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Abstract

In recent years, ozone (O_3) concentrations in the southeastern coastal areas of China have shown a gradual upward trend. As precursors and intermediates in the formation of O_3, carbonyl compounds play key roles in the atmospheric photochemical oxidation cycle. To explore the main pollution characteristics of carbonyl compounds in a typical coastal city in southeast China, ambient samples were collected in Fuzhou (The provincial capital of Fujian province, located on the southeast coast of China) and analyzed using high-performance liquid chromatography with ultraviolet detection. The study was continuously carried out at an urban site (Jinjishan) and a suburban site (Gushan) in Fuzhou from May 8 to 20, 2018. The total concentration of 16 carbonyl compounds at the urban site was 15.45 ± 11.18 ppbv, and the total concentration at the suburban site was 17.57 ± 12.77 ppbv. Formaldehyde (HCHO), acetaldehyde, and acetone were the main species detected in the samples, and acetone had the highest concentration among the species detected. The suburban site had a higher formaldehyde/acetaldehyde ratio and lower acetaldehyde/propionaldehyde ratio than the urban site, implying that biogenic sources potentially contributed to the carbonyl compound concentrations at the suburban site. The results of an observation-based model showed that anthropogenic hydrocarbons promoted HCHO production on May 17 at the urban site. Compared to biogenic emissions, anthropogenic activity is a more important source of carbonyl compounds.

Introduction

Carbonyl compounds are precursors of O_3 and secondary organic aerosols, and play key roles in the atmospheric photochemical oxidation cycle. The impact of carbonyl compounds on O_3 pollution has become a hot topic in the field of atmospheric chemistry research (*Finlayson-Pitts & Pitts, 1997; Zhu et al., 2019*). These species can control the generation rates and efficiency of hydroxyl (HO_2) and peroxyalkyl (RO_2) groups in the atmosphere through their photolysis and reactions with OH radicals. Carbonyls are also important intermediates in the photo-oxidation of volatile organic compounds (VOCs) and important precursors of peroxyacetyl nitrate (PAN) and organic acids, which means they have an important influence on the potential effect of atmospheric oxidation on O_3 pollution.

Carbonyl compounds undergo oxidation reactions with atmospheric oxidants to affect the equilibrium relationship in the photochemical oxidant cycle. At the same time, they are oxidized to form less volatile organic compounds, which gradually enter the particulate phase through condensation and adsorption processes and then form secondary organic aerosols (*Crutzen and Andreae, 1990, Brey and Fischer, 2016*). Carbonyls also have a direct negative impact on human health. Most aldehydes and ketones are strongly irritating, and can cause respiratory infections, sensitization, carcinogenesis, and mutation. Most of the unhealthy symptoms induced by carbonyl compounds are irritation to the eyes and lungs (*WHO, 2000*). Among them, the International Agency for Research on Cancer classifies formaldehyde as the first category of human carcinogens (*IARC, 2006*), which can cause nasopharyngeal cancer (*IARC, 2004*), and may also be related to leukemia (*Zhang et al., 2009*).

Carbonyl compounds are abundant components in ambient air. They are mainly formed by the oxidation of biogenic and anthropogenic hydrocarbons (*Zhu et al., 2019*), and are also directly emitted from natural and anthropogenic sources *(Singh et al., 1995; Wu & Wang, 2015; Xiang et al., 2017; Zarzana et al., 2017)*. Generally, anthropogenic sources are significant in urban areas. Biological sources of carbonyl compounds are also considered important.

In China, the concentrations of carbonyl compounds in the atmosphere are usually high. For example, the atmospheric concentrations of carbonyl compounds measured in Beijing showed that the environmental level of carbonyl compounds is 3-5 times of that in Hong Kong *(Pang & Mu, 2006)*. The concentration of HCHO in Guangzhou is 3 times that in Japan and 2 times that in Hong Kong (*Feng et al., 2005; Sin et al., 2001; Tago et al., 2005*). The high concentrations of carbonyl compounds may be important contributors to serious atmospheric photochemical pollution in Chinese cities.

Fuzhou is a city with relatively good air quality in China, ranking 6th out of 168 key cities in China for ambient air quality in 2019. However, ozone concentrations show an increasing trend year by year. Fuzhou's current O_3 pollution situation is likely to be a brand-new challenge for China to

106 face after $PM_{2.5}$ pollution is controlled. Therefore, the situation in Fuzhou deserves attention. The
107 carbonyl compounds are important precursors of O_3, and the study of its characteristics is of great
108 significance to the control of O_3 pollution. As important precursors of O_3, VOCs and NOx have
109 attracted wide attention (*Hong et al., 2019; Wang et al., 2017*). However, most research to date
110 has focused on non-methane hydrocarbons and carbonyl compounds have received limited
111 attention. This research focuses on Fuzhou carbonyl compounds to explore their pollution
112 characteristics and their relationship with ozone concentration. In this study, carbonyl compounds
113 in ambient air were investigated using offline 2,4-dinitrophenylhydrazine (DNPH) cartridge
114 sampling with high-performance liquid chromatography (HPLC) analysis. Fuzhou is in the
115 western part of the Taiwan Strait and is subject to weaker winds during the monsoon exchange
116 period in May and is less affected by regional transmission. Sixteen carbonyl compounds were
117 analyzed in samples collected from May 8 to 20, 2018 in Fuzhou.
118

Materials & Methods
Sampling sites
121 Two observation sites were chosen on the rooftop of the Jinjishan Environmental Protection
122 Building (Jijishan site: JJS) and in the Gushan Scenic Area (Gushan site: GSS) in the suburbs of
123 Fuzhou, China (Fig. 1).
124

125 Fuzhou is located on the southeast coast of China. The JJS site was located 30 m above the ground
126 at the foot of the southwest Jinjishan mountain in the Jin'an district, Fuzhou. The Jin'an River was
127 located to the west of this site and Jinjishan Park to the northeast. The site was surrounded by
128 residential areas and was considered a typical urban site with no pollution sources. The GSS site
129 was located on the top of the Songtao Building of the Gushan Scenic Area Management
130 Committee. This site was located to the south of the east side of Fuzhou city and north of the
131 Minjiang River. The GSS was selected by China National Environmental Monitoring Center
132 (CNEMC) as a suburban background site as it was surrounded by green trees and had no pollution
133 sources. This site was located about 8 km away from the JJS site.
134

Carbonyls sampling and analysis
136 The sampling and analysis procedures used were based on the Environmental Protection Agency
137 method TO-11A (*US EPA, 1999*). Ambient carbonyls were collected on silica cartridges coated
138 with acidified DNPH (IC-DN3501, Agela Technologies, China). The sampling flow rate was 0.8
139 L/min. The sampling pumps in this study are all vacuum pumps with a rated voltage of 24v, and
140 soap film flowmeters are used for flow calibration before sampling (*Zhang et al. 2018*). Samples
141 were collected at a 2 h intervals beginning at 00:00 (UTC+8) from May 8 to 20, 2018. The
142 sampling duration was 2 h with 12 atmospheric samples collected each day: 00:00-02:00; 02:00-
143 04:00; 04:00-06:00; 06:00-08:00; 08:00-10:00; 10:00-12:00; 12:00-14:00; 14:00-16:00; 16:00-
144 18:00; 18:00-20:00; 20:00-22:00; 22:00-00:00. A total of 156 carbonyl compound samples were
145 collected at each site. An O_3 scrubber loaded with potassium iodide (KI 140, Agela Technologies,

146 China) was installed in front of the cartridge to eliminate O_3. Two cartridges in series were sampled
147 to evaluate the collection efficiency before application to the first sample collection in the field.
148 Over 98% of carbonyls were detected in the first cartridge. After sampling, the cartridges were
149 sealed with Teflon caps immediately, placed in an aluminum foil bag to protect them from light,
150 and stored in a refrigerator (< 4°C). Throughout the sampling process, blank samples were
151 collected at each location. Blank samples were collected by passive sampling, which involved
152 opening a sealed cartridge and placing it in the ambient air at the same time as a cartridge was used
153 for active air sampling. Six cartridges were collected every 12 hours, and the concentration of
154 blank samples with no sampling for 12 hours had been deducted from the concentration of each
155 sample. Two filed blank samples were collected both before and after the sampling process. At the
156 end of the sample collection period, all the samples were transported to the Laboratory of
157 Atmospheric Photochemical Simulation at the Chinese Research Academy of Environmental
158 Sciences (Beijing, China) in a heat-resistant incubator maintained at 0°C and then analyzed within
159 1 month.
160
161 In the sampling cartridges, the ambient carbonyls reacted with DNPH to form stable hydrazone
162 derivatives. These derivatives were eluted slowly from the cartridges into a volumetric flask using
163 5 mL of acetonitrile (HPLC grade, J.T. Baker, USA). No DNPH or derivatives remained in the
164 cartridges after this elution. Because we several eluted cartridges were chosen to be eluted with 5
165 ml of acetonitrile again, and no residual carbonyl compounds in the second eluted solutions were
166 detected. This shows that 5 ml of acetonitrile is enough to elute all the carbonyl compounds in the
167 cartridges. The extracts were then analyzed by HPLC (LC20A, Shimadzu, Japan) with UV-Vis
168 detection at 360 nm. The separation column was a Inertsil ODS-P reversed-phase column (250 ×
169 4.6 mm i.d., 5 μm particle size; Shimadzu, Japan) at 40°C. The mobile phase consisted of
170 acetonitrile and water and the following gradient elution was used: 0–20 min, 60% acetonitrile;
171 20–30 min, 60% to 100% acetonitrile; 30–32 min, 100% to 60% acetonitrile; and 32–40 min, 60%
172 acetonitrile. The total flow rate was 1.0 mL/min and the injection volume was 20 μL. A mixed
173 calibration standard of 15 DNPH-carbonyl derivatives (Supelco, Bellefonte, PA), which contained
174 HCHO, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, butyraldehyde,
175 benzaldehyde, isovaleraldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde,
176 hexaldehyde, and 2,5-dimethylbenzaldehyde, and a calibration standard of methacrylaldehyde
177 (MACR) were diluted to 0.03, 0.06, 0.09, 0.15, 0.24, 0.30, and 0.45 μg/mL. Details for the
178 detection of the 16 carbonyl compounds are given in Table 1.
179
180 **Other measurements**
181 The O_3 concentrations were measured by a UV photometric O_3 analyzer (Model 49i, Thermo
182 Fisher Scientific, USA). The NO and NO_2 concentrations were measured by a chemiluminescence
183 instrument (Model 42i, Thermo Fisher Scientific) coupled with a molybdenum oxide catalytic
184 converter. The SO_2 and CO concentrations were measured by a pulsed fluorescence analyzer
185 (Model 43i, Thermo Fisher Scientific) and an infrared absorption analyzer (Model 48i, Thermo

186   Fisher Scientific), respectively. The $PM_{2.5}$ concentrations were measured by a multiangle
187   absorption photometer (Model 5012, Thermo Fisher Scientific). The pollutants data (including O_3,
188   CO, NO_2, SO_2, $PM_{2.5}$) came from the National Environmental Monitoring Station in Fuzhou. All
189   instruments in these sites are maintained by a professional service company every day and are
190   turned on during the carbonyl compound sampling period.
191
192   The VOCs concentrations were determined on an O_3 pollution day (May 17) at the JJS site. Four
193   samples were collected in 3.2-L stainless steel canisters at 8:00, 14:00, 18:00, and 21:00 local time.
194   Fifty-seven VOCs species of Photochemical Assessment Monitoring Stations (PAMS) were
195   identified using a gas chromatograph equipped with a flame ionization detector and a mass
196   spectrometry detector (EPA/600-R-98/161, Technical Assistance Document for Sampling and
197   Analysis of Ozone Precursors) at the same laboratory in Chinese Research Academy of
198   Environmental Sciences. Meteorological data for the temperature, relative humidity, wind speed,
199   wind direction, and pressure were obtained from the National Climate Data Center of the National
200   Oceanic and Atmospheric Administration (*National Climatic Data Center*).
201

Observation-based model

203   For quantification of the in situ photochemical production and sensitivity analysis of carbonyl
204   compounds, an observation-based model (OBM) was utilized in this study. This model has been
205   successfully applied in previous studies (*He et al., 2019; Mellouki et al., 2015; Xue et al., 2014;*
206   *Yang et al., 2018; Zhang et al., 2019*). Briefly, it is built on the Master Chemical Mechanism,
207   which is a near-explicit mechanism describing the oxidation of 143 primary VOCs together with
208   the latest IUPAC inorganic nomenclature *(Jenkin et al., 2003; Saunders et al., 2003)*. In this study,
209   the model was updated to the newest version of the Master Chemical Mechanism (*MCM website*).
210   In the calculations, the observed concentrations of O_3, NO, NO_2, SO_2, CO, and VOCs, and the
211   temperature, relative humidity, and pressure were interpolated to a time resolution of 1 h and
212   processed as the model input data sets. We only analyzed the case at JJS station on May 18, 2018
213   because of the VOCs data limited.
214

Results

Concentration level

217   Fig. 2 shows the measured time series of major carbonyl compounds, O_3, NO_2, SO_2, CO, $PM_{2.5}$,
218   and meteorological parameters at the JJS and GSS sites in Fuzhou from May 8 to 20, 2018. The
219   average concentrations of O_3, NO_2, SO_2, CO, and $PM_{2.5}$ during the observation period at the GSS
220   site were 48.29 ppbv, 6.99 ppbv, 2.67 ppbv, 0.47 ppmv, and 29.40 μg/m^3, respectively. At the JJS
221   site, the corresponding average concentrations were 40.44 ppbv, 14.18 ppbv, 1.63 ppbv, 0.62
222   ppmv, and 31.06 μg/m^3 (Table 2).
223
224   During the observation period, the concentrations of carbonyl compounds at the JJS and GSS sites
225   were relatively low from May 8 to 11, and the. This may have been caused by low temperatures

226   (average temperature was 21.3 ℃) that were not conducive to the formation of carbonyl
227   compounds or strong southwesterly winds that facilitated dispersion of the pollutants. From May
228   12 to 18, the carbonyl compound concentrations at the two sites greatly increased, which may have
229   been caused by high temperatures (average temperature was 27.1 ℃) and strong easterly winds
230   facilitating the formation and accumulation of pollutants. On May 19 and 20, the temperature
231   dropped and the wind direction changed, which resulted in decreases in the concentrations of
232   carbonyl compounds at the two sites. The O_3 concentration changes were consistent with those for
233   the carbonyl compounds during the observation period. The O_3 concentration remained at a low
234   level from May 8 to 11, greatly increased from May 12 to 18, and slightly decreased on May 19
235   and 20. In addition, from May 12 to 20, the GSS site showed large diurnal variations in the
236   concentrations of O_3 and the carbonyl compounds, and these concentrations peaked at almost the
237   same time (around noon), which indicated that photochemical reactions were the main contributor
238   to O_3 and carbonyl compound formation during the day at the GSS site. A similar situation was
239   also observed at the JJS site. However, from May 13 to 19 at the JJS site, no obvious daily trends
240   were observed in the carbonyl compound concentrations. These results suggested that
241   anthropogenic sources around the site had considerable contributions in addition to the
242   contribution of photochemical reactions during the day. These observations indicate that the
243   photochemical pollution phenomena occur in Fuzhou.
244   The overall trends for the carbonyl compounds at the two sites were similar, with a peak in the
245   middle of the day, but the carbonyl compound composition varied greatly with time.
246
247   Among the carbonyl compounds detected at the GSS site from May 8 to 11, the dominant carbonyl
248   compound was acetaldehyde, followed by HCHO. From May 12 to 13, the concentration of
249   acetaldehyde increased sharply, and the main reason for this was the overall increase in the
250   concentration of carbonyl compounds. In addition, the concentrations of other carbonyl
251   compounds also increased. From May 14 to 17, the concentration of acetaldehyde decreased and
252   that of acetone increased rapidly. The increasing trend of acetone is due to the conversion of
253   acetaldehyde and the gradual accumulation of acetone. In addition, changes in wind direction and
254   the influence of other man-made pollution sources may be the cause of this phenomenon. The
255   concentration of acetone was much higher than that of any other species. During the observation
256   period, the concentrations of the species varied greatly. The daily concentration changes were
257   basically the same, indicating a stable source of the carbonyl compounds. From May 18 to 20, the
258   total concentration of carbonyl compounds declined as the acetone concentration decreased.
259
260   From May 8 to 14, the JJS site was similar to the GSS site and the carbonyl compound
261   concentration was relatively low. Starting on May 14, the concentration of acetaldehyde increased
262   greatly and the concentration of acetone increased slightly, which was the main reason for the large
263   increase in the carbonyl compound concentration. From May 15 to 18, the concentration of acetone
264   increased rapidly and it became the main species, followed by acetaldehyde and HCHO, and the
265   concentrations of the compounds continued to increase. From May 18 to 20, the concentration of

266 acetone began to decrease relative to the previous period (May 15 to 18) but the concentration
267 remained high and it was still the dominant species, followed by acetaldehyde and HCHO.
268
269 Table 3 shows the average concentrations and ranges of the 16 carbonyl compounds detected at
270 the GSS and JJS sites in Fuzhou. The total average concentration (± standard deviation) of carbonyl
271 compounds at the GSS site was 17.57 ± 12.77 ppbv and the range was 1.11–53.22 ppbv. The total
272 average concentration of carbonyl compounds at the JJS site was slightly lower than that at the
273 GSS site, which was 15.45 ± 11.18 ppbv with a range of 0.04–46.83 ppbv.
274

Diurnal variations in the ambient Carbonyl compounds

276 Fig. 3 shows diurnal variation of the total carbonyl compound and O_3 concentrations at the GSS
277 and JJS sites from May 18 to 20, 2018. Both sites showed diurnal variation. It is well-known that
278 atmospheric photochemical reactions are one of the important production routes of carbonyl
279 compounds in ambient air and an important method of O_3 generation. The intensity of solar
280 radiation directly affects reaction rates in atmospheric photochemistry. Therefore, the intensity of
281 solar radiation has an important influence on the concentrations of carbonyl compounds and O_3.
282 At the same time, anthropogenic emissions are also important and can affect the concentrations of
283 carbonyl compounds, which directly affect the diurnal variation of carbonyl compounds.
284

285 Diurnal variation of the total carbonyl compounds at the GSS site showed a distinct single peak
286 during the observation period. Overall, the total concentration of carbonyl compounds was much
287 higher during the day than at night, with concentrations beginning to increase around 05:00 and
288 peaking at around 12:00–14:00 when solar radiation was the strongest. As solar radiation
289 decreased, the concentration decreased rapidly from 14:00 to 19:00 and stabilized after 19:00.
290 From 19:00 to 05:00 the next day, the concentrations of the carbonyl compounds did not vary
291 much and were maintained at low levels relative to those observed during the day. During the
292 observation period, the daily change in the O_3 concentration at the GSS site also showed a single
293 peak, and the trend was similar to that observed for the carbonyl compounds.
294

295 Diurnal variation at the JJS site was different to that at the GSS site. Generally, variation in the
296 concentrations of carbonyl compounds at the JJS site showed multiple peaks. Similar to the GSS
297 site, the JJS site had higher concentrations of carbonyl compounds during the day than at night;
298 however, the JJS site had much higher concentrations at night (19:00–07:00) than the GSS site,
299 indicating a persistent source of pollution. During the day, the carbonyl compounds showed a peak
300 at 07:00, concentrations then rose from 05:00 to 07:00 before decreasing slightly from 07:00 to
301 09:00. As solar radiation increased, the concentrations of the carbonyl compounds increased again
302 after 09:00. Between 13:00 and 15:00, the atmospheric photochemical reaction rate reached its
303 daytime peak, and the highest carbonyl compound concentrations were reached at 15:00. From
304 15:00 to 19:00, as solar radiation decreased, the concentrations of the carbonyl compounds
305 gradually decreased, and between 19:00 to 23:00, a late peak for the carbonyl compounds was

306   reached and then the concentrations began to decrease. The diurnal variation of O_3 at the JJS site
307   basically showed a single peak that was consistent with the variation observed for the carbonyl
308   compounds from 9:00 to 19:00. This indicated that the concentrations of the carbonyl compounds
309   were mainly affected by atmospheric photochemical reactions during this period.
310
311   Fig. 4 shows diurnal variation of the main carbonyl compounds at the two sites from May 8 to 20,
312   2018. The overall diurnal variation trend for these compounds was similar to that of the total
313   carbonyl compounds. The concentrations of acetaldehyde and acetone at the GSS site were much
314   higher than those of other species, indicating that this was the main species that affected diurnal
315   variation. The diurnal variation of acetaldehyde at the JJS site was consistent with the change in
316   the total carbonyl compounds, indicating that it was one of the main species that affected the total
317   diurnal variation of carbonyl compounds at the JJS site. In addition, the high concentration of
318   acetone also affected the diurnal variation trend of the total carbonyl compounds at the JJS site to
319   a certain extent.
320

321   **Discussion**
322   **Comparison of urban and suburban stations**
323   The carbonyl compounds at the GSS site, which had less human activity than the JJS site, mainly
324   arise from secondary generation via photochemical reactions. By contrast, at the JJS site, in
325   addition to secondary generation, human activity in the surrounding area has a high contribution
326   to the carbonyl compound concentrations.
327
328   The JJS site was located in an urban area, the pollution sources were more complex than at the
329   GSS site, and the carbonyl compound sources may also be more complex. Although the GSS site
330   was located in a forested area with a single main source of carbonyl compounds, it was close to
331   the JJS site and could be affected pollutants transported from other areas. This may be the main
332   reason why the concentration of carbonyl compounds at the GSS site was slightly higher than that
333   at the JJS site.
334
335   Fig. 5 shows the average contributions of different carbonyl compounds at the two sites. Acetone
336   was the most abundant carbonyl compound at the GSS and JJS sites, which could be attributed to
337   its chemical stability and long atmospheric lifetime. Acetone released from various sources
338   accumulates in the atmosphere (*Atkinson, 2000; Dai et al., 2012*) , and the most important sources
339   are natural sources (*Janson et al., 2001*), with pine trees accounting for a higher share of emissions.
340   Among the anthropogenic sources, motor vehicle exhaust emissions are more significant (*Ho KF*
341   *et al., 2015*). The average concentration of acetone at the GSS site was 7.45 ± 8.13 ppbv (Table
342   3), accounting for 42.26% of the total concentration of the 16 carbonyl compounds. The average
343   acetone concentration at the JJS site (6.82 ± 8.11 ppbv) (Table 3) was slightly lower than that at
344   the GSS site, accounting for 44.14% of the total concentration of the 16 carbonyl compounds.
345   These results were comparable to the acetone concentrations measured by Yang et al. in Beijing

346   (*Yang et al., 2018*). They were also similar to the concentrations measured by Lü et al. in
347   Guangzhou, where acetone was one of the species with the highest concentrations (*Lü et al., 2010*).
348   The compound with the second highest concentration at the GSS site was acetaldehyde (4.41 ±
349   4.36 ppbv, 25.01% of the total) (Table 3), and the third was HCHO (2.54 ± 2.09 ppbv, 14.41% of
350   the total) (Table 3). Similar to the GSS site, the species with second highest concentration at the
351   JJS site was acetaldehyde (4.84 ± 3.63 ppbv, 31.35% of the total), and the third was HCHO
352   oxidation (1.64 ± 0.75 ppbv, 10.64% of the total) (Table 3). Higher concentration of MACR could
353   be caused by the abundant vegetation at the GSS site, which would produce more MACR than at
354   the JJS site (*Duane et al., 2002; Riemer et al., 1998*).
355
356   **Diurnal variation analysis**
357   The concentration of carbonyl compounds at GSS sites has an obvious single-peak diurnal
358   variation trend, which is basically consistent with the change of solar radiation intensity during a
359   day, indicating that the concentration of carbonyl compounds is mainly caused by atmospheric
360   photochemical reactions. However, there is no significant diurnal variation in the concentration of
361   carbonyl compounds from the whole-time variation at the JSS site, indicating that the
362   concentration of carbonyl compounds is not only influenced by atmospheric photochemical
363   reactions, but also by certain anthropogenic factors.
364
365   The highest concentrations of acetone could be observed at the two sites at any time. Atmospheric
366   oxidation affects the atmospheric lifetime of carbonyl compounds. The photolysis reactions of
367   HCHO and acetaldehyde take about 4 h and 6 days, respectively, and their lifetimes initiated by
368   OH radicals are about 1.2 days (HCHO) and 8.8 h (acetaldehyde) (*Dai et al., 2012*). Acetone is
369   more stable and has a longer lifetime (60 days uptake by photolysis and 53 days uptake by reaction
370   with OH radicals) than those of HCHO and acetaldehyde. Therefore, acetone accumulates in the
371   atmosphere easily and its concentration is higher than those of other carbonyl compounds such as
372   HCHO and acetaldehyde (*Atkinson, 2000; Possanzini et al., 2007*). This further explains why the
373   acetone concentration is much higher than other carbonyl compounds.
374
375   **Source apportionment of carbonyl compounds using ratio methods**
376   The sources of carbonyl compounds can be roughly determined from the ratio of the concentrations
377   of atmospheric formaldehyde/acetaldehyde (F/A) to that of acetaldehyde/propionaldehyde (A/P)
378   (*Shepson et al., 1991*). Fig. 6 and Fig. 7 show statistical analysis of the F/A and A/P ratios during
379   the day and night at the GSS and the JJS sites from May 8 to 21.
380
381   The F/A value in the atmosphere is generally between 1–10. Generally, the amount of
382   formaldehyde produced by biogenic-derived hydrocarbons through atmospheric photochemical
383   reactions is higher than the amount of acetaldehyde. Therefore, the F/A ratio is higher in areas
384   with high forest or vegetation coverage than in urban areas *(Possanzini et al., 1996; Shepson et
385   al., 1991*). Overall, the F/A value at the GSS site (daytime: 0.19–1.38, nighttime: 0.10–1.42) first

386 decreased and then increased during the observation period. The GSS site was located in a forested
387 area and there was one main source of carbonyl compounds. However, the F/A values at the GSS
388 site were much lower than those in typical forested areas, which may be related to the regional
389 transportation of pollutants. During the observation period, the F/A value at the JJS site (daytime:
390 0.18–0.69, nighttime: 0.10–1.43) also first decreased and then increased.
391
392 Overall, the F/A value at the GSS site was slightly higher than that at the JJS site during the
393 observation period. This may be because the vegetation coverage at the GSS site was higher than
394 that at the JJS site as the GSS site was in a forested area. Therefore, the F/A value at the GSS site
395 was higher than that at the urban JJS site. However, because the GSS site was located close to an
396 urban area, the F/A value was lower than that in typical forested area because of the impact of
397 pollutant transportation. The F/A values were slightly higher at night than during the day at both
398 sites, which could be attributed to the fact that formaldehyde and acetaldehyde were removed at
399 night mainly by reactions with NO_3 radicals. Acetaldehyde reacted at a higher rate than
400 formaldehyde at night. From May 12 to 13, a sudden increase in the GSS acetaldehyde
401 concentration led to a decrease in its F/A value to slightly lower than that at the JJS site.
402
403 Generally, the A/P ratio can be used to indicate the presence of man-made pollutants because
404 propionaldehyde is considered only to be associated with anthropogenic sources *(Shepson et al.,*
405 *1991)*. Therefore, the lower the A/P value, the greater the influence of anthropogenic sources. The
406 A/P at the GSS website was between 2.22–23.64 during the day and 2.20–28.77 at night, while at
407 the JJS site, the A/P was between 2.52–31.62 during the day and 2.99–39.09 at night.
408 Propionaldehyde is mainly related to anthropogenic emissions, and acetaldehyde may come from
409 secondary generation or primary emission. The A/P value at the JJS site was higher than the A/P
410 value at the GSS site. From the A/P ratio, the GSS site seems to be more severely affected by man-
411 made sources, which may be due to the GSS site producing more acetaldehyde. And the GSS site
412 was affected by pollutant transportation from the source area (Table 3), and the concentration of
413 propionaldehyde was slightly higher than that at the JJS site.
414
415 The ratio of the concentrations of atmospheric formaldehyde/acetaldehyde (F/A) and
416 acetaldehyde/propionaldehyde (A/P) can be analyzed the relative contribution of anthropogenic
417 and biogenic sources. However, there were some arguments that the ratios of F/A and A/P often
418 have large variations due to different sources of pollution and meteorological conditions
419 (*Grosjean, 1992; Ho et al., 2015*), thus we should use it with caution. Furthermore, the ratio
420 method also fails to identify different photochemical production. Thus we will discuss the sources
421 of gaseous carbonyls more detail in the next section.
422
423 **Source apportionment of carbonyl compounds using observation-based model**
424 Carbonyls production at the JJS site was observed on May 17, 2018 and simulated by an OBM
425 model (Fig. 8). The simulated distribution of HCHO from photochemical production was

426 compared with the observed HCHO concentration. Peaks appeared during the day and valleys
427 appeared during the night. This was similar to the trend observed for O_3, and indicated that the
428 HCHO photochemical reaction had a large contribution during the day. The highest in situ HCHO
429 was 0.64 ppbv/h at 12:00, and this value was lower than those measured in a previous study in
430 Beijing on July 23 and 24, 2008 (*Yang et al., 2018*). One aspect of the figure is of interest, two
431 large increases were observed in HCHO in the early morning and after dusk. Rush hour traffic
432 occurs during these two periods and vehicle emissions are a major source of HCHO at such times
433 (*Cao et al., 2016; Tsai et al., 2014*). In addition, the nocturnal boundary layer build ups rapidly
434 after sunset, and unfavorable dilution conditions may contribute to increases in the HCHO
435 concentration (*Brown & Stutz, 2012*).
436
437 The highest observed rate of acetaldehyde appeared at dusk, because the major source of
438 acetaldehyde is anthropogenic emission and it accumulated during daytime. But the highest in situ
439 photochemical rate was 0.92 ppbv/h at 11:00 due to higher photolysis rate of acetaldehyde in the
440 afternoon. Acetone has a lower in situ photochemical rate indicated photochemical generation is
441 the minor source of acetone. And it has a higher background value (the lowest value of acetone,
442 about 16 ppbv) , means it may be affected by local pollution sources on this day. Others represent
443 the sum of other carbonyl compounds. Similar to formaldehyde, it affected by photochemical
444 production during the daytime and anthropogenic emission during the nighttime.
445
446 At 3:00 p.m., the net HCHO generation rate showed a decreasing trend, indicating that the on-site
447 HCHO generation rate was lower than the HCHO destruction rate. In fact, many simulations
448 showed that the concentration of OH radicals was highest in the afternoon during the day (*Tan et
449 al., 2019; Zong et al., 2018*). The photolysis of formaldehyde is an important source of OH
450 radicals. Negative values occur when the rate of formaldehyde photolysis is greater than the sum
451 of the production rate and the primary release. It has been reported in many articles that the
452 concentration of formaldehyde decreases between 14:00 and 18:00, and according to the published
453 literature, this phenomenon is most pronounced in summer (*de Blas et al., 2019; Jiang et al., 2016;
454 Jiang et al., 2019; Yang et al., 2019*).
455
456 Fig. 9 shows that the model-calculated relative incremental reactivities (RIR) of the major
457 precursors for secondary formation of carbonyl compounds on May 17, 2018. We further identified
458 key precursors by calculating the RIR (*Cardelino & Chameides, 1995*), which has been applied in
459 many previous studies (*Tan et al., 2018; Yang et al., 2018*). All VOCs species were categorized as
460 biogenic or anthropogenic hydrocarbons (AHCs). The AHCs were divided into the following four
461 subgroups: alkanes, alkenes, alkynes, and aromatics. All kinds of carbonyl compounds production
462 were VOC-limited, and the dominant position was AHC. The RIRs for the NOx were negative.
463 But the dominant species of different carbonyl compounds were different. Alkenes were dominant
464 and aromatics followed for formaldehyde. For acetaldehyde and other carbonyl compounds,
465 alkanes and alkenes both were important for its chemical generation, followed by aromatics. And

466   alkanes dominate the formation of acetone. Therefore, anthropogenic VOCs emissions should be
467   reduced for carbonyl compounds controlling.
468

Conclusions

470   The characteristics and sources of 16 carbonyls compounds were measured in May 2018 in the
471   southeastern coastal city of Fuzhou, China. The concentration at the urban site was 15.45 ± 11.18
472   ppbv and the concentration at the suburban site was 17.57 ± 12.77 ppbv. HCHO, acetaldehyde,
473   and acetone were the main species in Fuzhou city, and acetone had the highest concentration. The
474   F/A and A/P ratios were used to determine the sources of the carbonyl compounds. Suburban areas
475   with high vegetation coverage had high F/A values, whereas urban areas were greatly affected by
476   human activities and the A/P values were higher. HCHO production was VOC-limited, and AHCs
477   were dominant and particularly sensitive to reactive alkenes. The RIR for NOx were negative and
478   NOx would generally have a negative influence on attempts to control HCHO production. In
479   summary, both anthropogenic emission and biogenic emissions sources were important source of
480   OVOCs in Fuzhou, and the impact of anthropogenic emission was greater, deserve more attention
481   in the future control of ozone precursors, both in Fuzhou and other cities of China.
482

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489

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661
662

Figure 1

Google earth map showing the location of the Fuzhou sample sites of JJS and GSS.

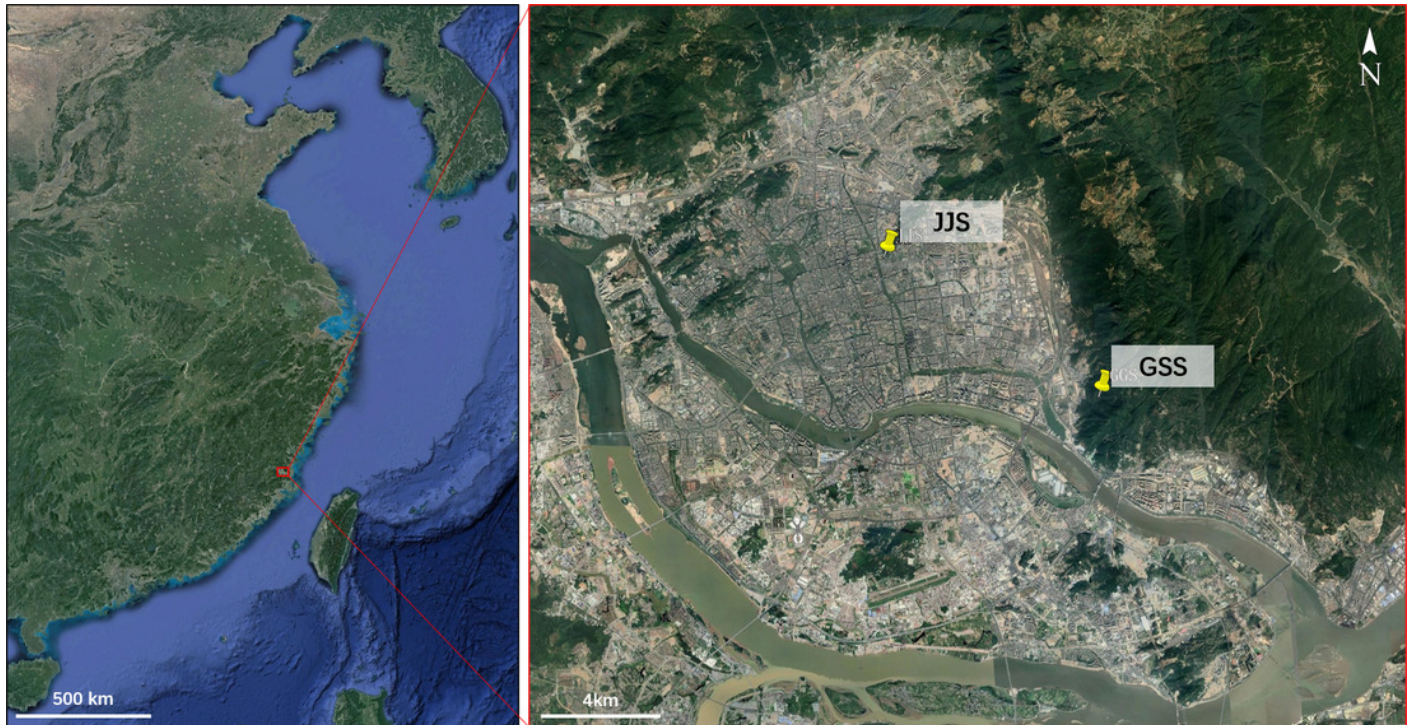



Figure 2

Time series of carbonyl compounds, O₃, NO₂, SO₂, CO, PM₂.₅, and meteorological parameters at GSS and JJS sites from May 5 to 20, 2018.

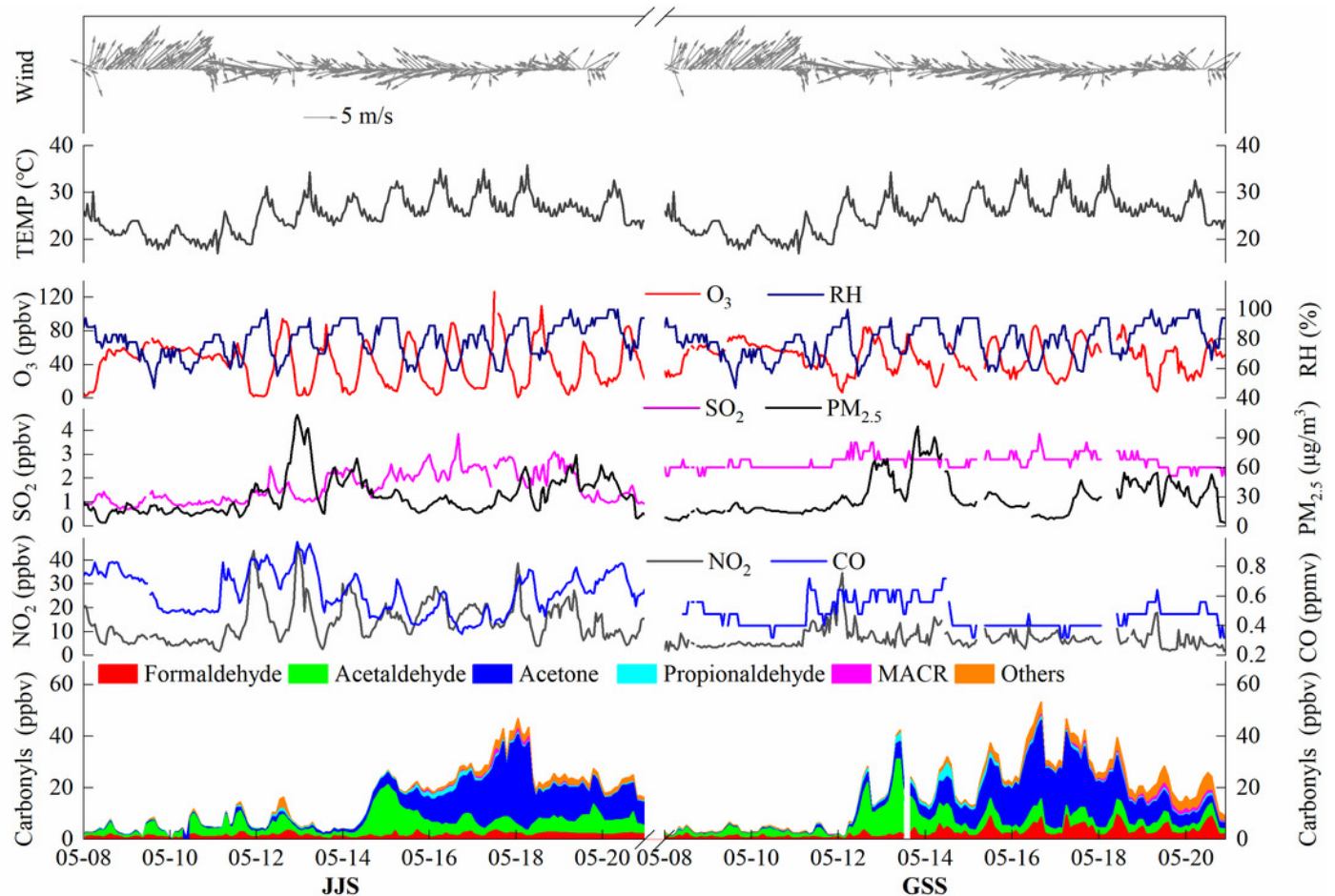



Figure 3

Diurnal variations of the total carbonyl compounds and O_3 at GSS and JJS sites from May 8 and 20, 2018.

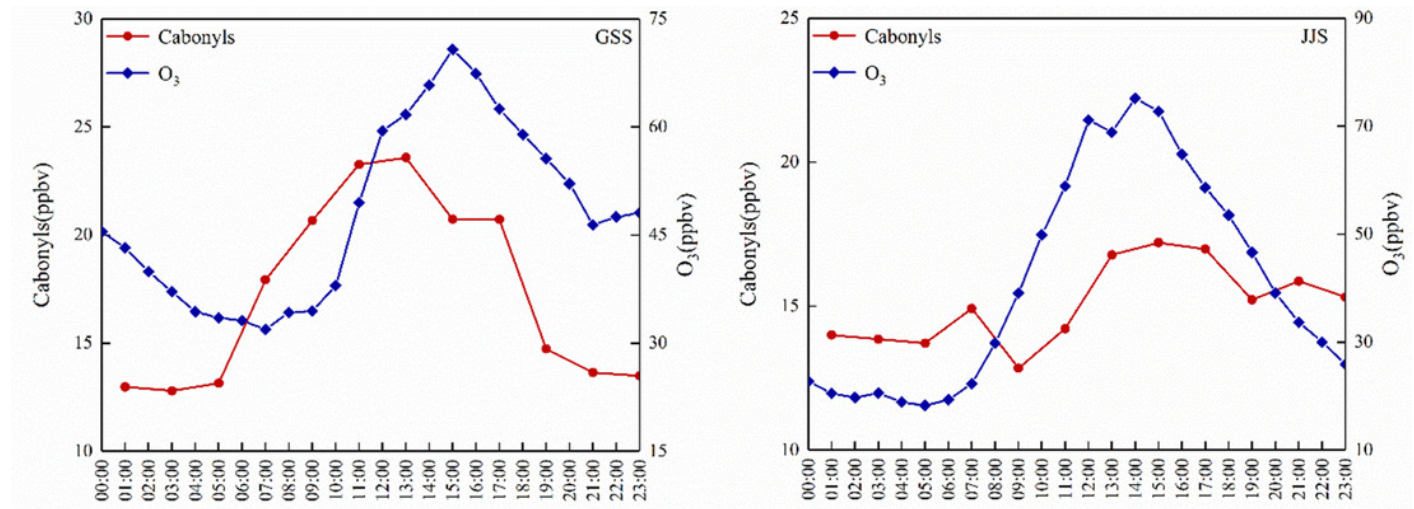



Figure 4

Diurnal variations of main carbonyl compounds at GSS and JJS sites from May 8 and 20, 2018.

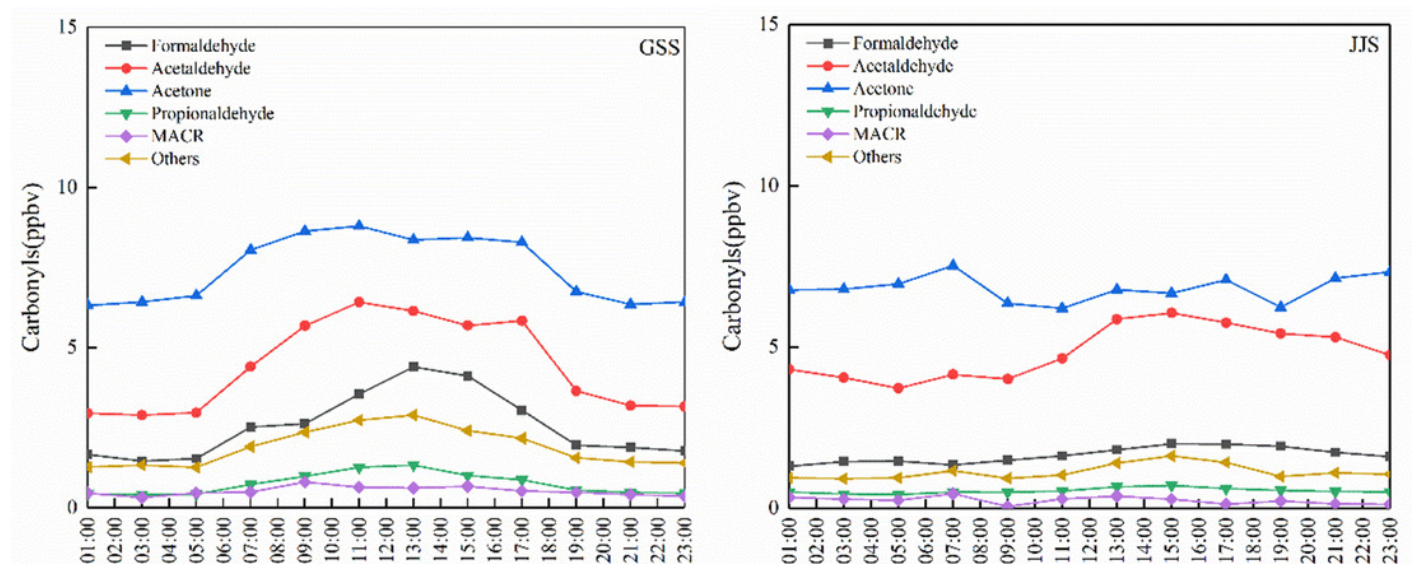



Figure 5

Proportions of main carbonyl compounds at GSS and JJS sites from May 8 to 20, 2018.

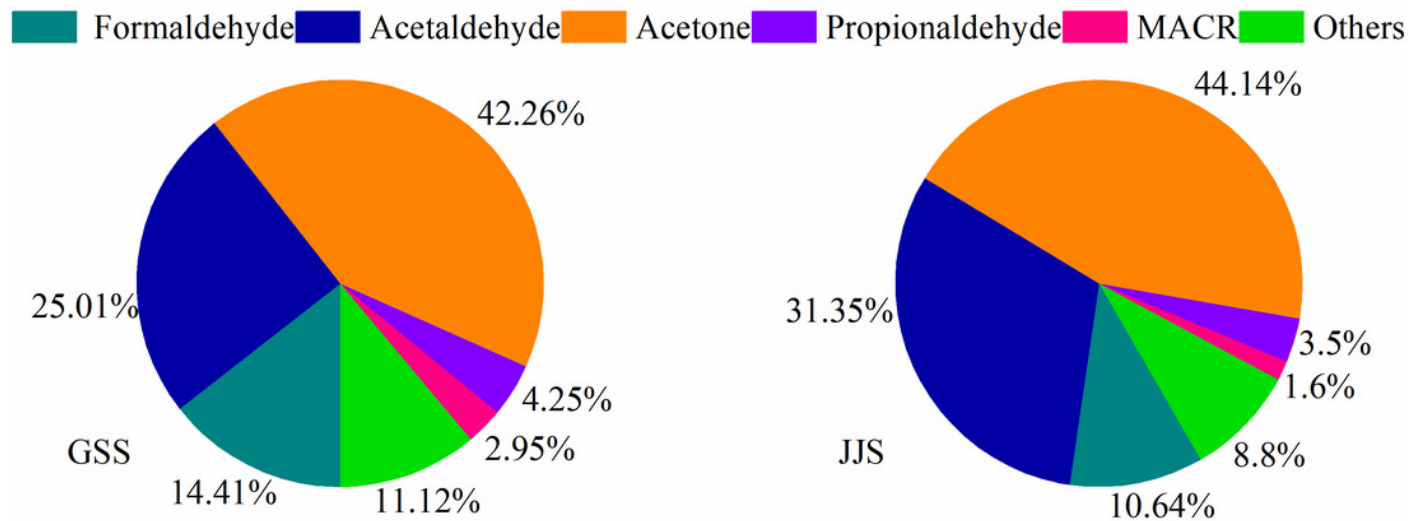



Figure 6

Ratios of formaldehyde to acetaldehyde (F/A) during the day and night at GSS and JJS sites from May 8 and 20, 2018.

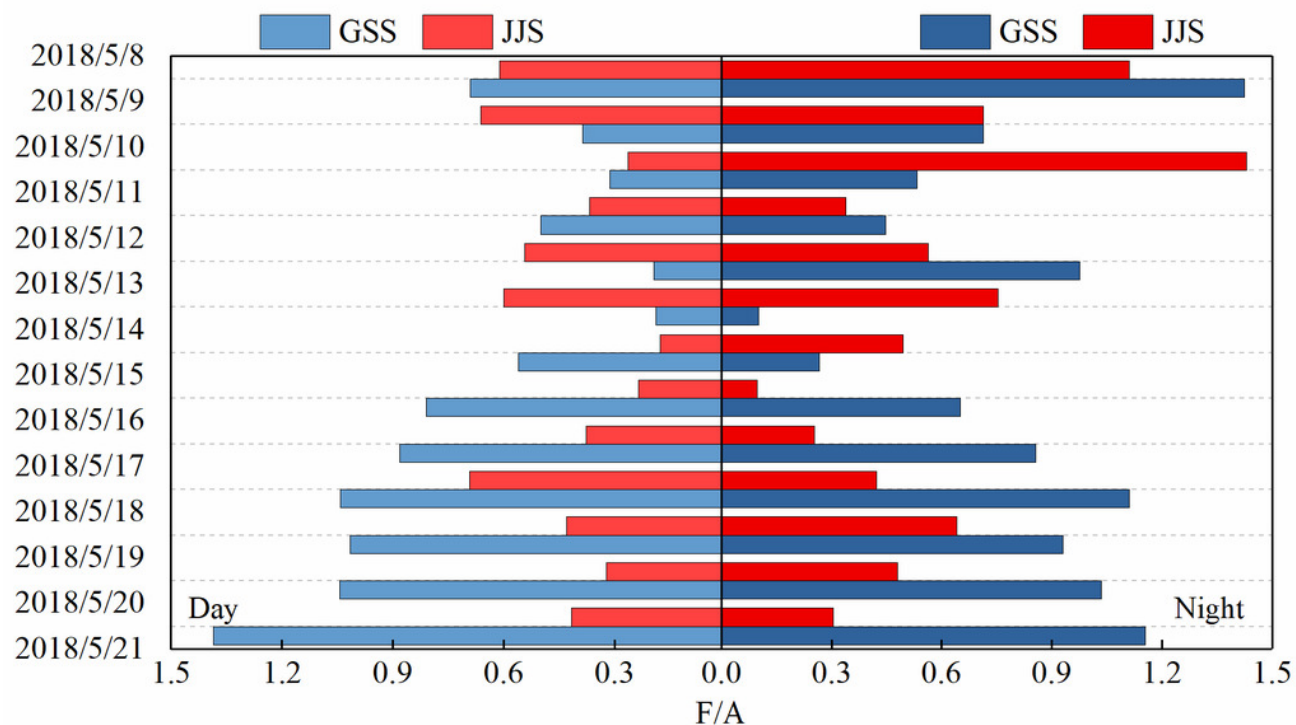



Figure 7

Ratios of acetaldehyde to propionaldehyde (A/P) during the day and night at GSS and JJS sites from May 8 and 20, 2018.

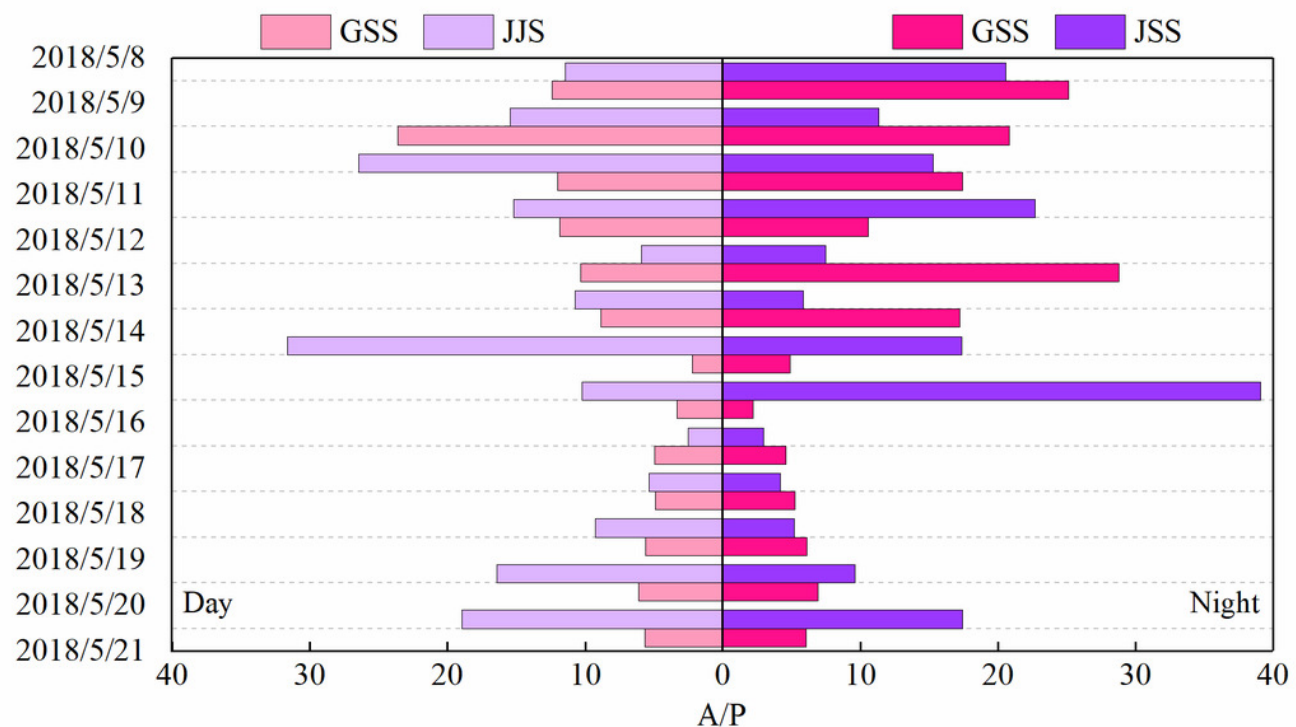



Figure 8

The simulated and observed HCHO production rate on May 17, 2018.

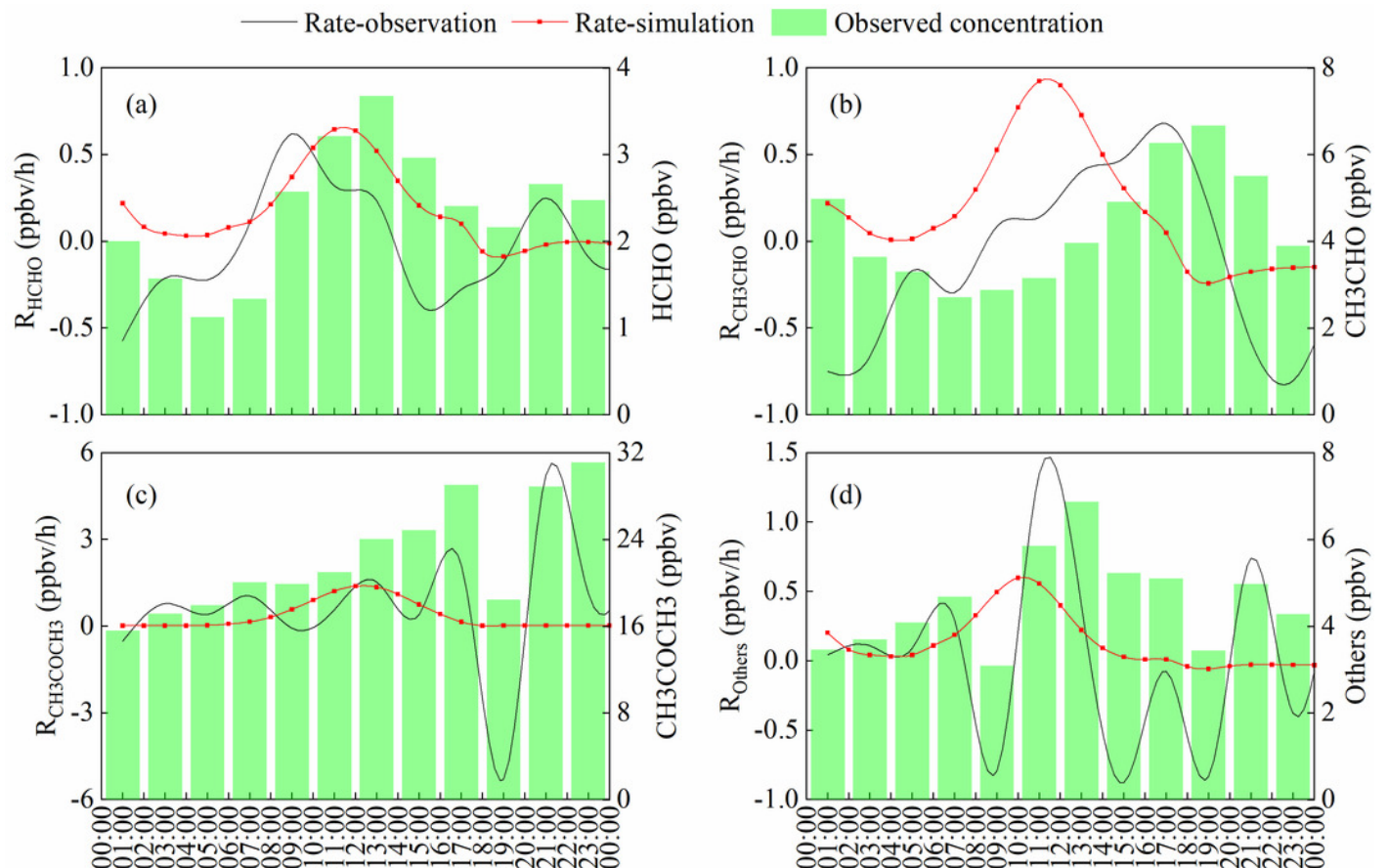
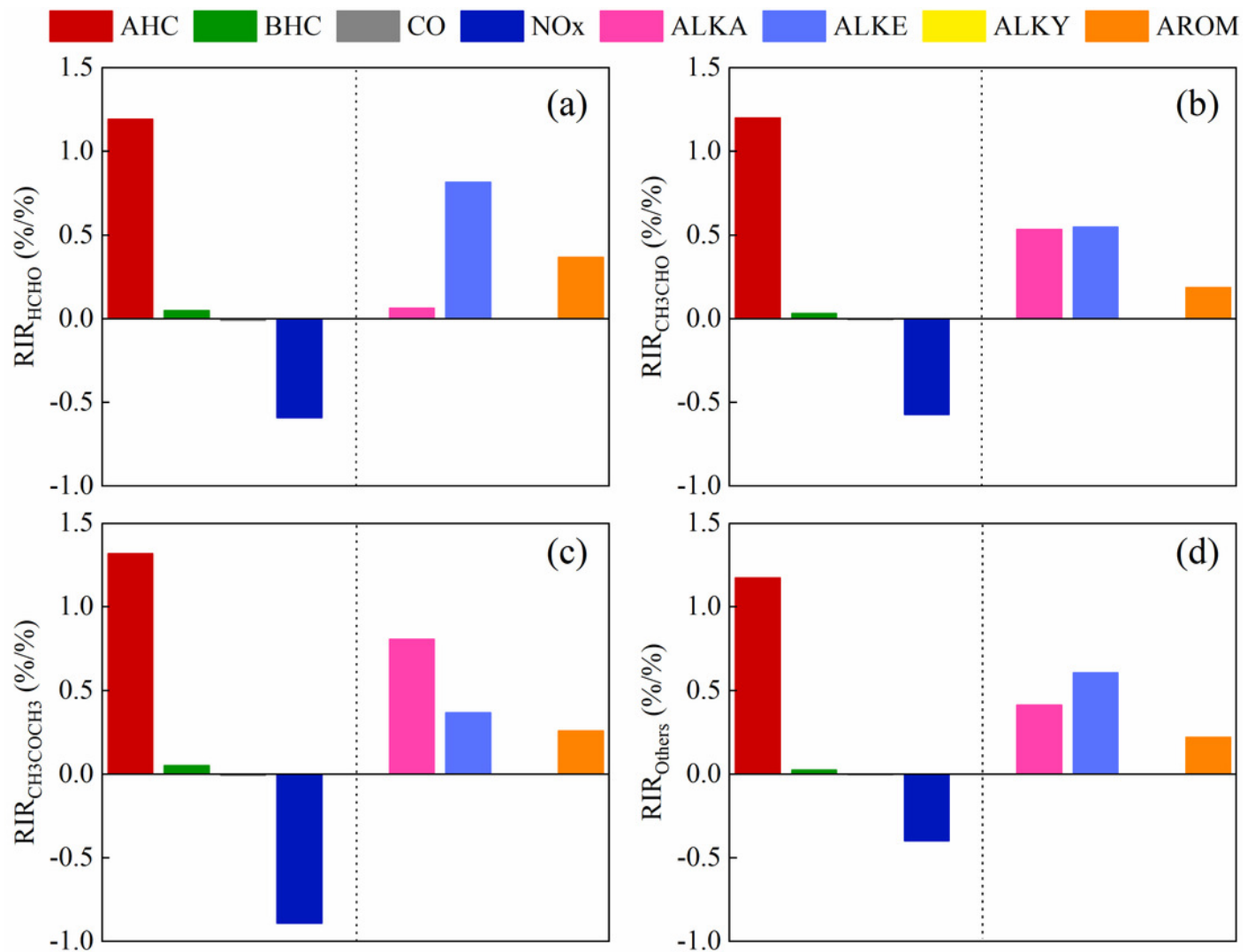



Figure 9

The model-calculated RIR of the major precursors for the secondary formation of HCHO on May 17, 2018.

Detection information of 16 carbonyl compounds by HPLC/UV.

1   **Table 1.** Detection information of 16 carbonyl compounds by HPLC/UV.

Species	Retention time (min)	Correlation coefficient (R^2)	Detection limit (ppbv)	Quantitation limit (ppbv)
Formaldehyde	4.97	1.0000	0.022	0.073
Acetaldehyde	6.24	1.0000	0.022	0.073
Acrolein	7.83	1.0000	0.023	0.076
Acetone	8.13	1.0000	0.026	0.085
Propionaldehyde	8.70	1.0000	0.028	0.092
Crotoraldehyde	10.55	1.0000	0.031	0.102
n-Butyraldehyde	12.00	0.9998	0.035	0.104
Benzaldehyde	13.31	0.9994	0.036	0.109
Isovaleraldehyde	16.20	0.9996	0.049	0.164
Valeraldehyde	17.13	0.9980	0.048	0.159
o-Tolualdehyde	18.32	0.9992	0.050	0.166
m-Tolualdehyde	18.95	0.9982	0.050	0.166
p-Tolualdehyde	19.76	0.9978	0.054	0.180
Hexaldehyde	24.21	0.9998	0.034	0.114
2,5-Dimethylbenzaldehyde	24.75	0.9998	0.031	0.102
MACR	11.67	0.9994	0.033	0.110

Concentrations of $PM_{2.5}$, SO_2, O_3, CO, NO_2 at GSS and JJS sites

Table 2. Concentrations of other pollutants at GSS and JJS sites.

Compound	Mean ±SD[1]		Number of samples	
	GSS	JJS	GSS	JJS
$PM_{2.5}$ (µg/m^3)	29,40±18.83	31.06±19.36	n=311	n=311
SO_2 (ppb)	2.67±0.34	1.65±0.66	n=311	n=311
O_3 (ppb)	48.29±18.03	40.70±25.37	n=311	n=311
CO (ppm)	0.47±0.09	0.63±0.14	n=311	n=311
NO_2 (ppb)	6.99±4.15	14.22±8.45	n=311	n=311

Concentrations of carbonyl compounds at GSS and JJS sites

Table 3. Concentrations of carbonyl compounds at GSS and JJS sites.

Compound	Mean ±SD[1] (ppbv)		Range (ppbv)	
	GSS	JJS	GSS	JJS
Formaldehyde	2.54±2.09	1.64±0.75	0.23-9.63	0.08-3.68
Acetaldehyde	4.41±4.36	4.84±3.63	0.48-29.07	0.02-19.61
Acrolein	BDL[2]	BDL	BDL	BDL
Acetone	7.45±8.13	6.82±8.11	0.03-30.55	BDL-35.18
Propionaldehyde	0.75±0.82	0.54±0.51	BDL-5.28	BDL-2.20
Crotonaldehyde	0.08±0.08	0.07±0.07	BDL-0.34	BDL-0.29
Butyaldehyde	1.28±1.3	0.80±0.92	BDL-4.57	BDL-3.95
Benzaldehyde	0.05±0.03	BDL	BDL-0.22	BDL-0.15
Isovaleraldehyde	0.48±0.43	0.19±0.53	BDL-2.27	BDL-3.71
Valeraldehyde	BDL	BDL	BDL	BDL-0.20
o-Tolualdehyde	BDL	BDL	BDL	BDL
m-Tolualdehyde	BDL	BDL	BDL-0.05	BDL-0.05
p-Tolualdehyde	BDL	BDL	BDL	BDL
Hexaldehyde	0.06±0.05	0.22±0.34	BDL-0.36	BDL-1.01
2,5-Diemthybenzaldehyde	BDL	BDL	BDL	BDL
MACR	0.52±0.57	0.24±0.42	BDL-2.01	BDL-2.37
Total Carbonyl compounds	17.57±12.77	15.45±11.18	1.11-53.22	0.04-46.83

3   [1] SD means standard deviations in pptv

4   [2]BDL: below detection limit