

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, O₃ 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 C₂ – C₄ alkanes across initial period, O₃ 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:

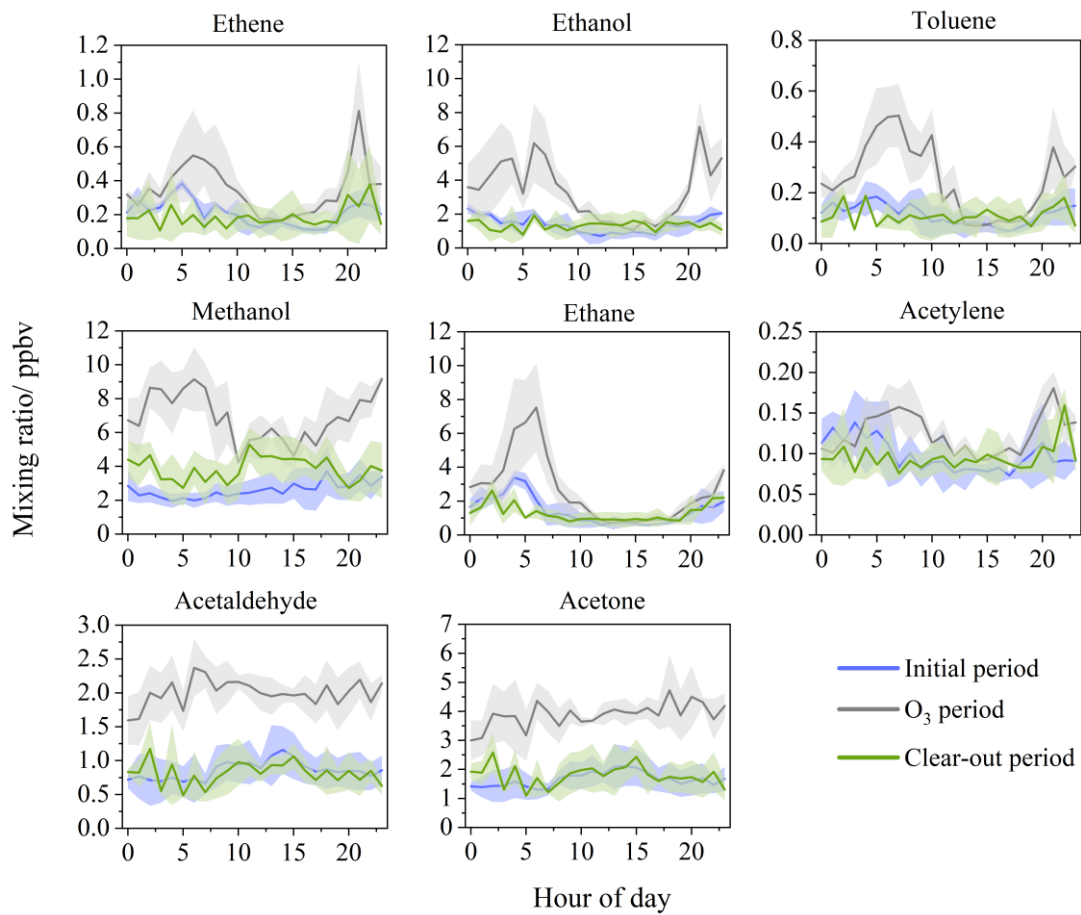


Figure 1. Campaign averaged diel mixing ratio of selected VOCs during different periods: ethene, ethanol, toluene, methanol, ethane, acetylene, acetaldehyde, and acetone. The shaded area represents one standard deviation from the mean.

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

References

- 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.

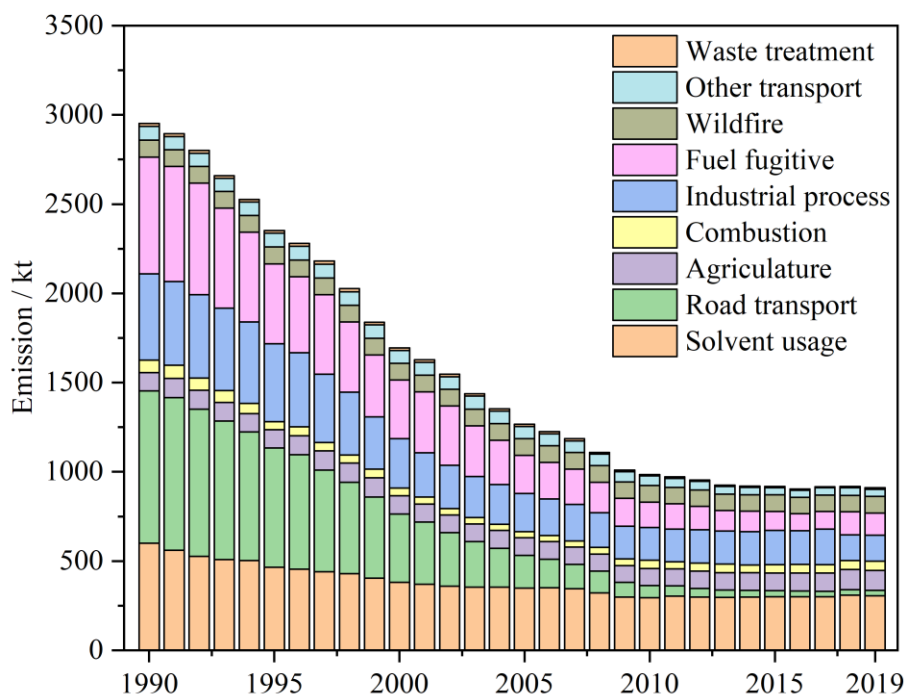


Figure 2. Emissions of VOCs from anthropogenic sources in the UK between 1990-2019. Data: UK National Atmospheric Emissions Inventory (<https://naei.beis.gov.uk/>, last access 07 September 2023).

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 speciation changes are shown in Figure 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 role 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 corresponding changes in ozone production rate was obtained.

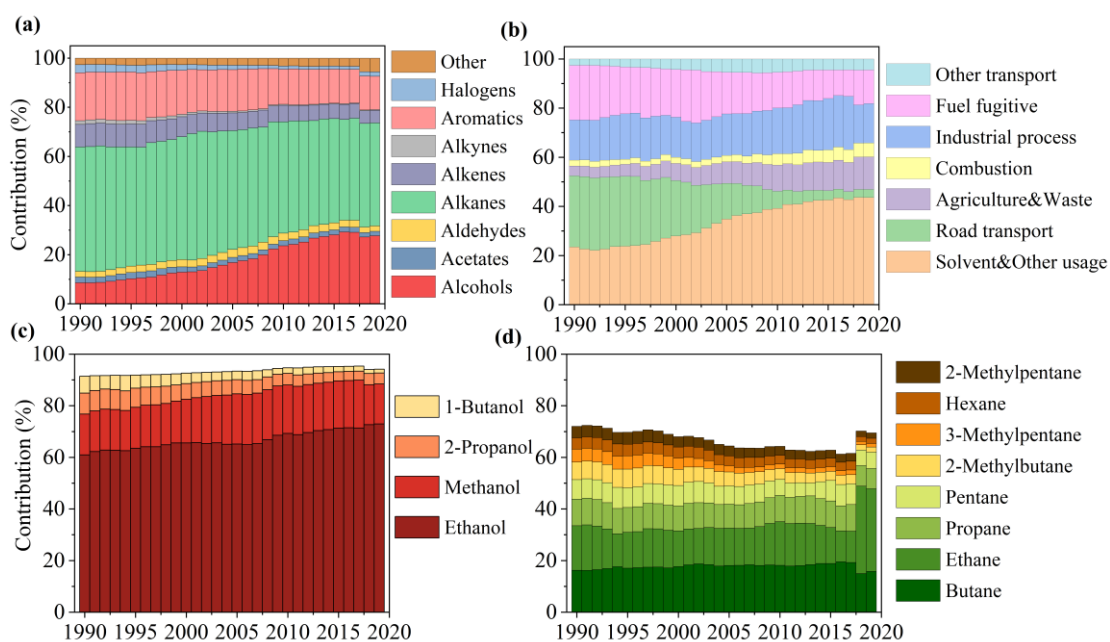


Figure 3. Contributions to annual national UK emissions of VOCs between 1990-2019 by: (a) functional group; (b) by major emissions reporting sector; (c) for four individual alcohols in the overall sub-class of alcohols; (d) for eight individual alkanes in the sub-class of all alkanes.

- 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).

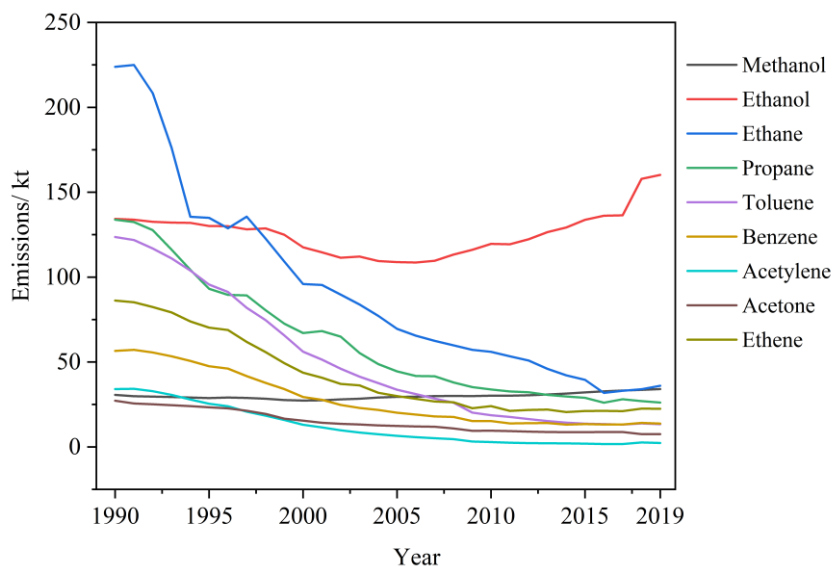


Figure 4. Estimated trends (1990 – 2019) in the UK emissions of selected species corresponding to different VOCs classes.

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 O₃ (P(O₃)). 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 O₃ 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 O₃ formation in all periods. The simulation of O₃ production using the box model without constraining observed OVOCs slightly underestimated average daily maximum O₃ mixing ratio and P(O₃), compared to the scenario with all observed OVOCs species constrained. The underestimation for average daily maximum mixing ratio of O₃ was 4.8%, 6.9%, and 5.1% in initial period, O₃ period, and clear-out period, respectively. In this case, the underestimation of average daily maximum P(O₃) 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.

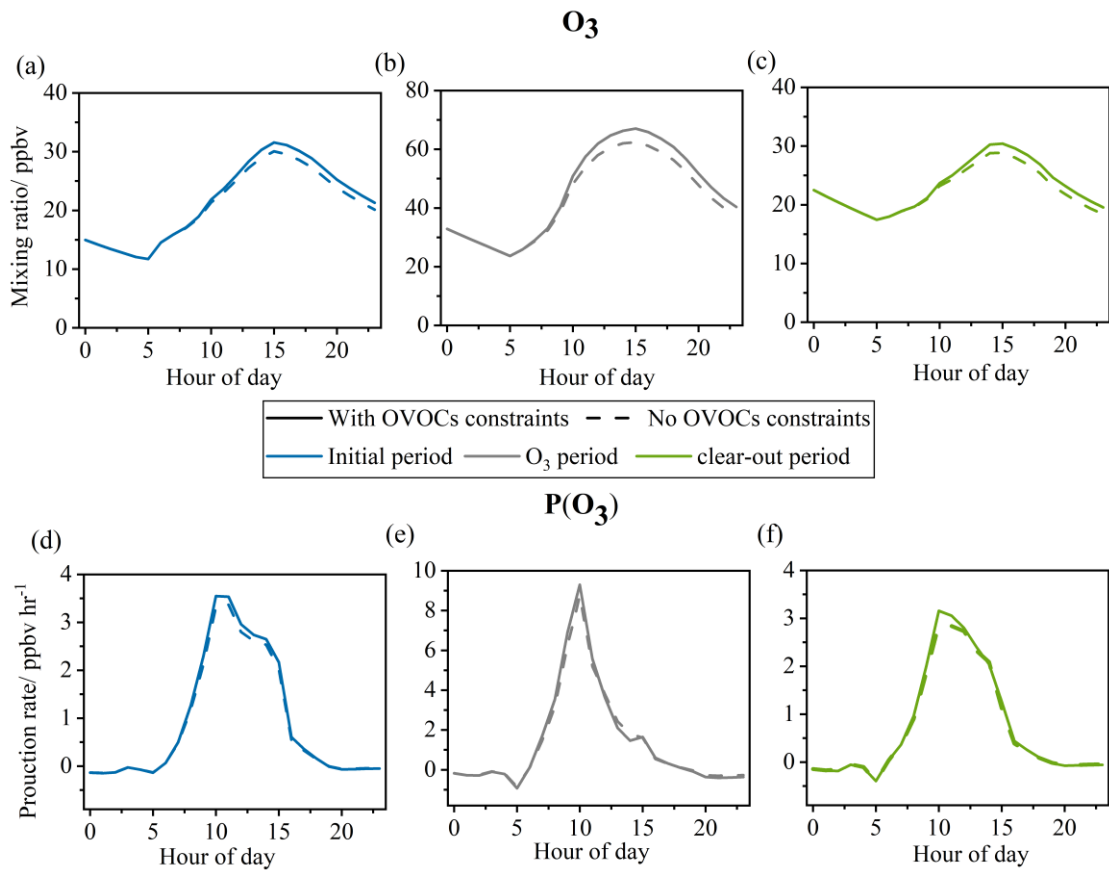


Figure 5. Modelled O₃ mixing ratio (a, b, c) and P(O₃) (d, e, f) with and without photodegradable OVOCs during the select periods.