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 investigate the impact of gaseous carbonyls on regional ozone pollution, 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 10.70±4.16 to 35.18±13.37 ppbv, 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. Sites with higher average ozone concentrations during observations were mainly in the VOCs-limited regime, while others were in the transitional regime. 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 precursors of secondary 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.

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

1. Introduction

Atmospheric carbonyl compounds play a pivotal role in tropospheric chemistry, acting as crucial precursors to both ozone (O_3) and secondary organic aerosols (SOA), a fact recognized for decades (Altshuller, 1993; Grosjean and Seinfeld, 1989). Their importance has been confirmed by numerous studies over the years(Guo et al., 2004; Hallquist et al., 2009; Wang et al., 2020; Ye et al., 2021; Coggon et al., 2019), highlighting their significant contribution to atmospheric photochemistry and air pollution. Over the past two decades, severe air pollution in China has driven substantial research efforts to understand the contributions of carbonyl compounds to these environmental challenges. Studies have shown that photolysis of carbonyl compounds is a major source of RO_X radicals (Grosjean and Seinfeld, 1989; Zhang et al., 2016). These compounds can be photolyzed and react with OH radicals to form a large number of HO_2 and RO_2 radicals, which increase the atmospheric oxidation capacity and

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participate in the NOx photochemical cycle, leading to ozone formation (Zhang et al., 2016; Meng et al., 2017). Additionally, dialdehydes such as glyoxal and methylglyoxal undergo heterogeneous reactions with aqueous particulate matter, rapidly forming SOA (Lou et al., 2010; Xue et al., 2016; Yuan et al., 2012). Ambient carbonyl compounds not only affect the environment but also pose direct health risks to humans. They can harm ecosystems through deposition and adsorption processes (Yang et al., 2018). They also pose direct health risks to humans, including sensitization, carcinogenesis, and mutagenicity (Fuchs et al., 2017).

Recent research has increasingly focused on understanding the spatial and temporal variability of carbonyl compounds in highly polluted regions, particularly in China, where rapid industrialization has led to severe air quality challenges. Xue et al. (2013) and Duan et al. (2012) reported typical ambient concentrations of carbonyl compounds ranging from a few μg·m^{-3} to tens of μg·m^{-3} in urban areas, depending on the specific compounds and regions studied. For example, formaldehyde concentrations in highly polluted areas can exceed 10 μg·m^{-3}. Shen et al. (2013) and Fu et al. (2008) observed significant diurnal variation, with higher concentrations of carbonyl compounds during the daytime, particularly in the afternoon, driven by photochemical production. Concentrations can increase by as much as 50-100% during peak sunlight hours compared to nighttime levels. Pang and Mu (2006) and Rao et al. (2016) identified key sources of carbonyl compounds, including vehicular emissions, industrial activities, and secondary formation from VOC oxidation in the atmosphere. In urban environments, vehicular emissions are often a dominant primary source, while secondary formation contributes significantly during daytime due to photochemical processes. The results highlight severe and spatiotemporal variations of carbonyl pollution in China. High levels are found mainly in the North China Plain(NCP), the Yangtze River Delta(YRD), and the Pearl River Delta(PRD)(Duan et al., 2008; Shao et al., 2009; Tan et al., 2018; Wang et al., 2018; Xue et al., 2014, 2013; Yang et al., 2017). Urban areas generally exhibit higher carbonyl levels than suburban and rural areas due

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to human activities(Xue et al., 2013). Despite the progress made, significant gaps remain in understanding the spatiotemporal distribution and source apportionment of carbonyl compounds, particularly in urban agglomerations. Existing research has primarily focused on urban areas in rapidly developing regions like the NCP, YRD, and PRD. Moreover, studies have often emphasized the overall role of VOCs in ozone pollution, with less attention given to specific carbonyl compounds and their individual contributions to atmospheric oxidation capacity and ozone formation (Meng et al., 2017).

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

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

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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.

In this context, 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 limited understanding of the distribution, sources, and specific roles of carbonyl compounds across the entire CPUA and their contributions to regional ozone pollution and mutual air transport mechanisms.

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删除了: analyzed the online observation data of VOCs in Chengdu from June to September 2019 and found that the aromatic hydrocarbons and alkenes in VOCs contributed greatly to the formation of ozone in Chengdu in summer.

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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 obvious pollution sources, with convenient transportation and power supply. The distribution of specific sites is shown in Fig. 1.

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Ozone concentrations were measured using the UV absorption method with a Thermo O_3 analyzer (Model 49i), with data sourced from national control stations near each sampling site. Nitrogen dioxide (NO_2) was measured by chemiluminescence following chemical conversion to nitric oxide (NO) using a molybdenum catalyst; however, this method is known to have interferences from other NOz species. Carbon monoxide (CO) was measured via infrared absorption with a Thermo instrument (Model 20). All Thermo instruments were carefully maintained and calibrated daily at 01:00 to ensure measurement accuracy. Measurements for ozone, NO_2, and CO were collected with a time resolution of one hour. Simultaneously, meteorological parameters—temperature, relative humidity (RH), wind speed, and direction—were recorded at each observation site using an automatic weather station (PC-4, JZYG, China), also at a one-hour resolution.

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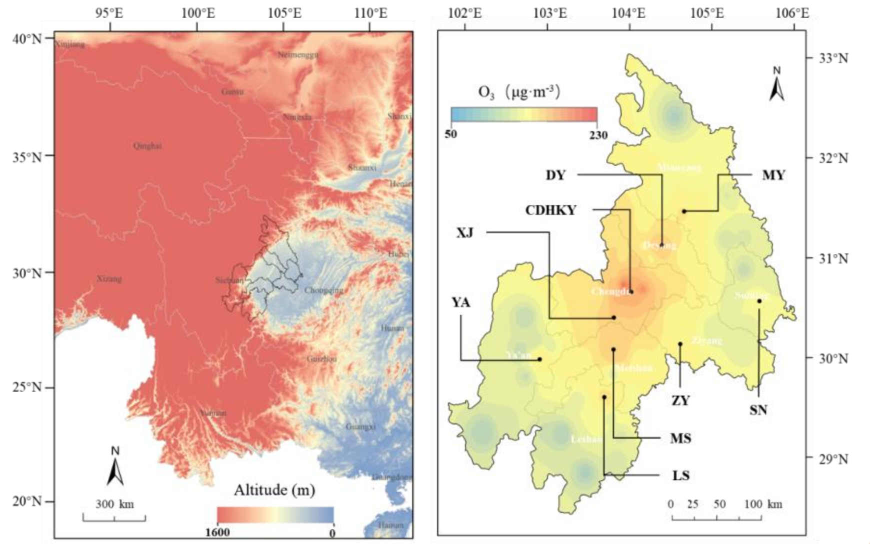
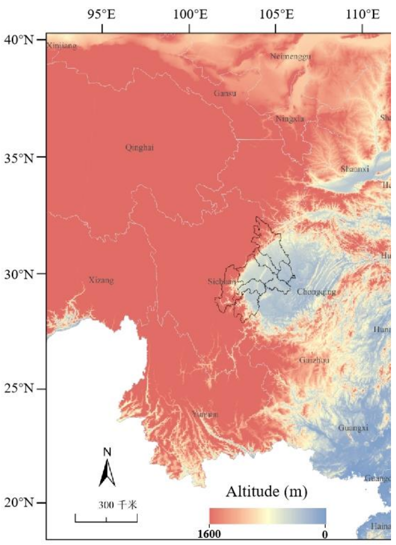


Figure 1. Distribution of sampling sites. The left panel shows the elevation map of the Sichuan Basin, highlighting the geographical features of the region, with elevation data sourced from the Geospatial Data Cloud (https://www.gscloud.cn/#page1/2). The right panel presents the spatial distribution 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



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(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 $L\ min^{-1}$. 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.

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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 sample was taken into an HPLC sample bottle, and sealed and stored in a refrigerator at <4 °C 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 limit of detection of the device was 0.56~5.57 ng·mL^{-1}, and the limit of quantification was 1.87~18.56 ng·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 °C.

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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

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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

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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):

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

Where, $[OVOC]_i$ was the observed concentration of the i^{th} (i=1 to n) carbonyl compound, in molecule·cm^{-3}; $k_i(OH)$ was the rate constants of the i^{th} 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).

$$OFP = MIR_i \times [OVOC]_i \quad (2)$$

Where, MIR was the maximum incremental reactivity of the i^{th} 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 i^{th} carbonyl compound, in μg·m^{-3}. The unit of OFP is μg·m^{-3}, representing the potential ozone formation.

(2) Observation-based model (OBM)

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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. 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.

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Relative Incremental Reactivity (RIR) was first used by Cardelino and Chameides (1995) to simulate the response of ozone to precursor changes through scenario tests using box model calculations. RIR was calculated by assuming that the concentration of a given carbonyl compound precursor decreased by a certain proportion could cause the change of the concentration of the carbonyl compound, so as to further judge the effect of VOCs on the formation of carbonyl compounds. Combining the concentrations and activity levels of 15 carbonyl compounds during the observation period, this study focused on formaldehyde, acetaldehyde, and acetone as the primary research targets. The impacts of various AVOCs（anthropogenic VOCs）, including alkanes, alkenes, alkynes, and aromatic hydrocarbons, as well as BVOCs（biogenic VOCs） like isoprene, on the formation of formaldehyde, acetaldehyde, and acetone were assessed using observation-based OBM classification. Specific species of anthropogenic source VOCs (alkanes, alkenes, alkynes, and aromatic hydrocarbons) and biogenic VOCs (isoprene) are detailed in Table S3.

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VOCs observations, conventional gases (NO_2, CO and SO_2) and meteorological parameters (temperature, relative humidity and pressure) were imputed into the model. It was assumed that the pollutants are well mixed. Under the constraints of the measured hourly concentration data of pollutants, the atmospheric chemical process was simulated to obtain the source-effect relationship of the measured pollutants. By assuming the reduction of the source effect, the RIRs of different carbonyl compounds precursors were calculated, and the sensitivities of carbonyl compounds to different pollutants were obtained, and then the secondary formation mechanism of carbonyl compounds was determined. The formula to calculate the RIR is as follows:

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

$$P_Y = \mathrm{Y}_{\text{net formation}} - Y_{\text{net consumption}} \quad (4)$$

Where X was a specific species; $P_Y(X)$ was the net formation rate of species y; S(X) was the total amount of emissions of species X in a certain period, i.e., the source effect of species X. ΔS(X) was the change in total emissions of X caused by the hypothetical change in source effect, $\Delta P_Y(X)$ was the change in $P_Y(X)$ after the change in source effect S(X), and RIR(X) was the relative incremental reactivity of species X. The species Y in this study were formaldehyde, acetaldehyde and acetone, respectively, and pollutant X was reduced by 20%.

The absolute RIR of the precursor reflects the sensitivity of carbonyl compounds formation to the precursor. The higher the absolute RIR, the more sensitive the carbonyl compounds formation to the precursor. A positive RIR value indicates that reducing the species can reduce the formation rate of species Y, and a negative RIR value indicates that reducing the species can increase the formation rate of species Y.

2.4.4 Sources Analysis

(1) Multi-linear regression model

There is a good correlation between concentrations of compounds of the same or similar source in the atmosphere. Based on this property, it was assumed that the primary and secondary sources of carbonyl compounds were linearly correlated with the selected tracers, and then a quantitative source model was established by multiple linear statistical regression analysis (Kanjanasiranont et al., 2016a; Li et al., 2010; Ling et al., 2017; Luecken et al., 2012; Lui et al., 2017; Wang et al., 2017). In general, CO is the marker product of typical anthropogenic combustion source emissions, mainly from vehicle exhaust emissions and coal combustion. Ozone, as an indicator of photochemical smog, is a typical secondary formation pollutant. In this study, CO and ozone were selected as the tracers of primary source and secondary source of carbonyl compounds, respectively. The formula is as follows:

$$[carbonyl] = \beta_0 + \beta_1[CO] + \beta_2[O_3] \qquad (6)$$

Where [carbonyl], [CO] and [O_3] represented the observed mixing ratios of carbonyl compounds, CO and ozone, respectively, in ppbv. β_0, β_1 and β_2 were coefficients obtained by multiple linear regression fitting model, in ppbv/ppbv. β_0 represented the background concentration of a given carbonyl compound, β_1 represented the emission ratio of the carbonyl compound relative to CO. β_1[CO] and β_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 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

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 volatile organic compounds (VOCs), 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

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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

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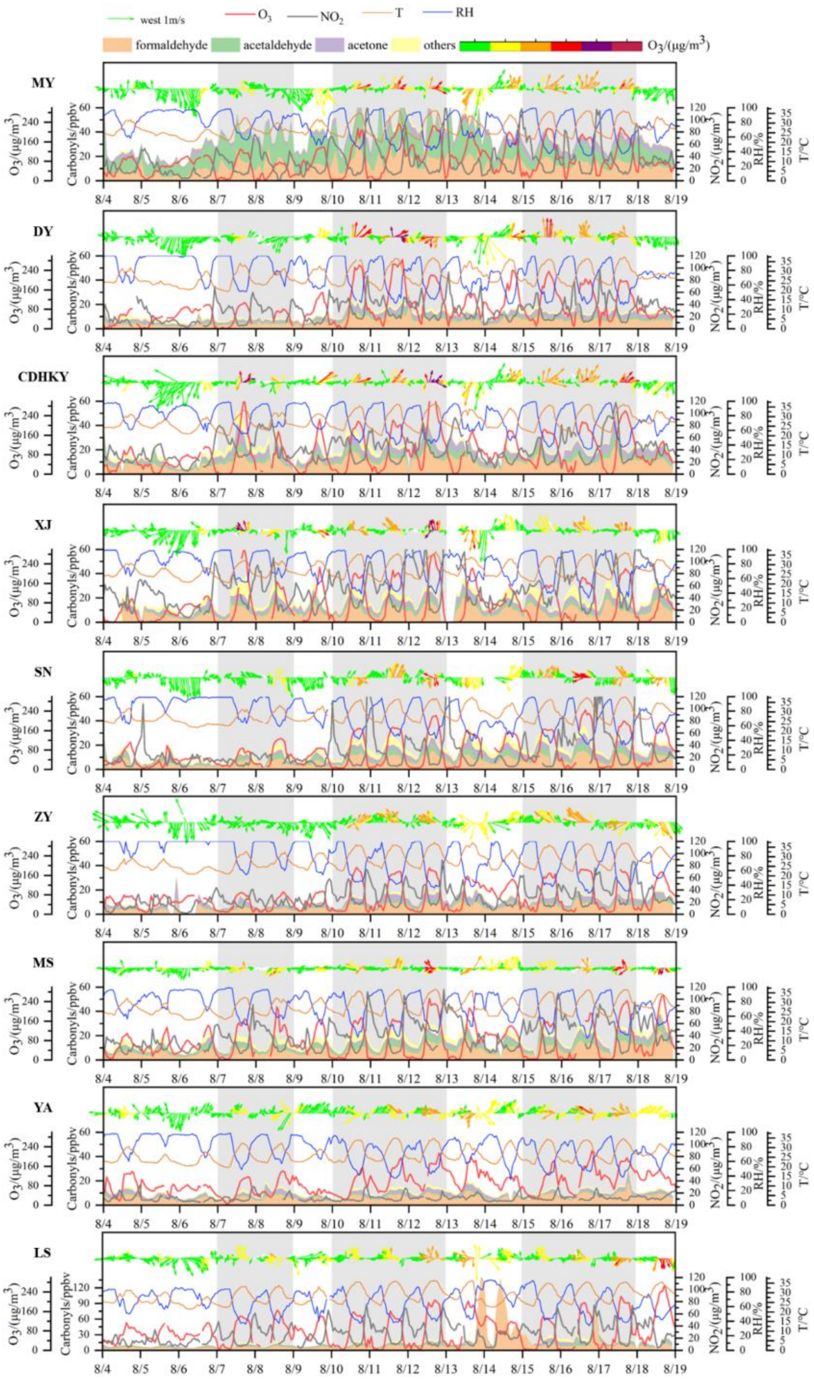


Figure 2. Overview of air quality at each site during the observation period. The gray shaded parts respectively represent the three heavy ozone pollution episodes (EP1, EP2,EP3).

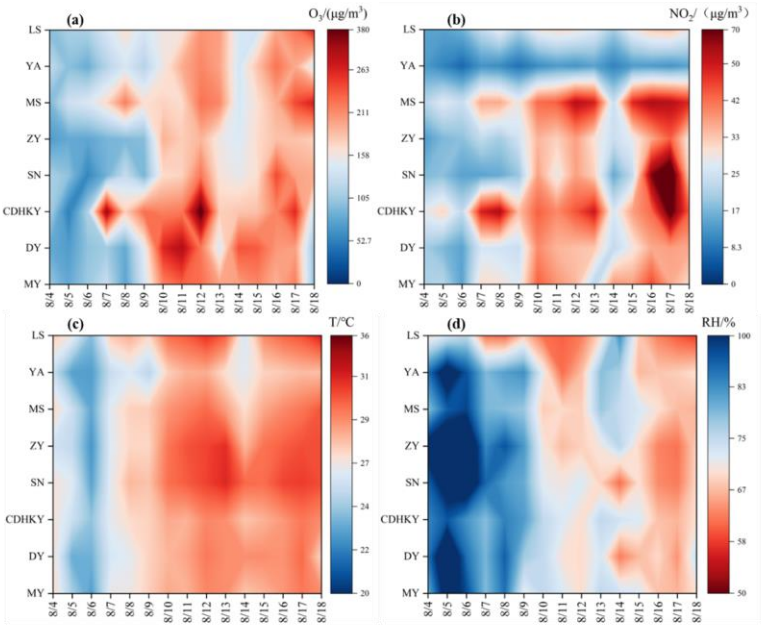
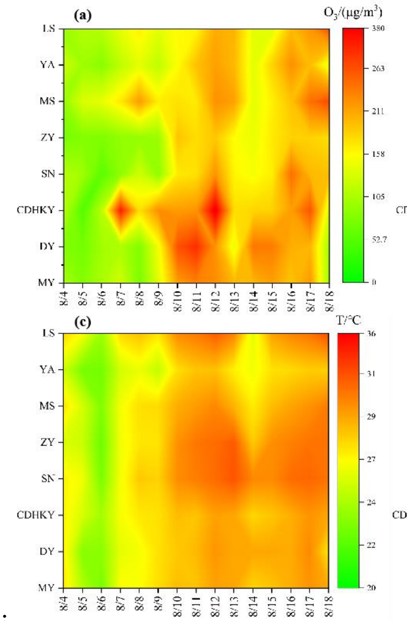


Figure 3. Temporal and spatial variations of (a) ozone concentration, (b) NO$_2$ concentration, (c) temperature and (d) humidity in the CPUA during the observation period.

3.2 Comparative characterization of carbonyl compounds

3.2.1 Ambient levels

During the observation period, we utilized 2,4dinitrophenylhydrazine (DNPH) cartridge and high-performance liquid chromatography (HPLC) analysis technique to quantify 15 carbonyl compounds. The concentrations and relative proportions of these compounds are summarized in Table 1. The average total concentration of the 15 carbonyls in the CPUA was 17.35 ± 5.31 ppb. Overall, areas with elevated concentrations of carbonyl compounds were primarily concentrated in and around Chengdu in both northern and southern directions. MY site, located to the north of Chengdu, exhibited the highest concentration of carbonyl compounds (35.18 ± 13.37



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ppb), while YA site, situated southwest of Chengdu, showed the lowest concentration (10.70 ± 4.16 ppb).

Table 1. Daily mean ± standard error of carbonyl compound mixing ratios (ppbv) at each site in the CPUA during the observation period. Sum: the total sum of carbonyl compound mixing ratios across all compounds at each site.

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Carbonyls	MY	DY	CDHKY	XJ	SN	ZY	MS	YA	LS
formaldehyde	12.82±6.52	6.06±2.82	10.09±4.21	8.87±4.39	6.98±3.56	5.84±2.69	8.47±4.15	6.36±2.40	6.55±3.35
acetaldehyde	16.65±7.38	1.54±0.77	3.65±2.15	2.33±1.07	2.62±1.74	1.40±0.61	3.24±1.60	0.88±0.68	1.63±1.32
acetone	4.36±1.70	2.80±1.19	4.51±2.25	3.70±1.21	3.14±1.70	3.23±1.73	2.15±1.14	2.18±1.08	2.91±1.63
propionaldehyde	0.41±0.22	0.24±0.14	0.39±0.27	0.39±0.17	0.34±0.22	0.28±0.14	0.41±0.18	0.20±0.15	0.31±0.16
crotoraldehyde	0.20±0.21	0.10±0.11	0.23±0.34	0.05±0.07	0.23±0.08	0.19±0.27	0.15±0.21	0.36±0.24	0.12±0.24
butyaldehyde	0.22±0.48	0.22±0.28	0.40±0.57	0.94±1.67	0.26±0.18	0.06±0.18	0.44±0.46	0.25±0.16	0.02±0.06
benzaldehyde	0.00±0.04	0.02±0.06	0.04±0.11	0.21±0.20	0.08±0.10	0.00±0.01	0.00±0.01	0.00±0.00	0.01±0.04
isovaleraldehyde	0.01±0.14	0.03±0.09	0.08±0.14	0.08±0.13	0.05±0.10	0.01±0.05	0.68±0.42	0.04±0.07	0.06±0.12
valeraldehyde	0.00±0.00	0.25±0.09	0.30±0.59	0.63±0.36	0.85±0.65	0.00±0.00	0.00±0.00	0.00±0.02	0.77±0.47
o-Tolualdehyde	0.46±0.52	0.36±0.29	0.45±0.19	0.00±0.00	0.00±0.00	0.23±0.17	0.43±0.33	0.18±0.22	0.16±0.17
m-Tolualdehyde	0.00±0.02	0.04±0.10	0.04±0.09	0.17±0.17	0.30±0.13	0.00±0.03	0.00±0.02	0.00±0.02	0.01±0.05
p-Tolualdehyde	0.00±0.00	0.01±0.05	0.01±0.04	0.00±0.00	0.00±0.00	0.00±0.00	0.01±0.04	0.00±0.02	0.00±0.02
hexaldehyde	0.00±0.01	0.34±0.25	0.41±0.69	0.57±0.47	0.95±0.65	0.02±0.18	0.78±0.58	0.00±0.01	0.10±0.32
2,5-diemthybenzaldehyde	0.01±0.03	0.00±0.01	0.00±0.01	0.05±0.12	0.00±0.00	0.00±0.01	0.01±0.02	0.00±0.01	0.00±0.01
MACR	0.03±0.20	0.14±0.17	0.26±0.34	1.05±1.10	0.26±0.21	0.19±0.16	0.42±0.36	0.24±0.22	0.81±0.88
Sum	35.18±13.37	12.16±4.84	20.84±8.85	19.04±8.1	16.05±7.73	11.47±4.89	17.19±7.61	10.70±4.16	13.46±6.12

Fig.S1 illustrates the relationship between ozone concentration and carbonyl compounds concentration at each site during the observation period. It is evident that the spatial distribution of carbonyl compound concentrations is similar to that of ozone concentration. Regions with severe ozone pollution tend to exhibit higher concentrations of carbonyl compounds. The variation in carbonyl compound concentrations is primarily attributed to anthropogenic emissions and prevailing summer wind directions in the CPUA. Chengdu is the most economically developed city in the CPUA, with notably higher GDP and industrial production values than other regions. Chengdu’s major industries include coal-fired power plants, chemical plants, metallurgy and building materials plants, and high concentrations of carbonyls were observed in here. The unique basin climate of the CPUA, characterized by intense sunlight and stable atmospheric conditions, facilitates the accumulation of pollutants. Large amount of industrial emissions and strong photochemical reaction contributes to ozone pollution. Additionally, during the summer, prevailing northerly winds in the CPUA facilitate the downwind transport of pollutants from upwind sources, leading to regional pollution. It is noteworthy that the concentration of carbonyl compounds at the MY site significantly exceeds that at the CDHKY site. Mianyang, with its industrial roots, consistently maintains its position as the second-highest GDP contributor in Sichuan Province. The electronics information industry stands as Mianyang's primary economic driver, constituting approximately half of the city's total output value. Studies investigating the volatile organic compound (VOC) source profile in Chengdu(Zhou et al., 2021) reveal that ethanol and carbonyls predominantly characterize electronics manufacturing emissions.

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3.2.2 Compositional characteristics

According to the composition characteristics of 15 carbonyl compounds in the 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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that the city likely experiences higher concentrations of these pollutants compared to other regions across the country. However, more extensive temporal data would be beneficial to fully validate this pattern at a national scale. Comparing our findings to international studies, the FAT concentrations at the CDHKY site were lower than those reported in Rio De Janeiro, Brazil(da Silva et al., 2016), during July to October 2013 (35.43 ppb), but higher than those in Bangkok, Thailand(Kanjanasiranont et al., 2016b), Orleans, France(Jiang et al., 2016), and the United States(Murillo et al., 2012), with values of 9.05 ppb, 6.12 ppb, and 5.76 ppb, respectively.

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3.3 Temporal variations of carbonyl compounds

The diurnal variation of the total mixing ratio of ambient carbonyl compounds and ozone concentration around each site in the CPUA during the observation period is shown in Fig. 4. According to the observation results, the diurnal trend of ozone concentration at each site showed a "unimodal" variation characteristic, that was, it gradually increased from the morning to the peak of one day at noon, and then decreased. The diurnal variation of the total mixing ratio of carbonyl compounds at each site generally showed a characteristic of high during the daytime and low at night. The concentration of carbonyl compounds during the day (6:00-16:00) was 48.8% higher than that at night (18:00-4:00) at the XJ site. This indicated that the concentration of carbonyl compounds increased by photochemical production during the daytime. Additionally, deposition processes, particularly dry deposition at night, likely contribute to the observed diurnal variation in carbonyl levels. The diurnal variation characteristics of each site were different. For example, the diurnal variation characteristics of carbonyl compounds concentration at CDHKY, XJ and SN sites were consistent with those of ozone. The diurnal variation of carbonyl compounds concentrations at other sites showed "double peaks", peaking at 10:00-12:00 and 18:00-20:00, respectively. The concentrations of carbonyl compounds at night were also higher at MY, DY and LS sites. The diurnal minimum values of the total concentration of carbonyl compounds and ozone concentration appeared at similar time, usually at

4:00 a.m. or 6:00 a.m. The first peak of the total mixing ratio of carbonyl compounds occurred earlier than the maximum ozone concentration of the day. The first peak of the total mixing ratio of carbonyl compounds mostly occurred between 10:00 and 12:00. And the maximum ozone concentration mostly occurs between 14:00 and 16:00. This was related to the fact that carbonyl compounds were important precursors of ozone.

In general, the diurnal variation of the total concentration of carbonyl compounds on pollution days and clean days was high during the daytime and low at night. The total mixing ratio of carbonyl compounds on pollution days was 22.8%-66.2% higher than that on clean days. At the same time, the increase of concentration of carbonyl compounds during the daytime on pollution days was higher than that on clean days. This suggested that the increase in the concentration of carbonyl compounds during the daytime contributed to ozone pollution.

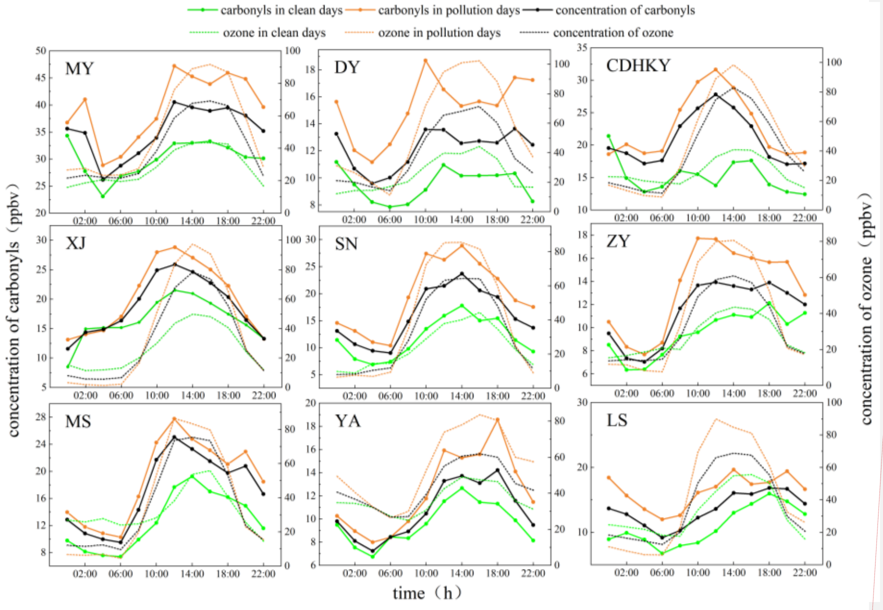

Figure 4. Diurnal variations of carbonyl compounds and ozone concentrations at each site in the CPUA during the observation period

3.4 Atmospheric photochemical reactivity of carbonyl compounds

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

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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.

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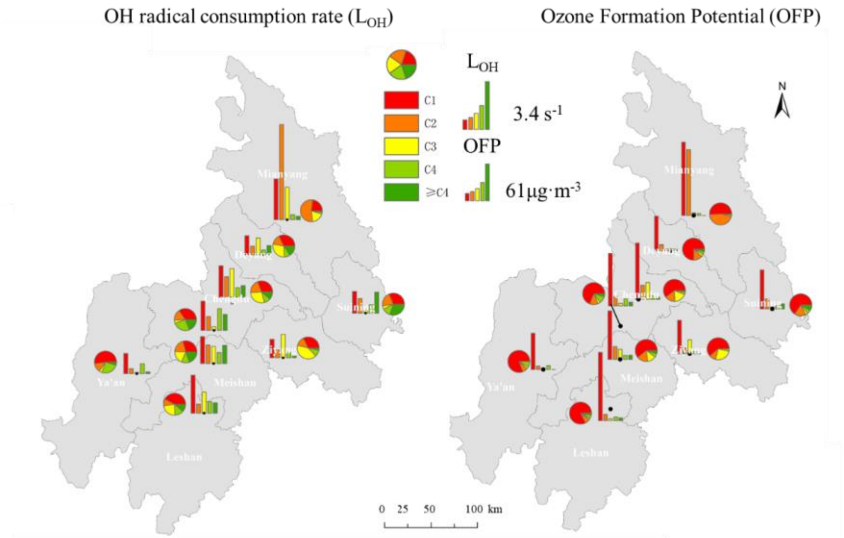

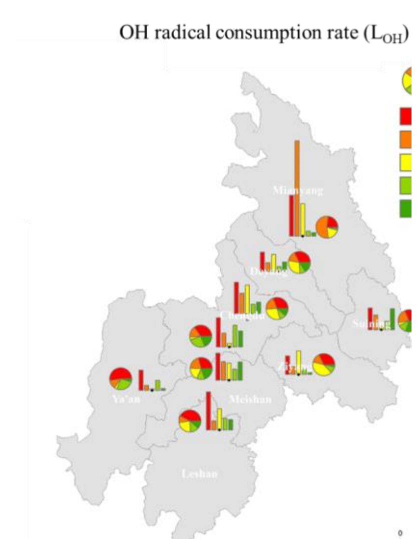

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Figure 5. L_{OH} and OFP of carbonyl compounds at each site in the CPUA during the observation

period

3.5 Sensitivity analysis of ozone formation based on formaldehyde to NO_2 ratio (FNR)

The change of O_3 formation sensitivity of each site in the CPUA during the observation period is shown in Fig.6. As can be seen from the Fig. 6, most sites remain in the VOCs-limited regime during the cleaning period and EP1 to EP3. Economically developed city such as Chengdu, Meishan, with high levels of formaldehyde and NO_2, remain in the VOCs-limited regime. Ya'an as a city with the lowest GDP ranking in the CPUA, with low levels of formaldehyde and NO_2, remain in the transitional regime.

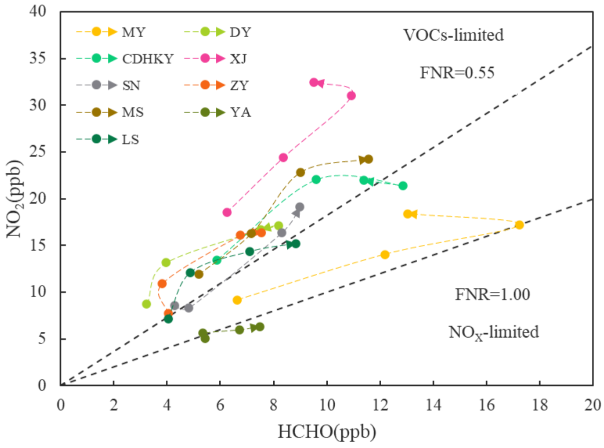

Figure 6. The change of O_3 formation sensitivity of each site in the CPUA during the observation period. The arrows represent time step from clean period to EP1 to EP2 to EP3.

The daily variation of O_3 formation sensitivity and ozone concentration at each site in the CPUA during the observation period is shown in Fig. S4. The mean FNR of each site ranged from 0.48 to 1.29 during the observation period. The FNRs were lower than 0.55±0.16 at XJ, DY, ZY, CDHKY, and MS, and higher than 1.0 at LS, SN, YA and MY. At the same time, the mean ozone concentration at each site was between 138 and 192 μg·m^{-3}. The mean ozone concentration in XJ, DY, CDHKY and MS was 166-192 μg·m^{-3}, it was 150-164 μg·m^{-3} in LS, SN, YA and MY. Therefore, it could be seen 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.

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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 52.4%, 80.3%, and 58.5%, respectively. The most significant increases in secondary concentrations were observed at the SN site, while relatively smaller increases were observed at LS and XJ.

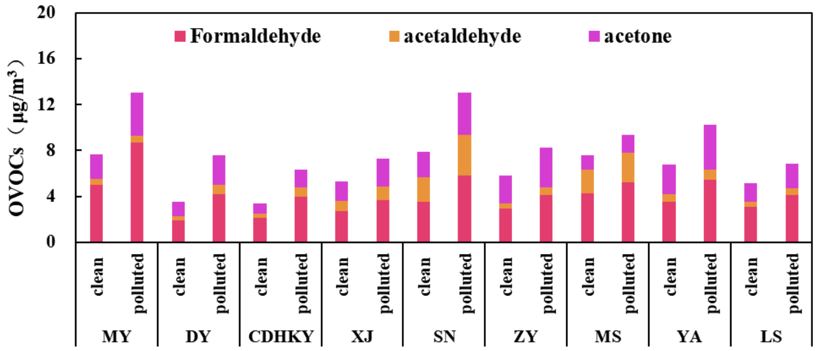

Figure 7. Concentrations of formaldehyde, acetaldehyde and acetone in secondary formation under different pollution conditions at each site in the CPUA during the observation period

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,

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and acetone at the MY, SN, ZY, YA, and LS sites on these days. The OBM analysis allowed us to assess the impact of anthropogenic VOCs (alkanes, alkenes, alkynes, aromatics) and biogenic VOCs (e.g., isoprene) on carbonyl compound formation in the context of regional ozone pollution events (Fig.8). Overall, the sensitivities of different anthropogenic source and plant source VOCs to formaldehyde, acetaldehyde and acetone was consistent among sites. For formaldehyde, reducing alkenes in anthropogenic source VOCs and plant VOCs was the most effective way to control formaldehyde concentration, while reducing alkenes in anthropogenic source VOCs was also beneficial to reduce the formation of acetaldehyde. For acetone with low reactivity, the alkanes in anthropogenic source VOCs were the most sensitive to the formation of acetone, followed by alkenes and BVOCs. Only the RIR value of alkanes were greater than zero, and the RIR values of both alkenes and BVOCs were less than zero, indicating that reducing alkanes could reduce the formation of acetone, while reducing alkenes and BVOCs was not conducive to acetone concentration control.

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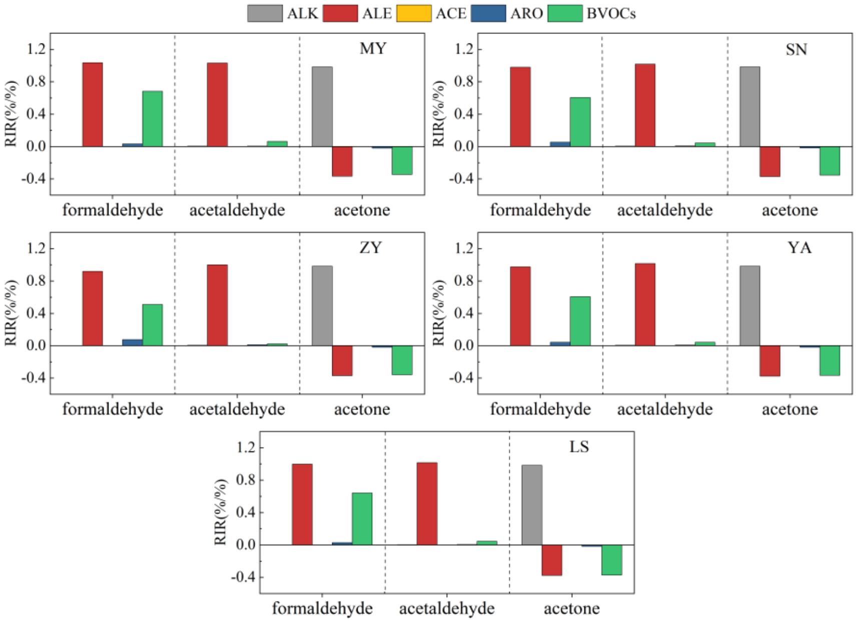

Figure 8. Mean RIRs of formaldehyde, acetaldehyde and acetone to different anthropogenic source VOCs and biogenic source VOCs at MY, SN, ZY, YA and LS sites on August 11th, 12th and

16th

3.6.3 Influence of regional transportation contribution

The TrajStat trajectory model was used to calculate and cluster the 24-hour backward trajectories of air quality at the sampling sites. The backward trajectory during sampling is shown in Fig.S5. During the observation period, the pollution of carbonyl compounds in the cities of the CPUA was affected by the mutual transport among cities in Sichuan Province, especially along the MY-DY-CDHKY route. In addition, the surrounding provinces and cities of Sichuan Province (Gansu and Chongqing) also contributed to the carbonyl compounds of the CPUA.

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The potential sources of carbonyl compounds at different pollution stages at the CDHKY 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.

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.

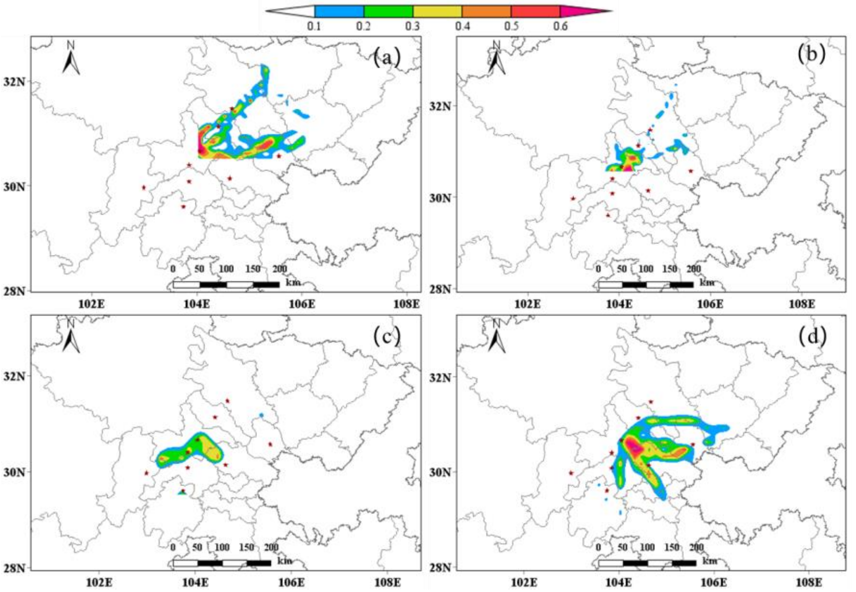

Figure 9. Analysis of potential sources of carbonyl compounds at different periods at the CDHKY site during the observation period (a) August 4th-6th (b) August 7th-9th (c) August 10th-13th (d) August 15th-18th

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4. Conclusions

During a concurrent atmospheric observation campaign conducted at nine sites in the CPUA from August 4th to 18th, 2019, three regional heavy ozone pollution episodes, labeled 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 17.35 ± 5.31 ppb. Spatial analysis revealed a positive correlation between carbonyl levels and ozone concentrations, particularly concentrated around Chengdu in both northern and southern directions. Formaldehyde (36.4%-64.3%), acetone (12.4%-28.1%), and acetaldehyde (8.2%-47.3%) constituted the predominant species by volume concentration. Intriguingly, Chengdu exhibited FAT concentrations surpassing national and international levels, indicating heightened levels compared to other regions. Diurnal variations showed peaks during the day and lows at night, with notable spikes on ozone pollution days. A distinctive "weekend effect" was observed, particularly evident in carbonyl compounds associated with motor vehicle emissions, such as acetaldehyde and acetone, peaking during morning rush hours and nighttime on weekends. This suggests significant contributions from both daytime photochemical processes and nighttime vehicular emissions to carbonyl compounds. At the MY site, 48.6% of the total volatile organic compounds (VOCs) ozone formation potential (OFP) was attributed to the 15 carbonyl compounds, emphasizing their substantial impact on ozone formation, especially formaldehyde and acetaldehyde.

Ground-level observations of FNR were utilized to assess the sensitivity of ground-level ozone formation. FNR from ground-level observations were used to determine 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. Carbonyl compound sources include primary emissions and secondary formation processes. Multivariate linear regression quantitatively analyzed formaldehyde, acetaldehyde, and acetone sources. Secondary formation contributed over 30% on average to formaldehyde, acetaldehyde, and acetone, despite primary emissions being primary sources. 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. 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-DY-CDHKY route. Establishing a collaborative prevention and control mechanism among cities within the CPUA and neighboring provinces and cities is crucial to effectively address carbonyl compounds and ozone pollution in the region in the future.

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

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

Competing interests. The contact author has declared that none of the authors has any competing interests.

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References

Altshuller, A. P. (1993). Atmospheric chemistry of VOCs and NOx: Implications for ozone formation. *Environmental Science & Technology*, 27(6), 1104–1117. doi:10.1021/es00043a001

Atkinson, R., Arey, J., 2003. Atmospheric Degradation of Volatile Organic Compounds. Chem. Rev. 103, 4605–4638. https://doi.org/10.1021/cr0206420

Bao, J., Li, H., Wu, Z., Zhang, X., Zhang, H., Li, Y., Qian, J., Chen, J., Deng, L., 2022. Atmospheric carbonyls in a heavy ozone pollution episode at a metropolis in Southwest China: Characteristics, health risk assessment, sources analysis. Journal of Environmental Sciences 113, 40–54. https://doi.org/10.1016/j.jes.2021.05.029

Cardelino, C., Chameides, W., 1995. An observation-based model for analyzing ozone precursor relationships in the urban atmosphere. J. Air Waste Manage. Assoc. 45, 161–180.

Coggon, M. M., Veres, P. R., Yuan, B., et al. (2019). Emissions of organic carbonyl compounds from biomass burning: A global source of reactive carbon to the atmosphere. *Environmental Science & Technology*, 53(20), 11401–11412.

da Silva, D.B.N., Martins, E.M., Corrêa, S.M., 2016. Role of carbonyls and aromatics in the formation of tropospheric ozone in Rio de Janeiro, Brazil. Environ Monit Assess 188, 289. https://doi.org/10.1007/s10661-016-5278-3

Duan, J., Guo, S., Tan, J., Wang, S., Chai, F., 2012. Characteristics of atmospheric carbonyls during haze days in Beijing, China. Atmospheric Research 114–115, 17–27. https://doi.org/10.1016/j.atmosres.2012.05.010

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带格式的: 正文, 缩进: 左侧: 0 厘米, 悬挂缩进: 7.2 字符

Duan, J., Tan, J., Yang, L., Wu, S., Hao, J., 2008. Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing. Atmospheric Research 88, 25–35. https://doi.org/10.1016/j.atmosres.2007.09.004

Fu, T.-M., Jacob, D.J., Wittrock, F., Burrows, J.P., Vrekoussis, M., Henze, D.K., 2008. Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols. Journal of Geophysical Research: Atmospheres 113. https://doi.org/10.1029/2007JD009505

Fuchs, H., Tan, Z., Lu, K., Bohn, B., Broch, S., Brown, S.S., Dong, H., Gomm, S., Häseler, R., He, L., Hofzumahaus, A., Holland, F., Li, X., Liu, Y., Lu, S., Min, K.-E., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Yinson, Wahner, A., Zhang, Yuanhang, 2017. OH reactivity at a rural site (Wangdu) in the North China Plain: contributions from OH reactants and experimental OH budget. Atmospheric Chemistry and Physics 17, 645–661. https://doi.org/10.5194/acp-17-645-2017

Grosjean, D., & Seinfeld, J. H. (1989). Parameterization of the formation potential of secondary organic aerosols. *Atmospheric Environment*, 23(8), 1733–1747. doi:10.1016/0004-6981(89)90058-9

Guo, H., Wang, T., Simpson, I.J., Blake, D.R., Yu, X.M., Kwok, Y.H., Li, Y.S., 2004. Source contributions to ambient VOCs and CO at a rural site in eastern China. Atmospheric Environment 38, 4551–4560. https://doi.org/10.1016/j.atmosenv.2004.05.004

Hallquist, M., Wenger, J. C., Baltensperger, U., et al. (2009). The formation, properties, and impact of secondary organic aerosol: Current and emerging issues. *Atmospheric Chemistry and Physics*, 9, 5155–5236. doi:10.5194/acp-9-5155-2009

Ho, K.F., Ho, S.S.H., Huang, R.-J., Dai, W.T., Cao, J.J., Tian, L., Deng, W.J., 2015. Spatiotemporal distribution of carbonyl compounds in China. Environmental Pollution 197, 316–324. https://doi.org/10.1016/j.envpol.2014.11.014

Hong, Q., Zhu, L., Xing, C., Hu, Q., Lin, H., Zhang, C., Zhao, C., Liu, T., Su, W., Liu, C., 2022. Inferring vertical variability and diurnal evolution of O3 formation sensitivity based on the vertical distribution of summertime HCHO and NO2 in Guangzhou, China. Science of The Total Environment 827, 154045. https://doi.org/10.1016/j.scitotenv.2022.154045

Hu, J., Wang, P., Ying, Q., Zhang, H., Chen, J., Ge, X., Li, X., Jiang, J., Wang, S., Zhang, J., Zhao, Y., Zhang, Y., 2017. Modeling biogenic and anthropogenic secondary organic aerosol in China. Atmospheric Chemistry and Physics 17, 77–92. https://doi.org/10.5194/acp-17-77-2017

Jiang, Z., Grosselin, B., Daële, V., Mellouki, A., Mu, Y., 2016. Seasonal, diurnal and nocturnal variations of carbonyl compounds in the semi-urban environment of Orléans, France. Journal of Environmental Sciences, Changing Complexity of Air Pollution 40, 84–91. https://doi.org/10.1016/j.jes.2015.11.016

带格式的: 正文, 缩进: 左侧: 0 厘米, 悬挂缩进: 7.2 字符

删除了: Guenther, A.B., Jiang, X., Heald, C.L., Sakulyanontvittaya, T., Duhl, T., Emmons, L.K., Wang, X., 2012. The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. Geoscientific Model Development 5, 1471–1492. https://doi.org/10.5194/gmd-5-1471-2012

带格式的: 正文, 缩进: 左侧: 0 厘米, 悬挂缩进: 7.2 字符

Kanjanasiranont, N., Prueksasit, T., Morknoy, D., Tunsaringkarn, T., Sematong, S., Siriwong, W., Zapaung, K., Rungsiyothin, A., 2016a. Determination of ambient air concentrations and personal exposure risk levels of outdoor workers to carbonyl compounds and BTEX in the inner city of Bangkok, Thailand. Atmospheric Pollution Research 7, 268–277. https://doi.org/10.1016/j.apr.2015.10.008

Kanjanasiranont, N., Prueksasit, T., Morknoy, D., Tunsaringkarn, T., Sematong, S., Siriwong, W., Zapaung, K., Rungsiyothin, A., 2016b. Determination of ambient air concentrations and personal exposure risk levels of outdoor workers to carbonyl compounds and BTEX in the inner city of Bangkok, Thailand. Atmospheric Pollution Research 7, 268–277. https://doi.org/10.1016/j.apr.2015.10.008

Li, N., Fu, T.-M., Cao, J., Lee, S., Huang, X.-F., He, L.-Y., Ho, K.-F., Fu, J.S., Lam, Y.-F., 2013. Sources of secondary organic aerosols in the Pearl River Delta region in fall: Contributions from the aqueous reactive uptake of dicarbonyls. Atmospheric Environment, Improving Regional Air Quality over the Pearl River Delta and Hong Kong: from Science to Policy 76, 200–207. https://doi.org/10.1016/j.atmosenv.2012.12.005

Li, Y., Shao, M., Lu, S., Chang, C.-C., Dasgupta, P.K., 2010. Variations and sources of ambient formaldehyde for the 2008 Beijing Olympic games. Atmospheric Environment 44, 2632–2639. https://doi.org/10.1016/j.atmosenv.2010.03.045

Ling, Z.H., Zhao, J., Fan, S.J., Wang, X.M., 2017. Sources of formaldehyde and their contributions to photochemical O3 formation at an urban site in the Pearl River Delta, southern China. Chemosphere 168, 1293–1301. https://doi.org/10.1016/j.chemosphere.2016.11.140

Liu, J., Li, X., Tan, Z., Wang, W., Yang, Y., Zhu, Y., Yang, S., Song, M., Chen, S., Wang, H., Lu, K., Zeng, L., Zhang, Y., 2021. Assessing the Ratios of Formaldehyde and Glyoxal to NO2 as Indicators of O3–NOx–VOC Sensitivity. Environ. Sci. Technol. 55, 10935–10945. https://doi.org/10.1021/acs.est.0c07506

Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.C., Fuchs, H., Häseler, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., Hofzumahaus, A., 2010. Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results. Atmospheric Chemistry and Physics 10, 11243–11260. https://doi.org/10.5194/acp-10-11243-2010

Luecken, D.J., Hutzell, W.T., Strum, M.L., Pouliot, G.A., 2012. Regional sources of atmospheric formaldehyde and acetaldehyde, and implications for atmospheric modeling. Atmospheric Environment 47, 477–490. https://doi.org/10.1016/j.atmosenv.2011.10.005

Lui, K.H., Ho, S.S.H., Louie, P.K.K., Chan, C.S., Lee, S.C., Hu, D., Chan, P.W., Lee, J.C.W., Ho, K.F., 2017. Seasonal behavior of carbonyls and source characterization of formaldehyde (HCHO) in ambient air. Atmospheric

Environment 152, 51–60. https://doi.org/10.1016/j.atmosenv.2016.12.004

Monks, P. S., Archibald, A. T., Colette, A., Cooper, O., Coyle, M., Derwent, R., ... & Williams, M. L. (2015). Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer. *Atmospheric Chemistry and Physics*, 15(15), 8889-8973.

Murillo, J.H., Marín, J.F.R., Román, S.R., 2012. Determination of carbonyls and their sources in three sites of the metropolitan area of Costa Rica, Central America. Environ Monit Assess 184, 53–61. https://doi.org/10.1007/s10661-011-1946-5

Pang, X., Mu, Y., 2006. Seasonal and diurnal variations of carbonyl compounds in Beijing ambient air. Atmospheric Environment 40, 6313–6320. https://doi.org/10.1016/j.atmosenv.2006.05.044

Rao, Z., Chen, Z., Liang, H., Huang, L., Huang, D., 2016. Carbonyl compounds over urban Beijing: Concentrations on haze and non-haze days and effects on radical chemistry. Atmospheric Environment, Air Pollution in the Beijing – Tianjin – Hebei (BTH) region, China 124, 207–216. https://doi.org/10.1016/j.atmosenv.2015.06.050

Sahu, L. K., & Saxena, P. (2015). High time-resolved volatile organic compounds measurements at an urban location in India: Sources, variability, and role in ozone formation. *Environmental Science and Pollution Research*, 22(5), 3975-3986.

Schroeder, J.R., Crawford, J.H., Fried, A., Walega, J., Weinheimer, A., Wisthaler, A., Müller, M., Mikoviny, T., Chen, G., Shook, M., Blake, D.R., Tonnesen, G.S., 2017. New insights into the column CH2O/NO2 ratio as an indicator of near-surface ozone sensitivity. Journal of Geophysical Research: Atmospheres 122, 8885–8907. https://doi.org/10.1002/2017JD026781

Shao, M., Lu, S., Liu, Y., Xie, X., Chang, C., Huang, S., Chen, Z., 2009. Volatile organic compounds measured in summer in Beijing and their role in ground-level ozone formation. Journal of Geophysical Research: Atmospheres 114. https://doi.org/10.1029/2008JD010863

Shen, X., Zhao, Y., Chen, Z., Huang, D., 2013. Heterogeneous reactions of volatile organic compounds in the atmosphere. Atmospheric Environment 68, 297–314. https://doi.org/10.1016/j.atmosenv.2012.11.027

Tan, Z., Lu, K., Jiang, M., Su, R., Dong, H., Zeng, L., Xie, S., Tan, Q., Zhang, Y., 2018. Exploring ozone pollution in Chengdu, southwestern China: A case study from radical chemistry to O3-VOC-NOx sensitivity. Science of The Total Environment 636, 775–786. https://doi.org/10.1016/j.scitotenv.2018.04.286

Tonnesen, G.S., Dennis, R.L., 2000. Analysis of radical propagation efficiency to assess ozone sensitivity to hydrocarbons and NO x : 2. Long-lived species as indicators of ozone concentration sensitivity. Journal of Geophysical Research: Atmospheres 105, 9227–9241. https://doi.org/10.1029/1999JD900372

Vermeuel, M.P., Novak, G.A., Alwe, H.D., Hughes, D.D., Kaleel, R., Dickens, A.F., Kenski, D., Czarnetzki, A.C., Stone, E.A., Stanier, C.O., Pierce, R.B., Millet,

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带格式的: 正文, 缩进: 左侧: 0 厘米, 悬挂缩进: 7.2 字符

D.B., Bertram, T.H., 2019. Sensitivity of Ozone Production to NOx and VOC Along the Lake Michigan Coastline. Journal of Geophysical Research: Atmospheres 124, 10989–11006. https://doi.org/10.1029/2019JD030842

Wang, C., Huang, X.-F., Han, Y., Zhu, B., He, L.-Y., 2017. Sources and Potential Photochemical Roles of Formaldehyde in an Urban Atmosphere in South China. Journal of Geophysical Research: Atmospheres 122, 11,934-11,947. https://doi.org/10.1002/2017JD027266

Wang, Y., Guo, H., Zou, S., Lyu, X., Ling, Z., Cheng, H., Zeren, Y., 2018. Surface O3 photochemistry over the South China Sea: Application of a near-explicit chemical mechanism box model. Environmental Pollution 234, 155–166. https://doi.org/10.1016/j.envpol.2017.11.001

Wang, Y., Wang, H., Zhang, X., et al. (2020). Formation of secondary organic aerosols from carbonyl compounds: Insights from field observations and simulations. *Atmospheric Chemistry and Physics*, 20, 6177–6189.

Xue, L., Gu, R., Wang, T., Wang, X., Saunders, S., Blake, D., Louie, P.K.K., Luk, C.W.Y., Simpson, I., Xu, Z., Wang, Z., Gao, Y., Lee, S., Mellouki, A., Wang, W., 2016. Oxidative capacity and radical chemistry in the polluted atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe photochemical smog episode. Atmospheric Chemistry and Physics 16, 9891–9903. https://doi.org/10.5194/acp-16-9891-2016

Xue, L.K., Wang, T., Gao, J., Ding, A.J., Zhou, X.H., Blake, D.R., Wang, X.F., Saunders, S.M., Fan, S.J., Zuo, H.C., Zhang, Q.Z., Wang, W.X., 2014. Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes. Atmospheric Chemistry and Physics 14, 13175–13188. https://doi.org/10.5194/acp-14-13175-2014

Xue, L.K., Wang, T., Guo, H., Blake, D.R., Tang, J., Zhang, X.C., Saunders, S.M., Wang, W.X., 2013. Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: results from the Mt. Waliguan Observatory. Atmospheric Chemistry and Physics 13, 8551–8567. https://doi.org/10.5194/acp-13-8551-2013

Xue, L., Wang, T., Louie, P. K. K., Luk, C. W. Y., Blake, D. R., Gao, J., & Lee, S. H. (2013). Increasing external effects negate local efforts to control ozone air pollution: A case study of Hong Kong and implications for other Chinese cities. Environmental Science & Technology, 47(17), 10299-10305.

Yang, X., Xue, L., Wang, T., Wang, X., Gao, J., Lee, S., Blake, D.R., Chai, F., Wang, W., 2018. Observations and Explicit Modeling of Summertime Carbonyl Formation in Beijing: Identification of Key Precursor Species and Their Impact on Atmospheric Oxidation Chemistry. Journal of Geophysical Research: Atmospheres 123, 1426–1440. https://doi.org/10.1002/2017JD027403

Yang, X., Xue, L., Yao, L., Li, Q., Wen, L., Zhu, Y., Chen, T., Wang, X., Yang, L., Wang, T., Lee, S., Chen, J., Wang, W., 2017. Carbonyl compounds at Mount Tai in the North China Plain: Characteristics, sources, and effects on ozone formation.

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带格式的: 正文, 缩进: 左侧: 0 厘米, 悬挂缩进: 7.2 字符

Atmospheric Research 196, 53–61. https://doi.org/10.1016/j.atmosres.2017.06.005

Ye, Z., Xie, S., Wu, Y., et al. (2021). Characterization of carbonyl compounds and their contributions to ozone and secondary organic aerosol formation in a megacity. *Environmental Science & Technology*, 55(14), 9465–9474.

Yuan, B., Chen, W., Shao, M., Wang, M., Lu, S., Wang, Bin, Liu, Y., Chang, C.-C., Wang, Boguang, 2012. Measurements of ambient hydrocarbons and carbonyls in the Pearl River Delta (PRD), China. Atmospheric Research, Remote Sensing of Clouds and Aerosols: Techniques and Applications - Atmospheric Research 116, 93–104. https://doi.org/10.1016/j.atmosres.2012.03.006

Zhang, X., Chen, Z.M., Zhao, Y., 2010. Laboratory simulation for the aqueous OH-oxidation of methyl vinyl ketone and methacrolein: significance to the in-cloud SOA production. Atmospheric Chemistry and Physics 10, 9551–9561. https://doi.org/10.5194/acp-10-9551-2010

Zhang, X., Wu, Z., He, Z., Zhong, X., Bi, F., Li, Y., Gao, R., Li, H., Wang, W., 2022. Spatiotemporal patterns and ozone sensitivity of gaseous carbonyls at eleven urban sites in southeastern China. Science of The Total Environment 824, 153719. https://doi.org/10.1016/j.scitotenv.2022.153719

Zhang, Y., Wang, X., Wen, S., Herrmann, H., Yang, W., Huang, X., Zhang, Z., Huang, Z., He, Q., George, C., 2016. On-road vehicle emissions of glyoxal and methylglyoxal from tunnel tests in urban Guangzhou, China. Atmospheric Environment 127, 55–60. https://doi.org/10.1016/j.atmosenv.2015.12.017

Zhang, Z., Zhang, Y., Wang, X., Lü, S., Huang, Z., Huang, X., Yang, W., Wang, Y., Zhang, Q., 2016. Spatiotemporal patterns and source implications of aromatic hydrocarbons at six rural sites across China's developed coastal regions. Journal of Geophysical Research: Atmospheres 121, 6669–6687. https://doi.org/10.1002/2016JD025115

Zhou, Z., Tan, Q., Deng, Y., Lu, C., Song, D., Zhou, X., Zhang, X., Jiang, X., 2021. Source profiles and reactivity of volatile organic compounds from anthropogenic sources of a megacity in southwest China. Science of The Total Environment 790, 148149. https://doi.org/10.1016/j.scitotenv.2021.148149

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