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Chemical characteristics of dicarboxylic acids and related organic compounds in PM_{2.5} during biomass-burning and non-biomass-burning seasons at a rural site of Northeast China[☆]



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ABSTRACT

Fine particulate matter (PM_{2.5}) samples were collected using a high-volume air sampler and pre-combusted quartz filters during May 2013 to January 2014 at a background rural site (47°35' N, 133°31' E) in Sanjiang Plain, Northeast China. A homologous series of dicarboxylic acids (C₂–C₁₁) and related compounds (oxoacids, α -dicarbonyls and fatty acids) were analyzed by using a gas chromatography (GC) and GC-MS method employing a dibutyl ester derivatization technique. Intensively open biomass-burning (BB) episodes during the harvest season in fall were characterized by high mass concentrations of PM_{2.5}, dicarboxylic acids and levoglucosan. During the BB period, mass concentrations of dicarboxylic acids and related compounds were increased by up to >20 times with different factors for different organic compounds (i.e., succinic (C₄) acid > oxalic (C₂) acid > malonic (C₃) acid). High concentrations were also found for their possible precursors such as glyoxylic acid (ω C₂), 4-oxobutanoic acid, pyruvic acid, glyoxal, and methylglyoxal as well as fatty acids. Levoglucosan showed strong correlations with carbonaceous aerosols (OC, EC, WSOC) and dicarboxylic acids although such good correlations were not observed during non-biomass-burning seasons. Our results clearly demonstrate biomass burning emissions are very important contributors to dicarboxylic acids and related compounds. The selected ratios (e.g., C₃/C₄, maleic acid/fumaric acid, C₂/ ω C₂, and C₂/levoglucosan) were used as tracers for secondary formation of organic aerosols and their aging process. Our results indicate that organic aerosols from biomass burning in this study are fresh without substantial aging or secondary production. The present chemical characteristics of organic compounds in biomass-burning emissions are very important for better understanding the impacts of biomass burning on the atmosphere aerosols.

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1. Introduction

Organic aerosols could contribute 20%–50% of the total mass of fine particulate matter (e.g., particulate matter with a diameter smaller than or equal to 2.5 μ m or PM_{2.5}), in which 40%–80% of the organic aerosols are water-soluble (Timonen et al., 2010; Zhang

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et al., 2007, 2016). Dicarboxylic acids (diacids) and related polar organic compounds are one of the most abundant water-soluble organic compounds from aerosols reported in various environments including urban (Ho et al., 2007; van Pinxteren et al., 2014), continental background (Limbeck and Puxbaum, 1999), mountainous (Kawamura et al., 2013) and remote atmosphere (Wang and Kawamura, 2006; Kawamura et al., 1996). Dicarboxylic acids can play important roles in organic aerosol budget via secondary organic aerosol formation and also global/regional climate directly by changing the solar radiation or indirectly by acting as cloud condensation nuclei (Peng et al., 2001; Kumar et al., 2003; Kawamura and Bikkina, 2016).

Diacids in aerosols may be primarily emitted from fossil fuels combustion (Kawamura and Kaplan, 1987) and biomass burning (Narukawa et al., 1999) or formed as secondary organic aerosols from atmospheric oxidation of unsaturated fatty acids (Kawamura et al., 1996) and cyclic alkenes (Hatakeyama et al., 1987), and also from aqueous processing of volatile organic compounds (VOCs) and intermediates (Lim et al., 2013; Carlton et al., 2007; Lim et al., 2005; Carlton et al., 2006; Yu et al., 2005; Sorooshian et al., 2007; Sorooshian et al., 2006; Zhang et al., 2016). High loadings of diacids have been recently reported in aerosols significantly influenced by biomass burning emissions (Kawamura et al., 2013; Kundu et al., 2010; Narukawa et al., 1999).

Northeast China is one of the most productive agricultural regions in China, where agricultural waste burning during the harvest seasons (e.g., early October) occurs frequently. Haze episodes with remarkably high PM_{2.5} levels (up to >400 $\mu\text{g}/\text{m}^3$) due to intensive open biomass burning in this region have recently been reported (Cao et al., 2016). Despite the importance of biomass burning aerosols in the region, little is known about the chemical compositions of organic aerosols such as diacids and related organic compounds. Here, we present the measurement results on molecular distributions and concentrations of diacids and related organic compounds in PM_{2.5} samples collected at a rural background site of Sanjiang in Northeast China during different seasons including biomass-burning and non-biomass-burning periods. Our results can be used to better characterize the chemical compositions of organic aerosols from biomass burning especially for open burning of agricultural waste in China.

2. Experimental

2.1. Study site

Aerosol sampling was conducted in the Sanjiang Plain in northeast China, which is located at the Sanjiang Marsh Wetland Ecological Experimental Station, Chinese Academy of Sciences

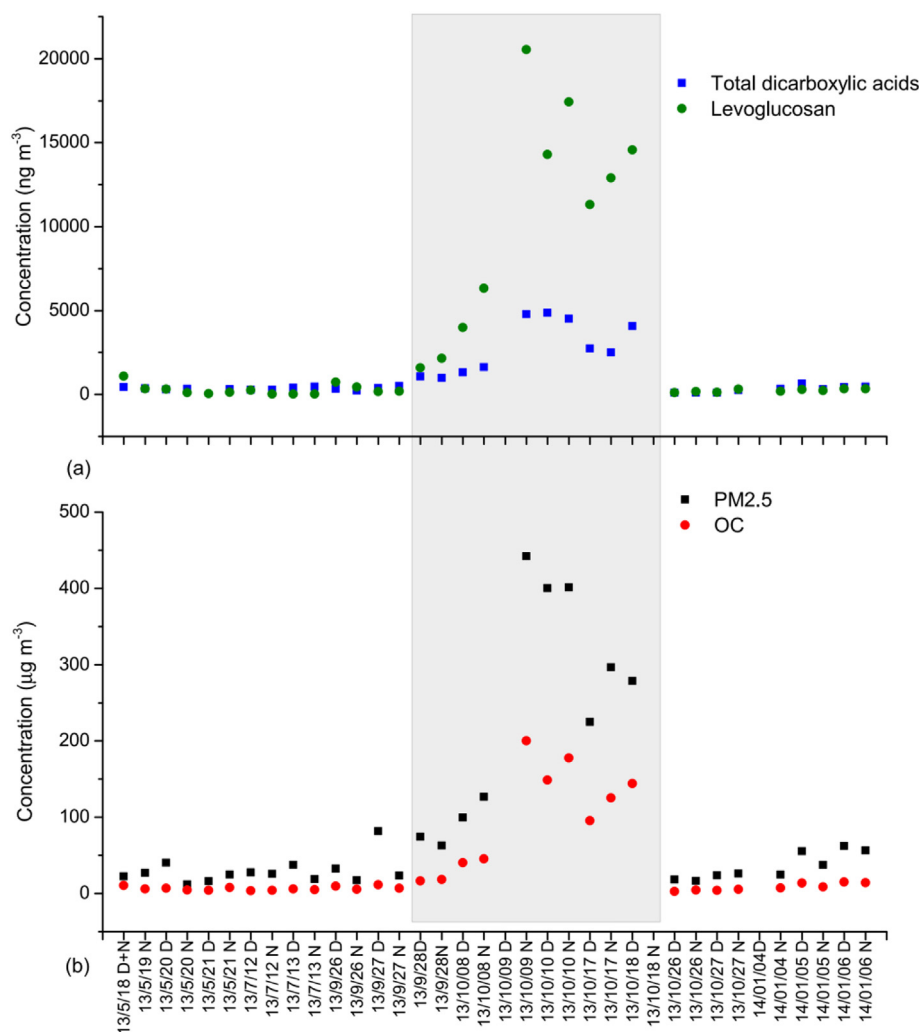


Fig. 1. Temporal variations of mass concentrations of (a) total dicarboxylic acids and levoglucosan and (b) PM_{2.5} and OC during the sampling period in the Sanjiang Plain, Northeast China. Shaded area represents the biomass burning periods. D and N denote daytime and nighttime, respectively.

(47°35' N, 133°31' E). PM_{2.5} samples were collected on pre-heated (i.e., 450 °C for about 6 h) quartz filters (25 × 20 cm) using a high volume air sampler (~1 m³/min) from May 2013 to January 2014. Day time samples (n = 15) were collected from 07:00–18:00 LT and nighttime samples (n = 17) were collected from 19:00–06:00 LT. In total, 32 PM_{2.5} samples were collected, including 10 samples were collected during intensive open field burning days. 4 field blanks were collected by putting the blank filters on the sampling holder for 30s without sampling. The filter samples were placed in aluminum foils, packed in air-tight polyethylene bags and stored at –20 °C before analysis. PM_{2.5} mass concentration was analyzed gravimetrically (Sartorius MC5 electronic microbalance) with ±1 µg sensitivity before and after sampling (e.g., T: 25 °C and RH: 45 ± 5%).

2.2. Chemical analysis

The analytical procedures of diacids and related compounds have been reported elsewhere (Zhang et al., 2016). Briefly, samples were extracted with 10 mL organic-free ultrapure water for 3 times to extract diacids and related organic compounds by ultrasonic bath. The insoluble particles were filtered and then concentrated using a vacuum rotary evaporator (~40 °C). 14% BF₃/n-butanol was added to derivatize the extracts at 100 °C by converting the carboxyl groups to dibutyl esters and aldehyde groups to butoxy acetals (Zhang et al., 2016). These derivatized samples were dissolved in 50 µl of n-hexane, concentrated and 2 µl solution were injected into a gas chromatograph (Agilent 6890, USA) using a HP-5 fused silica capillary column (25 m × 0.2 mm ID × 0.52 µm film thickness) and a flame ionization detector (FID) for the determination of targeted compounds. Quantifications were performed by the comparison of GC peaks and retention times of authentic standards. The peaks of dicarboxylic acids and related compounds were confirmed by a GC-MS system (Agilent 7890, USA) with similar GC column conditions. The concentrations of field blanks were less than 15% of those examined aerosol samples, and the data reported in this study were all corrected by the field blanks.

The analytical procedures of levoglucosan were well reported elsewhere (Sang et al., 2011). An area of 2.01 cm² of the quartz filter sample was punched into a plastic vessel, and extracted for 30 min with 4 mL of Ultra-Pure water (18.2 MΩ cm⁻¹, Millipore, USA) by an ultrasonic bath. The extracted solution was filtered with a syringe filter (0.22 µm, ANPEL Laboratory Technologies, China), and then detected using a Dionex ICS 5000 + system (Thermo Fisher Scientific, USA). The separation was performed on Dionex CarboPac MA1 Analytical Column (4 × 250 mm) together with the CarboPac MA 1 guard column (4 × 50 mm) at 30 °C using ultra-pure water (eluent A) and 1.0 M NaOH. The elution was run as the following time-gradient with 0.4 mL min⁻¹ flow rate: 15–34 min for 30% eluent B, 34–45 min for 48% eluent B, and 45–60 min for 48–65% eluent B. The sample injection loop volume was 200 µL. Levoglucosan's concentrations were quantified by a standard calibration curve. The chemicals, including levoglucosan (≥99%) and NaOH (50% wt.% solution in H₂O), were obtained from J&K Scientific (China). The recoveries for diacids were obtained by a spike experiment using authentic standards, showing recovery of >82% for oxalic acid and more than 85% for other diacids and levoglucosan. All present results were not further corrected for recovery. The field blank showed less than 5% of the real samples and was subtracted for all samples. The organic carbon (OC) and elemental carbon (EC) were measured using a thermal/optical OC/EC analyzer with the NIOSH protocol (Sunset Laboratory, USA) (Birch and Cary, 1996; Cao et al., 2016). K⁺ was measured by an ion chromatograph (761 Compact IC, Metrohm, Switzerland), and WSOC was measured by a TOC analyzer (Shimadzu, TOC-V_{CSH}, Japan), which have been

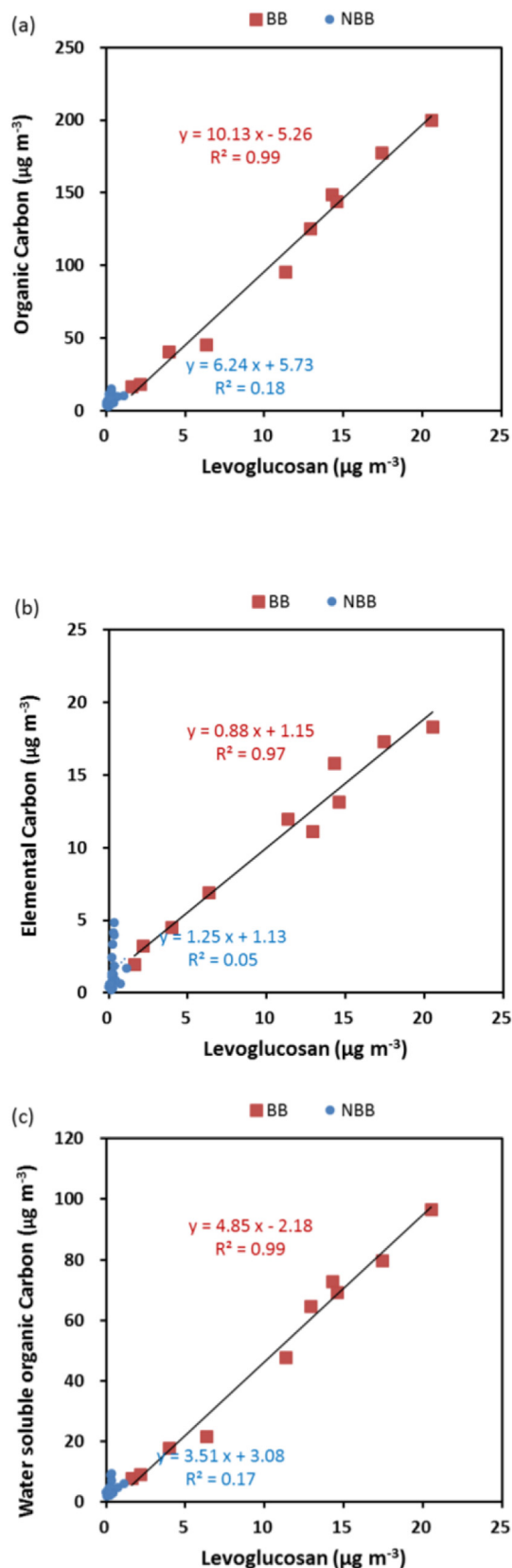


Fig. 2. Relations between levoglucosan and (a) organic carbon, (b) elemental carbon, and (c) water soluble organic carbon in PM_{2.5} samples collected in the Sanjiang Plain, Northeast China during the biomass burning (BB) and non-biomass burning (NBB) periods.

described in Cao et al. (2016).

3. Results and discussion

3.1. Identification of biomass-burning episodes

The temporal variations of mass concentrations of PM_{2.5}, OC, total diacids, and levoglucosan are illustrated in Fig. 1. From the end of the September, their values started to increase until reaching the maxima in early October. The biomass burning episodes in this study were then defined a period between from 28th September to 18th October 2013, during which concentrations of PM_{2.5}, OC, total diacids and levoglucosan were significantly elevated. Such high biomass-burning activities during this period were also supported by MODIS fire maps (Cao et al., 2016). Levoglucosan (lev.), which was widely used as marker of biomass burning aerosols (Liu et al., 2013; Simoneit et al., 1999), was increased by 20 times during the biomass burning (BB) episode compared to non-biomass burning (NBB) periods, suggesting a significant impact of biomass burning emissions on aerosol mass.

During the BB episode, levoglucosan significantly correlates

with OC, EC and WSOC (Fig. 2), suggesting an important contribution from biomass burning emissions to carbonaceous aerosols. However, such a good correlation was not observed during the other sampling periods. The biomass burning events could also be evidenced by the measurements of water-soluble potassium (K^+), stable carbon isotope composition, and MODIS fire map during the same period (Cao et al., 2016). We also conducted correlation analyses for diacids and related compounds with biomass burning tracers such as levoglucosan and K^+ during the NBB and BB periods. As shown in Figs. 3 and 4, the mass concentrations of dicarboxylic acids, oxoacids and α -dicarbonyls show strong correlations with levoglucosan and K^+ during the BB periods whereas such correlations were not found during the NBB periods. High correlation between dicarboxylic acids and levoglucosan has also been reported by Cong et al. (2015) in which the biomass burning plume was captured on the northern slope of Mt. Everest. It should be noted that levoglucosan concentrations were not very high even during the winter suggesting biomass burning emissions were not important contributors of wintertime aerosols in this area. In the following sections, the whole sampling periods were divided into the BB and NBB periods (Fig. 1) to better characterize the chemical

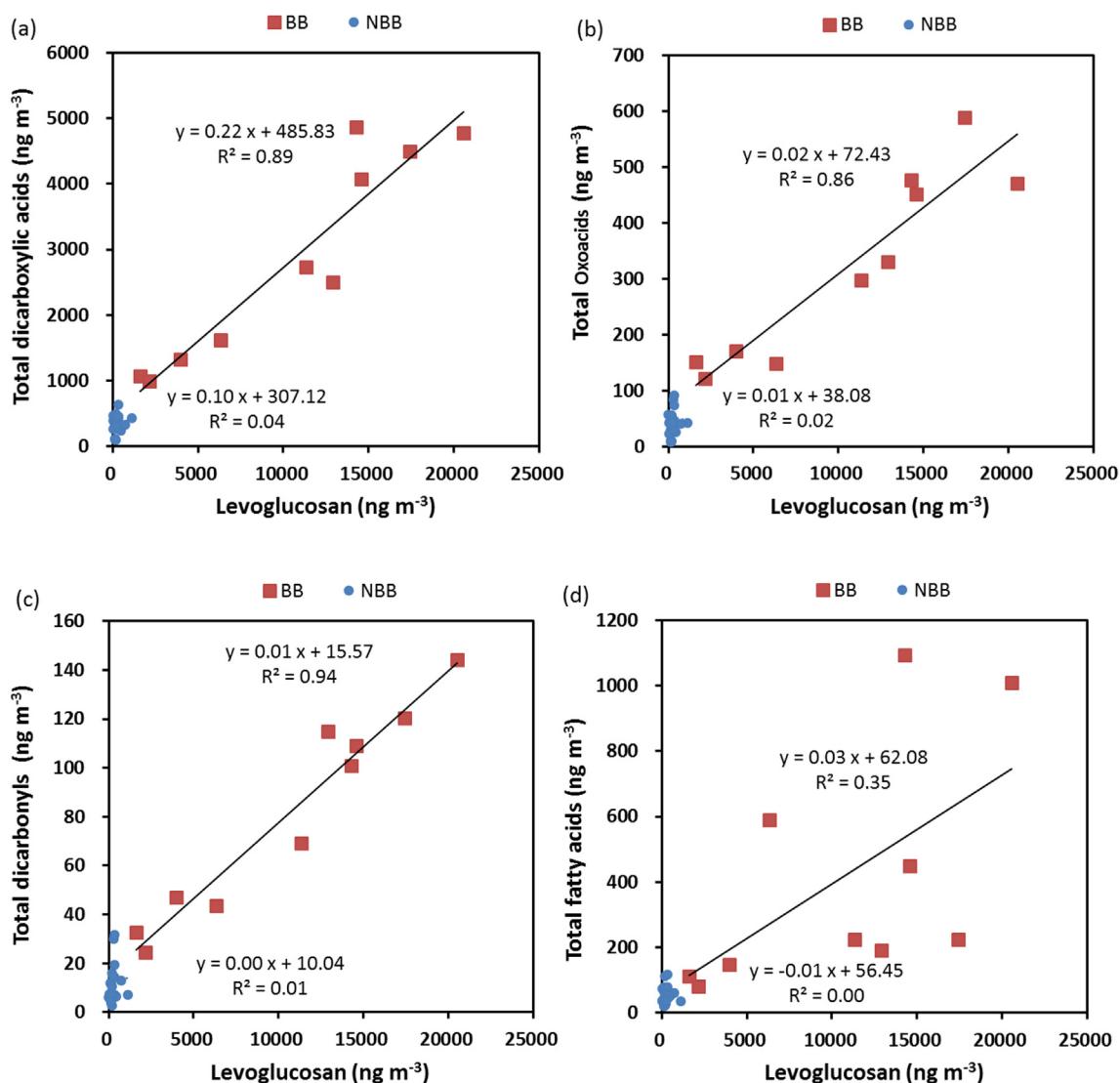


Fig. 3. Relations between levoglucosan and (a) dicarboxylic acids, (b) oxoacids, (c) α -dicarbonyls and (d) fatty acids in PM_{2.5} samples collected in the Sanjiang Plain, Northeast China during the non-biomass burning (NBB) and biomass burning (BB) periods.

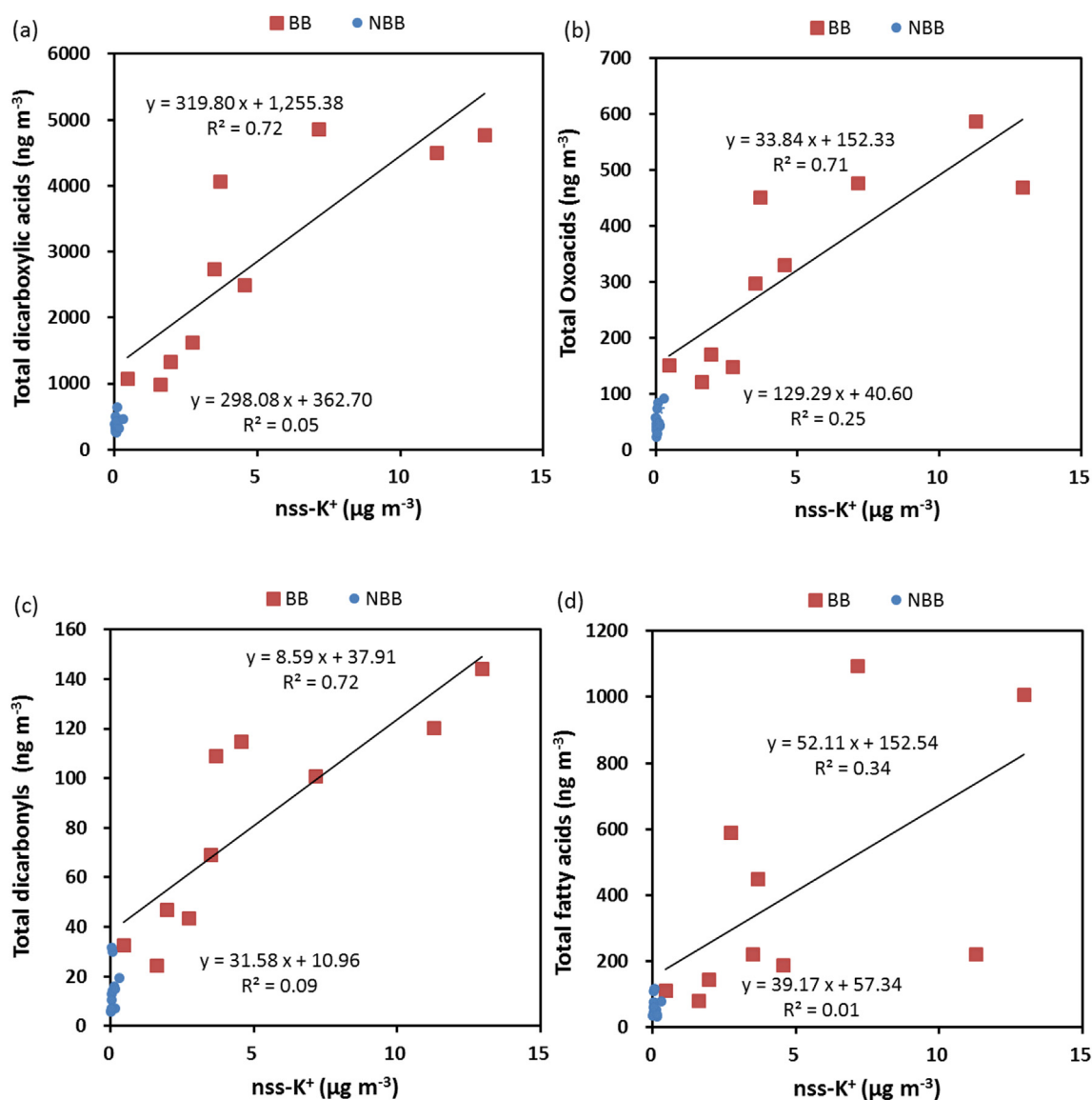


Fig. 4. Relations between non-sea-salt potassium ($nss-K^+$) and (a) dicarboxylic acids, (b) oxoacids, (c) α -dicarbonyls and (d) fatty acids in PM_{2.5} samples collected in the Sanjiang Plain, Northeast China during the biomass burning (BB) and non-biomass burning (NBB) periods.

compositions of diacids and related compounds in biomass burning emissions.

3.2. Molecular compositions of diacids and related compounds in BB and NBB periods

Table 1 shows mass concentrations of dicarboxylic acid, oxoacids, α -dicarbonyls and fatty acids in PM_{2.5} samples collected in Sanjiang. The total concentrations of identified dicarboxylic acids and related compounds ranged from 1.2×10^3 to $6.5 \times 10^3\ ng\ m^{-3}$ and 138–873 $ng\ m^{-3}$, during the BB and NBB periods, respectively. During the BB periods, the average concentrations of dicarboxylic acids, oxoacids, α -dicarbonyls and fatty acids were 2.8×10^3 , 321, 80.7 and 412 $ng\ m^{-3}$, respectively, 8.5, 7.7, 7.3, 7.5 times higher than those during the NBB periods (335, 41.7, 11.1 and 55.0, $ng\ m^{-3}$, respectively), suggesting biomass burning emissions are very important sources of dicarboxylic acids and related compounds. In this study, both day and night samples were analyzed to investigate diurnal variations of diacids (Fig. 5); however, no clear diurnal

trend was found possibly due to complex variations of boundary layer height, photochemical production and emission sources.

The diacid levels during the BB periods are much higher than those reported in 14 Chinese cities (i.e., 892 $ng\ m^{-3}$) (Ho et al., 2007), aerosols (i.e., 109 $ng\ m^{-3}$) on the northern slope of Mt. Everest (Cong et al., 2015) and fine particles (i.e., 121–917 $ng\ m^{-3}$) in the Kanto Plain, Japan (Kumagai et al., 2010), and slightly higher than those from biomass burning aerosols from the North China Plain (i.e., 1702 $ng\ m^{-3}$) (Kawamura et al., 2013) and at a pasture site in Rondonia, Brazil (i.e., 2180 $ng\ m^{-3}$) (Kundu et al., 2010). This clearly suggests that biomass burning could serve as an important source of dicarboxylic acids.

As shown in Fig. 6, the mass concentrations of identified organic compounds were much higher during BB than those in NBB seasons, and relative abundance of some organic compounds were also significantly different. Oxalic acid (C_2) was found as the most abundant diacid in both BB and NBB aerosols followed by succinic acid (C_4), which have been recognized as the predominant species in aerosols collected in China. The relative abundances of C_2 in total

Table 1

Concentrations of dicarboxylic acids, oxoacids, α -dicarbonyls and fatty acids detected in PM_{2.5} aerosol samples collected in the Sanjiang Plain, Northeast China during the biomass burning and non-biomass burning periods.

Compounds (ng m ⁻³)	Biomass burning (n = 10)				Non-biomass burning (n = 22)			
	Min.	Max.	Ave.	S.D.	Min.	Max.	Ave.	S.D.
Dicarboxylic acids								
Oxalic, C ₂	562	2.3 E+03	1.2 E+03	659	35.7	316	155	76.5
Malonic, C ₃	28.6	230	106	72.4	4.2	57.7	25.2	14.1
Succinic, C ₄	149	1.3 E+03	749	470	16.2	56.6	39.7	10.7
Glutaric, C ₅	27.1	190.8	101	62.3	2.8	13.5	8.0	2.6
Adipic, C ₆	12.2	60.4	32.0	19.6	0.7	12.5	4.7	2.9
Pimelic, C ₇	4.6	19.4	10.3	5.9	0.8	10.7	4.4	2.8
Suberic, C ₈	0.8	6.7	3.2	2.0	0.1	16.0	1.9	3.8
Azelaic, C ₉	28.5	266	146	86.7	2.6	24.4	11.5	6.6
Sebacic, C ₁₀	1.1	10.8	4.4	3.6	0.4	8.9	2.2	2.1
Undecanedioic, C ₁₁	2.5	29.7	15.6	10.1	0.1	2.7	0.8	0.6
Total saturated straight chain diacids	845	4.3 E+03	2.4 E+03	1.3 E+03	70.8	453	257	105
Methylmalonic, iC ₄	1.8	62.4	15.1	18.4	0.2	3.7	1.9	1.0
Methylsuccinic, iC ₅	11.3	280	56.2	81.1	0.4	10.1	3.8	2.2
Methylglutaric, iC ₆	0.4	5.0	2.0	1.4	0.2	17.3	3.0	3.7
Total branched chain diacids	20.8	344	73.3	97.0	2.5	23.5	8.2	4.6
Maleic, M	8.3	60.4	40.7	19.4	2.5	12.6	6.7	2.3
Fumaric, F	2.7	20.0	7.6	5.8	0.9	45.6	5.3	9.3
Methylmaleic, mM	6.2	128	59.0	42.8	1.0	14.6	4.7	3.3
Phthalic, Ph	38.2	153	88.9	44.2	9.5	104	31.9	24.0
Isophthalic, iPh	0.8	38.4	21.5	12.9	0.1	9.5	2.4	2.6
Terephthalic, tPh	10.2	90.5	30.5	24.5	2.0	23.2	9.5	5.8
Total unsaturated diacids	91.6	433	248	130	21.1	162	60.5	33.2
Hydroxysuccinic, hC ₄	7.2	65.4	34.0	21.4	0.2	5.4	1.5	1.4
Ketomalonic, kC ₃	11.2	171	69.1	50.2	2.3	13.5	5.6	2.8
Ketopimelic, kC ₇	3.8	14.3	9.3	3.8	0.2	5.4	2.0	1.8
Total oxo and hydroxy diacids	3.6	240	56.1	72.9	3.6	19.6	8.9	3.8
Total Dicarboxylic acids	993	4.9 E+03	2.8 E+03	1.6 E+03	104	641	335	131
Oxoacids								
Glyoxylic, ω C ₂	15.6	66.3	40.1	18.5	0.5	14.9	5.9	3.8
3-oxopropanoic, ω C ₃	38.3	146	87.3	42.0	3.4	50.9	15.4	10.6
4-oxobutanoic, ω C ₄	8.6	48.2	26.2	14.7	0.5	14.8	4.9	4.3
5-oxopentanoic, ω C ₅	38.4	287	134	83.3	0.2	16.6	5.5	4.6
7-oxoheptanoic, ω C ₇	3.6	22.6	12.3	7.4	0.3	4.6	1.6	1.0
8-oxooctanoic, ω C ₈	3.1	18.8	9.0	5.9	0.3	10.2	3.7	2.3
9-oxononoic, ω C ₉	4.0	19.6	10.1	5.6	0.4	7.5	3.0	2.1
Pyruvic, Pyr	0.6	6.6	1.9	1.9	0.1	2.9	0.8	0.8
Total oxoacids	121	588	321	150	8.7	92.2	41.7	22.1
α-Dicarbonyls								
Glyoxal, Gly	12.4	69.9	42.2	23.5	0.9	19.0	4.6	4.6
Methylglyoxal, MeGly	12.2	74.2	38.5	19.8	1.7	13.8	6.5	3.8
Total α -dicarbonyls	24.5	144	80.7	42.3	2.6	31.6	11.1	7.7
Fatty acids								
Myristic acid, C14:0	28.4	172	100	53.9	4.3	56.7	17.9	12.1
Palmitic, C16:0	24.0	245	106	78.2	9.0	69.3	24.1	14.5
Stearic acid, C18:0	5.3	59.1	21.8	18.2	0.6	12.8	4.6	3.3
Oleic acid, C18:1	7.4	613	168	249	1.4	24.3	7.6	5.6
Arachidic acid, C20:0	1.9	17.0	7.9	5.4	0.2	1.4	0.5	0.4
Behenic acid, C22:0	0.2	24.6	8.0	7.2	0.2	1.6	0.6	0.5
Total fatty acids	80.8	1.1 E+03	412	372	18.7	117	55.0	26.4
Total (all detected species)	1.2 E+03	6.5 E+03	3.7 E+03	2.1 E+03	138	873	443	176
PM _{2.5} (μ g m ⁻³)	62.8	479	261	163	11.9	81.7	31.7	17.3
OC (μ g m ⁻³)	16.6	200	101	67.6	2.9	15.1	7.4	3.5

saturated straight-chain (C₂–C₁₁) diacids were 60% and 52% in the NBB and BB seasons, respectively (Fig. 6). The predominance of C₂ could be due to biomass burning emissions, photochemical oxidation and aging process of longer chain organic acids (Mkoma and Kawamura, 2013). It is interesting to note that the relative abundance of C₂ was declined in the BB events, which was due to an enhanced production of C₄. As shown in Fig. 6, both mass concentrations and relative abundance of C₄ are much higher than

those of C₃ during the BB events, which have been previously reported in biomass burning emissions (Kawamura et al., 2013; Kundu et al., 2010; Cong et al., 2015). Moreover, the C₄/C₂ ratios in biomass burning aerosols (0.6 ± 0.2) were almost twice the ratios in the NBB periods (0.3 ± 0.1) due to relatively high abundant C₄ in biomass burning aerosols. This comparison indicates that the relative abundance of C₄ (i.e., C₄/C₂) may be a good signal for biomass burning emissions.

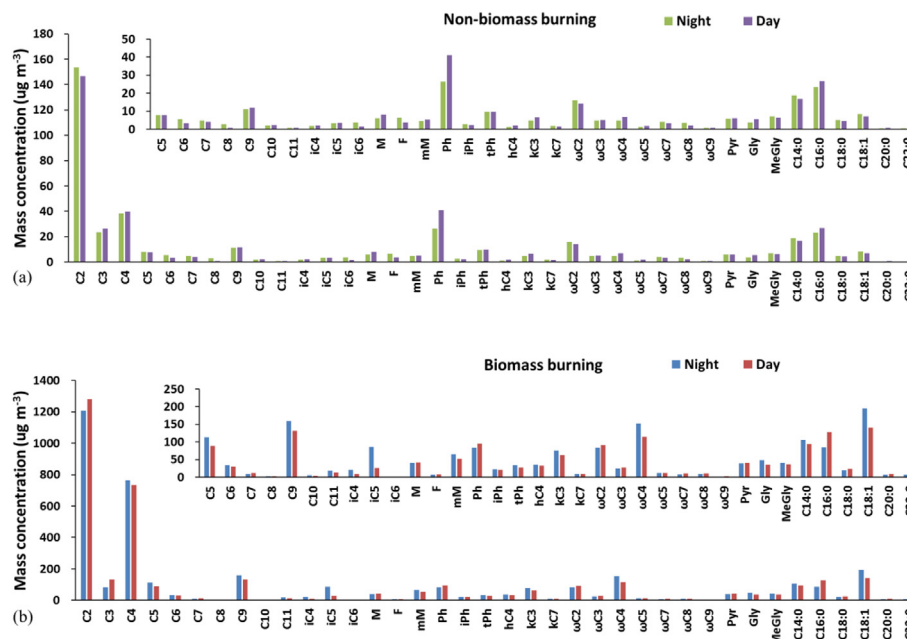


Fig. 5. Averaged molecular distributions of dicarboxylic acids, oxocarboxylic acids, α -dicarbonyls and fatty acids in PM_{2.5} aerosol samples collected in the Sanjiang Plain, Northeast China during (a) the non-biomass-burning and (b) biomass-burning periods.

Among the longer chain saturated n-dicarboxylic acids (C₅–C₁₁), glutaric (C₅) acid is the most abundant followed by azelaic (C₉) and adipic (C₆) acids. No significant difference was observed for their relative abundance in the total saturated n-dicarboxylic diacids in the BB and NBB periods. C₅ and C₆ are mainly produced by atmospheric oxidation of cyclohexene and methylenecyclohexane from anthropogenic emissions (Hamilton et al., 2006; Muller et al., 2007), whereas C₉ can be formed as oxidation products of biogenic unsaturated fatty acids (e.g., oleic acid, C_{18:1}) (Kawamura and Gagosian, 1987). The absolute concentrations of C₅, C₆ and C₉ in the BB period was significantly increased during the BB period, indicating that these organic acids can be either primarily emitted by biomass burning emissions or formed as oxidation productions from associated precursors from biomass combustion. Oleic acid can be directly emitted either from anthropogenic sources such as biomass burning and cooking or from biogenic sources such as higher plants and soils (Rogge et al., 1993). In our study, oleic acid was increased by > 20 times during the BB period, suggesting that oleic acid is strongly enriched in biomass burning emissions. Thus, a large fraction of C₉ may be also produced by photochemical oxidation of C_{18:1} in biomass burning emissions.

Phthalic acids can be emitted from combustion processor or formed as oxidation of aromatic hydrocarbons (e.g., naphthalenes) (Kawamura and Kaplan, 1987; Kawamura and Yasui, 2005; Wang et al., 2006; Kautzman et al., 2010). At Sanjiang, three phthalic acids (phthalic acid, o-isomer; terephthalic acid, p-isomer; and isophthalic acid, m-isomer) were analyzed with the order of o-isomer (Ph) > p-isomer (tPh) > m-isomer (iPh) during the BB and NBB periods, which is consistent with previous studies (Kawamura et al., 2013; Kundu et al., 2010). However, iPh was increased by 8 times whereas the other two isomers were increased only by 2 or 3 times during the BB season, suggesting that iPh is relatively more enriched in biomass burning aerosols. Another important feature is that Ph concentrations and Ph/EC ratios are higher during daytime than nighttime for almost all the samples, indicating an important contribution from secondary production.

The most abundant oxoacid in the NBB season was glyoxylic acid

(ω C₂), an important precursor of oxalic acid. However, 4-oxobutanoic (ω C₄) became a dominant compound of ketoacids with an average concentration of 134 ng m⁻³ followed by ω C₂ during the BB season, which was >24 times larger than that in the NBB season. Such an enhancement has not been reported in aerosols that are significantly influenced by biomass burning. ω C₄ can be further transformed to C₄, which was also supported by a good correlation (i.e., $r = 0.94$, $p < 0.01$) between C₄ and ω C₄ in biomass burning aerosols.

Concentrations of α -dicarbonyls are one or two orders of magnitude lower than those of diacids (Table 1), although their concentrations are also increased during the BB events. Glyoxal (Gly) and methylglyoxal (MeGly) can be produced by atmospheric oxidation of volatile organic compounds (VOCs) from both biogenic (e.g., isoprene and monoterpenes) and anthropogenic emissions (e.g., toluene, xylene) and they are also involved in the SOA formation as intermediates (Lim et al., 2013; Fu et al., 2008; Carlton et al., 2007). Interestingly, Gly showed higher concentrations in biomass burning aerosols whereas MeGly is more abundant in the NBB aerosols, suggesting that biomass burning emission produce more Gly than MeGly. Furthermore, during the BB events, these two α -dicarbonyls show good correlations ($r > 0.85$, $p < 0.01$) with C₂ and pyruvic (Pyr) acid, implying a possible reaction mechanism: (e.g., CH₃COCOOH or HCO–CHO or CH₃COCHO) → HCO–COOH → HOOC–COOH (Carlton et al., 2006, 2007, 2009; Lim et al., 2013).

3.3. Photochemical aging of dicarboxylic acids and related compounds

Succinic acid (C₄) can be degraded into malonic acid (C₃), and thus the C₃/C₄ ratio could be used an indicator of photochemical aging of organic aerosols (Cong et al., 2015; Fu et al., 2013). The C₃/C₄ ratios in the BB periods ranged from 0.06 to 0.55 with a mean of 0.18 ± 0.14 , which was lower than those of urban (0.7) (Ho et al., 2007), mountainous (0.51) (Cong et al., 2015) and marine remote aerosols (>0.6) (Fu et al., 2013). The *cis* maleic acid (M) can be transformed to *trans* fumaric acid (F) during photochemical aging

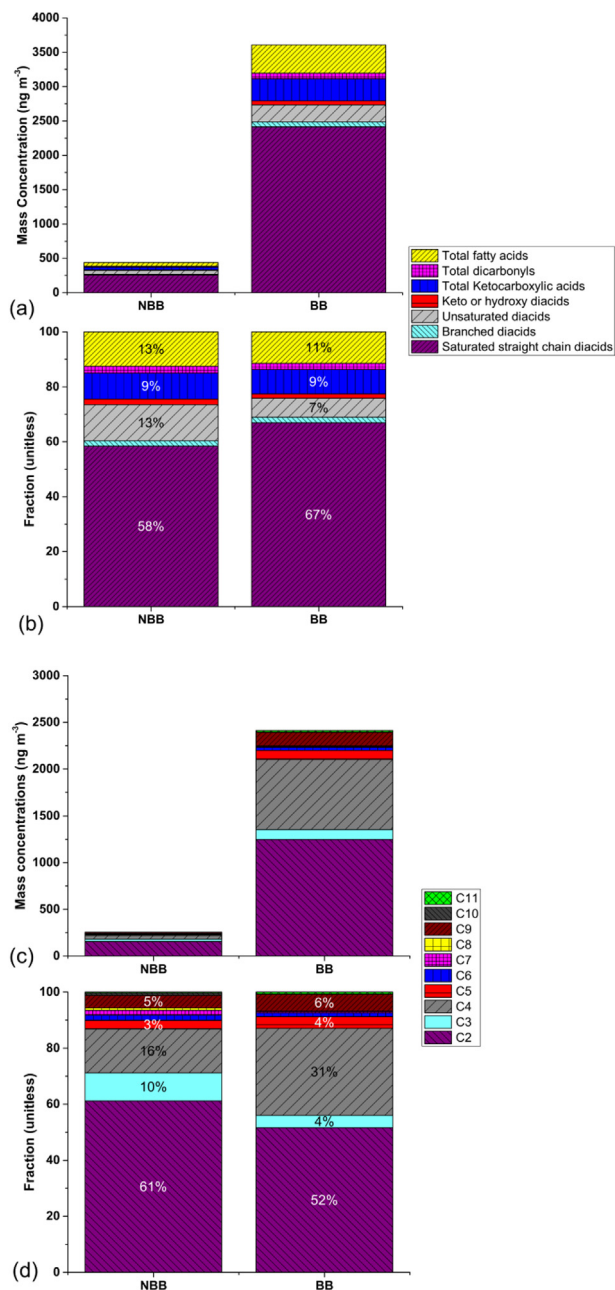


Fig. 6. Average mass concentrations ($\mu\text{g m}^{-3}$) of (a) identified organic compounds, (b) relative abundances of identified compounds, (c) average mass concentrations dicarboxylic acids and (d) relative abundances of dicarboxylic acids in ambient PM_{2.5} samples collected in the Sanjiang Plain, Northeast China during the non-biomass burning (NBB) and biomass burning (BB) periods.

and thus F/M ratio could be used as a tracer of photochemical transformation. The mean value of F/M ratio in NBB aerosols was 0.56 ± 0.48 , which was similar to that (0.5) of urban aerosols (Ho et al., 2007). In BB aerosols, the mean values of C_3/C_4 and F/M ratio were reduced to 0.18 ± 0.14 (0.06–0.55) and 0.23 ± 0.16 (0.05–0.48), respectively, suggesting that organic aerosols in BB aerosols in this study are very fresh without substantial further photochemical transformation after aerosols were formed. Indeed, Cao et al. (2016) also found that the inorganic aerosols influenced by the biomass burning plumes were mostly fresh emitted and less-aged.

Oleic acid can be directly emitted either from anthropogenic

sources such as biomass burning and cooking or from biogenic sources such as higher plants and soils (Rogge et al., 1993). The ratio of $C_{18:1}/C_{18:0}$ was used to determine the level of aerosol aging in previous study (Bendle et al., 2007). Lower values indicate that the air masses are more aged. The ratios of $C_{18:1}/C_{18:0}$ in BB and NBB aerosols were 5.2 and 1.9, respectively, again indicating the BB aerosols were less aged. The relative abundances of diacids and related compounds to levoglucosan (e.g., C_2/lev) ranges from 0.2 to 12.7 (mean: 1.6 ± 2.9) during the NBB periods, which was much higher than those (i.e., ranging from 0.1 to 0.4 with a mean of 0.2 ± 0.1) from BB aerosols. The C_2/lev ratio in BB aerosols from our study was slightly higher than those (i.e., 0.05) reported in fresh plumes of Savanna fires. Gao et al. (2003) found that diacids to levoglucosan ratios were increased in aged plumes due to secondary production of diacids. Thus, the lower diacids ratios with respect to levoglucosan suggests that secondary production of diacids is not significant and organic aerosols in biomass burning emission in our study are less aged. Therefore, the chemical composition of diacids reported here may represent the chemical characteristics of fresh biomass burning aerosols in this region. It should be noted that fuel types and combustion conditions may also lead to variation in these ratios, which require further studies.

4. Conclusions

Fine particulate matter (PM_{2.5}) samples were collected during May 2013 to January 2014 at Sanjiang, a background rural site in Northeast China. Intensive open biomass burning (e.g. open rice residues burning) episodes during the fall harvest season were characterized by high mass concentrations of PM_{2.5}, dicarboxylic acids and levoglucosan. The molecular distributions of dicarboxylic acids, oxocarboxylic acids, α -dicarbonyls and fatty acids in biomass burning and non-biomass burning aerosols are analyzed. During biomass-burning seasons, mass concentrations of diacids and related compounds were increased by up to >20 times with different enrichment factors (i.e., succinic (C₄) acid > oxalic (C₂) acid > malonic (C₃) acid, see Fig. 5). High concentrations were also found for their possible precursors (e.g., glyoxylic (ω C₂), 4-oxobutanoic (ω C₄), pyruvic (Pyr) acids, glyoxal (Gly) and methylglyoxal (MeGly) as well as fatty acids. During the biomass burning episodes, levoglucosan shows strong correlations with carbonaceous aerosols (OC, EC, WSOC) and diacids although such good correlations were not observed in non-biomass-burning seasons. These results clearly demonstrate that biomass-burning emissions significantly contribute to diacids and related compounds as well as carbonaceous aerosols. The selected ratios such as C_3/C_4 , F/M, C_2/ω C₂, $C_{18:1}/C_{18:0}$ and C_2/lev , which can be used for tracers of aerosols aging and secondary formation, further strengthening and supporting our previous conclusions that both organic and inorganic aerosols derived from biomass burning in this study are fresh without substantial aging or secondary production. Therefore, the chemical composition of diacids and related compounds reported here can be used a good characteristic of fresh biomass burning aerosols in the studied region.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2017.08.045>.

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