Evaluation of modelled versus observed NMVOC compounds at EMEP sites in Europe

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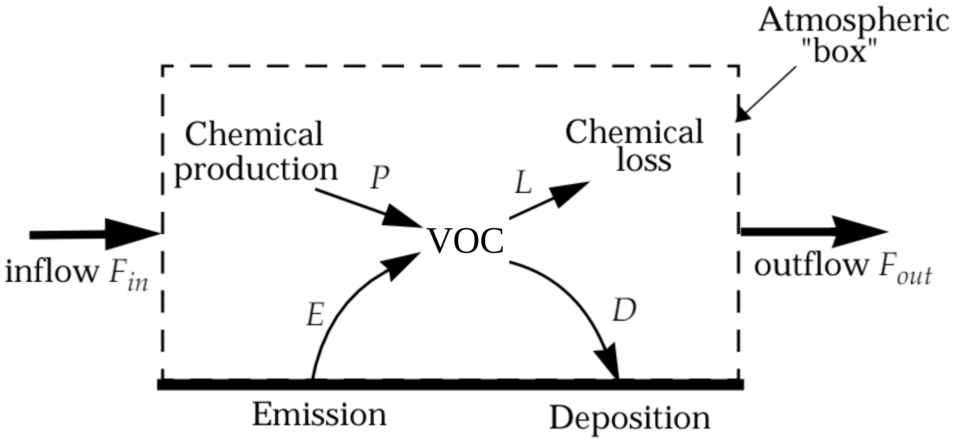
Challenges in model-measurement comparisons

- **Emissions** are often reported as a total mass of VOC: need to be converted to emissions of individual VOCs
- Many VOCs are lumped into different groups in **models**: cannot be compared with measured individual VOC concentrations
- The availability, quality, and consistency of **measurement** data can vary dramatically



Aims and progress

- Increase the VOC species set in the EMEP model with tracers for individual compounds: allows a direct model-measurement comparison
- Employ the model in assessing the 'goodness' of current emission inventories
- The first intensive VOC comparison study among EMEP in years: **Ge et al., ACPD, 2024**

Chemistry Transport Model: EMEP MSC-W

- **Chemistry mechanism**:CRIv2R5Em and EmChem19rc have been utilised to develop VOC tracers
- **Meteorology & resolution**: ECMWF at 0.1° × 0.1°
- **Tracers (_T)**: take explicit emissions and follow species-specific losses to give pure concentrations

Green: for existing lumped surrogate

Blue: newly added species

Orange: have secondary production

CRIv2R5Em	Species			
Shorter-chain alkane	C2H6_T	C3H8	NC4H10_T	IC4H10_T
Longer-chain alkane	NC5H12_T	IC5H12_T	NC6H14_T	NC7H16_T
Alkene	C2H4_T	C3H6_T	TBUT2ENE	
Alkyne	C2H2			
Aromatics	BENZENE	TOLUENE	OXYL_T	
Alcohol	CH3OH	C2H5OH_T	NPROPOL	IPROPOL
Aldehyde	HCHO	CH3CHO		
Dialdehyde	GLYOX	MGLYOX		
Ketone	CH3COCH3	MEK		
Carboxylic acid	HCOOH	CH3CO2H		
Biogenic VOC	C5H8	α-PINENE	β-PINENE	XTERPENE
Rest†	OTH_ALKANE_T			

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

GenChem v1.0 – a chemical pre-processing and testing system for atmospheric modelling

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Geoscientific Model Development
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Emissions: inventory and speciation profile

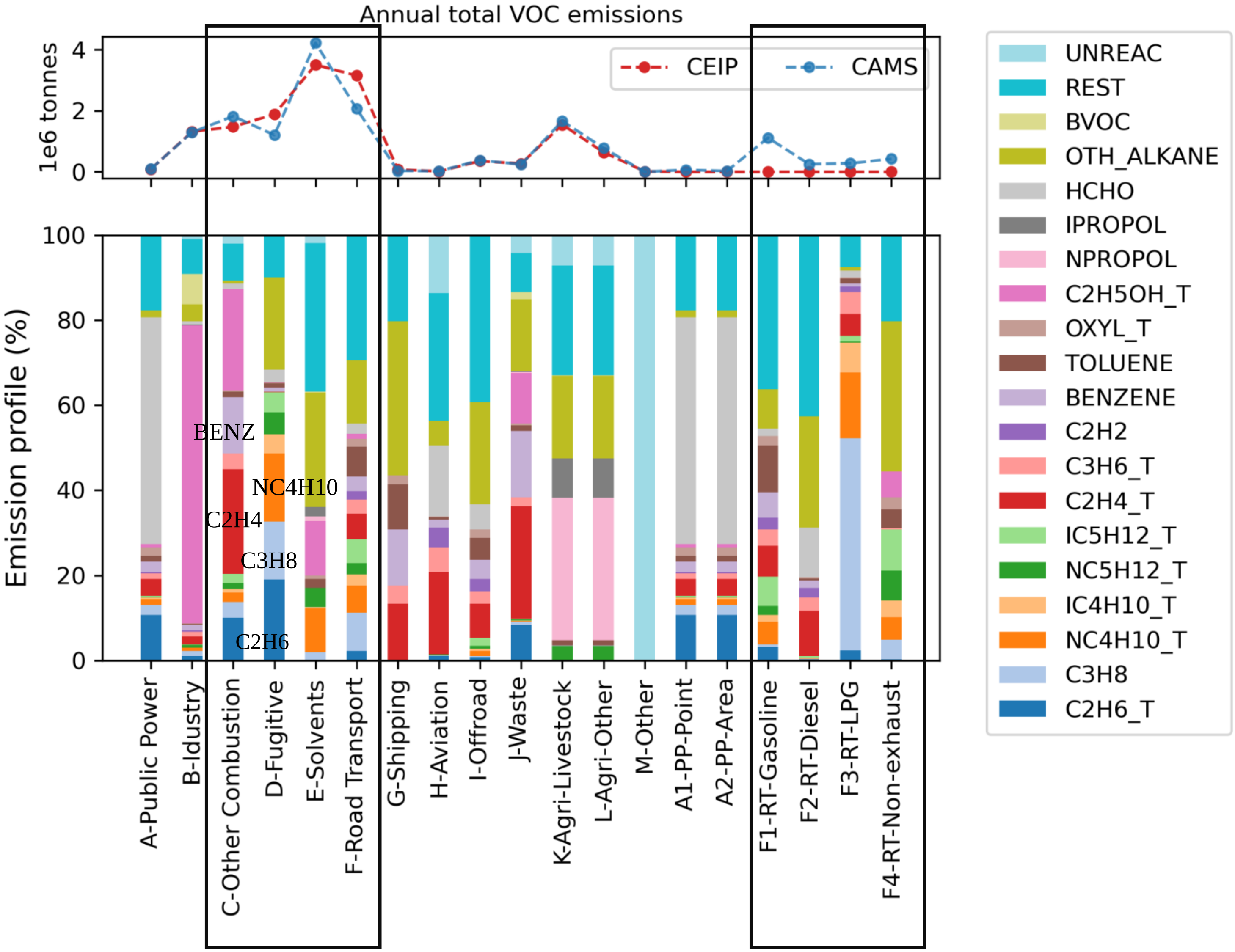
- **Anthropogenic emissions**: CAMS and CEIP inventory
- **Anthropogenic VOC (AVOC) profiles**: UK NAEI
- **BVOC emissions**: calculated online from temperature, radiation and land-cover data (Simpson et al., 1999, 2012)
- **Biomass burning (BB)**: FINN - Fire INventory from NCAR

FINN species	C2H6	C3H8	ALK4	ALK4	C2H4	C2H2	PRPE	XYLE	BENZ	TOLU	CH2O	GLYX	MGLY
EMEP species	C2H6_T	C3H8	NC4H10_T	IC4H10_T	C2H4_T	C2H2	C3H6_T	OXYL_T	BENZENE	TOLUENE	HCHO	GLYOX	MGLYOX
Factor	1	1	0.6255	0.3745	1	1	1	1	1	1	1	1	1

(Andreae, ACP, 2019)

Emissions: species mapping

- **Large emitting sectors**: Solvents, Road Transport, Other Combustion, Fugitive
- **Large VOC emissions**: C2H6, C3H8, C2H4, Benzene, etc.
- **CAMS**: sector-F Road Transport (RT) are reported in four sub-sectors, each with their own distinct emission profiles



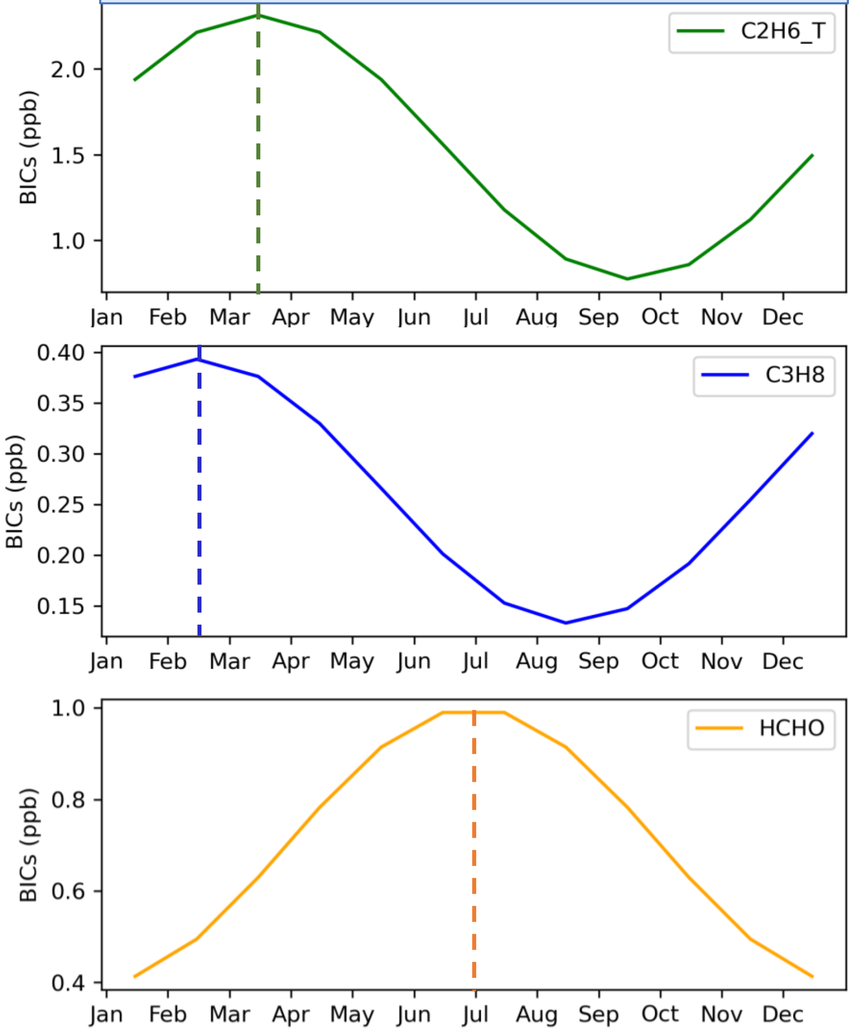
Boundary and initial conditions (BICs)

- The model specifies the BICs of many species using measurements from Mace Head, Ireland and a cosine function to describe monthly fields (Simpson et al., 2012, 2015; Grant et al., 2011; Waked et al., 2016)
- Monthly near-surface concentration χ_0:

$$\chi_0 = \chi_{\text{mean}} + \Delta\chi \times \cos(2\pi \frac{d_{mm} - d_{max}}{n_y})$$

model species	χ_{mean} (ppb)	$\Delta\chi_{mean}$ (ppb)	d_{max}
C2H6_T	1.544	0.77	75
C2H2	0.456	0.23	75
C3H8	0.263	0.13	45
NC4H10_T	0.095	0.05	45
IC4H10_T	0.044	0.02	45
NC5H12_T	0.026	0.01	45
IC5H12_T	0.026	0.01	45
OTH_ALKANE_T	1.546	0.77	45
HCHO	0.7	0.3	180

BICs examples



Measurements

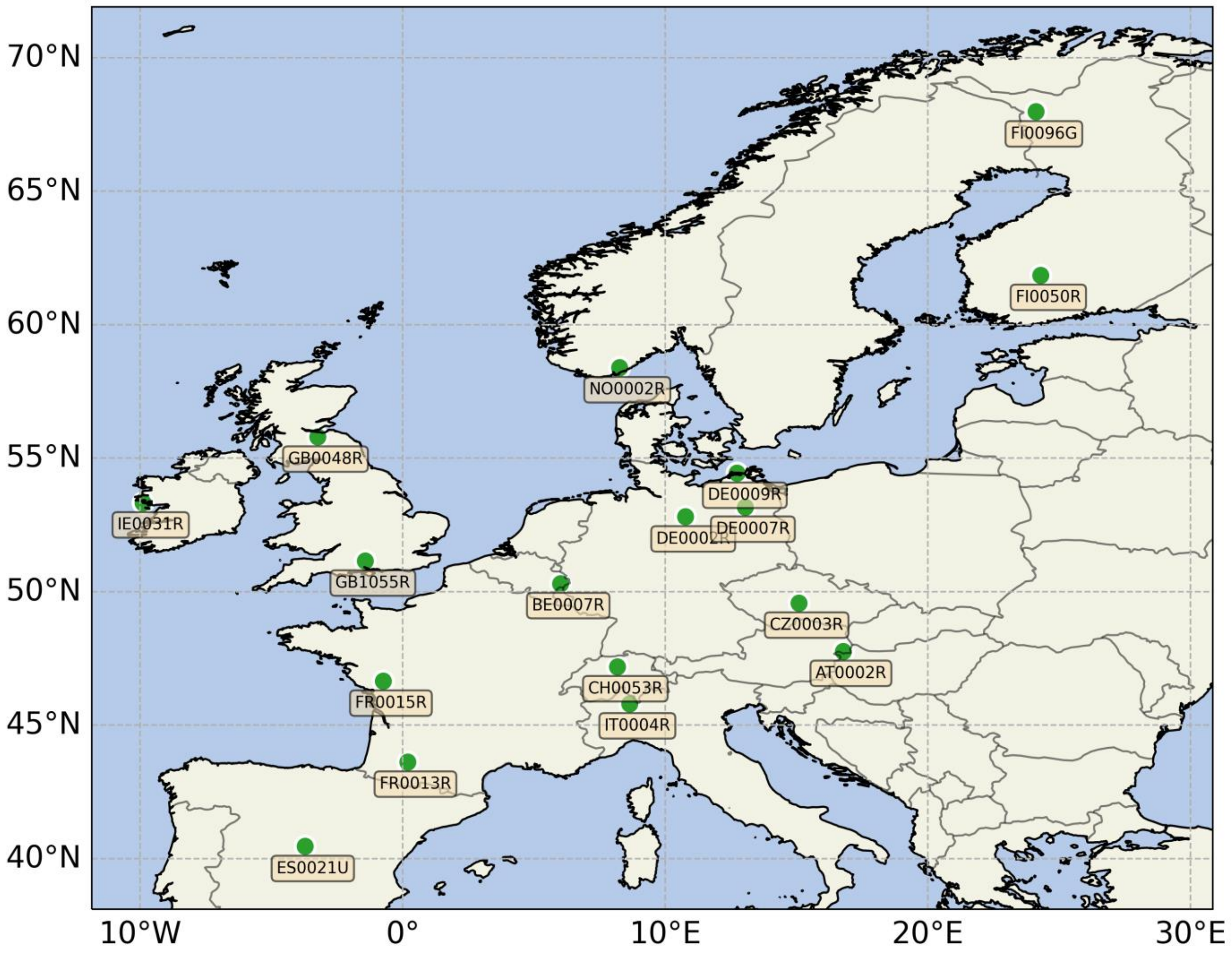
- Measurement data are compiled from the EBAS platform: ebas-data.nilu.no

- The model-measurement agreement is intrinsically constrained by differences in:

  - The number of sites per species

  - Sampling techniques (Online GC, steel canisters)

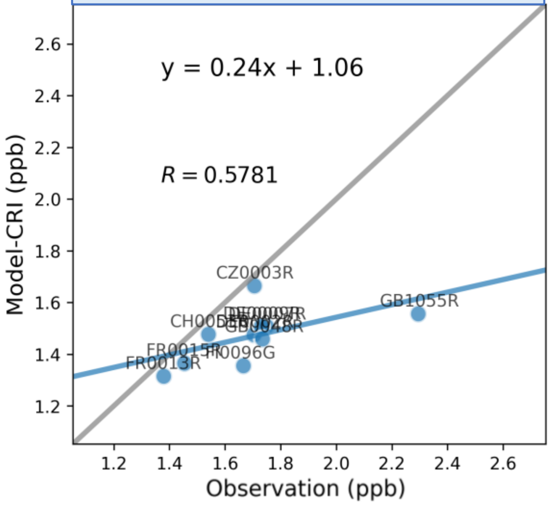
  - Sampling duration and frequency



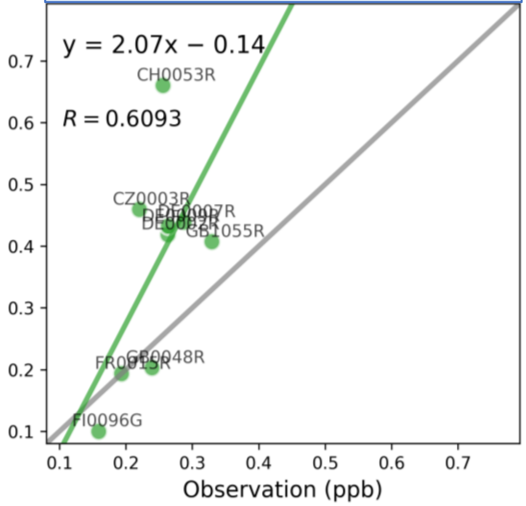
Alkane species: shorter-chain alkanes

- Agreement that ethane has the highest annual concentrations among these alkanes (~ 1.6 ppb);
- Modelled ethane also shows good temporal agreement with observations
- Clear model overpredictions for NC4H10_T but underpredictions for IC4H10_T

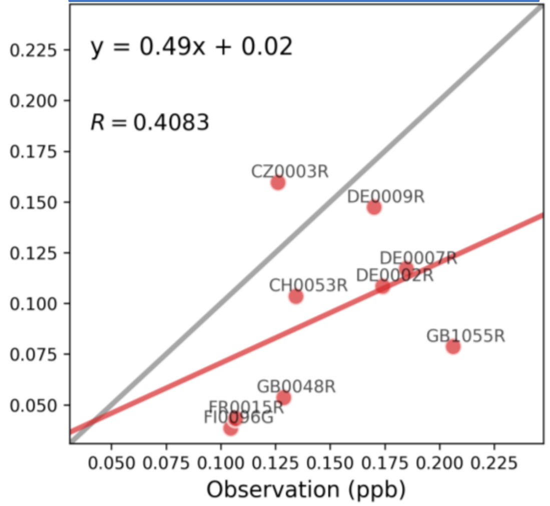
C2H6_T



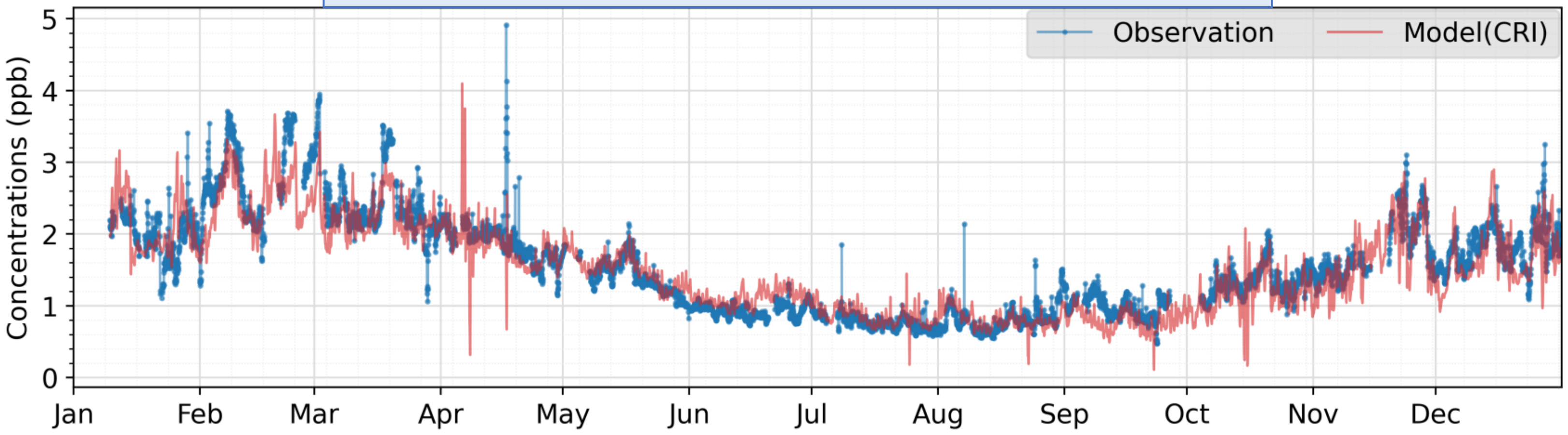
NC4H10_T



IC4H10_T

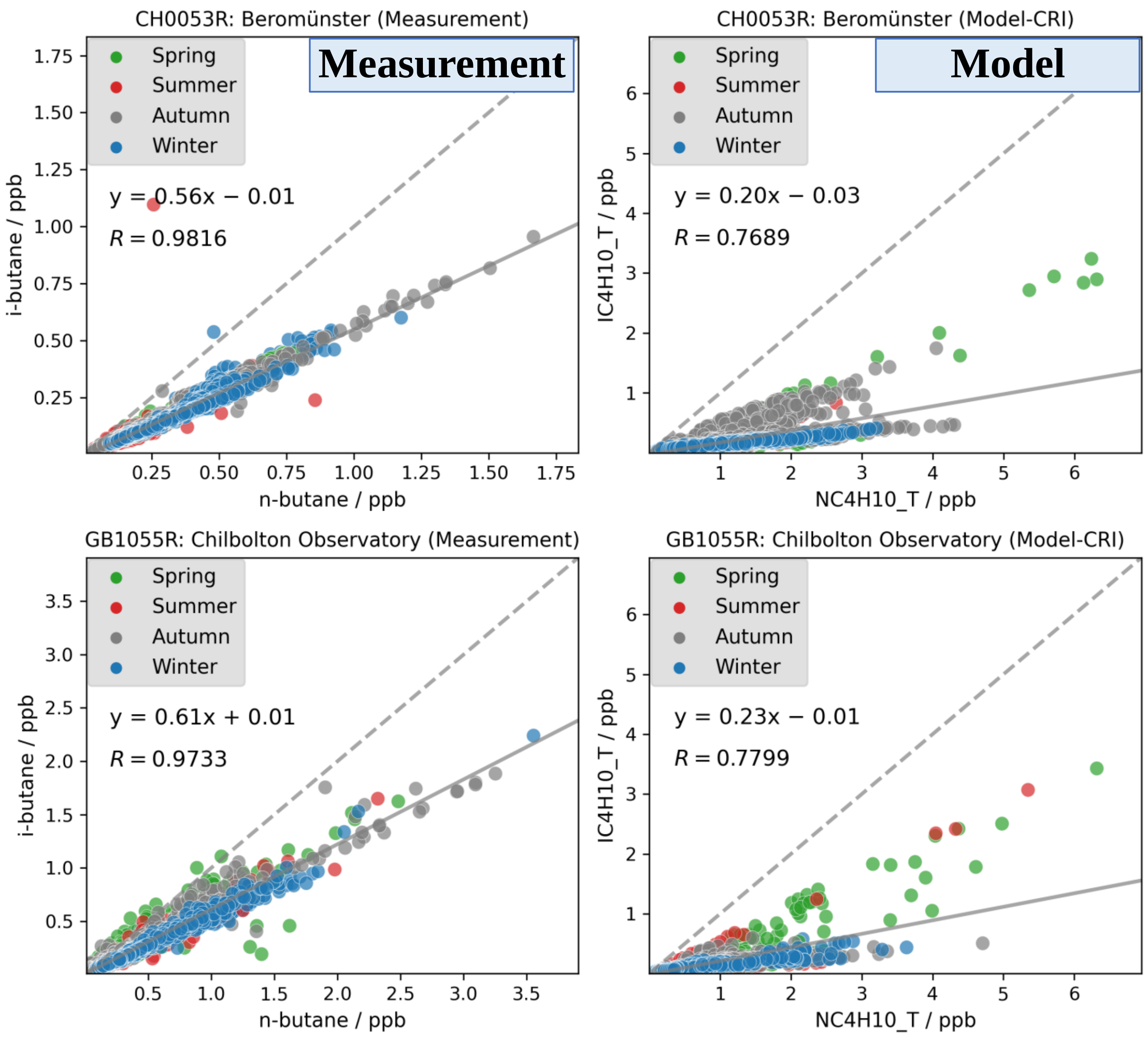


C2H6_T: CH0053R, Beromünster, 2018



VOC ratios: i-/n-butane

- Similar sources and chemical loss rates: similar lifetimes of 3-4 days (Helmig et al., 2014; Zhang et al., 2013; Watson et al., 2008)
- Strong linear correlations between i- and n-butane are observed in both measurement and model data: common sources
- Measurement data: $i/n \approx 0.6$, similar across different seasons; same as the values in other measurement studies (Helmig et al., 2014)
- Model results: $i/n \approx 0.2$, ratios are lower in winter compared to e.g., spring



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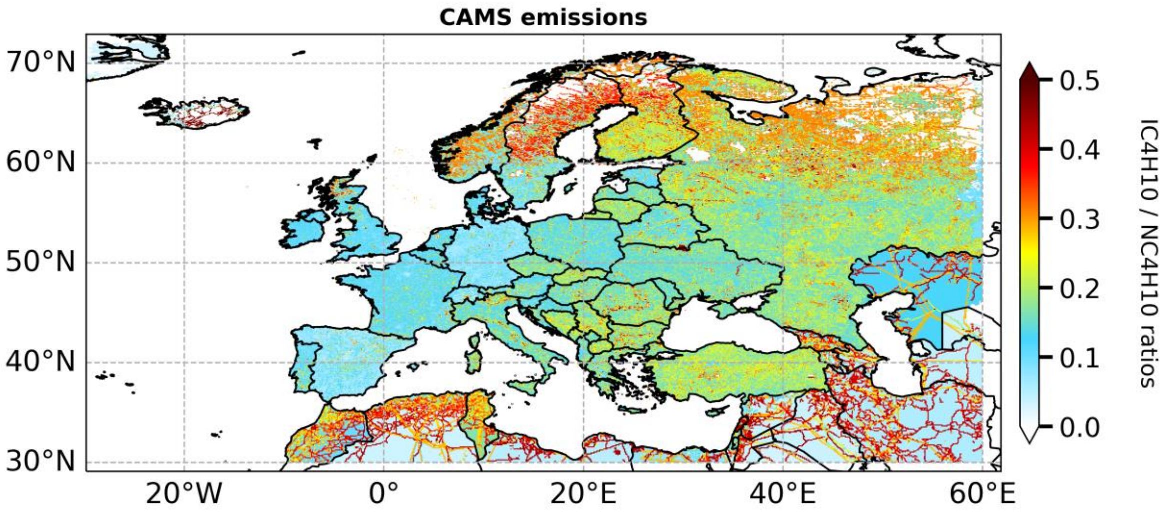
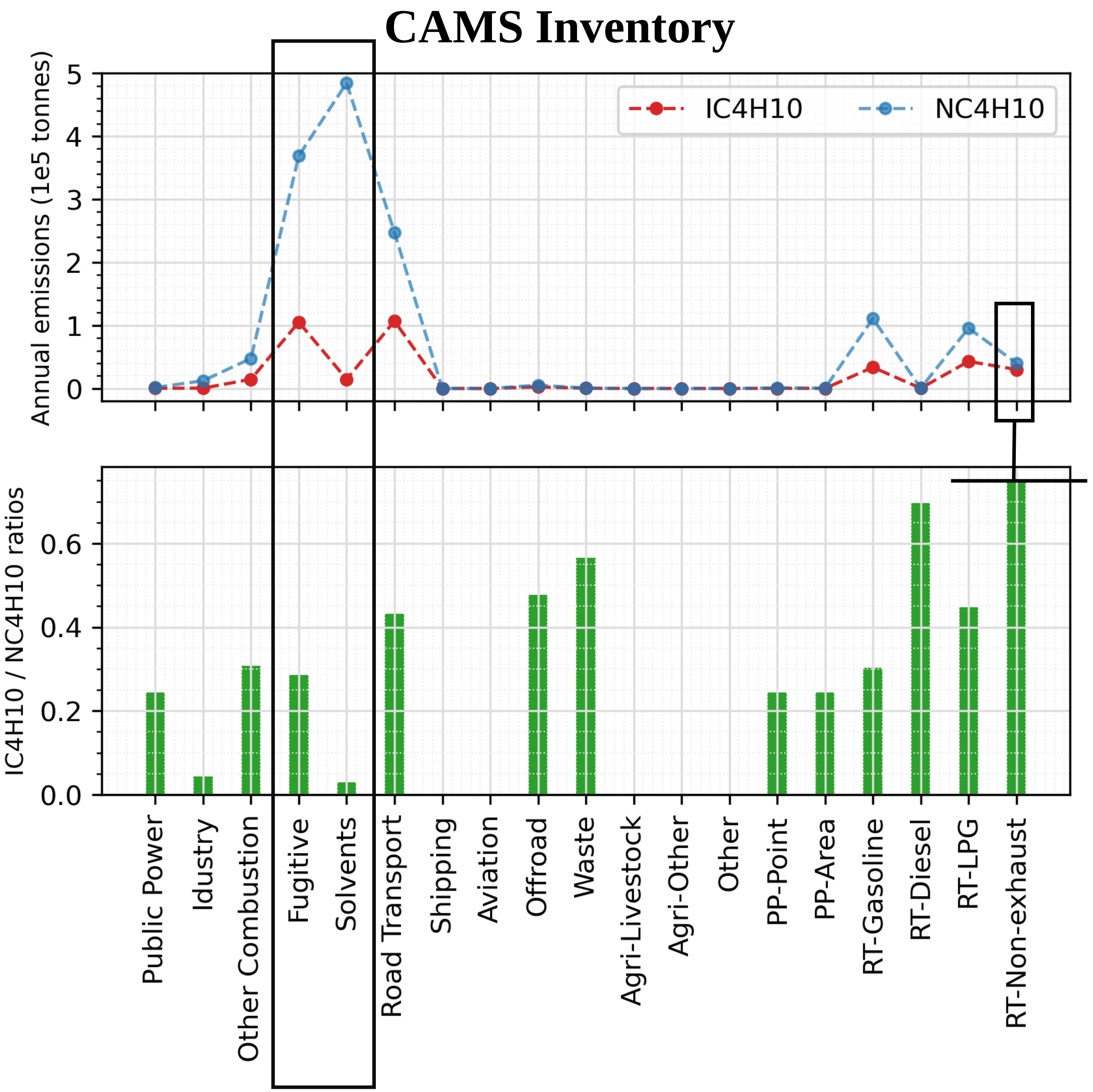
VOC ratios: i-/n-butane in emissions

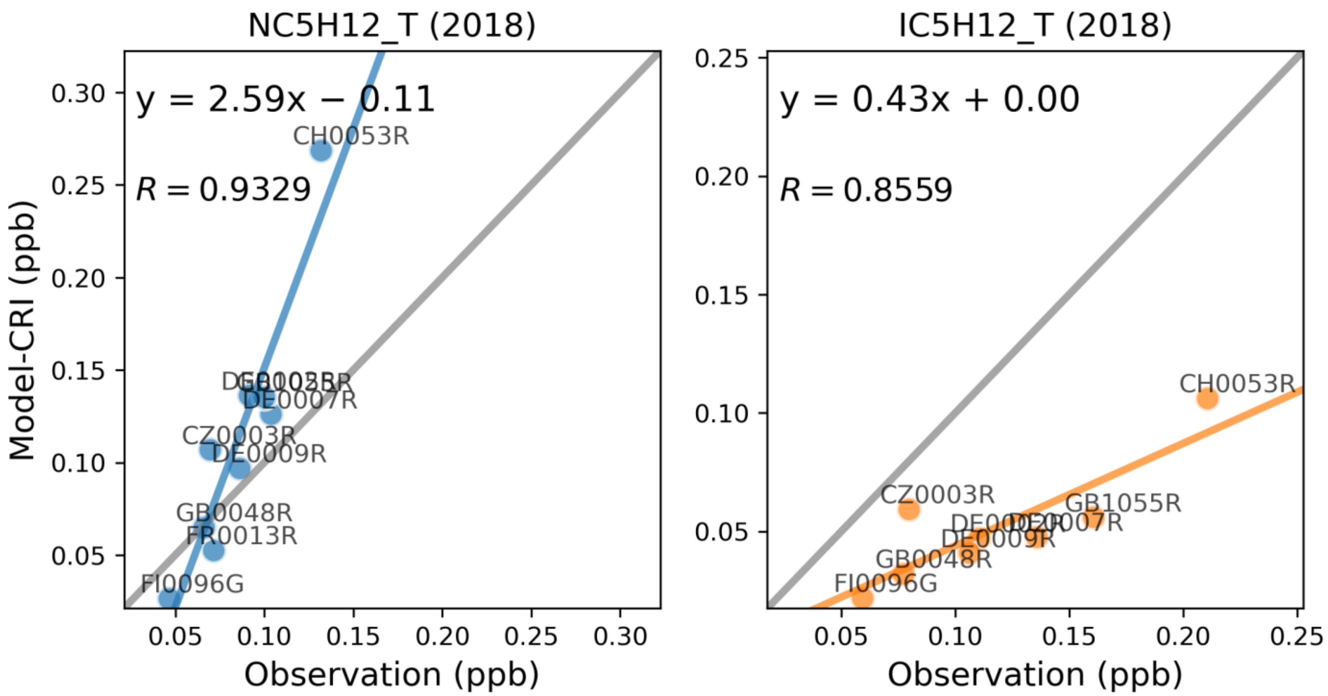




- The ratio in BICs ≈ 0.5; ≈ 0.6 in BB emissions
- Examining individual sectors: solvent is the largest contributor but has a ratio < 0.05, followed by fugitive sector with a ratio of 0.28.
- Possible explanations: the speciation of solvent sector is biased (e.g., missing i-butane emissions while overestimating n-butane), or contributions from road transport-non-exhaust sectors are underestimated

Alkane species: i- and n-pentane

- Similar sources (traffic exhaust, fuel evaporation) and lifetimes (ca. 2 days)
- Strong model-measurement linear correlations are found for both species despite the low concentrations (annual means ~ 0.1 ppb)
- Albeit i-pentane contributes comparable emissions to n-pentane, the model significantly underestimates i-pentane concentrations
- Several studies suggest that i-pentane emissions are not adequately captured in emission inventories despite its significance within urban environments (Coll et al., 2010; Borbon et al., 2002)

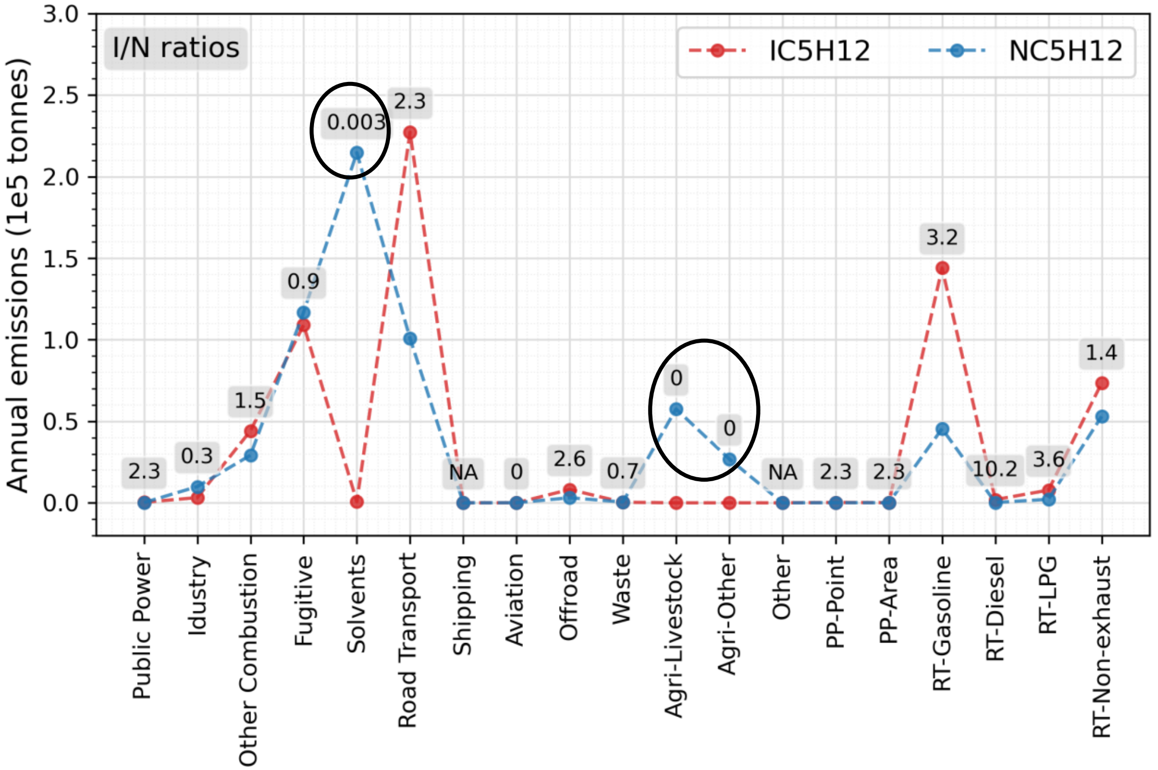


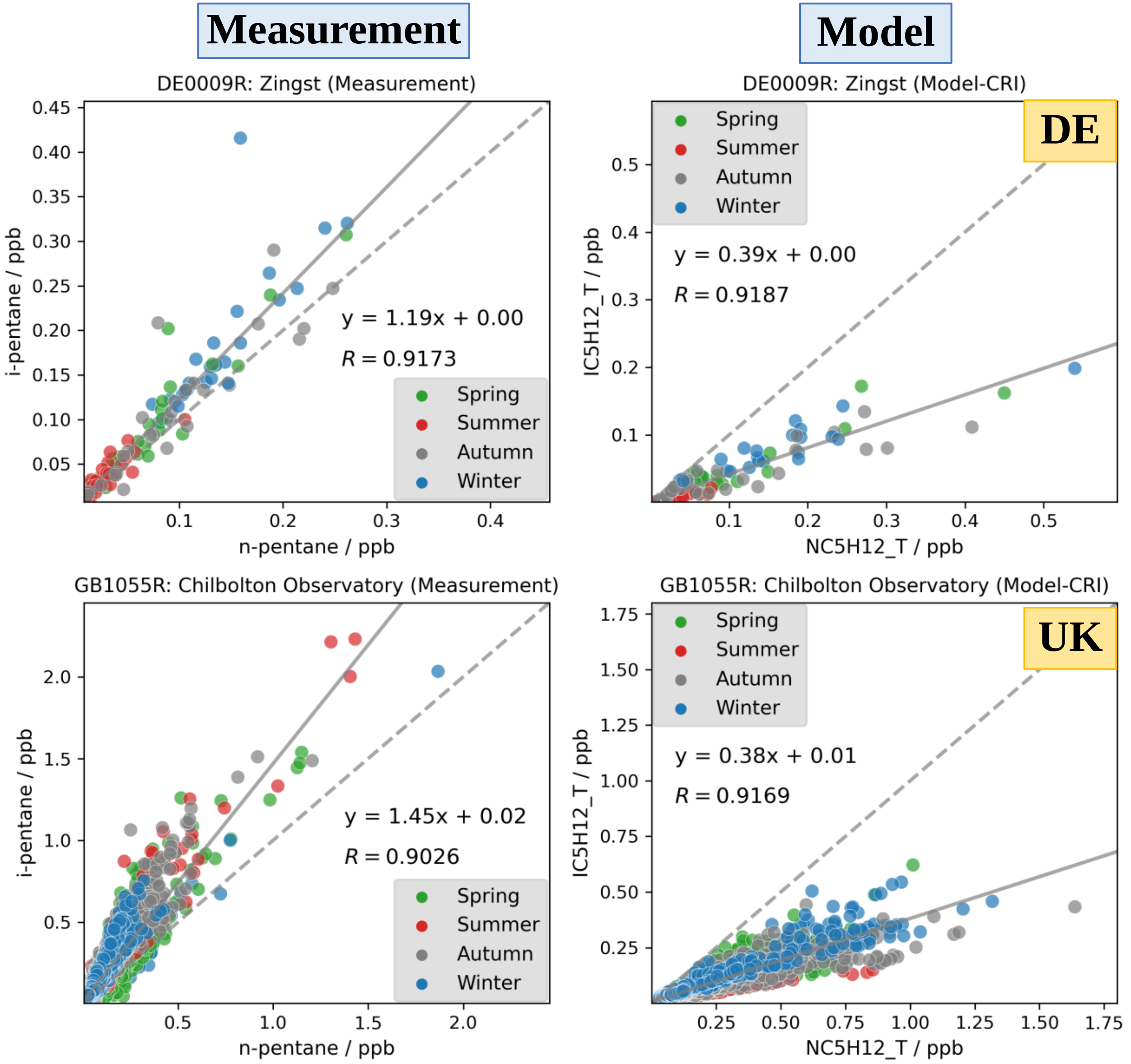
Species	N	Mean_O	Mean_M	NMB	NME
N5H12_T	9	0.085	0.113	32%	43%
IC5H12_T	9	0.117	0.051	-56%	56%

Comparison statistics. N is the number of sites. Mean_O and Mean_M refer to the annual average concentrations (in ppb) of observation (O) and model (M) over all sites, respectively. NMB is the Normalised Mean Bias, and NME is the Normalised Mean Error.

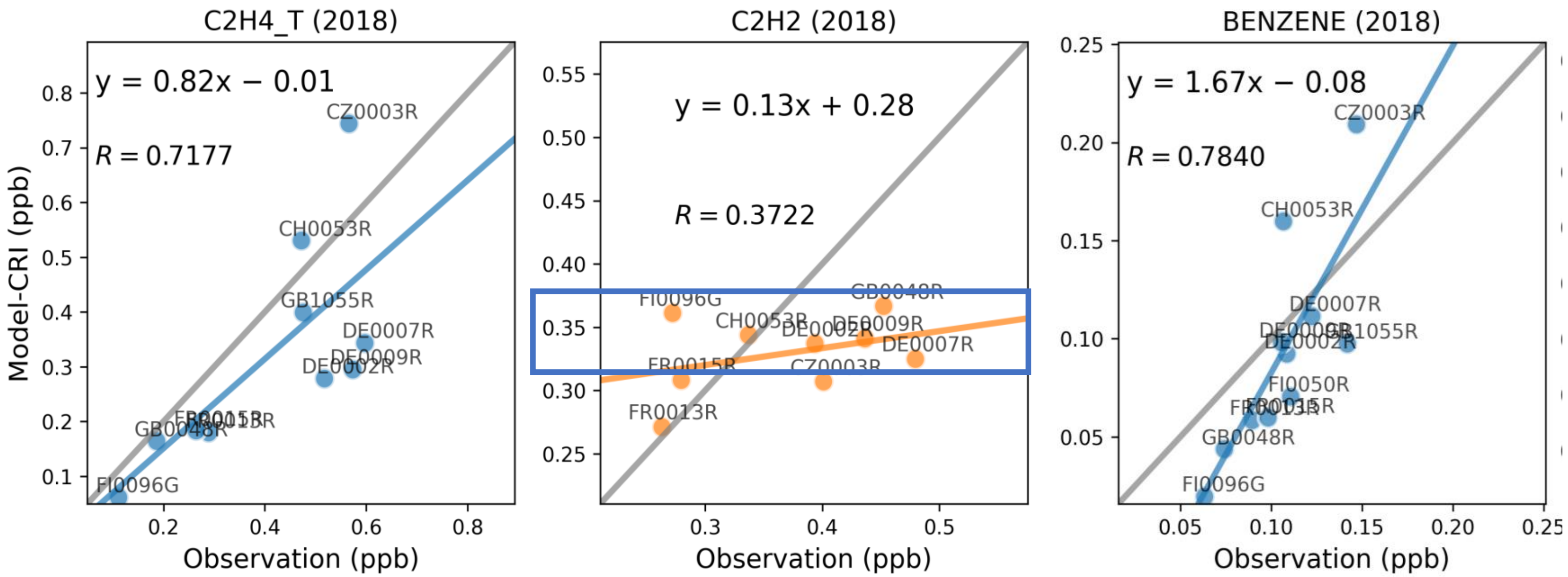
VOC ratios: i-/n-pentane

- Measurements affected by anthropogenic sources: i/n = 1.7~2.9 (Helmig et al., 2014; Bourtsoukidis et al., 2019); same BICs; BB and oceanic emissions: 0.5~0.7 (not modelled)
- Modelled ratios are much smaller than measured ratios, which is driven by large n-pentane emissions from solvent sector
- Agricultural VOCs: need more emission measurements





Unsaturated VOCs: ethene, ethyne and benzene



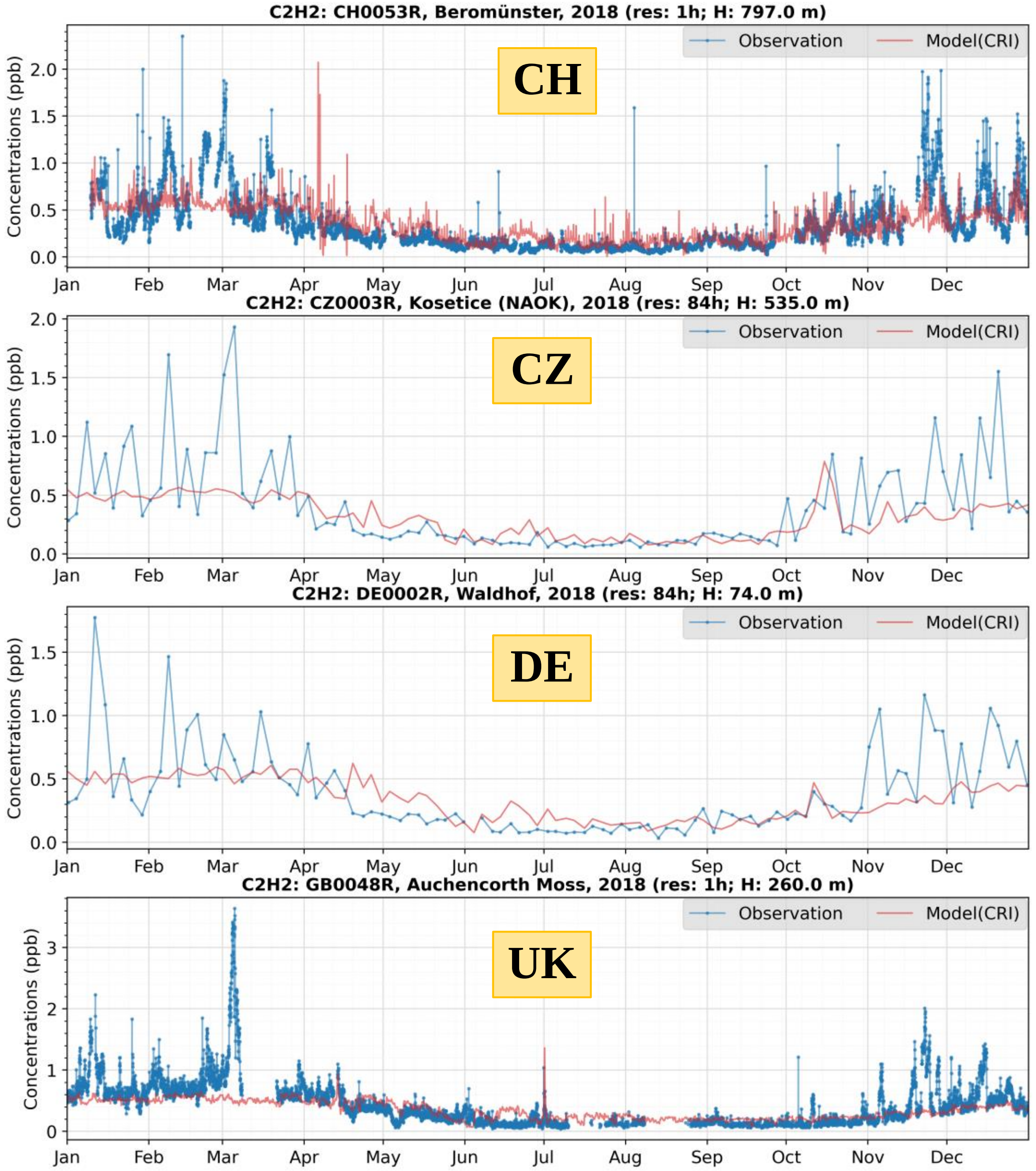
C2H2 (ppb)	Previous run (Ge et al., 2023)	This study
N	7	9
R	-0.18	0.37
Mean_O	0.396	0.368
Mean_M	0.035	0.329
NMB	-91%	-11%

- Mixed results: good agreement for ethene and benzene but not for ethyne
- The different model performance points to shortcomings in the spatial patterns and magnitudes of ethyne emissions
- Modelled ethyne levels cluster around 0.35 ppb: mainly determined by its BICs
- Compared to the previous model run (no BICs and BB emissions), current model underestimation is improved
- Inputs of anthropogenic emissions are too small to significantly affect the model outputs

Unsaturated VOCs: ethene, ethyne and benzene

- Modelled ethyne: little seasonal variation; missing winter ethyne emissions (e.g., transport and industrial combustion)
- Measured benzene is closely correlated with ethyne in winter: common sources of the two species
- Model results show poor correlation: problematic ethyne emissions (given the good model performance for benzene)

BENZENE/C2H2	Summer		Winter	
	Obs	Mod	Obs (R)	Mod (R)
Beromünster	0.26 (0.82)	0.33 (0.57)	0.34 (0.96)	0.98 (0.63)
Kosetice	0.26 (0.47)	0.35 (0.62)	0.29 (0.93)	0.46 (0.15)
Waldhof	0.24 (0.77)	-0.00 (-0.01)	0.30 (0.99)	-0.20 (-0.11)
Neuglobsow	0.31 (0.88)	0.00 (0.01)	0.31 (0.99)	-0.02 (-0.01)
Zingst	0.17 (0.83)	-0.03 (-0.13)	0.30 (0.97)	-0.77 (-0.40)
Pallas	0.11 (0.43)	-0.03 (-0.48)	0.28 (0.94)	-0.04 (-0.06)
Peyrusse Vieille	0.04 (0.09)	-0.07 (-0.58)	0.24 (0.91)	-0.40 (-0.22)
La Tardiere	0.25 (0.41)	-0.10 (-0.63)	0.29 (0.93)	0.17 (0.15)
Auchencorth Moss	0.18 (0.76)	0.08 (0.34)	0.19 (0.89)	0.03 (0.04)



Summary: more info at Ge et al., ACPD, 2024

- This model evaluation study adapts the EMEP model to assess the accuracy of recent emission inventories and the agreement between modeled and measured VOC concentrations. The agreement varies by species, suggesting potential biases in emissions estimates for certain VOCs and sectors

- Discrepancies between modeled and measured i-to-n-butane and i-to-n-pentane ratios suggest **biases in solvent sector** speciation profiles or **underestimates of transport sector totals** in current inventories

- Disparate model performance for ethene, benzene, and ethyne suggests limitations in representing spatial, temporal, and emission magnitude patterns for ethyne from **combustion-related sectors**

- **Agricultural sectors** need more attention

Acknowledgement

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