1 **Distribution and stable carbon isotopic composition of dicarboxylic**

2 **acids, ketocarboxylic acids and α-dicarbonyls in fresh and aged**

3 **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 ($\delta^{13}C$) 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 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 C_2 $\delta^{13}C$ values for aged biomass samples were higher than those of urban aerosols but lower than marine or mountain aerosols, and the C_2 $\delta^{13}C$ became isotopically heavier during aging. Relationships between the reduction in volatile organic compounds (VOCs), such as toluene, benzene, and isoprene, and increase in dicarboxylic acids after 2-day aging indicate that these volatile organic compounds led to the formation of dicarboxylic acids.

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

1. Introduction

48   Dicarboxylic acids (diacids), ketocarboxylic acids and α-dicarbonyls are

49   common components of the atmospheric organic aerosol, accounting for 1–3% of the

50   total organic carbon in urban areas and >10% of the carbon mass in remote regions

51   (Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999; Kerminen et al.,

52   2000; Zhao et al., 2018). Due to their high water-solubility and other physicochemical

53   properties, diacids affect the hygroscopic growth of particulate matter (PM), and these

54   compounds are involved in the activation of cloud condensation nuclei and formation

55   of ice nuclei (Kawamura and Bikkina, 2016). Diacids and related compounds have

56   been found in a wide variety of environments including urban settings (Ho et al., 2006;

57   Kawamura and Ikushima, 1993; Meng et al., 2020; Sorathia et al., 2018; Wang et al.,

58   2002, 2006, 2012), mountains ranges (Kawamura et al., 2013; Kunwar et al., 2019),

59   and remote marine atmospheres (Hoque et al., 2020; Kawamura and Usukura, 1993).

60   They also have been reported in both the Arctic and Antarctic aerosols (Kawamura et

61   al., 1996a, b; Narukawa et al., 2002, 2003) as well as polar ice cores (Legrand and De

62   Angelis, 1996; Kawamura et al., 2001). Various studies have assessed the molecular

63   distributions, temporal variability, and sources of diacids in different air-sheds.

64   There are both primary and secondary sources for dicarboxylic acids (Mkoma

65   and Kawamura, 2013). Primary sources include emissions from fossil fuel combustion

66   (Kawamura and Kaplan, 1987;Rogge et al., 1993), cigarette burning (Rogge et al.,

67   1994), cooking (Rogge et al., 1991), and biomass burning (BB) (Narukawa et al.,

68   1999; Schauer et al., 2001). Of these, BB was found to be an important source of

69   dicarboxylic acids and related compounds over regional and global scales (Kundu et

70   al., 2010). Emissions from BB not only compose a major source of primary particles

71   but also introduce aerosol precursors to the atmosphere (Akagi et al., 2011; Gilman et

72   al., 2015; Reid et al., 2005). Secondary sources include particles produced by

73   chemical/photochemical oxidation reactions of volatile organic compounds, especially

74   those emitted from primary sources (Lim et al., 2013; Carlton et al., 2006, 2007).

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

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

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

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

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

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

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

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

83   Although high concentrations of diacids have been detected in biomass

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

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

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

87   data are available on the specific dicarboxylic acids emitted from burning of

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

89   composition of dicarboxylic acids in both fresh and aged BB aerosols to advance

90   current understanding of the potential environmental and climatic effects.

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

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

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

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

95   composition (δ^{13}C) of selected dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls,

96   and benzoic. The objectives of this study were to (1) investigate the emissions of

97   dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls from crop residue burning;

98   (2) evaluate the effects of atmospheric aging processes on dicarboxylic acids and

99   related compounds; and (3) investigate reactions of volatile organic carbon

100   compounds (VOCs) with oxalic acid and intermediates that form in the aging process

101   to explore potential formation mechanisms of selected organic acids.

102   **2. Methods**

103   **2.1. Preparation and collection of fresh and aged BB aerosols**

104   Fresh smoke was generated by burning dry biomass fuels (i.e., rice, maize, and

105   wheat straw) in an ~8 m^3 combustion chamber (Tian et al., 2015), and the smoke was

106   then passed through a Potential Aerosol Mass-Oxidation Flow Reaction (PAM-OFR)

107   (Aerodyne Research, LLC, Billerica, MA, USA) to simulate aging processes (Cao et

108   al., 2020). The experimental setup is illustrated in supplementary Fig. S1. Detailed

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

110   et al., 2020, 2021; Niu et al., 2020). The PAM-OFR can be used to simulate an

111   environment with extremely high oxidant concentrations with short residence times

112   (Kang et al., 2007).

113   For each test, ~100 g of the biomass fuel was burned on a combustion platform

114   inside the combustion chamber. Each sampling period lasted 120–180 min, during

115   which an equal amount of fuel was added to the platform 10 times at regular intervals.

116   The entire burning cycle, including ignition, flaming, smoldering, and extinction,

117   intends to simulate real-world source characterization without the use of combustor or

118   heat preservation. Smoldering was the major driver of the combustion process.

119   A portion of the diluted smoke was drawn through a quartz fiber filter (47 mm

120   diameter, Whatman QM/A, Maidstone, UK) at 5 L min^{-1} using a mini-Vol PM$_{2.5}$

121   sampler (Airmetrics, OR, USA) to capture fresh emission, and another portion (~9 L

122   min^{-1}) was drawn into a 19-L cylinder PAM-OFR (with a diameter of 20 cm and

123   length of 60 cm) to simulate atmospheric aging. The aging times are selected to

124   represent lifetimes of regional air pollutants prior to arrival at a receptor (Chow et al.,

125   2019). Three oxidants (O$_3$, •OH, and •HO$_2$) were generated in the PAM chamber

126   using irradiation from ultraviolet (UV) lamps. The UV lamps operated at a voltage of

127   2 and 3.5 V, and the OH exposure values (OH$_{exp}$) in the chamber were estimated at

128   2.6×10^{11} and 8.8×10^{11} molecules-sec/m^3, respectively. These levels corresponded

129   to ~2 and 7 day of aging (Watson et al., 2019), assuming that a representative

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

131   aerosols were sampled following the reactions in the PAM-OFR chamber. Each test

132   was conducted in triplicate to account for experimental errors and to provide a

133   measure of variability, which was calculated as standard deviations. A total of 36

134   samples were collected and analyzed for chemical composition.

2.2. Sample extraction, derivatization, and quantification

135

136 For dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls analyzing, one

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

138 (18.2 MΩ) water (Milli-Q, Merch, France) and ultrasonication. The pH of the aerosol

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

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

141 step improves the recovery of smaller diacids, such as oxalic acid (Hegde and

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

143 evaporator under vacuum and then reacted with 14% BF_3/n-butanol at 100 ℃ for 1 h

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

145 After derivatization, n-hexane was added and washed with pure water three times

146 to remove the water-soluble inorganics such as hydrogen fluoride and boric acid. The

147 hexane layer was concentrated to near dryness using a rotary evaporator under

148 vacuum and a N_2 blow-down technique, and then the esters and acetals of target

149 analytes were dissolved in known amounts of n-hexane. Finally, the hexane layers

150 were concentrated to 100 μL and analyzed using a capillary gas chromatography (GC;

151 HP 6890, Agilent Technology, Santa Clara, CA, USA) equipped with a split/splitless

152 injector and a flame ionization detector (FID). Peak identification was performed by

153 comparing the GC retention times with those of authentic standards and confirmed by

154 a thermal desorption (TD) unit coupled with a gas chromatograph/mass spectrometric

155 detector (TD-GC/MS, Models 7890A/5975C, Agilent Technology, Santa Clara, CA,

156 USA). The detection limits for those organic compounds were 0.1 ng m^{-3}, and the

157 analytical errors, based on the replicate analyses, were less than 15%. Recoveries of

158 the target compounds were 83% for oxalic acid and 87% to 110% for the other

159 species.

2.3 Emission factor calculations

160

161 Concentrations of the various species in the aged samples were affected by their

162 initial emission, also undergo degradation and production through secondary chemical

163 processes. Fresh and aged fuel-based emission factors (EF) for each measured

164 chemical compound were calculated by dividing its filter mass by the mass of

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165 combusted dry biomass fuel (Andreae and Merlet, 2001; Li et al., 2020; Tian et al.,

166 2015); that is:

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

167 where EF_i (mg kg^{-1}) is the EF of chemical compound i for the specific crop; m_i (mg)

168 is the mass of chemical compound i collected on the filter; v_{Stk} is the average stack

169 flow velocity (m s^{-1}) at standard conditions; D is the stack cross section (m^2); t_{sample} is

170 the sampling duration (s); Q_p is the sampling volume through the filter (m^3) at

171 standard temperature and pressure; and m_{fuel} is the mass of burned biomass fuel (kg,

172 dry weight).

173 The dilution ratio (DR) was determined from the CO_2 concentrations measured at

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

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

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

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

177 smoke.

2.4. Stable carbon isotope composition of dicarboxylic acids

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

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

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

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

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

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

185 measured $\delta^{13}C$ values of derivatives and the derivatizing agent (BF$_3$/n-butanol)

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

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

188 values.

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3. Results and Discussion

3.1. Emission factors for dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls

Fresh and aged $PM_{2.5}$ EFs for a homologous series of dicarboxylic acids, 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 severely order-of-magnitude with higher EFs after atmospheric aging. The highest fresh EF (i.e. EF_{fresh}) was found for wheat straw ranging 44 - 122 mg kg^{-1} for succinic acid and 67-102 mg kg^{-1} for glyoxal, higher than those found in maize and rice. The arithmetic means and standard deviations for the EF_{fresh} of total dicarboxylic acids from burning of rice, maize, and wheat straws were 84 ±36, 130 ±47, and 307 ±141 mg kg^{-1}, respectively.

As is shown Fig. 1, distributions of dicarboxylic acids in fresh emissions varied by crop types and species. Of the saturated n-dicarboxylic acids, succinic acid (C_4) acid was the most abundant species in the maize and wheat straw with average EF_{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 EF_{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 oxalic acid (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).

Similar to the diacids, the highest EF_{fresh} for ketocarboxylic acids and α-dicarbonyls were also found in wheat straw samples, with 44 ±31 and 138 ±91 mg kg^{-1}, respectively. Glyoxal (Gly) was the highest α-dicarbonyls, with average EF_{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 methylglyoxal (mGly) in polluted aerosols collected from China (Pavuluri et al., 2010;Ho et al., 2007). Benzoic acid also was determined, and its EF_{fresh} for rice, maize, and wheat aerosols were 1.9 ±0.2, 2.5 ±0.4, and 3.1 ±0.3 mg

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

219   **3.2. Effects of atmospheric aging processes**

220   3.2.1 Dicarboxylic acids

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

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

223   aged/fresh ratios implies that the bulk of the total dicarboxylic acids were secondarily

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

225   the formation of diacids as ratios of average aged/fresh increased from 9.1 (2-day) to

226   10.8 (7-day) (Table S1).

227   As shown in Fig. 2, oxalic acid (C_2) was the most abundant of all measured

228   diacids among three crops, with the highest EF_{aged} found in wheat (1412 ± 328 mg/kg)

229   after 7-day aging. The aged/fresh (A/F) ratios for oxalic acid increased by ~27% from

230   50.8 (2-day) to 64.5 (7-day) (Table S1). These results are further evidence that $PM_{2.5}$

231   oxalic acid is largely produced by secondary photochemical processes rather than

232   direct emissions in biomass burning. This also is a likely reason why C_2 is often the

233   most abundant diacid in ambient samples, especially in the oceanic and other remote

234   areas (Hoque et al., 2020;Kawamura and Usukura, 1993;Kawamura and Sakaguchi,

235   1999;Kunwar and Kawamura, 2014;Hegde and Kawamura, 2012;Kawamura and

236   Bikkina, 2016;Wang et al., 2012). Two-day aging appeared to be sufficient for maize,

237   with degradation after 7-day. This may partial due to the low VOCs produced in

238   maize burn (Niu et al., 2020). The A/F ratios in Fig. 3 showed that 2-day aging is

239   sufficient for many of the diacids.

240   Succinic acid (C_4) ranked second in abundance after C_2, with 7-8 folds increased

241   in EF after 2- and 7-day aging wheat. Although malonic acid (C_3) is mainly produced

242   by the photochemical oxidation of succinic acid, it also can be formed through the

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

244   In the atmosphere, C_4 is typically more abundant than C_3 originated from BB,

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

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

247   abundances of C_3 and C_4 with A/F ratios increased from 16.2 to 31.1 for malonic acid,

248 and from 5.7 to 8.0 in succinic acid from 2- to 7-day of aging (Table S1). These

249 findings add to the evidence that these diacids are produced by the photo-oxidation of

250 primary pollutants emitted from combustion process. Lower EFs and higher A/F ratios

251 in aged and fresh malonic acid than those of succinic acid may be attributed to rapid

252 oxidation rate of C_3 or decarboxylation processing of C_4 diacid during aging (Zhao et

253 al., 2018).

254 As mentioned above, C_9 (azelic acid) is thought to be mainly formed through the

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

256 Gagosian, 1987). Average EFs in azelic acid were low, ranging from 18 ± 7.3 mg kg^{-1}

257 (fresh), to 51 ± 14 mg kg^{-1} (2-day), with A/F ratios of C_9 of 2.8, and 2.2 for the 2- and

258 7-day samples, respectively, suggesting that azelic acid is relatively stable with short

259 residence time. Fig.3 shows that A/F ratios of other long-chain dicarboxylic acids and

260 branched dicarboxylic acids did not show apparent changes between the 2- and 7-day

261 samples, which may be due to the degradation of long-chain dicarboxylic acids

262 (Enami et al., 2015;Legrand et al., 2007;Miyazaki et al., 2010). It is also possible that

263 the laboratory combustion experiment did not produce adequate quantities of certain

264 diacids. For example, C_5 and C_6 are commonly formed by reactions of cycloolefins

265 emitted from anthropogenic sources with O_3 (Hatakeyama et al., 1985), and phthalic

266 acid as a product of the photochemical oxidation of aromatic hydrocarbon compounds

267 (Kawamura and Ikushima, 1993). Additional laboratory experiments may be needed

268 to reify different atmospheric process.

269 3.2.2 Ketocarboxylic acids and α-carbonyls

270 In contrast to the dicarboxylic acids, aging process were not apparent in

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

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

273 5.4 (2-day) to 3.3 (7-day). This suggests the possibility that the degradation of these

274 intermediates to oxalic acid is faster than their formation by oxidation after 2 days of

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

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

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

278   pyruvic acid (Pyr) and glyoxylic acid (ωC_2) and then further oxidized to C_2 (Wang et

279   al., 2012;Warneck, 2003).

280   **3.3. Comparisons of diagnostic ratios of dicarboxylic acids in fresh and aged**

281   **aerosols**

282   Patterns in the relative abundances of dicarboxylic acids have been used to

283   evaluate biogenic versus anthropogenic source strengths and the photochemical

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

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

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

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

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

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

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

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

292   0.1 to 0.6 in C_2/total diacids and 0.2 to 0.5 in C_3/C_4 with photochemically oxidization

293   rune pronounced.

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

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

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

297   potential oxidation pathways from precursor glyoxylic to oxalic acids. Similarly, the

298   Gly/mGly ratios in the biomass burning samples were higher in the fresh $PM_{2.5}$

299   samples (3.8) compared to the 2-day aged (2.3) and 7-day (2.0) aging, indicating the

300   degradation for Gly proceeds more rapidly than mGly, and that is consistent with the

301   decline Gly/mGly ratios in aged aerosols (Cheng et al., 2013).

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

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

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

305   burning emissions in a large aerosol chamber (<0.03) (Kalogridis et al., 2018). The

306   largest difference was found for C_2/C_4, varied from <1 for fresh aerosol in Siberian

307   biomass burning (Kalogridis et al., 2018), to 25.2 from forest fire in Thailand

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

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

310   2014), marine aerosol, Pacific ocean (14.3) (Kawamura and Sakaguchi, 1999), and

311   ambient island Okinawa, Japan (15.5) (Kunwar and Kawamura, 2014). These C_2/C_4

312   ratios are ~63% to 142% higher than these reported in this study. Overall, these

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

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

315   marine environments.

316   **3.4. Stable carbon isotopes**

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

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

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

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

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

322   because isotopic fractionation result from chemical reactions or phase transfer

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

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

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

326   2-day and -19.1 to -15.5 ‰ (-17.3 ± 1.7 ‰) for 7-day aged samples (Table 3).

327   Table 3 shows that aged maize samples reported the a heaviest $\delta^{13}C$ signatures

328   than those of rice and wheat. This is likely because maize is a C_4 plant, whereas wheat

329   and rice are both C_3 plants. Song et al. (2018) showed that $\delta^{13}C_{TC}$ in C_4 plants is

330   isotopically heavier than in C_3 plants. Moreover, the $\delta^{13}C$ of C_2 is more abundant in 7-

331   than 2-day samples (Table 3) with -13.1 ± 1.6 ‰ (2-day) and -7.1 ± 1.4 ‰ (7-day) in

332   maize; -26.2 ± 1.8 ‰ (2-day) and -20.8 ± 3.3 ‰ (7-day) in rice and -26.5 ± 0.2 ‰

333   (2-day) and -24.0 ± 0.5 ‰ (7-day) in wheat combustion. The $\delta^{13}C$ data for C_3, C_4 and

334   ωC_2 (Table S2) showed similar trends, consistent with previous studies. For example,

335   Zhao et al. (2018) found that the $\delta^{13}C$ values of C_2 were related to aging. Pavuluri and

336   Kawamura (2016) analyzed diacids, ωC_2, and Gly for $\delta^{13}C$ in anthropogenic and

337   biogenic aerosol samples by UV irradiation, and reported more $\delta^{13}C$ less negative

338   with longer irradiation times. During atmospheric oxidation reactions, organic

339   compounds react with OH radicals, causing the release of CO_2 and CO which contain

340   relatively the lighter ^{12}C isotope and thus leaving the remaining substrate enriched in

341   ^{13}C (Hoefs, 1997; Sakugawa and Kaplan, 1995).

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

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

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

345   (-21.8 ± 2.8‰) (Zhao et al., 2018) and Liaocheng (-19.8 ± 3.1‰) (Meng et al., 2020)

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

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

348   western pacific and southern ocean aerosol (-16.8 ± 0.8‰) (Wang and Kawamura,

349   2006), but it was significantly lighter than that of samples from the Korea Climate

350   Observatory at Gosan (-13.7 ± 2.5‰), which is a mountain background site in East

351   Asia (Zhang et al., 2016).

352   **3.5. Relationships between volatile organic carbon compounds and dicarboxylic**

353   **acids**

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

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

356   increases in dicarboxylic acids from fresh to 2-day aged BB samples. Significant

357   (0.01 <p < 0.05) correlations (R) were observed for toluene with Gly (R = 0.75),

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

359   that toluene was converted to diacids during the aging processes. Indeed, it has been

360   reported that the photooxidation of toluene is a potential source of secondary organic

361   aerosol (SOA) in urban air (Sato et al., 2007), and the major chemical components of

362   the SOA include hemiacetal, peroxy hemiacetal oligomers and dicarboxylic acids. It

363   also can be seen that benzene had significant correlations with mGly and C_2 (R>0.59

364   in Fig.5), implying that the oxidation of benzene led to diacid formation. And we can

365   see that the slope of the correlation between the decrease of toluene and benzene and

366   the increase of the precursor (Pyr and ωC_2) is significantly higher than that of oxalic

367   acid.

368   On the global scale isoprene is the most important precursor for C_2, contributing

369   70% to the global C_2, while anthropogenic VOCs contribute 21% to C_2 production

370   (Myriokefalitakis et al., 2011). Thus, it is not surprising that isoprene correlated with

371   C_2 (R=0.58) (Fig.5). In addition, several alkenes and alkanes also had a significant

372   correlation with C_2 (Table S3), indicating that these species may react in secondary

373   oxidation processes to generate oxalic acid. Previous studies have confirmed that

374   dicarboxylic acids can be oxidation products of aromatic hydrocarbons (Borrás and

375   Tortajada-Genaro, 2012), cycloolefins (Hamilton et al., 2006), and may originated

376   from diesel vehicle exhaust (Samy and Zielinska, 2010). However, no significant

377   correlation was found between decreases in VOCs and increases in 7-day aged

378   dicarboxylic acids. For the longer aging times, the particulate phase compounds may

379   be further oxidized to generate other compounds besides diacids.

4. Conclusions

381   The emission factors (EFs) of dicarboxylic acids and related compounds in

382   experimentally produced fresh and aged biomass burning aerosols were compared.

383   For fresh emissions, succinic acid (C_4) was the most abundant diacid species followed

384   by azelaic acid (C_9). After atmospheric aging, C_2 dominated the diacids, with elevated

385   emission factors. Ratios of aged to fresh (A/F) for C_2 increased from 50.8 (2-day) to

386   64.5 (7-day). These results suggest that the dicarboxylic acids in the atmosphere

387   largely originated from secondary photochemical processes as opposed to primary

388   emissions from biomass burning. The 2-day A/F ratios 2.8 of azelaic acid (C_9)

389   degraded by 27% after 7-days, suggesting that this species is relatively stable with

390   short residence time.

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

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

393   3.3, respectively. These results suggest that after 2-day aging, the net degradation of

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

395   samples, the $\delta^{13}C$ of C_2, C_3, C_4 and ωC_2 in 7-day samples became more positive or

396   isotopically heavier after the additional aging, likely due to kinetic isotope

397   fractionation effects. Moreover, the $\delta^{13}C$ values for the aged maize samples in both

398   the 2- and 7-day samples were significantly more positive than those of rice and

399   wheat. This is likely due to differences in their photosynthetic pathways as maize is a

400   C_4 plant, while wheat and rice are both C_3 plants. The correlations between VOCs

401   (benzene, toluene, isoprene, etc.) and oxalic acid (C_2) and intermediates indicated that

402   the oxidation of VOCs led to the formation of diacids. The results provide in-depth

403   understanding of SOAs formation in regions greatly affected by biomass burning.

Data availability

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

406   corresponding authors.

Author contribution

408   Junji Cao and Jianjun Li conceived and designed the study. Minxia Shen

409   contributed to the literature search, samples and data analysis, and manuscript writing.

410   Jianjun Li, Junji Cao, Judith C. Chow and John G. Watson contributed to manuscript

411   revision. Kin Fai Ho, Wenting Dai, Suixin Liu, Ting Zhang, Qiyuan Wang, Jingjing

412   Meng carried out the particulate samples and supervised the experiments. All authors

413   commented on the manuscript and reviewed the manuscript.

Declaration of Competing Interest

415   The authors declare that they have no known competing financial interests or

416   personal relationships that could have appeared to influence the work reported in this

417   paper.

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A: Dicarboxylic acids; B: Ketocarboxylic acids; C: α-dicarbonyls
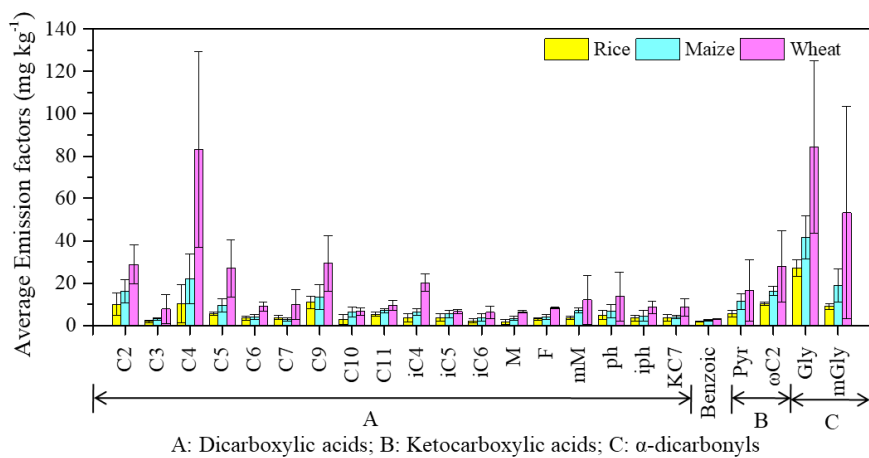
Figure 1 Average emission factors of dicarboxylic acids and related compounds in fresh $PM_{2.5}$ aerosols from biomass burning.

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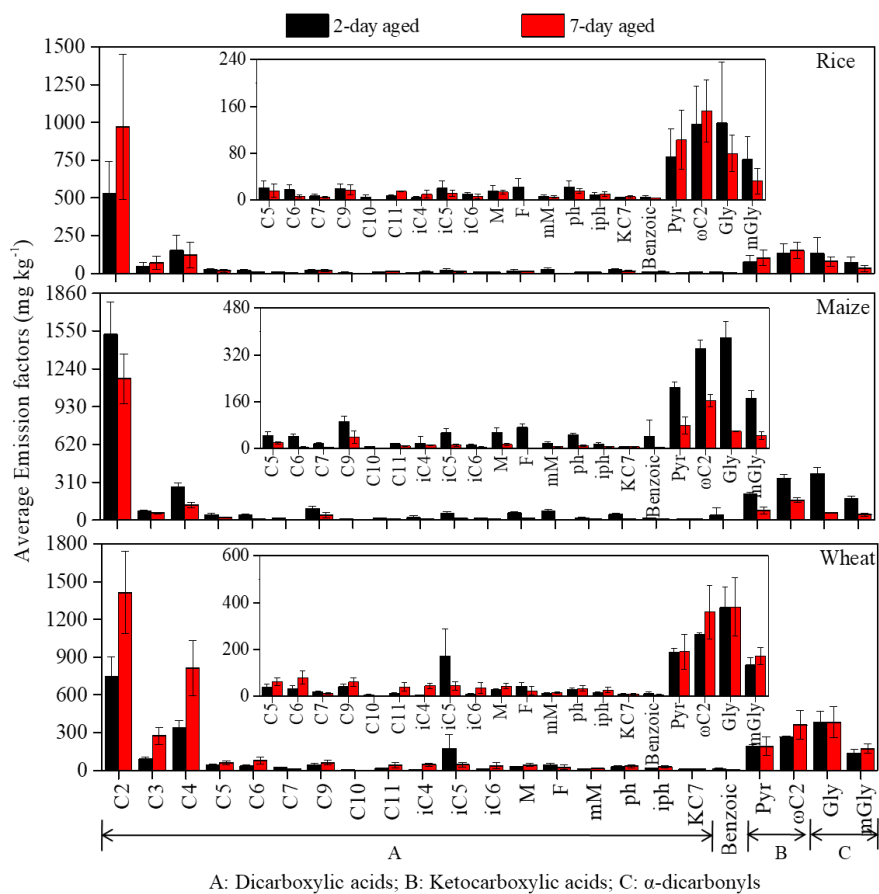
Figure 2 Comparison between 2- and 7-day aged average PM$_{2.5}$ emission factors of A: dicarboxylic acids, B: ketocarboxylic acids, and C: α-carbonyls for laboratory combustion of rice, maize, and wheat straw.

A: Dicarboxylic acids; B: Ketocarboxylic acids; C: α-dicarbonyls
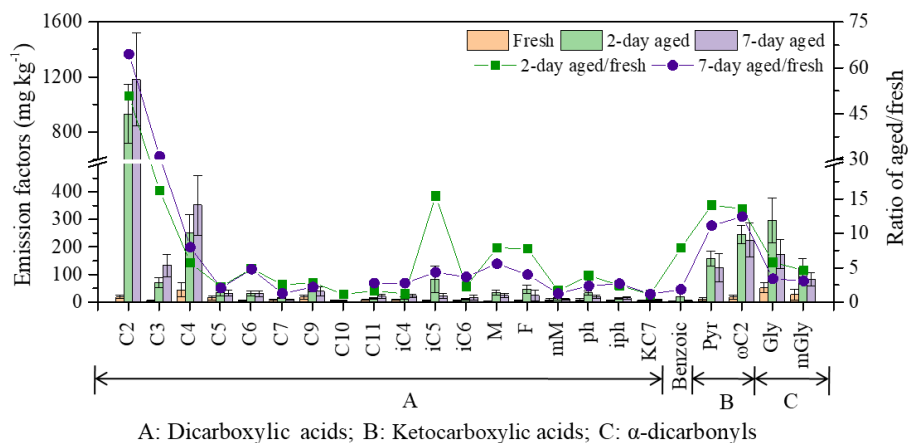
Figure 3 Average emission factors of dicarboxylic acids and related compounds from biomass burning experiment for the fresh, 2- and 7-day aged $PM_{2.5}$ aerosols. The squares and dots denote the ratios of aged to fresh (A/F) sample for the dicarboxylic acids and related compounds after 2- and 7-day aging.
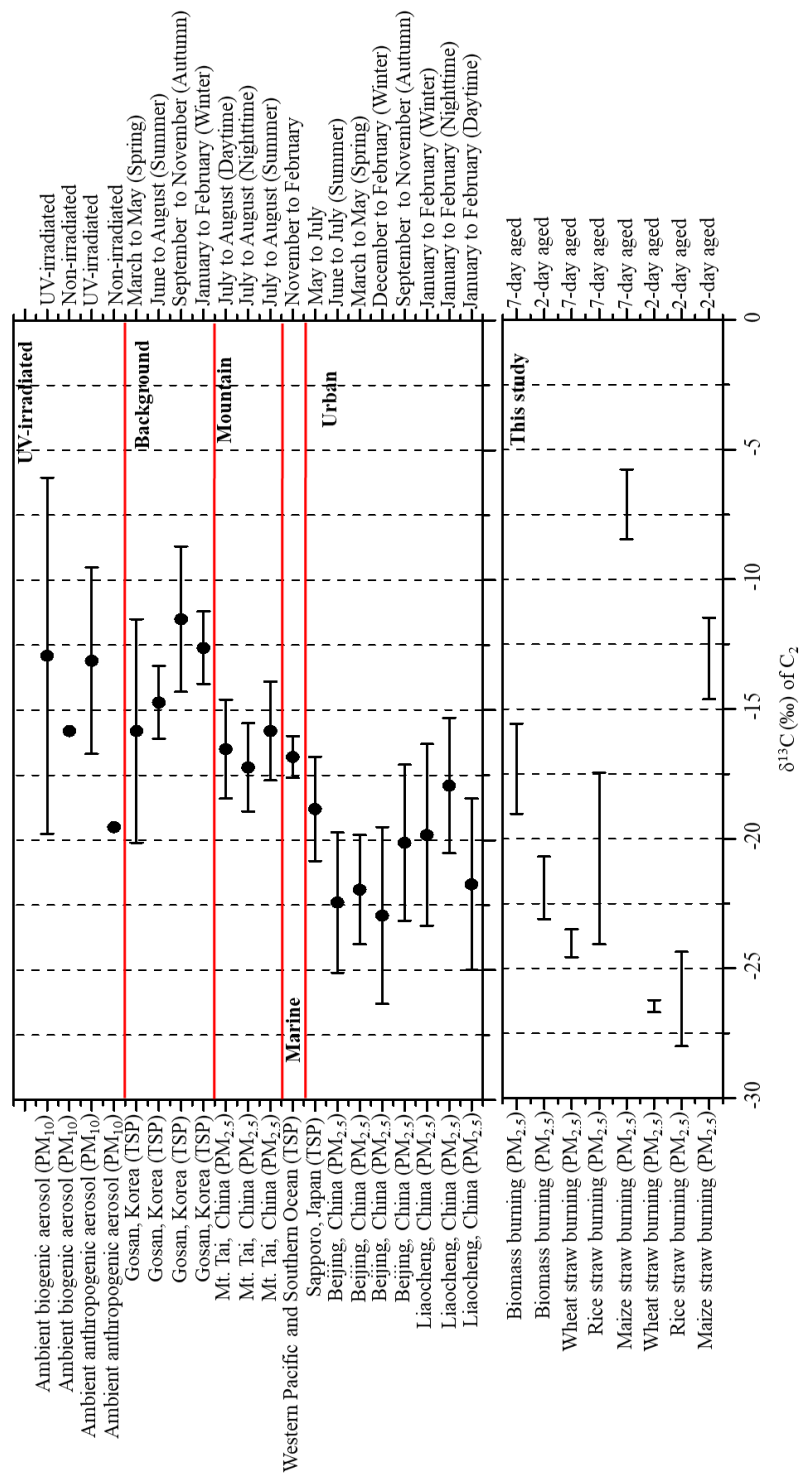
Figure 4 Stable carbon isotope ratios (δ^{13}C, ‰) of C$_2$ in aerosols from selected environments.

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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).

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

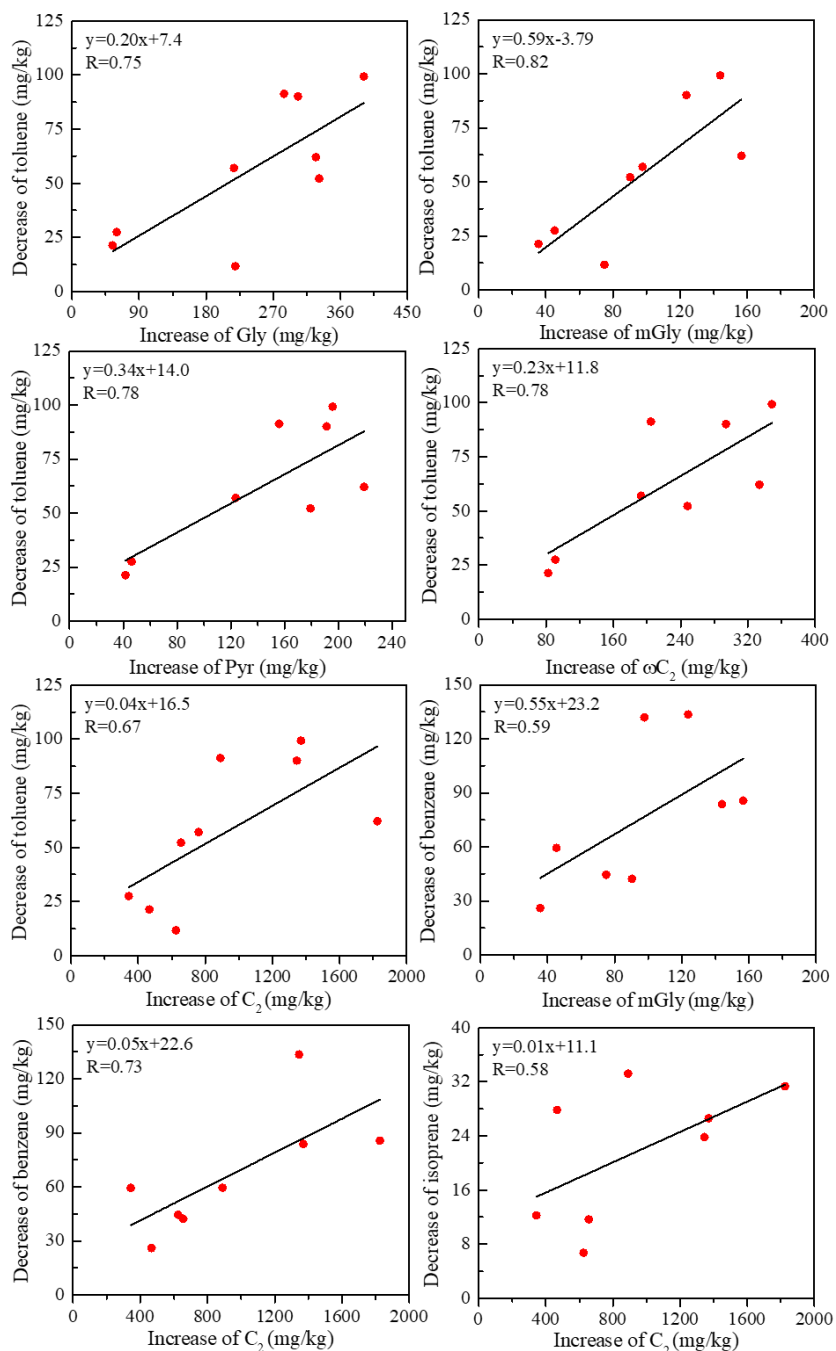| Compounds	Rice-2 day aged		Rice-7 day aged		Maize-2 day aged		Maize-7 day aged		Wheat-2 day aged		Wheat-7 day aged	
	Fresh	2-d aged	Fresh	7-d aged	Fresh	2-d aged	Fresh	7-d aged	Fresh	2-d aged	Fresh	7-d aged
I. Dicarboxylic acids												
Oxalic, C_2	5.1±0.9	527±214	15±10	971±482	8.1±2.2	1522±268	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±14	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).

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738 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 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)
	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)
Urban	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)
	North Pacific	TSP	1.4	5.3	0.5	0.01	2.0	Kawamura et al. (1993)
Marine area	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	<1	/	/		Kawamura et al. (1987)
	Siberian (biomass burning, chamber)	$PM_{2.5}$	<0.03		/	/	/	Kalogridis et al. (2018)
Laboratory simulation	Fresh (biomass burning, chamber)	$PM_{2.5}$	0.2	0.7	0.1	1.3	3.8	This study
	2-day aged (biomass burning, chamber)	$PM_{2.5}$	0.3	3.8	0.6	0.3	2.3	
	7-day aged (biomass burning, chamber)	$PM_{2.5}$	0.5	6.4	0.6	0.2	2.0	

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[1] See compund list in Table 1

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

Sampling site	Particle size	Min[1]	Max	Ave.	Std.	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.	
	$PM_{2.5}$	-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.	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.	
	$PM_{2.5}$	-20.1	-12.1	-16.5	1.9	Jul. to Aug. (Summer)	
Background							
Gosan, 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.	
	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	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-day aged	This study
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	
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	

742 [1]Min, Max, Ave, and Std stand for minimum, maximum, arithmetic mean, and standard deviation.

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