



Spatial distributions of airborne di-carbonyls in urban and rural areas in China



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ABSTRACT

Gaseous glyoxal and methylglyoxal concentrations were characterized in nine cities of China during 2010–2011. The average summer (winter) glyoxal and methylglyoxal concentrations were 36.4–178.4 (12.3–241.4) and 67.8–359.4 (28.4–530.0) ng/m³, respectively. In summer, the highest average glyoxal concentration was in Guangzhou (GZ), while the lowest was in Shanghai (SH). In winter, Xiamen (XM) showed the highest average methylglyoxal concentration and Yantai (YT) reported the lowest. Both di-carbonyls showed distinct seasonal variations. The maximum average methylglyoxal concentration was approximately twice as much as glyoxal, which is consistent with the results of other studies. Glyoxal-to-methylglyoxal ratios showed that there was a consistent direct source of emissions in remote areas such as Qinghai Lake and Lhasa in both seasons ($r \geq 0.9$). Pearson's correlation analysis suggested possible similar sources formation ($R \geq 0.7$) for the two di-carbonyls in winter. Multiple linear regression analyses demonstrated that every 1 °C temperature increase could lead to a > 2% increase in the concentration of the di-carbonyls in both seasons. There was a greater percentage gain for glyoxal in winter than in summer for the same temperature increase. The northeast monsoon occurs in winter, and for every 1 ms⁻¹ increase in wind speed, >20% of the di-carbonyls can be transferred out of China. This study is useful to understand about the secondary organic aerosol formation in the areas, the statistical analysis can provide information about the relationships between these carbonyls in atmosphere.

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1. Introduction

Glyoxal (CHOCHO) and methylglyoxal (CH₃COCHO) are bi-functional carbonyls that commonly exist in ambient air in the troposphere. Previous studies have shown that these di-carbonyls could be a significant source of secondary organic aerosol (SOA) (Fu et al., 2008; Schwier et al., 2010). These compounds are tracers for the oxidation of a number of hydrocarbons (e.g. isoprene) and can be produced by oxidation of volatile organic compounds (VOCs) via various anthropogenic and biogenic activities. Common sources of glyoxal and methylglyoxal are the oxidation of aromatic hydrocarbons (Kleindienst et al., 2004; Smith et al., 1999; Smith et al., 1998) and motor vehicle exhausts (Ortiz et al., 2013). These chemical compounds are also important ring-cleavage products in OH-radical initiated reactions (Calvert et al., 2002; Smith

et al., 1999; Volkamer et al., 2001). The sources of glyoxal and methylglyoxal are ~45 Tg and 140 Tg per annum, respectively, at a global level (Fu et al., 2008).

The atmospheric lifetime of glyoxal and methylglyoxal are estimated to be 2.9 and 1.6 h, respectively, according to the GEOS-Chem global 3-D chemical transport model (Fu et al., 2008). One of the characteristics common to glyoxal and methylglyoxal is large hydration constants. The large constants allow moderate-to-high water solubility, and they may be trapped in aqueous aerosols and cloud droplets, eventually forming low-volatility products partitioned in the condensed phase (Tan et al., 2012; Sedehi et al., 2013; Lim et al., 2013). Glyoxal has a high Henry's law constant ($>3.6 \times 10^5$ M/atm), which favors its existence in aerosols, leading to oligomer formation (Betters and Hoffmann, 1988; Carlton et al., 2007; Liggio et al., 2005; Loeffler et al., 2006). Methylglyoxal is an important precursor of peroxyacetyl nitrate (PAN) (Munger et al., 1995). Di-carbonyls are precursors of oxalic acid, which is considered the most abundant organic species in atmospheric particles. The presence of oxalic acid in aerosols can convert aerosols into cloud condensation nuclei (CCN), thereby causing climate change (Kawamura et al., 2013).

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Mutagenic and genotoxic properties of glyoxal and methylglyoxal have been reported in the past (Murata-Kamiya and Kamiya, 2001; Ueno et al., 1991a, 1991b; Ueno et al., 1991c). The underlying mechanism involves the promotion of cellular oxidation by attacking the anti-oxidative mechanisms of cells and the major pathway is presumably by the formation of DNA adducts (Al-Enezi et al., 2006; Mehta et al., 2009; Shangari et al., 2003; Shangari et al., 2007).

China is the world's most populous country with a population of approximately 1.35 billion (National Bureau of Statistics of China, 2012). The country is undergoing rapid modernization with robust economic growth (>7.0% annual GDP growth for more than two decades) (National Bureau of Statistics of China, 2012). The downside is that the country is suffering from severe environmental degradation (e.g. frequent haze episodes, desertification, etc.) (Ma et al., 2012; Sun and Fang, 2001; Zhu and Wang, 1993). A thorough understanding of health, climate, and air quality is high on environmental policymakers' agendas, not only nationally, but also worldwide.

There is currently a lack of knowledge about di-carbonyls in the Chinese urban atmosphere, and information about their concentration distribution in ambient air across the country remains scarce. It is therefore important to identify glyoxal and methylglyoxal in the gaseous phase to understand how these compounds are cycled in the atmosphere. The present study involved the sampling of a wide area of China (nine sampling locations) and the dataset created can further be used to compare with experimentally constrained model prediction outputs. This study provides information to verify the presence of these short lived gases and further evidence of CHOCHO and CH₃COCHO sources in China. The data are useful to understand further about the SOA formation in the areas. Relationships between CHOCHO/CH₃COCHO in the gaseous phase and several environmental parameters (temperature, relative humidity and wind speed) are investigated by statistical approach, which can supply further information about the production of these compounds and show the connections between these carbonyls in the atmosphere.

The aims of this study are to: 1) investigate seasonal and spatial characteristics of di-carbonyls in ambient air at nine sampling sites in China; 2) identify correlations between unique seasonal/spatial characteristics of di-carbonyls and meteorological factors (temperature, relative humidity and wind speed); 3) evaluate the effects of meteorological factors on glyoxal/methylglyoxal concentration variations during summer/winter using multiple linear regression analyses.

2. Materials and methods

2.1. Sampling locations

A nationwide survey of ambient di-carbonyls was conducted simultaneously in nine cities (14–18 sampling days in each city) during summer (between 7th of August 2010 and 9th of September 2010) and winter (between 23rd of December 2010 and 26th of January 2011). Two di-carbonyls were collected from ambient air using the classic 2,4-dinitrophenylhydrazine (DNPH) derivatization method followed by applying high-performance liquid chromatography (HPLC) for analysis (USEPA, 1999). Nine sampling sites in China were chosen within the area 23–39°N, 91–121°E. The idea was to include both economically well-developed and economically underdeveloped cities. The seven urban sampling sites are Beijing (BJ), Chengdu (CD), Guangzhou (GZ), Shanghai (SH), Wuhan (WH), Xiamen (XM) and Yantai (YT), and the two rural sites are at Qinghai Lake, Qinghai (QH) and Lhasa, Tibet (TB) (Fig. 1). Further general information about the sampling locations is given in Table S1 (Supplementary material).

2.2. Sample collection

Samples were collected daily and integrated over 24-h intervals (from 10:00 a.m. onwards). The total sampling days at different locations were Beijing (Summer: 14; Winter: 14), Chengdu (Summer: 14; Winter: 13), Guangzhou (Summer: 16; Winter: 15), Shanghai (Summer: 14; Winter: 10), Wuhan (Summer: 13; Winter: 15), Xiamen (Summer: 11; Winter: 12) and Yantai (Summer: 13; Winter: 15), Qinghai Lake, Qinghai (Summer: 15; Winter: 14) and Lhasa, Tibet (Summer: 17; Winter: 18). Air samples were collected in silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55–105 μm particle size, 125Å pore size; Waters Corporation, Milford, MA) at a flow rate of 0.7 L/min. A total of 127 and 130 samples were collected in summer and winter, respectively. Collection efficiencies were measured under different field conditions by sampling carbonyls in two identical cartridges connected in series. The collection efficiencies were harmonized to 100% using Eq. (1):

$$\text{Collection efficiency} = (1 - A_b/A_f) \quad (1)$$

where A_f and A_b represent the amount of carbonyls collected on the

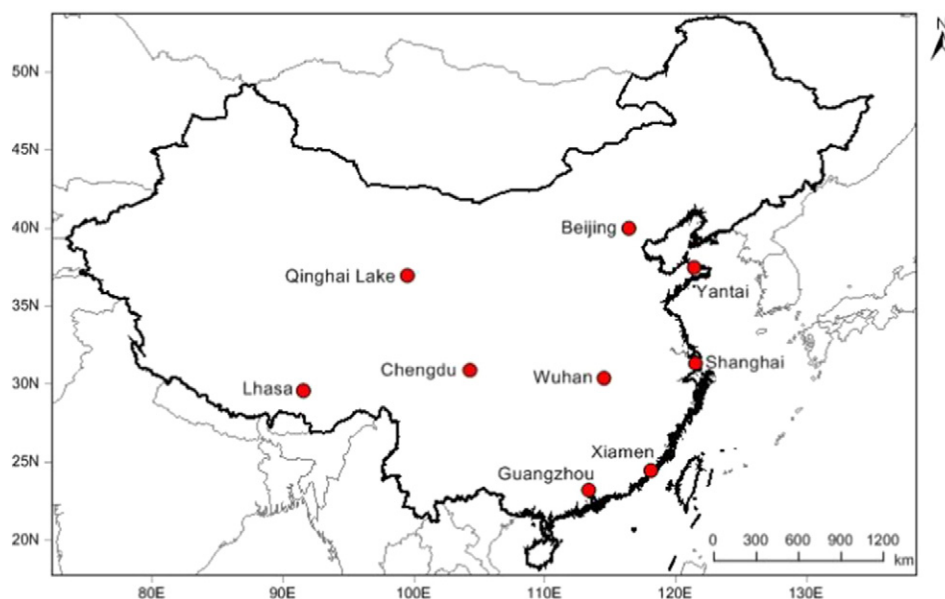


Fig. 1. Map showing sampling sites in the campaign.

front and back sampling tubes, respectively. No detectable breakthrough was observed under these sampling times and flow rates. The flow rate was checked in the field prior to the start and end of each sampling period using a calibrated flow meter (Gilibrator Calibrator; Gilian Instruments, W. Caldwell, NJ). A Teflon filter assembly (Whatman, Clifton, NJ) coupled with an ozone scrubber (Sep-Pak; Waters Corporation) was installed in front of the DNPH-silica cartridge to remove any particulate matter and to prevent possible ozone disturbance (Dai et al., 2012a, 2012b; Spaulding et al., 1999). Collocated samples were collected to ensure collection reproducibility (>95%) in the field for all samplers. One cartridge was reserved for a field blank at each sampling trip and was handled in the same manner as other sample cartridges. The amount of carbonyls detected in the cartridges was corrected against the field blank to work out the final carbonyl concentration in air. The DNPH-coated cartridges were stored in the refrigerator at <4 °C after sampling and prior to analysis. Acetone and different meteorological factors such as temperature, relative humidity and wind speed were collected and analyzed throughout the sampling period.

2.3. Analytical method

Acetonitrile (ACN), tetrahydrofuran (THF) (HPLC/GCMS grade, J&K Scientific Ltd., Ontario, Canada), DNPH and pyridine (Sigma Corporation, USA) and Milli-Q ultrapure water were used (Millipore, Milford, MA, USA) in the analysis. DNPH derivatizing agent was prepared by adding DNPH (250 mg) and 10 µL concentrated hydrochloric acid (HCl) to a 25-mL volumetric flask, which was filled up with ACN and pyridine solution (4:1). An aliquot of the sample (20 × Φ14-mm punches) was cut and transferred to a vial and subsequently added to the DNPH derivatizing agent (4 mL). The derivatized samples were first reacted at 70 °C (30 min) and then ultrasonicated (15 min) (Wang et al., 2002). This step was repeated and the extractant was filtered through a 0.22-µm membrane filter to remove unwanted particles. The filtrate sample was washed with pyridine before transfer to a 5-mL volumetric flask. The calibration standard of di-carbonyls was prepared by adding glyoxal and methylglyoxal (Sigma, St. Louis, MO) to acetonitrile with DNPH (1 mL in concentration of 100 µg/mL) in acidic solution. The solution was allowed to stand for complete derivatization (>6 h, 25 °C). Each calibration solution was filled up to 2.0 mL in a concentration ratio of 8:2 (v/v) acetonitrile/pyridine (HPLC/GCMS grade; Sigma). The di-carbonyl DNP-hydrazone used for calibration purposes was in the concentration range of 0.01–2.00 µg/mL. Calibration was performed ($R^2 > 0.9$). The extractants were analyzed by high-performance liquid chromatography (HPLC) (Agilent, Santa Clara, CA, USA) coupled with a photodiode array detector (DAD). The instrument specification is listed in Table S2 (Supplementary material). 20-µL samples were used for the analysis. The limit of detection (LOD) was calculated by analyzing a minimum of seven replicates of standard solution containing analytes at a concentration of 0.015 µg/mL. The LOD can be estimated with Eq. (2):

$$\text{LOD} = t(n-1, 1-\alpha = 99\%) \times S \quad (2)$$

$t(n-1, 1-\alpha = 99\%)$ denotes the student's *t*-distribution value at $(n-1)$ degrees of freedom and S is the standard deviation of the replicates. Quality assurance (QA) was implemented to ensure data quality. QA is a set of guidelines for sample handling, routine calibration, performance assurance and data processing. The tolerance level was also established in the guidelines. The measurement precision is in the range of 1.7–4.6% for the di-carbonyls. Glyoxal and methylglyoxal were quantified and the recovery rates were $96 \pm 5\%$ and $93 \pm 6\%$, respectively. The acetone analysis can be referred to Dai et al. (2012a, 2012b) for further information.

2.4. Statistical data analysis

Pearson's correlation coefficient analysis was performed to identify the correlation between glyoxal/methylglyoxal and meteorological factors (temperature, relative humidity and wind speed) during summer 2010/winter 2011. Multiple linear regression analysis was further applied to identify relationships between variables. A general regression equation is listed below.

$$[a] = b_0 + b_1[T] + b_2[R] + b_3[W] \quad (3)$$

where a denotes the dependent variable of glyoxal or methylglyoxal, and the three independent variables are temperature (T), relative humidity (R) and wind speed (W); b_0 , b_1 , b_2 , and b_3 are the coefficients of the linear regression model. b_0 is a constant, while b_1 , b_2 , and b_3 are the coefficients of the independent effects of T , R , and W (subject to per unit change) on glyoxal/methylglyoxal concentration. For further information about the regression model, the reader is referred to Giorgini et al. (2015) and Ocak and Turalioglu (2008). All the data were analyzed using IBM SPSS statistics 21.0 (IBM®, New York, NY) or using GraphPad Prism software (Version 5 for Windows). The significance level was set at $p < 0.05$. The purpose of the analysis was to initially measure the degree of the relationship between linear related variables, followed by further regression analysis to study the cause of effect of a relation between two variables (or more).

3. Results and discussion

3.1. Seasonal variations

Table 1 shows a descriptive analysis of gaseous glyoxal and methylglyoxal concentrations during summer and winter in the cities sampled. Overall maximum average concentration in summer and winter shows that methylglyoxal concentration was higher than glyoxal concentration (an approximately two-fold difference). This finding is consistent with other reported studies (e.g. Kawamura et al., 2013) and can be explained by methylglyoxal having a longer lifetime than glyoxal (2.9 vs. 1.6 h), which leads to methylglyoxal enrichment on aerosol surfaces (Fu et al., 2008). The average concentrations of glyoxal and methylglyoxal show statistically significant differences between seasons (paired *t*-test; glyoxal ($p = 0.001$) and methylglyoxal ($p = 0.005$)).

The seasonal average glyoxal concentration comparison (summer (S) vs. winter (W)) shows that $S > W$ in cities BJ, GZ, YT, and QH whereas $W > S$ in cities SH, WH, CD, TB, and XM. The same also applied for the seasonal average methylglyoxal concentration. Cities where $S > W$ could favor the atmospheric photo-oxidation of volatile organic compounds (VOCs) and hence secondary source formation of the di-carbonyls (Fu et al., 2008).

On the contrary, for those cities where $W > S$, primary di-carbonyl emissions could be the dominated source. Stable atmospheric stratification coupled with heating fuel usage in winter could further enhance di-carbonyl accumulation (Dai et al., 2012a, 2012b). The aforementioned factors could possibly lead to the above seasonal variations of the glyoxal concentration.

3.2. Concentrations of di-carbonyls in sampling locations

The glyoxal concentrations in the two seasons are presented in Fig. 2. In summer, GZ has the highest average glyoxal concentration and SH records the lowest. The average glyoxal concentration is in the range of 36.4–178.4 ng/m³ while the glyoxal concentration in SH is 4.9 times lower than in GZ. No consistent spatial trends (e.g. inland vs. coastal) were observed in summer, as the sampling cities are remote from each other. The average summer glyoxal concentrations in the nine cities were all higher than in the suburban atmosphere at Saitama in Japan

Table 1
Pearson correlation coefficients (R) of glyoxal/methylglyoxal and meteorological factors during winter and summer (R ≥ 0.70 and 0.05 significance level).

		Glyoxal	Methylglyoxal	Temperature	Relative humidity	Wind speed
Summer	Glyoxal	1	0.59** ^a	0.25* ^b	−0.12	0.14
	Methylglyoxal		1	0.45**	−0.17	0.14
	Temperature			1	0.13	−0.52
	Relative humidity				1	0.10
	Wind Speed					1
Winter	Glyoxal	1	0.80** ^a	0.39**	0.16	−0.40**
	Methylglyoxal		1	0.43**	0.25**	−0.36**
	Temperature			1	0.37**	0.01
	Relative humidity				1	−0.002
	Wind Speed					1

^a**Correlation is significant at the 0.01 level (2-tailed).

^b*Correlation is significant at the 0.05 level (2-tailed).

(Ortiz et al., 2006). The glyoxal concentration in GZ is comparable to Xi'an, China in summer for a one year sampling campaign (sampled in every 12 days), which is seriously polluted (Dai et al., 2012a, 2012b). The magnitude of the average glyoxal concentration in summer in all cities is in the following order: GZ > XM > CD > BJ > WH > YT > QH > TB > SH.

During winter, YT reports the lowest average glyoxal concentration and XM reports the highest. The average glyoxal concentration is in the range 12.3–241.4 ng/m³ while the glyoxal concentration in XM is 19.6 times higher than that in YT. The maximum average winter glyoxal concentration is higher than in summer. The magnitude of the average glyoxal concentration in winter is in the following order: XM > SH > CD > WH > TB > BJ > GZ > QH > YT. GZ and SH showed the highest glyoxal concentrations in summer and winter, respectively. Both of these cities also showed a large fluctuation in glyoxal concentration between seasons.

Since GZ (~12 million population) is one of the ten most populous cities in China and is the center of heavy industry (e.g. car manufacturing, petrochemical and electronic industries) in the Pearl River Delta, different industrial processes (anthropogenic activities) favor di-carbonyl emissions (Guangzhou Statistical Bureau, 2015). The decrease in glyoxal concentration from summer to winter could be possibly be

due to lower temperatures, solar radiation and relative humidity, which suppresses photochemical reactions (e.g. the oxidation of volatile organic compounds from anthropogenic sources (Chan et al., 2006)). Conversely, the increase in glyoxal concentration from summer to winter at SH could be due to the prevalent southeasterly wind direction transferring contaminated air masses (e.g. containing di-carbonyls) from western inland China to the coastal region. SH (~23 million population) is located at the heart of the Yangtze River Delta and is the most populous city in China. High consumption of heating fuels in winter, coupled with larger scale industrial emissions, could possibly be additional sources of di-carbonyls, potentially driving the rapid increase in concentrations in winter (Shanghai Statistical Bureau, 2015; Dai et al., 2012a, 2012b).

It is noted that the top four glyoxal concentrations in both seasons all occur in urban areas (megacities), suggesting that the observed high concentrations could be due to high acetylene emissions. Acetylene is the second largest source of glyoxal and the most important anthropogenic precursor (Fu et al., 2008). Its rather long lifetime (~18 days) in the troposphere makes it an ideal source for glyoxal formation (Fu et al., 2008). Acetylene can be commonly identified in emissions from the petrochemical industry (Na et al., 2001) and other industrial

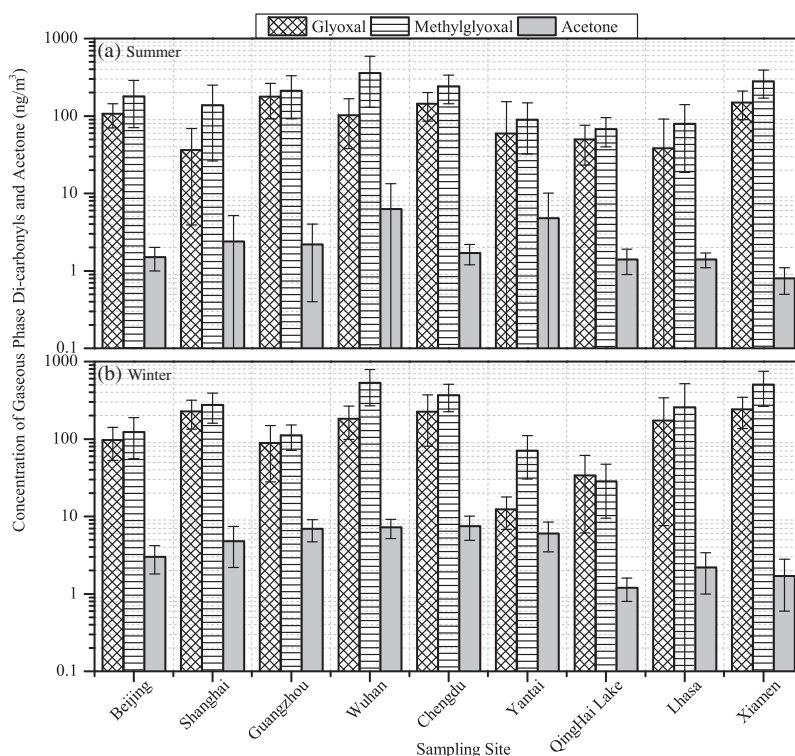


Fig. 2. Concentration of gaseous phase di-carbonyls and acetone in Chinese cities during winter and summer.

activities (e.g. acetylene gas plants, fuel combustion emissions, gasoline evaporation and solvent usage) (Borbon et al., 2002; Kang et al., 2001; Watson et al., 2001). It is expected that urban cities contain more of these manufactories and activities than rural areas (e.g. QH), which explains why the highest glyoxal concentrations occur in cities.

The concentration of methylglyoxal in the two seasons is shown in Table 1. In summer, WH shows the highest average methylglyoxal concentration and QH reports the lowest. The average methylglyoxal concentration is in the range 67.8–359.4 ng/m³ and methylglyoxal concentration in WH is ~5.3 times higher than in QH. The magnitude of the average methylglyoxal concentration in summer is in the following order: WH > XM > CD > GZ > BJ > SH > YT > TB > QH.

During winter, the average methylglyoxal concentration is in the range 28.4–530.0 ng/m³. The methylglyoxal concentration in QH is ~18.7 times lower than that in WH. The magnitude of the average methylglyoxal concentration in winter is in the order: WH > XM > CD > SH > TB > BJ > GZ > YT > QH. The methylglyoxal concentrations at QH remained the lowest across seasons. QH is remote and isolated from urban areas as well as human activities (~150 km away from Xining city, ~3200 m altitude). The observed concentrations could be naturally occurring site-specific background concentrations generated largely by strong solar radiation (Meng et al., 2013). This hypothesis is strengthened because the average methylglyoxal concentration in summer (67.8 ng/m³) was higher than in winter (28.4 ng/m³). WH shows the highest methylglyoxal concentrations during both seasons. Acetone is the second largest source of methylglyoxal formation (i.e. •OH radical oxidation) due to its long atmospheric lifetime (~22 days) in the troposphere (Fu et al., 2008). The average acetone concentration at WH in summer and winter was ranked first and second highest among the nine cities, respectively (Table 1). The concentrations are comparable with a previous study at Nanning, China (Guo et al., 2016). The high methylglyoxal concentration observed could be explained by the high acetone concentration, which enhances methylglyoxal formation at WH.

A previous study showed that isoprene is the most important precursor for both di-carbonyls via oxidation of NO₃ and OH. Under the OH oxidation, intermediates such as glycolaldehyde (HOCH₂CHO) and hydroxyacetone (HOCH₂COCH₃) can be produced before the di-carbonyls formation (Fu et al., 2008). Further studies are required to quantify the di-carbonyls concentrations relationships with the mechanisms involved. The importance of the potential health implications of di-carbonyls in ambient air cannot be underestimated. Previous studies have shown that di-carbonyls are able to induce inflammatory cytokine expression by pulmonary epithelial cells (A549) in a simulated indoor air environment (Anderson et al., 2010). Although its concentration in indoor air is usually not comparable with outdoor air, this study showed that di-carbonyls are capable of stimulating the release of pro-inflammatory mediators in lung epithelial cells. Such a result warrants further investigation into the effects of glyoxal and methylglyoxal “in vitro” in outdoor air.

3.3. Statistical analysis of relationships between di-carbonyls and meteorological factors

3.3.1. Relationship between Glyoxal and methylglyoxal in sampling locations

Figs. 3 and 4 show the relationship between glyoxal and methylglyoxal concentrations in the sampled cities in two seasons. Consistent positive correlations were observed for BJ, QH, TB and XM in summer and winter. Fair correlations between summer and winter at BJ ($r \geq 0.5$) could possibly be due to persistent additional sources for formation. BJ is enclosed by mountains in the north, northwest and west, which could potentially trap primary and secondary sources of glyoxal/methylglyoxal within the city.

Strong correlations were observed at QH, TB and XM ($r \geq 0.9$ at all three cities), implying that consistent direct sources (either possibly

from primary emissions or secondary sources due to long range transport) dominated throughout both seasons. QH and TB are remote from any anthropogenic activities and the primary source could be biogenic emissions. A previous study showed biomass combustion could produce low levels of the di-carbonyls at QH (Meng et al., 2013), and household burning of yak dung is a major energy source in Tibet (Xiao et al., 2015). A past study showed abundance of di-carbonyls in Xiamen (~2.2 million populations) is comparably less to Shanghai (~16.7 million populations). Primary source emissions could dominate at Xiamen over Shanghai, although further studies are necessary (Ho et al., 2007).

Variation in positive correlations across seasons (summer (S) vs. winter (W)) were identified at WH, SH, GZ, CD and YT. S > W at WH whereas W > S in SH, GZ, CD and YT. The majority of the cities show that W > S, potentially because of the higher temperature, coupled with strong local photochemical reactions, generating additional sources of di-carbonyls.

3.3.2. Correlation analysis

Pearson's correlation analysis was applied to identify correlations between overall glyoxal/methylglyoxal concentrations against meteorological factors in the two seasons (Table 1). A similar analysis has been applied in Xi'an, China (Ho et al., 2014). The analysis was performed solely to determine the means, to investigate statistical inferences about the relationships between concentrations and locations, not to explain large portions of the variance.

Weak positive correlations ($R \geq 0.3$) were shown between glyoxal/methylglyoxal and temperatures in the two seasons. This suggests that regardless of season, temperature alone did not strongly correlate with glyoxal/methylglyoxal concentration. The significance values confirm the linear relationships are statistically reliable between temperature and di-carbonyls concentrations. The correlation coefficients are low, reflecting large day-to-day variability in the concentration data, possibly due to large meteorological variability.

In summer, only a moderate positive correlation ($R \geq 0.5$) was observed between glyoxal and methylglyoxal. This could be due to different vertical pollutants mixing and the high intensity of solar radiation amplifying photochemical degradation (secondary formation), which eclipses the importance of local source emissions (direct primary formation) in summer compared to winter.

During winter, a strong positive correlation ($R \geq 0.7$) was observed between glyoxal and methylglyoxal, suggesting that the two compounds possibly share similar sources formation. Weak negative correlations ($R \geq 0.3$) were reported between glyoxal/methylglyoxal and wind speeds in winter. This confirms that lower wind speeds could be associated with higher glyoxal/methylglyoxal accumulation.

3.3.3. Multiple linear regression analysis

Table 2 shows overall glyoxal/methylglyoxal concentration changes against the per-unit change in meteorological factors over the two seasons. Those meteorological factors not reported were not associated with glyoxal and methylglyoxal concentration variation in the model. A similar approach has been applied to investigate source characteristics of airborne carbonyls using multiple linear regression models to evaluate the impact of traffic sources and meteorological conditions on the carbonyl concentrations in a past study (Liu et al., 2006).

A 1% increase in relative humidity change led to a 3.7 ng/m³ decrease in methylglyoxal concentration during summer. In summer, a 1 °C temperature increase caused concentration increase of 2.1 ng/m³ (~2.1%) for glyoxal and 9.9 ng/m³ (~5.4%) for methylglyoxal. Increase in methylglyoxal concentration was 2.6 times higher in terms of percentage gain. This finding is consistent with the overall maximum average concentration, which showed that methylglyoxal concentration was approximately two times higher than that of glyoxal in the summer. The temperature was significantly associated with glyoxal and showed a strong, significant association with methylglyoxal ($p < 0.05$).

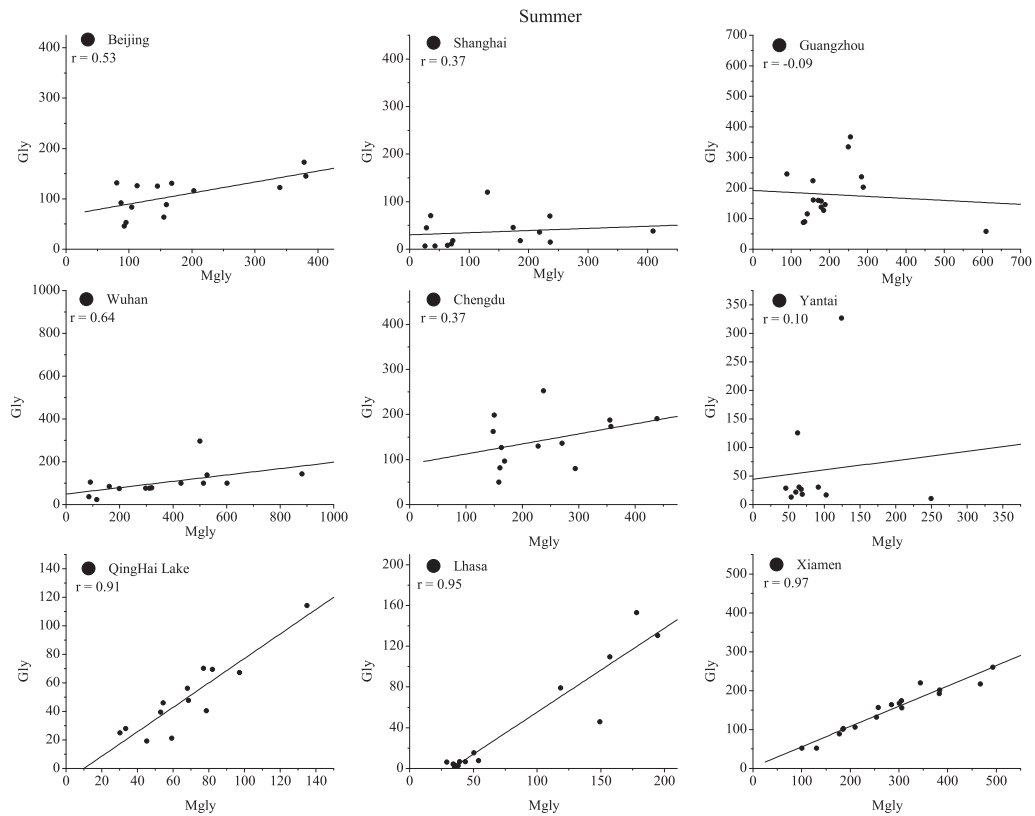


Fig. 3. Relationships between glyoxal and methylglyoxal concentrations in sampling sites during summer.

In winter, a temperature increase of 1 °C led to an increase of 6.8 ng/m³ (~4.8%) in glyoxal concentration and 12.7 ng/m³ (~5.0%) in methylglyoxal concentration. The temperatures showed a strong

significant association with glyoxal and methylglyoxal. In winter, the percentage change in glyoxal concentration was ~2.3 times higher than methylglyoxal with the same unit of temperature change. This

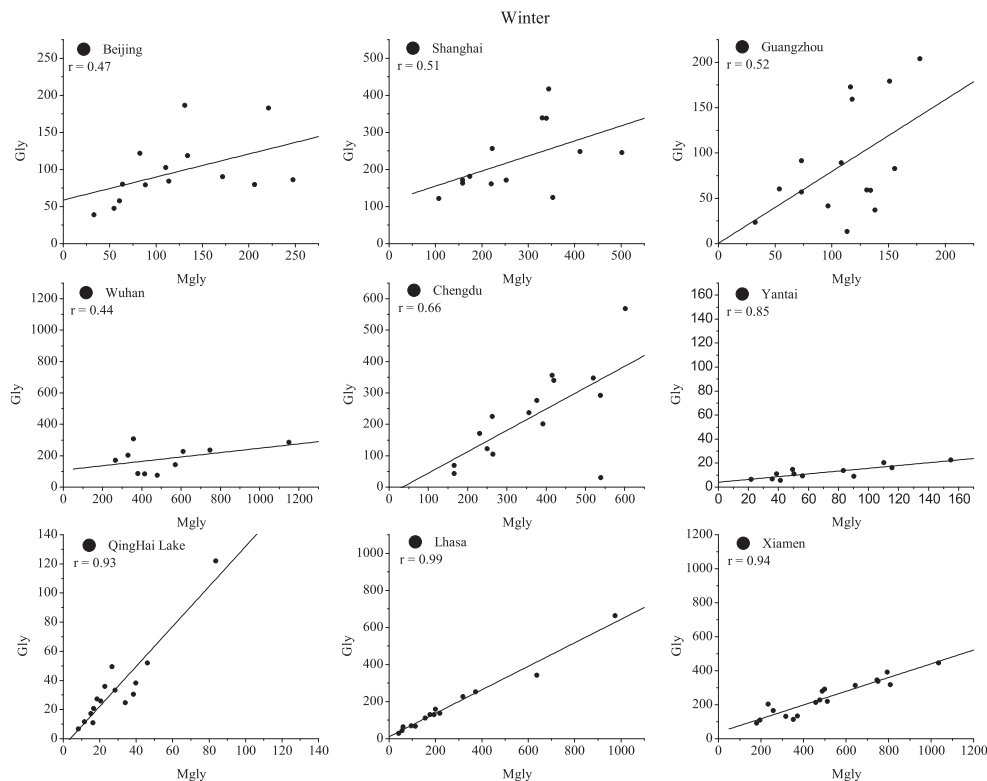


Fig. 4. Relationships between glyoxal and methylglyoxal concentrations in sampling sites during winter.

Table 2
Change in glyoxal/methylglyoxal against per unit change in meteorological factors during winter and summer.

Concentrations (ng/m ³)	Glyoxal (a) ⁱ Coefficient (95% C.I.)	Methylglyoxal (a) Coefficient (95% C.I.)
Summer^b		
T (b ₁) ^e	2.1 (0.5, 3.6) ^{a,d*}	9.9 (6.0, 13.8) ^{d***}
R (b ₂) ^f	−0.9 (−2.0, 0.3)	−3.7 (−6.5, −0.9) ^{d*}
W (b ₃) ^g	9.4 (−3.6, 22.5)	28.5 (−3.8, 60.9)
C (b ₀) ^h	53.3 (−29.9136.5)	101.1 (−104.9307.0)
Winter^c		
T (b ₁)	6.8(4.0.9.6) ^{d***}	12.7(7.5.17.8) ^{d***}
R (b ₂)	−0.2(−1.3, 0.9)	0.7(−1.2, 2.7)
W (b ₃)	−31.7(−43.8, −19.7) ^{d***}	−52.9 (−74.9, −30.9) ^{d***}
C (b ₀)	237.1 (171.4, 302.8) ^{d***}	352.7 (232.7, 472.8) ^{d***}

^a Results were estimated by multiple regression model.

^b Summer (N = 75 sampling days).

^c Winter (N = 119 sampling days).

^d *p < 0.05; **p < 0.005; ***p < 0.0005.

^e T denotes temperature (°C).

^f R denotes relative humidity (%).

^g W denotes wind speed (ms^{−1}).

^h C denotes constant (ng/m³).

ⁱ a denotes dependent variable of glyoxal or methylglyoxal concentration (ng/m³).

could potentially be due to cold air masses in winter having higher pressure, leading to a higher particle collision frequency between the radicals and precursors for glyoxal formation. Methylglyoxal shows only minimal variation between seasons in percentage gain, suggesting that the rate-determining step might not be collision rate. In winter, a wind speed increase of 1 ms^{−1} led to a concentration decrease of 31.7 ng/m³ (~−22.2%) for glyoxal and 52.9 ng/m³ (~−21.0%) for methylglyoxal. The Chinese monsoon is influenced by the huge land mass of Siberia. The winter monsoon is driven by the differential warming and cooling over the land and ocean. The temperature differences give rise to pressure differences, which in turn generate air flow from land to sea, which eventually causes the northeast monsoon to prevail and drive the glyoxal and methylglyoxal towards Southeast Asia (Junmei and Ren Juzhang, 2004; Xu, 2001; Yihui and Chan, 2005; Xu et al., 2006).

4. Conclusions

Concentration of gaseous glyoxal and methylglyoxal collected in nine Chinese cities during summer 2010 and winter 2011 were characterized. Overall maximum average concentrations showed that methylglyoxal concentrations were approximately two times greater than those of glyoxal in both seasons due to possible methylglyoxal enrichment in the troposphere. Both of the di-carbonyls exhibited statistically significant differences between seasons.

The glyoxal concentration was highest in GZ in summer and XM in winter. High glyoxal concentrations were consistently found in megacities, which could be possibly due to high acetylene emissions. The highest methylglyoxal concentration was observed at WH in both seasons. This could be due to high acetone concentration enhancing methylglyoxal formation. Glyoxal-to-methylglyoxal ratios showed that consistent direct emissions dominated in QH and TB, where anthropogenic activity is insignificant. Conversely, seasonal variations dominated in urban areas, which could be due to enhanced secondary source formation.

Pearson's correlation analysis showed a strong positive correlation (R ≥ 0.7) between glyoxal and methylglyoxal, suggesting that possible similar sources for the two di-carbonyls in winter. Multiple linear regression analysis demonstrated that temperature rises could lead to a concentration increase for both of the di-carbonyls. There was a greater percentage gain in glyoxal concentrations in winter, which could be due to cold air masses having a higher particle collision frequency between

radicals and precursors. During winter, the northeast monsoon occurs, driving >20% di-carbonyls towards Southeast Asia.

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Appendix A. Supplementary data

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