and on oceanic nutrient deposition are continuing to be investigated [e.g., *Artaxo et al.*, 1994; *Charlson et al.*, 1992; *Husar et al.*, 1997; *Intergovernmental Panel on Climate Change*, 1995; *Li et al.*, 1996; *Moulin et al.*, 1997; *Penner*, 1995; *Penner et al.*, 1994; *Prospero et al.*, 1996; *Sokolik and Toon*, 1996; *Swap et al.*, 1992; *Tegen et al.*, 1996]. Another major concern is the potential detrimental human health effects of fine aerosol particulate matter with the associated microbes, spores, and toxic organic compounds (e.g., PAHs) [*Abelson*, 1998; *Hannigan et al.*, 1998; *Prospero*, 2001]. The primary study area has been the North Atlantic Ocean and the export of Saharan dust over the ocean has been estimated to be about  $10^9$  ton/year [*D'Almeida*, 1986]. However, the Indian and northwestern Pacific Oceans are currently also active research areas under the auspices of the Aerosol Characterization Experiments (ACE) projects. This is a companion paper of *Simoneit et al.* [2004a], where we reported on the same compound classes using an identical technique for the aerosol particles collected over the western North Pacific rim using the C-130 aircraft.

[4] 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  $2 \times 10^7$  ton/year [*Buat-Ménard et al.*, 1989]. Most of this carbon is of a contemporary biological origin and is associated with transport of mineral dust by major wind systems seasonally active from the continents to the oceans [e.g., *Gagosian and Peltzer*, 1986; *Kawamura and Gagosian*, 1990; *Kawamura and Usukura*, 1993; *Kawamura et al.*, 2004; *Prospero*, 1996b, 2001; *Simoneit*, 1977; *Simoneit et al.*, 1988]. 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 oceanic atmosphere. Major oxidative-photochemical reactions alter the organic matter composition during transport, forming derivative products with higher oxygen contents, i.e., greater polarity, which are ideal as cloud condensation nuclei (complementing the inorganic species such as  $\text{SO}_x$ ,  $\text{NO}_x$ ). Thus molecular characterization and provision of mass balance closure of the initial and downwind aerosols continues to be of interest.

[5] One aspect of the ACE-Asia project in the northwestern Pacific region is to determine the organic compounds and their sources in the aerosol particles [*Huebert et al.*, 2003]. The Asian continent has been inferred as a source of oceanic dust [e.g., *Gagosian et al.*, 1981] and that was the case during the sampling campaign in April–May 2001 as confirmed by satellite and other observations. The proposed source regions for the Asian dusts are the deserts and loess regions of northern China and Mongolia. Preliminary organic compound compositions of samples of desert sands from northern China have been presented [*Simoneit et al.*, 2001] and one organic tracer analysis has been reported for a sample from Beijing taken on a 290 m tower, downwind from the sources [*Simoneit et al.*, 1991b]. Here we present a general assessment of the organic tracer composition of aerosols from ground stations at Gosan (also Kosan) on Jeju (also Cheju) Island, Korea, in Sapporo on Hokkaido Island, Japan, and in Chichi-jima Island in the western North Pacific, as well as from the North Pacific on the R/V *Ronald H. Brown* during the ACE-Asia project. One-year observation at Gosan site [*Kawamura et al.*, 2004] and 4-year observation at Chichi-jima [*Mochida et al.*, 2003a] for water-soluble dicarboxylic acids ( $\text{C}_2$ – $\text{C}_{10}$ ) in aerosols have been reported elsewhere.

## 2. Materials and Methods

### 2.1. Samples

[6] Atmospheric particles were collected on quartz fiber filters using high-volume air samplers during the ACE-Asia

**Table 1.** Atmospheric Particulate Matter Samples, Dates, Locations, Total Suspended Particles, Organic Carbon, and Elemental Carbon During the ACE-Asia Campaign<sup>a</sup>

Sample	Date Acquired	Location	TSP, $\mu\text{g m}^{-3}$	OC, $\mu\text{g m}^{-3}$	EC, $\mu\text{g m}^{-3}$	OC/EC Ratios	OC, %
G1	8–9 April 2001	Gosan, Jeju Island	110	7.2	0.81	8.9	90
G3	10–11 April 2001	Gosan, Jeju Island	440	8.6	2.0	4.3	81
G4	11–12 April 2001	Gosan, Jeju Island	270	8.1	1.4	5.8	85
G5	12–13 April 2001	Gosan, Jeju Island	170	3.9	1.3	3.0	75
G14	21–22 April 2001	Gosan, Jeju Island	140	7.5	1.4	5.4	84
G20	27–28 April 2001	Gosan, Jeju Island	260	6.7	0.8	8.4	89
G30	14–17 May 2001	Gosan, Jeju Island	120	n.d.	n.d.		
S2033	8–10 April 2001	Sapporo	230	14	3.2	4.4	81
S2039	14–16 April 2001	Sapporo	66	6.7	1.7	3.9	80
S2443	28 June to 5 July 2001	Sapporo	40	4	0.65	6.2	86
S2447	11–12 Sept. 2001	Sapporo	31	1.5	1.9	0.8	44
S2504	10–12 Jan. 2002	Sapporo	40	4.5	2.1	2.1	68
C181	9–12 April 1990	Chichi-jima Island	62	1.4	0.52	2.7	73
C188	3–6 June 1990	Chichi-jima Island	16	0.28	0.41	0.7	41
C221	17–20 Sept. 1991	Chichi-jima Island	280	0.76	0.04	19.0	95
RB1(2329) <sup>b</sup>	16–17 March 2001	R/V <i>Ronald H. Brown</i>	23	0.00	0.01		
RB2(2332) <sup>b</sup>	18–19 March 2001	R/V <i>Ronald H. Brown</i>	24	0.49	0.10	4.9	83
RB3(2333) <sup>b</sup>	19 March 2001	R/V <i>Ronald H. Brown</i>	n.d.	n.d.	n.d.		
RB4(2350) <sup>b</sup>	2–3 April 2001	R/V <i>Ronald H. Brown</i>	130	1.4	0.53	2.6	73
RB5(2357) <sup>b</sup>	6 April 2001	R/V <i>Ronald H. Brown</i>	65	3.9	0.56	7.0	87
RB6(2360) <sup>b</sup>	Apr. 7–8, 2001	R/V <i>Ronald H. Brown</i>	120	5.2	0.93	5.6	85
RB7(2376) <sup>b</sup>	14–15 April 2001	R/V <i>Ronald H. Brown</i>	60	2.9	0.62	4.7	82
RB8(2384) <sup>b</sup>	19–20 April 2001	R/V <i>Ronald H. Brown</i>	270	12	2.6	4.6	82

<sup>a</sup>TSP was weighed in the laboratory with air conditioning, but relative humidity was not controlled; n.d., not determined.

<sup>b</sup>Approximate location shown in Figure 1.

campaign in 2001 spring to autumn at island sites: Gosan on Cheju (Jeju) Island (Korea), and Sapporo on Hokkaido Island (Figure 1). Aerosol samples from Chichi-jima (Japan) were collected in 1990 to 1991. Marine aerosol samples were also collected over the western North Pacific, the East China Sea and the Sea of Japan during the cruise of the R/V *Ronald H. Brown* in the same time period (Figure 1). Aliquots of filters were prepared for high-molecular-weight organic compound characterization, organic carbon analyses, and dicarboxylic acid analyses.

## 2.2. Extraction and Derivatization

[7] The samples of filter aliquots were sonicated three times for 10 min each with dichloromethane/methanol (2:1; v/v). The solvent extract was filtered through quartz wool packed in a Pasteur pipette, and concentrated by use of a rotary evaporator and then under blow-down with dry nitrogen gas. Aliquots of the total extracts were reacted with N, O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and pyridine for 3 h at 70°C to derive the trimethylsilyl derivatives of carboxylic acids, alcohols and sugars. This procedure derivatizes COOH and OH groups to the corresponding trimethylsilyl (TMS) esters and ethers, respectively.

## 2.3. Gas Chromatography–Mass Spectrometry

[8] Gas chromatography–mass spectrometry (GC-MS) analyses of the derivatized total extracts 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 DB-5 (30 m × 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness). The GC operating conditions were as follows: temperature hold at 50°C for 2 min, increase from 50° to 300°C at a rate of 6°C min<sup>-1</sup> with final isothermal hold at 300°C for 20 min. Helium was used as carrier gas. The sample was injected splitless with the injector temperature at 300°C. The silylated extracts

were diluted (to 1:1) with *n*-hexane prior to injection. The mass spectrometer was operated in the electron impact mode (EI) 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. GC-MS response factors were determined using authentic standards. Recoveries of levoglucosan, glucose, sucrose, palmitic acid, and stearic acid were better than 80%.

## 2.4. OC and EC Measurements

[9] The amounts of organic carbon (OC) and elemental carbon (EC) on the filter punches (2 cm<sup>2</sup>) were determined using a thermal-optical OC/EC analyzer from Sunset Laboratory (Tigard, OR). OC was evolved under a stream of ultrahigh-purity He while heating the sample in four temperature steps to 870°C. To evolve EC and pyrolyzed OC, the sample was first cooled to 550°C and then heated under a mixture of 2% O<sub>2</sub> + 98% He in six temperature steps to a final temperature of 900°C. The transmittance through the filter was monitored with a He-Ne laser throughout the analysis to correct for the pyrolytic conversion of OC to EC.

## 3. Results and Discussion

[10] The samples for this study, locations, and ambient conditions are summarized in Table 1 and the general locations are shown in Figure 1. Ground stations were located in Gosan, Sapporo and Chiji-jima. Marine aerosols over the North Pacific (see locations 1–8 in Figure 1) were sampled during the cruise of the R/V *Ronald H. Brown*. The sampling periods covered the ACE-Asia dust event in April 2001 and extended to fall of 2001 and winter of 2002 for the stations in Sapporo. The concentrations of the organic compounds in the samples considered here are listed and





**Table 3.** Organic Compounds Identified in Aerosol Particulate Matter Sampled on Board the R/V *Ronald H. Brown*<sup>a</sup>

Compound	Composition	M.W.	RB1 (2329)	RB2 (2332)	RB3 (2333)	RB4 (2350)	RB5 (2357)	RB6 (2360)	RB7 (2376)	RB8 (2384)
<i>n</i> -Alkanes										
Nonadecane	C <sub>19</sub> H <sub>40</sub>	268							0.09	
Eicosane	C <sub>20</sub> H <sub>42</sub>	282		0.09	0.20				0.08	0.96
Heneicosane	C <sub>21</sub> H <sub>44</sub>	296	0.03	0.18	0.47	0.14	0.08	0.54	0.08	2.52
Docosane	C <sub>22</sub> H <sub>46</sub>	310	0.04	0.20	0.46	0.26	0.10	0.56	0.40	3.00
Tricosane	C <sub>23</sub> H <sub>48</sub>	324	0.06	0.19	0.50	0.30	0.20	1.28	0.72	3.24
Tetracosane	C <sub>24</sub> H <sub>50</sub>	338	0.11	0.22	0.60	0.62	0.24	1.39	0.64	2.16
Pentacosane	C <sub>25</sub> H <sub>52</sub>	352	0.18	0.35	0.87	0.86	0.34	2.89	1.04	2.76
Hexacosane	C <sub>26</sub> H <sub>54</sub>	366	0.19	0.37	0.83	0.84	0.30	1.93	0.64	1.80
Heptacosane	C <sub>27</sub> H <sub>56</sub>	380	0.19	0.40	0.83	1.02	0.35	3.21	1.28	2.88
Octacosane	C <sub>28</sub> H <sub>58</sub>	394	0.12	0.28	0.67	0.84	0.26	1.50	0.56	1.68
Nonacosane	C <sub>29</sub> H <sub>60</sub>	408	0.10	0.30	0.76	1.20	0.50	3.00	1.60	3.60
Triacontane	C <sub>30</sub> H <sub>62</sub>	422	0.07	0.17	0.67	0.96	0.28	1.07	0.40	1.44
Hentriacontane	C <sub>31</sub> H <sub>64</sub>	436	0.07	0.23	0.70	1.10	0.33	2.14	1.04	2.16
Dotriacontane	C <sub>32</sub> H <sub>66</sub>	450	0.04	0.09	0.43	0.52	0.18	0.86	0.16	0.96
Tritriacontane	C <sub>33</sub> H <sub>68</sub>	464	0.03	0.08	0.40	0.60	0.19	0.86	0.28	0.96
Tetracontane	C <sub>34</sub> H <sub>70</sub>	478			0.17	0.12	0.06	0.43	0.08	0.36
Total			<b>1.3</b>	<b>3.2</b>	<b>8.6</b>	<b>9.4</b>	<b>3.4</b>	<b>21.6</b>	<b>9.1</b>	<b>30.5</b>
CPI (19-34) <sup>b</sup>			1.1	1.2	1.2	1.3	1.4	1.7	2.1	1.6
Squalene	C <sub>30</sub> H <sub>50</sub>	410		2						
Plant Wax Alkanes <sup>c</sup>										
Tricosane	C <sub>23</sub> H <sub>48</sub>	324				0.04		0.31		0.66
Pentacosane	C <sub>25</sub> H <sub>52</sub>	352	0.03	0.06	0.16	0.13	0.05	1.23	0.40	0.80
Heptacosane	C <sub>27</sub> H <sub>56</sub>	380	0.03	0.08	0.08	0.18	0.05	1.50	0.68	1.14
Nonacosane	C <sub>29</sub> H <sub>60</sub>	408	0.01	0.08	0.11	0.30	0.23	1.72	1.02	2.09
Hentriacontane	C <sub>31</sub> H <sub>64</sub>	436	0.02	0.10	0.15	0.36	0.10	1.18	0.76	0.96
Tritriacontane	C <sub>33</sub> H <sub>68</sub>	464	0.01	0.04	0.10	0.28	0.07	0.22	0.16	0.30
Total			<b>0.10</b>	<b>0.38</b>	<b>0.60</b>	<b>1.29</b>	<b>0.50</b>	<b>6.16</b>	<b>3.02</b>	<b>5.95</b>
PAH										
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	202	-	-	-	0.012	-	0.10	0.50	-
Pyrene	C <sub>16</sub> H <sub>10</sub>	202	-	-	-	0.008	-	0.08	0.40	-
Benzo(ghi)fluoranthene	C <sub>18</sub> H <sub>10</sub>	226	-	-	-	-	-	0.02	0.15	-
Benz(a)anthracene	C <sub>18</sub> H <sub>12</sub>	228	-	-	-	0.003	-	-	0.10	-
Chrysene	C <sub>18</sub> H <sub>12</sub>	228	-	-	-	-	-	0.02	0.25	-
Benzo(b/k)fluoranthene	C <sub>20</sub> H <sub>12</sub>	252	-	-	-	0.007	-	0.06	0.40	-
Benzo(e)pyrene	C <sub>20</sub> H <sub>12</sub>	252	-	-	-	-	-	0.04	0.20	-
Benzo(a)pyrene	C <sub>20</sub> H <sub>12</sub>	252	-	-	-	-	-	-	0.10	-
Indeno(1,2,3-cd)pyrene	C <sub>22</sub> H <sub>12</sub>	276	-	-	-	-	-	-	0.20	-
Benzo(ghi)perylene	C <sub>22</sub> H <sub>12</sub>	276	-	-	-	-	-	-	0.20	-
1,3,5-Triphenylbenzene	C <sub>24</sub> H <sub>18</sub>	306	-	-	-	-	-	0.02	0.05	-
Total						<b>0.03</b>		<b>0.34</b>	<b>2.4</b>	
<i>n</i> -Alkanoic acids										
Dodecanoic acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	200	0.08	0.9	4.6				8.82	4.05
Tetradecanoic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	228	0.21	1.5	5.8	1	1.56	3.20	20.16	4.56
Pentadecanoic acid	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	242	0.07	0.6	2.5	0.3	0.63	1.50	8.40	2.03
Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	256	1.2	3.2	15.2	2.4	2.50	11.50	42.00	22.80
Heptadecanoic acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	270	0.01	0.08	0.4		0.23	0.69	2.10	0.51
Octadecanoic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	284	0.13	0.6	3.9	0.7	1.03	4.26	7.14	6.59
Nonadecanoic acid	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	298					0.08	0.12	0.02	
Eicosanoic acid	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	312		0.03	0.05	0.1	0.27	1.15	0.63	0.76
Heneicosanoic acid	C <sub>21</sub> H <sub>42</sub> O <sub>2</sub>	326					0.13	0.58	0.04	
Docosanoic acid	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	340		0.03	0.05	0.1	0.42	1.96	0.08	1.01
Tricosanoic acid	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	354					0.30	1.04	0.04	
Tetracosanoic acid	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>	368		0.05	0.07	12	0.55	2.30	0.13	1.01
Pentacosanoic acid	C <sub>25</sub> H <sub>50</sub> O <sub>2</sub>	382					0.11	0.46	0.02	
Hexacosanoic acid	C <sub>26</sub> H <sub>52</sub> O <sub>2</sub>	396		0.02	0.02	0.1	0.28	1.04	0.04	0.51
Heptacosanoic acid	C <sub>27</sub> H <sub>54</sub> O <sub>2</sub>	410					0.08	0.35		
Octacosanoic acid	C <sub>28</sub> H <sub>56</sub> O <sub>2</sub>	424					0.22	0.81	0.04	0.25
Nonacosanoic acid	C <sub>29</sub> H <sub>58</sub> O <sub>2</sub>	438						0.12		
Triacontanoic acid	C <sub>30</sub> H <sub>60</sub> O <sub>2</sub>	452						0.46		
CPI (12-30) <sup>b</sup>			10	9.3	10.1	11	4.5	5.8	7.2	14.2
<i>n</i> -Alkenoic acids										
Hexadecenoic acid	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	254	0.04	0.8	2.07	0.2		1.15	12	1.01
Octadecenoic acids	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	282	0.02	0.38	1.84	0.2		1.04	9	2.03
Total aliphatic acids			<b>11.8</b>	<b>17.5</b>	<b>46.6</b>	<b>16.1</b>	<b>12.9</b>	<b>39.5</b>	<b>117.9</b>	<b>61.3</b>
Glyceric acid	C <sub>3</sub> H <sub>6</sub> O <sub>4</sub>	106	0.3	2.2	1.7		15	18	5	21
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	122	0.2	0.2	0.3	3.2	2	1.2	0.8	3.9
Dicarboxylic acids										
Malonic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	104	0.1	1.5	3.8	5.6	21	23	2.5	16
Succinic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	118	0.6	7	3.3	2.2	70	58	11	50
Glutaric acid	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	132	0.1	2.2	2.4		14	13	3	11
Adipic acid	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	146					8	22	2.5	10

Table 3. (continued)

Compound	Composition	M.W.	RB1 (2329)	RB2 (2332)	RB3 (2333)	RB4 (2350)	RB5 (2357)	RB6 (2360)	RB7 (2376)	RB8 (2384)
Malic acid	C <sub>4</sub> H <sub>6</sub> O <sub>5</sub>	134		0.2	0.8				3	26
1,2-Benzenedicarboxylic acid	C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>	166			1.2		11.4	11.6	7	18
1,3-Benzenedicarboxylic acid	C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>	166			0.1		2.2	2.6	2.1	4.1
1,4-Benzenedicarboxylic acid	C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>	166			0.1		3.1	4	3.1	9
Total			<b>0.8</b>	<b>10.9</b>	<b>11.7</b>	<b>7.8</b>	<b>129.7</b>	<b>134.2</b>	<b>34.2</b>	<b>124.9</b>
<i>n</i> -Alkanols										
Docosanol	C <sub>22</sub> H <sub>46</sub> O	326							0.6	
Tetracosanol	C <sub>24</sub> H <sub>50</sub> O	354							0.5	
Hexacosanol	C <sub>26</sub> H <sub>54</sub> O	382							2	
Octacosanol	C <sub>28</sub> H <sub>58</sub> O	410							1.3	
Triacosanol	C <sub>30</sub> H <sub>62</sub> O	438							0.5	
Nonacosan-10-ol	C <sub>29</sub> H <sub>60</sub> O	424							1.3	
Total									<b>6.2</b>	
Steroids										
Cholesterol	C <sub>27</sub> H <sub>46</sub> O	386	0.24	0.8	1.2			2	3.6	0.8
β-Sitosterol	C <sub>29</sub> H <sub>50</sub> O	414								3.2
Triterpenoids										
Lupa-2,19(22)-dienol	C <sub>30</sub> H <sub>48</sub> O	424							0.3	0.2
Friedelin	C <sub>30</sub> H <sub>50</sub> O	426	0.04	0.15						0.1
Anhydrosaccharides										
Levoglucofan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	162	0.2	1.3	0.4	0.6	28	40	15	27
Mannosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	162					1.2	2.8	0.2	0.9
Saccharides										
Sucrose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	342			1.8		0.6	1.2	3.7	422
Mycose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	342			0.2		0.3	0.8	1.8	16
Sorbitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	182								1
α-Fructose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	180								1
β-Fructose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	180								3
α-Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	180			4		1.2	3.1	5	5
β-Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	180			3		1.4	4	3.5	22
Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	92	6	15	32	-	8.1	7	9	12
Total			<b>6</b>	<b>15</b>	<b>41</b>	<b>0</b>	<b>11.6</b>	<b>16.1</b>	<b>23</b>	<b>482</b>
Lignin products										
4-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	138				3	1.5	3	2	
Vanillic acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	168				0.3		0.4	0.2	
Total						<b>3.3</b>	<b>1.5</b>	<b>3.4</b>	<b>2.2</b>	
Phthalates										
Dibutyl phthalates	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	278			2.2	0.5				
Diethyl phthalate	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	390	3.8	3.3	7.6	18	9.7	83	4.8	27
Total			<b>3.8</b>	<b>3.3</b>	<b>9.8</b>	<b>18.5</b>	<b>9.7</b>	<b>83</b>	<b>4.8</b>	<b>27</b>

<sup>a</sup>Values are given in ng m<sup>-3</sup>.

<sup>b</sup>CPI as defined in Table 2.

<sup>c</sup>Calculated by subtraction of the nonbiogenic *n*-alkanes [Simoneit *et al.*, 1991a].

categorized as classes in Table 2 for the ground stations and in Table 3 for the samples on board the R/V *Ronald H. Brown*. Typical examples of organic compositions of aerosol particles are discussed and shown in the following text and figures.

### 3.1. Ground Stations: Gosan (Kosan) and Sapporo

#### 3.1.1. General Results

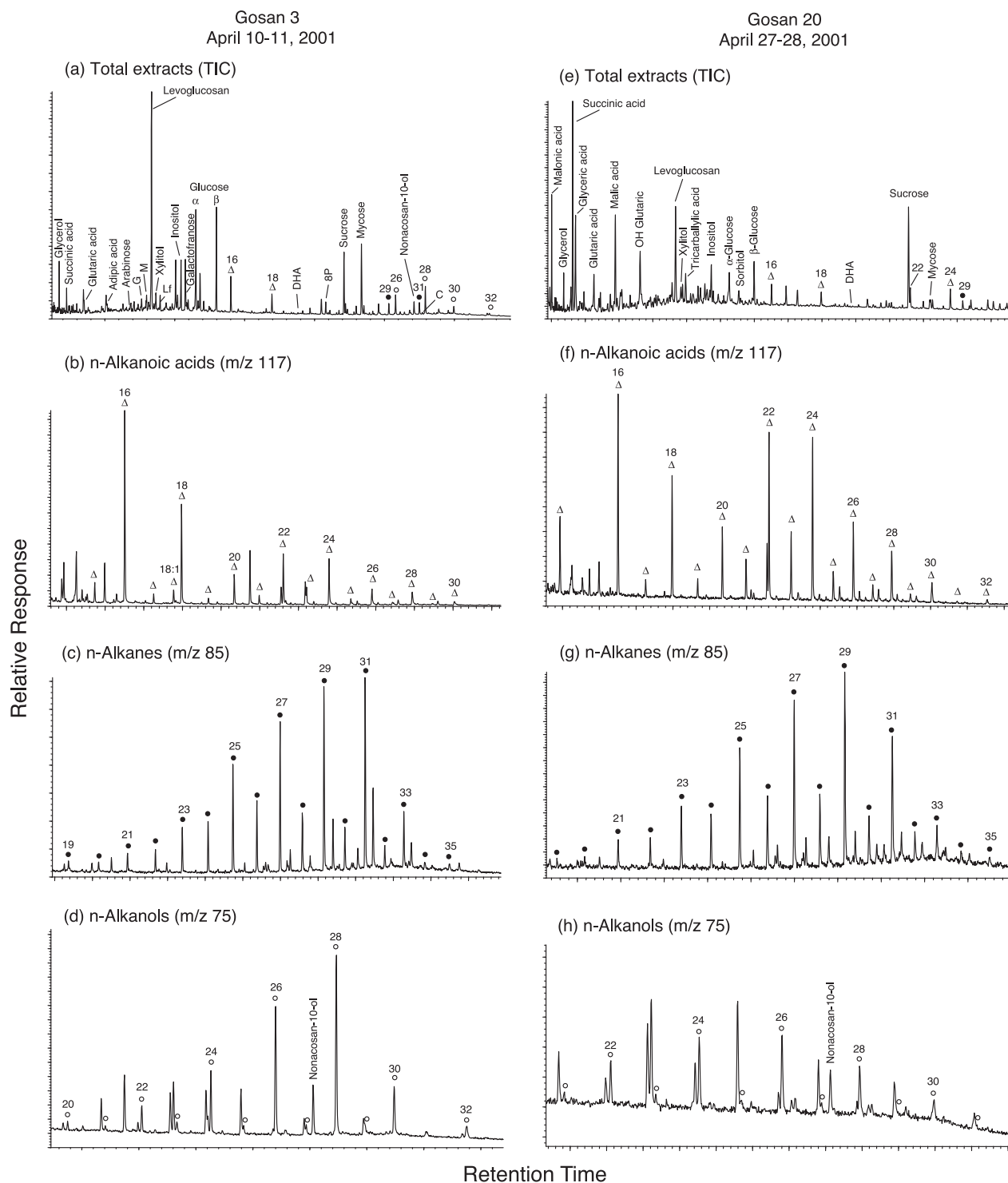
[11] The total suspended particles (TSP) in the atmosphere during the dust period at the land stations ranged from 142–440 μg m<sup>-3</sup>, compared to 31–120 μg m<sup>-3</sup> during other times (Table 1). The TSP for the shipboard samples varied from 23–270 μg m<sup>-3</sup> with low values far from continental outflow (Table 1). The Chichi-jima samples had high TSP during April and September. The organic carbon (OC) contents were high during the dust episode (3.9–14 μg m<sup>-3</sup> for the land stations and 5–12 μg m<sup>-3</sup> for the shipboard samples, Table 1) and lower during other times. Elemental carbon (EC or black C) increased only slightly during the dust event and ranged from 0.65 to 3.2 μg m<sup>-3</sup> for the land stations, from 0.53 to 2.6 μg m<sup>-3</sup> for samples taken on the

mobile platform and from 0.01 to 0.10 μg m<sup>-3</sup> for background marine samples (Table 1). OC is several times more abundant than EC (OC/EC ratios: 2–9), except for few samples collected in urban Sapporo and Chichi-jima (ratios: 0.7–0.8). The OC/EC ratios obtained at Gosan site (average 6.0) are higher than those of Sapporo (average 3.5). In contrast, the ratios obtained on board R/V *Ron H. Brown* (average 4.9) are consistent with those (average 3.7) reported for offshore of Japan [Lim *et al.*, 2003].

[12] The major resolved components of the total aerosol extracts are water-soluble saccharides and dicarboxylic acids with minor hydrophobic lipids from higher plant waxes and fossil fuel sources (*n*-alkanes, *n*-alkanols, *n*-alkanoic acids) (e.g., Figures 2a, 2e, and 3a).

#### 3.1.2. Water-Soluble Compounds

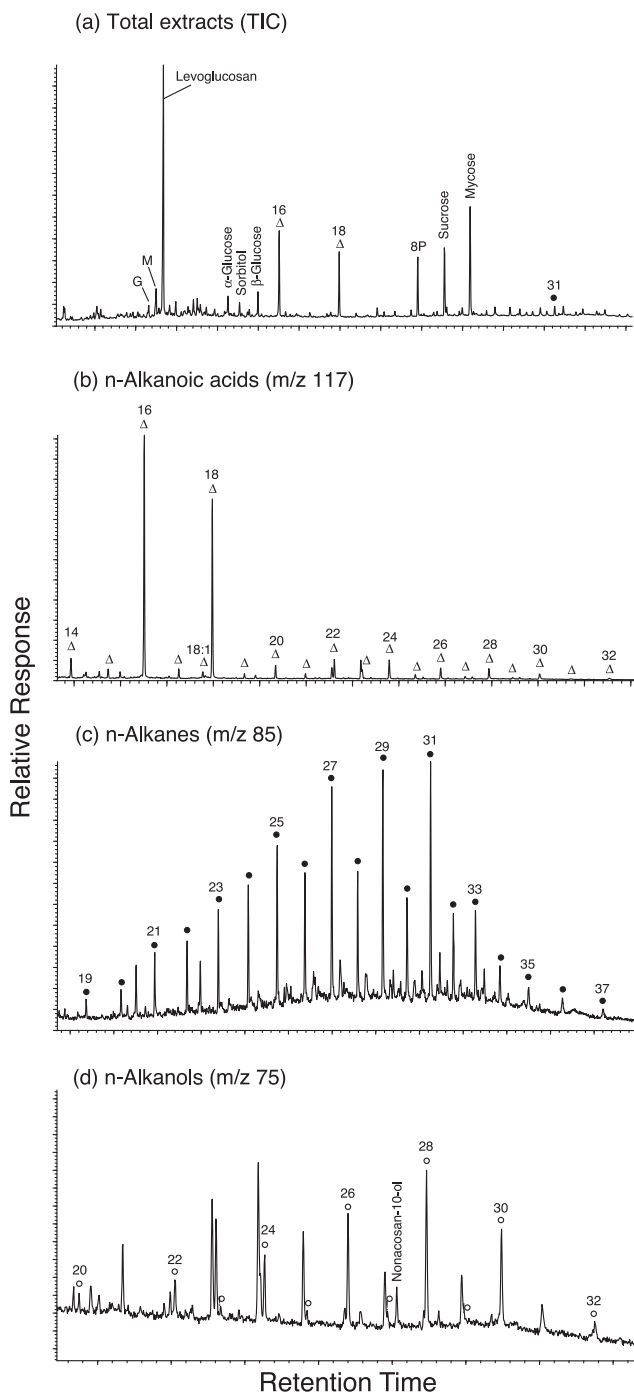
[13] The saccharides are composed of levoglucosan (1,6-anhydro-β-D-glucopyranose, I, chemical structures are given in Figure 5), with minor mannosan (II), galactosan (III), and 1,6-anhydro-β-D-glucofuranose (levoglucosan isomer, IV), and primary saccharides consisting of α- and β-glucose (V), inositols (VI), sucrose (VII) and mycose



**Figure 2.** Salient features of the GC-MS data for total extracts of aerosol samples from Gosan: (a–d) G3 and (e–h) G20 as the trimethylsilyl derivatives. Shown are total ion current traces (Figures 2a and 2e),  $m/z$  117 key ion plots for *n*-alkanoic acids (Figures 2b and 2f),  $m/z$  85 key ion plots for *n*-alkanes (Figures 2c and 2g), and  $m/z$  75 key ion plots for *n*-alkanols (Figures 2d and 2h) (numbers refer to carbon chain length of homologous compounds; solid circles, *n*-alkanes; open circles, *n*-alkanols; triangles, *n*-alkanoic acids; G, galactosan; M, mannosan; Lf, 1,6-anhydro- $\beta$ -D-glucofuranose; OH Glutaric, hydroxyglutaric acid; DHA, dehydroabietic acid; 8P, dioctyl phthalate; C, cholesterol; S,  $\beta$ -sitosterol).



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**Figure 3.** Salient features of the GC-MS data for total extracts of aerosol sample (S2033) from Sapporo. (a) Total ion current traces, (b)  $m/z$  117 plots for  $n$ -alkanoic acids, (c)  $m/z$  85 plots for  $n$ -alkanes, and (d)  $m/z$  75 plots for  $n$ -alkanols (numbers and symbols as in Figure 2).

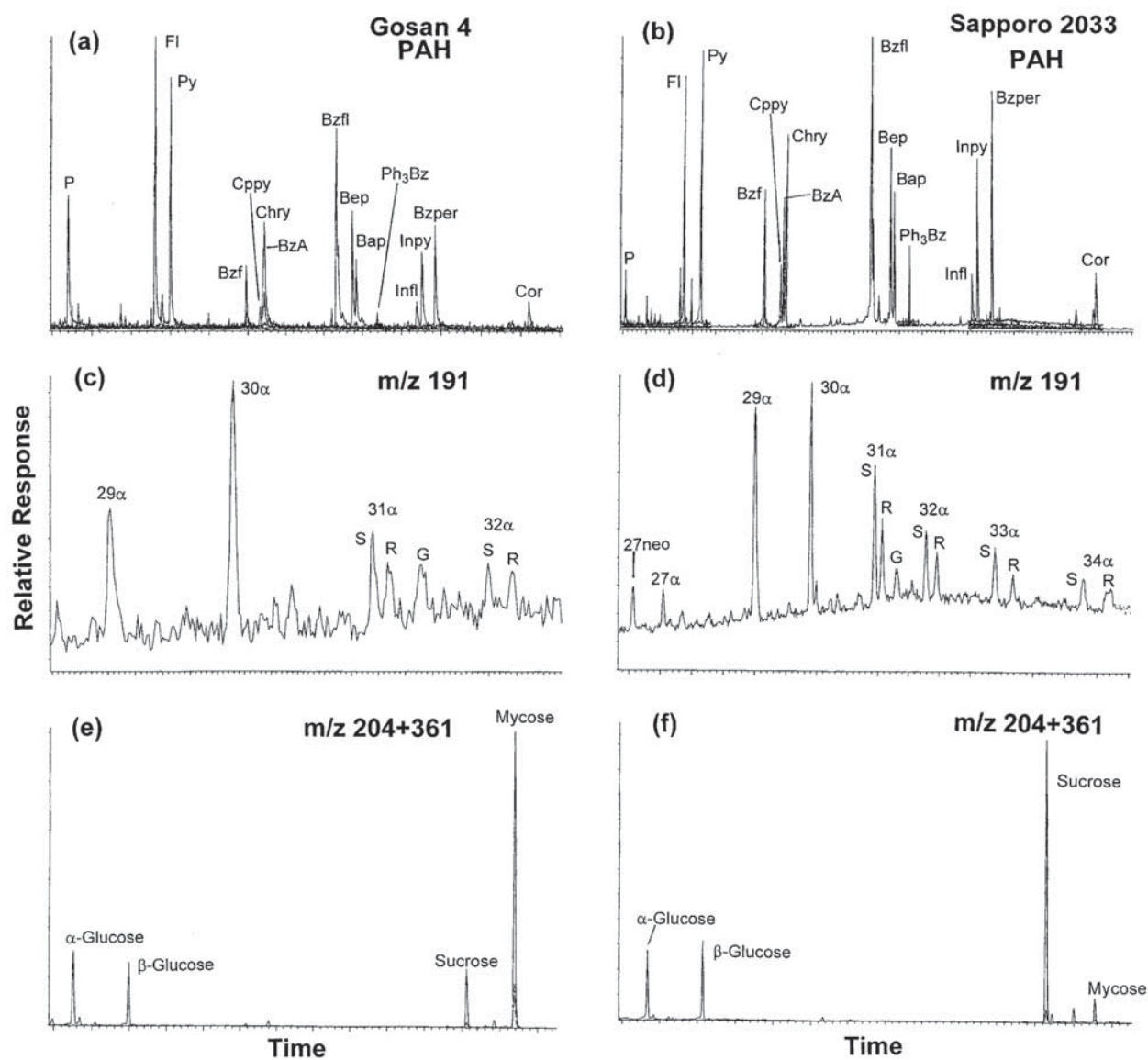
(trehalose VIII). In addition there is the series of saccharide polyols (alditols, i.e., reduced sugars) ranging from sorbitol (D-glucitol, IX), xylitol (X), to glycerol (XI). Minor amounts of other monosaccharides (e.g., arabinose,  $\alpha$ - and  $\beta$ -fructose,

galactofuranose) are found in some samples. Levoglucosan, with mannosan, galactosan, and 1,6-anhydro- $\beta$ -D-glucofuranose (I–IV) are the key tracers for smoke particulate matter from burning of biomass (i.e., thermal alteration products from cellulose [Simoneit *et al.*, 1999]) and have concentrations from 7 to 78  $\text{ng m}^{-3}$  (Table 2). These compounds have been found in aerosols over the ocean and thus are stable during long-range transport [Simoneit and Elias, 2000; Fraser and Lakshmanan, 2000]. The primary saccharides (e.g., glucose, sucrose, trehalose, etc.) and the saccharide polyols (e.g., sorbitol, xylitol, etc.) have concentrations ranging from 14 to 574  $\text{ng m}^{-3}$  (Table 2) and are candidate tracers for surface soil dust. Saccharides are a major fraction of soil organic matter [Gleixner *et al.*, 2002] and have been characterized in riverine particulate matter [da Cunha *et al.*, 2002]. These compounds are present at relatively low atmospheric concentrations during the early spring and become dominant into the summer season, paralleling the agricultural tilling practices on the Asian continent that resuspend soil dust into the passing aerosols. The characterization, atmospheric chemistry, and implications of these sugars are under further study.

[14] Secondary oxidation products of organic compounds are found mainly as short-chain dicarboxylic acids ranging from oxalic acid to adipic acid and aromatic acids (e.g., benzoic, benzenedicarboxylic acids) [Kawamura and Sakaguchi, 1999; Mochida *et al.*, 2003b]. The dicarboxylic acids detected in these total extracts are malonic, succinic, glutaric, and adipic acids ( $C_3$ – $C_6$ ) and the aromatic acids (e.g., 1,2-, 1,3- and 1,4-benzenedicarboxylic acids), with concentration ranges from 8 to 302  $\text{ng m}^{-3}$  (Table 2). Malonic and succinic acids are somewhat depleted because of the volatility of the trimethylsilyl esters used in this method compared to the data from the direct analyses, where the  $C_2$ – $C_6$  dicarboxylic acids were determined by separate specific analyses [e.g., Mochida *et al.*, 2003b; Kawamura *et al.*, 2004]. Some aerosol samples also contain hydroxydicarboxylic acids, mainly malic, and hydroxyglutaric acids ( $C_4$ – $C_5$ ), which may be secondary oxidation products from the saccharides. Thus the saccharides and dicarboxylic acids comprise the major water-soluble organic compounds of these aerosols.

### 3.1.3. Aliphatic Lipids

[15] The lipid components, secondary in concentration in these aerosols (Table 2), are derived from terrestrial plant waxes. This is illustrated by the key ion plots for the total extract GC-MS data as the  $m/z$  85 plot for  $n$ -alkanes,  $m/z$  117 plot for  $n$ -alkanoic acids as the TMS esters, and  $m/z$  75 for the  $n$ -alkanols as the TMS ethers (Figures 2 and 3). The  $n$ -alkanes typically range from  $C_{19}$  to  $C_{35}$  and in some cases (especially in Sapporo) to  $C_{39+}$ , with a strong odd carbon number predominance (carbon preference index, CPI, ranges from 1.2 to 6.0) and carbon number maxima ( $C_{\text{max}}$ ) at  $C_{29}$  or  $C_{31}$ . Volatile compound blow-off from the filters over the 1–2-day acquisition time has depleted mainly the  $n$ -alkanes  $<C_{21}$ , and therefore the petroleum tracers (i.e., pristane and phytane) for urban traffic emissions are not detectable. The heavier components from petroleum product utilization (i.e., urban traffic) are present as  $n$ -alkanes  $>C_{21}$  with no carbon number predominance and traces of biomarkers (hopanes and steranes) [Simoneit, 1984, 1985]. Leaf surface (epicuticular) wax input to aerosols is recog-



**Figure 4.** Examples of key ion plots for PAHs and biomarkers: G4 (Figures 4a, 4c, and 4e) and S2033 (Figures 4b, 4d, and 4f). (a and b) Sums of  $m/z$  178, 202, 226, 228, 252, 276, 300 and 306 for P, phenanthrene; FI, fluoranthene; Py, pyrene; Bzf, benzo(ghi)fluoranthene; Cppy, cyclopenta(cd)pyrene; BzA, benz(a)anthracene; Chry, chrysene; Bzfl, benzo(ghi)fluoranthenes; Bep, benzo(e)pyrene; Bap, benzo(a)pyrene; Ph<sub>3</sub>Bz, 1,3,5-triphenylbenzene; Infi, indeno(1,2,3-cd)fluoranthene; Inpy, indeno(1,2,3-cd)pyrene; Bzper, benzo(ghi)perylene; and Cor, coronene; (c and d)  $m/z$  191 fragmentogram for hopanes (numbers refer to carbon skeleton; G, gammacerane; S and R, configuration at C-22); and (e and f)  $m/z$  204 and 361 fragmentogram for glucose and sucrose isomers.

nized by the  $n$ -alkanes from C<sub>21</sub>-C<sub>35</sub> with a strong odd carbon number predominance, and  $n$ -alkanoic acids from C<sub>20</sub>-C<sub>32</sub> and  $n$ -alkanols from C<sub>22</sub>-C<sub>30</sub>, both with strong even carbon number predominances [Simoneit, 1989]. The contribution of epicuticular wax to the total  $n$ -alkanes has been estimated by the subtraction of the smooth alkane envelope from the total alkanes [Simoneit *et al.*, 1991a], and the wax alkane concentrations are listed in Table 2 and plotted in a separate figure as discussed below.

[16] The  $n$ -alkanoic acids (fatty acids) range mainly from C<sub>12</sub> to C<sub>32</sub>, with C<sub>max</sub> at 16, 18 and minor C<sub>max</sub> at 22 or 24

and strong even carbon number predominances (CPI range 1.9 to 2.6 for C<sub>20</sub>-C<sub>32</sub>, Table 2) (Figures 2b, 2f, and 3b). There are only traces of alkenoic acids (e.g., C<sub>18:1</sub>) indicating that the organic matter of these aerosols is aged and has been transported over significant distances. There is also no palmitoleic acid (C<sub>16:1</sub>) detectable as it is found in the marine aerosols discussed below. The alkenoic acids are rapidly oxidized once in the atmosphere [e.g., Kawamura and Gagosian, 1987]. The  $n$ -alkanoic acids <C<sub>20</sub> have multiple sources and thus only indicate a biogenic input. The  $n$ -alkanoic acids from C<sub>20</sub> to C<sub>32</sub> are interpreted to

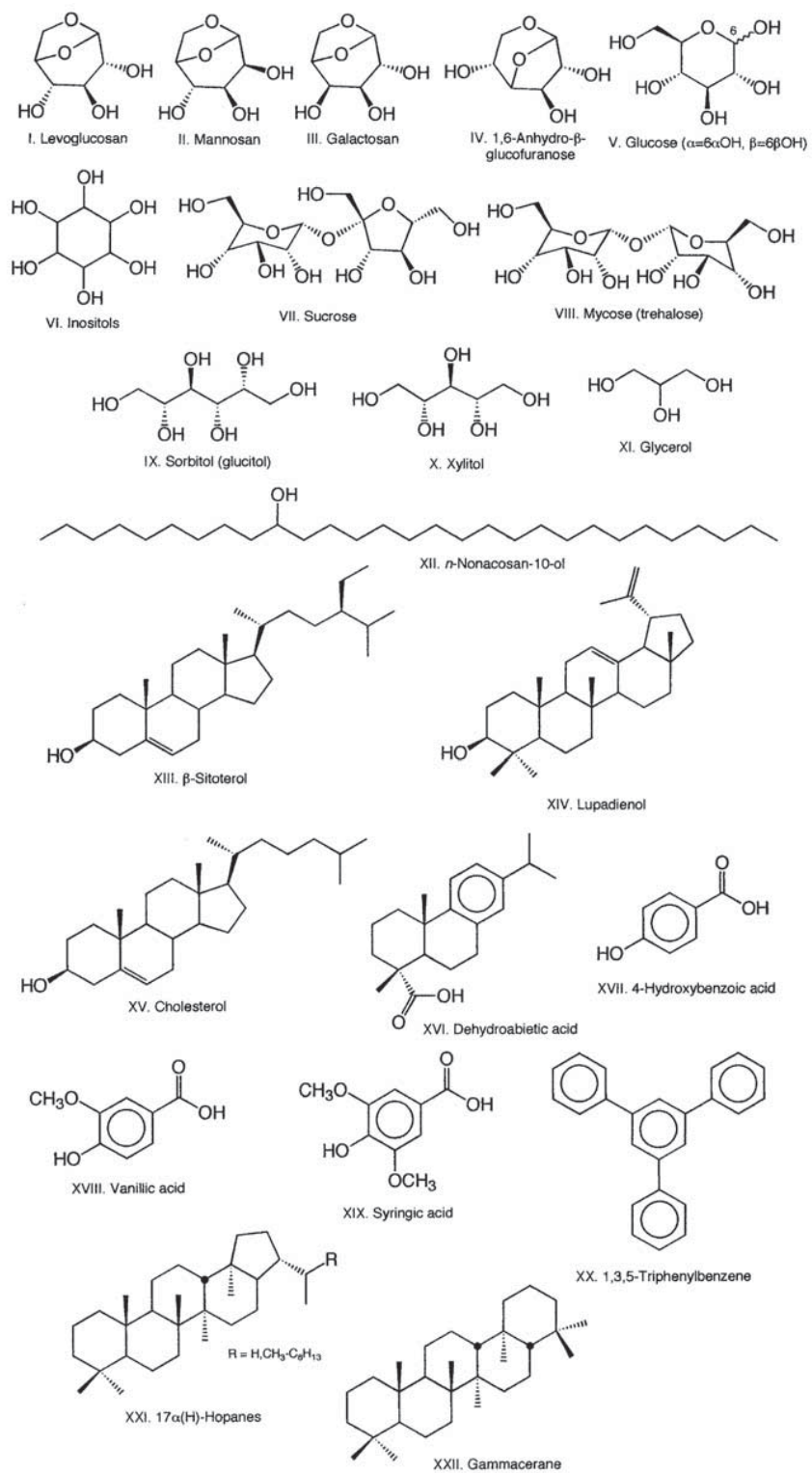


Figure 5. Chemical structures cited.

derive from higher plant waxes and they have very similar distributions of  $C_{22} \approx C_{24} > C_{26} < C_{28}$  for most of the ground station samples during the same time interval (compare Figures 2b, 2f, and 3b). This distribution changes later in the season (e.g., Figure 2).

[17] The *n*-alkanols (fatty alcohols) range from  $C_{20}$  to  $C_{32}$ , with strong even carbon number predominances (essentially no odd numbered alkanols, CPI all  $>4$ , Table 2) and  $C_{\max}$  at  $C_{28}$  during the dust event and at  $C_{26}$  afterward (Figures 2d, 2h, and 3d). All aerosol samples contain *n*-nonacosan-10-ol (XII) at unusually high levels (Table 2). The normal alkanols indicate an input of plant waxes and noncosan-10-ol indicates an input of waxes from forests consisting of both soft and hardwoods [Oros and Simoneit, 2001a, 2001b]. Some of these alkanols may also be injected into the atmosphere by smoke from biomass burning [Oros and Simoneit, 2001a, 2001b; Simoneit, 2002], which is supported by the presence of  $\beta$ -sitosterol (XIII) and in some samples lupadienol (XIV) (Table 2). The latter lupadienol is an altered natural product and its precursor and  $\beta$ -sitosterol occur as internal lipids, which can become airborne by volatilization during burning [Simoneit, 2002]. Cholesterol (XV) is found in most of these samples (Table 2) and indicates an input from marine (algal) sources and possibly from emissions from cooking in urban areas [e.g., Rogge et al., 1991; Schauer et al., 1999; Simoneit et al., 1983].

#### 3.1.4. Biomass-Burning Tracers

[18] Biomass burning injects numerous organic compounds from the fuels directly into the atmosphere, and on the basis of the major tracers detected, both the process and the types of fuels can be assessed [Simoneit, 2002]. The major markers for burning of anything that contains cellulose are levoglucosan (I) with lesser amounts of the other anhydrosaccharides (II–IV) mentioned above. Levoglucosan is found in all aerosol samples analyzed here (range 0.2–74  $\text{ng m}^{-3}$ , Table 2), often as the major organic compound, and indicates that biomass burning is impacting the whole western Pacific region.

[19] The secondary tracers for biomass burning are various natural product compounds or their derivatives [Simoneit, 2002].  $\beta$ -Sitosterol (XIII) is a directly emitted phytosterol present in all vegetation and is thus not fuel specific but indicates biomass burning. High concentrations of  $\beta$ -sitosterol (XIII) were reported in the marine aerosols from the western North Pacific during the 1991 El Niño forest fire event occurred in Indonesia and other Southeast Asian countries [Kawamura et al., 2003]. Lupadienol (XIV) is indicative for burning of hardwood. Another secondary tracer from biomass-burning emissions is dehydroabietic acid (XVI), the key marker for smoke from burning of conifer wood [Standley and Simoneit, 1994; Oros and Simoneit, 2001a; Rogge et al., 1998; Simoneit, 1999]. Dehydroabietic acid is present as a minor component in these samples (Table 2), indicating significant softwood burning during winter-spring in the aerosol source regions. Lignin is the other major biopolymer of wood and upon burning yields phenolic tracers in the smoke characteristic of the fuel type [Hawthorne et al., 1988; Simoneit et al., 1993, 1996]. The major tracers for lignin burning products in oxidized aerosols are 4-hydroxybenzoic acid (XVII) indicative of grasses and other nonwoody vegetation, vanillic acid (XVIII) indicative of mainly softwood but also

hardwood, and syringic acid (XIX) indicative of hardwood [Simoneit et al., 1993]. These three phenolic compounds are found in most of the aerosol samples analyzed here (Table 2) and the concentrations are similar for Gosan and Sapporo indicating an upwind source on the Asian continent. These compounds are also present in the marine aerosol samples taken near land (Table 3). The predominance of 4-hydroxybenzoic acid in all cases supports the interpretation that the biomass fuels being burned are primarily grasses (e.g., dung, agricultural refuse, bamboo, etc.) [e.g., Sheesley et al., 2003].

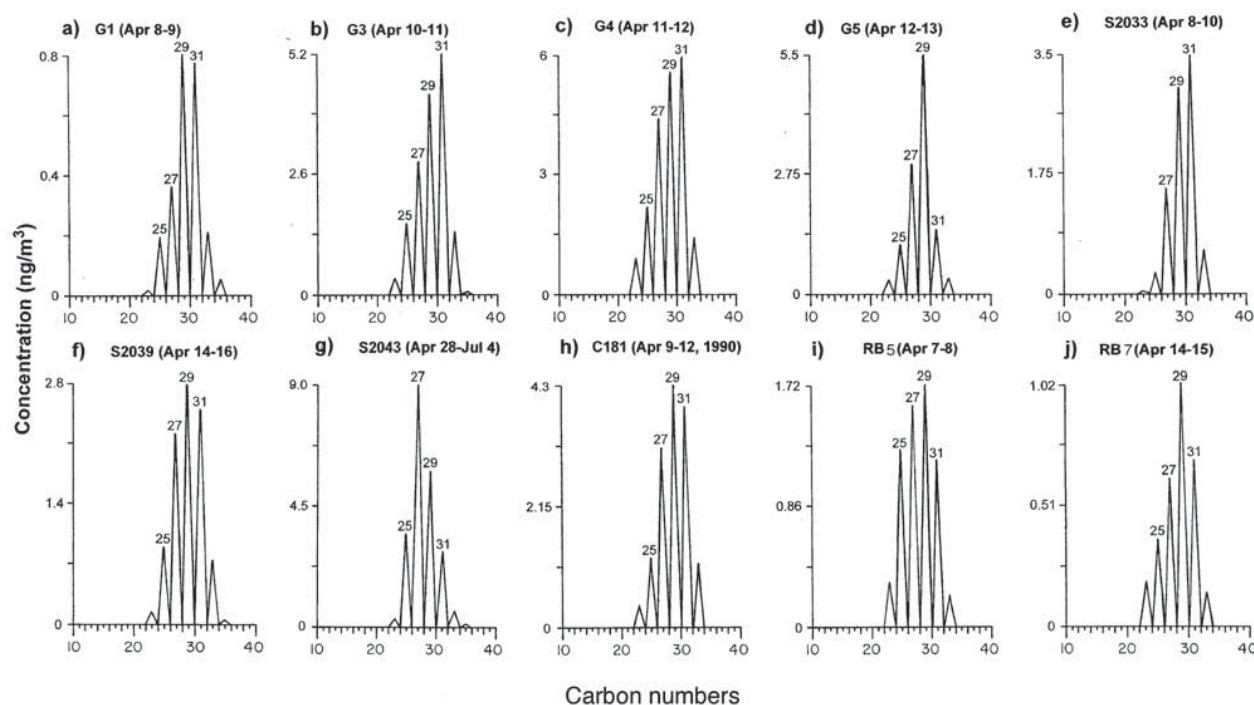
#### 3.1.5. PAHs

[20] Examples of typical PAH compositions and confirming biomarkers are shown in Figure 4. The PAHs range from phenanthrene to coronene (Figures 4a and 4b) and their total concentrations are significant, ranging from 0.005 to 7.8  $\text{ng m}^{-3}$  in Gosan and 1.7 to 19.3  $\text{ng m}^{-3}$  in Sapporo (Table 2). Their distribution patterns are similar during the dust event, indicating common sources. 1,3,5-Triphenylbenzene (XX) is present at significant concentrations indicating a major input source of PAHs from incineration of refuse [Fu et al., 1997]. 1,3,5-Triphenylbenzene has been detected in particles from solid waste incinerators and from burning of plastics [Tong et al., 1984; Karasek and Tong, 1985]. It may be a useful urban tracer. Similar PAH distributions have also been reported for various cities in China [Simoneit et al., 1991b; Fu et al., 1997; Okuda et al., 2002] with total PAH concentrations of 8–450  $\text{ng m}^{-3}$ . Retene from burning conifer wood is not detectable in any of these samples. PAHs are of health concerns because of their carcinogenicity, genotoxicity, and endocrine disrupting potential. 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 (Table 2). The Bap/Bep values for samples from urban areas of China ranged from 0.1 to 1.0 [Simoneit et al., 1991b; Okuda et al., 2002]. Benzo[a]pyrene has a shorter atmospheric lifetime than benzo[e]pyrene because of photochemical degradation [Lane, 1989]. 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 [Oros and Simoneit, 2000].

[21] The urban aerosols of China also contained equivalent concentrations of oxy-PAHs as 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) [Simoneit et al., 1991b]. Oxy-PAHs are not significant components of these samples, probably reflecting their greater reactivity toward further atmospheric oxidation upon emission to for example the benzenedicarboxylic acids and/or entrapment in coal tar emissions.

#### 3.1.6. Biomarker Confirmations

[22] The compositions of the hopane biomarkers characteristic of petroleum utilization are shown for two examples in Figures 4c and 4d. They are present at trace levels (Table 2) and are thus utilized for confirmation of urban traffic emissions. The hopanes consist of only the 17 $\alpha$ (H) series (XXI), ranging from  $C_{27}$  to  $C_{35}$  (no  $C_{28}$ ) with the fully mature configuration for the homologs  $>C_{30}$ . Gammacerane (XXII) is present and these compositions match those reported earlier



**Figure 6.** Distribution plots of the odd carbon number alkanes attributable to plant wax in the aerosols (see Table 1 for information on the samples).

for some urban areas of China [Simoneit *et al.*, 1991b]. Steranes and carotane detected in urban aerosols of China during the 1980's were below the detection limit in these samples.

[23] Examples of key ion traces ( $m/z$  204 + 361) for GC-MS confirmation of the glucose and sucrose anomers are shown in Figures 4e and 4f. Although these compounds are dominant resolved peaks in most of the total ion current traces (e.g., Figures 2a, 2e, and 3a), such key ion plots allow confirmation of trace levels of an anomer. The interconversion of sucrose to its suspected aldol anomer during atmospheric transport is still under investigation.

### 3.1.7. Wax Alkanes

[24] The  $n$ -alkane distributions attributable to vascular plant wax in these samples have been calculated as described (Table 2; Simoneit *et al.* [1991a]) and plotted (Figure 6). None of these distributions are the same and even the air parcel over Gosan moving to Sapporo over a 2-day period shows slightly different  $n$ -alkane distributions (e.g., Figure 6a versus Figure 6e or Figure 6c versus Figure 6f). This variation may reflect source attributes or additional local input. Nevertheless, the  $C_{\max}$  at 29 or 31 reflects a more tropical source region [Simoneit, 1977, 1979], confirming the long-range transport of these aerosols from Southeast Asia to the sampling locations. A minor contribution of  $n$ -alkanes from  $C_{34}$  to  $>C_{37}$ , especially for samples from Sapporo (Figure 3c and Table 2), should be pointed out. These long-chain alkanes are interpreted to be the high-molecular-weight distribution of paraffin wax ( $C_{\max}$  at 28), a petroleum product used for example to coat food containers such as paper milk and juice cartons. The enhanced contents of phthalates in the Sapporo aerosol samples ( $24\text{--}86\text{ ng m}^{-3}$ ) compared to those from Gosan

( $2\text{--}23\text{ ng m}^{-3}$ , Table 2) and the possible presence of paraffin wax indicate fugitive emissions from burning of urban refuse [Didyk *et al.*, 2000]. Source tests from such sources have not yet been conducted.

## 3.2. Ground Station: Chichi-jima

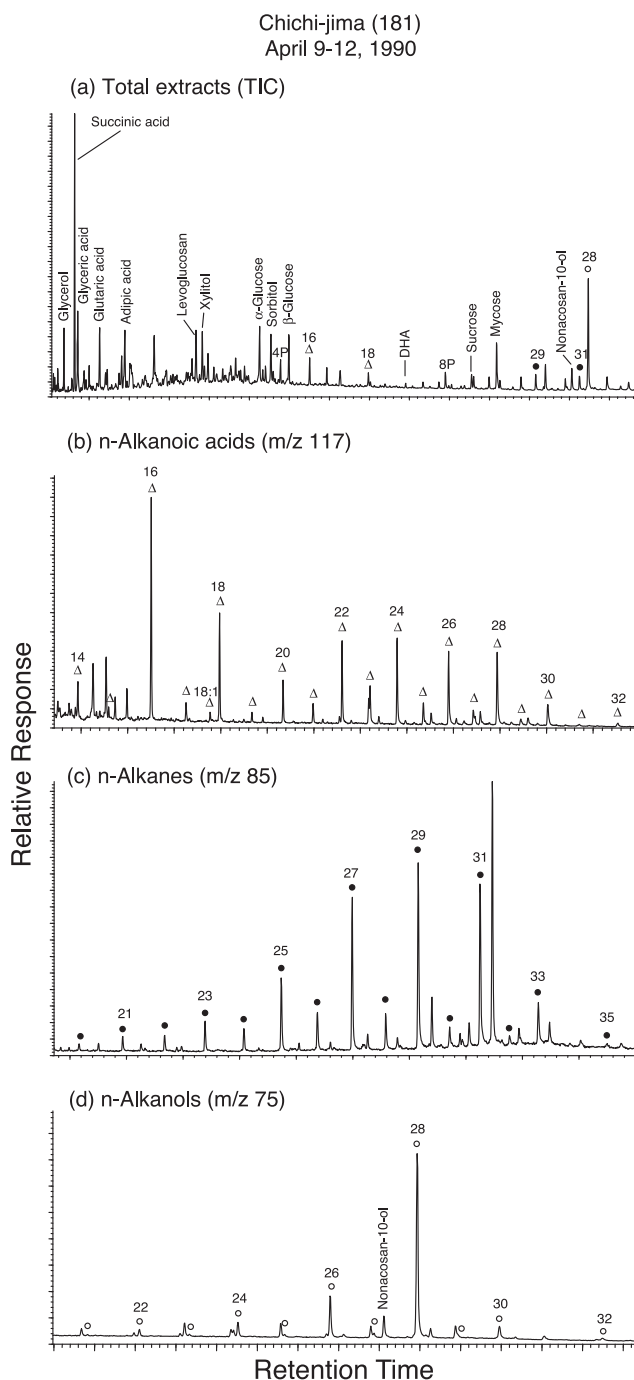
[25] Chichi-jima is located to the southeast of the major dust outflow trajectories from Asia, but is still impacted (Figure 1). The organic compositions of typical aerosol samples taken on the island in 1990 and 1991 during dust episodes are given in Table 2 and an example is shown in Figure 7.

### 3.2.1. Water-Soluble Compounds

[26] The dominant compounds are water-soluble saccharides and their derivatives and dicarboxylic acids with minor amounts of plant wax lipids, phthalates, and dehydroabietic acid. The saccharides and derivatives consist of glycerol (XI), glyceric acid, xylitol (X), sorbitol (IX),  $\alpha$ - and  $\beta$ - glucose (V), sucrose (VII), and sucrose aldol (VIII), with a lesser amount of levoglucosan (I) (Table 2). Levoglucosan and dehydroabietic acid indicate an input from biomass burning with a significant amount of softwood [Simoneit, 2002]. The saccharides are interpreted to derive from soil dust. The dicarboxylic acids, ranging from succinic to adipic acids ( $C_4\text{--}C_6$ ), and the benzenedicarboxylic acids (Table 2) are oxidation products from other organic compounds, reflecting the long-range transport of the aerosols.

### 3.2.2. Lipid Compounds

[27] The lipid compounds of the example aerosol taken in April 1990 are shown in the key ion plots (Figures 7b–7d). The dominant aliphatic homologs are derived from terrestrial plant wax as indicated by the  $n$ -alkanes, ranging from



**Figure 7.** Salient features of the GC-MS data for the total extract of an aerosol sample taken on Chiji-jima in 1990. (a) Total ion current trace, (b)  $m/z$  117 plot for *n*-alkanoic acids, (c)  $m/z$  85 plot for *n*-alkanes, and (d)  $m/z$  75 plot for *n*-alkanols (numbers and symbols as in Figure 2). Here, 4P, dibutyl phthalate.

$C_{21}$  to  $C_{35}$  with  $C_{max}$  at 29 and  $CPI = 4.8$ , the *n*-alkanoic acids  $>C_{20}$  with  $C_{max}$  at 24 and  $CPI = 3.2$ , and the *n*-alkanols, ranging from  $C_{22}$  to  $C_{30}$  with  $C_{max}$  at 28. Nonacosan-10-ol is also derived from terrestrial plant wax. The wax alkanes have been replotted after subtraction of the even carbon numbered homologs (Figure 6h) and

clearly show the  $C_{max}$  at 29. The source region for this plant wax is interpreted to be tropical areas on the basis of the high  $C_{max}$  of these lipids. Marine-derived lipids are minor and consist mainly of *n*-alkanoic acids  $>C_{20}$  for this example (Figure 7b). However, during June the terrestrial wax component is small and the marine lipids are major, with a dominance of saccharides (Table 2). In that case the saccharides, especially the alditols (polyols), may also have a marine origin. This is consistent with the seasonal trend of lipid distributions observed for Chichi-jima aerosols [Kawamura *et al.*, 2003], where concentrations of terrestrial lipids are generally high in winter/spring and low in summer/autumn. Petroleum and coal hydrocarbons, PAH and biomarkers, from continental urban areas or marine traffic are not detectable in these aerosol samples. The minor amounts of phthalates may indicate an input from urban areas as, for example, smoke from garbage burning or contaminants.

### 3.3. Mobile Station: R/V *Ronald H. Brown*

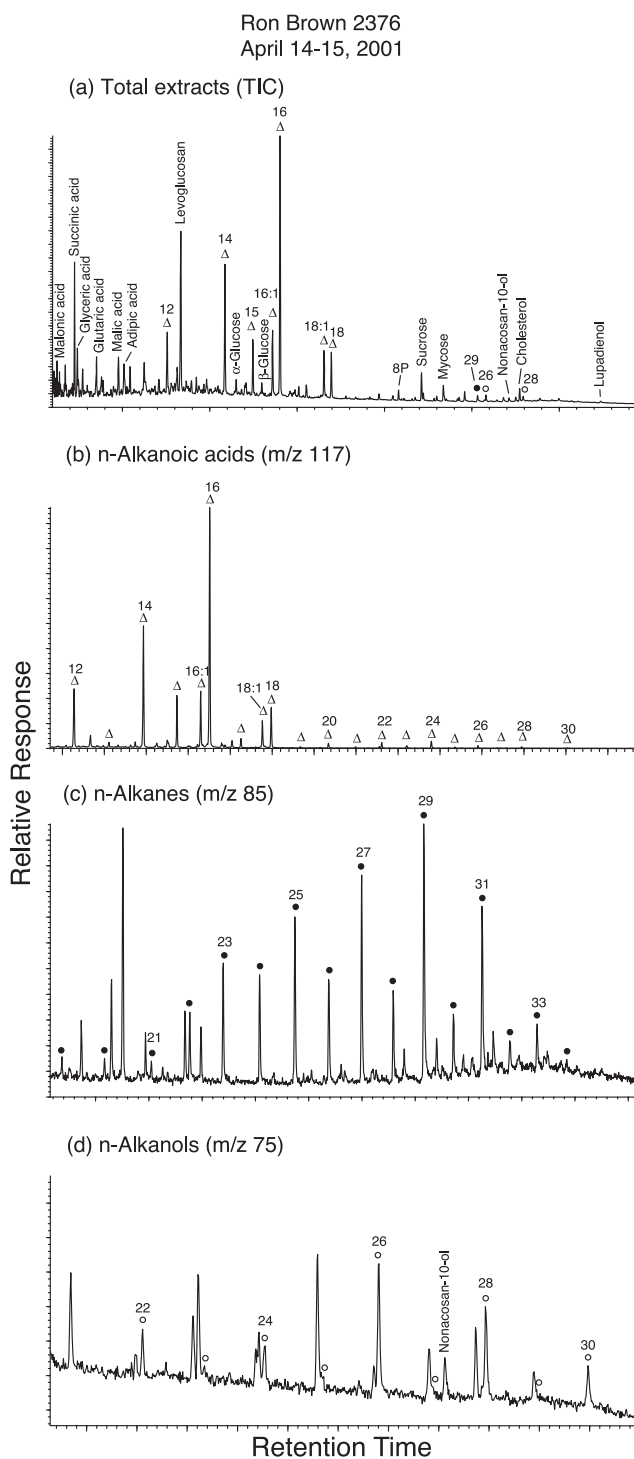
[28] The organic compound signatures of the aerosols collected during the cruise of the R/V *Ronald H. Brown* from Hawaii to the east Asian region (Figure 1) changed from solely marine to dominantly terrestrial sources. The data are summarized in Table 3 and typical examples of GC-MS data are illustrated in Figure 8.

#### 3.3.1. Marine Aerosol Composition

[29] Samples RB1-3 have mainly marine-derived lipid components ( $2-37 \text{ ng m}^{-3}$ ) and secondary oxidation products (e.g., dicarboxylic acids) become superimposed for samples closer to land (e.g., samples 5-6). The marine lipids are composed of *n*-alkanoic acids  $<C_{20}$ , significant amounts of monounsaturated fatty acids (i.e., hexadecenoic and octadecenoic acids, Table 3), cholesterol (XVI), and glycerol (XI). The high amount of glycerol may reflect hydrolysis of fatty acid glycerides from the marine lipid pool in the sea surface slick, which can become part of the aerosol with the other lipid markers by wind activity [Simoneit *et al.*, 1991c]. The dicarboxylic acids ( $1-134 \text{ ng m}^{-3}$ , Table 3, e.g., Figure 8a) become more prevalent in the samples nearer land and consist of succinic to adipic acids and the benzenedicarboxylic acids.

#### 3.3.2. Terrestrial Tracers

[30] Levoglucosan (I) is detectable in all samples ( $0.2-40 \text{ ng m}^{-3}$ ), indicating biomass-burning smoke is spread over the western North Pacific. Dehydroabietic acid (XI), the secondary biomass-burning tracer specific for conifer wood, is not detectable. The terrestrial lipids are found as minor components in aerosols taken near land (mainly samples 6-10,  $3-27 \text{ ng m}^{-3}$ ). They consist of *n*-alkanes ranging from  $C_{21}$  to  $C_{33}$ , with  $C_{max}$  at 29 or 31 and  $CPI$  values from 1.1 to 2.1, *n*-alkanoic acids  $>C_{20}$  ( $CPI$  from 4.5-11.0) and  $C_{max}$  at 24, and *n*-alkanols from  $C_{22}$  to  $C_{30}$ , with  $C_{max}$  at 26, as well as nonacosan-10-ol (XIII) (Table 3 and Figure 8). Minor amounts of sterols and triterpenoids are also found in some samples (Table 3). The plant wax alkanes are replotted after subtraction of the even carbon numbered homologs for two examples (Figures 6i and 6j), thus showing the  $C_{max}$  more clearly. These homolog distributions and  $C_{max}$  confirm the terrestrial plant wax origin and a semitropical to temperate source region of the minor aliphatic components, with their transport from Asia to the ocean. At sea level these continental aerosols are admixed and even overwhelmed with



**Figure 8.** Salient features of the GC-MS data for total extracts of marine aerosol samples (RB7) taken on board the R/V *Ronald H. Brown* from the North Pacific. (a) Total ion current trace, (b)  $m/z$  117 plot for *n*-alkanoic acids, (c)  $m/z$  85 plot for *n*-alkanes, and (d)  $m/z$  75 plot for *n*-alkanols (numbers and symbols as in Figure 2).

marine-derived organic matter from the sea slick. The *n*-alkane distributions of the marine samples (e.g., Figure 8c) reflect traces of petroleum-derived hydrocarbons with no carbon number preference (CPI = 1.1) and  $C_{\max}$  at

26. Petroleum biomarkers were not detectable but the alkane distribution can be interpreted to be derived from diesel exhaust particulate matter (i.e., marine ship traffic) which had become resuspended from the sea surface by wind action and had the volatiles removed by evaporation or once on the filter by blow-off [Simoneit *et al.*, 1991c]. The *n*-alkanoic acids derived from marine emissions are mainly composed of the homologs  $<C_{20}$  ( $C_{\max} = 16$ ) with high contents of alkenoic acids, especially palmitoleic acid ( $C_{16:1}$ ) common in phytoplankton (compare Figure 8b). The saccharides and phthalates (Table 3) are found in most samples, but PAHs or other terrestrial tracers from urban anthropogenic activity are not detectable. The sources of the sometimes dominant saccharides are not clear at this time, they may have both a terrigenous and marine origin.

### 3.4. Emission Sources

[31] The organic compound groups characterized and quantitated for these aerosols can be apportioned to seven emission sources and to significant oxidation reactions during long-range transport, which produces secondary products. This apportionment is based on the extensive emission profile studies of organic compound compositions carried out for major stationary and fugitive sources in Los Angeles, CA and other regions [e.g., Rogge *et al.*, 1991, 1998; Fraser *et al.*, 1998; Oros and Simoneit, 2000, 2001a, 2001b; Simoneit, 1989, 1999, 2002]. The source strengths in terms of organic compound tracers can thus be modeled and apportioned [Schauer *et al.*, 1996]. These source groups are summarized in Table 4 and plotted for selected samples in Figure 9. The terrestrial natural background compounds are the vascular plant wax lipids and they range from 4.6 to 24% of the total identified compound mass (TCM) during the dust season (Table 5, especially G5, S2033, and C181 in Figures 9b–9d). The emissions from fossil fuel utilization range from 5–29% at Gosan and 19–58% of TCM at Sapporo for petroleum markers and 0.0–2.6% of TCM at Gosan and 0.3–2.9% at Sapporo for coal-derived PAHs (both coal and petroleum are summed in Figure 9). Thus there is an additional input of petroleum hydrocarbons from the Sapporo urban area to the organic matter transported over long range from Asia (Figure 9c). The high PAH levels compared to the petroleum-derived alkanes and unresolved complex mixture (UCM) of branched and cyclic hydrocarbons indicate coal as the major source for PAH [Oros and Simoneit, 2000]. Emissions from possible burning of refuse range from about 1 to 24% of TCM and probably reflect the influences of local urban and onboard ship emissions (e.g., G5, S2033 and RB7 in Table 5 and Figures 9b, 9c, and 9f).

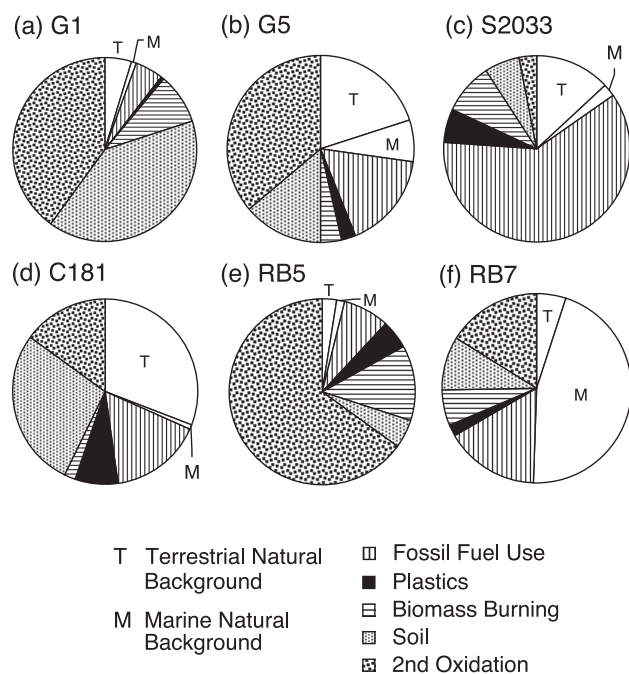
[32] Biomass burning, as reflected by wood smoke markers accounts for 5–12% of TCM during the major dust period (G1–G20, S2033, S2039, and RB4–8 in Table 5 and Figures 9a, 9c, and 9e). The value rises to 13% during the winter in Sapporo and has been reported at much higher levels in other regions [e.g., Schauer *et al.*, 2002]. During summer the wood smoke impact decreases (<3% of TCM). The saccharides compose from 13 to 26% of TCM and have isolated higher values over the ocean (up to 63%, Table 5, e.g., G1–G30, S2039, S2443, RB1–3 and RB8). These compounds are interpreted to represent viable biomass as in soil and possibly in marine particulate matter. Saccharides

Table 4. Total Compound Group Yields<sup>a</sup>

Compound Groups	Gosan					Sapporo					Chichi-jima					R/V Ronald Brown								
	G1	G3	G4	G5	G14	G20	G30	S2033	S2039	S2443	S2447	S2504	C181	C188	C221	RB1	RB2	RB3	RB4	RB5	RB6	RB7	RB8	
Lipids																								
Plant wax lipids																								
<i>n</i> -Alkanes <sup>b</sup>	2.3	15.7	18.8	12.7	91.6	11.1	14.5	16.6	9.4	22.1	7.8	8	4.5	0.06	1.9	0.1	0.38	0.6	1.29	0.5	6.16	3.02	5.95	
<i>n</i> -Alkanols	5	48.3	58.7	23	134	25	15.5	33	16	38	0.8	8.3	22	0	4.6	0	0	0	0	0	0	6.2	0	
<i>n</i> -Alkanoic acids <sup>c</sup>	33	3.7	37.5	24	81.3	26.8	19.4	36	22	13.2	2.7	5.8	5	0.47	6.1	0	0.6	0.7	1.4	5.44	21.1	2.9	13.1	
Total	<b>40.3</b>	<b>67.7</b>	<b>115</b>	<b>59.7</b>	<b>307</b>	<b>63</b>	<b>49.4</b>	<b>86</b>	<b>47.4</b>	<b>73.3</b>	<b>11.3</b>	<b>24.1</b>	<b>29.5</b>	<b>0.53</b>	<b>12.6</b>	<b>0.1</b>	<b>1</b>	<b>1.3</b>	<b>2.7</b>	<b>5.9</b>	<b>27.2</b>	<b>12.1</b>	<b>19</b>	
Fossil fuel (coal/petroleum)																								
<i>n</i> -Alkanes <sup>b</sup>	7.3	19.1	26.4	6.7	58.7	14.7	19	64.2	26.2	9.4	20.8	69.2	2.5	0.24	2.6	1.16	2.78	8	8.09	2.9	15.4	6.07	24.5	
UCM <sup>d</sup>	3.7	95.5	132	33.5	294	74	95	321	131	47	104	346	12.5	1.2	13	5.8	13.9	40	40.5	14.5	77	30.5	123	
Total	<b>44.3</b>	<b>114.6</b>	<b>158</b>	<b>40.2</b>	<b>353</b>	<b>88.7</b>	<b>114</b>	<b>385</b>	<b>157</b>	<b>56.4</b>	<b>125</b>	<b>415</b>	<b>15</b>	<b>1.4</b>	<b>15</b>	<b>7.0</b>	<b>16.7</b>	<b>48</b>	<b>48.6</b>	<b>17.4</b>	<b>92.4</b>	<b>36.6</b>	<b>148</b>	
PAHs	0.4	3.95	7.46	7.8	7.7	0	0.75	19.3	1.7	12	1.2	5.1	0.08	0	0	0	0	0	0.03	0	0.34	2.4	0	
Marine lipids																								
Alkanoic acids <sup>c</sup>	7	2.3	23.7	10.2	14.6	0	2.9	107	37	8.5	13.3	10.3	0.6	2.73	1.5	1.76	6.96	35.8	3.86	2.95	11.6	107.8	34	
Sterols	0.26	0.75	9	10.8	14.5	0.7	0	3.8	0.8	1.1	0.015	0.7	0.3	0.03	0.01	0.24	0.8	1.2	0	0	2	3.6	4	
Polar compounds																								
Saccharides (soil resuspension)	352	210	69	40	574	100	291	41	152	95	93	14	27	29	24	6	15	41	0	12	16.4	23	482	
Anhydrosaccharides (biomass burning)	78	60	28	12	72	29	8	62	59	7	26	73	1.4	0.5	1.2	0.2	1.3	0.4	0.6	29	43	15	28	
Dicarboxylic, glyceric and benzoic acids (Secondary oxidation)	347	197	131	104	103	176	83	20	25	23	8	8.3	14	5	0.05	1.3	13.3	13.7	11	147	153	40	169	
Plastics																								
Phthalates	5	5	6	7.3	23	2	12	39	24	28	86	38	7	7	17	4	3	10	19	10	83	5	27	
Total all compounds + UCM	<b>874</b>	<b>661</b>	<b>547</b>	<b>292</b>	<b>1469</b>	<b>459</b>	<b>561</b>	<b>667</b>	<b>504</b>	<b>304</b>	<b>364</b>	<b>589</b>	<b>95</b>	<b>46</b>	<b>72</b>	<b>20.6</b>	<b>58</b>	<b>151.4</b>	<b>85.8</b>	<b>224</b>	<b>429</b>	<b>246</b>	<b>911</b>	

<sup>a</sup>Values are given in ng m<sup>-3</sup>.<sup>b</sup>Plant wax alkanes are calculated as the excess odd homologs-adjacent even homologs average [Simoneit et al., 1991a, 1991c], and the difference from the total alkanes is the petroleum-derived amount.<sup>c</sup>Plant wax alkanolic acids are apportioned as the sum of all homologs >C<sub>20</sub> and the equal increment of C<sub>22</sub> or C<sub>24</sub> equivalent to C<sub>18</sub> for those <C<sub>20</sub>.<sup>d</sup>UCM is estimated on the basis of a U:R (unresolved: resolved compounds) of 5 for emissions from vehicle traffic in a Los Angeles tunnel [Fraser et al., 1998].





**Figure 9.** Pie diagrams showing the source strengths of organic matter in aerosols from (a and b) Gosan, (c) Sapporo, (d) Chichi-jima, and (e and f) on board the R/V *Ronald H. Brown* (see Table 1 for information on the samples).

have been characterized in urban aerosols, which contain entrained soil dust [e.g., *Didyk et al.*, 2000] and in agricultural soils [*Simoneit et al.*, 2004b]. Thus saccharides are used here as tracers for soil resuspension by agricultural tilling or wind erosion.

[33] The marine lipid input to these aerosols is reflected mainly by the apportioned fatty acid (<C<sub>20</sub>, including C<sub>16:1</sub> and C<sub>18:1</sub>) content, which ranges from 1 to 12% of TCM for the Gosan and Sapporo locations and from 1–45% of TCM for the samples taken on board the R/V *Ronald H. Brown* (see Table 5 and Figure 9f). Obviously, the marine samples contain more autochthonous components such as phytoplankton lipids, but the long-range continental signature is still dominant.

[34] The secondary products derived from oxidative reactions of the organic compounds during transport consist mainly of aliphatic dicarboxylic acids, dihydroxy carboxylic (glyceric) acid and aromatic acids. This compound group varies from 3–40% of TCM for the aerosols from the land stations (e.g., S2033 versus G1 and G5, Figures 9a, 9b, and 9c) and from 6–66% of TCM for those taken on board the ship (e.g., RB1, RB5, and RB7, see Table 5 and Figures 9e and 9f). The remote marine atmosphere has a higher proportion of secondary oxidation products than the atmosphere downwind from Asia at Gosan and Sapporo. This has been demonstrated earlier on prior cruise in the western Pacific [e.g., *Kawamura and Sakaguchi*, 1999;

**Table 5.** Relative Percentages of the Various Compound Source Groups in the Total Compound Mass of the Extractable Organic Matter From the Aerosols

Sample	Natural <sup>a</sup>		Urban <sup>a</sup>			Biomass Burning <sup>b</sup>	Soil Resuspension <sup>c</sup>	Secondary Oxidation Products <sup>d</sup>	Total Water-Soluble Compounds <sup>e</sup>
	Plant Wax Lipids	Marine Lipids	Petroleum	PAHs (Coal)	Plastics				
Gosan									
G1	4.6	0.8	5	0.05	0.6	9	40	40	89
G3	10.2	0.5	17	0.6	0.8	9	32	30	71
G4	21	6	29	1.4	1.1	5	13	24	42
G5	20	7.2	14	2.6	2.5	4	14	36	54
G14	21	2	24	0.5	1.6	5	39	7	51
G20	14	0.2	19	0.00	0.4	6	22	38	66
G30	8.8	0.5	20	0.1	2.1	1.4	52	15	68
Sapporo									
S2033	13	2.2	58	2.9	5.8	9	6	3	19
S2039	9.4	7.5	31	0.3	5	12	30	5	47
S2443	24	3.2	19	0.4	9.2	2.3	31	7.6	41
S2447	3.1	3.7	34	0.3	24	7	26	2	35
S2504	4.2	2	73	0.9	6.7	13	3	2	14
Chichi-jima									
C181	31	0.9	16	0.08	7.4	2	28	15	45
C188	1.2	0.06	3.1	0.0	15	1	63	11	75
C221	18	2.1	22	0.0	24	1.7	33	0.07	35
Mobile: R/V <i>Ronald H. Brown</i>									
RB1	0.5	10	34	0.0	19	1	29	6	36
RB2	1.7	13.5	29	0.0	5	2	26	23	51
RB3	0.9	24	32	0.0	6.6	0.3	27	9	36
RB4	3.1	4.5	57	0.04	22	0.7	0	13	14
RB5	2.6	1.3	8	0.0	5	13	5	66	84
RB6	6.3	2.9	22	0.08	19	10	4	36	50
RB7	4.9	45	15	1.0	2	6	9	16	31
RB8	2	4.2	16	0.0	3	3	53	19	75

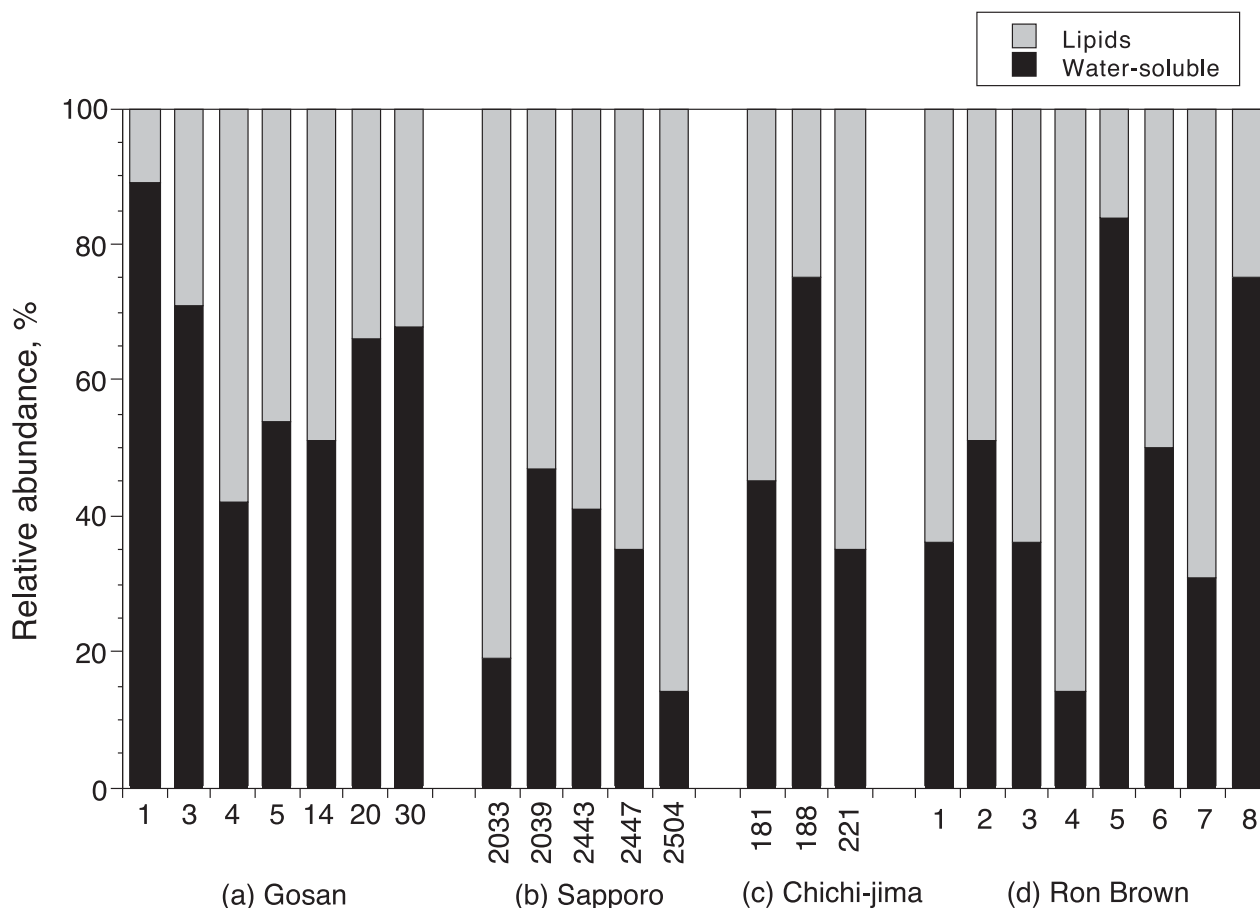
<sup>a</sup>Totals from Table 4 divided by total of all compounds plus UCM.

<sup>b</sup>(Total anhydrosaccharides + resin acids)/(total for biomass burning).

<sup>c</sup>(Total saccharides)/(total for soil resuspension).

<sup>d</sup>(Total dicarboxylic glyceric and benzoic acids)/(total for secondary oxidation) (from Table 4).

<sup>e</sup>Water-soluble compounds: sum of biomass burning, soil resuspension, and secondary oxidation products.



**Figure 10.** Bar graphs showing the lipid versus water-soluble compounds in the aerosols from (a) Gosan, (b) Sapporo, (c) Chichi-jima Island, and (d) on board the R/V *Ronald H. Brown*. Numbers under the bars refer to sample ID (see Table 1).

*Sempéré and Kawamura, 2003*]. The terrestrial compounds have been subjected to thorough oxidation during transport as also supported by low concentrations of unsaturated fatty acids.

### 3.5. Water-Soluble Organic Compounds

[35] The water solubility of the carbonaceous organic fraction of aerosols is a major open question in climate models [*Facchini et al., 1999*]. Oxalic acid, with the other short-chain dicarboxylic acids, has been documented as the dominant water-soluble components of organic aerosol matter [e.g., *Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999; Kawamura et al., 2004*]. Here we add the following groups of organic compounds to the list of water-soluble organic matter on the basis of their complete aqueous solubility properties: saccharides, anhydrosaccharides, and secondary oxidation products such as aliphatic dicarboxylic, dihydroxy carboxylic, and aromatic acids. The sums of these water-soluble compounds range from 14 to 89% of TCM for all the samples analyzed here and are about 40–70% of TCM (Table 5) during the dust episode at the ground stations. Bar graphs showing the total lipid versus water-soluble compounds are illustrated in Figure 10 for all samples analyzed. These water-soluble fractions are unusually high and when coupled with the

oxalic and malonic acid contents determined separately [e.g., *Mochida et al., 2003a, 2003b; Kawamura et al., 2004*] make essentially the total compound mass soluble in water (e.g., G1 and G3 in Figure 10). The Gosan, Chichi-jima, and R/V *Ronald H. Brown* (RB2, RB5, and RB6) have a greater proportion of water-soluble organic matter because of the long-range transport of the aerosols. The samples from Sapporo and RB1, RB3, RB4, and RB7 have a higher proportion of lipids because of additional input from urban emissions being superimposed on the aerosol from the Asian continent. This is quite different from other urban aerosols such as Los Angeles, California, or Santiago, Chile, where the bulk of the organic compounds are hydrophobic [e.g., *Schauer et al., 1996; Didyk et al., 2000*]. 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 [*Simoneit and Elias, 2000*].

### 3.6. Contributions of Each Compound Classes to Aerosol OC: Mass Closure for Organics

[36] Table 6 presents contribution of each compound class to total OC in aerosols collected from Gosan, Sapporo, Chichi-jima and R/V *Ron H. Brown*. The results for total *n*-alkanes show that higher relative abundances (>1%) of

**Table 6.** Contribution of Each Organic Compound Class to Total Organic Carbon in Aerosols<sup>a</sup>

Compound Class <sup>b</sup>	Gosan		Sapporo		Chichi-jima		R/V <i>Ron H. Brown</i>	
	Range	Average	Range	Average	Range	Average	Range	Average
Total <i>n</i> -alkanes	0.1–1.7	0.57	0.53–1.6	1.0	0.09–0.50	0.34	0.07–0.57	0.34
UCM hydrocarbons (fossil fuel) <sup>c</sup>	0.44–3.3	1.3	1.0–6.6	3.4	0.37–1.5	0.86	0.87–2.5	1.4
Wax alkanes (higher plant)	0.03–1.0	0.31	0.10–0.47	0.26	0.02–0.86	0.36	0.01–0.10	0.06
PAHs (combustion)	0.00–0.20	0.07	0.02–0.29	0.13	0.005	0.005	0.002–0.09	0.03
Fatty acids (biogenic)	0.31–0.98	0.58	0.27–1.0	0.62	0.31–1.6	0.78	0.16–1.1	0.82
Diacids (C <sub>3</sub> –C <sub>8</sub> )	0.60–1.7	0.96	0.07–0.24	0.15	0.003–0.43	0.39	0.20–1.1	0.79
<i>n</i> -Alcohols (higher plant)	0.06–1.5	0.56	0.04–0.77	0.27	0.04–1.3	0.89	0.34	0.34
Anhydrosaccharides (biomass burning)	0.14–0.49	0.29	0.07–0.78	0.44	0.04–0.08	0.06	0.003–0.37	0.18
Other saccharides	0.3–2.0	1.2	0.12–2.5	0.94	0.80–1.2	2.1	0.1–1.7	0.69
Lignin products	0.01–0.06	0.03	0.01–0.04	0.03	0.03–0.52	0.21	0.02–0.14	0.06
Phthalates (plasticizer)	0.02–0.23	0.09	0.21–4.1	1.1	0.31–1.7	1.2	0.12–1.2	0.52
Total compounds	3.8–12	6.0	4.3–16	8.1	4.5–9.3	6.6	2.8–5.7	4.9

<sup>a</sup>Values are given in percent. Results for minor species such as steroidal alcohols, benzoic acid, glyceric acid, and dehydroabietic acid are not presented here. However, they are all included in total compounds as shown above.

<sup>b</sup>Compound concentrations (ngC m<sup>-3</sup>) were calculated for each species and then divided by OC (μgC m<sup>-3</sup>).

<sup>c</sup>UCM hydrocarbon-carbon was calculated assuming that UCM carbon/mass ratio is equivalent to that of C<sub>28</sub> alkane. See Table 4 for UCM data.

OC were found in the aerosols from ground stations at Gosan and Sapporo, whereas those of Chichi-jima and Ron Brown samples are less than 0.6%. UCM hydrocarbons of fossil fuel combustion origin are found to compose 0.4–6.6% of aerosol OC, where the highest value (6.6%) was obtained in Sapporo and the lowest value (0.4%) was in Chichi-jima. The values from Sapporo are similar with those (1–6%, average 4%) reported for the aerosols from Tokyo [Kawamura *et al.*, 1995]. This indicates that local emissions of UCM hydrocarbons from fossil fuel combustion sources largely contribute to OC in the urban atmosphere. Relatively high UCM/OC ratios were also obtained at Gosan and the offshore of Japanese Islands during the cruise of R/V *Ron Brown*. This indicates that anthropogenic combustion sources also affect on the organic composition of remote aerosols. Other class of compounds that importantly contribute to OC includes biogenic fatty acids (0.2–1.6%), photochemically derived diacids (0.003–1.7%), *n*-alcohols (0.04–1.5%), anhydrosaccharides (0.003–0.78%), saccharides (0.1–2.5%) and phthalates (0.02–4.1%). However, sum of these organic compounds determined account for only less than 16% of OC.

[37] Although oxalic acid that is the most abundant diacid species was not determined in this study and malonic acid is possibly underestimated as stated above, optimal contribution of these diacids to OC should be less than 10% [Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999]. With the consideration of oxalic and malonic acids, the maximum total amounts of identifiable organic compounds are at most 26% of OC. This indicates that major portion (three quarters) of organic aerosols studied in the Asian Pacific region is unknown in terms of chemical structures. They may include amino acids, peptides, amines, and fulvic and humic acids, etc. Our organic analytical study demonstrates that soil-derived organic materials are sometimes detected as major species in aerosols (see Figures 9a and 9d), suggesting that humic substances may substantially be present in atmospheric particles and significantly contribute to the aerosol OC. Humic and fulvic acids are one of the most abundant organic fractions of soil organic matter as well as humin (kerogen) [e.g., Schnitzer and Khan, 1972; Stevenson, 1982]. Thus humic materials may be emitted to the atmosphere during strong winds,

followed by uplift process of air mass and be subjected to long-range atmospheric transport. It is of interest to note that organic carbon is enriched in fine aerosol fraction when soil particles are emitted to the air under a strong wind condition [Zenchelsky *et al.*, 1976].

[38] Matsumoto *et al.* [2001] isolated fatty acids collected in June 1999 from Sapporo and conducted compound-specific radiocarbon analysis of individual fatty acids using accelerator mass spectrometry (AMS). They found that <sup>14</sup>C ages of C<sub>24</sub> plus C<sub>26</sub> fatty acids to be 5860 (±200) years, suggesting that these terrestrial fatty acids had been stored in geochemical reservoirs such as soils at least for hundreds to thousands of years and then emitted to the atmosphere followed by long-range atmospheric transport from the Asian continent. They also analyzed the humic-like substances for <sup>14</sup>C, which were left in the acidified fraction of the CH<sub>2</sub>Cl<sub>2</sub>/methanol extracts of the aerosols after the fatty acids were removed. The humic-like substances are insoluble in acidified solution and nonextractable with CH<sub>2</sub>Cl<sub>2</sub>. They were isolated, converted to CO<sub>2</sub>, and then subjected to AMS measurement. The humic-like substances showed an age of ca. 5000 years, again suggesting that aerosol particles contain fairly old carbons probably derived from aged soil organic matter transported long distances from the Asian continent.

#### 4. Conclusions

[39] The primary inputs of organic compounds to ACE-Asia aerosols are as follows: (1) natural emissions of terrestrial plant wax and marine lipids based on the alkanolic acid, alkanol, and alkane distributions; (2) smoke from biomass burning (mainly nonconifer fuels) using levoglucosan and dehydroabietic acid as the tracers; (3) soil resuspension due to spring agricultural activity as inferred from major primary and reduced sugars (e.g., sucrose, glucose, sorbitol); and (4) urban/industrial emissions from fossil fuel use based on the biomarkers in this case from coal and petroleum. Significant secondary products derive from the oxidation of atmospheric organic matter during long-range transport and consist of dicarboxylic acids, aromatic acids, and hydroxy carboxylic acids (e.g., glyceric acid).

[40] The organic compound compositions of these samples are very different from those reported for aerosol particles of the Atlantic Ocean [Simoneit and Elias, 2000] and from the data reported earlier for the Pacific [e.g., Gagosian et al., 1981]. The major external sources recognized in these samples are: (1) the plant wax composition which fits with an origin from the deserts of northwestern China; (2) high levels of tracers from biomass-burning smoke and from agricultural soil resuspension; and (3) high levels of PAHs mainly from coal combustion. The water-soluble fraction of the total organic matter is high and consists of the saccharides, anhydrosaccharides, and the secondary dicarboxylic acids. The organic source apportionment needs to be coupled with the inorganic/mineralogical composition data to provide the appropriate weighting of desert dust versus soil dust.

[41] Comparison of each compound class to OC further supported the source strength and source apportionment obtained by the molecular signature and concentrations. Although measured compound classes in the aerosols explained up to 16% of OC, a mass closure approach for organic compounds demonstrated that we still have a significant fraction (>80% of OC) whose chemical structures are unknown. Our molecular analyses of organic aerosols suggest that this fraction may contain soil-derived organic geopolymers such as humic and fulvic acids that are abundantly present in soil reservoirs and can be emitted to the atmosphere by wind motions.

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