**Manuscript number:** EGUSPHERE-2024-4178

**Title:** Diagnosing $O_3$ formation and $O_3$-NOX-VOC sensitivity in a heavily polluted megacity of central China: A multi-method systematic evaluation over the warm seasons from 2019 to 2021

This manuscript presents a comprehensive investigation of O3 pollution in Zhengzhou over the warm seasons from 2019 to 2021, utilizing observational data and model simulations (CMAQ, PMF, and OBM) to provide insights into the O3-NOx-VOC sensitivity and to propose effective control strategies. Significant improvements are needed in terms of novelty, logistics, and writing. Below are my main comments.

**Response:** We appreciated it very much for the reviewer's positive comments and valuable suggestions. Below are the point-to-point responses to all of the comments (The comments are marked in black color and the responses are marked in dark blue color). The major changes that have been made according to these responses were marked in yellow color in the highlighted copy of the revised manuscript. And our own minor changes were marked in red font. Note that the following line numbers are shown in the corrected version.

**Major comments**

1. More comprehensive analysis of O3 pollution characteristics in Zhengzhou. The title describes Zhengzhou as "a heavily polluted megacity of central China," yet the manuscript does not provide sufficient evidence to justify this statement. Additionally, comparisons with other urban areas should be incorporated into the results discussion.

**Response:** Thanks for your suggestions. Zhengzhou is a typical heavily polluted city in central China, facing severe air pollution issues in recent years. According to various studies, the air quality in Zhengzhou has consistently been poor, especially with high concentrations of pollutants such as $PM_{2.5}$ and $O_3$. The introduction of this paper will briefly outline the pollution status of Zhengzhou, further confirming its classification as a heavily polluted city through the reference of relevant literature. In section 2.1 of the methods, we have focused on explaining Zhengzhou as a major polluted megacity in central China.

In chapters concerning the concentration characteristics of VOCs and VOCs source analysis, we have compared and analyzed domestic and international research findings to enrich the manuscript. By incorporating studies from different countries and regions, a more comprehensive understanding of Zhengzhou's pollution characteristics and trends can be achieved, thus providing more accurate evidence for pollution control. The updates and tables are shown below.

Table S3 presents a comparison between the concentration characteristics of VOCs in this study and those reported in domestic and international literature. The concentration of VOCs in Zhengzhou (90.3 ± 52.8 μg/m³; 2019-2021) is higher than that of most international urban regions, aligning with other regions in China, such as Beijing (101.5 ± 65.2 μg/m³; 2016) (Liu et al., 2021). In contrast, cities like Istanbul (40-60 μg/m³), Athens (50.3 μg/m³; 2016-2017), and Vitória, Brazil (24.1 ± 29.6 μg/m³; 2022-2024) show significantly lower levels in the concentration of VOCs, reflecting regional disparities in emission control and industrial development (Thera et al., 2019; Panopoulou et al., 2021; Galvão et al., 2025). The VOCs in Zhengzhou are mainly composed of dichloromethane, acetone, ethane, isopentane, and n-hexane, indicating mixed sources from solvents and vehicular emissions, different from other cities where industrial and traffic emissions are more specialized. This finding suggests that there is an urgent need for targeted abatement efforts to reduce the concentration of VOCs and alleviate ozone pollution in a rapidly growing city like Zhengzhou.

**Table S3** Comparative analysis of VOCs pollution characteristics in Zhengzhou and other cities

| No. | Time Period | Location | Site Type | VOCs Concentration | Dominant VOCs Species / Composition | Reference |
|---|---|---|---|---|---|---|
| 1 | May-Sep 2019-2021 | Zhengzhou City, China | Urban site | 90.3 ± 52.8 μg/m³ | Dichloromethane, Acetone, Ethane, Isopentane, n-Hexane | This study |
| 2 | Summer 2019 | Coastal Tokyo Bay, Japan (Yokohama area) | Industrial site (Ushioda) | 86 μg/m³ (Range: 29–199 μg/m³) | Propane (6.9 μg/m³) > Ethyl acetate (6.0 μg/m³) > n-Butane (5.2 μg/m³) > Ethane (5.0 μg/m³) > Ethyl acetate (4.8 μg/m³) | Fukusaki et al., 2021 |
| | | Port-industrial mixed area (Yokohama Tower) | Port-industrial mixed site | 70 μg/m³ (Range: 20–255 μg/m³) | Toluene (5.1 μg/m³) > Propane (4.9 μg/m³) > Ethyl acetate (4.8 μg/m³) > Ethyl acetate (3.8 μg/m³) > Ethane (3.5 μg/m³) | |
| 3 | Jan-Nov 2010 | Greater Paris Metropolitan Area, France | Urban site | / | Alkanes: 39.1%, Oxygenated VOCs: 36.5%, Aromatics: 16.9%, Alkenes + Alkynes + Dienes: 7.5% | Baudic et al., 2016 |
| 4 | [Data missing] | Beşiktaş District, Istanbul, Turkey | Urban site | 40–60 μg/m³ (Average range) | Oxygenated VOCs: 43.9% (≈17 μg/m³), Alkanes: 26.3% (≈16 μg/m³), Aromatics: 20.7% (≈18 μg/m³), Alkenes: 4.8% (≈3 μg/m³) | Thera et al., 2019 |
| 5 | Mar 2016 – Feb 2017 | Athens, Greece | Urban site | 50.3 μg/m³ | Toluene: 6.7 μg/m³, Isopentane: 6.5 μg/m³, Ethane: 4.2 μg/m³, m/p-Xylene: 4.0 μg/m³, n-Butane: 3.8 μg/m³ | Panopoulou et al., 2021 |
| 6 | Jul 2022 – Apr 2023; Dec 2023 – Mar 2024 | Vitória, Brazil | Urban site | 24.1 ± 29.6 μg/m³ | n-Pentane (4.59 μg/m³), Benzene (3.09 μg/m³), 1,2,4-Trimethylbenzene (1.49 μg/m³), Ethylbenzene (2.41 μg/m³) | Galvão et al., 2025 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 7 | 2017 | Taiwan | Urban & industrial sites | 53.4–76.0 μg/m³ | Alkanes (46.5–55.3%) > Aromatics (28.0–42.2%) > Alkenes (7.4–11.4%) > Alkynes (1.2–5.5%) | Huang et al., 2020 |
| 8 | Jan-Jul 2016 | Beijing, Jing-Jin-Ji Region, China | Urban site | 101.5 ± 65.2 μg/m³ | Alkanes > OVOCs > Halogenated hydrocarbons > Aromatics > Alkenes > Alkynes | Liu et al., 2021 |
| 9 | Jul-Dec 2019 | Hefei, Yangtze River Delta Region, China | Urban site | 68.79 μg/m³ | Alkanes > OVOCs > Halogenated hydrocarbons > Aromatics > Alkenes > Alkynes | Wang et al., 2022 |

Table S4 presents a comparison of source apportionment between Zhengzhou and other cities. During the observation period, the main sources of VOCs in Zhengzhou comprise vehicle emissions (31%), solvent use (24%), and industrial processes (21%), collectively accounting for 76% of the total pollution, highlighting the dominant role of traffic and industrial pollution. In contrast, cities like Paris and Turkey have significantly lower proportions of vehicle emissions (15% and 15.8%, respectively) (Baudic et al., 2016; Thera et al., 2019). The proportion of solvent use in Zhengzhou (21%) is similar to that in the cities of the Yangtze River Delta but higher than that in Turkey and other regions (Zhang et al., 2025; Thera et al., 2019). The severity of biogenic pollution in Zhengzhou is lower, a phenomenon particularly evident in cities with richer vegetation cover, such as Athens (Kaltsonoudis et al., 2016). The source apportionment structure in Zhengzhou reflects its typical characteristics as an industrial city, with significant pressure from traffic emissions, as well as notable contributions from solvent use and industrial processes, while biogenic sources contribute relatively little.

**Table S4** Source analysis of VOCs in Zhengzhou and comparison with other cities.

| No. | City/Location | Study Period | Site Type | PMF Source Apportionment (%) | Reference |
|---|---|---|---|---|---|
| 1 | Central Plains (Zhengzhou, Henan), China | Jan 2019-Sep 2021 | Urban | Vehicle emissions: 32.4%; Solvent use: 24.8%; Industrial processes: 18.3%; LPG/NG combustion: 12.6%; Combustion sources: 8.9%; Biogenic: 3.0% | This study |
| 2 | Jing-Jin-Ji Region (Beijing), China | 1 Jun-31 Aug 2020 | Urban | Gasoline exhaust: 23.5%; Biogenic: 19.2%; Fuel evaporation: 15.7%; Diesel exhaust: 15.2%; Solvents: 14.3%; Industrial processes: 12.1% | Li et al., 2024 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | North China (Changzhi, Shanxi), China | 2-30 Jun 2021 | Urban | Gasoline vehicles: 27.0%; Coal combustion: 20.3%; Diesel vehicles: 15.9%; Industrial processes: 15.1%; Solvents: 14.0%; Biogenic: 7.6% | Niu et al., 2024 |
| 4 | Yangtze River Delta (Suzhou, Jiangsu), China | 2015-2022 | Urban | Fossil fuel combustion: 20.4%; Solvents: 17.7%; Gasoline evaporation: 16.7%; Diesel exhaust: 12.6%; Natural gas: 10.8%; Industrial: 9.7%; Vehicle exhaust: 7.7%; Biogenic: 4.5% | Zhang et al., 2025 |
| 5 | Yangtze River Delta (Tongxiang, Zhejiang), China | 1 May-25 Jul 2021 | Urban | Solvents & gasoline: 32.3%; Temperature-dependent sources: 28.1%; Vehicle exhaust: 19.9%; Manufacturing: 14.4%; Petrochemical: 7.8% | Qu et al., 2025 |
| 6 | Taiwan Region (Taipei), China | Mar 2020-Feb 2021 | Urban | Industrial solvents: 11.97-37.62%; Household emissions: 14.67-31.62%; Biogenic: 1.7-25.21%; Diesel vehicles: 5.74-19.03%; Petrochemicals: 5.43-18.67%; Gasoline vehicles: 4.51-12.34% | Chen et al., 2023 |
| 7 | Vitória, Brazil (ES Site) | Jul 2022-Apr 2023; Dec 2023-Mar 2024 | Urban site | Vehicle exhaust: 46%; Coke ovens: 26%; Solvents: 13%; Industrial processes: 11%; Fuel evaporation: 4% | Galvão et al., 2025 |
| 8 | Paris Metropolitan Area, France | 15 Jan-22 Nov 2010 | Urban | Natural gas + background: 23%; Solvents: 20%; Wood burning: 17%; Vehicle exhaust: 15%; Biogenic: 15%; Gasoline evaporation: 10% | Baudic et al., 2016 |
| 9 | Athens, Greece | 3-26 Jul 2012 (Summer) | Urban | Traffic: 37.1%; Biogenic VOCs: 26.2%; Secondary oxidized VOCs: 19.3%; Biogenic oxidized VOCs: 18.4% | Kaltsonoudis et al., 2016 |
| 10 | Beşiktaş District, Istanbul, Turkey | 14-30 Sep 2014 | Urban | Mixed area emissions: 36.3%; Natural gas evaporation: 25.9%; Road transport: 15.8%; Solvents (toluene): 14.2%; Biogenic terpenes: 7.8% | Thera et al., 2019 |

2. More details on the CMAQ model configuration. The current version lacks a detailed description of the CMAQ model configuration. Essential aspects such as horizontal and vertical resolution, meteorological condition, chemical mechanisms, emission inventories, and boundary conditions should be explicitly stated. Additionally, Fig.S2 is too blurred, and the information it expresses should be described in detail in manuscript.

**Response:** Thank you very much for your valuable feedback. I have added more details about the CMAQ model configuration in the manuscript and summarized them in Table S1. Additionally, Figure S2 has been updated. The revised manuscript and figures are presented below.

"The decoupled direct method (DDM) is simulated using the WRF/CMAQ model, with detailed configuration information provided in the papers published by our research group. Additionally, the WRF/CMAQ setup is summarized in Table S1. More specifically, the WRF/CMAQ model is configured with four nested domains: 36 km for East Asia, 12 km for central and eastern China, 4 km for Henan Province, and 1 km for Zhengzhou (Fig. S2). WRF provides meteorological inputs for CMAQ, using 6-h FNL global reanalysis data as initial and boundary conditions. The SAPRC-99 gas-phase photochemical mechanism and AERO6 aerosol module are utilized in the CMAQ model, with modified heterogeneous chemistry for SO2 to sulfate and NO2 to nitrate conversion (Hu et al., 2014). The clean continental IC/BC is used in the 36-km simulation, and the nested domain IC/BC is derived from the parent domains. The CMAQ output within the first five days is discarded to minimize IC influence. The anthropogenic emission data of China are obtained based on the 2016 MEIC inventory (at a resolution of 0.25° × 0.25°), while the emission data of other regions are collected from the REAS2 inventory. The emission data of Henan Province (4-km domain) are acquired based on the local data from Bai et al. (2020). The biogenic emission data of all domains are generated using MEGAN (version 2.10), with the windblown dust emission data generated online in CMAQ simulations."

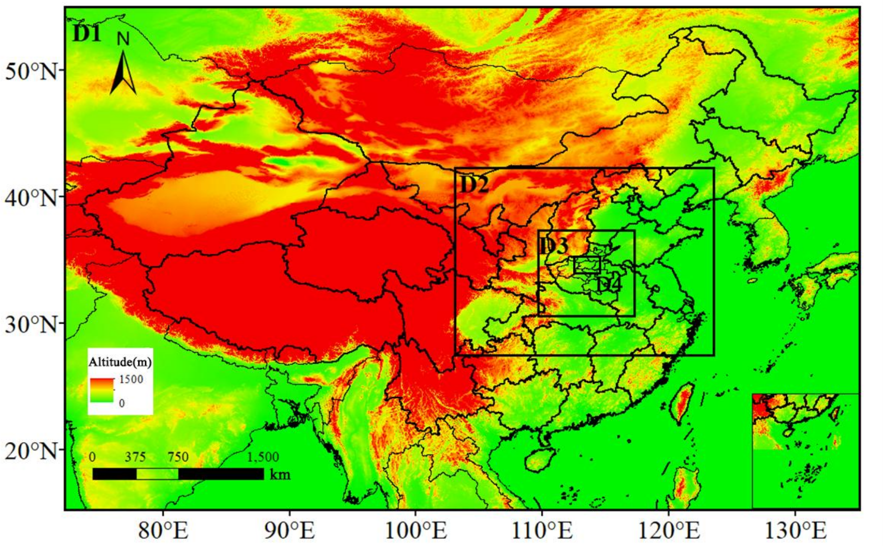


**Fig. S2** Four-level nested domains used in the WRF/CMAQ simulations. D1, D2, D3 and D4 have horizontal resolutions of 36, 12, 4 and 1 km, respectively.

**Table S1** Key parameter settings for the mode section.

| Main parameters | Content |
|---|---|
| WRF Vertical resolution (eta_levels) | 1.000, 0.996, 0.99, 0.98, 0.97, 0.96, 0.95, 0.94, 0.93, 0.92, 0.91, 0.895, 0.88, 0.865, 0.85, 0.825, 0.8, 0.775, 0.75, 0.72, 0.69, 0.66, 0.63, 0.6, 0.57, 0.54, 0.51, 0.475, 0.44, 0.405, 0.37, 0.33, 0.29, 0.25, 0.21, 0.175, 0.145, 0.115, 0.09, 0.065, 0.045, 0.025, 0.01, 0.000 |
| Microphysics scheme | New Thompson et al. (scheme 8) |

| | |
|---|---|
| Longwave radiation | Rapid Radiative Transfer Model |
| Shortwave radiation | Goddard shortwave scheme |
| Land-surface scheme | Unified Noah land-surface model |
| Surface layer scheme | MYJ surface scheme |
| Boundary layer parameterization | Yonsei University scheme (Non-local -K scheme 1) |

3. Different methods were included, including CMAQ, PMF and OBM. However, no clear connections and intercomparison were introduced for these methods. Were these methods really necessary?

**Response:** Thank you for your careful review and valuable comments. Regarding your suggestion about the connection between model selection and methodology, I have carefully considered it and made corresponding adjustments and additions. Below is my response:

This study is based on three years of real-time observational data from Zhengzhou and utilizes a combination of multiple models (CMAQ, PMF, and OBM) to identify the characteristics of ozone precursor pollutants and their influence on ozone formation. We selected these models based on their respective strengths and aligned them with the specific research objectives. Specifically, CMAQ and PMF are used for source apportionment of ozone and VOCs, respectively. Although PMF is widely used in source apportionment, it has been insufficiently applied in ozone source apportionment studies. Therefore, this paper strengthens the research on the source apportionment of ozone and its precursors, and the findings show that ozone and its precursors in Zhengzhou are mainly influenced by motor vehicle emissions, which is one of the innovative contributions of this study.

Furthermore, in the study of ozone sensitivity, we employed a variety of methods, including the ratio method, OBM's RIR and EKMA methods, and the CMAQ's DDM method. By coupling these multiple approaches, we aim to overcome the limitations of any single method. We recognize that each method has its advantages and limitations, and thus combining them allows for a more comprehensive understanding of the ozone sensitivity characteristics.

4. Describe the main improvement or innovation compared with your previous study.

Wang, X. D., Yin, S. S., Zhang, R. Q., Yuan, M. H., and Ying, Q.: Assessment of summertime O3 formation and the O3-NOx-VOC sensitivity in Zhengzhou, China using an observation-based model, Sci. Total Environ., 813, 152449, 2022.

**Response:** This study introduces several improvements and innovations compared to the previous research conducted by members of our research group:

The previous study relied on data collected over a one-month period, capturing three instances of ozone pollution characteristics. However, the short duration of this dataset introduced a higher degree of randomness and larger potential errors. In contrast, this study utilizes three years of observation data and, following the GB3095-2012 standard, systematically classifies ozone pollution levels. We comprehensively analyzed the characteristics and formation mechanisms of ozone and its precursors under different pollution levels, ensuring more reliable and robust results.

This paper goes beyond the traditional approach of source apportionment for volatile organic compounds (VOCs) by conducting a detailed source tracing for both ozone and its precursors. Unlike previous studies that focused solely on VOCs, our research offers a more holistic understanding of the sources of ozone in Zhengzhou, providing critical data for targeted emission reduction strategies.

While the previous study used the OBM model to assess ozone sensitivity, this research takes a more comprehensive approach by incorporating the ratio method, OBM model, and CMAQ-DDM methods. This multi-method approach enables a more thorough and integrated evaluation of ozone sensitivity, providing a broader perspective on the findings.

5. In referencing previous studies, should write as Huang et al. (2019) instead of Huang (2019) (line 73). Do this for the other references.

**Response:** Thank you for your detailed review and valuable feedback. Regarding the reference format issue you raised, we have made the necessary revisions based on your suggestion. Specifically, we have changed "Huang (2019)" to "Huang et al. (2019)" throughout the manuscript, including in line 73, and have made similar adjustments to the other references.

**Detailed comments:**

1. Line 40-41: The phrase "precursor emissions" is inaccurate, please revise for clarity.

**Response:** Thank you for your valuable comments. Regarding your feedback on the phrase "precursor emissions," we agree that this term may not be clear in the context. To improve clarity, we have revised the sentence accordingly. Specifically, we have removed "precursor emissions" and clarified the message by directly referring to "VOC emissions." Revised sentence:

"The results demonstrated that reducing vehicle emissions should be prioritized to mitigate ozone pollution in Zhengzhou, as transportation emissions accounted for 64% and 31% of ozone and VOC emissions, respectively."

2. Line 42: Should be "observation-based model (OBM)".

**Response:** We have revised the phrase to "observation-based model (OBM)" as recommended.

3. Line 59: "Continue to increase" should be revised to "continue increasing."

**Response:** Accepted.

4. Line 61: Clarify the distinction between "VOC" and "VOCs" and explain why this differentiation is necessary.

**Response:** Sorry for the misunderstanding. "VOCs" is typically used to refer to a group of volatile organic compounds, as it represents a collection of different chemical substances. We have made the necessary revisions throughout the manuscript to ensure consistency, and all instances have been updated to "VOCs."

5. Lines 71–72: The sentence structure is overly complex.Lines 83: can provide abbreviation for "Yangtze River Delta" here and then use it later.

**Response:** Thank you for your suggestion. The introduction has been rewritten, and I have hired a professional editing company to polish it.

6. Lines 264-265: I do not understand the logic here. It's not surprising that the model has a better performing in simulating NO2 since it was directly emitted. The logic does not make sense at all here.

**Response:** Apologies for any confusion caused. Based on your suggestion, this sentence has been corrected to: On the contrary, the simulation of nitrogen dioxide is generally more accurate, as $NO_2$ is directly emitted, leading to better model performance in simulating $NO_2$."

7. Line 325: "specie" should be corrected to "species".

**Response:** Thank you for your suggestion; the correction has been implemented as advised.

8. Line 338: Please define MDA8 correctly.

**Response:** Thank you for your suggestion. Following the published literature, this section has been updated to "the maximum daily average 8-hour (MDA8) O3 concentrations."

9. Line 384: Clearly define "non-polluted," "lightly polluted," and "moderately polluted" periods.

**Response:**Thank you very much for your suggestion. The definitions for different pollution scenarios have been established, and this section has been updated to:

"According to the GB 3095-2012 standard, MDA8 O3 concentrations exceeding 160 and 215 μg/m³ are defined as light pollution and moderate pollution, respectively. The average VOCs concentrations for non-pollution, light pollution, and moderate pollution periods were 84.7±51.0, 96.6±53.4, and 105.3±59.4 μg/m³, respectively."

10. Line 402: Mark the P1–P4 phases in Fig. S5 to improve readability.

**Response:**Thank you for your suggestions. The Fig. S5 has been redrawn as shown below.

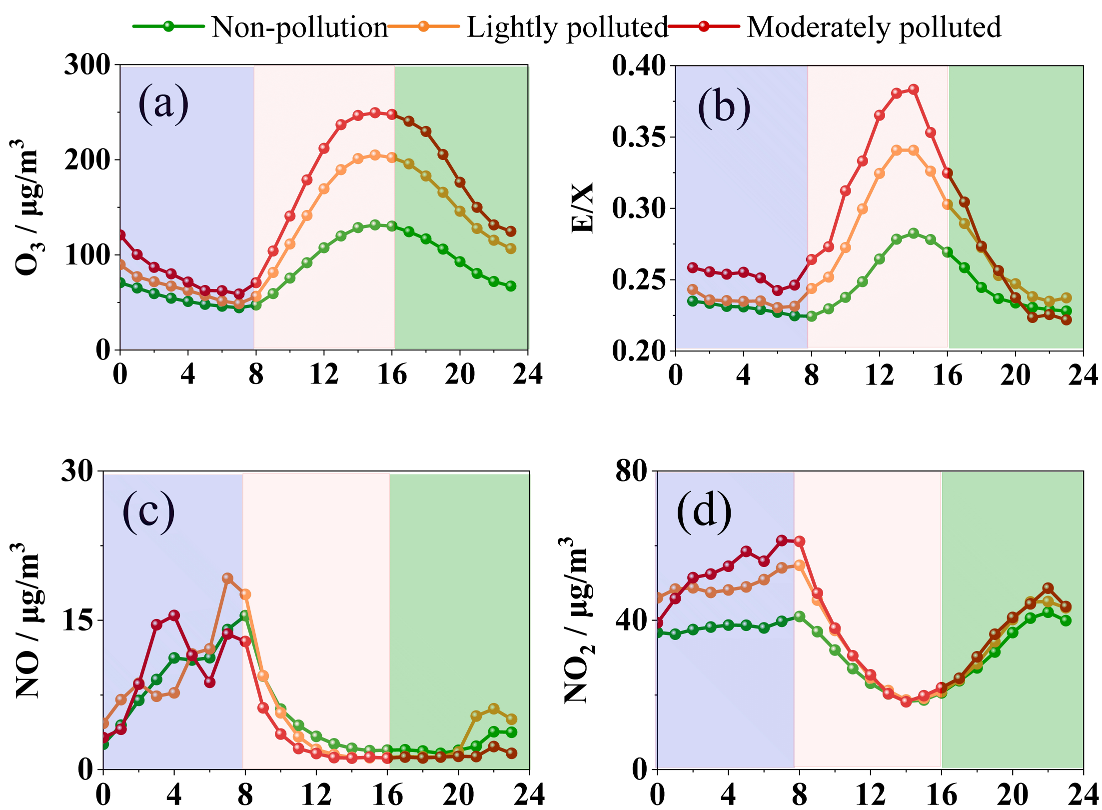


**Fig. S5** Diurnal variation distribution of pollutants during different pollution periods. The light blue, light red, and light green shadows represent stages P1, P2, and P3, respectively.

11. Line 474: How did the authors conclude that "cross-regional mitigation measures" are required? Please provide a clear rationale.

**Response:** Thank you for your valuable comment. We concluded that "cross-regional mitigation measures" are required based on the observation of relatively high $O_3$ concentrations in areas surrounding Zhengzhou, as shown in Fig. 3b. These high concentrations in neighboring regions suggest that ozone pollution is not confined to a single locality but is instead a regional issue, likely influenced by factors such as wind patterns, transportation, industrial emissions, and urbanization, which affect multiple areas within Henan Province.

$O_3$ pollution in Zhengzhou and surrounding areas is interconnected, meaning that measures taken in one region alone may not be sufficient to effectively reduce the overall $O_3$ levels. Therefore, to achieve meaningful reductions in ozone concentrations, coordinated efforts across regions are necessary, addressing both local emissions and regional transport of pollutants. This would require collaboration between neighboring regions to implement effective air quality management strategies, such as controlling emissions from transportation and industries that affect multiple areas simultaneously.

12. Line 496: Clarify whether the "power sector" is equivalent to "electricity".

**Response:** Thank you for your valuable comment. We confirm that "power sector" is equivalent to "electricity" in this context. To avoid any potential ambiguity, we have standardized the term to "electricity" and made the corresponding revisions in the text.

13. Lines 713–714: Please label the relevant regions in Fig. 10 to enhance readability.

**Response:** Thank you very much for your suggestions. I have updated Fig. 10 based on your feedback.

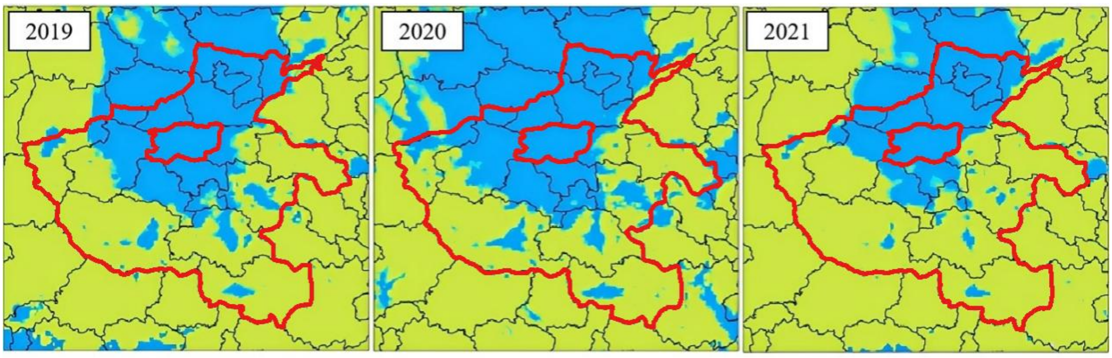


**Fig. 10** Spatial comparison of $O_3$-NOx-VOCs sensitive regime from 2019 to 2021 in

Zhengzhou.

14. Conduct a thorough grammatical revision and refine sentence structures throughout the manuscript.

**Response:**Thank you for your feedback. The manuscript has been professionally edited by a specialized agency, and here is the proof of editing.

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CERTIFICATE OF EDITING

This is to certify that the paper titled **Diagnosing $O_3$ formation and $O_3$-NOX-VOC sensitivity in a heavily polluted megacity of central China: A multi-method systematic evaluation over the warm seasons from 2019 to 2021** commissioned to us by **Shijie Yu, Hongyu Liu, Hui Wang, Fangcheng Su, Beibei Wang, Minghao Yuan, Kunao Song, Zixian Wang, Daoqing Xu, Ruiqin Zhang** has been edited for English language, grammar, punctuation, and spelling by Enago, the editing brand of Crimson Interactive Consulting Co., Ltd..

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