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### ► To cite this version:

Yingnan Zhang, Likun Xue, Can Dong, Tao Wang, Abdelwahid S Mellouki, et al.. Gaseous carbonyls in China's atmosphere: Tempo-spatial distributions, sources, photochemical formation, and impact on air quality. *Atmospheric Environment*, 2019, 214, pp.116863. 10.1016/j.atmosenv.2019.116863 . insu-02263523

**HAL Id: insu-02263523**

**<https://insu.hal.science/insu-02263523>**

Submitted on 5 Aug 2019

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# Gaseous carbonyls in China's atmosphere: tempo-spatial distributions, sources, photochemical formation, and impact on air quality

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## Abstract

Carbonyls are an important class of oxygenated volatile organic compounds that play a crucial role in tropospheric chemistry as intermediates in the formation of ozone (O<sub>3</sub>) and secondary organic aerosols. Over the last two decades, China's severe air pollution has led atmospheric chemists to devote substantial efforts to investigate the contribution of carbonyl compounds to the observed phenomena. This study reviews the major findings with regard to the gas-phase atmospheric chemistry of carbonyls in China, including their chemical compositions, temporal and spatial distributions, source apportionments, photochemical formation mechanisms, and impact on tropospheric oxidative capacity, air quality, and human health. Extremely high levels of carbonyls have frequently been observed in China's most rapidly developing regions, such as the North China Plain, the Yangtze River Delta, and the Pearl River Delta, but observational data from other regions are relatively scarce. Primary emissions and photochemical formation are major sources of carbonyls. Alkenes, aromatics, and isoprene have been identified as major precursors on a national scale. In addition, an increasing number of studies has focused on the effects of carbonyls on O<sub>3</sub> formation, radical chemistry, the formation of secondary organic aerosols, and human health. The photolysis of oxygenated volatile organic compounds was recognized as a dominant pathway to ROx production, which further influences O<sub>3</sub> formation, mainly via HO<sub>2</sub>+NO or RO<sub>2</sub>+NO. Dicarboxyls (such as glyoxal and methylglyoxal) make important contributions to secondary organic aerosol formation via irreversible uptake by aqueous particles. Indoor and outdoor carbonyls often pose a significant threat to human health. This review also includes recommendations from the perspective of emissions, observations, photochemical formation mechanisms, and the effects of carbonyls to guide future research and provide scientific support for the formulation of mitigation policies to address photochemical air pollution.

**Key words:** Carbonyls; Human health; Ozone; Photochemical formation; Secondary organic aerosol

## 38 1. Introduction

39 Carbonyls are important members of the family of oxygenated volatile organic  
40 compounds (OVOCs), which have a significant influence on the formation of ozone (O<sub>3</sub>) and  
41 secondary organic aerosol (SOA) and hence play key roles in tropospheric chemistry (Calvert  
42 et al., 2011; Mellouki et al., 2015; Shen et al., 2013; and references therein). In recent decades,  
43 photochemical air pollution, characterized by high concentrations of O<sub>3</sub> and other secondary  
44 contaminants, has become a major environmental concern in China due to its rapid urbanization  
45 and industrialization (Xue et al., 2014; Wang et al., 2017b; and references therein). Due to the  
46 significance of carbonyls in O<sub>3</sub> formation, investigation of their pollution characteristics,  
47 sources, relationships with precursors, and impact on air quality is essential to better understand  
48 and control photochemical pollution.

49 Extensive studies have been conducted in the United States and Europe to investigate the  
50 pollution characteristics and formation mechanisms of photochemical smog since the mid-20th  
51 century. In contrast, only in the last three decades has China realized the severity of its  
52 photochemical air pollution, and finding solutions to photochemical pollution problems has  
53 become a top priority. Most studies have focused on the characteristics and formation  
54 mechanisms of surface O<sub>3</sub> because it is regarded as the principal constituent of photochemical  
55 smog (Wang et al., 2017b; and references therein). In the lower troposphere, O<sub>3</sub> is formed  
56 mainly via photochemical reactions that involve volatile organic compounds (VOCs) and  
57 nitrogen oxides (NO<sub>x</sub>) (Atkinson, 2000; Atkinson and Arey, 2003). Among these precursors,  
58 the pollution characteristics of hydrocarbons have rapidly attracted considerable attention  
59 because of their complexity and our poor understanding of them. More and more studies have  
60 focused on the sources and photochemistry of VOCs (e.g., Guo et al., 2006; Guo et al., 2004b;  
61 Xue et al., 2013). In particular, carbonyls have been dissected from VOCs as a research hotspot  
62 due to their great reactivity and important contributions to the formation of O<sub>3</sub> and aerosols.

63 Despite its late start, China has made some promising progress in gaseous carbonyls  
64 research. In particular, in the last 20 years, several field observations have been carried out  
65 across China, and more than 25 carbonyl species have been monitored. Basic information on  
66 major carbonyls is provided in Table 1. The collected data show that various aspects of  
67 carbonyls have been investigated. Analyses of the temporal and spatial distributions of  
68 carbonyls have been widely performed (Cheng et al., 2014; Dai et al., 2012; Guo et al., 2016;  
69 Ho et al., 2014a; Ho et al., 2015; Ho et al., 2002; Lui et al., 2017a; Lui et al., 2017c; Pang and  
70 Lee, 2010; Pang and Mu, 2006), but few studies have focused on the sources or photochemical  
71 mechanisms of carbonyls, or their influence on atmospheric chemistry, air quality, and human  
72 health (Ling et al., 2017; Liu et al., 2009; Wang et al., 2017a; Xue et al., 2016; Yang et al.,  
73 2018), so these aspects are relatively poorly understood. In addition, most studies have focused  
74 on the characteristics of gaseous carbonyls; observational data on high-molecular weight  
75 carbonyls are relatively scarce. High-molecular weight carbonyls are semivolatile and largely  
76 partitioned into the particle phase, and their gas-phase concentrations are generally very low.  
77 This review article focuses on the most abundant gas-phase carbonyl compounds. Considering  
78 recent advances and the underlined needs, a critical review of the atmospheric chemistry of  
79 gaseous carbonyls in China's prevailing conditions is timely.

80 In this review, we summarize the main findings of studies of gaseous carbonyl compounds  
81 in China and provide suggestions for future research. Section 2 briefly reviews the atmospheric  
82 chemistry of carbonyls, Section 3 summarizes field studies on and techniques for measuring  
83 carbonyls across China, and Section 4 presents the chemical compositions and tempo-spatial  
84 variations of carbonyls. Section 5 presents the source apportionment results and contributions  
85 of various sources to ambient carbonyls in various regions, and Section 6 summarizes the  
86 photochemical formation mechanisms of several major carbonyl species based on numerical  
87 modeling studies. Section 7 reviews assessments of the effects of carbonyls on O<sub>3</sub> formation,  
88 atmospheric oxidizing capacity, SOA formation, and human health, and Section 8 summarizes  
89 the current findings and gives recommendations for future studies. Overall, this review aims to  
90 comprehensively summarize the current understanding of atmospheric carbonyls pollution in  
91 China, which should help to enlighten future research and aid in the formulation of control  
92 strategies to address regional air pollution.

## 93 **2. Brief review of atmospheric chemistry of carbonyls**

94 Carbonyls are organic molecules that contain at least a carbonyl group (C=O), and mainly  
95 include aldehydes and ketones. The chemical fates of carbonyls in the atmosphere are  
96 determined in large part by their structures and physical properties. For a given carbon number,  
97 carbonyls usually have lower vapor pressure than the corresponding parent alkanes, indicating  
98 the more polar nature of carbonyls. In addition, most carbonyls have low Henry's law constants,  
99 below 10<sup>3</sup> M atm<sup>-1</sup>, so their physical removal (including wet and dry deposition) is not  
100 important (Calvert et al., 2011; Mellouki et al., 2015). Notable exceptions, including glyoxal  
101 (GLY) and methylglyoxal (MGLY), are extremely water-soluble and can easily hydrate and  
102 polymerize even at low humidity, hence contributing to SOA formation (Shen et al., 2013; and  
103 references therein). Owing to their distinctive structures and physical properties, carbonyls play  
104 an active role in tropospheric chemistry.

105 Figure 1 illustrates the major atmospheric chemical processes of carbonyls, including their  
106 sources and sinks. The sources of carbonyl species in the troposphere are classified as primary  
107 or secondary. Carbonyls can be emitted directly from sources such as vehicular emissions,  
108 biomass burning, industrial activities, and biogenic emissions (Guenther et al. 2012; Ho et al.,  
109 2007; Ma et al., 2016; Mason et al., 2001; Zhang et al., 2016). Secondary carbonyls are formed  
110 via the photochemical oxidation of VOCs, mainly via RO+O<sub>2</sub> reactions (Yang et al., 2018).  
111 Specifically, in the presence of sunlight, the OH-initiated degradation of VOCs leads to the  
112 production of alkyl peroxy radicals (RO<sub>2</sub>), which then rapidly oxidize NO into NO<sub>2</sub> and form  
113 RO radicals (Atkinson and Arey, 2003; Seco et al., 2007). Carbonyls can then be formed by  
114 reactions of RO+O<sub>2</sub>. From the perspective of sources, OVOCs are important intermediate  
115 products that are formed during radical recycling circles. OVOCs also play significant roles in  
116 the radical-initiation processes because the photolysis of OVOCs presents a significant primary  
117 source of radicals in the atmosphere (Xue et al., 2016).

118 The most important loss pathways of carbonyls are photolysis and reactions with OH  
119 radicals. As mentioned above, the photolysis of carbonyls has been shown to make an important  
120 contribution to the primary production of HO<sub>2</sub> and RO<sub>2</sub> radicals (Jia et al., 2018; Li et al., 2018;  
121 Liu et al., 2012a; Xue et al., 2016; Xue et al., 2013). These radicals then participate in the NO<sub>x</sub>

122 chemical cycle, oxidizing NO to NO<sub>2</sub> and thus affecting O<sub>3</sub> formation (Wang et al., 2018). The  
123 oxidation of carbonyls by OH forms an acyl peroxy radical (generally for aldehydes) or an  
124 alkyl peroxy radical (mainly for ketones), both of which then undergo radical recycling and  
125 termination as RO<sub>2</sub>. The heterogeneous loss of aqueous particles, which commonly occurs for  
126 dicarbonyls such as GLY and MGLY, also serves as an important sink of carbonyls (Fu et al.,  
127 2008; Hu et al., 2017; Li et al., 2013a). When these two dicarbonyls are in contact with aqueous  
128 particles and cloud droplets, SOA is rapidly produced. Another loss pathway of carbonyls is  
129 reaction with O<sub>3</sub>/NO<sub>3</sub>, which is an important fate of unsaturated carbonyls. Studies have shown  
130 that the dominant sources and sinks may vary between regions and carbonyl species.

### 131 **3. Field observations over China**

132 Field studies of carbonyls began relatively late in China. Tables S1-S4 list the field  
133 observations collected from articles published between 2000 and 2018. Although these  
134 references may not be exhaustive, we believe that they are sufficiently comprehensive to reflect  
135 the situation of carbonyls pollution in China. The measurement campaigns have been  
136 concentrated in the rapidly developing regions of the North China Plain (NCP), the Yangtze  
137 River Delta (YRD), and the Pearl River Delta (PRD). Extremely high levels of carbonyls,  
138 indicating severe carbonyls pollution, have been frequently observed (Figures 2a-d) due to the  
139 thriving industry and high population density. In contrast, limited efforts have been devoted to  
140 slow-developing areas.

141 In the late 1990s, measurement campaigns were conducted in urban Qingdao, a coastal  
142 city on the NCP. Tan et al. (2002) analyzed the seasonal variations in 11 aldehydes and ketones,  
143 explored their interrelationships, and qualitatively identified their sources. The increasing  
144 number of field studies conducted across China over the next 20 years identified more than 25  
145 carbonyl species. Moreover, the number of field studies has drastically increased in the NCP  
146 and PRD regions since 2005, especially in 2008 for the purpose of controlling air pollution and  
147 preparing to host the Beijing Olympic Games. Note that these field observations were not  
148 limited to urban areas; they were conducted in various environments, including suburban, rural,  
149 mountain, and forest sites, to investigate the spatial distribution of carbonyls across China.  
150 Carbonyls levels were generally higher in urban sites (Cheng et al., 2014; Lui et al., 2017c;  
151 Yuan et al., 2012a). In addition, some field observations were conducted to examine the  
152 influence of various meteorological factors (e.g., haze, a lack of haze, dust storms, wind, and  
153 wet precipitation) on carbonyls levels (Duan et al., 2012; Pang et al., 2009a; Zhang et al., 2014).  
154 Other aspects, such as emission factors, have also been investigated. For example, to measure  
155 the on-road vehicle emissions of carbonyls, Ho et al. (2007) and Zhang et al. (2016) carried out  
156 measurements in tunnels in Hong Kong and Guangzhou, respectively. However, such  
157 investigations are relatively scarce in China.

158 Tables S1-S4 also show the measurement methods and analysis techniques used in each  
159 observational campaign. The various techniques used to measure and analyze carbonyls can be  
160 classified into two categories: online and offline. Offline methods were especially widely  
161 adopted during the measurement campaigns conducted before 2006. For example, many studies  
162 used silica cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) to collect air samples  
163 for high-performance liquid chromatography (HPLC) analysis (Lü et al., 2010; Pang and Mu,

164 2006; Wang et al., 2007). Although the DNPH-HPLC method has been widely used, its  
165 limitations include poor sensitivity and a strong dependence on the relative humidity (Pang et  
166 al., 2011). Some alternative offline approaches have been also developed. Altemose et al. (2015)  
167 used dansylhydrazine to derivatize carbonyls followed by HPLC analysis. Several other  
168 derivatization agents such as O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine and  
169 pentafluorophenyl hydrazine have also been used to absorb carbonyls, followed by analysis  
170 with thermal desorption–gas chromatography–mass spectrometry (Ho and Yu, 2002, 2004;  
171 Pang et al., 2011). Szuleiko and Kim (2015) summarized commonly used derivatization agents  
172 and analytical methods for carbonyls analysis and indicated that DNPH-HPLC remains the  
173 most common choice among the offline methods mentioned above. Since 2006, differential  
174 optical absorption spectroscopy has been used to measure carbonyls (Kawamura et al., 2013;  
175 Ling et al., 2017; Nan et al., 2017), and Kawamura et al. (2013) compared the performances of  
176 multi-axis differential optical absorption spectroscopy and filter sampling–gas chromatography  
177 measurements. In addition, Shao et al. (2009) used gas chromatography–flame ionization  
178 detection–mass spectrometry (MS) to achieve the continuous monitoring of carbonyls in China  
179 at a high time resolution. Online methods such as proton transfer reaction–mass spectrometry  
180 (PTR-MS; including PTR-QMS, PTR-IT-MS, PTR-TOF-MS, PTR-TOF-CIMS, and PTR-ID-  
181 CIMS) were then successively applied (Kanaya et al., 2009; Ma et al., 2016; Yuan et al., 2017;  
182 Yuan et al., 2016). Detailed information on these online methods has been published elsewhere  
183 (Chi et al., 2007; Cui et al., 2016; Ho and Yu, 2004; Inomata et al., 2008; Wang et al., 2014b).  
184 Although offline methods have been widely used, they have some disadvantages. One  
185 disadvantage is that the length of the derivatization time makes it difficult to characterize the  
186 continuous evolution process of carbonyls. The application of online methods has achieved  
187 continuous online measurements of carbonyls in the atmosphere at the trace level. Nevertheless,  
188 some carbonyl species still cannot be detected with these novel methods (Chen et al., 2014;  
189 Kawamura et al., 2013; Nan et al. 2017; Wang et al., 2014b). For example, PTR-MS can only  
190 detect species with a proton affinity greater than that of water and cannot distinguish  
191 isomeric/isobaric compounds (Blake et al., 2009; Yuan et al., 2017). Formaldehyde and  
192 acetaldehyde cannot be detected with online gas chromatography–MS because they do not  
193 produce unique ions in the MS (Pang et al., 2011). Further developments in measurement  
194 techniques for carbonyls are required to provide high-quality data and cover more species in  
195 future studies.

196 It is noteworthy to mention that most of these field observations were carried out by the  
197 research community and that carbonyls have not been listed as a target by the national air  
198 quality monitoring network. Very recently, Chinese government agencies have begun to attach  
199 greater importance to the measurement of carbonyls after realizing their significance in ozone  
200 pollution. In 2017, the Ministry of Ecology and Environment of the People’s Republic of China  
201 issued a series of regulations to promote the development of OVOC measurement, including  
202 both manual and automatic monitoring (<http://www.mee.gov.cn/>). For example, some air  
203 quality monitoring stations in key regions and/or cities have been asked to perform routine  
204 measurements of 13 major carbonyls (see Table 1) with the same method (i.e., DNPH-HPLC  
205 and gas chromatography–flame ionization detection–MS), so a picture of nationwide carbonyls  
206 levels across China seems around the corner.

#### 207 **4. Chemical compositions and tempo-spatial distributions**

208 Historical data show that formaldehyde (HCHO), acetaldehyde (CH<sub>3</sub>CHO), and acetone  
209 (CH<sub>3</sub>COCH<sub>3</sub>) are the three most abundant carbonyl species in field studies, but the most  
210 abundant species vary between sites. The contributions of these three species to the total  
211 observed carbonyl compounds generally exceed 70% (Guo et al., 2014a; Guo et al., 2016; Yang  
212 et al., 2017). In addition, the mixing ratios of two dicarbonyl compounds (i.e., GLY and MGLY)  
213 that are crucial players in the formation of O<sub>3</sub> and SOA have also shown high concentration  
214 levels in China (Ho et al., 2014a; Rao et al., 2016).

215 Figures 2a-d show the spatial distributions of major carbonyl species over China.  
216 Carbonyls pollution is obviously much more severe in the NCP, YRD, and PRD regions than  
217 in other areas. Of these three severely polluted regions, the PRD has a slightly better carbonyls  
218 pollution situation. Within a given region, higher levels of carbonyls were usually observed at  
219 urban sites than at suburban and rural sites. Megacities such as Beijing, Shanghai, Guangzhou,  
220 and Hong Kong have severe carbonyls pollution. High levels of HCHO (exceeding 20 ppbv),  
221 CH<sub>3</sub>CHO (exceeding 10 ppbv), and CH<sub>3</sub>COCH<sub>3</sub> (exceeding 6 ppbv) have been frequently  
222 observed in Beijing (Altemose et al., 2015; Duan et al., 2008; He et al., 2016; Pang and Mu,  
223 2006). Observational data for carbonyls other than the top three carbonyl species are relatively  
224 limited because they have high reactivities and low concentration levels. Nevertheless,  
225 observational data for propionaldehyde (C<sub>2</sub>H<sub>5</sub>CHO), butyraldehyde (C<sub>3</sub>H<sub>7</sub>CHO), GLY, and  
226 MGLY have also been collected. The spatial distributions of these four carbonyl species differ  
227 slightly from those of the three abundant species. In addition to the NCP, YRD, and PRD  
228 regions, Taiwan also showed elevated levels of C<sub>2</sub>H<sub>5</sub>CHO (>1 ppbv) and C<sub>3</sub>H<sub>7</sub>CHO (>2 ppbv)  
229 (Huang et al., 2008; Lü et al., 2010; Lü et al., 2009; Shi et al., 2011; Wang et al., 2010a). Figures  
230 3a-b show that GLY and MGLY in limited studies were found to exhibit high levels in Beijing  
231 and Xi'an (>0.3 ppbv and >1 ppbv for GLY and MGLY, respectively) (Ho et al., 2014a; Rao et  
232 al., 2016). GLY generally has a greater concentration than MGLY due to its longer lifespan (2.9  
233 vs. 1.6 h) (Fu et al., 2008). Dai et al. (2012) reported similar data in which the GLY  
234 concentrations were higher than those of MGLY in Xi'an in winter. However, at the same site,  
235 MGLY exhibited higher levels than GLY during summer, which may be attributed to seasonal  
236 variations in the sources of dicarbonyls.

237 The status of carbonyls pollution in China is less optimal than that of other countries. For  
238 example, levels of major carbonyl species (HCHO+CH<sub>3</sub>CHO+CH<sub>3</sub>COCH<sub>3</sub>) exceeding 20 ppbv  
239 have frequently been observed in Beijing (e.g., Duan et al., 2012; Duan et al., 2008; He et al.,  
240 2016; Pang and Mu., 2006; Rao et al., 2016; Yang et al., 2018), on par with those of Los Angeles  
241 (19.2 ppbv in 2008-2010) (Warneke et al., 2012) and Campeche, Mexico (37.1 ppbv in the  
242 summer of 2004) (Cerón et al., 2007), which have experienced the world's most serious  
243 photochemical pollution.

244 Four year-round observation campaigns are carefully selected to elucidate the seasonal  
245 variations in carbonyls in various regions (Huang et al., 2008; Lü et al., 2010; Lui et al., 2017c;  
246 Pang and Mu, 2006). These four measurements were conducted in urban areas of Beijing (from  
247 November 2004 to October 2005), Shanghai (from January to October 2007), Guangzhou  
248 (from January to November 2005), and Hong Kong (from January to December 2013),

249 respectively. These studies were chosen to obtain a comprehensive understanding of the severe  
250 carbonyls pollution characteristics in typical fast-developing regions of China. Although a time  
251 gap separates these four observation campaigns, we believe that it should have little effect on  
252 the seasonal variations of carbonyls. Figure 4 shows that HCHO and CH<sub>3</sub>CHO were  
253 significantly more abundant in summer than in winter in Beijing, Shanghai, and Guangzhou.  
254 This difference can be explained by the stronger photochemical activities in summer and was  
255 confirmed with <sup>13</sup>C isotope evidence by Guo and Chen (2013). In Hong Kong, both HCHO and  
256 CH<sub>3</sub>CHO exhibited their maximum levels in autumn, and similar levels were seen in summer  
257 and winter. The reason for this distinct seasonal pattern is that Hong Kong is frequently  
258 influenced by clean marine air masses under prevailing southerly or southeasterly winds in  
259 summer, which alleviates carbonyls pollution to some degree. Autumn is the most  
260 photochemically polluted season in Hong Kong due to the regional transport of continental air  
261 masses from mainland China via the winter monsoon and the sunny weather at low latitudes  
262 (Wang et al., 2009b). Another exception is the seasonal pattern in Xiamen, where higher levels  
263 of both HCHO and CH<sub>3</sub>CHO were found in winter than in summer, which may be attributed  
264 to the stronger sea-land breeze circulation during summer (Ho et al., 2015).

265 The diurnal patterns in carbonyls levels have been also examined. Liu et al. (2015)  
266 reported the diurnal patterns of several carbonyl species measured at PKU in urban Beijing in  
267 July 2008. Levels of HCHO, CH<sub>3</sub>CHO, and CH<sub>3</sub>COCH<sub>3</sub> peaked at noon after a daytime buildup,  
268 following the trend of O<sub>3</sub>, thus indicating the significance of secondary production during the  
269 day. These carbonyl species then reached another peak in early evening, which may be  
270 attributed to primary vehicle emissions. At Mount Tai, Yang et al. (2017) observed an evening  
271 peak in carbonyls that could be ascribed to regional transport. In addition, diurnal variations in  
272 carbonyls in some studies are not clear-cut (Cheng et al., 2014; Guo et al., 2014a; Guo et al.,  
273 2016; Huang et al., 2008; Lü et al., 2010; Rao et al., 2016; Yuan et al., 2012b). In general, the  
274 mixing ratios of carbonyls are related to many factors, including their sources (both primary  
275 emissions and secondary formation), sinks, regional transport, and meteorological conditions.  
276 Seasonal variations and diurnal patterns roughly reflect the influences of these factors on the  
277 ambient carbonyls levels.

## 278 **5. Source apportionment**

279 The sources of carbonyls are rather complex. Several methods have been used to diagnose  
280 or quantify the major sources of ambient carbonyls, and detailed information on these methods  
281 can be found in the Supplementary Materials. Here, we focus on the major findings of the  
282 source apportionment studies in a few regions.

### 283 **5.1 North China Plain**

284 Many studies have attempted to identify the principal sources of carbonyls and quantify  
285 their contributions to ambient carbonyls levels in the NCP. Although various methods have  
286 been used, source apportionment results have consistently demonstrated the dominance of the  
287 secondary formation of carbonyls in summer. For example, Pang and Mu (2006) conducted an  
288 intensive measurement campaign from November 2004 to October 2005 in urban Beijing and  
289 found a strong correlation between carbonyls and O<sub>3</sub> in summer. In addition, the calculated  
290 C<sub>1</sub>/C<sub>2</sub> ratios exhibited the highest average values (e.g., 1.94) in summer, which suggests the



291 importance of photo-oxidation of biogenic hydrocarbons. Later, during the summer of 2014,  
292 Yang et al. (2017) used the multilinear regression method and found that secondary formation  
293 made the largest contribution to the carbonyls level (except  $\text{CH}_3\text{COCH}_3$ ) at Mount Tai, a  
294 regional site in the central NCP. Liu et al. (2009) used the photochemical age-based  
295 parameterization method and found that nearly half of the  $\text{CH}_3\text{CHO}$ ,  $\text{C}_2\text{H}_5\text{CHO}$ , and  $\text{C}_3\text{H}_7\text{CHO}$   
296 in urban Beijing were attributed to secondary anthropogenic sources, whereas the measured  
297 alcohols ( $\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OH}$ ) and ketones ( $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{COC}_2\text{H}_5$  [methyl ethyl  
298 ketone]) were mainly from primary sources. Secondary formation usually made a larger  
299 contribution to reactive aldehydes than to inert alcohols and ketones. This conclusion was also  
300 confirmed by Yuan et al. (2012b), who also reported that biogenic VOCs accounted for a large  
301 part (36%) of HCHO formation at PKU in urban Beijing. In contrast, Chen et al. (2014)  
302 identified a much lower contribution of biogenic sources to HCHO at the same site based on  
303 the results of a positive matrix factorization model. The cause of this discrepancy may be that  
304 the biogenic sources identified by the positive matrix factorization model represented relatively  
305 fresh emissions, whereas secondary formation from biogenic sources was also considered by  
306 Yuan et al. (2012b).

307 In comparison, carbonyls were reported to come mainly from primary anthropogenic  
308 emissions in winter, when the photochemistry is relatively weak (Ho et al., 2015; Pang and Mu,  
309 2006). In winter 2004, Pang and Mu (2006) found a significant correlation between carbonyls  
310 and CO, an anthropogenic emission tracer, over urban Beijing, thus suggesting the importance  
311 of anthropogenic emissions (especially vehicular emissions) to carbonyls levels. Furthermore,  
312 the results of principal component analysis showed that gasoline and diesel engine exhausts  
313 are the principal components of vehicle emissions, which make an important contribution to  
314 ambient carbonyls (Rao et al., 2016). However, Chen et al. (2014) found that secondary  
315 formation dominated carbonyls sources not only in summer (with a contribution of 46.0%), but  
316 also in winter (with a contribution of 51.2%). In addition, coal burning for heat during winter  
317 was identified as an important component of primary anthropogenic emissions (Chen et al.,  
318 2014).

## 319 **5.2 Yangtze River Delta**

320 Source apportionment studies in the YRD region are relatively limited compared to those  
321 in the NCP and PRD regions. In the YRD region, primary emissions were identified as  
322 important sources of carbonyls in spring and autumn. Huang et al. (2009) reported that the  
323 ambient carbonyls in urban Shanghai in April 2008 were dominated by vehicle emissions  
324 during the day and industrial emissions at night. The importance of industrial emissions was  
325 also confirmed by Ma et al. (2016), who used a multilinear regression approach to show that  
326 industrial activities made the largest contribution (59%) to HCHO in April 2015 in an industrial  
327 zone of Zhejiang province. In contrast, Wang et al. (2015) used the same method and found  
328 that industrial emissions made a relatively smaller contribution (19%) to HCHO at a rural site  
329 in Nanjing, Jiangsu province;  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$  dominated (>50%). These results  
330 prove the variability of carbonyls sources in various parts of the YRD region. One point in  
331 common is that the contribution of photochemical formation to carbonyls was relatively low in  
332 both studies due to weaker photochemical reactions during spring and autumn in the YRD

333 region.

### 334 **5.3 Pearl River Delta**

335 Severe photochemical smog episodes are frequently observed in the PRD region during  
336 autumn because of its distinct meteorological conditions. Intensive measurement campaigns  
337 were conducted from September to November 2010 at a mountain site (TMS) and an urban site  
338 (TW) in Hong Kong (Guo et al., 2013; Ling et al., 2016). The positive matrix factorization  
339 model results were similar at these two sites. Secondary formation (including in-situ  
340 photochemical production and the transport of secondary products) was identified as the major  
341 contributor to HCHO (>50%) and CH<sub>3</sub>CHO (>45%). Meanwhile, secondary formation and  
342 vehicle emissions made the greatest contribution (>65%) to the ambient CH<sub>3</sub>COCH<sub>3</sub> level.  
343 These findings indicate the importance of photochemical formation. In addition, carbonyls  
344 were more likely to be primary emissions in urban areas than in rural areas, as confirmed by  
345 Lui et al. (2017c). In addition to autumn, Ling et al. (2017) showed strong photochemical  
346 activities in summer, but the prevailing southerly and southeasterly winds from the oceans  
347 alleviated carbonyls pollution during summer, whereas the northeasterly winds in autumn  
348 aggravated the pollution. Wang et al. (2017a) investigated the source category contributions to  
349 HCHO in different seasons. They used the photochemical age-based parameterization method  
350 and found that the contributions of biogenic sources (including both primary and secondary  
351 biogenic sources) to HCHO were much higher during summer (41%) and autumn (39%) than  
352 during spring (26%) and winter (28%). In contrast, the contributions of primary anthropogenic  
353 emissions during spring (20%) and winter (18%) were double those during summer (9%) and  
354 autumn (9%).

355 Some studies also identified primary emissions as important sources of carbonyls (Feng  
356 et al., 2005; Guo et al., 2004a; Ho et al., 2002; Lü et al., 2009; Yuan et al., 2010), so the emission  
357 profiles of vehicular emissions and biomass burning were investigated in the PRD region. Two  
358 tunnel tests were successively conducted in Hong Kong and Guangzhou (Ho et al., 2007; Zhang  
359 et al., 2016). Ho et al. (2007) reported a range of 21.7 to 68.9 mg veh<sup>-1</sup> km<sup>-1</sup> of emission factors  
360 of a combination of 15 monocarbonyls. Furthermore, HCHO presented the highest emission  
361 factor throughout the sampling period, followed by CH<sub>3</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub> (Ho et al., 2012).  
362 Higher emission factors of carbonyls were observed in summer than in winter, partly due to the  
363 higher temperature. Zhang et al. (2016) reported average emission factors of 1.18 and 0.52 mg  
364 veh<sup>-1</sup> km<sup>-1</sup> for GLY and MGLY, respectively. The higher emission factor of GLY usually  
365 accompanies a higher proportion of gasoline vehicles, whereas a higher proportion of diesel  
366 vehicles was responsible for the higher emission factors of monocarbonyls and MGLY. In  
367 addition, biomass burning was also found to exert a significant influence on ambient carbonyls  
368 in specific circumstances. Wang et al. (2016) suggested that biomass burning could serve as a  
369 primary source of OVOCs and promote the production of secondary OVOCs by emitting their  
370 precursors. Yuan et al. (2010) reported an enhancement of 10% to 18% of OVOCs during  
371 biomass burning plumes at a receptor site in the PRD region. Yuan et al. (2013) and Mo et al.  
372 (2016) both reported that OVOC emissions were significantly underestimated in the current  
373 emission inventory, possibly due to the poor understanding of the emission characteristics of  
374 nonvehicle primary sources. In addition to anthropogenic emissions, some studies have

375 reported biogenic emissions of carbonyls. In China, the total biogenic VOC emissions were  
376 reported to range from 35 to 50 Tg/y from 1981 to 2003, among which the contributions of  
377 OVOCs ranged from 30% to 40% (Li and Xie, 2014). Moreover, Guenther et al. (2012)  
378 identified CH<sub>3</sub>COCH<sub>3</sub> (43.7 Tg/y), CH<sub>3</sub>CHO (20.7 Tg/y), and HCHO (5.0 Tg/y) as the three  
379 most abundant primary biogenic carbonyl species on a global scale. However, great uncertainty  
380 remains in the evaluation of biogenic carbonyls emissions.

381 As discussed above, secondary formation generally dominated the carbonyls sources in  
382 China, but the importance of the contributions from primary emissions should not be  
383 overlooked. However, current knowledge of carbonyls sources remains far from sufficient to  
384 provide scientific support for carbonyls abatement strategies. First, the means to accurately  
385 characterize primary emissions (both anthropogenic and biogenic) is a major work underway  
386 and is urgently needed to aid in compiling the current emission inventories. Second, the  
387 photochemical formation mechanisms of some reactive carbonyl species remain poorly  
388 understood, so more relevant studies are needed.

## 389 **6. Photochemical formation mechanisms**

390 The source apportionment results elucidate the necessity to comprehensively understand  
391 the secondary formation mechanisms of carbonyls. The methods commonly used to investigate  
392 the photochemical formation mechanisms of carbonyls are based on chemical models.  
393 Investigations have included monocarbonyls, among others. Important dicarbonyls such as  
394 GLY and MGLY are also involved. Below we summarize the major findings regarding the  
395 photochemical formation mechanisms of monocarbonyls and dicarbonyls.

### 396 **6.1 Monocarbonyls**

397 In China, the photochemical formation mechanisms of monocarbonyls such as HCHO,  
398 CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, and CH<sub>3</sub>COC<sub>2</sub>H<sub>5</sub> have been investigated with an observation-based  
399 box model coupled with chemical mechanisms. Previous studies showed that models could  
400 well reproduce the diurnal variations and concentrations of secondary products such as O<sub>3</sub>,  
401 HCHO, and GLY (Li et al., 2014; Ling et al., 2017).

402 Li et al. (2014) and Ling et al. (2017) conducted field observations in the PRD region in  
403 July 2006 at a semirural site (BG) and an urban site (GPEMC), respectively, and further refined  
404 the secondary formation pathways of HCHO. Li et al. (2014) found that isoprene oxidation  
405 contributed most to the secondarily formed HCHO (43%), followed by oxidation of  
406 anthropogenic alkenes (29%), aromatics (15%), and alkanes (13%). In contrast, Ling et al.  
407 (2017) showed that alkenes (including isoprene) made an overwhelming contribution (77%) to  
408 the photochemical production of HCHO, followed by aromatics (20%) and alkanes (3%).  
409 Trans-2-butene was identified as the largest contributor (16%) of the individual VOC  
410 precursors, whereas isoprene made a smaller contribution (9.6%). The differences between the  
411 results of Li et al. (2014) and Ling et al. (2017) are likely the result of differences in the  
412 chemical compositions of first-generation VOC precursors between urban and rural areas. The  
413 photochemical formation mechanism of CH<sub>3</sub>COCH<sub>3</sub> differs greatly from that of HCHO. Guo  
414 et al. (2013) used the observation-based box model to investigate the photochemical precursors  
415 of CH<sub>3</sub>COCH<sub>3</sub> from September to November 2010 at a mountain site (TMS) and an urban site

416 (TW) in Hong Kong. C<sub>3</sub>-C<sub>6</sub> alkanes were found to be the largest contributor to the secondary  
417 formation of CH<sub>3</sub>COCH<sub>3</sub> at both sites, making an average contribution of 28.7% at TMS and  
418 54.5% at TW. This result is also consistent with that of Jacob et al. (2002), who confirmed the  
419 oxidation of C<sub>3</sub>-C<sub>5</sub> isoalkanes as a dominant source of the in situ formation of CH<sub>3</sub>COCH<sub>3</sub> in  
420 the northern hemisphere. The contributions of C<sub>2</sub>-C<sub>3</sub> alkenes to secondarily formed  
421 CH<sub>3</sub>COCH<sub>3</sub> were comparable at the two sites (20.0% at TMS and 16.1% at TW). Furthermore,  
422 the most important of all measured VOC precursors was identified to be i-butene at TMS and  
423 i-butane at TW, with the two compounds contributing 20% and 30%, respectively.

424 In the NCP region, the relationships between monocarbonyls and their precursors were  
425 also investigated using box models. As mentioned above, many observation campaigns were  
426 carried out in 2008 to improve air quality and prepare for the Beijing Olympic Games. During  
427 that period, two intensive measurements conducted from July to August 2008 were selected for  
428 comparison. These two measurements were carried out by Liu et al. (2015) in the PKU and by  
429 Yang et al. (2018) at the Chinese Research Academy of Environmental Sciences (both in urban  
430 areas). These two studies investigated the photochemical formation mechanisms of carbonyls  
431 from different perspectives. Yang et al. (2018) identified five major pathways responsible for  
432 the formation of secondary HCHO and CH<sub>3</sub>CHO: OVOC photolysis, O<sub>3</sub>+OVOCs,  
433 OH+OVOCs, radical propagation reactions, and RO+O<sub>2</sub> reactions. Of these, RO+O<sub>2</sub> reactions  
434 made the largest contribution to the in situ formation of HCHO (~85%) and CH<sub>3</sub>CHO (~70%).  
435 One point that must be clarified is that the target carbonyls were excluded from the OVOC  
436 precursors mentioned above. As for the first-generation VOC precursors, the further refinement  
437 of the RO+O<sub>2</sub> formation routes suggested that anthropogenic alkenes played an important role  
438 in the production of RO (~30%). Liu et al. (2015) investigated the photochemical formation  
439 mechanisms of carbonyls from the perspective of precursors and showed that anthropogenic  
440 alkenes made the largest contribution to the photochemical formation of HCHO (54%),  
441 CH<sub>3</sub>CHO (91%), and CH<sub>3</sub>COCH<sub>3</sub> (60%), whereas alkanes were predominantly responsible for  
442 the in situ formation of CH<sub>3</sub>COC<sub>2</sub>H<sub>5</sub> (>95%). As for individual VOC precursors, the oxidation  
443 of isoprene made the largest contribution (30%) to secondary HCHO. In addition, the loss rates  
444 of HCHO were governed both by reactions with OH and by photolysis, whereas CH<sub>3</sub>CHO  
445 losses were dominated by reactions with OH (Yang et al., 2018). Such studies of the detailed  
446 photochemical processes of carbonyls remain limited in other regions, and more efforts are  
447 needed.

## 448 **6.2 Dicarbonyls**

449 The photochemical formation mechanisms of GLY and MGLY have also been  
450 investigated (Chan Miller et al., 2016; Liu et al., 2012b; Yang et al., 2018). Fu et al. (2008)  
451 conducted a detailed simulation based on a global three-dimensional model (GEOS-Chem) and  
452 found that isoprene dominated the secondary formation of GLY and MGLY on a global scale,  
453 whereas acetylene and acetone were the second most important precursors for GLY and MGLY,  
454 respectively. However, the photochemical formation mechanisms of GLY and MGLY in China  
455 differ significantly from those on a global scale. Liu et al. (2012b) quantified the missing source  
456 of GLY in China by comparing the vertical column densities observed by SCIAMACHY and  
457 those simulated by a three-dimensional regional chemical transport model. Inverse modeling

458 was then applied to calculate the emission adjustment for each grid, and the results showed a  
459 substantial underestimation of aromatics emissions (by a factor of 4 to 10) in the VOC emission  
460 inventories over China, which well explained the missing source of GLY. Later, Chan Miller et  
461 al. (2016) identified the PRD region as a hotspot of GLY based on satellite observations from  
462 the Ozone Monitoring Instrument. In contrast with the results of Liu et al. (2012b), they found  
463 good agreement between the observed GLY enhancements and the current VOC emission  
464 inventories. The difference in the results was attributed to the combined effects of bias in the  
465 satellite data and underestimation of GLY production from aromatics oxidation. Based on  
466 MCM v3.2 (Master Chemical Mechanism, a nearly-explicit chemical mechanism), the  
467 aromatics emitted by industrial sources were determined as a dominant contributor to GLY  
468 formation in the PRD region (Chan Miller et al., 2016). Yang et al. (2018) investigated the  
469 photochemical formation mechanisms of GLY and MGLY in urban Beijing. RO+O<sub>2</sub> and  
470 OH+OVOCs reactions were identified as the dominant formation pathways for both GLY and  
471 MGLY. Furthermore, aromatics made the largest contribution of all first-generation VOC  
472 precursors to the formation of GLY (>43%) and MGLY (39%). The dominant first-generation  
473 VOC precursors responsible for secondarily formed GLY and MGLY in Beijing are similar to  
474 those identified in the PRD region (i.e., aromatics).

475 Overall, some progress has been made in gaining a better understanding of the  
476 photochemical formation mechanisms of carbonyls in China. Nonetheless, most studies have  
477 focused on the identification of important precursors; the detailed photochemical processes of  
478 carbonyls have not been fully addressed. Moreover, most work has been concentrated in the  
479 NCP and PRD regions, with few studies considering other regions of China. More work is  
480 needed to further unravel the detailed formation mechanisms of carbonyls with a wider spatial  
481 coverage in China.

## 482 **7. Effects of carbonyls on atmospheric chemistry, air quality, and human** 483 **health**

### 484 **7.1 Atmospheric oxidative capacity and radicals**

485 OVOCs play crucial roles in radical chemistry. First, they exert a significant influence on  
486 radical initiation reactions. As mentioned in Section 2, OVOC photolysis is acknowledged as  
487 a major primary source of ROx radicals. Xue et al. (2016) used box modeling analysis to  
488 quantify the radical budget of a prolonged severe photochemical smog episode in Hong Kong  
489 and found that OVOC photolysis (except for HCHO photolysis) made an overwhelming  
490 contribution (47%) to daytime primary ROx production. Moreover, the photolysis of HCHO  
491 was an important source of HO<sub>2</sub>. The dominance of OVOC photolysis to RO<sub>2</sub>+HO<sub>2</sub> production  
492 was also found in many other areas, such as Beijing, Lanzhou, and Waliguan (see Table 2 and  
493 references therein). Despite this similarity, RO<sub>2</sub>+HO<sub>2</sub> production from OVOC photolysis was  
494 much more efficient in polluted urban areas than in rural or remote areas.

495 OVOCs also play an important role in radical recycling cycles, which further influence  
496 the atmospheric oxidizing capacity. Generally, OH is the largest contributor to the atmospheric  
497 oxidizing capacity. Some studies have calculated the OH reactivity to track the contributions  
498 of various VOC groups to OH oxidation. Table 2 summarizes the related studies of OH

499 reactivity in China. In the PRD region, Lou et al. (2010) compared the measured and calculated  
500 OH reactivity and found a discrepancy of a factor of ~2. Further examination suggested that  
501 the missing reactivity was attributed to a lack of measurement data for OVOCs (mainly  
502 aldehydes and ketones), suggesting the significant contributions of carbonyls to OH reactivity.  
503 Yuan et al. (2012a) calculated that that OH reactivity was dominated by OVOCs. The  
504 dominance of OVOCs to OH reactivity in the PRD region was also confirmed by Xue et al.  
505 (2016) and Li et al. (2018) based on model simulations. In the NCP region, Yang et al. (2018)  
506 and Fuchs et al. (2017) reported the dominant contributions of OVOCs to OH reactivity. Of all  
507 OVOC species, HCHO and CH<sub>3</sub>CHO were identified as the largest contributors to OH  
508 reactivity (Duan et al., 2012; Fuchs et al., 2017; Shao et al., 2009; Yang et al., 2018). In addition,  
509 OVOCs (especially carbonyls) usually dominated OH reactivity in rural areas, whereas alkenes  
510 tended to dominate OH reactivity in urban areas. Overall, OVOCs not only behaved as a  
511 predominant radical source via photolysis but also as a major contributor to the atmospheric  
512 oxidizing capacity via OH-initiated degradation.

## 513 **7.2 O<sub>3</sub> formation**

514 The worsening O<sub>3</sub> pollution situation has caused wide public concern, and many studies  
515 have investigated O<sub>3</sub>-precursor relationships (e.g., Duan et al., 2008; Tan et al., 2018; Wang et  
516 al., 2018; Xue et al., 2014; Xue et al., 2013). However, most studies have focused on  
517 hydrocarbons; relatively limited attention has been paid to the contributions of OVOCs to O<sub>3</sub>.  
518 A close relationship has been assumed to exist between O<sub>3</sub> and OVOCs because high levels of  
519 O<sub>3</sub> and OVOCs are often monitored concurrently during photochemical pollution episodes  
520 (Wang et al., 2018; Yang et al., 2017). A clear understanding of the role played by carbonyls  
521 during O<sub>3</sub> formation is essential for air pollution control.

522 Based on the PBM-MCM model, Wang et al. (2018) found that HCHO photolysis  
523 dominated HO<sub>2</sub> formation and that HO<sub>2</sub> then further oxidizes NO to NO<sub>2</sub>, facilitating the  
524 formation of O<sub>3</sub>. Some studies evaluated the O<sub>3</sub>-precursor relationships based upon O<sub>3</sub>  
525 formation potential (OFP) calculations and model sensitivity tests. Yuan et al. (2012a)  
526 calculated the OFP of various VOC groups measured in the PRD region and found that  
527 aromatics made the largest contribution to the OFP at most urban sites, whereas carbonyls  
528 usually dominated the OFP in rural areas. In contrast, Duan et al. (2008) found that carbonyls  
529 dominated the OFP (40%) at an urban site in Beijing. This discrepancy reveals the different  
530 formation regimes of O<sub>3</sub> in various regions of China. However, one common conclusion is that  
531 of the carbonyl species, HCHO and CH<sub>3</sub>CHO usually exhibited the highest OFP due to their  
532 relatively high reactivity and abundance. Some studies were based on model-calculated relative  
533 incremental reactivity. Yang et al. (2018) identified carbonyls as the most sensitive precursors  
534 responsible for O<sub>3</sub> formation in Beijing. Wang et al. (2018) calculated the relative incremental  
535 reactivity values for each VOC precursor to O<sub>3</sub> production over the South China Sea. They  
536 showed that HCHO exhibited the highest relative incremental reactivity value on both episode  
537 days and non-episode days (Here, the episode days refer to days with maximum hourly average  
538 O<sub>3</sub> value exceeding 100 ppbv [China's Grade II Standard]). Cutting carbonyls emissions would  
539 be an effective way to alleviate O<sub>3</sub> pollution in these regions.

540 The studies mentioned above have demonstrated that carbonyls make important

541 contributions to O<sub>3</sub> formation. These findings are useful for the formulation of effective ozone  
542 pollution control strategies. However, most of these studies have focused on the sensitivity of  
543 O<sub>3</sub> formation to the bulk of carbonyls, to which secondary formation contributed a large  
544 proportion. Control policies can only reduce primary emissions. Thus, more efforts are needed  
545 to better quantify the contributions of primary carbonyl species to O<sub>3</sub> formation in China.

### 546 **7.3 SOA formation**

547 Heterogeneous reactions are an important sink of carbonyls and an important source of  
548 SOA. As previously mentioned, GLY and MGLY usually exhibit high levels in China. These  
549 two small dicarbonyls have relatively high reactivity and water solubility (Shen et al., 2013;  
550 and references therein). They can easily hydrate and polymerize even at low humidity. This  
551 distinct feature makes GLY and MGLY important contributors to SOA formation. Fu et al.  
552 (2008) added the known sources and sinks of GLY and MGLY to the GEOS-Chem model and  
553 found that the yield of global SOA increased by 38%, thus indicating their significant  
554 contributions to SOA formation on a global scale.

555 Investigations of the relationships between carbonyls and SOA formation in China are  
556 relatively limited. Yuan et al. (2013) reported a discrepancy between measured and calculated  
557 SOA and attributed it partly to the lack of measurement data for GLY. Li et al. (2013a) improved  
558 the representation of the gas-phase and aqueous-phase chemistry of dicarbonyls (GLY and  
559 MGLY) in the community multiscale air quality (CMAQ) modeling system to simulate SOA  
560 levels over the PRD region and made comparisons with observations. The simulated average  
561 SOA concentration was in better agreement with the observed mean SOA concentration after  
562 the improvement. Furthermore, dicarbonyls were found to make a large contribution (~53%)  
563 to the simulated surface SOA formation, mainly via irreversible uptake by aqueous particles,  
564 whereas the contributions of dicarbonyls to SOA via gas-phase reactions can be negligible (Li  
565 et al., 2013a). This finding was consistent with that of Hu et al. (2017), who used the CMAQ  
566 model to study the tempo-spatial distribution of SOA in China and found that the reactive  
567 surface uptake of GLY and MGLY was an important formation pathway for SOA, with  
568 respective contributions of 14% to 25% and 23% to 28%.

569 Some laboratory experiments have also investigated the roles of monocarbonyls in SOA  
570 formation. The heterogeneous reactions of carbonyls can occur on various aerosol surfaces,  
571 including mineral particles, sea salt, and soot particles. Therefore, some laboratory studies have  
572 provided reliable uptake coefficients and identified the reaction products under various  
573 conditions (Shen et al., 2013; and references therein). Some studies have also attempted to  
574 quantify the contributions of some monocarbonyls to SOA formation. For example, assuming  
575 the partition efficiency of both oxalic and malonic acid to be 100%, the aqueous OH-oxidation  
576 of methacrolein and methyl vinyl ketone was reported to make maximum contributions of 8.8%  
577 and 23.8% to SOA formation, respectively, after a 7-h reaction (Zhang et al., 2010). However,  
578 the detailed formation mechanisms of SOA from carbonyls across China remain unclear and  
579 warrant further investigation.

### 580 **7.4 Human health**

581 The World Health Organization has classified several carbonyl species (e.g., HCHO and

582 CH<sub>3</sub>CHO) as toxic air pollutants and even human carcinogens. In the last two decades, the  
583 Chinese government has issued a series of standards to regulate indoor exposure to toxic  
584 carbonyl species, but few focused on outdoor carbonyls. Indoor carbonyls often exhibit high  
585 levels, and some even exceed the national standard (Huang et al., 2011; Lü et al., 2016; Lui et  
586 al., 2017b; Wang et al., 2007; Weng et al., 2009). Therefore, studies have been conducted to  
587 investigate the detrimental effects of both indoor and outdoor carbonyls on human health in  
588 China.

589 Based on numerous experimental studies and historical data, Cogliano et al. (2005)  
590 confirmed the carcinogenicity (e.g., nasopharyngeal cancer, leukemia, and sinonasal cancer) of  
591 HCHO in humans and animals. The acute and chronic toxicity effects of HCHO apart from  
592 carcinogenicity were also investigated (Cogliano et al., 2005; Tang et al., 2009; and references  
593 therein). Such laboratory studies of other carbonyl species are very scarce in China, and more  
594 investigations are urgently needed. In addition, few studies have focused on personal exposure  
595 levels and risk assessments. For example, Ho et al. (2015) conducted field studies in nine  
596 Chinese cities and assessed the potential health risks of HCHO and CH<sub>3</sub>CHO using a simple  
597 risk-calculation model. High cumulative cancer risks were found in summer in all cities except  
598 for Xiamen, a coastal city in southeast China. Furthermore, the highest risk was observed at  
599 Chengdu in summer and Wuhan in winter. High exposure and health risks of HCHO and  
600 CH<sub>3</sub>CHO were also found in public places in Hangzhou and Shanghai (Feng et al., 2010; Weng  
601 et al., 2009). In addition, Ho et al. (2014b), Huang et al. (2011), and Lü et al. (2016) investigated  
602 the health risks of indoor carbonyls at a university in Xiamen, two residential kitchens in Hong  
603 Kong, and a library in Guangzhou, respectively. Each identified HCHO exposure as a valid  
604 occupational health and safety concern. Furthermore, Tang et al. (2009) elucidated the indoor  
605 and outdoor exposure levels and health effects of HCHO across China in detail. Overall, these  
606 limited results revealed the high risk of exposure to carbonyls in China. More studies of the  
607 health impact of carbonyls are needed, and essential measures to protect human health should  
608 be taken.

## 609 **8. Summary and outlook**

610 Significant progress has been achieved in the last 20 years in the study of ambient  
611 carbonyls in China's atmosphere. A number of field observations have been conducted at  
612 various surface sites across China. The results have revealed the severity and tempo-spatial  
613 variations of carbonyls pollution in China. Photochemical formation was identified as the  
614 dominant source of ambient carbonyls, but primary emissions also made important  
615 contributions in specific circumstances. Alkenes, aromatics, and isoprene usually dominated  
616 the secondary formation of carbonyls. Carbonyls are acknowledged as important precursors of  
617 O<sub>3</sub> and SOA. For O<sub>3</sub>, carbonyls usually dominate the OFP in rural areas, and for SOA,  
618 dicarbonyls such as GLY and MGLY make important contributions to SOA formation, mainly  
619 via irreversible uptake by aqueous particles. In addition, few studies have revealed the high  
620 exposure and health risk of both indoor and outdoor carbonyls in China.

621 Despite the abovementioned progress, more efforts are still needed to gain a thorough  
622 understanding of the role of carbonyls in tropospheric chemistry, O<sub>3</sub> and SOA formation, and  
623 human health. The following directions are recommended for future study.



- 624 (1) The current field observations remain far from sufficient to comprehensively reflect  
625 the carbonyls pollution situation across China. Although high-molecular weight  
626 carbonyls play a significant role in aerosol formation, the observational data available  
627 are very scarce because they are largely partitioned into the particle phase and thus  
628 exhibit low gas-phase concentrations. More studies should be conducted to investigate  
629 the characteristics of high-molecular weight carbonyls. Furthermore, the vertical  
630 distribution profiles for gaseous carbonyls remain unclear. In addition, most ground  
631 observations have been concentrated in fast-developing regions, such as the NCP,  
632 YRD, and PRD. It is strongly suggested that more field studies be conducted on other  
633 overpopulated and fast-developing regions. This suggestion also applies to other more  
634 reactive carbonyl species that should receive more attention.
- 635 (2) The emission patterns of primary sources (especially the non-vehicle primary sources)  
636 remain poorly understood. The combined efforts of the research community and  
637 government agencies are needed to accurately characterize the primary emissions and  
638 develop a national species-specific carbonyls emission inventory in China.
- 639 (3) Most studies have focused on identifying dominant precursors; little attention has been  
640 paid to the detailed photochemical formation processes of carbonyls. To some extent,  
641 such an investigation is impeded by the accurate representation of chemical  
642 mechanisms of carbonyls in models, which is still considered a difficulty in current  
643 research. We recommend that more laboratory experiments be conducted to update the  
644 chemical mechanisms that can be incorporated into models to better identify dominant  
645 precursors and investigate the detailed photochemical formation mechanisms of  
646 carbonyls. It can also help to precisely quantify the contributions of isoprene and other  
647 important biogenic VOCs to carbonyls.
- 648 (4) Due to the limitations of observation techniques, few studies have focused on the  
649 effects of carbonyls on O<sub>3</sub> and SOA. Ways of better dissecting the contributions of  
650 primary and secondary carbonyls to O<sub>3</sub> and better understanding the formation  
651 mechanisms of SOA from carbonyls remain significant challenges that require further  
652 investigation. In addition, research and control policy making should attach equal  
653 importance to indoor and outdoor exposure to carbonyls.

## 654 **Acknowledgements**

655 This work was funded by the National Natural Science Foundation of China (41675118,  
656 91544213), the National Key Research and Development Program of China  
657 (2016YFC0200500), the Qilu Youth Talent Program of Shandong University, the Jiangsu  
658 Collaborative Innovation Center for Climate Change, and the Taishan Scholars (ts201712003).

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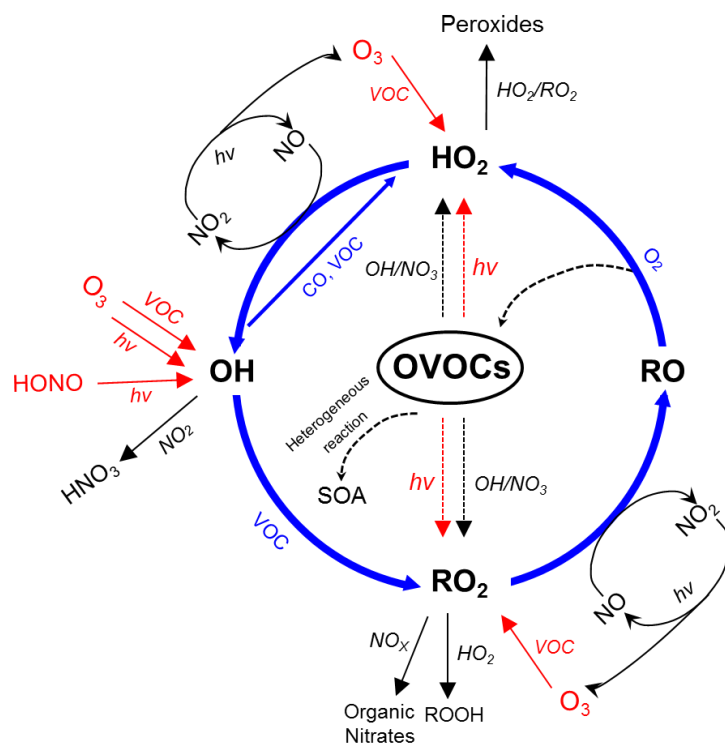
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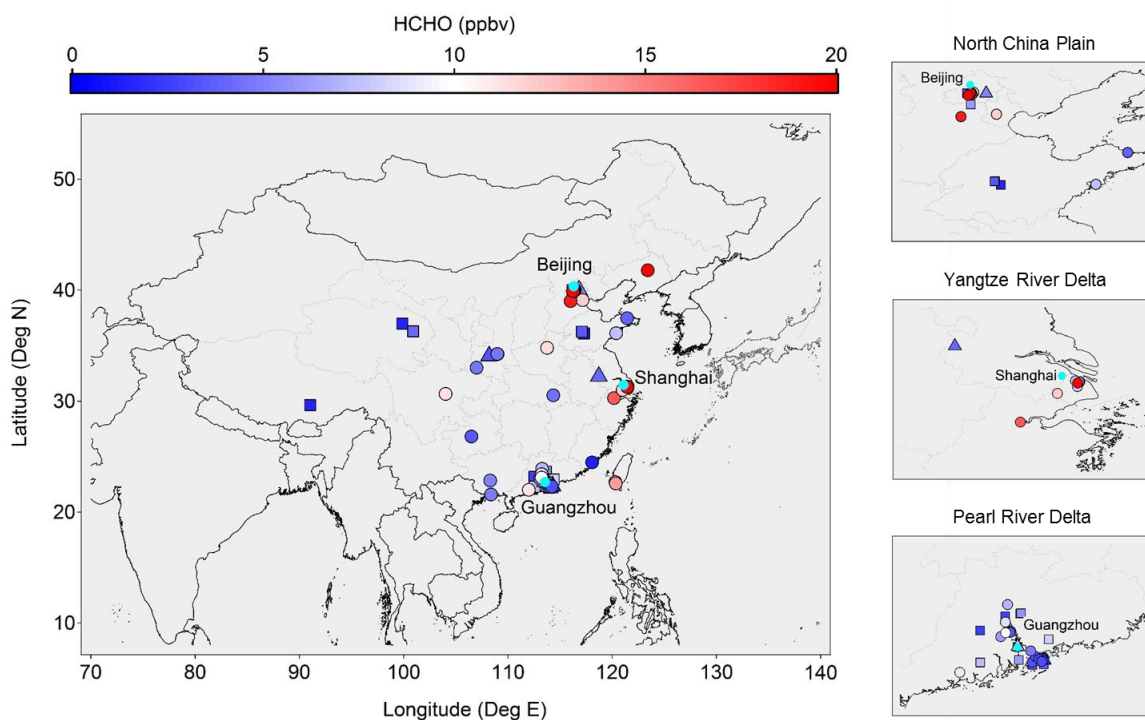
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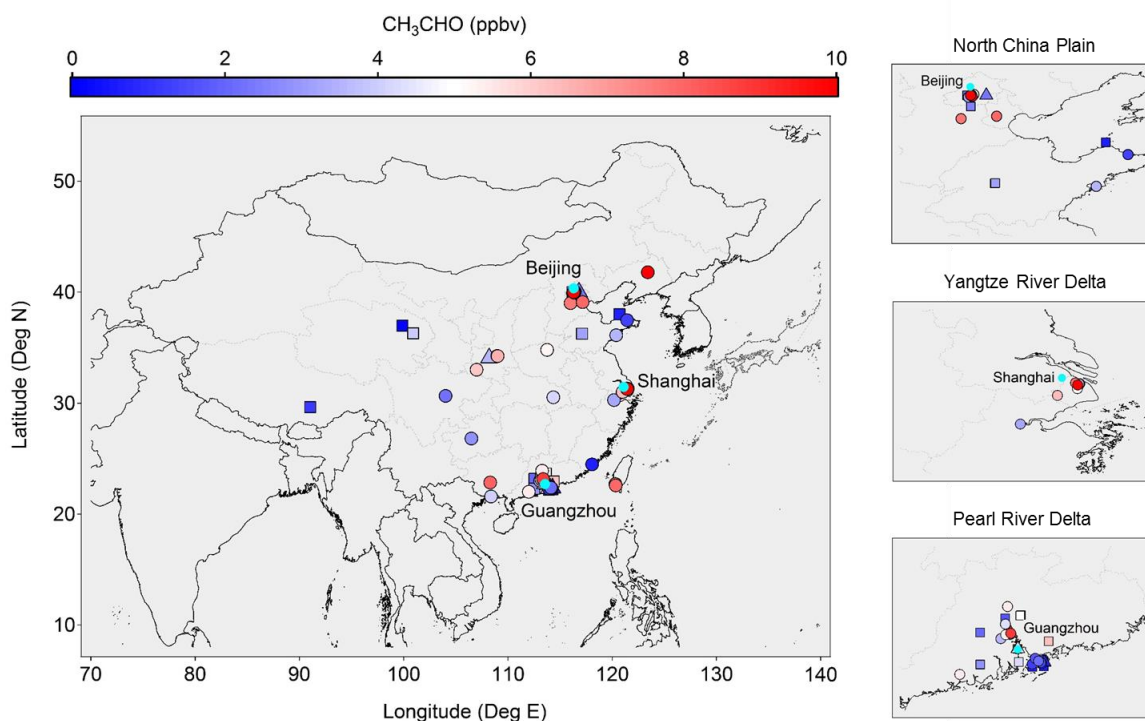
1007 **Figure 1.** Major chemical processes of OVOCs in the atmosphere. The red and blue lines  
 1008 indicate the initiation and recycling pathways of radicals. The dotted lines indicate chemical  
 1009 processes in which OVOCs directly involved.



1010

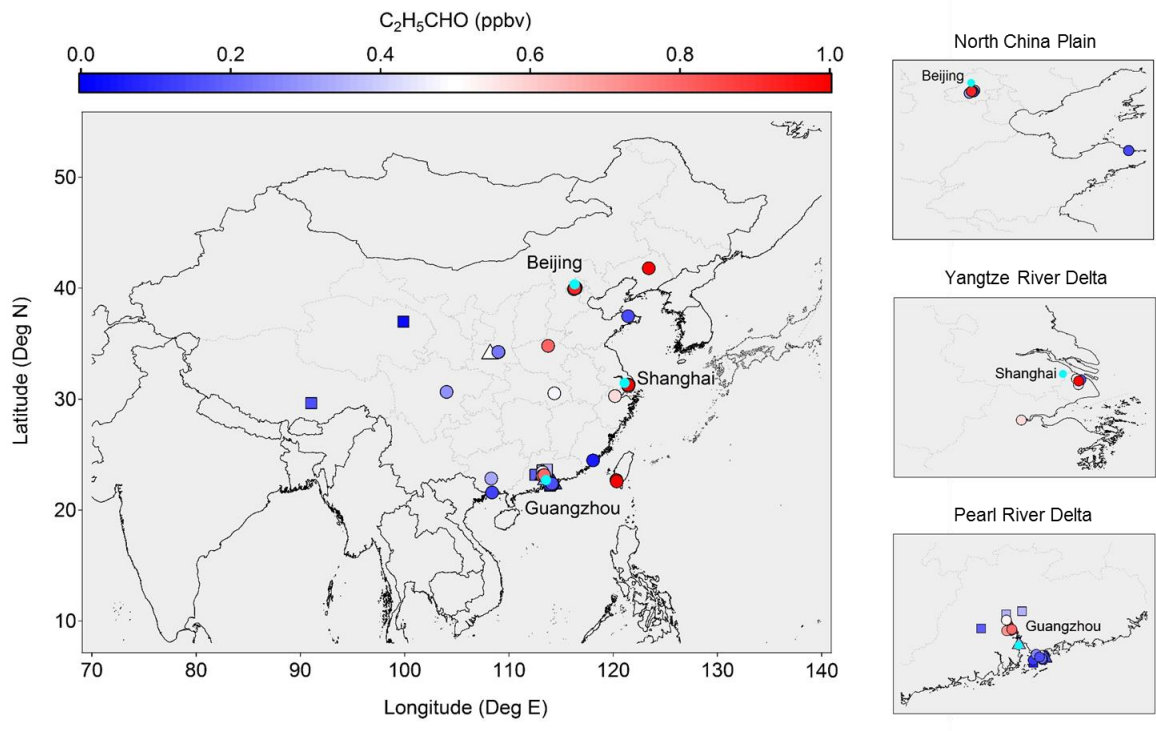
1011 **Figure 2a.** Spatial distributions of HCHO levels (ppbv) in China. Urban, suburban, rural sites  
 1012 are marked as circles, triangles and squares, respectively. The observation data are taken from

1013 Altemose et al. (2015), Cheng et al. (2014), Chi et al. (2008), Dai et al. (2012), Duan et al.  
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1020 al. (2011), Tan et al. (2002), Wang et al. (2007), Wang et al. (2009a), Wang et al. (2017a), Wang  
1021 et al. (2010a), Wang et al. (2014a), Wang et al. (2010b), Weng et al. (2009), Xu et al. (2010),  
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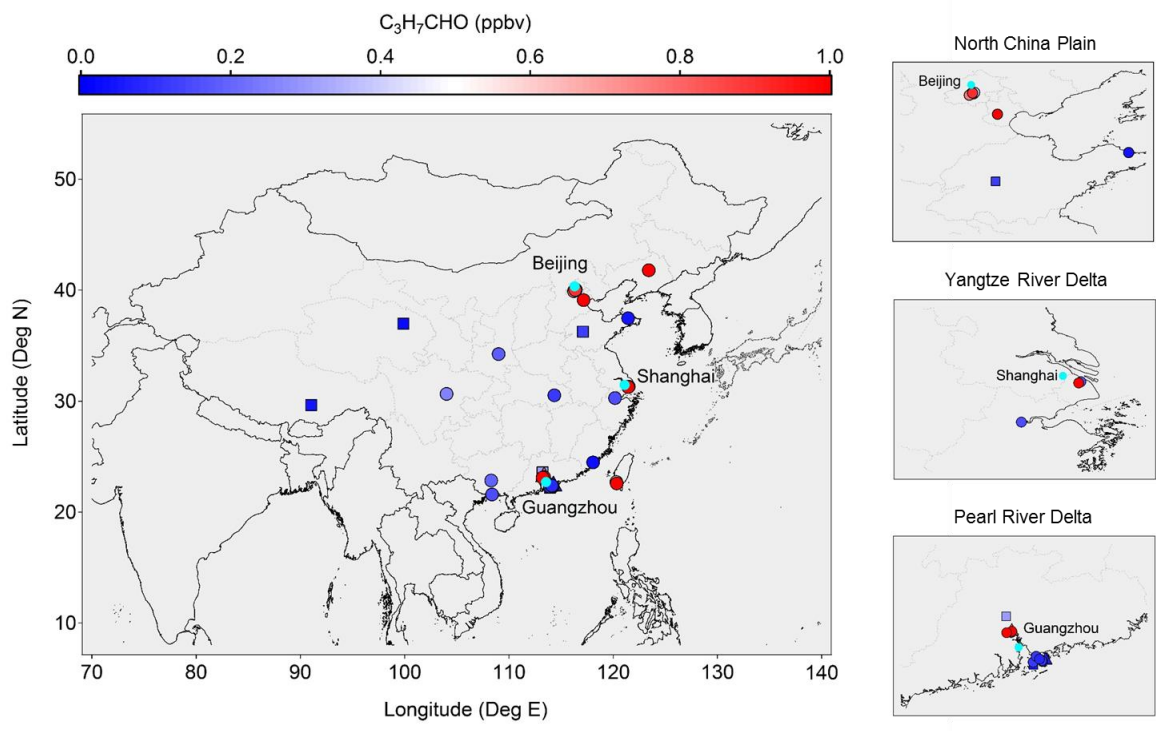
1023  
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**Figure 2b.** The same to Figure 2a but for  $\text{CH}_3\text{CHO}$ .



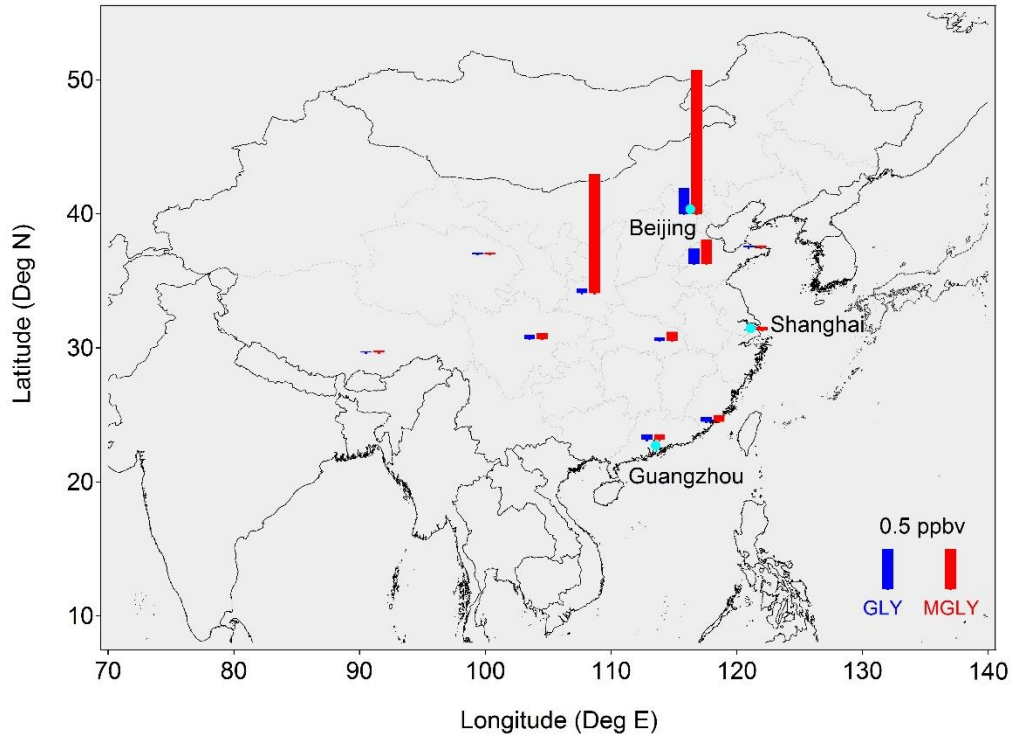
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**Figure 2c.** The same to Figure 2a but for  $C_2H_5CHO$ .

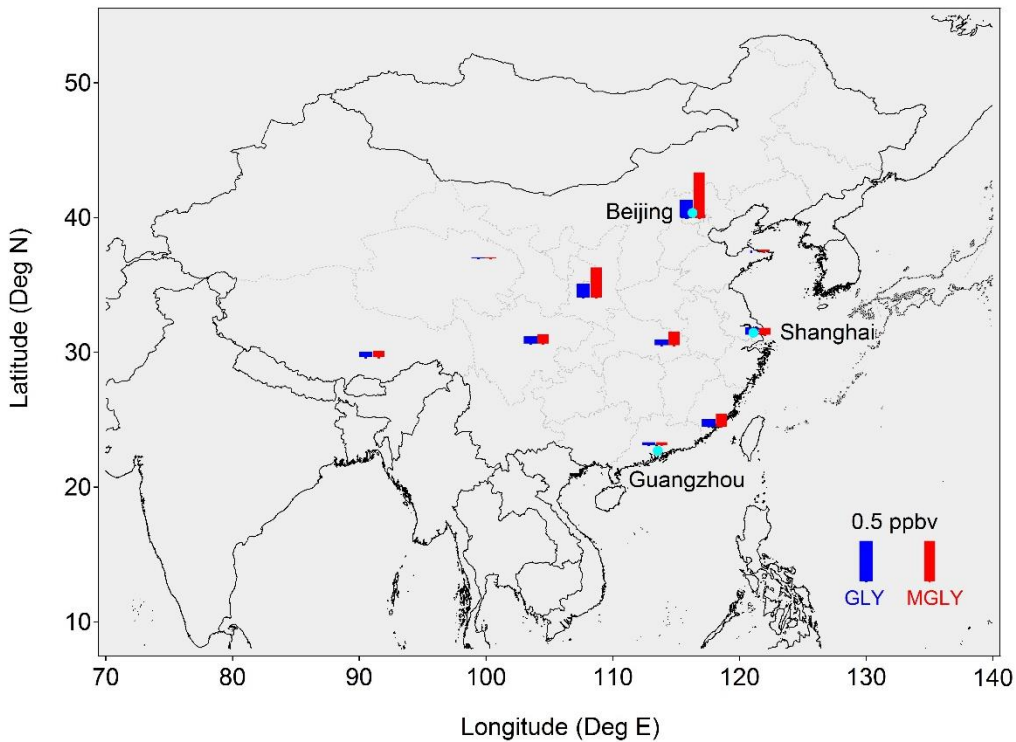


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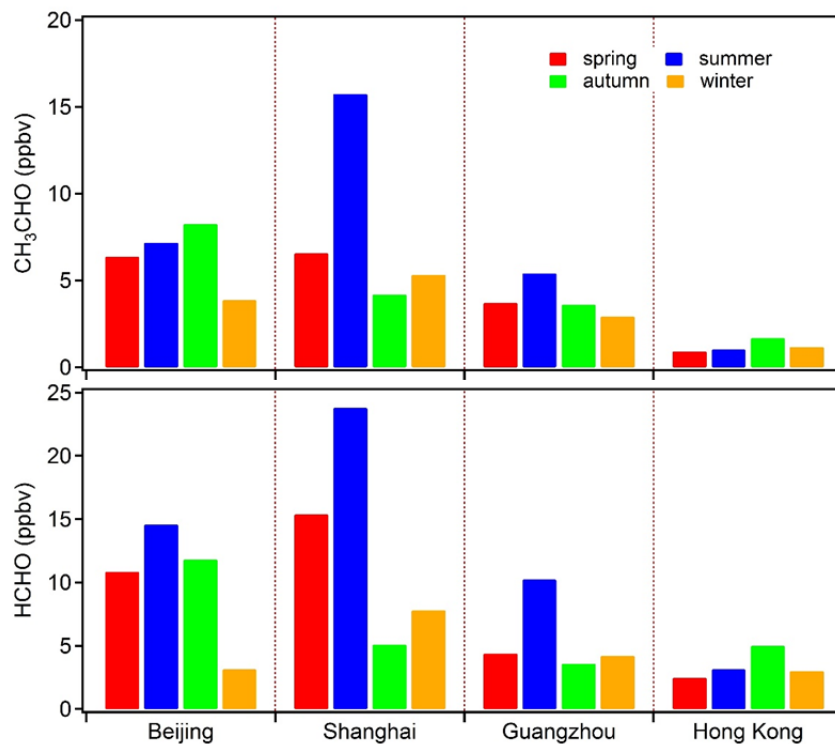
**Figure 2d.** The same to Figure 2a but for  $C_3H_7CHO$ .



1029  
 1030 **Figure 3a.** Spatial distributions of GLY and MGLY levels (ppbv) in China in summer. The  
 1031 observation data are taken from Ho et al. (2014a), Ho et al. (2015), Kawamura et al. (2013),  
 1032 Lui et al. (2017a), and Rao et al. (2016).



1033  
 1034 **Figure 3b.** The same to Figure 3a but for data in winter.



1035  
 1036 **Figure 4.** Seasonal variations of HCHO and CH<sub>3</sub>CHO in Beijing, Shanghai, Guangzhou, and  
 1037 Hong Kong, respectively. The observation data are taken from Huang et al. (2008), Lü et al.  
 1038 (2010), Lui et al. (2017c), and Pang and Mu (2006).

**Table 1.** Summary of basic information of major carbonyl species that have ever been observed in China.

Species	Molecular formula	J (s <sup>-1</sup> )	Methods available	K <sub>OH</sub> (× 10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
Formaldehyde	HCHO	9.02 × 10 <sup>-5</sup>	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: PTR-MS, PTR-TOF-MS, PTR-ID-CIMS, LP-DOAS, MAX-DOAS;	8.5
Acetaldehyde	CH <sub>3</sub> CHO	7.31 × 10 <sup>-6</sup>	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: PTR-MS, PTR-TOF-CIMS, PTR-TOF-MS;	15.3
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	-	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS, PTR-TOF-CIMS, PTR-TOF-MS;	0.18
Acrolein	CH <sub>2</sub> CHCHO	1.42 × 10 <sup>-6</sup>	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS;	21.6
Propionaldehyde	C <sub>2</sub> H <sub>5</sub> CHO	1.18 × 10 <sup>-5</sup>	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: GC-MS/FID;	18.7
Crotonaldehyde	CH <sub>3</sub> CHCHCHO	6.61 × 10 <sup>-6</sup>	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS;	36
Methacrolein	CH <sub>2</sub> C(CH <sub>3</sub> )CHO	-	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS;	32
Methyl ethyl ketone	CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub>	-	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS, PTR-TOF-CIMS, PTR-TOF-MS;	1.1
Butyraldehyde	C <sub>3</sub> H <sub>7</sub> CHO	1.98 × 10 <sup>-5</sup>	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: GC-MS/FID;	23.7
Benzaldehyde	C <sub>6</sub> H <sub>5</sub> CHO	3.12 × 10 <sup>-4</sup>	Offline: DNPH-HPLC, PFPH-TD-GC/MS;	12.6
Pentanal	C <sub>4</sub> H <sub>9</sub> CHO	1.80 × 10 <sup>-5</sup>	Offline: DNPH-HPLC; Online: PTR-MS;	26.6
m-Tolualdehyde	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	-	Offline: DNPH-HPLC;	16.8
Hexaldehyde	C <sub>5</sub> H <sub>11</sub> CHO	2.41 × 10 <sup>-5</sup>	Offline: DNPH-HPLC;	28.5

Cyclohexanone	C <sub>6</sub> H <sub>10</sub> O	-	Offline: DNPH-HPLC;	6.4
p-Tolualdehyde	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	-	Offline: DNPH-HPLC;	16.8
o-Tolualdehyde	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	2 × 10 <sup>-4</sup>	Offline: DNPH-HPLC;	18.9
2,5-Dimethyl-benzaldehyde	(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	-	Offline: DNPH-HPLC;	31.5
Heptaldehyde	C <sub>6</sub> H <sub>13</sub> CHO	1.13 × 10 <sup>-5</sup>	Offline: DNPH-HPLC, PFPH-TD-GC/MS;	29.6
Octylaldehyde	C <sub>8</sub> H <sub>16</sub> O	-	Offline: DNPH-HPLC, PFPH-TD-GC/MS;	30
Nonanaldehyde	C <sub>9</sub> H <sub>18</sub> O	-	Offline: DNPH-HPLC;	32
Decylaldehyde	C <sub>10</sub> H <sub>20</sub> O	-	Offline: DNPH-HPLC;	30
Undecanal	C <sub>11</sub> H <sub>22</sub> O	-	Offline: DNPH-HPLC;	-
Methyl vinyl ketone	CH <sub>3</sub> COCHCH <sub>2</sub>	-	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-TOF-CIMS, PTR-MS;	3.9
Glyoxal	CHOCHO	1.40 × 10 <sup>-4</sup>	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: MAX-DOAS;	9
Methylglyoxal	CHOCOCH <sub>3</sub>	1.45 × 10 <sup>-4</sup>	Offline: DNPH-HPLC, PFPH-TD-GC/MS;	13

The  $k_{OH}$  values were under conditions of 298 K and 1 bar; the  $k_{OH}$  values and photolysis frequencies are taken from Calvert et al. (2011) and Mellouki et al. (2015).



**Table 2.** Summary of studies of radical source and OH reactivity in China.

Site	Measurement period	Type	Dominant primary source of OH	Dominant contributor to OH reactivity	Dominant primary source of HO <sub>2</sub>	Dominant primary source of RO <sub>2</sub>	Reference
<sup>a</sup> CRAES, Beijing	Jul.-Aug. 2008	Urban	O <sub>3</sub> photolysis	OVOCs	OVOCs photolysis	OVOCs photolysis	Yang et al. (2018)
<sup>a</sup> PKU, Beijing	Aug. 2005	Urban	-	Alkenes	-	-	Shao et al. (2009)
	Aug. 2006	Urban	-	OVOCs	-	-	Shao et al. (2009)
	Aug. 2007	Urban	HONO photolysis	-	OVOCs photolysis	OVOCs photolysis	Liu et al. (2012a)
Yufa, Beijing	Aug. 2006	Rural	-	Alkenes, OVOCs	-	-	Shao et al. (2009)
Mazhuang, Tai'an	Jul. 2007	Rural	O <sub>3</sub> photolysis	-	-	-	Wang et al. (2010b)
Wangdu, Hebei	Jun.-Jul. 2014	Rural	-	OVOCs	-	-	Fuchs et al. (2017)
<sup>a</sup> FDU, Shanghai	Apr.-Aug. 2013	Urban	HONO photolysis	-	-	-	Nan et al. (2017)
Baiyunshan, Guangzhou	Jul. 2006	Urban	-	Alkenes	-	-	Yuan et al. (2012a)
Huijingcheng, Foshan	Jul. 2006	Urban	-	Alkenes	-	-	Yuan et al. (2012a)
Wanqingsha, Guangzhou	Jul. 2006	Suburban	-	OVOCs	-	-	Yuan et al. (2012a)
Tangjia, Zhuihai	Jul. 2006	Rural	-	Isoprene	-	-	Yuan et al. (2012a)
Tianhu, Guangzhou	Oct.-Nov. 2008	Rural	-	OVOCs	-	-	Yuan et al. (2012a)
Jinguowan, Huizhou	Jul. 2006	Rural	-	OVOCs	-	-	Yuan et al. (2012a)
Jaingmen	Oct.-Nov. 2008	Rural	-	OVOCs	-	-	Yuan et al. (2012a)

Hok Tsui, Hongkong	2012	Rural	O <sub>3</sub> photolysis	OVOCs	OVOCs photolysis	OVOCs photolysis	Li et al. (2018)
Tung Chung, Hongkong	Aug. 2011	Suburban	HONO photolysis	OVOCs	OVOCs photolysis	OVOCs photolysis	Xue et al. (2016)
Shenzhen	Summer, 2016	Urban	HONO photolysis	-	-	-	Wang et al. (2017a)
Chengdu	Sep.-Oct. 2016	Suburban	-	Alkenes	-	-	Tan et al. (2018)
Lanzhou	Jun.-Aug. 2013	Urban	O <sub>3</sub> photolysis	-	HCHO photolysis	OVOCs photolysis	Jia et al. (2018)
Lanzhou	Jun.-Aug. 2013	Industrial	O <sub>3</sub> photolysis	-	HCHO photolysis	OVOCs photolysis	Jia et al. (2018)
Mt. Waliguan	Apr.-May and Jul.-Aug. 2003	Mountain	O <sub>3</sub> photolysis	-	HCHO photolysis	OVOCs photolysis	Xue et al. (2013)

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<sup>a</sup> CRAES: Chinese Research Academy of Environmental Sciences; PKU: Peking University; FDU: Fudan University;