Dear Dr. Eleanor:

Thank you for giving us the opportunity to submit a revised draft of our manuscript titled "The impact of multi-decadal changes in VOCs speciation on urban ozone chemistry: A case study in Birmingham, United Kingdom." to the journal of *Atmospheric Chemistry and Physics*. We sincerely appreciate the time and effort and you and the reviewers have dedicated to providing your insightful feedbacks on our paper.

We have incorporated changes in responding to all reviewers' valuable comments and suggestions. Revised texts within the revised manuscript have been marked by red color, and newly added Table/Figure captions have been highlighted by yellow. We have also corrected grammar errors/fragment sentences throughout the manuscript, and these changes have been marked by green color.

Below are point-by-point responses to the reviewers' comments and concerns.

Best Regards,
Jianghao Li (on behalf of all co-authors)

Reviewer #1

I think that the presentation quality requires substantial improvements in three aspects, as follows.

1) The VOC observed datasets are poorly presented. This manuscript did not thoroughly discuss the trend of speciated VOCs but lumped the species into functional groups. It is impossible to evaluate the model evaluation processes without VOC-specific information. In addition, FID is not a common analytical tool to quantify oxygenated VOCs, which requires a thorough description of the analytical characteristics;

Authors' reply: We very much appreciate the time and effort you have put into your comments. Your advice about completing descriptions on VOCs observed datasets is most helpful for improving the quality of this manuscript. We have now added figures and manuscript texts to increase the information on important VOCs species. Please see specific changes as follows:

- Campaign averaged mixing ratio of the individual VOCs species have been added in supplement material, as shown below:

Table 1. Average mixing ratio 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

- A table that summarizes mean mixing ratio of the top 10 species in initial period, O_3 period, and clear-out period have been added into supplement material, as shown below:

Table 2. Average mixing ratio (ppbv) of the top 10 species in selected periods at Birmingham Supersite.

Ranking	**Initial period**		**O_3 period**		**Clear-out period**	
	Species	Concentration	Species	Concentration	Species	Concentration
1	methanol	2.60 ± 0.90	methanol	6.45 ± 2.03	methanol	3.92 ± 1.82
2	acetone	1.66 ± 0.53	acetone	3.90 ± 0.80	acetone	1.80 ± 0.94
3	ethane	1.43 ± 1.40	ethanol	3.33 ± 2.27	ethanol	1.42 ± 0.01
4	ethanol	1.40 ± 1.08	ethane	2.32 ± 1.79	ethane	1.22 ± 0.88
5	acetaldehyde	0.85 ± 0.31	acetaldehyde	2.00 ± 0.38	acetaldehyde	0.82 ± 0.41
6	propane	0.48 ± 0.37	propane	1.05 ± 0.84	propane	0.49 ±0.38
7	n-butane	0.37 ± 0.31	n-butane	0.75 ± 0.57	n-butane	0.35 ± 0.31
8	ethene	0.21 ± 0.17	i-butane	0.39 ± 0.32	i-butane	0.24 ± 0.33
9	i-butane	0.19 ± 0.16	ethene	0.35 ± 0.20	ethene	0.19 ± 0.14
10	isoprene	0.13 ± 0.12	i-pentane	0.32 ± 0.23	i-pentane	0.13 ± 0.11

Average mixing ratios of the top 10 species in selected periods at Birmingham Supersite are listed in Table 2. The top 10 species were represented by methanol, acetone, ethanol, acetaldehyde, and C_2 – C_4 alkanes across initial period, O_3 period, and clear-out period. The top individual species contributing to the total VOCs were methanol (10.3% – 33.6%) and acetone (15.5% – 17.1%), regardless of the subdivided periods. The results highlight large emissions of ethane, propane, n-butane, and i-butane associated with Natural Gas (NG), Liquefied Petroleum Gas (LPG), and propellant use, fuel combustion and evaporation. Above description has been added into the revised manuscript **Page 9 Line 254-260**.

- A figure of diurnal variations of ethene, ethanol, toluene, methanol, ethane, acetylene, acetaldehyde, and acetone in the selected period have been added into supplement material, as shown below:

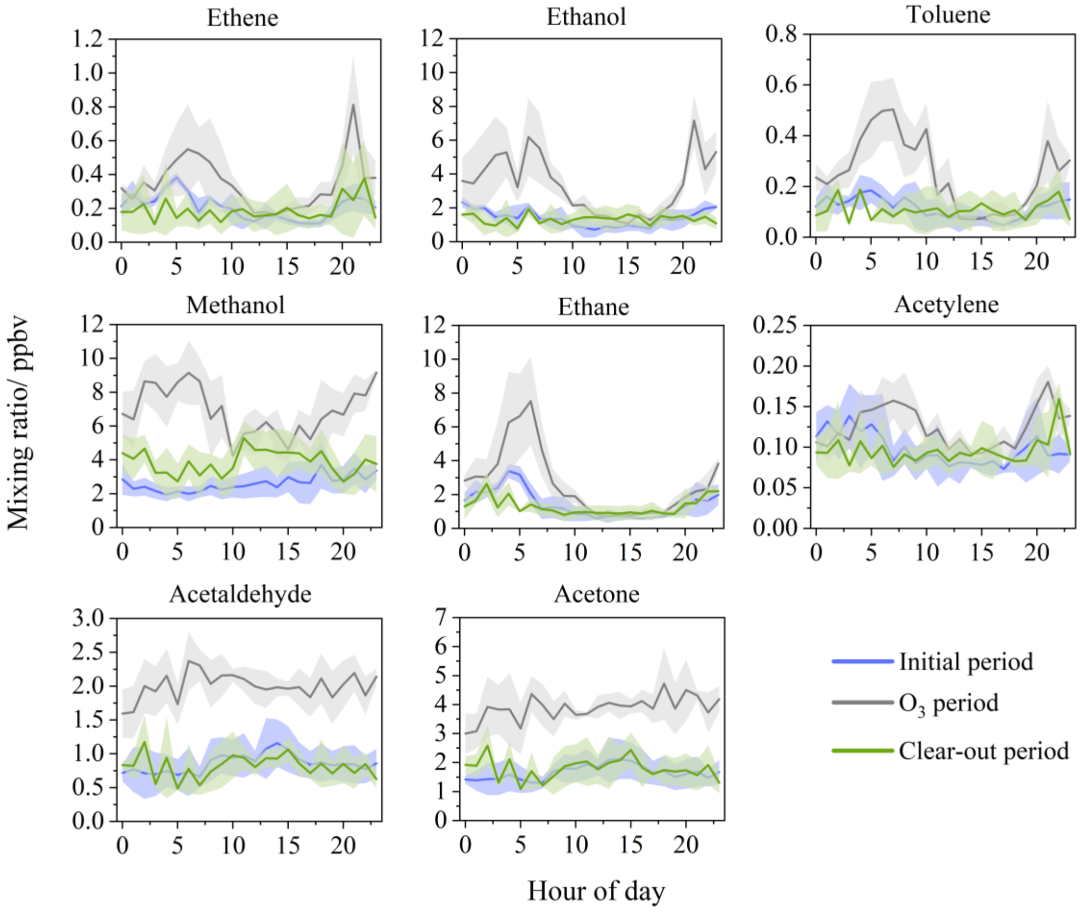

Figure 1. Campaign averaged diel mixing ratio of selected VOCs during different periods: ethene, ethanol, toluene, methanol, ethane, acetylene, acetaldehyde, and acetone. The shaded area represents one standard deviation from the mean.

The general diel profiles for all selected VOCs, except for ethane, showed bimodal pattern (Figure 1). Concentrations were much higher during the night, and lower in the day, due to they were subject to photochemical losses during the daytime. The bimodal pattern is less apparent for methanol and acetone, as they are abundant species originating from many anthropogenic sources in urban areas. For example, methanol was the most abundant species measured at a roadside in UK using Thermal Desorption-Gas Chromatography coupled with Flame Ionization Detection (TD-GC-FID) (Cliff et al., 2023). A separate study on gasoline and diesel vehicle exhausts reported methanol and acetone were the largest OVOCs emitted (Wang et al., 2022). Gkatzelis et al. (2021) conducted Positive Matrix factorization (PMF) analysis based on observed VOCs dataset in New York City, and concluded that acetone was the second most abundant species in measurements and was most attributed to volatile consumer product emissions (90%). (See Section 3.3 for further discussions for anthropogenic sources of OVOCs). Above texts have been added into the revised manuscript **Page 11 Line 278-289**.

- As for your comment “FID is not a common analytical tool to quantify oxygenated VOCs, which requires a thorough description of the analytical characteristics,” the method being used here has been in use, and reported in literature, for more than 20 years – see: Hopkins, J. R., Lewis, A. C., and Read, K. A.: A two-column method for long-term monitoring of non-methane hydrocarbons (NMHCs) and oxygenated volatile organic. The method has been used in support of more than 40 publications by the York research group over the years. The challenges of calibration are no different to MS detection. Here we use direct calibration using 4 ppbv gas standard cylinders and the use of carbon response for this instrument is tightly controlled, with regular carbon-wise responses calculated for all species. Detection limits for this instrument are not higher than 0.1 ppbv and are typically in the 5-10 pptv range. Table 3 lists which species were directly calibrated, and which used equivalent carbon numbers for quantification. Additionally, please see Table 1 for effective carbon numbers of species which used carbon-wise responses. These tables have now been added into the revised supplement. Calibration sequence has been added into the revised manuscript **Page 6 Line 151-156**.

Table 3. 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

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Cliff, S. J., Lewis, A. C., Shaw, M. D., Lee, J. D., Flynn, M., Andrews, S. J., Hopkins, J. R., Purvis, R. M., and Yeoman, A. M.: Unreported VOC emissions from road transport including from electric vehicles, Environmental science & technology, 10.1021/acs.est.3c00845, 2023.

Gkatzelis, G. I., Coggon, M. M., McDonald, B. C., Peischl, J., Gilman, J. B., Aikin, K. C., Robinson, M. A., Canonaco, F., Prevot, A. S., and Trainer, M.: Observations confirm that volatile chemical products are a major source of petrochemical emissions in US cities, Environmental science & technology, 55, 4332-4343, 10.1021/acs.est.0c05471, 2021.

Hopkins, J. R., Lewis, A. C., and Read, K. A.: A two-column method for long-term monitoring of non-methane hydrocarbons (NMHCs) and oxygenated volatile organic compounds (o-VOCs), Journal of Environmental Monitoring, 5, 8-13, 10.1039/B202798D, 2003.

Wang, S., Yuan, B., Wu, C., Wang, C., Li, T., He, X., Huangfu, Y., Qi, J., Li, X.-B., and Sha, Q. e.: Oxygenated volatile organic compounds (VOCs) as significant but varied contributors to VOC emissions from vehicles, Atmospheric Chemistry and Physics, 22, 9703-9720, 10.5194/acp-22-9703-2022, 2022.

2) The emission inventory's speciation information is not thorough enough. All inventory information is presented in a lumped fashion except for alkane. It is vague how this information was integrated into the box model framework;

Authors' reply: The National Atmospheric Emission Inventory (NAEI) estimates emissions of over 600 different VOCs from anthropogenic sources. Due to the large number of VOCs species, we showed the decadal changes (1990 – 2019) of VOCs emissions from the perspective of the source sectors and VOCs classes, rather than attempting to represent such a large range of individual species.

From the perspective of the source sectors: First, decadal changes in 9 emission sectors were presented (Figure 2). Second, all observed VOCs (excluding isoprene) were attributed to the 2019 emission inventory sectors (Table 4). This makes a key assumption that the VOCs, NO_x, and CO at the observation site are affected directly in the same proportion that VOCs are reported in national amounts in the NAEI. Then, corresponding relative contributions of every VOCs species, NO_x, and

CO emitted from the six emission inventory sectors were integrated into the photochemical box model. In this sense, whilst species are bulked together for presentation purposes, they are treated explicitly in the chemical modeling. The ozone sensitivity of those sources was explicitly examined under different scenarios.

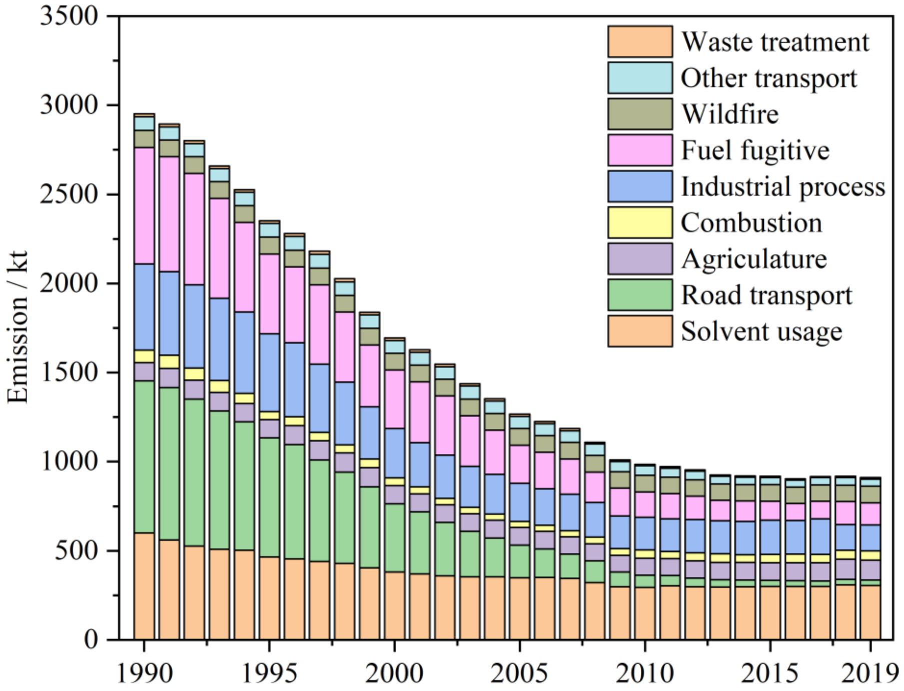

Figure 2. Emissions of VOCs from anthropogenic sources in the UK between 1990-2019. Data: UK National Atmospheric Emissions Inventory (https://naei.beis.gov.uk/, last access 07 September 2023).

Table 4. Relative contributions (%) of ozone precursors emitted from the six emission inventory sectors.

	road transport	**fuel fugitive**	**agriculture**	**industrial process**	**combustion**	**solvents**	**SUM**
ethane	6.0	48.6	39.1	2.1	2.9	0.0	98.7
butanes	34.9	35.2	0.0	1.4	1.2	27.0	99.8
propanes	82.0	9.9	0.0	0.7	0.5	6.7	99.8
C>=6 alkanes	39.5	31.3	0.0	2.2	1.5	22.8	97.2
acetylene	85.8	7.6	–	2.7	0.0	–	96.2
ethene	8.6	86.9	–	4.5	–	–	100.0
butenes	96.1	0.7	–	0.7	1.5	–	99.0
propene	64.1	34.1	–	1.8	–	–	100.0
pentenes	100.0	–	–	–	–	–	100.0
1,3-butadiene	76.0	3.3	–	3.5	11.0	–	93.8
toluene	80.0	3.8	0.3	0.6	1.1	10.3	96.1
xylenes	72.0	1.3	0.3	1.0	1.3	21.6	97.6
other aromatics	71.3	2.9	–	1.8	5.3	12.6	94.0
acetaldehyde	69.0	–	0.2	13.0	0.0	–	82.1
acetone	17.0	–	–	15.4	0.2	65.6	98.3
methanol	–	0.0	–	3.0	–	96.8	99.8
ethanol	7.3	0.1	11.9	48.8	5.8	25.3	99.1
NO_x	33.3	–	3.9	18.4	28.0	–	83.5
CO	14.5	1.2	–	32.3	34.0	–	82.0

From the perspective of the VOCs classes: The specaiation changes are shown in Figrue 3. Results highlighted dominant contributions from alkanes and alcohols in mass terms, the former decreasing as gasoline sources declined, the other increasing as non-industrial solvent and food and drink industry processes emissions followed a different pattern (Figure 3 (a), (b)). We then emphasized the roel of key individual species from alkanes and alcohols (Figure 3 (c), (d)). Contributions of methanol and ethanol to the total alcohol emissions were high over 1990 – 2019 period, increasing from 76.8% in 1990 to 88.4% in 2019. In order to understand the role of the speciation changes in ozone chemistry, we developed a scenario that decreased the mixing ratio of all observed alkanes (this covers the 7 major species in the emission inventory for alkanes) and increased the mixing ratio of methanol and ethanol since they represent most of the national alcohol group emissions. The scenario was further integrated into the box model, and corrseponding changes in ozone production rate was obtained.

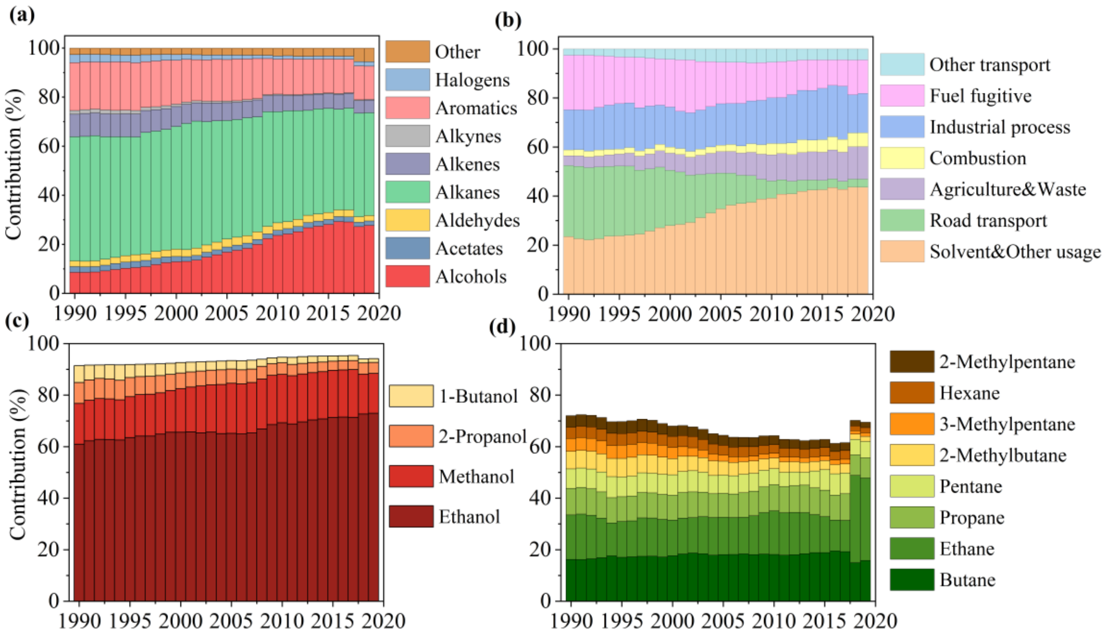

Figure 3. Contributions to annual national UK emissions of VOCs between 1990-2019 by: (a) functional group; (b) by major emissions reporting sector; (c) for four individual alcohols in the overall sub-class of alcohols; (d) for eight individual alkanes in the sub-class of all alkanes.

- We hope that above explanation helps understand how speciation changes are integrated into the box model in this study. It is inevitably a challenge to produce a concise representation of sectors and emissions, when the underlying VOC complexity is very high. We hope this assures the reviewer that individual VOC species effects are properly included in the modelling and later conclusions. In responding to the concerns on emission inventory's speciation information, Figure 4 describes UK emission trends of individual species from different VOCs classes. This has been added into the revised supplement material. The result highlights a national trend since 1990 of decreasing emissions of ethane associated with natural gas leakage, toluene and propane associated with on-road petrol evaporation, as well as reductions of benzene, ethene, and acetylene associated with tailpipe exhaust. Meanwhile, the reduced emissions have been accompanied with increases in emissions of methanol and ethanol. The increase in methanol is largely attributed to increased emissions from car-care products (i.e., non-aerosol products). The increase in ethanol is due to increased domestic and industrial solvent usage. The above text has been added into revised manuscript **Page 14-15 Line 364-370**. Additionally, please see our previous publication for detailed information on NAEI estimated UK emissions of VOCs over 1990 – 2017 (Lewis et al., 2020).

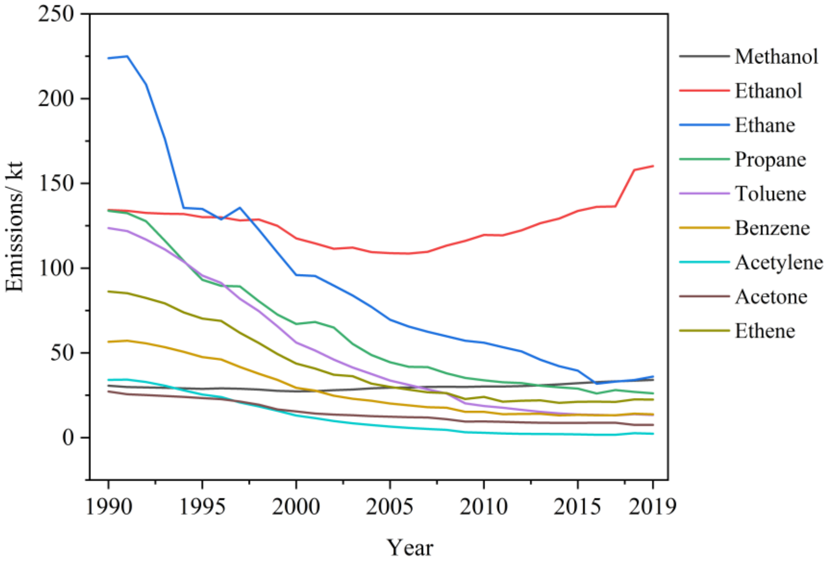

Figure 4. Estimated trends (1990 – 2019) in the UK emissions of selected species corresponding to different VOCs classes.

References

Lewis, A. C., Hopkins, J. R., Carslaw, D. C., Hamilton, J. F., Nelson, B. S., Stewart, G., Dernie, J., Passant, N., and Murrells, T.: An increasing role for solvent emissions and implications for future measurements of volatile organic compounds, Philosophical Transactions of the Royal Society A, 378, 20190328, 10.1098/rsta.2019.0328, 2020.

3) The sensitivity tests of the box model need to be conducted and thoroughly discussed. The oxidation product accumulation in the box model frame must be verified by comparing it with the observed value. This is particularly important as this study concludes that OVOCs play an important role in ozone production. Therefore, it is important to present a quantitative discussion of how much of OVOCs in the studied area is coming from direct emission vs photochemical production.

Authors' Reply: This is a good point to raise and we have adapted the manuscript in response. The reactivity of OVOCs arising through secondary formation at the Birmingham Supersite is a key issue when simulating impacts of changes in primary emissions of OVOCs on production rate of O_3 ($P(O_3)$). The text below and figures show results from the two scenarios are now included in the revised manuscript **Page 12 Line 307-318** and supplement material.

- In order to understand contributions of O_3 formation from direct emissions and secondary formations of OVOCs, we developed two modelling scenarios: (1) all OVOCs species were constrained to observed mixing ratio; (2) all OVOCs species were unconstrained. (2) allowed secondary formations of OVOCs by oxidations of their precursor VOCs. As shown in Figure 5, secondary formations of OVOCs had little impact on O_3 formation in all periods. The simulation of O_3 production using the box model without constraining observed OVOCs slightly underestimated average daily maximum O_3 mixing ratio and $P(O_3)$, compared to the scenario with all observed OVOCs species constrained. The underestimation for average daily maximum mixing ratio of O_3 was 4.8%, 6.9%, and 5.1% in initial period, O_3 period, and clear-out period, respectively. In this case, the underestimation of average daily maximum $P(O_3)$ was 5.1%, 6.0%, and 9.3% in the three periods, respectively. The results demonstrated that in the Birmingham case study, primary emissions of OVOCs played central role in the *in -situ* ozone production.

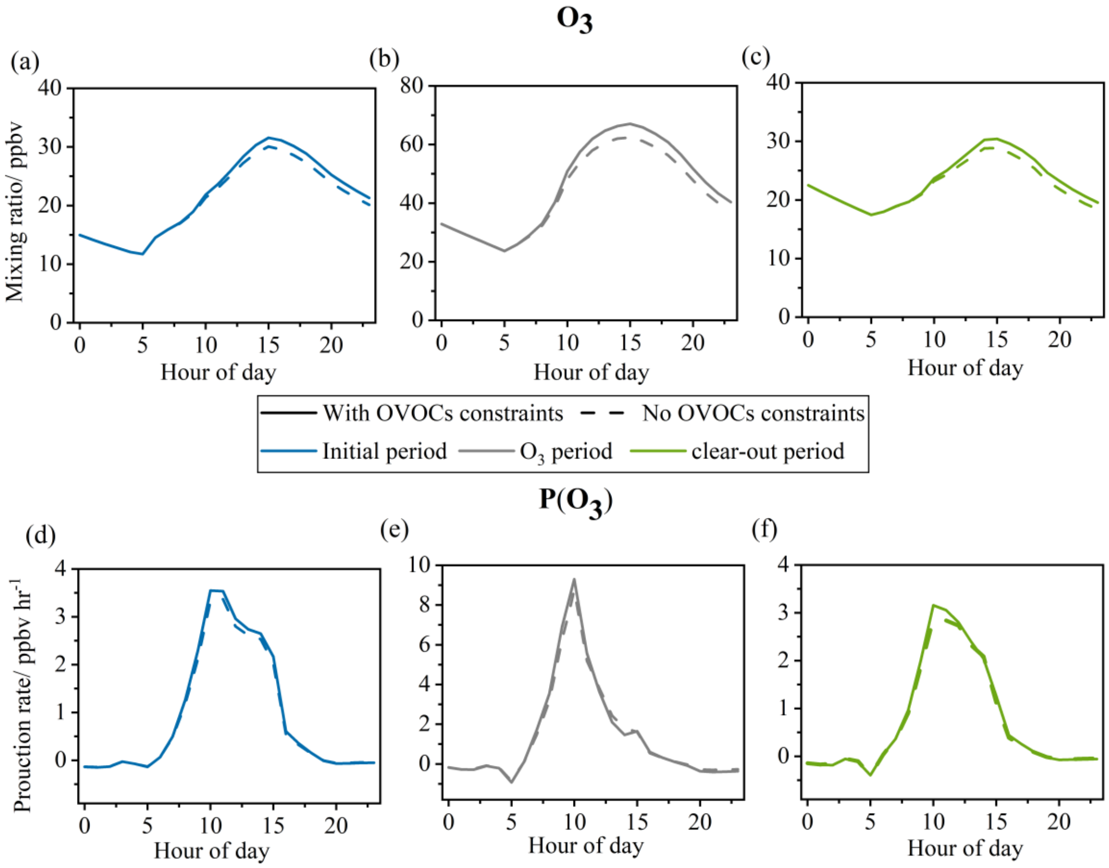

Figure 5. Modelled O_3 mixing ratio (a, b, c) and $P(O_3)$ (d, e, f) with and without photodegradable OVOCs during the select periods.

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

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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

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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**.

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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.