

EXPRESS LETTER

Distributions and diurnal changes of low molecular weight organic acids and α -dicarbonyls in suburban aerosols collected at Mangshan, North China

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Aerosol samples were collected at Mangshan in the north of Beijing, China in autumn 2007 and analyzed for α,ω -dicarboxylic acids (C_2 – C_{12}), ketoacids (ωC_2 – ωC_4 , ωC_9 , pyruvic acid) and α -dicarbonyls (glyoxal and methylglyoxal). Oxalic (C_2) acid was found as the most abundant species, followed by succinic (C_4) and malonic (C_3) acids. Concentrations of most compounds, except for C_2 and some other species, were higher in daytime than nighttime, indicating that diacids are produced by photochemical oxidation of organic precursors emitted from anthropogenic sources such as fossil-fuel combustion in Beijing, and are transported to Mangshan area by the northerly wind in daytime. Phthalic acid (Ph) was detected as the 4th most abundant diacid both in daytime and nighttime samples, indicating that anthropogenic sources significantly contribute to the organic aerosols. However, lower adipic (C_6)/azelaic (C_9) acid ratios in nighttime than daytime suggest that biogenic source makes more contribution to the aerosols in nighttime. Higher ratios of C_2 /total diacids in nighttime than daytime suggest the aging of aerosols proceed more in nighttime, probably due to the aqueous phase oxidation of biogenic precursors. This study demonstrates that water-soluble organic aerosols are secondarily produced in the vicinity of Beijing by the oxidation of both anthropogenic and biogenic precursors.

Keywords: dicarboxylic acids, ketoacids, α -dicarbonyls, anthropogenic and biogenic emissions, secondary organic aerosols

INTRODUCTION

China has been facing serious air pollution problems due to huge usage of fossil fuels. One fourth of global primary anthropogenic organic aerosols are generated in China, approximately 70% of which originate from coal burning (Streets *et al.*, 2004). Beijing, the capital of China and one of the biggest mega-cities in the world, is located in northern China with a population of over 15.4 million, 4 million automobiles and several huge industrial regions. This city has been suffering a persistent air pollution problem. To control the air quality of Beijing, the chemical processes, atmospheric transport and chemical compositions of aerosols need to be understood. In summer 2006, CAREBEIJING (Campaign of Air Quality Research in Beijing) field program was carried out, including intensive observations in the city center and also in the south part of Beijing city (Ho *et al.*, 2010).

However, comprehensive observations of atmospheric gaseous and aerosol components had not been performed in the north of Beijing. Over the city area, dominant winds

come from the south in daytime and the north in nighttime during August to September. It was thus expected that polluted air masses are transported from Beijing area to the north, where we could catch the air parcels at Mangshan site, 40 km north of Beijing. During the long-range atmospheric transport, polluted aerosols and their precursors would be subjected to photochemical processes in daytime whereas air masses coming from the north may be less affected by the pollutants in nighttime. In this study, we analyzed atmospheric aerosols collected at Mangshan, a vicinity of Beijing, for water-soluble organic acids and aldehydes to better understand the status of air pollution and evaluate its contribution to the regional air quality in the north of Beijing.

SAMPLES AND METHODS

Aerosol sampling was carried out at Mangshan site (40°16' N, 116°17' E) (Fig. 1), where the biggest forest park of Beijing area exists. This site is surrounded by forests, and the mountain areas are expanded to the north of Mangshan. In contrast, populous, urbanized and industrialized areas including Beijing, Tianjin and Hebei Province locate in the south of the site. The sampling site is situated at elevation of about 600 m above sea level.

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Three-hour daytime samples ($n = 26$) (from 9 to 12, 12 to 15, 15 to 18 h), 9-hour daytime samples ($n = 12$) (from 9 to 18 h), and 15-hour nighttime samples (from 18 to 9 h) ($n = 20$) were collected together with 4 field blank samples from 15th September to 5th October 2007 using a high-volume air sampler and pre-combusted quartz fiber filters without any size-cut device. Meteorological parameters including temperature, relative humidity, and wind direction were measured at the sampling site. The average temperature and relative humidity at Mangshan were 25°C and 57% in daytime and 17°C and 78% in nighttime. The wind from the south-southeast dominated in daytime whereas the wind from the north-east dominated in nighttime.

Detailed analytical procedures for the determination of dicarboxylic acids and related compounds are described in Kawamura and Ikushima (1993) and Kawamura (1993). Briefly, aliquots of the filter samples are extracted with Milli Q water under ultrasonication. The extracted carboxylic acids and α -dicarbonyls are concentrated using a rotary evaporator and then derivatized to dibutyl esters and dibutoxyacetals with 14% borontrifluoride (BF_3) in *n*-butanol at 100°C. The derivatives are determined using a capillary gas chromatography. Authentic diacid dibutyl esters are used for the peak identification and quantification as external standards. Recoveries of diacid standards spiked to quartz filter were more than 70%. The analytical errors for the major organic species were <10% based on replicate analyses of filter samples. Levels of field blanks were below 10% of actual samples. The data reported here were all corrected against the field blanks.

RESULTS AND DISCUSSION

A homologous series of α,ω -dicarboxylic acids (C_2 – C_{12}), ketocarboxylic acids (ωC_2 – ωC_4 , ωC_9 , and pyruvic acid), α -dicarbonyls (glyoxal and methylglyoxal) and aromatic (phthalic, iso-/tere-phthalic) dicarboxylic acids were detected in the samples. Table 1 presents concentrations of 30 water-soluble organic species in the Mangshan aerosols for daytime and nighttime.

The concentrations of total dicarboxylic acids ranged from 105 to 3060 ng m^{-3} , with an arithmetical average of 1090 ng m^{-3} in daytime and 1210 ng m^{-3} in nighttime. These values are higher than those (90–1370 ng m^{-3} , av. 480 ng m^{-3}) reported in urban Tokyo, Japan (Kawamura and Ikushima, 1993), but are close to those reported in 14 Chinese cities (319 to 1940 ng m^{-3} , av. 904 ng m^{-3} in winter, and 211 to 2160 ng m^{-3} , av. 892 ng m^{-3} in summer) (Ho *et al.*, 2007), and are also close to those (300 to 2100 ng m^{-3}) reported in Nanjing, China (Wang *et al.*, 2002). We found that oxalic acid (C_2) was the most abundant diacid, followed by malonic acid (C_3) or succinic acid (C_4). C_2 can be primarily generated by fossil fuel

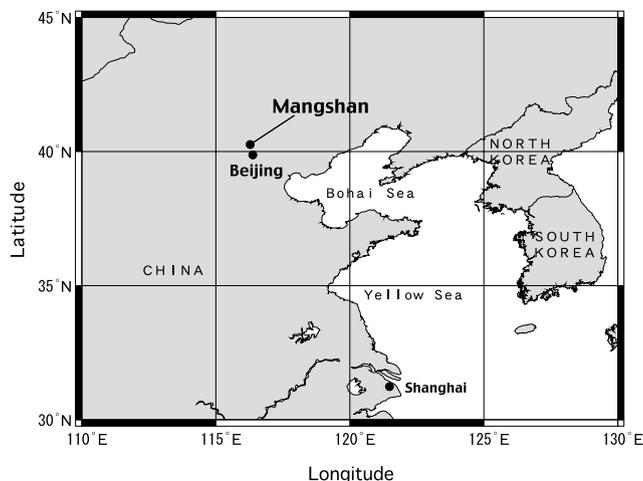


Fig. 1. A map of Northeast China with a sampling site at Mangshan.

combustion (Kawamura and Kaplan, 1987) and biomass burning (Narukawa *et al.*, 1999) and secondarily formed by the oxidation of volatile organic compounds (VOCs) and other organic precursors in gas phase and/or aerosol phase (Kawamura *et al.*, 1996, 2005). Aqueous phase chemistry in aerosol/cloud/fog droplets is also important in the production of C_2 (Warneck, 2003; Miyazaki *et al.*, 2009).

Concentrations of total ketocarboxylic acids ranged from 12.7 to 321 ng m^{-3} , with an arithmetical average of 131 ng m^{-3} in day samples and 98 ng m^{-3} in night samples. They have been considered as intermediates in the oxidation of monoacids and other precursors in the atmosphere, resulting in diacids (Kawamura and Ikushima, 1993; Kawamura *et al.*, 1996). α -Dicarbonyls showed concentrations ranging from 3.5 to 289 ng m^{-3} , with an arithmetical average of 51.5 ng m^{-3} in daytime and 59.8 ng m^{-3} in nighttime. Glyoxal (Gly) and methylglyoxal (MeGly) are gas-phase oxidation products of numerous VOCs such as benzene, toluene, xylene (Volkamer *et al.*, 2001), ethylene (Ervens *et al.*, 2004), isoprene (Zimmermann and Poppe, 1996) and terpene (Fick *et al.*, 2004), and could act as precursors of secondary organic aerosols via heterogeneous processes (Kroll *et al.*, 2005; Liggio *et al.*, 2005).

Concentrations of most compounds, except for C_2 and azelaic acid (C_9) were higher in daytime than nighttime, indicating that diacids are produced by photochemical oxidation of organic precursors emitted from anthropogenic sources such as fossil-fuel combustion in Beijing, and are transported to Mangshan area by the northward wind in daytime. Phthalic acid (Ph), which is produced by the atmospheric oxidation of anthropogenic aromatic hydrocarbons such as naphthalene (Kawamura and

Table 1. Concentrations of low molecular weight dicarboxylic acids, ketocarboxylic acids, and α -dicarbonyls in aerosol samples from Mangshan

Compounds, ng m ⁻³	Day			Night		
	Minimum	Maximum	Average	Minimum	Maximum	Average
Dicarboxylic acids						
Oxalic, C ₂	53.2	1300	607	57.6	1880	806
Malonic, C ₃	29.3	233	123	16.6	169	88.5
Succinic, C ₄	11.0	270	115	11.1	286	107
Glutaric, C ₅	2.91	72.4	34.2	3.46	78.3	27.8
Adipic, C ₆	1.40	44.1	19.7	1.18	45.7	15.2
Pimelic, C ₇	N.D.	21.1	6.16	0.32	15.9	6.15
Suberic, C ₈	N.D.	24.3	1.23	N.D.	2.19	0.53
Azelaic, C ₉	1.05	74.4	24.0	1.82	64.1	27.8
Sebacic, C ₁₀	N.D.	5.82	2.56	0.29	5.04	1.91
Undecanedioic, C ₁₁	N.D.	5.27	1.62	0.14	7.66	2.80
Dodecanedioic, C ₁₂	N.D.	1.64	0.58	0.11	5.63	1.35
Methylmalonic, iC ₄	0.22	11.5	6.22	1.30	6.78	3.90
Methylsuccinic, iC ₅	1.36	37.8	14.2	1.21	26.7	12.8
2-Methylglutaric, iC ₆	0.34	8.57	2.40	0.20	19.5	2.96
Maleic, M	0.37	84.3	15.3	0.14	135	18.7
Fumaric, F	1.28	16.4	7.23	1.37	19.0	8.61
Methylmaleic, mM	1.33	26.0	9.07	0.84	25.7	9.29
Malic, hC ₄	N.D.	11.9	3.25	0.09	9.28	1.32
Phthalic, Ph	7.01	218	66.7	5.00	203	42.4
Isophthalic, iPh	0.44	18.0	8.06	0.76	15.3	6.88
Terephthalic, tPh	0.60	29.8	9.90	0.32	21.5	10.3
Ketomalonic, kC ₃	0.41	6.52	2.60	0.37	5.26	1.73
4-Ketopimelic, kC ₇	N.D.	16.2	6.06	0.54	10.3	4.13
Total diacids	112	2540	1090	105	3060	1210
Ketocarboxylic acids						
Pyruvic	2.04	73.8	24.7	1.52	67.0	21.0
Glyoxylic, ω C ₂	11.8	195	82.1	10.1	121	58.6
3-Oxopropanoic, ω C ₃	2.62	47.0	19.1	1.82	17.6	7.80
4-Oxobutanoic, ω C ₄	2.39	35.0	17.3	0.86	23.2	10.5
9-Oxononanoic, ω C ₉	N.D.	11.6	3.90	0.09	15.4	5.51
Total ketoacids	16.3	321	131	12.7	232	97.9
α-Dicarbonyls						
Glyoxal, Gly	3.15	35.3	14.9	2.59	33.8	12.6
Methylglyoxal, Megly	1.01	242	36.6	0.96	255	47.2
Total dicarbonyls	4.16	277	51.5	3.55	289	59.8

N.D. = Not detected.

Kaplan, 1987), clearly showed higher concentrations relative to total diacids in daytime than nighttime (Fig. 2(b)). This suggests that anthropogenic sources are more important in daytime than nighttime. Because the wind blew from the south to the north during daytime travelling over the urban and industrial regions, the organic precursors emitted from vehicular exhaust and fossil fuel combustion in the city area may be transported to Mangshan area. In nighttime, the wind blew from the north where the forest locates toward the south, thus it is likely that the aerosols, which are emitted in the south area and transported to the north in daytime, come back with the northerly wind

in nighttime.

C₆ acid is produced by the atmospheric oxidation of anthropogenic cyclohexene (Hatakeyama *et al.*, 1987), whereas C₉ is from biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987). Thus C₆/C₉ ratio can be used to evaluate the relative contributions from anthropogenic and biogenic sources to organic aerosols (Kawamura and Yasui, 2005). In this study, C₆/C₉ ratios show peaks in daytime (av. 0.93) and show minima in nighttime (av. 0.61) (Fig. 2(c)). This result supports that biogenic organic compounds are important as a source of organic aerosols in Mangshan, in particular during

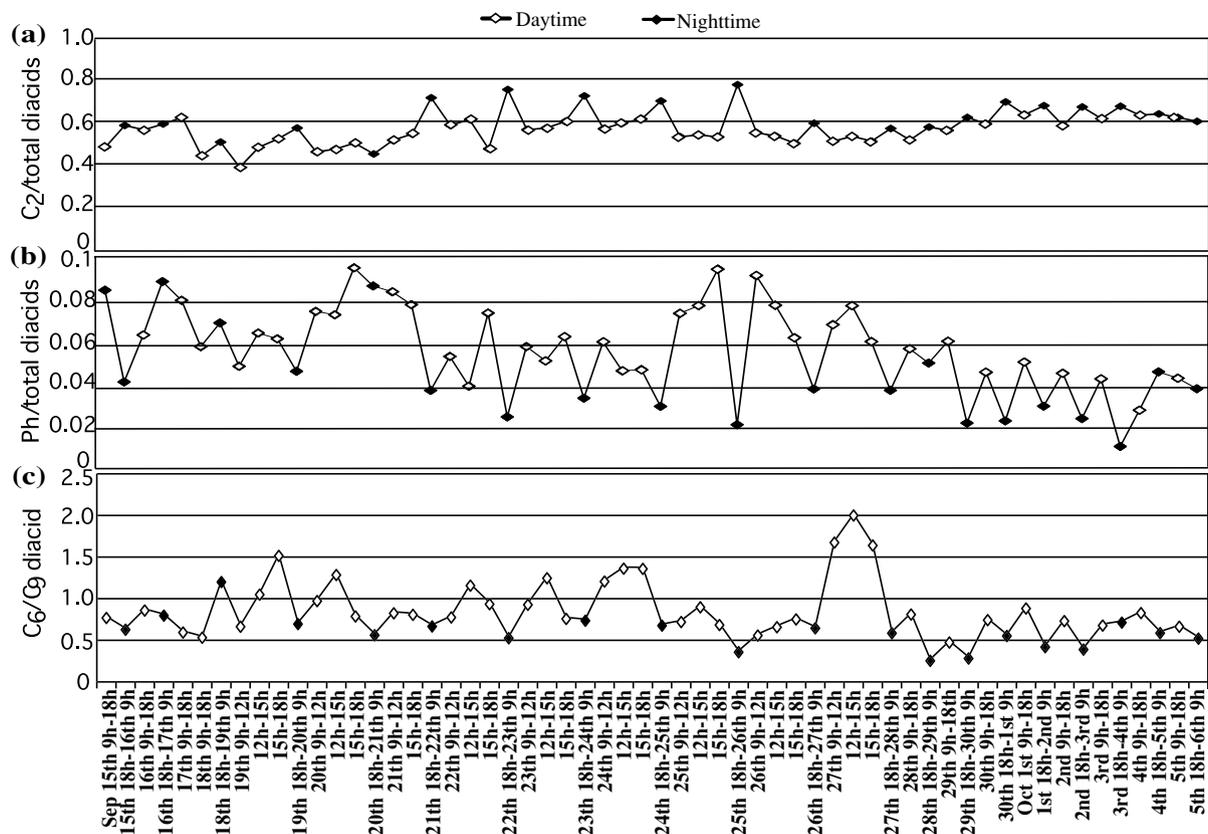


Fig. 2. Temporal variations of (a) C_2 /total diacid concentration ratios, (b) Ph/total diacid concentration ratios, and (c) C_6/C_9 concentration ratios in the aerosol samples collected at Mangshan.

nighttime. Concentrations of C_{11} – C_{12} diacids, which are the oxidation production of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987), are also higher in nighttime than daytime within the same date; daytime/nighttime concentration ratios of C_{11} and C_{12} are 0.64 and 0.62, respectively. This result also emphasizes the important contribution of biogenic source to organic aerosols in nighttime.

We found that, within the same date, the concentrations of C_2 are lower in daytime than nighttime and average concentration ratio of C_2 in daytime to nighttime is 0.77. Because C_2 can be produced by the oxidations of longer-chain diacids (Kawamura *et al.*, 1996), C_2 /total diacid ratio can be used to evaluate the aging process of organic aerosols (Kawamura and Sakaguchi, 1999). With the progress of aerosol aging, the ratio should become higher. In fact, the C_2 /total diacid ratios show peaks in nighttime (Fig. 2(a)), indicating that the nighttime aerosols were more aged. Because the anthropogenic aerosols that are emitted from the industrial regions and travel to the north come back to the sampling site by the northerly wind in nighttime, aging of these aerosols might occur during the transport and thus contribute to the high

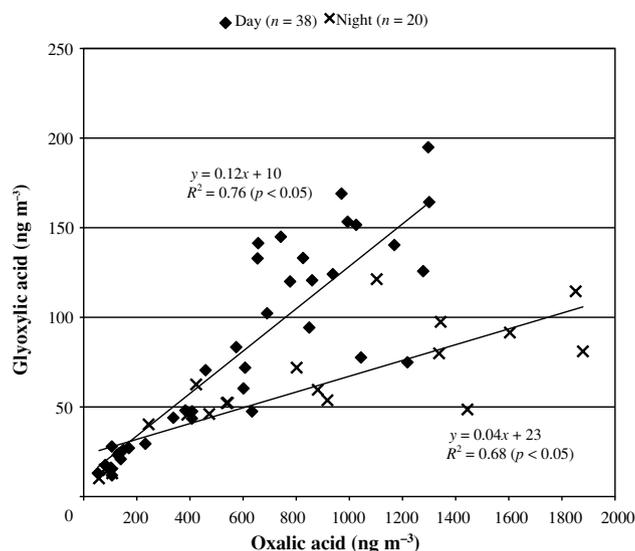


Fig. 3. Correlation plots for the concentrations of oxalic acid (C_2) and glyoxylic acid (ωC_2) in Mangshan aerosols during daytime and nighttime.

C₂/total diacid ratios.

Aqueous phase chemistry in aerosol/cloud/fog droplets is also important in the production of C₂ (Warneck, 2003; Miyazaki *et al.*, 2009). Since there is no sunlight and the relative humidity was quite high in nighttime (up to 100%, 78% on average), we suppose that C₂ was produced in aqueous phase during the nighttime aging process. Biogenic and anthropogenic VOCs can react with oxidants to produce MeGly and Gly in gas phase in both daytime and nighttime. In daytime, important oxidants are OH radical (Fan and Zhang, 2004) and O₃ (Kamens *et al.*, 1982). In contrast, the main oxidant in nighttime is NO₃, which only react with biogenic VOCs such as isoprene and monoterpene emitted in the forest area (Warneke *et al.*, 2004). Hence, biogenic VOCs also act as the important source in nighttime. MeGly and Gly can be further hydrated in aqueous phase to form CH₃COCH(OH)₂ and (OH)₂CHCH(OH)₂, respectively. Hydrated MeGly is further oxidized to result in pyruvic acid, acetic acid, hydrated glyoxylic acid, and finally oxalic acid. Hydrated Gly can be oxidized to ωC₂, and finally to C₂ (Lim *et al.*, 2005). Aqueous phase reactions are mainly initiated by NO₃ in nighttime (Harrmann *et al.*, 2000), as well as H₂O₂ (in the presence of H₂SO₄) (Claeys *et al.*, 2004). However, the mechanisms of aqueous phase reactions in nighttime are complex and are not fully understood at present. Further studies on the formation of C₂ in aqueous phase by oxidants including O₃ and H₂O₂ are needed.

In this study, we found that C₂ is more produced in nighttime whereas the concentrations of ωC₂ become lower in nighttime than daytime (see Fig. 3). This result is consistent with the higher ratio of C₂/total diacids in nighttime (Fig. 2(a)). Thus, it is reasonable to consider that C₂ is partly produced via the oxidation of ωC₂, which is derived from MeGly and Gly. These α-dicarbonyls may be produced by the oxidation of biogenic precursors emitted in daytime from the northern forest, then transported southward to Mangshan in nighttime and react with NO₃ and other oxidants in aqueous phase to result in C₂. In contrast, in daytime, C₂ is primarily produced from anthropogenic sources, e.g., motor exhaust and fossil fuel combustion in the city area, and also is secondarily produced by the photochemical oxidation of anthropogenic precursors during the atmospheric transport.

SUMMARY AND CONCLUSIONS

Molecular compositions of low molecular weight dicarboxylic acids and related compounds were studied in the aerosol samples collected from Mangshan in the north of Beijing, China. Oxalic (C₂) acid was detected as the most abundant diacid, followed by succinic (C₄) or malonic (C₃) acids. We found phthalic acid is the fourth

most abundant diacid with higher concentrations in daytime than nighttime. This can be explained by the photochemical oxidation of anthropogenic organic precursors, which were emitted from Beijing and its industrial regions, and then transported to Mangshan area by the southerly wind in daytime. In nighttime, anthropogenic aerosols, which are emitted from the city area and transported to the north in daytime, move back to the south by the northerly wind. Simultaneously, in nighttime, C₂ is generated by the aqueous phase oxidation of MeGly and Gly, which are oxidation products of biogenic hydrocarbons. This study demonstrates that secondary organic aerosols are significantly produced in the vicinity of Beijing via the oxidation of both anthropogenic and biogenic organic precursors.

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