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 for 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)~~of 50.8 to 64.5~~, 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-day but decreased after 7-day aging, indicating short residence time and further atmospheric degradation from 2- to 7-days. The δ^{13}C values of C_2 ~~δ^{13}C values~~ 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 ~~δ^{13}C~~ became isotopically heavier during aging. Relationships between the reduction in volatile organic compounds (VOCs), such as toluene, benzene, and isoprene, and increase in diacids~~dicarboxylic acids~~ after 2-day aging indicate that these VOCs~~volatile organic compounds~~ led to the formation of diacids~~dicarboxylic acids~~. However, no significant correlation was found between decreases in VOCs and increases in 7-day aged diacids. In addition, the A/F of C_2 was 50.8 at 2 days and 64.5 at 7 days, indicating that the conversion of VOCs to C_2 was almost completed within 2 days. For the longer aging times, the particulate phase compounds may undergo further degradation in the oxidation processes.

Keywords: Biomass burning, Dicarboxylic acids, Atmospheric aging, Stable carbon isotope, VOCs

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 air-sheds.

There are both primary and secondary sources for diacids~~dicarboxylic acids~~ (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~~dicarboxylic acids~~ 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).

82   Being one of the major contributors to the global budget of aerosols, BB

83   emissions are of particular concern because they impact air quality, visibility, climate,

84   and human health (Hodshire et al., 2019). As the largest developing country and one

85   that burns large quantities of biomass, China has long suffered from severe air

86   pollution from BB (Chen et al., 2016; Fullerton et al., 2008). Domestic crop residues

87   (eg. rice, maize, and wheat straw) and firewood are the most significant energy

88   sources in most rural areas, and these are commonly used for cooking and heating (Li

89   et al., 2021; Tao et al., 2018).

90   Diacids, ketocarboxylic acids and α-dicarbonyls are products of BB (Agarwal et

91   al., 2010). Although these acids have been measured in ambient air in some areas

92   dominated by BB sources (FaLkovich et al., 2005; Kundu et al., 2010; Kawamura et

93   al., 2013), there have been few BB sources emission (e.g., chamber) measurements. It

94   was reported that BB smokes was found to contain large amounts of gaseous

95   pollutants, such as VOCs, nitrogen oxides (NOx), sulfur dioxide (SO_2), and ammonia

96   (NH_3) (Akagi et al., 2011; Andreae and Merlet, 2001). Gas-phase compounds,

97   especially VOCs, can be partition to the particle phase through nucleation,

98   condensation, and heterogeneous chemical reactions, creating secondary organic

99   aerosol (SOA) and adding to aerosol mass (Hodshire et al., 2019; Lim et al., 2019).

100   Oxalic acid (C_2), the most abundant species of diacids (Kawamura and Sakaguchi,

101   1999) and is formed by various VOCs in cloud droplets through photochemical

102   oxidation and liquid phase reactions. It is of interest to quantify emission factors (EFs)

103   of diacids and related compounds during the combustion of different biomass fuels in

104   the laboratory. Kalogridis et al. (2018) performed small-scale fire experiments using

105   the Large Aerosol Chamber (LAC, 1800 m^3) with a focus on BB from Siberian boreal

106   coniferous forests, and presented experimental data on EFs of diacids. However, this

107   study only focused on the EFs of diacids of fresh pollutants that directly emitted from

108   BB, so it is necessary to further investigation of molecular composition of aged BB

109   aerosols. Although high concentrations of diacids have been detected in biomass

110   combustion (FaLkovich et al., 2005; Kundu et al., 2010), it is still unclear on the

111   distribution of diacids directly emitted by BB (Jaffrezo et al., 1998) or compared to

112 those formed secondarily from percursors (Allen et al., 2004). In addition, limited

113 data are available on the specific diacidsdicarboxylic acids emitted from burning of

114 agricultural residues. Therefore, it is important to investigate the molecular

115 composition of diacids dicarboxylic acids in both fresh and aged BB aerosols to

116 advance current understanding of the potential environmental and climatic effects.

117 In this study, rice, maize, and wheat straw were selected for laboratory

118 simulations of fresh and aged BB aerosols. The study was conducted with the use of a

119 combustion chamber and oxidation flow reactor (OFR). Fresh and aged BB aerosols

120 were chemically analyzed for molecular characteristics and the stable carbon isotopic

121 composition (δ^{13}C) of selected diacidsdicarboxylic acids, ketocarboxylic acids,

122 α-dicarbonyls, and benzoic. The objectives of this study were to (1) investigate the

123 emissions of dicarboxylic acidsdiacids, ketocarboxylic acids and α-dicarbonyls from

124 crop residue burning; (2) evaluate the effects of atmospheric aging processes on

125 dicarboxylic acidsdiacids and related compounds; and (3) investigate reactions

126 relationship between of volatile organic carbon compounds (VOCs) with oxalic

127 acidC_2 and intermediates that form in the aging process to explore potential formation

128 mechanisms of selected organic acids.

2. Methods

2.1. Preparation and collection of fresh and aged BB aerosols

131 The experimental setup is illustrated in supplementary Fig. S1. Detailed

132 procedures for sample preparation and collection may be found in previous studies (Li

133 et al., 2020, 2021; Niu et al., 2020). Briefly, Fresh fresh smoke was generated by

134 burning dry biomass fuels (i.e., rice, maize, and wheat straw) in an ~8 m³ combustion

135 chamber (Tian et al., 2015), and the smoke was then passed through a Potential

136 Aerosol Mass-Oxidation Flow Reaction (PAM-OFR) (Aerodyne Research, LLC,

137 Billerica, MA, USA) to simulate aging processes in timescale of hours to days. The

138 biomass combustion chamber with a volume of ~8 m³ (1.8m (W)× 1.8m (L) ×2.2m

139 (H)), which was made of 3 mm thick aluminum to withstand high-temperature heating.

140 The combustion chamber was equipped with a thermoanemometer, an air purification

system, a heated sampling line, a dilution sampler, and so on. More detailed information about the design and evaluation of combustion chamber were described in Tian et al. (2015). ~~(Cao et al., 2020). The experimental setup is illustrated in supplementary Fig. S1. Detailed procedures for sample preparation and collection may be found in previous studies (Li et al., 2020, 2021; Niu et al., 2020). The PAM-OFR can be used to simulate an environment with extremely high oxidant concentrations with short residence times (Kang et al., 2007).~~

In order to get sufficient aerosols 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. ~~without the use of combustor or heat preservation.~~ 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. ~~For each test, ~100 g of the biomass fuel was burned on a combustion platform inside the combustion chamber. Each sampling period lasted 120-180 min, during which an equal amount of fuel was added to the platform 10 times at regular intervals. The entire burning cycle, including ignition, flaming, smoldering, and extinction, intends to simulate real-world source characterization without the use of combustor or heat preservation.~~ Smoldering was the major driver of the combustion process. A portion of the diluted smoke by 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 mini-Vol 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). ~~A portion of the diluted smoke was drawn through a quartz fiber filter (47 mm diameter, Whatman QM/A, Maidstone, UK) at 5 L min^{-1} using a mini-Vol PM$_{2.5}$ sampler (Airmetrics, OR, USA) to capture fresh emission, and a~~ Another portion of the exhaust (~9 L min^{-1}) was directed through a ~~drawn into~~ a 19-L cylinder PAM-OFR (with a diameter of 20 cm and length of 60 cm) to simulate atmospheric aging. Residence time of PAM-OFR

171 is estimated to be 90 ± 1 s at flow rate of 9 L min^{-1} (Li et al., 2021). ~~The aging times~~

172 ~~are selected to represent lifetimes of regional air pollutants prior to arrival at a~~

173 ~~receptor (Chow et al., 2019).~~ Three oxidants (O$_3$, •OH, and •HO$_2$) were generated in

174 the PAM chamber using irradiation from ultraviolet (UV) lamps. The OH exposure

175 values (OH$_{exp}$) can be calculated by the concentration of SO$_2$ and CO at the OFR inlet

176 and outlet in a laboratory setting. Relative humidity (RH) inside the OFR was varied

177 by passing different amounts of carrier gas through the OFR humidifier (MH-110).

178 Additional details on smoke generation condition, test study and evaluation of the

179 PAM-OFR were described by Cao et al. (2020).

180 In this study, ~~The~~ the UV lamps operated at a voltage of 2 and 3.5 V, ~~and the OH~~

181 ~~exposure values (~~OH$_{exp}$~~)~~ in the chamber were estimated at 2.6×10^{11} and 8.8×10^{11}

182 molecules-sec/m^3, respectively. These levels corresponded to ~2 and 7 day of aging

183 (Chow et al., 2019; Watson et al., 2019), assuming ~~that~~ a representative atmospheric

184 •OH level of 1.5×10^6 molecules/m^3 (Mao et al., 2009). The aged aerosols were

185 sampled by another mini-Vol PM$_{2.5}$ sampler (5 L min^{-1}) following the reactions in the

186 PAM-OFR chamber. Each test was conducted in triplicate to account for experimental

187 errors and to provide a measure of variability, which was calculated as standard

188 deviations. A total of 36 samples were collected and analyzed for chemical

189 composition.

190 **2.2. Sample extraction, derivatization, and quantification**

191 For diacids~~dicarboxylic acids~~, ketocarboxylic acids and α-dicarbonyls analyzing,

192 one quarter of each filter sample was extracted three times (15 min each) with purified

193 (18.2 MΩ) water (Milli-Q, Merch, France) and ultrasonication. The pH of the aerosol

194 extracts was adjusted to 8.5 to 9.0 using a 0.1 M potassium hydroxide solution prior to

195 drying that convert carboxylic acids into their salts (Bikkina et al., 2021). This drying

196 step improves the recovery of smaller diacids, such as ~~oxalic acid~~C$_2$ (Hegde and

197 Kawamura, 2012). Water extracts were concentrated to near dryness with a rotary

198 evaporator under vacuum and then reacted with 14% BF$_3$/n-butanol at 100 °C for 1 h

199 to derivatize carboxyl groups to dibutyl esters and oxo groups to dibutoxyacetals.

200 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 chromatography (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 ~~oxalic acid~~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, also undergo degradation and production through secondary chemical processes. Fresh and aged fuel-based ~~emission factors~~ (EF$_S$) 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:

$$EF_i = \frac{m_i \times v_{Stk} \times D \times t_{sample}}{Q_p \times m_{fuel}} \times DR$$

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

230   the stack, diluted stack, and background, where:

231    $$DR = \frac{CO_{2,Stk} - CO_{2,Bkg}}{CO_{2,Dil} - CO_{2,Bkg}}$$

232   where $CO_{2,Stk}$ is the CO_2 concentration in the stack; $CO_{2,Bkg}$ the background CO_2

233   concentration in the atmosphere; and $CO_{2,Dil}$ the CO_2 concentration in the diluted

234   smoke.

235   **2.4. Stable carbon isotope composition of diacids~~dicarboxylic acids~~**

236   Stable carbon isotopic determinations ($\delta^{13}C$) of diacids~~dicarboxylic acids~~,

237   ketocarboxylic acids, and α-dicarbonyls followed the techniques of Kawamura and

238   Watanabe (2004). The isotope values of the derivatized samples were determined

239   using a gas chromatography–isotope ratio mass spectrometer (GCIR-MS; Thermo

240   Fisher, Delta V Advantage, Franklin, MA, USA). The $\delta^{13}C$ values were then

241   calculated for free organic acids using an isotope mass balance equation based on the

242   measured $\delta^{13}C$ values of derivatives and ~~the derivatizing agent~~ (BF_3/n-butanol~~)~~

243   (Kawamura and Watanabe, 2004). To ensure the analytical error of the $\delta^{13}C$ values

244   less than 0.2‰, each aerosol sample was analyzed in triplicate, to obtain the average

245   values.

246   **3.   Results and Discussion**

247   **3.1. Emission factors for ~~dicarboxylic acids~~diacids, ketocarboxylic acids,**

248   **α-dicarbonyls**

249   Fresh and aged $PM_{2.5}$ EFs for a homologous series of ~~dicarboxylic acids~~diacids,

250   ketocarboxylic acids (glyoxylic acid, ωC_2 and pyruvic acid, Pyr), α-dicarbonyls

251   (glyoxal, Gly and methylglyoxal, mGly) and benzoic acid are presented in Table 1.

252   The EFs for most fresh and aged diacids varied by severely order-of-magnitude with

253   higher EFs after atmospheric aging. The highest fresh EF (i.e. EF_{fresh}) was found for

254   wheat straw ranging 44 - 122 mg kg^{-1} for succinic acid (C$_4$) and 67-102 mg kg^{-1} for

255   ~~glyoxal~~Gly, higher than those found in maize and rice. The arithmetic means and

256   standard deviations for the EF_{fresh} of total ~~dicarboxylic acids~~diacids from burning of

257   rice, maize, and wheat straws were 84 ± 36, 130 ± 47, and 307 ± 141 mg kg^{-1},

258 respectively.

259 As is shown Fig. 1, distributions of diacids~~dicarboxylic acids~~ in fresh emissions

260 varied by crop types and species. Of the saturated n-dicarboxylic acids, ~~succinic acid~~

261 ~~(~~C_4~~)~~ acid was the most abundant species in the maize and wheat straw with average

262 EF_{fresh} of 22 ± 12 and 83 ± 46 mg kg^{-1}, respectively. Azelaic acid (C_9) and C_4 were the

263 most abundant species from rice burning with EF_{fresh} of 11 ± 2.9 and 10 ± 9.0 mg kg^{-1},

264 respectively. These findings are consistent with the fresh smoke aerosols in Siberian

265 BB plumes (Kalogridis et al., 2018), in which C_4 and C_9 were more abundant than

266 ~~oxalic acid (~~C_2~~)~~. Previous studies also showed C_9 to be an oxidation product of

267 unsaturated fatty acids in biomass smoke (Kawamura and Gagosian, 1987; Kawamura

268 et al., 2013; Agarwal et al., 2010; Cao et al., 2017). $\underline{C_2}$ is the most abundant species of

269 diacids and is one of the final products of SOA reaction chain. In the fresh BB sample,

270 C_2 emissions were lower due to the short aging time.

271 Similar to the diacids, the highest EF_{fresh} for ketocarboxylic acids and

272 α-dicarbonyls were also found in wheat straw samples, with 44 ± 31 and 138 ± 91 mg

273 kg^{-1}, respectively. ~~Glyoxal (~~Gly~~)~~ was the highest α-dicarbonyls, with average EF_{fresh}

274 of 27 ± 3.9, 42 ± 10, and 84 ± 41 mg kg^{-1} for rice, maize and wheat straw,

275 respectively. This is consistent with previous studies which showed that Gly is often

276 more abundant than ~~methylglyoxal (~~mGly~~)~~ in polluted aerosols collected from China

277 (Pavuluri et al., 2010; Ho et al., 2007). Benzoic acid also was determined, and its

278 EF_{fresh} for rice, maize, and wheat aerosols were 1.9 ± 0.2, 2.5 ± 0.4, and 3.1 ± 0.3 mg

279 kg^{-1} (Table 1).

280 **3.2. Effects of atmospheric aging processes**

281 3.2.1 ~~Dicarboxylic acids~~Diacids

282 The EF_{aged} of 2- and 7-day diacids were 1650 ± 438 and 1957 ± 598 mg/kg,

283 respectively (Table S1); approximately 10 times greater than the EF_{fresh}. High

284 aged/fresh (A/F) ratios implies that the bulk of the total diacids were secondarily

285 produced through aging processes. Longer exposure time in the atmosphere increased

286 the formation of diacids as ratios of average ~~aged/fresh~~ A/F increased from 9.1 (2-day)

287 to 10.8 (7-day) (Table S1). As shown in Fig. 2, ~~oxalic acid (~~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) after 7-day aging. These results provide further evidence that C_2 is produced mainly through secondary photochemical processes rather than direct emissions from BB. The aged/fresh (A/F) ratios for oxalic acid increased by ~27% from 50.8 (2-day) to 64.5 (7-day) (Table S1). These results are further evidence that $PM_{2.5}$ oxalic acid is largely produced by secondary photochemical processes rather than direct emissions in biomass burning. This at is one possible also is a likely reason why 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 ratio of C_2 after 2-day aging was 50.8, and the change from 2~ to 7 day was relatively small, only increasing by 13.7 (Table S1). These results meant that 2-day aging may be sufficient for most diacids formation. It can be inferred that although diacids is still generated at 7-day aging, a large number of VOCs may have been oxidized at 2-day aging and transferred to the particle phase by condensation, adsorption and other ways. Especially for maize straw, the EF_{aged} of total detected organics at 7-day aging (1844 ± 344 mg/kg) was lower than that of at 2-day aging (3530 ± 626 mg/kg), which was mainly due to predominant role of particulate diacids degradation in longer aging time. This phenomenon is consistent with the change of EF_S of VOCs (precursors of C_2) during maize straw combustion. The decreases in of ΣVOC_{EF} after 2-day aging (1227 mg/kg) were comparable with those of 7-day aging (884 mg/kg) for maize straw (Niu et al., 2020). Two-day aging appeared to be sufficient for maize, with degradation after 7-day. This may partial due to the low VOCs produced in maize burn (Niu et al., 2020). The A/F ratios in Fig. 3 showed that 2-day aging is sufficient for many of the diacids.

As shown in Fig. 2, oxalic acid (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) after 7-day aging. The aged/fresh (A/F) ratios for oxalic acid increased by ~27% from 50.8

328 Succinic acid (C$_4$) ranked second in abundance after C$_2$, with 7-8 folds increased

329 in EF after 2- and 7-day aging wheat. Although malonic acid (C$_3$) is mainly produced

330 by the photochemical oxidation of C$_4$succinic acid, it also can be formed through the

331 incomplete combustion of fossil fuels and biomass (Kawamura and Ikushima, 1993).

332 In the atmosphere, C$_4$ is typically more abundant than C$_3$ originated from BB,

333 vehicular engine exhaust and biogenic emissions (Fu et al., 2013; Kawamura and

334 Kaplan, 1987; Kundu et al., 2010). Fig. 3 shows atmospheric aging increased the

335 abundances of C$_3$ and C$_4$ with A/F ratios increased from 16.2 to 31.1 for C$_3$malonic

336 acid, and from 5.7 to 8.0 in C$_4$succinic acid from 2- to 7-day of aging (Table S1).

337 These findings add to the evidence that these diacids are produced by the

338 photo-oxidation of primary pollutants emitted from combustion process. Lower EFs

339 and higher Higher A/F ratios in aged and fresh C$_3$malonic acid than those of

340 C$_4$succinic acid may be attributed to rapid oxidation formation rate of C$_3$ or

341 decarboxylation processing of C$_4$ diacid during aging (Zhao et al., 2018).

342 As mentioned above, C$_9$ (azelic acid) is thought to be mainly formed through the

343 photochemical oxidation of unsaturated fatty acids emitted by plants (Kawamura and

344 Gagosian, 1987). Average EFs in C$_9$azelic acid were low, ranging from 18 ±7.3 mg

345 kg^{-1} (fresh), to 51 ± 14 mg kg^{-1} (2-day), with A/F ratios of C$_9$ of 2.8, and 2.2 for the

346 2- and 7-day samples, respectively, suggesting that C$_9$azelic acid is relatively stable

347 with short residence time. Fig.3 shows that A/F ratios of other long-chain dicarboxylic

348 acids~~diacids~~ and branched ~~dicarboxylic acids~~diacids did not show apparent changes

349 between the 2- and 7-day samples, which may be due to the degradation of long-chain

350 diacids~~dicarboxylic acids~~ (Enami et al., 2015;Legrand et al., 2007;Miyazaki et al.,

351 2010). It is also possible that the laboratory combustion experiment did not produce

352 adequate quantities of certain diacids. For example, glutaric acid (C_5) and adipic acid

353 (C_6) are commonly formed by reactions of cycloolefins emitted from anthropogenic

354 sources with O_3 (Hatakeyama et al., 1985), and phthalic acid as a product of the

355 photochemical oxidation of aromatic hydrocarbon compounds (Kawamura and

356 Ikushima, 1993). Additional laboratory experiments may be needed to reify different

357 atmospheric process.

358 3.2.2 Ketocarboxylic acids and α-carbonyls

359 In contrast to the ~~dicarboxylic acids~~diacids, aging process were not apparent in

360 ketocarboxylic acids as A/F ratios reduced by 16% from 13.8 (2-day) to 11.9 (7-day).

361 Similar phenomenon was found for α-carbonyls with A/F ratios reduced by 64% from

362 5.4 (2-day) to 3.3 (7-day). This suggests the possibility that the degradation of these

363 intermediates to ~~oxalic acid~~C_2 is faster than their formation by oxidation after 2 days

364 of aging. Fig.3 also show apparent reduction EF of 33-42% from 2- to 7-day aging for

365 ~~glyoxal (~~Gly~~)~~ and ~~methylglyoxal (~~mGly~~)~~ which may be due to the fact ~~that~~ both Gly

366 and mGly initially can be oxidized to less volatile polar organic acids including

367 ~~pyruvic acid (~~Pyr~~)~~ and ~~glyoxylic acid (~~ωC$_2$~~)~~ and then further oxidized to C_2 (Wang et

368 al., 2012;Warneck, 2003).

369 **3.3. Comparisons of diagnostic ratios of ~~dicarboxylic acids~~diacids in fresh and**

370 **aged aerosols**

371 Patterns in the relative abundances of ~~dicarboxylic acids~~diacids have been used

372 to evaluate biogenic versus anthropogenic source strengths and the photochemical

373 processing of organic aerosols (Kawamura et al., 2012). Previous studies have shown

374 that C_4 can be directly oxidized into C_2 or via C_3 into C_2 (Jung et al., 2010;

375 Sorooshian et al., 2007), with C_2 being an end-product of the photochemical oxidation

376 (Wang et al., 2012). The ratios of C_3/C_4, C_2/C_4 and C_2/total diacids can be regarded as

377 indicators of aerosol aging (Cheng et al., 2013; Kunwar et al., 2019; Meng et al., 2018;

378 Pavuluri et al., 2010), with higher ratios indicative of more aged aerosols (Kawamura

379 and Sakaguchi, 1999). As shown in Table 2, the ratios in this study showed a clear

380 atmospheric aging trend from fresh to 7-day aging with ratios of 0.7 to 6.4 for C_2/C_4,

381 0.1 to 0.6 in C_2/total diacids and 0.2 to 0.5 in C_3/C_4, indicating obvious photochemical

382 oxidation. ~~with photochemically oxidization rune pronounced.~~

383 Ratios of $\omega C_2/C_2$ and Gly/mGly can also be used to evaluate the oxidation of

384 organic aerosols (Cheng et al., 2013, 2015; Kawamura et al., 2013). In the study,

385 apparent reduction of the $\omega C_2/C_2$ ratios from 1.3 (fresh) to 0.2 (7-day) supports the

386 potential oxidation pathways from precursor glyoxylic to oxalic acids. Aqueous-phase

387 oxidation by OH is faster for Gly than for mGly, and the abundance of Gly relative to

388 mGly is an indicator of aerosol aging (Cheng et al., 2013). The ratio of Gly/mGly in

389 xi'an samples was lower in haze days than in clean days, and lower in summer than in

390 winter. Similarly, the Gly/mGly ratios in the aged ~~biomass burning~~BB samples were

391 higher in the fresh PM$_{2.5}$ samples (3.8) compared to the 2-day ~~aged~~ (2.3) and 7-day

392 (2.0) aging~~, indicating the degradation for Gly proceeds more rapidly than mGly, and~~

393 ~~that is consistent with the decline Gly/mGly ratios in aged aerosols (Cheng et al.,~~

394 ~~2013)~~.

395 Ratios of C_3/C_4, C_2/diacids, $\omega C_2/C_2$, and Gly/mGly are similar among studies.

396 Except for the higher C_3/C_4 ratio of 3.9 found in marine aerosols of over the pacific

397 region (Kawamura and Sakaguchi, 1999), and lower C_3/C_4 ratios in Siberian

398 ~~biomass burning~~BB emissions in a large aerosol chamber (<0.03) (Kalogridis et al.,

399 2018). The largest difference was found for C_2/C_4, varied from <1 for fresh aerosol in

400 Siberian ~~biomass burning~~BB (Kalogridis et al., 2018), to 25.2 from forest fire in

401 Thailand (Boreddy et al., 2020). Elevated C_2/C_4 ratios exceeding 10 were found in

402 aged ambient Xi'an, China (10.4) (Cheng et al., 2013), Mt. Hua, China (10.7) (Meng

403 et al., 2014), marine aerosol, Pacific ocean (14.3) (Kawamura and Sakaguchi, 1999),

404 and ambient island Okinawa, Japan (15.5) (Kunwar and Kawamura, 2014). These

405 C_2/C_4 ratios are ~63% to 142% higher than these reported in this study. Overall, these

406 comparisons show the importance of photochemical aging, however, the atmospheric

407 oxidation evidently was more extensive in aerosols from some remote mountain and

408   marine environments.

3.4. Stable carbon isotopes of diacids

410   Stable carbon isotope ratios ($\delta^{13}C$) can provide insights into the sources of

411   aerosols, Pavuluri and Kawamura (2016) reported that average $\delta^{13}C$ values for C_2

412   from biogenic aerosols (-15.8‰) were less negative—i.e., contained more ^{13}C and

413   was isotopically enriched than those from anthropogenic aerosols (-19.5‰). Data for

414    $\delta^{13}C$ also can provide information on the processing or aging of organic aerosols

415   because isotopic fractionation result from chemical reactions or phase transfer

416   (Pavuluri and Kawamura, 2016; Zhang et al., 2016). Mass loading of $\delta^{13}C$ for diacids

417   in the fresh BB samples were too low to be detected by the GCIR-MS, but the $\delta^{13}C$

418   values for C_2 ranged from -23.3 to -21.0 ‰ (with an average of -21.9 ± 1.2 ‰) in

419   2-day and -19.1 to -15.5 ‰ (-17.3 ± 1.7 ‰) for 7-day aged samples (Table 3).

420   Table 3 shows that the average $\delta^{13}C$ values of C_2 from aged maize samples

421   ~~reported the a heaviest $\delta^{13}C$ signatures~~ higher than those of rice and wheat. ~~This is~~The

422   reason for the isotope difference may be that ~~likely because~~ maize is a C_4 plant,

423   ~~whereas~~ while wheat and rice are both C_3 plants. Song et al. (2018) showed that

424    $\delta^{13}C_{TC}$ in C_4 plants is isotopically heavier than in C_3 plants. Moreover, the $\delta^{13}C$ of C_2

425   is more abundant in 7- than 2-day samples (Table 3) with -13.1 ± 1.6 ‰ (2-day) and

426   -7.1 ± 1.4 ‰ (7-day) in maize; -26.2 ± 1.8 ‰ (2-day) and -20.8 ± 3.3 ‰ (7-day) in

427   rice and -26.5 ± 0.2 ‰ (2-day) and -24.0 ± 0.5 ‰ (7-day) in wheat combustion. The

428    $\delta^{13}C$ data for C_3, C_4 and ωC_2 (Table S2) showed similar trends, consistent with

429   previous studies. For example, Zhao et al. (2018) found that the $\delta^{13}C$ values of C_2

430   were related to aging. Pavuluri and Kawamura (2016) analyzed diacids, ωC_2, and Gly

431   for $\delta^{13}C$ in anthropogenic and biogenic aerosol samples by UV irradiation, and

432   reported more $\delta^{13}C$ less negative with longer irradiation times. During atmospheric

433   oxidation reactions, organic compounds react with OH radicals, causing the release of

434   CO_2 and CO which contain relatively the lighter ^{12}C isotope and thus leaving the

435   remaining substrate enriched in ^{13}C (Hoefs, 1997; Sakugawa and Kaplan, 1995).

436   A comparison of $\delta^{13}C$ values for C_2 in the aerosols from selected environments is

437   shown in ~~Figure~~ Fig. 4. Average $\delta^{13}C$ value (-21.9 ± 1.2 ‰) of 2-day aged biomass

438   burning of C_2 was comparable to those reported for urban regions, such as Beijing

439   (-21.8 ± 2.8‰) (Zhao et al., 2018) and Liaocheng (-19.8 ± 3.1‰) (Meng et al., 2020)

440   (Table 3). With continued aging, the C_2 $\delta^{13}C$ of the 7-day samples (-17.3 ± 1.7 ‰)

441   was more similar in samples from Mt. Tai (-16.5 ± 1.8‰) (Meng et al., 2018) and

442   western ~~pacific~~ Pacific and ~~southern~~ Southern ~~ocean~~ Ocean aerosol (-16.8 ± 0.8‰)

443   (Wang and Kawamura, 2006), but it was significantly lighter than that of samples

444   from the Korea Climate Observatory at Gosan (-13.7 ± 2.5‰), which is a mountain

445   background site in East Asia (Zhang et al., 2016).

3.5. Relationships between decreases VOCs~~volatile organic carbon compounds~~

446

447   **and increases diacids~~dicarboxylic acids~~**

448   During the chamber experiment (Niu et al., 2020) concerning measured the VOC

449   compounds. Table S3 presents the correlations between decreases in VOCs and

450   increases in ~~dicarboxylic acids~~diacids from fresh to 2-day aged BB samples.

451   Significant ($0.01 < p < 0.05$) correlations (R) were observed for toluene with Gly (R =

452   0.75), mGly (R = 0.81), Pyr (R =0.78), ωC_2 (R = 0.78) and C_2 (R = 0.67) (Fig. 5),

453   suggesting that toluene was converted to diacids during the aging processes. Indeed, it

454   has been reported that the photooxidation of toluene is a potential source of secondary

455   organic aerosol (SOA) in urban air (Sato et al., 2007), and the major chemical

456   components of the SOA include hemiacetal, peroxy hemiacetal oligomers and

457   ~~dicarboxylic acids~~diacids. It also can be seen that benzene had significant correlations

458   with mGly and C_2 (R>0.59 in Fig.5), implying that the oxidation of benzene led to

459   diacid formation. Photooxidation of Gly and mGly is a major global and regional

460   source of C_2 diacid, and the two formation pathways are Gly-ωC_2-C_2 and

461   mGly-Pyr-ωC_2-C_2, respectively (Yasmeen et al., 2010; Wang et al., 2012). As shown

462   in the Fig.5, the slope (0.20~0.59) between the decrease of toluene and the increase of

463   intermediates (Gly, mGly, Pyr and ωC_2) is significantly higher than C_2 (0.04). Same

464   thing with benzene, the slope between decrease of benzene and increase of mGly is

465   0.55, while C_2 is only 0.05. ~~And we can see that the slope of the correlation between~~

466   ~~the decrease of toluene and benzene and the increase of the precursor (Pyr and ωC₂) is~~

467   ~~significantly higher than that of oxalic acid.~~

On the global scale isoprene is the most important precursor for C_2, contributing 70% to the 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 ~~oxalic acid~~C_2. Previous studies have confirmed that ~~dicarboxylic acids~~diacids can be oxidation products of aromatic hydrocarbons (Borrás and Tortajada-Genaro, 2012), cycloolefins (Hamilton et al., 2006), and may originated from diesel vehicle exhaust (Samy and Zielinska, 2010). However, no significant correlation was found between decreases in VOCs and increases in 7-day aged diacids~~dicarboxylic acids~~. For the longer aging times, the particulate phase compounds may be further oxidized to generate other compounds besides diacids. Such a correlation between decreases VOCs and increases diacids again suggests that 2-day 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 was dominated by oxalic acid (C_2)~~dominated the diacids~~, with elevated EFs~~emission factors~~. Ratios of aged to fresh (A/F) for C_2 increased from 50.8 (2-day) to 64.5 (7-day). These results suggest that the ~~dicarboxylic acids~~diacids in the atmosphere largely originated from secondary photochemical processes as opposed to primary emissions from ~~biomass burning~~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 ratio of 2-day and 7-day aging, it was found that 2 days of aging is sufficient for many diacids. The 2-day A/F ratios 2.8 of azelaic acid (C_9) degraded by 27% after 7-days, suggesting that this species is relatively stable with short residence time.

497   Decreasing trends in EFs were found for ketocarboxylic acids and α-dicarbonyls,

498   from 2-day to 7-day aging with A/F ratios reduced from 13.8 to 11.9 and from 5.4 to

499   3.3, respectively. These results suggest that after 2-day aging, the net degradation of

500   these intermediates was faster than their rates of formation. Compared with 2-day

501   samples, the $\delta^{13}C$ of C_2, malonic acid (C_3), C_4 and glyoxylic acid (ωC_2) in 7-day

502   samples became more positive or isotopically heavier after the additional aging, likely

503   due to kinetic isotope fractionation effects. Moreover, the $\delta^{13}C$ values for the aged

504   maize samples in both the 2- and 7-day samples were significantly more positive than

505   those of rice and wheat. This may be due to their different plant types with maize

506   being~~This is likely due to differences in their photosynthetic pathways as maize is~~ a

507   C_4 plant, while wheat and rice are both C_3 plants. The correlations between volatile

508   organic compounds (VOCs) ~~(benzene, toluene, isoprene, etc.)~~ and ~~oxalic acid (C_2)~~ and

509   intermediates indicated that the oxidation of VOCs led to the formation of diacids.

510   This correlation exists only at 2-day aging, but does not exist at 7-day aging, probably

511   because the longer the aging time, the particle phase compounds may be further

512   oxidized to other compounds. ~~The results provide in depth understanding of SOAs~~

513   ~~formation in regions greatly affected by biomass burning.~~

514   Diacid are highly water-soluble in nature and thus their high abundances due to

515   BB and intense photochemical aging would enhance the ability of aerosols to act as

516   cloud condensation nuclei and modify the water-uptake properties of aerosol particles.

517   Therefore, it is necessary to better understand the chemical and physical properties of

518   the constituents of water-soluble organic smoke, as they may have a significant

519   impact on climate forcings through indirect aerosol effects. The results provide

520   in-depth understanding of secondary organic aerosol (SOAs) formation in regions

521   greatly affected by BB.

Data availability

523   The data involved in this study will be provided when they are asked from the

524   corresponding authors.

Author contribution

Junji Cao and Jianjun Li conceived and designed the study. Minxia Shen contributed to the literature search, samples and data analysis, and manuscript writing. Jianjun Li, Junji Cao, Judith C. Chow and John G. Watson contributed to manuscript revision. Kin Fai Ho, Wenting Dai, Suixin Liu, Ting Zhang, Qiyuan Wang, Jingjing Meng carried out the particulate samples and supervised the experiments. All authors commented on the manuscript and reviewed the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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A: Dicarboxylic acids; B: Ketocarboxylic acids; C: α-dicarbonyls

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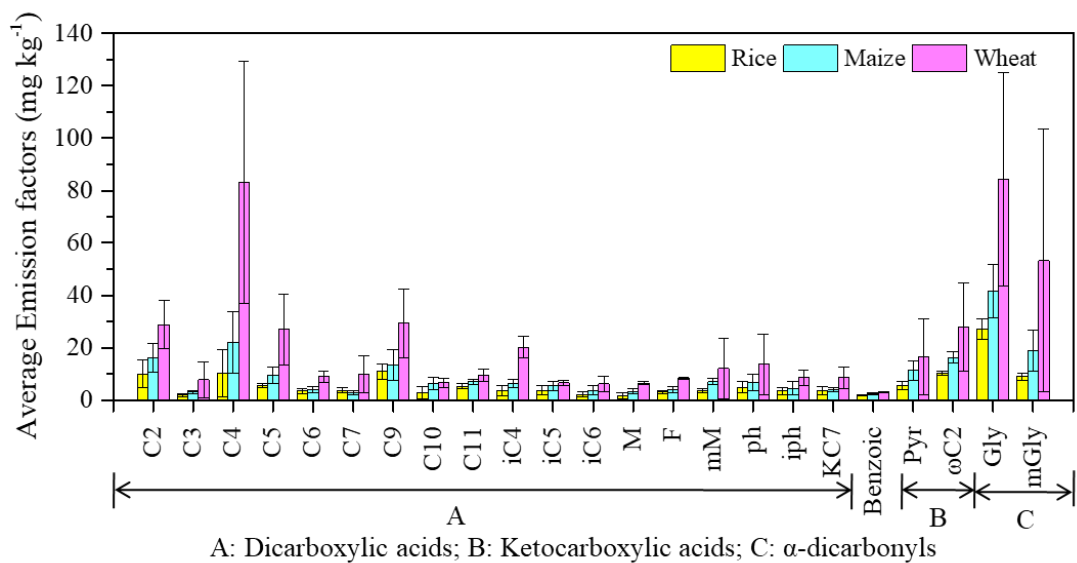
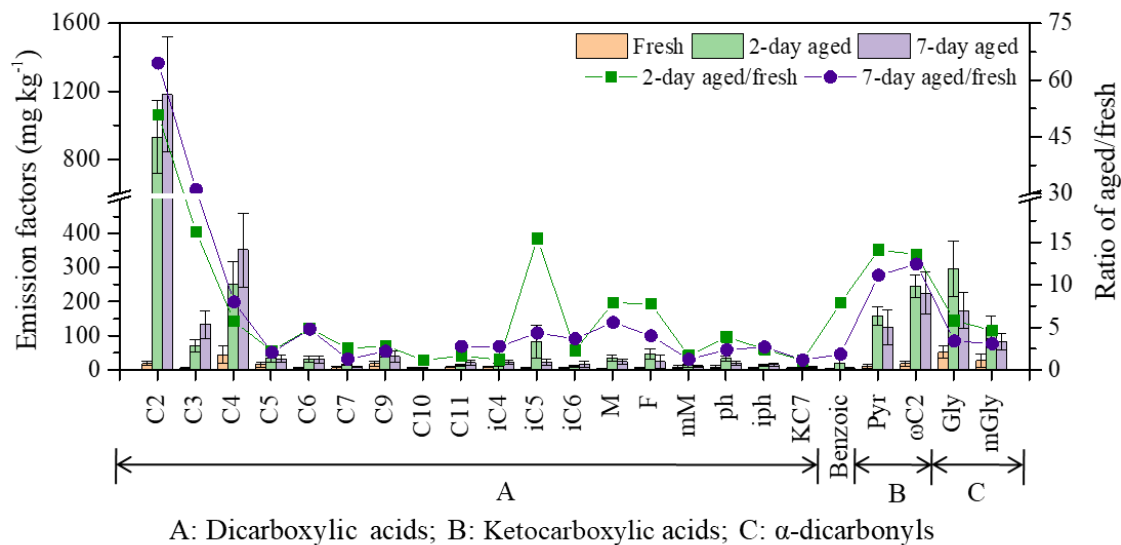

844 Figure 1 Average emission factors of dicarboxylic acids and related compounds in

845 fresh PM$_{2.5}$ aerosols from biomass burning.

Figure 2 Comparison between 2- and 7-day aged average PM$_{2.5}$ emission factors of A: dicarboxylic acids, B: ketocarboxylic acids, and C: α-carbonyls for laboratory combustion of rice, maize, and wheat straw.

851
852 Figure 3 Average emission factors of dicarboxylic acids and related compounds from
853 biomass burning experiment for the fresh, 2- and 7-day aged PM$_{2.5}$ aerosols. The
854 squares and dots denote the ratios of aged to fresh (A/F) sample for the dicarboxylic
855 acids and related compounds after 2- and 7-day aging.

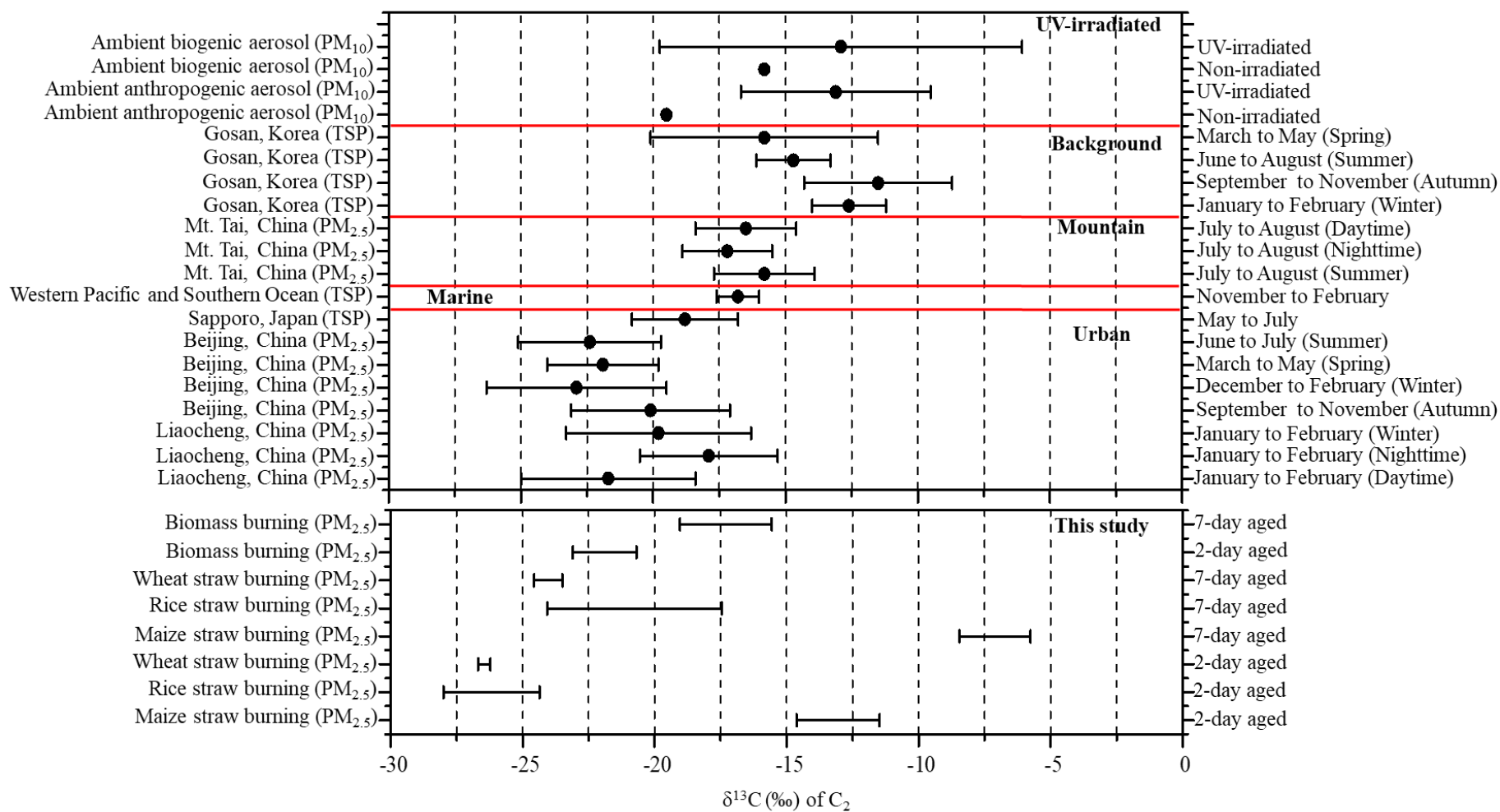



Figure 4 Stable carbon isotope ratios ($\delta^{13}C$, ‰) of C_2 in aerosols from selected environments.

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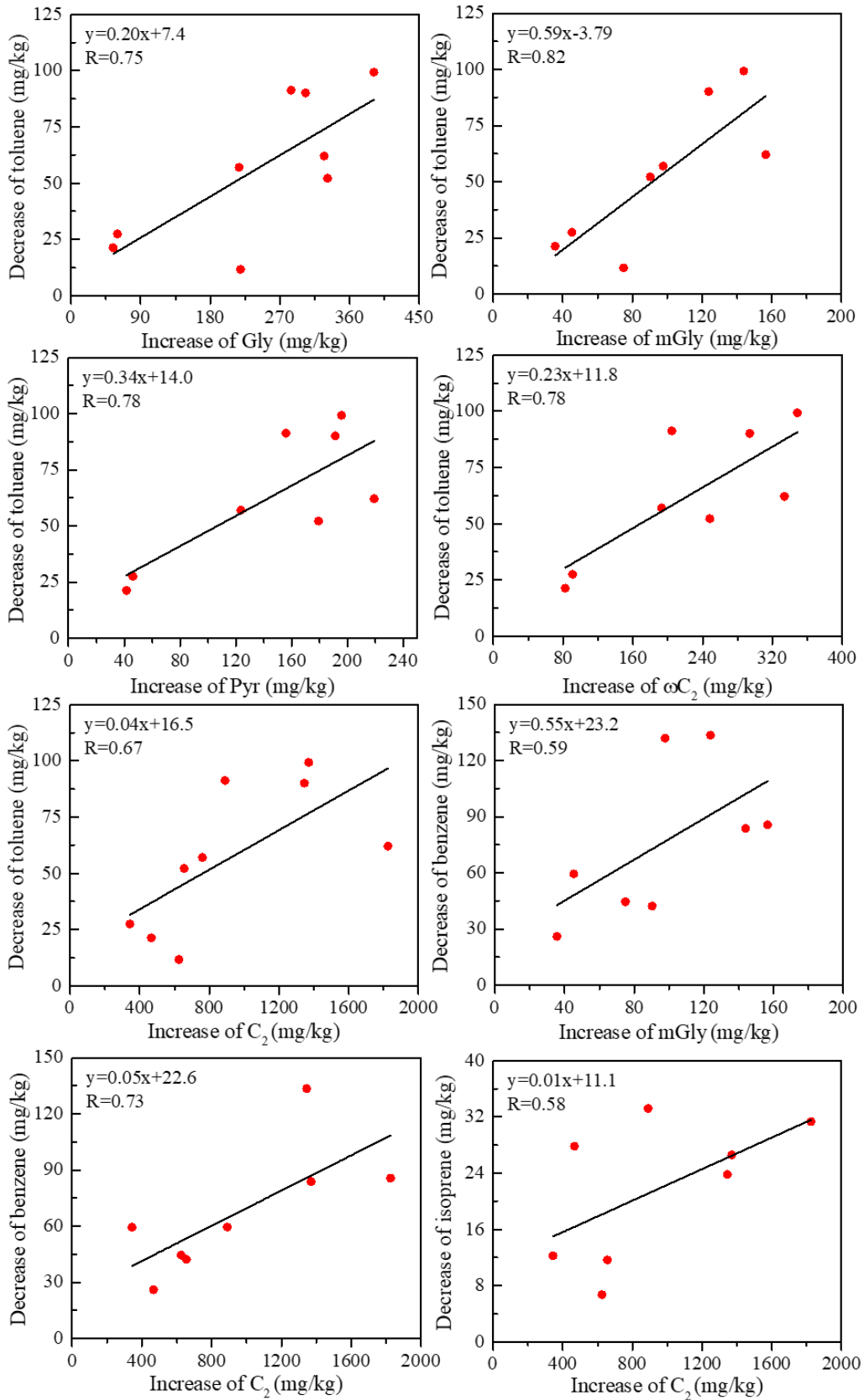
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859 Figure 5 Regressions between the decreases of specific VOCs (toluene, benzene and

860 isoprene) and increases of C_2 and its intermediates methylglyoxal (mGly), Glyoxal,

861 (Gly), Pyruvic acid (Pyr) and Glyoxylic (ωC_2).

862   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 day aged		Rice-7 day aged		Maize-2 day aged		Maize-7 day aged		Wheat-2 day aged		Wheat-7 day 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[a]	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

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

863 Table 2 Comparison of mass ratios of C_3/C_4, C_2/C_4, C_2/total diacids, $\omega C_2/C_2$ and Gly/mGly in fresh and aged aerosols collected from biomass
864 burning with the different locations around the World

	Sampling site	Particle size	C_3[1]$/C_4$	C_2/C_4	C_2/total diacids	$\omega C_2/C_2$	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 et al. (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)
	DoiAngKhang, 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)
	Motor Exhausts		0.35					Kawamura et al. (1987)
	Siberian (biomass burning, chamber)	PM$_{2.5}$	<0.03	<1	/	/	/	Kalogridis et al. (2018)
Laboratory simulation	Fresh (biomass burning, chamber)	PM$_{2.5}$	0.2	0.7	0.1	1.3	3.8	
	2-day aged (biomass burning, chamber)	PM$_{2.5}$	0.3	3.8	0.6	0.3	2.3	This study
	7-day aged (biomass burning, chamber)	PM$_{2.5}$	0.5	6.4	0.6	0.2	2.0	

865 [1] See compund list in Table 1

 Table 3 Stable carbon isotope ratios ($\delta^{13}C$, ‰) of C_2 in atmospheric aerosols from selected
867   locations

Sampling site	Particle size	Min[1]	Max	Ave.	Std.	Sampling interval	References
Urban							
	PM$_{2.5}$	-31.8	-16.6	-21.7	3.3	Jan. to Feb. (Daytime)	
Liaocheng, China	PM$_{2.5}$	-26.5	-14.1	-17.9	2.6	Jan. to Feb.	Meng et al. (2020)
	PM$_{2.5}$	-31.8	-14.1	-19.8	3.5	Jan. to Feb. (Winter)	
	PM$_{2.5}$	-23.7	-15.0	-20.1	3.0	Sep. to Nov.	
Beijing, China	PM$_{2.5}$	-27.2	-14.8	-22.9	3.4	Dec. to Feb. (Winter)	Zhao et al. (2018)
	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							
	PM$_{2.5}$	-19.4	-13.0	-15.8	1.9	Jul. to Aug. (Daytime)	
Mt. Tai, China	PM$_{2.5}$	-20.1	-12.1	-17.2	1.7	Jul. to Aug.	Meng et al. (2018)
	PM$_{2.5}$	-20.1	-12.1	-16.5	1.9	Jul. to Aug. (Summer)	
Background							
	TSP	-15.0	-10.6	-12.6	1.4	Mar. to May (Spring)	
Gosan, Korea	TSP	-14.1	-7.5	-11.5	2.8	Jun. to Aug.	Zhang et al. (2016)
	TSP	-16.7	-13.2	-14.7	1.4	Sep. to Nov.	
	TSP	-20.5	-10.1	-15.8	4.3	Jan. to Feb. (Winter)	
UV-irradiated							
Ambient anthropogenic	PM$_{10}$			-19.5		Non-irradiated	
	PM$_{10}$			-13.1	3.6	UV-irradiated	Pavuluri and Kawamura (2016)
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-day aged	
Rice straw	PM$_{2.5}$	-28.2	-24.6	-26.2	1.8	2-day aged	
Wheat straw	PM$_{2.5}$	-26.7	-26.3	-26.5	0.2	2-day aged	
Maize straw	PM$_{2.5}$	-9.1	-6.0	-7.1	1.4	7-day aged	This study
Rice straw	PM$_{2.5}$	-23.7	-17.2	-20.8	3.3	7-day aged	
Wheat straw	PM$_{2.5}$	-24.6	-23.5	-24.0	0.5	7-day aged	
Biomass burning	PM$_{2.5}$	-23.3	-21.0	-21.9	1.2	2-day aged	
	PM$_{2.5}$	-19.1	-15.5	-17.3	1.7	7-day aged	

868   [1]Min, Max, Ave, and Std stand for minimum, maximum, arithmetic mean, and standard deviation.

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