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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 (O₃) 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 O₃ 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 O₃ formation, mainly via HO₂+NO or RO₂+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 (O₃) 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 O₃ 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 O₃ 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 O₃ because it is regarded as the principal constituent of photochemical
55 smog (Wang et al., 2017b; and references therein). In the lower troposphere, O₃ is formed
56 mainly via photochemical reactions that involve volatile organic compounds (VOCs) and
57 nitrogen oxides (NO_x) (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 O₃ 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 O₃ 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 10³ M atm⁻¹, 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+O₂ 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 (RO₂), which then rapidly oxidize NO into NO₂ and form
113 RO radicals (Atkinson and Arey, 2003; Seco et al., 2007). Carbonyls can then be formed by
114 reactions of RO+O₂. 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 HO₂ and RO₂ 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_x

122 chemical cycle, oxidizing NO to NO₂ and thus affecting O₃ 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 RO₂. 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 O₃/NO₃, 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 (CH₃CHO), and acetone
209 (CH₃COCH₃) 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 O₃ 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 CH₃CHO (exceeding 10 ppbv), and CH₃COCH₃ (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 (C₂H₅CHO), butyraldehyde (C₃H₇CHO), 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 C₂H₅CHO (>1 ppbv) and C₃H₇CHO (>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+CH₃CHO+CH₃COCH₃) 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 CH₃CHO 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 ¹³C isotope evidence by Guo and Chen (2013). In Hong Kong, both HCHO and
256 CH₃CHO 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 CH₃CHO 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, CH₃CHO, and CH₃COCH₃ peaked at noon after a daytime buildup,
268 following the trend of O₃, 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 O₃ in summer. In addition, the calculated
290 C₁/C₂ 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 CH_3COCH_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 CH_3CHO , $\text{C}_2\text{H}_5\text{CHO}$, and $\text{C}_3\text{H}_7\text{CHO}$
296 in urban Beijing were attributed to secondary anthropogenic sources, whereas the measured
297 alcohols (CH_3OH and $\text{C}_2\text{H}_5\text{OH}$) and ketones (CH_3COCH_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; CH_3CHO and CH_3COCH_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 CH₃CHO (>45%). Meanwhile, secondary formation and
342 vehicle emissions made the greatest contribution (>65%) to the ambient CH₃COCH₃ 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⁻¹ km⁻¹ of emission factors
360 of a combination of 15 monocarbonyls. Furthermore, HCHO presented the highest emission
361 factor throughout the sampling period, followed by CH₃CHO and CH₃COCH₃ (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⁻¹ km⁻¹ 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_3COCH_3 (43.7 Tg/y), CH_3CHO (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_3CHO , CH_3COCH_3 , and $\text{CH}_3\text{COC}_2\text{H}_5$ 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_3 ,
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_3COCH_3 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_3COCH_3 from September to November 2010 at a mountain site (TMS) and an urban site

416 (TW) in Hong Kong. C₃-C₆ alkanes were found to be the largest contributor to the secondary
417 formation of CH₃COCH₃ 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 C₃-C₅ isoalkanes as a dominant source of the in situ formation of CH₃COCH₃ in
420 the northern hemisphere. The contributions of C₂-C₃ alkenes to secondarily formed
421 CH₃COCH₃ 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 CH₃CHO: OVOC photolysis, O₃+OVOCs,
433 OH+OVOCs, radical propagation reactions, and RO+O₂ reactions. Of these, RO+O₂ reactions
434 made the largest contribution to the in situ formation of HCHO (~85%) and CH₃CHO (~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+O₂ 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 CH₃CHO (91%), and CH₃COCH₃ (60%), whereas alkanes were predominantly responsible for
442 the in situ formation of CH₃COC₂H₅ (>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 CH₃CHO
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+O₂ 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 HO₂. The dominance of OVOC photolysis to RO₂+HO₂ 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, RO₂+HO₂ 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 CH₃CHO 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 O₃ formation**

514 The worsening O₃ pollution situation has caused wide public concern, and many studies
515 have investigated O₃-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 O₃.
518 A close relationship has been assumed to exist between O₃ and OVOCs because high levels of
519 O₃ 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 O₃ formation is essential for air pollution control.

522 Based on the PBM-MCM model, Wang et al. (2018) found that HCHO photolysis
523 dominated HO₂ formation and that HO₂ then further oxidizes NO to NO₂, facilitating the
524 formation of O₃. Some studies evaluated the O₃-precursor relationships based upon O₃
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 O₃ in various regions of China. However, one common conclusion is that
531 of the carbonyl species, HCHO and CH₃CHO 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 O₃ formation in Beijing. Wang et al. (2018) calculated the relative incremental
535 reactivity values for each VOC precursor to O₃ 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 O₃ value exceeding 100 ppbv [China's Grade II Standard]). Cutting carbonyls emissions would
539 be an effective way to alleviate O₃ pollution in these regions.

540 The studies mentioned above have demonstrated that carbonyls make important

541 contributions to O₃ 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 O₃ 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 O₃ 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 CH₃CHO) 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 CH₃CHO 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 CH₃CHO 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 O₃ and SOA. For O₃, 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, O₃ 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 O₃ and SOA. Ways of better dissecting the contributions of
650 primary and secondary carbonyls to O₃ 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.

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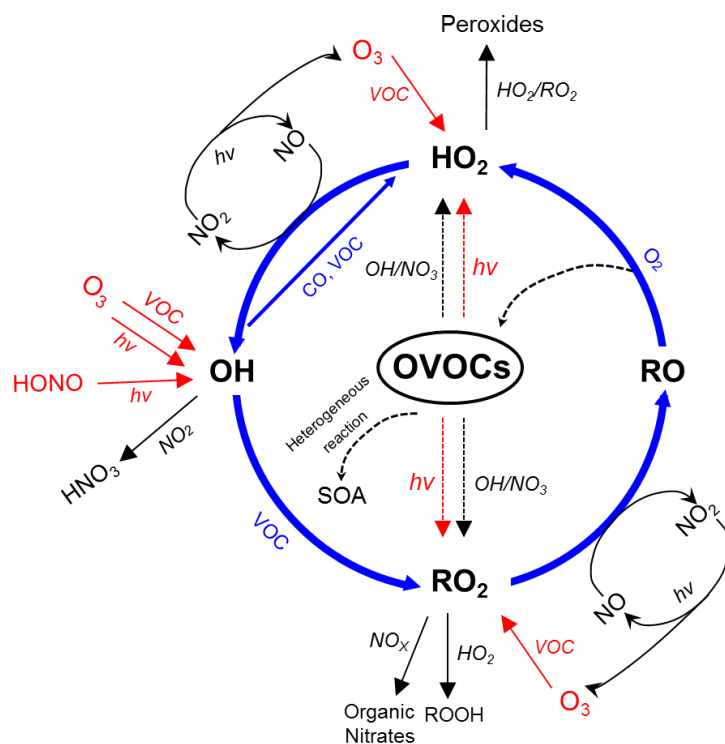
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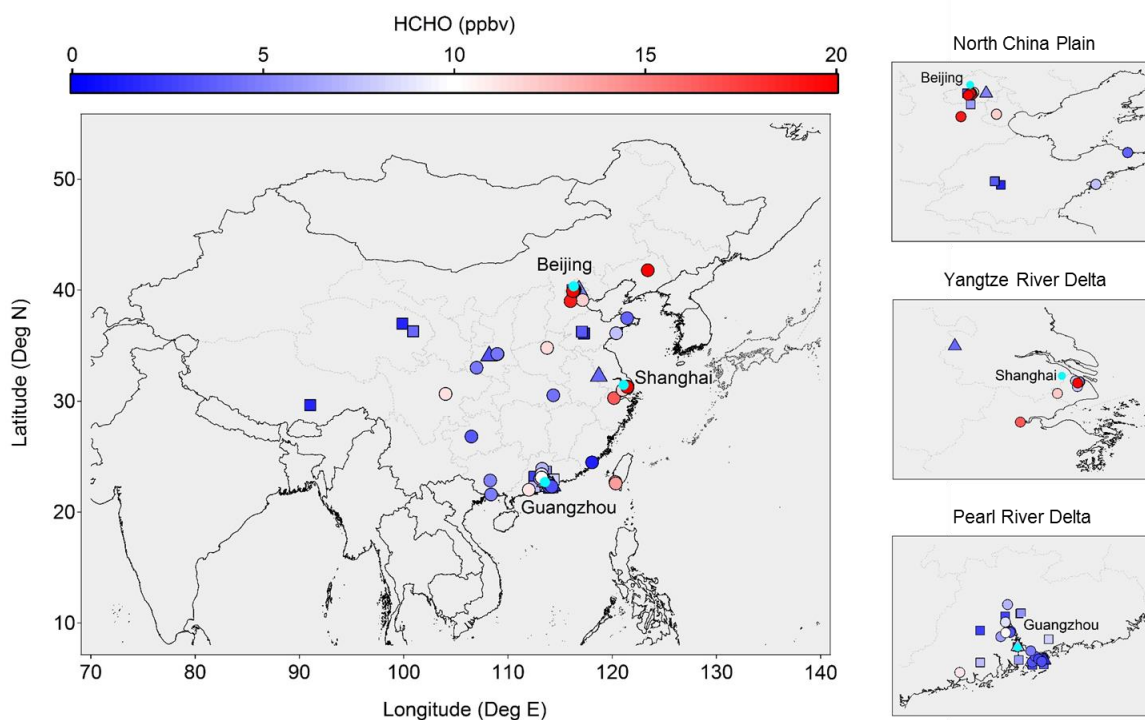
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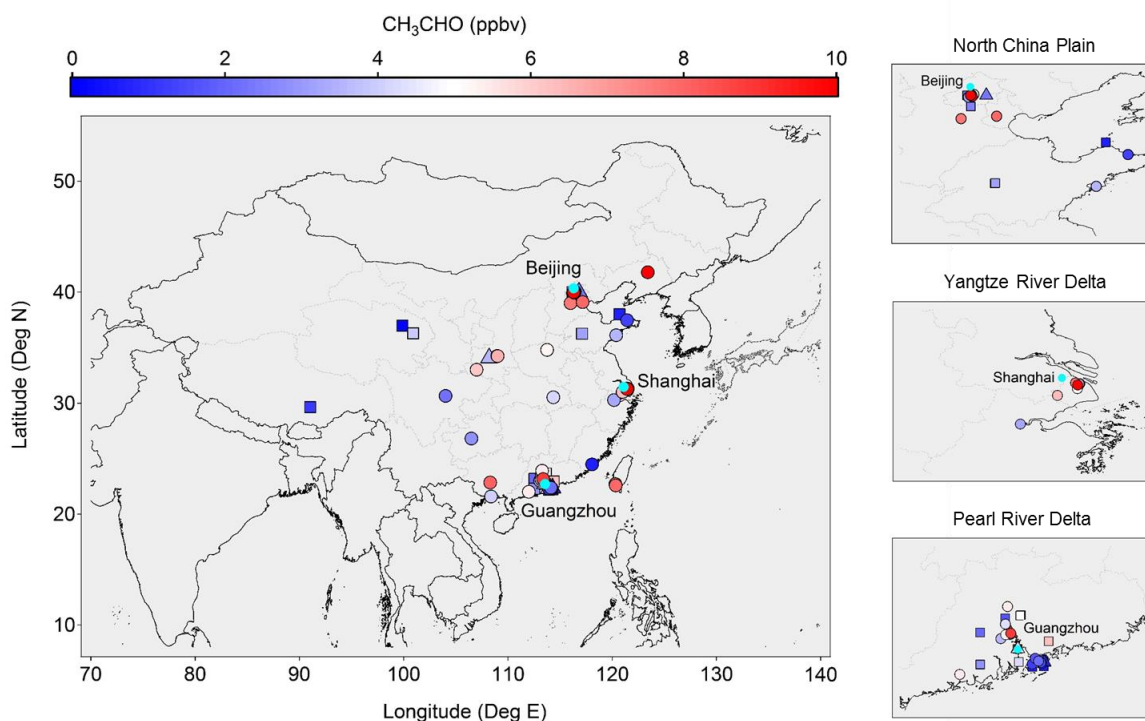
1007 **Figure 1.** Major chemical processes of OVOCs in the atmosphere. The red and blue lines
 1008 indicate the initiation and recycling pathways of radicals. The dotted lines indicate chemical
 1009 processes in which OVOCs directly involved.



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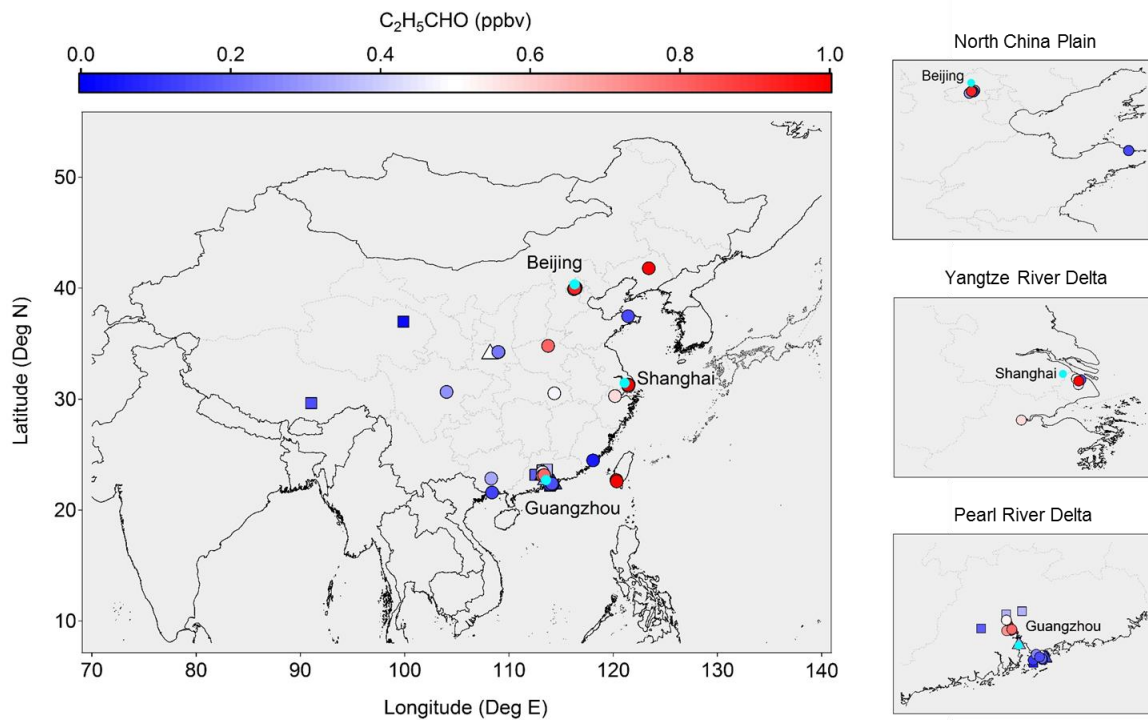
1011 **Figure 2a.** Spatial distributions of HCHO levels (ppbv) in China. Urban, suburban, rural sites
 1012 are marked as circles, triangles and squares, respectively. The observation data are taken from

1013 Altemose et al. (2015), Cheng et al. (2014), Chi et al. (2008), Dai et al. (2012), Duan et al.
1014 (2012), Duan et al. (2008), Guo et al. (2009), Guo et al. (2013), Guo et al. (2014a), Guo et al.
1015 (2016), He et al. (2016), Ho et al. (2014a), Ho et al. (2015), Ho et al. (2002), Huang et al.
1016 (2008), Huang et al. (2009), Jiang (2015), Kanaya et al. (2009), Li et al. (2010), Li et al. (2018),
1017 Ling et al. (2016), Ling et al. (2017), Liu et al. (2015), Liu et al. (2012a), Lü et al. (2010), Lü
1018 et al. (2009), Lui et al. (2017a), Lui et al. (2017c), Ma et al. (2016), Mu et al. (2007), Nan et al.
1019 (2017), Pang and Lee (2010), Pang and Mu (2006), Rao et al. (2016), Shao et al. (2009), Shi et
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),
1022 Yang et al. (2018), Yang et al. (2017), Yu et al. (2008), and Yuan et al. (2012a).



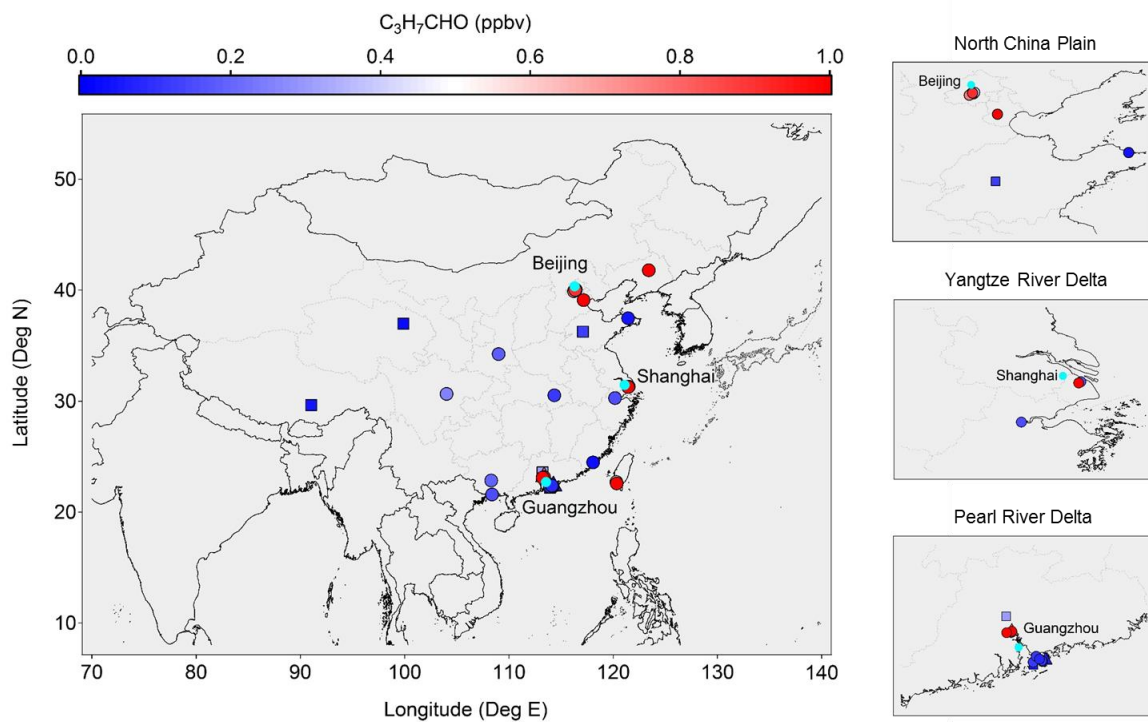
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Figure 2b. The same to Figure 2a but for CH_3CHO .



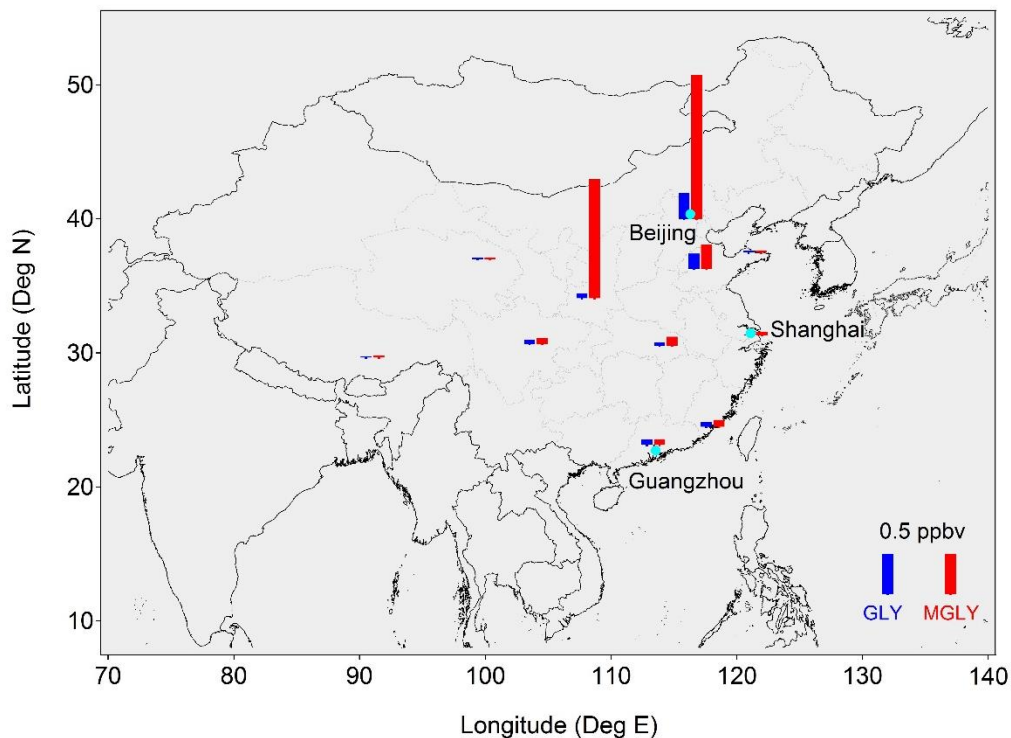
1025
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Figure 2c. The same to Figure 2a but for C_2H_5CHO .

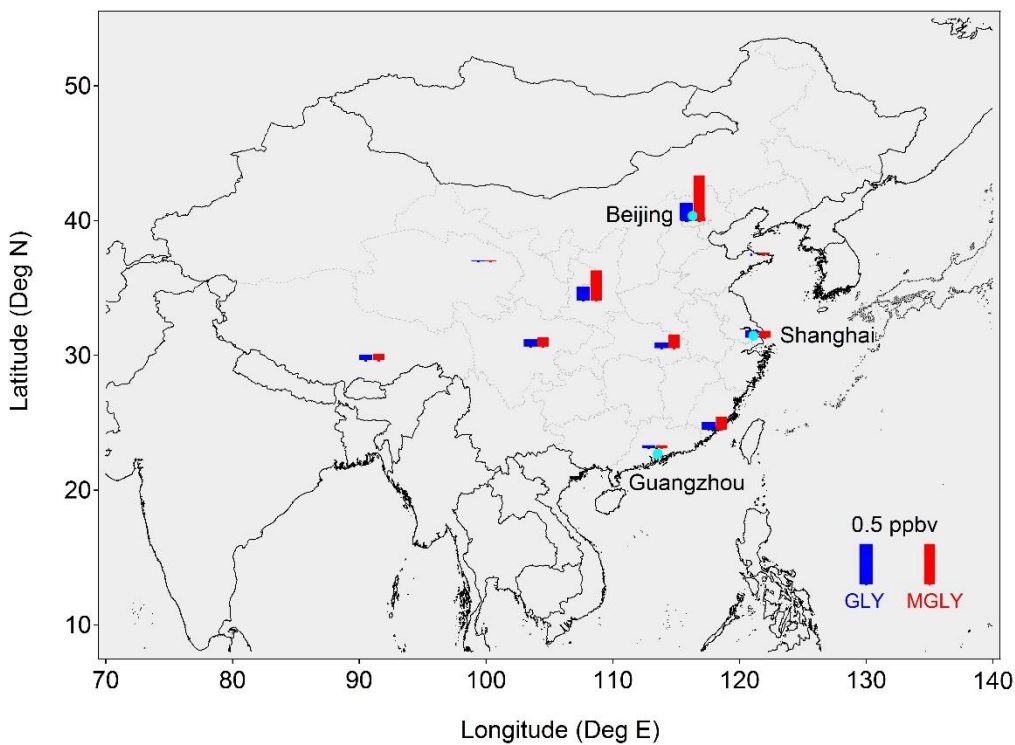


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1028

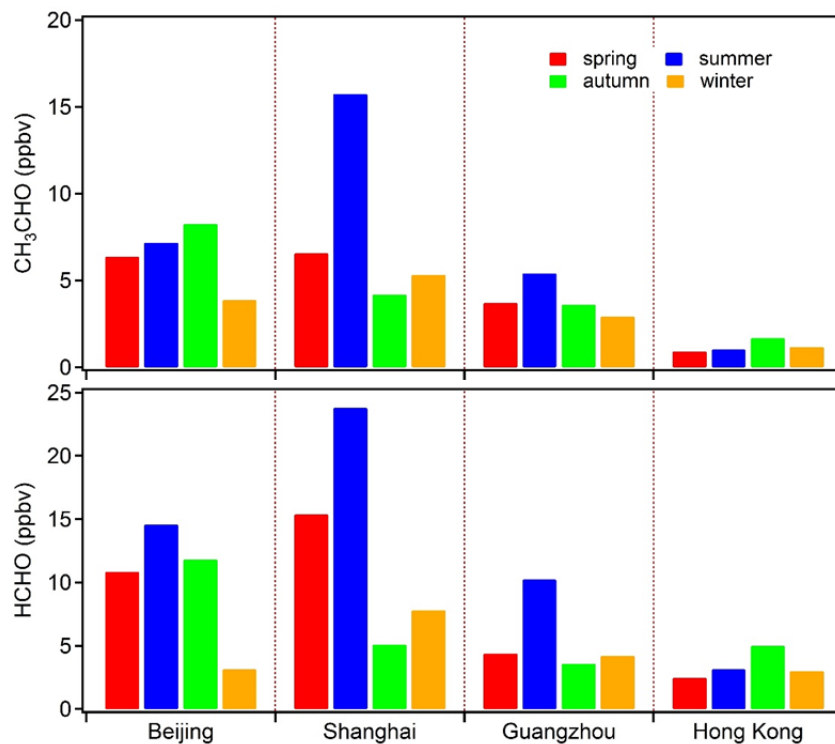
Figure 2d. The same to Figure 2a but for C_3H_7CHO .



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 CH₃CHO 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 ⁻¹)	Methods available	K _{OH} (× 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)
Formaldehyde	HCHO	9.02 × 10 ⁻⁵	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: PTR-MS, PTR-TOF-MS, PTR-ID-CIMS, LP-DOAS, MAX-DOAS;	8.5
Acetaldehyde	CH ₃ CHO	7.31 × 10 ⁻⁶	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: PTR-MS, PTR-TOF-CIMS, PTR-TOF-MS;	15.3
Acetone	CH ₃ COCH ₃	-	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS, PTR-TOF-CIMS, PTR-TOF-MS;	0.18
Acrolein	CH ₂ CHCHO	1.42 × 10 ⁻⁶	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS;	21.6
Propionaldehyde	C ₂ H ₅ CHO	1.18 × 10 ⁻⁵	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: GC-MS/FID;	18.7
Crotonaldehyde	CH ₃ CHCHCHO	6.61 × 10 ⁻⁶	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS;	36
Methacrolein	CH ₂ C(CH ₃)CHO	-	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS;	32
Methyl ethyl ketone	CH ₃ COC ₂ H ₅	-	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-MS, PTR-TOF-CIMS, PTR-TOF-MS;	1.1
Butyraldehyde	C ₃ H ₇ CHO	1.98 × 10 ⁻⁵	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: GC-MS/FID;	23.7
Benzaldehyde	C ₆ H ₅ CHO	3.12 × 10 ⁻⁴	Offline: DNPH-HPLC, PFPH-TD-GC/MS;	12.6
Pentanal	C ₄ H ₉ CHO	1.80 × 10 ⁻⁵	Offline: DNPH-HPLC; Online: PTR-MS;	26.6
m-Tolualdehyde	CH ₃ C ₆ H ₄ CHO	-	Offline: DNPH-HPLC;	16.8
Hexaldehyde	C ₅ H ₁₁ CHO	2.41 × 10 ⁻⁵	Offline: DNPH-HPLC;	28.5

Cyclohexanone	C ₆ H ₁₀ O	-	Offline: DNPH-HPLC;	6.4
p-Tolualdehyde	CH ₃ C ₆ H ₄ CHO	-	Offline: DNPH-HPLC;	16.8
o-Tolualdehyde	CH ₃ C ₆ H ₄ CHO	2 × 10 ⁻⁴	Offline: DNPH-HPLC;	18.9
2,5-Dimethyl-benzaldehyde	(CH ₃) ₂ C ₆ H ₃ CHO	-	Offline: DNPH-HPLC;	31.5
Heptaldehyde	C ₆ H ₁₃ CHO	1.13 × 10 ⁻⁵	Offline: DNPH-HPLC, PFPH-TD-GC/MS;	29.6
Octylaldehyde	C ₈ H ₁₆ O	-	Offline: DNPH-HPLC, PFPH-TD-GC/MS;	30
Nonanaldehyde	C ₉ H ₁₈ O	-	Offline: DNPH-HPLC;	32
Decylaldehyde	C ₁₀ H ₂₀ O	-	Offline: DNPH-HPLC;	30
Undecanal	C ₁₁ H ₂₂ O	-	Offline: DNPH-HPLC;	-
Methyl vinyl ketone	CH ₃ COCHCH ₂	-	Offline: DNPH-HPLC; Online: GC-MS/FID, PTR-TOF-CIMS, PTR-MS;	3.9
Glyoxal	CHOCHO	1.40 × 10 ⁻⁴	Offline: DNPH-HPLC, PFPH-TD-GC/MS; Online: MAX-DOAS;	9
Methylglyoxal	CHOCOCH ₃	1.45 × 10 ⁻⁴	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 ₂	Dominant primary source of RO ₂	Reference
^a CRAES, Beijing	Jul.-Aug. 2008	Urban	O ₃ photolysis	OVOCs	OVOCs photolysis	OVOCs photolysis	Yang et al. (2018)
^a 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 ₃ photolysis	-	-	-	Wang et al. (2010b)
Wangdu, Hebei	Jun.-Jul. 2014	Rural	-	OVOCs	-	-	Fuchs et al. (2017)
^a 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 ₃ 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 ₃ photolysis	-	HCHO photolysis	OVOCs photolysis	Jia et al. (2018)
Lanzhou	Jun.-Aug. 2013	Industrial	O ₃ photolysis	-	HCHO photolysis	OVOCs photolysis	Jia et al. (2018)
Mt. Waliguan	Apr.-May and Jul.-Aug. 2003	Mountain	O ₃ photolysis	-	HCHO photolysis	OVOCs photolysis	Xue et al. (2013)

^a CRAES: Chinese Research Academy of Environmental Sciences; PKU: Peking University; FDU: Fudan University;