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MRes in Environmental Engineering

Analysis and research on the change of ozone concentration in the near-surface atmosphere during the new crown epidemic in Zhejiang Province

By

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Abstract

With the rapid development of China's economy, ozone pollution has become increasingly serious in many cities and regions. It has become an important air pollutant second only to particulate pollutants. It is a research hotspot in the field of atmospheric environmental chemistry. China has implemented strict control measures, residents' travel and production activities have been strictly restricted, and the intensity of anthropogenic pollutant emissions has dropped to the lowest level in history favorable opportunity.

This study selects Zhejiang Province, relatively developed in the Yangtze River 8 Delta region, as a specific research object. Based on the National Urban Air Quality 9 10 Real-time Release Platform of China Environmental Monitoring Station monitoring data, 11 major cities in Zhejiang Province(Hangzhou, Jiaxing, Ningbo, Wenzhou, 11 Wenling, Huzhou, Shaoxing, Jinhua, Quzhou, Lishui, and Taizhou) are systematically 12 explored before and after the outbreak of the COVID-19. The temporal and spatial 13 changes of the near-surface ozone concentration and the number of days exceeding 14 the standard characteristics (including interannual, seasonal, monthly, weekly, and 15 intraday variations). The results show that after the outbreak, the ozone concentration 16 changes at representative sites in cities at the same latitude are consistent with those 17 before the outbreak and still show a gradual increase from west to east. But cities in 18 the same longitude no longer show a decreasing trend from north to south. For the 19 characteristics of the time change, after the outbreak, the difference in ozone 20 21 concentration between seasons decreased, and the ozone concentration in winter increase, and the peak of ozone concentration appeared on Tuesday or Friday, no 22 23 longer showing the "weekend effect". At the same time, the ozone concentration increases from 0:00 to 9:00 compared with the data before the outbreak, 24

In addition, this paper further selects Jinhua City, a representative city in central Zhejiang Province, to explore the influence factors of ozone concentration before and after the outbreak, including meteorological and pollution factors. The results show that for meteorological factors, before and after the outbreak, ozone concentration is positively correlated with temperature but negatively correlated with relative humidity. After the outbreak, the correlation between ozone concentration and temperature decreased than before, while the correlation between ozone concentration and relative humidity increase slightly. For polluting gases, before and after the outbreak, the monthly trend of ozone concentration is negatively correlated with the concentrations of NO₂, SO₂, PM_{2.5}, and PM₁₀. After the outbreak, the concentrations of PM_{2.5}, PM₁₀, and ozone have been on an upward trend until March. the ozone concentration has increase compared with the data before outbreak, but SO₂ and NO₂ have decreased significantly. Therefore, when formulating the ozone control measures in Zhejiang Province, the control of the emission of pollution factors should be strengthened.

8 *Keywords:* Zhejiang Province; ozone concentration; COVID-19

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1 Chapter One Introduction

2 1.1 Research background and significance

With the continuous acceleration of urbanization, industrialization, and 3 regional economic integration in my country, the number of motor vehicles, 4 energy use, and population has rapidly expanded, the high-density emission of 5 pollutants, and the mutual transmission of pollutants between different cities and 6 7 regions. All kinds of atmospheric pollution problems have become increasingly 8 prominent, especially the compound air pollution with fine particulate matter (PM_{2.5}) and ozone (O3) as the main pollutants. PM_{2.5} is widely concerned by the 9 people of China as early as 2010. It has always plagued and affected people's lives 10 as the primary pollutant. But compared with PM2.5, ozone pollution is most easily 11 12 overlooked, and it is also one of the most harmful air pollutions. At present, the pollution formed by the combination of particulate matter and ozone is a 13 14 prominent form of air pollution in China. Due to the weak visibility of ozone pollution, it is easy to be ignored (Aneja et al., 2004), and the formation principle 15 of ozone is complex, making it difficult to control. Therefore, Even though various 16 17 localities take measures to reduce the PM2.5 concentration year by year, the ozone concentration is increasing year by year, becoming another important pollutant that 18 affects the national ambient air quality after PM2.5 (Liu Xin, 2020). 19

20 Ozone, a blue gas with a fishy smell, plays a very important role in the chemistry of Earth's atmosphere. Most of the ozone on Earth is concentrated in the 21 stratosphere, which absorbs most of the ultraviolet radiation from sunlight, 22 protecting humans, animals, and plants from short-wave ultraviolet rays. However, 23 a small part of ozone exists in the troposphere because of its strong oxidative 24 activity. It strongly irritates the eyes and respiratory tract when the environmental 25 concentration is high and seriously endangers human health. In addition, ozone is a 26 27 greenhouse gas, which also has an important impact on climate change and air quality (Aneja et al., 2004), so it has become one of the research hotspots of 28 29 environmental scholars in various countries in recent years. To cope with the increasing air pollution problem and improve air quality, the government has also 30

successively issued a series of laws, regulations, and action plans. The emission of
 primary pollutants has been greatly reduced, but the ozone concentration has not
 fallen but risen, and ozone pollution has intensified.

4 In January 2020, the novel coronavirus (COVID-2019) epidemic spread across the country, causing serious impacts on the economy, industrial production, 5 and social life. China has taken stringent measures, including the closing of 6 restaurants, shopping malls, and schools, as well as imposing restrictions on public 7 transportation, to halt the progression of the new crown epidemic and protect 8 human health (such as planes, trains, buses, etc. and even private cars), reducing 9 10 people's social interaction and non-essential business. Anthropogenic sources such 11 as transportation emissions and industrial sources are major contributors to urban air pollutants (Lelieveld et al., 2015). Strict control measures include blocking 12 traffic routes, restricting non-essential activities of the population, closing factories, 13 14 schools, etc. (Zhao Xue et al., 2021). These measures have dramatically changed people's way of life, minimizing the large number of motor vehicles used for daily 15 activities in cities. During the epidemic prevention and control period, the number 16 of motor vehicles in large cities has dropped sharply, which has brought 17 anthropogenic emissions of volatile organic compounds (VOCs) under control. 18 Lockdowns during the COVID-19 pandemic reduced anthropogenic air pollutant 19 20 emissions and thus provided a favorable opportunity to assess the impact of anthropogenic sources on air quality in urban agglomerations (Ki and Task Force 21 22 -NCO, 2020; Rasool et al., 2020).

23 Zhejiang Province is located in the economically developed Yangtze River Delta region. The province with the highest economic and industrial activities is 24 25 the largest energy consumer and has the most pollution in China (Zhang et al., 2022). In recent years, Zhejiang's economy has continued to develop, and the city's 26 status has been continuously improved. At the same time, the problem of urban 27 photochemical pollution represented by ozone has become increasingly prominent. 28 This study investigated the gaseous pollution of eleven major cities in Zhejiang 29 Province (Hangzhou, Jiaxing, Ningbo, Wenzhou, Wenling, Huzhou, Shaoxing, 30 31 Jinhua, Quzhou, Lishui, and Taizhou) from January 1, 2019, to December 31, 2020. The continuous observation data of pollutants (ozone, nitrogen dioxide, sulfur 32 dioxide, PM_{2.5}, and PM₁₀) and meteorological parameters (temperature, humidity) 33

are analyzed to explore the temporal and spatial distribution and variation 1 2 characteristics of ozone concentration in the lower troposphere in different cities before and after the outbreak. Jinhua City, the central city of Zhejiang Province, is 3 selected to study the impact of various pollution factors and meteorological 4 elements on ozone concentration and further analyze the changes in ozone 5 generation before and after the closure of the city, and provide theoretical support 6 7 for formulating and improving ozone control policies.

8

1.2 Research status 9

10

1.2.1 Sources and hazards of ozone

There are two main sources of tropospheric ozone: natural and anthropogenic. 11 Natural sources include stratospheric input and tropospheric photochemical 12 reactions. Many studies have shown that the stratosphere can transport ozone to 13 the troposphere under certain atmospheric conditions, resulting in a local increase 14 in ozone concentration. Photochemical reaction refers to the part generated from 15 the reaction of naturally occurring nitrogen oxides (NOx) (soil, lightning, and 16 stratospheric transport) and biologically emitted VOCs and generates ozone 17 components through photochemical reactions. The source of tropospheric ozone in 18 anthropogenic sources is the main cause of ozone pollution. In terms of chemical 19 definition, ozone pollution is a secondary reaction formed by a series of 20 photochemical reactions of oxygen in the atmosphere, NOx emitted from motor 21 vehicle exhaust, industrial waste gas, etc., and volatile organic compounds (VOCs) 22 under the condition of solar ultraviolet radiation Pollution (An Junlin et al., 2009). 23 Among them, NOx mainly refers to NO and NO₂. Human activities mainly cause 24 the increase in ozone content, and the main generation source is anthropogenic 25 VOCs. Among the anthropogenic VOCs emissions, industrial sources, such as 26 waste gas from heavy petrochemical production (including petroleum distillation, 27 pyrolysis integration, and material synthesis), coal-fired power generation, and 28 other biomass combustion are the main sources of emissions, accounting for up to 29 55%, and Ozone generation contributed significantly; followed by traffic sources 30 and living sources. Among them, automobiles are an important source of pollution 31

in urban areas. The exhaust gas of automobiles is rich in NO and VOCs,
 accounting for about 20% respectively, and contributes greatly to ozone generation.
 However, this point reflects different generative characteristics in other regions
 (Wu Kai et al., 2017).

Ozone is a light blue gas mainly present in the stratosphere of the atmosphere. 5 The ozone layer can block ultraviolet radiation and protect humans from 6 ultraviolet rays (Yan Jiapeng, 2015). Ozone pollution occurs when the ozone 7 concentration in the air near the ground is higher than 120 μ g/m3. When the 8 9 hourly concentration of ozone exceeds 260 µ g/m3, people begin to feel uncomfortable, such as sore throat, dizziness, headache, and vision loss, which 10 lead to an increase in the incidence of respiratory and cardiovascular diseases 11 (Yang Guiying, 2010; Liao Zhiheng and Fan Shaojia). , 2015). Numerous studies 12 have also confirmed that elevated ozone concentration inhibits plant growth, 13 resulting in poor crop quality and reduced yield (Feng et al., 2014; Mao Bing et al., 14 2016; Feng Zhaozhong et al., 2018). The increase of ozone concentration will 15 affect the main nutrients contained in soybean and then affect the quality of 16 soybean (Wang Chunyu et al., 2019); in the research on the effect of ozone 17 concentration on Dongguan rice and Beijing winter wheat, it is shown that the 18 19 increase of atmospheric ozone concentration, Dongguan rice yield The relative 20 decrease of 2.7%, and the relative reduction in winter wheat yield in Beijing by 12.85% (Geng Chunmei et al., 2014); Avnery (Avnery et al., 2011) and others 21 believe that the increase of ozone concentration makes the global wheat, corn, 22 soybean, and other major crops decline. The drop is as high as 15%. When the 23 hourly ozone concentration exceeds 320 μ g/m3, plants will dry up or even die. In 24 addition, ozone pollution mainly affects plants' normal growth by affecting plants' 25 photosynthesis and may also affect the ecological environment (Kou Taiji et al., 26 2009). Some studies also show that high ozone concentrations will also have a 27 certain impact on the climate. For example, Zhou Renjun et al. (Zhou Renjun and 28 Chen Yuejuan, 2007) have shown that the total amount of ozone on the 29 Qinghai-Tibet Plateau from May to July is significantly related to the temperature 30 in summer and winter in my country, and the next spring. Negative correlation and 31 positive correlation with precipitation. It can be seen that the harm of ozone 32

concentration changes to human health, ecological environment, and economic
 development cannot be underestimated.

3 1.2.2 Research status of ozone pollution

4 **1.2.2.1 Ozone concentration monitoring**

At present, the means of obtaining ozone concentration are mainly through 5 site monitoring and remote sensing monitoring. The ground monitoring site has the 6 characteristics of real-time monitoring, short data monitoring time interval, and 7 long-term continuous observation. To solve the ozone pollution problem and 8 strengthen the monitoring of the temporal and spatial distribution of ground ozone, 9 the ground monitoring of ozone in my country started in 2008, from the initial six 10 pilot cities to the routine monitoring of 1497 national control points in more than 11 300 cities, which provides the basic conditions for the research on the temporal 12 and spatial distribution characteristics of ozone pollution in my country. The 13 14 research on ozone pollution's temporal and spatial distribution characteristics is carried out on national, regional, and city scales. 15

On the national scale, by analyzing the ozone pollution situation of 338 cities 16 17 in my country in 2016 and combining the topography and meteorological conditions of each city, my country is divided into ten ozone pollution control 18 19 areas according to the ozone pollution situation (Ma Pengfei et al. ., 2021). Analysis of ozone in 338 cities in my country over three years from 2015 to 2017 20 is carried out using spatial interpolation of ground-monitoring station data. 2020. 21 At the provincial, regional, and key urban agglomeration scales, the time-based 22 analysis of ground-level ozone in four regions of the Northwestern Mediterranean 23 Basin from 1994 to 2001, including coastal, mountainous, terrestrial and urban 24 areas, showed that the ozone concentration in coastal areas decreased by 22%, the 25 mountain area increase by 14%, and there is no significant change in inland and 26 the urban regions (Rojas and Venegas, 2013). The analysis of ozone concentration 27 28 in Beijing and its surrounding areas showed that meteorology is the main factor leading to the spatial variation of ozone in this area (Tang et al., 2012), after 29 dividing Sichuan Province into five major regions, in the exploration of the 30 temporal and spatial distribution of ozone concentration and pollution in the 31 different areas from 2015 to 2016, the temporal and spatial distribution of ozone 32

has obvious regional differences (Li Polan et al., 2018). The more commonly used
methods for investigating the temporal variation and spatial heterogeneity of ozone
concentration including the use of statistical methods and geographic detectors, or
through the Moran index, Kriging interpolation and hot-spot analysis methods.
(Peng Chao et al. al., 2018; Huang Xiaogang et al., 2019)

6

1.2.2.2 Spatial and temporal characteristics of ozone pollution

7 In recent years, economic activities in the Yangtze River Delta region have 8 developed rapidly, and the ozone concentration in urban air has been increasing yearly (Shanyuanyuan et al., 2016b; Chen Chao et al., 2019). Many scholars have 9 10 analyzed the characteristics of ozone pollution in Zhejiang and its relationship with meteorological conditions to analyze the ozone generation mechanism, change 11 12 elements, meteorological conditions, and control strategies that affect ozone concentration in this region. Research on the temporal and spatial characteristics of 13 ozone pollution in the Yangtze River Delta region shows that the highest ozone 14 concentration will occur in the year in late spring and early summer, and there are 15 also high ozone events in September (Wang Huixiang et al., 2003). 16

Among the studies on the spatiotemporal distribution of urban ozone, a study 17 investigating the differences in the weekend effect of ozone between urban and 18 rural areas in southern Italy showed an overall decrease in total ground-level ozone 19 over the weekend (Schipa et al., 2009). In exploring ozone pollution and 20 21 spatiotemporal characteristics in Xuchang City from 2014 to 2016, ozone pollution showed an increasing trend with time (Wang Aiqin et al., 2017). The analysis of 22 the spatiotemporal characteristics of annual ozone concentration showed that the 23 ozone concentration in Xuzhou is high in summer and low in winter (Shang Jing, 24 25 2018). Another study explored the spatial distribution of ozone by using passive measurement methods to monitor ozone concentrations in industrial cities in 26 27 Turkey (Pekey and Ozaslan, 2013).

In addition, many domestic studies have investigated the sources and concentrations of volatile organic compounds in the ambient air during special periods of human ozone emission (such as the Spring Festival and other major events). The research on the concentration of volatile organic compounds during the Spring Festival in Beijing showed that the concentration of volatile organic

compounds decreased by about 60% during the Spring Festival and pointed out 1 2 that fireworks and firecrackers during the Spring Festival are important sources of acetonitrile, aromatic hydrocarbons, CO, SO₂, and NO_x, emphasizing the control 3 of fireworks and firecrackers and the importance of discharge (Li et al., 2019). The 4 research on the changes in the concentration of volatile organic compounds, the 5 potential and sources of ozone generation during the Beijing Olympics showed 6 that automobile exhaust and solvent volatilization are the two major sources of 7 volatile organic compounds, and aromatic hydrocarbons have the greatest potential 8 9 for ozone generation in the atmosphere in Beijing. Compounds accounted for 47%, followed by alkenes with 40%, and alkanes with the lowest 13% (Wu Fangkun et 10 al., 2010). During the above major events, local pollutant reduction efforts are 11 strong, but the impact of pollutant migration in surrounding areas could not be 12 ignored (Jia Haiying et al., 2017). 13

14 **1.2.2.3 Factors Affecting Ozone Pollution**

Atmospheric ozone generation and pollution concentrations are influenced by a combination of local sources (photochemical reaction generation and removal), regional transport (input and output), and stratospheric ozone intrusion. The photochemical reaction substances that generate ozone are based on precursors (mainly NOx and VOCs). The necessary conditions include sufficient solar radiation and air temperature, while wind, precipitation, and relative humidity play a role in the transmission, removal, and deposition of ozone concentration.

In addition to local photochemical reactions affecting the level of near-surface 22 23 ozone concentrations, weather systems, and meteorological conditions are also closely related to ozone concentrations (Aneja et al., 2004; Geng et al., 2009). 24 25 Most scholars conduct correlation analysis on ozone concentration from two perspectives of local and overall meteorological conditions. In the exploration of 26 27 the influence of meteorological elements on ozone concentration in Beijing, by comparing the size of the same meteorological component on the day when the 28 29 ozone concentration reaches the standard and the day when the ozone concentration exceeds the standard, it is concluded that the wind speed and 30 pressure levels on an exceeding day are lower than those on the meeting day. The 31 temperature and humidity levels on an exceeding day are lower than the standard 32

day. The conclusion is higher than the target date (Wang Zhanshan et al., 2018). In 1 2 the research on the annual average ozone concentration in Nanjing, the correlation analysis results of meteorological elements at different levels of ozone 3 concentration show that the correlation between ozone concentration and 4 temperature is the best at the normal level, and the relationship between ozone 5 concentration and humidity and wind speed is the second level exceeding the 6 standard. Relevance is the best. The correlation analysis results of ozone 7 concentration and meteorological elements such as temperature, humidity, and 8 9 wind in Xi'an from January to April 2013 show that the ozone concentration is the 10 highest when the temperature is high, low humidity, and the wind direction is southeasterly and southerly (Liu Song et al., 2017). In addition, in the correlation 11 analysis of the average ozone concentration in my country from 2014 to 2017 and 12 meteorological factors such as temperature, humidity, and 24-h precipitation, 13 ozone concentration is positively correlated with temperature, and negatively 14 correlated with humidity and precipitation in the past 24 hours (Liu Yulian et al., 15 2018). More studies have shown that the ozone concentration is inseparable from 16 the pressure, and ozone mainly occurs in the type of weather controlled by high 17 18 pressure (Zhu Yuxiu and Xu Jialiu, 1994; Hong Shengmao et al., 2009). The ozone concentration is significantly higher on sunny days with few clouds than on cloudy 19 and rainy days (Shan et al., 2010). In addition, meteorological factors such as 20 temperature, relative humidity, wind direction, and wind speed affect the 21 22 near-surface ozone concentration (Ding Guoan et al., 1995; Tan Jianguo et al., 2007; Sun Guojin et al., 2020). 23

24 Precursor concentration level is one of the important factors affecting ozone 25 generation. Overseas studies on ozone precursor-related issues are earlier. In 1953, Haggen-Smit proposed that the precursors of near-ground ozone formation are 26 NOx and VOCs. Ozone precursors can affect ozone generation, but the 27 relationship between the two is complex and easily influenced by other 28 environmental factors, showing a nonlinear relationship. In some cases, controlling 29 a single precursor will not significantly reduce ozone concentration but may 30 aggravate ozone pollution (Miranda et al., 2005; Chen et al., 2020). Emissions of 31 large amounts of NOx and SO₂ in the Asia-Pacific coastal areas can significantly 32 increase regional ozone concentrations (Akimoto and Narita, 1994). The in-depth 33

advancement of domestic industrialization and urbanization has increase the 1 2 emission of anthropogenic VOCs and NOx, resulting in a continuous increase in ozone concentration in urban areas and frequent occurrence of ozone pollution 3 incidents. The change in ozone concentration in China from 2013 to 2019 showed 4 that the massive emission of VOCs is one of the important reasons for the 5 continuous increase in ozone concentration (Li et al., 2020). The observation of 6 7 ozone concentration in the northern mountainous area of Beijing over six weeks in summer found that the massive emission of VOCs and NOx led to an increase in 8 9 the level of ozone concentration in Beijing, and NOx played an important role in ozone generation in Beijing (Wang et al., 2006). In the VOCs observations carried 10 out in the cities and suburbs of the Pearl River Delta, it is found that ethylene, 11 toluene, and m/para-xylene are the main precursors of ozone generation in the 12 Pearl River Delta region and contributed greatly to ozone generation (Zhang et al., 13 2022). 14

The presence of particulate matter in the atmosphere can reduce the 15 photolysis rate of ozone precursors, thereby affecting ozone production in the 16 atmosphere. A study of near-surface photochemical pollution in Mexico found that 17 the presence of aerosols reduced the rate of NO₂ photolysis, resulting in a 20% 18 reduction in ozone concentrations (Castro et al., 2001). In a study in the summer of 19 20 2011 in North China, it is found that the presence of aerosols resulted in a decrease in ozone photolysis rate, OH radicals, and boundary layer ozone concentrations (Li 21 22 et al., 2020). When exploring the effect of atmospheric particulate matter on ozone in Nanjing, it is found that PM2.5 can affect ozone concentration by changing the 23 photolysis rate and heterogeneous reactions of ozone (Guo et al., 2018). Typically, 24 25 the resulting photolysis rate effect results in a greater ozone reduction when particle concentrations are higher, whereas heterogeneous reactions dominate at 26 low concentrations. Furthermore, in typical VOC-sensitive regions, the ozone 27 concentration can even be increase by heterogeneous reactions. By simulating the 28 sensitivity of NOx and VOCs in summer anthropogenic emissions in my country, 29 it can be seen that the emissions of precursors have a relatively weaker effect on 30 ozone than changes in PM2.5 concentration (Irei et al., 2016). In exploring the 31 ozone concentration exceeding the standard in each city of Beijing-Tianjin-Hebei 32 through the filtering method, there is a 90.4% probability that changes in pollutant 33

emissions cause the increasing ozone pollution. Pollutants can be divided into two 1 2 aspects, one is the decrease in particulate matter concentration (contributing 27.3%), and the other is the increase in precursor concentration (contributing 3 63.1%); the impact of meteorological conditions on ozone pollution is only 9.6% 4 probability (Yu Yijun et al., 2020). It can be seen that the reduction of particulate 5 matter concentration has the most important contribution to the increase of ozone 6 concentration in the Beijing-Tianjin-Hebei region, which means that we need to 7 further reduce the emission of precursors such as NOx and VOCs to offset the 8 9 reduction of PM2.5. And cause the reverse effect of ozone increase.

10

1.2.2.4 Ozone Sensitivity Analysis

Currently, the research methods for the sensitivity of near-ground ozone 11 12 mainly include the sensitivity test method, source tracer method, and indicator. The sensitivity test method determines the sensitivity of the precursor by adjusting 13 the model's input parameters and outputting the change of ozone concentration 14 under different emission scenarios. Wang Xuesong et al. (Wang Xuesong et al., 15 2009) used the source tracing method combining an air quality model and ozone 16 source identification technology to analyze the source of ozone concentration in 17 the Beijing area. A specific threshold determines the ratio of certain intermediates 18 or products in the photochemical reaction to determine the required control 19 precursors in the region (Wu Lin et al., 2017). However, H2O2 and HN ozone are 20 not easy to monitor, and data are difficult to obtain. The indicators received based 21 22 on the ozone monitoring instrument (OMI) satellite data have the advantages of 23 good temporal and spatial continuity, wide monitoring range, and little human interference and have been widely used in ozone sensitivity analysis research. OMI 24 satellite data are used in a study to explore the ozone sensitivity of 25 Beijing-Tianjin-Hebei and surrounding areas in summer from June to September 26 2005 to 2016 (Wu Weiling et al., 2018). The temporal and spatial variation 27 characteristics of ozone sensitivity of different land-use types in the Pearl River 28 Delta from 2005 to 2016 are explored through OMI satellite data and MODIS land 29 cover classification products. Between the edge of the Pearl River Delta and the 30 31 first two control areas: the developed area is mainly a VOCs/co-controlled area, the more developed area is primarily the same control area, and the less developed 32 area is the Nq control area (Zhuang Liyue et al., 2019). When exploring the spatial 33

distribution characteristics of ozone control areas in the central and eastern regions
of my country from 2005 to 2014, the OMI satellite data is also used. It is found
that the major cities in Shandong, Yujin, Beijing-Tianjin-Hebei, the Yangtze River
Delta, and the Pearl River Delta belong to VOC control areas. The surrounding
towns belong to the collaborative Control area, and the other regions belong to the
NOx control area (Shan et al., 2016a).

7

1.2.2.5 The impact of COVID-19 on ozone concentration

8 During the COVID-19 pandemic, motor vehicle traffic, industrial operations, building construction, and shopping malls have all been significantly reduced due 9 10 to the implementation of social distancing policies. Human and industrial activities are reduced to a minimum, and the discharge of primary pollutants is greatly 11 12 reduced. Comparing the concentration changes of air pollutants before and after the "partial blockade" in Rio de Janeiro, Brazil, it is found that CO and NO2 13 decreased significantly, by 30.3-48.5% and 16.8-53.8%, respectively. And PM10 14 concentrations only dropped in the first few weeks of the partial lockdown. In 15 contrast, ozone concentrations increase by 67% compared to pre-lockdown 16 (Dantas et al., 2020). Similarly, in São Paulo (Li et al., 2020), Barcelona (Mahato 17 et al., 2020), London (Sharma et al., 2020), and many cities in India (Sicard et al., 18 2020; Tobias et al., 2020b) observed similar trends. In addition, after analyzing the 19 ozone concentrations in four southern European cities (Nice, Rome, Valencia, and 20 Turin) and Wuhan, China, during the lockdown period in 2017-2020, it is found 21 22 that during the lockdown period in 2020, Nice, Rome, Turin, Valencia The ozone concentration in Wuhan and Wuhan increase by 24%, 14%, 27%, 2.4%, and 36% 23 respectively, of which the increase in ozone in Wuhan is the largest. It is inferred 24 25 that the increase in ozone concentration is mainly due to the sharp drop in NOx emissions, resulting in a reduction in NO titration depletion of ozone (Sicard et al., 26 2020). 27

In addition, studies have shown that although PM_{2.5} in the Yangtze River Delta region decreased during the epidemic blockade, it still maintained a high level, with high background pollution and residues (Li et al., 2019). The concentration of PM_{2.5} in Wuhan has decreased significantly, but its chemical composition and sources have a complex nonlinear response to air pollution

control measures, requiring regional joint control (Zhang et al., 2022). After the 1 2 epidemic prevention and control, HONO in the Shijiazhuang area decreased by about 31%, NO by 62%, and NO₂ by about 36% (Liu Xinjun et al., 2022). Wang 3 Shenbo et al. (2020) showed that apart from ozone, PM2. 5 and NO decreased 4 significantly in Henan Province under the influence of the Spring Festival and the 5 epidemic, but the concentrations are still high. During the epidemic, all air 6 pollutants except ozone in Beijing-Tianjin-Hebei are generally in a downward 7 trend, and controlling industrial emissions is still the key to air pollution control 8 (Zhu Yifan et al., 2021). The above studies all show that the heavily polluted 9 weather has not disappeared due to the reduction of anthropogenic 10 emissions.VOCs are important precursors of ozone and PM2.5, and the emission 11 reduction of VOCs will be the key to realizing the coordinated control of ozone 12 and PM2.5 in my country (Zhang et al., 2022). The pollution characteristics and 13 source changes of VOCs before and after the epidemic prevention and control in 14 the Nanjing urban area are studied. It is found that the volume fraction of VOCs 15 decreased significantly after the epidemic prevention and control began, and the 16 contribution of the chemical industry and motor vehicle pollution sources to VOCs 17 18 decreased significantly (Tian Kaiwen et al., 2022). The research on the change characteristics, ozone generation potential, and source analysis of VOCs during the 19 20 epidemic prevention and control period in Jiyuan City shows that the volume fraction of VOCs during the epidemic prevention and control period has increase 21 22 compared with that before the epidemic prevention and control period. The contribution rate of TVOCs in Jiyuan City has been greatly reduced. Still, the 23 24 contribution of ethanol and chlorine-containing substances from disinfectants to TVOCs in Jiyuan City has increase significantly (Wang Hongguo et al., 2021). 25

26

1.3 Research purpose and content

27 **1.3.1 Research purpose**

Based on the sorting and summary of previous research work, this research relies on representative sites of 11 cities in Zhejiang Province (Hangzhou, Jiaxing, Ningbo, Wenzhou, Wenling, Huzhou, Shaoxing, Jinhua, Quzhou, Lishui, and Taizhou) January 2019- The monitoring data in December 2020 is divided into two stages: "before the outbreak" (2019) and "after the outbreak" (2020). From the data

perspective, the ozone in typical cities in Zhejiang Province before and after the 1 2 outbreak is explored from the two dimensions of time and space. The distribution characteristics of pollution, and Jinhua City, a city in central Zhejiang Province, is 3 selected as a representative to explore further the influencing factors of ozone 4 concentration and its correlation with precursors and meteorological factors and 5 analyze the possible causes of ozone pollution during the epidemic. In 6 7 epidemiological emergencies, formulating effective control strategies for air pollutants provides scientific guidance and technical support to provide reference 8 9 and a basis for environmental management and decision-making.

10 **1.3.2 Research content**

11 The specific research contents of this paper are set as follows:

(1) Spatial and temporal characteristics of ozone pollution in Zhejiang Provincebefore and after the outbreak of COVID-19

Statistical analysis of the hourly ozone concentration of 11 typical cities in Zhejiang Province from January 1, 2019, to December 31, 2020, is conducted to explore the same longitude (from north to south) and latitude (from west to east) in Zhejiang Province before and after the new crown epidemic.) represents the interannual, seasonal, monthly, weekly, and intraday variation characteristics of ozone concentration at urban sites.

20 (2) Analysis of the influencing factors of ozone pollution

Taking Jinhua City, a city in central Zhejiang Province, as a distinct research area by analyzing the change characteristics of meteorological factors such as temperature, relative humidity, and pollution factors such as PM2. Analyze the effects and possible mechanisms of meteorological factors and polluting gases on ozone concentration.

- 1
- 2

Chapter 2 Data and Methods

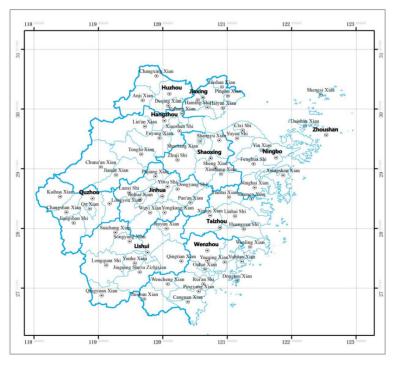
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2.1 Introduction to observation sites

The observation site in this study is located in Zhejiang Province, and the 4 regional locations of Zhejiang Province are 118° 01'E~123° 10'E, 27° 02'N~31 5 11'N, as shown in Figure 1. Zhejiang is one of the country's most economically 6 developed and populous provinces. The straight-line distance from east to west and 7 north to south in Zhejiang is about 450 kilometers, with a land area of 105,500 8 square kilometers, including 11 prefecture-level cities and 20 county-level cities, 9 with a resident population of more than 64.57 million and a GDP of more than 10 6,461.3 billion yuan. Zhejiang Province has a complex topography and naturally 11 12 slopes from the southwest to the northeast. Except for the east, which is adjacent to the East China Sea, the rest are surrounded by cities. The province's interior 13 14 consists of eight major water systems and several plains, hills, basins, and mountains. Zhejiang Province is located in the mid-subtropical zone with a 15 suitable climate. The average annual temperature is between 15 and 18 degrees. 16 The subtropical climate is humid, with four distinct seasons, mild temperatures 17 throughout the year, increase rainfall, and relatively good air quality. 18

According to the survey at the end of 2019, Zhejiang Province has ten 19 meteorological radar observation stations, 15 satellite cloud image-receiving 20 stations, and 3,082 regional automatic meteorological observation stations, which 21 can collect and analyze climate phenomenon data in the province extensively and 22 23 accurately. According to statistics: In 2019, the average number of haze days in Zhejiang Province is about 37 days, an increase of 15 days over the previous year; 24 the average annual concentration of PM2.5 The ambient air quality of the 11 25 districted cities is 31 micrograms/m3, which is higher than the previous year. A 26 decrease of 3.1%; among the 58 cities above the county level, the percentage of 27 days with good air quality is between 76.7% and 98.1%, with an average of 88.6%, 28 down 0.4 percentage points from the previous year; the percentage of days with 29

1 good air quality is 77.3 % to 100%, with an average of 94.0%, a decrease of 0.2%



2 from the previous year.

3 Figure 1 Geographical distribution map of major cities in Zhejiang Province

All the city sites involved in this paper (Table 1), including four cities in the northern part of Zhejiang Province (Huzhou, Jiaxing, Shaoxing, and Hangzhou), four cities in the southern part (Quzhou, Lishui, Wenzhou, and Wenling) and from west to east four cities (Quzhou, Jinhua, Taizhou, and Ningbo). Since the site involves 11 cities, this paper selects the atmospheric background station in Hangzhou to focus on the introduction to better convey the site information. Air quality monitoring stations in other regions operate similarly to this station.

11 Hangzhou Meteorological Monitoring Station is located in the southern suburbs of Hangzhou. It can more accurately collect atmospheric data in urban 12 areas at the West Lake Viewing Area and Hangzhou metropolitan area, eliminating 13 14 the influence of human factors. The monitoring station of the weather monitoring center The air quality monitoring station is located at an altitude of about 41.7 15 meters. The atmospheric composition sampling point is located on the large 16 platform on the third floor of the courtyard. PTFE tubing is used to collect gas 17 samples. The air quality monitoring station is surrounded by mountains in the west, 18 adjacent to West Lake, and mountains in the south. The urban construction group 19 in the center of Hangzhou, mainly residential areas and traffic sections, is 20

separated by the Qiantang River. The north and east sides of the air quality
 monitoring station are separated by the river, avoiding the industrial pollution
 source caused by the factory construction.

4

| Latitute | Longitude | Background | Sampling Duration |
|----------|--|---|---|
| 3053 | 11998 | Urban | Jan 2019-Dec 2020 |
| 3079 | 12074 | Urban | Jan 2019-Dec 2020 |
| 3005 | 12049 | Urban | Jan 2019-Dec 2020 |
| 3027 | 12006 | Urban | Jan 2019-Dec 2020 |
| 2891 | 11981 | Urban | Jan 2019-Dec 2020 |
| 2858 | 11857 | Urban | Jan 2019-Dec 2020 |
| 2846 | 11993 | Urban | Jan 2019-Dec 2020 |
| 2865 | 12142 | Urban | Jan 2019-Dec 2020 |
| 2920 | 12193 | Urban | Jan 2019-Dec 2020 |
| 2779 | 12009 | Urban | Jan 2019-Dec 2020 |
| 2836 | 12107 | Urban | Jan 2019-Dec 2020 |
| | 3053 3079 3005 3027 2891 2858 2846 2865 2920 2779 | 3053 11998 3079 12074 3005 12049 3027 12006 2891 11981 2858 11857 2846 11993 2865 12142 2920 12193 2779 12009 | 3053 11998 Urban 3079 12074 Urban 3005 12049 Urban 3027 12006 Urban 2891 11981 Urban 2858 11857 Urban 2846 11993 Urban 2865 12142 Urban 2920 12193 Urban 2779 12009 Urban |

Table 1. Location of air quality station, period of data collection

5

6 **2.2 Data sources**

The near-ground ozone data used in this paper comes from the national urban air quality real-time release platform of the China Environmental Monitoring Station. Air quality data types include PM2.5, PM10, SO2, NO2, ozone, CO, and Air Quality Index (AQI). The data used in this paper are PM2.5, PM10, SO2, NO2, and ozone data, which are hourly data monitored in real-time. This paper's Chinese surface meteorological data comes from the National Climatic Data Center, a National Oceanic and Atmospheric Administration subsidiary.

1 If the ozone mass concentration exceeds the standard value, refers to the 2 Ministry of Environmental Protection standard HJ633-2012 "Ambient Air Quality Index (AQI) Technical Regulations" and "Ambient Air Quality Standard" 3 (GB3095-2012). Data quality control for selecting outliers according to the 4 Ambient Air Quality Monitoring Specification. In addition, when classifying and 5 analyzing the data, the lack of hourly and average data due to power outages, 6 instrument maintenance, calibration, etc., during the observation period is 7 eliminated to ensure accuracy and reference values. In addition, records and 8 9 erroneous data related to instrument failures must be deleted. The data acquisition system saves and records raw data every minute to provide raw data for subsequent 10 research. Finally, according to the validity of the Ambient Air Quality Standards in 11 pollutant statistics, it takes at least 45 minutes per hour. Average concentration 12 values are at least 20 hours per day, hourly arithmetic averages are calculated using 13 5-minute average data, and daily arithmetic averages are calculated using hourly 14 data. 15

When analyzing the problem of ozone concentration, O3 concentration is an 16 evaluation index of pollution degree according to the provisions of the national 17 "Ambient Air Quality Standard" (GB30952012) (the primary standard is 100 18 μ g/m3). Since the raw monitoring data is long-term, with at least 14 hours per day, 19 the arithmetic means data of the valid daily mean is defined as the main analysis. 20 After synthesizing various field information, this paper determines that the effective 21 daily average of ozone is the maximum 8-hour moving average. SPSS 19.0 (IBM 22 Inc., Chicago, IL, US) software is used for data processing and analysis, and 23 Sigmaplot 14.0 is used for plotting. 24

25 Chapter 3 Results

3.1 Temporal and spatial variation characteristics of ozone

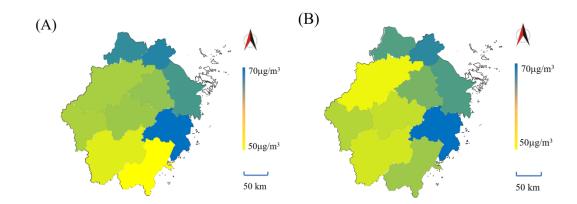
27 concentration

To explore the spatial distribution characteristics of ozone concentration in Zhejiang Province before and after the outbreak of the new crown epidemic, we selected representative sites in the north (Huzhou, Jiaxing, Shaoxing, Hangzhou) and usual sites in the south (Quzhou, Lishui, Wenzhou, Wenling) with the same
 longitude, respectively. And the representative stations (Quzhou, Jinhua, Taizhou,
 Ningbo) from west to east at the same latitude are studied.

4 **3.1.1 Interannual Variation of Ozone Concentration**

First, by analyzing the inter-annual spatial changes in ozone concentration at 5 each representative site before and after the outbreak (Fig. 2), it is found that before 6 7 the outbreak, the inter-annual changes in ozone concentration in cities in Zhejiang 8 Province decreased sequentially from north to south, and sequentially from west to east. Increase. After the outbreak, towns at the same latitude still showed a trend of 9 10 increasing interannual ozone concentration from west to east. From the longitude perspective, the ozone concentration changes in Hangzhou and Taizhou are different. 11 12 After the outbreak, the inter-annual average ozone concentration in Hangzhou is the lowest among the 11 cities (52.18 μ g/m3), while the ozone concentration in Taizhou 13 is the highest (69.29 μ g/m3). 14

15



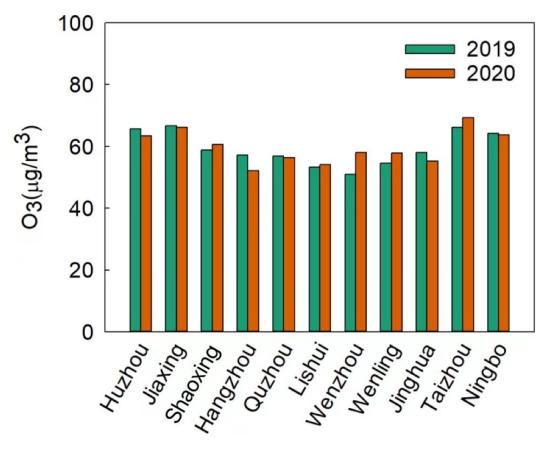
16 17

Figure 2 Spatial distribution of ozone concentration at each representative location in Zhejiang Province in 2019 (A) and 2020 (B)

18 19

Based on the spatial distribution characteristics of ozone concentration, we further explored the annual changes in ozone concentration in each representative site in Zhejiang Province in 2019 and 2020 (Fig. 3). The average annual change of ozone concentration in Zhejiang Province in 2019 and 2020 is between 50 and 80 µg/m3. Among them, the average ozone concentration value in Shaoxing, Wenzhou,

- 1 and Taizhou in 2020 is higher than in 2019. Overall, the annual mean value of ozone
- 2 concentration before and after the outbreak is not significantly different.
- 3



4 5

Figure 3 The annual change of ozone concentration at each representative site in Zhejiang Province

7

6

8 Based on the first-level ozone concentration limit (100 μ g/m3) specified in the National Ambient Air Quality Standard (GB3095-2012), we calculated the ozone 9 concentration exceeding the standard at each representative site (Fig. 4). Except for 10 Wenling, the annual number of days with ozone exceeding the standard exceeded 11 12 150 days in all cities. Among them, the days exceeding the standard ozone 13 concentration in Huzhou ranked first before and after the outbreak, while the rate of exceeding the standard ozone concentration in Wenling is the lowest. Among them, 14 15 the number of days where the ozone concentration exceeded the standard in Wenzhou and Wenling after the outbreak is slightly higher than the days before the 16 outbreak. Overall, the inter-annual ozone excess days in each city do not differ much 17

1 before and after the outbreak, which is consistent with the annual change in ozone

2 concentration.

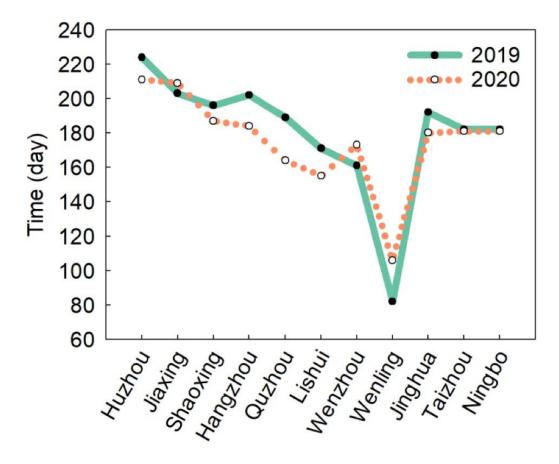


Figure 4 The number of days with excessive ozone concentration in Zhejiang Province in 2019 and 2020

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4 5

7

3.1.2 Seasonal variation characteristics of ozone concentration

8 The climate of Zhejiang Province is a temperate continental climate 9 characterized by a semi-humid and semi-arid climate, with hot summers and cold 10 winters. According to the characteristics of meteorology, March-May is defined as 11 spring, June-August is defined as summer, September-November is defined as autumn, 12 and December-February is defined as winter.

13

Before the outbreak, each city's seasonal spatial distribution of near-ground ozone concentration is significantly different (Figure 5). All representative city sites showed the highest in spring and summer, the lowest in winter, and fall in between. In

spring and summer, ozone concentrations in northern cities (Huzhou, Jiaxing, 1 2 Shaoxing, and Hangzhou) are higher than in southern cities (Quzhou, Lishui, Wenzhou, and Wenling). The city with the highest ozone concentration in spring and 3 summer is Jiaxing; the highest concentration in autumn is Quzhou; the highest 4 concentration in winter is Wenling. Lishui has the same attention in spring and 5 autumn, and the ozone concentration in Wenling is similar each season. Overall, the 6 7 seasonal differences in ozone concentration in northern cities are more obvious than 8 those in southern towns.

9

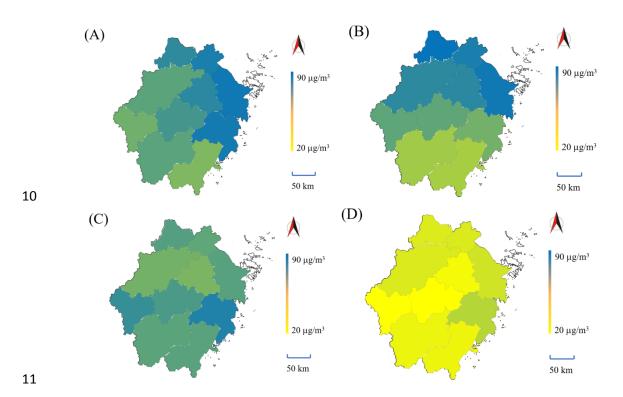


Figure 5 Spring (A), summer (B), autumn (C), and winter (D) of each representative location
 in Zhejiang Province in 2019

14

After the epidemic outbreak, the seasonal spatial distribution of near-ground ozone concentrations in various cities differed significantly. Each city's seasonal near-ground ozone concentration is the highest in spring, the lowest in winter, and between the two in spring and autumn. In spring and summer, the seasonal ozone concentration of northern cities is still higher than that of southern towns, and the seasonal ozone concentration of eastern cities is higher than that of western cities. For autumn and winter, Taizhou still maintains the highest seasonal ozone concentration, and the ozone concentration in the southwestern cities of Zhejiang Province is
 relatively high. In contrast, the seasonal ozone concentration in the northern cities
 decreases significantly (Figure 6).

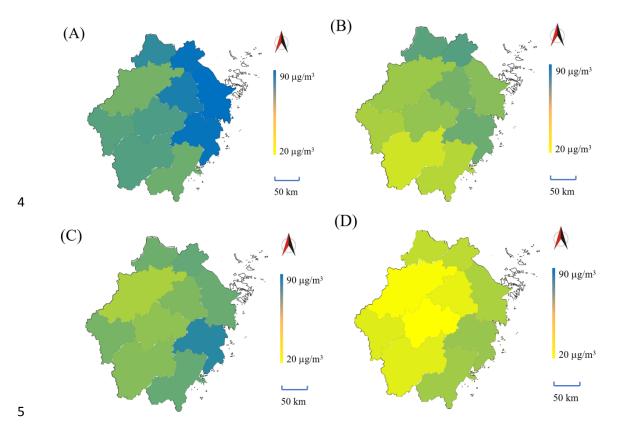


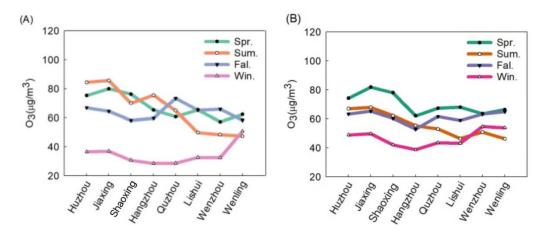
Figure 6 Spatial distribution of ozone concentration in spring (A), summer (B), autumn (C),
and winter (D) at each representative location in Jiang Province in 2020

8

9 From the seasonal changes in ozone concentration at each representative site before and after the outbreak (Fig. 7), it can be seen that before the outbreak, the 10 11 ozone concentration ranges in spring, summer, autumn, and winter are 57.16 μg/m3-82.26 μg/m3, 47.22 μg/m3-85.69 μg/m3, 58.10 μg/m3-78.64 μg/m3 12 13 and 28.30 μ g/m3-50.68 μ g/m3, with obvious "fault phenomenon," the largest difference in ozone concentration between seasons Over 50 µg/m3. After the 14 outbreak, the ozone concentration ranges in spring, summer, autumn and winter are 15 16 62.06 μg/m3-82.67 μg/m3, 46.17 μg/m3-67.94 μg/m3, 52.78 μg/m3-75.62 17 μ g, respectively /m3, 37.68 μ g/m3-55.95 μ g/m3. After the outbreak, the seasonal differences narrowed, and the maximum difference in ozone concentration between 18 seasons is less than 40 μ g/m3. The four-season differences in ozone concentration in 19 20 northern cities are also more significant than those in southern cities. Still, the

differences in ozone concentrations in four seasons in each city are significantly reduced. Meanwhile, the ozone concentration of each city in spring is higher than in summer, autumn and winter. Moreover, in the spring of 2020, Jiaxing and Hangzhou are the two cities with the highest and lowest ozone concentrations in the four seasons, respectively. In addition, we found that the ozone concentrations in the selected seven cities are all less than 100 μ g/m3, which met the required concentration limit.

7

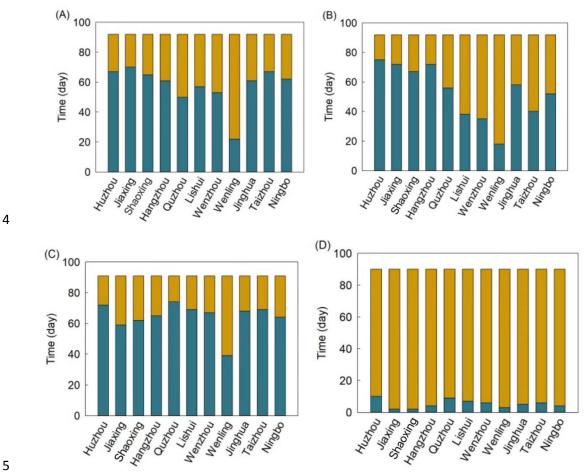


9 Figure 7 Changes in the mean ozone concentration in each season at each representative site
 10 in Zhejiang in 2019 (A) and 2020 (B)

11

8

12 We further calculated the number of days that the seasonal ozone concentration 13 exceeded the standard at each representative site before and after the outbreak. From the stacked column charts of the number of days with ozone concentration exceeding 14 the standard in spring (A), summer (B), autumn (C), and winter (D) before the 15 outbreak, it can be seen that in spring, except for Wenling, the monthly ozone days 16 exceeding the standard in ten cities Both are between 50-70 days, accounting for 17 about 2/3 of the spring days. In summer, the five towns of Huzhou, Jiaxing, Shaoxing, 18 Hangzhou, and Quzhou, continued to increase the number of days with excess ozone. 19 20 In contrast, the number of days with excess ozone in Wenling remained at 18 days, and the number of days with excess ozone in other cities decreased. In autumn, the 21 22 number of days with excess ozone in eleven cities increase, with Wenling reaching 39 days and the remaining ten cities with 55-75 days. In winter, the days with ozone 23 24 exceeding the standard dropped rapidly in 11 cities, reaching the lowest values in the



four seasons. The number of days exceeding the standard ozone did not exceed ten 1

2 days.

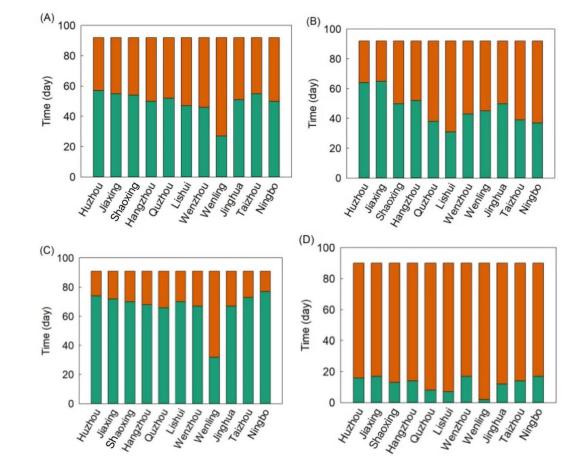
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Figure 8 Stacked column chart of the number of days with ozone concentration exceeding the 6 standard in spring (A), summer (B), autumn (C), and winter (D) at each representative site in 7 Zhejiang in 2019 (Note: blue represents the number of days exceeding the standard, and 8 9 vellow represents the number of days not exceeding the standard)

10

After the outbreak, the number of days when the ozone concentration exceeded 11 the standard in spring (A), summer (B), autumn (C), and winter (D) at each 12 representative station (Fig. 9) is as follows: In spring, except for Wenling, the ozone 13 concentration in the other ten cities The monthly excess days are between 45-60 days. 14 15 In summer, the number of days with excessive ozone in three cities, Huzhou, Jiaxing, and Wenling, continued to rise. In contrast, the days with excessive ozone in other 16 17 cities decreased. Lishui has the least ozone days, exceeding the standard among the eleven cities. In autumn, the number of days with excess ozone in eleven cities 18

increase, with 32 days in Wenling and more than 60 days in the remaining ten cities.
In winter, the number of days with ozone exceeding the standard dropped rapidly in
eleven cities, reaching the lowest values in the four seasons. The number of days
exceeding the standard ozone did not exceed 20 days. Among them, Wenling has the
least number of ozone exceeding days in winter, only two days.





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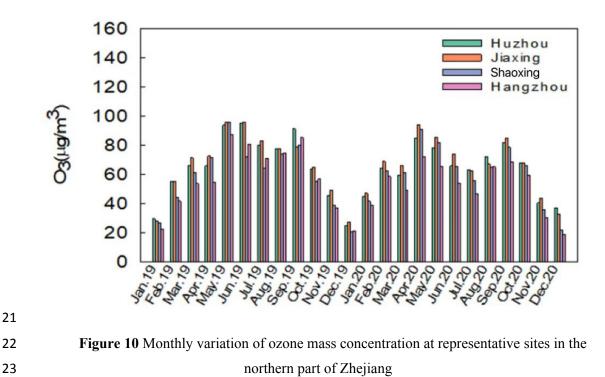
Figure 9 Stacked column chart of the number of days with ozone concentration exceeding the
standard in spring (A), summer (B), autumn (C), and winter (D) at each representative site in
Zhejiang in 2020 (Note: green represents the number of days exceeding the standard, and
orange represents the number of days not exceeding the standard)

12

13 **3.1.3** Monthly variation characteristics of ozone concentration

Figure 10 shows the monthly changes in ozone concentration values in 4 cities in the northern part of Zhejiang Province before and after the epidemic outbreak. Before the outbreak, the monthly variation characteristics of ozone concentration did not differ much among the four northern cities. The monthly variation trend of the overall ozone concentration shows a less obvious "M"-shaped curve, that is, a bimodal characteristic of first increase and then decrease. The ozone concentration

in the two cities of Huzhou and Jiaxing gradually increase from January to June 1 2 2019, reached the highest value in June, then dropped from June to August, rose again from August to September, and then increase from September to December. 3 Month and then gradually decrease. The ozone concentration in Shaoxing and 4 Hangzhou began to increase significantly from January to May 2019, gradually 5 decreased from May to July, reached the minimum value in July, rose again from 6 7 July to September, and then increase again in December 2019. month to the lowest value. Overall, the ozone concentrations in Huzhou and Jiaxing are higher than 8 9 those in Shaoxing and Hangzhou. At the same time, the monthly ozone concentrations in Huzhou, Jiaxing, Shaoxing, and Hangzhou did not exceed the 10 first-level concentration limit (100 μ g/m3) specified in the ambient air quality 11 standard (GB3095-2012). After the outbreak, the changing trend of ozone 12 concentration in the four northern cities roughly showed an "M"-shaped curve. The 13 four cities had high ozone concentration levels in April and September 2020. They 14 dropped significantly in July of the same year, reaching the lowest ozone 15 concentration levels for the year. At the same time, Hangzhou is the city with the 16 lowest ozone content among the four cities, and it is also the city with the fastest 17 18 drop in ozone from April 2020 to June 2020. Compared with 2019, we found that the ozone concentration in January and February 2020 in the four cities increase 19 20 faster than in the same period in 2019.

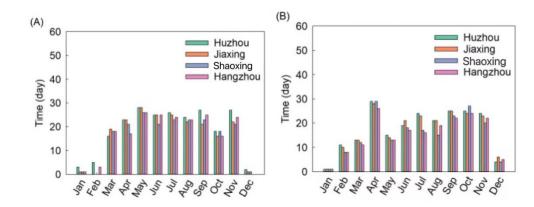




26

1 The monthly exceeding days of ozone concentration at representative sites in the 2 northern part of Zhejiang before and after the outbreak showed that the ozone concentration in four cities had fewer exceeding days in January, February, and 3 December 2019. The ozone concentration in Jiaxing and Shaoxing is even higher than 4 2. The monthly average is less than 100 μ g/m3. Hangzhou did not show the ozone 5 concentration exceeding the standard in December 2019. The concentrations in the 6 7 four cities are the lowest in January 2020, then rose in April, reaching the maximum number of days with excess ozone (Figure 11(B)). Compared with the number of days 8 9 with ozone exceeding the standard before the outbreak, the ozone exceeding the standard in February 2020 is the most abnormal. The number of days in which the 10 ozone exceeding the standard is exceeded in the four cities is 1.17, 1.24, 1.41, and 11 1.40 times that of February 2019, respectively. 12

13



14

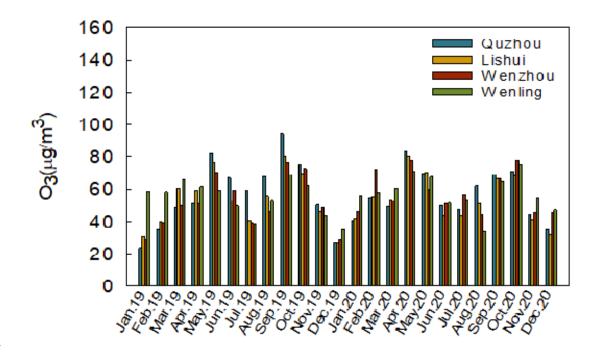
15 16

Figure 11 Monthly exceeding days of ozone concentration in 2019 (A) and 2020 (B) at representative sites in the northern part of Zhejiang

17

18 Figure 12 shows the monthly changes in ozone concentration values in four cities in southern Zhejiang Province (Quzhou, Lishui, Wenzhou, and Wenling) 19 20 before and after the outbreak. For the four southern cities, Quzhou, Lishui, and Wenzhou all showed an "M"-shaped curve for the monthly changes in ozone 21 22 concentration before the outbreak; that is, it gradually increase from January to May, and from May to It gradually decreased in July, reached a minimum value in July, 23 24 then rose, and finally steadily reduced to a minimum value from September to December. Among them, the change in ozone concentration in Quzhou is the most 25 obvious among the four southern cities, reaching peaks in May and September, 26 respectively. However, the ozone concentration in Wenling did not change 27

significantly from January to May, and then an inverted "V" curve appeared. For the
ozone concentrations in the four southern cities, January and February 2020 also
rose faster than the same period in 2019.



4

5 6

Figure 12 Monthly variation of ozone mass concentration at representative sites in the southern part of Zhejiang

7 Figure 13 shows the monthly number of days when the ozone concentration value exceeded the standard before and after the outbreak in the four cities in 8 9 southern Zhejiang Province (Quzhou, Lishui, Wenzhou, and Wenling) before and after the outbreak. For the four southern cities, the trend of monthly ozone 10 concentration exceeding days in the four cities in 2019 showed an "M" shape. In 11 January 2019, ozone concentrations in the four cities did not exceed 100 µg/m3. The 12 number of excess ozone days rose to a peak in May, followed by a decline in June, 13 July, and August. The three cities of Quzhou, Lishui, and Wenzhou had more than 14 15 20 days of ozone exceeding the standard from October to December and then dropped significantly in December. However, the days when the ozone 16 concentration in Wenling exceeded the standard dropped substantially in November, 17 only one day. 18

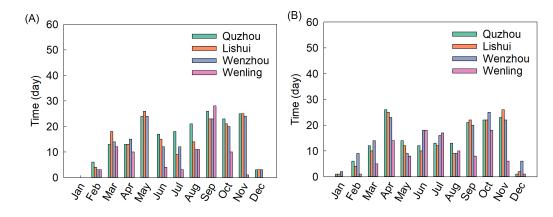


Figure 13 Monthly exceeding days of ozone concentration in 2019 (A) and 2020 (B) at representative sites in the southern part of Zhejiang

1 2

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4

Figure 14 shows the monthly changes in ozone concentration values before and 5 after the outbreak in the four cities in Zhejiang Province from west to east. The 6 monthly variation characteristics of ozone concentration in 2019 did not differ much 7 among the four cities. The monthly variation trend of the overall ozone 8 concentration is an "M"-shaped curve, a bimodal characteristic of first increase and 9 then decrease. The ozone concentration in the four cities gradually increase from 10 January to May 2019, reached the highest value in May, then gradually decreased 11 from May to July, rose again from July to September, reached a small peak, and then 12 reached a small peak in September. From January to December, it gradually 13 decreases again. At the same time, the monthly ozone concentrations of the four 14 cities did not exceed the first-level concentration limit (100 μ g/m3) specified in the 15 ambient air quality standard (GB3095-2012). In 2020, the changing trend of ozone 16 concentration in four cities from west to east also showed an "M"-shaped curve. The 17 18 four cities had high ozone concentration levels in April and September 2020. They dropped significantly in July of the same year, reaching the lowest ozone 19 concentration levels for the year. 20

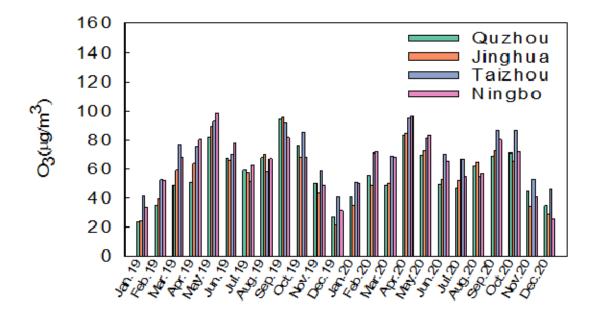
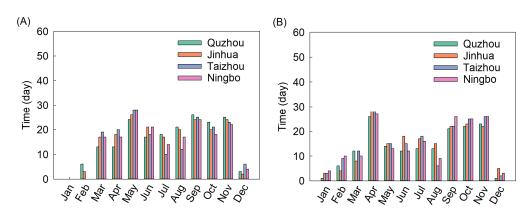


Figure 14 Monthly variation of ozone mass concentration at representative sites in Zhejiang from west to east

The monthly excess days of ozone concentration in 4 cities from west to east in 4 Zhejiang Province (Quzhou, Jinhua, Taizhou, and Ningbo) before and after the 5 6 outbreak of the epidemic show that the trend of the monthly excess days of ozone concentration in 4 cities in 2019 is "M"-shaped. In January 2019, the number of days 7 with no extra ozone concentration in the four cities. The four cities reached their 8 peaks in May and September, respectively, followed by the minimum number of 9 excess days in the four cities in December. From January to August 2020, the 10 number of days with excessive ozone concentration showed an inverted "V" shape. 11 The four cities reached their respective maximums in April, exceeding 25 days. The 12 monthly ozone concentration in the four cities exceeded 20 days from September to 13 November and decreased significantly in December (Figure 15). 14



15

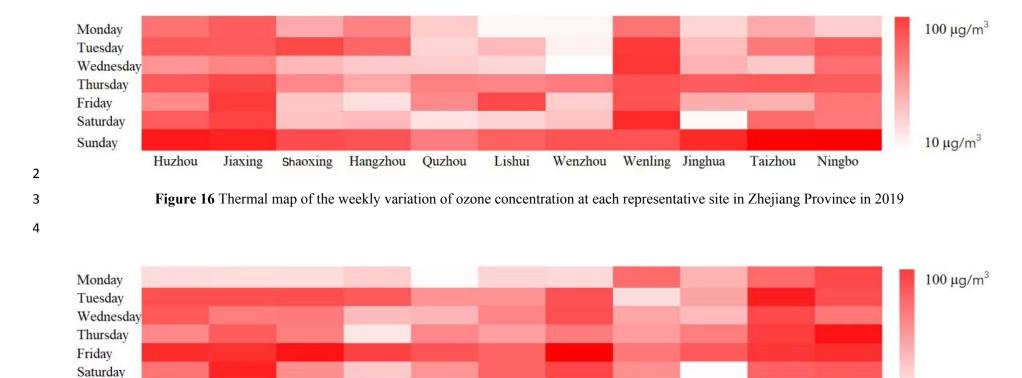
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Figure 15 The number of days with monthly ozone concentration exceeding the standard in
 2019 (A) and 2020 (B) at representative sites in Zhejiang from west to east

1 3.1.4 Weekly variation characteristics of ozone concentration

Ozone concentration data before and after the epidemic outbreak are analyzed 2 in this paper to determine the characteristics of weekly ozone changes in various 3 regions of Zhejiang Province. The results are shown in Figures 16 and Figure 17. 4 The weekly trend of ozone concentration varies in the different areas. Before the 5 outbreak, the weekly ozone concentration in Huzhou, Jiaxing, and Wenling is 6 always high. The rest of the cities showed other trends, with Quzhou showing a 7 trough in ozone concentration on Tuesday and Shaoxing, Hangzhou, Lishui, 8 9 Wenzhou, and Taizhou showing troughs on Wednesday. Quzhou, Lishui, and Jinhua 10 experienced troughs in ozone concentration on Saturday. Overall, eleven cities saw their peak ozone concentrations on Sunday. After the outbreak, Taizhou and Ningbo 11 12 always maintained high ozone concentrations. At the same time, Huzhou, Jiaxing, Shaoxing, Hangzhou, Quzhou, Lishui, Wenzhou, and Jiaxing showed a unimodal 13 14 trend but dropped to a low value on Sunday.



Lishui

Figure 17 The heat map of the weekly variation of ozone concentration at each representative site in Zhejiang Province in 2020

Quzhou

Wenzhou

Wenling Jinghua

Taizhou

Ningbo

1

Sunday

5

6

Huzhou

Jiaxing

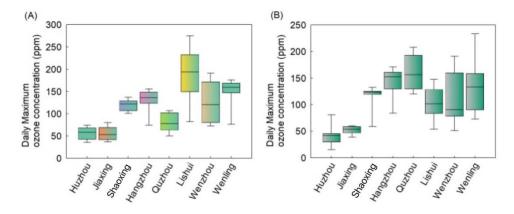
Shaoxing Hangzhou

 $20 \,\mu\text{g/m}^3$

1 3.1.4 Characteristics of intraday variation of ozone concentration

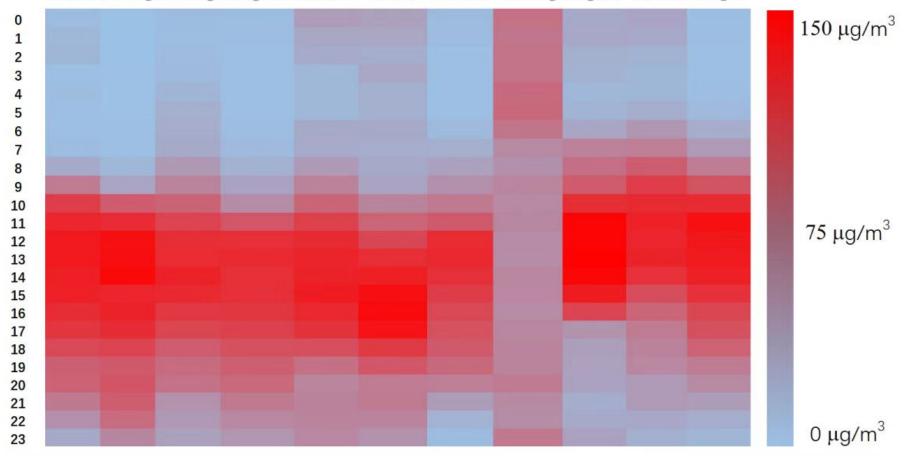
2 The intraday change (24-hour) heat map of ozone concentration at each representative site is analyzed before and after the outbreak. We found that before the outbreak, the 3 hourly variation of ozone concentration in Wenling is between 45-76 g/m3. Except 4 5 for Wenling, the other cities showed higher ozone concentration from 10:00 am to 6:00 pm (Figure 18). After the outbreak, the ozone concentration in Wenling 6 decreased with time, and the remaining cities maintained a high ozone concentration 7 from 10:00 am to 11:00 pm. In addition, the ozone concentration in each city between 8 0:00 and 9:00 increase compared with the same period before the outbreak (Figure 19). 9

Subsequently, we further described the distribution of maximum ozone 10 concentrations in 8 cities in Zhejiang Province before and after the outbreak in the 11 form of boxplots (Figure 20). Before the outbreak, the daily maximum ozone 12 13 concentration in Zhejiang Province gradually increase from north to south. Lishui and Wenzhou had the largest changes in the daily maximum ozone concentration before 14 the outbreak, and Lishui had higher values than other cities. The maximum ozone 15 concentration range in Huzhou and Jiaxing is less than 100 g/L, which does not 16 exceed the first-level concentration limit specified in the ambient air quality standard 17 18 (GB3095-2012). After the outbreak, the daily maximum ozone concentration range in Huzhou and Jiaxing in Zhejiang Province is still the first-level concentration. And the 19 daily ozone concentration in southern cities is significantly higher than that in 20 21 northern cities, which is consistent with the seasonal ozone variation.



22

Fig. 20. The daily maximum ozone concentration trend is the boxplot for 2019 (A) and 2020 (B).



Huzhou Jiaxing Shaoxing Hangzhou Quzhou Lishui Wenzhou Wenling Jinghua Taizhou Ningbo

Figure 18 Hourly changes of ozone concentration at each representative site in Zhejiang Province in 2019

1 2

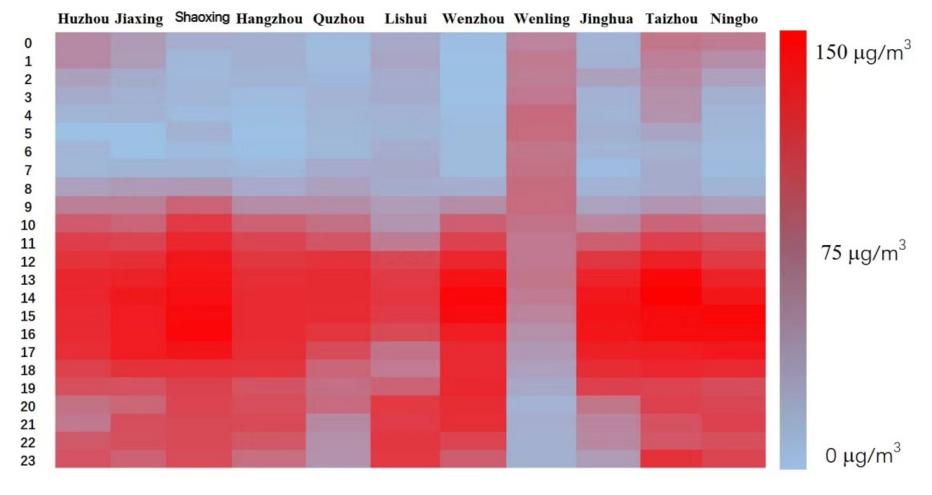


Figure 19 Hourly changes of ozone concentration at each representative site in Zhejiang Province in 2020

3.2 Analysis of factors affecting ozone concentration

From the perspective of meteorological conditions, ozone precursors NO₂, SO₂, PM_{2.5}, and PM₁₀ particulate pollutants, the influencing factors of near-ground ozone are analyzed. Considering the amount of data and the influence of excluded geographical space on ozone concentration, we choose Zhejiang Province. The central city of Jinhua is used as a distinct research area to analyze the influencing factors of ozone concentration, and the period is from January 2019 to December 2020.

8

3.2.1 Analysis of the impact of meteorological elements on near-surface ozone

9 Zhejiang Province will implement a fully closed management from January 27, 10 2020, and cities will gradually lift the closure control from April. To better explore 11 the influence of meteorological elements on ozone concentration before and after the 12 epidemic containment period, we chose Jinhua City, Zhejiang Province, during the 13 epidemic containment period in March 2020 and the period when the epidemic did not 14 occur in March 2019 for comparative analysis.

Figure 21 shows the distribution of the daily maximum ozone concentration in 15 Jinhua City before and after the outbreak and its scatter plot with the daily maximum 16 dry bulb temperature change. Before the outbreak, the maximum ozone concentration 17 in Jinhua City is proportional to the maximum dry bulb temperature, and the 18 correlation is high; the daily ozone concentration increase with the increase of 19 dry-bulb temperature. In March 2019, the maximum ozone concentration in Jinhua 20 21 exceeded the first-class standard (100 (g/m3)) is 18 days, and the number of days when the maximum temperature exceeded 15°C is 19 days. For the monthly mean value of 22 ozone, the mean value of ozone in March 2019 is 60.17 µg/m3, and the mean value of 23 temperature is 13.5 °C. After the outbreak, the daily maximum ozone concentration in 24 Jinhua is still proportional to the daily maximum temperature, and the temperature has 25 26 a greater impact on the ozone concentration. In Jinhua City, the daily maximum ozone concentration exceeds the first-class standard (100 μ g/L) for 12 days, and the daily 27 maximum temperature exceeds 15 °C for 21 days. For the monthly average ozone 28 29 value, the average ozone value in March 2020 is 74.88 µg/m3, and the average temperature value is 13.9° C. 30

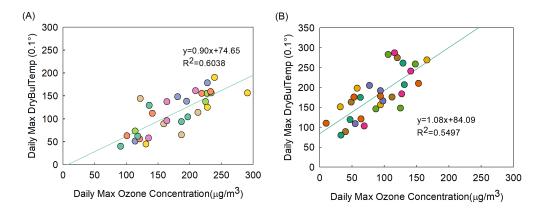


Fig. 21. Scatter plots of daily maximum ozone concentration and DryBulTemp for March 2019 (A) and March 2020 (B)

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Figure 22 shows the daily maximum concentration distribution of ozone 5 concentration and the daily maximum relative humidity before and after the outbreak 6 7 in Jinhua City, Zhejiang Province. Before the outbreak, the maximum ozone concentration in Jinhua City is inversely proportional to the maximum relative 8 9 humidity; the daily ozone concentration decreased with the increase in relative 10 humidity. In March 2019, Jinhua's daily maximum ozone concentration exceeded the first-class standard (100 µg/m3) for 18 days, and the daily maximum relative 11 12 humidity exceeded 90% for 21 days. For the monthly average ozone value, the average value of ozone in March 2019 is 60.17 µg/m3, and the average value of 13 relative humidity is 62.79%. After the outbreak, the daily maximum ozone 14 concentration in Jinhua City in March 2020 is still inversely proportional to the daily 15 maximum relative humidity, and the impact of relative humidity on ozone 16 concentration became greater. In Jinhua City, the daily maximum ozone concentration 17 exceeded the first-class standard (100 µg/L) for 12 days, and the daily maximum 18 relative humidity exceeded 80% for 19 days. 19

20

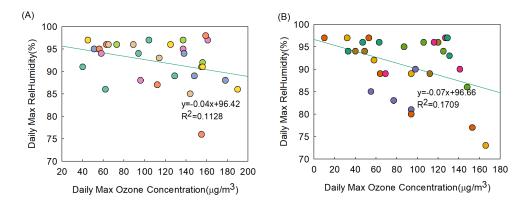


Fig. 22. Scatter plots of daily maximum ozone concentration and relative humidity for March 2019 (A) and March 2020 (B)

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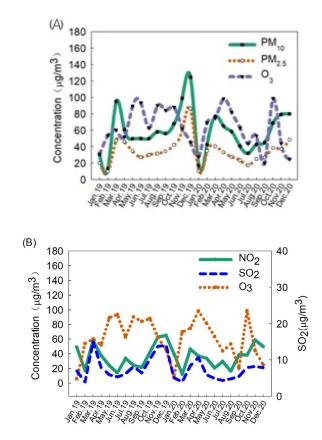
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3.2.1 Analysis of the impact of polluting gases on near-surface ozone

Ozone is mainly produced by reacting precursors such as NOx, CO, and VOCs
under suitable meteorological conditions. Due to the lack of observational data on
VOCs, only the relationship between particulate matter and precursors such as NO2,
SO2, and ozone concentration is analyzed. The monthly relationship between PM2.5,
PM10, NO2, SO2, and ozone concentration in Jinhua City before and after the
outbreak.

Before the outbreak, the monthly trends of PM2.5 and PM10 in Jinhua are 12 13 consistent, and the concentration of PM_{2.5} is always lower than that of PM₁₀. The volatility of the two in 2019 peaked in March and October, respectively. A trough 14 15 appeared in February 2019. The specific performance is as follows: PM2.5 and PM10 showed a downward trend in January-February 2019, rose sharply in February-March, 16 17 and then increase significantly in September-October, reaching the maximum value of the year in October. PM2.5 and PM10 ushered in the trough again in January 2020 and 18 reached the minimum value in 2020. The two showed a "V"-shaped trend after a small 19 20 rebound in March, and then fell again in June 2020, and then gradually increase 21 (Figure 23 (A)). NO₂ and SO₂ remained consistent before and after the outbreak, and the SO₂ concentration is lower than the NO₂ concentration. 22

The two peaked in March, August, and October 2019, respectively, and there are obvious troughs in February 2019 and February 2020. The fluctuations in 2019 peaked in March and October, respectively. A trough appeared in February 2019 (Fig. 23(B)). The ozone concentration showed a "wave"-like change before the outbreak. 1 The ozone concentration showed an upward trend from January to March 2019. After 2 a slight decline in April, it rose until June and again ushered in a small wave trough in 3 July and September. After a slight increase in the ozone concentration in October 2019, the value plummeted in January 2020; the ozone concentration continued to rise 4 until April 2020 before ushering in a three-month decline again. After peaking in 5 August 2020, ozone concentrations reached a trough in September, but their 6 7 concentrations are still slightly higher than in January. Ozone concentrations rose 8 significantly in September 2020, with a peak. Overall, the ozone trend in 2020 is "M" 9 (Figure 23).



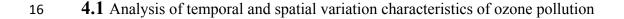
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Figure 23 Monthly changes of ozone and PM10, PM2.5, SO2 and NO2 concentrations in
 Jinhua City (A and B)

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15 Chapter 4 Discussion



17 4.1.1 Analysis of the interannual variation characteristics of ozone pollution

1 Before the outbreak, the inter-annual spatial variation of urban ozone 2 concentration in Zhejiang Province showed a decrease from north to south and an increase from west to east. After the outbreak, cities at the same latitude still showed 3 that the inter-annual ozone concentration gradually increase from west to east. Still, 4 the inter-annual ozone concentration before and after the outbreak is not much 5 different, indicating that the epidemic containment did not significantly affect the 6 inter-annual change in ozone concentration. Influences. Taizhou, Wenzhou, and 7 Ningbo are close to the East China Sea, and the ozone level is at a high level 8 9 throughout the year, probably because the local temperature difference is small 10 throughout the year, and the annual average temperature in the region is around 20 ° C. Many previous studies have shown that the distribution of pollutants is related 11 to areas (Li Polan et al., 2018; Yu Yijun et al., 2020; Yue Yanyu et al., 2021). The 12 13 interannual ozone concentration in northern cities is significantly higher than that in southern cities, mainly because the climates of the north and south of my country are 14 quite different. The dry air in the north is more conducive to ozone production, 15 while the relatively humid air in the south is conducive to deposing ozone precursors. 16 Stratospheric ozone transport to the troposphere is another important reason for 17 supporting high ozone concentrations in the northern regions. Tobias et al. (2020a) 18 19 combined satellite and ground observations. They found that NO2 in East Asia, 20 Europe, and North America decreased significantly after the controlled epidemic, 21 while ozone is compared with the climate average in previous years. The signal is mainly rising in East Asia and Europe and declining in North America, reflecting 22 regional differences in ozone response. 23

The year-to-year changes in the number of days with ozone pollution exceeding 24 the standard also reflect regional differences in ozone. Huzhou has the highest 25 number of days with ozone concentration exceeding the standard before and after 26 the epidemic outbreak. Huzhou is the northernmost city in Zhejiang Province, and 27 28 its relatively dry climate provides ozone production conditions. On the other hand, Wenling had the fewest ozone-exceeding days before and after the outbreak. 29 30 Wenling is located in the southeast of Zhejiang Province, near the East China Sea, 31 and the temperature is relatively stable throughout the year. Secondly, Wenling is a 32 prefecture-level city in Taizhou City, and the anthropogenic sources of ozone pollution, such as nitrogen oxides and VOCs emitted by motor vehicle exhaust,
 industrial iste gas, etc., are less than in other cities.

3

4.1.2 Analysis of seasonal variation characteristics of ozone pollution

The ozone distribution in different seasons is not uniform, showing obvious 4 time-varying characteristics. Before and after the outbreak, 11 cities in Zhejiang 5 6 Province showed that the ozone concentration in spring and summer is higher than in 7 autumn and winter. This phenomenon is not difficult to understand. The photochemical reaction process that leads to ozone formation is affected by 8 meteorological conditions such as light and temperature. The climatic conditions of 9 high temperature and high ultraviolet intensity in summer are more conducive to 10 forming and accumulating ozone, resulting in higher ozone concentration in summer. 11 At the same time, the height of the boundary layer in summer is high, the atmospheric 12 turbulence is strong, and the vertical transport process of ozone is obvious, resulting 13 in the peak ozone concentration. My country's winter temperature is generally low, so 14 the ozone pollution in winter is relatively slight. Seasonal changes in ozone are also 15 reflected in space. In spring and summer, ozone pollution is most severe in the 16 northern regions (Huzhou, Jiaxing, Shaoxing, and Hangzhou). The ozone 17 concentration in cities from north to south gradually decreased each season. The 18 possible reason is that the cities in the south are in the rainy season in June and July. 19 20 The frequent precipitation will affect the sunshine and temperature, leading to a slightly lower ozone concentration in June and July. The decrease in ozone 21 concentration in southern cities may also be caused by the climatic characteristics of 22 the prevailing southwest monsoon in summer. The low value of ozone concentration 23 in winter is related to intense radiation and temperature. In autumn, the center of 24 gravity of ozone pollution gradually shifts to the south. In winter, the ozone pollution 25 26 in Zhejiang Province is more than that of northern cities. In winter, the ozone 27 pollution situation in the province is relatively moderate. Only a few towns have high ozone concentration levels, mainly in coastal areas with relatively warm winter 28 29 climates.

In addition, the city's economic development and transportation level will also affect the seasonal variation of ozone concentration. When the city has the characteristics of low regional GDP and low road freight volume, the ozone pollution problem in summer and autumn is relatively moderate. However, some economically and industrially developed transportation hubs, such as Beijing, Shanghai, Shenyang, Zhengzhou, Chongqing, and other cities, often suffer from ozone pollution in summer. For example, in the summer of 2017, the daily maximum 8-hour average of ozone concentration in Shanghai once reached 285 µg/m3, which seriously exceeded the national secondary concentration limit. % or more, the second-level concentration limit exceeds the standard by nearly 50% (Yu Xinyang et al., 2022).

8 It is worth noting that before the outbreak, the maximum difference in ozone concentration between seasons could reach nearly 50 μ g/m3. This phenomenon has an 9 inseparable relationship with temperature. Low temperature has no obvious effect on 10 ozone concentration. As the temperature increases, the ozone concentration shows an 11 upward trend. After the temperature reaches 23 $^{\circ}$ C, the ozone increase trend 12 increases significantly. When the temperature reaches 35 ° C, the ozone 13 concentration increases. It can be increase to about 200µg/m3. When the temperature 14 reaches the highest value, the ozone concentration also reaches the extreme value. 15 High temperature and high radiation intensity in summer accelerate photochemical 16 reactions to generate ozone (Chen et al., 2020). Although coal consumption is large in 17 winter, due to low temperature and weak solar radiation, the photochemical reaction 18 that generates ozone is inhibited, and the ozone concentration is the lowest. After the 19 outbreak, the largest difference in ozone concentration between seasons narrowed, 20 mainly because the highest ozone concentration in the spring and the lowest in winter 21 22 after the outbreak increase, respectively. When conducting the seasonal analysis of ozone concentration, we divided January, February, and December 2020 into the 23 winter months after the outbreak. This result indicates that the seasonal ozone 24 25 concentration in each city increase after the outbreak.

26 4.1.3 Analysis of monthly variation characteristics of ozone pollution

According to the monthly changes of ozone concentration in eleven cities, the trend of monthly changes before and after the outbreak is "M"-shaped, reaching the maximum monthly changes in ozone concentration in June and September, respectively, and a trough in July. This trend is mainly because solar radiation is an important factor affecting ozone production. The solar radiation intensity varies significantly with the month (Pekey and Ozaslan, 2013). In summer, the sun shines

directly on the Tropic of Cancer, which makes Zhejiang Province in the northern 1 2 hemisphere face the strongest and longest ultraviolet radiation in a year. In addition, fewer clouds in the high sky, and the temperature near the ground rises, which is 3 prone to photochemical pollution, resulting in 6 The ozone concentration is higher 4 around the month. In winter, the temperature drops, the solar radiation is weak, and 5 there is more static and stable weather, so the ozone concentration is low. During the 6 high-temperature month of July, the decrease in ozone concentration may be related to 7 the large rainfall in July in Zhejiang Province. In the case of precipitation weather, the 8 9 sky is generally densely covered with dark clouds, and the thick cloud layer has a 10 strong absorption effect on the short-wave radiation of solar ultraviolet light from the upper boundary of the atmosphere, which will reduce the rate of photochemical 11 reactions that form ozone, thereby causing near-ground Ozone production is limited. 12 The study of Wang Mei et al. (2019) showed that the effect of rainfall on ozone is 13 related to the magnitude of rainfall; moderate rain and heavy rain have a scavenging 14 effect on ozone concentration, among which moderate rain has the best scavenging 15 effect, and trace drizzle and light rain have a significant impact on ozone 16 concentration. Enhancement effect; the first and second days of continuous 17 18 precipitation had a scavenging impact on ozone concentration, and the third day's effect changed from scavenging to promoting. In addition, the individual weather with 19 20 better sunlight in September (Duan Yuxiao et al., 2001) and the concentration changes of other pollutants may be the reasons for the small peak of ozone concentration at 21 22 this time (Wang Xijiao et al., 2015).

By comparing related cities in longitude and latitude, we found that the number 23 of days in which the ozone concentration exceeded the standard in March 2020 is 24 25 significantly higher than that in March 2019. Still, the cities in the southwest showed the number of days exceeding the standard monthly after the outbreak. Falling 26 situation. After June, the decrease in ozone concentration in southern cities may be 27 caused by the prevailing southwest monsoon in summer. At the same time, in the 28 southwestern region of my country, the change of ozone concentration is greatly 29 affected by ultraviolet radiation, and the transport of stratospheric ozone to the 30 troposphere is another important reason supporting the decline of ozone concentration 31 in this region. We're guessing this should be closely related to COVID-19; in 32 December 2019, China experienced the coronavirus outbreak. The rapid increase in 33

confirmed cases and 55 deaths have led the government to implement preventive 1 2 measures. From January 23 to 29, 2020, China activated a level 1 public health emergency response and imposed strict travel restrictions, involving 1.358 billion 3 people. As a result, traffic, construction, and light industrial activity have decreased 4 significantly. For example, on January 30, 2020, total traffic in China dropped by 5 87.7% compared to the same period last year. The coronavirus outbreak has had a 6 major impact on society and the economy. The study also found that particulate 7 matter can increase the optical thickness of the aerosol, weaken solar radiation, and 8 9 then affect ozone generation (Miranda et al. 2005). In the context of the 2020 10 coronavirus epidemic, March is in a period of epidemic-controlled lockdown, which has resulted in the shutdown of many factories. The emission of ozone-forming 11 precursors has dropped significantly due to human factors. 12

After the outbreak caused ozone concentrations to drop after March, ozone 13 14 concentrations returned to normal levels, thus the lowest emission levels in March. Emissions fell slightly in August, which may also be the result of a rebound in the 15 outbreak in August, leading to renewed lockdowns in some areas and a corresponding 16 reduction in ozone concentrations due to human factors. However, lockdowns are 17 only regional, so the drop in August is not as dramatic as in March. The monthly high 18 ozone concentration at each site is concentrated in May and September, and the air 19 20 pressure in summer is generally low. In the context of the 2020 coronavirus epidemic, March is in a period of epidemic-controlled lockdown, which has resulted in the 21 22 shutdown of many factories. The emission of ozone-forming precursors has dropped significantly due to human factors. After the outbreak caused ozone concentrations to 23 drop after March, ozone concentrations returned to normal levels, thus the lowest 24 25 emission levels in March. Emissions fell slightly in August, which may also be the result of a rebound in the outbreak in August, leading to renewed lockdowns in some 26 areas and a corresponding reduction in ozone concentrations due to human factors. 27 However, lockdowns are only regional, so the drop in August is not as dramatic as in 28 March. The monthly high ozone concentration at each site is concentrated in May and 29 September, and the air pressure in summer is generally low. The monthly ozone 30 variation is consistent with the seasonal variation, and both showed that the ozone 31 concentration increase during the prevention and control stage. Studies have shown 32 33 that ozone concentration and air pressure are negatively correlated. Relatively low air

pressure usually occurs in summer, a period of high ozone concentration. Liu Jiaojiao et al. (Liu Jiaojiao et al., 2014) pointed out that the increase in ozone concentration is closely related to the decrease in atmospheric pressure. When the atmospheric pressure drops more than 0.4 kPa, the ozone mass concentration is higher; Under the increase control, the air pressure is high, and there is more sunny, hot, and high-temperature weather, which is conducive to the generation of ozone, so the air pressure on the over-standard day is high.

8

4.1.4 Analysis of weekly variation characteristics of ozone pollution

Before the outbreak, cities had their peak ozone concentrations on Sundays. 9 Stephens et al. (2008) pointed out that ozone pollution has a "weekend effect"; ozone 10 concentration on rest days is higher than on working days. Our results show that 11 12 ozone concentrations in cities in Zhejiang Province showed a clear "weekend effect" before the outbreak, and the ozone concentrations are lower during workdays. After 13 the outbreak, the peak of ozone concentration appeared on Tuesday or Friday, and the 14 "weekend effect" is not very obvious. However, Das et al. (2021) compared the main 15 air pollutants during the epidemic closure period with the atmospheric pollutants on 16 weekdays and weekends in the same period of history. They found that the weekend 17 effect of ozone during the period of closure is more obvious than that in the same 18 period in history, which is consistent with ours. The results are inconsistent. We 19 speculate that the possible reason is related to the high frequency of human productive 20 activities during the working day. The epidemic has limited people's travel for work, 21 22 resulting in people choosing off-peak travel for safety reasons and the large discharge of industrial pollutants, so the ozone concentration is higher than that on rest days. In 23 addition, our study found that the spatial characteristics of the weekly ozone changes 24 at each representative site before the outbreak showed that the ozone concentration in 25 26 each city decreased sequentially from north to south and increase sequentially from 27 west to east. The spatial characteristics are consistent. After the outbreak, the weekly ozone concentration in various urban sites at the same latitude still showed a gradual 28 29 increase from west to east; however, in terms of longitude, Wenzhou, a southern city, 30 performed abnormally, and the weekly change in ozone concentration increase 31 instead.

4.1.5 Analysis of intraday variation characteristics of ozone pollution

The photochemical reaction process mainly controls ozone formation, and 2 changes in photochemical reaction conditions will inevitably affect the appearance of 3 ozone. In a day, as the sun rises in the east and sets in the west, meteorological 4 conditions such as sunshine duration and temperature will change during the day, and 5 the concentrations of ozone precursors such as NOx and VOCs also vary with 6 people's daily activities. Fluctuations occur, and these changes undoubtedly lead to 7 changes in ozone concentrations at different times of the day. The daily variation of 8 9 ozone generally presents a "single peak" trend, and the daily variation of ozone 10 concentration depends on atmospheric diffusion conditions and the intensity of photochemical reactions. Generally, the ozone concentration is the lowest between 8 11 12 and 9 o'clock, starting at 9 o'clock; with the gradual increase of the sun's altitude angle, the intensity of solar radiation from the upper atmosphere increases, and the 13 14 photochemical reaction becomes more intense. The ozone concentration increases at 18-20 times to the highest value. From 8 to 9 o'clock the next day, the photochemical 15 reaction weakened at night, which reduced the amount of ozone generated. The 16 impact of ground deposition on ozone and the emission of human activities in the 17 evening peak (especially the emission of traffic) led to an increase in nitric oxide and 18 19 ozone. It is consumed by the continuous reaction of nitric oxide (Wang Xuesong et al., 2009), so the ozone concentration at this time continues to decrease until it reaches the 20 lowest level in the early morning. Solar radiation can promote photochemical 21 reactions, and photochemical reactions can accelerate the production of ozone. 22

23 Therefore, the ozone concentration in a day generally shows the characteristics of high during the day and low at night. At night, because the sunshine hours are 0, 24 the photochemical reaction of ozone is very weak, and the concentration is at a low 25 26 value; after sunrise, with the strengthening of solar radiation, the decomposition of 27 oxygen molecules in the atmosphere is enhanced, and at the same time, the temperature rises, and the secondary photochemical reaction of ozone The rate 28 29 increases, the concentration begins to rise. The maximum concentration is reached at 15:00-16:00, which lags behind the strongest period of solar radiation, which is 30 31 mainly related to the reaction time of photochemical reaction to generate secondary pollutant ozone (An Junlin et al., 2009; Wang Hong et al., 2011; Wang Lei et al., 32 33 2018), the period of strongest radiation is also the period of rapid accumulation of

ozone concentration. Then, as the solar radiation weakened, the ozone concentration 1 2 began to decrease again. Its diurnal variation characteristics are consistent with those in Chengdu and other regions (Wu Kai et al., 2017). Before and after the outbreak, 3 except for Wenling, each representative city station's daily high ozone concentration 4 showed a decreasing order from north to south, consistent with the seasonal, monthly, 5 and weekly ozone concentration changes before the outbreak. At the same time, after 6 the outbreak, the ozone concentration in each city between 0:00 and 9:00 increase 7 compared with the same period before the outbreak. This result also shows that the 8 9 epidemic containment will lead to an increase in ozone concentration.

10

4.2 Analysis of factors affecting ozone concentration

11 4.2.1 Influence of meteorological elements on ozone concentration

12 To explore the correlation of meteorological elements to ozone pollution, we choose two commonly used meteorological indicators, temperature, and relative 13 14 humidity. There is a good correlation between temperature and ozone concentration. It is similar to the research results in the literature (Cheng Nianliang et al., 2016; Jiang 15 Lulu et al., 2016; Wu Kai et al., 2017), the higher the temperature and the stronger the 16 sunshine, the more conducive to the generation of ozone. Due to the photochemical 17 reaction of ozone precursors under the action of solar radiation, ozone is generated. 18 The stronger the solar radiation, the radiation effect of surface warming, the higher the 19 atmospheric temperature, and the faster the photochemical reaction of ozone 20 21 precursors promotes ozone generation and the near ground. The increase in ozone 22 concentration and the greenhouse effect of atmospheric ozone accumulation make its 23 pollution more serious, and the surface temperature rises higher, resulting in the climate warming and self-feedback warming effect of ozone (Mao Bing et al., 2016). 24 25 In addition, some studies have shown that evaporation has a close positive correlation with the near-surface atmospheric temperature, so the change of evaporation can 26 27 reflect the evolution of near-surface air temperature in the region to a certain extent, 28 so the effect of evaporation on ozone also reflects the impact of temperature on its In 29 addition, with the increase of temperature, along with the enhancement of surface evaporation and vegetation transpiration, the volatilization of volatile substances 30 31 (including VOCs) on the surface and vegetation is enhanced, which promotes the 32 formation of ozone. Generated (Yijun Yu et al., 2020). Compared with before the

outbreak, the ozone concentration increase significantly after the outbreak. Still, the concentrations of precursors such as NO₂ and SO₂ are lower than in the same period in previous years. Still, the ozone concentration did not decrease but increase, proving to a certain extent that the meteorological elements during the period significantly impacted ozone. Concentration increases contribute significantly.

The atmosphere's water vapor and ozone will react to generate free radicals such 6 as OH and HO2. These free radicals can trigger photochemical reactions in the 7 atmosphere and are an important "fuse" for photochemical reactions. Therefore, water 8 vapor concentration (relative humidity) also affects photochemical reactions and 9 atmospheric ozone concentration. Our research shows that the ozone concentration 10 before and after the outbreak negatively correlates with relative humidity; high 11 12 relative humidity is not conducive to ozone generation. Junlin et al. (2009) found a critical value of photochemical reaction intensity at about 60% relative humidity. 13 When the relative humidity is greater than 60%, the ozone concentration decreases 14 with the increase of relative humidity. The ozone generation results from the 15 combined action of local photochemical pollution and regional transport (Cheng 16 Nianliang et al., 2016). At the same time, studies have shown that the high humidity 17 environment is conducive to the wet growth of particulate matter, the increase of 18 PM2.5 concentration, and the inhibition of ozone generation (Wang Hong et al., 2011). 19 20 After the outbreak, the relative humidity of the air decreased, thereby increasing the ozone concentration. Humid air conditions not only make solar radiation attenuated 21 by the extinction mechanism under the action of water vapor (Liu Jingmiao et al., 22 2003) but also facilitate the occurrence of dry ozone deposition. Regional short-term 23 precipitation can remove some nitrogen oxides. 24

25 Meanwhile, on rainy days, the cloud layer is thicker, and the solar radiation is weak, which is not conducive to the volatilization of organic matter in the precursor, 26 and also weakens the photochemical reaction (Liang Biling et al., 2017). In the case of 27 high relative humidity, the free radicals -H and -OH contained in water vapor in the 28 29 air quickly decompose ozone into oxygen molecules, reducing the ozone concentration (Cheng Nianliang et al., 2016); water vapor also affects the sun through 30 31 extinction mechanism. The radiation causes the attenuation of ultraviolet radiation, reducing the ozone concentration (Wang Lei et al., 2018). 32

1 4.2.2 Analysis of the influence of polluting gases on ozone concentration

Before the outbreak, the monthly variation trend of ozone concentration is 2 negatively correlated with the concentrations of NO₂, SO₂, PM_{2.5}, and PM₁₀. The 3 ozone concentration first increase and then decreased, and the other four pollutants 4 decreased first and then increase. The trend of SO₂ and NO₂ in the city is the same, 5 and the trend of PM2.5 and PM10 concentration is the same. According to relevant 6 research, NO2 and SO2 are both precursors of ozone and reactants of PM2.5 (Li Hong 7 et al., 2019). PM2.5 mainly comprises secondary components such as sulfates, nitrates, 8 9 ammonium salts, and secondary organic aerosols, while PM10 also contains many 10 crustal elements. May-September is the high incidence period of ozone pollution in Zhejiang Province. This period coincides with the high-temperature season in 11 12 Zhejiang Province.

In addition, due to the instability of the atmosphere, the diffusion of pollutants is 13 strong, the concentration of PM2.5 is reduced, and the visibility of the atmosphere is 14 enhanced. The amount of radiation increases accordingly, and ozone precursors, 15 especially NO2 and SO2, are prone to photochemical reactions to generate ozone 16 under these conditions. The concentrations of NO2 and SO2 decrease, and the amount 17 of ozone increases. The ozone concentration is at the lowest in January, November, 18 and December. Due to the low average temperature in winter in Zhejiang Province, 19 20 and it is prone to the stable atmospheric formation, no wind or downwind, especially in the heating season, more pollutants are discharged. And it is not easy to diffuse; the 21 22 pollution of PM2.5 is strengthened, the radiation of sunlight is blocked, and pollutants such as NO₂ and SO₂ are easily converted into secondary particulate pollution. Under 23 these conditions, ozone is not easily generated, so the concentration is relatively low. 24 At the same time, Yu Yijun et al. (2020) found through research and analysis that the 25 26 most important factor for the increase of ozone concentration in Beijing, Hengshui, 27 and other regions is the decrease in PM2.5 concentration, which also means that we must effectively offset the reduction in PM2.5 concentration. The reverse effect, so that 28 29 the ozone concentration also decreases, requires further reduction of the emission of precursor substances. 30

After the outbreak, the ozone concentration increase rapidly from January to May 2020, and compared with before the outbreak, the ozone concentration increase,

but SO₂ and NO₂ showed a downward trend. This occurrence does not seem 1 2 surprising. SO₂ mainly comes from fuel combustion and industrial production emissions, while NO₂ mainly comes from industry, coal-burning sources, and vehicle 3 exhaust emissions. Zhejiang Province launched the first-level response to public 4 health emergencies on January 23, 2020. Under strict prevention and control measures, 5 the movement of people is restricted, and traffic emissions are reduced. At the same 6 time, some studies have shown that the migration index of Zhejiang Province dropped 7 significantly after the Spring Festival after the epidemic outbreak (FU et al., 2019). 8 9 Zhejiang Province, as a province with a large inter-provincial floating population, the 10 decline in the migration index after the holiday shows that the degree of resumption of work and production after the holiday has been affected. In addition, Tobias et al. 11 (2020a) found a significant decrease in NO2 and a significant increase of 33%-57% in 12 the ozone-8 h sliding maximum through the observation data of the Barcelona area. 13 Das t et al. (2021) used the WRFCHIMERE model to simulate the situation of 14 epidemic containment and no epidemic containment in Western Europe during the 15 same period. They found that containment measures would lead to a large reduction in 16 primary NO₂ emissions, a small reduction in fine particulate matter, and a small 17 18 decrease in ozone concentration. Most areas showed an increase, and the more densely populated areas, the greater the growth. After the closure of the city, the 19 20 concentrations of SO₂ and NO₂ all declined, but the concentrations of PM_{2.5}, PM₁₀, and ozone are on the rise as time went on until March. So emissions are not the only 21 22 factor determining pollution during the COVID-19 control period; there are other factors such as transmission, atmospheric chemistry, and deposition. 23

24

1

2 Chapter 5 Conclusions and Outlook

3 5.1 Research conclusions

This study takes eleven cities in Zhejiang Province as the research objects, 4 selects the ozone concentration data in 2019 before the outbreak of the new crown 5 epidemic and in 2020 after the outbreak, and used statistical methods to analyze the 6 temporal and spatial distribution characteristics of ozone concentration in Zhejiang 7 Province and the number of days when the ozone concentration exceeded the standard. 8 9 Including interannual, seasonal, monthly, weekly, daily, and hourly changes and selecting Jinhua, the central city of Zhejiang Province, to further explore the 10 relationship between ozone concentration and meteorological factors and other 11 pollutants. The main conclusions are as follows: 12

(1) Before the outbreak of the new crown epidemic, the spatial changes of ozone
concentration on different time scales in Zhejiang Province showed a decrease from
north to south, and cities at the same latitude showed a gradual increase from west to
east. After the outbreak of the new crown epidemic, different The spatial variation
trend of urban ozone concentration is generally similar to that before the epidemic,
but there are local anomalies in the changes in the same longitude. For example,
Wenling, a seaside city, is greatly affected by temperature changes.

20 (2) The interannual variation of ozone concentration and the number of days with 21 excess concentration are not significantly different before and after the outbreak of the 22 new crown epidemic. The seasonal changes in ozone concentration and the number of days with extra concentration show that the ozone concentration in spring and 23 summer is higher than in autumn and winter. Still, the ozone concentration between 24 seasons after the outbreak occurs. The difference in concentration decreased; the 25 weekly variation of ozone concentration showed an obvious "weekend effect" before 26 the outbreak, but the peak of ozone concentration appeared on Tuesday or Friday after 27 the outbreak; intraday changes in ozone concentration are all 18- The highest value of 28 ozone concentration is reached between 20:00, but after the outbreak, the ozone 29 30 concentration increase from 0:00 to 9:00 compared with the data before the outbreak.

(3) Before and after the outbreak of the new crown epidemic, ozone concentration and 1 2 temperature changes showed a positive correlation, which increase with the rise of temperature but is negatively correlated with relative humidity. After the new crown 3 epidemic outbreak, the correlation between ozone concentration and temperature 4 decreased compared to before the outbreak. In contrast, the correlation between ozone 5 concentration and relative humidity increase slightly. In addition, the monthly trend of 6 7 ozone concentration is negatively correlated with NO2, SO2, PM2.5, and PM10 concentrations before and after the outbreak of the new crown epidemic. After the 8 9 outbreak, the concentrations of PM2.5, PM10, and ozone have been on an upward trend 10 until March. Compared with the data before the outbreak, the ozone concentration has increase, but SO₂ and NO₂ have decreased significantly. 11

12 **5.2 Deficiencies and Prospects**

13 The shortcomings of this study and the areas that need to be improved are as 14 follows:

(1) Research on regional scale issues: This study mainly focuses on comparing and
analyzing urban ozone concentration in Zhejiang Province. According to relevant air
pollution research, it is found that there is a regional transmission of air pollutants, so
ozone pollution in Zhejiang Province is also related to surrounding areas. Study the
region's scope and the ozone pollution problem between regions.

(2) Research time scale problem: This study only selects the air pollutants in the two
years from 2019 to 2020, the temporal and spatial distribution of the concentration
data can reflect a certain trend of change. However, since the station pollutant data
before 2019 and after 2020 are not obtained, the explanatory power of the long-term
change characteristics of ozone pollution in the study area is not strong. Multi-year
data is added to analyze the change characteristics.

(3) Problems on selecting research indicators: VOCs are another important ozone
precursors. Due to the lack of data acquisition channels, this paper fails to analyze the
impact of VOCs and their interaction with other factors on ozone deeply. Therefore,
data acquisition channels should be expanded to obtain more detailed multi-year data
to ensure the scientificity and rigor of the research results.

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