Reviewer #2

The manuscript entitled " The impact multi-decadal of changes in VOCs speciation on urban ozone chemistry: A case study in Birmingham, United Kingdom" aimed to quantify the impacts of the real-world changes in VOCs sources on urban O_3 production rate, and also evaluate the relative importance of different VOCs functional group classes on the O_3 production. The manuscript provides some valuable advice for the pollution control of O_3 in the area with relative clean air quality. I therefore suggest a necessary revision of this manuscript before final publication in Atmospheric Chemistry and Physics.

Authors' reply: We appreciate the reviewer's efforts in recognizing the contribution of our results to the research field of urban ozone pollution. We have been able to incorporate changes in responding to the reviewer's valuable feedbacks. Revised texts within the manuscript have been marked by red color, and newly added Table/Figure captions have been highlighted by yellow.
Here is a point-by point response to the reviewer's comments.

1) The innovation of the paper needs further unearthing, as there are already many similar literatures;

Authors' reply: We value the reviewer's efforts in comparing our study to those in the existing literatures. Throughout the revised Introduction, we have enriched literature reviews (**Page 3, Line 60-62, Line 81-85** in revised manuscript) on previous O_3 studies. The current research gap has been clearly stated (**Page 3-4, Line 88-92** in revised manuscript), and the significance of our results has been pointed out (**Page 4, Line 102-104** in revised manuscript). The innovation of this paper is briefly denoted as follows:

- Over the last decades, there have been extensive studies investigating controlling factors of *in -situ* production of O_3 from the perspective of chemical control regime and reactivity of O_3 precursors (please see detailed literature review on **Page 2-3 Line 47-63** in revised manuscript). For example, a recent study in a coastal city of China applied observation-constrained box model to clarify sensitivity of O_3 production and OH reactivity of VOCs classes during a high O_3 event in 2019 autumn. The results indicated that the O_3 production at

the urban site was VOC-sensitive. Aromatics, alkenes, and alkanes were the primary reduction target for the ozone pollution control, which showed the highest OH reactivity and played a leading role in radical recycling and O_3 production (Liu et al., 2022).

Since VOC emissions are often the limiting factor in photochemical production of urban ozone, the issue of shifts in major VOC emissions (detailed discussion please see **Page 3 Line 64-88** in revised manuscript) and their resulting impacts on urban ozone chemistry have been addressed worldwide. The increasing role for volatile chemical product (VCP) emissions in urban ozone chemistry has been taken into account. In North America and Europe cities, OVOCs emitted from volatile chemical products (VCP) can outweigh fossil fuel sources for urban VOCs. Modelling results showed that the additional OVOCs from VCP emissions were the most important species for urban O_3 production, increasing the daily maximum O_3 mixing ratio by as much as 10 ppbv in Los Angeles and 11 ppbv in New York (Coggon et al., 2021; Qin et al., 2021).

Although investigations on *in-situ* urban ozone chemistry and attributions of O_3 production from important VOC sources have been extensively conducted in atmospheric modeling studies, there has been limited reporting on the evaluation of real-world emission changes in VOCs speciation. From the perspective of *in-situ* O_3 production, the benefit of substantial reductions on vehicle emissions, whilst there has been a parallel increasing role for non-industrial solvent usage remains unclear. What effect this shift in speciation is having on ozone chemistry is less well studied. Therefore, by incorporating the detailed NAEI VOCs emission inventories over the period of 1990-2019 into a box model, O_3 formation in Birmingham is used as a case study to quantify the impacts of the real-world changes in VOCs sources on urban O_3 production rate. The study makes a major advance since it couples both highly detailed *in- situ* measurements along with a multi-year highly speciated inventory, something that has not been available to other studies. The results help understand impacts of decades of abating different VOCs-emitting sectors on urban O_3 production, and outline the implications for future O_3 control strategies.

References

Coggon, M. M., Gkatzelis, G. I., McDonald, B. C., Gilman, J. B., Schwantes, R. H., Abuhassan, N.,

Aikin, K. C., Arend, M. F., Berkoff, T. A., Brown, S. S., Campos, T. L., Dickerson, R. R., Gronoff, G., Hurley, J. F., Isaacman-VanWertz, G., Koss, A. R., Li, M., McKeen, S. A., Moshary, F., Peischl, J., Pospisilova, V., Ren, X., Wilson, A., Wu, Y., Trainer, M., and Warneke, C.: Volatile chemical product emissions enhance ozone and modulate urban chemistry, Proc Natl Acad Sci U S A, 118, 10.1073/pnas.2026653118, 2021.

Liu, T., Hong, Y., Li, M., Xu, L., Chen, J., Bian, Y., Yang, C., Dan, Y., Zhang, Y., and Xue, L.: Atmospheric oxidation capacity and ozone pollution mechanism in a coastal city of southeastern China: analysis of a typical photochemical episode by an observation-based model, Atmospheric Chemistry and Physics, 22, 2173-2190, 10.5194/acp-22-2173-2022, 2022.

Qin, M., Murphy, B. N., Isaacs, K. K., McDonald, B. C., Lu, Q., McKeen, S. A., Koval, L., Robinson, A. L., Efstathiou, C., and Allen, C.: Criteria pollutant impacts of volatile chemical products informed by near-field modelling, Nature sustainability, 4, 129-137, 10.1038/s41893-020-00614-1, 2021.

2) In this study only 38 VOCs species were detected, which was much less than the photochemical species requirements of PAMS and also not conducive to the operation of the OBM model. It is also necessary for the author to explain the quality control of the online VOCs monitoring instrument;

Authors' reply:

■ Thank you for your comment. The up-to-dated 2017 PAMS target list includes 27 priority compounds and 37 optional compounds (Addtional Revisions to the PAMS Compound Target List, last accessed 2024-Jan-30). We agree with you that the measured 38 VOCs species at Birmingham Supersite was much less than the PAMS requirements. Nevertheless, the measured species in this study covered 20 of the 27 priority compounds. Mixing ratios of alkanes, alkenes, aromatics, and oxygenated VOCs species with high OH reactivities were well-recorded at the sampling site. In terms of the model performance, the mixing ratios of modelled O_3 during the initial period, O_3 period, and clear-out period were significantly correlated with those of the observed O_3 ($R^2 = 0.9$ at all periods, $P < 0.05$).

From the perspective of O_3 formation mechanism, *in-situ* production of O_3 is driven by radical

chemistry. Therefore, even a simplified NO_x-O_3-VOC mechanism with limited numbers of VOCs input can describe the most important features of chemical formation of O_3 (Seinfeld and Pandis, 2016). For example, a recent study applied a box model constrained by NO_x and a single compound, propane, to evaluate the chemical regime of urban O_3 in major cities in China, Japan, and the United States (Wolf et al., 2022). It was concluded that the elevated O_3 in Chinese cities and the slowed reduction of O_3 in Japan and US were likely attributed to decreased NO_x emissions.

- Regarding your comments on the quality control of the online VOCs monitoring instrument, This was completed regularly since the instrument is used for long-term monitoring and reports to national air quality networks. Direct calibration using 4 ppbv gas standard cylinders and the use of carbon response for this instrument was tightly controlled, with regular carbon-wise responses calculated for all species as a cross check. Calibration sequences of the 4 ppbv calibration used in this study are run at regular intervals, with responses analyzed as a function of time. FID response has been verified to be stable over the lifetime of the GC-FID instrument, and did not drift in any observable way over the sample analyzing period for this study. Detection limits for this instrument are not higher than 0.1 ppbv and are typically in the 5-10 pptv range. We have added Table 1 and Table 2 into the supplement material. Table 1 lists which species were directly calibrated, and which used equivalent carbon numbers for quantification. Table 2 lists effective carbon numbers of species which used carbon-wise responses. Additionally, Descriptions on GC-FID instrument has been fully revised, and the calibration sequence has been added in the revised manuscript onto **Page 6, Line 151-156**.

Table 1. Species quantified and their corresponding quantification method used in this study.

Species	Quantification method
ethane	4 ppbv gas standard cylinders
propane	4 ppbv gas standard cylinders
i-butane	4 ppbv gas standard cylinders
n-butane	4 ppbv gas standard cylinders
i-pentane	4 ppbv gas standard cylinders
n-pentane	4 ppbv gas standard cylinders
2-methylpentane	4 ppbv gas standard cylinders
hexane	4 ppbv gas standard cylinders
heptane	4 ppbv gas standard cylinders
i-octane	4 ppbv gas standard cylinders
ethene	4 ppbv gas standard cylinders
propene	4 ppbv gas standard cylinders
t-2-butene	4 ppbv gas standard cylinders
1-butene	4 ppbv gas standard cylinders
c-2-butene	4 ppbv gas standard cylinders
1,3-butadiene	4 ppbv gas standard cylinders
t-2-pentene	4 ppbv gas standard cylinders
c-2-pentene	4 ppbv gas standard cylinders
isoprene	4 ppbv gas standard cylinders
acetylene	4 ppbv gas standard cylinders
benzene	4 ppbv gas standard cylinders
toluene	4 ppbv gas standard cylinders
ethylbenzene	4 ppbv gas standard cylinders
m-xylene	4 ppbv gas standard cylinders
p-xylene	4 ppbv gas standard cylinders
o-xylene	4 ppbv gas standard cylinders
1,3,5-trimethoxybenzene	4 ppbv gas standard cylinders
1,2,4-trimethoxybenzene	4 ppbv gas standard cylinders
1,2,3-trimethoxybenzene	4 ppbv gas standard cylinders
cyclopentane	effective carbon number using toluene as reference
3-methylpentane	effective carbon number using toluene as reference
nonane	effective carbon number using toluene as reference
i-butene	effective carbon number using toluene as reference
acetaldehyde	effective carbon number using toluene as reference
acetone	effective carbon number using toluene as reference
methanol	effective carbon number using toluene as reference
ethanol	effective carbon number using toluene as reference

Table 2. Average concentration in ppbv and effective carbon number (ECN) of the measured VOCs at Birmingham Supersite over August, 2022.

	Species	Mean	SD	ECN
Alkanes	ethane	1.69	1.48	–
	propane	0.65	0.57	–
	i-butane	0.27	0.27	–
	n-butane	0.50	0.46	–
	cyclopentane	0.03	0.04	5.00
	i-pentane	0.19	0.17	–
	n-pentane	0.09	0.10	–
	2-methylpentane	0.05	0.05	–
	3-methylpentane	0.03	0.03	5.00
	hexane	0.03	0.03	–
	heptane	0.02	0.02	–
	i-octane	0.02	0.02	–
	nonane	0.06	0.03	9.00
Alkenes	ethene	0.26	0.20	–
	propene	0.10	0.08	–
	t-2-butene	0.01	0.01	–
	1-butene	0.02	0.02	–
	i-butene	0.02	0.01	4.00
	c-2-butene	0.00	0.00	–
	1,3-butadiene	0.01	0.01	–
	t-2-pentene	0.00	0.01	–
	c-2-pentene	0.01	0.01	–
	isoprene	0.12	0.13	–
Alkyne	acetylene	0.11	0.06	–
Aromatics	benzene	0.07	0.05	–
	toluene	0.16	0.14	–
	ethylbenzene	0.04	0.04	–
	m-xylene	0.11	0.12	–
	p-xylene	0.04	0.04	–
	o-xylene	0.04	0.05	–
	1,3,5-trimethoxybenzene	0.01	0.01	–
	1,2,4-trimethoxybenzene	0.05	0.06	–
	1,2,3-trimethoxybenzene	0.01	0.02	–
OVOCs	acetaldehyde	1.09	0.59	1.00
	acetone	2.21	1.13	2.00
	methanol	3.72	2.35	0.75
	ethanol	1.79	1.60	1.50

References

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, John Wiley & Sons, 2016.

Wolf, M. J., Esty, D. C., Kim, H., Bell, M. L., Brigham, S., Nortonsmith, Q., Zaharieva, S., Wendling, Z. A., de Sherbinin, A., and Emerson, J. W.: New insights for tracking global and local trends in exposure to air pollutants, Environmental Science & Technology, 56, 3984-3996, 10.1021/acs.est.1c08080, 2022.

3) Is the research based on case study representative in evaluating photochemical pollution in a certain region?

Authors' reply: Thank you for pointing this out. The Birmingham Supersite has been operated for many years and represents a typical UK urban background environment (Please see detailed description on surroundings of the site in revised manuscript **Page 4 Line 108-112**). As a case study in Birmingham, we evaluated the impacts of changes in VOC sources and speciation on the O_3 production. The evaluation is based on the national trend of VOC emissions that hold for Birmingham where on-road emissions, residential combustion, gas leakage, and non-industrial solvent usage are dominant sources for O_3 precursors. However, the results we obtained in this study may not hold for cities near large industrial VOC sources (i.e., oil and natural gas production (Edwards et al., 2014); steel and cement production (Yao et al., 2021)) can significantly affect composition and chemical reactivity of ambient VOCs. So whilst no location can every truly be considered as 'typical', this site is one that has been used for many years as being representative for a city with a mix of residential, business, energy and road traffic emission sources, and in turn is therefore very similar in nature to many other UK cities.

- In responding to your comment, we have added "The attribution of VOCs sources based on the NAEI data can be thought of as representative for this case study as a typical urban environment, but it might not hold for cities near large industrial VOC sources (i.e., oil refinery and industrial production sites), since they can significantly affect composition and chemical reactivity of ambient VOCs." in the revised manuscript **Page 15 Line 379-383**.

References

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Yao, S., Wang, Q., Zhang, J., Zhang, R., Gao, Y., Zhang, H., Li, J., and Zhou, Z.: Ambient volatile organic compounds in a heavy industrial city: Concentration, ozone formation potential, sources, and health risk assessment, Atmospheric Pollution Research, 12, 101053, 10.1016/j.apr.2021.101053, 2021

4) The research result showed that road transport played the most important VOC role in the case study ozone photochemistry despite it only contributing 3.3% of national VOCs emissions in 2019. Since the proportion of emissions from road transportation is so limited, how to further control?

Authors' reply: In support of Net Zero proposed by International Energy Agency, UK and many countries in the world delivered plans to promote electric-fuel hybrid and full-electric vehicles. UK government announced a commitment to phasing-out sales of new internal combustion engine vehicles by 2030. The target is set by 2035 in European countries. Government of China has been implementing policies on reduction/exemption of tax, as well as subsides on buying full-electric vehicles since 2012 (Wang et al., 2017). The widespread policy will over time lead to significant VOCs reductions from on-road transportation and related fuel (i.e., gasoline, natural gas, and liquefied petroleum gas (LPG)) usages.

We believe that this question is already well answered through Figures 5 and 6 and the Conclusion section (detailed discussion please see revised manuscript **Page 15-18**). In combination these demonstrate that further reducing road transport emissions, ultimately to 100% abatement, does continue to deliver further reductions in $P(O_3)$. Once 100% abated, however, the remaining

VOC sources such as solvents control $P(O_3)$ rates.

References

Wang, N., Pan, H., and Zheng, W.: Assessment of the incentives on electric vehicle promotion in China, Transportation Research Part A: Policy and Practice, 101, 177-189, 10.1016/j.tra.2017.04.037, 2017.