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Evaluation of modelled versus observed non-methane volatile organic compounds at European Monitoring and Evaluation Programme sites in Europe

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S1. EmChem19rc species

Table S1. Summary of current primary VOC species in EmChem19rc. Species denoted by $^{\circ}$ are newly added VOC tracers; species denoted by * are tracers for existing lumped surrogates; species formatted in italic indicate those that have secondary production from other VOCs including lumped surrogates. TBUT2ENE represents 2-butene; NPROPOL_T and IPROPOL_T represent 1-propanol and 2-propanol respectively; GLYOX and MGLYOX represent glyoxal and methylglyoxal respectively; MEK represents methyl ethyl ketone. XTERPENE is a lumped surrogate for other biogenic species.

EmChem19rc	**Species**			
Shorter-chain alkane	C2H6_T*	C3H8_T$^{\circ}$	NC4H10_T*	IC4H10_T$^{\circ}$
Longer-chain alkane	NC5H12_T$^{\circ}$	IC5H12_T$^{\circ}$	NC6H14_T$^{\circ}$	NC7H16_T$^{\circ}$
Alkene	C2H4_T*	C3H6_T*	TBUT2ENE_T$^{\circ}$	
Alkyne	C2H2_T$^{\circ}$			
Aromatics	BENZENE	TOLUENE	OXYL_T*	
Alcohol	*CH3OH*	C2H5OH_T*	NPROPOL_T$^{\circ}$	IPROPOL_T$^{\circ}$
Aldehyde	*HCHO*	*CH3CHO*		
Dialdehyde	*GLYOX*	*MGLYOX*		
Ketone	CH3COCH3_T$^{\circ}$	*MEK*		
Carboxylic acid	HCOOH_T$^{\circ}$	CH3CO2H_T$^{\circ}$		
Biogenic VOC	C5H8	α-PINENE	β-PINENE_T$^{\circ}$	XTERPENE
Rest†	OTH_ALKANE_T$^{\circ}$			

Notes †: Rest includes other alkanes and some other species.

S2. Emission sectors and time factors

Table S2 details the 19 emission sectors incorporated in the model, which comprise 13 GNFR sectors and additional 6 subsectors as defined by the CAMS emission inventory. CEIP provides emission data from these 13 GNFR sectors, treating sectors A and F collectively (i.e., without individual data for subsectors A1, A2, F1, F2, F3, F4). By contrast, CAMS reports emissions from the same 13 GNFR sectors, but it divides the emissions from sectors A and F into their respective subsectors. Figs. S1 and S2 illustrate the monthly factors for two countries, the UK and Switzerland, see Sect. 2.3.

Table S2. Relations between EMEP, GNFR_CAMS and SNAP emission sectors

EMEP code	SNAP	GNFR_CAMS code	Source
1	1	A	Public Power
2	3	B	Industry
3	2	C	Other Stationary Combustion
4	5	D	Fugitive
5	6	E	Solvents
6	7	F	Road Transport
7	8	G	Shipping
8	8	H	Aviation
9	8	I	Offroad
10	9	J	Waste
11	10	K	Agri - Livestock
12	10	L	Agri - Other
13	3	M	Other
14	1	A1	PublicPower & Point
15	1	A2	PublicPower & Area
16	7	F1	Road Transport Exhaust - Gasoline
17	7	F2	Road Transport Exhaust - Diesel
18	7	F3	Road Transport Exhaust - LPG
19	7	F4	Road Transport Non-Exhaust

Notes: The EMEP codes 1–19 are used in the EMEP model. The SNAP codes 1–11 are from the earlier EMEP model version.

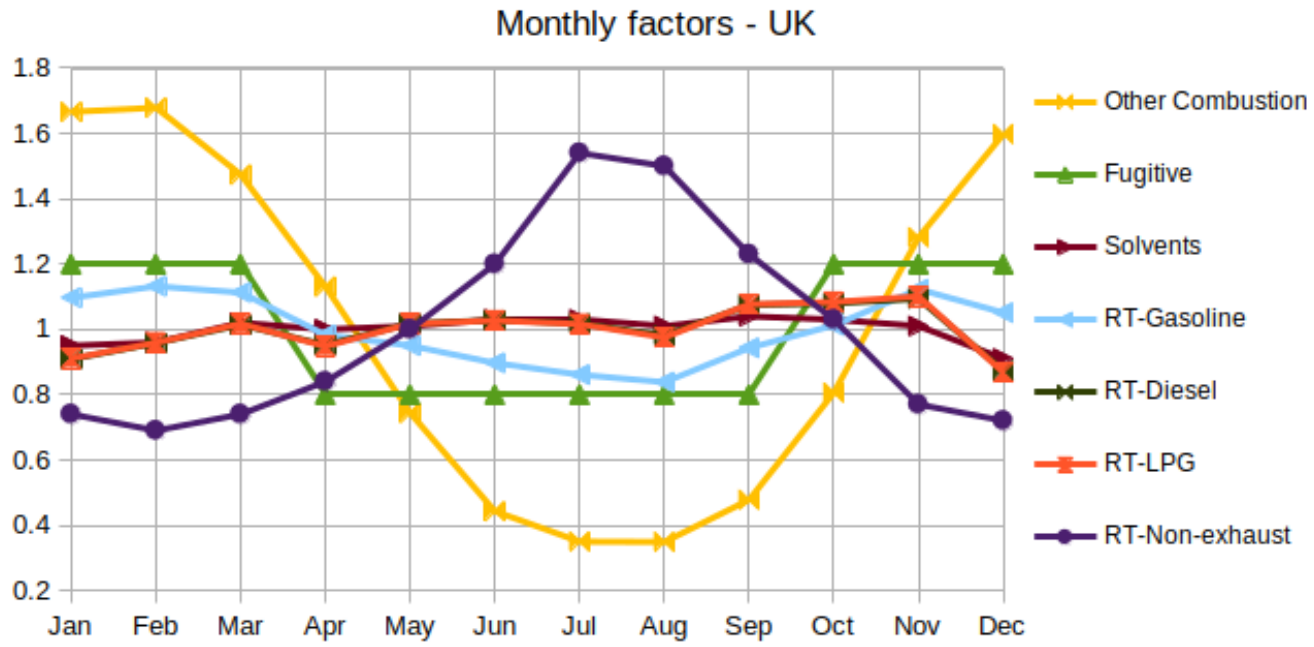


Figure S1. Monthly factors of VOC emissions for the UK, derived from CAMS_TEMPO (Guevara et al., 2021).

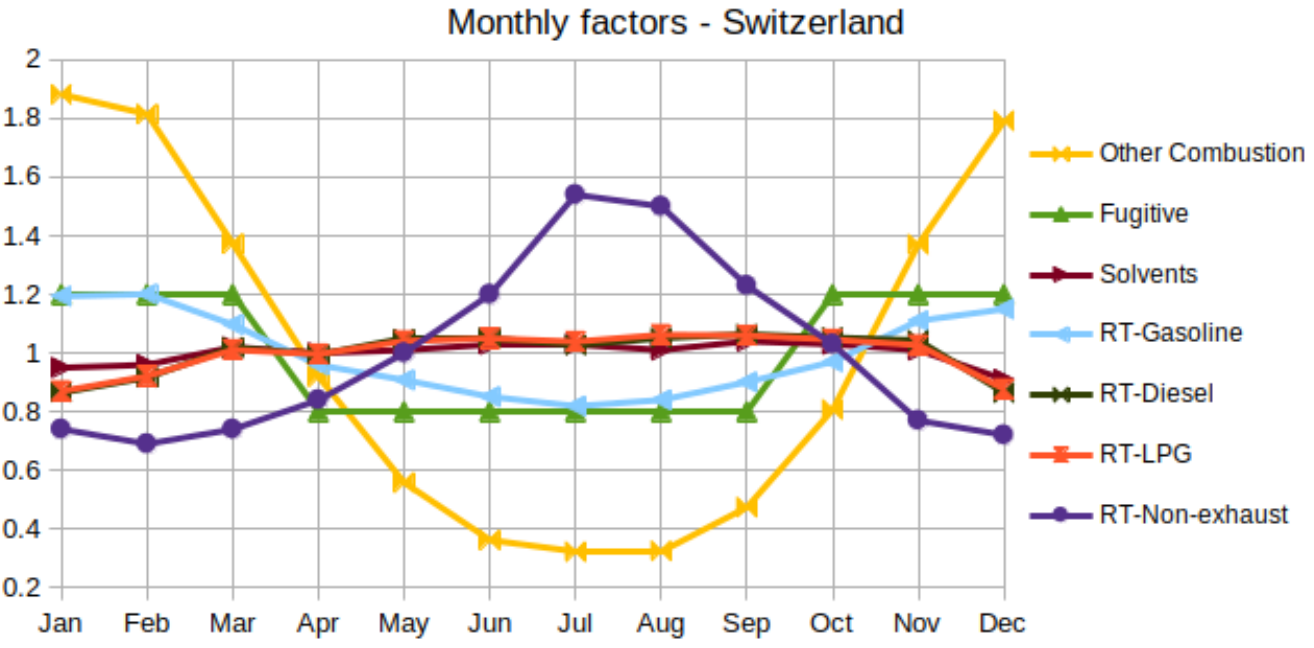


Figure S2. As Fig. S1, but for Switzerland

S3. Measurement sites

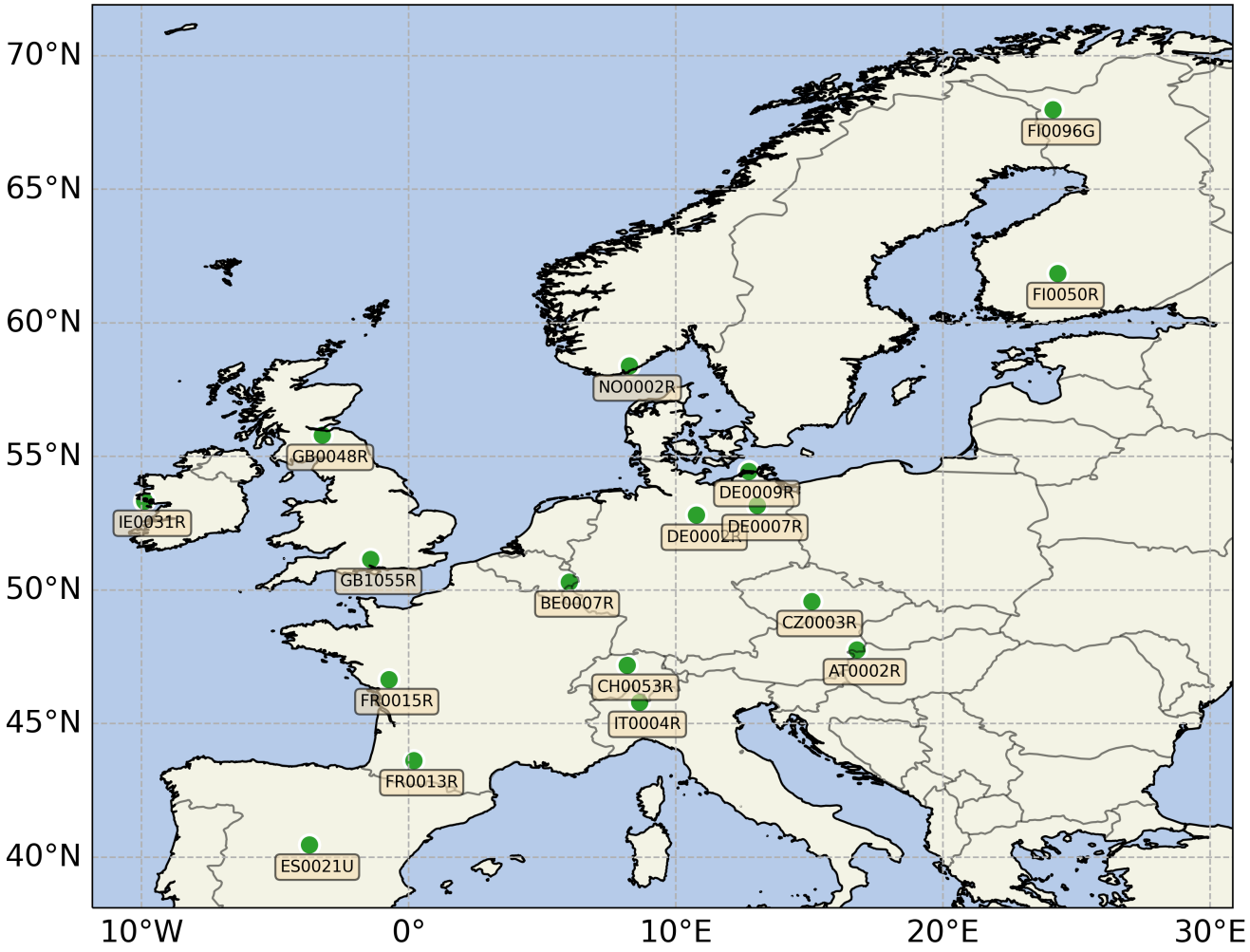


Figure S3. Locations of measurement sites providing VOC measurement used in this study

S4. Lifetimes of VOCs

Table S3. Atmospheric lifetimes of selected VOCs, calculated using CRIv2R5Em rates (the same as MCM rates), and obtained from Seinfeld and Pandis (1998), assuming OH of 1.5×10^6 molecules cm^{-3} (12 hour daytime average), 30 ppb O_3 (24h average), 1 ppt NO_3 (12h night average).

	Lifetime due to:			
	OH	O_3	NO_3	$h\nu$
ethane†	32 d			
propane†	7.2 d			
n-butane†	3.28 d		n.e.	
i-butane†	3.52 d			
n-petane†	1.93 d			
i-petane†	2.09 d			
n-hexane†	1.42 d			
n-heptane†	1.10 d			
ethyne†	10.2 d			
ethene†	5.8 min	10.1 d	6.1 yr	
isoprene†	1.85 h	1.23 d	17.3 h	
benzene†	6.3 d			
toluene†	1.37 d		n.e.	
o-xylene†	13.6 h		n.e.	
n-butane	5.7 d		2.8 yr	
benzene	12 d			
toluene	2.4 d		1.9 yr	
m-xylene	7.4h		200 d	
HCHO	1.5 d		80 d	4 h
C5H8	1.7 h	1.3 d	0.8 h	

† calculated from CRIv2R5Em rates, for 25°C, with n.e. denoting not estimated (reactions are not included in the mechanism).

S5. Alkanes comparisons

Table S4. Annual mean shorter-chain alkanes concentrations (ppb) for observation (Obs) and model (Mod) data in 2018, presented in Fig. 3. The 'n.a.' stands for 'not available', meaning that either the species is not measured at the monitoring site or its observation data does not meet the 65% data-capture threshold for the year.

2018 sites	C2H6_T		C3H8_T		NC4H10_T		IC4H10_T	
	Obs	Mod	Obs	Mod	Obs	Mod	Obs	Mod
CH0053R	1.539	1.478	0.598	0.391	0.256	0.661	0.134	0.104
CZ0003R	1.705	1.666	0.540	0.342	0.220	0.460	0.126	0.160
DE0002R	1.704	1.476	0.693	0.316	0.263	0.419	0.174	0.109
DE0007R	1.748	1.508	0.709	0.326	0.287	0.439	0.185	0.117
DE0009R	1.730	1.508	0.674	0.304	0.263	0.432	0.170	0.147
FI0096G	1.665	1.356	0.521	0.210	0.159	0.100	0.104	0.039
FR0013R	1.379	1.316	0.583	0.220	n.a.	n.a.	n.a.	n.a.
FR0015R	1.454	1.366	0.507	0.232	0.193	0.194	0.107	0.043
GB0048R	1.735	1.459	0.665	0.266	0.239	0.203	0.129	0.054
GB1055R	2.294	1.557	1.109	0.358	0.329	0.407	0.206	0.079

Table S5. Annual mean shorter-chain alkanes concentrations (ppb) for observation (Obs) and model (Mod) data in 2019, presented in Fig. 4. The 'n.a.' stands for 'not available', meaning that either the species is not measured at the monitoring site or its observation data does not meet the 65% data-capture threshold for the year.

2019 sites	C2H6_T		C3H8_T		NC4H10_T		IC4H10_T	
	Obs	Mod	Obs	Mod	Obs	Mod	Obs	Mod
CH0053R	1.549	1.449	0.569	0.369	0.265	0.600	0.128	0.094
CZ0003R	1.524	1.590	0.479	0.318	0.180	0.351	0.111	0.098
DE0002R	1.728	1.532	0.739	0.352	0.292	0.504	0.171	0.137
DE0007R	1.648	1.500	0.700	0.329	0.284	0.464	0.169	0.136
DE0009R	1.713	1.485	0.739	0.317	0.298	0.450	0.177	0.137
FI0096G	1.588	1.324	0.520	0.207	0.165	0.106	0.091	0.040
FR0013R	1.374	1.364	0.476	0.227	0.196	0.253	0.096	0.095
GB0048R	1.910	1.448	0.675	0.267	0.265	0.268	0.133	0.091
GB1055R	2.348	1.710	1.207	0.406	0.450	0.479	0.256	0.100

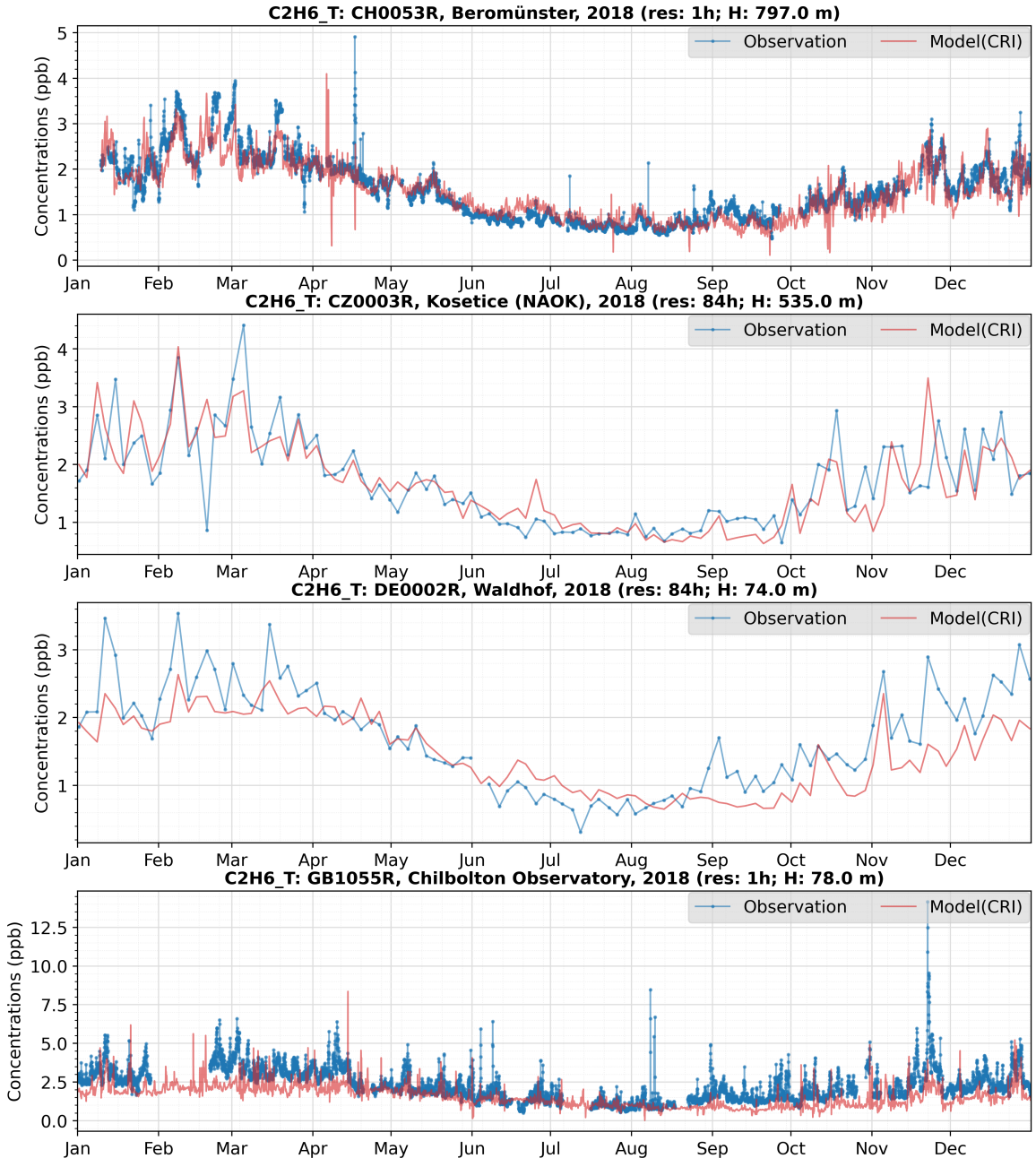


Figure S4. Time series of modelled and measured ethane concentrations in 2018.

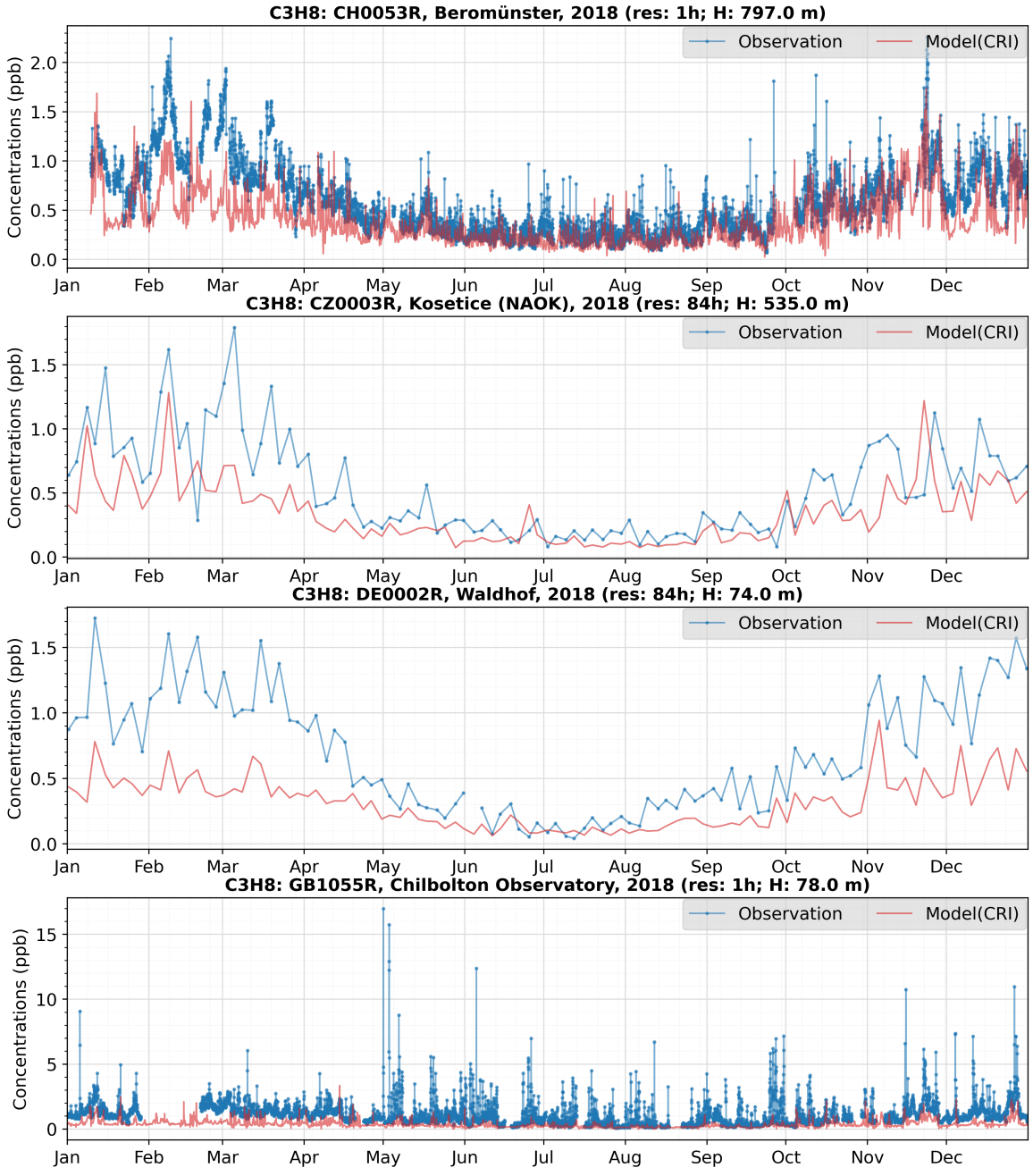


Figure S5. Time series of modelled and measured propane concentrations in 2018.

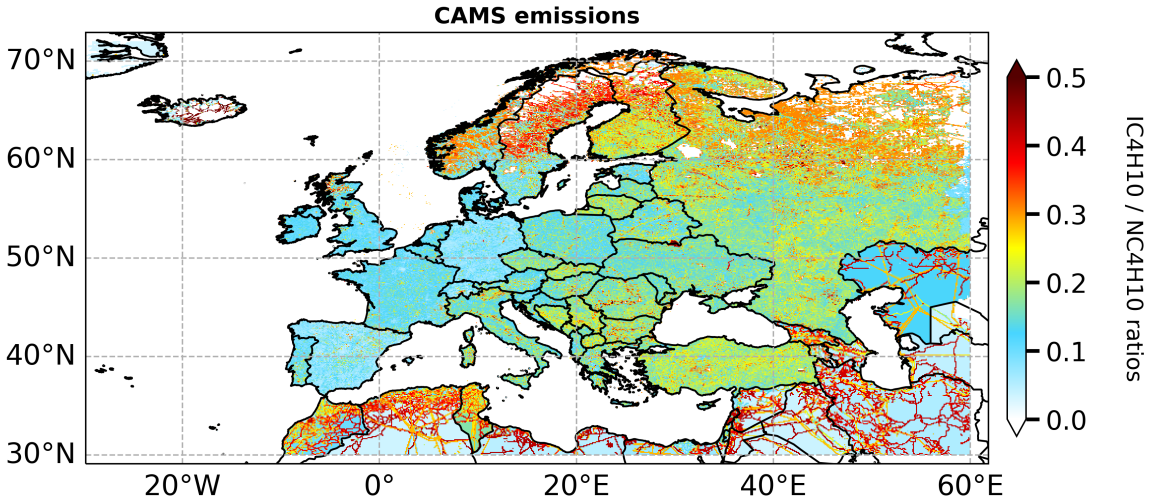


Figure S6. Map of iso-butane to n-butane emitting ratios using the CAMS emission inventory

Table S6. Annual mean longer-chain alkanes concentrations (ppb) for observation (Obs) and model (Mod) data in 2018, presented in Fig. 8. The 'n.a.' stands for 'not available', meaning that either the species is not measured at the monitoring site or its observation data does not meet the 65% data-capture threshold for the year.

2018 sites	NC5H12_T		IC5H12_T		NC6H14_T	
	Obs	Mod	Obs	Mod	Obs	Mod
CH0053R	0.132	0.269	0.211	0.106	0.025	0.057
CZ0003R	0.069	0.107	0.080	0.059	0.019	0.023
DE0002R	0.092	0.136	0.110	0.047	0.033	0.028
DE0007R	0.104	0.126	0.136	0.048	0.029	0.026
DE0009R	0.086	0.097	0.106	0.041	0.025	0.020
FI0096G	0.046	0.027	0.059	0.022	0.012	0.003
FR0013R	0.072	0.053	n.a.	n.a.	n.a.	n.a.
FR0015R	n.a.	n.a.	n.a.	n.a.	0.023	0.022
GB0048R	0.066	0.065	0.077	0.032	n.a.	n.a.
GB1055R	0.100	0.135	0.161	0.056	n.a.	n.a.

S6. Unsaturated NMHCs

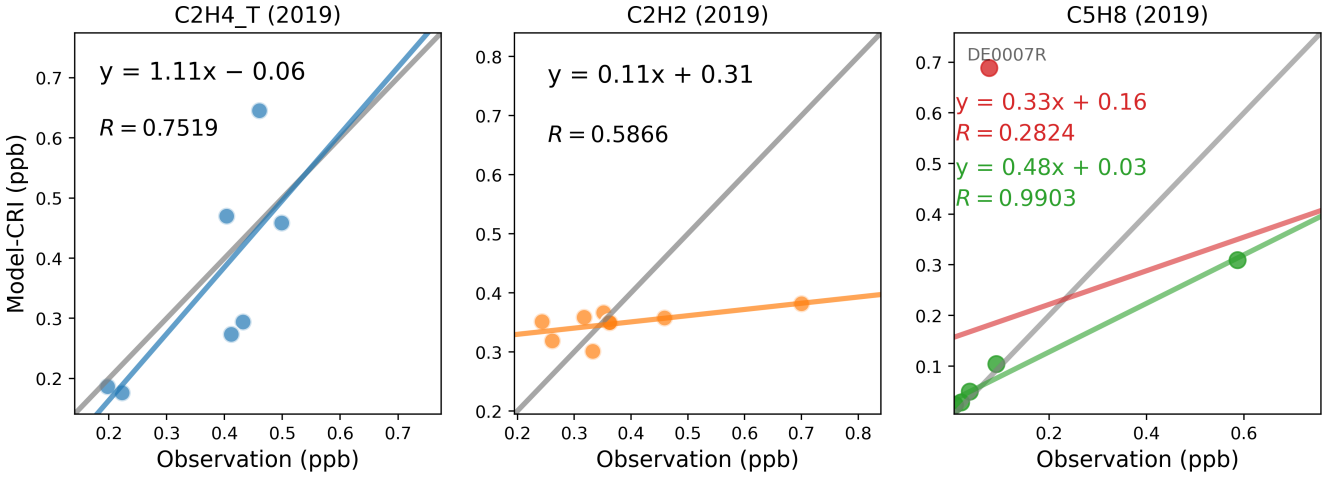


Figure S7. Scatter plots of annual mean modelled and measured ethene, ethyne, and isoprene concentrations in 2019. The term 'CRI' indicates that the model data is calculated using the CRIv2R5Em mechanism. In each plot, the grey line is the 1:1 line, and the other coloured line is the least-squares regression line. For isoprene, the outlier site is plotted in red; the red line is the regression line with the outlier; the green line is the regression line without the outlier. Detailed site codes and their respective data values for each figure panel are provided in Table F2.

Table S7. Annual mean ethene, ethyne, and isoprene concentrations (ppb) for observation (Obs) and model (Mod) data in 2018, presented in Fig. 11. The 'n.a.' stands for 'not available', meaning that either the species is not measured at the monitoring site or its observation data does not meet the 65% data-capture threshold for the year.

2018 sites	C2H4_T		C2H2		C5H8	
	Obs	Mod	Obs	Mod	Obs	Mod
CH0053R	0.472	0.531	0.337	0.344	0.026	0.031
CZ0003R	0.565	0.744	0.401	0.307	n.a.	n.a.
DE0002R	0.517	0.279	0.394	0.337	0.051	0.064
DE0007R	0.597	0.344	0.479	0.325	0.174	1.108
DE0009R	0.574	0.296	0.436	0.341	0.175	0.148
FI0050R	n.a.	n.a.	n.a.	n.a.	0.122	0.083
FI0096G	0.111	0.062	0.272	0.361	0.013	0.029
FR0013R	0.288	0.180	0.263	0.272	0.608	0.335
FR0015R	0.264	0.184	0.279	0.308	0.329	0.091
GB0048R	0.187	0.165	0.452	0.367	n.a.	n.a.
GB1055R	0.476	0.400	n.a.	n.a.	n.a.	n.a.

Table S8. Annual mean ethene, ethyne, and isoprene concentrations (ppb) for observation (Obs) and model (Mod) data in 2019, presented in Fig. S7. The 'n.a.' stands for 'not available', meaning that either the species is not measured at the monitoring site or its observation data does not meet the 65% data-capture threshold for the year.

2019 sites	C2H4_T		C2H2		C5H8	
	Obs	Mod	Obs	Mod	Obs	Mod
CH0053R	0.404	0.470	0.317	0.358	0.019	0.028
CZ0003R	0.460	0.645	0.332	0.301	n.a.	n.a.
DE0002R	0.432	0.294	0.352	0.367	0.037	0.050
DE0007R	0.412	0.273	0.361	0.349	0.077	0.689
DE0009R	n.a.	n.a.	0.362	0.350	0.091	0.104
FI0096G	n.a.	n.a.	0.243	0.351	0.007	0.023
FR0013R	0.223	0.176	0.261	0.319	0.587	0.309
GB0048R	0.198	0.187	0.459	0.358	n.a.	n.a.
GB1055R	0.499	0.459	0.700	0.382	n.a.	n.a.

Table S9. Annual mean benzene, toluene, and o-xylene concentrations (ppb) for observation (Obs) and model (Mod) data in 2018, presented in Fig. 12. The 'n.a.' stands for 'not available', meaning that either the species is not measured at the monitoring site or its observation data does not meet the 65% data-capture threshold for the year.

2018 sites	BENZENE		TOLUENE		OXYL_T	
	Obs	Mod	Obs	Mod	Obs	Mod
CH0053R	0.107	0.160	0.194	0.152	0.020	0.033
CZ0003R	0.147	0.209	0.070	0.077	0.008	0.010
DE0002R	0.109	0.092	0.094	0.072	0.015	0.012
DE0007R	0.122	0.112	0.093	0.068	0.014	0.012
DE0009R	0.106	0.098	0.071	0.069	0.010	0.009
FI0050R	0.111	0.071	0.120	0.041	n.a.	n.a.
FI0096G	0.063	0.020	n.a.	n.a.	n.a.	n.a.
FR0013R	0.090	0.059	n.a.	n.a.	n.a.	n.a.
FR0015R	0.098	0.060	0.097	0.032	n.a.	n.a.
GB0048R	0.074	0.044	n.a.	n.a.	n.a.	n.a.
GB1055R	0.142	0.098	0.110	0.060	0.020	0.015

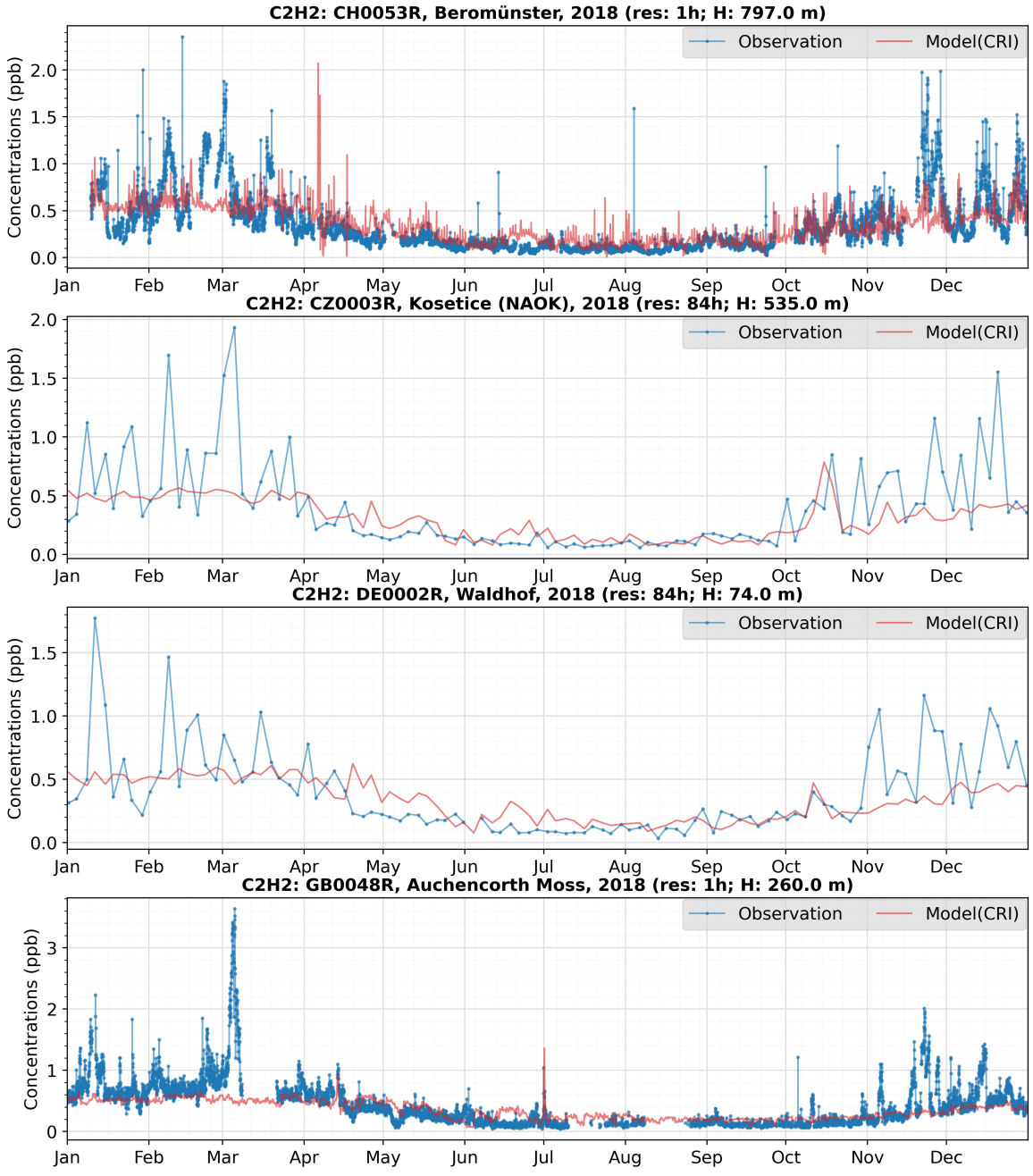


Figure S8. Time series comparisons of ethyne in 2018

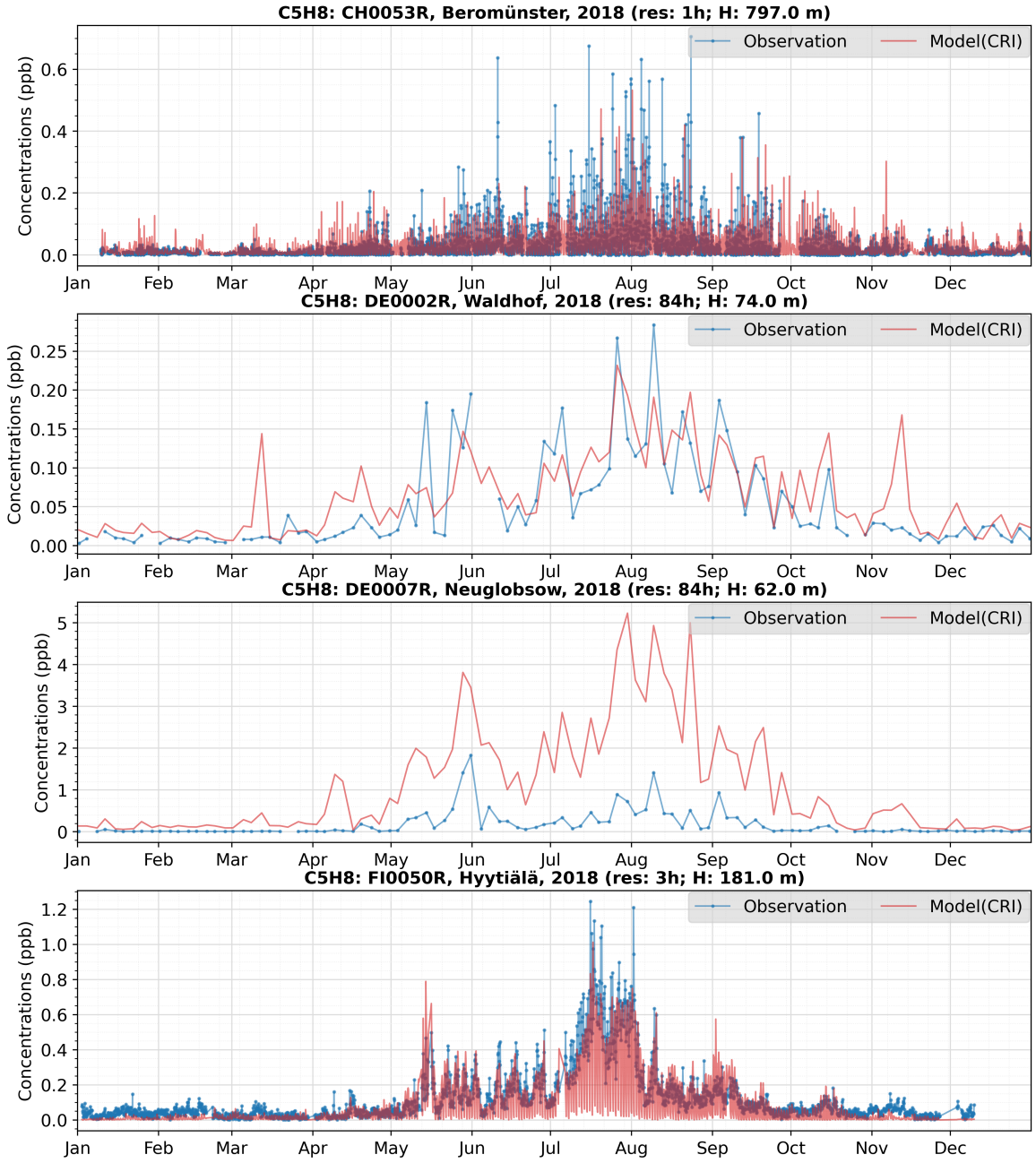


Figure S9. Time series of modelled and measured isoprene concentrations in 2018.

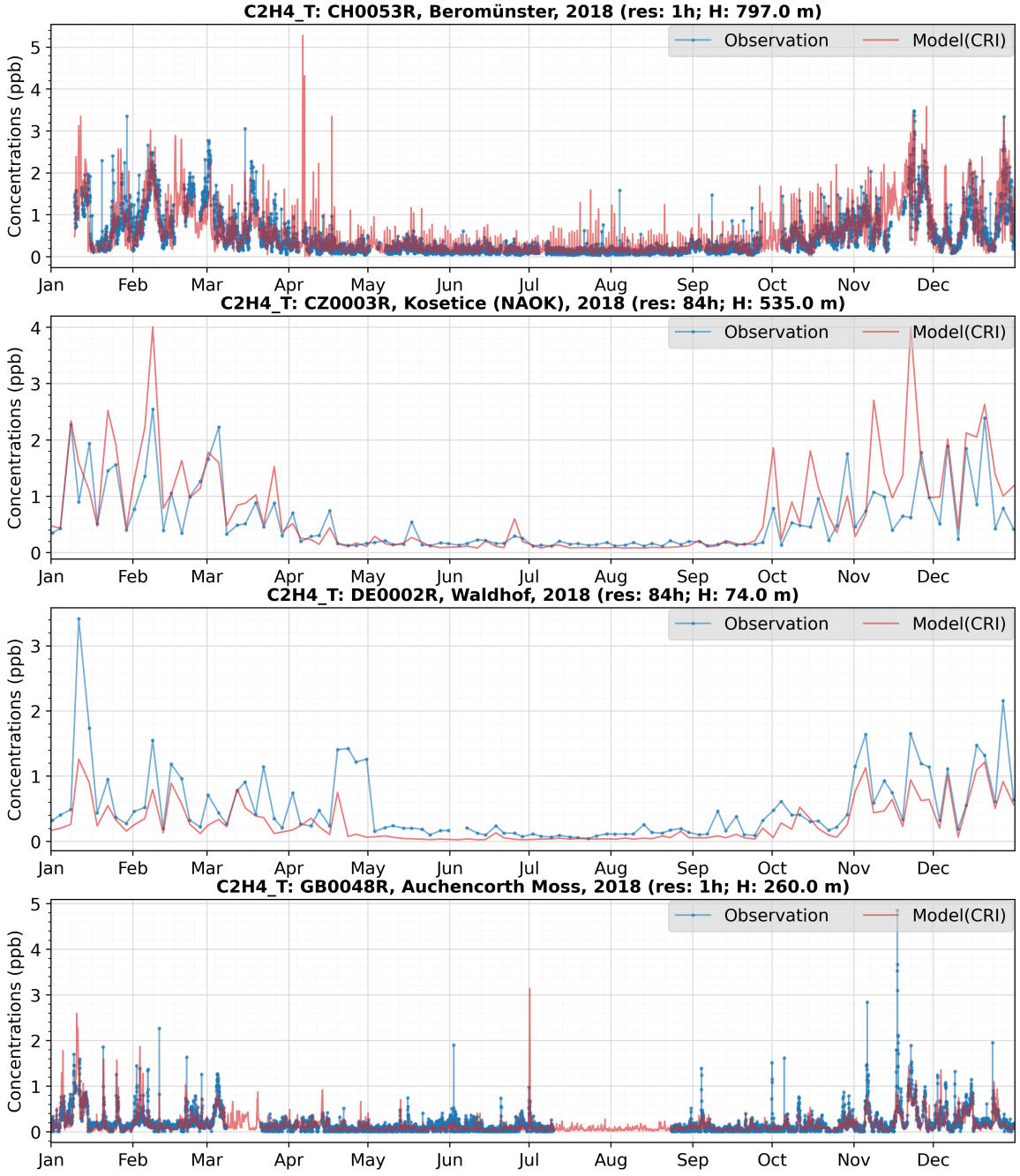


Figure S10. Time series of modelled and measured ethene concentrations in 2018.

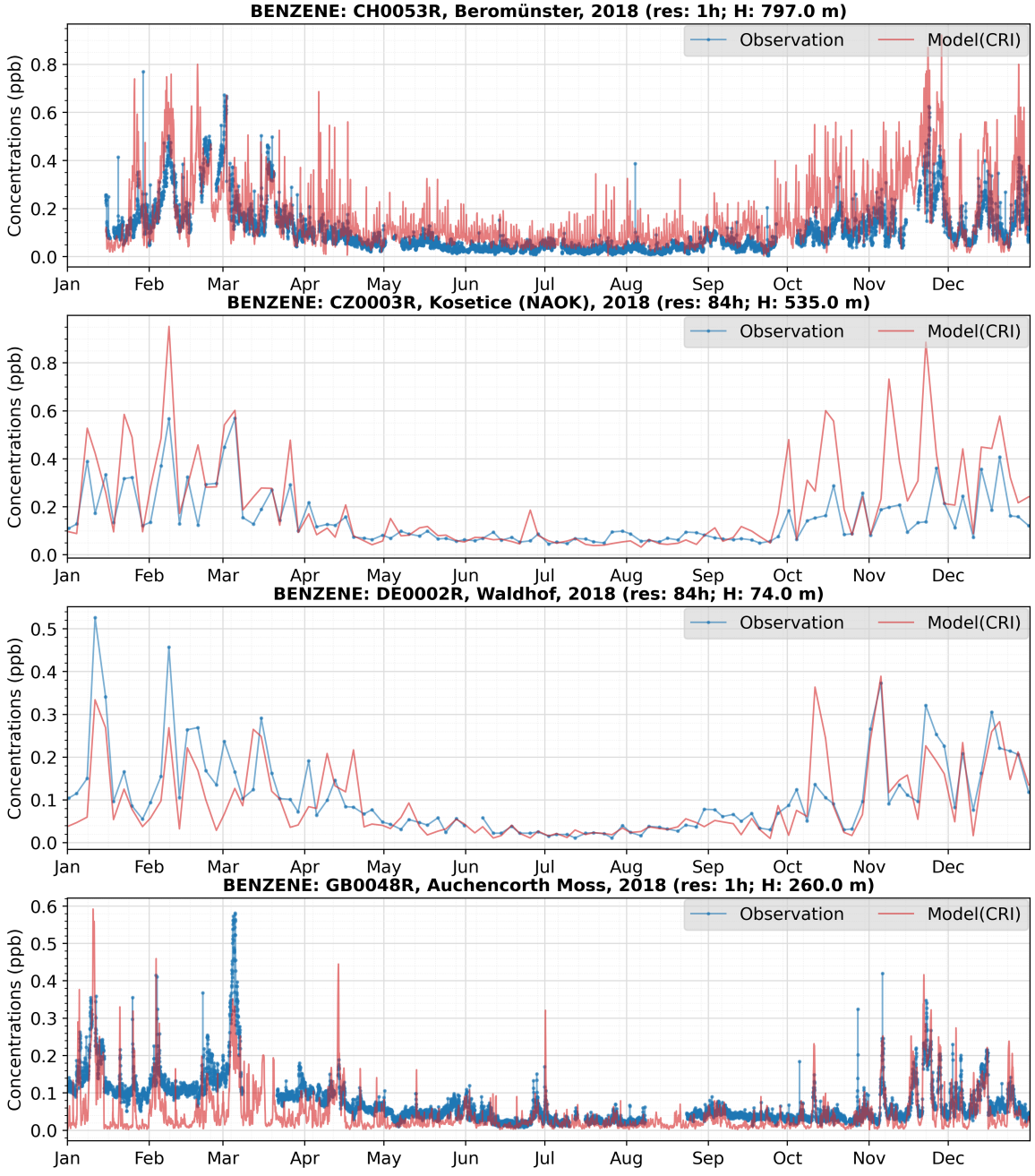


Figure S11. Time series of modelled and measured benzene concentrations in 2018.

S7. OVOCs

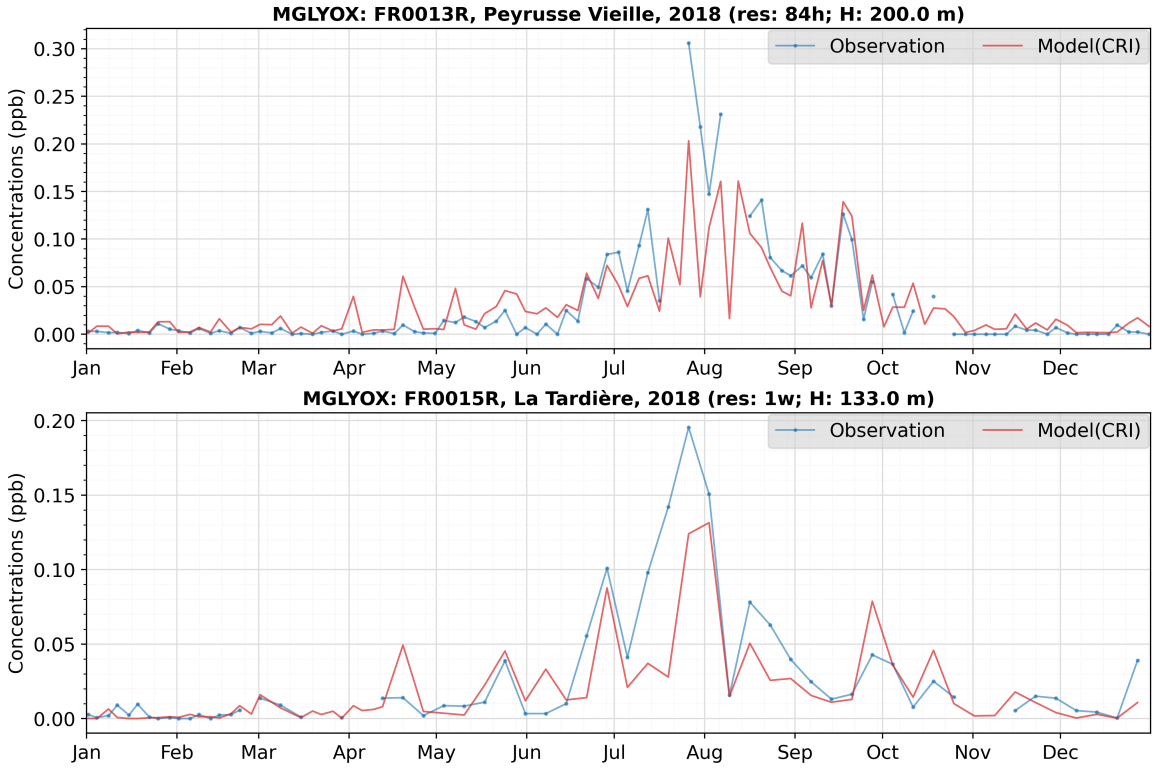


Figure S12. Time series of modelled and measured methylglyoxal concentrations in 2018.

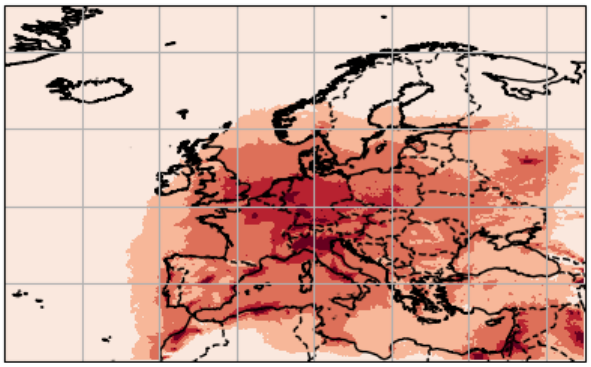
Table S10. Average methanal and methylglyoxal concentrations (ppb) for observation (Obs) and model (Mod) data during 2022 IMP, presented in Fig. 15.

2022 IMP	HCHO		MGLYOX	
	Obs	Mod	Obs	Mod
AT0002R	2.054	1.386	0.254	0.047
BE0007R	2.644	1.717	0.150	0.074
CZ0003R	1.679	0.931	0.098	0.013
DE0007R	1.492	0.995	0.040	0.016
ES0021U	4.056	2.401	0.109	0.082
GB0048R	2.221	0.995	0.051	0.033
GB1055R	2.354	1.972	0.087	0.082
IE0031R	1.004	0.385	0.055	0.002
IT0004R	4.769	2.241	0.179	0.055
NO0002R	0.959	0.537	0.015	0.006

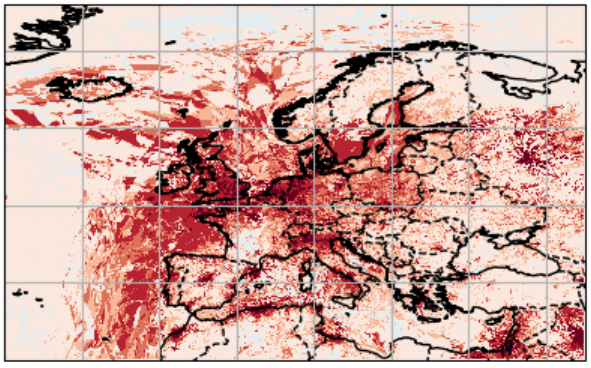
S8. Impacts of changing emission speciation on modelled ozone concentrations

As discussed in Sect. 3.6, we have made model calculations with both a reference run (nDef), and a sensitivity test (Sol6) in which the VOC speciation of solvents was replaced by the more reactive mix from GNFR sector F1. We have investigated changes in mean of daily maximum ozone (MDMax O_3), the 4th highest daily maximum 8-hour ozone (4MDA8), and in the highest daily maximum 8-hour ozone (1MDA8). Figure S13(a) and (b) shows that this change of speciation has only small impacts on MDMax O_3 and 4MDA8, with changes below 1 ppb in the majority of areas. The 1MDA8 values, Fig. S13(c), show a bigger response, of more than 5 ppb in some areas, but in very localised regions such as southern UK, the Po Valley in northern Italy, or near Madrid in Spain. These areas coincide with areas of high NOx emissions as expected - ozone chemistry is most sensitive to VOC emissions in such regions (Seinfeld and Pandis, 1998).

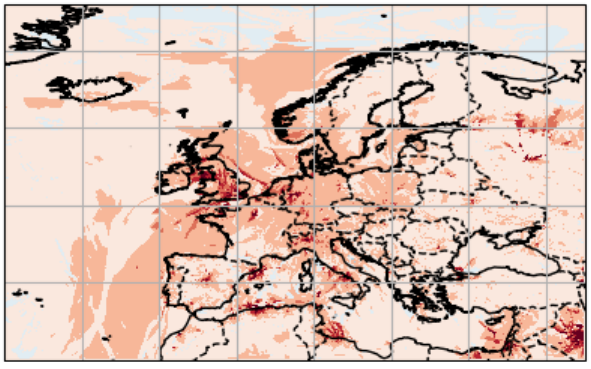
Figure S14 illustrates some of these changes for the Madrid region in more detail. The distribution of MDMax O_3, Fig. S14(a), shows maximum values north of the city centre, with much lower values to the east - these areas correspond to the high NOx emission areas (Fig.S14(e)). The changes in MDMax O_3, 1MDA and 4MDA are shown in Fig.S14(b)-(d). It is notable that VOC impacts can be significant (here over 20 ppb for 4MDA8 and 1MDA8), but are restricted to grid squares within 20–30 km of the major emission sources.



(a) Δ MDMax O_3 (ppb), Sol6 - nDef

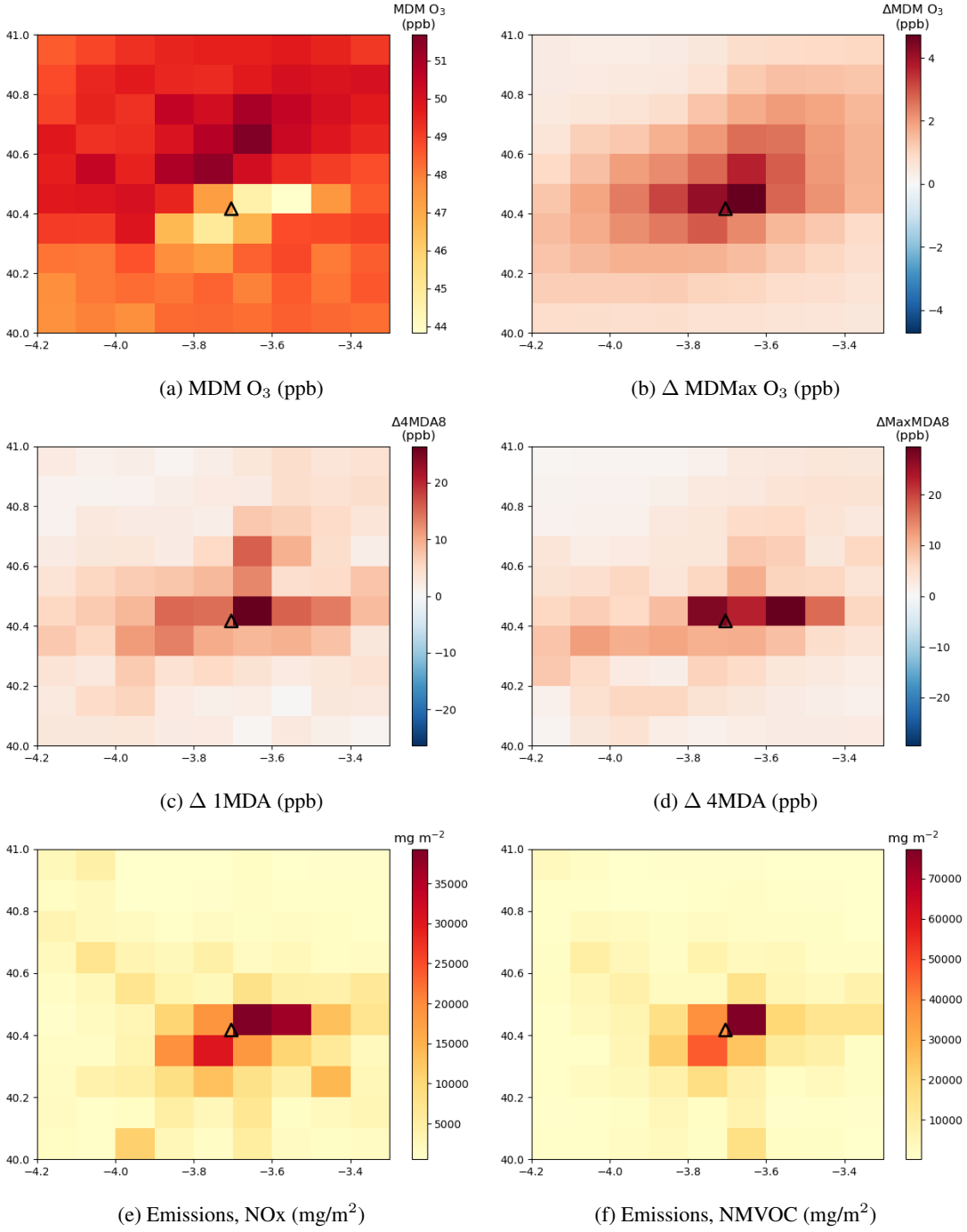


(b) Δ 4MDA8 (ppb), Sol6 - nDef



(c) Δ 1MDA8 (ppb), Sol6 - nDef

Figure S13. Results of sensitivity tests with solvent speciation replaced by that of gasoline exhaust. Plots show differences (Sol6 - nDef, see text) for: (a) Mean of daily maximum O_3, (b) 4^{th} highest MDA8 (c) highest daily MDA8.



(a) MDM O_3 (ppb)

(b) Δ MDMax O_3 (ppb)

(c) Δ 1MDA (ppb)

(d) Δ 4MDA (ppb)

(e) Emissions, NOx (mg/m^2)

(f) Emissions, NMVOC (mg/m^2)

Figure S14. Results of sensitivity tests for an area of Spain surrounding Madrid (marked with triangle): (a) base-case calculations of mean of daily maximum ceO3 (MDM O_3), (b) change in MDM O_3 when solvent speciation changed, (c) change in 4^{th} highest MDA8 when solvent speciation changed, (d) change in highest MDA8 when solvent speciation changed. Figs. (e) and (f) illustrate the emissions for NOx and NMVOC. Calculations with EmChem19 chemistry, CAMS-REG emissions, $0.1\times0.1^\circ$ resolution.