

High Loadings of Water-soluble Oxalic Acid and Related Compounds in PM_{2.5} Aerosols in Eastern Central India: Influence of Biomass Burning and Photochemical Processing

Dhananjay K. Deshmukh¹, Kimitaka Kawamura¹, Tarun Gupta², Md. Mozammel Haque³, Yan-Lin Zhang³, Dharmendra K. Singh^{1,4}, Ying I. Tsai^{5*}

¹ Chubu Institute for Advanced Studies, Chubu University, Kasugai 487-8501, Japan

² Department of Civil Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

³ Yale-NUIST Center on Atmospheric Environment, School of Applied Meteorology, Nanjing University of Information Science and Technology, Nanjing 210044, China

⁴ Institute of Research on Catalysis and the Environment of Lyon (IRCELYON), French National Centre for Scientific Research (CNRS), Villeurbanne 69100, France

⁵ Department of Environmental Engineering and Science, Chia Nan University of Pharmacy and Science, Tainan 71710, Taiwan

ABSTRACT

Water-soluble organic compounds are important constituents of atmospheric aerosols and have been recognized as unique fingerprints to identify atmospheric processes. Fine aerosol samples (PM_{2.5}) were collected at Ambikapur (23.1°N and 83.2°E) in eastern central India from March to June 2017. The samples were analyzed for water-soluble dicarboxylic acids (C₂–C₁₂), glyoxylic acid (ω C₂), glyoxal (Gly), methylglyoxal (MeGly), organic carbon (OC), elemental carbon (EC) and water-soluble OC (WSOC). Oxalic acid (C₂) was detected as the most abundant species, followed by succinic (C₄) and malonic (C₃) acids. Temporal variation in concentrations of C₂ diacid and related compounds was pronounced from early to late April when biomass burning (BB) was dominant in eastern central India. Strong positive correlations of C₂ diacid and related compounds with levoglucosan (r = 0.83-0.99) further demonstrate that organic aerosols (OAs) were affected by BB in eastern central India. Strong positive correlations of C₂ with saturated diacids (C₃–C₉: r = 0.78-0.97), ω C₂ (r = 0.98), Gly (r = 0.96) and MeGly (r = 0.84) suggest that their sources and formation processes were similar and oxalic acid might be produced via the photochemical degradation of precursor compounds. The relatively high ratios of WSOC to OC (avg. 0.69) and C₃ to C₄ diacid (avg. 0.95) suggest that water-soluble OAs were photochemically processed during the campaign. The total water-soluble organic compounds detected in Ambikapur PM_{2.5} samples accounted for an average of 1.9% (1.1–3.1%) of OC. Our results demonstrate that BB and photochemical processing caused high levels of water-soluble organic compounds over eastern central India.

Keywords: Water-soluble organic aerosols; Dicarboxylic acids; Secondary formation; Photochemical production; Biomass burning emission.

INTRODUCTION

Organic aerosols (OAs) are abundant in the troposphere and are crucial determinants of air quality and climate (Decesari *et al.*, 2001; Kanakidou *et al.*, 2005). OAs are emitted directly to the atmosphere from primary sources (Gilardoni, 2017; Khan *et al.*, 2018). They are also secondarily produced in

* Corresponding author.

Tel.: +886-6-266-0208; Fax: +886-6-266-9090 *E-mail address:* mtsaiyi@mail.cnu.edu.tw the atmosphere by the photochemical oxidation of volatile organic compounds (VOCs) (Kroll and Seinfeld, 2008; Shiraiwa *et al.*, 2013). New particle formation also occurs via the photooxidation of VOCs (Vana *et al.*, 2016). The photooxidation products of OAs are highly water-soluble and typically contain several functional groups such as carboxyl (COOH), carbonyl (CO) and hydroxyl (OH) groups (Hallquist *et al.*, 2009; Wang *et al.*, 2015).

Dicarboxylic acids and related polar compounds, including oxocarboxylic acids and α -dicarbonyls, are known to be ubiquitous in atmospheric aerosols and comprise a significant fraction of OAs (Kawamura and Yasui, 2005; Pavuluri *et al.*, 2010; Tsai *et al.*, 2015). They are directly released to the

atmosphere from primary sources such as fossil fuel combustion and biomass burning (Kundu *et al.*, 2010; Tsai *et al.*, 2013; Cong *et al.*, 2015). They are also produced in the atmosphere by secondary processes via photochemical oxidation of VOCs and unsaturated fatty acids (UFAs) derived from anthropogenic and biogenic sources (Pavuluri *et al.*, 2015; Kundu *et al.*, 2016). Diacids are an important organic compound class of secondary organic aerosol (SOA) because of their high abundance in the water-soluble organic carbon (WSOC) fraction of atmospheric aerosols (Decesari *et al.*, 2006; Kawamura *et al.*, 2013). Claeys *et al.* (2004) and Fu *et al.* (2008) have proposed that anthropogenic VOCs are rather a minor source of SOA precursors compared to those of biogenic VOCs on a global scale.

Oxalic acid (C_2) is often reported as the dominant species among diacids in atmospheric aerosols. Laboratory and field studies have proposed the production of C₂ diacid by photooxidation of precursors such as glyoxal (Gly) and methylglyoxal (MeGly) in aqueous-phase (Carlton et al., 2009; Ervens et al., 2011). It has been suggested that C₂ is also produced by photochemical oxidation of higher homologues of diacids (C₃-C₁₂) in aerosol aqueous-phase (Pavuluri et al., 2015; Zhang et al., 2016). Brooks et al. (2002) have shown that the presence of C_2 diacid affects both deliquescence relative humidity and hygroscopicity of atmospheric aerosols. The atmospheric abundances of diacids have a significant influence on regional radiative forcing through direct aerosol effects on cloud and fog formation processes (Pradeep Kumar et al., 2003; Gierlus et al., 2012). Biomass burning emission causes a significant perturbation to global atmospheric chemistry (Stocks et al., 2000; Akagi et al., 2011; Grell et al., 2011; Lin et al., 2017; Popovicheva et al., 2017; Pani et al., 2018; Liang et al., 2019). It has an impact of direct and indirect effects on the radiative forcing of atmospheric aerosol particles and climate change (Li et al., 2017; Martins et al., 2018; Bukowiecki et al., 2019; Huang et al., 2019). Chemical compounds in aerosol particles are used as tracers to determine the sources such as biomass burning emission (Decesari et al., 2006; Wang et al., 2009; Lee et al., 2016; Du et al., 2017; Cui et al., 2018; Popovicheva et al., 2019; Priyadharshini et al., 2019).

South Asia is experiencing severe air pollution due to rapid economic growth and urbanization (Ramanathan and Ramana, 2005; Srivastava and Ramachandran, 2013). The air pollution in India is enhancing anthropogenic aerosols in the South Asian atmosphere (Ramanathan *et al.*, 2007; Gustafsson *et al.*, 2009). The major source of air pollution in India is industrial and vehicular emissions (Sharma and Maloo, 2005; Das *et al.*, 2006; Pal *et al.*, 2018), coal and biomass burning (Ram *et al.*, 2012; Pachauri *et al.*, 2013; Sahu and Kota, 2017). Dumping of domestic and municipal solid waste into open landfills and subsequent open burning are also common in India (Chowdhury *et al.*, 2007; Pavuluri *et al.*, 2010).

Biomass burning and combustion of biofuels are identified as the major sources of OAs in eastern central India (Giri *et al.*, 2013; Nirmalkar *et al.*, 2015; Deshmukh *et al.*, 2016). Verma *et al.* (2007, 2008, 2010) found high loadings of fine mode aerosols (avg. 239 μ g m⁻³) and coarse mode aerosols (avg. 245 µg m⁻³) as well as gaseous pollutants such as sulfur dioxide (SO₂) (avg. 95.2 µg m⁻³) and nitrogen dioxide (NO₂) (avg. 115 μ g m⁻³) in the atmosphere of eastern central India. The results of Giri et al. (2013) represented that the dominant components of OAs in eastern central India are from fossil fuel utilization and the burning of biomass and plastics. Nirmalkar et al. (2015) also reported biomass burning and fossil fuel combustion as the dominant emission sources leading to high levels of OAs in eastern central India. They reported that the combustion of coal for cooking is a common source of air pollution not only in rural areas but also in the cities. Eastern central India is also a receptor site of transported aerosols from the Indo-Gangetic-Plain (IGP), where aerosol particles are enriched with biomass burning products and industrial emissions. Nevertheless, numerous air improvement schemes implemented in urban areas have not been applied widely in rural areas. The investigation on the origin and atmospheric processing of OAs from rural sites are needed to understand the air quality in eastern central India. The high ambient temperature and intense solar radiation during summertime may induce enhanced production of secondary OAs in the atmosphere of eastern central India. Eastern central India is thus a unique place to investigate the sources and atmospheric processing of OAs.

We collected fine aerosol samples (PM_{2.5}) at the city of Ambikapur in eastern central India from March to June 2017. We analyzed the samples for water-soluble dicarboxylic acids (C₂–C₁₂), glyoxylic acid (ω C₂), α -dicarbonyls (C₂–C₃), elemental carbon (EC), organic carbon (OC) and water-soluble OC (WSOC). The purpose of this research is to evaluate the mass loadings of water-soluble organic compounds and examine their sources and formation processes in PM_{2.5} aerosols over eastern central India. The results from this work are expected to improve the understanding of atmospheric processing and the impacts of water-soluble organic compounds of PM_{2.5} aerosols in the atmosphere of eastern central India.

MATERIALS AND METHODS

Description of the Sampling Area and Local Meteorology

The location of the sampling site in Ambikapur (23.1°N and 83.2°E), India and its surroundings in South Asia are shown in Fig. 1. Ambikapur is situated in the Sarguja district in the Chhattisgarh state of India. The total area of Ambikapur is approximately 1983 km², with a population of 214,575. It is located in an upland region at an elevation of 623 m above sea level. Ambikapur extends into southeastern parts of the Vindhyachal-Baghelkhand region of peninsular India. It is represented by extremely rich vegetation. Nearly 58% of the Sarguja district is forested. The sampling area represents a unique rural location in eastern central India with relatively low anthropogenic emissions.

Meteorological data during the campaign for the observation site were acquired from the local meteorological station. The temporal changes in meteorological parameters at the campaign site during the collection of aerosol samples are shown in Fig. 2. The ambient air temperature ranged from 11 to 46°C with an average of 29°C. The relative humidity ranged from 5 to 88% with an average of 33%. The prevailing wind



Fig. 1. A map showing the location of sampling site Ambikapur (23.1°N and 83.2°E) in eastern central India and its surroundings in South Asia. The map was downloaded from Map data © 2018 Google.



Fig. 2. The average variations of meteorological parameters during the collection of aerosol samples at the campaign site in eastern central India.

direction during the campaign was westerly and northwesterly and wind speed ranged from 1.5 to 25 km h^{-1} with an average of 4.5 km h^{-1} . The rainfall event occurred during June. The total amount of rainfall was 385 mm during the campaign.

PM_{2.5} Aerosol Sample Collection and Gravimetric Determination

PM_{2.5} aerosol samples were collected in Ambikapur on a terrace of a building approximately 15 m above ground level

using a Thermo Andersen high-volume sampler (USA) at a flow rate of 1.1 ± 0.1 m³ min⁻¹. The samples were collected on quartz fiber filters (QFFs) during the campaign from March 1 to June 25 in 2017. All QFFs were pre-combusted at 500°C for 6 h before use. The sampling duration was 24 h for each sample to acquire enough material for the analysis of several chemical components in aerosol particles. A total of 30 PM_{2.5} samples were collected every 3 days during the campaign together with 3 field blanks.

The mass concentration of PM_{2.5} aerosol particles was determined by gravimetric analysis. Aerosol-laden and blank filters were equilibrated for 24 h at $25 \pm 2^{\circ}$ C and $40 \pm 5\%$ relative humidity before weighing on an analytical balance. All weight measurements were repeated three times to ensure reliability. The PM_{2.5} aerosol mass was determined as the difference between the mass of each filter prior and post sampling. The aerosol particle sample and blank filters were placed in pre-combusted (450°C for 6 h) clean glass bottles with Teflon-lined cap. They were appropriately stored in darkness at -20° C until chemical analysis to avoid a potential loss of volatile and semi-volatile organic compounds and microbial decomposition of organics.

Measurement of Carbonaceous Components

Elemental carbon (EC) and organic carbon (OC) concentrations in aerosol samples were measured using a Sunset Lab Carbon Analyzer following the Integrated Monitoring Protected Visual Environments (IMPROVE) protocol described in detail in Wang *et al.* (2005). The sample filter of 16 mm in diameter was placed in a glass tube inside the thermal desorption chamber of the analyzer, and then stepwise heating was applied. Helium (He) was used as a carrier gas. A non-dispersive infrared (NDIR) detector was used to measure the evolved carbon dioxide (CO₂) during the oxidation at each temperature step. The analytical errors from the replicate analysis of aerosol samples (n = 3) were 3% for EC and 5% for OC.

Water-soluble organic carbon (WSOC) was measured on a Shimadzu Total Organic Carbon (TOC-V_{CSH}) Analyzer equipped with a catalytic oxidation column and NDIR detector following a protocol described in detail in Miyazaki *et al.* (2011). The area of 2.11 cm² from each aerosol sample filter was extracted with ultrapure water in a 20 mL glass vial under ultrasonication in an ice-water bath. The specific resistance of 18.2 MΩ-cm at 25°C is considered to be pure water for the extraction of the samples. The extracts were filtered through a 0.22 µm pore size syringe filter in a precleaned glass vial. Potassium hydrogen phthalate was used to achieve the external calibration of WSOC. Replicate analysis of aerosol samples (n = 3) showed an analytical error of 5% in the determination of WSOC.

Measurement of Dicarboxylic Acids and Related Polar Compounds

Water-soluble dicarboxylic acids (C_2-C_{12}), glyoxylic acid (ωC_2) and α -dicarbonyls (C_2-C_3) were measured in aerosol samples using capillary gas chromatograph (GC) equipped with a flame ionization detector (FID) following a protocol described in Kawamura and Ikushima (1993). A filter area of 2.01 cm² from each aerosol sample was cut into small pieces and extracted with ultrapure water (10 mL × 3) in a glass vial with a Teflon-lined screw cap under ultrasonication (10 min × 3) to isolate the ample amount of aerosol particles retained on the sample filter. The extracts were then filtered through a Pasteur pipette packed with pre-combusted (500°C for 6 h) quartz wool to remove particles and filter debris. The pH of the extracts was adjusted between 8.5 and 9.0 using 0.01 M potassium hydroxide (KOH) solution to increase the recoveries of smaller diacid such as oxalic acid (Hegde and Kawamura, 2012; Wang *et al.*, 2012). The extracts were evaporated to near dryness using a rotary evaporator under vacuum and derivatized by boron trifluoride (BF₃) dissolved in *n*-butanol at 100°C for 1 hour. The derivatives were dissolved in *n*-hexane and then washed with ultrapure water to remove the impurities. The hexane layer was further concentrated using a rotary evaporator under vacuum and the derivatives were dissolved into a known volume of *n*-hexane after gentle nitrogen blow-down to near dryness.

Two µL of the sample was injected into a Hewlett-Packard (HP) 6890 model GC-FID. Peak identification of identified diacids and related compounds in the samples was conducted by comparing the GC retention times with those of authentic standards. Quantification of detected compounds was performed by the comparison of GC-FID responses of the derivatives with those of authentic diacid dibutyl ester. Free diacids and related compounds were spiked onto the pre-combusted QFF and measured using the protocol described above to test the recovery. The recoveries were in the range of 85 to 90% for C2 diacid and better than 95% for other diacids and related compounds. Replicate analysis of aerosol samples (n = 3) showed that analytical errors on the above procedure to measure diacids and related compounds were within 6%, excluding decanedioic (C_{10}), undecanedioic (C_{11}) and dodecanedioic acid (C_{12}) , for which analytical error was between 7.8 to 8%.

Measurement of Levoglucosan and Oleic Acid

Levoglucosan and oleic acid (C18:1) were measured using gas chromatograph-mass spectrometer (GC-MS) following a protocol explained in Fu et al. (2010). An aliquot of a filter (2.01 cm^2) was extracted with a mixture of dichloromethane (CH_2Cl_2) and methanol (CH_3OH) $(10 mL \times 3)$ using ultrasonication (10 min \times 3). The solvent extracts were filtered through a Pasteur pipette packed with pre-combusted (500°C for 6 h) guartz wool and then concentrated to near dryness using a rotary evaporator under vacuum and nitrogen blow-down technique. The extracts were reacted using 50 µL of N,O-bis(trimethylsilyl)trifluoroacetamide including 1% trimethylsilyl (TMS) chloride and 10 µL of pyridine at 70°C for 3 h to convert the OH group to corresponding TMS ether and the COOH group to TMS esters. The derivatized fractions were diluted with a known volume of *n*-hexane containing an internal standard of *n*-C₁₃ alkane (1.43 ng μ L⁻¹) before injection into a GC-MS. The GC-MS analysis of the samples was performed on an HP 6890 model GC coupled with an HP 5973 model mass detector. The recoveries were found to be 90% for levoglucosan and 85% for oleic acid. Replicate analysis of aerosol samples (n = 3) showed that analytical errors on this procedure were 6% for levoglucosan and 8% for oleic acid.

Field blank filters were extracted and analyzed like the real samples by the procedure described above. However, the levels of detected chemical species in blank filters were in the range of 0.2 to 3% of the real samples. The reported concentrations of chemical components were corrected for the field blanks. The data reported here were not adjusted for recoveries.

In order to investigate the influence of long-range transport on the chemical composition of aerosols at Ambikapur, 5 days backward trajectories of air masses starting at 500 m above ground level were computed every day from 1 March to 25 June 2017 using Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Draxler and Rolph, 2013). Fire spots data were obtained from the Fire Information for Resource Management System (FIRMS) (https://firms.modaps.eosdis.nasa.gov) operated by the National Aeronautics and Space Administration (NASA) of the United States. The air mass backward trajectories arriving over the campaign site together with fire spots during the collection of aerosol samples is shown in Fig. 3.

RESULTS AND DISCUSSION

Concentrations of PM2.5 and Carbonaceous Aerosols

The statistical summaries of concentrations of carbonaceous

species measured in $PM_{2.5}$ samples are given in Table 1. $PM_{2.5}$ aerosol concentrations in Ambikapur ranged from 32.3 to 286 µg m⁻³ with an average of 153 µg m⁻³. Central Pollution Control Board (CPCB) considered $PM_{2.5}$ aerosol particle as one of the criteria pollutants in India in 2009 with a 24 h average limit value of 60 µg m⁻³. Frequencies of 24 h $PM_{2.5}$ aerosol concentration levels exceeding 60 µg m⁻³ at Ambikapur were 86% during the sampling period. This result suggests that more efforts should be taken to control $PM_{2.5}$ aerosol pollution in eastern central India.

The concentrations of EC ranged from 0.90 to 15.1 μ g m⁻³ (avg. 6.05 μ g m⁻³) and concentrations of OC ranged from 5.30 to 65.7 μ g m⁻³ (avg. 33.5 μ g m⁻³). The concentrations of WSOC ranged from 3.18 to 53.2 μ g m⁻³ with a mean of 24.2 μ g m⁻³ during the campaign. The correlations among carbonaceous components give information about the source of carbonaceous aerosols. Fossil fuel combustion and biomass burning primarily emit OC and WSOC. They are also secondarily produced in the atmosphere by photochemical



Longitude (°E)

Fig. 3. The air mass backward trajectories over the campaign site together with Moderate Resolution Imaging Spectroradiometer (MODIS) fire images during the collection of aerosol samples. The round symbol is the location of the sampling site Ambikapur in eastern central India.

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Compounds	Abbreviation	Chemical formula	Mean	S.D. ^a	Min. ^b	Max.°
PM _{2.5} aerosols ^d			153	77.5	32.3	286
Carbonaceous species ^d						
Elemental carbon	EC		6.05	3.82	0.90	15.1
Organic carbon	OC		33.5	17.2	5.30	65.7
Water-soluble organic carbon	WSOC		24.2	14.7	3.18	53.2
Dicarboxylic acids ^e						
Saturated normal-chain diacids						
Oxalic	C_2	HOOC-COOH	853	549	136	2025
Malonic	C_3	HOOC-CH ₂ -COOH	222	142	32.2	531
Succinic	C_4	HOOC-(CH ₂) ₂ -COOH	262	204	29.1	766
Glutaric	C ₅	HOOC-(CH ₂) ₃ -COOH	48.7	34.1	5.33	133
Adipic	C_6	HOOC-(CH ₂) ₄ -COOH	38.1	29.1	4.20	103
Pimelic	C_7	HOOC-(CH ₂) ₅ -COOH	27.1	20.3	1.50	80.3
Suberic	C_8	HOOC-(CH ₂) ₆ -COOH	15.1	10.3	3.82	45.5
Azelaic	C ₉	HOOC-(CH ₂) ₇ -COOH	123	127	18.6	485
Decanedioic	C_{10}	HOOC-(CH ₂) ₈ -COOH	10.9	8.51	0.87	32.6
Undecanedioic	C11	HOOC-(CH ₂) ₉ -COOH	10.6	7.13	1.09	26.0
Dodecanedioic	C ₁₂	HOOC-(CH ₂) ₁₀ -COOH	9.25	7.57	1.03	27.2
Unsaturated aliphatic diacids						
Maleic	М	HOOC-CH=CH-COOH	25.7	24.8	2.31	108
Fumaric	F	HOOC-CH=CH-COOH	18.1	21.1	1.63	103
Unsaturated aromatic diacids						
Phthalic	Ph	HOOC-(C ₆ H ₄)-COOH	57.1	41.3	8.90	151
Terephthalic	tPh	HOOC-(C ₆ H ₄)-COOH	6.97	4.09	1.20	15.0
Total diacids			1727	1185	288	4606
Oxocarboxylic acid ^e						
Glyoxylic	ωC_2	OHC-COOH	79.0	54.3	13.0	193
α-Dicarbonyls ^e						
Glyoxal	Gly	OHC-CHO	32.7	23.5	6.20	83.5
Methylglyoxal	MeGly	CH ₃ -C(O)-CHO	19.0	14.7	3.49	51.8
Total α-dicarbonyls			51.7	36.3	9.69	127

Table 1. Concentrations of aerosol mass (PM_{2.5}), elemental carbon (EC), organic carbon (OC), water-soluble organic carbon (WSOC), water-soluble dicarboxylic acids (C_2 - C_{12}), glyoxylic acid (ωC_2) and α -dicarbonyls (C_2 - C_3) in eastern central India.

^aStandard deviation. ^bMinimum. ^cMaximum. ^dConcentrations are in µg m⁻³. ^cConcentrations are in ng m⁻³.

processes, whereas EC is only primarily produced from combustion sources such as fossil fuel combustion and biomass burning (Wang *et al.*, 2005; Huang *et al.*, 2006). The correlations among carbonaceous components in PM_{2.5} samples are shown in Fig. 4. Positive correlations of EC with OC (r = 0.83) and WSOC (r = 0.85) were found in Ambikapur aerosols. We also found a strong correlation between WSOC and OC (r = 0.98). These results suggest that carbonaceous components in PM_{2.5} aerosols in Ambikapur had common emission sources. The stronger correlation of WSOC with OC suggests that these components had very similar sources and were produced by similar secondary processes in the atmosphere of eastern central India.

Fossil fuels and biomass burning emissions and secondary aerosol formation are characterized by a specific ratio of OC to EC in atmospheric aerosols (Ram *et al.*, 2008; Sandradewi *et al.*, 2008; Saarikoski *et al.*, 2008; Yang *et al.*, 2017). A higher ratio implies biomass burning and secondary processes as a major source of carbonaceous aerosols. Alternatively, lower ratios are characteristic of emissions from fossil fuels. Sandradewi *et al.* (2008) reported an average OC/EC ratio of 1.1 for vehicular emission and 7.3 for wood burning emission. Saarikoski et al. (2008) documented OC/EC ratios of 0.71 for vehicular emission and 6.6 for biomass combustion. Watson et al. (2001) reported the OC/EC ratios of 1.1 for vehicular emission and 2.7 for coal combustion, while OC/EC ratio of 9.0 was found in biomass burning emission. We have assessed the OC/EC ratios in Ambikapur PM_{2.5} samples to classify the sources of carbonaceous aerosols. OC/EC ratios ranged from 3.12 to 12.0 with an average of 6.34 in Ambikapur aerosol samples. The values observed are within the ranges reported for biomass burning emission but higher than those reported for vehicular emission, as discussed above. These results suggest that biomass burning may be the main source of carbonaceous aerosols in eastern central India. The contribution of vehicular emission to carbonaceous aerosols may be minor in a rural site in eastern central India. It is noteworthy that OC/EC ratios from SOA formation are usually higher than those from vehicular emission (Ram et al., 2012; Peng et al., 2018; Sorathia et al., 2018). The high OC/EC ratios in Ambikapur samples may suggest a contribution of photochemically processed aerosols over eastern central India.

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Fig. 4. The correlations among elemental carbon (EC), organic carbon (OC) and water-soluble organic carbon (WSOC) in PM_{2.5} aerosols.

Water-soluble organic compounds are derived from various emission sources. The mass concentration ratio of WSOC to OC is therefore a unique tracer to the origin and transformation features of carbonaceous aerosols and SOA formation in the atmosphere. High WSOC/OC ratios (0.5-0.8) were related to biomass burning emission or formation of secondary organic carbon whereas low ratios (0.06-0.26)were related to fossil fuel combustion such as vehicular emission (Ram and Sarin, 2010; Kaul et al., 2011; Huang et al., 2013). WSOC/OC ratios in Ambikapur aerosol samples ranged from 0.52 to 0.88 with an average of 0.69. This result suggests that a considerable fraction of WSOC was secondarily produced by the photochemical oxidation of VOCs of biomass burning origin in the atmosphere of eastern central India. Decesari et al. (2006) and Gierlus et al. (2012) proposed that SOA could constitute a major fraction of water-soluble organic compounds. Relatively high contributions of WSOC in OC in Ambikapur samples further suggest more SOA production in the atmosphere of eastern central India.

Molecular Characteristics of Water-soluble Organic Compounds

We analyzed a homologous series (C_2-C_{12}) of normalchain saturated diacids as well as unsaturated aliphatic and aromatic diacids in PM2.5 samples. We also detected glyoxylic acid (ωC_2) and α -dicarbonyls (C_2 - C_3) in Ambikapur aerosol samples. Their mean concentrations and ranges in PM_{2.5} aerosols together with abbreviation and chemical formula are given in Table 1. The concentrations of total diacids ranged from 288 to 4606 ng m⁻³ with a mean of 1727 ng m⁻³. The contribution of the sum of diacids-C to OC in Ambikapur PM_{2.5} samples ranged from 0.9 to 2.9% with an average of 1.8%. These values are similar to those estimated in aerosol samples from Hong Kong (1.12 to 2.47%) (Ho et al., 2006), Chinese cities (avg. 1.3%) (Ho et al., 2007) and biomass burning derived aerosols collected during davtime (avg. 1.7%) and nighttime (avg. 1.4%) at Rondônia in Brazil (Kundu et al., 2010), however they are lower than those reported in aerosol samples from Sapporo in Japan (avg. 4.8%) (Aggarwal and Kawamura, 2008).

The average molecular characteristics of diacids are shown in Fig. 5. Molecular characteristics of measured water-soluble organic compounds show the predominance of oxalic acid (C_2) followed by succinic (C_4) and malonic (C_3) acids. Concentrations of C₂ ranged from 136 to 2025 ng m⁻³ with a mean of 853 ng m⁻³. Relative abundances of C₂ in total diacids in the Ambikapur aerosols ranged from 42 to 67% with an average of 51%. Azelaic acid (C_9) is the fourth most abundant species, followed by ωC_2 and phthalic acid (Ph) in Ambikapur samples. The photooxidation of UFAs such as C_{18:1} produces C₉ diacid in the atmosphere (Hung et al., 2005; Pavuluri et al., 2015). UFAs originate from terrestrial higher plants as well as emission from biomass burning (Hays et al., 2005; Deshmukh et al., 2018). This result suggests that the photochemical alteration of UFAs is significant in the atmosphere of eastern central India. ωC_2 is produced by the photooxidation of α -dicarbonyls such as Gly and MeGly (Volkamer et al., 2001; Lim et al., 2005). Ph is an aromatic diacid that has been reported to originate from multiple anthropogenic sources such as primarily from fossil fuel combustion and biomass burning and secondarily from the photooxidation of polycyclic aromatic hydrocarbons (Kawamura and Yasui, 2005). Phthalates may also produce Ph in the atmosphere (Ho et al., 2007; Pavuluri et al., 2010). We found that Gly is more abundant than MeGly in Ambikapur aerosols (Fig. 5). This result may suggest that fossil fuel combustion and biomass burning emissions are more critical than emissions from terrestrial higher plants at the campaign site because Gly is often more abundant than MeGly in aerosol particles derived from combustion sources (Ho et al., 2006; Wang et al., 2012).

Comparison of Molecular Characteristics and Concentrations of Water-soluble Organic Compounds in Ambikapur with Previous Studies

The average concentrations of diacids and related compounds in Ambikapur are presented in Table 2 together



Dicarboxylic acids and related compounds

Fig. 5. Molecular characteristics of water-soluble organic compounds measured in PM_{2.5} aerosols.

Table 2. Average concentrations^a of water-soluble diacids and related compounds measured in Ambikapur aerosols and different sites in Asia and other regions.

C 1-	Ambikapur,	Chennai,	Hong	14 Cities	Sapporo,	Mt.	Morogoro,	Vienna,
Compounds	India	India ^b	Kong ^c	of China ^d	Japan ^e	Everest ^f	Tanzania ^g	Austria ^h
Dicarboxylic acids								
C_2	853	241	268	513	192	138	189.8	340
C_3	222	37.2	47.6	50.9	77	15.4	18.4	244
C_4	262	27.7	33.0	71.8	58	28.6	23.8	117
C_5	48.7	11.4	6.95	30.0	13	4.86	3.9	26.0
C_6	38.1	9.4	12.7	23.5	5.1	2.34	11.1	117
C_7	27.1	9.0	1.40	6.34	2.6	1.46	0.8	
C_8	15.1	15.5	2.56	9.06	1.1	0.79	3.0	
C ₉	123	32.4	9.06	31.6	6.5	2.24	10.8	
C_{10}	10.9	4.6	1.47	2.49	1.3	0.73		
C_{11}	10.6	4.2	3.27	5.18	1.0	0.40		
C ₁₂	9.25	0.6	0.53	0.91	0.12	0.15		
М	25.7	2.3	12.4	5.04	4.1	5.71	2.1	
F	18.1	1.3	3.38	2.47	2.1	1.20	3.1	
Ph	57.1	21.5	89.9	102	17	16.3	12.8	18.0
tPh	6.97	61.3			2.6	3.04	2.6	
Total diacids	1726	502.9	526	892	406	235	289	862
Oxocarboxylic acid								
ωC_2	79.0	17.3	18.5	23.9	22	6.27	20.9	22
α-Dicarbonyls								
Gly	32.7	2.9	0.19	2.72	4.6	0.84	4.7	
MeGly	19.0	4.2	10.0	2.47	5.1	0.98	1.0	
Total α-dicarbonyls	51.7	7.1	10.2	5.19	9.7	1.82	5.7	

See Table 1 for abbreviation. ^aConcentrations are in ng m⁻³. ^bPM₁₀ samples collected in summer (Pavuluri *et al.*, 2010). ^cPM_{2.5} samples collected in summer (Ho *et al.*, 2007). ^eTSP samples collected in summer (Aggarwal and Kawamura, 2008). ^fTSP samples collected in summer (Cong *et al.*, 2015). ^gPM_{2.5} samples collected in wet and dry season (Mkoma and Kawamura, 2013). ^hTSP samples collected in June (Limbeck and Puxbaum, 1999).

with those reported from different sites in Asia and other regions. Molecular distribution of water-soluble organic compounds with a predominance of C_2 diacid in Ambikapur is similar to previous reports of urban (Kawamura and Ikushima, 1993; Limbeck and Puxbaum, 1999; Huang *et al.*, 2005;

Hsieh *et al.*, 2008; Deshmukh *et al.*, 2016), rural (Legrand *et al.*, 2007; Mkoma and Kawamura, 2013) and marine aerosols (Kawamura and Sakaguchi, 1999; Mochida *et al.*, 2003; Wang *et al.*, 2006). The predominance of oxalic acid is not surprising because this diacid is the final product of

photooxidation of several VOCs and UFAs in the atmosphere (Lim et al., 2005; Sorooshian et al., 2006; Legrand et al., 2007). C_2 may also be emitted directly to some extent from anthropogenic sources such as fossil fuel combustion and biomass burning (Kawamura and Yasui, 2005; Cong et al., 2015). Nevertheless, the secondary production of C_2 diacid may be more significant in the atmosphere than the primary emission (Huang and Yu, 2007). The concentration level of C₂ (avg. 853 ng m⁻³) in Ambikapur aerosols is higher than those reported in Chennai (avg. 241 ng m⁻³), Hong Kong (avg. 268 ng m⁻³), Chinese cities (avg. 513 ng m⁻³), Sapporo (avg. 192 ng m⁻³) and Vienna (avg. 340 ng m⁻³) (Limbeck and Puxbaum, 1999; Pavuluri et al., 2010; Ho et al., 2006; Ho et al., 2007; Aggarwal and Kawamura, 2008). It is noteworthy that the level of C₂ in Ambikapur is several times higher than in biomass burning derived aerosol particles collected on the northern slopes of the Himalayas (avg. 138 ng m⁻³) (Cong et al., 2015).

The predominance of succinic acid (C₄) over malonic acid (C₃) in Ambikapur aerosols (Fig. 5) differs from the studies of Chennai (Pavuluri et al., 2010), Hong Kong (Ho et al., 2006) and Sapporo aerosols (Aggarwal and Kawamura, 2008), where OAs experienced significant photochemical processing in the warmer season and C₃ diacid was more abundant than C₄ diacid. This unique feature of diacids in Ambikapur aerosols may likely be related to the strength of emission sources in eastern central India. The greater abundance of C₄ over C₃ diacid has been found in aerosol particles collected in the heavily polluted atmosphere in northern cities in China (Ho et al., 2007), biomass burning derived aerosols in Rondônia (Kundu et al., 2010) and Mt. Everest (Cong et al., 2015). This result suggests the prominence of biomass burning episodes in eastern central India during the campaign. Another key feature of Ambikapur aerosols is that the concentration level of C₉ diacid (avg. 123 ng m⁻³) is several times higher than those in Chennai (avg. 32.4 ng m⁻³), Hong Kong (avg. 9.06 ng m⁻³), Chinese cities (avg. 31.6 ng m⁻³), Sapporo (avg. 6.5 ng m⁻³) and Himalayan aerosols (avg. 2.24 ng m⁻³) (Ho et al., 2006; Ho et al., 2007; Aggarwal and Kawamura, 2008; Pavuluri et al., 2010; Cong et al., 2015). We found that the level of C₉ diacid in Ambikapur aerosols is also substantially higher than that (avg. 22 ng m^{-3}) reported in biomass burning derived aerosols in Rondônia (Kundu et al., 2010). Azelaic acid is a tracer for evaluating the photochemical processing of UFAs such as oleic acid in the atmosphere (Kawamura and Gagosian, 1987; Mochida et al., 2003; Enami et al., 2015; Pavuluri et al., 2015; Deshmukh et al., 2018). These results and comparisons suggest that aerosols from Ambikapur experienced considerable photochemical processing of UFAs in the atmosphere during the campaign.

It is noteworthy that glyoxal is an immediate precursor of glyoxylic acid and that glyoxylic acid directly produces oxalic acid via photooxidation (Volkamer *et al.*, 2001; Lim *et al.*, 2005). The concentrations of ωC_2 (avg. 79.0 ng m⁻³) and Gly (avg. 32.7 ng m⁻³) in Ambikapur aerosols are substantially higher than those in Chennai (avg. 17.3 and 2.9 ng m⁻³), Hong Kong (avg. 18.5 and 0.19 ng m⁻³), China (avg. 23.9 and 2.72 ng m⁻³), Sapporo (avg. 22 and 4.6 ng m⁻³) and Himalayan aerosols (avg. 6.27 and 0.84 ng m⁻³) (Ho *et al.*, 2006; Ho *et*

al., 2007; Aggarwal and Kawamura, 2008; Pavuluri *et al.*, 2010; Cong *et al.*, 2015). The high abundances of ωC_2 and Gly in Ambikapur aerosols may serve as a key precursor of oxalic acid in the atmosphere of eastern central India.

Temporal Changes in the Concentrations of PM_{2.5} and Associated Chemical Species: Role of Emission Sources and Meteorological Parameters

The temporal variations in the concentrations of PM_{2.5} and carbonaceous components are shown in Fig. 6. The concentrations of PM_{2.5} were relatively stable from 1-25 March 2017, excluding one sample that was collected on 13 March 2017. PM_{2.5} concentrations then increased from 29 March to 10 April 2017 and slightly decreased on 14 April and increased again on 22-26 April 2017. The concentrations of PM_{2.5} significantly decreased from 30 April to 25 June 2017. The EC levels were relatively stable at the beginning of the campaign from 1-25 March 2017 and then increased from 29 March to 2 April 2017 and decreased on 6 April with a maximum on 10 April and then decreased from the middle of April to late June 2017. The temporal patterns in the concentrations of OC and WSOC are very similar to those of PM_{2.5}. The similar temporal changes show that OC and WSOC are the key components of PM_{2.5} in Ambikapur aerosols. High levels of PM_{2.5} as well as OC and WSOC were observed during 2-30 April 2017.

The backward trajectories presented in Fig. 3 reveal that air masses mostly came from the IGP areas during March 2017. Most of the air masses originated from the Arabian Sea were passing through western and central India and moved to the campaign site during April and June 2017, whereas the samples collected during May 2017 showed mixed air masses. Verma et al. (2010) investigated that atmospheric transport may control the levels of aerosol particles and associated chemical species in eastern central India. Nevertheless, we presume the substantial contribution of locally produced aerosol particles than transported aerosols at Ambikapur in eastern central India. The emission strength of biomass burning and meteorological parameters might be critical factors that influence the atmospheric levels of PM2.5 and associated chemical components in eastern central India.

It is noteworthy that biomass burning mostly from forest fires was seen during the collection of samples in eastern central India. We further checked such emission strength for different months using the Moderate Resolution Imaging Spectroradiometer (MODIS) satellite and the results of MODIS fire spots are presented in Fig. 3. The results show that there were higher numbers of fire spots in eastern central India from early to late April than the rest of the campaign (Fig. 3(b)). We also detected high numbers of fire spots in central India during April 2017, which can produce a substantial amount of PM2.5 aerosols and transport to the campaign site together with the air masses originated from the Arabian Sea. The concentrations of PM2.5 and carbonaceous components were very low from early to late June when fire activities dropped significantly in eastern central India. The low levels of PM_{2.5} and carbonaceous components during June 2017 may also be due to that the samples collected



Fig. 6. Temporal variations in the concentrations of PM_{2.5} aerosols and carbonaceous components.

during this month have an influence of pristine air masses from the Arabian Sea. It is notable that rainfall events also occurred occasionally from late May to late June with a total rainfall of 381 mm. The low levels of $PM_{2.5}$ and carbonaceous components from late May to late June were possibly due to the substantial decline of fire events and the washout of aerosols by rain. These results strongly suggest that biomass burning had a significant influence on the levels of $PM_{2.5}$ and carbonaceous components over eastern central India.

Temporal changes in the concentrations of C_2 and some major diacids and related compounds are shown in Fig. 7. The concentrations of C_2 diacid are higher during early to late April than early to late March and then they continuously decreased from early May to late June. The temporal variations of higher congeners such as shorter chain (C_3 – C_6) and longer chain (C_9) diacids and Ph acid are similar to that of C_2 diacid. ωC_2 oxoacid and both Gly and MeGly were also enriched in samples where C_2 showed high abundances. These results suggest that C_2 and related compounds had similar sources in Ambikapur aerosols. These variations are similar to those of OC and WSOC. Their concentrations decreased towards the end of the campaign. These results further suggest that diacids and related compounds were closely linked with biomass burning emission in eastern central India. This is further demonstrated in section 3.5 employing the correlation of diacids and related compounds with a tracer of biomass burning emission.

Sources Assessment by Using a Tracer Compound

Levoglucosan is produced explicitly during the pyrolysis of cellulose and hemicellulose and has therefore been widely used as a tracer of biomass burning emission (Bhattarai *et al.*, 2019). Diacids and related compounds were present abundantly in the plumes of biomass burning fires (Kundu *et al.*, 2010; Cong *et al.*, 2015; Deshmukh *et al.*, 2018). We examined the correlations of PM_{2.5} aerosols and measured chemical compounds with levoglucosan. We found that PM_{2.5} presents a strong positive correlation with levoglucosan (r =0.96) (Fig. 8(a)). This result suggests biomass burning as a major source of PM_{2.5} in eastern central India. We found that correlation coefficients for OC (r = 0.95) and WSOC (r =0.97) with levoglucosan are higher than that of EC with



Fig. 7. Temporal variations in the concentrations of water-soluble dicarboxylic acids and related compounds in $PM_{2.5}$ aerosols.

levoglucosan (r = 0.83) in PM_{2.5} samples (Figs. 8(b)–8(d)). High WSOC to OC ratios as discussed earlier together with a strong correlation of WSOC with levoglucosan further suggest that biomass burning in conjunction with SOA formation was a major contributor of water-soluble OAs over eastern central India.

Carlton *et al.* (2006) proposed that photochemical oxidation of VOCs and other organic precursors are the major source of C₂ diacid in atmospheric aerosols along with some primary contribution from fossil fuel combustion and biomass burning. C₂ diacid presented a strong positive correlation with levoglucosan (r = 0.99) during the campaign (Fig. 9(a)). The homologues higher than C₂ diacid (C₃-C₆) also presented strong correlations (r = 0.95-0.96) with levoglucosan (Figs. 9(b)–9(e)). These results suggest that biomass burning contributed significantly to the production of C₂ and related diacids in PM_{2.5} samples. It is noteworthy that Ph acid presented a strong correlation with levoglucosan (r = 0.93)

in Ambikapur samples (Fig. 9(g)). Polycyclic aromatic hydrocarbons may also be produced from biomass burning in a similar manner in fossil fuel combustion processes (Mao et al., 2018; Han et al., 2020), which can be further degraded to Ph acid in the atmosphere. This result demonstrates that the origin of Ph acid in Ambikapur was associated with biomass burning emission. A strong correlation of C9 diacid with levoglucosan (r = 0.95) was found in PM_{2.5} samples (Fig. 9(f)). This result suggests that biomass burning was a major source of C₉ diacid in Ambikapur aerosols. The biomass burning materials are mostly of biogenic origin and therefore biomass may contain a substantial amount of UFAs such as C_{18:1} (Hays et al., 2005; Deshmukh et al., 2018). C_{18:1} is highly labile because of the double bond at the carbon-9 position. The biomass burning-derived C18:1 may therefore be photooxidized to C₉ diacid after its emission to the atmosphere. We detected C_{18:1} in Ambikapur aerosol samples with a concentration range of 8.2 to 115 µg m⁻³ with an average of



Fig. 8. The correlations of elemental carbon (EC), organic carbon (OC) and water-soluble organic carbon (WSOC) with levoglucosan in $PM_{2.5}$ aerosols.

33.9 µg m⁻³. The significant positive correlation of C_{18:1} with levoglucosan (r = 0.92) strongly suggests biomass burning origin of oleic acid in Ambikapur aerosols (Fig. 9(h)). ω C₂ is strongly correlated (r = 0.97) with levoglucosan (Fig. 10(a)), demonstrating that ω C₂ was closely linked with biomass burning emission in eastern central India. The correlation of Gly with levoglucosan (r = 0.96) is relatively stronger than that of MeGly with levoglucosan (r = 0.83) in PM_{2.5} samples (Figs. 10(b) and 10(c)). Isoprene is the main precursor of Gly and MeGly (Guenther *et al.*, 2006; Myriokefalitakis *et al.*, 2011). Fu *et al.* (2008) reported that the global contribution of isoprene to MeGly formation is nearly 79%, whereas it is only 47% for Gly. Gly and MeGly are also produced from acetylene and alkenes as well as aromatics originating from anthropogenic sources (Volkamer *et al.*, 2007; Chan *et al.*, 2009; Galloway *et al.*, 2011). Such findings may suggest that biomass burning derived anthropogenic hydrocarbons may be the source of Gly and MeGly in Ambikapur aerosols.

Assessment of Photochemically Processed vs. Unprocessed Aerosols and Atmospheric Processing of Aromatic Hydrocarbons vs. Unsaturated Fatty Acids

Diagnostic concentration ratios of diacids have been used previously to assess the sources together with atmospheric processes for diacids in the atmosphere (Kawamura and Sakaguchi, 1999; Mochida et al., 2003; Kawamura and Yasui, 2005; Ho et al., 2006; Pavuluri et al., 2010; Wang et al., 2012; Kawamura et al., 2013; Kundu et al., 2016; Sorathia et al., 2018). Kawamura and Ikushima (1993) proposed that the malonic acid to the succinic acid ratio (C_3/C_4) is a unique tracer to evaluate the photochemical production of diacids because C₄ diacid photochemically dissociates to C₃ diacid in the ambient atmosphere. The C_3/C_4 ratios in Ambikapur aerosols ranged from 0.69 to 1.30 with an average of 0.95 during the campaign. These values are significantly higher than those of photochemically unprocessed aerosol particles derived from anthropogenic sources such as wood smoke and food cooking fumes (0.07-0.25) (Wu et al., 2015) and vehicular emission (avg. 0.35) (Kawamura and Kaplan, 1987), but significantly lower than those of photochemically processed aerosol particles collected in the equatorial central Pacific (1.5-10) (Kawamura and Sakaguchi, 1999) and western North Pacific (1.2-3.8) (Mochida et al., 2003).

The average C_3/C_4 diacid ratio of 0.95 in Ambikapur aerosols is likely due to the high contribution of photochemically unprocessed aerosol particles produced from biomass burning mainly during early to late April compared to photochemically processed aerosols in the atmosphere. We found that C₃/C₄ ratios were relatively low (0.69-0.87) in the samples collected during 2-30 April 2017 compared with the remainder of the sampling period (0.81–1.30) (Fig. 11). The samples collected during 2-30 April 2017 were more influenced by biomass burning emission as discussed previously based on fire spots and high levels of levoglucosan. It is noteworthy that Ambikapur aerosols are slightly more photochemically processed in the atmosphere than those of aerosol particles collected during the biomass burning episodes in Rondônia in Brazil during nighttime (avg. 0.59) (Kundu et al., 2010) and Himalayan region (avg. 0.51) (Cong et al., 2015). Nevertheless, the degree of photochemical processing in Ambikapur aerosols is not as strong as long-range transported aerosols collected in the equatorial central Pacific (Kawamura and Sakaguchi, 1999) and western North Pacific (Mochida et al., 2003).

The fumaric acid (F) to maleic acid (M) ratio (F/M) can also be applied to evaluate the aging of aerosols because *trans* isomer (F) could be produced by the photoisomerization of *cis* isomer (F) in the atmosphere (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999). The F/M ratios in Ambikapur aerosols ranged from 0.55 to 0.99 with an average of 0.73. This value is much lower than those reported for marine aerosols in the North Pacific (avg. 3.2) (Kawamura and Sakaguchi, 1999), where photoisomerization of maleic acid to fumaric acid occurs in the marine atmosphere during long-range atmospheric transport. The low F/M ratios in



Fig. 9. The correlations of water-soluble dicarboxylic acids and oleic acid with levoglucosan in PM_{2.5} aerosols.

Ambikapur samples suggest that isomerization of M to F by photochemical transformation was not significant. Lower F/M ratios were also reported in polluted aerosol samples collected at urban sites in India (avg. 0.57) (Pavuluri *et al.*, 2010), Hong Kong (avg. 0.27) (Ho *et al.*, 2006), China (avg. 0.49) (Ho *et al.*, 2007), Japan (avg. 0.51) (Aggarwal and Kawamura, 2008) and site intensively impacted by biomass burning emission (avg. 0.21) (Cong *et al.*, 2015). The temporal variation of F/M ratios indicates that the ratios were relatively low (0.55–0.68) in the samples that were more influenced by biomass burning emission compared with the rest of the samples (Fig. 11). This finding confirms that the Ambikapur aerosols were rather fresh and originated from biomass burning during the campaign.

The concentration ratio of phthalic acid to azelaic acid (Ph/C₉) has frequently been used to evaluate the source strength of anthropogenic versus biogenic emissions because Ph is produced by the oxidation of aromatic hydrocarbons such as naphthalene derived from anthropogenic sources whereas C₉ diacid is produced by the oxidation of UFAs such as oleic acid derived from biogenic sources (C_{18:1}) (Kawamura and Yasui, 2005; Ho *et al.*, 2007; Kawamura *et*

al., 2013). Ph acid is also emitted from motor vehicles via fossil fuel combustion (Kawamura and Yasui, 2005). Aromatic hydrocarbons may also be produced during biomass burning and oxidized to Ph acid in the atmosphere. Although C₉ diacid is produced by the oxidation of UFAs released from terrestrial higher plants (Agarwal *et al.*, 2010; Wang *et al.*, 2012), biomass burning also produces UFAs abundantly (Hays *et al.*, 2005).

Biomass burning may be technically defined as an anthropogenic activity, as this is the case for at least 90% of all fires globally (Kawamura *et al.*, 2013). However, biomass burning materials are mostly of biogenic origin. We presume that these possible primary sources and secondary processes of Ph and C₉ diacids may slightly complicate the situation of using Ph/C₉ ratios to distinguish the strength of anthropogenic and biogenic sources of diacids. Based on their immediate precursors Ph/C₉ ratio may therefore be used to assess the atmospheric processing of UFAs versus aromatic hydrocarbons (Kundu *et al.*, 2016; Deshmukh *et al.*, 2018). Ph/C₉ ratios in Ambikapur aerosols ranged from 0.30 to 0.88 with a mean value of 0.60. This result suggests that Ambikapur aerosols experienced more atmospheric processing



Fig. 10. The correlations of glyoxylic acid and α -dicarbonyls with levoglucosan in PM_{2.5} aerosols.

of UFAs than aromatic hydrocarbons during the campaign. We found that Ph/C₉ ratios are very low (0.30-0.49) when levels of levoglucosan (Fig. 11) are high. This result suggests that the production of azelaic acid might be enhanced due to the fast oxidation of C_{18:1} derived from biomass burning in the atmosphere of eastern central India.

Possible Formation Process of Oxalic Acid in PM_{2.5} Aerosols in Eastern Central India

Although it is widely accepted that the secondary production of C_2 diacid overwhelms the contribution from

primary sources, little is known about its secondary production from different precursor compounds such as UFAs (Kawamura and Gagosian, 1987; Kawamura and Sakaguchi, 1999), oxocarboxylic acids (Lim et al., 2005; Legrand et al., 2007) and α -dicarbonyls (Lim *et al.*, 2005; Carlton *et al.*, 2006). We performed correlation analyses for C₂ diacid with higher homologues of diacids (C3-C12), glyoxylic acid and adicarbonyls (Gly and MeGly) to investigate the formation process of oxalic acid in eastern central India. The results of these correlation analyses are presented in Table 3. Biomass burning produces large amounts of UFAs such as C_{18:1} in the atmosphere (Hays et al., 2005; Li et al., 2019), which is a precursor of C₉ diacid in the atmosphere via photooxidation (Hung et al., 2005; Pavuluri et al., 2015). We found strong correlations of C2 diacid with higher homologues of diacids $(C_3-C_9: r = 0.78-0.97)$ and $C_{18:1} (r = 0.91)$ in PM_{2.5} samples. It has been proposed that C₉ diacid can be degraded to C₂ diacid via intermediate compounds such as C3-C8 diacids via photochemical chain reactions (Wang et al., 2012; Enami et al., 2015; Pavuluri et al., 2015). These correlations indicate that diacids and oleic acid had a similar source and were simultaneously produced via photochemical degradation of oleic acid to result in C2 diacid over eastern central India.

Photooxidation of Gly and MeGly is a major global and regional source of C₂ diacid in the atmosphere (Volkamer *et al.*, 2001; Carlton *et al.*, 2009). Photooxidation of Gly and MeGly produces the intermediate ω C₂ that is further oxidized to C₂ diacid (Lim *et al.*, 2005; Yasmeen *et al.*, 2010; Wang *et al.*, 2012). The correlation coefficient of C₂ with Gly (r =0.96) is relatively stronger than that of C₂ with MeGly (r =0.84) in PM_{2.5} samples. It is noteworthy that the correlation of ω C₂ with Gly is also stronger (r = 0.95) than that of ω C₂ with MeGly (r = 0.85). These results and a strong correlation of C₂ with ω C₂ (r = 0.98) suggest that C₂ diacid as well as ω C₂ and Gly had common emission sources and that the production of oxalic acid from the photooxidation of glyoxal may be more important in eastern central India.

CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

Water-soluble dicarboxylic acids, glyoxylic acid and α -dicarbonyls were detected in PM_{2.5} aerosol samples collected from March to June 2017 in the city of Ambikapur



Fig. 11. Temporal variations in the mass concentration ratios of water-soluble diacids in PM_{2.5} aerosols.

Table 3. Pearson correlation^a analysis of concentrations of measured water-soluble diacids and related compounds in $PM_{2.5}$ aerosols.

	C ₂	C ₃	C4	C5	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	М	F	Ph	ωC_2	Gly
C ₃	0.97															
C ₄	0.97	0.99														
C ₅	0.96	0.96	0.96													
C_6	0.96	0.95	0.97	0.97												
C ₇	0.78	0.80	0.83	0.84	0.82											
C_8	0.85	0.82	0.84	0.85	0.85	0.84										
C ₉	0.95	0.95	0.97	0.95	0.95	0.84	0.85									
C ₁₀	0.55	0.45	0.45	0.52	0.44	0.34	0.36	0.41								
C ₁₁	0.63	0.63	0.68	0.67	0.65	0.77	0.53	0.66	0.60							
C ₁₂	0.51	0.59	0.61	0.67	0.61	0.83	0.60	0.58	0.13	0.58						
М	0.60	0.64	0.68	0.72	0.67	0.91	0.74	0.70	0.23	0.65	0.88					
F	0.68	0.69	0.74	0.77	0.72	0.90	0.79	0.78	0.32	0.68	0.74	0.95				
Ph	0.93	0.93	0.95	0.96	0.95	0.81	0.80	0.94	0.49	0.69	0.62	0.65	0.70			
ωC_2	0.98	0.94	0.94	0.95	0.96	0.76	0.85	0.93	0.52	0.59	0.48	0.57	0.67	0.92		
Gly	0.96	0.95	0.96	0.96	0.96	0.83	0.85	0.97	0.45	0.67	0.62	0.67	0.72	0.96	0.95	
MeGly	0.84	0.77	0.80	0.78	0.84	0.70	0.76	0.82	0.51	0.56	0.35	0.51	0.60	0.79	0.85	0.80

See Table 1 for abbreviation. ^aSignificance level is ≤ 0.001 for the correlation where *r* is ≥ 0.56 whereas significance level is ≤ 0.005 for the correlation where *r* is 0.50 to 0.55.

in eastern central India. The molecular characteristics of water-soluble organic compounds showed the predominance of oxalic acid (C₂) followed by succinic (C₄) and malonic (C₃) acids. The peak concentrations of C₂ diacid and related compounds were observed during early to late April when biomass burning episodes prevailed in eastern central India. MODIS fire images and strong positive correlations of C₂ diacid and related compounds with levoglucosan suggest that biomass burning was the main source of water-soluble OAs in eastern central India.

The diagnostic concentration ratio of C_3 to C_4 diacid suggests a greater contribution of photochemically less processed aerosol particles derived from biomass burning than photochemically aged aerosols whereas the ratios of Ph to C_9 implied that the atmospheric processing of unsaturated fatty acids was more significant than that of aromatic hydrocarbons in the atmosphere of eastern central India. Strong positive correlations of C_2 diacid with saturated diacids (C_3 – C_9), glyoxylic acid and α -dicarbonyls suggest their common sources and formation processes in the atmosphere of eastern central India. Our results demonstrate that intense biomass burning together with photochemical processing enhanced the atmospheric abundance of water-soluble organic compounds in a rural area in eastern central India.

Our results have an implication for the radiative forcing of aerosols in South Asia. Lathem *et al.* (2013) have proposed that water-soluble OAs derived from biomass burning significantly contribute to the solar radiation balance as they can act as cloud condensation nuclei and may have an impact on the hygroscopic behavior of aerosol particles and the lifetime of clouds in the atmosphere. Severe biomass burning emission and photochemical processing of biomass burning derived organic precursors in the Ambikapur site increased the atmospheric burden of water-soluble OAs in eastern central India and may have an impact on the regional climate. Biomass burning in eastern central India not only determines the high loading of OAs but also affects the air quality and climate in the outflow region.

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