Exploring the Crucial Role of Atmospheric Carbonyl Compounds in Regional Ozone heavy Pollution: Insights from Intensive Field Observations and Observation-based modelling in the Chengdu Plain Urban Agglomeration, China

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Abstract. Gaseous carbonyl compounds serve as crucial precursors and intermediates in atmospheric photochemical reactions, significantly contributing to ambient ozone formation. To determine whether the impact of carbonyl compounds on regional ozone pollution is driven by their abundance or by specific secondary chemical processes, simultaneous field observations and observation-based modelling of ambient carbonyls were conducted at nine sites within the Chengdu Plain Urban Agglomeration (CPUA), China during August 4-18, 2019, when three episodes of regional heavy ozone pollution occurred across eight cities within CPUA. Throughout the study, the total mixing ratios of 15 carbonyls ranged from 10.7 ± 4.2 to 35.2 ± 13.4 ppbv. The spatial distribution reveal that regions with higher concentrations of carbonyl compounds, such as around Chengdu, are also areas with more severe ozone pollution. Both the abundance and the

36 chemical reactivity of carbonyl compounds, especially formaldehyde and acetaldehyde,

37 play crucial roles in ozone formation in the CPUA. On ozone pollution days, carbonyl

38 concentrations significantly increased by 22.8% to 66.2%.While the abundance of

39 carbonyls is an important factor, their significant role in heavy ozone pollution within

40 the CPUA is primarily driven by secondary chemical processes, particularly those

41 involving alkenes and BVOCs. Sites with higher average ozone concentrations during

42 observations were mainly in the VOCs-limited regime, while others were in the

43 transitional regime. Additionally, the mutual transport of carbonyl compounds between

44 cities in the CPUA suggests that regional collaboration is essential to address ozone

45 pollution effectively. These findings offer valuable insights for developing effective

46 strategies to control regional ozone pollution.

47 **Keywords:** Gaseous Carbonyls; Ozone Heavy Pollution; Pollution Characteristics;
48 Atmospheric Photochemical Reactivity; Source Analysis; The Chengdu Plain Urban
49 Agglomeration, China

50 **1. Introduction**

51 Atmospheric carbonyl compounds play a pivotal role in tropospheric chemistry,

52 acting as crucial precursors to both ozone (O_3) and secondary organic aerosols (SOA),

53 a fact recognized for decades (Altshuller, 1993; Grosjean and Seinfeld, 1989). Their

54 importance has been confirmed by numerous studies over the years(Guo et al., 2004;

55 Hallquist et al., 2009; Wang et al., 2020; Ye et al., 2021; Coggon et al., 2019),

56 highlighting their significant contribution to atmospheric photochemistry and air

57 pollution. Over the past two decades, severe air pollution in China has driven substantial

58 research efforts to understand the contributions of carbonyl compounds to these

59 environmental challenges. Studies have shown that photolysis of carbonyl compounds

60 is a major source of RO_X radicals (Grosjean and Seinfeld, 1989; Zhang et al., 2016).

61 These compounds can be photolyzed and react with OH radicals to form a large number

62 of HO_2 and RO_2 radicals, which increase the atmospheric oxidation capacity and

63 participate in the NOx photochemical cycle, leading to ozone formation (Zhang et al.,

删除了： in which formaldehyde (48.1%), acetone (19.9%), and acetaldehyde (17.5%) were most abundant within the CPUA. Ambient levels of carbonyls and ozone showed some positive correlations in space (especially pronounced around Chengdu in both northern and southern directions) and in diurnal variations with higher concentrations of carbonyls during ozone pollution episodes. Photochemical reactivity analysis emphasized the significant contributions of carbonyls, especially formaldehyde and acetaldehyde, to ozone formation.

删除了： The ozone formation sensitivity for sites experiencing severe ozone pollution were classified as VOCs-limited regime, while others were categorized as transitional regime.

删除了： Local primary emissions, mutual air transportation among cities within the CPUA and photochemical secondary processes were recognized to contribute significantly to the production or the contamination of carbonyls in ambient air, with alkenes and alkanes being important secondary precursors of carbonyls. This study highlights the pivotal role of carbonyls in heavy ozone pollution within the CPUA, China, providing valuable scientific insights to guide the development of effective countermeasures for regional ozone pollution control in the future.

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108 2016; Meng et al., 2017). Additionally, dialdehydes such as glyoxal and methylglyoxal

109 undergo heterogeneous reactions with aqueous particulate matter, rapidly forming SOA

110 (Lou et al., 2010; Xue et al., 2016; Yuan et al., 2012). Ambient carbonyl compounds

111 not only affect the environment but also pose direct health risks to humans. They can

112 harm ecosystems through deposition and adsorption processes (Yang et al., 2018). They

113 also pose direct health risks to humans, including sensitization, carcinogenesis, and

114 mutagenicity (Fuchs et al., 2017).

115   Recent research has increasingly focused on understanding the spatial and

116 temporal variability of carbonyl compounds in highly polluted regions, particularly in

117 China, where rapid industrialization has led to severe air quality challenges. Xue et al.

118 (2013) and Duan et al. (2012) reported typical ambient concentrations of carbonyl

119 compounds ranging from a few µg·m⁻³ to tens of µg·m⁻³ in urban areas, depending on

120 the specific compounds and regions studied. For example, formaldehyde concentrations

121 in highly polluted areas can exceed 10 µg·m⁻³. Shen et al. (2013) and Fu et al. (2008)

122 observed significant diurnal variation, with higher concentrations of carbonyl

123 compounds during the daytime, particularly in the afternoon, driven by photochemical

124 production. Concentrations can increase by as much as 50-100% during peak sunlight

125 hours compared to nighttime levels. Pang and Mu (2006) and Rao et al. (2016)

126 identified key sources of carbonyl compounds, including vehicular emissions, industrial

127 activities, and secondary formation from VOC oxidation in the atmosphere. In urban

128 environments, vehicular emissions are often a dominant primary source, while

129 secondary formation contributes significantly during daytime due to photochemical

130 processes. The results highlight severe and spatiotemporal variations of carbonyl

131 pollution in China. High levels are found mainly in the North China Plain(NCP), the

132 Yangtze River Delta(YRD), and the Pearl River Delta(PRD)(Duan et al., 2008; Shao et

133 al., 2009; Tan et al., 2018; Wang et al., 2018; Xue et al., 2014, 2013; Yang et al., 2017).

134 Urban areas generally exhibit higher carbonyl levels than suburban and rural areas due

135 to human activities(Xue et al., 2013). Despite the progress made, significant gaps

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删除了: In addition, ambient carbonyl compounds could also be removed through wet and dry deposition, and soil and ocean adsorption, thereby adversely affecting the ecological environment

下移了 [1]: The sources of Atmospheric carbonyl compounds can be divided into primary source and secondary source. Primary sources mainly include incomplete combustion of fossil fuels and biomass, industrial emissions, catering business emissions, and plant releases, etc; And secondary source is mainly from the secondary formation of atmospheric photochemical oxidation of VOCs (Xue et al., 2013).

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243 remain in understanding the spatiotemporal distribution and source apportionment of
244 carbonyl compounds, particularly in urban agglomerations. Existing research has
245 primarily focused on urban areas in rapidly developing regions like the NCP, YRD, and
246 PRD. Moreover, studies have often emphasized the overall role of VOCs in ozone
247 pollution, with less attention given to specific carbonyl compounds and their individual
248 contributions to atmospheric oxidation capacity and ozone formation (Meng et al.,
249 2017).

250   Monitoring carbonyl compounds in the atmosphere is challenging due to their
251 typically low concentrations (ppt-ppb levels), necessitating highly sensitive analytical
252 methods. The diversity of carbonyl compounds, including multiple isomers, requires
253 highly selective analytical techniques for differentiation. Current measurement
254 technologies limit our understanding of the spatiotemporal distribution of carbonyl
255 compounds, affecting the accurate assessment of their environmental behavior, sources,
256 and transport (Xue et al., 2013; Sahu and Saxena, 2015). While numerous studies have
257 explored the role of carbonyl compounds in ozone production, many focus on general
258 mechanisms rather than specific compounds or regional variations (Atkinson and Arey,
259 2003; Monks et al., 2015).

260   Atmospheric carbonyl compounds originate from both primary and secondary
261 sources (Pang and Mu, 2006; Rao et al., 2016). Primary sources include the incomplete
262 combustion of fossil fuels and biomass, industrial emissions, emissions from the
263 catering industry, and releases from plants. Secondary sources arise from the
264 atmospheric photochemical oxidation of VOCs (Xue et al., 2013), particularly
265 alkenes, aromatics, and isoprene, which typically dominate the secondary formation of
266 carbonyls. However, distinguishing between primary and secondary contributions
267 remains challenging. Existing source apportionment methods, such as characteristic
268 species ratios and multiple linear regression, often lack the resolution to differentiate
269 these sources accurately, especially for non-vehicular emissions and secondary
270 formation. The limitations of these methods underscore the need for more advanced

approaches to better quantify the secondary formation mechanisms of carbonyl compounds and their regional impact on ozone formation. Despite significant advancements in studying atmospheric carbonyls, key gaps remain in understanding their precise spatiotemporal distribution and source apportionment. Specifically, there is a need for studies that examine how carbonyls vary across different environments—urban, suburban, and rural—and during varying pollution events. Without such targeted analysis, our understanding of the behavior of carbonyl compounds and their contribution to ozone pollution remains incomplete, particularly in regions experiencing severe pollution.

This study focuses on atmospheric carbonyl compounds and their roles in photochemical pollution within the Chengdu Plain Urban Agglomeration (CPUA) of China. The CPUA includes eight cities: Chengdu, Mianyang, Deyang, Leshan, Meishan, Yaan, Suining, and Ziyang. This region has a developed economy and a high degree of internationalization. The CPUA is located on the western edge of the Sichuan Basin, surrounded by mountain ranges, which easily block airflow. The unique climatic environment of the CPUA features low wind speeds year-round, high frequency of static winds, short hours of sunshine, frequent winter inversions, and a pronounced heat island effect in summer. These climatic characteristics significantly impact the variations in air pollutant concentrations, making the region prone to ozone pollution in summer and haze pollution in winter (Li et al., 2013; Hu et al., 2017; Zhang et al., 2010). Although previous studies have shown that ozone formation in urban Chengdu is primarily VOCs-limited (Tan et al., 2018), with aromatic hydrocarbons and alkenes contributing significantly to ozone generation in summer (Xu et al., 2020), these studies mainly focus on single cities and overall VOCs. There is still limited understanding of whether the significant roles of carbonyl compounds in ozone formation are primarily due to their abundance or whether specific chemical reactions involving carbonyls drive this process. This study aims to address these gaps by investigating the spatial distribution, sources, and specific chemical pathways of carbonyl compounds across

the entire CPUA and assessing their contributions to regional ozone pollution and inter-city air transport mechanisms.

To address these research gaps, this study involves an intensive field observation experiment conducted by the Sichuan Academy of Environmental Sciences, Peking University, Sichuan University and Chinese Academy of Environmental Sciences. Atmospheric carbonyl compounds were observed at nine sites in eight cities within the CPUA for 15 days during a period of heavy ozone pollution in August 2019. Samples were analyzed using 2,4-dinitrophenylhydrazine solid phase adsorption/high performance liquid chromatography (HPLC). The study aims to characterize the atmospheric carbonyl compounds in the CPUA, assess their influence on photochemical pollution, identify key carbonyl compounds that may play crucial roles in heavy ozone pollution in the CPUA, and evaluate the contribution of primary emissions, air pollution transport, and secondary generation to key carbonyl compounds through a combination of multivariate linear regression modeling and Observation-Based Modeling (OBM). This research aims to provide technical support for controlling carbonyl compounds pollution in the CPUA and to reduce their contributions to ozone pollution.

2. Materials and methods

2.1 Observation Sites Profile

In this study, a total of 9 off-line sampling sites for atmospheric carbonyl compounds were set up in 8 cities in the CPUA from August 4th to 18th, 2019(table S1). Considering that this study focused on the pollution characterization of carbonyl compounds in urban areas, one urban site was selected in each city. In addition, in order to compare and study the pollution characteristics of carbonyl compounds in the suburbs, a suburban site was set up in Xinjin County, Chengdu. For the selection of urban sites in each city, priority is given to those choices of set-up in the vicinity of the state-controlled site, and the perimeter of the sites should be open, unobstructed and no

430 obvious pollution sources, with convenient transportation and power supply. The

431 distribution of specific sites is shown in Fig. 1.

432   Ozone concentrations were measured using the UV absorption method with a

433 Thermo O_3 analyzer (Model 49i), with data sourced from national control stations near

434 each sampling site. Nitrogen dioxide (NO_2) was measured by chemiluminescence

435 following chemical conversion to nitric oxide (NO) using a molybdenum catalyst;

436 however, this method is known to have interferences from other NOz species. Carbon

437 monoxide (CO) was measured via infrared absorption with a Thermo instrument

438 (Model 20). All Thermo instruments were carefully maintained and calibrated daily at

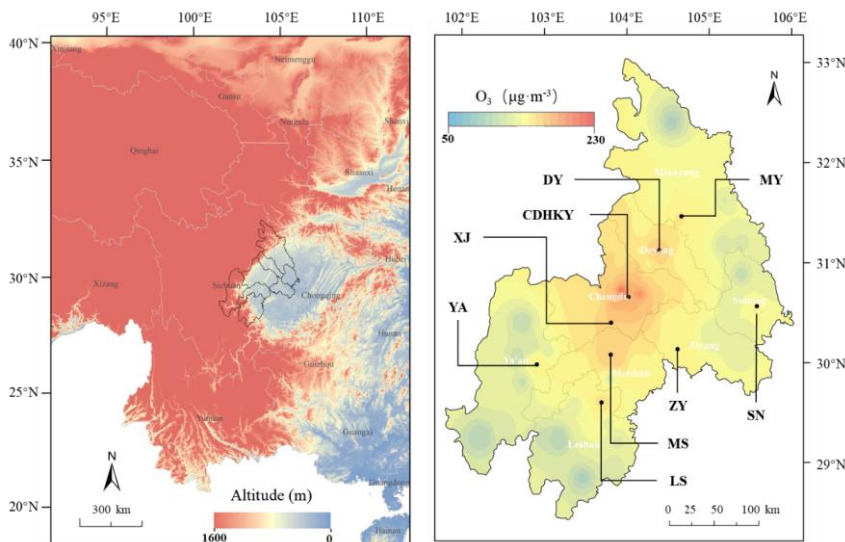
439 01:00 to ensure measurement accuracy. Measurements for ozone, NO_2, and CO were

440 collected with a time resolution of one hour. Simultaneously, meteorological

441 parameters—temperature, relative humidity (RH), wind speed, and direction—were

442 recorded at each observation site using an automatic weather station (PC-4, JZYG,

443 China), also at a one-hour resolution.

444

445 **Figure 1.** Distribution of sampling sites. The left panel shows the elevation map of the Sichuan

446 Basin, highlighting the geographical features of the region, with elevation data sourced from the

447 Geospatial Data Cloud (https://www.gscloud.cn/#page1/2). The right panel presents the spatial

448 distribution of ozone concentrations in the CPUA during the observation period (August 4–18,

2019), with ozone data obtained from national control stations near each sampling site. Black dots represent the locations of the sampling sites, labeled as follows: MY (Mianyang), DY (Deyang), CDHKY (Chengdu Environmental Science Research Institute), XJ (Xinjin), SN (Suining), ZY (Ziyang), MS (Meishan), YA (Ya'an), and LS (Leshan). The color bar in the top left corner corresponds to interpolated ozone concentrations, with each color representing a concentration gradient.

2.2 Samples Collection

The sampling of atmospheric carbonyl compounds mainly referred to the TO-11A standard of the United States Environmental Protection Agency (US EPA) and the Chinese environmental protection standard HJ 683-2014 High Performance Liquid Chromatography Method for the Determination of Atmospheric Carbonyl Compounds, and the sampling was carried out by using silica gel sampling tubes (IC-DN3501 from Tianjin Bonna-Agela) coated with DNPH (2,4-dinitrophenylhydrazine). In this study, an automatic sampler for carbonyl compounds (Zhang et al., 2019) was used to continuously collect atmospheric carbonyl compounds. From August 4th to 18th, 2019, air samples were collected every 2 hours with a sampling flow rate of 0.8 $L\cdot min^{-1}$. In addition, in order to prevent the impact of ozone and rainwater in the atmospheric air on sample collection, a potassium iodide ozone removal column (KI 140 from Tianjin Bonna-Agela) was installed and a water removal agent made by ourselves (Bao et al., 2022; Wang et al., 2020) was added at the front end of the sample tube. Two blank samples were collected before and after the sampling, and blank samples were also collected for different batches of sampling tubes. The samples were frozen at -18°C and analyzed within one month.

Atmospheric VOCs were sampled using SUMMA tanks, stainless steel tanks with electropolished and silanized inner walls, manufactured by Entech in the United States, with a sampling volume of 3.2 liters. The sampling was controlled by a constant current integral sampler to sampling for an average of 1 hour. From August 4th to 18th, 2019, two VOCs samples were collected each day at each site, at 8:00-9:00 and 14:00-15:00 (no samples were taken under special weather conditions, such as rain). On August 11th, 12th and 16th, six samples were collected per day to capture diurnal variations under

ozone pollution events, at the following times: 8:00-9:00, 10:00-11:00, 12:00-13:00, 14:00-15:00, 16:00-17:00, and 18:00-19:00.

2.3 Samples Analysis

The carbonyl compounds samples were qualitatively and quantitatively analyzed by using High Performance Liquid Chromatography (HPLC) (LC-20AD, Shimadzu, Japan) and an ultraviolet detector (SPD-20A, Shimadzu, Japan), mainly based on the US EPA TO-11A standard and the Chinese HJ 683-2014 standard. The DNPH sampling column after sampling was slowly eluted into a volumetric flask using acetonitrile (chromatographically pure, Thermo Fisher Scientific China) to 5.0 mL. Then 1.5 mL of the sample was transferred into an HPLC sample bottle, and sealed and stored in a refrigerator at <4 ℃ to complete the pre-treatment. Prior to sample analysis, a standard solution of the concentration gradient was prepared using TO-11A standard solution (Supelco, USA) and used as the external standard. The correlation coefficient (R^2) of the standard curve was greater than 0.995. The detection limit of the device was 0.56~5.57 $ng \cdot mL^{-1}$, and the quantification limit was 1.87~18.56 $ng \cdot mL^{-1}$ (Table S2). Then 20 μL of the pretreated sample was extracted through the autosampler and injected into the HPLC/UV system, detected by a UV detector with a wavelength of 360 nm, qualified by retention time value, quantified by peak area value, and the qualitative and quantitative analysis data of carbonyl compounds were obtained after conversion. The HPLC conditions referred to Chinese environmental protection standard HJ 683-2014: binary gradient washing was performed using acetonitrile and water, 60% acetonitrile was held for 20 mins, acetonitrile was increased linearly from 60% to 100% within 20-30 mins, and acetonitrile was reduced to 60% again within 30-32 mins and held for 8 mins; the column oven was kept at 40 ℃. It should be noted that while the sampling and analysis method was effective for most carbonyl compounds, ketones, including methyl vinyl ketone (MVK), were not well sampled during the field observations. As a result, data for MVK and other ketones were missing. During the observation period, DNPH cartridges and HPLC analysis technique were used to detect a total of 15

carbonyl compounds (Table S2).

The atmospheric VOCs were analyzed using the TO-14 and TO-15 methods, which are recommended by the US EPA. These methods involve frozen preconcentration coupled with gas chromatography and mass spectrometry (GC-MS). TO-15 is a method for detecting and quantifying a wide range of VOCs from air samples. The VOCs were pre-concentrated by the Entech7100 system at a low temperature, then quantified by an Agilent GC-MS. During the sample analysis, four internal standard gases (bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5, and 4-bromofluorobenzene) were used. A multi-point calibration curve was created using a standard gas containing 118 VOCs, including PAMS compounds, TO-15 target analytes, and carbonyl compounds. PAMS (Photochemical Assessment Monitoring Stations) compounds are a subset of hydrocarbons known to contribute to ozone formation, such as ethane, ethylene, propane, and others.

2.4 Data Analysis

2.4.1 Ozone pollution assessment criteria

According to the Technical Regulation on Ambient Air Quality Index (on trial), National Environmental Protection Standard of the People's Republic of China HJ 633—2012, days with an ozone pollution index (IAQI) of 100 or higher during the observation period were designated as pollution days, while days with an IAQI below 100 were considered clean days. This study compared the pollution characteristics of carbonyl compounds between pollution days and clean days. Additionally, the concentrations of formaldehyde, acetaldehyde, and acetone observed during the summer of 2009-2013 in economically developed and industrialized areas such as Beijing, Shanghai, and Guangzhou in China, as well as locations in South America (Brazil), Asia (Thailand), Europe (France), and North America (United States), were selected and compared.

2.4.2 Ozone formation sensitivity

Previous studies have shown that the formaldehyde to NO_2 ratio (FNR) can be used to determine the sensitivity of O_3-NOx-VOCs (Schroeder et al., 2017; Tonnesen and Dennis, 2000; Vermeuel et al., 2019). Most studies used satellite remote sensing-based FNR, but the FNR column concentration ratios inverted by satellite remote sensing mainly represented the average photochemical of the troposphere, and the concentration distributions of HCHO and NO_2 in the vertical direction were inconsistent (Hong et al., 2022; Schroeder et al., 2017). So, there is a large uncertainty to develop ground-level ozone pollution prevention and control measures. In this study, sensitivity analysis of ground-level ozone formation was carried out based on the ratio of ground-level HCHO to NO_2 during the observation period at the 9 sites of 8 cities in the CPUA. FNR < 0.55±0.16 and FNR > 1.0±0.3 were defined to VOCs-limited and NOx-limited, respectively, and FNR ratio ranged from 0.55±0.16 to 1.0±0.3 defined to NO_X and VOCs co-limited (Liu et al., 2021; Zhang et al., 2022).

2.4.3 Exploration of Secondary Formation Mechanisms

(1) Atmospheric chemical reactivity

In this study, the contribution of atmospheric chemical reactivity of carbonyl compounds to ozone formation was evaluated using the OH free radical consumption rate (L_{OH}) and ozone formation potential (OFP):

$$L_{OH} = [OVOC]_i \times k_i(OH) \tag{1}$$

Where, $[OVOC]_i$ was the observed concentration of the ith (i=1 to n) carbonyl compound, in molecule·cm^{-3}; $k_i(OH)$ was the rate constants of the ith carbonyl compound reacting with OH radicals, in cm^3·(molecule·s)$^{-1}$. The unit of L_{OH} is s^{-1}, representing the rate of OH radical consumption. The selected $k_i(OH)$ values were from literature (Atkinson and Arey, 2003).

$$OFP = MIR_i \times [OVOC]_i \tag{2}$$

Where, MIR was the maximum incremental reactivity of the ith carbonyl compound, in g O_3·(g VOC)$^{-1}$ (grams of ozone formed per gram of volatile organic

compound), and the MIR values of each species were from California Code of Regulations (https://govt.westlaw.com); [OVOC]$_i$ was the mass concentration of the ith carbonyl compound, in $\mu g \cdot m^{-3}$. The unit of OFP is $\mu g \cdot m^{-3}$, representing the potential ozone formation.

(2) Observation-based model (OBM)

The Observation-Based Model (OBM) is a box model that uses actual observational data to evaluate the sensitivity of secondary pollutant formation mechanisms to their precursor emissions. By constraining the model with atmospheric observation data, typical secondary pollutants and parameters such as NO_X, SO_2, CO, VOCs, temperature, humidity, pressure, and JNO_2 are input into the model as hourly observational data to calculate the chemical formation and consumption of secondary pollutants and free radicals. In this study, the OBM model used the Master Chemical Mechanism (MCM) (v3.3.1, mcm.leeds.ac.uk), which is a nearly detailed chemical mechanism that describes the chemical processes of 143 VOC species from emission to degradation in the atmosphere, including approximately 6,700 species and 17,000 inorganic and organic reactions. In this version of the MCM, a total of 19 carbonyl compounds are included, comprising 9 aldehydes and 10 ketones. Of these, 9 carbonyl compounds were measured in this study, including formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde, butyraldehyde, isovaleraldehyde, valeraldehyde, and hexaldehyde. The MCM chemical mechanism can simulate atmospheric photochemical reaction processes under near-real conditions and calculate the concentrations of highly reactive species, quantifying the reaction rates of all species involved. For VOCs, especially carbonyls, that were not directly measured, the MCM uses estimated values derived from emission inventories, literature data, and assumptions based on similar species to provide estimates for their concentrations and reaction rates.

Relative Incremental Reactivity (RIR) was first used by Cardelino and Chameides

634 (1995) to simulate the response of ozone to precursor changes through scenario tests

635 using box model calculations. RIR was calculated by assuming that the concentration

636 of a given carbonyl compound precursor decreased by a certain proportion could cause

637 the change of the concentration of the carbonyl compound, so as to further judge the

638 effect of VOCs on the formation of carbonyl compounds. Combining the concentrations

639 and activity levels of 15 carbonyl compounds during the observation period, this study

640 focused on formaldehyde, acetaldehyde, and acetone as the primary research targets.

641 The impacts of various AVOCs(anthropogenic VOCs)including alkanes, alkenes,

642 alkynes, and aromatic hydrocarbons, as well as BVOCs(biogenic VOCs)like isoprene,

643 on the formation of formaldehyde, acetaldehyde, and acetone were assessed using

644 observation-based OBM classification. Specific species of anthropogenic source VOCs

645 (alkanes, alkenes, alkynes, and aromatic hydrocarbons) and biogenic VOCs (isoprene)

646 are detailed in Table S3.

647   VOCs observations, conventional gases (NO_2, CO and SO_2) and meteorological

648 parameters (temperature, relative humidity and pressure) were imputed into the model.

649 It was assumed that the pollutants are well mixed. Under the constraints of the measured

650 hourly concentration data of pollutants, the atmospheric chemical process was

651 simulated to obtain the source-effect relationship of the measured pollutants. By

652 assuming the reduction of the source effect, the RIRs of different carbonyl compounds

653 precursors were calculated, and the sensitivities of carbonyl compounds to different

654 pollutants were obtained, and then the secondary formation mechanism of carbonyl

655 compounds was determined. The formula to calculate the RIR is as follows:

656
$$RIR(X) = \left[\frac{\Delta P_Y(X)/P_Y(X)}{\Delta S(X)/S(X)}\right] \qquad (3)$$

657
$$P_Y = Y_{\text{net formation}} - Y_{\text{net consumption}} \qquad (4)$$

658   Where X was a specific species; $P_Y(X)$ was the net formation rate of species y;

659 S(X) was the total amount of emissions of species X in a certain period, i.e., the source

660 effect of species X. $\Delta S(X)$ was the change in total emissions of X caused by the

661 hypothetical change in source effect, $\Delta P_Y(X)$ was the change in $P_Y(X)$ after the change

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666 in source effect S(X), and RIR(X) was the relative incremental reactivity of species X.

667 The species Y in this study were formaldehyde, acetaldehyde and acetone, respectively,

668 and pollutant X was reduced by 20%.

669 The absolute RIR of the precursor reflects the sensitivity of carbonyl compounds

670 formation to the precursor. The higher the absolute RIR, the more sensitive the carbonyl

671 compounds formation to the precursor. A positive RIR value indicates that reducing the

672 species can reduce the formation rate of species Y, and a negative RIR value indicates

673 that reducing the species can increase the formation rate of species Y.

674 **2.4.4 Sources Analysis**

675 **(1) Multi-linear regression model**

676 There is a good correlation between concentrations of compounds of the same or

677 similar source in the atmosphere. Based on this property, it was assumed that the

678 primary and secondary sources of carbonyl compounds were linearly correlated with

679 the selected tracers, and then a quantitative source model was established by multiple

680 linear statistical regression analysis (Kanjanasiranont et al., 2016a; Li et al., 2010; Ling

681 et al., 2017; Luecken et al., 2012; Lui et al., 2017; Wang et al., 2017). In general, CO is

682 the marker product of typical anthropogenic combustion source emissions, mainly from

683 vehicle exhaust emissions and coal combustion. Ozone, as an indicator of

684 photochemical smog, is a typical secondary formation pollutant. In this study, CO and

685 ozone were selected as the tracers of primary source and secondary source of carbonyl

686 compounds, respectively. The formula is as follows:

687
$$[carbonyl] = \beta_0 + \beta_1[CO] + \beta_2[O_3] \tag{6}$$

688 Where [carbonyl], [CO] and [O_3] represented the observed mixing ratios of

689 carbonyl compounds, CO and ozone, respectively, in ppbv. β_0, β_1 and β_2 were

690 coefficients obtained by multiple linear regression fitting model, in ppbv/ppbv. β_0

691 represented the background concentration of a given carbonyl compound, β_1

692 represented the emission ratio of the carbonyl compound relative to CO. β_1[CO] and

$\beta_2[O_3]$ represented the concentrations of carbonyl compound in primary emission and secondary formation, respectively, in ppbv.

In addition, the relative contribution of primary emissions, secondary formation and background concentrations of carbonyl compounds can be calculated using the following formula:

$$P_{primary} = \frac{\beta_1[CO]_i}{(\beta_0 + \beta_1[CO]_i + \beta_2[O_3]_i)} \times 100\% \qquad (7)$$

$$P_{secondary} = \frac{\beta_2[O_3]_i}{(\beta_0 + \beta_1[CO]_i + \beta_2[O_3]_i)} \times 100\% \qquad (8)$$

$$P_{background} = \frac{\beta_0}{(\beta_0 + \beta_1[CO]_i + \beta_2[O_3]_i)} \times 100\% \qquad (9)$$

Where, $P_{primary}$ represented the contribution of the primary emission of a given carbonyl compound, %; $P_{secondary}$ represented the contribution of the secondary formation of the carbonyl compound species, %; $P_{background}$ represented the contribution of the carbonyl compounds species from sources other than primary emissions and secondary formation, %.

(2) Backward trajectory model

The effects of long-distance air mass transport on the pollution of carbonyl compounds in the CPUA were studied using MeteoInfo software and TrajStat plug-in (http://www.meteothink.org/downloads/index.html). In this model, meteorological data were relevant meteorological data from the global date assimilation system (GDAS) database (ftp://arlftp.arlhq.noaa.gov/pub/archives/gdasl). A trajectory simulation height of 500 m above ground level (AGL) was selected. The duration of backward trajectory was 48 h. The daily start time was 00:00 UTC. The analog frequency was 2 h. The backward trajectory diagram was calculated. Meanwhile, the clustering method in TrajStat software and the Euclidean distance algorithm were used to cluster the airflow trajectory to the CPUA. And then the statistical analysis was carried out in combination with the corresponding pollutant mass concentration characteristics.

3. Results and Discussion

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3.1 Overview of air quality during observation period

Due to the influence of cooling and precipitation caused by cold air intrusion, the early observation period (from August 4th to 6th, 2019) in the Chengdu Plain Urban Agglomeration (CPUA) experienced slightly lower temperatures (25.1°C) and higher humidity (87.6%). These conditions were unfavorable for ozone formation. Although ozone itself is not easily removed by rain, precipitation reduces ozone pollution by washing away its precursors, such as nitrogen oxides (NOx) and polar volatile organic compounds (VOCs), such as aldehydes, ketones, and others, decreasing sunlight exposure, and enhancing atmospheric dispersion. However, as temperatures increased and humidity dropped in the subsequent days, more favorable conditions for ozone formation emerged, leading to heavy and persistent regional ozone pollution in the CPUA. By August 12th, the mean temperature had gradually increased to 29.1°C, while it averaged 27.7°C from August 13th to 14th. During this time, cumulative precipitation reached 975 mm, resulting in temporary alleviation of ozone pollution. Subsequently, temperatures rose again from August 15th to 18th, with the mean temperature persisting above 28.4°C for several days, accompanied by a decrease in humidity to a minimum of 64.8% on August 17th. Overall, during the observation period (from August 4th, 2019, 0:00 to August 18th, 2019, 24:00), three episodes of severe ozone pollution occurred, namely EP1 (August 7th to 9th), EP2 (August 10th to 13th), and EP3 (August 15th to 18th), as depicted in Fig. 2.

Fig.3 illustrates the temporal and spatial variations of ozone and NO_2 concentrations, as well as temperature and humidity at each site during the observation period. After observing the spatial distribution of ozone concentration during EP1, it's evident that the severity of pollution reached heavily polluted levels, with Chengdu recording an MDA8 concentration of 297 $\mu g \cdot m^{-3}$ on August 7th. This distribution demonstrated a radial decrease from Chengdu to the surrounding areas. However, the subsequent episodes, EP2 and EP3, exhibited even broader ranges of ozone pollution and more pronounced spatial movements. During the early stages of EP2 and EP3 (from

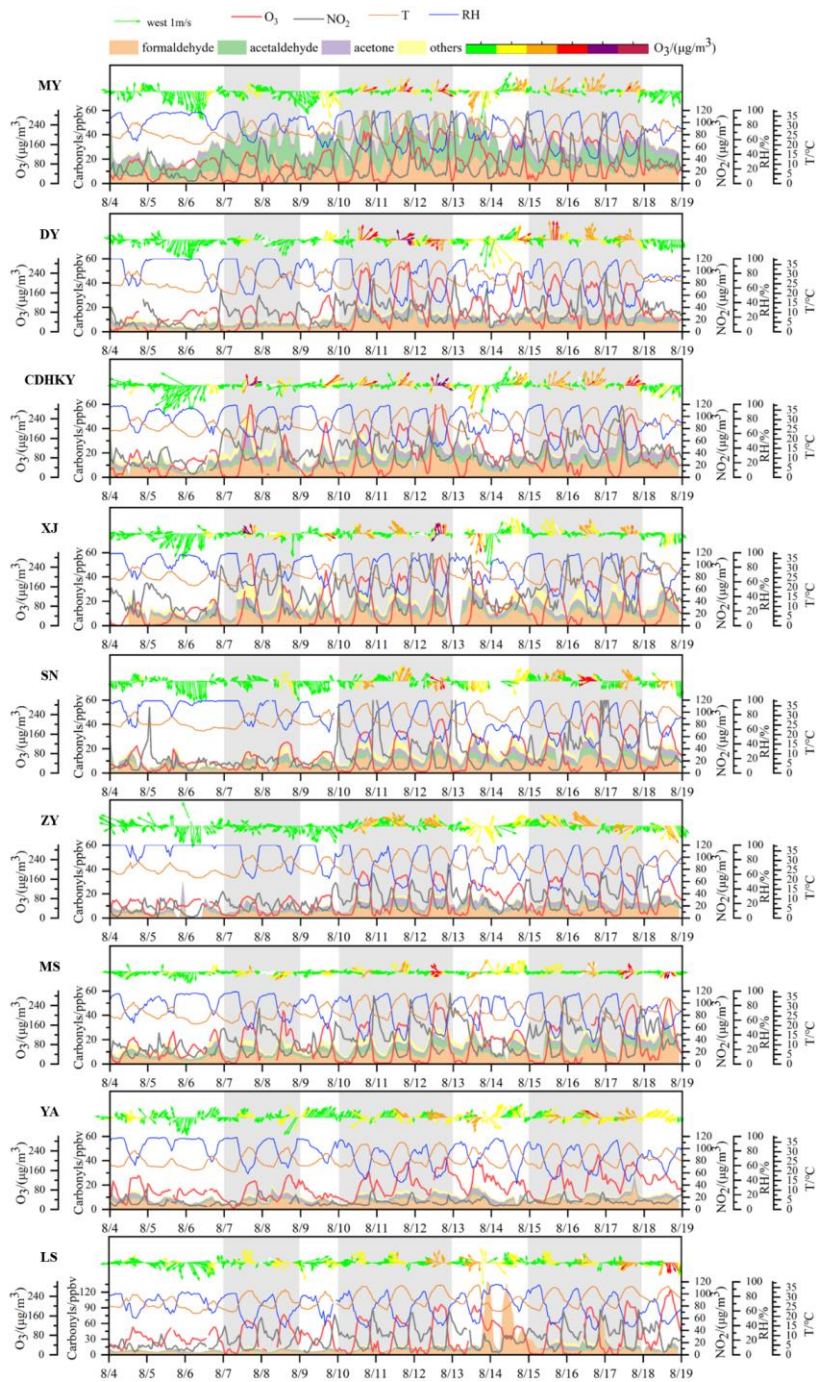
August 10th to 11th and from August 14th to 15th, respectively), high ozone concentrations were observed in the Chengdu-Deyang-Mianyang region. In the middle stages (August 12th and from August 16th to 17th, respectively), influenced by northerly airflow, regions with high ozone concentrations expanded to the central (Meishan, Ziyang, and Suining) and southwestern (Leshan and Ya'an) parts of the CPUA. In the later stages (August 13th and August 18th), under the influence of northwesterly airflow, regions with high ozone concentrations (Meishan and Leshan) moved southward again, while ozone pollution in other areas of the CPUA gradually weakened. On August 11th to 12th and August 16th to 17th, ozone concentrations in the eight cities of the CPUA reached light pollution levels or higher, with the heaviest pollution recorded on August 12th. Specifically, Deyang, Mianyang, Suining, and Meishan reached moderate pollution levels, while Chengdu reached heavy pollution with a concentration of 324 $\mu g \cdot m^{-3}$.

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Figure 2. Overview of air quality at each site during the observation period. The gray shaded parts

772   respectively represent the three heavy ozone pollution episodes (EP1, EP2,EP3).

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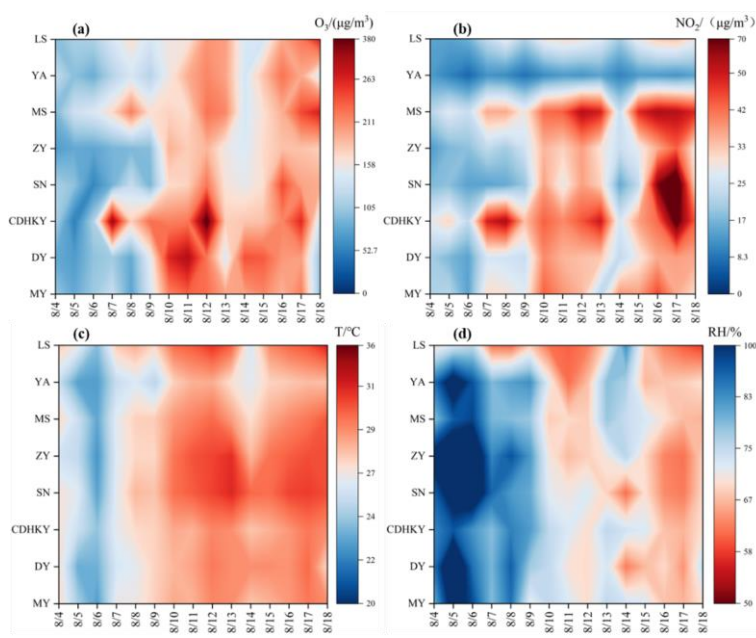
774   **Figure 3.** Temporal and spatial variations of (a) ozone concentration, (b) NO₂ concentration, (c)

775   temperature and (d) humidity in the CPUA during the observation period.

776   **3.2 Comparative characterization of carbonyl compounds**

777   **3.2.1 Ambient levels**

778   During the observation period, we utilized 2,4dinitrophenylhydrazine (DNPH)

779 cartridge and high-performance liquid chromatography (HPLC) analysis technique to

780 quantify 15 carbonyl compounds. The concentrations and relative proportions of these

781 compounds are summarized in Table 1. The average total concentration of the 15

782 carbonyls in the CPUA was 17.4 ± 5.3 ppb. Overall, areas with elevated concentrations

783 of carbonyl compounds were primarily concentrated in and around Chengdu in both

784 northern and southern directions. MY site, located to the north of Chengdu, exhibited

785 the highest concentration of carbonyl compounds (35.2 ± 13.4 ppb), while YA site,

786 situated southwest of Chengdu, showed the lowest concentration (10.7 ± 4.2 ppb).

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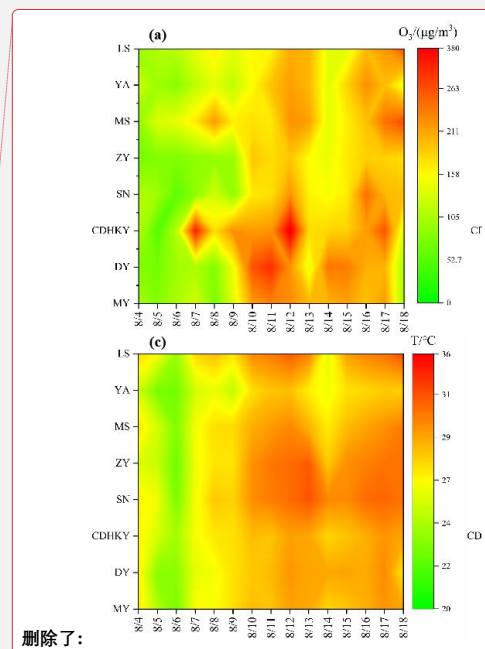
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796 **Table 1.** Daily mean ± standard error of carbonyl compound mixing ratios (ppbv) at each site in

797 the CPUA during the observation period. Sum: the total sum of carbonyl compound mixing ratios

798 across all compounds at each site.

Carbonyls	MY	DY	CDHKY	XJ	SN	ZY	MS	YA
formaldehyde	12.8±6.5	6.1±2.8	10.1±4.2	8.9±4.4	7.0±3.6	5.8±2.7	8.5±4.2	6.4±2.4
acetaldehyde	16.7±7.4	1.5±0.8	3.7±2.2	2.3±1.1	2.6±1.7	1.4±0.6	3.2±1.6	0.9±0.7
acetone	4.4±1.7	2.8±1.2	4.5±2.3	3.7±1.2	3.1±1.7	3.2±1.7	2.2±1.1	2.2±1.1
propionaldehyde	0.4±0.2	0.2±0.1	0.4±0.3	0.4±0.2	0.3±0.2	0.3±0.1	0.4±0.2	0.2±0.1
crotoraldehyde	0.2±0.2	0.1±0.1	0.2±0.3	0.1±0.1	0.2±0.1	0.2±0.3	0.2±0.2	0.4±0.2
butyaldehyde	0.2±0.5	0.2±0.3	0.4±0.6	0.9±1.7	0.3±0.2	0.1±0.2	0.4±0.5	0.3±0.2
benzaldehyde	0.0±0.0	0.0±0.1	0.0±0.1	0.2±0.2	0.1±0.1	0.0±0.0	0.0±0.0	0.0±0.0
isovaleraldehyde	0.0±0.1	0.0±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.0±0.1	0.7±0.4	0.0±0.0
valeraldehyde	0.0±0.0	0.3±0.1	0.3±0.6	0.6±0.4	0.9±0.7	0.0±0.0	0.0±0.0	0.0±0.0
o-Tolualdehyde	0.5±0.5	0.4±0.3	0.5±0.2	0.0±0.0	0.0±0.0	0.2±0.2	0.4±0.3	0.2±0.1
m-Tolualdehyde	0.0±0.0	0.0±0.1	0.0±0.1	0.2±0.2	0.3±0.1	0.0±0.0	0.0±0.0	0.0±0.0
p-Tolualdehyde	0.0±0.0	0.0±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
hexaldehyde	0.0±0.0	0.3±0.3	0.4±0.7	0.6±0.5	1.0±0.7	0.0±0.2	0.8±0.6	0.0±0.0
2,5-diemthybenzaldehyde	0.0±0.0	0.0±0.0	0.0±0.0	0.1±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
MACR	0.0±0.2	0.1±0.2	0.3±0.3	1.1±1.1	0.3±0.2	0.2±0.2	0.4±0.4	0.2±0.2
Sum	35.2±13.4	12.2±4.8	20.8±8.9	19.0±8.1	16.1±7.7	11.5±4.9	17.2±7.6	10.7±4.2

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1237

1238   Fig.S1 illustrates the relationship between ozone concentration and carbonyl

1239   compounds concentration at each site during the observation period. It is evident that

1240   the spatial distribution of carbonyl compound concentrations is similar to that of ozone

1241   concentration. Regions with severe ozone pollution tend to exhibit higher

1242   concentrations of carbonyl compounds. The variation in carbonyl compound

1243   concentrations is primarily attributed to anthropogenic emissions and prevailing

1244   summer wind directions in the CPUA. Chengdu is the most economically developed

1245   city in the CPUA, with notably higher GDP and industrial production values than other

1246   regions. Chengdu's major industries include coal-fired power plants, chemical plants,

1247   metallurgy and building materials plants, and high concentrations of carbonyls were

1248   observed in here. The unique basin climate of the CPUA, characterized by intense

1249   sunlight and stable atmospheric conditions, facilitates the accumulation of pollutants.

1250   Large amount of industrial emissions and strong photochemical reaction contributes to

1251   ozone pollution. Additionally, during the summer, prevailing northerly winds in the

1252   CPUA facilitate the downwind transport of pollutants from upwind sources, leading to

1253   regional pollution. It is noteworthy that the concentration of carbonyl compounds at the

1254   MY site significantly exceeds that at the CDHKY site. Mianyang, with its industrial

1255   roots, consistently maintains its position as the second-highest GDP contributor in

1256   Sichuan Province. The electronics information industry stands as Mianyang's primary

1257   economic driver, constituting approximately half of the city's total output value. Studies

1258   investigating the volatile organic compound (VOC) source profile in Chengdu(Zhou et

1259   al., 2021) reveal that ethanol and carbonyls predominantly characterize electronics

1260   manufacturing emissions.

1261   **3.2.2 Compositional characteristics**

1262   According to the composition characteristics of 15 carbonyl compounds in the

1263   ambient air of each city during the observation period(Table S4).Formaldehyde was

the most abundant carbonyl found in these sites followed by acetone and acetaldehyde, which is widely observed in previous studies. The measured ratios of formaldehyde, acetone, and acetaldehyde across different sites ranged from 36.4% to 59.4% (average 48.1%), 12.4% to 28.1% (average 19.9%), and 8.2% to 47.3% (average 17.5%), respectively. In this study, the total measured of formaldehyde, acetaldehyde, and acetone(FAT)account for over 78% of the total carbonyls concentrations. At the MY and ZY sites, this proportion even exceeded 90%. It is noteworthy that isobutyraldehyde (MACR) ranks fourth in the volume concentration of 15 carbonyls measured in the ambient air surrounding XJ, accounting for 5.3%. MACR, a characteristic product of isoprene photooxidation from biogenic sources, possibly originates from the abundant vegetation surrounding XJ. It reflects the period's relatively active photochemical reactions, with substantial contributions from secondary formation to the measured carbonyls composition.

The observed levels of FAT in different areas were influenced by various factors including sampling period, geographic location, meteorological conditions, chemical removal, and source emissions(Z. Zhang et al., 2016). Despite these influences, comparisons remain valuable in providing an overview of ambient carbonyl levels in the CPUA. During the summer of 2010, a national wide survey of ambient monocarbonyl compounds were conducted simultaneously in nine sites (Ho et al., 2015)found that the total FAT concentration was highest in Chengdu (14.96 ppb), followed by Beijing (11.83 ppb), and Wuhan (11.70 ppb). Beijing, as the capital of China, and Wuhan, being one of the top ten most populous cities in China, played significant roles in this comparison. In our study, the CDHKY site within CPUA exhibited the highest FAT concentration, with values of 18.25 ppb, surpassing those recorded in 2010. Furthermore, the total FAT concentrations observed at the CPUA and XJ sites, with values of 14.99 ppb and 14.90 ppb respectively in our study, closely resemble those reported in August 2010 in Chengdu. The consistently high levels of carbonyl compounds observed in Chengdu, both in 2010 and our current study, indicate

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1297   that the city likely experiences higher concentrations of these pollutants compared to

1298   other regions across the country. However, more extensive temporal data would be

1299   beneficial to fully validate this pattern at a national scale. Comparing our findings to

1300   international studies, the FAT concentrations at the CDHKY site were lower than those

1301   reported in Rio De Janeiro, Brazil(da Silva et al., 2016), during July to October 2013

1302   (35.43 ppb), but higher than those in Bangkok, Thailand(Kanjanasiranont et al., 2016b),

1303   Orleans, France(Jiang et al., 2016), and the United States(Murillo et al., 2012), with

1304   values of 9.05 ppb, 6.12 ppb, and 5.76 ppb, respectively.

1305   **3.3 Temporal variations of carbonyl compounds**

1306   The diurnal variation of the total mixing ratio of ambient carbonyl compounds and

1307   ozone concentration around each site in the CPUA during the observation period is

1308   shown in Fig. 4. According to the observation results, the diurnal trend of ozone

1309   concentration at each site showed a "unimodal" variation characteristic, that was, it

1310   gradually increased from the morning to the peak of one day at noon, and then decreased.

1311   The diurnal variation of the total mixing ratio of carbonyl compounds at each site

1312   generally showed a characteristic of high during the daytime and low at night. The

1313   concentration of carbonyl compounds during the day (6:00-16:00) was 48.8% higher

1314   than that at night (18:00-4:00) at the XJ site. This indicated that the concentration of

1315   carbonyl compounds increased by photochemical production during the daytime.

1316   Additionally, deposition processes, particularly dry deposition at night, likely

1317   contribute to the observed diurnal variation in carbonyl levels. The diurnal variation

1318   characteristics of each site were different. For example, the diurnal variation

1319   characteristics of carbonyl compounds concentration at CDHKY, XJ and SN sites were

1320   consistent with those of ozone. The diurnal variation of carbonyl compounds

1321   concentrations at other sites showed "double peaks", peaking at 10:00-12:00 and 18:00-

1322   20:00, respectively. The concentrations of carbonyl compounds at night were also

1323   higher at MY, DY and LS sites. The diurnal minimum values of the total concentration

1324   of carbonyl compounds and ozone concentration appeared at similar time, usually at

1328   4:00 a.m. or 6:00 a.m. The first peak of the total mixing ratio of carbonyl compounds

1329   occurred earlier than the maximum ozone concentration of the day. The first peak of

1330   the total mixing ratio of carbonyl compounds mostly occurred between 10:00 and 12:00.

1331   And the maximum ozone concentration mostly occurs between 14:00 and 16:00. This

1332   was related to the fact that carbonyl compounds were important precursors of ozone.

1333   In general, the diurnal variation of the total concentration of carbonyl

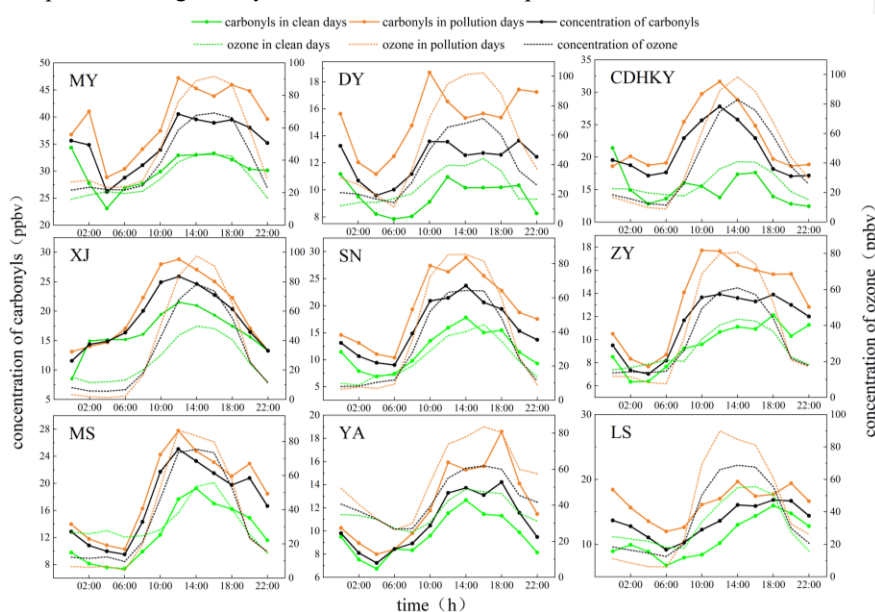
1334   compounds on pollution days and clean days was high during the daytime and low at

1335   night. The total mixing ratio of carbonyl compounds on pollution days was 22.8%-

1336   66.2% higher than that on clean days. At the same time, the increase of concentration

1337   of carbonyl compounds during the daytime on pollution days was higher than that on

1338   clean days. This suggested that the increase in the concentration of carbonyl

1339   compounds during the daytime contributed to ozone pollution.

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1341   **Figure 4.** Diurnal variations of carbonyl compounds and ozone concentrations at each site in the

1342   CPUA during the observation period

1343   **3.4 Atmospheric photochemical reactivity of carbonyl compounds**

1344   During the observation period, the total OH radical consumption rate (L_{OH}) and

total ozone formation potential (OFP) of the 15 carbonyl compounds at each site are depicted in Fig.5. The ranking of total L_{OH} and total OFP at each site is consistent, except for the YA and ZY sites with lower concentrations of carbonyl compounds, where the atmospheric photochemical reactivity ranking also aligns with the concentration. Among all sites, the MY and CD sites display the highest reactivity, while the YA and ZY sites exhibit the lowest reactivity. During the observation period, carbonyl compounds significantly contributed to ozone formation. The contributions to total VOCs (alkanes, alkenes, alkynes, aromatics, and carbonyl compounds) OFP at the MY, SN, ZY, YA, and LS sites ranged from 19.5% to 48.6%. Formaldehyde and acetaldehyde were identified as the most reactive species in the atmosphere, surpassing other carbonyl compounds in reactivity due to their higher concentrations and inherent reactivity, especially formaldehyde. However, acetone exhibited high inertness and a prolonged atmospheric lifetime, leading to its accumulation in ambient air with concentrations higher than other carbonyl compounds except for formaldehyde and acetaldehyde. Thus, despite its elevated concentration, acetone's reactivity remained relatively low.

Figure 5. L_{OH} and OFP of carbonyl compounds at each site in the CPUA during the observation

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1405   period

1406   **3.5 Sensitivity analysis of ozone formation based on formaldehyde to NO₂ ratio (FNR)**

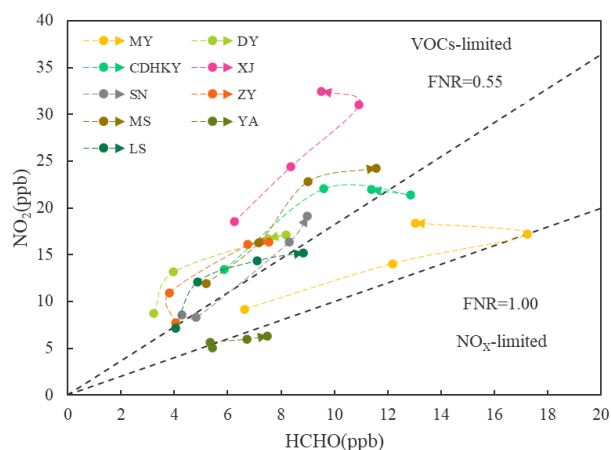
1407   The change of O_3 formation sensitivity of each site in the CPUA during the

1408   observation period is shown in Fig.6. As can be seen from the Fig. 6, most sites remain

1409   in the VOCs-limited regime during the cleaning period and EP1 to EP3. Economically

1410   developed city such as Chengdu, Meishan, with high levels of formaldehyde and NO_2,

1411   remain in the VOCs-limited regime. Ya'an as a city with the lowest GDP ranking in the

1412   CPUA, with low levels of formaldehyde and NO_2, remain in the transitional regime.

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1414   **Figure 6.** The change of O_3 formation sensitivity of each site in the CPUA during the observation

1415   period. The arrows represent time step from clean period to EP1 to EP2 to EP3.

1416   The daily variation of O_3 formation sensitivity and ozone concentration at each

1417   site in the CPUA during the observation period is shown in Fig. S4. The mean FNR of

1418   each site ranged from 0.48 to 1.29 during the observation period. The FNRs were lower

1419   than 0.55±0.16 at XJ, DY, ZY, CDHKY, and MS, and higher than 1.0 at LS, SN, YA

1420   and MY. At the same time, the mean ozone concentration at each site was between 138

1421   and 192 $\mu g \cdot m^{-3}$. The mean ozone concentration in XJ, DY, CDHKY and MS was 166-

1422   192 $\mu g \cdot m^{-3}$, it was 150-164 $\mu g \cdot m^{-3}$ in LS, SN, YA and MY. Therefore, it could be seen

1423   that most of the sites with high mean ozone concentrations during the observation

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period, like CDHKY, XJ, MS and Deyan sites, were in the VOCs-limited regime, and most of the stations with low mean ozone concentrations during the observation period such as YA, SN, MY and LS were in the transitional regime. It was worth noting that the mean ozone concentration at ZY site (only 138 $\mu g \cdot m^{-3}$) during the observation period was much lower than that of other sites, but most of the ZY site was in VOCs-limited regime, which was mainly related to the low concentration of formaldehyde. In addition, the FNR value of the MY site was also relatively high, which was mainly caused by the high concentration of formaldehyde.

Based on the ratio of formaldehyde to NO_2 mixing ratio, most sites remain in the VOCs-limited regime during the observation period. And the sites with heavy ozone pollution were in the VOCs-limited regime, and the sites with light ozone pollution were in the transitional regime. Photochemical reactivity (L_{OH} and OFP) analysis showed that formaldehyde and acetaldehyde contributed significantly to the enhancement of atmospheric oxidation and ozone formation potential. Therefore, when heavy ozone pollution occurs in the CPUA, special attention should be paid to the control of VOCs, especially formaldehyde and acetaldehyde in carbonyl compounds, under the coordinated control of NOx and VOCs. Overall, this study reveals the important contribution of carbonyl compounds to ozone pollution in the CPUA, and provides scientific support for the establishment of ozone pollution prevention and control measures.

3.6 Source Analysis of carbonyl compounds

3.6.1 Quantitative source analysis of key carbonyl compounds

The table S7 provides a summary of the background and primary emissions concentrations of formaldehyde, acetaldehyde, and acetone at nine sites across the eight cities of the CPUA, along with the proportion of secondary formation contributing to their concentrations. Background concentrations and primary emissions of formaldehyde, acetaldehyde, and acetone ranged from 50% to 80%, 46% to 83%, and

45% to 78%, respectively. Secondary formation accounted for 20% to 50%, 17% to 54%, and 22% to 55% of their concentrations, respectively. Notably, in SN and YA, the secondary formation of formaldehyde contributed half of the observed concentration, indicating it as the predominant source, while acetaldehyde's secondary formation also prevailed in these sites. Conversely, acetone, with lower reactivity, primarily originated from background concentrations and primary emissions at other sites except YA. Moreover, background concentrations and primary emissions were identified as the main contributors to carbonyl compounds in XJ and LS.

Fig.7 illustrates the secondary formation concentrations of formaldehyde, acetaldehyde, and acetone at each site in the CPUA under both clean and polluted conditions. Under polluted conditions, the secondary concentrations of formaldehyde, acetaldehyde, and acetone exceeded those in clean conditions by 58.8%, 54.6%, and 57.6%, respectively. The most significant increases in secondary concentrations were observed at the SN site, while relatively smaller increases were observed at LS and XJ.

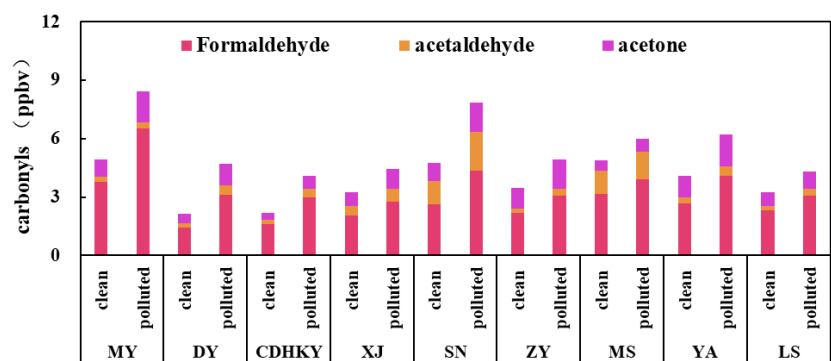



Figure 7. Concentrations of formaldehyde, acetaldehyde and acetone in secondary formation under different pollution conditions at each site in the CPUA during the observation period

3.6.2 Exploration of secondary formation mechanism of key carbonyl compounds

In this study, we utilized VOC data collected on August 11, 12, and 16, when all eight cities in the CPUA were experiencing mild to severe ozone pollution. We calculated the Relative Incremental Reactivity (RIR) of formaldehyde, acetaldehyde,

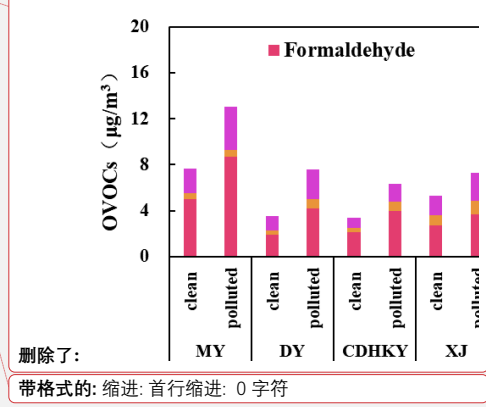
1489 and acetone at the MY, SN, ZY, YA, and LS sites on these days. The OBM analysis

1490 allowed us to assess the impact of anthropogenic VOCs (alkanes, alkenes, alkynes,

1491 aromatics) and biogenic VOCs (e.g., isoprene) on carbonyl compound formation in the

1492 context of regional ozone pollution events (Fig.8). Overall, the sensitivities of different

1493 anthropogenic source and plant source VOCs to formaldehyde, acetaldehyde and

1494 acetone was consistent among sites. For formaldehyde, reducing alkenes in

1495 anthropogenic source VOCs and plant VOCs was the most effective way to control

1496 formaldehyde concentration, while reducing alkenes in anthropogenic source VOCs

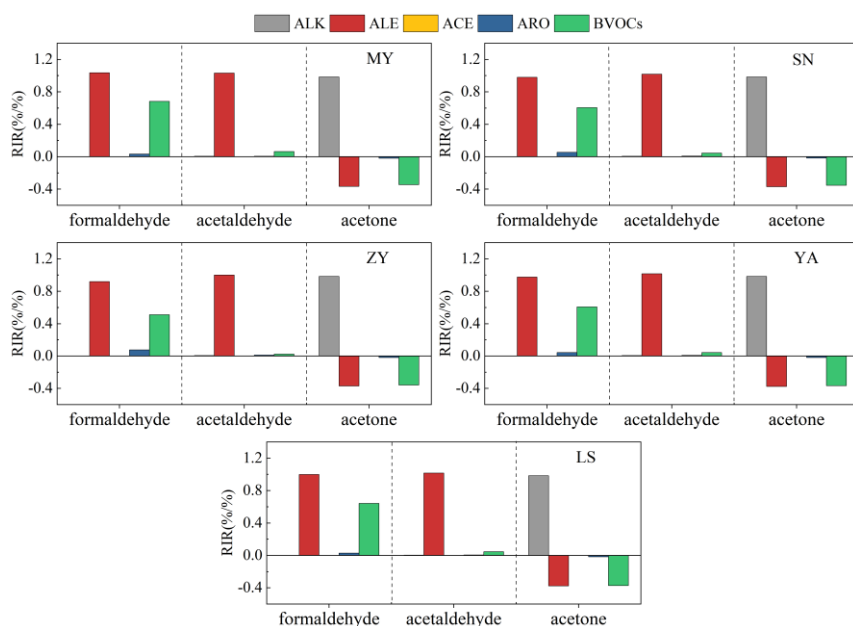
1497 was also beneficial to reduce the formation of acetaldehyde. For acetone with low

1498 reactivity, the alkanes in anthropogenic source VOCs were the most sensitive to the

1499 formation of acetone, followed by alkenes and BVOCs. Only the RIR value of alkanes

1500 were greater than zero, and the RIR values of both alkenes and BVOCs were less than

1501 zero, indicating that reducing alkanes could reduce the formation of acetone, while

1502 reducing alkenes and BVOCs was not conducive to acetone concentration control.

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1504 **Figure 8.** Mean RIRs of formaldehyde, acetaldehyde and acetone to different anthropogenic

1505 source VOCs (alkanes (ALK), alkenes (ALE), alkynes(ACE), aromatics (ARO))and biogenic

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1507   VOCs (BVOCs)at MY, SN, ZY, YA and LS sites on August 11th, 12th and 16th.

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1508   **3.6.3 Influence of regional transportation contribution**

1509   The TrajStat trajectory model was used to calculate and cluster the 24-hour
1510   backward trajectories of air quality at the sampling sites. The backward trajectory
1511   during sampling is shown in Fig.S5. During the observation period, the pollution of

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1512   carbonyl compounds in the cities of the CPUA was affected by the mutual transport
1513   among cities in Sichuan Province, especially along the MY-DY-CDHKY route. In
1514   addition, the surrounding provinces and cities of Sichuan Province (Gansu and
1515   Chongqing) also contributed to the carbonyl compounds of the CPUA.

1516   The potential sources of carbonyl compounds at different pollution stages at the
1517   CDHKY during the observation period are shown in Fig. 9. It can be seen from the
1518   figure that there are differences in the potential sources of carbonyl compounds among
1519   different pollution stages at the CDHKY site. The concentration of local carbonyl
1520   compounds in CDHKY was high during the early observation period and EP1, which
1521   existed local sources, and was also affected by the northern airflow, and carbonyl
1522   compounds was also affected by the transport from MY, DY and other northern regions.
1523   Under the effect of the continuous northern airflow, the local source emissions
1524   decreased during EP1, and the potential source of carbonyl compounds changed to from
1525   the junction between CDHKY and ZY. During EP3, under the combined influence of
1526   the western airflow, the contribution of transport from SN and ZY to carbonyl
1527   compounds increased, while emissions from local sources also increased.

删除了: The potential sources of carbonyl compounds at different pollution stages at the Chengdu Institute of Environmental Sciences site during the observation period are shown in Fig. 9. It can be seen from the figure that there are differences in the potential sources of carbonyl compounds among different pollution stages at the CDHKY site. The concentration of local carbonyl compounds in CDHKY was high during the early observation period and EP1, which existed local sources, and was also affected by the northern airflow, and carbonyl compounds was also affected by the transport from MY, DY and other northern regions. Under the effect of the continuous northern airflow, the local source emissions decreased during EP1, and the potential source of carbonyl compounds changed to from the junction between CDHKY and ZY. During EP3, under the combined influence of the western airflow, the contribution of transport from SN and ZY to carbonyl compounds increased, while emissions from local sources also increased.
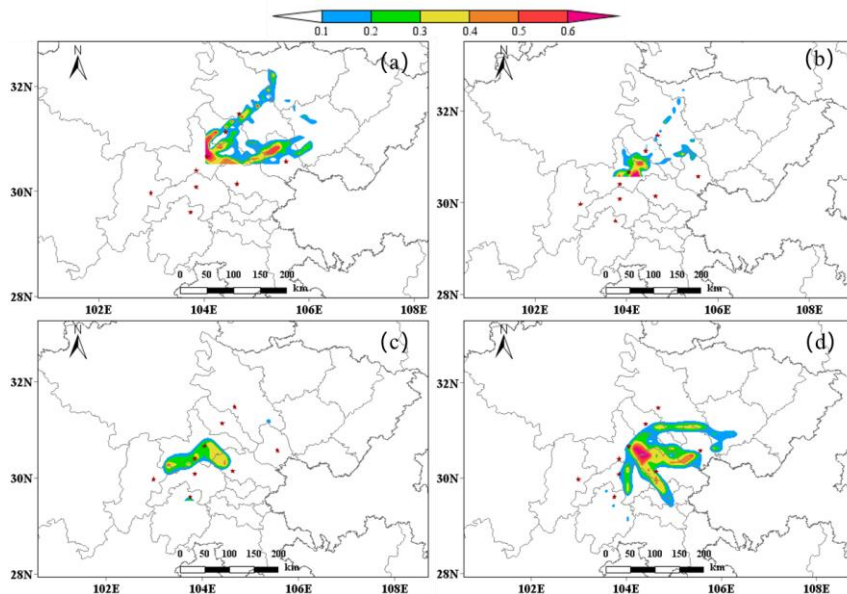
Figure 9. Analysis of potential sources of carbonyl compounds at different periods at the CDHKY site during the observation period (a) August 4th-6th (b) August 7th-9th (c) August 10th-13th (d) August 15th-18th

4. Conclusions

During a comprehensive atmospheric observation campaign conducted at nine sites across the CPUA from August 4th to 18th, 2019, three regional heavy ozone pollution episodes(EP1 to EP3) were observed. This study extensively examines the concentration variations, atmospheric chemical reactivity, and sources of carbonyls during this period. The average total concentrations of 15 carbonyl compounds across the nine sites within eight cities of the CPUA were measured at 17.4 ± 5.3 ppb. Spatial analysis indicated that areas with higher carbonyl concentrations were concentrated around Chengdu, extending both north and south. Notably, regions with elevated carbonyl compound concentrations also tended to experience more severe ozone pollution. Formaldehyde (36.4%-64.3%), acetone (12.4%-28.1%), and acetaldehyde (8.2%-47.3%) constituted the predominant species by volume concentration. Chengdu

exhibited FAT concentrations surpassing national and international levels, indicating heightened levels compared to other regions.

Compared to clean days, carbonyl compound concentrations were significantly higher on ozone pollution days, with increases ranging from 22.8% to 66.2%. Between 19.5% and 48.6% of the total volatile organic compound (VOC) ozone formation potential (OFP) was attributed to the 15 carbonyl compounds, highlighting their substantial contribution to ozone formation, particularly formaldehyde and acetaldehyde. While primary emissions are the main sources of these compounds, secondary formation processes contributed over 30% on average to the concentrations of formaldehyde, acetaldehyde, and acetone. Under ozone pollution conditions, the secondary formation concentrations of these three compounds were notably higher than on clean days, with increases of 58.8%, 54.6%, and 57.6%, respectively, emphasizing the critical role of secondary processes in exacerbating regional ozone pollution. OBM modeling revealed that formaldehyde and acetaldehyde primarily originated from the secondary formation of alkenes and BVOCs, while acetone mainly stemmed from the secondary formation of alkanes. These findings highlight that while the concentration of carbonyl compounds is important, their significant impact on ozone formation is primarily driven by secondary chemistry. Specifically, the secondary formation of these compounds from alkenes and biogenic BVOCs plays a key role in this process.

Ground-level observations of the formaldehyde to NO$_2$ ratio (FNR) were utilized to assess the sensitivity of ground-level ozone formation. Analysis of FNR revealed that sites experiencing heavy ozone pollution exhibited lower FNRs, indicating a VOCs-limited regime, while sites with lighter ozone pollution were categorized into a transitional regime. Furthermore, it is recommended to establish a scientific control mechanism for both NOx and VOCs, with special attention to formaldehyde, acetaldehyde, and acetone, and their alkenes precursors. Additionally, considering the regional nature of pollution, this study suggests that carbonyl compound pollution is influenced by mutual transport among cities within the CPUA, notably along the MY-

1635 DY-CDHKY route. Establishing a collaborative prevention and control mechanism
1636 among cities within the CPUA and neighboring provinces and cities is crucial to
1637 effectively address carbonyl compounds and ozone pollution in the region in the future.
1638

1639 **Data availability.** Observational data including meteorological parameters and air
1640 pollutants used in this study are available from the corresponding authors upon request
1641 (lihong@craes.org.cn).
1642

1643 **Author contributions.** Hong Li and Jiemeng Bao designed this study. Xin Zhang,
1644 Zhenhai Wu, Jiemeng Bao, Li Zhou, Qinwen Tan, and Fumo Yang coordinated the
1645 selection of field observation sites, including locations for both VOCs and carbonyls
1646 grid sampling. Qinwen Tan and Hefan Liu supported the collection of carbonyls at one
1647 site. Zhenhai Wu and Xin Zhang assisted in carbonyls sampling; Xin Zhang and
1648 Yunfeng Li assisted in carbonyls sample analysis and data collection. Li Zhou and
1649 Hefan Liu organized the analysis of VOCs measurements. Jun Qian, Junhui Chen, and
1650 Liqun Deng provided support in project funding application. Jiemeng Bao performed
1651 the data analysis and wrote the paper with contributions from all co-authors; Hong Li
1652 reviewed the paper, provided comments and finalized it.
1653

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