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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/m^3, 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 that the same emission sources ($R \geq 0.7$) were present 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.

Keywords:

Glyoxal, Methylglyoxal, Ambient Air, Correlation Analysis, Multiple Linear Regression

1. Introduction

Glyoxal (CHOCHO) and methylglyoxal (CH_3COCHO) 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). The 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). Production rates 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 can be secured in aqueous aerosols and cloud droplets, eventually forming low-volatility products partitioned in the condensed phase. 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 (Betterton and Hoffmann, 1988; Carlton et al., 2007; Liggio et al., 2005; Loeffler et al., 2006). Methylglyoxal is an important precursor of peroxyacetylnitrate (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). Mutagenic and genotoxic properties of glyoxal and methylglyoxal have been reported in the past (Murata-Kamiya and Kamiya, 2001; Ueno et al., 1991a, b; 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.

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 cites (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-dinitophenylhydrazine (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 ^{O}N, 91-121 ^{O}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) (Figure 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). Air samples were collected in 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) 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 equation 1:

$$\textit{Collection efficiency} = (1 - A_b/A_f) \qquad \text{(eq. 1)}$$

where A_f and A_b represent the amount of carbonyls collected on the 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., 2012; 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. Different meteorological factors such as temperature, relative humidity and wind speed were recorded 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) were all purchased. Milli-Q ultrapure water was used (Millipore, Milford, MA, USA). DNPH derivatizing agent was prepared by adding DNPH (250 mg) and 10 μL concentrated hydrochloride 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 hours, 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 equation 2:

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

$t(n-1, 1-\alpha = 99\%)$ 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 ± 5% and 93 ± 6%, respectively.

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.

$$[a] = b_0 + b_1[T] + b_2[R] + b_3[W] \qquad \text{(eq. 3)}$$

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.

3.0 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 have high solar radiation, relative humidity and temperature along with atmospheric precursors, which could be factors contributing to the atmospheric photo-oxidation of volatile organic compounds (VOCs) (Fu et al., 2008). This is an important secondary source of the studied di-carbonyls. For those cities where W > S, primary di-carbonyl emissions dominated due to low temperature, which could potentially deter oxidant formation and hence suppress photochemical reactions. Stable atmospheric stratification coupled with heating fuel usage in winter could further enhance di-carbonyl accumulation (Dai et al., 2012).

3.2 Concentrations of Di-carbonyls in Sampling Locations

The glyoxal concentrations in the two seasons are presented in Table 1. 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/m^3 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 (Ortiz et al., 2006). The glyoxal concentration in GZ is comparable to Xi'an, China in summer, which is seriously polluted (Dai et al., 2012). 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/m^3 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. 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. 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 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/m^3 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/m^3. 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/m^3) was higher than in winter (28.4 ng/m^3). WH shows the highest methylglyoxal concentrations during both seasons. Acetone is the second largest source of methylglyoxal formation (i.e. $^\bullet$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 high methylglyoxal concentration observed could be explained by the high acetone concentration, which enhances methylglyoxal formation at WH. 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

Figures 2 and 3 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 (vegetation emissions in particular). 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 2). 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 formation. Rather, other meteorological factors have to be taken into account. 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 intensity of solar radiation amplifying photochemical degradation, which eclipses the importance of local source emissions in summer compared to winter. During winter, a strong positive correlation ($R \geq 0.7$) was observed between glyoxal and methylglyoxal, suggesting that the emission sources are the same for the two di-carbonyls. Weak negative correlations were reported between glyoxal/methylglyoxal and wind speeds. This confirms that lower wind speeds, coupled with winter conditions, could favor higher glyoxal/methylglyoxal accumulation.

3.3.3 Multiple Linear Regression Analysis

Table 3 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 1% increase in relative humidity change led to a 3.7 ng/m^3 decrease in methylglyoxal concentration during summer. In summer, a 1 °C temperature increase caused concentration increase of 2.1 ng/m^3 (~2.1%) for glyoxal and 9.9 ng/m^3 (~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 ($p < 0.05$). In winter, a temperature increase of 1 °C led to an increase of 6.8 ng/m^3 (~4.8%) in glyoxal concentration and 12.7 ng/m^3 (~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 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/m^3 (~−22.2%) for glyoxal and 52.9 ng/m^3 (~−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.

4.0 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 significantly 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 the source for the two di-carbonyls in winter is the same. 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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References

Al-Enezi, K.S., Alkhalaf, M., Benov, L.T., 2006. Glycolaldehyde induces growth inhibition and oxidative stress in human breast cancer cells*, Free Radic. Biol. Med. 40,1144-1151.

Anderson, S.E., Jackson, L.G., Franko, J., Wells, J., 2010. Evaluation of dicarbonyls generated in a simulated indoor air environment using an in vitro exposure system, Toxicol. Sci. 115, 453-461.

Betterton, E.A., Hoffmann, M.R., 1988. Henry's law constants of some environmentally important aldehydes, Environ. Sci. Technol. 22, 1415-1418.

Borbon, A., Locoge, N., Veillerot, M., Galloo, J., 2002. Guillermo, R., Characterisation of NMHCs in a French urban atmosphere: overview of the main sources, Sci. Total Environ. 292, 177-191.

Calvert, J.G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T.J., Yarwood, G., 2002. The mechanisms of atmospheric oxidation of aromatic hydrocarbons. Oxford University Press, New York.

Carlton, A.G., Turpin, B.J., Altieri, K.E., Seitzinger, S., Reff, A., Lim, H.J., Ervens, B., 2007. Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmos. Environ. 41, 7588-7602.

Chan, L.Y., Chu, K.-W., Zou, S.-C., Chan, C.-Y., Wang, X.-M., Barletta, B., Guo, H., Tsai, W.-Y., 2006. Characteristics of nonmethane hydrocarbons (NMHCs) in industrial, industrial-urban, and industrial-suburban atmospheres of the Pearl River Delta (PRD) region of south China, J. Geophys. Res. Atmos. 111, D11304.

Dai, W.-T., Ho, S.S.H., Ho, K.-F., Cao, J.-J., 2012. Characterization of particulate-phase high molecular weight mono-carbonyls (C#> 5) and dicarbonyls in urban atmosphere of Xi'an, China, Aerosol Air Qual. Res. 12, 892-901.

Fu, T.M., Jacob, D.J., Wittrock, F., Burrows, J.P., Vrekoussis, M., Henze, D.K., 2008. Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J. Geophys. Res. Atmos. 113, D15303.

Giorgini, P., Rubenfire, M., Das, R., Gracik, T., Wang, L., Morishita, M., Bard, R.L., Jackson, E.A., Fitzner, C.A., Ferri, C., 2015. Higher fine particulate matter and temperature levels impair exercise capacity in cardiac patients, *Heart* 101, 1293-1301.

Kang, D., Aneja, V.P., Zika, R.G., Farmer, C., Ray, J.D., 2001. Nonmethane hydrocarbons in the rural southeast United States national parks, J. Geophys. Res. Atmos. 106, 3133-3155.

Kawamura, K., Okuzawa, K., Aggarwal, S.G., Irie, H., Kanaya, Y., Wang, A., 2013. Determination of gaseous and particulate carbonyls (glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, nonanal and decanal) in the atmosphere at Mt. Tai, Atmos. Chem. Phys. 13, 5369-5380.

Kleindienst, T., Conver, T., McIver, C., Edney, E., 2004. Determination of secondary organic aerosol products from the photooxidation of toluene and their implications in ambient PM2.5, J. Atmos. Chem. 47, 79-100.

Liggio, J., Li, S.-M., McLaren, R., 2005. Heterogeneous reactions of glyoxal on particulate matter: Identification of acetals and sulfate esters, Environ. Sci. Technol. 39, 1532-1541.

Loeffler, K.W., Koehler, C.A., Paul, N.M., De Haan, D.O., 2006. Oligomer formation in evaporating aqueous glyoxal and methyl glyoxal solutions, Environ. Sci. Technol. 40, 6318-6323.

Ma, J., Xu, X., Zhao, C., Yan, P., 2012. A review of atmospheric chemistry research in China: Photochemical smog, haze pollution, and gas-aerosol interactions, Adv. Atmos. Sci. 29, 1006-1026.

Mehta, R., Wong, L., O'Brien, P.J., 2009. Cytoprotective mechanisms of carbonyl scavenging drugs in isolated rat hepatocytes, Chem. Biol. Interact. 178, 317-323.

Meng, J., Wang, G., Li, J., Cheng, C., Cao, J., 2013. Atmospheric oxalic acid and related secondary organic aerosols in Qinghai Lake, a continental background site in Tibet Plateau, Atmos. Environ. 79, 582-589.

Munger, J.W., Jacob, D.J., Daube, B.C., Horowitz, L.W., Keene, W.C., Heikes, B.G., 1995. Formaldehyde, glyoxal, and methylglyoxal in air and cloudwater at a rural mountain site in central Virginia, J. Geophys. Res. Atmos. 100, 9325-9333.

Murata-Kamiya, N., Kamiya, H., 2001. Methylglyoxal, an endogenous aldehyde, crosslinks DNA polymerase and the substrate DNA, Nucleic Acids Res. 29, 3433-3438.

Na, K., Kim, Y.P., Moon, K.-C., Moon, I., Fung, K., 2001. Concentrations of volatile organic compounds in an industrial area of Korea, Atmos. Environ. 35, 2747-2756.

National Bureau of Statistics of China, China Stastical Yearbook, (2012).

Ocak, S., Turalioglu, F.S., 2008. Effect of Meteorology on The Atmospheric Concentrations of Traffic-Related Pollutants in Erzurum, Turkey, J. Int. Environ. Appl. Sci. 3, 325-335.

Ortiz, R., Hagino, H., Sekiguchi, K., Wang, Q., Sakamoto, K., 2006. Ambient air measurements of six bifunctional carbonyls in a suburban area, Atmos. Res. 82, 709-718.

Ortiz, R., Shimada, S., Sekiguchi, K., Wang, Q., Sakamoto, K., 2013. Atmospheric Concentrations of Semivolatile Bifunctional Carbonyl Compounds and the Contribution from Motor Vehicles, Asian J. Atmos. Environ. 7, 152-160.

Schwier, A.N., Sareen, N., Mitroo, D., Shapiro, E.L., McNeill, V.F., 2010. Glyoxal-methylglyoxal cross-reactions in secondary organic aerosol formation, Environ. Sci. Technol. 44, 6174-6182.

Shangari, N., Bruce, W., Poon, R., O'brien, P., 2003. Toxicity of glyoxals-role of oxidative stress, metabolic detoxification and thiamine deficiency, Biochem. Soc. Trans. 31, 1390-1393.

Shangari, N., Mehta, R., O'Brien, P.J., 2007. Hepatocyte susceptibility to glyoxal is dependent on cell thiamin content, Chem. Biol. Interact. 165, 146-154.

Smith, D., Kleindienst, T., McIver, C., 1999. Primary product distributions from the reaction of OH with m-, p-xylene, 1,2,4- and 1,3,5-trimethylbenzene, J. Atmos. Chem. 34, 339-364.

Smith, D., McIver, C., Kleindienst, T., 1998. Primary product distribution from the reaction of hydroxyl radicals with toluene at ppb NOx mixing ratios, J. Atmos. Chem. 30, 209-228.

Spaulding, R.S., Frazey, P., Rao, X., Charles, M.J., 1999. Measurement of hydroxy carbonyls and other carbonyls in ambient air using pentafluorobenzyl alcohol as a chemical ionization reagent, Anal. Chem. 71, 3420-3427.

Sun, B., Fang, T., Desertification in China and its control. 2001. Sustainable land use in deserts, Springer, 418-426.

Ueno, H., Nakamuro, K., Sayato, Y., Okada, S., 1991a. Characteristics of mutagenesis by glyoxal in Salmonella typhimurium: contribution of singlet oxygen, Mutat. Res. Fund. Mol. Res. Mut. 251, 99-107.

Ueno, H., Nakamuro, K., Sayato, Y., Okada, S., 1991b. DNA lesion in rat hepatocytes induced by in vitro and in vivo exposure to glyoxal, *Mutation Research/Genetic Toxicology* 260, 115-119.

Ueno, H., Segawa, T., Hasegawa, T., Nakamuro, K., Maeda, H., Hiramatsu, Y., Okada, S., Sayato, Y., 1991c. Subchronic oral toxicity of glyoxal via drinking water in rats, Toxicol. Sci. 16, 763-772.

USEPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition: Compendium Method TO-11A Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology], (1999).

Volkamer, R., Platt, U., Wirtz, K., 2001. Primary and secondary glyoxal formation from aromatics: Experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene, and p-xylene, J. Phys. Chem. A 105, 7865-7874.

Wang, G., Niu, S., Liu, C., Wang, L., 2002. Identification of dicarboxylic acids and aldehydes of PM10 and PM2. 5 aerosols in Nanjing, China, Atmos. Environ. 36, 1941-1950.

Watson, J.G., Chow, J.C., Fujita, E.M., 2001. Review of volatile organic compound source apportionment by chemical mass balance, Atmos. Environ. 35, 1567-1584.

Zhu, Z., Wang, T., 1993. Trends of desertification and its rehabilitation in China, Desertification Control Bulletin, 22, 27-30.

Figure Legend

List of Tables

Table 1	Concentration of Gaseous Phase Di-carbonyls and Acetone in Chinese Cities during winter and summer
Table 2	Pearson Correlation Coefficients (R) of Glyoxal/Methylglyoxal and Meteorological Factors during winter and summer ($R \geq 0.70$ and 0.05 significance level).
Table 3	Change in Glyoxl/Methylglyoxal against Per Unit Change in Meteorological Factors during winter and summer

List of Figures

Figure 1	Map showing sampling sites in the campaign
Figure 2	Relationships between glyoxal and methylglyoxal concentrations in sampling sites during summer
Figure 3	Relationships between glyoxal and methylglyoxal concentrations in sampling sites during winter

Table 1 Concentration of Gaseous Phase Di-carbonyls and Acetone in Chinese Cities during winter and summer

	Concentration (ng/m^3)	Summer		Winter	
		Average ± SD[a]	Median	Average ± SD	Median
Beijing	Glyoxal	106.9 ± 36.7	119	96.9 ± 43.9	85.3
	Methylglyoxal	178.6 ± 108.0	150.1	122.7 ± 66.7	112
	Acetone	1.5 ± 0.5	1.3	3.0 ± 1.2	2.7
Shanghai	Glyoxal	36.4 ± 32.5	27.3	226.1 ± 91.8	181.8
	Methylglyoxal	137.8 ± 111.5	101.8	274.7 ± 115.3	252.4
	Acetone	2.4 ± 2.8	1.4	4.8 ± 2.6	3.7
Guangzhou	Glyoxal	178.4 ± 86.3	158.6	88.7 ± 60.9	60.2
	Methylglyoxal	212.4 ± 120.0	178.2	111.4 ± 39.9	116.3
	Acetone	2.2 ± 1.8	1.6	6.9 ± 2.2	5.9
Wuhan	Glyoxal	102.5 ± 64.5	92.7	182.2 ± 83.8	186.7
	Methylglyoxal	359.4 ± 229.6	316.3	530.0 ± 262.1	446.1
	Acetone	6.3 ± 7.0	3.1	7.2 ± 2.0	6.7
Chengdu	Glyoxal	143.6 ± 57.6	136	225.9 ± 145.1	225.7
	Methylglyoxal	240.7 ± 96.3	228.1	366.4 ± 140.9	376.5
	Acetone	1.7 ± 0.5	1.6	7.5 ± 2.6	7.2
Yantai	Glyoxal	59.1 ± 94.4	27	12.3 ± 5.5	11
	Methylglyoxal	90.0 ± 57.7	67.4	70.6 ± 40.2	53.1
	Acetone	4.8 ± 5.3	3.2	6.0 ± 2.5	5.2
QingHai Lake	Glyoxal	49.6 ± 26.4	46.1	33.8 ± 27.7	27.3
	Methylglyoxal	67.8 ± 27.9	68	28.4 ± 18.9	22.8
	Acetone	1.4 ± 0.5	1.6	1.2 ± 0.4	1.3
Lhasa	Glyoxal	38.4 ± 52.9	6.6	173.7 ± 166.1	130
	Methylglyoxal	79.5 ± 60.8	43.7	257.7 ± 259.3	184.1
	Acetone	1.4 ± 0.3	1.3	2.2 ± 1.2	1.9
Xiamen	Glyoxal	149.7 ± 59.7	156.5	241.4 ± 105.2	224.1
	Methylglyoxal	280.4 ± 110.7	284.5	506.3 ± 243.8	482
	Acetone	0.8 ± 0.3	0.7	1.7 ± 1.1	1.7

[a] SD denotes standard deviation

Table 2 Pearson Correlation Coefficients (R) of Glyoxal/Methylglyoxal and Meteorological Factors during winter and summer ($R \geq 0.70$ 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	0.1
	Wind Speed					1
Winter	Glyoxal	1	0.80**	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)

Table 3 Change in Glyoxl/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]	[a]2.1 (0.5, 3.6)*[d]	9.9 (6.0, 13.8)***[d]
R (b_2)[f]	-0.9 (-2.0, 0.3)	-3.7 (-6.5, -0.9)*
W (b_3)[g]	9.4 (-3.6, 22.5)	28.5 (-3.8, 60.9)
C (b_0)[h]	53.3 (-29.9,136.5)	101.1 (-104.9,307.0)
Winter[c]		
T (b_1)	6.8(4.0,9.6)***	12.7(7.5,17.8)***
R (b_2)	-0.2(-1.3, 0.9)	0.7(-1.2, 2.7)
W (b_3)	-31.7(-43.8, -19.7)***	-52.9 (-74.9, -30.9)***
C (b_0)	237.1 (171.4, 302.8)***	352.7 (232.7, 472.8)***

[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 deontes relative humidity (%)

[g] W deonotes wind speed (ms^{-1})

[h] C denotes constant (ng/m^3)

[i] a denotes dependent variable of glyoxal or methylglyoxal concentration (ng/m^3)

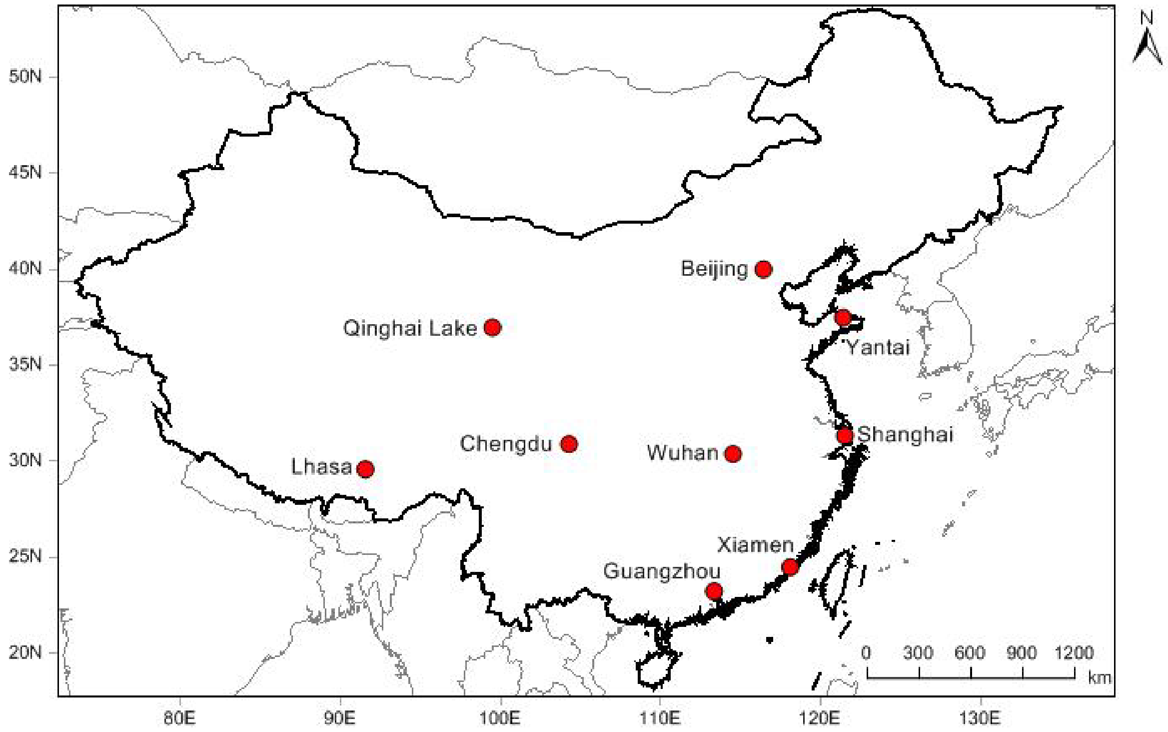

Figure 1 Map showing Sampling Sites in the Campaign

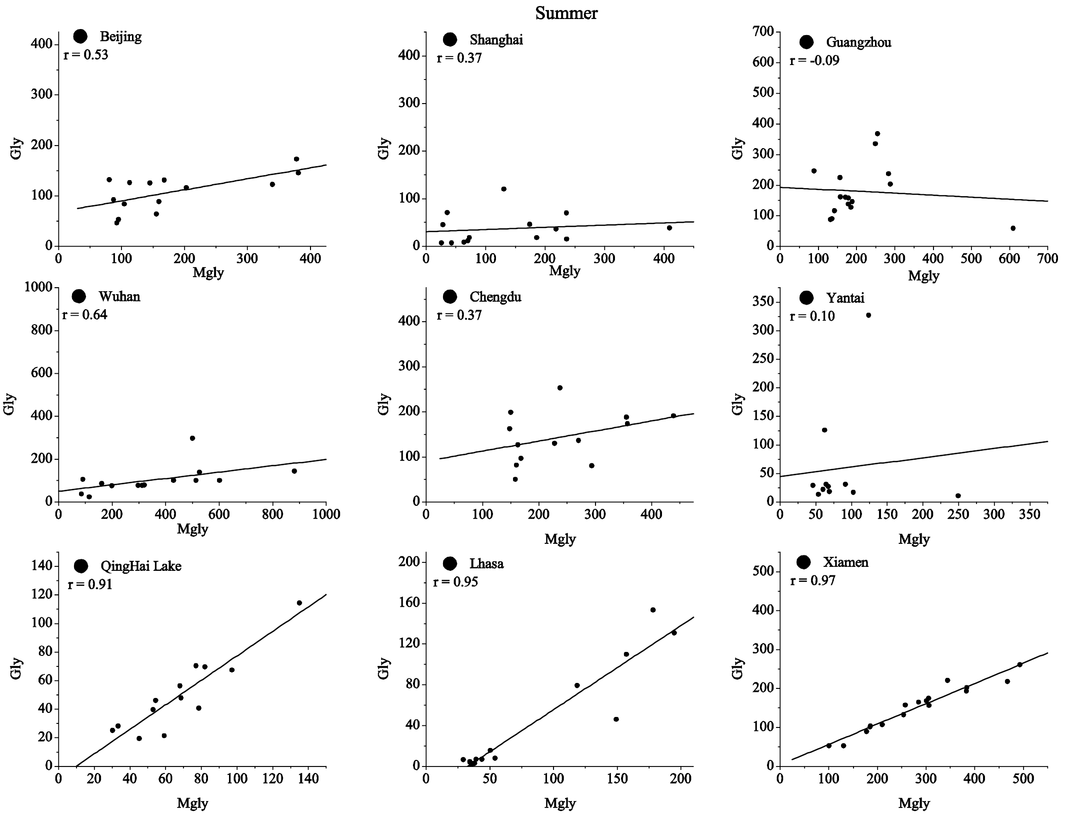

Figure 2 Relationships between glyoxal and methylglyoxal concentrations in sampling sites during summer

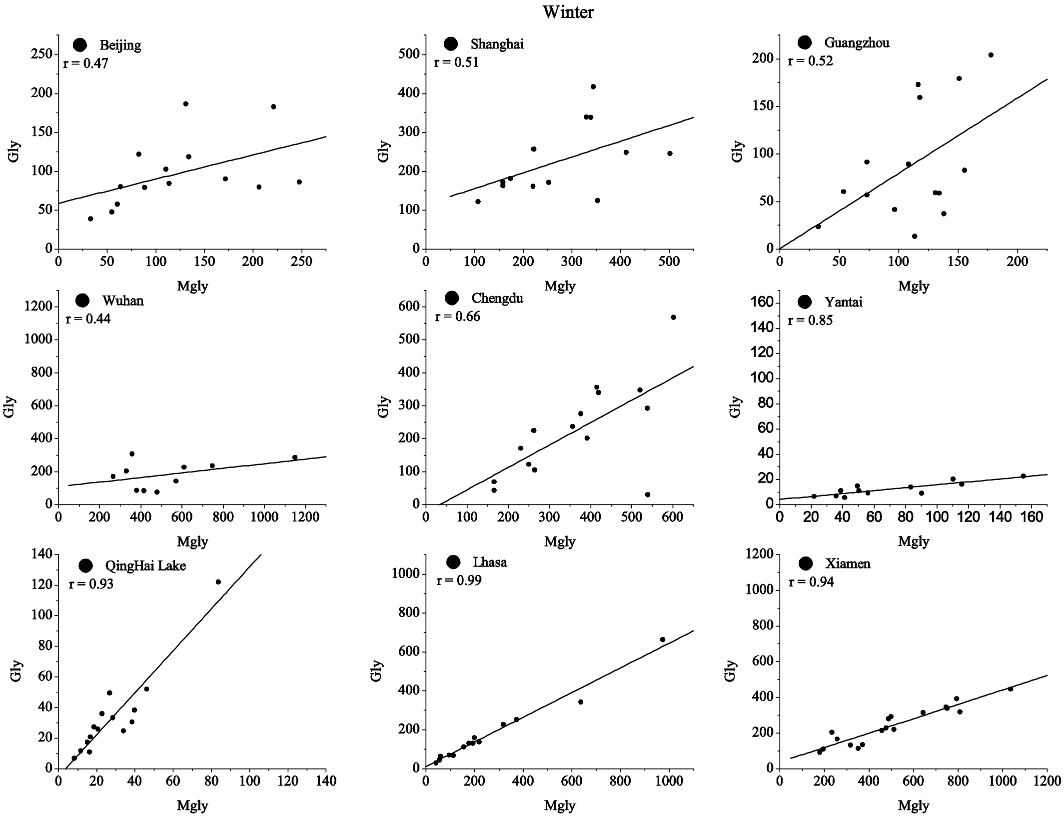

Figure 3 Relationships between glyoxal and methylglyoxal concentrations in sampling sites during winter