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The impact of multi-decadal changes in VOC speciation on urban ozone chemistry: a case study in Birmingham, United Kingdom

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Table S1. 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 S2. Average mixing ratio in ppbv and effective carbon number (ECN) value 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

Table S3. Descriptive statistics (Mean ± SD) of concentrations of the measured air pollutants and meteorological parameters in selected periods.

Air pollutants (ppbv)	**Initial Period**	**O_3 Period**	**Clear–out Period**
O_3	21.6 ± 8.5	31.5 ± 19.1	26.7 ± 10.7
CO	99.0 ± 57.7	120.4± 34.5	102.3 ± 29.9
NO	0.6 ± 0.6	0.8 ± 2.0	0.6 ± 1.1
NO_2	2.5 ± 3.7	7.6 ± 7.8	3.6 ± 4.1
Parameter	**Initial Period**	**O_3 Period**	**Clear–out Period**
temperature (°C)	18.2 ± 4.1	20.8 ± 5.3	18.1 ± 2.8
relatively humidity (%)	65.5 ± 16.9	58.3 ± 19.1	75.7 ± 15.6
wind speed (m s^{-1})	1.7 ± 1.2	1.5 ± 0.9	1.9 ± 1.3

Table S4. 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

Table S5. 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

Figure Captions

Figure S1. Average contributions (%) of different measured VOCs functional groups to the overall measured total of VOCs and the mean concentrations of the sum of all measured VOCs in each of the three periods.

Figure S2. 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.

Figure S3. Diurnal variations of the modelled average OH reactivity (*k*(OH)) for VOCs, CO, and NO_x in initial period(a), O_3 period (b), and clear–out period (c).

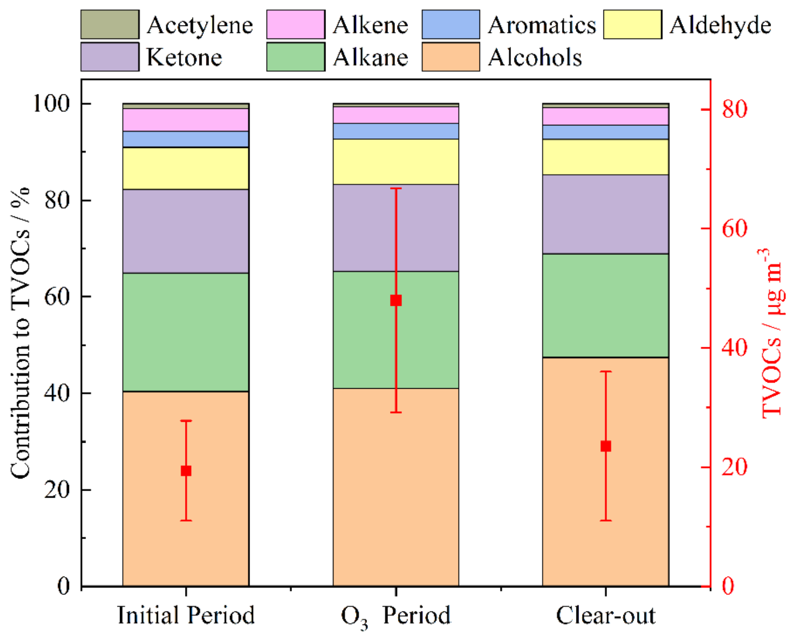
Figure S4. Modelled average chemical budgets of O_3 in the selected periods.

Figure S5. Modelled O_3 (a, b, c) and $P(O_3)$ (d, e, f) with and without all observed photodegradable OVOCs constrained in the selected periods.

Figure S6. 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).

Figure S7. UK National Atmospheric Emissions Inventory estimated trends (1990-2019) of emissions of selected VOCs.

Figure S8. Modelled RIRs for anthropogenic sources in selected periods during 08:00-16:00 LST.



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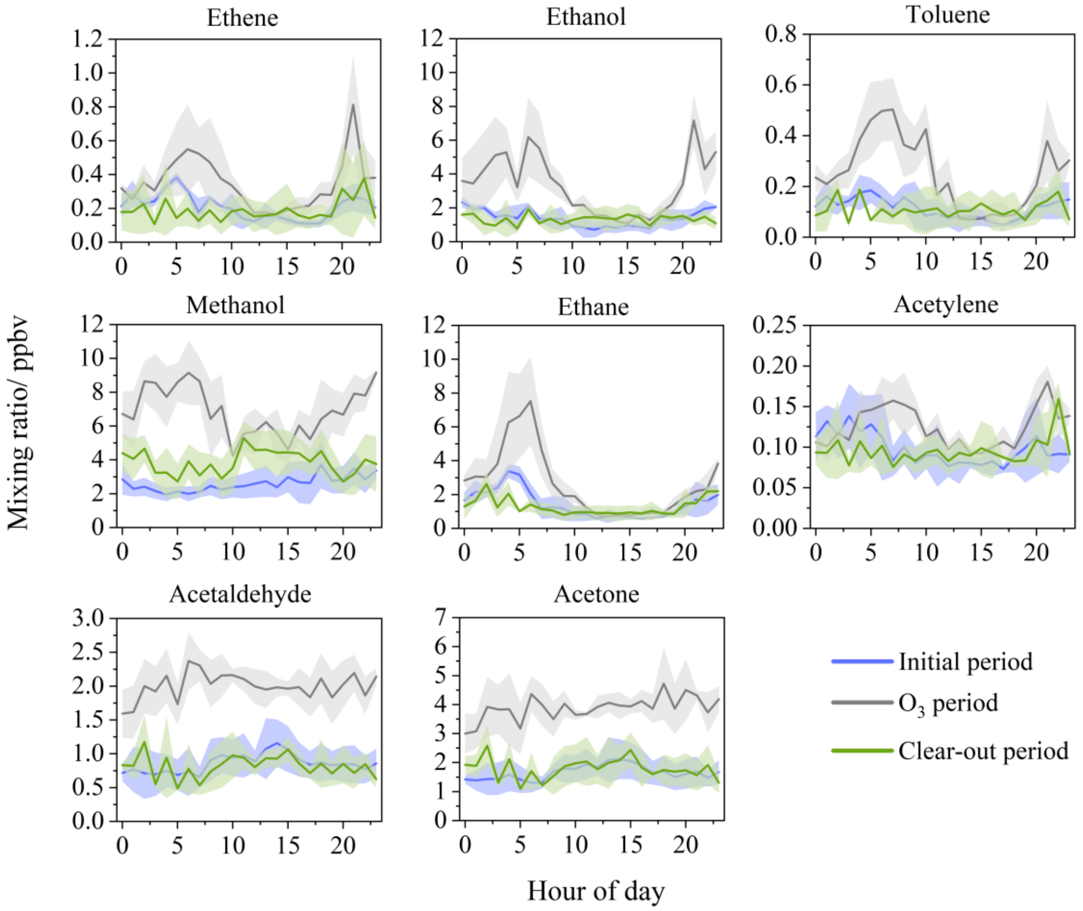

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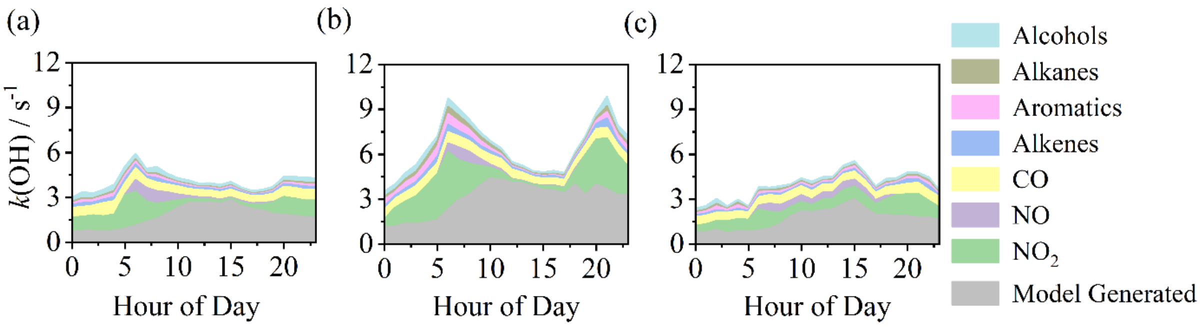

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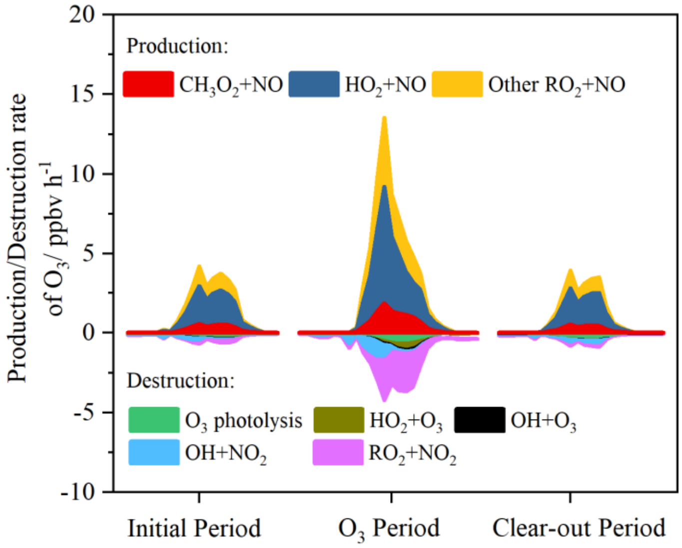

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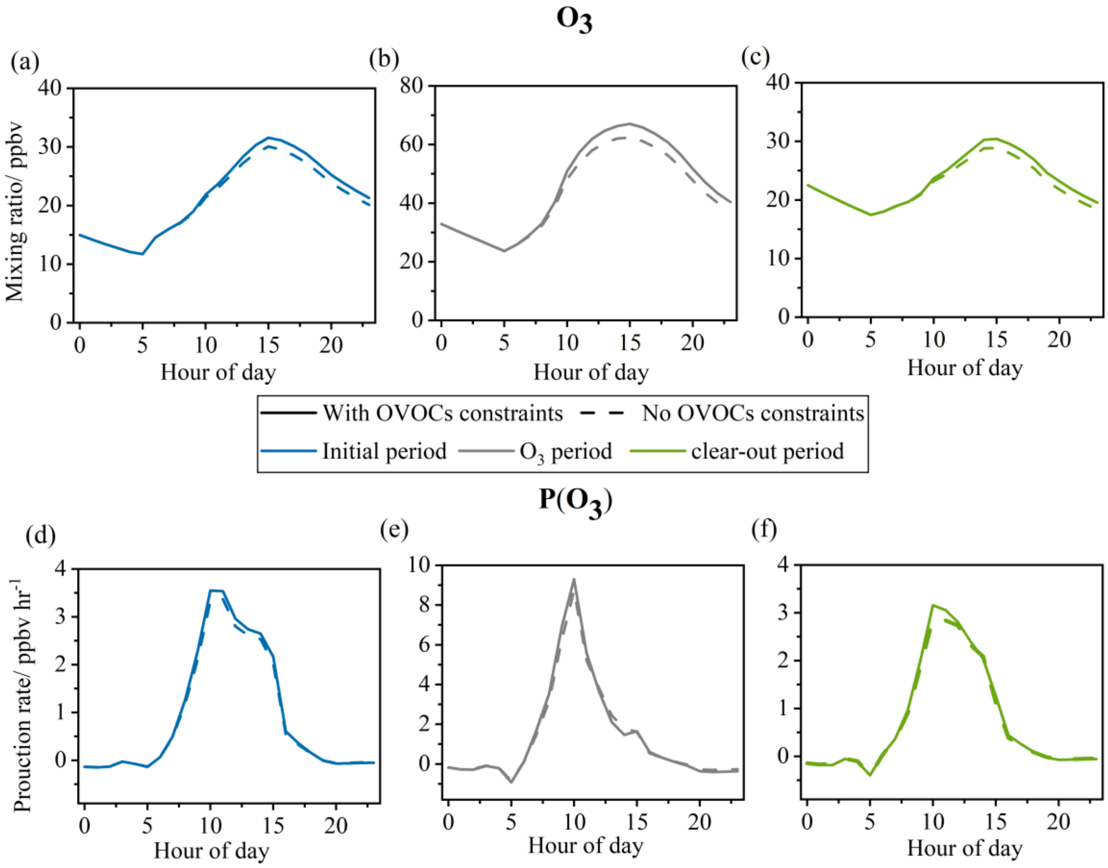

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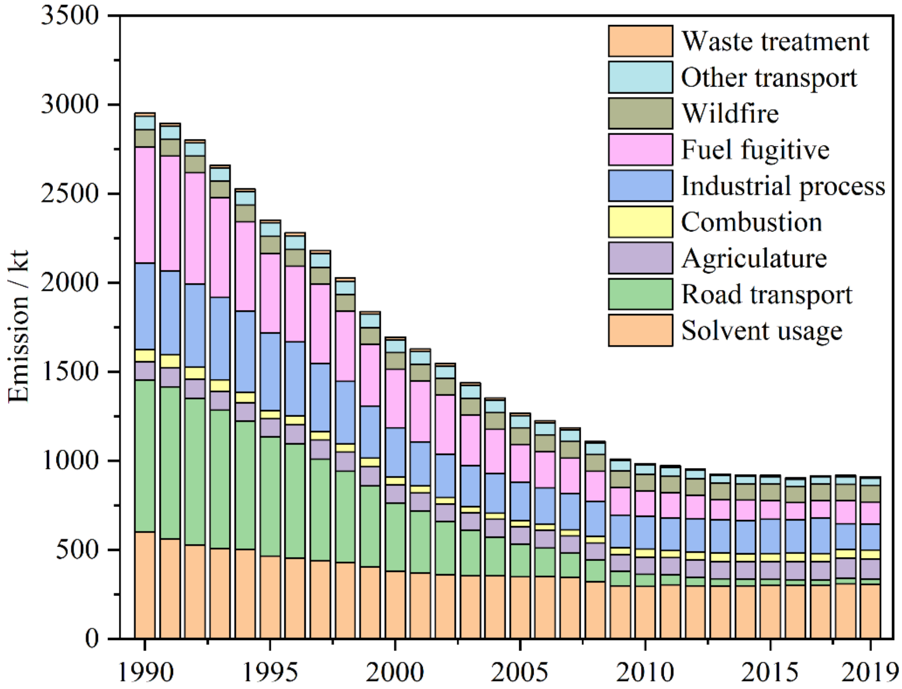

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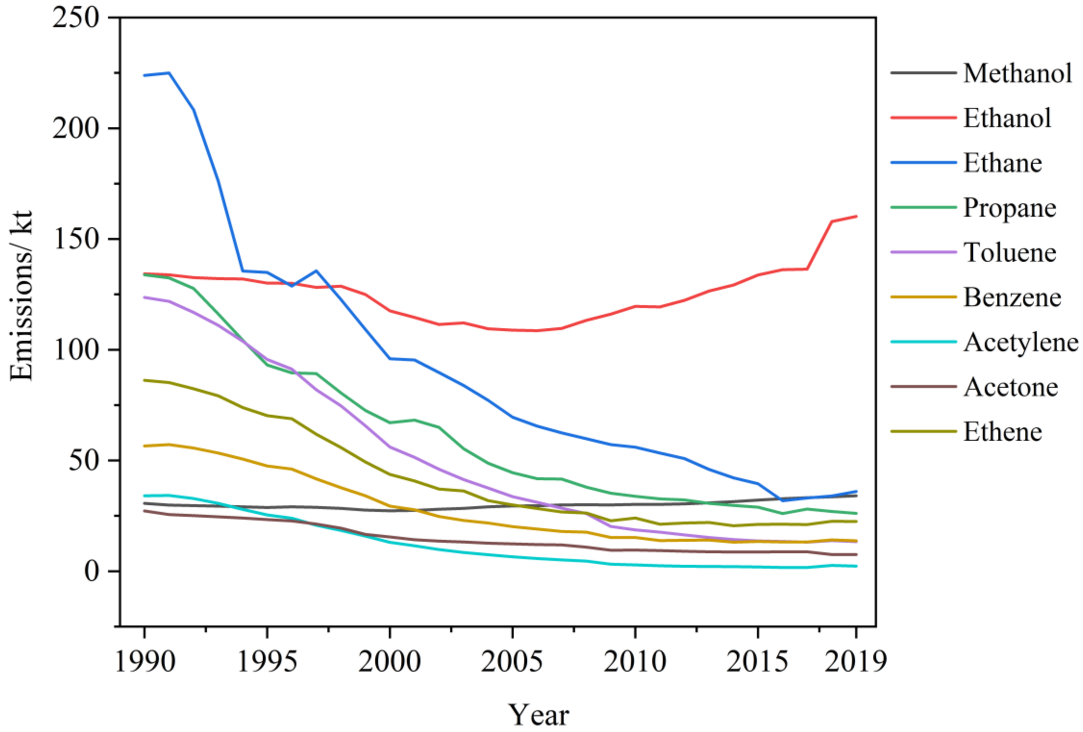
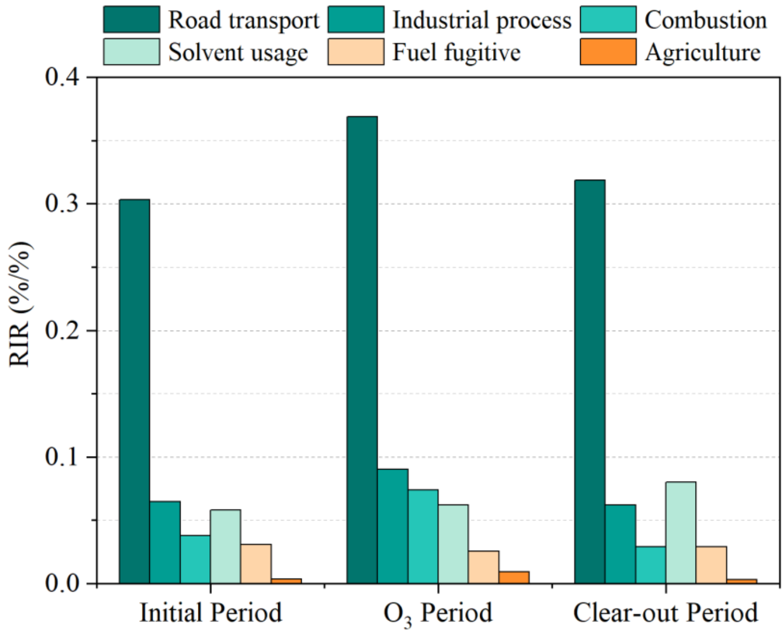


Figure S7. UK National Atmospheric Emissions Inventory estimated trends (1990-2019) of emissions of selected VOCs.



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