Response to Reviewers comments:

Reviewer #2: The article from Dai et al., "Significant influence of oxygenated volatile organic compounds on atmospheric chemistry analysis: A case study in a typical industrial city in China", investigates the contribution of volatile organic compounds, including oxygenated VOC, to ozone formation potential using ambient data from five observation sites around Zibo, an industrial city in the North China Plain, and an observation-based model (OBM).

The topic covered by the study can help assessing correct strategies to mitigate urban air pollution, therefore I find the study of interest to the atmospheric sciences community and in scope with the journal. However, in its current form, the methodology used by the authors is not described with enough clarity and for this reason it is hard to assess the robustness of the study and the presented results. For this reason, I would suggest publication after some major revisions are considered.

Response: We thank the reviewer for the positive and constructive comments. Below is our point-by-point response to each comment, marked in blue. Changes made to the main text are marked in blue in the revised manuscript file.

General comments:

1. The main comment I have concerns the methodology used by the authors. The experimental methods used by the authors are not sufficiently presented. The authors use measurements from five observation sites collected during five days using online gas-chromatography (GC) and offline gas-chromatography. While offline GC can require extensive timing for both sampling and analysis and can be limited by samples availability, I wonder if there is any particular reason why the online field campaigns lasted for short time periods and if the limited sampling time is representative to the field

sites and conditions? Can the authors explain this choice, maybe related to previous studies conducted in the same area? The authors should also provide some information about the sampling and analytical methods used (type of analysis, GC column characteristics, desorption and separation methods, sampling inlets characteristics, use of any ozone scrubber during the sampling, samples storage) and uncertainty associated to the results. As the whole discussion is based on comparing the results among different sites there should be mention that the analytical techniques and sampling are comparable, was any test conducted to prove that?

Response: Thank you for the detailed feedback and for highlighting the importance of clarifying the methodology. We understand the concerns regarding the representativeness and comparability of our sampling and analytical methods.

For question 1, The short-term sampling campaign conducted in August 2021 was strategically designed to capture VOC and OVOC concentrations across multiple sites during a representative ozone pollution episode. To ensure comprehensive temporal coverage, we collected 1-3 hourly samples at each station, resulting in 8-10 samples per station every day, which effectively captured the diurnal variability of atmospheric composition. Throughout the observation period, we obtained a total of 39 valid samples from both the suburban (TZ) and industrial (XD) stations, while the upwind (CQ), downwind (CD), and urban (ZL) stations yielded 49 valid samples each. This sampling strategy provided robust datasets that accurately represent the spatial and temporal variations of VOC and OVOC concentrations during the study period.

For question 2, we have revised the descriptions of VOC and OVOC measurements methods. Please refer to Lines 129-151:

“A mixture of 56 PAMS target species (Spectra Gases Inc., USA, Table S2) was used for the calibration of the GC-FID system. Each VOC analyzer provided measurements with a 1-hour temporal resolution. More detailed descriptions of these instruments can be found in previous studies (Li et al., 2023; Wang et al., 2014; Yang et al., 2022; Zheng et al., 2023). Overall, the detection limits for most VOC species are below 0.1 ppb. Additionally, 18 oxygenated VOCs species were collected by 2,4-dinitrophenylhydrazine (DNPH) sorbent tubes in conjunction with an automated sampler for a period of 1 or 3 hour per sample. A 47 mm quartz filter membrane is attached to the front of the sampling tube to filter particulate matter. An ozone scrubber (silica gel column tubing coated with potassium iodide) was placed at the front of the air inlet to avoid ozone interference. OVOCs were derivatized in cartridges to hydrazones during sampling. The cartridges were eluted with 3 ml of acetonitrile and stored at 0-4 °C immediately. Then the eluants were analyzed using an Agilent HPLC, equipped with ultraviolet absorption detector (UVD), quadruple pump, and Agilent TM C18 reversed column (250 mm×4.6 mm, 5.0 µm). A gradient elution was used, and the mobile phase was mixing of acetonitrile, tetrahydrofuran and water. The analysis was carried out using a ternary gradient elution program at a flow rate of 1.2 mL/min, with detection wavelength of 360 nm, and sample volume of 10 µL at a column temperature of 45 °C. More details about OVOC samplings and analysis can be found in Peng et al. (2023). The lower limit of detection for OVOCs were <0.1 ppb (Peng et al., 2023). A total of 271 valid OVOCs samples were collected during the campaign. At the industrial (XD) and suburban (TZ) stations, 8 samples were collected per day at 3-hour intervals. At the urban (ZL), upwind (CQ) and downwind (CD) stations, 10 samples were collected per day, with 7 samples collected at 1-hour intervals during 7:00-21:00 LT, and 3 samples collected at 3-hour intervals during the night (1:00-6:00 and 22:00-1:00^{+1} LT), and totaling 59 valid samples per station.”

For question 3, while we did not conduct specific tests to evaluate inter-site comparability. However, the VOC analyzing instruments used at the five sites were operated and maintained by the same organization, following standardized protocols. These instruments were regularly calibrated using identical standard gas mixtures to maintain measurement accuracy and consistency. For offline OVOC sampling, we employed uniform methodologies across all sites, including the use of identical sampling instruments, standardized collection techniques, consistent sample preservation procedures, and the same analytical protocols. This comprehensive approach to quality control and methodological standardization ensures that the observational data from the five sites are directly comparable and maintain consistent data quality throughout the study period.

2. The calculation-modelling methods miss some information as well. It is not easy to follow section 2.2 as many acronyms are present and several assumptions considered. Could the authors adjust this section in a way that it is clear which assumptions are considered and why? Could the authors provide the different equations used in their calculations and model with more detail? There is no mention on how the ozone formation potential is calculated and which data are used for that.

Response: Thank you for your detailed feedback regarding the calculation and modeling methods in Section 2.2 in the origin manuscript. We apologize for any confusion or questions that may have arisen due to the unclean expression. We recognize the importance of providing clear and comprehensive explanations for readers to fully understand our methodology.

(1) Clarification of assumptions and calculation methods of OVOC budget:

In our analysis of the OVOC budget, we assume that variations in the mixing ratios of OVOCs within a given air mass are driven by four factors: chemical production and loss, emissions, transport, and deposition. This assumption underpins our calculations and is discussed in added Section 2.3, Lines 201-218, where the relevant descriptions and methodologies are introduced in detail:

"At a given site, variations in OVOCs mixing ratios are mainly influenced by in-situ photochemical production and chemical loss, emissions, regional transport, and deposition (Tan et al., 2018a; Xue et al., 2014a; Zhang et al., 2021). The change rate of observed OVOCs (R_{Meas}) is calculated by Equation (1). The in-situ photochemical production of OVOC ($R_{ChemProd}$) is mainly caused by the oxidation of VOCs, while their in-situ chemical loss ($R_{ChemLoss}$) includes photolysis and reactions with oxidants (OH, NO_3, and O_3) (https://mcm.york.ac.uk/MCM/, last access: 13 Jan 2025) (Atkinson, 2000; Atkinson and Arey, 2003; Jenkin et al., 2015; Saunders et al., 2003). The in-situ net OVOCs chemical production ($R_{NetProd}$) (Equation (2)) and their removal by deposition (R_{Dep}) are calculated hourly according to the OBM simulation. The OBM primarily accounts for atmospheric photochemical reactions, and deposition within the boundary layer. However, previous studies have reported that the OBM lacks an explicit representation of transport processes and emissions (Wolfe et al., 2016; Zhang et al., 2021), making it challenging to disentangle their respective contributions. Therefore, emissions and transport are combined to a single term ($R_{Emis\&Trans}$) to represent their contributions collectively. If the $R_{Emis\&Trans}$ is positive, it is considered a net import of emissions/transport, whereas a negative suggests a net export. The emissions and regional transport of OVOCs ($R_{Emis\&Trans}$) are computed as Equation (3).

$$R_{Meas} = \sum_{i} \frac{d([OVOC]_i)}{dt} \tag{1}$$

$$R_{NetProd} = \sum_{i} (R_{ChemProd,i} - R_{ChemLoss,i}) \tag{2}$$

$$R_{Emis\&Trans} = (R_{Meas} - R_{NetProd} - \sum_{i} R_{Dep,i}) \tag{3}$$

where $[OVOC]_i$ is the mixing ratios of OVOC species i constrained in OBM, 15 in total (Table S2). dt is the time-step of modeling, $d[OVOC]_i$ refer to the change in mixing ratio of OVOC species i."

(2) Description of the methodology for calculating ozone formation potential (OFP):

To calculate the potential of VOCs contributed to O_3 formation, we used the Maximum Incremental Reactivity (MIR) approach. The relevant methodology description has been added. Please refer to Section 2.4, Lines 233-240:

"**2.4 Evaluation of ozone formation potential and atmospheric oxidation capacity**

Different VOC species vary in their capability to form ozone, and their potential to produce O_3 can be evaluated by the maximum incremental reactivity (MIR) (Carter, 2010). The ozone formation potential (OFP) calculated for each VOC species represents its maximum contribution to ozone production (Bufalini and Dodge, 1983). The OFP of VOCs is calculated as follows:

$$OFP_i = [VOC]_i \times MIR_i \tag{6}$$

where OFP_i is the OFP of VOC species *i* ($\mu g\ m^{-3}$), $[VOC]_i$ is the atmospheric concentration of VOC species *i* ($\mu g\ m^{-3}$), MIR_i is the maximum incremental reactivity coefficient of the VOC species *i* (g O_3/g VOCs) (Table S2) from Carter, 2010a."

The MIR data of VOC species has been added, please refer to Table S2 in the supplement information:

Table S1 VOCs species and their names in Master Chemical Mechanism (MCMv3.3.1), minimum detection limits (MDL), and maximum incremental reactivity coefficient (MIR).

"—" means that the species is not listed in the mechanism.

Species	MCM name	MDL (ppb)	MIR	Species	MCM name	MDL (ppb)	MIR
Alkanes				**BVOCs**			
Ethane	C2H6	0.079	0.28	Isoprene	C5H8	0.02	10.61
Propane	C3H8	0.046	0.49	**Alkynes**			
Isobutane	IC4H10	0.022	1.23	Acetylene	C2H2	0.032	0.95
n-Butane	NC4H10	0.027	1.15	**Aromatics**			
Cyclopentane	—	0.016	1.15	Benzene	BENZENE	0.012	0.72
Isopentane	IC5H12	0.087	2.39	Toluene	TOLUENE	0.013	4.00
n-Pentane	NC5H12	0.031	1.31	Ethylbenzene	EBENZ	0.014	3.04
2,2-Dimethylbutae	M22C4	0.014	1.17	m-Xylene	MXYL	0.027	9.75
2,3-Dimethylbutane	M23C4	0.019	0.97	Styrene	STYRENE	0.014	1.73
2-Methylpentane	M2PE	0.031	1.50	o-Xylene	OXYL	0.012	7.64
3-Methylpentane	M3PE	0.012	1.80	Isopropylbenzene	IPBENZ	0.014	2.52
n-Hexane	NC6H14	0.011	1.24	n-Propylbenzene	PBENZ	0.013	2.03
Methylcyclopentane	—	0.011	2.19	m-Ethyltoluene	METHTOL	0.032	7.39
2,4-Dimethylpentane	—	0.013	1.55	p-Ethyltoluene	PETHTOL	0.014	4.44
Cyclohexane	CHEX	0.016	1.25	1,3,5-Trimethylbenzene	TM135B	0.012	11.76
2-Methylhexane	M2HEX	0.012	1.19	1,2,4-Trimethylbenzene	TM124B	0.011	8.87
3-Methylhexane	M3HEX	0.013	1.61	1,2,3-Trimethylbenzene	TM123B	0.011	11.97
2,3-Dimethylpentane	—	0.013	1.34	o-Ethyltoluene	OETHTOL	0.013	5.59
2,2,4-Trimethylpentane	—	0.012	1.26	m-Diethylbenzene	—	0.011	7.10
n-Heptane	NC7H16	0.012	1.07	p-Diethylbenzene	—	0.011	4.43

Species	MCM name	MDL (ppb)	MIR
Methylcyclohexane	—	0.011	1.70
2,3,4-Trimethylpentane	—	0.013	1.03
2-Methylheptane	—	0.013	1.07
3-Methylheptane	—	0.013	1.24
n-Octane	NC8H18	0.012	0.90
n-Nonane	NC9H20	0.013	0.78
n-Decane	NC10H22	0.011	0.68
n-Undecane	NC11H24	0.018	0.61
n-Dodecane	NC12H26	0.048	0.55
Alkenes			
Ethylene	C2H4	0.057	9.00
Propylene	C3H6	0.022	11.66
trans-2-Butene	TBUT2ENE	0.013	15.16
1-Butene	BUT1ENE	0.023	9.73
cis-2-Butene	CBUT2ENE	0.016	14.24
trans-2-Pentene	TPENT2ENE	0.012	10.56
1-Pentene	PENT1ENE	0.093	7.21
cis-2-Pentene	CPENT2ENE	0.011	10.38
1-Hexene	HEX1ENE	0.014	5.49
OVOCs			
Formaldehyde	HCHO	0.007	9.46
Acetaldehyde	CH3CHO	0.016	6.54
Acetone	CH3COCH3	0.009	0.36
Acrolein	ACR	0.008	7.45
Propionaldehyde	C2H5CHO	0.026	7.08
Crotonaldehyde	C4ALDB	0.042	9.39
Butyraldehyde	C3H7CHO	0.048	5.97
Benzaldehyde	BENZAL	0.055	-0.67
Cyclohexanone	CYHEXONE	0.058	1.35
3-Methylbutyraldehyde	C3ME3CHO	0.058	4.97
Pentanal	C4H9CHO	0.038	5.08
o-Tolualdehyde	OXYLAL	0.072	0.00
m-Tolualdehyde	MXYLAL	0.089	0.00
Hexaldehyde	C5H11CHO	0.060	4.35
Heptaldehyde	C6H13CHO	0.034	3.69
Octanal	—	0.029	3.16
Nonanal	—	0.032	0.00
Decanal	—	0.035	0.00

3. I suggest also to improve harmonization between the main text's manuscript and the supplementary information. In the current form, there are many points discussed in the main text that are not immediately clear to the reader, as the main text misses to recall the corresponding information or figure actually presented in the supplement. Some of the information presented in the supplement could be included in the main text to improve clarity.

Response: Thank you for your valuable suggestion. We have reorganized the key information to present the key charts in the main text's manuscript. The adjusted charts have been marked in blue in the main text's manuscript.

Specific comments:

1. line 16. What type of stations?

Response: To clarify, the five stations mentioned in Line 16 are urban, suburban, industrial, upwind, and downwind stations. The relevant descriptions have been revised, please refer to Lines 16-18:

"In this study, 74 VOCs (including 18 OVOCs) were measured at five representative stations (urban, suburban, industrial, upwind, and downwind stations) in Zibo, an industrial city in the North China Plain."

2. Line 18. Previous studies conducted where?

Response: Previous studies conducted most in Chinese cities, offering a statistical basis for comparison.

The related description has been revised, please refer to Lines 18-19:

"The VOCs level in Zibo (44.6±20.9 ppb) is in the upper-middle range (> 32 ppb) compared to previous studies conducted in most Chines cities, with OVOCs contributing for 30.0%~37.8%."

3. Line 81. 5-day field campaign: are they representative to the sites and conditions?

Response: Yes, we consider these 5 days of observations to be representative.

Firstly, the short-term observations are typical of ozone-polluted days and are representative for analyzing photochemistry. And we collected 1-3 hourly samples at each station, resulting in 8-10 samples per station every day, which effectively captured the diurnal variability of atmospheric composition. Throughout the observation period, we obtained a total of 39 valid samples from both the suburban (TZ) and industrial (XD) stations, while the upwind (CQ), downwind (CD), and urban (ZL) stations yielded 49 valid samples each. This sampling strategy provided robust datasets that accurately represent the spatial and temporal variations of OVOC concentrations during the study period.

Secondly, the VOC analyzing instruments used at the five sites were operated and maintained by the same organization, following standardized protocols. These instruments were regularly calibrated using identical standard gas mixtures to maintain measurement accuracy and consistency. For offline OVOC sampling, we employed uniform methodologies across all sites, including the use of identical sampling instruments, standardized collection techniques, consistent sample preservation procedures, and the same analytical protocols. This comprehensive approach to quality control and methodological standardization ensures that the observational data from the five sites are directly comparable and maintain consistent data quality throughout the study period.

4. Section 2.1 please provide information about the methods as suggested in my general comment

Response: Thanks for your suggestion. We have added information about the methods in Section 2.1, please refer to the General comments 1.

5. Line 107. PAMS=?

Response: PAMS is the Photochemical Assessment Monitoring Stations, including 28 alkanes, 16 aromatics, 10 alkenes, acetylene, and isoprene. The relevant descriptions have been added clearly, please refer to Lines 107-109:

"Site-scale wind patterns can affect the levels and spatial distribution of OVOCs and PAMS (target VOC species from the Photochemical Assessment Monitoring Stations, including include 29 alkanes, 16 aromatics, 9 alkenes, isoprene, and acetylene) across sites."

6. I would suggest to include here a list of the measured compound, and the classification method considered by the authors to recall the chemical compounds in subsequent analysis.

Response: Thank you for your suggestion. We have provided a categorized list of VOCs here. Pease refer to Table S2, please refer to general comments 2.

7. Section 2.2 Please provide information about the methods and calculations as suggested in my general comment

Response: Thanks for your suggestion. We have made the relevant revision under your general comment 2 (1). And the related information about methods and calculations has been moved to Section 2.3, Lines 201-218.

8. Figure. 2 It is hard to see the contribution from acetylene in the figure.

Response: Thank you for your careful check-up. We have modified the color of acetylene, please refer to Figure 2.

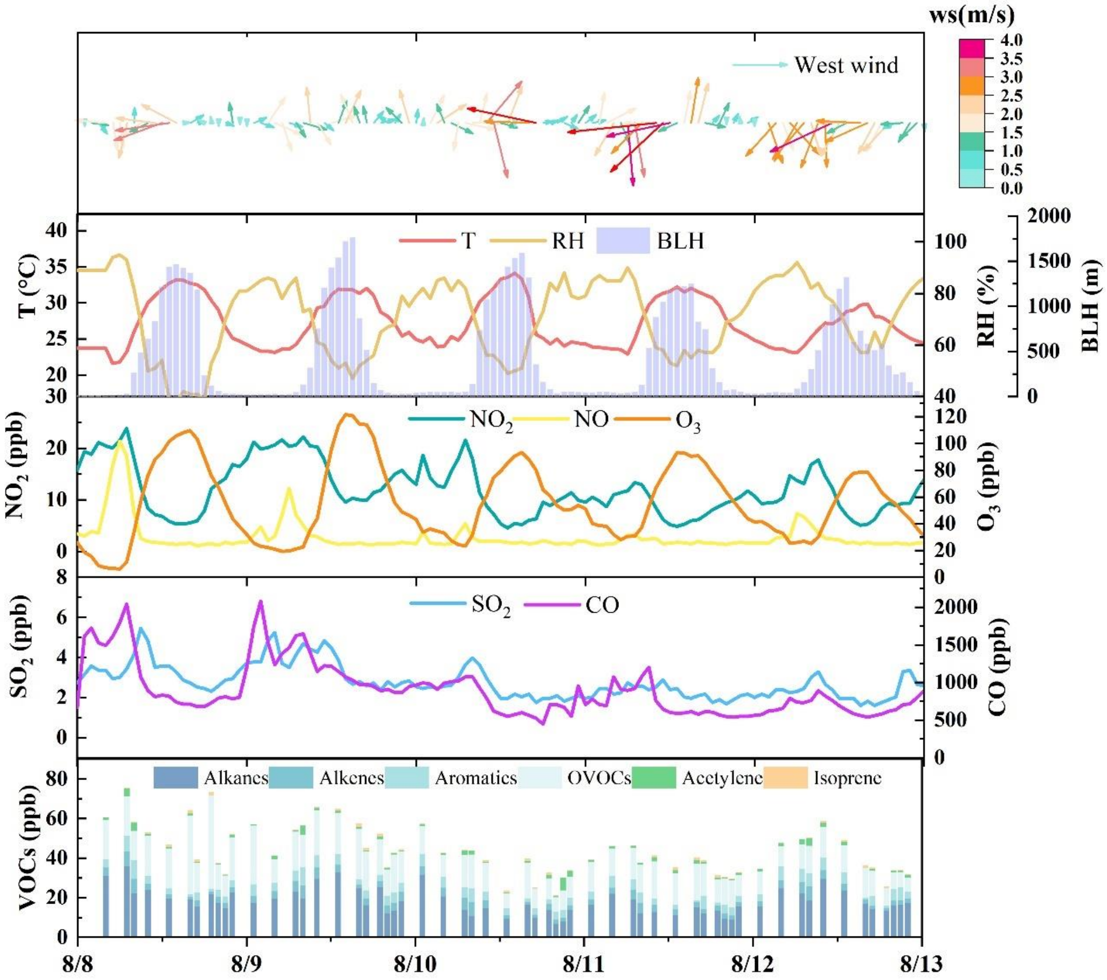

Figure 1. Time profiles of pollutant mixing ratios and meteorological parameters in Zibo from August 8 to 12, 2021. The meteorological data were from ZL, the central site of Zibo, and the pollutants data were the average of the five sites. The hourly PAMS (including alkanes, alkenes, aromatics, acetylene, and isoprene) data were aligned with the 1/3-hour sampling intervals of the OVOCs data to ensure comparability between the two datasets.

9. Line 195. Is this also seen by the largest concentration of aromatics?

Response: Are you referring to the TZ station? While it is close to the oil field, its aromatic levels are not the highest among the five stations. However, it does exhibit the highest levels of alkanes.

10. Line 198. Transport from where to where. Is this also the site where the largest concentration of O_3 is formed?

Response: For question 1, O_3 and its precursors were transported from the northeast to the southwest, i.e., sequentially from upwind (CQ) to urban stations (ZL), and then to downwind stations (CD).

For question 2, yes, O_3 concentration at the downwind site (CD) is higher than at any other site. And the O_3 concentration increases sequentially from the northeast to southwest (CQ → ZL → CD).

The relevant descriptions have been revised, please refer to Lines 288-294:

"The downwind site (CD) has slightly lower NO_2 level (10.8±5.1 ppb) and lower TVOCs mixing ratios (35.7±12.5 ppb) than urban site (ZL, 14.8±6.5 and 40.6±10.3 ppb, respectively) and upwind site (CQ, 12.7±8.1 and 42.3±15.4 ppb, respectively), and has higher O_3 mixing ratio (58.6±30.0 ppb) than CQ and ZL station. This may be attributed to the sequential transport of O_3 and its precursors from the upwind station (CQ) to urban station (ZL), and subsequently to the downwind station (CQ), driven by the dominant northeasterly winds (**Error! Reference source not found.** (b), Figure S1)."

11. Line 214. Please provide the method to determine OFP

Response: The method of calculating OFP has been added in Section 2.4, Lines 233-240. Please refer to general comments 2 (2) for details.

12. Line 215. What are the contributions of other classes of VOC?

Response: In addition to OVOC, aromatics contribute the second largest share of OFP with 10.2%~41.2%. Alkanes (10.3%–24.6%) and alkenes (11.4%~23.1%) contributed comparable proportions, and BVOC (2.1%~7.6%) has the lowest share.

The relevant expressions have been refined, please refer to Lines 308-312:

"The mean OFP in Zibo during the observation is 410.4±197.2 μg m^{-3}, with OVOCs accounting for the largest proportion (31.5%~55.9%), followed by aromatics (10.2%~41.2%). Alkanes (10.3%–24.6%) and alkenes (11.4%~23.1%) make comparable proportions, while BVOCs accounted for only 2.1%~7.6% of the total OFP (Figure 5 (b))."

13. Line 216. Which OVOC contributes the largest? The authors can provide here the OVOC speciation.

Response: Thanks for your suggestion. We have added relevant content that complements the top three contributing OVOCs species. Please refer to Lines 328-332:

"Among OVOC species, HCHO is the dominant contributor to OFP across the five sites (56.6~202.0 μg m^{-3}). This is consistent with previous studies (Duan et al., 2008; Huang et al., 2020; Zhou et al., 2024). The top four OVOC species are formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde, which cumulatively contributed 91%~95% of the OFP from OVOCs (Table S5)."

14. Line 233. Please include a table with measured concentrations, OFP from each measured VOC

and VOC group.

Response: We have added a table with measured concentrations, OFP from each measured VOC and VOC groups. Please refer to Table S5.

Table S5. Measured mixing ratios, ozone formation potential from VOC species and groups.

Species/Groups	VOC mixing ratios (mean±std) (ppb)					OFP (mean±std) (μg m^{-3})				
	CD	CQ	TZ	XD	ZL	CD	CQ	TZ	XD	ZL
TVOCs	35.7±12.5	42.3±15.4	58.5±35.0	49.6±19.0	40.6±10.3	279.4±101.2	464.2±162.3	456.3±295.3	422.9±166.9	441.1±174.5
Alkanes	13.2±6.2	16.5±8.5	30.2±21.0	23.3±11.2	13.5±5.6	36.0±19.3	47.8±25.4	66.5±39.9	103.9±51.7	46.7±21.9
Alkenes	3.3±1.8	3.3±1.6	2.9±1.7	2.8±1.3	5.6±3.0	57.1±30.4	57.5±30.5	52.1±30.8	50.6±27.2	101.8±56.8
Aromatics	4.0±1.7	7.0±3.6	2.2±1.2	3.1±1.5	6.3±4.7	73.4±29.1	191.3±111.3	46.6±24.8	48.4±23.0	125.3±116.2
OVOCs	10.7±5.0	14.5±6.7	22.1±22.5	17.9±8.5	14.6±4.8	102.3±51.2	146.2±70.7	254.9±276.1	194.7±101.0	148.9±55.7
Acetylene	4.4±4.1	0.4±0.7	0.0±0.0	1.9±1.6	0.0±0.0	4.8±4.5	0.5±0.8	0.0±0.1	2.1±1.7	0.0±0.1
Isoprene	0.2±0.2	0.6±0.6	1.1±0.8	0.7±0.5	0.6±0.7	5.8±7.7	20.8±17.8	34.9±25.8	23.0±16.3	18.1±23.6
Benzene	1.0±0.5	0.3±0.2	0.2±0.3	1.1±0.6	1.2±0.5	2.4±1.3	0.6±0.4	0.4±0.7	2.7±1.5	3.0±1.3
Toluene	1.2±0.5	1.2±0.9	1.4±1.0	0.9±0.5	1.6±1.3	19.3±7.5	20.0±15.2	23.6±15.9	14.5±8.2	25.8±21.4
Ethylbenzene	0.3±0.2	0.4±0.5	0.1±0.1	0.2±0.1	0.7±0.3	4.4±2.7	6.3±7.7	0.9±0.8	3.0±1.0	9.5±4.8
m-Xylene	0.4±0.2	1.2±1.2	0.1±0.1	0.4±0.2	0.3±0.1	17.2±9.0	53.8±56.1	3.6±2.6	16.7±8.0	12.5±5.9
Styrene	0.5±0.4	0.8±1.1	0.1±0.0	0.3±0.3	0.6±0.4	3.7±3.4	6.8±8.5	0.6±0.3	2.3±2.5	4.6±3.0
o-Xylene	0.2±0.1	0.7±0.8	0.1±0.0	0.1±0.1	1.5±2.2	6.0±3.9	23.6±29.3	2.1±1.4	5.1±2.4	53.2±79.4
Isopropylbenzene	0.0±0.1	0.4±0.5	0.0±0.1	0.0±0.1	0.2±0.1	0.2±0.4	5.3±6.9	0.2±0.3	0.1±0.2	2.8±1.7
n-Propylbenzene	0.0±0.1	0.4±0.5	0.0±0.1	0.0±0.1	0.0±0.1	0.5±0.4	4.0±5.3	0.1±0.3	0.2±0.4	0.0±0.1
m-Ethyltoluene	0.1±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.1	4.1±1.8	0.0±0.1	1.0±1.2	1.0±1.5	0.3±0.6
p-Ethyltoluene	0.0±0.1	0.3±0.3	0.0±0.1	0.0±0.1	0.1±0.1	1.0±0.6	7.1±6.6	0.3±0.5	0.0±0.1	1.3±1.8
1,3,5-Trimethylbenzene	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.0±0.1	2.6±2.3	13.6±15.3	1.2±2.0	0.0±0.1	0.0±0.1
1,2,4-Trimethylbenzene	0.1±0.1	0.3±0.3	0.2±0.1	0.0±0.1	0.0±0.1	2.6±3.1	13.7±13.4	7.4±3.6	2.3±2.4	0.2±0.7
1,2,3-Trimethylbenzene	0.0±0.1	0.3±0.3	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.0	18.1±17.2	3.1±2.1	0.0±0.1	6.5±4.9
o-Ethyltoluene	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.0±0.1	1.2±1.4	7.0±7.0	0.8±0.8	0.6±0.9	0.7±0.9
m-Diethylbenzene	0.1±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.1±0.1	6.0±2.6	7.2±10.2	1.1±1.5	0.0±0.1	2.4±2.9

Species/Groups	VOC mixing ratios (mean±std) (ppb)					OFP (mean±std) (μg m^{-3})				
	CD	CQ	TZ	XD	ZL	CD	CQ	TZ	XD	ZL
p-Diethylbenzene	0.1±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.1±0.1	2.0±1.4	4.1±5.5	0.3±0.5	0.0±0.1	2.7±1.1
Ethylene	1.4±1.2	1.8±0.9	1.6±1.2	1.4±0.6	2.7±1.4	15.5±13.6	20.4±9.6	17.9±13.1	15.3±6.7	29.9±15.3
Propylene	0.4±0.4	0.9±0.7	0.7±0.5	0.6±0.4	1.6±1.5	8.8±8.0	20.7±15.6	14.6±11.8	12.5±8.2	36.0±33.9
trans-2-Butene	0.1±0.1	0.0±0.1	0.0±0.1	0.2±0.2	0.4±0.2	2.0±2.4	0.0±0.1	1.6±2.5	6.5±7.8	14.0±8.5
1-Butene	0.0±0.1	0.0±0.1	0.0±0.1	0.1±0.2	0.2±0.2	1.2±1.6	1.0±1.1	1.0±1.7	3.2±4.1	5.0±3.7
cis-2-Butene	0.0±0.1	0.3±0.2	0.0±0.1	0.1±0.1	0.1±0.1	0.7±1.9	10.2±8.0	0.3±0.8	3.7±4.8	2.3±4.0
trans-2-Pentene	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.1	0.0±0.1	0.7±1.5	1.0±1.3	2.0±2.5	0.1±0.3	0.0±0.1
1-Pentene	0.0±0.1	0.1±0.1	0.0±0.1	0.0±0.1	0.2±0.2	0.2±0.7	1.8±1.3	0.9±1.6	0.5±0.6	3.9±4.8
cis-2-Pentene	0.0±0.1	0.1±0.1	0.3±0.3	0.0±0.1	0.0±0.1	0.0±0.1	1.9±3.2	10.6±9.5	0.3±0.9	0.6±1.4
1-Hexene	1.4±1.0	0.0±0.1	0.2±0.2	0.4±0.7	0.5±0.4	28.1±20.3	0.4±0.6	3.2±3.5	8.4±13.7	10.1±8.9
Ethane	4.0±1.5	3.3±1.6	4.4±3.9	2.4±0.8	0.0±0.1	1.5±0.6	1.2±0.6	1.7±1.5	0.9±0.3	0.0±0.1
Propane	2.8±1.7	3.9±2.4	13.3±11.1	4.1±2.3	3.2±0.8	2.7±1.6	3.7±2.3	12.8±10.7	4.0±2.2	3.1±0.8
Isobutane	0.8±0.6	1.4±1.4	1.0±1.2	1.3±1.1	3.2±1.4	2.6±1.9	4.5±4.6	3.2±3.9	4.1±3.4	10.3±4.5
n-Butane	1.6±0.9	2.4±2.4	4.4±3.6	2.9±2.5	0.9±0.5	4.7±2.8	7.0±7.2	13.0±10.9	8.7±7.6	2.7±1.6
Cyclopentane	0.1±0.1	0.3±0.2	2.5±2.2	0.3±0.5	1.6±0.9	0.3±0.3	0.9±0.8	8.9±7.8	1.2±1.7	5.9±3.1
Isopentane	1.3±0.7	0.4±0.8	0.0±0.1	8.6±5.0	0.1±0.1	10.3±5.5	3.4±5.9	0.0±0.1	66.2±38.5	0.6±0.5
n-Pentane	0.7±0.6	0.3±0.5	0.0±0.1	1.3±1.2	1.4±0.8	3.1±2.4	1.4±2.3	0.0±0.1	5.5±5.0	6.0±3.2
2,2-Dimethylbutae	0.1±0.1	0.1±0.1	0.0±0.1	0.0±0.1	0.8±0.6	0.6±0.6	0.4±0.6	0.2±0.5	0.0±0.1	3.8±2.7
2,3-Dimethylbutane	0.1±0.2	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.5±0.6	0.1±0.1	0.9±0.8	0.1±0.2	0.1±0.1
2-Methylpentane	0.2±0.1	0.2±0.2	0.0±0.1	0.4±0.3	0.4±0.2	0.9±0.8	1.0±0.9	0.0±0.1	2.4±1.8	2.0±0.9
3-Methylpentane	0.3±0.2	0.3±0.2	0.0±0.1	0.3±0.1	0.3±0.2	1.9±1.4	2.0±1.6	0.0±0.1	2.3±1.0	2.0±1.1
n-Hexane	0.6±0.4	0.2±0.3	0.0±0.1	0.6±0.2	0.1±0.1	2.7±2.0	0.9±1.4	0.1±0.4	2.7±1.1	0.4±0.4

Species/Groups	VOC mixing ratios (mean±std) (ppb)					OFP (mean±std) (μg m^{-3})				
	CD	CQ	TZ	XD	ZL	CD	CQ	TZ	XD	ZL
Methylcyclopentane	0.1±0.1	0.1±0.2	0.0±0.0	0.0±0.1	0.7±0.5	0.9±0.9	0.9±1.3	0.0±0.1	0.1±0.5	5.5±3.8
2,4-Dimethylpentane	0.1±0.1	0.0±0.1	0.2±0.2	0.2±0.1	0.1±0.1	0.8±0.4	0.2±0.3	1.2±1.3	1.2±0.9	1.0±1.0
Cyclohexane	0.1±0.1	0.2±0.3	0.0±0.1	0.1±0.1	0.2±0.1	0.6±0.3	1.1±1.3	0.0±0.1	0.4±0.4	0.9±0.4
2-Methylhexane	0.0±0.1	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.1	0.2±0.3	0.3±0.3	0.0±0.1	0.3±0.3	0.2±0.3
3-Methylhexane	0.1±0.1	0.3±0.3	0.0±0.1	0.1±0.1	0.0±0.1	0.7±0.5	2.1±2.4	0.0±0.1	0.7±0.6	0.1±0.1
2,3-Dimethylpentane	0.0±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.0±0.1	0.6±0.7	0.8±0.8	0.4±0.5	0.7±0.3
2,2,4-Trimethylpentane	0.0±0.1	0.1±0.1	2.5±1.7	0.0±0.1	0.0±0.1	0.1±0.2	0.9±0.7	16.4±10.7	0.2±0.3	0.0±0.1
n-Heptane	0.1±0.1	0.4±0.3	0.6±0.4	0.2±0.1	0.0±0.1	0.4±0.4	2.1±1.6	2.8±2.1	0.8±0.4	0.2±0.2
Methylcyclohexane	0.0±0.1	0.2±0.2	0.0±0.1	0.1±0.1	0.1±0.1	0.2±0.4	1.3±1.5	0.2±0.5	1.0±0.9	0.7±0.6
2,3,4-Trimethylpentane	0.0±0.1	0.2±0.2	0.2±0.4	0.0±0.1	0.0±0.1	0.0±0.1	1.2±1.2	1.2±2.0	0.0±0.1	0.0±0.1
2-Methylheptane	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.1	1.1±1.1	0.2±0.5	0.1±0.1	0.3±0.4
3-Methylheptane	0.0±0.1	0.8±0.5	0.2±0.2	0.0±0.1	0.0±0.1	0.2±0.3	4.9±3.2	1.5±1.3	0.1±0.2	0.0±0.1
n-Octane	0.0±0.1	0.3±0.3	0.1±0.1	0.0±0.1	0.0±0.1	0.1±0.1	1.2±1.4	0.4±0.5	0.2±0.2	0.1±0.2
n-Nonane	0.0±0.1	0.2±0.2	0.0±0.1	0.0±0.1	0.0±0.1	0.1±0.1	0.9±1.0	0.1±0.3	0.2±0.2	0.1±0.2
n-Decane	0.0±0.1	0.2±0.3	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.9±1.4	0.1±0.1	0.0±0.1	0.1±0.1
n-Undecane	0.0±0.1	0.2±0.2	0.1±0.0	0.0±0.1	0.0±0.1	0.1±0.1	0.8±0.9	0.3±0.2	0.1±0.2	0.0±0.1
n-Dodecane	0.0±0.1	0.2±0.2	0.1±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.8±0.9	0.3±0.2	0.0±0.0	0.0±0.1
Formaldehyde	4.5±2.3	6.6±3.5	15.9±20.0	8.1±4.3	7.8±3.8	56.6±29.1	83.3±44.4	202.0±253.8	103.2±54.8	99.1±48.0
Acetaldehyde	2.1±1.7	3.1±2.1	2.4±1.1	4.3±3.4	2.1±0.7	27.6±21.4	39.4±27.5	31.0±14.7	55.6±44.2	27.4±8.8
Acetone	2.6±1.5	2.9±1.8	1.9±1.2	2.6±1.0	2.7±1.6	2.4±1.4	2.7±1.6	1.8±1.2	2.4±0.9	2.5±1.5
Acrolein	0.0±0.1	0.0±0.1	0.0±0.1	0.1±0.2	0.0±0.1	0.0±0.1	0.2±0.6	0.0±0.2	1.4±4.6	0.1±0.3
Propionaldehyde	0.3±0.1	0.4±0.2	0.3±0.1	0.4±0.3	0.3±0.1	5.0±2.4	7.3±3.9	5.5±2.1	7.5±5.2	5.6±2.2
Crotonaldehyde	0.1±0.1	0.1±0.2	0.0±0.1	0.1±0.1	0.1±0.2	1.8±3.1	2.4±5.9	0.2±0.6	1.8±2.8	3.9±4.9
Butyraldehyde	0.2±0.1	0.2±0.3	0.2±0.1	0.8±0.9	0.1±0.1	3.5±2.6	4.7±5.2	3.4±2.3	14.7±16.7	2.8±2.4

Species/Groups	VOC mixing ratios (mean±std) (ppb)					OFP (mean±std) (μg m^{-3})				
	CD	CQ	TZ	XD	ZL	CD	CQ	TZ	XD	ZL
Benzaldehyde	0.1±0.1	0.2±0.1	0.2±0.1	0.3±0.6	0.2±0.1	-0.4±0.4	-0.8±0.4	-0.5±0.3	-1.0±1.9	-0.6±0.4
Cyclohexanone	0.0±0.1	0.1±0.2	0.1±0.1	0.1±0.1	0.2±0.2	0.1±0.2	0.9±0.9	0.7±0.6	0.5±0.4	1.1±1.2
Isovaleraldehyde	0.1±0.2	0.1±0.1	0.1±0.2	0.1±0.1	0.0±0.1	1.9±4.0	1.1±1.1	2.5±4.1	1.2±0.6	0.9±1.0
Pentanal	0.0±0.1	0.0±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.5±0.8	0.7±0.8	1.8±1.2	1.3±0.7	1.6±1.4
o-Tolualdehyde	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
m-Tolualdehyde	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
Hexaldehyde	0.1±0.2	0.2±0.2	0.3±0.2	0.3±0.2	0.2±0.2	2.7±3.0	2.9±4.0	4.9±3.2	4.9±3.3	3.5±3.7
Heptaldehyde	0.0±0.1	0.0±0.1	0.1±0.1	0.0±0.1	0.0±0.1	0.0±0.1	0.2±0.5	1.3±1.0	0.3±0.5	0.2±0.4
Octanal	0.0±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.6±1.3	1.4±1.3	1.6±1.4	1.2±1.0	1.3±1.4
Nonanal	0.3±0.2	0.3±0.1	0.3±0.3	0.3±0.1	0.3±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
Decanal	0.2±0.1	0.1±0.1	0.1±0.1	0.2±0.1	0.2±0.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0

15. Figure 4. There is a typo on the y axis title

Response: Thank you for pointing it out. We have corrected the typo in the y-axis caption of Figure 4 (b) and adjusted Figure 4.

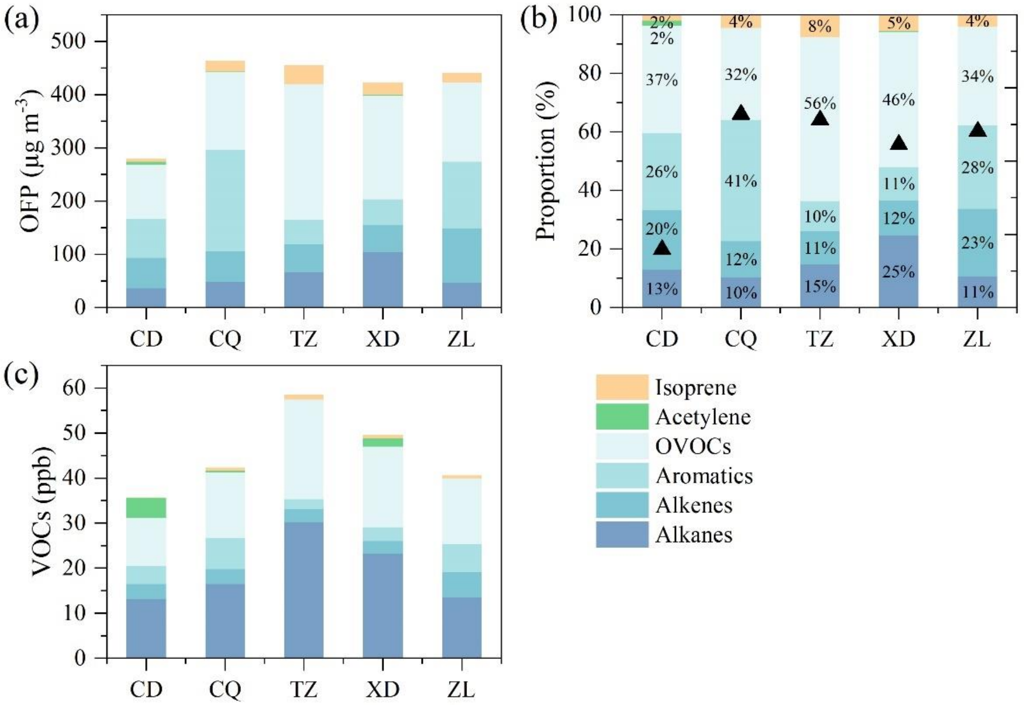

Figure 4. (a) Ozone formation potential (OFP) and (b) proportions of OFP contributed by VOC subgroups, along with (c) mixing ratios of VOC subgroups at five sites.

16. Line 296. Define acronym AOC and how this value is determined in the methods

Response: Thanks for point this out. We have added the definition of the acronym AOC and explained how this value is calculated in the Methodology Section 2.4. Please refer to Lines 241-248:

"Atmospheric oxidation capacity (AOC) is the core driving force of complex air pollution, influencing the removal rate of trace gases and the production rates of secondary pollutants (Liu et al., 2021). AOC is calculated based on the sum of oxidation rates of oxidants (OH, O_3, and NO_3) with primary pollutants (VOCs, CO, and CH_4) (Elshorbany et al., 2009; Geyer et al., 2001; Yang et al., 2022b). The formula is as follows:

$$AOC = \sum_{i} k_{Yi}[Y_i][X] \quad (7)$$

where Y_i represents primary VOCs (excluding OVOCs), CO and CH_4, X represents oxidants (OH, O_3 and NO_3) and k_{Yi} is the bimolecular rate constant for the reaction of Y_i with X. Atmospheric oxidation capacity determines the rate of Y_i removal."

17. Fig. 7 &8. What is b) representing?

Response: Thank you for your question. In Figure 7 and Figure 8, panel (b) represents the difference of corresponding sources and sinks of RO_x and O_3 between the Free and Base scenarios, respectively, illustrating the impact of OVOCs observationally constrained on the respective budgets. Specifically, in Figure 7(b), it shows the impact on the RO_x budget, while in Figure 8(b), it shows the impact on the O_3 budget. Figure 7 and 8 have been moved to Figures 8 and 9, respectively.

18. Line 318-319. Needed acronyms definition for O_3 formation, $P(O_3)$, $L(O_3)$ and how these values are determined.

Response: Thank you for pointing it out. We have added definitions and calculation methods in Section 2.3 of the Methodology, Lines 219-232:

"Considering the oxidation of NO to NO_2 by peroxyl radicals, the total oxidant ($O_x = O_3 + NO_2$) is generally used to characterize the chemical budget of O_3 (Kanaya et al., 2009; Xue et al., 2014b). The total chemical production of O_x through oxidations of NO by HO_2 and RO_2 radicals (Tan et al., 2018b), is defined as the production of O_3 ($P(O_3)$), which is calculated according to Equation (4):

$$P(O_3) = k_{HO2+NO}[HO_2][NO] + \sum k_{RO2,j+NO}[RO_2]_j[NO] \tag{4}$$

The chemical loss rate (L(O_3)) of O_3 is equal to the sum of loss rates of O_3 and NO_2, including O_3 photolysis, reactions of O_3 with OH, HO_2 and alkenes, as well as reactions of NO_2 with OH and RO_2, as well as the reaction of NO_3 with unsaturated VOCs (Chen et al., 2020; Liu et al., 2022; Xue et al., 2016, 2014b).

$$\begin{aligned} L(O_3) = {} & k_{O1D+H2O}[O1D][H_2O] + k_{O3+OH}[O_3][OH] \\ & + k_{O3+HO2}[O_3][HO_2] + k_{O3+alkenes}[O_3][alkenes] \\ & + k_{NO2+OH}[NO_2][OH] \\ & + \sum k_{NO2+RO2,j}[NO_2][RO_2]_j \\ & + \sum k_{NO3+VOC,i}[NO_3][VOC]_i \end{aligned} \tag{5}$$

The concentrations of radicals and intermediates are derived from the outputs of the OBM. The *k* values in Equations (4) and (5) rate constants of the corresponding reactions, which can be found from https://mcm.york.ac.uk/MCM/ (last access: 13 Jan 2025) or the study by Liu et al. (2022). The subscript '*j*' in Equation (4) and (5) denotes individual RO_2 species. The subscript '*i*' in Equation (5) represents individual VOC species. The net O_3 production rate can be obtained from the difference between P (O_3) and L(O_3)."

19. Line 339. Conducted in China or urban areas in general? What is the upper-middle range? A review of the existing studies would be helpful (if the review is the same presented in the SI, I suggest to include the review in the main text).

Response: Thank you for your comment. The previous studies were conducted in China (see Table S4). The upper-middle range refers to the range of VOC mixing ratios above the median value

(> 32 ppb), as determined from the literature review and data collection presented Table S4 in the SI. We have added a bar chart comparing VOCs by city in the main text for better clarity. Please refer to Figure 3.

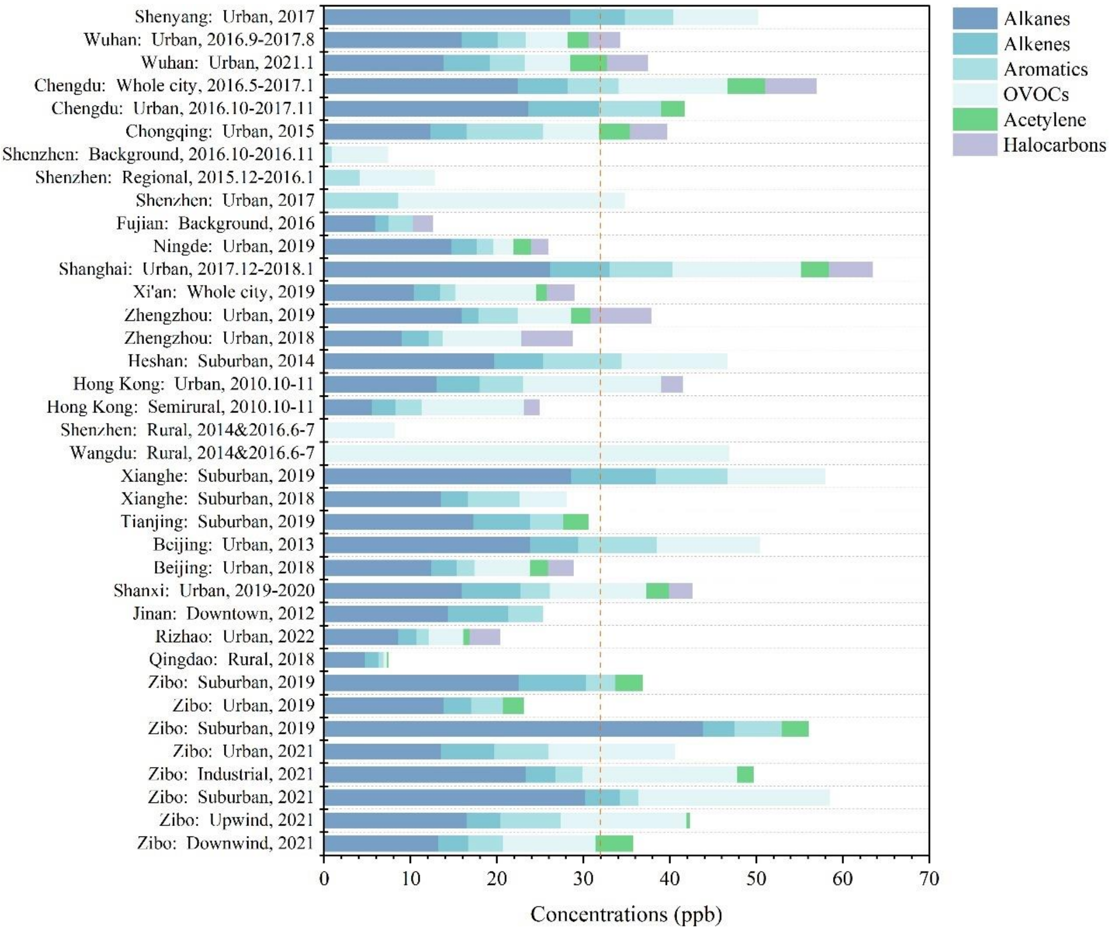

Figure 3. Comparison of VOC mixing ratios and compositions in this study with former studies based on Table S4. The red dash line represents the median levels (~32 ppb) of VOCs。

20. Line 348. Refer to SI where needed.

Response: Thanks for your suggestion. We have inserted the relevant chart to support the information, and have referred to Table S5 in the supporting information. Please refer to specific comment 14.

21. Line 356. Can the authors separate emissions from transport? For example using an auxiliary

method, such as a source apportionment method or ancillary measurements

Response: Thank you for the insightful comment regarding the separation of OVOC emissions from transport. The OBM is designed to simulate in-situ photochemical production, chemical loss, and deposition processes within a given air mass at a specific location. It does not explicitly account for emissions or regional transport processes (Wolfe et al., 2016), so emissions and transport were combined into a single term ($R_{Emis\&Trans}$) in our study. However, after many attempts, we apologize that we were unable to modify the emission and transmission contributions to OVOC. We would like to elaborate on the reasons for this.

While ancillary methods such as source assignment (e.g., the positive matrix factorization (PMF) model (Bon et al., 2011), the multiple linear regression (MLR) (Garcia et al., 2006; Zou et al., 2024), and the photochemical age-based parameterization method) (de Gouw et al., 2005; Huang et al., 2020), can theoretically help to isolate emissions during transportation, their application in separating transport and emissions was limited by the following factors:

1) Tracer representativeness:

    (1) Methods like MLR and PMF rely on tracer species to characterize sources. For example, CO, benzene, and toluene are commonly used as tracers for anthropogenic emissions (Huang et al., 2019; Zou et al., 2024). However, identifying tracers that specifically represent transport processes is challenging, as transport-influenced air masses often lack unique chemical markers.

    (2) In the photochemical age-based parameterization approach, the photochemical age is used to characterize aged air masses (de Gouw et al., 2005). However, this is to a large extent closely related to the secondary photochemical reactions, which does not allow

a better quantification of the contribution of transport.

2) Complexity of urban environments:
    (1) Photochemical age-based parameterization methods require a fixed emission ratio of each VOC relative to a selected tracer, which is often unavailable or highly variable in complex urban environments (Yuan et al., 2012; Zou et al., 2024).
    (2) These source apportionment methods also struggle to distinguish between primary and secondary sources, particularly when specific precursors are not well-defined or when multiple sources contribute to OVOCs.

Given these limitations, auxiliary methods are not well-suited to separate emissions from transport in the context of our study. We acknowledge that separating emissions from transport is crucial for a more comprehensive understanding of OVOCs sources and sinks. Integrating the OBM with regional chemical transport model (CTM) to explicitly may resolve emissions and transport dynamics.

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