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Source Distribution and Variation of Atmospheric di-carbonyl Compounds in Wanqingsha, Pearl River Delta, South China, from 2008 to 2011

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Abstract

Glyoxal (G) and methylglyoxal (MG) have received cautions for their roles in the atmospheric chemistry and formation of secondary organic aerosol. Mostly they come from the photochemical transformation of precursors like isoprene, aromatic compounds, acetylene and acetone etc. Here these two compounds were studied in Wanqingsha, the central sector of Pearl River Delta (PRD), south China, in deep-autumn from 2008-2011. Their concentrations (from tens of pptv to sub-ppbv) were determined together with some other related atmospheric compounds such as benzene, acetylene, CO etc. MG concentrations were mostly higher than G, which might be resulted from the high concentration level of acetone (about 10 ppbv). For the sources of di-carbonyl compounds, transport source (mainly vehicle emission and industry emission from upwind cities) and local emission (including mankind activity and biogenic emission) all contributed. The concentration ratio of glyoxal to formaldehyde (R_{GF}, < 0.04) indicated larger part of anthropogenic source. For 2008, the economic crisis caused the decreasing of the factory emission, and for 2010, the control measurement during the Asia Games cause the decreasing of transport source. The variation of R_{GF} and correlations between the detected compounds reflected the source variation during these two years.

Keywords: Glyoxal; Methylglyoxal; Source Distribution; Source Variation

Introduction

Glyoxal (G) and methylglyoxal (MG) were two di-carbonyl species of the smallest molecular weight in the atmosphere. They were the most abundant di-carbonyl compounds in atmosphere, both for gas phrase and particle phrase. Studies showed that they were indicator for atmospheric photochemistry, and recently works pointed that they might be strongly involved in the formation of secondary organic aerosol, SOA (Garcia et al., 2006; Kawamura et al., 1996; Liggio et al., 2005; Matsunaga et al., 2007) [1-4], and might contribute largely to the missing part of SOA between modeled and detected SOA (Liggio et al. 2005) [3]. These two compounds were concerned during the last ten years, more and more studies revealed the high yield of SOA even thought they were molecular with two or three carbons, which were thought to be impossible to form SOA before.

These two compounds had the directly emission of biomass burning (Hays et al., 2002) [5] and vehicle emission (Kean et al., 2001) [6], but mainly were produced in the photochemical process of many anthropogenic and biogenic volatile organic compounds (VOCs) (Volkamer et al., 2001, 2005) [7,8].

Among the VOCs, isoprene contributed the major part in the global scale. It was described that its contribution to glyoxal and methyglyoxal was nearly 50% and 80%, respectively (Fu et al., 2008) [9].

Acetylene (C_2H_2) was the second largest source of glyoxal and the most important anthropogenic precursor (Fu et al., 2008) [9]. It was emitted by combustion and had a global mean lifetime of 18 d against oxidation by OH radical. The measured molar yield of glyoxal from acetylene was 70% ± 30%. The resulting glyoxal might contribute to about 20% of the total glyoxal source, and the proportion should be larger in city atmosphere. Because of its long lifetime, acetylene provided a free tropospheric source of glyoxal and hence of SOA.

Aromatics were mainly emitted by combustion and solvent use. Chamber studies showed that they produce glyoxal and methylglyoxal in high yield (about 20%) during the ring-cleavage stage (Volkamer et al., 2001; Atkinson and Arey, 2003; Berndt and Boge, 2001) [7,10,11]. Benzene and toluene, with lifetimes exceeding days, enhanced the di-carbonyl concentrations in the outflow of anthropogenic emission regions.

Acetone was the second largest source of methylglyoxal and had a long atmospheric lifetime (22 d against OH oxidation and photolysis). Primary sources of acetone were mainly biogenic, including terrestrial vegetation and dissolved organic matter in the ocean (Jacob et al., 2002) [12]. But in city, combustion and solvent use were main primary source. In addition, acetone was produced in the atmosphere by OH oxidation of monoterpenes, methylbutenol, and isoalkanes. Acetone oxidation by OH in MCMv3.1 produced methylglyoxal and hydroxyacetone. Globally, Annual methylglyoxal production from primary acetone contributed about 7% of the global total methylglyoxal source (Fu et al., 2008) [9].

Glyoxal and methylglyoxal were removed from the atmosphere by photolysis, oxidation, dry and wet deposition, and irreversible uptake by aerosols and cloud droplets. Studies showed that photolysis was the main sink of glyoxal and methylglyoxal, the global glyoxal and methylglyoxal lifetime against photolysis was 4.9 h and 2.2h, respectively (Fu et al., 2008) [9], and glyoxal lifetime for clear-sky conditions at noon in Mexico City in April was as short as about 1.5 h (Volkamer et al., 2005) [8].

Few works were proceeded about di-carbonyl in China, especially in Pearl River Delta, south China, where there were high density of population and high speed economic develop. Here presented the work carried out in Wanqingsha, the core point in PRD, di-carbonyl compounds were detected with their precursors and related compounds in deep autumn during 2008-2011, their source distribution and variation were discussed.

Methodologies

Description of sampling site

The Pearl River Delta (PRD) region of south China covering an area about 41700 km^2 is among the highly industrialized and densely populated regions in China. It encompasses nine cities in Guangdong province, namely Guangzhou, Shenzhen, Zhuhai, Dongguan, Foshan, Jiangmen, Zhongshan, Zhaoq-ing and Huizhou, plus Hong Kong and Macau Special Administrative Regions constituting the greater PRD (Figure 1). The rapid growth in economy has resulted in fast increase in anthropogenic air pollutant emission in this region. In the PRD atmosphere, because of the high average temperature, the strong solar radiation and the high concentration of oxidizing gases (Zheng et al., 2010) [13], it is easy for photochemical reactions to occur. The carbonyl compound concentrations in the ambient atmosphere under different weather conditions and their possible sources had been reported (Lü, et al., 2009, 2010) [14,15]. These previous studies had shown that acetone (CH3COCH3), HCHO and CH3CHO were the dominant carbonyl compounds accounting for 60–70 % of the total carbonyl compounds, and vehicular exhaust was a major source of carbonyl compounds in the urban area of PRD. However, until now, there are no measurements to study situation of di-carbonyl compounds in the PRD region.

Figure 1: Location of sampling site Wanqingsha in Pearl River Delta, Guangdong Province, China

The field sampling site (22.711N, 113.549E), is located at Wanqingsha (WQS), a small town southernmost of Guangzhou in the center of the PRD (Figure 1). This small town is surrounded by farmlands, and very few textile and clothing workshops. So the local anthropogenic emissions are not remarkable and air pollutants are mainly from the surrounding cities. The site is 50 km to the southeast of Guangzhou urban center, 40 km to the southwest of Dong-guan, 50 km to the northwest of Shenzhen, and 25 km northeast of Zhongshan, making it a good regional monitoring station to characterize the air pollution in inner PRD.

Field sampling

Di-carbonyl compounds and related carbonyl compounds collection: The sampling site had been described elsewhere (Zhang et al., 2012) [16]. Briefly, measurements were conducted on the rooftop of a 15 m high building in a secondary school during four periods from November 25 to December 1, 2008; December 1 to 7 and 17 to 24, 2009; November 21 to 27, 2010; November 25-27 and November 30 to December 6 in 2011. The air samples were collected into silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55–105 μm particle size, 125 Å pore size; Waters Corporation, Milford, MA) with a sampling pump (Thomas, USA). Target compounds were trapped as 2, 4-dinitrophenylhydrazine derivatives. A one-meter copper tube (i.d. 6 mm) coated with saturated potassium iodide (KI), as ozone denuder, was connected to the upstream of the cartridge to avoid degradation of DNPH (as described by Lü, et al., 2009, 2010) [14,15]. The collection for carbonyl compounds were conducted from 0:00 to 4:00, 4:00 to 8:00, 8:00 to 12:00, 12:00 to 16:00, 16:00 to 20:00 and 20:00 to 24:00 at a flow rate of 1 L min^{-1}. The total sample numbers in 2008, 2009, 2010 and 2011 were 42, 76, 37, and 54, respectively.

Meteorological parameters, trace gas and VOCs collection: The meteorological parameters were measured by a mini weather station (Vantage Pro2™, Davis Instruments Corp., USA). Trace gases including O_3, NO-NO_2-NOx, SO_2 were also monitored online using Thermo Fischer Scientific instruments (Model 49i, 42i-TL, 43i-TLE). Detailed information about the measurements and quality control and quality assurance can be found elsewhere (Zhang et al. 2012, 2013) [16,17]. Time series of wind speed/direction, relative humidity, temperature and global solar radiation were showed elsewhere (Zhang, Wang et al. 2012) [16]. During most period of sampling, north wind was detected.

Ambient VOCs samples were collected during the same time as carbonyl compounds were collected using cleaned and evacuated 2-Liter electro-polished stainless steel canisters. The details were described elsewhere (Zhang et al., 2012) [16].

Di-carbonyl compounds and other carbonyl compounds analysis

The details of analytical procedures for the carbonyl compounds were described by Lü et al. (2009, 2010) [14,15] and Liu et al. (Liu et al., 2013) [18]. In brief, the sampled cartridges were eluted slowly with 2 mL of acetonitrile (ACN) into a 2-mL volumetric flask, stored in refrigerator until HPLC analyses. A 10-μL aliquot was injected into the HPLC system (Agilent 1200) installed with Agilent SB-C18 reverse column (250×4.6 mm, 5μm) for the carbonyl compounds analysis. The chromatographic conditions were as follow: the gradient mobile phase was 60–70 % ACN of water solution for 20 min, 70–100 % ACN for 3 min, 100 % ACN for 4 min, 100–60 % ACN for 1 min, and then 60 % ACN for 5 min. The mobile-phase flow rate was 1 mL min^{-1}. The column temperature was 40 ºC. A detector was UV detector set at 360 nm wavelength.

Calibration standards of the dicarbonyls were prepared by mixing glyoxal (CHO-CHO) and methylglyoxal (CH3-CO-CHO) in acetonitrile (1 mg/ml, Sigma, St. Louis, MO) with 1 mL of 200 μg mL^{-1} DNPH in an acidic ACN solution. The mixtures were allowed to stand at room temperature for at least 6 h for a complete derivatization. The final volume of each calibration mixture was made to be 1.0 mL with acetonitrile (HPLC/GCMS grade; Sigma). Concentrations of the di-carbonyl DNP-hydrazones in the calibration standards ranged from 0.02 to 2.0 μg mL^{-1}. Linearity was indicated by a correlation of determination (r^2) of at least 0.99. The cartridge extracts and calibration standards were analyzed by injecting 10 μL of the samples to a high-pressure liquid chromatography (HPLC) system. Method detection limits of these two compounds were < 0.01 μg/m^3 using 240 L sampling volume, determined by using seven replicate analyses of the working standard.

For other carbonyl compounds detection (e.g., formaldehyde, HCHO, and acetone, CH3-CO-CH3), at least three field blanks were analyzed during each sampling period. Identification and quantification of carbonyl compounds were based on their retention times and peak areas, respectively. The instrument was calibrated using seven standard concentrations (from 0.2 to 20 μg mL^{-1}). A very good linear relationship (r^2=0.999) was established between the concentration and response for all carbonyl compounds identified. Calibration standards ran daily to ensure the instruments being stabilized. Cartridge collection efficiency was determined with two cartridges in series, and over 95 % of the carbonyl compounds were found in the first cartridge. The second elution tests indicate complete recovery of all of the carbonyl compounds. Relative percent differences for a duplicate analysis were less than 5 %.

Labs analysis of VOCs and carbon monoxide (CO)

Air samples were analyzed using a Model 7100 pre-concentrator (Entech Instruments Inc., California, USA) coupled with an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). Detailed cryogenically concentration steps are described elsewhere (Zhang et al., 2012) [16]. Briefly, the VOCs inside the canister were first concentrated in a liquid-nitrogen cryogenic trap at -160 ^{o}C. The trapped VOCs were then transferred by pure helium to a secondary trap at - 40 ^{o}C with Tenax-TA as adsorbent. Majority of H$_2$O and CO$_2$ were removed during these two steps. The secondary trap was then heated to get target VOCs transferred by helium to a third cryo-focus trap at -170 ^{o}C. After the focusing step, the trap was rapidly heated and the VOCs were transferred to the GC-MSD/FID system. The mixture was first separated by an HP-1 capillary column (60 m × 0.32 mm × 1.0 mm, Agilent Technologies, USA) with helium as carrier gas, and then split into two ways: one is a PLOT-Q column (30 m × 0.32 mm × 2.0 mm, Agilent Technologies, USA) followed by FID detection, another is a 65 cm × 0.10 mm I.D stainless steel line followed by MSD detection. The GC oven temperature was programmed to be initially at -50 ^{o}C, holding for 3 min; increasing to 10 ^{o}C at 15 ^{o}C /min, then to 120 ^{o}C at 5 ^{o}C /mi, then to 250 ^{o}C at 10 ^{o}C/min, and finally holding for 10 min. The MSD was used in selected ion monitoring (SIM) mode and the ionization method was electron impacting (EI). CO in air samples was also analyzed by a gas chromatography (Agilent 6890 GC) equipped with a FID and a packed column (5 Å Molecular Sieve 60/80 mesh, 3 m × 1/8 inch). CO was first converted by Ni-based catalyst to CH$_4$ and then detected by FID after separation by the packed column.

Trace gas (SO2, O3, NOx) analysis

These three trace gases were analyzed by Thermo Fischier Scientific 43i-TLE, 49i and 42i-TL (USA), respectively. The air was pumped in continuously and analyzed; five-minute average data were stored in the memory of instruments. In this study, the four hour average data were supplied.

Results and Discussion

Meteorological conditions

During the sampling intervals from 2008-2011, details of meteorological conditions were showed in previous studies (Zhang et al., 2012; Liu et al., 2013b) [16,19]. Briefly, it was as below: average air temperature was about 16 ± 5, 15 ± 4, 21 ± 2, 19 ± 2 ^{o}C and the RH was 36 ± 11, 60 ± 18, 70 ± 9, 72 ± 13%, respectively during sampling time in 2008-2011. Prevailing wind directions were mostly north north east (NNE) or north north west (NNW), average wind speed was about 0-5 m s^{-1}.

Characteristic of di-carbonyl compounds and related VOCs, trace gases

As shown in Table 1, the four-hour-average concentrations of these two di-carbonyl compounds were listed. Most of their concentrations were low than 1 ppbv and varied in a large range. Commonly, the concentrations in daytime were higher than those in nighttime, which meant their photochemical formation in the daytime.

Glyoxal							methyl glyoxal			
year	type	N	mean	std	min	max	mean	std	min	max
2008	total	42	0.182	0.169	0	0.592	0.338	0.164	0.096	0.778
	day	21	0.280	0.189	-	-	0.428	0.170	-	-
	night	21	0.083	0.049	-	-	0.248	0.198	-	-
2009	total	77	0.056	0.045	0	0.178	0.316	0.177	0.021	0.924
	Day	40	0.054	0.059	-	-	0.336	0.195	-	-
	night	37	0.059	0.046	-	-	0.296	0.115	-	-
2010	total	38	0.225	0.156	0.036	0.649	0.424	0.265	0.090	1.39
	day	20	0.270	0.183	-	-	0.509	0.288	-	-
	night	18	0.167	0.115	-	-	0.312	0.217	-	-
2011	total	54	0.039	0.030	0	0.159	0.273	0.178	0.100	0.627
	day	30	0.051	0.030	-	-	0.241	0.101	-	-
	night	24	0.025	0.022	-	-	0.306	0.146	-	-

unit: ppb, v/v.

N: numbers of the samples for analysis.

Min: minimum data.

Max: maximum data.

Std: standard deviation.

Table 1: Four-hour-average concentrations of G and MG in Wanqingsha, in Autumn during 2008-2011

Some precursors of di-carbonyl compounds were listed in Table 2. Low concentration of isoprene was detected in WQS during the sampling period (about 0.1 ppb), which meant low biogenic source. For aromatic compounds, ethylbenzene, Xylene and benzene were all around 1 ppb, but toluene were mostly higher than 5 ppb, which would provide a important part of both G and MG. High level of acetylene (over 3 ppb), would give additional G, but really high level of acetone (mostly close to 10 ppb), would greatly increase the MG concentration level.

2008					2009				2010				2011			
	average	std	min	max	average	std	min	max	average	std	min	max	average	std	min	max
CO	944. 88	416. 42	310. 73	2421. 57	NA	NA	NA	NA	669. 36	130. 52	394. 08	991. 05	714. 06	187. 71	318. 73	1286. 04
SO2	45. 02	16. 57	14. 71	75. 88	22. 04	9. 11	7. 11	47. 93	7. 23	3. 38	1. 83	14. 86	NA	NA	NA	NA
NOx	58. 06	49. 19	12. 50	234. 71	54. 93	19. 87	23. 76	125. 41	17. 61	6. 29	8. 51	40. 22	41. 45	12. 46	24. 58	84. 67
O3	46. 83	34. 01	3. 40	121. 00	25. 68	22. 94	1. 59	78. 01	29. 33	13. 90	4. 35	58. 61	15. 30	14. 37	0. 79	53. 66
ethyl- benzene	0. 91	0. 86	0. 08	3. 86	1. 58	0. 77	0. 33	3. 29	1. 44	0. 88	0. 30	4. 54	2. 40	2. 04	0. 27	8. 73

2008	aver age	std	min	max	2009 aver age	std	min	max	2010 aver age	std	min	max	2011 aver age	std	min	max
m/p-Xylene	0.91	0.84	0.06	3.48	1.09	0.53	0.18	2.45	0.84	0.66	0.14	3.24	2.75	2.54	0.19	10.54
o-Xylene	0.39	0.35	0.02	1.34	0.46	0.22	0.14	1.03	0.10	0.08	0.01	0.39	1.13	1.03	0.09	3.98
Xylene	1.29	1.18	0.08	4.81	1.54	0.75	0.32	3.48	0.94	0.74	0.15	3.63	3.88	3.57	0.28	14.53
acetylene	3.86	0.79	1.96	5.17	4.61	1.34	2.11	9.79	4.55	1.42	2.19	10.34	3.59	1.30	0.93	7.97
Isoprene	0.15	0.16	0.02	0.80	0.07	0.04	0.02	0.21	0.13	0.15	0.02	0.79	0.08	0.06	0.01	0.35
Benzene	1.34	0.89	0.22	3.72	1.91	0.84	0.56	4.69	1.96	0.80	0.99	5.31	1.42	0.64	0.37	3.16
Toluene	4.23	3.51	0.27	13.00	5.76	2.80	0.75	11.93	7.90	7.01	0.67	37.29	7.85	6.03	0.83	23.02
formal-dehyde	8.51	4.36	1.84	23.15	7.67	3.65	0.75	17.50	6.42	3.04	2.16	16.90	5.90	3.07	0.76	12.49
acetone	8.83	5.44	1.75	23.05	7.36	2.65	3.28	13.67	6.01	2.52	2.20	14.38	5.35	2.47	0.59	10.24
propanal	0.56	0.29	0.086	1.56	0.47	0.18	0.08	0.88	0.89	0.62	0.18	2.56	0.36	0.16	0.06	0.83

TNA: not analyzed.

Min: minimum data.

Max: maximum data.

Std: standard deviation.

Table 2: Four-hour average concentrations of related VOCs and trace gases in WQS, 2008-2011 (unit: ppb, v/v)

For most sampling period, concentrations of MG was larger than G (G/MG < 1, Table 3), the reasons might be as follows. Firstly, for the important precursor isoprene, higher yield of MG was shown (about 25%) comparing to G (6.2%), (Fu et al, 2008) [9]; Secondly, high level of acetone concentration (about 10 ppbv) would produce more MG. And maybe there was another more reason, the higher yield of MG by the photooxidation of some aromatic compounds. As described by Nishino et al.(2010) [20], for the glyoxal and methylglyoxal yields by the aromatic compounds in atmospheric photochemistry, though equal yields were got for benzene and toluene (about 20%), yields of about 2-3 times higher for MG was got for most kinds of Xylene and trimethylbenzene, comparing to that of G.

For the concentration data of some trace gas listed in Table 2, CO was in the range of 300-900 ppb, SO_2 was 7-45ppb, NOx was 17-58ppb, O_3 was 15-45 ppb. For 2010, lowest concentration of SO_2 and NOx were detected, which might be the control measurement proceeded in the sampling time for Asia games (described below).

| type | | 2008 | | | 2009 | | | 2010 | | | 2011 | |
	G/F	A/MG	G/MG	G/F	A/MG	G/MG	G/F	A/MG	G/MG	G/F	A/MG	G/MG
Total concentration	0.022 ± 0.015	32.602 ± 28.226	0.502 ± 0.349	0.012 ± 0.010	22.138 ± 16.370	0.186 ± 0.138	0.036 ± 0.023	18.065 ± 10.823	0.652 ± 0.414	0.010 ± 0.014	20.961 ± 8.983	0.190 ± 0.171
Day concentration	0.028 ± 0.017	24.919 ± 16.193	0.659 ± 0.413	0.010 ± 0.010	23.614 ± 36.414	0.185 ± 0.157	0.034 ± 0.015	14.677 ± 5.392	0.568 ± 0.309	0.008 ± 0.005	25.354 ± 8.130	0.256 ± 0.166
Night concentration	0.016 ± 0.010	40.28 ± 35.314	0.345 ± 0.165	0.013 ± 0.010	20.623 ± 7.871	0.188 ± 0.116	0.036 ± 0.03	20.682 ± 14.485	0.706 ± 0.518	0.012 ± 0.020	16.230 ± 7.403	0.119 ± 0.148

Data were shown in arithmetic mean value ± standard deviation. G: glyoxal; MG: methyl glyoxal; F: formaldehyde; A: acetone.

Table 3: Concentration ratios of G/F (RGF), A/MG and G/MG in Wanqingsha, in Autumn during 2008-2011

Source distribution and variation of G and MG in WQS during 2008-2011

General conception about source contribution of G and MG in WQS: Though it had been reported that vehicle emission and biomass burning could emit G and MG, even in city with large amount of vehicles, direct emission of di-carbonyl compounds from vehicle was a still a very small part source. As described by Volkamer et al. (2005) [8], average molar CHOCHO emissions were expected at least two orders of magnitude lower than those of HCHO, so did MG. For G and MG, they mainly came from the photochemistry production of their precursors, such as aromatic compounds, isoprene and acetone, etc. (Fu et al; 2008) [9].

The main precursors of G and MG in WQS were listed in Table 2. These compounds could divide into two parts: biogenic compound (isoprene in this study), for its low concentration, might offer a small part of the total contribution; anthropogenic compounds, including acetylene, acetone, and aromatic compounds, might produce larger part of di-carbonyl. Previous studies have shown that most of them come from transport source, mainly from the upwind location of Guangzhou and Dongguan, during the sampling time in autumn (Zhang et al., 2012, 2013) [16,17]. And as we described above, sampling site located in a small town WQS, a small part of local emission would contribute to the anthropogenic source of these precursor compounds (Zhang et al., 2012, 2013) [16,17].

Totally, the precursors of di-carbonyl were mainly anthropogenic sources (transport and local), with a small part of local biogenic source.

Specialty in 2008 and 2010: For the sampling periods in 2008, the financial crisis (FC) affected greatly for the factories in PRD. Zhang et al. (2012) [16] reported significant drop in aromatic hydrocarbons (AHs) during November-December 2008 comparing to 2007. They pointed out that this drop was due to the reduction of emission from the Industries using AH-containing solvents under the influence of a decline in industrial activity. These compounds were mainly coming from vehicle exhausts and industrial emissions in PRD. And they all showed a remarkable drop in source proportion using PMF analysis. And for acetylene and acetone, industrial emission was an important source, which could expect that the drop of industry emission occurred in 2008.

At the same time, total vehicle number rose from ～4.2 million in 2007 to ～4.7 million in 2008 in the whole PRD region; and in Guangzhou and Dongguan, total vehicle numbers rose from 1,041,917 and 608,933 in 2007 to 1,171,731 and 701,600, respectively

(Zhang et al., 2012) [16]. In particular, the most striking increase of vehicle numbers was that of gasoline-powered sedan cars. Numbers of sedan cars in Guangzhou and Dongguan were 408,139 and 262,218 in 2007, and were 575,676 and 357,676 in 2008, with annual increase of 41% and 36%, respectively. This rapid increase of vehicle numbers in the PRD region would certainly lead to larger amount of VOCs emitted from vehicles to the ambient.

So in the sampling period, for the obvious drop of industrial emission and increasing of vehicle number, the source of precursors of di-carbonyl compounds was mainly vehicle emission.

In 2010, half of the motor vehicles were off the road due to the traffic restriction for the Asian Games in Guangzhou during the 2010 sampling period.

From 1 to 27 November and 5 to 21 December 2010, mandatory restrictions were implemented for personal vehicles, permitting them on roads only on alternate days depending on license plate numbers (odd-numbered vehicles on odd-numbered days and even-numbered vehicles on even-numbered days). During the Games, all construction activities were placed on. Point sources in PRD (e.g., factories) were supervised strictly to reduce emissions.

As a combination of both odd/even traffic restrictions and yellow-label vehicle restrictions, some studies estimated the total reductions of the mobile source were 35.6% of HC, 44.5% of CO, 24.8% of PM and 30.3% of NOx (Liu et al., 2013a; Yao, Zhang et al., 2013) [18,21]. As described in Table 2, all the compounds detected in WQS in 2010, showed a dramatic drop. Lowest compounds concentrations in 2010 were detected comparing to those in other years.

Source distribution confirmed by the analysis of concentration ratios: As previous studies pointed (Vrekoussis et al., 2010; Wittrock et al. 2006) [22,23], the concentration ratio of CHOCHO to HCHO (G/F), RGF, could classify the sources according to biogenic and/or anthropogenic emissions of the precursors. RGF of the ratio of 0.040-0.060 pointed to the existence of large proportion of biogenic emissions. RGFs below 0.040 were indicative of obvious anthropogenic emissions, which was often associated with high levels of NO2. The decrease of RGF could be explained by the existence of anthropogenic primary sources of HCHO. In addition, there were secondary sources for both CHOCHO and HCHO. The decreasing tendency of RGF with increasing NO2 was observed in many large cities, indicating that it was a common feature.

Here the RGF were listed in Table 3. Though the mean values of all these four years were less than 0.040, which showed large proportion of anthropogenic emissions, there were obvious increases in 2008 and 2010. As described above, anthropogenic source decreased during these two years, which caused the increase of RGF data. Especially in 2010, the ratios raised very close to 0.040 (average data of 0.036), showed the non-ignorable biogenic emission. As we described above, the traffic and factories source greatly decreased because of the Asia Games, so the proportion of the local biogenic source occupied a relative high proportion.

For concentration ratio of acetone/methyl-glyoxal, A/MG, acetone was a potential precursor of methyl-glyoxal (Fu et al., 2008) [19]. Therefore, A/M could be used to determine the impact of photochemistry in the atmosphere. During the photochemical reactions, acetone can be oxidized to form methyl-glyoxal in the atmosphere. The photochemical reaction was more favorable in summer, resulting in decreased concentrations of acetone but increased concentrations of methyl-glyoxal. As described by Liu et al. (2006) [24], the average A/M ratio (1.05) in summer was the lowest among the four seasons, comparing to the values in spring (1.88), winter (2.51) and fall (4.02). The same trend was observed in Montelibretti in Rome, Italy (Possanzini et al., 2007) [25], where the lowest A/M (2.52) was found in summer at the average temperature of 32.4 $^{\circ}$C whereas the A/M in autumn (22.6 $^{\circ}$C on average) and in winter (8.5 $^{\circ}$C on average) were both >4.0. In this research, no seasonal data were got for the comparison, only the data in deep autumn were shown in Table 3. The average A/M ratio for all these four years was about 20-30, similar to those detected in winter (21.3±5.1) in Xi'an (Dai et al., 2012) [26], but they were much higher than those of studies above. For different atmospheric pollutant condition and meterological condition, it was hard to draw a further conclusion on such limited data. More researches should be proceeded.

Correlation of di-carbonyl and related compounds: The correlations among di-carbonyls and other related compounds were evaluated by regression analysis, and their correlation coefficients (r) were shown in Tables 4, 5 and 6. Table 4 showed the Pearson correlation coefficient between concentrations of di-carbonyl compounds and their precursors, including aromatic compounds, acetylene and acetone. It indicated that there were overall good correlations among the years of 2009 and 2011, and bad correlations in 2008 and 2010. As we described above, in 2008 and 2010, the transport source of all these compounds decreased, which caused that all the sources (local and transport, anthropogenic and biogenic) were in similar level, and none of source could occupy the main part. Then, the correlations reflected the complex sources and expressed a bad correlation. For 2009 and 2011, transport source occupied large part of the sources, and the correlation coefficients were good, which meant the relatively simple source.

	2008 (N=42)							2009 (N =35)							2010(N=38)							2011 (N= 54)						
	G	MG	B	T	E	A	Ac	G	MG	B	T	E	A	Ac	G	MG	B	T	E	A	Ac	G	MG	B	T	E	A	Ac
G	1	0.756	-	-	-	-	-	1	-	0.449	0.357	0.578	0.403	0.578	1	0.442	-	-	-	0.325	-	1	-0.357	-	-	-0.343	-	-0.341
M		1	-	-	-	-	-		1	-	-	0.317	0.416	-		1	-	-	-	0.498	-		1	0.374	0.733	0.441	0.681	0.441
B			1	0.894	-	0.338	-			1	0.776	0.943	0.552	0.943			1	-	0.894	-	0.877			1	0.667	0.673	0.526	0.673
T				1	-	0.436	-				1	0.739	0.717	0.739				1	0.328	-	-				1	0.624	0.834	0.624
E					1	-	0.327					1	0.562	0.686					1	-	0.357					1	0.622	0.591
A						1	0.328						1	0.562						1	0.338						1	0.622
Ac							1							1							1							1

-: data too small (<0.3) to be listed here.

Data in common style: At the 0.05 level significantly correlated (bilateral). Data in Bold and Italic: At the 0.01 level significantly correlated (bilateral).

G: glyoxal; MG: methyl glyoxal; B: benzene; T: toluene; E: Ethyl benzene; A: acetone; Ac: acetylene. N: Numbers of the data used in correlation analysis.

Coefficients between di-carbonyl compounds and isoprene were all small and not shown here.

Table 4: Pearson correlation coefficient between concentrations of di-carbonyl compounds and their precursors

2008 (N=42)					2009 (N =35)					2010 (N= 38)					2011 (N= 54)				
	G	MG	NOx	ozone		G	MG	NOx	ozone		G	MG	NOx	ozone		G	MG	NOx	ozone
G	1	**0.756**	-0.231	**0.473**		1	0.229	**0.534**	-0.297		1	**0.442**	-0.409	**0.482**		1	**-0.357**	-0.089	**0.519**
MG		1	-0.170	**0.470**			1	0.369	0.125			1	-0.051	0.136			1	**0.397**	-0.087
NOx			1	**-0.621**				1	**-0.496**				1	**-0.611**				1	0.021
ozone				1					1					1					1

Data in common style: At the 0.05 level significantly correlated (bilateral) Data in

Bold: At the 0.01 level significantly correlated (bilateral).

G:glyoxal; MG: methyl glyoxal.

N: Numbers of the data used in correlation analysis.

Table 5: Pearson correlation coefficient between dicarbonyl, NOx and ozone

2008 (N = 42)						2009 (N = 35)					2010 (N = 38)					2011 (N = 54)				
	G	MG	F	A	P	G	MG	F	A	P	G	MG	F	A	P	G	MG	F	A	P
G	1	**0.756**	0.358	0.309	0.309	1	0.229	-0.085	0.406	0.244	1	**0.442**	**0.700**	**0.481**	0.577	1	**-0.357**	0.263	-0.068	**0.353**
MG		1	**0.458**	**0.488**	**0.496**		1	**0.523**	**0.617**	**0.629**		1	0.570	0.435	0.642		1	0.245	0.120	**0.378**
F			1	**0.903**	**0.868**			1	**0.543**	**0.709**			1	0.579	**0.700**			1	-0.417	**0.821**
A				1	**0.958**				1	**0.875**				1	**0.810**				1	-0.307
P					1					1					1					1

Data in common style: At the 0.05 level significantly correlated (bilateral) Data in Bold: At the

0.01 level significantly correlated (bilateral).

G:glyoxal; MG: methyl glyoxal; F: formaldehyde; A: acetaldehyde; P: propanal. N: Numbers of

the data used in correlation analysis.

Table 6: Pearson correlation coefficient between di-carbonyl and mono- carbonyl compounds

Otherwise, for MG versus acetone, good correlations were shown except in 2008, at that time, the industrial emission decreased dramatically. Acetone, as an important source of MG, showed the mixed source mainly from vehicle and industrial emission in WQS (Liu et al., 2013b) [19]. Good correlations in the common year meant one main source of acetone, industrial or vehicle. And if the vehicle source was the main source of acetone, there should be still good correlation data in 2008 when industry emission decreased. According to all these facts, we could see that industry emission was the main source of acetone [27].

Table 5 listed the coefficient between di-carbonyl, NOx and Ozone. G showed a good correlation with ozone in most time (except 2009), and MG only showed a good correlation in 2008. In some ways, G was a better indicator for atmospheric oxidation than MG. No correlations were detected between NOx and di-carbonyl compounds. None did for NOx and R_{GF} (data not show here).

Table 6 listed the coefficient between di-carbonyl and some mono-carbonyl compounds, good correlation were shown in most time (except 2011), which showed the similar source of sink of these carbonyl compounds (mainly photochemical formed and deleted). Something special for the photochemical characteristics might occur in 2011, more should be carried on to reveal it.

Conclusions

Atmospheric glyoxal and methylglyoxal were studied in WQS, in 2008-2011, together with their precursors and some related compounds. The di-carbonyl compounds concentrations varied from tens of ppt to ppb level, and they mainly came from the photooxidation of the precursors such as aromatic compounds, acetylene etc.. High level of acetone concentration might contribute the higher MG concentration than G. R_{GF} (<0.04) meant the main source of anthropogenic emission, and the increasing of R_{GF} during 2008 and 2010 showed the decreasing of anthropogenic emission, which accorded with the financial crisis in 2008 and the control measurement for the Asia Game in 2010. The correlation coefficients analysis also showed the similar result.

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