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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 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.

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). 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 (>3.6×10^5 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).

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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 CH_3COCHO sources in China. The data are useful to understand further about the SOA formation in the areas. Relationships between CHOCHO/CH_3COCHO 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 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°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

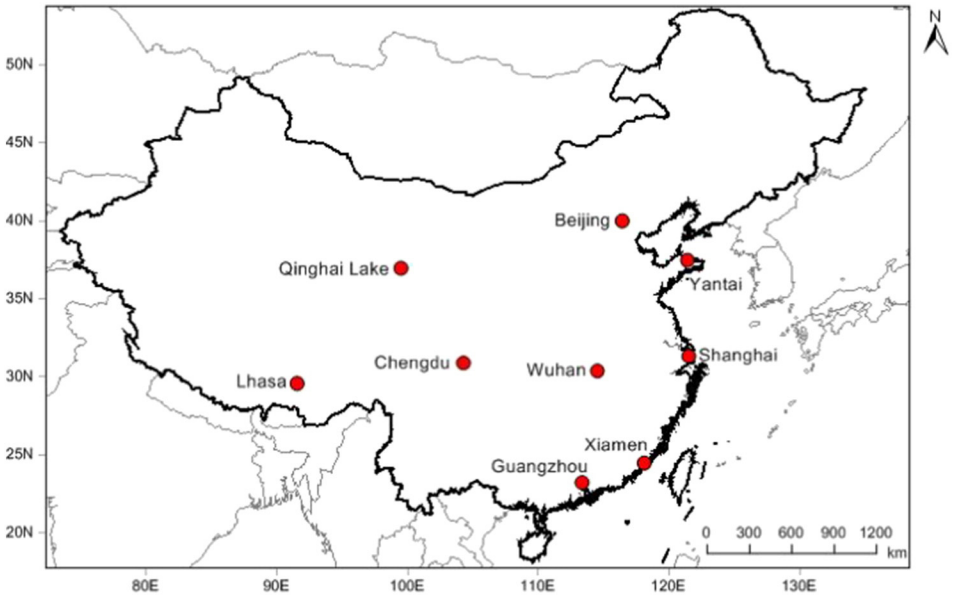

Fig. 1. Map showing sampling sites in the campaign.