Supplement of

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

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Table Captions

Table S1. Descriptive statistics (Mean ± SD) of the concentrations of measured gases and meteorological parameters at the Birmingham Supersite.

Table S2. Relative contributions of ozone precursors emitted from the six emission inventory source sectors.

Table S1. Descriptive statistics (Mean ± SD) of the concentrations of measured gases and meteorological parameters at the Birmingham Supersite.

Species (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)	1.7 ± 1.2	1.5 ± 0.9	1.9 ± 1.3

Table S2. Relative contributions of ozone precursors emitted from the six emission inventory source 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

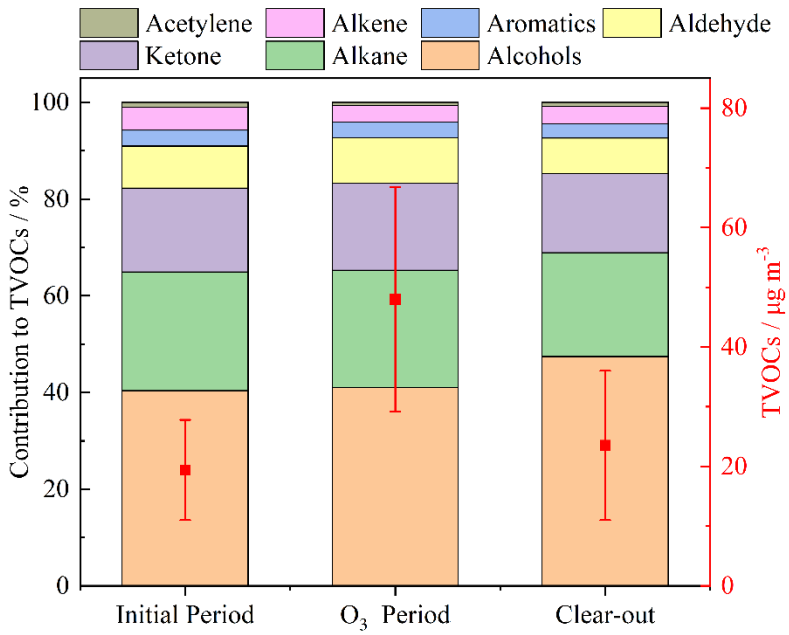
Figure S1. Average contributions of different measured VOCs functional groups to the overall measured total of VOCs and the mean concentrations of the sum of all measured VOCs in the each of the three periods.

Figure S2. Diurnal variations of the modelled average OH reactivity (k(OH)) for VOCs, CO, and NOx in initial period(a), O_3 period (b), and clear–out period (c).

Figure S3. Modelled average chemical budgets of O_3 in the selected periods.

Figure S4. 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 S5. Modelled RIRs for anthropogenic sources in selected periods during 08:00-16:00 LST.



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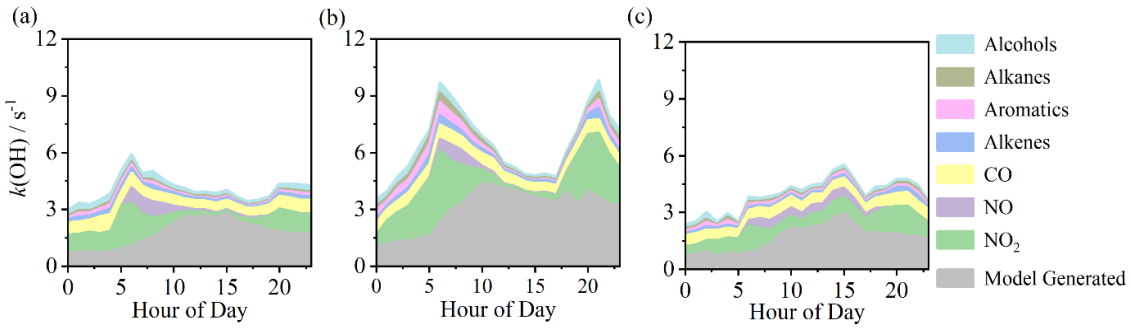

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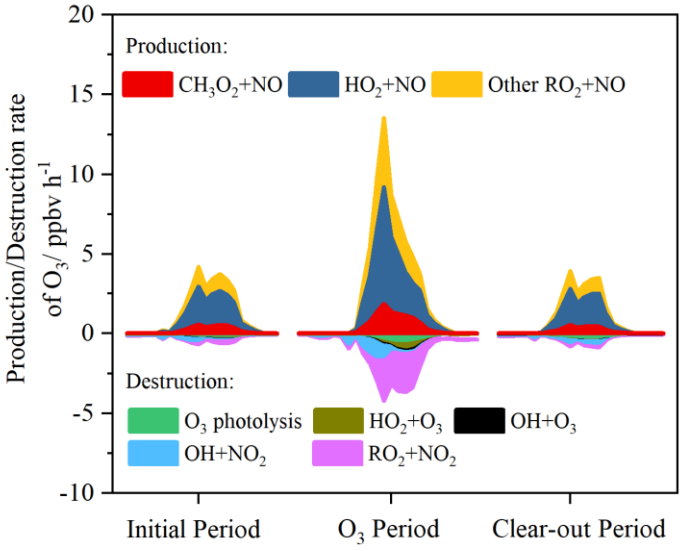

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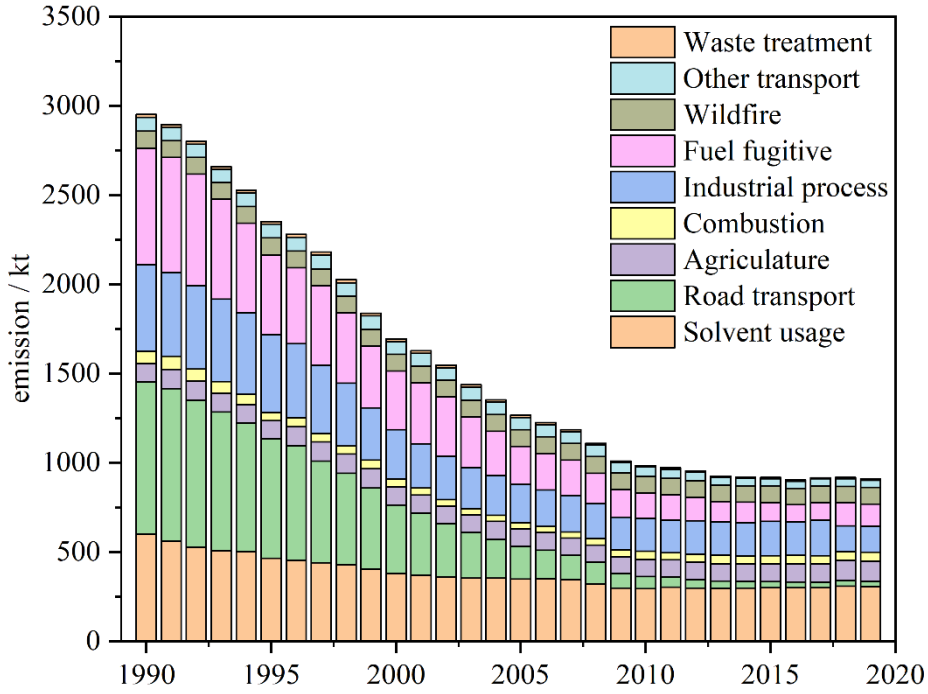

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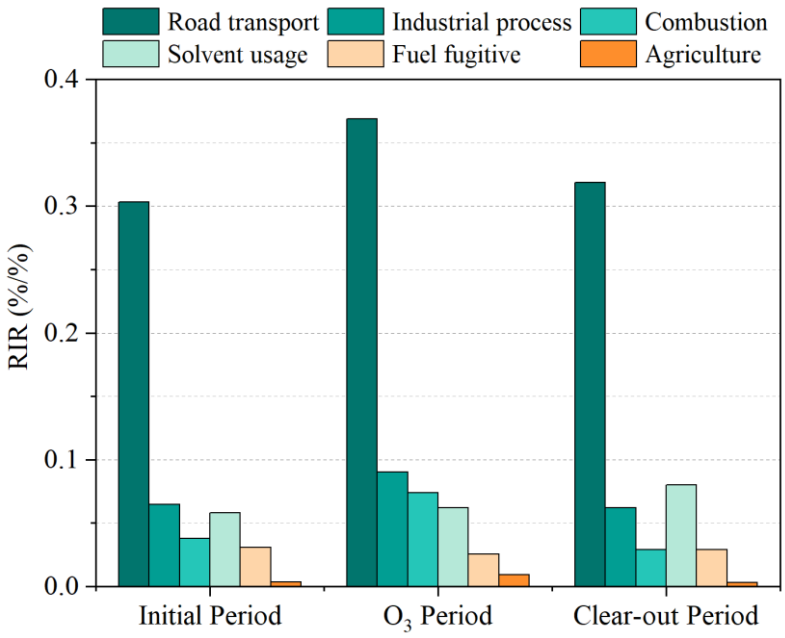

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