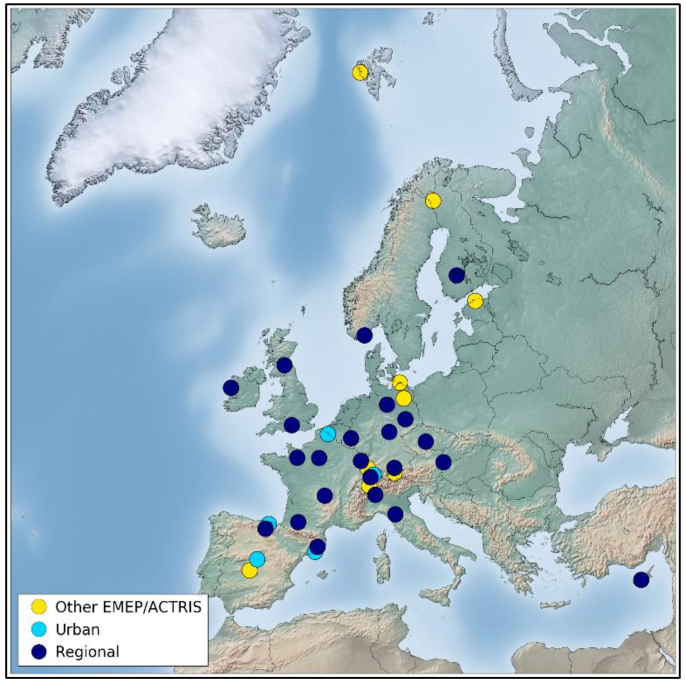
Intensive measurement periods

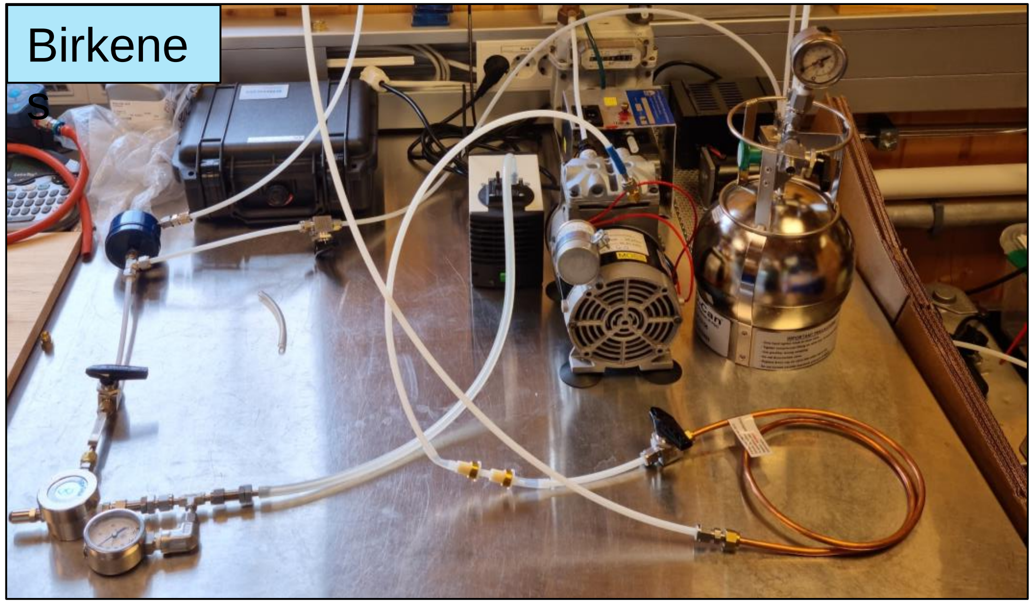
- summer 2022 on VOCs, SOA and ozone
- summer/autumn on VOCs

Wenche Aas, Sverre Solberg et al.

Background /Objectives

- High ozone episodes are typically underpredicted by atmospheric transport models. **Provide data for model improvement**
- Decrease in summer peaks, but the reductions are lower compared to the reductions in NMVOC and NOx emissions. **More insight in the VOC sources/emissions**
- VOC observations in EMEP is limited in respect of compounds (few sites with O-VOCs and terpenes) and frequency (grab sampling at several) **Get spatial information of range of VOC**
- Biogenic secondary organic aerosols (BSOA) important secondary pollutant of VOCs. **Tracer analysis to assess main sources of BSOA**





The setup for the one-week intensive sampling

- Sites already have ozone, NOx/NO_2 observations, several also EC/OC
- Forecasted the best week for high ozone levels

1) Extended the regular EMEP observations

✓ include missing VOC component groups (NMHC, OVOC, Monoterpenes)

✓ increase sampling frequency to daily sampling all the sites

✓ Equip sites with continuous sampling if available (i.e. PTR-(ToF)-MS, GC/FID)

2) Additional manual sampling.

Distributed devices and centralised analysis:

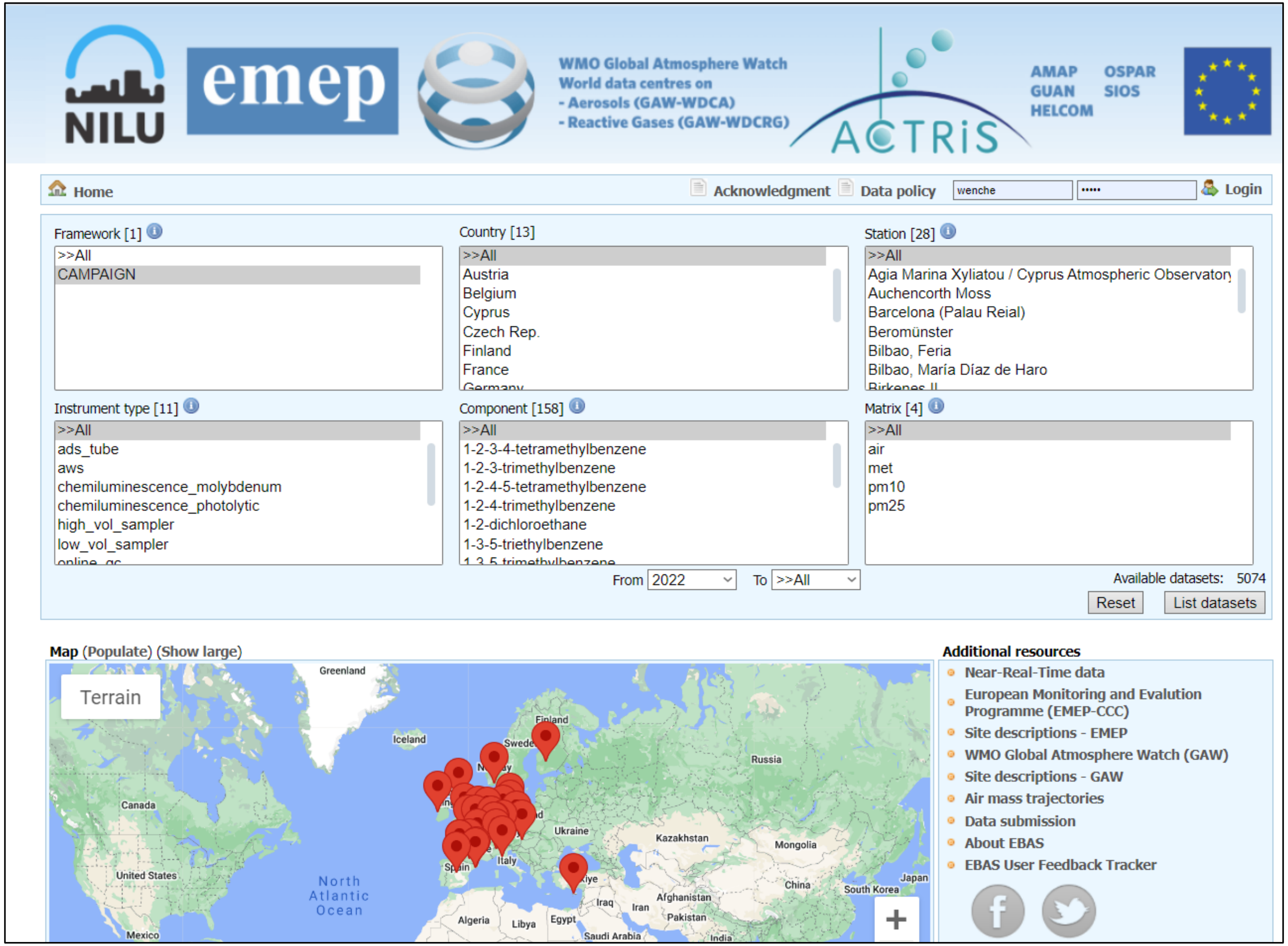
✓ NMHC:	Canister air sampling (FZ Jülich, Germany)
✓ O-VOCs:	DNPH cartridge (IMT, France)
✓ Monoterpenes:	Tenax tubes (FMI, Finland)
o SOA tracers:	Use part of EC OC filters from regular monitoring (IGE, France)

Sponsored by:

Data available in EBAS

- 5074 datasets
- 13 countries
- 28 sites
- 158 components

Tracers (46 different) yet to be added (end of May)



https://ebas-data.nilu.no

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Defined new naming convention for PTR-MS and PTR-ToF-MS

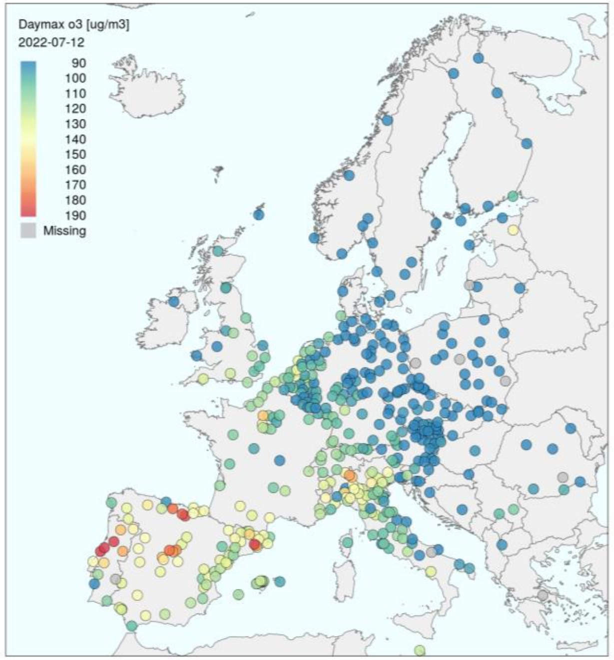
m/z (unit mass)				Ebas vocabulary new names (white) established names (green)	
QMS	Tof-MS	Parent ion composition	Compound attributions	PTR-ToF-MS	PTR-QMS
31	31.018	CH2OH+	Methanal (formaldehyde)	methanal	methanal
33	33.033	CH4OH+	Methanol	methanol	methanol
42	42.034	C2H3NH+	Acetonitrile	acetonitrile	acetonitrile
45	45.033	C2H4OH+	Ethanal (Acetaldehyde)	ethanal	ethanal
47	47.013	CH2O2H+	Formic acid	formic_acid	mass_47_organic_compounds
47	47.049	C2H6OH+	Ethanol	ethanol	
57	57.033	C3H4OH+	2-propenal (Acrolein),methylketene	mass_57.033_organic_compounds	mass_57_organic_compounds
57	57.070	C4H8H+	Butene, 2-methylpropene (Isobutylene), 1-Butanol, 2-Butanol	mass_57.070_organic_compounds	
59	59.049	C3H6OH+	Propanone (Acetone), Propanal	mass_59_organic_compounds	mass_59_organic_compounds
61	61.028	C2H4O2H+	Acetic acid, Hydroxyethanal (glycolaldehyde)	mass_61.028_organic_compounds	mass_61_organic_compounds
61	61.065	C3H8OH+	n-propanol (1-propanol), 2-Propanol	mass_61.065_organic_compounds	
63	63.026	C2H6SH+	dimethylsulfide	dimethylsulfide	dimethylsulfide
69	69.033	C4H4OH+	Furan	furan	mass_69_organic_compounds
69	69.070	C5H8H+	Isoprene (2-Methylbuta-1,3-dien), Cyclopentene	isoprene	
71	71.049	C4H6OH+	3-buten-2-one (Methyl vinyl ketone (MVK)), 2-methylpropenal (Methacrolein (MACR), 2-Methyl-2-propen-1-al), 2-Butenal (crotonaldehyde)	mass_71_organic_compounds	mass_71_organic_compounds
73	73.028	C3H4O2H+	Methylglyoxal, Acrylic acid (propenoic acid)	mass_73.028_organic_compounds	mass_73_organic_compounds
73	73.065	C4H8OH+	Butanal, 2-Methylpropanal (Isobutyraldehyde), 2-Butanone (methyl ethyl ketone (MEK)), Tetrahydrofuran	mass_73.065_organic_compounds	
75	75.044	C3H6O2H+	Methyl acetate (acetic acid methyl ester)	methyl_acetate	methyl_acetate
79	79.054	C6H6H+	Benzene	benzene	benzene
93	93.010	C3H5ClOH+	1-Chloropropan-2-one (Chloroacetone)	chloroacetone	mass_93_organic_compounds
93	93.033	C6H5O+	1,2 Epoxybenzene	epoxybenzene	
93	93.057	C6H7N +	Anilin	mass_93.06_organic_compounds	
93	93.055	C3H9O3+	Propanoic acid water cluster		
93	93.070	C7H8H+	Toluene, p-cymene	mass_93.070_organic_compounds	
93	93.091	C4H13O+	Ethanoldimer, Butanol-Water-Cluster	mass_93.091_organic_compounds	
105	105.070	C8H9+	Styrene	styrene	styrene
107	107.049	C7H6OH+	Benzaldehyde	benzaldehyde	mass_107_organic_compounds
107	107.086	C8H10H+	o-Xylene, m-Xylene, p-Xylene, ethylbenzene, C8-alkylbenzenes	mass_107.086_organic_compounds	
113	113.015	C6H5ClH+	chlorobenzene (monochlorobenzene -MCB)	chlorobenzene	chlorobenzene
121	121.101	C9H12H+	1,2,3-trimethylbenzene,1,2,4-trimethylbenzene,1,3,5-trimethylbenzen, C9-alkylbenzenes	mass_121_organic_compounds	mass_121_organic_compounds
137	137.132	C10H16H+	Monoterpenes	monoterpenes	monoterpenes

in cooperation with ACTRIS CiGas

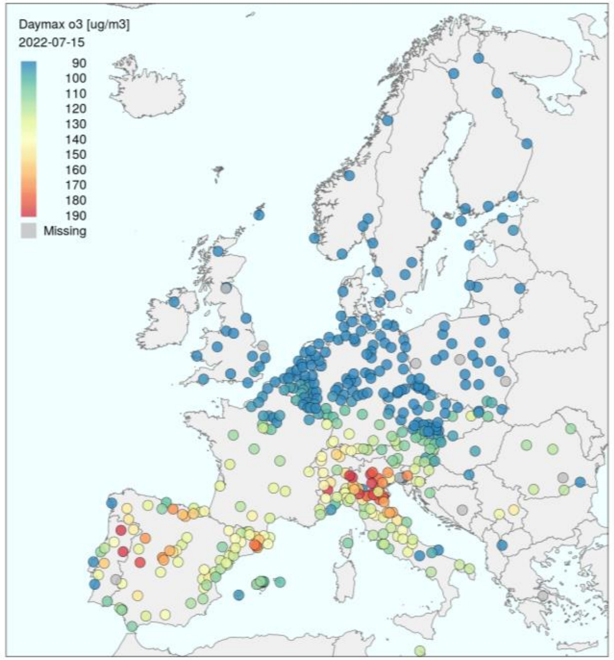
Groups (mz) in accordance to GLOVOCS («Master compound assignment guide for PTRMS users"): http://glovocs.creaf.cat/guide/

Ozone, daily maximum (Data from EEA)

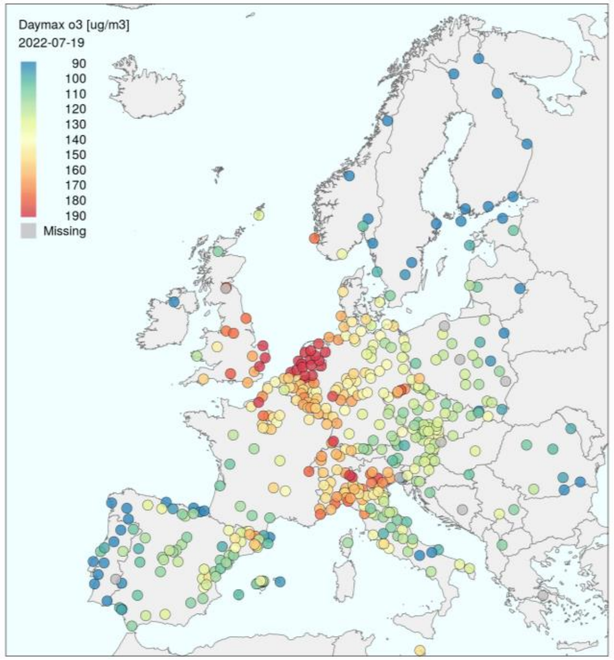
12. July



15. July

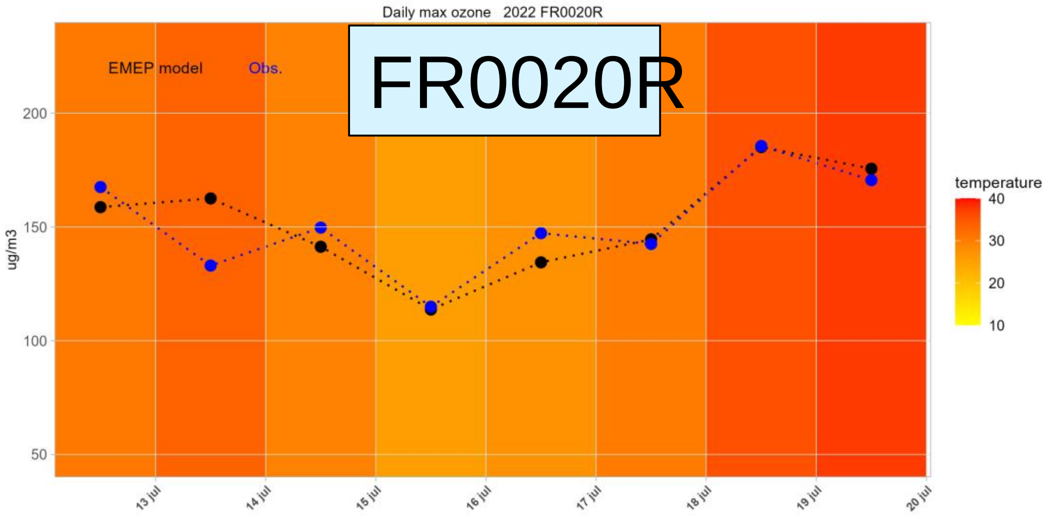


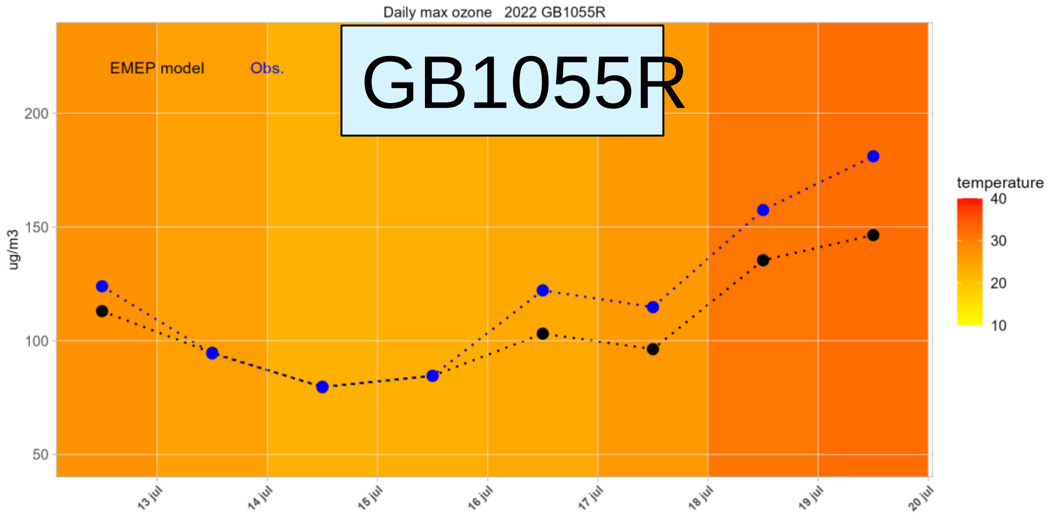
19. July

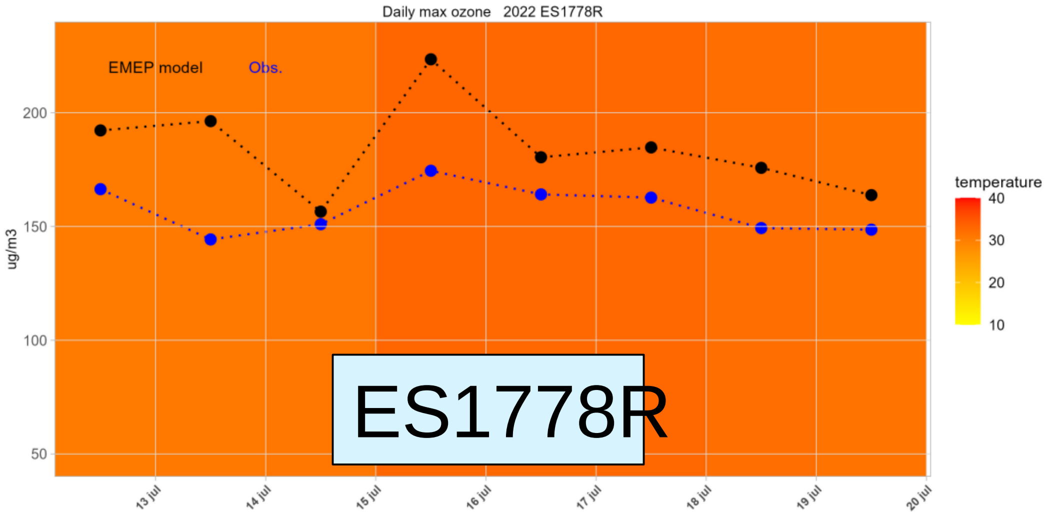


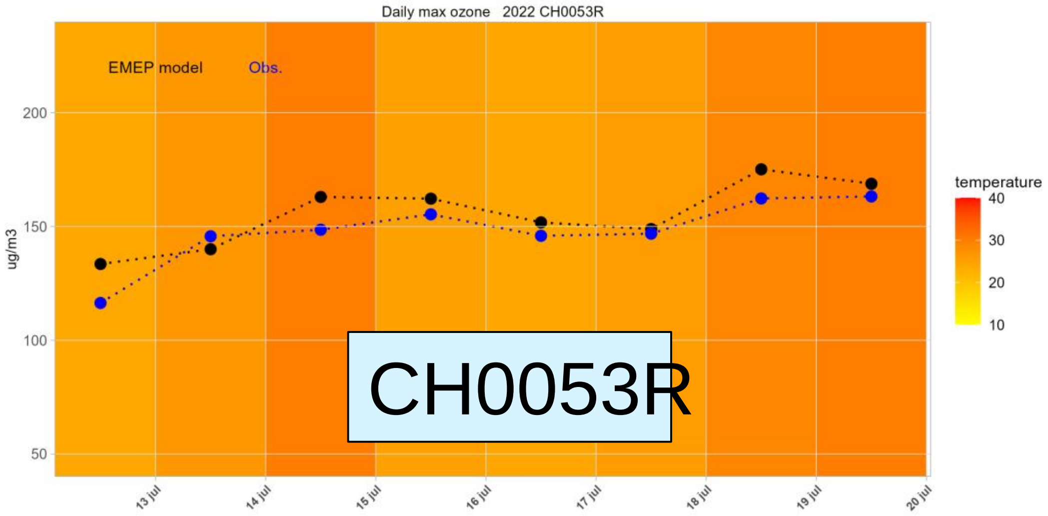
Does the EMEP model underpredict the ozone peaks?

Daily max obs (blue) and model (black), 12-19 July vs temperature (colourscale)



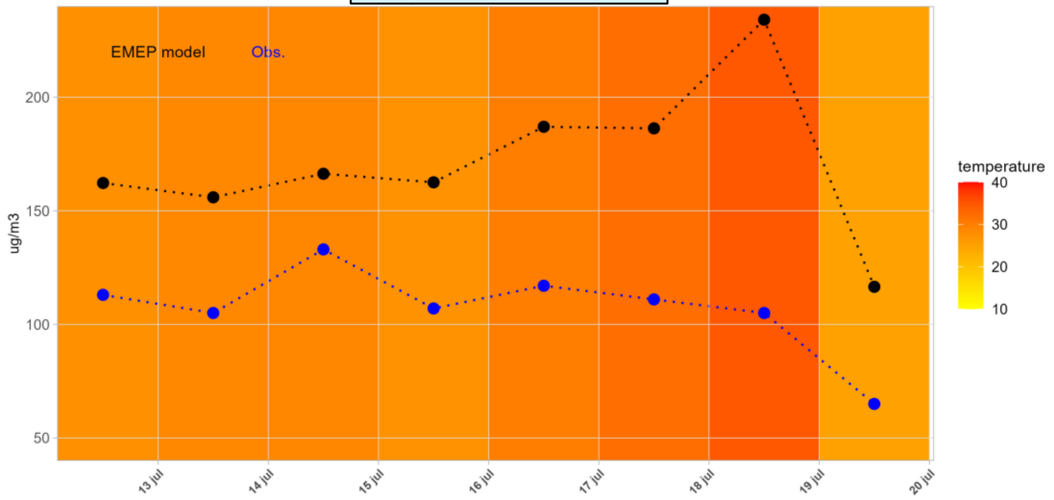




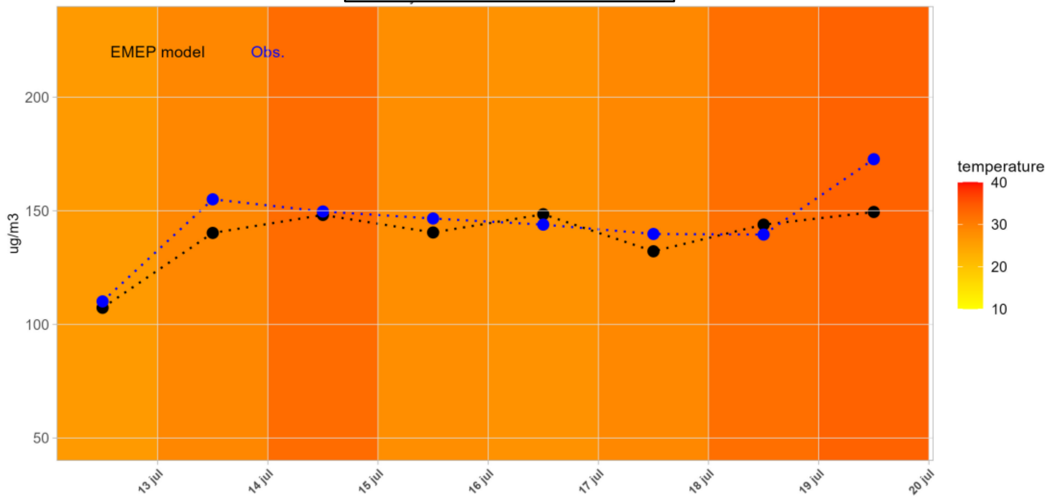


cont. urban sites

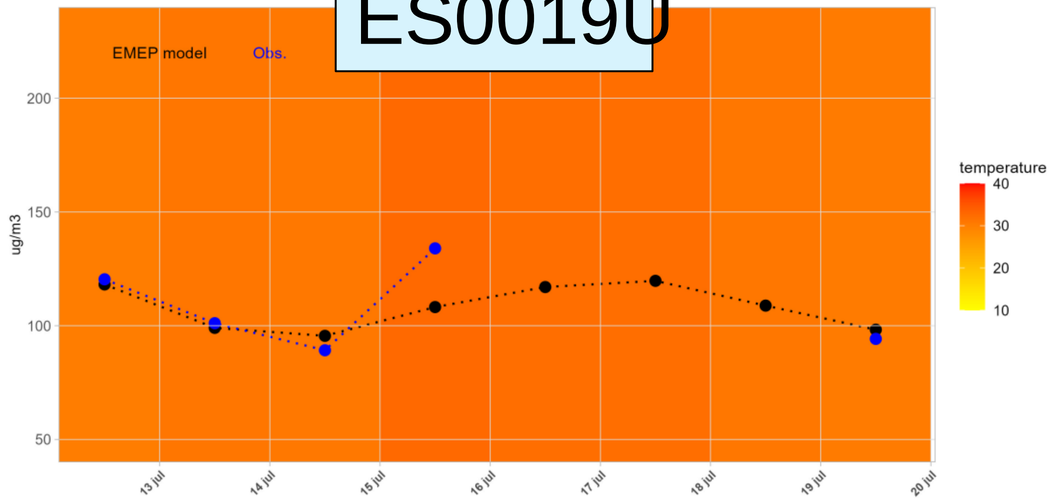
ES0025U



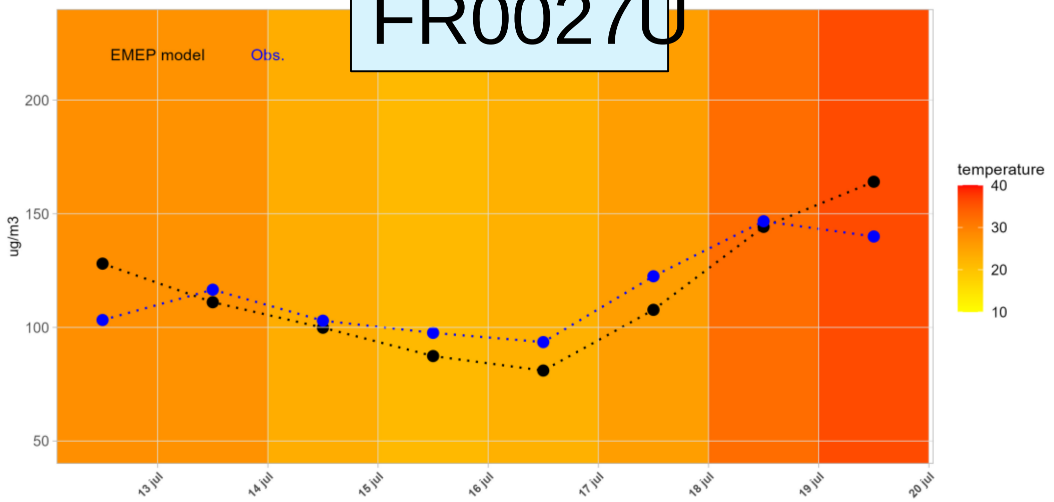
CH0010U



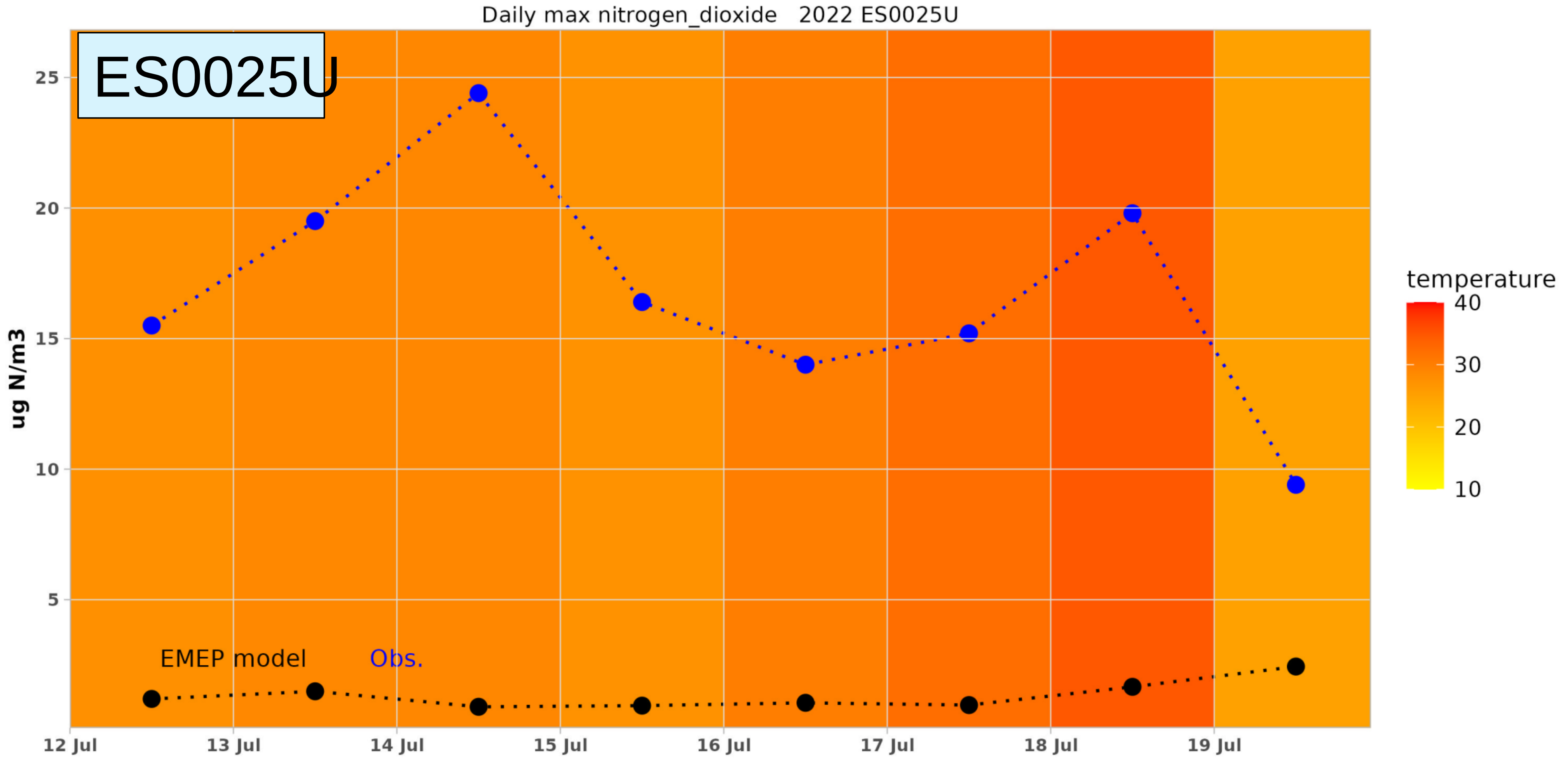
ES0019U



FR0027U

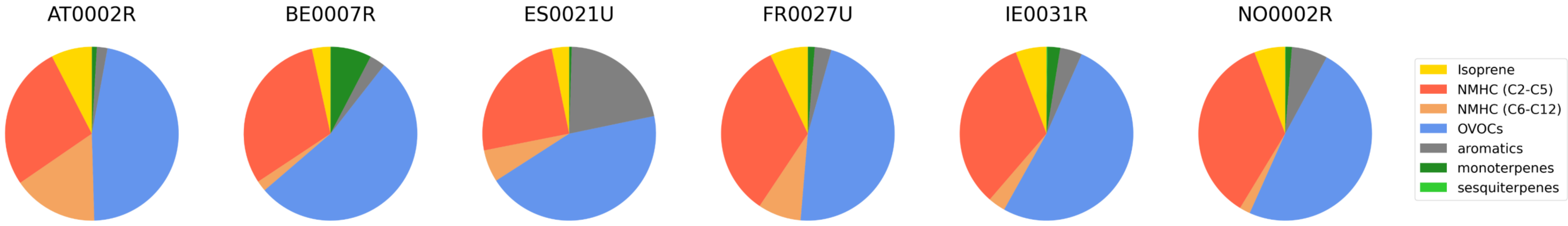


Important to get the Nox emissions right to get correct levels at urban sites –though difficult with representativity



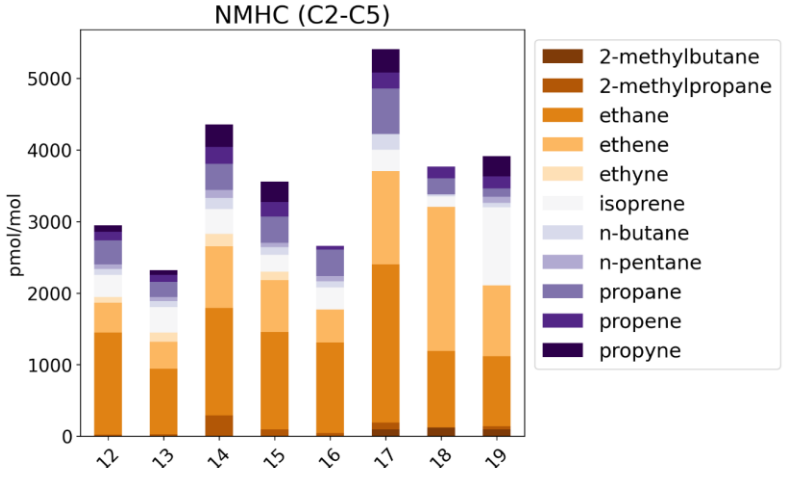
Distribution of different VOC groups at selected sites

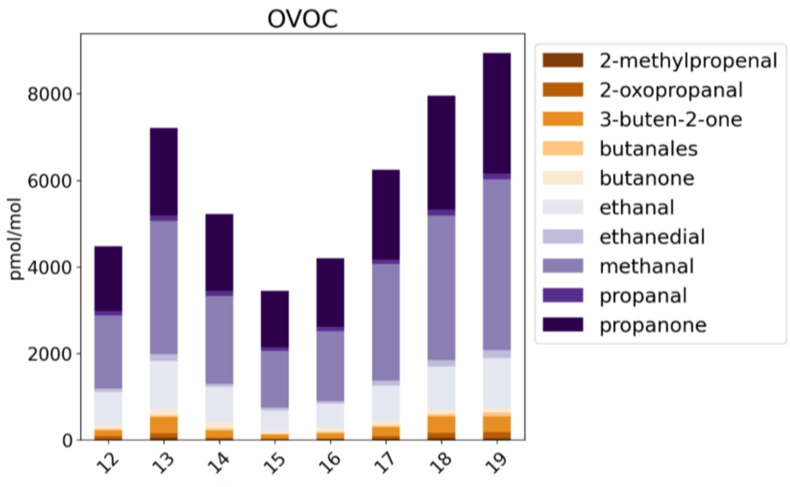
- Only compared components measured with comparable methods (central analysis).
- **All the sites are dominated by OVOCs and C2-C5 NMHCs**, and their relative contribution does not vary very much between the sites even though they are situated in quite different environments, some differences seen though:
  - Illmitz (AT0002R) that has a larger fraction of C6-C12 NMHCs.
  - Madrid (ES0021U) has the highest relative influence of aromatic VOCs
  - Viesalam (BE0007R) is situated in a forest and has relatively large contribution of monoterpenes

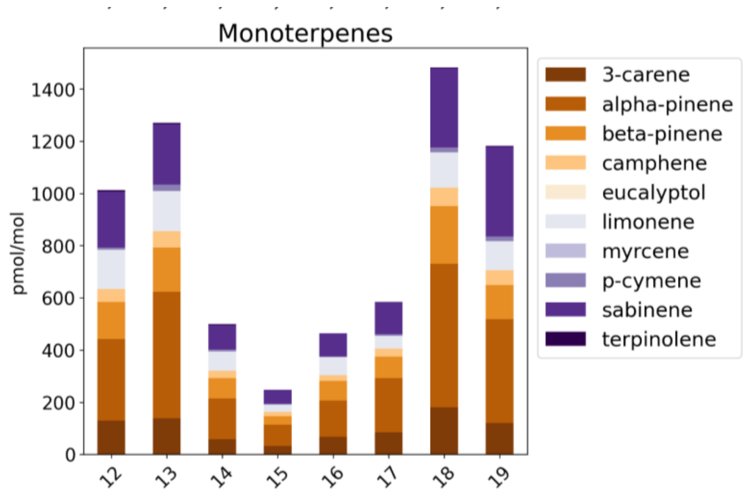


Detailed information on VOC speciation from central analyis

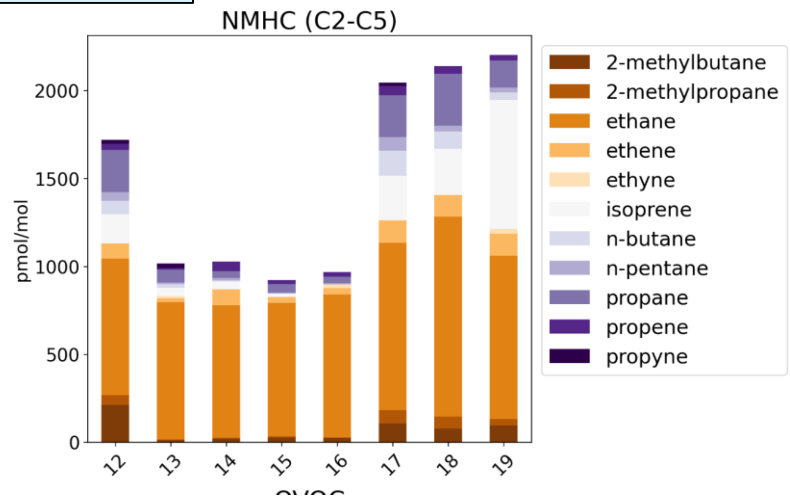
BE0007R

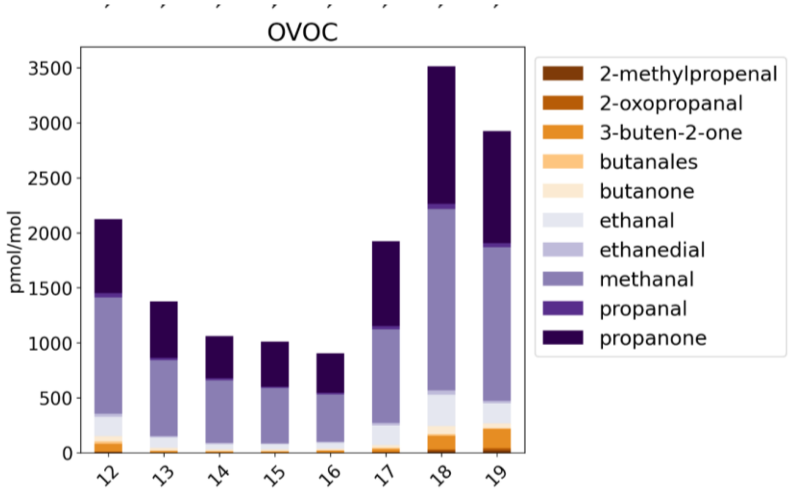


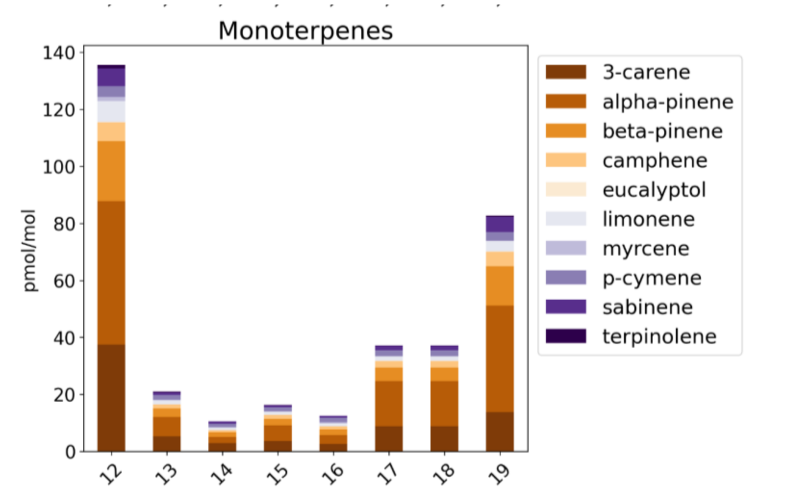




NO0002R



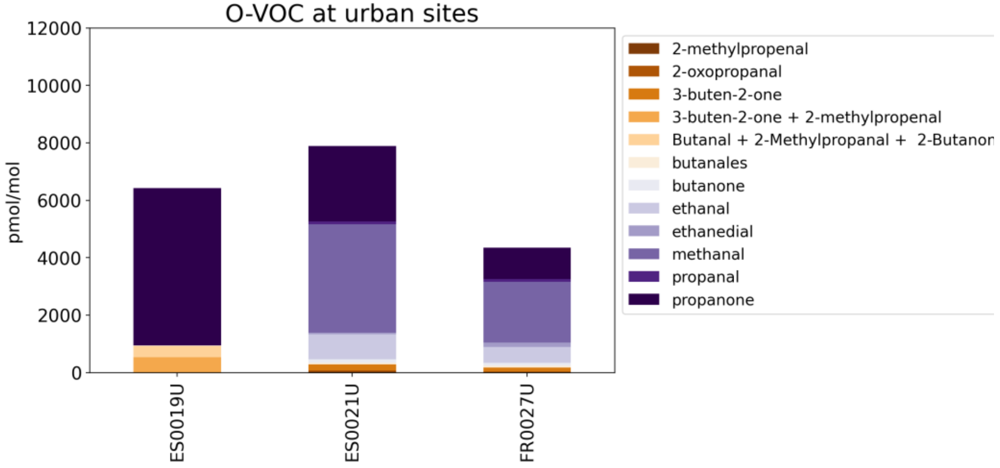


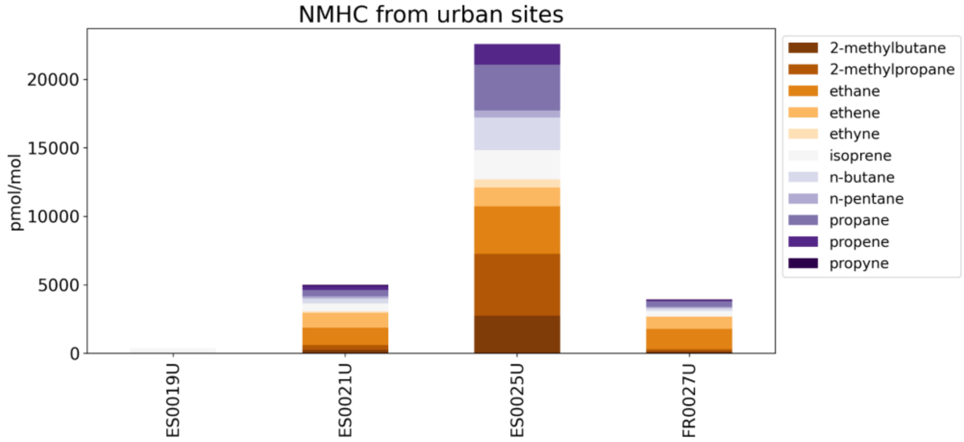


OVOCs

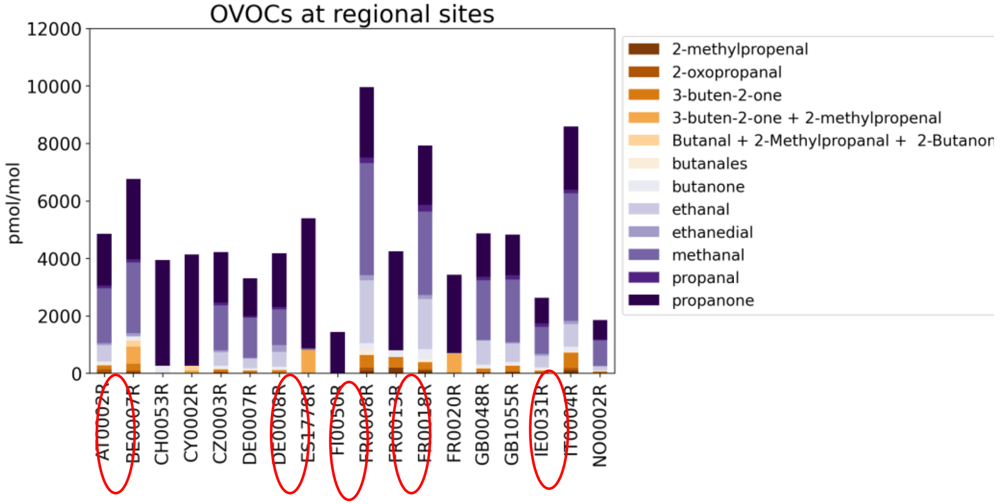
NMHCs

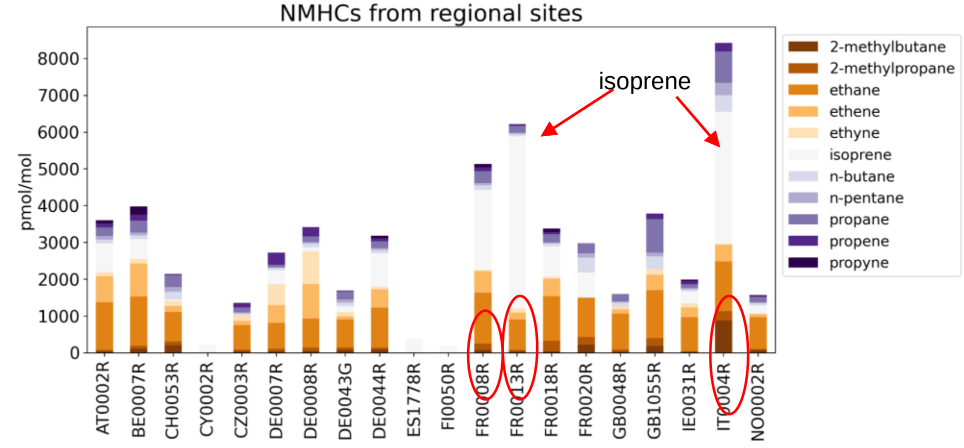
Urban sites





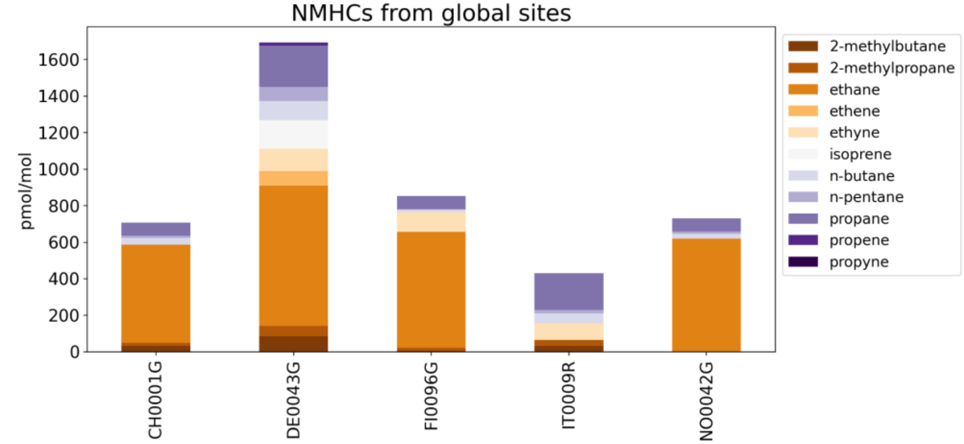
Regional sites





BE0007R, ES1778, FR0008R,FR0018 and IT0004R comparable to urban levels

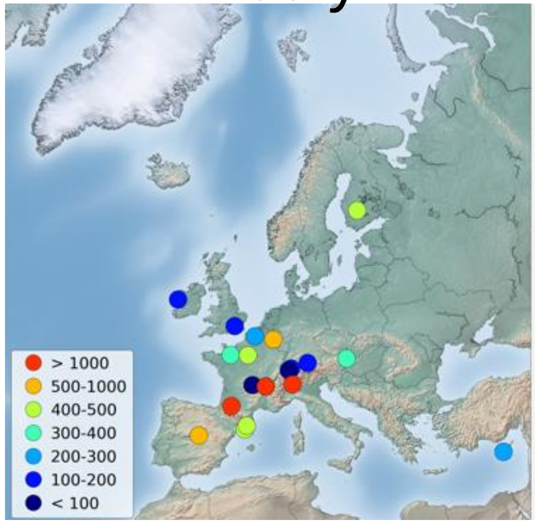
Global sites

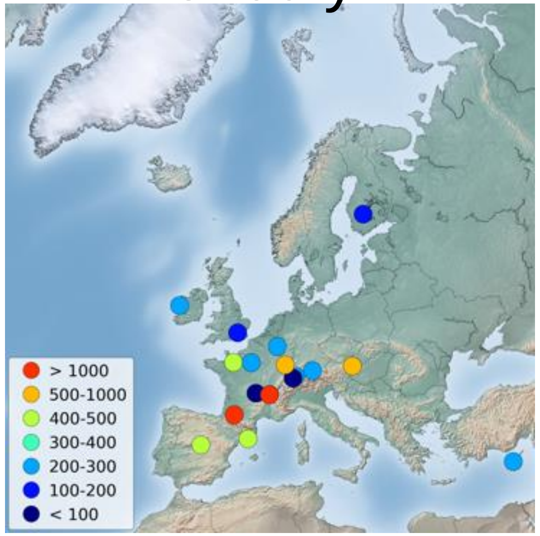


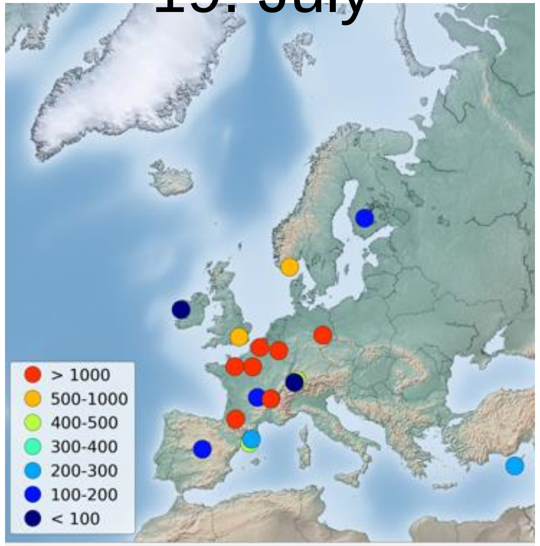
Spatial and temporal variation of selected VOCs

12. July | 15. July | 19. July

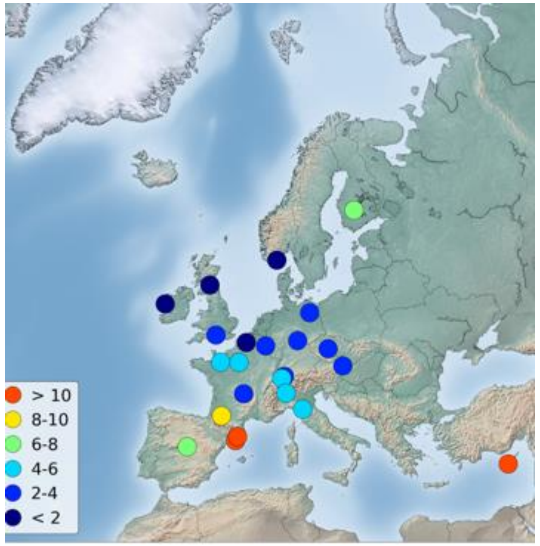
Isoprene

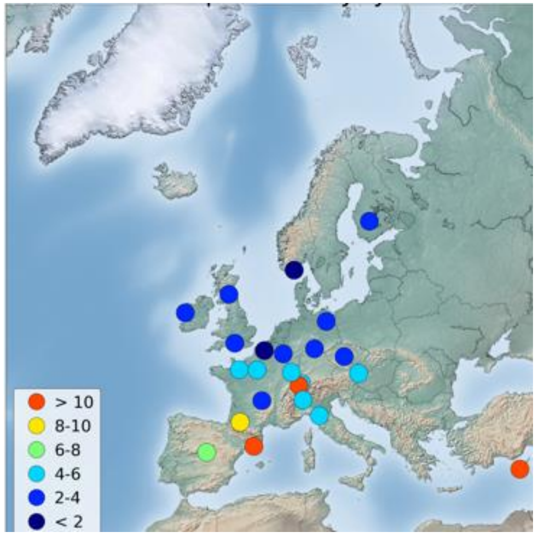


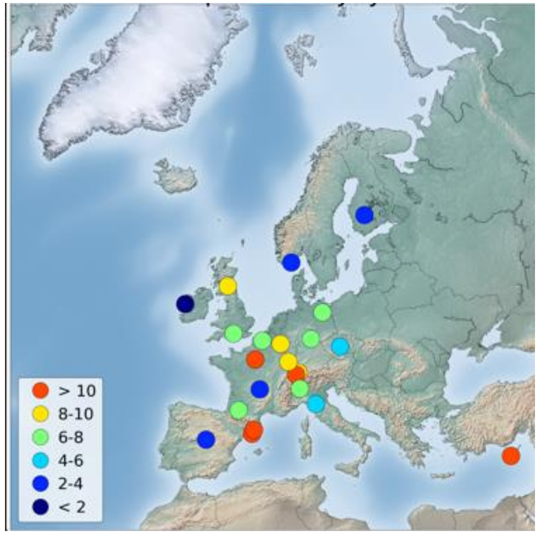




Propanone (acetone)





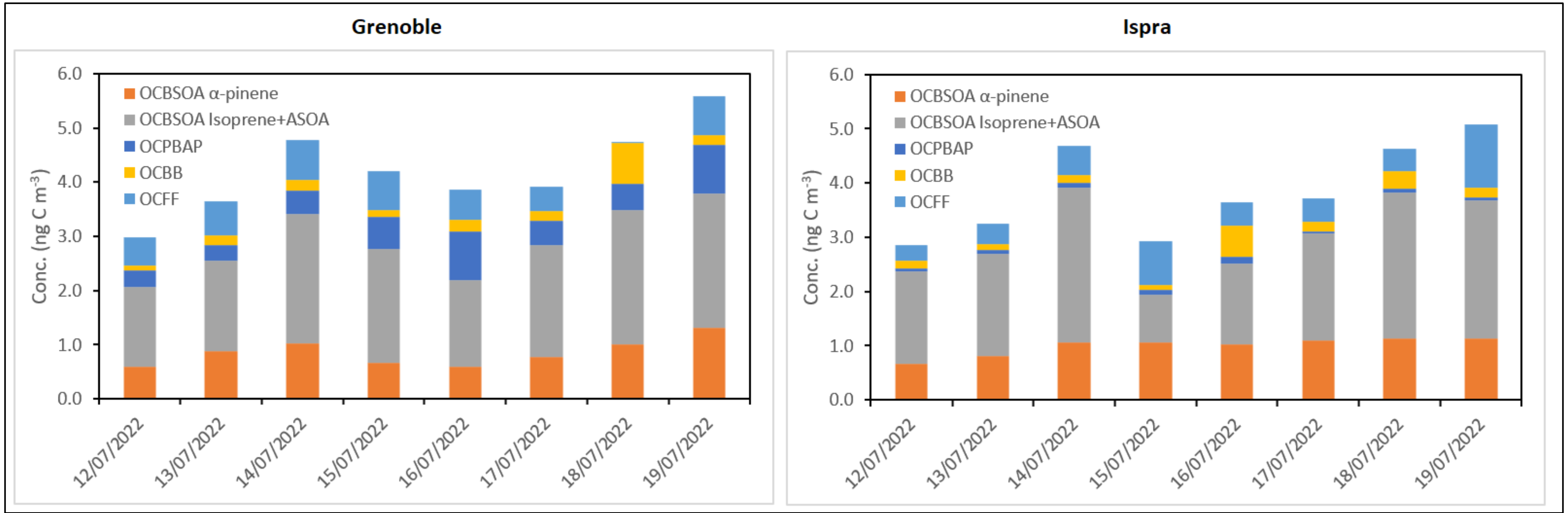


Tracers used for apportioned biogenic organic aerosols into secondary and primary categories, at Ispra and Grenoble

Organic aerosols during the intensive measurement week (IMP) was apportioned to:

- 20% from oxidation of α-pinene
- 50% from oxidation products of isoprene and anthropogenic emissions
- 13% -14% from fossil fuel (FF)
- 6% OC from biomass burning (BB)
- Primary biological particles (PBAP): 13% at Grenoble but only 2 % at Ispra

Up to 80% of organic aerosol was attributed to SOA



From the EMEP status report 1

Discussions

- The IMP period does not show a general underprediction of the ozone peaks
- Both ozone and VOC increase towards north during the IMP week
- Higher concentrations of NMHC in urban areas otherwise large variations between sites
- Relative concentrations between VOC groups similar across sites.

Further process on IMP 2022

- This IMP will probably not answer the question of which VOC may cause an underestimation of ozone during heat waves. Need a broader perspective and incl more models
- Publish a PAN European assessment of the various VOC levels dynamic during this heat wave –submit during 2024
- Include work on organic tracers -linked to the levels of the different VOCs

A new VOC intensive measurement campaign planned for 2024

- Discussed at TFMM web call meeting in October - invitation sent out in 2 April

Focus:

- **Speciated VOC emissions.** Knowledge gaps in speciated VOC emissions, **measurements near emission sources**, notably industrial and urban sites, including harbors. -include regional sites (preferably twin sites, wherever feasible.

- **Enhanced temporal resolution**. Acknowledging the varying lifetimes and evaporation potential of VOCs, our priority is **high temporal resolution** over extensive spatial coverage. May complement automated methods with manual sampling at selected sites to attain detailed specifications.

- **Extended duration.** In contrast to the one-week period of IMP-2022, IMP-2024 will span **an entire month**. This extended timeframe will enable us to better capture variations in emissions and facilitate comparisons with model calculations.

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- ESIG kindly offered to sponsor also the campaign

Feedback so far (not decided - potential sites)

Online –high resolution measurements

- France. Several French sites (local municipalities) are interested with online (GC and PTR-MS?) rural/urban. At least Strasbourg (urban site), Donon and Peyrusse Vieille (rural sites), -**September**
- Spain. Measurement campaign in Barcelona harbor **July?**
- Belgium. Vielsalm (forest), Engis (industrial/harbor influenced), Uccle in Brussels (semi-urban) PTR-MS
- Finland. SMEAR IV / Puijo, VocusPTR- MS (+ adsorbent tube samples for offline GC analysis.)
- Italy/Ispra online GC
- Switzerland. on-line instruments for NHMCs and OVOCs at Zuerich and at Beromuenster.
- Germany. Melplitz and (Eisenbahnstrasse (street canyon station) PTR-MS (ACTRIS – online GC for campaign

Manual

- Germany UBA 6-7 EMEP/ACTRIS stations -manual sampling)
- Spain. CIEMAT Madrid. VOC analysis with TENAX
- Italy. LIEFEREMY project urban NMVOC relevant for SOA formation.

Suggestion for VOC campaign in 2024

- One month sampling –**September**

- **High resolution measurements** (PTR-MS, GC-MS) at a variety of sites urban, industry, regional

- ITM Nord France will assist in coordinating and make QA/QC data available

- Possibly organise additional manual sampling and centralised analysis (ITM Nord) at selected sites to supplement the high-resolution measurements