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Hydroxy fatty acids in fresh snow samples from northern Japan: long-range atmospheric transport of Gram-negative bacteria by Asian winter monsoon

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Abstract

Hydroxy fatty acids (FAs) in fresh snow from Sapporo, one of the heaviest snowfall regions in the world, have been studied to ascertain the airborne bacterial endotoxin concentrations and their biomass. The presence of β-hydroxy FAs (C_9–C_{28}), constituents of Gram-negative bacteria (GNB), suggests long-range transport of soil microbes. Likewise, the occurrence of α- and ω-hydroxy FAs (C_9–C_{30} and C_9–C_{28}, respectively) in snow reveals their contribution from epicuticular waxes and soil microorganisms. Estimated endotoxin and GNB mass can aid in assessing their possible impacts on the diversity and functioning of aquatic and terrestrial ecosystems, as well as lethal effects on pedestrians through dispersal of microbes. Air mass back trajectories together with hydroxy FAs unveil their sources from Siberia, Russian Far East and North China by the Asian monsoon. This study highlights the role of fresh snow that reduces the human health risk of GNB and endotoxin by scavenging from the air.

1 Introduction

Lipid biomarkers from terrigenous plants, algae, fungi and soil microorganisms have been reported extensively in aerosols (Conte and Weber, 2002; Gagosian et al., 1987, 1981; Kawamura, 1995; Kawamura et al., 2003; Simoneit, 1977; Simoneit et al., 2004), sediments (Kawamura, 1995; Kawamura and Ishiwatari, 1984; Kawamura et al., 1987; Zhang et al., 2014), ice core (Sankelo et al., 2013) and rain/snow (Kawamura and Kaplan, 1986; Satsumabayashi et al., 2001; Yamamoto et al., 2011). These studies have utilized fatty acids as a proxy to assess the terrigenous contribution of higher plant waxes to various environmental samples owing to their abundant presence in biopolymers of plants and microorganisms. Similarly, certain hydroxy fatty acids (e.g., C_{10}–C_{18} β-hydroxy FAs) have been proposed as a tracer to understand the airborne bacterial transport (Tyagi et al., 2015).

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Among the airborne soil microbes, the Gram-negative bacterium (GNB) is one of the most extensively studied bacteria and is documented in aerosols, snow and rain samples (Morris et al., 2011b). Owing to considerable ground based emissions of GNB and its ability to act as cloud condensation nuclei (CCN), these plant pathogenic bacteria can influence the regional as well as global climate through cloud-aerosol interactions (Morris et al., 2011b and references therein). In particular, GNB contains β-hydroxy FAs (C_{10}–C_{18}) in their lipid A fraction of lipopolysaccharides (LPS) as constituents of outer cell membrane (Westphal, 1975). Moreover, the environmental toxic effects of GNB are, in part, due to the presence of β-hydroxy FAs present in LPS (endotoxin) (Larsson, 1994; Saraf et al., 1997; Spaan et al., 2008).

Apart from β-hydroxy FAs, other positional isomers such as α-, ω- and (ω-1)-hydroxy FAs have also been documented in various environmental archives viz. aerosols (Kawamura, 1995; Tyagi et al., 2015) and sediments (Kawamura, 1995; Wakeham et al., 2003; Zhang et al., 2014). Short chain α-hydroxy FAs (C_{12}–C_{18}) are the constituent biopolymers of fungi (Zelles, 1997), soil bacteria (Steinberger et al., 1999; Zelles and Bai, 1994) and protozoa (Ratledge and Wilkinson, 1988). In contrast, long chain α-hydroxy FAs (C_{16}–C_{26}) are abundant in plants, microalgae and cyanobacteria (Matsumoto and Nagashima, 1984). Likewise, ω- and (ω-1)-hydroxy FAs are highly cross-linked constituents of the cell walls of algae (Blokker et al., 1999) and plant seeds, suberin and cutin in terrestrial higher plants (Molina et al., 2006). In addition, ω- and (ω-1)-hydroxy FAs are the intermediates in the oxidation of monocarboxylic acids to dicarboxylic acids in sediments and marine aerosols (Kawamura, 1995; Kawamura and Gagosian, 1990). Further, specificity of hydroxylation in FAs depends on the type of microorganisms involved (Wakeham, 1999).

These tracer compounds in snow samples may be important to better understand the contribution of plant and pathogenic bacteria to regional vs. long-range atmospheric transport (Hines et al., 2003; Lee et al., 2004, 2007; Tyagi et al., 2015) as their presence in the atmosphere can affect the CCN and ice nuclei activity (Morris et al., 2011a). To the best of our knowledge, our study is the first to report α, β- and ω-hydroxy FAs

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in snow samples. Snow efficiently scavenges airborne particles including soil microbes and higher plant metabolites in the free boundary layer of troposphere. Since hydroxy FAs from GNB and plants are inert in nature, they do not undergo chemical modification during snow accumulation. Therefore, hydroxy FAs in fresh snow can be used as a tracer to assess the sources and transport pathways of microorganisms and plant metabolites.

In this study, we determined hydroxy FAs in fresh snow samples collected from Sapporo, Japan, to evaluate the qualitative contribution from GNB and higher plant metabolites. Our results support the hypothesis that these hydroxy FAs are important tracers to better understand the contribution of microorganisms to the organic matter in snow. More importantly, we also discuss the possible transformations of these chemical markers during long-range atmospheric transport.

2 Experimental methods

2.1 Site description and sample collection

Sapporo (43.07° N, 141.36° E) is the capital of Hokkaido, whose population is 1.9 million (June 2013). Sapporo receives cold and dry air masses with heavy snowfall during the Asian winter monsoon. The average temperature of Sapporo in winter goes up to ∼ 2 °C (Yamamoto et al., 2011). Snow cover over the ground and fallen leaves of deciduous plants suppresses the suspension of soil particles during winter whereas the emissions of plant biomarkers from local vegetation are minimal. During winter season, Asian monsoon affects the regional climate, air quality and human health in Japan, delivering anthropogenic aerosols and dust from China and Siberia (Yamamoto et al., 2011). Several studies have examined the chemical and isotopic composition of ambient aerosols in various types of air masses in Sapporo (Aggarwal and Kawamura, 2008; Pavuluri et al., 2013; Yamamoto et al., 2011) to better understand the impacts of anthropogenic and biogenic contributions from Siberia, North China and surrounding

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oceans. However, no study is available from Sapporo, which focuses on the transport of microorganisms using organic markers.

In this study, eleven fresh snow samples were collected from the rooftop of the Institute of Low Temperature Science (ILTS) building, Hokkaido University in Sapporo during intensive snow fall periods (January–March) in 2010 and 2011. On each sampling day, only fresh snow was collected using pre-cleaned stainless steel shovel and then placed into a clean glass jar (8 L), to which mercuric chloride ($HgCl_2$) was added to prevent microbial activity (Yamamoto et al., 2011). Each sample was collected after removing the surface snow (1–2 cm) to avoid any possible contamination from the dry deposition of local aerosols. Soon after the collection, glass jar was sealed with a Teflon lined screw cap and stored in a freezer room at −20 °C until analysis.

2.2 Identification and quantification of hydroxy FAs

The analytical protocol used for assessing the atmospheric abundances of hydroxy FAs is described in Yamamoto et al. (2011). In brief, the hydroxy FAs were first derivatized to methyl esters and then OH groups were derivatized to trimethylsilyl (TMS) ethers with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) (SUPELCO^{TM} Analytical) at 70 °C for 1 h. After the reaction, 50 µL of n-hexane solution containing 1.43 ng µL^{-1} of internal standard (C_{13} n–alkane/tridecane, Wako) was added to dilute the derivatives prior to GC/MS injection (Hewlett-Packard, Model 6890 GC coupled to Hewlett-Packard Model 5973 mass-selective detector, MSD). The GC was installed with a split/splitless injector and DB-5MS fused silica capillary column.

For the quantification of hydroxy FAs, the GC oven temperature was programmed from 50 °C (2 min) to 305 °C (15 min) at 5 °C min^{-1}. Data were acquired and processed with the Chemstation software. Structural identification and comparison of retention time of hydroxy FAs were performed using authentic TMS derivatives of n–C_{12} and n–C_{16} α-hydroxy FAs, n–C_{12}, n–C_{14}, n–C_{15}, and n–C_{16} β-hydroxy FAs and n–C_{16}, n–C_{20} and n–C_{22} ω-hydroxy FAs. The recoveries of authentic fatty acid standards were better than 92 ± 4 % with analytical error (average 4.1 %) for acidic compounds (Yamamoto

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et al., 2011). Laboratory blanks showed no contamination of any target compounds. The results of n-alkanes, n-alkanols and n-alkanoic acids (terrestrial biomarkers) in snow samples are reported in Yamamoto et al. (2011), which revealed a long-range atmospheric transport of terrestrial organic materials from Northeast Asia to North Japan by the Asian winter monsoon.

2.3 Estimation of endotoxin levels and mass loading of GNB

Since the endotoxins from GNB contain β-hydroxy FAs from C_{10} to C_{18}, previous studies attempted to quantify atmospheric abundances of endotoxins using the concentrations of ambient hydroxy FAs measured (Lee et al., 2004; Rietschel et al., 1984; Wilkinson, 1988). According to these studies, concentrations of endotoxins in snow samples were estimated by the mathematical expression as below.

Endotoxins (LPS, ng kg^{-1}) = [(Σ β-hydroxy FAs from C_{10} to C_{18}; nmol kg^{-1}) × 8000]/4

In the above formula, the average molecular weight of endotoxin corresponds to 8000 as reported by Mielniczuk et al. (1993). We also estimated the mass loading of airborne GNB using the approach initially suggested by Balkwill et al. (1988) and later on by Lee et al. (2004), in which they used the chemical marker to bacterial mass conversion factor of 15 nmol of β-hydroxy FAs (C_{10}–C_{18}) per mg dry cell weight. Therefore, we have converted the sum of mass concentrations of β-hydroxy FAs from C_{10} to C_{18} (in nmol kg^{-1}) into equivalent dry cell weight of GNB (i.e., in mg kg^{-1}) by normalizing with 15.

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3 Results and discussion

3.1 Air mass backward trajectory analysis

The air mass back-trajectories (AMBTs) provide a means to qualitatively assess the source regions of airborne pollutants over a receptor site. For this study, we have computed seven day isentropic AMBTs using hybrid single particle lagrangian integrated trajectory (HYSPLIT) model (Draxler and Rolph, 2013 and references therein). The meteorological parameters (GDAS data sets) from NOAA air resources laboratory were used as an input for the HYSPLIT model. Figure 1 shows the AMBT cluster at an arrival height of 500 m over Sapporo during sampling days of winter 2010 and 2011. In almost all snow-sampling periods in Sapporo, the AMBTs show plausible influence of air masses from Russia and Siberia via the long-range atmospheric transport.

3.2 Concentrations of hydroxy fatty acids

Homologues series of α-, β- and ω-hydroxy FAs were detected in fresh snow samples collected from Sapporo. Their mass concentrations are summarized in Tables 1 and 2 for winter 2010 and 2011, respectively. Based on two-year seasonal data on hydroxy FAs, we found that concentrations of α-hydroxy FAs are significantly higher than β- and ω-hydroxy FAs. The predominance of α-hydroxy FAs can be explained by the α-oxidation pathway of FAs, which generally occurs in plants, animals and bacteria (Cranwell, 1981 and references therein) whereas β- and ω-oxidation is specific to bacteria (Lehninger, 1975). A characteristic feature of our data is the predominance of C_{16} hydroxy FAs in all the types of hydroxy FAs measured. However, significant shifts were observed in the carbon numbers of the second most abundant β-hydroxy FAs (mostly C number > 16) and ω-hydroxy FAs (i.e., C number < 16; see Tables 1 and 2). A likely explanation for this observation is that β-hydroxy FAs above C_{16} were formed by β-oxidation of long chain FAs, which is a more common in microorganisms as discussed previously. In contrast, ω-hydroxy FAs below C_{16} are present in plants and microbes

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(Cardoso and Eglinton, 1983), in which ω-oxidation of fatty acids is secondary choice for microbial oxidation.

3.3 Molecular distributions

Figure 2 presents molecular distributions of α-hydroxy (C_9 to C_{30}), β- and ω-hydroxy FAs (C_9 to C_{28}) in snow samples from Sapporo during winter 2010 and 2011. Even carbon number predominance is noteworthy for α-, β- and ω-hydroxy FAs. α-Hydroxy FAs show molecular distributions with the order $C_{16} > C_{24} > C_{22}$ in both years (see Fig. 2a). Likewise, β-hydroxy FAs show the predominance of C_{16} followed by C_{18} or C_{20} and then by C_{14} in both winters. However, we found the predominance of C_{20}β-hydroxy FAs over C_{16} in one snow sample during 2010. Similarly, ω-hydroxy FAs showed dominance of C_{16} followed by the others as $C_{14} > C_{12} \sim C_{22} \sim C_{24}$ during snowfall in both the years.

Table S1 in the Supplement describes the statistically significant differences in the ratios of even to odd carbon numbers for α-, β-, and ω-hydroxy FAs in snow samples based on two-tailed unpaired *t* test. No significant differences were observed between 2010 and 2011 for the ratios of even to odd carbon number α-hydroxy FAs. In contrast, the difference is statistically significant between 2010 and 2011 for β- and ω-hydroxy FAs. In fact, the difference is extremely larger for ω-hydroxy FAs than that for β isomers. On average, even carbon numbered α-, β- and ω-hydroxy FAs in their total mass concentrations account for ~ 69, 68 and 84 %, respectively. The even carbon number predominance is also found in recent marine and lacustrine sediments (Cardoso and Eglinton, 1983; Goossens et al., 1986; Kawamura, 1995; Zhang et al., 2014).

Similar to our study, Volkman et al. (1980) documented the bimodal distribution of α-hydroxy FAs with peaks at C_{16} and C_{24} in the intertidal sediments from Victoria, Australia and attributed their contribution from sea grass (i.e., *Zostera muelleri*) detritus owing to similar distribution pattern. However, it is noteworthy that our AMBTs show a continental origin rather than the oceanic origin. Therefore, it is possible that waxes emitted from continental grasses via wind abrasion can be transported to Sapporo

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through the atmosphere. We speculate that α-hydroxy FAs (C_{16}–C_{28}) in Sapporo snow can be used as a tracer of plant waxes. Likewise, higher plant derived cutin and suberin have been suggested as a significant source of C_{16} to C_{22} α-, β- and ω-hydroxy FAs (Cardoso and Eglinton, 1983). In a similar way, it has been proposed that hydroxy FAs (C_{20}–C_{30}) are principally derived from terrestrial higher plants (Kawamura and Ishiwatari, 1984). Therefore, α-, β- and ω-hydroxy FAs (C_{16}–C_{22}) in snow samples can be related to their sources from terrestrial higher plants through long-range atmospheric transport.

Previous studies documented ubiquitous occurrence of these hydroxy FAs in soil microbes such as yeast and fungi (Van Dyk et al., 1994 and references therein) and in the LPS of GNB (Lee et al., 2007). In this regard, prior studies focussing on β-hydroxy FAs with the predominance of C_{16} and C_{18}, suggested the contributions from yeast and fungi (Stodola et al., 1967; Van Dyk et al., 1994 and references therein). Molecular distributions of β-hydroxy FAs show a predominance of C_{16} followed by C_{18} or C_{20} (see Fig. 2b), suggesting that they have been derived from soil microbes. Likewise, FAs < C_{20} are derived from marine phytoplankton (Kawamura, 1995 and references therein). β-Hydroxy FAs (C_{10}–C_{18}) have been proposed as a biomarker for soil microbes as they are the constituents of LPS of Gram-negative bacteria (Lee et al., 2004; Szponar et al., 2002). Hence, it is likely that β-hydroxy FAs in snow samples may have been significantly influenced by GNB and terrestrial higher plant metabolites.

Figure 3 depicts bar graphs, showing the relative abundances of α-, β- and ω-hydroxy FAs in the snow samples from Sapporo during winter. We found that the proportions of two classified groups (low molecular weight C_9–C_{19} and high molecular weight C_{20}–C_{30} or C_{20}–C_{28}) of α-, β- and ω-hydroxy FAs are very similar between 2010 and 2011 (Fig. 3). This observation is perhaps related to their common sources/transport pathways of α-, β- and ω-hydroxy FAs over Sapporo. This inference is further supported by the AMBTs computed at arrival heights of 500, 1000 and 1500 m (see Fig. 1 and Fig. S1 in the Supplement), indicating similar air mass transport pathway from Russia and Siberia.

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3.4 Endotoxin potency of GNB-impact via aeolian transport

Endotoxin in GNB determines their viability and potentially causes pathological effects on mammals (Lüderitz et al., 1981; Westphal, 1975). In particular, GNB contain LPS in their outer membrane. When bacteria multiply, die and lyse, LPS are released from the surface as a potential bacterial toxin, and therefore called as endotoxin (Westphal, 1975). In addition to intact bacterial cells, this endotoxin can trigger to cause allergies, respiratory problems and infections. Researchers have used LPS concentrations as a measure of GNB, primarily by Limulus Amebocyte Lysate (LAL) Assay which has limited specificity (Saraf et al., 1997). Endotoxin/LPS levels in various environmental samples such as dust (Andersson et al., 1999; Hines et al., 2000), aerosols (Lee et al., 2004, 2007; Walters et al., 1994), soils (Keinänen et al., 2003), sewage (Spaan et al., 2008) and marine dissolved organic matter (Wakeham, 1999) are often assayed by the analysis of β-hydroxy FAs.

As mentioned in Sect. 2.3, we have estimated the abundances of endotoxin and mass loading of GNB in fresh snow samples. This quantification is indeed crucial for assessing a likely allergic impact of endotoxin globally via long-range atmospheric transport. Here, we estimated the endotoxin concentrations in snow varied to be 424 to 1080 $\mathrm{ng\,kg^{-1}}$ (av. $789 \pm 237\,\mathrm{ng\,kg^{-1}}$) in 2010 and 36 to 1100 $\mathrm{ng\,kg^{-1}}$ (av. $579 \pm 435\,\mathrm{ng\,kg^{-1}}$) in 2011 samples. Although relative abundances of endotoxin during winter 2010 ($N = 5$) are higher than those of 2011 samples ($N = 6$), the two-tailed t test revealed no significant differences ($t = 0.96$; d$f = 9$; $P > 0.05$) with regard to mean concentrations of the two years.

In this study, we estimated dry mass concentrations of GNB in snow samples to be $26.3 \pm 7.9\,\mu\mathrm{g\,kg^{-1}}$ in 2010 v.s. $19.3 \pm 1.4\,\mu\mathrm{g\,kg^{-1}}$ in 2011. Lee et al. (2007) reported that airborne endotoxin is of crustal origin and thus can be transported long distances to the outflow region. Since the AMBTs reveal the impact of long-range transport from Russia and Siberia during the study period, we infer that estimated endotoxin concentrations and dry cell weight of GNB over Sapporo are derived from those source regions. Re-

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cently, Golokhvast (2014) documented the airborne biogenic particles in snow from Russian Far East that cause allergy for the pedestrians. So far, no literature is available on endotoxin and GNB concentrations in snow samples from East Asia in order to make a comprehensive comparison with the present study.

Overall, the presence of endotoxin and GNB in snow affirms that biogenic particles of soil microbes and their potential health impact should not be overlooked. Routine and long-term measurements of airborne chemical markers (hydroxy FAs in this study) could aid the monitoring of the microbial content in long-range transported air masses. Further studies are required to examine their distributions in the atmospheric environment and health effects on human beings in the regional and global perspectives during long-range atmospheric transport.

4 Conclusions

Although low temperature is considered to be a limiting factor for bacterial activity in air/snow, some studies have shown that bacteria can be metabolically active even at subzero temperatures (Polymenakou, 2012 and references therein). Figure 4 summarized the whole idea, which was addressed in this study. We conclude that fresh snow in Japan acts as a filter, which aids in reducing the burden of pathogenic microbes from the atmosphere via wet scavenging of these particles.

Owing to prolonged winters and thus, snow fall in Sapporo, it is likely that ambient bacterial endotoxin (LPS) is largely scavenged from the atmosphere by snow, which can decrease their effect on human health via inhalation (Jacobs, 1989; Milton, 1996). However, without snow scavenging, ambient bacterial endotoxin levels may stay high; having an influence on human health as well can be transported to further long distances (North Pacific). Overall, bacteria and their debris (biomass) can be evaluated in aerosols that are scavenged by snow in free troposphere without prior culture by the determination of hydroxy FAs for both LPS and GNB.

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Table 1. Mass concentrations (in ng kg^{-1}) of α-, β- and ω-Hydroxy fatty acids (FAs) measured in snow samples (N = 5) collected from Sapporo during winter 2010.

2010									
C-number	α-Hydroxy FAs			β-Hydroxy FAs			ω-Hydroxy FAs		
	range	mean ± S.E.	median	range	mean ± S.E.	median	range	mean ± S.E.	median
C_9	b.d.–7.1	2.4 ± 1.3	1.7	0.5–2.7	1.8 ± 0.47	2	b.d.–1.7	0.97 ± 0.4	1.4
C_{10}	b.d.–37.3	14.6 ± 7.6	10.9	1.7–6.5	4.6 ± 1.2	5.1	b.d.–5.1	1.7 ± 1.1	0
C_{11}	b.d.–35.1	21 ± 6.5	21.1	3.4–7.9	6.1 ± 0.8	6.2	b.d.–6.4	2.2 ± 1.4	0
C_{12}	b.d.–46.7	25.3 ± 7.8	22.6	8–10.1	9.2 ± 0.4	9.8	b.d.–95.6	47.2 ± 17.8	32.7
C_{13}	b.d.–45.2	20 ± 7.3	18	3.5–11.9	7.1 ± 1.8	6	b.d.–5.1	3.7 ± 0.9	4.4
C_{14}	b.d.–53.4	27.1 ± 8.5	27.6	16.6–40.9	23.5 ± 4.4	19.6	b.d.–196.7	101 ± 34.7	79.8
C_{15}	b.d.–44	18.6 ± 7.2	16.4	2.9–10.8	6.8 ± 1.4	6.7	b.d.–17	9.6 ± 3.1	12.8
C_{16}	b.d.–139	89.2 ± 23.6	97.8	21.7–79.4	45.1 ± 9.4	4.4	2.3–754.1	296 ± 129	256.3
C_{17}	b.d.–26.5	12.4 ± 4.4	10	3.1–10.7	7.5 ± 1.3	8.4	b.d.–12.6	7.1 ± 2	8.1
C_{18}	b.d.–44.7	26.2 ± 8.1	26.3	23.4–52.3	33.5 ± 6.6	29.1	b.d.–43.9	21.2 ± 6.9	21
C_{19}	b.d.–20.1	11.5 ± 3.4	11.5	5.3–21.7	10.4 ± 3.8	7.3	b.d.–12.2	5.5 ± 2	5.7
C_{20}	b.d.–46.6	25 ± 7.8	21.5	14.4–120	48.3 ± 25	29.2	0.2–45.6	17.2 ± 7.6	13.5
C_{21}	b.d.–21.1	12.1 ± 3.7	11.2	5.6–28.8	14.8 ± 5.4	13	b.d.–8.7	3.6 ± 1.4	3
C_{22}	b.d.–73.7	40.8 ± 13.1	37.7	11.2–30.4	19.5 ± 4.1	18.2	b.d.–318	96.4 ± 56.5	50.7
C_{23}	b.d.–32.8	18.5 ± 5.8	18.3	2.8–33.9	13.2 ± 7.1	8.1	b.d.–9.2	3.8 ± 1.6	3.6
C_{24}	b.d.–145	64 ± 25	56.8	6.2–29	15 ± 5.1	12.3	b.d.–72.4	24.1 ± 12.7	13
C_{25}	b.d.–39.1	18.4 ± 6.7	15.4	1.4–17.4	7.7 ± 3.4	5.9	b.d.–2.6	1.02 ± 0.5	1.2
C_{26}	b.d.–49.3	18.6 ± 9	15.8	b.d.–18	7.5 ± 3.8	6	b.d.–3.2	0.6 ± 0.6	0
C_{27}	b.d.–14.4	4.4 ± 2.8	1.1	b.d.–2.7	0.7 ± 0.7	0	b.d.–0.2	0.03 ± 0.03	0
C_{28}	b.d.–10.9	4 ± 2.5	0	b.d.–1.6	0.3 ± 0.3	0			
C_{29}	b.d.–0.54	0.1 ± 0.1	0						
C_{30}	b.d.–0.32	0.06 ± 0.06	0						
Total	432–774	593 ± 88	582	70–379	247 ± 52	252	2–1411	643 ± 228	530

Note: b.d. = below detection limit ≤ 0.02 ng kg^{-1}; S.E. (Standard Error) = $\sigma/N^{1/2}$, where σ refers to standard deviation of total samples (N).

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Table 2. Mass concentrations (in ng kg^{-1}) of α-, β- and ω-Hydroxy fatty acids (FAs) measured in snow samples (N = 6) collected from Sapporo during winter 2011.

2011									
C-number	α-Hydroxy FAs			β-Hydroxy FAs			ω-Hydroxy FAs		
	range	mean ± S.E.	median	range	mean ± S.E.	median	range	mean ± S.E.	median
C_9	b.d.–27.2	14.2 ± 5.7	13.8	1–8.5	5.1 ± 1.3	6	b.d.–16.4	11.0 ± 2.6	12.9
C_{10}	b.d.–65.4	30.9 ± 11.2	33.3	1.7–12.7	8.1 ± 1.8	8.8	b.d.–4.7	0.8 ± 0.8	0
C_{11}	19.8–66.6	34.2 ± 8.5	28.5	1.7–13.3	9.2 ± 1.9	10.1	b.d.–4.7	0.8 ± 0.8	0
C_{12}	20.7–60.4	36.5 ± 6.6	32.9	1.3–15.3	8.7 ± 2.2	8.8	b.d.–13.4	4.3 ± 2.7	0
C_{13}	b.d.–49.2	21.5 ± 8.2	21.8	4.5–15.8	9.1 ± 2.1	8.6	b.d.–7.3	2.1 ± 1.2	1
C_{14}	7.5–55.3	28.6 ± 7.7	28.4	4.5–25.5	13.7 ± 4	16.6	b.d.–61.5	17.7 ± 9.3	9.1
C_{15}	b.d.–77.6	29.2 ± 13.1	23.3	1.9–11.1	6.3 ± 1.8	7.7	b.d.–12.1	4.0 ± 2.2	3.9
C_{16}	14.3–186	94.0 ± 29.3	92.5	2.8–55.8	30.5 ± 10.2	32.8	b.d.–159	42.9 ± 24.7	19.4
C_{17}	2.8–29.3	15.3 ± 4.3	14.5	1.6–12.2	7.7 ± 2.2	9	b.d.–8.2	1.9 ± 1.3	0.3
C_{18}	8.0–55.8	31.3 ± 8.2	29.9	0.6–31.4	14.4 ± 5.3	13.6	b.d.–18.2	5.8 ± 2.8	3.9
C_{19}	b.d.–22.4	6.2 ± 4.4	0	1.9–10.9	6.5 ± 1.5	7.1	b.d.–6.5	1.5 ± 1.0	0.5
C_{20}	11.5–97.9	53.5 ± 18.6	47.3	1.2–43.4	23 ± 8.6	27.4	b.d.–10.5	3.3 ± 1.5	2.3
C_{21}	b.d.–95.2	29.1 ± 17.2	13	1.0–16.6	8.8 ± 3.2	8.8	b.d.–3.4	1.0 ± 0.5	0.6
C_{22}	13.4–109	60.8 ± 19.9	56.1	1.6–27.2	19.8 ± 6.1	25.2	b.d.–48.1	13.7 ± 7.4	8.2
C_{23}	8.1–58.1	32.2 ± 10.1	26.3	5.7–11.6	9.1 ± 1.7	10	b.d.–6.8	1.2 ± 1.1	0
C_{24}	12.3–92.2	74.9 ± 34	34	19.1–24.3	22.2 ± 1.6	23.1	b.d.–38	9.1 ± 6.0	3.2
C_{25}	2.6–51.3	18.4 ± 8.9	9.8	3.3–11.1	8.5 ± 2.6	11.1	b.d.–3.7	1.0 ± 0.6	0
C_{26}	2.6–52.0	24.2 ± 9	23.5	b.d.–15.9	6.4 ± 3.1	4	b.d.–10	2.2 ± 1.6	0.1
C_{27}	b.d.–5.6	2 ± 1.3	0	b.d.–9.2	3.3 ± 1.6	2.1			
C_{28}	b.d.–4.8	1.4 ± 0.9	0	b.d.–10.6	4.3 ± 2.1	2.3	b.d.–1.4	0.2 ± 0.2	0
C_{29}	b.d.–3.35	0.7 ± 0.67	0						
C_{30}	b.d.–0.60	0.12 ± 0.12	0						
Total	169–1279	639 ± 187	651	6–354	179 ± 64	170	27–422	149 ± 73	102

Note: b.d. = below detection limit ≤ 0.06 ng kg^{-1}. S.E. (Standard Error) = $\sigma/N^{1/2}$, where σ refers to standard deviation of total samples (N).

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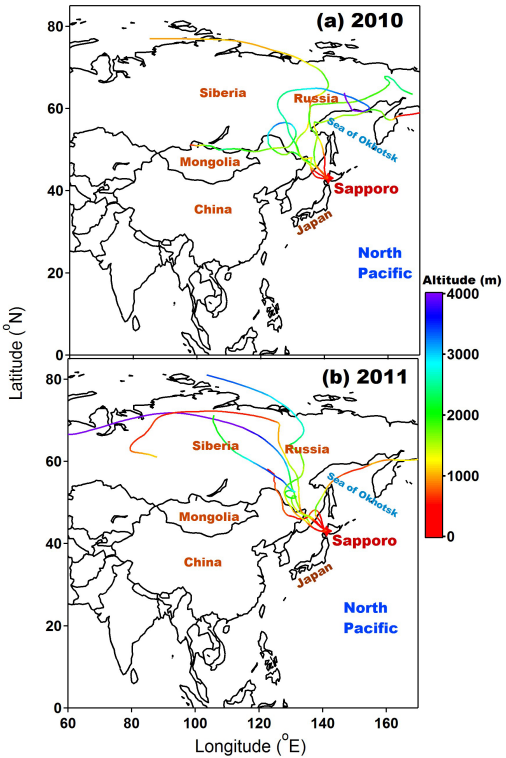

Figure 1. Air mass back trajectory cluster at an arrival height of 500 above ground level (a.g.l.) for the sampling days in **(a)** winter 2010 and **(b)** winter 2011.

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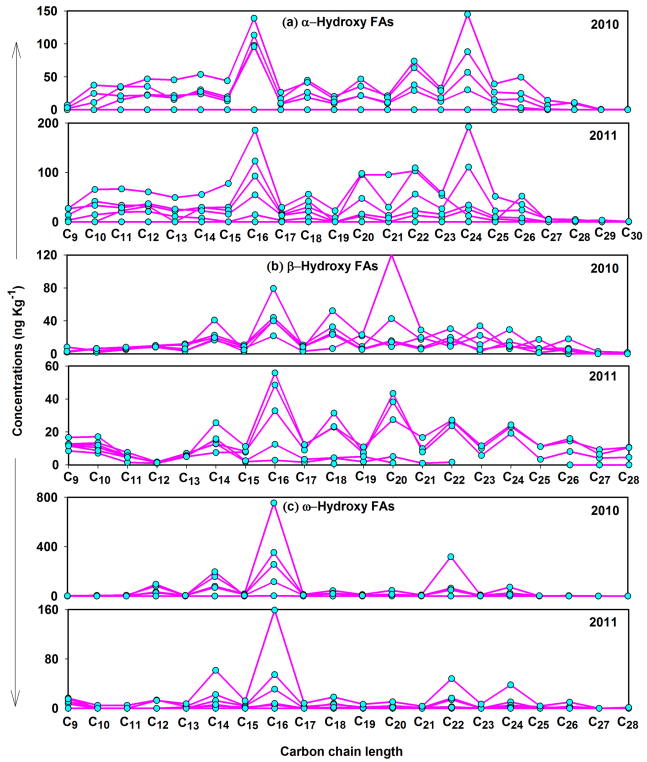

Figure 2. Molecular distributions of **(a)** α-Hydroxy fatty acids (FAs) (C_9–C_{30}), **(b)** β-Hydroxy FAs (C_9–C_{28}) and, **(c)** ω-Hydroxy FAs (C_9–C_{28}) in the snow samples collected from Sapporo during winter 2010 and 2011.

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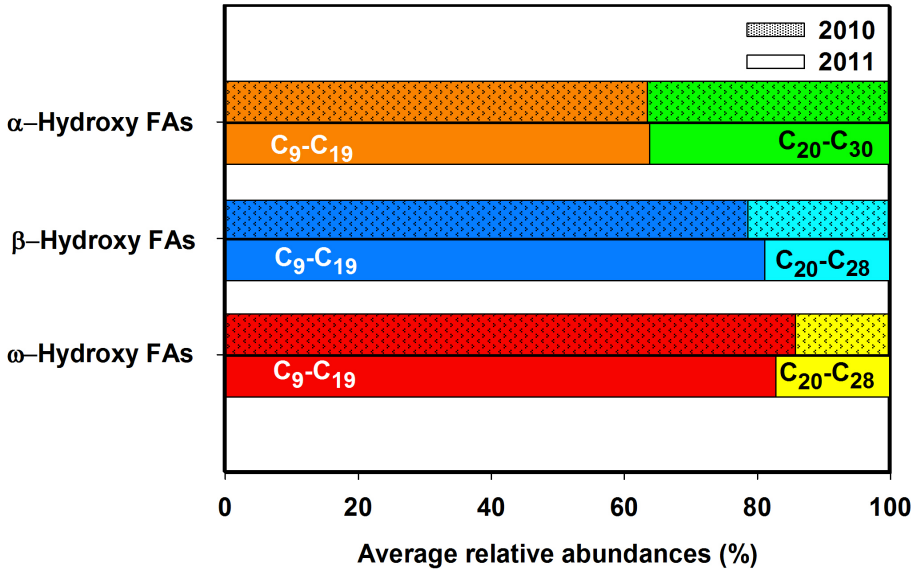

Figure 3. Bar graph, showing the relative abundances of low molecular weight (C_9–C_{19}), and high molecular weight fatty acids (C_{20}–C_{30} for α-Hydroxy; C_{20}–C_{28} for β- and ω-Hydroxy) in their total mass for the snow samples collected during winter 2010 and 2011. The upper and lower horizontal bars for each type of hydroxy fatty acids indicate the data for 2010 and 2011, respectively.

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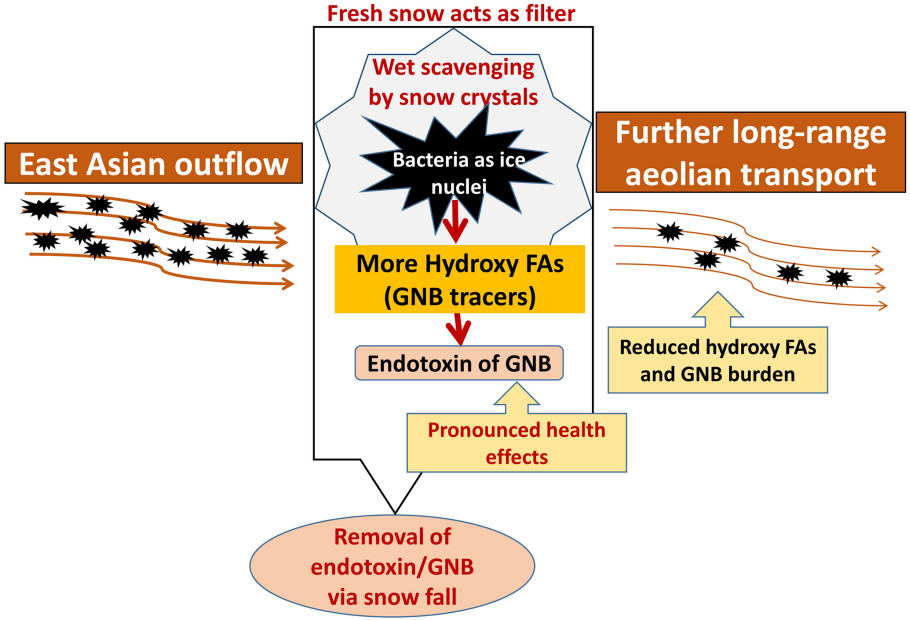

Figure 4. Conceptual model to explain the scavenging of hydroxy fatty acids (FAs) by fresh snow in the free troposphere. Snow fall in north Japan acts as a filter in reducing the hydroxy FAs (tracers of Gram-negative bacteria; GNB), which in turn results in the removal of endotoxin from the atmosphere and reduction in their health effects during long-range aeolian dust transport.

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