Dear Dr. Eleanor:

Thank you for taking time to review our submission for the second-round. Yours and the reviewer's concerns on the modelling assumptions have been carefully addressed in the manuscript. This includes: (1) in the Introduction, literature reviews of relevance to the use of emission inventories in ozone modelling and analyses on decadal trends of ozone have been added; (2) in the Results and Discussion, descriptions of modelling assumptions have been elaborated, and limitations of the modelling scenario have been added. Revised text within the manuscript have been marked by red. Please see below as our point-by-point responses to the reviewer's comments.

Best Regards,

Jianghao Li (on behalf of all co-authors)

Reviewer #1

The manuscript titled "The impact of multi-decadal changes in VOCs speciation on urban ozone chemistry: A case study in Birmingham United Kingdom" by Jianghao Li and colleagues focuses on the effects of changes in the speciation of volatile organic compounds (VOCs) on urban ozone production. The study, utilizing a photochemical box model and data from the UK National Atmospheric Emission Inventory (NAEI), evaluates the shift in VOC sources and their photochemical reactivities from 1990 to 2019. Key findings include a significant reduction in VOC emissions from road transport and increased emissions from alcohols due to solvent use and industry processes.

Evaluating the impacts of emission reduction on tropospheric ozone from scientific and policy perspectives is essential. I believe a few more clarifications are necessary to assess this study's main conclusion adequately.

1) The national emission inventory is utilized to interpolate the relative importance of different VOC sources and species in the historical context. Then, the analysis is applied to the *in -situ* observational dataset at a research site in Birmingham. I guess the study assumes that the emission sources and intensities directly correspond to each other between the local and national VOC emissions. It requires a thorough justification.

Authors' reply: In this study, we show the trends in anthropogenic VOC emissions from 1990 to 2019 estimated by the National Atmospheric Emission Inventory (NAEI). The emission reduction in VOCs from the anthropogenic sources described by NAEI were then developed into different modelling scenarios. We use this method to obtain the effect of emission reductions on ozone production sensitivity. According to the inventory, all observed pollutants investigated in this analysis can be almost entirely described by 6 source sectors (Table 1).

We agree that there is an overreaching assumption that the VOCs at the Birmingham Supersite are affected directly in the same proportion that VOCs are reported in national amounts in NAEI, and we reference this explicitly in the text. The Birmingham Supersite has been a major air quality research station operated for many years and is considered to represent a typical UK urban background environment. The analysis assumes that such a background location will reasonably

represent the national trends and distribution of VOC emissions for sources including on-road emissions, residential combustion, gas leakage, and non-industrial solvent usage. It should be noted however that the modelling completed here does not aim to exactly replicate the photochemistry of Birmingham, but to provide a starting point from which different sectors may have emissions reduced.

The technique that integrates emission inventories into box models has been commonly used in the research field of urban ozone pollution, since it provides a reasonable starting point for understanding how each inventory source sector may influence ozone production during a case study event. For example, Coggon et al. (2021) employed VOC emission flux from an emission inventory (fuel-based inventory of vehicle emissions with volatile chemical products) to evaluated contributions of each VOC emission sector to ozone production at an urban background site in New York City. Nelson et al. (2021) used emission inventories from Emission Database for Global Atmospheric Research (EDGAR) to investigate *in -situ* ozone production sensitivity to inventory source sectors at an urban site in Delhi.

As for the reviewer's concerns on using emission inventories in box models, we have specified limitations of this analysis in Line 410 – 414: 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 responding to your comment and to introduce the use of emission inventories in modelling studies, we have added above and additional relevant literature into the revised manuscript (For detailed information, please see Line 110 – 122).

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Table 1. 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

2) Emission changes do not necessarily occur directly in ambient concentration distributions as the atmospheric lifetime of different VOC species widely varies. The direct scaling of ambient VOCs by reflecting emission changes may be flawed.

Authors' reply: Ambient distribution in VOC speciation and concentration are affected by photochemical loss, anthropogenic/natural emissions, and advection process. It is inevitably a challenge to produce a concise representation of sectors and emissions when the underlying complexity of influence factor is very high. However from the perspective of ozone, the effect of reductions in O_3 precursors by sources can be obtained by varying source sectors from emission inventories. We developed model scenarios that vary model constrained concentrations according to their contributions to sources in the NAEI emission inventory. Although this may not accurately reflect how at fine geographic scales individual VOCs are distributed, it does adequately capture the ozone change since this is formed over multi-hour time scales and hence regional domains. The modelling is focused on reproducing integrated ozone production changes, not localized radical concentrations. It the paper was attempting to simulate the latter, then the reviewer's concern would be more relevant.

In the revised manuscript (Line 422 – 424), we have elaborated on the term 'emission change': …For this analysis, emission changes in these sectors can be obtained by reducing model constrained concentrations of VOCs, NO_x, and CO according to their contributions arising from individual emission sectors. At the end of the analysis, we have added limitations of the analysis (Line 439 – 445): It is important to acknowledge the limitation of this analysis. In the real world, reductions in ambient VOCs from the NAEI sectors are affected by photochemical loss rate and advection processes, potentially altering the proportion of VOCs that would be observed with each sector reduction at the measurement site. This would potentially be an important consideration if instantaneously radical budgets were being evaluated, but it is a less significant issue when integrated ozone production effects.

3) The underlying assumption is that all other natural conditions are identical and that only anthropogenic emissions have changed over time. This needs to be justified as natural NO_x emissions and mainly BVOC emissions might have changed. In addition, a broad discussion of how weather conditions have changed in the ozone photochemical context.

Authors' reply: Thank you for pointing this out. Ozone mixing ratios are largely influenced by precursor emission, surface regional transport, deposition, and stratosphere-atmosphere exchange. The interactions among ozone precursors play an important role in urban atmosphere. To implement successful ozone reduction strategies, a good understanding of the non-linear processing of its precursor is imperative. Hence, we focus on the impacts of VOC emissions in the context of historical changes on urban ozone production in this study.

In responding to your comments on influences of biogenic emissions and weather patterns, we have added literature reviews in the Introduction (revised manuscript Line 93 – 109) to discuss previous analyses on decadal trends of ozone. Here we briefly describe research that focuses on that published literature: Previous model analysis of decadal trends of ozone has centred on the association between extreme weather and ozone events and projected changes in ozone concentration under chemical regime change scenarios. This includes (1) understanding the role of anticyclonic conditions and higher temperature during late spring and summer in biogenic emissions and elevated ozone concentrations (Diaz et al., 2020; Hertig et al., 2020; Lewis et al., 2021; Finch and Palmer, 2020); (2) obtaining ozone sensitivities to VOCs, NO_x, and aerosol (Ivatt et al., 2022; Gouldsbrough et al., 2024); (3) investigating potential impacts of future climate change on occurrence of ozone event (Gouldsbrough et al., 2022; Liu et al., 2022).

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