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Identification of dicarboxylic acids and aldehydes of PM10 and PM2.5 aerosols in Nanjing, China

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Abstract

In this study aerosol samples of PM10 and PM2.5 collected from 18 February 2001 to 1 May 2001 in Nanjing, China were analyzed for their water-soluble organic compounds. A series of homologous dicarboxylic acids (C_{2-10}) and two kinds of aldehydes (methylglyoxal and 2-oxo-malonaldehyde) were detected by GC and GC/MS. Among the identified compounds, the concentration of oxalic acid was the highest at all the five sites, which ranged from 178 to 1423 ng/m^3. The second highest concentration of dicarboxylic acids were malonic and succinic acids, which ranged from 26.9 to 243 ng/m^3. Higher level of azelaic acid was also observed, of which the maximum was 301 ng/m^3. As the highest fraction of dicarboxylic acids, oxalic acid comprised from 28% to 86% of total dicarboxylic acids in PM10 and from 41% to 65% of total dicarboxylic acids in PM2.5. The dicarboxylic acids (C_2, C_3, C_4) together accounted for 38–95% of total dicarboxylic acids in PM10 and 59–87% of dicarboxylic acids in PM2.5. In this study, the total dicarboxylic acids accounted for 2.8–7.9% of total organic carbon (TOC) of water-soluble matters for PM10 and 3.4–11.8% of TOC for PM2.5. All dicarboxylic acids detected in this study together accounted for about 1% of particle mass. The concentration of azelaic acid was higher at one site than others, which may be resulted from higher level of volatile fat used for cooking. The amounts of dicarboxyic acids ($C_{2,3,4,9}$) and 2-oxo-malonaldehyde of PM2.5 were higher in winter and lower in spring. Compared with other major metropolitans in the world, the level of oxalic acid concentration of Nanjing is much higher, which may be contributed to higher level of particle loadings, especially for fine particles. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dicarboxylic acid; Aldehyde; Atmospheric aerosol; Spatial and temporal variations

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1. Introduction

Water-soluble organic compounds (WSOC) such as monocarboxylic acids, dicarboxylic acids and aldehydes have been taken as an important group of organic compounds identified in the atmospheric aerosols (Cautreels and Van Cauwenberghe, 1976; Grosjean et al., 1978; Rogge et al., 1993; Jacobson et al., 2000). Especially for dicarboxylic acids, they account for about 1–3% of the total particulate carbon in the urban and outskirt areas and even above 10% in the remote marine environment (Kawamura and Ikushima, 1993; Kawamura et al., 1996a, b; Sempere and Kawamura, 1996; Kawamura and Sakaguchi, 1999; Kerminen et al., 2000). Owing to high water solubility, the WSOC have the potential to modify the hygroscopic properties of atmospheric particles including particulate matter size and cloud condensation nuclei activity (Shulman et al., 1996; Cruz and Pandis, 1998; Jacobson et al., 2000). Galloway et al. (1976) reported that organic acids make negligible contribution to the acidity of rain-water. The same authors reached a similar conclusion from further investigations at Ithaca, New York and Hubbard

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Brook, New Hampshire (Likens et al., 1983). By contrast, other studies on organic acids of atmospheric aerosol in remote sites indicated that organic acids can lower the pH of rain (Galloway et al., 1982; Keene et al., 1983; Andreae et al., 1988, 1990). These WSOC have several different sources, including primary emissions from biomass burning and fossil fuel combustion, as well as photochemical oxidation of organic precursors of both anthropogenic and biogenic origin (Chebbi and Carlier, 1996). Monocarboxylic acids and dicarboxylic acids are the major constituents of the organic aerosol (Rogge et al., 1993; Limbeck et al., 2001) and have been extensively measured in urban, continental background (Dawson et al., 1980; Vainiotalo et al., 1983; Puxbaum et al., 1988; Wiley and Wilson, 1993), and remote atmosphere (Satsumabayashi et al., 1989; Hartmann et al., 1991; Helas and Bingemer, 1992; Kawamura et al., 1996a, b). However, concentration data of the organic acids from China have not been reported.

Chinese economic, industrial and demographic characteristics are different from those of North America and Europe (Zhang and Friedlander, 2000). High ambient suspended particulate loading has been a persistent problem in Nanjing, a typical metropolitan in China. For giving a comprehensive survey on the state of atmospheric particle pollution in Nanjing, a campaign has been performed from February to May 2001. The major fractions of pollutants such as polycyclic aromatic hydrocarbons, alkanes and water-soluble matters have been examined. As a part of this project, properties of the water-soluble matters were studied, including pH, conductivity, total organic carbon (TOC), water-soluble elements and ions (Wang et al., 2002). In order to further shed light on the chemical compositions and molecular distributions of water-soluble matter of atmospheric aerosols, this paper is devoted to chemical characterization of dicarboxylic acids, aldehydes and TOC of PM10 and PM2.5 aerosols at different sites in Nanjing city, as well as to their spatial and temporal variations.

2. Experimental part

2.1. Site description

Five sites were chosen for this study and noted in Fig. 1: (1) Suyuan Hotel (SY,32°03′18.2″N, 118°46′44.3″E); (2) Fuzi Temple (FZ,32°01′20.0″N, 118°47′04.7″E); (3) Ruijin village (RJ,32°01′58.2″N, 118°48′21.5″E); (4) Zhongshan Mausoleum (ZS, 32°03′42.9″N,118°50′47.9″E); and (5) Yangzi school (YZ,32°03′43.1″N,118°50′48.0″E). SY is located nearby Zhujiang highway, a heavy traffic center of Nanjing. RJ is a big residential area and located with FZ, a downtown, in the southern areas of the city. ZS is a scenery district and located in the east of Nanjing. YZ is a small residential area and lies in a large-scale petrochemical district, which is located in the northwestern Nanjing city.

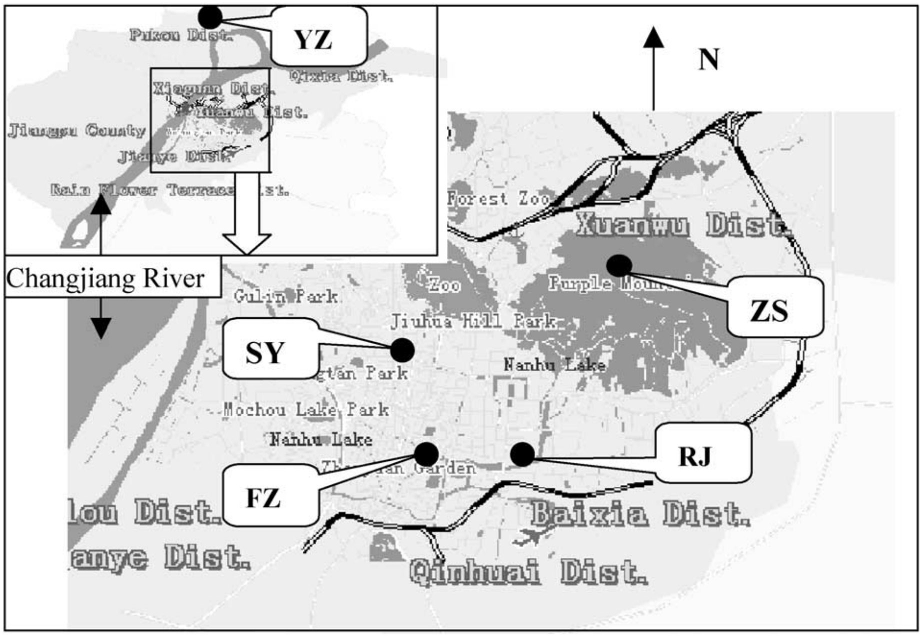

Fig. 1. Locations of five sampling sites.

2.2. Collection materials and sampling protocols

Two kinds of samplers have been used during the campaign. KC-2000 for PM10 (made in China) and Anderson GT22001 for PM2.5 (made in USA) are high volume air samplers, of which flow rates are 1.05 and 1.12 m^3/min, respectively.

The glass fiber filters ($200 \times 250\,mm^2$) was baked at 500°C for 2 h in order to eliminate organic species, conditioned in a desiccator for 24 h, and then weighted with Mettler AE240 electronic balance (limit of detection is 10 μg). After sampling, the filters were also equilibrated in the desiccator for 24 h prior to weight, and stored at −18°C before analysis.

PM10 and PM2.5 were simultaneously collected for 8 h from 8:30 a.m. to 4:30 p.m. at each site. The heights of the two air inlets were 1.5 m above the ground. The first sampling time (from 15 February to 1 March) represents the winter and the second sampling time (from 18 April to 1 May) represents the spring. Generally, air pollution of Nanjing city in both seasons is rather severe.

2.3. Determination for total organic carbon (TOC) of water-soluble species of the aerosols

One-fourth filter was cut into pieces, ultrasonically extracted with 25 ml pure water for 30 min, filtered, and then determined at 25°C for TOC of water-soluble species with Shimadzu TOC-5000 total organic analyzer (made in Japan).

2.4. Derivatization of organic acids and aldehydes of water-soluble species of the aerosols

One-fourth filter was cut into pieces, ultrasonically extracted with 25 ml × 3 pure water for 15 min to separate out WSOC. The extracts were concentrated to about 5 ml by a rotary evaporator under a vacuum and then filtered with a glass column packed with quartz wool to remove particles and filter debris. The filtrate was transferred to a 25-ml pear-shaped flask, further concentrated by rotary evaporation under a vacuum and then almost completely dried in a nitrogen stream. A 14% BF_3/*n*-butanol mixture (0.3 ml) was added into the pear-shaped flask stoppered with a ground-glass stopper and clamp and sealed with Teflon tape. The sample and reagent were reacted at 100°C for 30 min to convert the aldehyde and carboxyl groups to dibutyl acetal and butyl ester, respectively (Kawamura, 1993). The reaction products were extracted with 5 ml of *n*-hexane after adding pure water (3 ml) and acetonitrile (0.3 ml). The *n*-hexane layer was further washed with pure water (3 ml × 2) and concentrated to 1 ml in *n*-hexane by a stream of high pure nitrogen.

Glass apparatus was used after removing organic contaminants by rinsing with pure water and organic solvents.

2.5. Determination of the derivatives by GC and GC/MS

The above derivatives were analyzed by a capillary gas chromatography (Hewlett-Packard HP6890) equipped with a split/splitless injector, a HP-5 fused silica capillary column (0.32 mm i.d. × 25 m × 0.52), and an FID detector. The column oven temperature was programmed from 60°C to 280°C (hold 10 min) at 5°C/min. The identification was based on mass chromatograms obtained from major mass fragment ions of different classes of compounds. The individual components in the aerosol samples were identified using computer matches to standard reference mass spectra of the National Institute of Standards and Technology (NIST) library and the identification was confirmed by comparison to reference compounds available. For the identification of compounds, the a, b, c, and d labeling introduced by Rogge et al. (1991) was followed. Compounds were designated: (a) positive, when the sample spectrum, reference compound spectrum, and NIST-library spectrum were identical and also the retention times of the authentic compound and the sample compound were comparable; (b) probable, same as above, except that no authentic reference compound was available, but the NIST-library spectrum agreed very well with the sample spectrum; (c) possible, same as above, except that the sample mass fragmentation pattern contained additional ions from other compounds having minor peak co-elution; and (d) tentative, when the sample spectrum revealed additional mass fragments from one or more co-eluting compounds (noise) with substantial overlap. The retention times in the GC/MS mass chromatograms used for identification.

In this study, total 11 target compounds were identified. Their name, chemical structure and retention time are shown in Table 1.

3. Results and discussion

3.1. Background values of blank filter

Three sheets of blank filters were treated identically with the aerosol samples and tested for all target compounds. Although all filters were baked at high temperature (500°C) for 2 h, some target compounds were found, which probably come from the contamination during sampling and of the analysis reagents, as well as other artificial errors. Their background values are given in Table 2, calculated by the mass of target compounds in per square centimeter filter.

Table 1
Organic acids and related compounds identified in this study

Abbreviation	Name		Class	Structure	Molecular	R_t (min)
Me–Gly	Methylglyoxal		b	CH_3COCHO	$C_3H_4O_2$	6.23
C_3^a	2-Oxo-malonaldehyde		b	$HOCCOCHO$	$C_3H_2O_3$	21.88
C_2^{di}	Oxalic	Acid	a	$HOOCCOOH$	$C_2H_2O_4$	15.42
C_3^{di}	Malonic	Acid	a	$HOOCCH_2COOH$	$C_3H_4O_2$	17.62
C_4^{di}	Succinic	Acid	a	$HOOC(CH_2)_2COOH$	$C_4H_6O_4$	20.63
C_5^{di}	Glutaric	Acid	a	$HOOC(CH_2)_3COOH$	$C_5H_8O_4$	23.05
C_6^{di}	Adipic	Acid	a	$HOOC(CH_2)_4COOH$	$C_6H_{10}O_4$	25.62
C_7^{di}	Pimelic	Acid	a	$HOOC(CH_2)_5COOH$	$C_7H_{12}O_4$	27.73
C_8^{di}	Suberic	Acid	a	$HOOC(CH_2)_6COOH$	$C_8H_{14}O_4$	29.74
C_9^{di}	Azelic	Acid	a	$HOOC(CH_2)_7COOH$	$C_9H_{16}O_4$	31.87
C_{10}^{di}	Sebalic	Acid	a	$HOOC(CH_2)_8COOH$	$C_{10}H_{18}O_4$	33.77

R_t is the retention time of *n*-butyl derivative in GC.

Table 2
Background values of blank filter (ng/cm^2)

	Me–Gly	C_3^a	C_2^{di}	C_3^{di}	C_4^{di}	C_5^{di}	C_6^{di}	C_7^{di}	C_8^{di}	C_9^{di}	C_{10}^{di}
Blank	nd	nd	9.1	nd	nd	nd	nd	nd	nd	nd	nd
Blank	nd	nd	9.1	nd	6.2	7.1	nd	nd	nd	nd	nd
Blank	nd	nd	10.3	nd	nd	nd	9.8	nd	nd	nd	nd
Mean	nd	nd	9.5	nd	2.1	2.4	3.3	nd	nd	nd	nd

Nd: not detected.

Table 3
Recovery of dicarboxylic acids and aldehydes of aerosols

	Me–Gly	C_3^a	C_2^{di}	C_3^{di}	C_4^{di}	C_5^{di}	C_6^{di}	C_7^{di}	C_8^{di}	C_9^{di}	C_{10}^{di}
N	3	3	3	4	3	3	4	3	3	4	3
MR (%)	57	57	58	57	59	61	67	55	53	51	52

MR: mean recovery, N: the number of samples.

Most of the target compounds were not detected in blank filter. Amount of oxalic acid of blank filter is below 3% of oxalic acid of aerosol, and other dicarboxylic acids of blank filter are $<5\%$ of samples, respectively. The background values, therefore, are not the obstacle to accurately quantify the target compounds. Although phthalic acids was found in all samples, the data was omitted because the background value of phthalic acid prevails against aerosol samples and possibly decreases the quantitative accuracy of samples. It is necessary to note that quantitative results in this study were all corrected by the background values of blank filter.

3.2. Recovery of dicarboxylic acids and aldehydes

Dicarboxylic acids and aldehydes identified in this study were tested for their recovery. Procedures of recovery test are shown as follows: (1) 100 μg/ml dicarboxylic acids and aldehydes solution was prepared with dissolving the authentic standard compounds in pure water; (2) the standard solution (1 ml) was transported on one-fourth glass fiber filter by pipette; (3) the filter was equilibrated in desiccator for 24 h in order to remove water; (4) the filter adsorbing dicarboxylic acids and aldehydes was further treated identically with aerosol samples and determined for the recovery of target compounds. For the test accuracy, recovery of the target compounds were repeatedly determined for 3–4 times.

As a series of homologous compounds, dicarboxylic acids have the same chemical reaction activity during the esterization with *n*-butanol except phthalic acid, which result in the similar recovery (seen in Table 3). It was found that the recoveries of dicarboxylic acids and aldehydes could be much higher under higher level of the authentic standards concentrations. However, we believe that only the standards solution, of which organic acids and aldehydes concentrations are similar with aerosol samples, could match the target compounds. The quantitative outcomes of target compounds in this study were all corrected by the recovery.

3.3. Concentrations of dicarboxylic acids and aldehydes

Nine kinds of dicarboxylic acids (C_2–C_{10}) and two kinds of aldehydes (methylglyoxal, 2-oxo-malonaldehyde) were detected in this study. Tables 4 and 5, respectively, shows the concentration data of dicarboxylic acids and aldehydes of PM10 and PM2.5 aerosols at five sites in the winter (from 15 February to 1 March) and the spring (from 18 to 30 April). The most abundant dicarboxylic acids of PM10 or PM2.5 are oxalic acid, the smallest diacid species, followed by malonic and succinic acids. Oxalic acid was found in all samples with concentrations about 2–5 times higher than those of other carboxylic acids. This phenomenon

Table 4
Concentrations of dicarboxylic acids and aldehydes of PM10 at five sites (ng/m^3)

Site	SY		RJ		ZS		FZ		YZ	
Season	Winter	Spring	Winter	Spring	Winter	Spring	Winter	Spring	Winter	Spring
Time	02/15	04/18	02/16	04/22	02/18	04/26	02/22	04/25	03/01	04/30
PM10										
Me–Gly	12.5	nd	5.8	nd	13.9	9.7	22.2	nd	nd	14.2
C_3^{a}	62.5	13.1	20.9	20.9	211	nd	129	34.8	39.7	31.6
C_2^{di}	651	875	178	315	1388	621	1062	500	673	580
C_3^{di}	80.1	26.9	33.5	59.9	193	nd	159	76.4	106	88.6
C_4^{di}	87.3	65.3	28.9	61.6	243	nd	217	77.9	154	113
C_5^{di}	34.2	nd	15.8	26.7	65.3	nd	64.5	31.0	33.7	nd
C_6^{di}	21.5	nd	7.5	15.0	36.7	nd	31.4	102	20.5	28.6
C_7^{di}	16.7	nd	nd	13.0	28.4	nd	24.2	17.4	32.3	nd
C_8^{di}	18.7	nd	nd	50.1	31.9	nd	8.4	14.6	31.1	nd
C_9^{di}	152	228	32.5	301	79.9	29.6	98.8	220	99.1	nd
C_{10}^{di}	8.3	14.2	11.7	298	37.9	67.5	35.5	125	128	16.1
Total	1144	1223	335	1162	2328	728	1852	1198	1318	873
TOC (μ/m^3)	20.53	21.65	31.07	22.76	29.48	25.59	35.58	28.38	—	28.07
Total/TOC (%)	5.6	5.7	1.1	5.1	7.9	2.8	5.2	4.2	—	3.1
Total/PM (%)	0.2	0.2	0.2	0.6	0.7	0.3	0.6	0.3	0.4	1.0

TOC: total organic carbon of water-soluble matters; PM: particle mass; nd: not detected.

Table 5
Concentrations of dicarboxylic acids and aldehydes of PM2.5 at five sites (ng/m^3)

Site	SY		RJ		ZS		FZ		YZ	
Season	Winter	Spring	Winter	Spring	Winter	Spring	Winter	Spring	Winter	Spring
Time	02/15	04/18	02/16	04/22	02/18	04/26	02/22	04/25	03/01	04/30
PM2.5										
Me–Gly	217	30.1	35.3	nd	8.1	31.6	22.3	nd	19.6	41.4
C_3^{a}	112	28.0	45.4	31.4	83.8	25.6	162	34.8	96.0	34.9
C_2^{di}	935	477	363	288	844	505	1423	396	836	538
C_3^{di}	140	65.8	90.7	47.0	113	57.0	177	73.9	107	62.8
C_4^{di}	206	126	144	49.2	181	133	293	86.2	151	144
C_5^{di}	95.1	52.0	31.4	19.1	52.5	16.0	91.6	36.3	49.8	35.5
C_6^{di}	101	34.1	27.6	31.5	17.5	nd	43.3	29.2	57.1	26.6
C_7^{di}	115	12.5	15.9	11.3	16.3	nd	26.0	14.9	18.0	15.2
C_8^{di}	92.2	31.9	21.3	10.1	8.3	10.7	16.9	27.4	17.2	9.0
C_9^{di}	115	73.3	140	124	43.3	162	114	145	95.6	89.0
C_{10}^{di}	63.3	63.0	41.7	69.2	24.9	184	31.7	59.8	30.7	71.9
Total	2193	993	957	680	1392	1125	2401	908	1477	1069
TOC (μg/m^3)	18.54	20.14	17.45	19.89	18.45	24.71	29.60	17.84	25.63	20.33
Total/TOC (%)	11.8	4.9	5.5	3.4	7.5	4.6	8.1	5.1	5.8	5.3
Total/PM (%)	0.4	0.2	0.7	0.4	0.6	0.7	1.0	0.3	0.6	1.4

TOC: total organic carbon of water-soluble matters; PM: particle mass; nd: not detected.

is agreement with observations reported by Kawamura et al. (1995, 1996a, b), Sempere and Kawamura (1996) and Dabek-Zlotorzynska et al. (2001). Higher level of azelaic acid was also observed in this work. As the major fractions of dicarboxylic acids detected in this study, oxalic, malonic and succinic acids together comprised 38–95% of total dicarboxylic acids in PM10 and 59–87% of total dicarboxylic acids in PM2.5. Similar results are also reported by Kawamura (1993), who identified carboxylic acids and carbonyl compounds of aerosols and wet precipitation in Tokyo, Japan. As the most abundant acid in the samples of this study, oxalic acid comprised from 28% to 86% of total carboxylic acids in PM10 and 41–65% of total carboxylic acids in

PM2.5. As seen in Tables 4 and 5, the total dicarboxylic acids accounted for 2.8–7.9% of total organic carbon of water-soluble species (TOC) for PM10 and 3.4–11.8% of TOC for PM2.5. It was shown in our previous study (Wang et al., 2002) that about 10% of particle mass at the five sites was TOC. It suggests that the total dicarboxylic acids, which were detected in this study, accounted for about 1% of particulate mass.

Methylglyoxal and 2-oxo-malonaldehyde were almost observed in all samples, although amounts of the two aldehydes were relatively lower than dicarboxylic acids. They have been previously reported in rain, fog, mist and aerosol samples, as well as motor vehicle exhausts from the Los Angeles area (Steinberg and Kaplan, 1984; Kawamura et al., 1996a, b, 2000). As for their origin, many studies have taken them as the photo-oxidation products of aromatic hydrocarbons such as toluene (Nojima et al., 1974; Darnel et al., 1979; Takagi et al., 1980; Atkinson et al., 1980; Dumdei and O'Brien, 1984) and isoprene (Lee et al., 1995; Kawamura et al., 2000). They are also taken as the precursors of organic acids (Kawamura et al., 2000). As shown in Tables 4 and 5, methylglyoxal and 2-oxo-malonaldehyde accounted for about 1% of TOC. It was also observed in almost all samples that total/PM of PM2.5 had higher levels than those of PM10, which indicates that dicarboxylic acids and aldehydes, as secondary organic aerosol products, are more readily enriched in fine particles (Kawamura, 1993; Kawamura et al., 2000; Kubatova et al., 2000; Jacobson et al., 2000).

In this study more than about 90% fractions of TOC was unknown. Decesari et al. (2001) have shown that 87% of WSOC, on average, are neutral/basic compounds, mono- and dicarboxylic acids and polyacidic compounds. In addition, amino acids and peptides are also the significant constituents of WSOC (Yu et al., 1995, 1998).

3.4. *Spatial and temporal variations of dicarboxylic acids and aldehydes*

Spatial and temporal variations of the target compounds of PM10 and PM2.5 aerosols are shown in Figs. 2 and 3, respectively. Of all the five sites, dicarboxylic acids and aldehydes had the same spatial trend of concentration distribution. Among the detected compounds, oxalic acid was always the most abundant compound in the five sites, followed by malonic and succinic acids, except that azelaic acid presented at site RJ had higher level of concentration than malonic and succinic acids. Some papers have shown that azelaic acid originates from the oxidation of unsaturated fatty acids ($C_{18:1}$ and $C_{18:2}$) (Kawamura and Gagosian, 1987; Stephanou and Stratigaski, 1993). The site RJ is located in a big residential area and surrounded by many Chinese restaurants. We assumed that the fat used in cooking was volatized into air and oxidized into azelaic acid, which resulted in higher level of azelaic acid in the atmosphere.

In winter, the most amount of oxalic acid was observed at sites ZS (seen in Fig. 2(c)) and FZ (seen in Fig. 3(d)), which were 1388 ng/m^3 for PM10 and 1423 ng/m^3 for PM2.5, respectively. In spring, oxalic acid had the most amount at site SY, which was 875 ng/m^3 for PM10, and the similar concentrations at five sites for PM2.5. Compared to winter, the concentration of oxalic acid in spring was higher for PM10 and lower for PM2.5. With respect to the difference between winter and spring, oxalic, malonic and succinic acids and 2-oxo-malonaldehyde of PM2.5 had the higher level of concentrations in winter than in spring at all the five sites, except azelaic acid at sites ZS and FZ. But with respect to these compounds of PM10, a common trend of seasonal changes at all the five sites was not observed.

Of all the five sites, the amounts of the rest dicarboxylic acids (C_5–C_8, C_{10}) and Me–Gly were relatively lower, of which the variation trend of spatial and seasonal differences were not obvious.

The sources of atmospheric dicarboxylic acids include direct emissions from fossil fuel combustion, and photo oxidation of organic precursors of both anthropogenic and biogenic origin (Chebbi and Carlier, 1996). The formation pathways for particulate diacids are largely unknown. But they may be formed by condensation from the gas phase, by surface reaction on gas–particle interfaces, or by liquid-phase reaction in aqueous aerosol particle or in cloud or fog droplets. Diacids may also participate in new particle production by homogeneous nucleation with other vapors.

The oxalic acid concentrations of several typical metropolitans of the world are given in Table 6. Compared with other major cities, the level of oxalic acid concentration of Nanjing is much higher than Tokyo, New York and Los Angeles, and lower than Sao Paulo City. This difference may be contributed to higher level of particle loadings in the atmosphere, especially for fine particles. Our study results has shown that particle loadings of atmosphere in Nanjing, on average, were 331.4 μg/m^3 for PM10 and 244.5 μg/m^3 for PM2.5 during the survey (Wang et al., 2002), which are nearly four times of the National Ambient Air Standards of the United States and much higher than other cities.

4. Conclusions

The identification of nine kinds of dicarboxylic acids ($C_{2–10}$) and two kinds of aldehydes (methylglyoxyl and 2-oxo-malonaldehyde) present in PM10 and PM2.5 atmospheric aerosols in Nanjing, China has been done by GC and GC/MS. Among the detected compounds, oxalic acid was the most abundant compound at all the

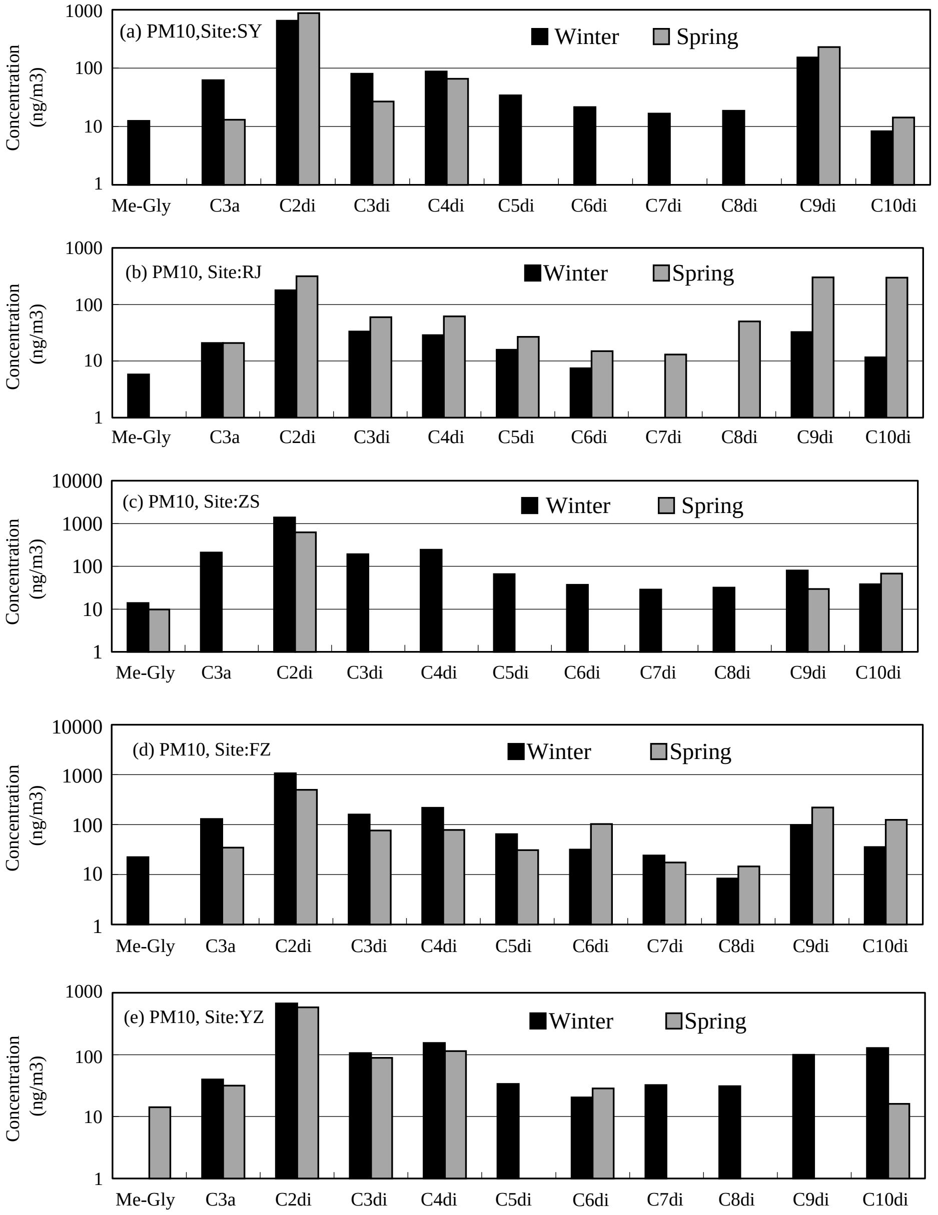

Fig. 2. Spatial and temporal differences of dicarboxylic acids and aldehydes of PM10 at five sites in the winter and the spring.

five sites, followed by malonic and succinic acids. The concentration of azelaic acid were also higher. As the highest fraction of dicarboxylic acids, oxalic acid comprised from 28% to 86% of total dicarboxylic acids in PM10 and from 41% to 65% of total dicarboxylic acids in PM2.5. The major dicarboxylic acids (C_2, C_3, C_4) together accounted for 38–95% of total dicarboxylic acids in PM10 and 59–87% of dicarboxylic acids in PM2.5. In this study, the total dicarboxylic acids accounted for 2.8–7.9% of TOC for PM10 and 3.4–11.8% of TOC for PM2.5. It means that the total dicarboxylic acids, detected in this study, accounted for about 1% of particle mass. Oxalic, malonic and succinic acids and 2-oxo-malonaldehyde of PM2.5 present higher levels in winter than in spring, but seasonal differences of these compounds of PM10 were not observed. We are interested to discover that the concentration of azelaic acid was higher at site RJ than at other sites, which may be resulted from higher level of volatile fat used for cooking. Compared with other major metropolitans, the

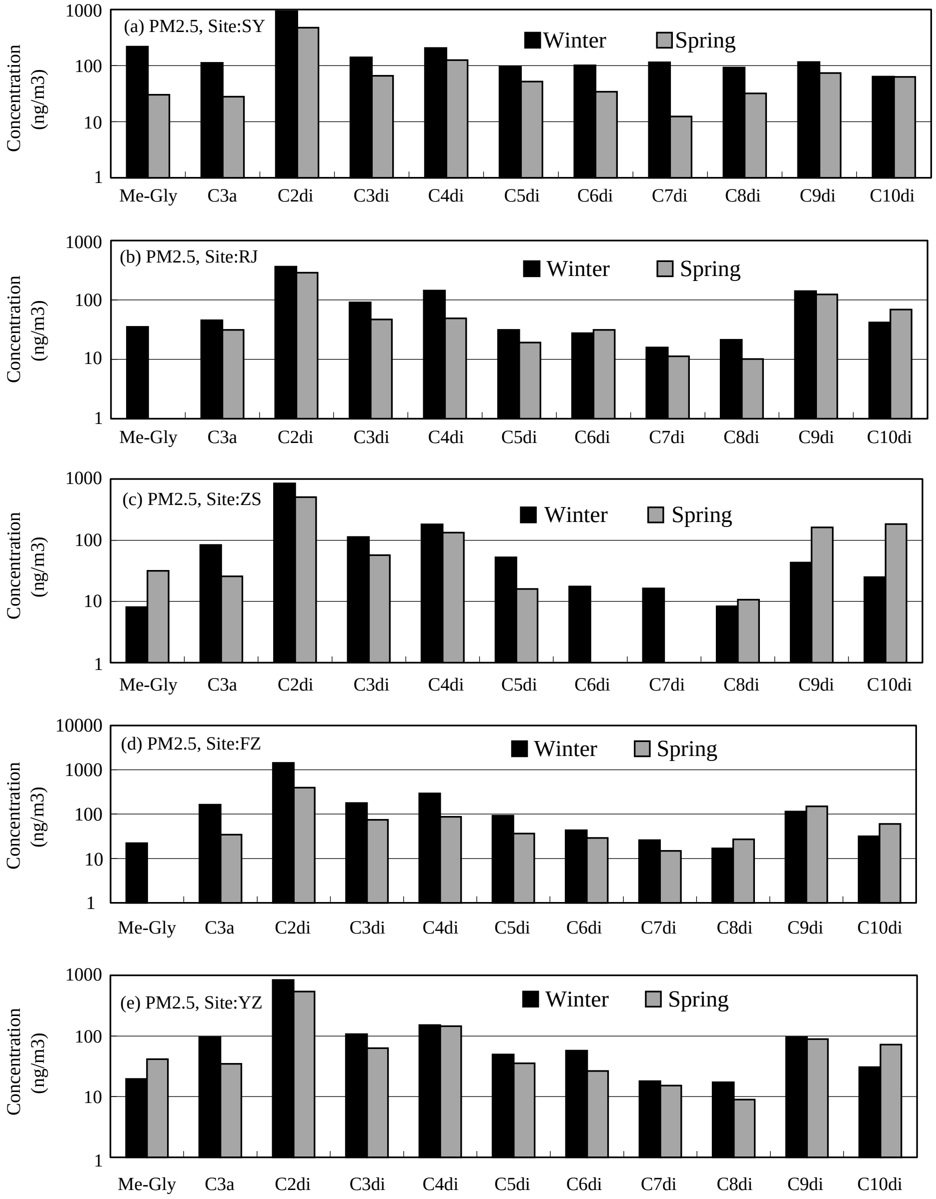

Fig. 3. Spatial and temporal differences of dicarboxylic acids and aldehydes of PM2.5 at five sites in the winter and the spring.

Table 6
Oxalic acid concentration of major metropolitans in the world

	Site	Author	Average concentration (μg/m^3)
Oxalic acid	Tokyo	Kawamura et al. (1993)	0.27
	New York	Grosjean (1988)	0.21
	Los Angeles	Kawamura et al. (1985)	0.49
	Colorado Mountain	Norton et al. (1983)	0.18
	Sao Paulo City, Brazil	Souza et al. (1999)	1.14
	Nanjing, China	This study	0.68 (PM10) 0.66 (PM2.5)

level of oxalic acid concentration of Nanjing is much higher than Tokyo, New York and Los Angeles, which may be contributed to higher level of particle loadings, especially for fine particles.

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