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Key Points:
- Impacts of biomass-burning emissions on soil microbes and plant metabolites
- Hydroxy fatty acids (FAs) in summertime aerosols collected over Mount Tai
- beta-Hydroxy FAs as tracers to assess endotoxin and Gram-negative bacteria in aerosols

Supporting Information:
- Supporting Information S1

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Impact of biomass burning on soil microorganisms and plant metabolites: A view from molecular distributions of atmospheric hydroxy fatty acids over Mount Tai

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Abstract Biomass burning events (BBEs) in the North China Plain is one of the principal sources of airborne pollutants in China and also for the neighboring countries. To examine the impact of BBEs on soil bacteria and other higher plant metabolites, their tracer compounds, hydroxy fatty acids (FAs), were measured in the bulk particulate matter (total suspended particles (TSP)) over Mount Tai during the period of wheat residue burning in June 2006. Higher inputs of epicuticular waxes and soil microorganisms during high BBEs (H; 6–14 and 27 June) relative to low BBEs (L; 15–26 and 28 June) were characterized by increased concentrations of homologous series of α-(C_9–C_{32}), β-(C_9–C_{32}), and ω-(C_{12}–C_{28}) hydroxy FAs in TSP samples. However, their relative abundances were not significantly different between H-BBEs and L-BBEs, suggesting their common source/transport pathways. We also found higher concentrations of trehalose and mannitol (tracers of soil microbes), and levoglucosan (tracer of biomass combustion) during H-BBEs than L-BBEs. These results are consistent with hydroxy FAs, suggesting that they are associated with biomass combustion processes of agricultural wastes as well as re-suspension of mineral dust and plant pathogens. In addition, enhanced concentrations of endotoxin and mass loading of Gram-negative bacteria during H-BBEs (117 endotoxin units (EU) m^{-3} and 390 ng m^{-3}, respectively) were noteworthy as compared to those in L-BBEs (22.5 EU m^{-3} and 75 ng m^{-3}, respectively). Back trajectory analysis and fire spots together with temporal variations of hydroxy FAs revealed an impact of biomass burning on emissions and atmospheric transport of bacteria and plant metabolites.

1. Introduction

Field burning of agricultural crop-residue is a traditional practice employed in South and East Asia for many years to clear and fertilize the lands, which emits a significant amount of organic compounds in the atmosphere on a global scale [*Andreae and Merlet*, 2001]. Several studies have been carried out to ascertain its impact on organic aerosols in terms of various organic compounds (e.g., diacids, sugars, and lipids) [*Fang et al*., 1999; *Kawamura et al*., 2013; *Wang et al*., 2009; *Wiesenberg et al*., 2009]. However, studies focusing on the role of this anthropogenic source (i.e., biomass burning) in terms of soil microbes and higher plant waxes have been limited in the literature [*Yang et al*., 2012].

The airborne microorganisms (e.g., bacteria, viruses, and fungal spores) and their long-range atmospheric transport have received considerable attention owing to their potential impacts on human health, animals, and plants. In addition, these bioaerosols can act as cloud condensation and ice nuclei [*Bauer et al*., 2003; *Bowers et al*., 2009; *Després et al*., 2012; *Huffman*, 2013]. However, knowledge on microbial aerosols is particularly deficient due to the absence of reliable measurement techniques and the limitations in culturing and quantification of microorganisms. Alternatively, the determination of certain chemical markers (e.g., hydroxy fatty acids) has been proven as an efficient means to assess the contribution from airborne Gram-negative bacteria (GNB) and higher plant metabolites [*Hines et al*., 2003; *Lee et al*., 2004, 2007; *Tyagi et al*., 2015a].

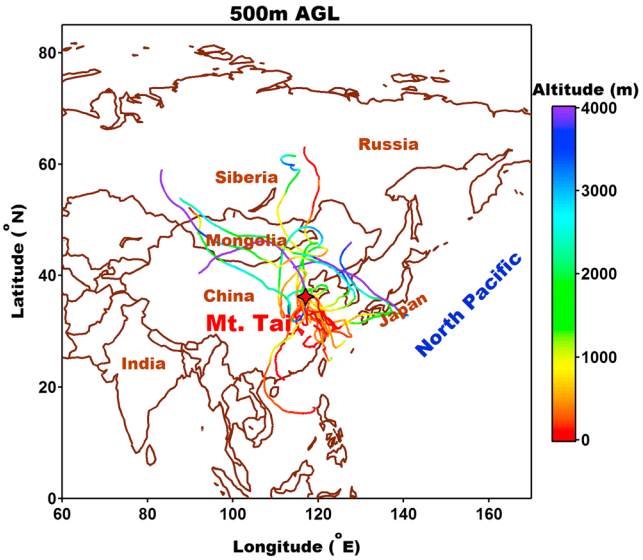

Figure 1. Geographical location of sampling site (Mount Tai; the red star indicates the site), together with the respective 3 day isentropic air mass back-trajectories (6–28 June 2006) at an arrival height of 500 m above ground level as calculated by the HYSPLIT model.

Hydroxy fatty acids (FAs) can be used as tracers for microorganisms such as bacteria, fungi as well as for algae, and higher plants during their transport via air [*Tyagi et al.*, 2015a]. Positional isomers (i.e., α-, β-, and ω-) of these hydroxy FAs have been identified in sediments [*Kawamura and Ishiwatari*, 1982; *Parker et al.*, 1982; *Perry et al.*, 1979; *Wakeham*, 1999], dust [*Fox et al.*, 1993; *Hines et al.*, 2003; *Saraf et al.*, 1997], lake waters and sediments [*Kawamura and Ishiwatari*, 1984; *Kawamura et al.*, 1987; *Zhang et al.*, 2014], snow [*Tyagi et al.*, 2015b], and continental [*Graham et al.*, 2003; *Lee et al.*, 2004] and marine aerosols [*Kawamura*, 1995; *Tyagi et al.*, 2015a]. Among the three isomers, β-hydroxy FAs (from C_{10} to C_{18}) have been reported as chemical markers for the GNB as they are abundant in their cell membrane and are also responsible for their toxic effects (e.g., respiratory problems and skin infections) [*Ratledge and Wilkinson*, 1988]. Similarly, short-chain α-hydroxy FAs (typically C_{12} to C_{20}) are the structural constituents of many soil microorganisms (e.g., bacteria, fungi, yeasts, and protozoa) [*Ratledge and Wilkinson*, 1988]. Long-chain α-, β-, and ω-hydroxy FAs (C_{16} to C_{32}) are abundant in microalgae, cyanobacteria [*Matsumoto and Nagashima*, 1984; *Matsumoto et al.*, 1984], sea grasses [*Volkman et al.*, 1999], and plant waxes [*Rogge et al.*, 1993; *Simoneit*, 1989]. Moreover, these α-, β-, and ω-hydroxy FAs can also act as intermediates of photochemical and microbial oxidation of long-chain monocarboxylic acids to dicarboxylic acids [*Volkman et al.*, 1998; *Wakeham*, 1999].

Concentrations and molecular distributions of hydroxy FAs and their spatiotemporal variability in the atmosphere are, in particular, useful to better assess the long-range transport of soil microbes and plant waxes. The mountain sites and high-altitude towers provide a means to assess the sources and transport pathways of atmospheric aerosols. To understand the impacts of biomass burning on soil- and plant-associated microbes (in particular GNB) as well as higher plant waxes, we measured hydroxy FAs in the aerosol samples collected over Mount Tai, located in the North China Plain (NCP). The objective of this study is to examine the impact of wheat residue burning on the emissions of airborne soil microorganisms and higher plant waxes over Mount Tai through the atmospheric abundances and molecular distributions of hydroxy FAs.

2. Materials and Methods

2.1. Sampling Site and Prevailing Meteorology

Aerosol samples (total suspended particles (TSP)) were collected at the summit of Mount Tai (36.25°N, 117.10° E; 1534 m above sea level), which is surrounded by flat lands (<200 m in altitude) and an independent peak in Shandong province, central East China (Figure S1 in the supporting information). Due to its sufficient elevation, Mount Tai intercepts the Asian outflow, and the mountain top is mostly covered with rocks and bushes. Since the summit of Mount Tai intervenes into in the free troposphere (i.e., above the planetary boundary layer) during nighttime, perhaps, it could serve as an ideal site to study the atmospheric chemistry [*Kanaya et al.*, 2013; *Kawamura et al.*, 2013] and also to trace the chemical markers of the soil microorganisms and plant metabolites. Moreover, prevailing meteorology dictates the physico-chemical properties of aerosols over Mount Tai. Generally, winds come from the west or southwest, however, during the periods of 8–10 and 14–15 June 2006; the northwest to north winds were dominated, delivering cold and dry air masses from Northern China and Siberia over Mount Tai (Figures 1 and S2) [*Kanaya et al.*, 2013].

2.2. Aerosol Samples Collection and Analyses

Total suspended particles (TSP) were collected on a day/night basis from 6 to 28 June 2006 ($n = 20$) as part of the Mount Tai Experiment (MTX2006) campaign. An overview of the aerosol collection and sampling site is given in our previous publications [*Kanaya et al*., 2013, and references therein]. The TSP samples were collected on precombusted (450°C for 6 h) quartz fiber filters, 20 × 25 cm, PALLFLEX®™ 2500QAT-UP, using a high-volume air sampler (flow rate: 1.0 m^3 min^{-1}). The filter samples including three blanks were placed individually in a cleaned glass bottle (150 mL) with a Teflon-lined screw cap and transported to the laboratory in Sapporo. After the collection, aerosol samples were stored at −20°C until analysis. More detailed description regarding the meteorological conditions and aerosol collection over Mount Tai can be seen in our previous publications [*Fu et al*., 2008; *Kanaya et al*., 2013; *Kawamura et al*., 2013].

2.3. Sample Extraction, Derivatization, and Gas Chromatography/Mass Spectrometry Analyses

Aerosol filter samples were analyzed for hydroxy FAs by using the detailed analytical protocol described in *Kawamura et al*. [2003]. Briefly, each filter aliquot (~10 cm^2) was saponified with 10 mL of 0.1 M KOH/methanol solution at 80°C for 2 h, followed by the ultrasonication with dichloromethane (DCM) (10 mL × 3). The extracts were combined and concentrated under vacuum, followed by the extraction of the neutral fraction with *n*-hexane/DCM (10:1) mixture. The remaining solution was acidified with 6 M HCl, and carboxylic acids were extracted with DCM. Furthermore, carboxylic acids were derivatized with 14% BF_3/methanol to their fatty acid methyl esters (FAMEs). FAMEs containing hydroxyl groups were then derivatized with N,O-*bis*-(trimethylsilyl) trifluoroacetamide (SUPELCO™ Analytical) at 70°C for 1 h to convert them into trimethylsilyl (TMS) ethers. After the reaction, 50 μL of *n*-hexane solution containing 1.43 ng μL^{-1} of internal standard (C_{13} *n*-alkane/tridecane, Wako) were added to dilute the derivatives prior to the injection to gas chromatography/mass spectrometry (GC/MS) (Agilent Technologies, Model 7890 GC coupled to Hewlett-Packard Model 5975 C inert XL EI/CI mass-selective detector with the Triple-Axis Detector). The GC was installed with a split/splitless injector and HP-5 fused silica column (Agilent 19091 J-202; 325°C; 19 m × 200 μm, 0.5 μm film thickness).

For the quantification of hydroxy FAs, the GC oven temperature was programmed from 50°C (2 min) to 120°C (15°C min^{-1}), then to 305°C (15 min) at 5°C min^{-1}. Helium was used as a carrier gas at a flow rate of 1 mL min^{-1}. Mass spectrometer was scanned from 50 to 650 Da and operated on electron impact (EI) mode at 70 eV. Data were acquired and processed with a Chemstation software. Identification of hydroxy FAs was performed by comparing retention times and mass spectra with those of authentic TMS derivatives of α-hydroxy FAs (*n*-C_{12} and C_{16}), β-hydroxy FAs (*n*-C_{12}, C_{14}, C_{15}, and C_{16}), and ω-hydroxy FAs (*n*-C_{16}, C_{20}, and C_{22}), which were also used as external standards. The recoveries of authentic β- and ω-hydroxy FA standards were better than 60% and 70%, respectively. Blank filters were also extracted as the real samples, and no target compounds were detected.

2.4. Endotoxin Levels and GNB Dry Mass

We estimated atmospheric abundances of endotoxin and mass loading of Gram-negative bacteria (GNB) on a basis of β-hydroxy FAs from C_{10} to C_{18} [*Hines et al*., 2003; *Lee et al*., 2004; *Tyagi et al*., 2015b; *Wilkinson*, 1988; *Zähringer et al*., 1993] using the mathematical expression as given below:

$$\text{Endotoxin}\left(\text{LPS},\ \text{ng m}^{-3}\right) = \left[\left(\Sigma(C_{10}\text{-}C_{18})\beta\text{-hydroxy FAs},\ \text{nmol m}^{-3}/4 \times 8000\right]\right. \quad (1)$$

In equation (1), endotoxin was assumed to have an average molecular weight of 8000 and to contain four β-hydroxy FAs [*Mielniczuk et al*., 1993]. The sum of β-hydroxy FAs in the mathematical expression represents total (lipopolysaccharide (LPS)-bound + free) hydroxy FAs. To convert the concentrations of β-hydroxy FAs to endotoxin units (EU), the value in nanograms (ng) was multiplied by 10 [*Pomorska et al*., 2007] and final endotoxin concentrations were reported in EU m^{-3}. In this study, a marker to bacterial mass conversion factor of 15 nmol of β-hydroxy FAs (C_{10}–C_{18}) per milligram dry cell weight is used to estimate the mass loading of GNB, which is consistent with previous studies [*Balkwill et al*., 1988; *Lee et al*., 2004; *Tyagi et al*., 2015b]. Here endotoxin concentrations and GNB dry mass were expressed in EU m^{-3} and ng m^{-3} of sampled air, respectively.

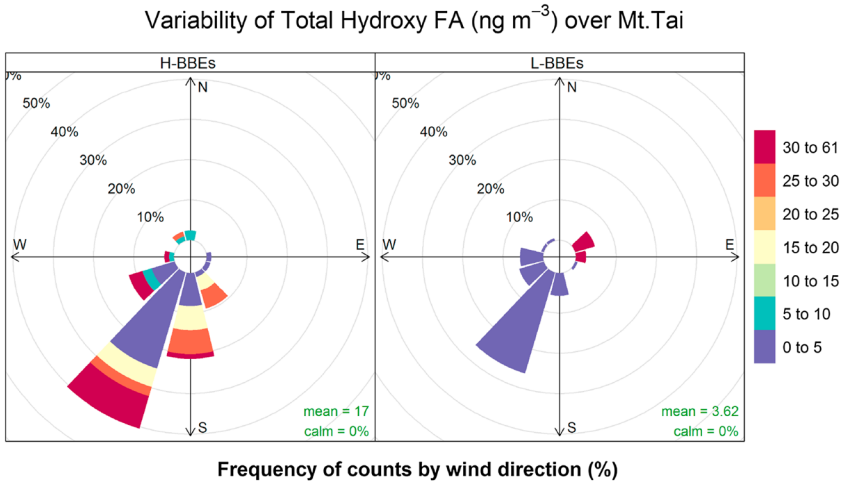

Figure 2. Pollution rose diagram for total hydroxy fatty acid mass concentration in ambient 790 aerosols (TSP) collected over Mt. Tai during MTX-2006 campaign.

3. Results and Discussion

3.1. Fire Counts, Pollution Rose, and Air Mass Backward Trajectory Analysis

To assess the probable source regions contributing to atmospheric abundances of hydroxy FAs over Mount Tai, 3 day isentropic air mass backward trajectories (AMBTs) were computed for the sampling days (Figure 1) using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, [*Draxler and Rolph*, 2013, and references therein]. The HYSPLIT model used the archived meteorological data sets (Global Data Assimilation System, from 1940 to present) from the National Oceanic and Atmospheric Administration (NOAA) air resources laboratory as an input file. Furthermore, the back trajectory analyses were combined with fire count data (obtained from https://earthdata.nasa.gov/data/near-real-time-data/firms) to identify the contribution of biomass-burning activities (specific for our sampling duration) in the NCP and Southeast Asia to the aerosols sampled over Mount Tai (Figure S3). This is to examine the contribution from various source regions and the influence of biomass-burning events (BBEs) on the atmospheric abundances of hydroxy FAs. The AMBT analyses revealed a generalized pattern with the maximum contribution from local sources such as Anhui, Jiangsu, Shandong, Henan, and Hebei in the NCP in early June of 2006 (Figures 1 and S2). However, occasionally, for some sampling days (mostly in the late June), AMBT analyses showed long-range transport from Russia, Siberia, Mongolia, eastern China, and southern part of Japan. The TSP samples from Mount Tai were also analyzed for biomass combustion tracers [*Fu et al.*, 2008].

We used pollution rose diagrams to examine the variability of atmospheric abundances of hydroxy FAs with wind frequency (i.e., percentage of winds blowing from a certain direction for a particular time period compared to total) and wind direction over Mount Tai. In general, high mass concentrations of total hydroxy FAs over Mount Tai are mostly associated with the atmospheric transport from South and Southwest. However, a sudden change in prevailing winds from South and Southwest to North was observed during 8–10 and 14–15 June 2006, while Mount Tai received air masses originated from East China during 22–25 June 2006 (Figure 2). The impact of wheat harvest residue burning emissions in the NCP on Mount Tai aerosols was documented by previous studies [*Fu et al.*, 2008; *Suthawaree et al.*, 2010; *Yamaji et al.*, 2010]. Consequently, we differentiated the concentration data of hydroxy FAs into two categories as days with high (H-BBEs: 6–7, 11–14, and 27 June 2006) and low biomass-burning emissions (L-BBEs: 15–26 and 28 June 2006). This classification was solely based on the relatively high concentrations of levoglucosan [*Fu et al.*, 2008], a pyrolysis product of cellulose and hemicellulose [*Simoneit et al.*, 1999], during H-BBEs ($>500\,ng\,m^{-3}$) compared to those observed during L-BBEs ($<120\,ng\,m^{-3}$). To assess a succinct influence of fire events in the NCP on the atmospheric abundances of soil microbes, hydroxy FAs were not assayed for the "clean period" (8–10 and 14–15 June) as explained in *Kanaya et al.* [2013].

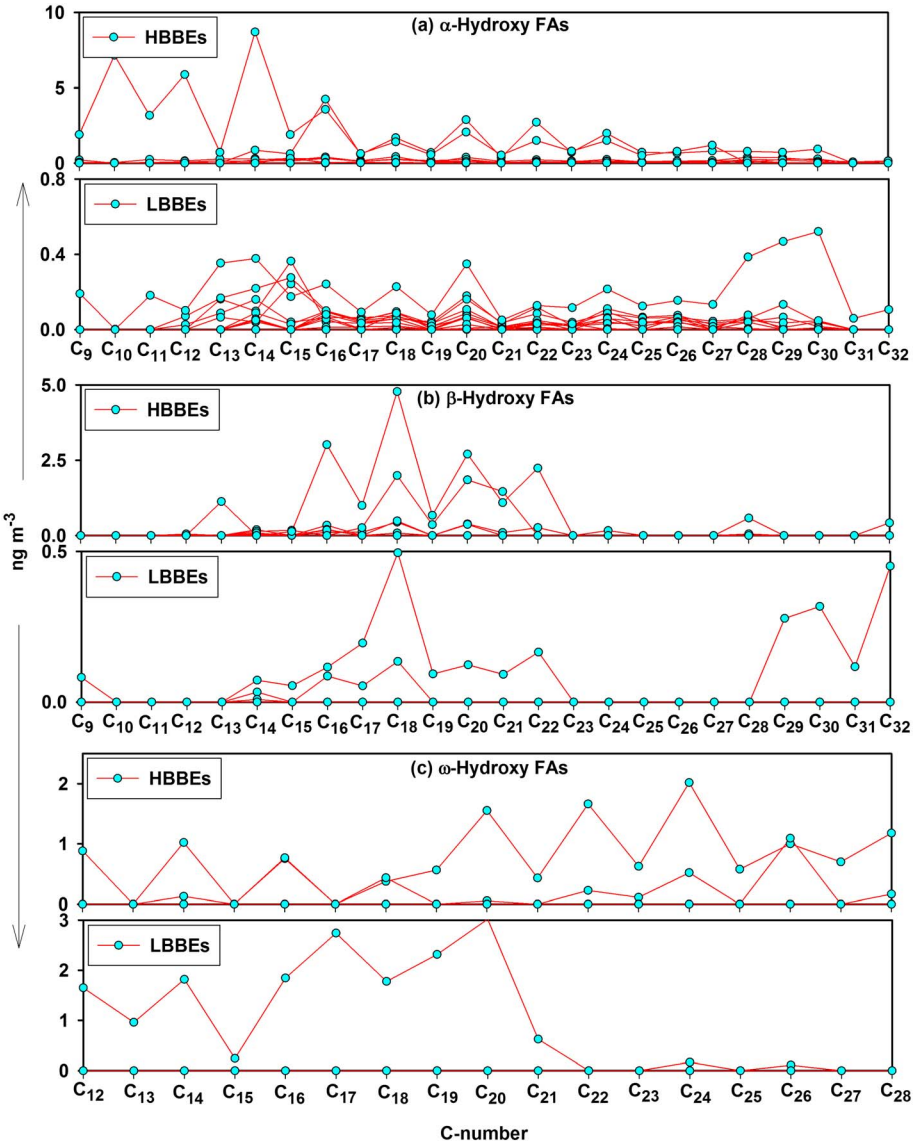

Figure 3. Molecular distributions of (a) α-hydroxy FAs (C_9–C_{32}), (b) β-hydroxy FAs (C_9–C_{32}), and (c) ω-hydroxy FAs (C_{12}–C_{28}) during high (H-BBEs, top) and low (L-BBEs, bottom) biomass-burning emissions in summertime aerosols collected over Mount Tai.

3.2. Molecular Distribution

We detected a homologues series of α-(C_9–C_{32})-hydroxy FAs during both H- and L-BBEs (Figure 3a). However, β- and ω-hydroxy FAs were found in relatively small number of samples ($n = 10$ and $n = 4$, respectively). In general, higher concentrations of α- and β-hydroxy FAs were detected by during H-BBEs (Table 1), which might be due to their contribution from open field burning in the NCP (also supported by the AMBTs). It has been suggested that soil- and plant-associated microbiota are the major sources of airborne hydroxy FAs [*Lee et al*., 2004; *Rogge et al*., 1993; *Zelles*, 1997; *Zogg et al*., 1997]). Therefore, we attribute the sources of hydroxy FAs over Mount Tai to the contribution from the soil microbes/plant pathogens associated with fugitive dust/aerosols from the agricultural fields in the NCP. Furthermore, Mount Tai is located within the NCP and significantly influenced by the emissions of organic aerosols derived from large-scale field burning activities in the NCP as supported by other molecular markers [*Kawamura et al*., 2013; *Fu et al*., 2008].

The measured β-hydroxy FAs are the structural cell membrane lipid components of soil microbes. The even carbon predominance of β-hydroxy FAs is a source specific indicator for the contribution from soil GNB.

Table 1. A Summary of α-, β-, and ω-Hydroxy Fatty Acids (FAs) Measured in Aerosols Collected Over Mount Tai During High (H-BBEs: 6–14 and 27 June 2006) and Low Biomass-Burning Emissions (L-BBEs: 15–26 and 28 June 2006) in the NCP[a]

	H-BBEs ($n = 8$; ng m^{-3})			L-BBEs ($n = 12$; ng m^{-3})		
Compounds	Mean ± SE	Range	Median	Mean ± SE	Range	Median
			α-Hydroxy FAs			
C_9	0.72 ± 0.59	0.06–1.89	0.22	0.19 ± 0.00	0.00–0.19	0.19
C_{10}	3.60 ± 3.56	0.04–7.16	3.60	0.002 ± 0.00	0.00–0.002	0.002
C_{11}	1.16 ± 1.01	0.05–3.17	0.24	0.18 ± 0.00	0.00–0.18	0.18
C_{12}	1.25 ± 1.16	0.04–5.87	0.12	0.07 ± 0.02	0.03–0.10	0.07
C_{13}	0.38 ± 0.17	0.15–0.72	0.27	0.17 ± 0.05	0.07–0.35	0.16
C_{14}	1.19 ± 1.07	0.07–8.70	0.25	0.13 ± 0.04	0.04–0.38	0.09
C_{15}	0.55 ± 0.23	0.13–1.90	0.31	0.19 ± 0.05	0.03–0.36	0.21
C_{16}	1.27 ± 0.69	0.02–4.25	0.31	0.09 ± 0.02	0.01–0.24	0.08
C_{17}	0.22 ± 0.09	0.01–0.63	0.12	0.04 ± 0.01	0.00–0.09	0.04
C_{18}	0.59 ± 0.26	0.03–1.69	0.27	0.08 ± 0.02	0.01–0.23	0.07
C_{19}	0.23 ± 0.11	0.03–0.70	0.11	0.03 ± 0.01	0.00–0.08	0.03
C_{20}	0.84 ± 0.43	0.02–2.88	0.25	0.10 ± 0.03	0.00–0.35	0.07
C_{21}	0.18 ± 0.07	0.03–0.53	0.08	0.02 ± 0.01	0.01–0.05	0.02
C_{22}	0.61 ± 0.07	0.02–2.71	0.11	0.05 ± 0.01	0.00–0.13	0.04
C_{23}	0.25 ± 0.11	0.02–0.80	0.10	0.03 ± 0.01	0.01–0.12	0.02
C_{24}	0.53 ± 0.27	0.01–1.98	0.14	0.08 ± 0.02	0.00–0.22	0.06
C_{25}	0.21 ± 0.09	0.02–0.72	0.10	0.05 ± 0.01	0.02–0.13	0.04
C_{26}	0.26 ± 0.10	0.02–0.78	0.13	0.06 ± 0.01	0.01–0.16	0.06
C_{27}	0.36 ± 0.17	0.02–1.19	0.16	0.04 ± 0.02	0.01–0.13	0.03
C_{28}	0.31 ± 0.11	0.07–0.78	0.22	0.09 ± 0.04	0.01–0.39	0.05
C_{29}	0.27 ± 0.11	0.02–0.72	0.23	0.14 ± 0.08	0.01–0.47	0.07
C_{30}	0.31 ± 0.16	0.04–0.93	0.19	0.11 ± 0.08	0.01–0.52	0.04
C_{31}	0.08 ± 0.00	0.00–0.08	0.08	0.06 ± 0.00	0.00–0.06	0.06
C_{32}	0.14 ± 0.00	0.14–0.15	0.14	0.11 ± 0.00	0.00–0.11	0.11
Subtotal	10.08 ± 5.50	0.17–44.46	3.35	1.04 ± 0.38	4.84–12.5	0.68
			β-Hydroxy FAs			
C_9				0.08 ± 0.00	0.00–0.08	0.08
C_{12}	0.03 ± 0.02	0.01–0.05	0.03			
C_{13}	1.13 ± 0.00	0.00–1.13	1.13			
C_{14}	0.09 ± 0.04	0.04–0.19	0.08	0.04 ± 0.02	0.01–0.17	0.03
C_{15}	0.10 ± 0.05	0.01–0.17	0.13	0.05 ± 0.00	0.00–0.05	0.05
C_{16}	0.77 ± 0.56	0.10–3.02	0.20	0.10 ± 0.01	0.09–0.12	0.10
C_{17}	0.46 ± 0.27	0.11–1.00	0.26	0.12 ± 0.07	0.05–0.20	0.12
C_{18}	1.56 ± 0.87	0.09–4.78	0.48	0.32 ± 0.18	0.13–0.50	0.32
C_{19}	0.52 ± 0.16	0.36–0.67	0.52	0.09 ± 0.00	0.00–0.09	0.09
C_{20}	1.33 ± 0.58	0.37–2.71	1.12	0.12 ± 0.00	0.00–0.12	0.12
C_{21}	0.88 ± 0.41	0.10–1.46	1.09	0.09 ± 0.00	0.00–0.09	0.09
C_{22}	1.25 ± 0.99	0.26–2.24	1.25	0.17 ± 0.00	0.00–0.17	0.17
C_{24}	0.16 ± 0.00	0.00–0.16	0.16			
C_{28}	0.32 ± 0.26	0.05–0.58	0.32			
C_{29}				0.28 ± 0.00	0.00–0.28	0.28
C_{30}				0.32 ± 0.00	0.00–0.32	0.32
C_{31}				0.12 ± 0.00	0.00–0.12	0.12
C_{32}	0.42 ± 0.00	0.00–0.42	0.42	0.45 ± 0.00	0.00–0.45	0.45
Subtotal	3.47 ± 2.06	0.00–16.8	0.93	0.25 ± 0.22	0.00–2.66	0.00
			ω-Hydroxy FAs			
C_{12}	0.88 ± 0.00	0.00–0.88	0.88	1.65 ± 0.00	0.00–1.65	1.65
C_{13}				0.96 ± 0.00	0.00–0.96	0.96
C_{14}	0.57 ± 0.45	0.13–1.02	0.57	1.82 ± 0.00	0.00–1.82	1.82
C_{15}				0.24 ± 0.00	0.00–0.24	0.24
C_{16}	0.76 ± 0.01	0.75–0.77	0.76	1.84 ± 0.00	0.00–1.84	1.84
C_{17}				2.74 ± 0.00	0.00–2.74	2.74
C_{18}	0.41 ± 0.03	0.38–0.44	0.41	1.78 ± 0.00	0.00–1.78	1.78
C_{19}	0.56 ± 0.00	0.00–0.56	0.56	2.32 ± 0.00	0.00–2.32	2.32
C_{20}	0.80 ± 0.75	0.05–1.55	0.80	3.02 ± 0.00	0.00–3.02	3.02
C_{21}	0.22 ± 0.22	0.00–0.43	0.22	0.63 ± 0.00	0.00–0.63	0.63
C_{22}	0.94 ± 0.72	0.23–1.66	0.94	1.42 ± 0.00	0.00–1.42	1.42
C_{23}	0.37 ± 0.26	0.11–0.63	0.37	0.59 ± 0.00	0.00–0.59	0.59

Table 1. (continued)

Compounds	H-BBEs ($n = 8$; ng m^{-3})			L-BBEs ($n = 12$; ng m^{-3})		
	Mean ± SE	Range	Median	Mean ± SE	Range	Median
C_{24}	1.27 ± 0.75	0.52–2.02	1.27	1.45 ± 1.28	0.17–2.73	1.45
C_{25}	0.58 ± 0.00	0.00–0.58	0.58	1.94 ± 0.00	0.00–1.94	1.94
C_{26}	1.05 ± 0.05	1.00–1.09	1.05	1.59 ± 1.48	0.11–3.07	1.59
C_{27}	0.70 ± 0.00	0.00–0.70	0.70	0.83 ± 0.00	0.00–0.83	0.83
C_{28}	0.67 ± 0.51	0.17–1.18	0.67	1.75 ± 0.00	0.00–1.75	1.75
Subtotal	8.42 ± 4.92	3.50–13.34	8.42	14.8 ± 14.5	0.28–29.3	14.80

[a]SE (standard error) = $\sigma/N^{1/2}$, *where* σ *refers to the standard deviation of total samples* (N).

Several studies have documented a similar feature that pertains to even carbon number predominance for the soil GNB worldwide. The AMBTs for the sampling days and cluster analysis revealed a dominant contribution from the NCP. Moreover, a lack of significant shift in the molecular distributions of β-hydroxy FAs could be expected if these are derived via in situ formation in the atmosphere or derived from industrial emissions. Further, we observed a significant correlation (Table 2) of β-hydroxy FAs with other soil microbe tracers (e.g., trehalose, a proxy for fungal spores in soils), indicating an impact of biomass-burning emissions and associated atmospheric processes in the NCP.

The molecular distributions of α-hydroxy FAs (Figure 3a) showed even C-number predominance during H-BBEs and followed the sequence as $C_{14} > C_{10} > C_{16} \approx C_{12}$. However, no such pattern in the molecular distributions of α-hydroxy FAs was observed during L-BBEs (Figure 3a). Furthermore, the relative abundance of even C-numbered α-hydroxy FAs to their total mass concentration (i.e., Σeven and odd C) was ~71% during H-BBEs and ~61% during L-BBEs. Moreover, total mass concentrations of α-hydroxy FAs were higher than those of β- and ω-isomers over Mount Tai in June 2006 (Table 1). *González-Pérez et al.* [2004] discussed the effect of biomass burning on soil organic matter. According to their study, lipid fraction of soil organic matter undergoes substantial changes (i.e., translocation of organic matter) as a result of high-temperature biomass combustion (e.g., forest fires). Interestingly, *Poole et al.* [2010] documented that β-hydroxy FAs and associated endotoxin levels were found to be highest in the atmospheric mineral dust from the agricultural fields. However, their study focuses on the settled agricultural dust from the fields rather than the re-suspended atmospheric mineral dust during fire activities (this study). Therefore, observed predominance of α-hydroxy FAs followed by β- and ω-hydroxy FAs over Mount Tai could be due to a prevalent change in their distribution pattern of lipid compounds during biomass-burning emissions in the NCP.

The molecular distributions of β-hydroxy FAs also exhibited even C-number predominance, among which C_{18} was dominant followed by C_{16} or C_{20} (Figure 3b). These observations were contrary to those reported in the sediments and cell membrane of GNB, where molecular distributions were characterized by the

Table 2. Pearson Correlation Coefficient (r) Among the Measured Hydroxy Fatty Acids (FAs) and Other Chemical Compounds in TSP Collected Over Mount Tai in the North China Plain During the Period of Wheat Residue Burning (6–28 June 2006)[a]

Parameter	[b]$\Sigma\alpha$-Hydroxy FAs	[c]$\Sigma\beta$-Hydroxy FAs	[d]$\Sigma\omega$-Hydroxy FAs	Galactosan	Mannosan	Levoglucosan	Arabitol	Mannitol	Trehalose
$\Sigma\alpha$-Hydroxy FAs	1.00								
$\Sigma\beta$-Hydroxy FAs	0.99	1.00							
$\Sigma\omega$-Hydroxy FAs	−0.02	0.11	1.00						
Galactosan	0.92	0.63	−0.04	1.00					
Mannosan	0.91	0.57	−0.05	0.95	1.00				
Levoglucosan	0.91	0.64	−0.05	0.99	0.98	1.00			
Arabitol	0.80	0.92	−0.03	0.83	0.79	0.83	1.00		
Mannitol	0.80	0.86	−0.05	0.72	0.71	0.72	0.96	1.00	
Trehalose	0.54	[d]0.71	−0.25	0.69	0.61	0.69	0.76	0.74	1.00

[a]Note that r-critical is the probability of n measurements (i.e., total number of samples) of two uncorrelated variables that would yield a correlation coefficient comparable to or greater than a particular value [*Pugh and Winslow*, 1966].
[b]For $\alpha-$ hydroxy FAs, $n = 16$; r-critical = 0.5; error = 5%.
[c]For $\beta-$ hydroxy FAs, $n = 7$; r-critical = 0.8; error = 3%; # correspond to r-critical = 0.7 with error of 8%.
[d]For $\omega-$ hydroxy FAs; correlation coefficients are rather weak due to the limited number of sample with detection ($n = 4$).

predominance of C_{16} and/or C_{14} [*Hedrick et al*., 2009; *Zhang et al*., 2014]. This could be due to an increased soil temperature of agricultural fields (i.e., up to 300°C) in the NCP during BBEs. LPS-derived β-hydroxy FAs are sensitive to soil temperature [*Zogg et al*., 1997]; thus, increased ground heating during biomass burning can affect their molecular distributions, emitting lower molecular weight species to gaseous phase. *Zogg et al*. [1997] examined the variability of molecular distribution of β-hydroxy FAs in soil for lower temperatures (5–25°C) than what is usually observed during BBEs (i.e., as high as 300–1000°C). Therefore, we attribute the observed shifts in molecular distributions of β-hydroxy FAs to their contribution from disturbed agricultural soils during BBEs in the NCP.

Moreover, at extremely high temperature, thermal evaporation or degradation of hydroxy FAs can occur in soil- and plant-associated bacteria. For example, molecular distributions of long-chain *n*-alkane from rye and maize combustion shifted to their short-chain homologues at 500°C, maximizing at C_{18} with the predominance of even C-numbered compounds [*Wiesenberg et al*., 2009]. Therefore, observed molecular distributions of hydroxy FAs during BBEs could be different than those from the complete absence of biomass combustion. Although the mass concentrations of atmospheric ω-hydroxy FAs were similar to those of both H-BBEs and L-BBEs, we observed significant shifts in the temporal variability of their molecular distributions over Mount Tai. Molecular distributions of ω-hydroxy FAs were also characterized by an even C-number predominance with the occurrence of high molecular weight (HMW) compounds ($>C_{20}$) during H-BBEs and of low molecular weight (LMW) compounds ($<C_{20}$) during L-BBEs (Figure 3c).

The even C-numbered predominance of hydroxy FAs in this study indicates the contribution from soil microbes and vascular plants. It has been suggested that lipids from terrestrial biomass (i.e., either soil organic matter or plant waxes), in particular saturated fatty acids, are characterized by the predominance of even C-numbered compounds [*Wiesenberg et al*., 2009]. For instance, saturated n-fatty acids from C_{20} to C_{32} with strong even/odd predominance are specific to epicuticular waxes [*Eglinton and Hamilton*, 1967; *Meyers*, 2003], which have been found in soils [*Morrison*, 1969], lake sediments [*Cranwell*, 1981], and deep-sea sediments [*Simoneit*, 1977]. Likewise, *Volkman et al*. [1998] documented a significant contribution of even C-numbered saturated hydroxy FAs from microalgal sources in lacustrine and intertidal sediments. The air mass back trajectory analyses for the sampling periods over Mount Tai showed an atmospheric transport from the NCP. Because the air masses had a substantial influence from BBEs in the NCP, even/odd carbon predominance of hydroxy FAs over Mount Tai indicates a significant contribution from microbial biomass associated with soil organic matter emitted during fire activities.

3.3. Average Temporal Concentration of Hydroxy FAs

The impact of the emissions of postharvest crop-residue burning in the NCP to TSP collected over Mount Tai was ascertained through the analyses of various organic markers such as diacids, sugars, and anhydrosugars [*Fu et al*., 2008; *Kawamura et al*., 2013]. Therefore, hydroxy FAs over Mount Tai can have a contribution either from biomass burning or an associated process during biomass combustion (e.g., re-suspension of soil-dust during fire activities). This inference was based on the covariability of atmospheric concentrations of hydroxy FAs (Figure 4) with levoglucosan (a proxy for BBEs), trehalose and mannitol (tracers for soil microbes) [*Fu et al*., 2008] over Mount Tai. Soil microbes or plant pathogen can also be transported long distances through synoptic-scale atmospheric circulations. For instance, numerous studies have documented a significance of long-range transport of Siberian forest fire-derived aerosols on the lipid class compounds [*Yamamoto et al*., 2011], dicarboxylic acids [*Aggarwal and Kawamura*, 2008; *Pavuluri et al*., 2013], and soil microbes [*Tyagi et al*., 2015b]. On a similar way, *Fang et al*. [1999] observed higher input of vascular plant markers (alkanes, alkanols, and alkanoic acids) in late September when BBEs were intense in Indonesia. Since Mount Tai also received a transported air mass from Mongolia and Siberia for some sampling days in late June, it is likely that soil microbes/plant pathogens from these regions are responsible to the measured hydroxy FAs.

The high concentrations of levoglucosan (400–5000 ng m^{-3}) during the study period indicate a significant contribution from biomass-burning activities. In contrast, trehalose and mannitol were found in surface soils of crop fields, being associated with fugitive dust in atmospheric particulate matter [*Rogge et al*., 2007]. Furthermore, trehalose was also found in aerosols sampled during the wheat straw burning [*Wang et al*., 2011]. Higher temperatures and convective currents generated during H-BBEs could result in the suspension of fugitive dust and associated microbial biomass from the agricultural fields in the

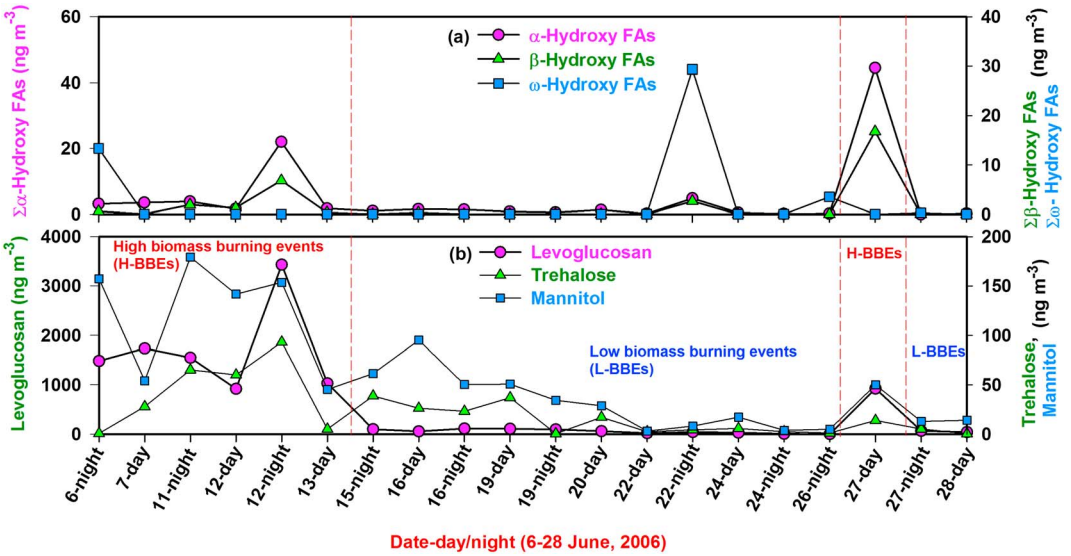

Figure 4. Temporal variability of concentrations of (a) α-, β-, and ω-hydroxy FAs and (b) levoglucosan, trehalose, and mannitol [*Fu et al.*, 2008] in aerosols collected over Mount Tai with respect to H-BBEs (6–14 and 27 June) and L-BBEs (15–26 and 28 June) in northern China during the summer of 2006.

NCP. Therefore, similar temporal trends of hydroxy FAs (present study) with levoglucosan, trehalose, and mannitol (Figure 4) revealed that biomass-burning activities could be an indirect source of soil microbes in airborne particulate matter via the injection of soil-dust particles.

In the previous studies, few reports discuss an impact of BBEs on airborne microorganisms. For example, forest fires lead to a significant reduction in the abundance of the bacterial biomass due to the heat shock generated by fire emissions [*Adeniyi*, 2010; *Neary et al.*, 1999; *Xiang et al.*, 2014]. In this study, we observed a sporadic decrease in atmospheric abundances of hydroxy FAs after BBEs, as evidenced by the apparently constant ratio of HMW/LMW hydroxy FAs (i.e., confirmed by the unpaired two-tailed *t* test; Table S1 in the supporting information). Being consistent with our results, higher abundances of HMW fatty acids (C_{20}–C_{30}) were also reported in the same TSP samples from Mount Tai [*Fu et al.*, 2008], suggesting the dominance of wheat straw burning in early June 2006. Thus, concentrations of hydroxy FA were lower just after the BBEs in the NCP.

3.4. Relative Abundances

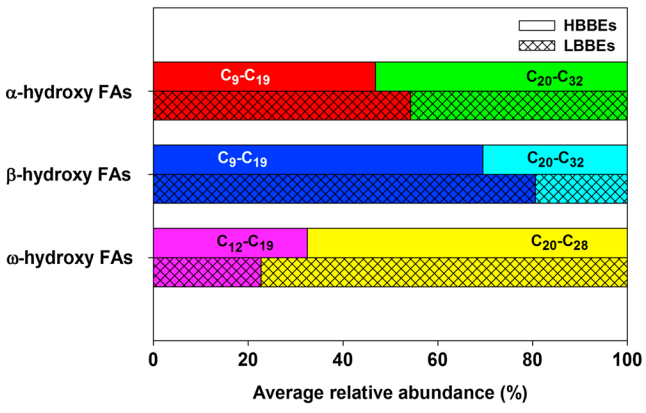

Figure 5. Relative abundances of low molecular weight (LMW) α-($C_9 - C_{19}$), β-($C_9 - C_{19}$), and ω-($C_{12} - C_{28}$)-hydroxy FAs and high molecular weight (HMW) α-($C_{20} - C_{32}$), β-($C_{20} - C_{32}$), and ω-($C_{20} - C_{28}$)-hydroxy FAs in the aerosols collected over Mount Tai during high and low biomass-burning emissions (H- and L-BBEs).

The relative abundances of two classified groups (i.e., LMW C_9–C_{19} and HMW C_{20}–C_{30} or C_{20}–C_{28}) of α-, β-, and ω-hydroxy FAs to their total mass concentrations were shown in Figure 5. The relative abundances of LMW α- and β-hydroxy FAs (C_9–C_{19}) were higher during L-BBEs (53% and 81%, respectively) than those observed during H-BBEs (49% and 70%, respectively). In particular, molecular distributions of α-hydroxy FAs were characterized by the predominance of LMW species during both L- and H-BBEs (Figure 3a). Although relative abundances of LMW β-hydroxy FAs showed a slight increase from H-BBEs to L-BBEs (similar to α-hydroxy FAs), they dominate in both

events. *Almendros et al*. [1988] observed significant differences in the molecular distributions of microbial lipids in soil after fire activities, with a dominant occurrence of LMW fatty acid homologues (i.e., $<C_{20}$). Therefore, observed predominance of LMW α- and β-hydroxy FAs (C_9–C_{19}) during L-BBEs could be attributed to changes in the molecular distributions of these compounds due to high-temperature biomass combustion in the NCP.

LMW β-hydroxy FAs and, to some extent, α-hydroxy FAs are specific to soil microbes [*Keinänen et al*., 2003; *Wilkinson*, 1988]. These patterns were also found (i.e., predominance of LMW β-hydroxy FAs in the total mass concentrations: Σ(LMW and HMW)) for remote marine aerosols collected over Chichijima Island in the North Pacific [*Tyagi et al*., 2015a]. Therefore, predominance of these two groups of LMW hydroxy FAs (α- and β-) during L-BBEs could represent their background (or undisturbed) signatures of soil microbes. In addition, a predominance of LMW α- and β-hydroxy FAs during H-BBEs could be caused by the charring process of biomass combustion, which usually occurs at high temperatures. As LMW hydroxy FAs have been assigned to soil microbes and plant pathogens (i.e., in particular GNB) and, hence, can be used as a marker for the residues of charred biomass coming from soil surfaces and plant where microbial activity is high.

One reason for changes in the molecular distribution of hydroxy FAs could be higher temperatures associated with biomass combustion, which affect the soil microbes. For instance, *Williams et al*. [2012] reported a substantial decrease (~25%) in GNB abundances, as estimated from phospholipids fatty acid analyses in soils followed by a forest fire. Similarly, predominance of LMW β-hydroxy FAs was also reported for springtime dust-laden aerosols sampled over the Chichijima Island [*Tyagi et al*., 2015a]. Therefore, observed predominance of LMW β-hydroxy FAs over Mount Tai during H- and L-BBEs could be due to their contribution from source specific soil microbes.

In contrast, the predominance of HMW ω-hydroxy FAs in both events (67% in H-BBEs and 77% in L-BBEs) could represent a significant contribution from higher plant waxes (e.g., suberin and cutin; Figure 5). However, LMW ω-hydroxy FAs were in part derived from ω-oxidation of long-chain hydroxy FAs [*Kawamura*, 1995] in soil microbes and might have contributions from higher plants. Overall, distributions of relative abundances in this study were attributed to their common source (i.e., sourced from fugitive dust inputs during H-BBEs/L-BBEs in the NCP) and/or long-range atmospheric transport over Mount Tai.

Among the measured hydroxy FAs, α-isomers dominate the total concentrations of hydroxy FAs during both H- and L-BBEs (~68% and 77%, respectively; Figure S4). The relative abundances of β-hydroxy FAs in total hydroxy FAs showed higher values (~21%) during H-BBEs than those (~2%) during L-BBEs. Although ω-hydroxy FAs (C_{12}-C_{28}) were detected only in few aerosol samples ($n = 4$), their contribution in H-BBEs (~11%) was lower than those observed in L-BBEs (~21%). These discrepancies can be explained on a basis of sources of hydroxy FAs as discussed in previous sections. The predominance of HMW α-hydroxy FAs (C_{20}-C_{32}) in their total mass concentrations was observed (i.e., 53%) during H-BBEs (Figure 5). This observation suggests the contribution from higher plants and also partly from α-oxidation of fatty acids [*Cranwell*, 1981]. In addition, α-isomers can also be produced from the photochemical oxidation of HMW FAs during their long-range atmospheric transport. Hence, these cannot be employed as specific tracers for plant waxes in the environmental samples.

3.5. Source Apportionment-Multiple Linear Regression Analysis

To assess the potential sources/transport pathways, multiple linear correlation matrices were computed among the measured hydroxy FAs and other chemical species (Table 2). It is important to state here that we have detected α-hydroxy FAs in almost all samples ($n = 19$), while β- and ω-hydroxy FAs were identified in limited numbers of samples ($n = 10$ and $n = 4$, respectively). The observed correlations of α- and β-hydroxy FAs with biomass-burning-derived sugar compounds (e.g., galactosan, mannosan, levoglucosan, and trehalose) were quenched by three outliers, in which two sampling dates correspond to H-BBEs (13 and 27 June 2006) and one is from L-BBEs (23 June 2006). Thus, these data points were excluded from the linear regression analyses to get a realistic correlation coefficient.

We found high concentrations of total α-hydroxy FAs (22 ng^{-3}), total β-hydroxy FAs (6.8 ng m^{-3}), and sugar compounds (galactosan: 103 ng m^{-3}, mannosan: 62 ng m^{-3}, levoglucosan: 3.43 μg m^{-3}, and trehalose: 93 ng m^{-3}) on 13 June 2011. Likewise, the TSP samples collected on 27 June 2006 also showed much higher concentrations of sugar compounds (galactosan: 14 ng m^{-3}, mannosan: 32 ng m^{-3}, levoglucosan:

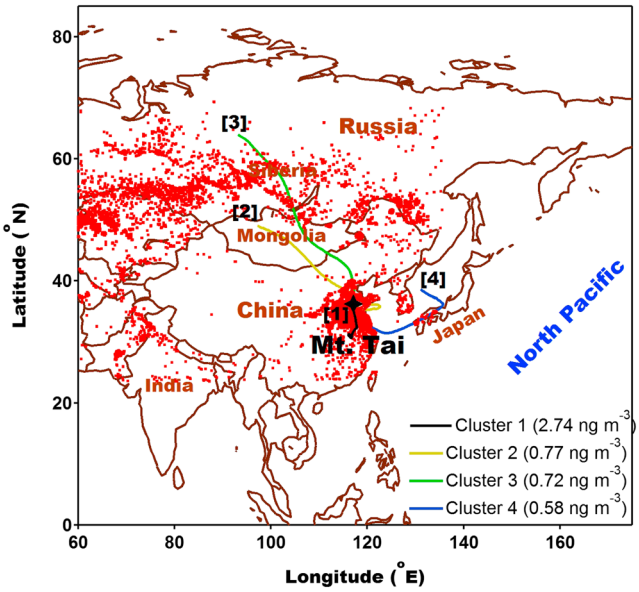

Figure 6. Mean horizontal plots of 7 day isentropic air mass back trajectories at 500 m aboveground level were grouped into four clusters as suggested by the NOAA HYSPLIT model. The colors black, yellow, green, and blue indicate the mean clusters from 1 to 4, respectively. The numbers in parenthesis indicate the concentrations of total ($\alpha+\beta+\omega$) hydroxy FAs (in ng m^{-3}) according to the fraction of trajectories coming from respective source regions. The triangle in black color indicates the location of the sampling site (Mount Tai) and hot spots (fire spots) distribution as red dots.

923 ng m^{-3}, and trehalose: 14 ng m^{-3}) than those collected before and after this date. We found a maximum concentration of total α-hydroxy FAs (44 ng m^{-3}) and total β-hydroxy FAs (17 ng m^{-3}) on 27 June 2006. The temporal shift in the concentrations of these compounds on 27 June 2006 is rather significant in levoglucosan and α-hydroxy FAs (~10-folds). Therefore, concurrent increase in the atmospheric abundances of α-hydroxy FAs and sugar compounds on these specific dates clearly indicates the more pronounced influence of biomass-burning activity in the NCP and subsequent transport to the summit of Mount Tai.

In contrast, we observed a decreasing trend in the mass concentrations of anhydrosugars (i.e., galactosan, mannosan, and levoglucosan) and trehalose on 23 June 2006, while atmospheric abundances of $\Sigma\alpha$- and β-hydroxy FAs increased by a factor of 5 and 10, respectively. The sudden declines in the mass concentrations of sugar compounds are consistent with those of other organic markers measured (e.g., dicarboxylic acids on 23 June 2006). We also observed a sudden shift in prevailing wind direction from Southwest to East over Mount Tai (see Figure 2) during 22–25 June, which was associated with a high-pressure front system located near Japan. Interestingly, for this sampling period, we observed exceptionally high concentrations of total ω-hydroxy FAs (22 ng m^{-3}), much higher than those of $\Sigma\alpha$- and β-hydroxy FAs (4.8 and 2.7 ng m^{-3}, respectively; Figure 2). Therefore, we excluded these three sampling dates (13, 23, and 27 June 2006) while examining the provinces of hydroxy FAs over Mount Tai.

Moderate to strong correlations of α-hydroxy FA with anhydrosugars (i.e., galactosan, mannosan, and levoglucosan: tracers for BBEs) [*Simoneit*, 2002], sugar polyols (e.g., arabitol and mannitol), and sugars (e.g., trehalose) are noteworthy during the study period. Likewise, good correlations were observed among β-hydroxy FAs (tracers for GNB) [*Tyagi et al*., 2015a], arabitol, mannitol, and trehalose (tracers for fungal spore and soil microbes) [*Fu et al*., 2008], suggesting their common source. This can be explained by the dust emissions from agricultural fields in the NCP, Mongolia, and Siberia.

3.6. Potential Sources and Transport Pathways of Hydroxy FAs

To identify the potential sources and transport pathways of hydroxy FAs over Mount Tai, we further performed cluster analysis by using PC-based HYSPLIT model [*Draxler and Rolph*, 2013, and references therein]. The principle behind the cluster analysis was to minimize the spread within the cluster and maximize the variability in between them using *k*-means clustering algorithm in which horizontal moving speed and direction were used as principal parameters [*Hartigan and Wong*, 1979]. We have identified four clusters, which provide information on the potential source regions of hydroxy FAs over Mount Tai (Figure 6). Moreover, fire count data were superimposed with the mean trajectory path of these clusters. This is to ascertain the influence of biomass combustion in the source regions on the emission and transport pathways of bacteria and plant waxes over Mount Tai.

The molecular distributions of hydroxy FAs over Mount Tai can be explained by their contribution from four geographical locations, accounting for 57% (cluster 1: the NCP), 16% (cluster 2: Mongolia), 15%

(cluster 3: Siberia), and 12% (cluster 4: maritime) of TSP samples. The average concentration of total hydroxy FAs (i.e., $\Sigma(\alpha+\beta+\omega)$-hydroxy FAs) multiplied by the percentage of air masses from each cluster (or source) provides a relevant source contribution to Mount Tai (Figure 6). The maximum percentage contribution (57%, cluster 1) of air masses over Mount Tai originates from the NCP (conc., ~2.74 ng m^{-3}) that includes regions such as Anhui, Jiangsu, Shandong, Henan, and Hebei. These regions are characterized by agricultural waste burning after wheat harvest [*Fu et al*., 2008]. Since the mean trajectory pathway is intercepted by BBEs in the NCP (Figures 6 and S3), we infer that biomass combustion and its associated process (e.g., soil- and plant-associated microorganisms) account for the high percentage contribution of hydroxy FAs over Mount Tai.

Long-range atmospheric transport of hydroxy FAs could be an important source of hydroxy FAs over Mount Tai because clusters '2' and '3' showed the contributions from Mongolia and Siberia (av. 0.77 and 0.72 ng m^{-3} of hydroxy FAs, respectively). Arid parts of these regions are the major sources of terrestrial organic matter (lipids) transported to Mount Tai [*Fu et al*., 2008] and further to the western North Pacific [*Kawamura et al*., 2003; *Tyagi et al*., 2015a, 2015b]. Mongolia (cluster 2) is characterized by arid climate, soil-derived particles, and the associated bacteria. Likewise, cluster 3 corresponds to the transport from Siberia (Russia), accounting for 15% of total hydroxy FAs. Since the mean AMBT for cluster 3 is intercepted by BBEs over Siberia (Figure 6), soil microbes and plant metabolites from this region could partly explain the observed concentrations of hydroxy FAs. *Agarwal et al*. [2010] documented an influence of Siberian BBEs on the chemical composition of organic aerosols over East Asia during summer. Hence, we inferred that transport from Siberian BBEs could be an important source of hydroxy FAs in TSP over Mount Tai during the summer of 2006.

Cluster 4 showed a minimal contribution to measured hydroxy FAs (av. 0.58 ng m^{-3}) by the maritime air masses that are traversing from the Sea of Japan to Mount Tai. Several studies suggested that cell metabolites from cyanobacteria and marine algae could be a source of hydroxy FAs [*Volkman et al*., 1998; *Wakeham et al*., 2003; *Wilkinson*, 1988] via sea-to-air emission of microlayer films. Therefore, we infer that the marine-derived contribution could explain, to some extent, the observed atmospheric abundances of hydroxy FAs over Mount Tai.

3.7. Endotoxin Levels and Dry Mass Loading of GNB

We estimated the endotoxin concentrations and dry mass of GNB using β-hydroxy FAs. Endotoxin/lipopolysaccharides (LPS), constituents of GNB cell membranes, are potential inflammatory agents and can lead to adverse health effects on human [*Poole et al*., 2010]. The airborne endotoxin was quantified in various occupational and industrial environments using an assay with kinetic chromogenic limulus amebocyte lysate (LAL) [*Binding et al*., 2004; *Lee et al*., 2004, and references therein]. However, LAL assay includes potential interferences from β-glucans originating from plants/moulds and is not sensitive enough to some bacteria [*Binding et al*., 2004; *Chow et al*., 2015; *Lee et al*., 2004].

Alternately, some studies estimated the endotoxin levels and bacterial dry mass using β-hydroxy FAs [*Lee et al*., 2004, 2007; *Tyagi et al*., 2015b]. These fatty acids are constituents of lipid A of LPS, which are responsible for the health effects of airborne endotoxin [*Binding et al*., 2004; *Ratledge and Wilkinson*, 1988]. Few studies addressed the health burden of prolonged exposure to endotoxin emitted from the different biomass combustion in homes [*Rosati et al*., 2005; *Semple et al*., 2010]. However, any single study has not been performed on airborne endotoxin measurement in open field biomass-burning emissions and their atmospheric transport to distant regions.

We report here the influence of biomass combustion on the emission and atmospheric transport of GNB and endotoxin (discussed in section 2.3) to Mount Tai. Endotoxin concentrations reported in this study (Table 3) are 5 times higher during H-BBEs (117 EU m^{-3}) compared to those estimated during L-BBEs (22.5 EU m^{-3}). These are consistent with the higher atmospheric abundances of GNB tracers (i.e., β-hydroxy FAs (C_{10}–C_{18}) during L-BBEs: 0.42 ng m^{-3} and H-BBEs: 2.15 ng m^{-3}). This could be caused by the increased emissions of GNB associated with soil-dust and plant pathogens during H-BBEs than those occurred during L-BBEs. Endotoxin levels in H-BBEs are slightly higher (117 ± 74 EU m^{-3}) than those documented in domestic wood-burning emissions from Nepal and Malawi (43 EU m^{-3} and 40 EU m^{-3}, respectively) [*Semple et al*., 2010]. However, endotoxin concentrations reported in the wood burning emissions [*Semple et al*., 2010] are comparable to those observed during L-BBEs (22.5 ± 14.6 EU m^{-3}). Surprisingly, *Rosati et al*. [2005]

Table 3. A Statistical Summary of the Estimated Endotoxin and Dry Mass of Gram-Negative Bacteria (GNB) in Summertime Aerosols Collected Over Mount Tai During High and Low Biomass-Burning Emissions (H- and L-BBEs) Occurred in the NCP in June 2006

Biomass-Burning Emissions	Mean ± SE	Range	Median
	Endotoxin (EU m^{-3})		
H-BBEs	117 ± 74	2–549	38
L-BBEs	22.5 ± 14.6	0.5–50.2	16.7
	Dry mass of GNB (ng m^{-3})		
H-BBEs	390 ± 246	7–1830	126
L-BBEs	75 ± 48.8	1.8–167	55.7

reported that endotoxin concentrations in domestic wood burning emissions from India varied from moderate to high levels (i.e., 24 EU m^{-3} and 190 EU m^{-3}) even for the short-term sampling time (<60 min).

The observed variability in the endotoxin concentrations between open biomass burning and indoor biomass combustion could be associated with the differences in the analytical method employed. However, dilution of sampled air masses from the BBEs during transport can partly explain the observed low abundances over Mount Tai. Being similar to our approach, *Lee et al*. [2004] estimated the endotoxin abundances using hydroxy FAs in particulate matter (PM) 10 collected at rural and urban environments (68.6 ± 11.5 EU m^{-3} and 123 ± 12.6 EU m^{-3}, respectively) in Hong Kong. The endotoxin levels from Mount Tai during H-BBEs are somewhat consistent with those documented by *Lee et al*. [2004]. A comparison of endotoxin levels over Mount Tai with those estimated for remote marine aerosols (av. 11 ± 1.21 EU m^{-3} at Chichijima Island) [*Tyagi et al*., 2015a] indicates a long-range transport of airborne pathogens from the continent to the open ocean. Further studies are required to examine the effects of these sustained airborne bacterial particles, which can be potentially pathogenic to densely populated cities during indoor and outdoor biomass burning.

The mass loadings of GNB (Table 3) during H-BBEs (390 ng m^{-3}) are higher than those reported in $PM_{2.5-10}$ aerosols at both rural (45 ± 1.5 ng m^{-3}) and urban sites (93 ± 1.4 ng m^{-3}) [*Lee et al*., 2004]. Higher mass loading of GNB in H-BBEs can be linked to the soil-dust emissions during biomass combustion and subsequent long-range atmospheric transport. Furthermore, GNB dry mass estimates from *Lee et al*. [2004] are comparable to those observed during L-BBEs (75 ng m^{-3}) in our study.

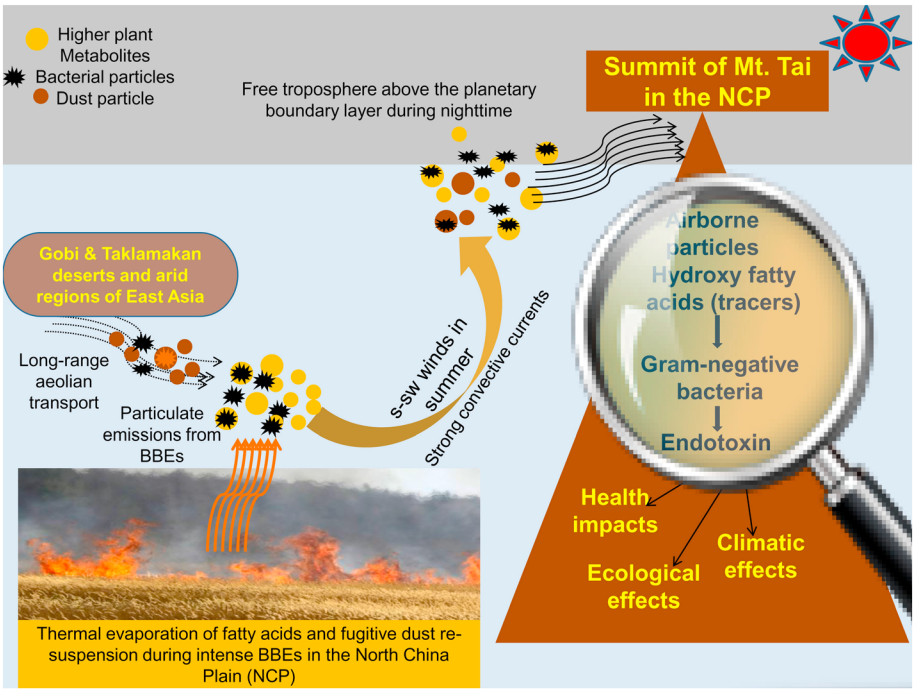

Figure 7. Conceptual model is to explain the atmospheric transport of hydroxy fatty acids (FAs) to high mountain sites. Higher abundances of bacterial tracers (hydroxy FAs) in re-suspended dust during biomass burning in the North China Plain (NCP) were observed in the aerosols collected at the summit of Mount Tai. Intense open field burning of agriculture residue can influence the microbial abundances and diversity in the atmosphere as well as their long-range transport, which can pose potential health impacts globally.

Every year, the NCP faces serious air pollution problem caused by the field burning of agricultural residues (e.g., wheat/rice straws) and soil-dust emissions in its rural areas. Studies have reported high abundances of organic compounds in Chinese urban cities [*Fu et al*., 2008, and references therein] and also in Changdao Island in the East China Sea [*Feng et al*., 2007]. These high concentrations are due to an increased usage of fossil fuels and wide spread biomass burning combined with soil emissions. The present study shows a significance of hydroxy FAs from wheat straw burning emissions in the NCP. In addition, our study raises the concern for upcoming risk factor of endotoxin emissions from biomass burning, which can affect human health in developing and developed nations via long-range atmospheric transport.

4. Conclusions

The present study shows an impact of biomass burning on the atmospheric abundances and molecular distributions of hydroxy FAs, potential tracers for soil microbes, plant pathogens, and higher plant waxes. Higher concentrations of hydroxy FAs were observed during H-BBEs than during L-BBEs. Estimated endotoxin concentrations during H-BBEs are also higher than the health-based occupational guidance limit (~90 EU m^{-3}) suggested by Dutch expert committee on Occupational Standards 2010 in Netherlands. Furthermore, these results are consistent with other organic tracers from biomass burning (e.g., levoglucosan, mannosan, and galactosan) and soil microbes (e.g., trehalose and mannitol). This observation highlights a significance of re-suspended dust from charred agricultural soils during fire emissions, which can act as a principal source of airborne soil microbes. Figure 7 summarizes the whole idea, which is addressed in this study. Overall, temporal shifts in the molecular distributions of these tracer compounds are likely associated with high temperatures occurred during agricultural residue combustion. However, the molecular distributions of hydroxy FAs from Mount Tai are different with respect to C-number predominance than those documented from the remote Island (Chichijima) in the western North Pacific, which also receives soil-borne microbes from the Asian dust.

We conclude that any types of biomass burning (outdoor/indoor) can severely influence the emission of soil- and airborne microbes and increase the risk of exposure to their potent pathogenic particles (endotoxin) regionally as well as globally. Further studies are required on the atmospheric abundances of hydroxy FAs that enhance our understanding on bacterial emissions, atmospheric transport, and their scavenging by particulate matter.

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