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Distribution and stable carbon isotopic composition of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in fresh and aged biomass burning aerosols

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Abstract. Biomass burning (BB) is a significant source of dicarboxylic acids (diacids) and related compounds that play important roles in atmospheric chemistry and climate change. In this study, a combustion chamber and oxidation flow reactor were used to generate fresh and aged aerosols from burned rice, maize and wheat straw to investigate atmospheric aging and the stable carbon isotopic (δ^{13}C) composition of these emissions. Succinic acid (C_4) was the most abundant species in fresh samples, while oxalic acid (C_2) became dominant after atmospheric aging. Of all diacids, C_2 had the highest aged to fresh emission ratios (A/F), suggesting that C_2 is largely produced through secondary photochemical processes. Compared with fresh samples, the emission factors of ketocarboxylic acids and α-dicarbonyls increased after 2 d but decreased after 7 d aging, indicating a short residence time and further atmospheric degradation from 2 to 7 d. The δ^{13}C values of C_2 for aged biomass samples were higher than those of urban aerosols but lower than marine or mountain aerosols, and the δ^{13}C values of C_2 became isotopically heavier during aging. Relationships between the reduction in volatile organic compounds (VOCs), such as toluene, benzene and isoprene, and increase in diacids after 2 d aging indicate that these VOCs led to the formation of diacids. However, no significant correlation was found between decreases in VOCs and increases in 7 d aged diacids. In addition, the A/F of C_2 was 50.8 at 2 d and 64.5 at 7 d, indicating that the conversion of VOCs to C_2 was almost completed within 2 d. For the longer aging times, the particulate-phase compounds may undergo further degradation in the oxidation processes.

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1 Introduction

Dicarboxylic acids (diacids), ketocarboxylic acids and α-dicarbonyls are common components of the atmospheric organic aerosol, accounting for 1 %–3 % of the total organic carbon in urban areas and > 10 % of the carbon mass in remote regions (Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999; Kerminen et al., 2000; Zhao et al., 2018). Due to their high water solubility and other physicochemical properties, diacids affect the hygroscopic growth of particulate matter (PM), and these compounds are involved in the activation of cloud condensation nuclei and formation of ice nuclei (Kawamura and Bikkina, 2016). Diacids and related compounds have been found in a wide variety of environments including urban settings (Ho et al., 2006; Kawamura and Ikushima, 1993; Meng et al., 2020; Sorathia et al., 2018; Wang et al., 2002, 2006, 2012), mountains ranges (Kawamura et al., 2013; Kunwar et al., 2019) and remote marine atmospheres (Hoque et al., 2020; Kawamura and Usukura, 1993). They also have been reported in both the Arctic and Antarctic aerosols (Kawamura et al., 1996a, b; Narukawa et al., 2002, 2003) as well as polar ice cores (Legrand and De Angelis, 1996; Kawamura et al., 2001). Various studies have assessed the molecular distributions, temporal variability and sources of diacids in different airsheds.

There are both primary and secondary sources of diacids (Mkoma and Kawamura, 2013). Primary sources include emissions from fossil fuel combustion (Kawamura and Kaplan, 1987; Rogge et al., 1993), cigarette burning (Rogge et al., 1994), cooking (Rogge et al., 1991) and biomass burning (BB) (Narukawa et al., 1999; Schauer et al., 2001). Of these, BB was found to be an important source of diacids and related compounds over regional and global scales (Kundu et al., 2010). Emissions from BB not only compose a major source of primary particles, but also introduce aerosol precursors to the atmosphere (Akagi et al., 2011; Gilman et al., 2015; Reid et al., 2005). Secondary sources include particles produced by chemical/photochemical oxidation reactions of volatile organic compounds (VOCs), especially those emitted from primary sources (Lim et al., 2013; Carlton et al., 2006, 2007).

Being one of the major contributors to the global budget of aerosols, BB emissions are of particular concern because they impact air quality, visibility, climate and human health (Hodshire et al., 2019). As the largest developing country and one that burns large quantities of biomass, China has long suffered from severe air pollution from BB (Chen et al., 2016; Fullerton et al., 2008). Domestic crop residues (e.g., rice, maize and wheat straw) and firewood are the most significant energy sources in most rural areas, and these are commonly used for cooking and heating (Li et al., 2021; Tao et al., 2018).

Diacids, ketocarboxylic acids and α-dicarbonyls are products of BB (Agarwal et al., 2010). Although these acids have been measured in ambient air in some areas dominated by BB sources (Falkovich et al., 2005; Kundu et al., 2010; Kawamura et al., 2013), there have been few BB source emission (e.g., chamber) measurements. It was reported that BB smoke was found to contain large amounts of gaseous pollutants, such as VOCs, nitrogen oxides (NO_x), sulfur dioxide (SO_2), and ammonia (NH_3) (Akagi et al., 2011; Andreae and Merlet, 2001). Gas-phase compounds, especially VOCs, can be partitioned to the particle phase through nucleation, condensation and heterogeneous chemical reactions, creating secondary organic aerosol (SOA) and adding to aerosol mass (Hodshire et al., 2019; Lim et al., 2019). Oxalic acid (C_2), the most abundant species of diacids (Kawamura and Sakaguchi, 1999), is formed by various VOCs in cloud droplets through photochemical oxidation and liquid-phase reactions. It is of interest to quantify emission factors (EFs) of diacids and related compounds during the combustion of different biomass fuels in the laboratory. Kalogridis et al. (2018) performed small-scale fire experiments using the Large Aerosol Chamber (LAC; 1800 m^3) with a focus on BB from Siberian boreal coniferous forests and presented experimental data on EFs of diacids. However, this study only focused on the EFs of diacids of fresh pollutants that were directly emitted from BB, so it is necessary to further investigate the molecular composition of aged BB aerosols. In addition, limited data are available on the specific diacids emitted from the burning of agricultural residues. Therefore, it is important to investigate the molecular composition of diacids in both fresh and aged BB aerosols to advance current understanding of the potential environmental and climatic effects.

In this study, rice, maize and wheat straw were selected for laboratory simulations of fresh and aged BB aerosols. The study was conducted with the use of a combustion chamber and oxidation flow reactor (OFR). Fresh and aged BB aerosols were chemically analyzed for molecular characteristics and the stable carbon isotopic composition ($\delta^{13}C$) of selected diacids, ketocarboxylic acids, α-dicarbonyls and benzoic acid. The objectives of this study were to (1) investigate the emissions of diacids, ketocarboxylic acids and α-dicarbonyls from crop residue burning; (2) evaluate the effects of atmospheric aging processes on diacids and related compounds; and (3) investigate the relationship between VOCs with C_2 and intermediates that form in the aging process to explore potential formation mechanisms of selected organic acids.

2 Methods

2.1 Preparation and collection of fresh and aged BB aerosols

The experimental setup is illustrated in the Supplement Fig. S1. Detailed procedures for sample preparation and collection may be found in previous studies (Li et al., 2020, 2021; Niu et al., 2020). Briefly, fresh smoke was generated by burning dry biomass fuels (i.e., rice, maize and wheat straw) in a combustion chamber, and the smoke was then passed through a potential aerosol mass oxidation flow reactor (PAM-OFR) (Aerodyne Research, LLC, Billerica, MA, USA) to simulate aging processes on the timescale of hours to days. The biomass combustion chamber had a volume of ∼ 8 m^3 (1.8 m (W) × 1.8 m (L) × 2.2 m (H)) and was made of 3 mm thick aluminum to withstand high-temperature heating. The combustion chamber was equipped with a thermo anemometer, an air purification system, a heated sampling line, a dilution sampler and so on. More detailed information about the design and evaluation of the combustion chamber was described in Tian et al. (2015).

In order to get sufficient aerosol samples for measurements of chemical composition, around 1 kg biomass fuels were burned inside the chamber in 10 burning cycles. The entire burning cycle, including ignition, flaming, smoldering and extinction, intends to simulate real-world source characterization. Each burning cycle, containing ∼ 100 g biomass fuels, lasts around 12–18 min. The fresh smoke was diluted by 4.6 times using clean air controlled by the flow balance. A portion of the diluted smoke by a dilution sampler (Model 18, Baldwin Environmental Inc., Reno, NV, USA) was drawn through a quartz fiber filter (47 mm diameter, Whatman QM/A, Maidstone, UK) at 5 L min^{-1} using a miniVol $PM_{2.5}$ sampler (Airmetrics, OR, USA) to capture fresh emission.

The PAM-OFR can be used to simulate an environment with extremely high oxidant concentrations with short residence times (Kang et al., 2007). Another portion of the exhaust (∼ 9 L min^{-1}) was directed through a 19 L cylinder PAM-OFR (with a diameter of 20 cm and length of 60 cm) to simulate atmospheric aging. The residence time of PAM-OFR is estimated to be 90 ± 1 s at flow rate of 9 L min^{-1} (Li et al., 2021). Three oxidants (O_3, ·OH and $·HO_2$) were generated in the PAM chamber using irradiation from ultraviolet (UV) lamps. The OH exposure values (OH_{exp}) can be calculated by the concentration of SO_2 and CO at the OFR inlet and outlet in a laboratory setting. Relative humidity (RH) inside the OFR was varied by passing different amounts of carrier gas through the OFR humidifier (MH-110). Additional details on smoke generation condition, test study and evaluation of the PAM-OFR were described by Cao et al. (2020).

In this study, the UV lamps operated at a voltage of 2 and 3.5 V, and OH_{exp} in the chamber was estimated at 2.6×10^{11} and 8.8×10^{11} molecules s m^{-3}, respectively. These levels corresponded to ∼ 2 and 7 d of aging (Chow et al., 2019; Watson et al., 2019), assuming a representative atmospheric ·OH level of 1.5×10^6 molecules m^{-3} (Mao et al., 2009). The aged aerosols were sampled by another miniVol $PM_{2.5}$ sampler (5 L min^{-1}) following the reactions in the PAM-OFR chamber. Each test was conducted in triplicate to account for experimental errors and to provide a measure of variability, which was calculated as standard deviations. A total of 36 samples were collected and analyzed for chemical composition.

2.2 Sample extraction, derivatization and quantification

For diacids, ketocarboxylic acids and α-dicarbonyls analysis, one-quarter of each filter sample was extracted three times (15 min each) with purified (18.2 MΩ) water (Milli-Q, Merch, France) and ultrasonication. The pH of the aerosol extracts was adjusted to 8.5 to 9.0 using a 0.1 M potassium hydroxide solution prior to drying that converts carboxylic acids into their salts (Bikkina et al., 2021). This drying step improves the recovery of smaller diacids, such as C_2 (Hegde and Kawamura, 2012). Water extracts were concentrated to near-dryness with a rotary evaporator under vacuum and then reacted with 14 % BF_3/n-butanol at 100 °C for 1 h to derivatize carboxyl groups to dibutyl esters and oxo groups to dibutoxyacetals.

After derivatization, n-hexane was added and washed with pure water three times to remove the water-soluble inorganics such as hydrogen fluoride and boric acid. The hexane layer was concentrated to near-dryness using a rotary evaporator under vacuum and a N_2 blow-down technique, and then the esters and acetals of target analytes were dissolved in known amounts of n-hexane. Finally, the hexane layers were concentrated to 100 µL and analyzed using a capillary gas chromatograph (GC; HP 6890, Agilent Technology, Santa Clara, CA, USA) equipped with a split/splitless injector and a flame ionization detector (FID). Peak identification was performed by comparing the GC retention times with those of authentic standards and confirmed by a thermal desorption (TD) unit coupled with a gas chromatograph/mass spectrometric detector (TD-GC/MS, Models 7890A/5975C, Agilent Technology, Santa Clara, CA, USA). The detection limits for those organic compounds were 0.1 ng m^{-3}, and the analytical errors, based on the replicate analyses, were less than 15 %. Recoveries of the target compounds were 83 % for C_2 and 87 % to 110 % for the other species.

2.3 Emission factor calculations

Concentrations of the various species in the aged samples were affected by their initial emission and also undergo degradation and production through secondary chemical processes. Fresh and aged fuel-based EFs for each measured chemical compound were calculated by dividing its filter mass by the mass of combusted dry biomass fuel (Andreae and Merlet, 2001; Li et al., 2020; Tian et al., 2015); that is

$$\mathrm{EF}_i = \frac{m_i \times v_{\mathrm{Stk}} \times D \times t_{\mathrm{sample}}}{Q_{\mathrm{p}} \times m_{\mathrm{fuel}}} \times \mathrm{DR}, \quad (1)$$

where EF_i (mg kg^{-1}) is the EF of chemical compound i for the specific crop, m_i (mg) is the mass of chemical compound i collected on the filter, v_{Stk} is the average stack flow velocity (m s^{-1}) at standard conditions, D is the stack cross section (m^2), t_{sample} is the sampling duration (s), Q_{p} is the sampling volume through the filter (m^3) at standard temperature and pressure, and m_{fuel} is the mass of burned biomass fuel (kg, dry weight).

The dilution ratio (DR) was determined from the CO_2 concentrations measured at the stack, diluted stack and background, where

$$\mathrm{DR} = \frac{\mathrm{CO}_{2,\mathrm{Stk}} - \mathrm{CO}_{2,\mathrm{Bkg}}}{\mathrm{CO}_{2,\mathrm{Dil}} - \mathrm{CO}_{2,\mathrm{Bkg}}}, \tag{2}$$

where $\mathrm{CO}_{2,\mathrm{Stk}}$ is the CO_2 concentration in the stack, $\mathrm{CO}_{2,\mathrm{Bkg}}$ the background CO_2 concentration in the atmosphere and $\mathrm{CO}_{2,Dil}$ the CO_2 concentration in the diluted smoke.

2.4 Stable carbon isotope composition of diacids

Stable carbon isotopic determinations (δ^{13}C) of diacids, ketocarboxylic acids and α-dicarbonyls followed the techniques of Kawamura and Watanabe (2004). The isotope values of the derivatized samples were determined using a gas chromatography–isotope ratio mass spectrometer (GCIR-MS; Thermo Fisher, Delta V Advantage, Franklin, MA, USA). The δ^{13}C values were then calculated for free organic acids using an isotope mass balance equation based on the measured δ^{13}C values of derivatives and BF_3/n-butanol (Kawamura and Watanabe, 2004). To ensure the analytical error of the δ^{13}C values less than 0.2 ‰, each aerosol sample was analyzed in triplicate to obtain the average values.

3 Results and discussion

3.1 Emission factors for diacids, ketocarboxylic acids and α-dicarbonyls

Fresh and aged $PM_{2.5}$ EFs for a homologous series of diacids, ketocarboxylic acids (glyoxylic acid, ωC_2, and pyruvic acid, Pyr), α-dicarbonyls (glyoxal, Gly, and methylglyoxal, mGly) and benzoic acid are presented in Table 1. The EFs for most fresh and aged diacids varied by several orders of magnitude, with higher EFs after atmospheric aging. The highest fresh EF (i.e. $\mathrm{EF}_{\mathrm{fresh}}$) was found for wheat straw ranging 44–122 mg kg^{-1} for succinic acid (C_4) and 67–102 mg kg^{-1} for Gly, higher than EFs found in maize and rice. The arithmetic means and standard deviations for the $\mathrm{EF}_{\mathrm{fresh}}$ of total diacids from burning of rice, maize and wheat straws were 63 ± 24, 117 ± 39 and 285 ± 135 mg kg^{-1}, respectively.

As is shown Fig. 1, distributions of diacids in fresh emissions varied by crop type and species. Of the saturated n-dicarboxylic acids, C_4 acid was the most abundant species in the maize and wheat straw, with average $\mathrm{EF}_{\mathrm{fresh}}$ of 22 ± 12 and 83 ± 46 mg kg^{-1}, respectively. Azelaic acid (C_9) and C_4 were the most abundant species from rice burning, with $\mathrm{EF}_{\mathrm{fresh}}$ of 11 ± 2.9 and 10 ± 9.0 mg kg^{-1}, respectively. These findings are consistent with the fresh smoke aerosols in Siberian BB plumes (Kalogridis et al., 2018), in which C_4 and C_9 were more abundant than C_2. Previous studies also showed C_9 to be an oxidation product of unsaturated fatty acids in biomass smoke (Kawamura and Gagosian, 1987; Kawamura et al., 2013; Agarwal et al., 2010; Cao et al., 2017). C_2 is the most abundant species of diacids and is one of the final products of the SOA reaction chain. In the fresh BB sample, C_2 emissions were lower due to the short aging time.

Similar to the diacids, the highest $\mathrm{EF}_{\mathrm{fresh}}$ for ketocarboxylic acids and α-dicarbonyls was also found in wheat straw samples, with 44 ± 31 and 138 ± 91 mg kg^{-1}, respectively. Gly was the highest α-dicarbonyl, with an average $\mathrm{EF}_{\mathrm{fresh}}$ of 27 ± 3.9, 42 ± 10 and 84 ± 41 mg kg^{-1} for rice, maize and wheat straw, respectively. This is consistent with previous studies which showed that Gly is often more abundant than mGly in polluted aerosols collected from China (Pavuluri et al., 2010; Ho et al., 2007). Benzoic acid also was determined, and its $\mathrm{EF}_{\mathrm{fresh}}$ for rice, maize and wheat aerosols was 1.9 ± 0.2, 2.5 ± 0.4 and 3.1 ± 0.3 mg kg^{-1} (Table 1).

3.2 Effects of atmospheric aging processes

3.2.1 Diacids

The $\mathrm{EF}_{\mathrm{aged}}$ of 2 and 7 d diacids was 1650 ± 438 and 1957 ± 598 mg kg^{-1}, respectively (Table S1), approximately 10 times greater than the $\mathrm{EF}_{\mathrm{fresh}}$. High aged / fresh emission ratios (A/F) imply that the bulk of the total diacids were secondarily produced through aging processes. Longer exposure time in the atmosphere increased the formation of diacids as ratios of average A/F increased from 9.1 (2 d) to 10.8 (7 d) (Table S1). As shown in Fig. 2, C_2 was the most abundant of all measured diacids among three crops, with the highest EF_{aged} found in wheat (1412 ± 328 mg kg^{-1}) after 7 d aging. These results provide further evidence that C_2 is produced mainly through secondary photochemical processes rather than direct emission from BB. That is one possible reason that C_2 is often the most abundant diacid in ambient samples, especially in the oceanic and other remote areas (Hoque et al., 2020; Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999; Kunwar and Kawamura, 2014; Hegde and Kawamura, 2012; Kawamura and Bikkina, 2016; Wang et al., 2012). In addition, we found that the A/F of C_2 after 2 d aging was 50.8, and the change from 2 to 7 d was relatively small, only increasing by 13.7 (Table S1). These results meant that 2 d aging may be sufficient for most diacid formation. It can be inferred that although diacids are still generated at 7 d aging, a large number of VOCs may have been oxidized at 2 d aging and transferred to the particle phase by condensation, adsorption and other ways. Especially for maize straw, the $\mathrm{EF}_{\mathrm{aged}}$ of total detected organics at 7 d aging (1844 ± 344 mg kg^{-1}) was lower than that of at 2 d aging (3530 ± 626 mg kg^{-1}), which was mainly due to the predominant role of particulate diacid degradation in longer aging time. This phenomenon is consistent with the change of EFs of VOCs (precursors of C_2) during maize straw combustion.

Table 1. Emission factors (EFs; mg kg^{-1}) of fresh and aged dicarboxylic acids and related compounds from rice, maize and wheat straw burning.

Compounds	Rice – 2 d aged		Rice – 7 d aged		Maize – 2 d aged		Maize – 7 d aged		Wheat – 2 d aged		Wheat – 7 d aged	
	Fresh	2 d aged	Fresh	7 d aged	Fresh	2 d aged	Fresh	7 d aged	Fresh	2 d aged	Fresh	7 d aged
I. Dicarboxylic acids												
Oxalic, C_2	5.1 ± 0.9	527 ± 214	15 ± 10	971 ± 482	8.1 ± 2.2	1522 ± 268	24 ± 8.8	1158 ± 202	18 ± 15	742 ± 160	39 ± 3.4	1412 ± 328
Malonic, C_3	2.4	46 ± 26	1.4 ± 0.7	70 ± 42	3.6	74 ± 8.4	2.7 ± 0.6	56 ± 9.0	12 ± 13	89 ± 18	3.6 ± 0.8	273 ± 70
Succinic, C_4	< DL*	152 ± 100	10 ± 9.0	120 ± 85	9.3 ± 12	268 ± 35	35 ± 12	124 ± 23	44 ± 72	335 ± 62	122 ± 21	813 ± 217
Glutaric, C_5	< DL	21 ± 12	5.4 ± 0.8	16 ± 11	8.9	44 ± 13	10 ± 3.1	20 ± 2.8	28 ± 23	41 ± 12	27 ± 3.7	61 ± 16
Adipic, C_6	< DL	18 ± 8.6	3.5 ± 0.9	6.4 ± 2.2	< DL	42 ± 6.4	4.1 ± 1.1	5.8 ± 0.7	12	33 ± 11	5.5 ± 2.2	79 ± 28
Pimelic, C_7	5.0	7.4 ± 2.7	2.4 ± 0.9	4.9 ± 1.7	< DL	18 ± 2.1	2.8 ± 0.9	5.5 ± 0.3	16 ± 12	21 ± 3.1	4.0 ± 1.6	13 ± 2.8
Azelaic, C_9	11 ± 1.8	19 ± 8.8	11 ± 3.9	18 ± 8.4	10 ± 3.2	91 ± 21	17 ± 8.4	39 ± 22	23 ± 20	41 ± 12	35 ± 6.5	61 ± 19
Sebacic, C_{10}	2.8 ± 2.3	5.0 ± 4.6	< DL	< DL	6.2 ± 2.3	7.0 ± 0.5	< DL	< DL	6.6 ± 1.7	5.7 ± 3.1	< DL	< DL
Undecanedioic, C_{11}	< DL	7.6 ± 1.5	5.4 ± 1.1	15 ± 1.2	6.7 ± 1.2	18 ± 1.5	7.5 ± 0.8	8.9 ± 2.1	11.2	14 ± 2.8	7.9 ± 2.4	40 ± 19
Methylmalonic, iC_4	3.6	4.8 ± 1.8	3.7 ± 1.9	10 ± 6.8	3.8 ± 0.2	19 ± 22	9.1 ± 2.9	11 ± 2.1	< DL	5.7 ± 1.4	20 ± 4.2	46 ± 12
Mehtylsuccinic, iC_5	< DL	20 ± 13	3.8 ± 1.7	12 ± 5.5	< DL	54 ± 16	5.6 ± 1.8	12 ± 3.5	< DL	172 ± 114	6.6 ± 1.0	45 ± 19
Methylglutaric, iC_6	< DL	9.8 ± 2.7	2.1 ± 1.0	6.1 ± 3.6	3.4	12 ± 3.4	4.0 ± 1.9	5.7 ± 1.4	7.4 ± 4.9	8.3 ± 2.9	5.1 ± 1.0	37 ± 23
Maleic, M	< DL	16 ± 8.9	1.6 ± 1.2	14 ± 3.5	2.8 ± 1.1	56 ± 14	4.0 ± 1.0	14 ± 3.6	9.6	29 ± 3.8	3.4 ± 0.6	43 ± 11
Fumaric, F	< DL	22 ± 15	3.1 ± 0.6	< DL	< DL	73 ± 13	4.0 ± 1.1	< DL	13	43 ± 15	3.6 ± 0.3	24 ± 19
Methylmaleic, mM	4.5 ± 0.7	6.7 ± 2.1	2.5 ± 0.8	5.6 ± 2.4	7.3 ± 0.5	18 ± 5.3	6.6 ± 1.9	6.5 ± 1.2	19 ± 22	12 ± 3.4	5.5 ± 0.8	16 ± 4.7
Phthalic, Ph	4.0 ± 0.5	23 ± 10	5.8 ± 3.5	16 ± 4.3	3.8 ± 1.0	47 ± 6.5	10 ± 5.4	11 ± 2.6	10 ± 12	29 ± 6.9	17 ± 12	33 ± 12
Isophthalic, iPh	4.1	8.7 ± 3.8	2.9 ± 1.3	11 ± 3.6	3.9	17 ± 3.9	5.2 ± 2.7	7.3 ± 1.3	9.7 ± 2.7	16 ± 2.6	7.6 ± 3.1	27 ± 11
Ketopimelic, kC_7	< DL	4.4 ± 0.6	3.6 ± 1.6	6.0 ± 1.8	< DL	6.5 ± 1.9	3.9 ± 0.7	6.3 ± 0.6	13 ± 7.6	9.3 ± 2.5	4.5 ± 0.4	8.9 ± 3.1
Subtotal	43 ± 6.2	919 ± 437	83 ± 41	1300 ± 665	78 ± 23	2386 ± 440	155 ± 55	1491 ± 279	252 ± 206	1645 ± 437	318 ± 64	3032 ± 814
II. Ketocarboxylic acids												
Pyruvic acid, Pyr	4.6	74 ± 48	6.5 ± 3.1	103 ± 50	8.1 ± 3.5	210 ± 17	15 ± 4.3	79 ± 29	21 ± 25	189 ± 15	13 ± 4.0	190 ± 75
Glyoxylic, ωC_2	11 ± 0.3	129 ± 65	9.6 ± 1.3	152 ± 53	16 ± 2.0	341 ± 30	17 ± 2.5	164 ± 21	33 ± 27	265 ± 4.9	23 ± 6.3	359 ± 114
Subtotal	16 ± 0.4	203 ± 113	16 ± 4.4	255 ± 103	24 ± 5.5	551 ± 48	32 ± 6.8	243 ± 50	53 ± 52	454 ± 20	35 ± 10	550 ± 189
III. α-Dicarbonyls												
Glyoxal, Gly	32 ± 1.1	132 ± 104	22 ± 6.7	79 ± 31	39 ± 8.6	380 ± 54	44 ± 12	60 ± 1.7	102 ± 71	380 ± 87	67 ± 11	382 ± 125
Methylglyoxal, mGly	15 ± 0.5	70 ± 39	2.8 ± 2.2	33 ± 22	30 ± 13	172 ± 28	7.6 ± 2.6	46 ± 13	91 ± 96	135 ± 31	16 ± 4.0	172 ± 37
Subtotal	47 ± 1.6	202 ± 143	25 ± 8.9	112 ± 53	69 ± 22	551 ± 82	52 ± 14	106 ± 15	192 ± 167	515 ± 118	83 ± 15	554 ± 161
Benzoic acid, Ha	< DL	5.4 ± 2.1	1.9 ± 0.2	3.8 ± 0.3	< DL	42 ± 57	2.5 ± 0.4	4.0 ± 1.1	< DL	12 ± 7.8	3.1 ± 0.3	6.0 ± 2.0
Total detected organics	105 ± 8.2	1329 ± 695	127 ± 54	1671 ± 821	171 ± 50	3530 ± 626	241 ± 76	1844 ± 344	498 ± 425	2626 ± 583	439 ± 90	4141 ± 1166

[*] < DL denotes emissions below method detection limit (MDL).

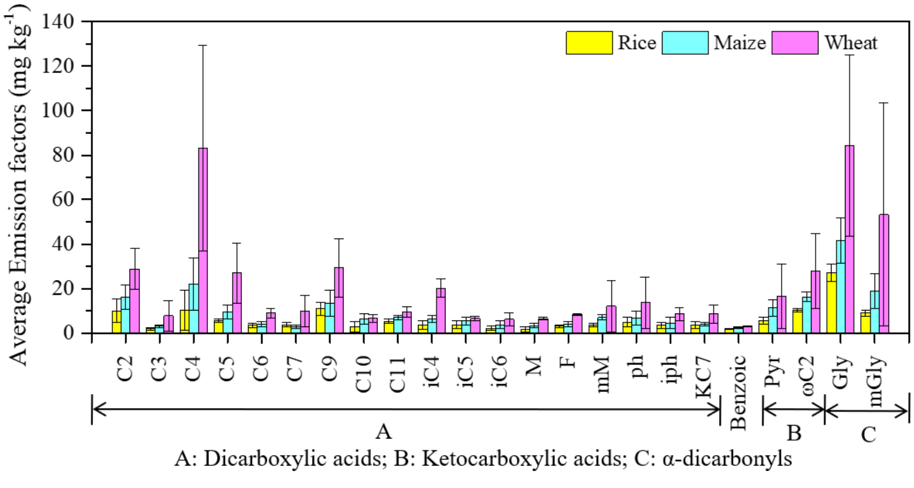

Figure 1. Average emission factors of dicarboxylic acids and related compounds in fresh $PM_{2.5}$ aerosols from biomass burning.

The decreases in of ΣVOC_{EF} after 2 d aging (1227 mg kg^{-1}) were comparable with those of 7 d aging (884 mg kg^{-1}) for maize straw (Niu et al., 2020).

C_4 ranked second in abundance after C_2, with a 7–8-fold increase in EF after 2 and 7 d aging wheat. Although malonic acid (C_3) is mainly produced by the photochemical oxidation of C_4, it also can be formed through the incomplete combustion of fossil fuels and biomass (Kawamura and Ikushima, 1993). In the atmosphere, C_4 is typically more abundant than C_3 originated from BB, vehicular engine exhaust and biogenic emissions (Fu et al., 2013; Kawamura and Kaplan, 1987; Kundu et al., 2010). Figure 3 shows atmospheric ag-

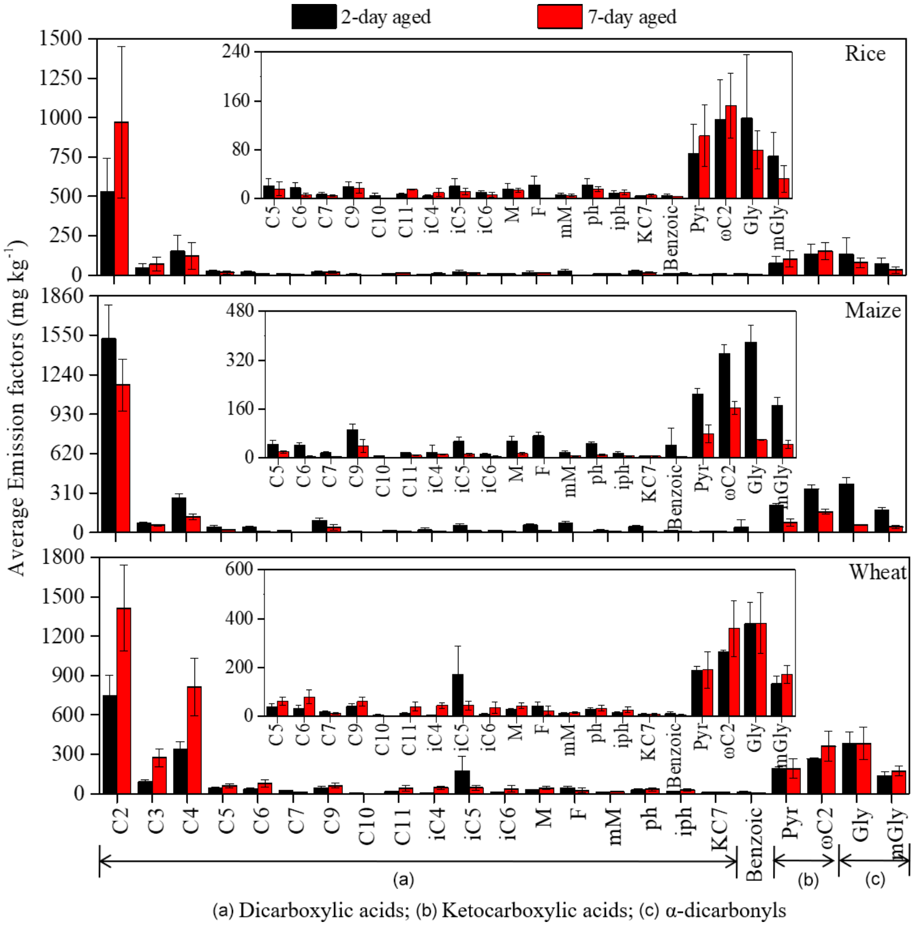

Figure 2. Comparison between 2 and 7 d aged average $PM_{2.5}$ emission factors of the sections marked as follows: (a) dicarboxylic acids, (b) ketocarboxylic acids and (c) α-carbonyls for laboratory combustion of rice, maize and wheat straw.

ing increased the abundances of C_3 and C_4, with A/F increasing from 16.2 to 31.1 for C_3 and from 5.7 to 8.0 in C_4 from 2 to 7 d of aging (Table S1). These findings add to the evidence that these diacids are produced by the photooxidation of primary pollutants emitted from combustion process. Higher A/F in aged and fresh C_3 acid than in C_4 acid may be attributed to the rapid formation rate of C_3 or decarboxylation processing of C_4 diacid during aging (Zhao et al., 2018).

As mentioned above, C_9 is thought to be mainly formed through the photochemical oxidation of unsaturated fatty acids emitted by plants (Kawamura and Gagosian, 1987). Average EFs in C_9 acid were low, ranging from $18 \pm 7.3\,\mathrm{mg\,kg^{-1}}$ (fresh) to $51 \pm 14\,\mathrm{mg\,kg^{-1}}$ (2 d), with an A/F of C_9 of 2.8 and 2.2 for the 2 and 7 d samples, respectively, suggesting that C_9 is relatively stable with a short residence time. Figure 3 shows that A/F of other long-chain diacids and branched diacids did not show apparent changes between the 2 and 7 d samples, which may be due to the degradation of long-chain diacids (Enami et al., 2015; Legrand et al., 2007; Miyazaki et al., 2010). It is also possible that the laboratory combustion experiment did not produce adequate quantities of certain diacids. For example, glutaric acid (C_5) and adipic acid (C_6) are commonly formed by reactions of cycloolefins emitted from anthropogenic sources with O_3 (Hatakeyama et al., 1985) and phthalic acid as a product of the photochemical oxidation of aromatic hydrocarbon compounds (Kawamura and Ikushima, 1993). Additional laboratory experiments may be needed to reify different atmospheric process.

3.2.2 Ketocarboxylic acids and α-carbonyls

In contrast to the diacids, aging process were not apparent in ketocarboxylic acids as A/F reduced by 16 % from 13.8 (2 d) to 11.9 (7 d). A similar phenomenon was found for α-carbonyls, with A/F reduced by 64 % from 5.4 (2 d) to 3.3 (7 d). This suggests the possibility that the degradation of these intermediates to C_2 is faster than their formation by oxidation after 2 d of aging. Figure 3 also show apparent reduction EF of 33 %–42 % from 2 to 7 d aging for Gly and mGly, which may be due to the fact both Gly and mGly initially can be oxidized to less volatile polar organic acids including Pyr

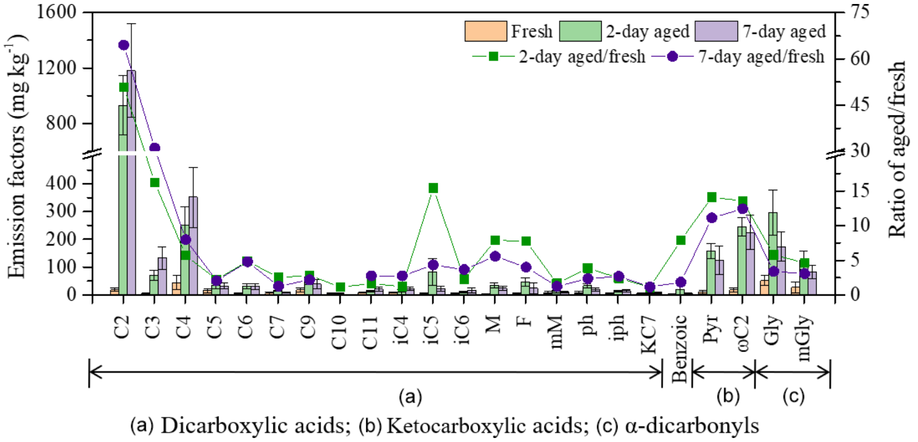

Figure 3. Average emission factors of dicarboxylic acids and related compounds from biomass burning experiment for the fresh, 2 and 7 d aged $PM_{2.5}$ aerosols. The squares and dots denote the ratios of aged to fresh (A/F) emission samples for the dicarboxylic acids and related compounds after 2 and 7 d aging.

and ωC_2 and then further oxidized to C_2 (Wang et al., 2012; Warneck, 2003).

3.3 Comparisons of diagnostic ratios of diacids in fresh and aged aerosols

Patterns in the relative abundances of diacids have been used to evaluate biogenic versus anthropogenic source strengths and the photochemical processing of organic aerosols (Kawamura et al., 2012). Previous studies have shown that C_4 can be directly oxidized into C_2 or via C_3 into C_2 (Jung et al., 2010; Sorooshian et al., 2007), with C_2 being an end product of the photochemical oxidation (Wang et al., 2012). The ratios of C_3 / C_4, C_2 / C_4 and C_2 / total diacids can be regarded as indicators of aerosol aging (Cheng et al., 2013; Kunwar et al., 2019; Meng et al., 2018; Pavuluri et al., 2010), with higher ratios indicative of more aged aerosols (Kawamura and Sakaguchi, 1999). As shown in Table 2, the ratios in this study showed a clear atmospheric aging trend from fresh to 7 d aging, with ratios of 0.7 to 6.4 for C_2 / C_4, 0.1 to 0.6 in C_2 / total diacids and 0.2 to 0.5 in C_3 / C_4, indicating obvious photochemical oxidation.

Ratios of ωC_2 / C_2 and Gly / mGly can also be used to evaluate the oxidation of organic aerosols (Cheng et al., 2013, 2015; Kawamura et al., 2013). In the study, apparent reduction of the ωC_2 / C_2 ratios from 1.3 (fresh) to 0.2 (7 d) supports the potential oxidation pathways from precursor glyoxylic to oxalic acids. Aqueous-phase oxidation by OH is faster for Gly than for mGly, and the abundance of Gly relative to mGly is an indicator of aerosol aging (Cheng et al., 2013). The ratio of Gly / mGly in Xi'an samples was lower on haze days than on clean days and lower in summer than in winter. Similarly, the Gly / mGly ratios in the aged BB samples were higher in the fresh $PM_{2.5}$ samples (3.8) compared to the 2 d (2.3) and 7 d (2.0) aging.

Ratios of C_3 / C_4, C_2 / diacids, ωC_2 / C_2 and Gly / mGly are similar among studies, except for the higher C_3 / C_4 ratio of 3.9 found in marine aerosols of over the Pacific region (Kawamura and Sakaguchi, 1999) and lower C_3 / C_4 ratios in Siberian BB emissions in a large aerosol chamber (< 0.03) (Kalogridis et al., 2018). The largest difference was found for C_2 / C_4, which varied from < 1 for fresh aerosol in Siberian BB (Kalogridis et al., 2018) to 25.2 from forest fire in Thailand (Boreddy et al., 2021). Elevated C_2 / C_4 ratios exceeding 10 were found in the aged ambient atmosphere of Xi'an, China (10.4) (Cheng et al., 2013), Mt. Hua, China (10.7) (Meng et al., 2014), marine aerosol, Pacific Ocean (14.3) (Kawamura and Sakaguchi, 1999), and the ambient atmosphere of Okinawa Island, Japan (15.5) (Kunwar and Kawamura, 2014). These C_2 / C_4 ratios are $\sim 63\,\%$ to $142\,\%$ higher than these reported in this study. Overall, these comparisons show the importance of photochemical aging; however, the atmospheric oxidation evidently was more extensive in aerosols from some remote mountain and marine environments.

3.4 Stable carbon isotopes of diacids

Stable carbon isotope ratios (δ^{13}C) can provide insights into the sources of aerosols. Pavuluri and Kawamura (2016) reported that average δ^{13}C values for C_2 from biogenic aerosols ($-15.8\,‰$) were less negative; i.e., they contained more ^{13}C and were isotopically more enriched than those from anthropogenic aerosols ($-19.5\,‰$). Data for δ^{13}C can also provide information on the processing or aging of organic aerosols because isotopic fractionation results from chemical reactions or phase transfer (Pavuluri and Kawamura, 2016; Zhang et al., 2016). Mass loading of δ^{13}C for diacids in the fresh BB samples was too low to be detected by the GCIR-MS, but the δ^{13}C values for C_2 ranged from $-23.3\,\%$ to $-21.0\,‰$ (with an average of $-21.9 \pm 1.2\,‰$) in

Table 2. Comparison of mass ratios of C_3 / C_4, C_2 / C_4, C_2 / total diacids, ωC_2 / C_2 and Gly / mGly in fresh and aged aerosols collected from biomass burning at different locations around the world.

	Sampling site	Particle size	C_3^* / C_4	C_2 / C_4	C_2 / total diacids	ωC_2 / C_2	Gly / mGly	References
Mountain	Mt. Hua	PM_{10}	2.0	10.7	0.6	0.06	0.6	Meng et al. (2014)
	Mt. Tai	TSP	0.8	5.3	0.6	0.1	0.5	Kawamura et al. (2013)
	Mt. Fuji	TSP	0.6	1.9	0.5	0.05	1.2	Kunwar et al. (2019)
Urban	Tokyo, Japan	TSP	1.0	4.2	0.5	0.2	0.7	Kawamura and Yasui (2005)
	Liaocheng, China	$PM_{2.5}$	0.4	3.6	0.6	0.1	1.0	Meng et al. (2020)
	Fairbanks	$PM_{2.5}$	1.2	4.2	0.5	0.1	1.4	Deshmukh et al. (2018)
	Doi Ang Khang, Thailand	$PM_{2.5}$	0.5	25.2	0.6	0.1	2.0	Boreddy et al. (2021)
	Beijing, China	$PM_{2.5}$	0.8	6.8	0.5	0.1	0.6	Zhao et al. (2018)
	Xi'an, China	PM_{10}	0.8	10.4	0.6	0.1	0.7	Cheng et al. (2013)
Marine area	North Pacific	TSP	1.4	5.3	0.5	0.01	2.0	Kawamura et al. (1993)
	Eastern North Pacific	TSP	1.1	4.3	0.5	0.004	0.2	Hoque et al. (2020)
	Western North to equatorial Pacific	TSP	3.9	14.3	0.6	–	–	Kawamura et al. (1999)
Island	Okinawa	TSP	1.9	15.5	0.8	0.06	0.5	Kunwar et al. (2014)
Laboratory simulation	Motor exhausts		0.35					Kawamura et al. (1987)
	Siberian (biomass burning, chamber)	$PM_{2.5}$	< 0.03	< 1	–	–	–	Kalogridis et al. (2018)
	Fresh (biomass burning, chamber)	$PM_{2.5}$	0.2	0.7	0.1	1.3	3.8	This study
	2 d aged (biomass burning, chamber)	$PM_{2.5}$	0.3	3.8	0.6	0.3	2.3	
	7 d aged (biomass burning, chamber)	$PM_{2.5}$	0.5	6.4	0.6	0.2	2.0	

* See compound list in Table 1.

2 d and −19.1 ‰ to −15.5 ‰ (−17.3 ± 1.7 ‰) for 7 d aged samples (Table 3).

Table 3 shows that the average δ^{13}C values of C_2 from aged maize samples were higher than those of rice and wheat. The reason for the isotope difference may be that maize is a C_4 plant, while wheat and rice are both C_3 plants. Song et al. (2018) showed that $\delta^{13}C_{TC}$ in C_4 plants is isotopically heavier than in C_3 plants. Moreover, the δ^{13}C of C_2 is more abundant in 7 than 2 d samples (Table 3), with −13.1 ± 1.6 ‰ (2 d) and −7.1 ± 1.4 ‰ (7 d) in maize; −26.2 ± 1.8 ‰ (2 d) and −20.8 ± 3.3 ‰ (7 d) in rice and −26.5 ± 0.2 ‰ (2 d) and −24.0 ± 0.5 ‰ (7 d) in wheat combustion. The δ^{13}C data for C_3, C_4 and ωC_2 (Table S2) showed similar trends, consistent with previous studies. For example, Zhao et al. (2018) found that the δ^{13}C values of C_2 were related to aging. Pavuluri and Kawamura (2016) analyzed diacids, ωC_2 and Gly for δ^{13}C in anthropogenic and biogenic aerosol samples by UV irradiation and reported more δ^{13}C less negative with longer irradiation times. During atmospheric oxidation reactions, organic compounds react with OH radicals, causing the release of CO_2 and CO which contain relatively the lighter ^{12}C isotope and thus leaving the remaining substrate enriched in ^{13}C (Hoefs, 1997; Sakugawa and Kaplan, 1995).

A comparison of δ^{13}C values for C_2 in the aerosols from selected environments is shown in Fig. 4. The average δ^{13}C value (−21.9 ± 1.2 ‰) of 2 d aged biomass burning of C_2 was comparable to the values reported for urban regions, such as Beijing (−21.8 ± 2.8 ‰) (Zhao et al., 2018) and Liaocheng (−19.8 ± 3.1 ‰) (Meng et al., 2020) (Table 3). With continued aging, the $C_2 \delta^{13}$C of the 7 d samples (−17.3 ± 1.7 ‰) was more similar in samples from Mt. Tai (−16.5 ± 1.8 ‰) (Meng et al., 2018) and western Pacific and Southern Ocean aerosol (−16.8 ± 0.8 ‰) (Wang and Kawamura, 2006), but it was significantly lighter than that of samples from the Gosan Climate Observatory at Gosan, South Korea (−13.7 ± 2.5 ‰), which is a mountain background site in East Asia (Zhang et al., 2016).

3.5 Relationships between decreases in VOCs and increases in diacids

The chamber experiment (Niu et al., 2020) measured VOC compounds. Table S3 presents the correlations between decreases in VOCs and increases in diacids from fresh to 2 d aged BB samples. Significant ($0.01 < p < 0.05$) correlations (R) were observed for toluene with Gly ($R = 0.75$), mGly ($R = 0.81$), Pyr ($R = 0.78$), ωC_2 ($R = 0.78$) and C_2 ($R = 0.67$) (Fig. 5), suggesting that toluene was converted to diacids during the aging process. Indeed, it has been reported that the photooxidation of toluene is a potential source of secondary organic aerosol (SOA) in urban air (Sato et al., 2007), and the major chemical components of SOA include hemiacetal, peroxy hemiacetal oligomers and diacids. It also can be seen that benzene had significant correlations with mGly and C_2 ($R > 0.59$ in Fig. 5), implying that the oxidation of benzene led to diacid formation. Photooxidation of Gly and mGly is a major global and regional source of C_2 diacid, and the two formation pathways are Gly–ωC_2–C_2 and mGly–Pyr–ωC_2–C_2, respectively (Yasmeen et al., 2010; Wang et al., 2012). As shown in Fig. 5, the slope (0.20–0.59) between the decrease of toluene and the increase of intermediates (Gly, mGly, Pyr and ωC_2) is significantly higher than C_2 (0.04). This was the same for benzene; the slope between

Table 3. Stable carbon isotope ratios (δ^{13}C, ‰) of C_2 in atmospheric aerosols from selected locations.

Sampling site	Particle size	Min*	Max	Avg	SD	Sampling interval	References
Urban							
Liaocheng, China	$PM_{2.5}$	−31.8	−16.6	−21.7	3.3	Jan to Feb (daytime)	Meng et al. (2020)
	$PM_{2.5}$	−26.5	−14.1	−17.9	2.6	Jan to Feb (nighttime)	
	$PM_{2.5}$	−31.8	−14.1	−19.8	3.5	Jan to Feb (winter)	
Beijing, China	$PM_{2.5}$	−23.7	−15.0	−20.1	3.0	Sep to Nov (autumn)	Zhao et al. (2018)
	$PM_{2.5}$	−27.2	−14.8	−22.9	3.4	Dec to Feb (winter)	
	$PM_{2.5}$	−25.0	−16.6	−21.9	2.1	Mar to May (spring)	
	$PM_{2.5}$	−27.0	−19.1	−22.4	2.7	Jun to Jul (summer)	
Sapporo, Japan	TSP	−22.4	−14.0	−18.8	2.0	May to Jul	Aggarwal et al. (2008)
Marine							
Western Pacific and Southern Ocean	TSP	−27.1	−6.7	−16.8	0.8	Nov to Feb	Wang and Kawamura (2006)
Mountain							
Mt. Tai, China	$PM_{2.5}$	−19.4	−13.0	−15.8	1.9	Jul to Aug (daytime)	Meng et al. (2018)
	$PM_{2.5}$	−20.1	−12.1	−17.2	1.7	Jul to Aug (nighttime)	
	$PM_{2.5}$	−20.1	−12.1	−16.5	1.9	Jul to Aug (summer)	
Background							
Gosan, S. Korea	TSP	−15.0	−10.6	−12.6	1.4	Mar to May (spring)	Zhang et al. (2016)
	TSP	−14.1	−7.5	−11.5	2.8	Jun to Aug (summer)	
	TSP	−16.7	−13.2	−14.7	1.4	Sep to Nov (autumn)	
	TSP	−20.5	−10.1	−15.8	4.3	Jan to Feb (winter)	
UV-irradiated							
Ambient anthropogenic aerosol	PM_{10}			−19.5		Non-irradiated	Pavuluri and Kawamura (2016)
	PM_{10}			−13.1	3.6	UV-irradiated	
Ambient biogenic aerosol	PM_{10}			−15.8		Non-irradiated	
	PM_{10}			−12.9	6.9	UV-irradiated	
This study							
Maize straw	$PM_{2.5}$	−14.9	−12.1	−13.1	1.6	2 d aged	This study
Rice straw	$PM_{2.5}$	−28.2	−24.6	−26.2	1.8	2 d aged	
Wheat straw	$PM_{2.5}$	−26.7	−26.3	−26.5	0.2	2 d aged	
Maize straw	$PM_{2.5}$	−9.1	−6.0	−7.1	1.4	7 d aged	
Rice straw	$PM_{2.5}$	−23.7	−17.2	−20.8	3.3	7 d aged	
Wheat straw	$PM_{2.5}$	−24.6	−23.5	−24.0	0.5	7 d aged	
Biomass burning	$PM_{2.5}$	−23.3	−21.0	−21.9	1.2	2 d aged	
	$PM_{2.5}$	−19.1	−15.5	−17.3	1.7	7 d aged	

* Min, max, avg and SD stand for minimum, maximum, arithmetic mean and standard deviation.

the decrease of benzene and the increase of mGly is 0.55, while for C_2 it is only 0.05.

On the global scale, isoprene is the most important precursor for C_2, contributing 70 % to global C_2, while anthropogenic VOCs contribute 21 % to C_2 production (Myriokefalitakis et al., 2011). Thus, it is not surprising that isoprene correlated with C_2 ($R = 0.58$) (Fig. 5). In addition, several alkenes and alkanes also had a significant correlation with C_2 (Table S3), indicating that these species may react in secondary oxidation processes to generate C_2. Previous studies have confirmed that diacids can be oxidation products of aromatic hydrocarbons (Borrás and Tortajada-Genaro, 2012) and cycloolefins (Hamilton et al., 2006) and may originate from diesel vehicle exhaust (Samy and Zielinska, 2010). However, no significant correlation was found between decreases in VOCs and increases in 7 d aged diacids. For the longer aging times, the particulate-phase compounds may be further oxidized to generate other compounds besides diacids. Such a correlation between decreases in VOCs and

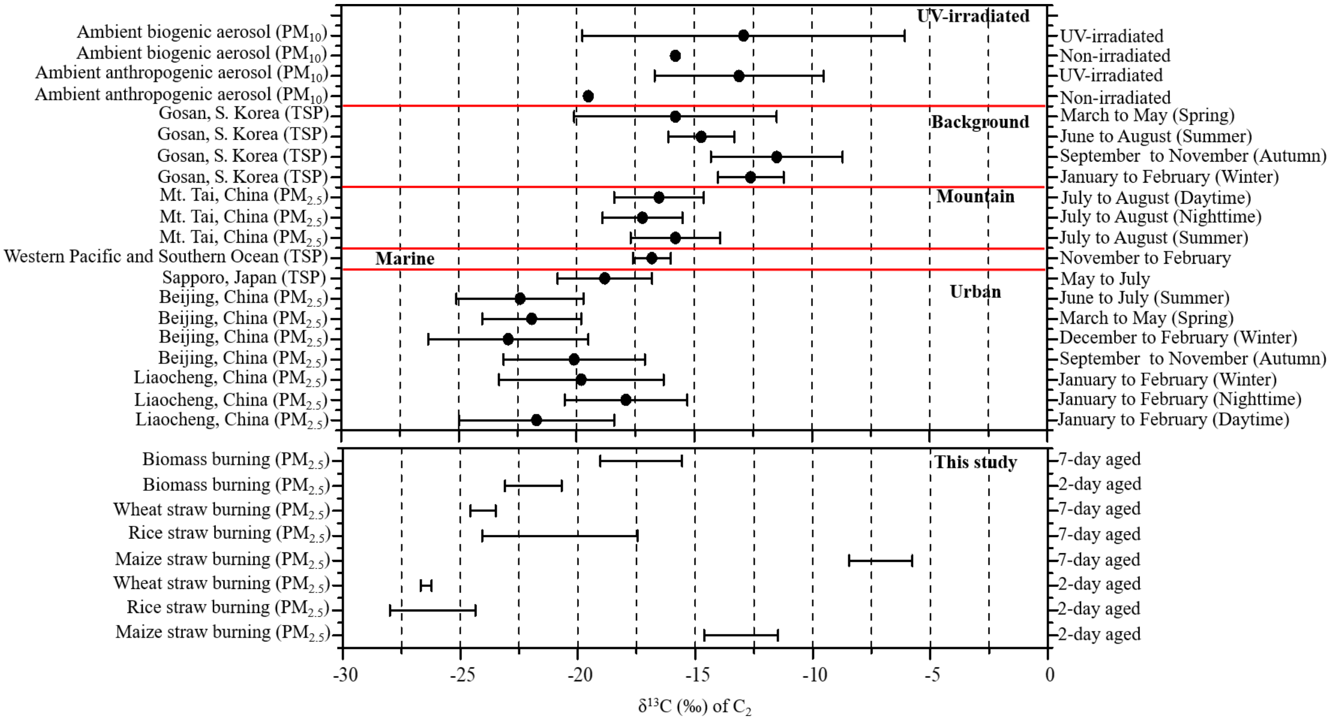

Figure 4. Stable carbon isotope ratios (δ^{13}C, ‰) of C_2 in aerosols from selected environments.

increases in diacids again suggests that 2 d aging may be sufficient to oxidize VOCs to diacids.

4 Conclusions

The emission factors (EFs) of dicarboxylic acids (diacids) and related compounds in experimentally produced fresh and aged biomass burning (BB) aerosols were compared. For fresh emissions, succinic acid (C_4) was the most abundant diacid species followed by azelaic acid (C_9). After atmospheric aging, diacids were dominated by oxalic acid (C_2), with elevated EFs. Ratios of aged to fresh (A/F) emissions for C_2 increased from 50.8 (2 d) to 64.5 (7 d). These results suggest that the diacids in the atmosphere largely originated from secondary photochemical processes as opposed to primary emissions from BB. It is confirmed for the first time whether the contribution of BB source to diacids is formed by primary emission or secondary oxidation. In addition, by comparing the EFs and A/F of 2 and 7 d aging, it was found that 2 d of aging is sufficient for many diacids. Moreover, the 2 d A/F of azelaic acid (C_9), 2.8, degraded by 27 % after 7 d, suggesting that this species is relatively stable with short residence time.

Decreasing trends in EFs were found for ketocarboxylic acids and α-dicarbonyls, from 2 to 7 d aging, with A/F reducing from 13.8 to 11.9 and from 5.4 to 3.3, respectively. These results suggest that after 2 d aging, the net degradation of these intermediates was faster than their rates of formation. Compared with 2 d samples, the δ^{13}C of C_2, malonic acid (C_3), C_4 and glyoxylic acid (ωC_2) in 7 d samples became more positive or isotopically heavier after the additional aging, likely due to kinetic isotope fractionation effects. Moreover, the δ^{13}C values for the aged maize samples in both the 2 and 7 d samples were significantly more positive than those of rice and wheat. This may be due to their different plant types, with maize being a C_4 plant, while wheat and rice are both C_3 plants. The correlations between volatile organic compounds (VOCs) and C_2 or intermediates indicated that the oxidation of VOCs led to the formation of diacids. This correlation exists only at 2 d aging but does not exist at 7 d aging, probably because the longer the aging time, the further the particle phase compounds may be oxidized to other compounds.

Diacids are highly water-soluble in nature, and thus their high abundances due to BB and intense photochemical aging would enhance the ability of aerosols to act as cloud condensation nuclei and modify the water-uptake properties of aerosol particles. Therefore, it is necessary to better understand the chemical and physical properties of the constituents of water-soluble organic smoke, as they may have a significant impact on climate forcings through indirect aerosol effects. The results provide in-depth understanding of secondary organic aerosol (SOA) formation in regions greatly affected by BB.

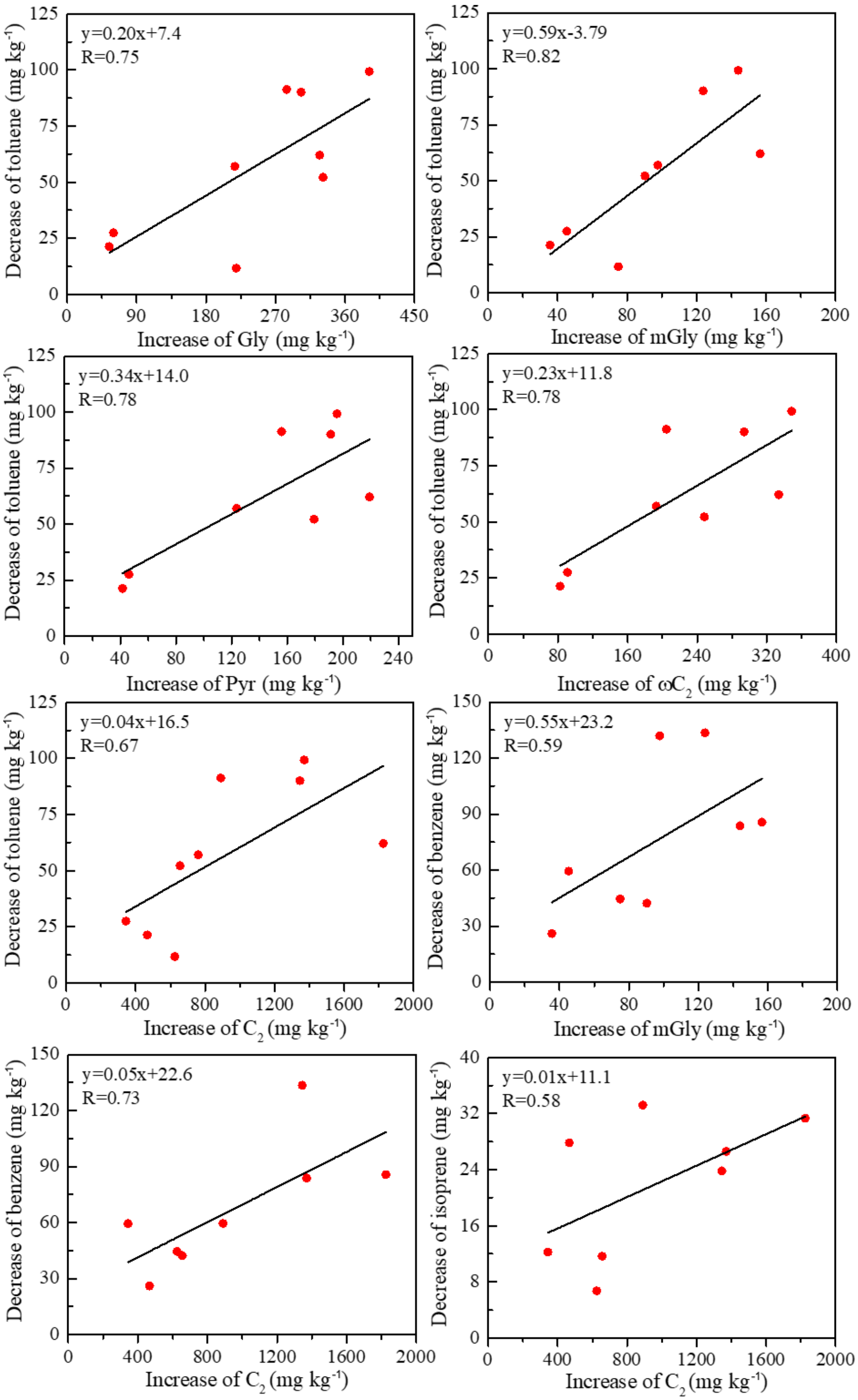

Figure 5. Regressions between the decreases of specific VOCs (toluene, benzene and isoprene) and increases of C_2 and its intermediates, methylglyoxal (mGly), glyoxal, (Gly), pyruvic acid (Pyr) and glyoxylic (ωC_2).

Data availability. Data can be made available upon request from the corresponding authors.

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-22-7489-2022-supplement.

Author contributions. JC and JL conceived and designed the study. MS contributed to the literature search, sample and data analysis, and manuscript writing. JL, JC, JCC and JGW contributed to manuscript revision. KFH, WD, SL, TZ, QW and JM carried out the particulate samples and supervised the experiments. All authors commented on the manuscript and reviewed the manuscript.

Competing interests. The contact author has declared that neither they nor their co-authors have any competing interests.

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