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DNPH VOC Sampling and Analysis during the EMEP Intensive Measurement Period 12-19/07/2022 Overview of the results

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Oxygenated Volatile Organic Compounds (oxy-VOCs)

- **Most abundant** VOCs in ambient air
- **Key compounds** as tracers of primary sources as well as chemical processes (secondary formation)
- **Adverse health effect** (formaldehyde, acrolein...)
- Tracers of solvent use significantly growing source

- Have the key sources of emission of NMVOCs changed over the past two decades?

Quick answer: Yes. There has been a substantial reduction in emissions of short-chain hydrocarbons related to fossil fuels and combustion and an increase in the relative contributions of VOCs emitted from solvent and product use. Solvents and the use of chemicals in industry and domestic products, and other non-combustion sources, are estimated to account for ~70% of UK emissions in 2017 according to the NAEI. Over the last decade there has been a growth in the estimated national emissions of oxygenated VOCs, including ethanol, methanol, butanone and acetone.

NMVOC in the UK, 2020: <http://uk-air.defra.gov.uk>

DNPH, derivatization / HPLC - UV



Low capital cost; easy sampling, one instrument for many sites



Very low time resolution

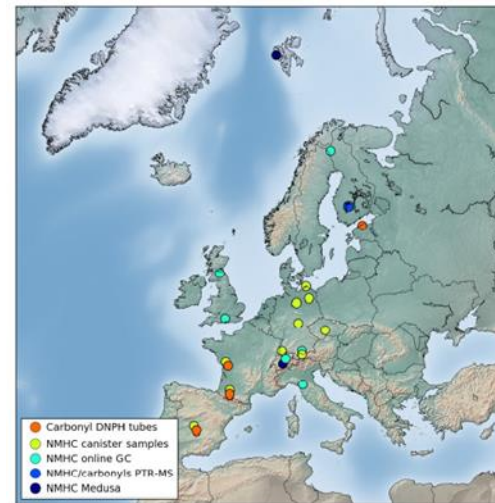
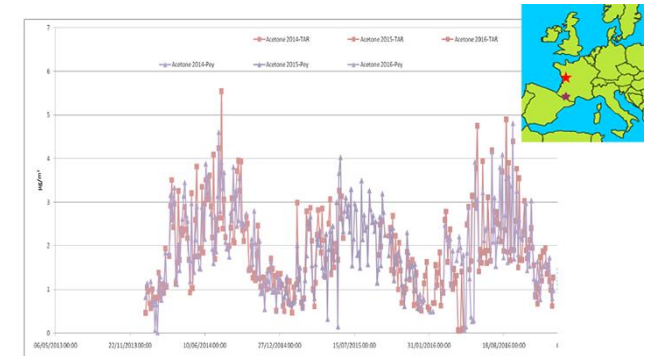


Figure 1: Monitoring sites for VOC in 2018.

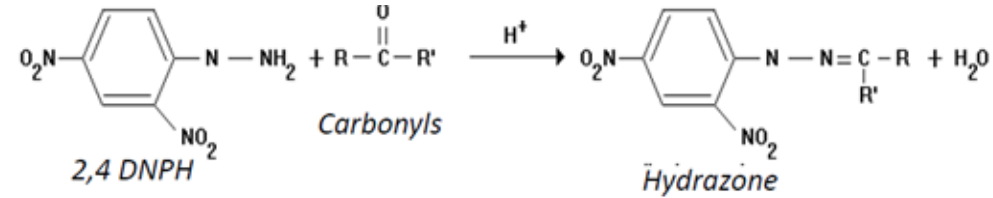


Acetone:
High seasonal variability &
Consistency between sites

BACKGROUND AND MOTIVATION - VOC MONITORING : *IMPLEMENTATION DURING EIMP*



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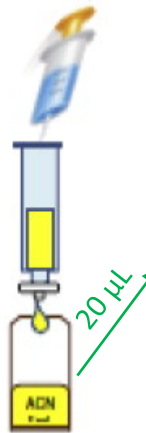


Automatic sampler SYPAC
(Tera env. co.)

3 mL
acetonitrile

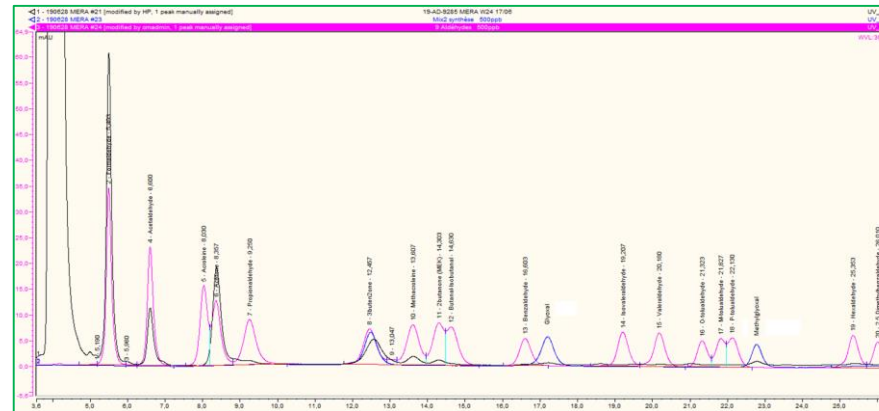


DNPH cartridges
stored at -21°C,
analysis within 3 weeks



HPLC-UV (365nm)

Standard: Apel Riemer; SUPELCO for verification
DL: ~10-30 ppt
Uncertainty: 10-20%



11 OVOCs C₁-C₇

- formaldehyde
- acetaldehyde
- acetone
- acrolein
- propanal
- methylvinylketone
- ethylmethylketone
- methacrolein
- butanal + isobutanal
- glyoxal
- methylglyoxal

DNPH METHOD OPTIMIZATION/EVALUATION: COLLECTION EFFICIENCIES VS. RH UNDER # LEVELS

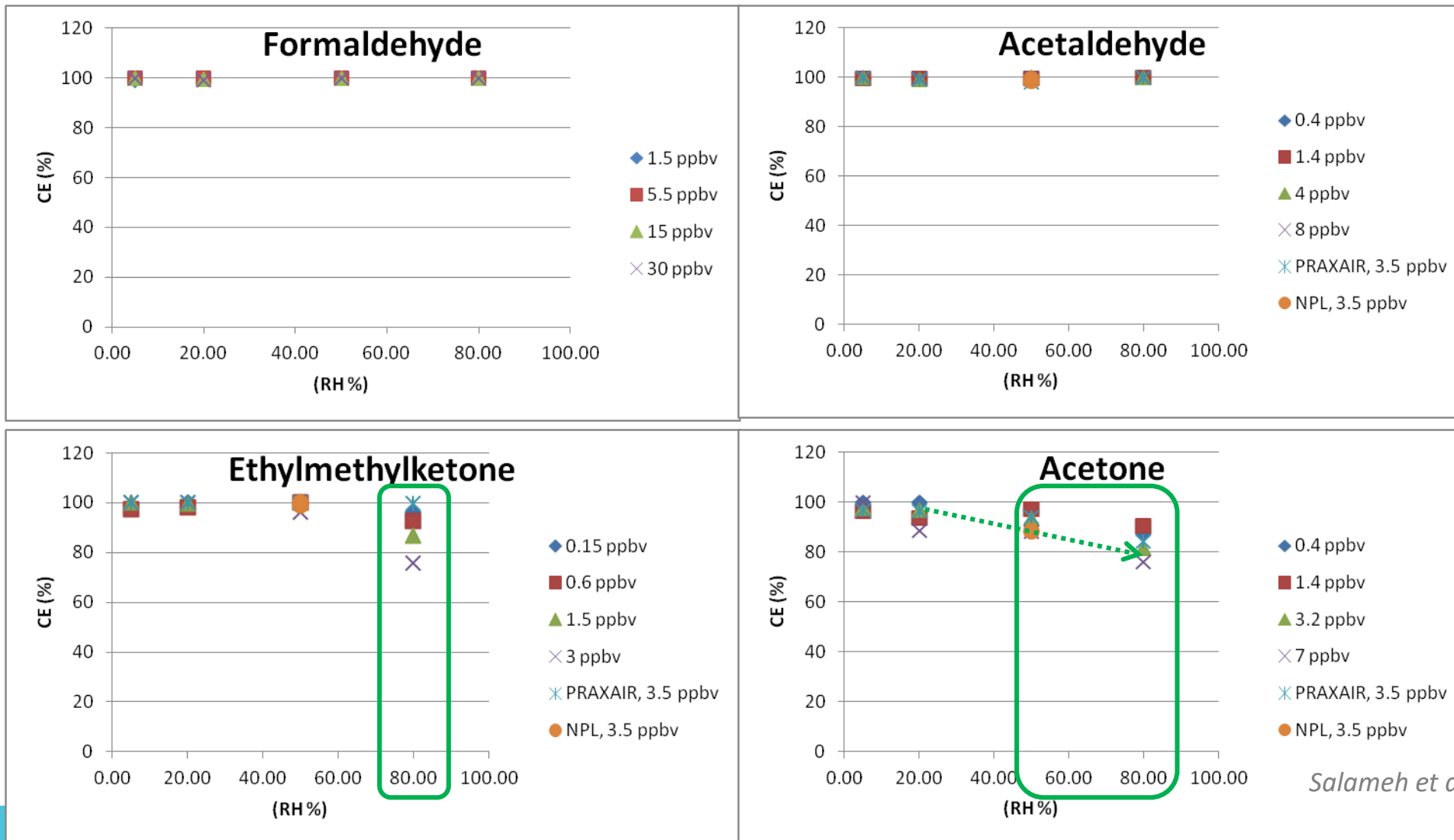


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Collection efficiencies vs. RH under # levels

$$CE = (C1 / (C1 + C2)) * 100$$





- **IMT contribution:** sending 17 DNPH cartridges (1 as a transport blank) + 2 cartridges to be used in series/sampling; and a KI/Cu ozone scrubber; & performing analysis: **17 DNPH/site * 16 sites = 272 DNPH + blanks, calibration standard throughout the analysis**
- **Frequency:** 8 days (1 day outside ozone episode) of continuous measurement with DNPH cartridges for 4 hours, at 12-16h UTC
- **Flow rate:** 1.5 L/min, if not possible 1L/min
- **Precautions:** leak tests; inox filter of 2 µm; ozone scrubber (KI)
- **Analysis:** blanks subtracted, reproducibility of the calibration standard

IMPLEMENTATION DURING EIMP: 17 SITES



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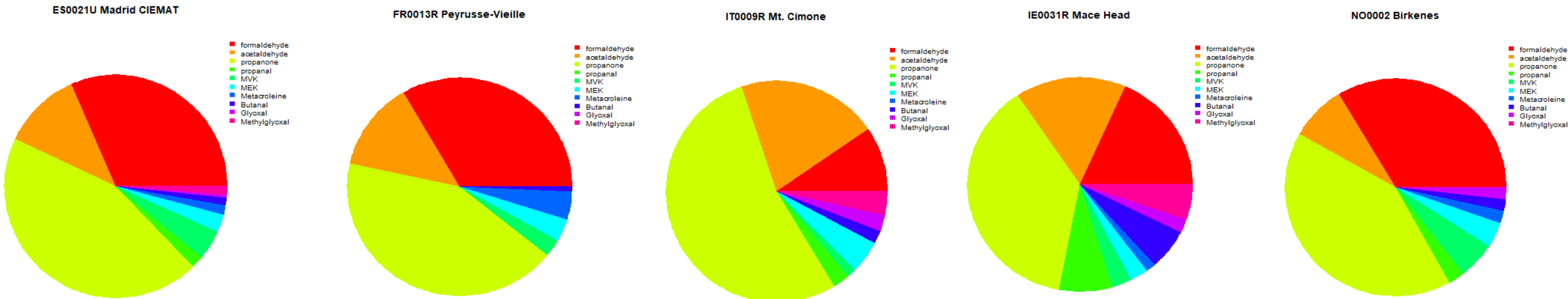
Sites	Centralised analysis			
	O-VOCs DNPH	NMHC Canister	terpenes Tenax	tracers (BSOA) from ECOC filter
AT0002R Illmitz	X	X	X	X
BE0007R TMNT09 Vielsalm	X	X	X	X
CZ0003R Kosetice	x		x	(X)
CY0002R Agia Marina Xyliatou (CAO)				(X)
DE0007R Neuglobsow	X		X	X
DE0008R Schmücke	X		X	X
DE0044R Melpitz		(X)	X	X
ES0019U Barcelona				X
ES1778R Montseny				X
ES0021U Madrid CIEMAT	X	X	X	X
FR0013R Peyrusse Vieille			X	X
FR0018R La Coulonche	X	X	X	X
FR0008R Donon	X	X	X	X
FR0020R SIRTÀ				X
FR0027U Villeneuve d'Ascq	X	X	X	
FR0030R Puy de Dome	X			X
GB0048R Auchencorth Moss	X		X	X
GB1055R Chilbolton Observatory	X		X	X
IE0031R Mace Head	X	X	X	
IT00004R Ispra	X		X	X
IT0009R Mt. Cimone	X		X	X
NO0002 Birkenes	A	A	A	X

OVERVIEW OF THE RESULTS



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- Major compounds at all the sites: propanone (max. $10 \mu\text{g}/\text{m}^3$), formaldehyde (max. $9 \mu\text{g}/\text{m}^3$), and acetaldehyde (max. $7 \mu\text{g}/\text{m}^3$)
- propanone, formaldehyde, and acetaldehyde contribute to over 85% of all oxy-VOCs at all sites

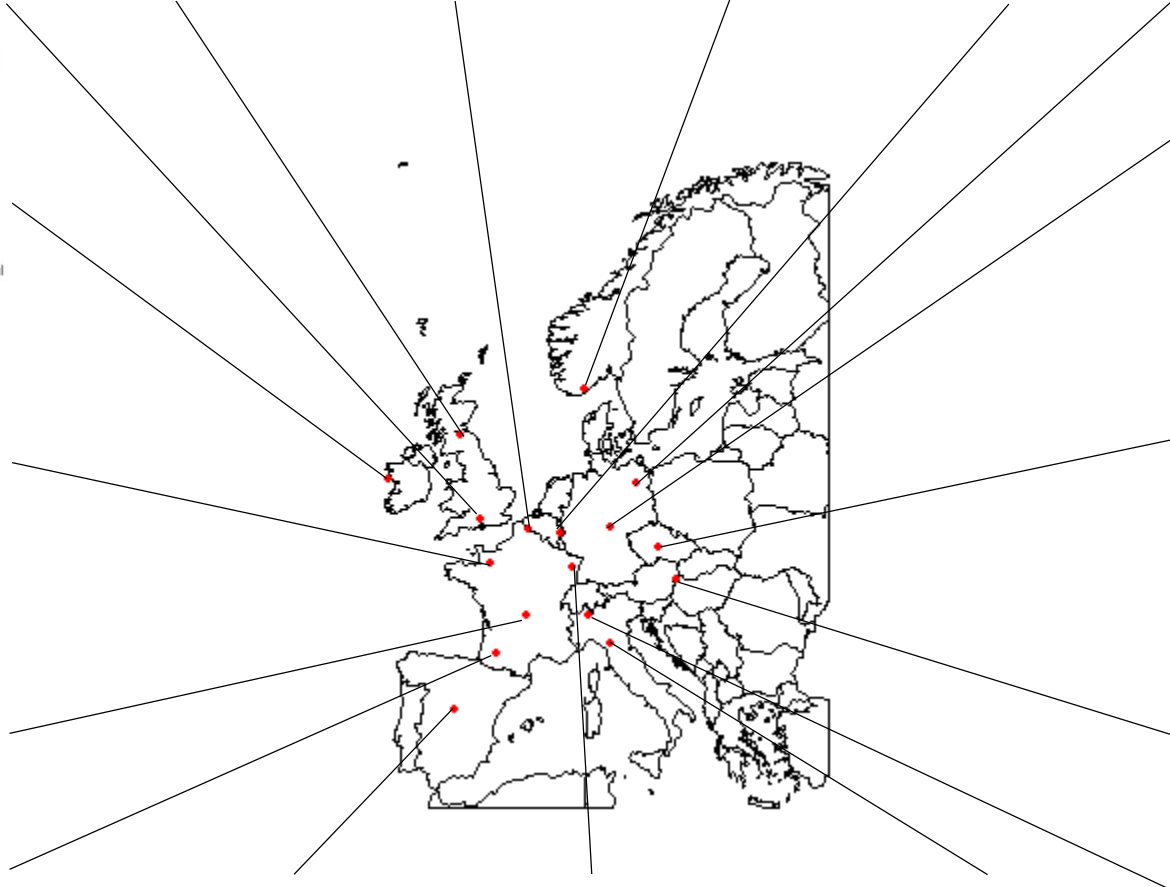
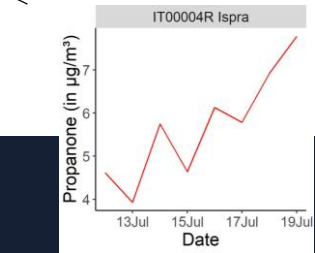
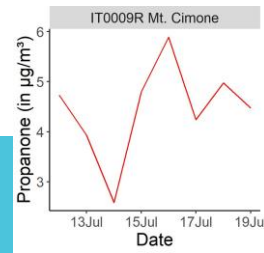
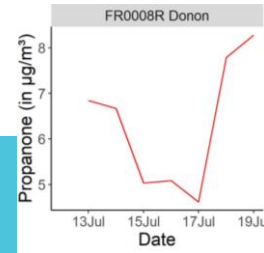
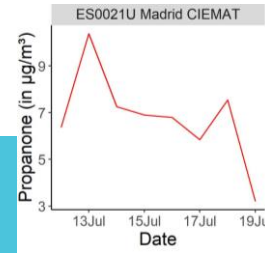
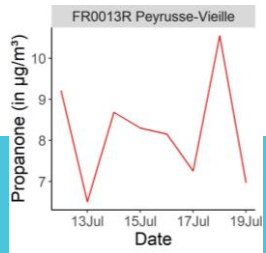
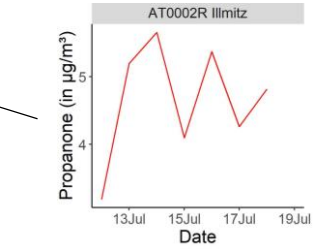
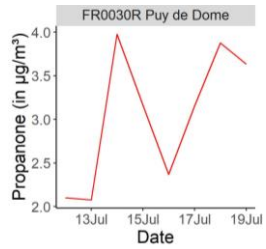
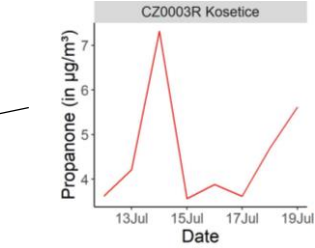
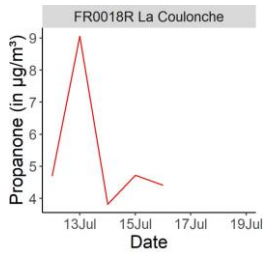
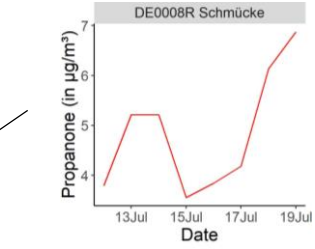
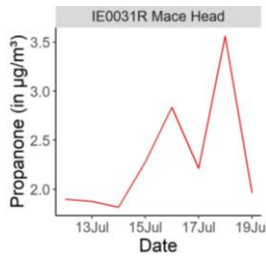
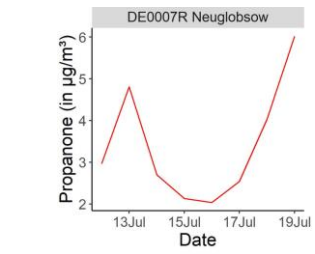
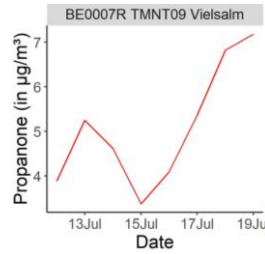
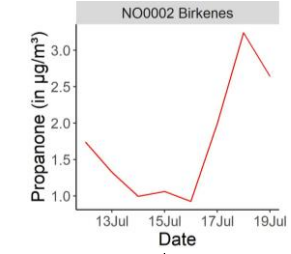
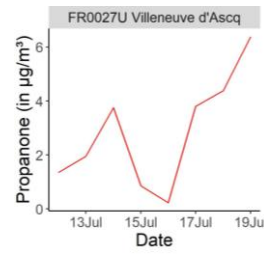
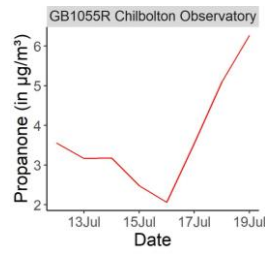
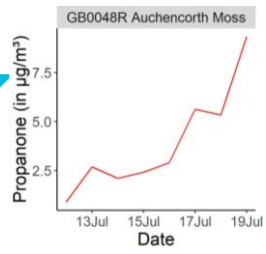


Example of the contribution of the different oxy-VOCs, on 12/07/2022 at different sites

Propanone



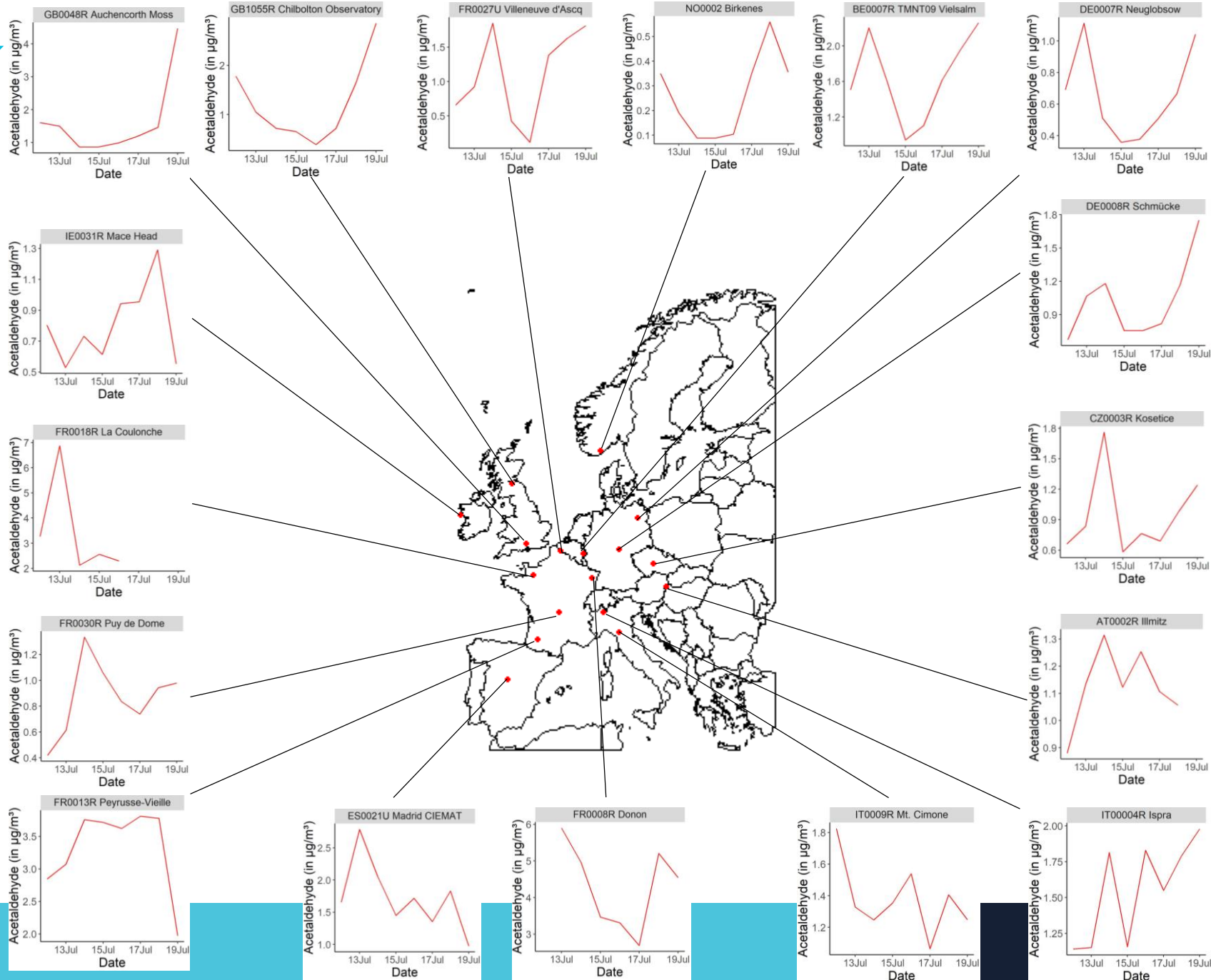
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Acetaldehyde



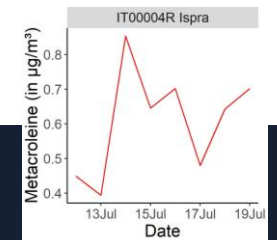
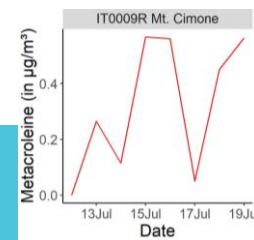
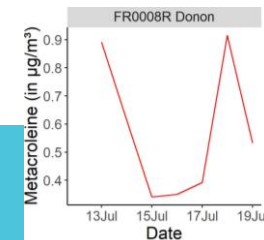
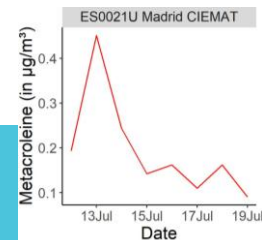
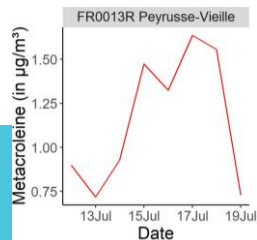
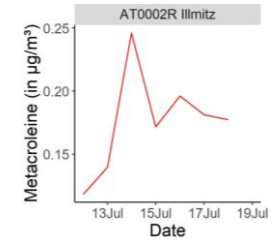
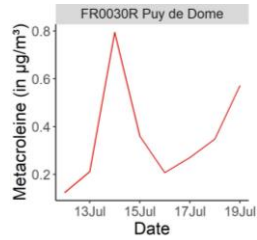
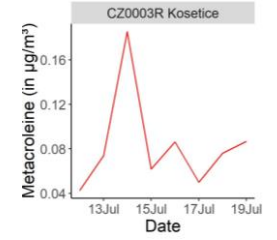
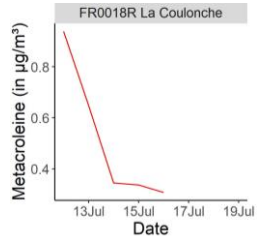
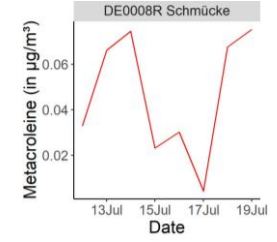
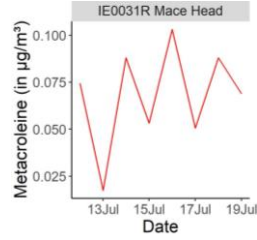
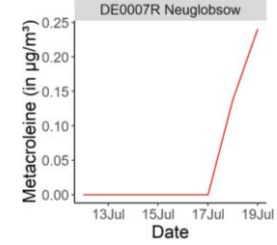
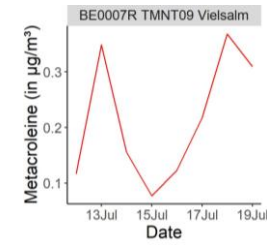
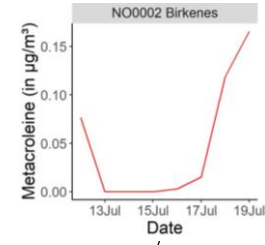
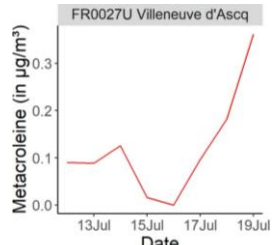
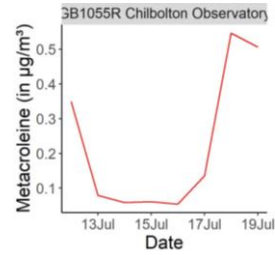
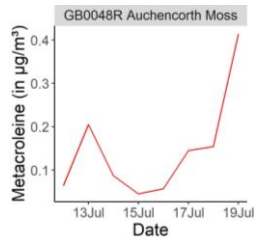
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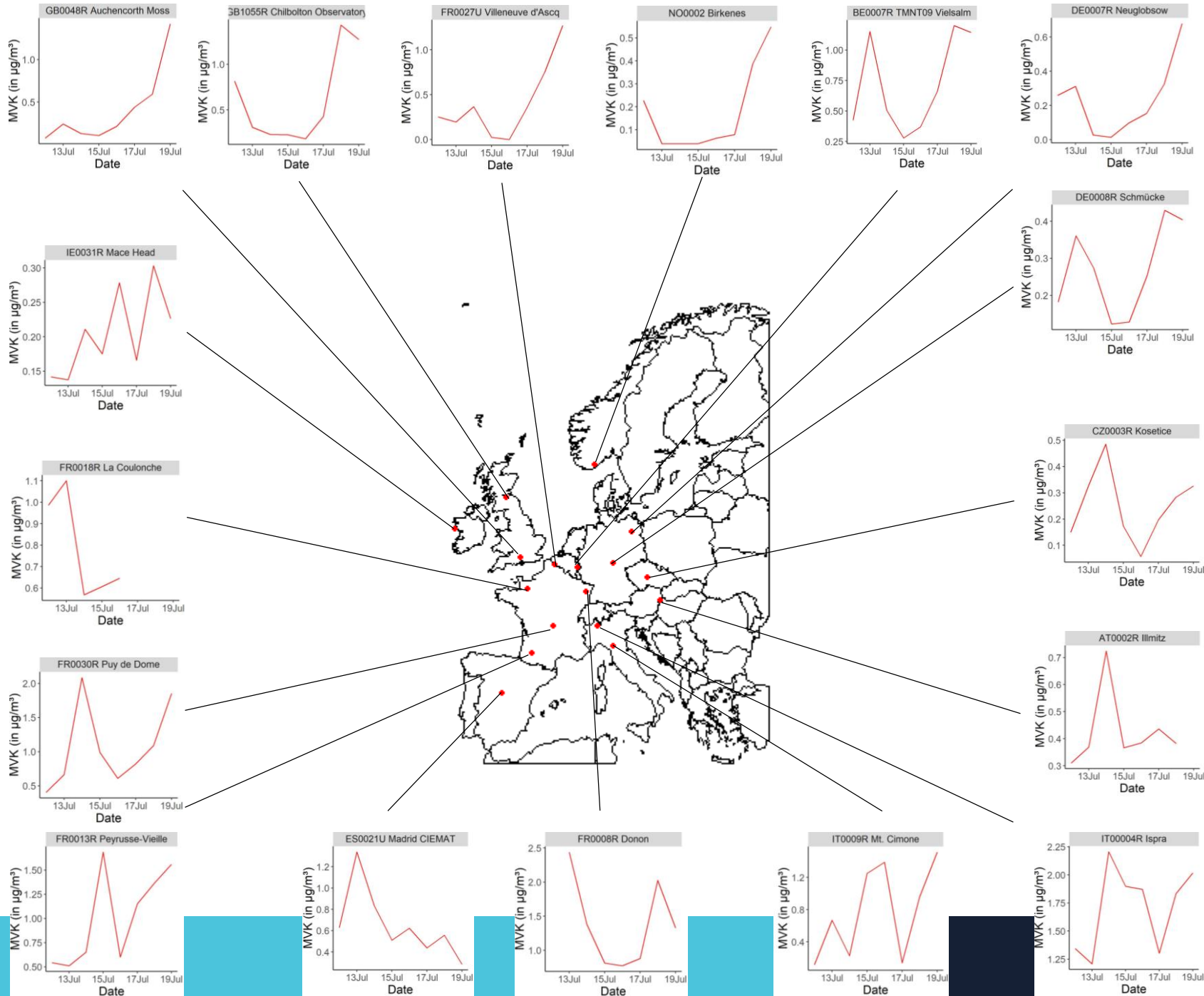


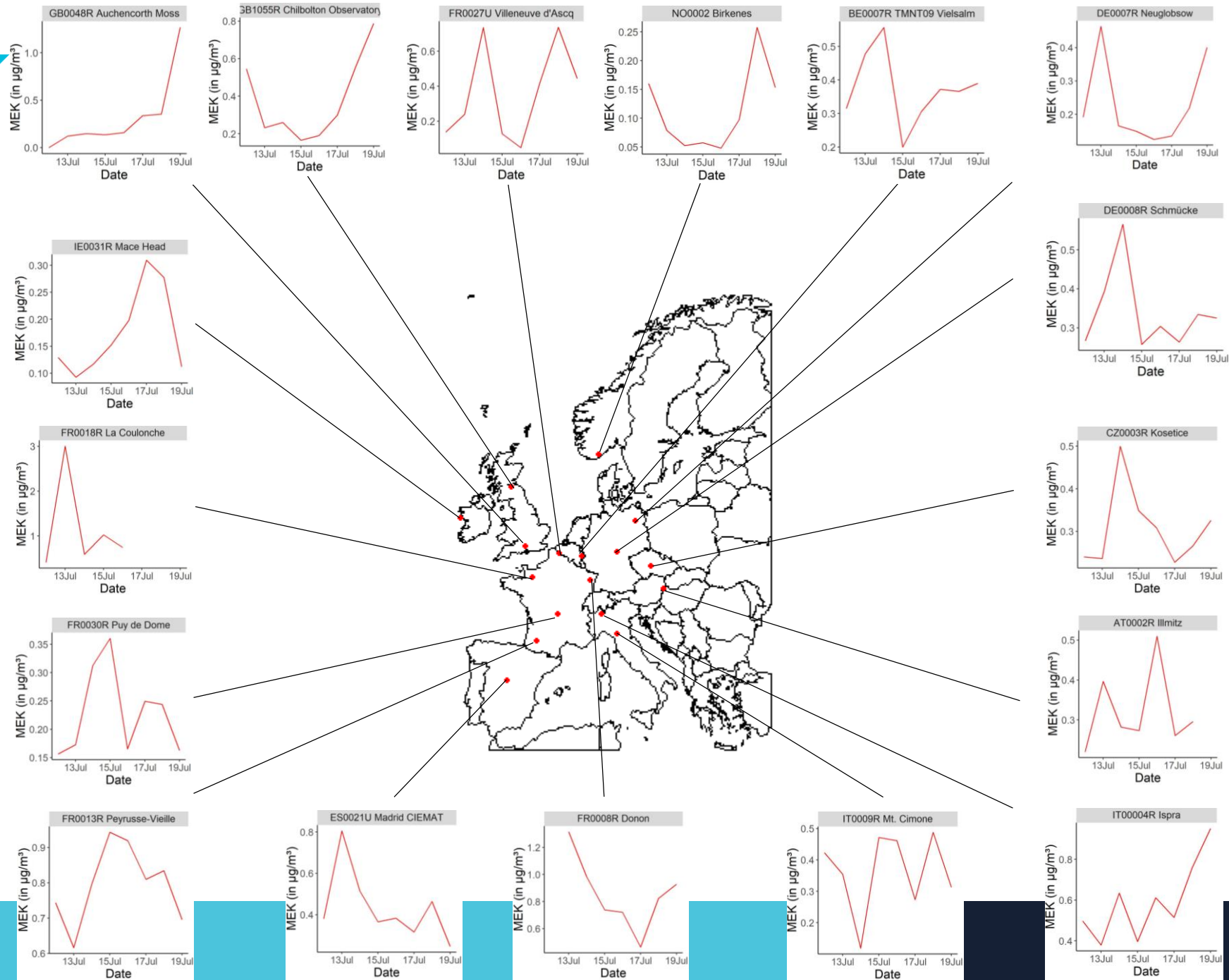
Methacrolein



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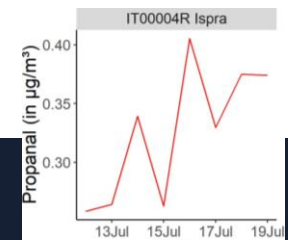
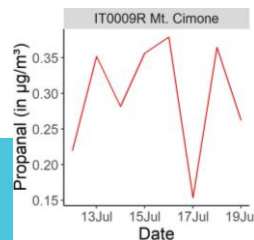
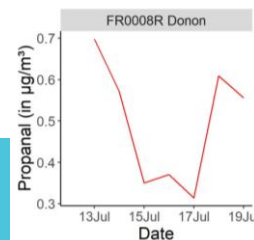
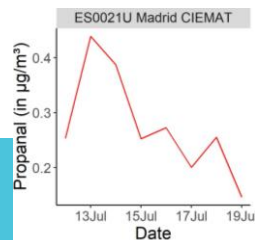
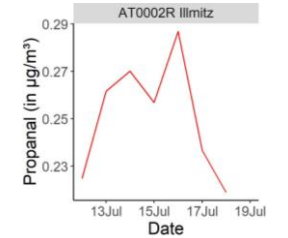
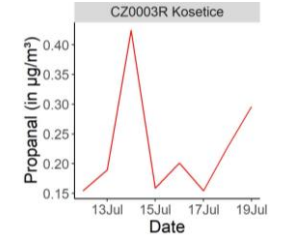
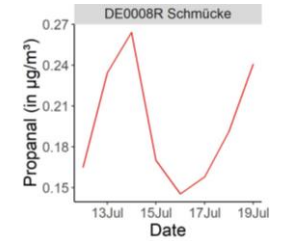
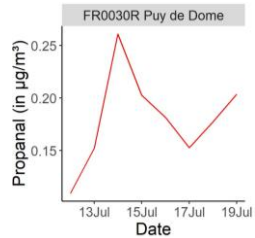
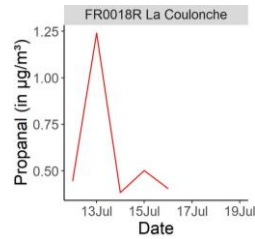
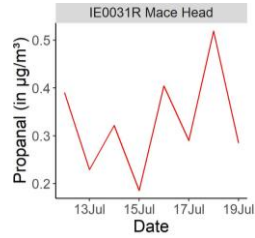
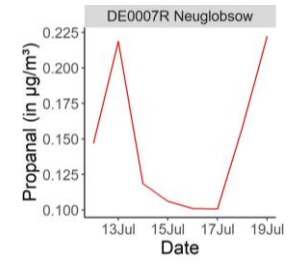
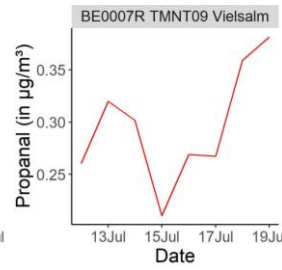
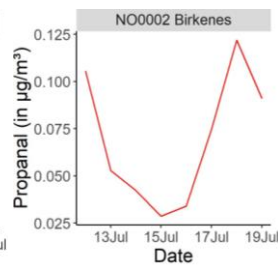
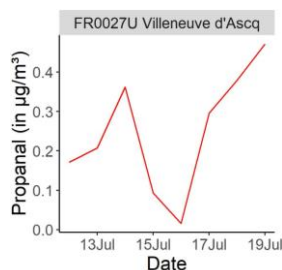
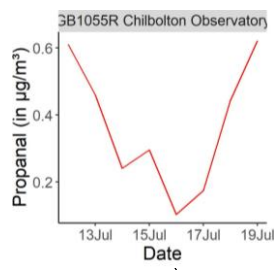
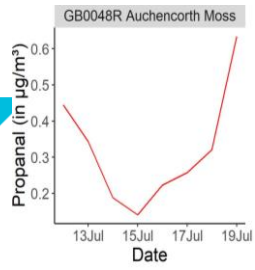


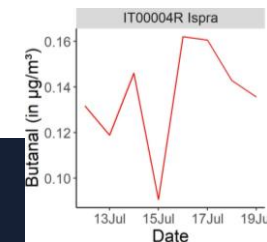
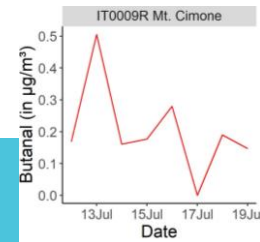
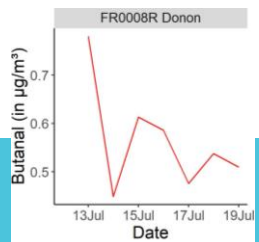
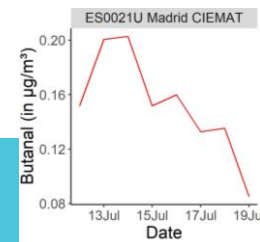
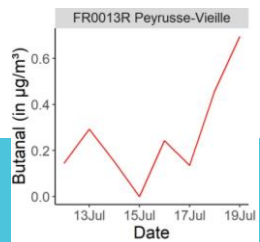
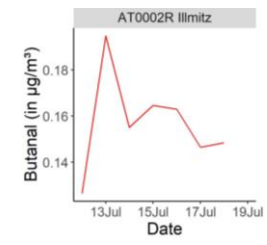
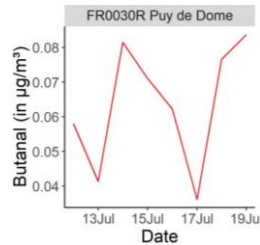
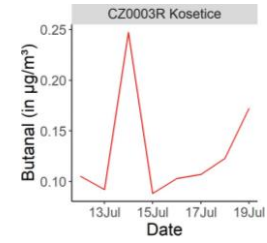
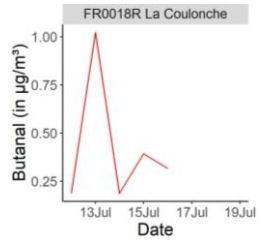
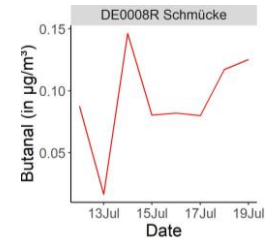
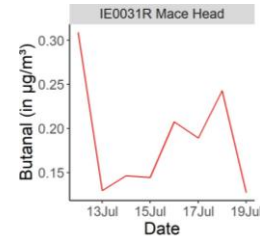
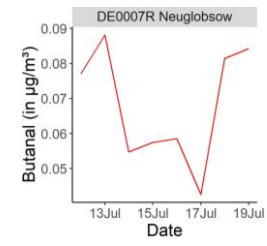
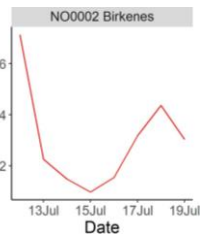
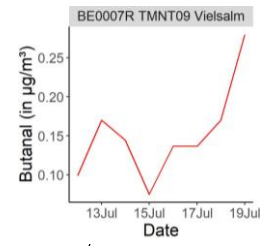
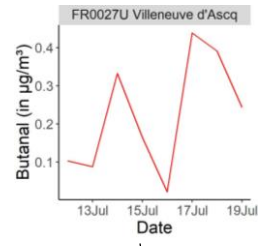
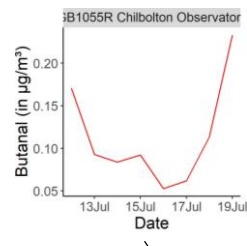
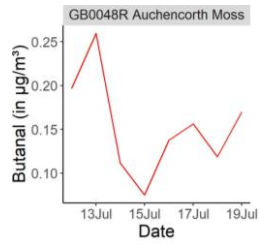


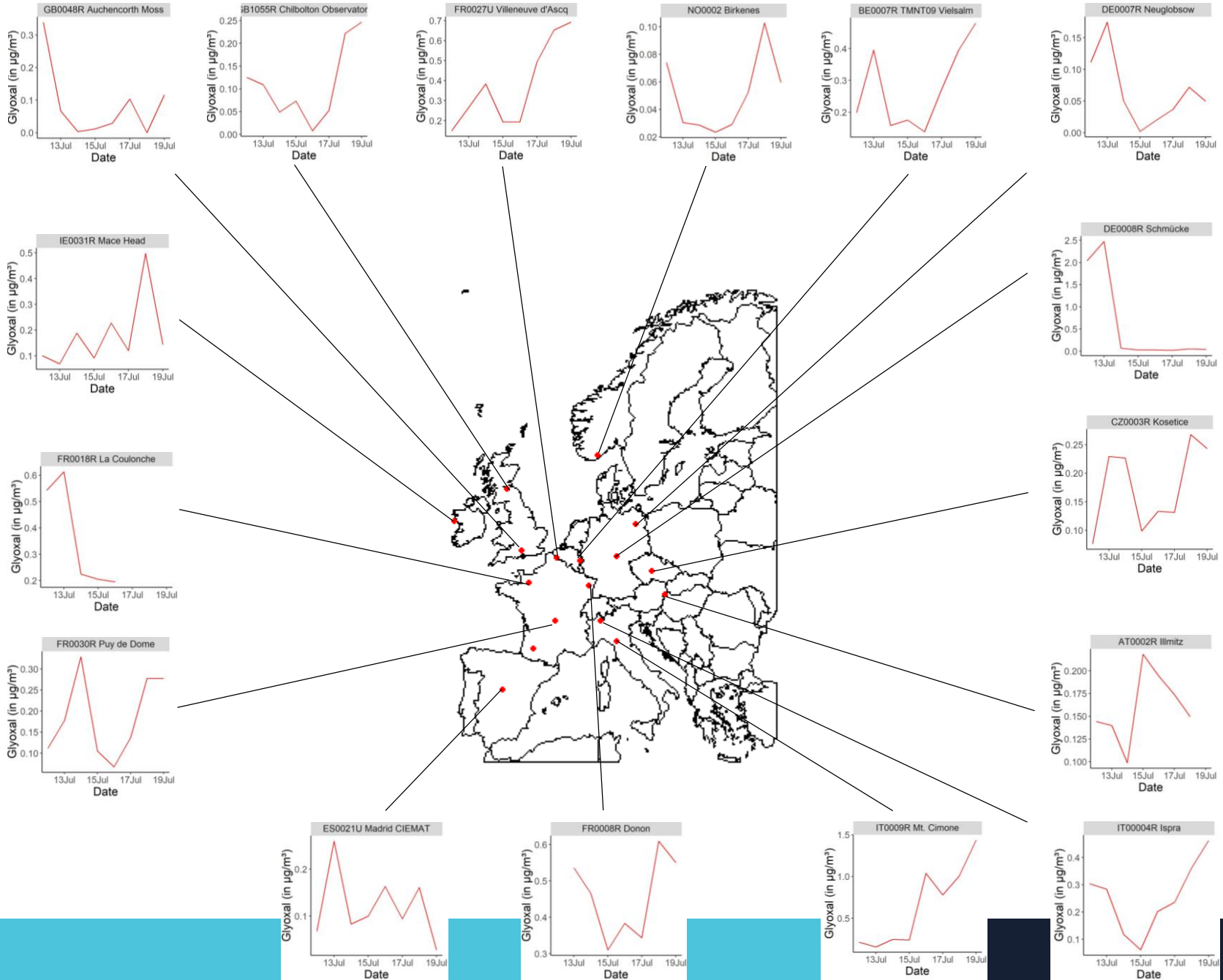
Propanal



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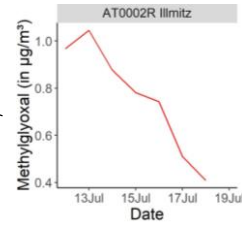
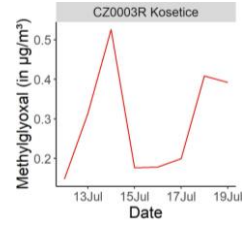
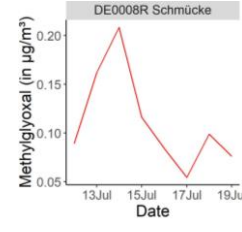
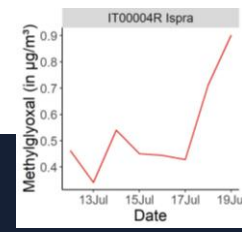
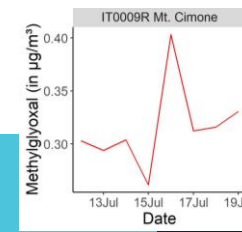
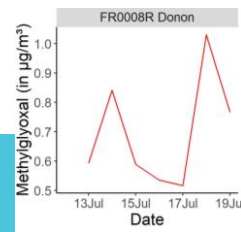
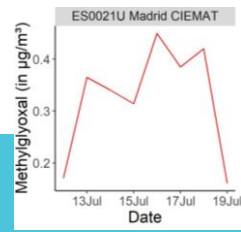
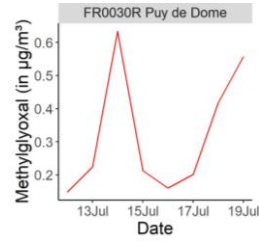
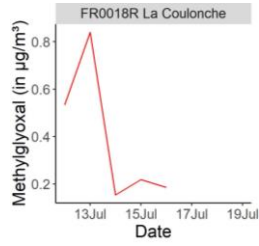
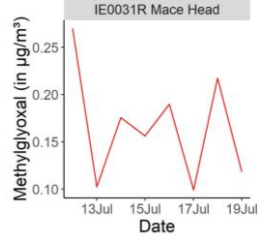
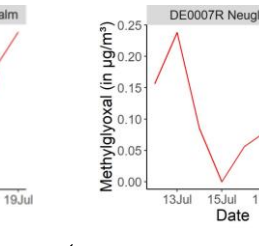
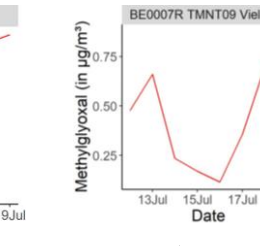
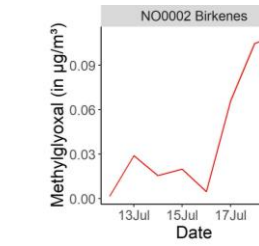
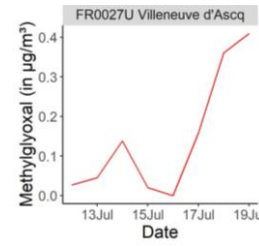
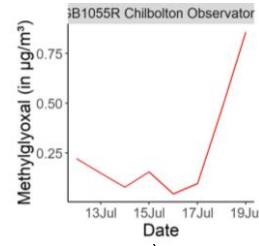
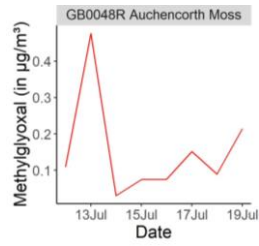




Methylglyoxal



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WAY FORWARD

- **Data sent to NILU -> sampling sites for reporting**
- **Results will be published in a common paper with other partners (EMEP – TFMM meeting 10-12 May)**

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