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EMEP

Co-operative Programme for Monitoring and Evaluation
of the Long-Range Transmission of Air Pollutants in Europe

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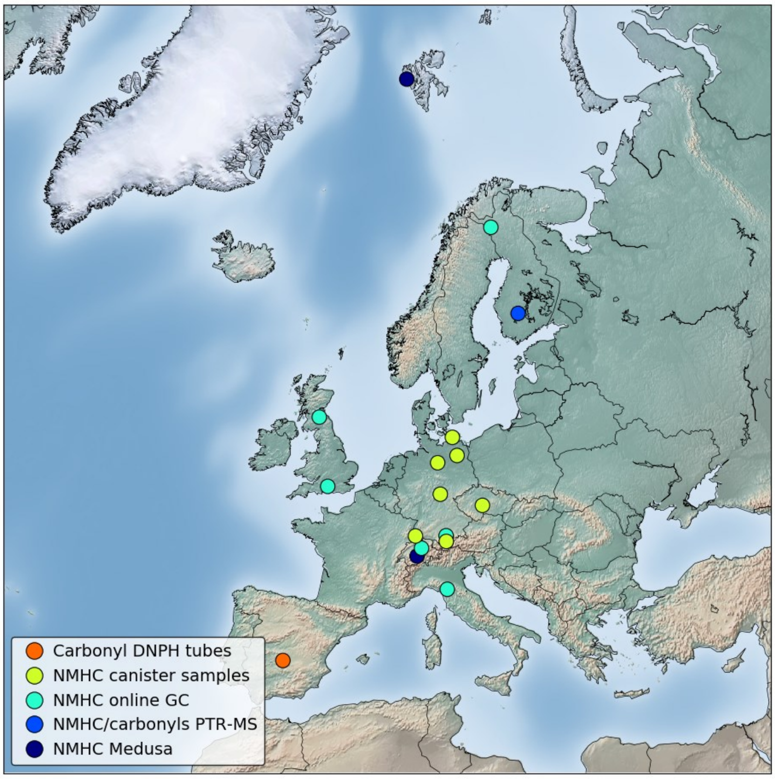

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VOC measurements 2021

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Summary

This report presents VOC (volatile organic compound) measurements carried out during 2021 at EMEP monitoring sites. In total, 17 sites reported VOC-data from EMEP VOC sites this year. Some of the datasets are considered preliminary and are not included in the report.

The monitoring of VOC has become more diverse with time in terms of instrumentation. Starting in the early 1990s with standardized methods based on manual sampling in steel canisters and adsorption tubes with subsequent analyses at the lab, the methods now consist of a variety of instruments and measurement principles, including automated continuous monitors and manual flask samples.

Within the EU infrastructure project ACTRIS, data quality issues related to measurements of VOC are important topics. Most of the institutions providing VOC-data to EMEP are participating in the ACTRIS infrastructure project, either as formal partners or on a voluntary basis. Participation in ACTRIS means an extensive effort with data-checking including detailed discussions between the ACTRIS community and individual participants. There is no doubt that this extensive effort has benefited the EMEP-program substantially and has led to improved data quality in general.

In general, the levels in 2021 agree well with previous 5-years period, showing similar geographical patterns as in the previous years. Changes in instrumentation, procedures and station network with time make it difficult to provide a rigorous and pan-European assessment of long-term trends of the observed VOCs. In this report, we have estimated the trends in individual NMHCs over the 2001-2021 period for one single station (Hohenpeißenberg), using a newly developed method, a so-called GAM (generalized additive model), that removes the effect of anomalies in the meteorology.

The results indicate substantial reductions in the observed levels of the NMHCs over the 2001-2021 period. Furthermore, significant differences in the trends for the various species are found. Strongest declines are found for benzene, toluene, ethene, and i-pentane which dropped more than 50 % during this 20 year's period. Next to this group, propane, ethyne, n-butane, i-butane, and n-pentane dropped 20-25 % whereas no trend is seen for ethane. These trend numbers refer to the trends adjusted for variations in meteorology.

These reductions are in line with the emission data from the so-called EMEP-West region although a quantitative comparison species by species could not be done since the EMEP emission data are given for the sum of NMHC and not for individual substances.

Please note that this is a corrected version (published 20 September 2023) of the original report published 15 September 2023. The correction includes new map plots (Fig. 3) since these plots were wrong in the original version of the report.

Please use this corrected version in all future work and disregard the original version.

VOC measurements 2021

1. Introduction

1.1 Historical background

The EMEP VOC monitoring programme was initiated at the EMEP Workshop on Measurements of Hydrocarbons/VOC in Lindau, 1989 (EMEP/CCC, 1990). A three-fold objective of the measurement programme was defined at the workshop:

- Establishing the current ambient concentrations
- Compliance monitoring ("Do the emission control programme lead to a reduction of atmospheric concentrations?")
- Support to the transboundary oxidant modelling (prognostic and diagnostic)

The Workshop recommended that as a first step it would be sufficient with VOC monitoring at 10-15 rural sampling sites and taking two samples per week centred at noon GMT at each station. Collection in stainless steel canisters and analyses by high resolution gas chromatography was recommended for the detection of light hydrocarbons, whereas impregnated adsorbent tubes sampling combined with high performance liquid chromatography (HPLC) was recommended for the detection of carbonyls.

VOC measurements within EMEP started with the collection of grab samples of light hydrocarbons in mid-1992 and measurements of carbonyls in 1993. Initially, five stations were included in the monitoring programme: Rucava (LV0010), Košetice (CZ0003), Waldhof (DE0002), Tänikon (CH0032) and Donon (FR0008). Since then, the number and selection of VOC measurement sites have changed several times.

EMEP VOC measurements are reported annually and presented in reports for consideration by EMEP-TFMM and the EMEP Steering Body. Previous results from the EMEP VOC programme have been presented in annual reports (e.g. Solberg, 2022 and references therein). An EMEP expert meeting on VOC measurements was organised in Berlin, 1994 (EMEP/CCC, 1995), and an evaluation of the measurement programme was made in 1995 (Solberg et al., 1995).

VOC-data from the EMEP-network have been published and documented in numerous publications, e.g. Waked et al. (2016), Hellen et al. (2015), Hoerger et al. (2015), Malley et al. (2015), Tørseth et al. (2012), Worton et al. (2012), Sauvage et al. (2009), Plass-Dülmer et al. (2009), Plass-Dülmer et al. (2002), Hakola et al. (2006), Borbon et al. (2004), Solberg et al. (2001), and Solberg et al. (1996). Details about the VOC monitoring program are given in the EMEP annual reports such as Solberg (2022) and references therein.

2. Status of the measurement programme in 2021

2.1 The station network

The locations of the EMEP monitoring sites for VOC in 2021 are shown in Figure 1 and an overview of the measurement programme and the responsible laboratories is given in Table 1. In total, 17 measurement sites and 10 laboratories are included in the list. Some data, as explained later, are not included in this report since they are still regarded as preliminary, either due to data format technicalities, or due to unresolved questions relating to data quality.

The measured VOCs consist of different groups of species which could be split into non-methane hydrocarbons hereafter named NMHC and oxygenated species hereafter named OVOC. Monitoring of NMHC is carried out at all sites, whereas OVOC are measured at fewer sites.

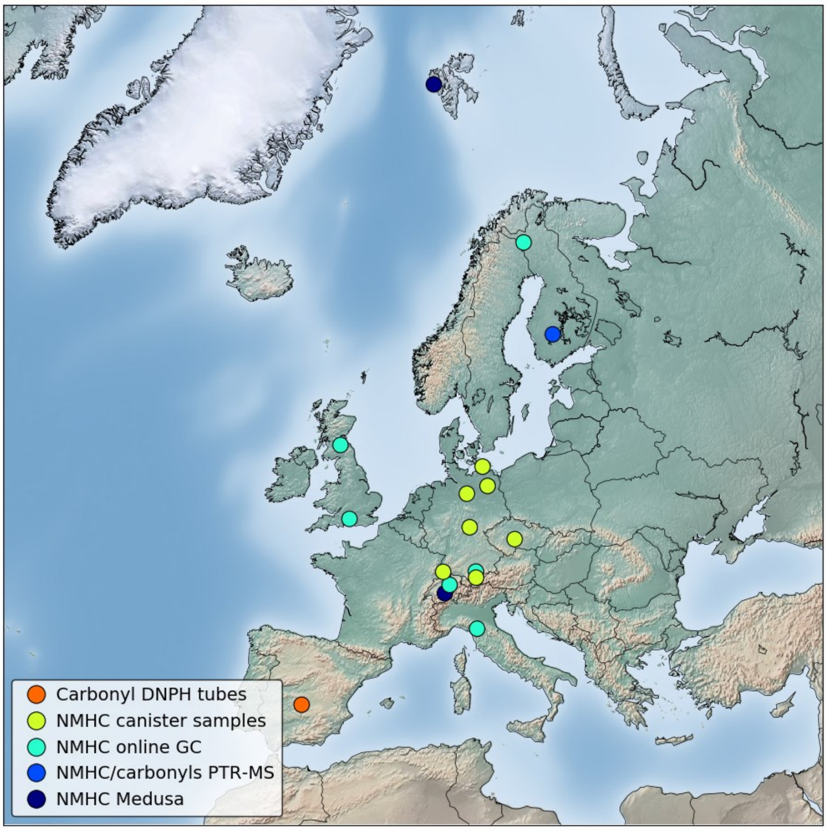


Figure 1: Monitoring sites for VOC in 2021.

The NMHC monitoring at EMEP sites has become more diverse with time in terms of instrumentation. Starting in the early 1990s with a standardized method based on manual sampling in steel canisters and subsequent lab analyses, the methods now comprise a variety of instruments and measurement principles, including PTR-MS (Hyytiälä), Medusa monitors (Zeppelin Mountain and Jungfraujoch) and specialized online GC monitors for hydrocarbons.

For OVOC the original EMEP method is based on sampling in DNPH adsorption tubes with subsequent lab analyses, and this method is still the method used at one remaining site in Spain (ES0001). In addition, OVOC are measured by the PTR-MS at Hyytiälä and by the new GC-GC FID/FID system at Beromünster in Switzerland.

Although many sites have contributed to the EMEP VOC programme since the early 1990s, very few sites have long and continuous time series. This poses a substantial problem for making reliable long-term trend assessments of VOC at European background sites. Additionally, shifts in instrumentation imply possible breaks in the time series. At some sites these shifts are a matter of upgrading the GC monitor, with minor effects on the measured values, while at other sites they represent significant breaks in the data time series. The VOC network has also changed due to stations being closed or moved (like e.g. CH0005 that was replaced with CH0053 in 2018).

As given in Table 1, some of the data series were considered questionable and not included in this report. NMHC data from San Pablo (ES0001) have for several years shown substantial differences compared to the expected levels and compared to the other sites. The differences become particularly evident when inspecting ratios of specific NMHCs which is used as a tool for quality assurance within ACTRIS.

The data from Chilbolton observatory, located in southern England, reflect the influence of populated areas in the whole of southern England, including e.g. road traffic emissions, and show a number of short-term spikes in the data. Data from Auchencorth Moss in Scotland, a rural location around 20 km south of Edinburgh also show very spiky hourly time series with peak levels of propane, n-butane and other species. The high concentrations are mainly seen during periods with winds from the northern sector, pointing to fresh anthropogenic emissions from the urban area around Edinburgh as well as from petroleum refineries in the same direction. It turns out that for both these sites, most of the spikes are of short duration while daily average levels seem fine.

NMHC data for all sites from UBA in Germany, i.e. Waldhof, Schauinsland, Neuglobsow, Schmücke, Zingst, and Zugspitze pose significant problems this year as in many previous years. This concerns in particular alkenes with three or more C-atoms (propene and higher) but also aromatics (o-xylene) and higher alkanes. All these data have been invalidated by NILU in 2021 as in many preceding years. Additionally, UBA’s data are traditionally submitted very late which delays and complicates the data processing. UBA wants to be included in the QA procedures for VOCs within ACTRIS-2 on a voluntary basis but the very late delivery of data makes this difficult or impossible.

Table 1: VOC monitoring at EMEP sites in 2021. The columns give the station names, site code, and the sampling frequencies for hydrocarbons (HC) and carbonyl compounds (Carb). The institute responsible for the chemical analyses is also given. Whether the station is part of the ACTRIS-2 project is also indicated.

Station	Code	HC[1)]	Institute[2)]	Carb[1)]	Method	ACTRIS	Comment
Zeppelin Mtn.	NO0042	Cont.	NILU	-	MEDUSA	y	
Pallas	FI0096	Cont.	FMI	-	GC/MS	y	
Hyytiälä	FI0050	Cont	UHel	-	PTR-MS.	y	
Auchencorth Moss	GB0048	Cont.	Ricardo	-	GC/MS	y	
Chilbolton Obs.	GB1055	Cont.	Ricardo	-	GC/MS	y	
Waldhof	DE0002	Reg.	UBA	-	Canister samples	y[3)]	Twice//week
Schauinsland	DE0003	Reg.	UBA	-	“	y[3)]	“
Neuglobsow	DE0007	Reg.	UBA	-	“	y[3)]	“
Schmücke	DE0008	Reg.	UBA	-	“	y[3)]	“
Zingst	DE0009	Reg.	UBA	-	“	y[3)]	“
Zugspitze	DE0054	Reg.	UBA	-	“	y[3)]	“
Hohenpeissenberg	DE0043	Daily	DWD	-	GC/FID	y	2/day (noon, midnight)
Košetice	CZ0003	Reg.	CHMI	-	Canister samples	y	Twice/week
Jungfraujoch	CH0001	Cont.	EMPA	-	MEDUSA	y	
Beromünster	CH0053	Cont.	EMPA	-	GC/FID	y	
Mt. Cimone	IT0009	Cont.	UU	-	GC/MS	y	
San Pablo	ES0001	Reg.	MMA	Reg.	Canister/DNPH samples	n	Twice/week. Prelim. NMHC data not included in the report.

1) Reg. = regularly (2-3 samples per week), Cont. = continuously
2) CHMI = Czech Hydrometeorological Institute
DWD = Deutscher Wetterdienst

IMT LD = Institut Mines Telecom Lille Douai
EMPA = Swiss Federal Lab. for Materials Testing and Research
FMI = Finnish Meteorological Institute
UHel = Univ. Helsinki
UBA = Umweltbundesamt (Germany)
UU = University of Urbino
MMA = Minestrio de Medio Ambiente
3) Participated voluntarily in ACTRIS-2 without being a formal partner. Significant problems with data quality

3. VOC concentrations in 2021

3.1 General levels

Time series of the diurnal means of all compounds at all stations during 2021 are given in the Appendix. Figure 2 shows the spread of data values for all station and species in 2021 in box and whisker plots together with the corresponding data during 2016-2020. The sites are arranged from north to south going from left to right in the panels. Thus, the panels in Figure 2 indicate both the north-to-south differences, the deviation of the 2021 concentration levels relative to the previous five years' climatology as well as the spread in 2021 data at each site separately.

For C_2–C_5 hydrocarbons there is a striking similarity between the variation in levels in 2021 compared to the 5-year climatology whereas for heavier compounds there are larger differences.

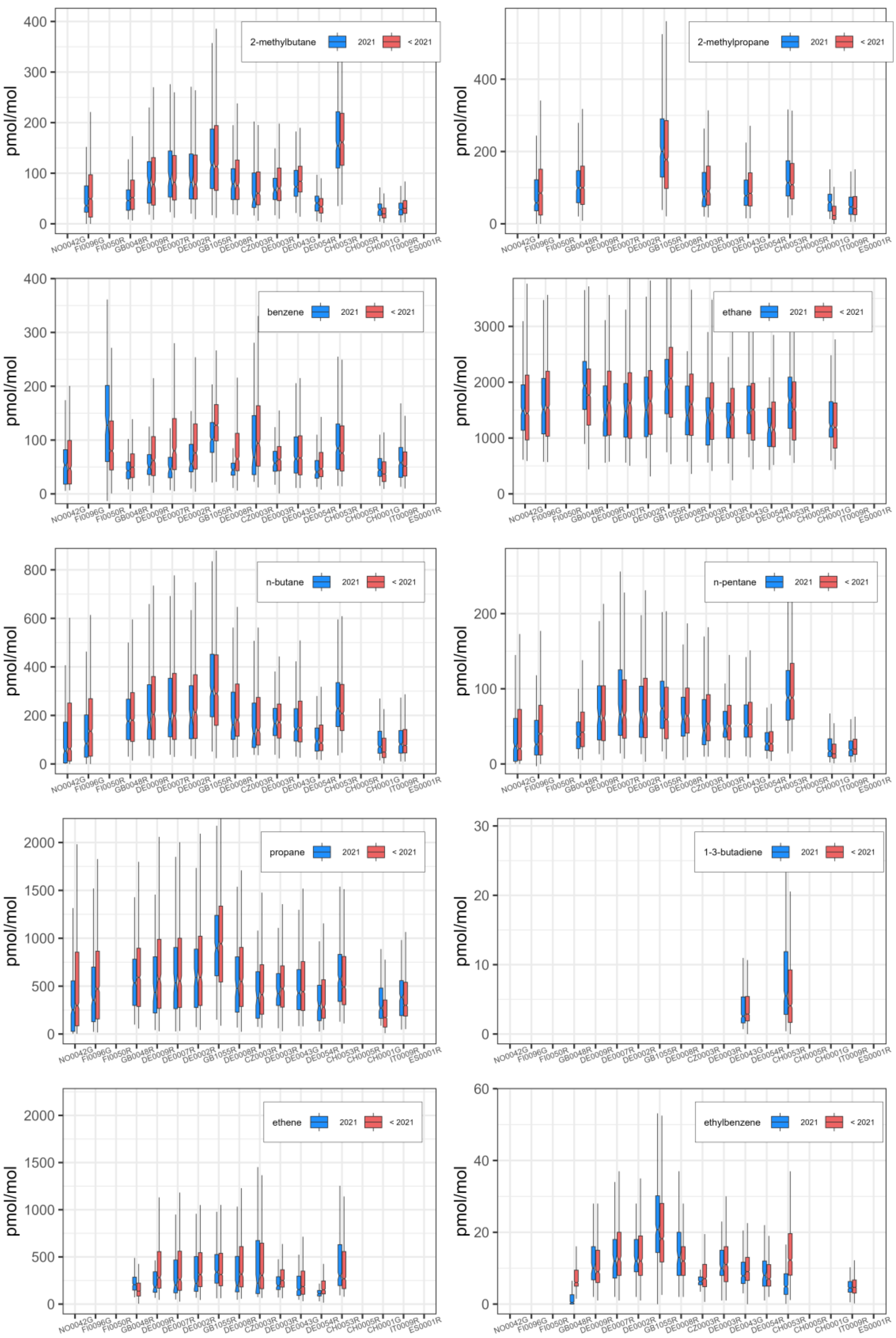
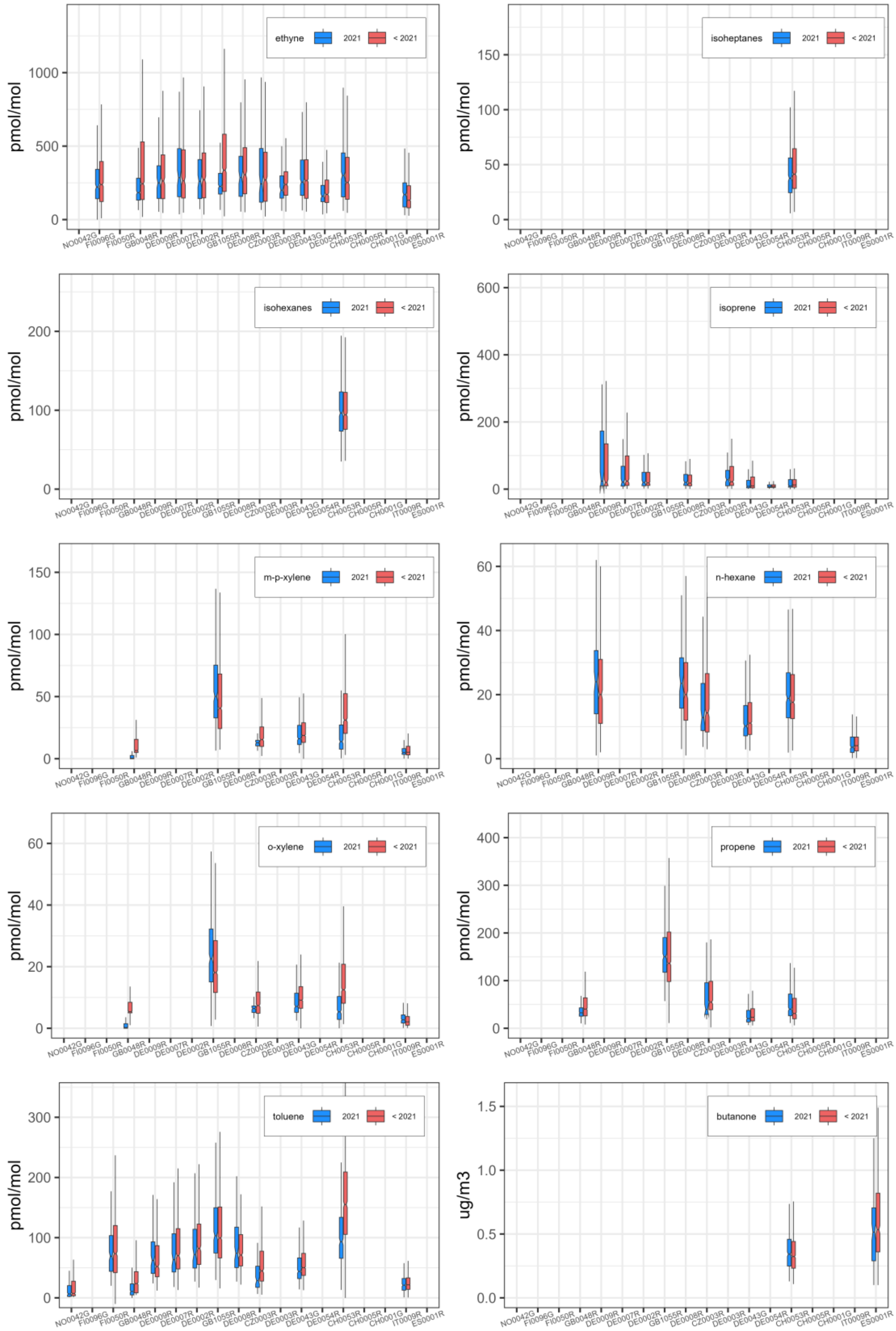


Figure 2: Box- and whisker-diagrams for VOCs based on all measurements in 2021 (blue) compared to the levels during 2016-2020. The boxes enclose the 25- and 75-percentile with the median marked inside.



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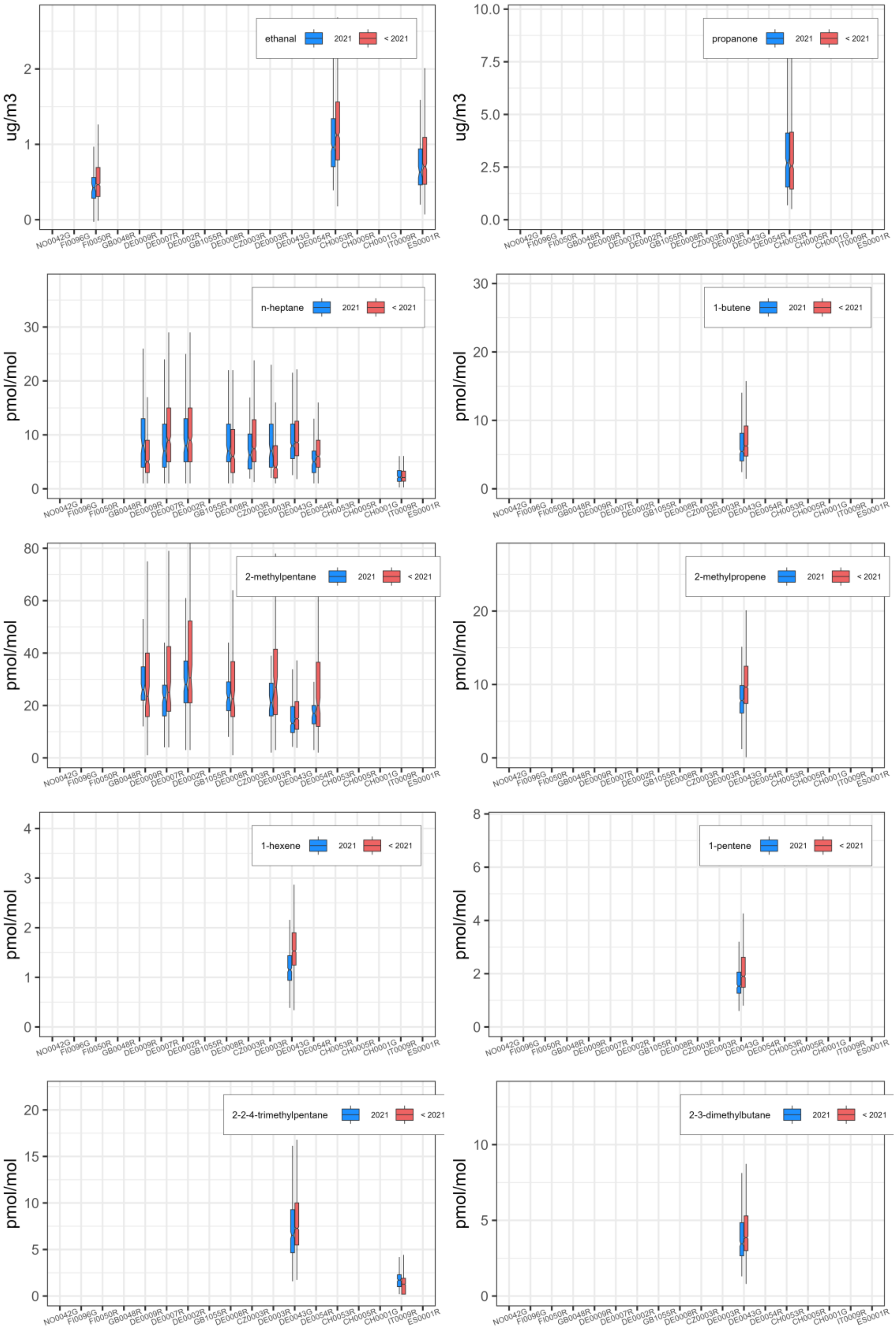

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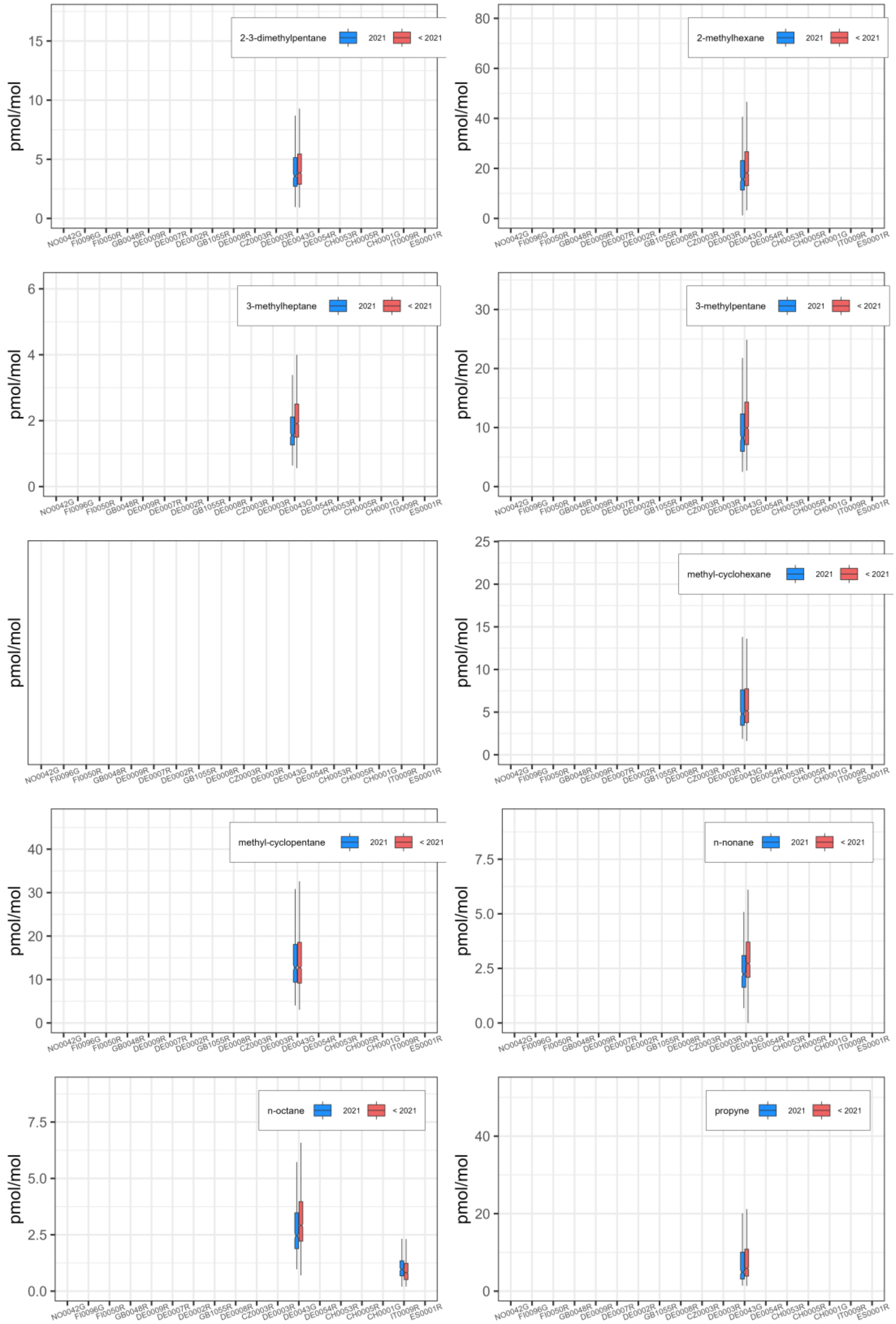

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3.2 Regional distribution of VOC

Figure 3 shows maps with the stations' annual median concentrations of VOCs in 2021. Note that since the steel canisters are all sampled at daytime (normally at noon), a bias could be inherent in these plots when compared with the 24 h daily average values from online GCs. A bias for other species is also likely to a varying extent. Some of the mountain stations (Zugspitze, Hohenpeissenberg and Mt Cimone) are influenced by diurnal venting of the planetary boundary layer and will receive upslope polluted air masses at daytime when the vertical mixing is sufficiently strong and cleaner free tropospheric air at night. The station at Jungfraujoch (3578 m asl) will on the other hand most of the time be located in the free troposphere, above the planetary boundary layer.

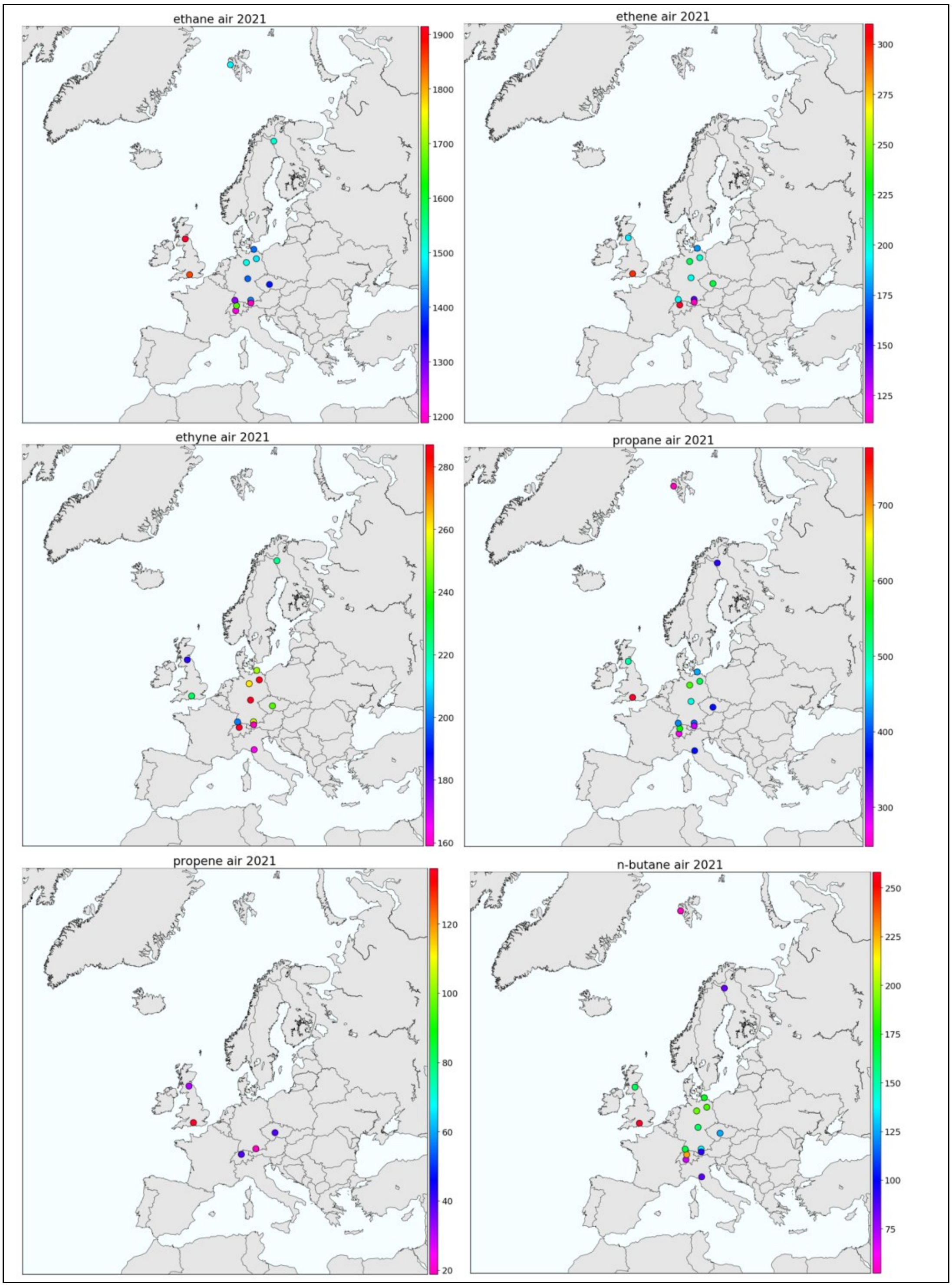
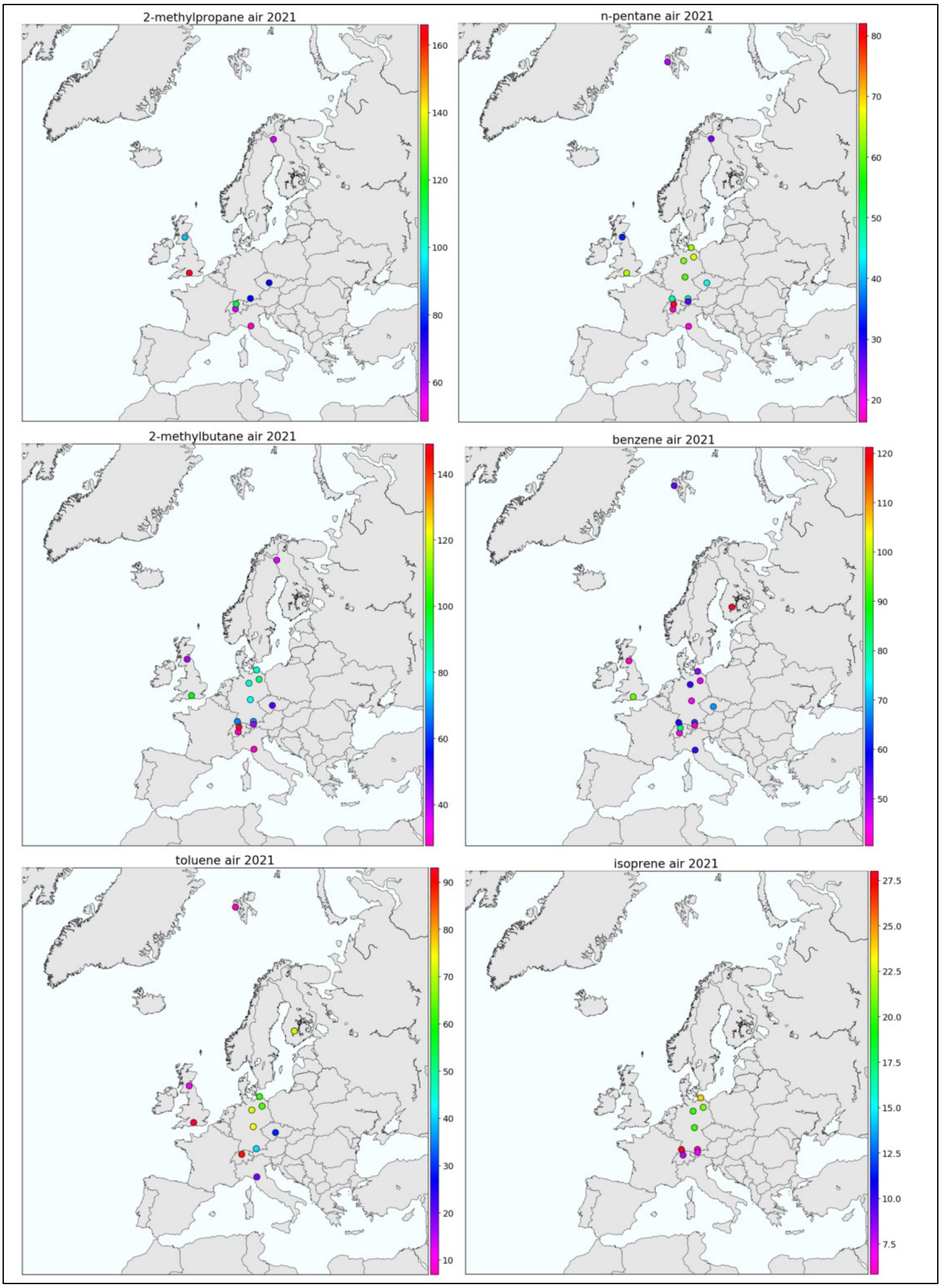


Figure 3: Annual median concentration of VOCs in 2021.



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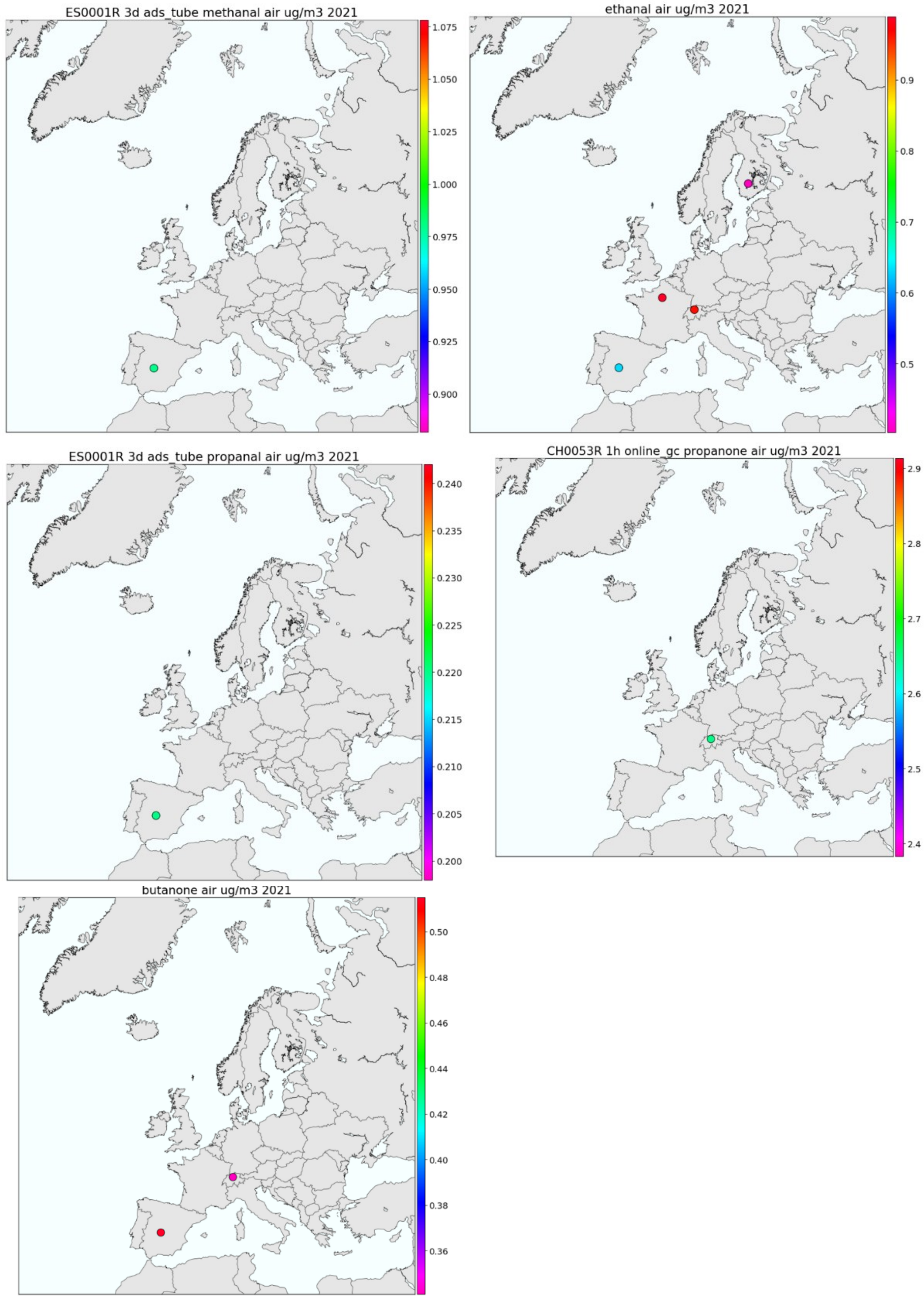


Figure 3 (contd.).

4. Long-term trends in VOC

According to the official emission data, there have been marked reductions in anthropogenic emissions of VOCs during the last decades in Europe. Overview tables with reported emission trends for individual countries have been published on the CEIP website at https://www.ceip.at/. Detailed information on the sectoral level can also be accessed in WebDab.

There are substantial differences in the emission trends between countries and regions. For the area defined as "EMEP-West", there has been an overall reduction in VOC emissions of more than 40 % for the period 2000-2020 (Fagerli et al., 2022) and for individual countries such as Germany, France, UK, Italy, Spain, and Poland, the reductions have been 43%, 54%, 56%, 46%, 38% and 17%, respectively, as given in the same report.

For the area defined as "EMEP-East", however, the emission data including so-called gap-filling indicate a nearly flat development from 2000 to 2020 for NMVOC. As stated in the EMEP Status report (Fagerli et al., 2022), the emission estimates for EMEP-East are, however, much more uncertain than the data for EMEP-West.

Declines in the measured concentrations of hydrocarbons have been reported from suburban/urban sites at several locations. Based on a network of high-frequency continuous monitoring of C_2-C_8 hydrocarbons in the UK, mostly at urban/suburban locations, Derwent et al. (2014) found substantial declines in concentrations with recent levels close to an order of magnitude below the levels in the early 1990s. They estimated exponential declines in concentrations of the order of -11% y^{-1} to -22% y^{-1} for the period 1994-2012. They also found a marked difference between ethane and propane on one side which showed relatively stable levels, while other alkanes showed pronounced declines.

Long-term monitoring data from an urban network in Switzerland (Hüglin, pers. comm.) also show strong declines in the concentrations of NMHC and OVOC from the start of the 1990s to the present.

Various trend studies have been carried out for VOC-data from EMEP rural sites as well. Sauvage et al. (2009) and Waked et al. (2016) found clear decreases at the French EMEP sites of most NMHCs. Ethane was an exception to this and showed more stable levels.

Analyses of the twenty years NMHC monitoring at the EMEP/GAW site Pallas in Northern Finland revealed a significant downward trend only for ethyne (Hellen et al., 2015). They concluded that other source regions than the EU were dominating the NMHC levels at the site. Based on source area estimates, they found that the Eastern parts of the continent were the main source regions for high concentrations at Pallas.

A simple 1:1 relationship between observed VOC concentrations at rural background sites and the overall European emission numbers is not to be expected. Interannual variations in atmospheric transport patterns, vertical mixing, photochemical oxidation as well as spatial differences in emission reductions complicate the analyses.

Furthermore, various procedures for trend analyses in terms of mathematical method, selection of time periods and stations etc. could give different results. In previous VOC annual reports (Solberg et al., 2022) daily measurements of selected VOCs at five EMEP sites were analyzed with two separate statistical methods: The method used for trace gases in the AGAGE project (Simmonds et al., 2006) as well as best-fit seasonal trend curves calculated by non-linear least squares fit using a standard statistical package (Markwardt, 2009). In addition to these two methods the Mann-Kendall/Theil-Sen's slope methodology (MK) was applied to the annual median concentrations (Bronaugh and Werner, 2019; Sen, 1968).

In the present report a GAM (generalized additive model) has been used based on the AirGAM model (Walker et al., 2023). This is an air quality trend and prediction model recently developed at NILU in cooperation with the European Environment Agency (EEA). AirGAM is based on nonlinear regression and is capable of estimating trends in daily measured pollutant concentrations at air quality monitoring stations, discounting for the effects of trends and time variations in corresponding meteorological data.

AirGAM was applied to daily levels of hydrocarbons measured at Hohenpeissenberg (DE0043) during the period 2001-2021 together with daily values of temperature, humidity, wind speed, wind direction, and mixing height as compiled from ECMWF met data in the same way as described in Walker et al. (2023). The same model set-up as used for NO_2 (Solberg et al., 2021) was used for these hydrocarbons, implying that daily mean values of all the meteorological covariates were used in the regression and furthermore, that a log-based approach was assumed, i.e. the logarithm of the daily hydrocarbon levels was used as the dependent variable.

The trend during 2001-2021 in the relative concentration levels of the NMHCs with 2001 being the reference year is shown in Figure 4 while Figure 5 shows the daily mean levels as observed and predicted with the AirGAM model.

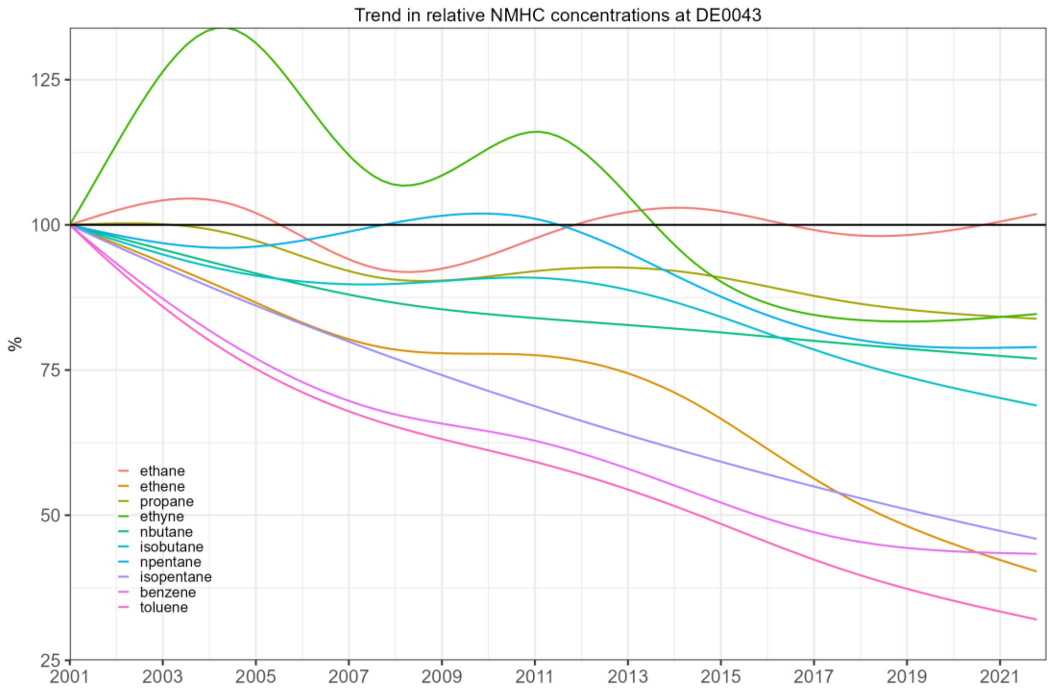


Figure 4: Meteorological adjusted trend in relative concentrations of NMHCs at Hohenpeissenberg as calculated by the AirGAM model (Walker et al., 2023).

The results shown in Figure 4 indicate a substantial reduction in the NMHCs measured at DE0043 and, furthermore, significant differences in the trends for the various species. Strongest declines are found for benzene, toluene, ethene, and i-pentane which dropped more than 50 % during this 20 year's period. Next to this group, propane, ethyne, n-butane, i-butane, and n-pentane dropped 20-25 % whereas no trend is found for ethane. These trend numbers refer to the trends adjusted for variations in meteorology.

These marked reductions in observed NMHC levels in Europe since 2000 are in line with the emission data from the EMEP-West region as mentioned above. A quantitative comparison species by species could not be done since the EMEP emission data are given for NMHC as a whole and not for individual substances.

The reliability of the AirGAM model could be judged from Figure 5 showing the agreement between the observed and modelled daily mean values during 2021 for 10 anthropogenic NMHCs from ethane to toluene plus isoprene. It is important to keep in mind that AirGAM is a statistical model (or tool) that is based purely on observed relationships between air quality data and meteorological parameters without any parameterization of physical processes. This makes it well suited for analyzing historical data while the model could of course not be used for predicting the effects of emission changes. The results in Figure 5 show a close agreement between observed and predicted daily values in 2001 although some spikes in the observed data are not reproduced by AirGAM.

As part of the long-term trend estimates using AirGAM, the lockdown periods in 2020 were taken out of the regression model since it is expected that the level of emissions dropped during these periods.

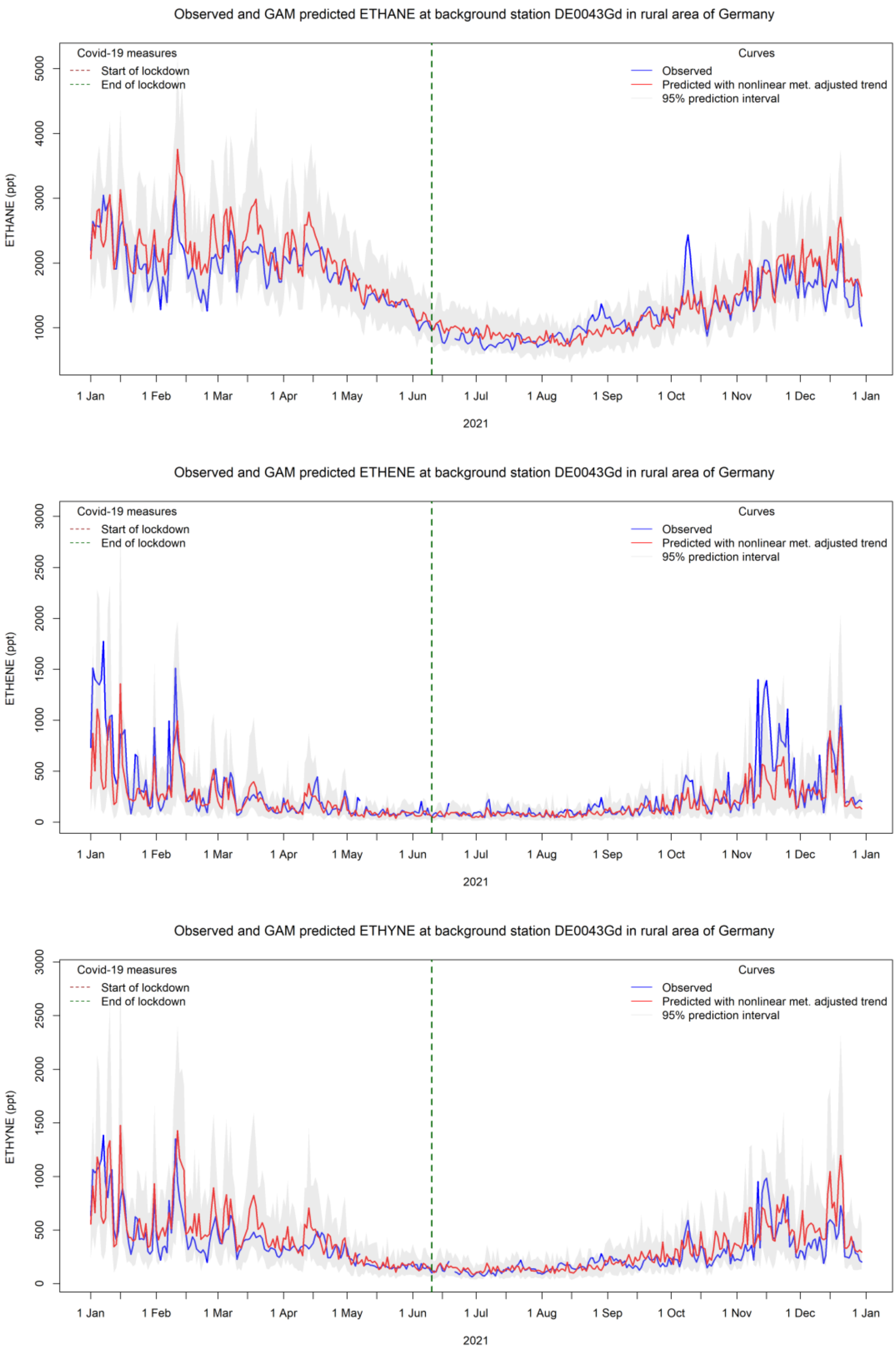
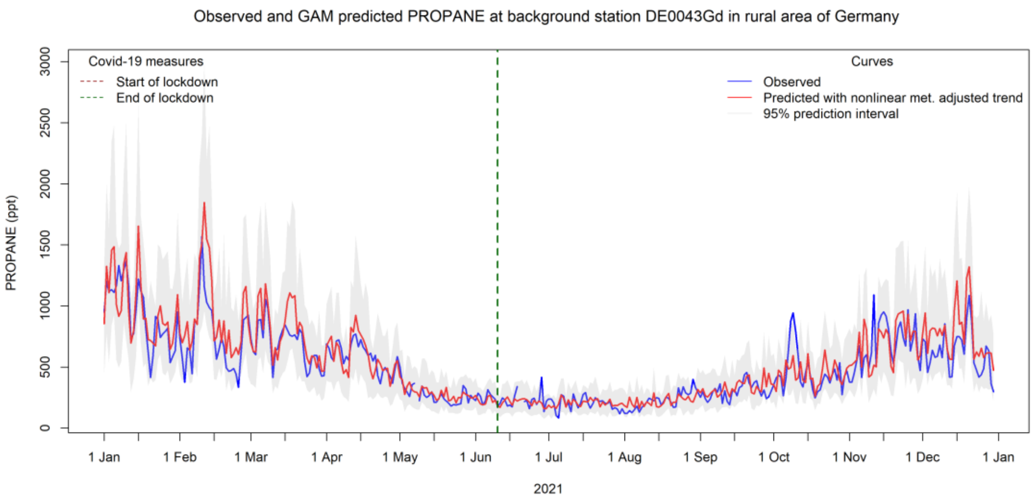
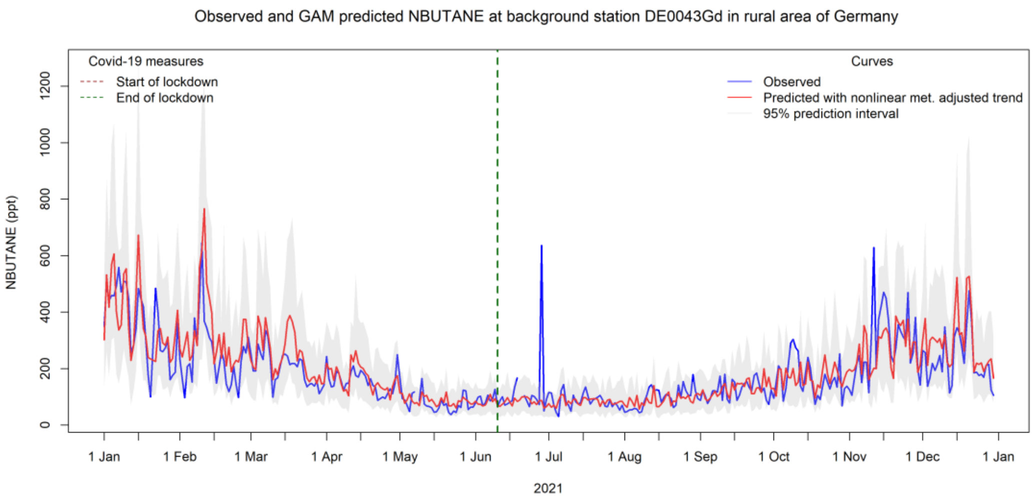
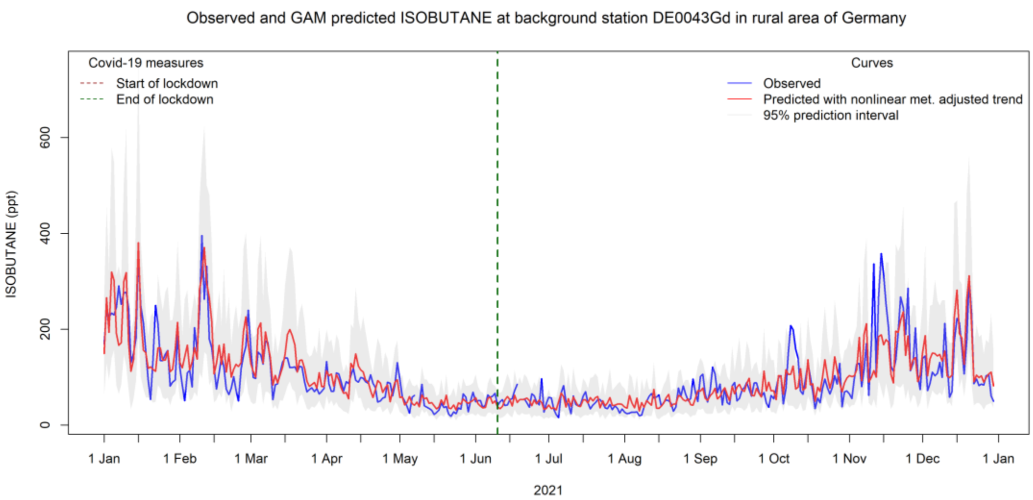


Figure 5: Daily concentrations of selected NMHCs as observed (blue) and modelled by AirGAM (red) at Hohenpeissenberg in 2021. The end of lockdown periods in Germany is indicated by a dashed vertical line.







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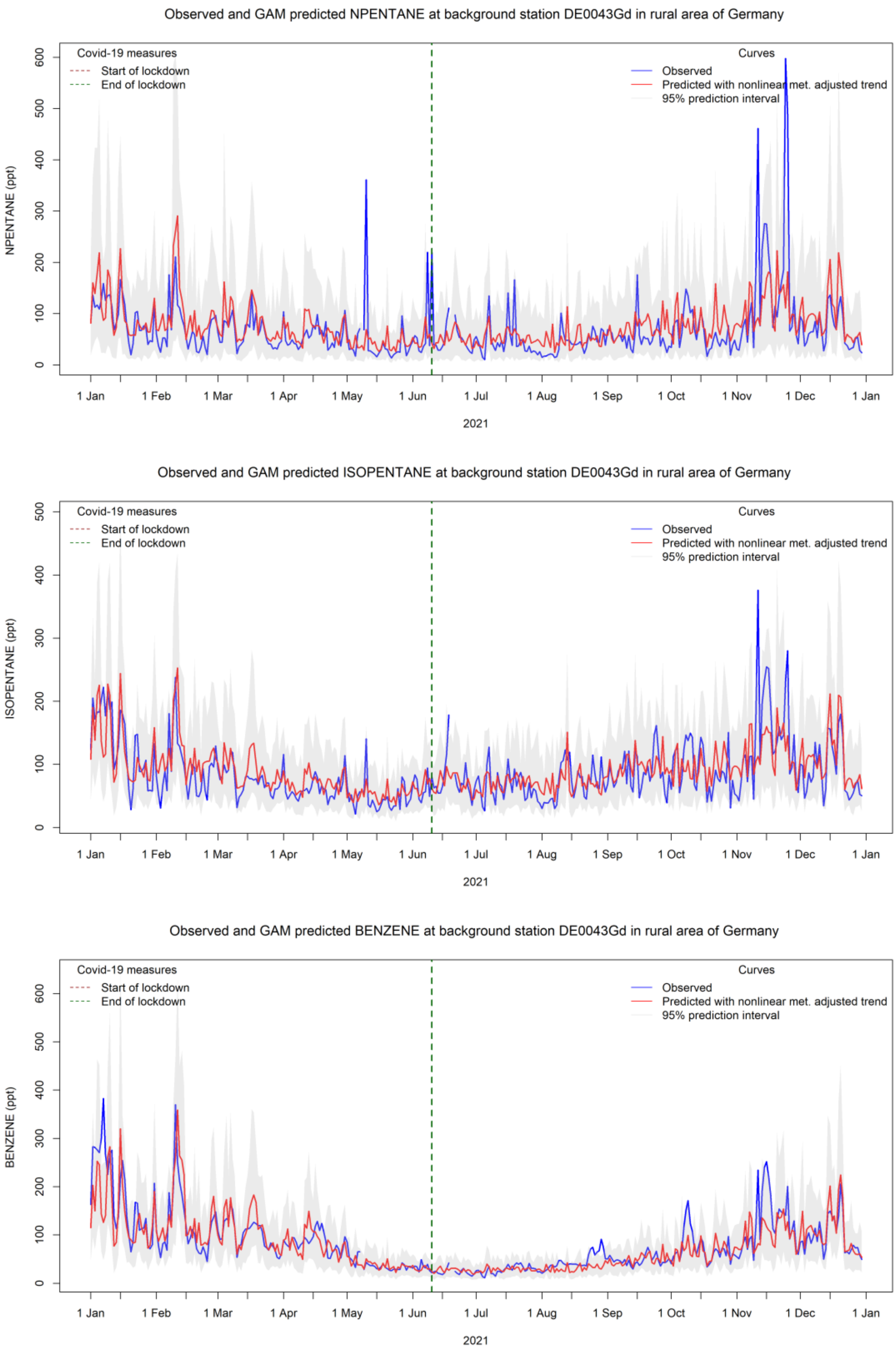

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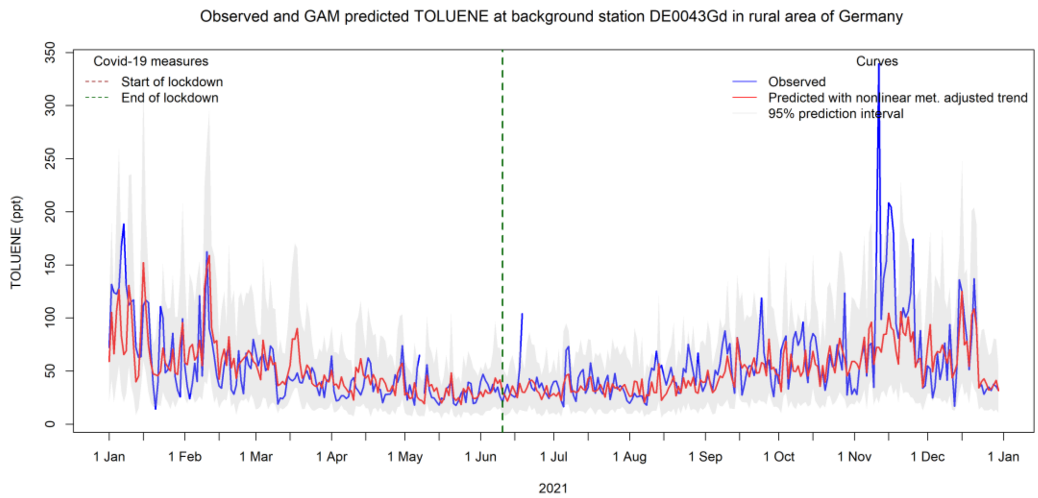

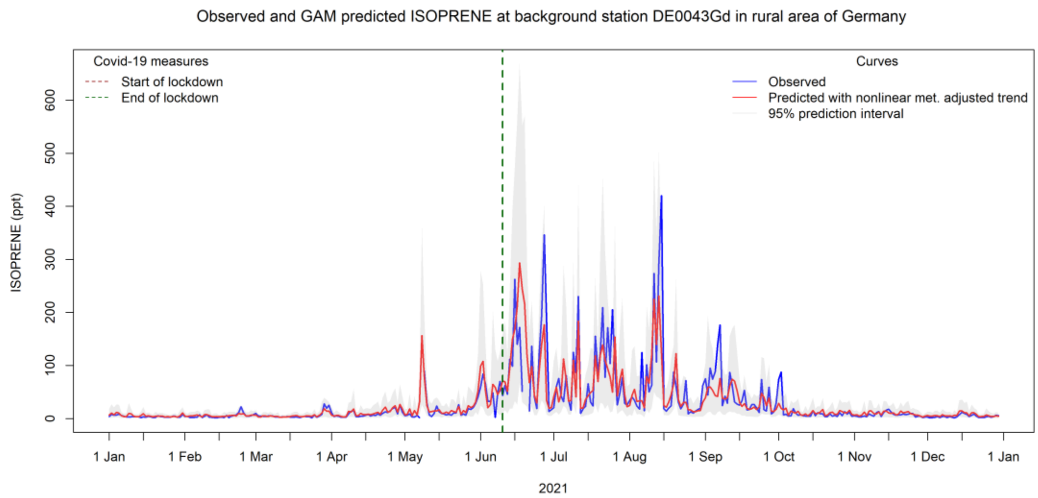

Figure 5 (contd.).

5. Acknowledgement

Data originators for individual datasets can be found as part of the metadata by visiting http://ebas.nilu.no. A special thanks to the providers of data for 2020: Heidi Hellen (FMI), Ilona Ylivinkka (UHEL), Toivo Truuts (EERC), Jitka Privoznikova (CHMI), James Dernier (Ricardo), Bryan Hellack (UBA), Therese Salameh (IMT), Norbert Schmidbauer (NILU), Arduini Jgor (UU), Fernandez Monistrol Jose Antonio (MMA).

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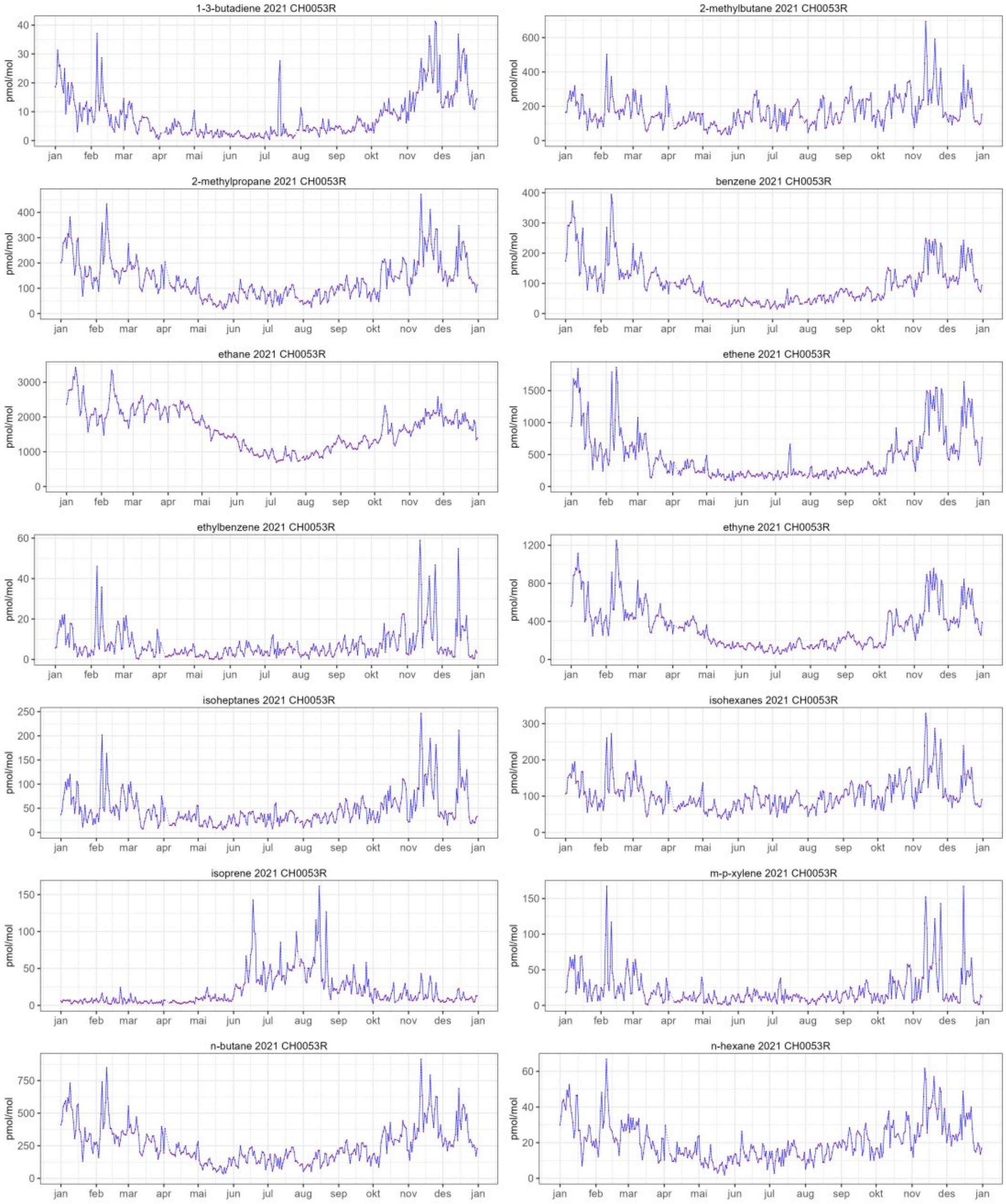
Appendix 1

Time series of daily means of VOCs measured in 2021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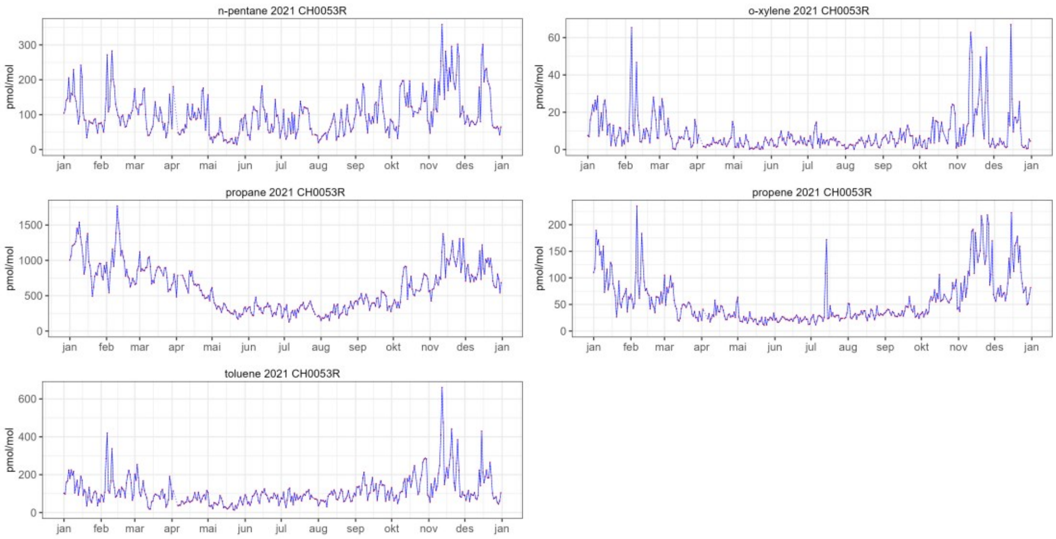
ethane 2021 CH0053R
ethene 2021 CH0053R
ethylbenzene 2021 CH0053R
ethyne 2021 CH0053R
isoheptanes 2021 CH0053R
isohexanes 2021 CH0053R
isoprene 2021 CH0053R
m-p-xylene 2021 CH0053R
n-butane 2021 CH0053R
n-hexane 2021 CH0053R
pmol/mol
jan feb mar apr mai jun jul aug sep okt nov des jan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o-xylene 2021 CH0053R
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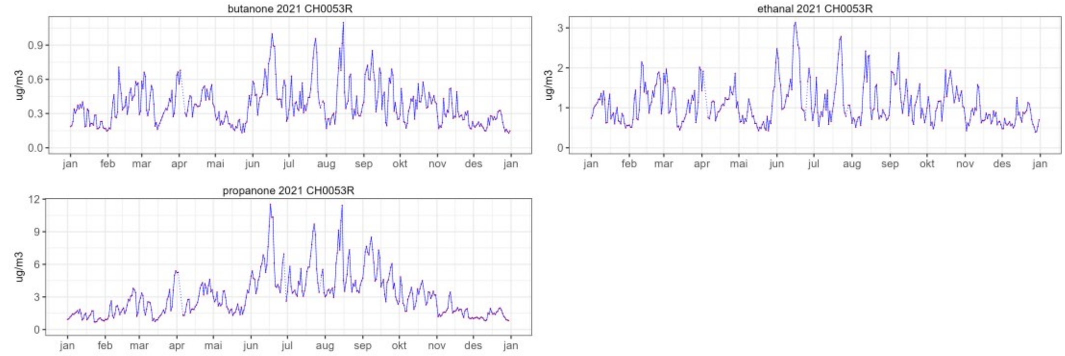
pmol/mol
jan feb mar apr mai jun jul aug sep okt nov des jan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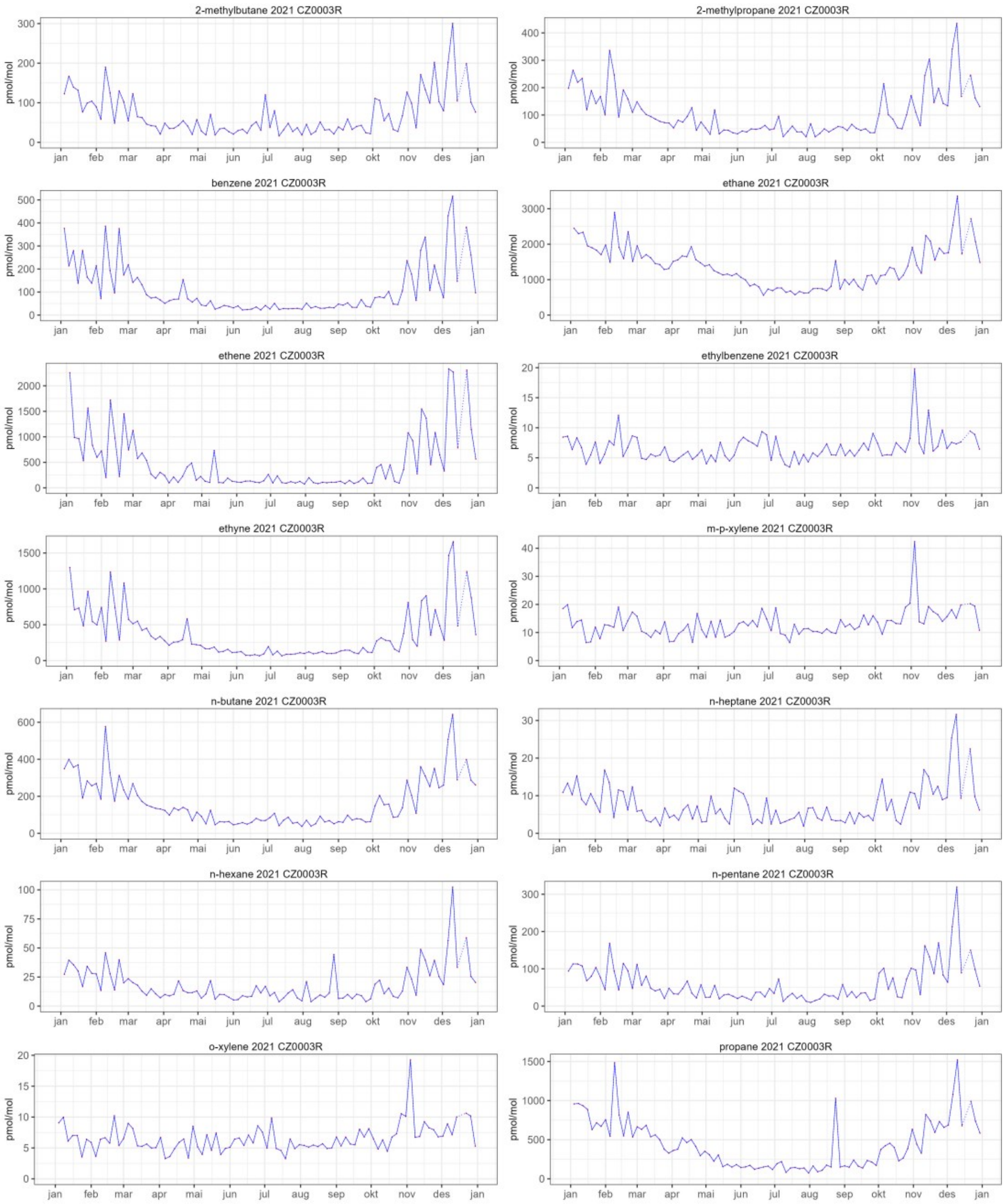
0.3
0.6
0.9
jan feb mar apr mai jun jul aug sep okt nov des jan
ethanal 2021 CH0053R
ug/m3
0
1
2
3
jan feb mar apr mai jun jul aug sep okt nov des jan
propanone 2021 CH0053R
ug/m3
0
3
6
9
12
jan feb mar apr mai jun jul aug sep okt nov des jan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benzene 2021 CZ0003R
ethane 2021 CZ0003R
ethene 2021 CZ0003R
ethylbenzene 2021 CZ0003R
ethyne 2021 CZ0003R
m-p-xylene 2021 CZ0003R
n-butane 2021 CZ0003R
n-heptane 2021 CZ0003R
n-hexane 2021 CZ0003R
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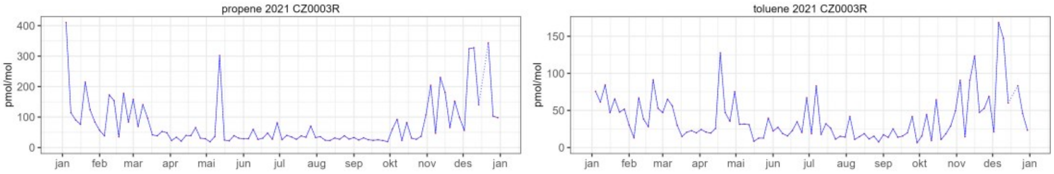
o-xylene 2021 CZ0003R
propane 2021 CZ0003R
pmol/mol
jan feb mar apr mai jun jul aug sep okt nov des jan


propene 2021 CZ0003R
pmol/mol
400
300
200
100
0
jan
feb
mar
apr
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jun
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aug
sep
okt
nov
des
jan
toluene 2021 CZ0003R
pmol/mol
150
100
50
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jan
feb
mar
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mai
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sep
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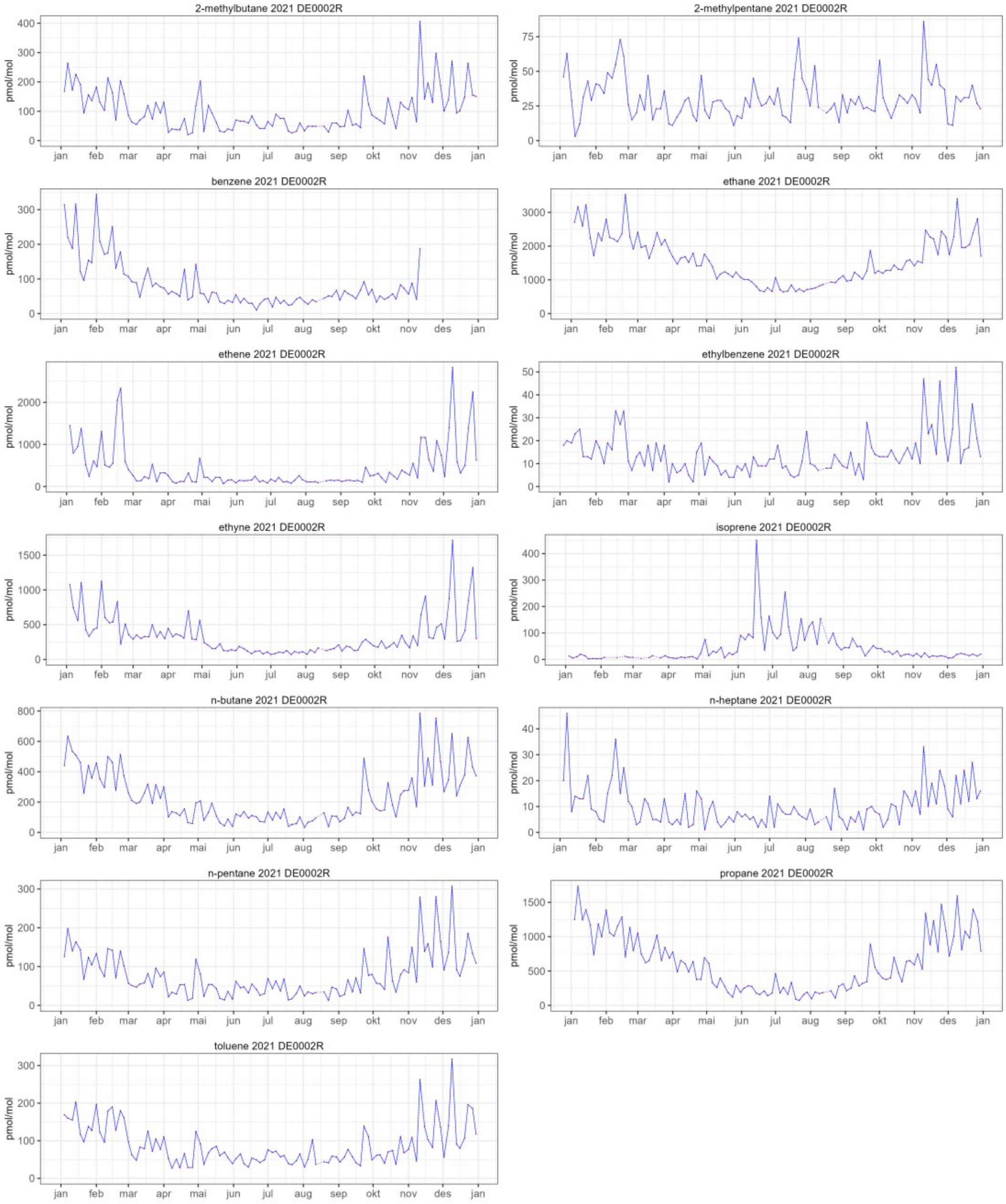
jan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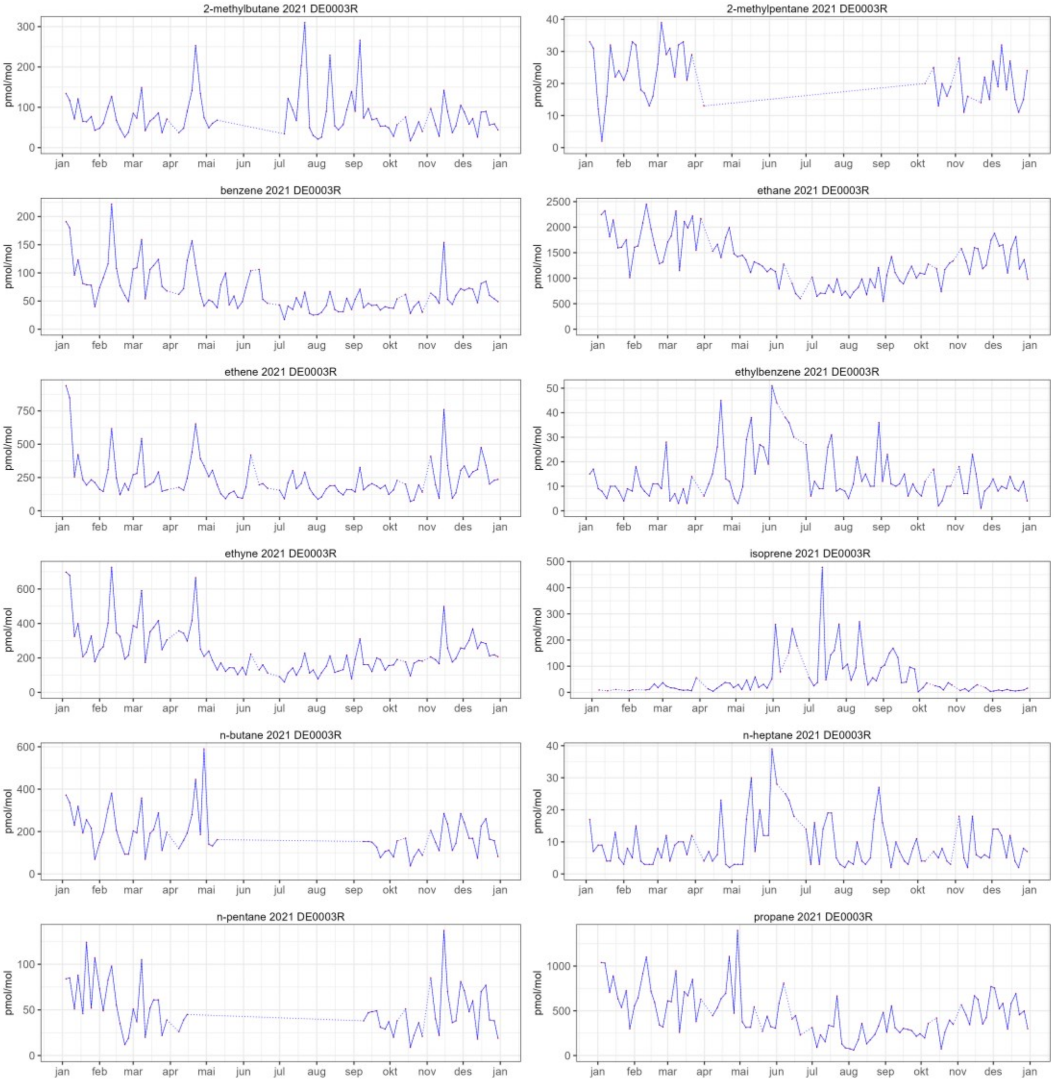
ethene 2021 DE0002R
ethylbenzene 2021 DE0002R
ethyne 2021 DE0002R
isoprene 2021 DE0002R
n-butane 2021 DE0002R
n-heptane 2021 DE0002R
n-pentane 2021 DE0002R
propane 2021 DE0002R
toluene 2021 DE0002R
pmol/mol
jan feb mar apr mai jun jul aug sep okt nov des jan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benzene 2021 DE0003R
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ethylbenzene 2021 DE0003R
ethyne 2021 DE0003R
isoprene 2021 DE0003R
n-butane 2021 DE0003R
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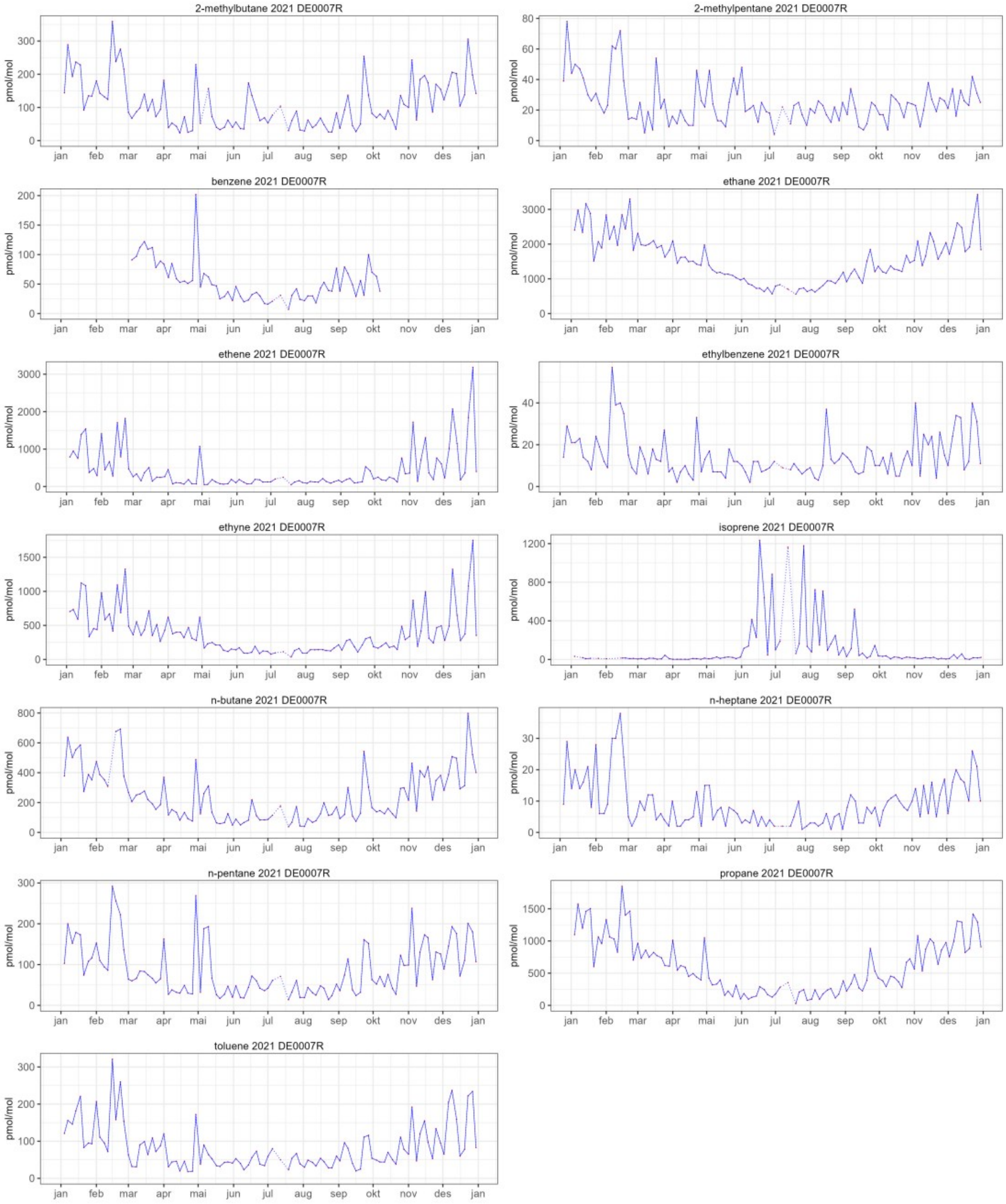
n-pentane 2021 DE0003R
propane 2021 DE0003R
pmol/mol
jan feb mar apr mai jun jul aug sep okt nov des jan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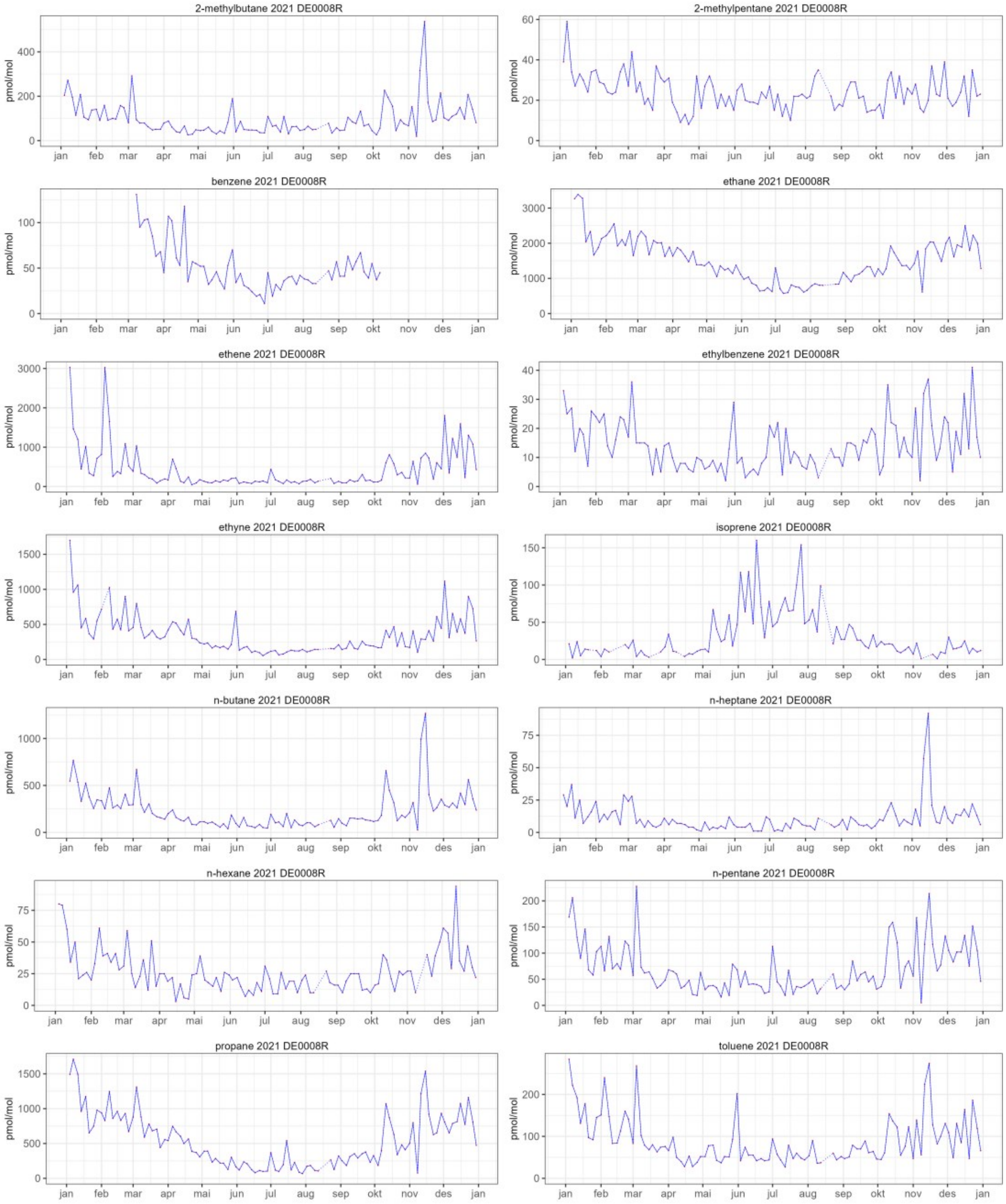
2-methylpentane 2021 DE0007R
benzene 2021 DE0007R
ethane 2021 DE0007R
ethene 2021 DE0007R
ethylbenzene 2021 DE0007R
ethyne 2021 DE0007R
isoprene 2021 DE0007R
n-butane 2021 DE0007R
n-heptane 2021 DE0007R
n-pentane 2021 DE0007R
propane 2021 DE0007R
toluene 2021 DE0007R
pmol/mol
jan feb mar apr mai jun jul aug sep okt nov des jan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benzene 2021 DE0008R
ethane 2021 DE0008R
ethene 2021 DE0008R
ethylbenzene 2021 DE0008R
ethyne 2021 DE0008R
isoprene 2021 DE0008R
n-butane 2021 DE0008R
n-heptane 2021 DE0008R
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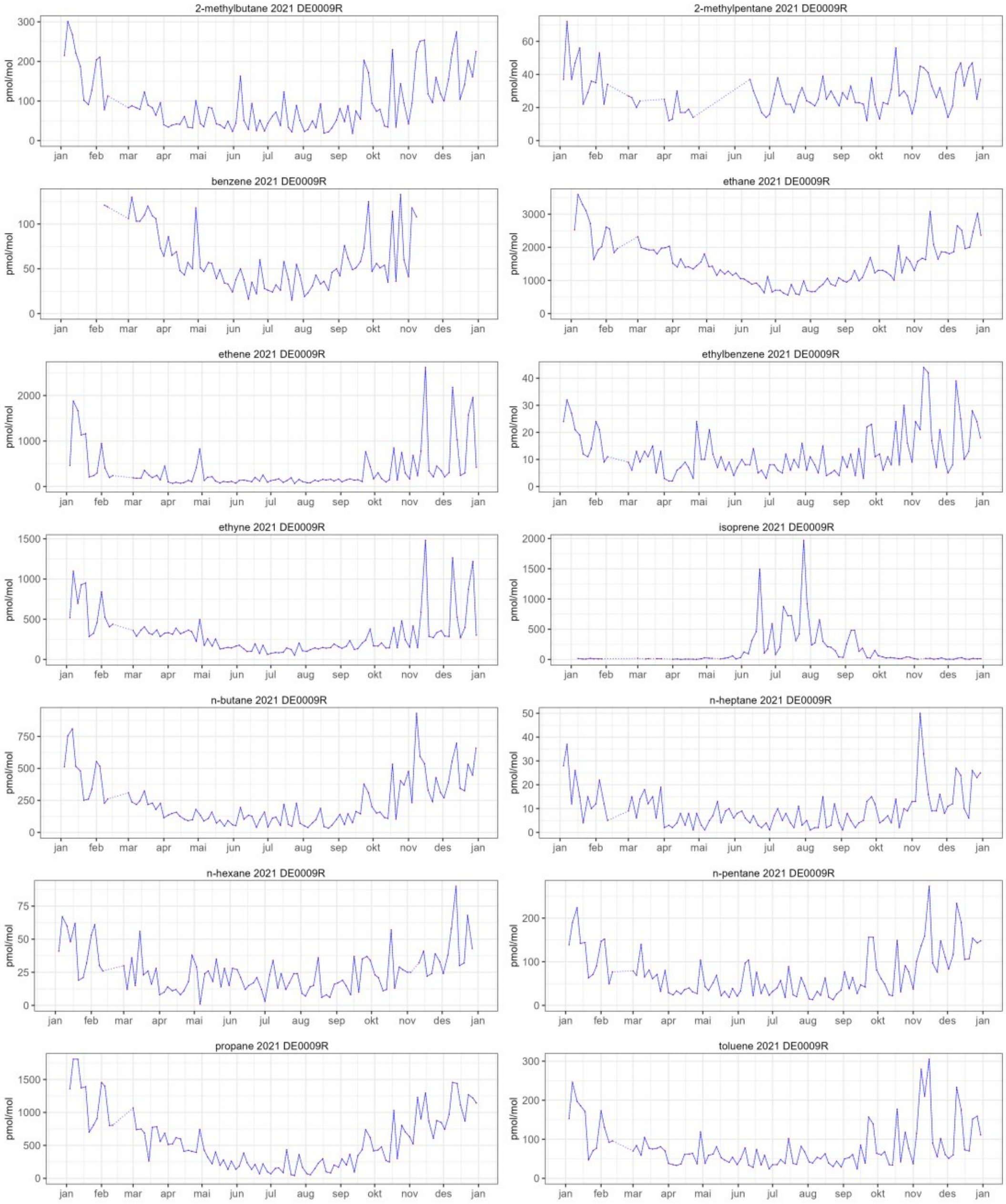
toluene 2021 DE0008R
pmol/mol
jan feb mar apr mai jun jul aug sep okt nov des jan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2-methylpentane 2021 DE0009R
benzene 2021 DE0009R
ethane 2021 DE0009R
ethene 2021 DE0009R
ethylbenzene 2021 DE0009R
ethyne 2021 DE0009R
isoprene 2021 DE0009R
n-butane 2021 DE0009R
n-heptane 2021 DE0009R
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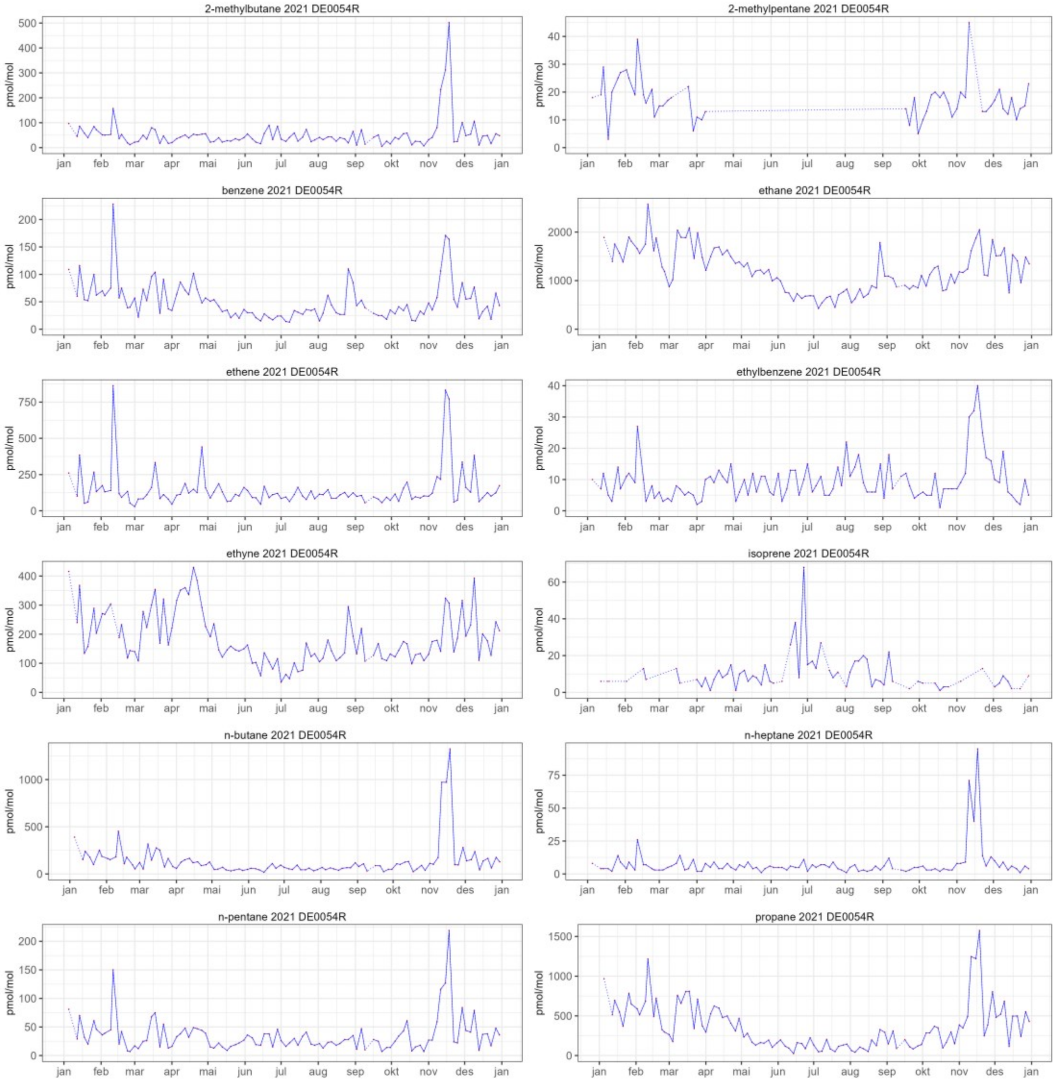
propane 2021 DE0009R
toluene 2021 DE0009R
pmol/mol
jan feb mar apr mai jun jul aug sep okt nov des jan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ethyne 2021 DE0054R
isoprene 2021 DE0054R
n-butane 2021 DE0054R
n-heptane 2021 DE0054R
n-pentane 2021 DE0054R
propane 2021 DE0054R
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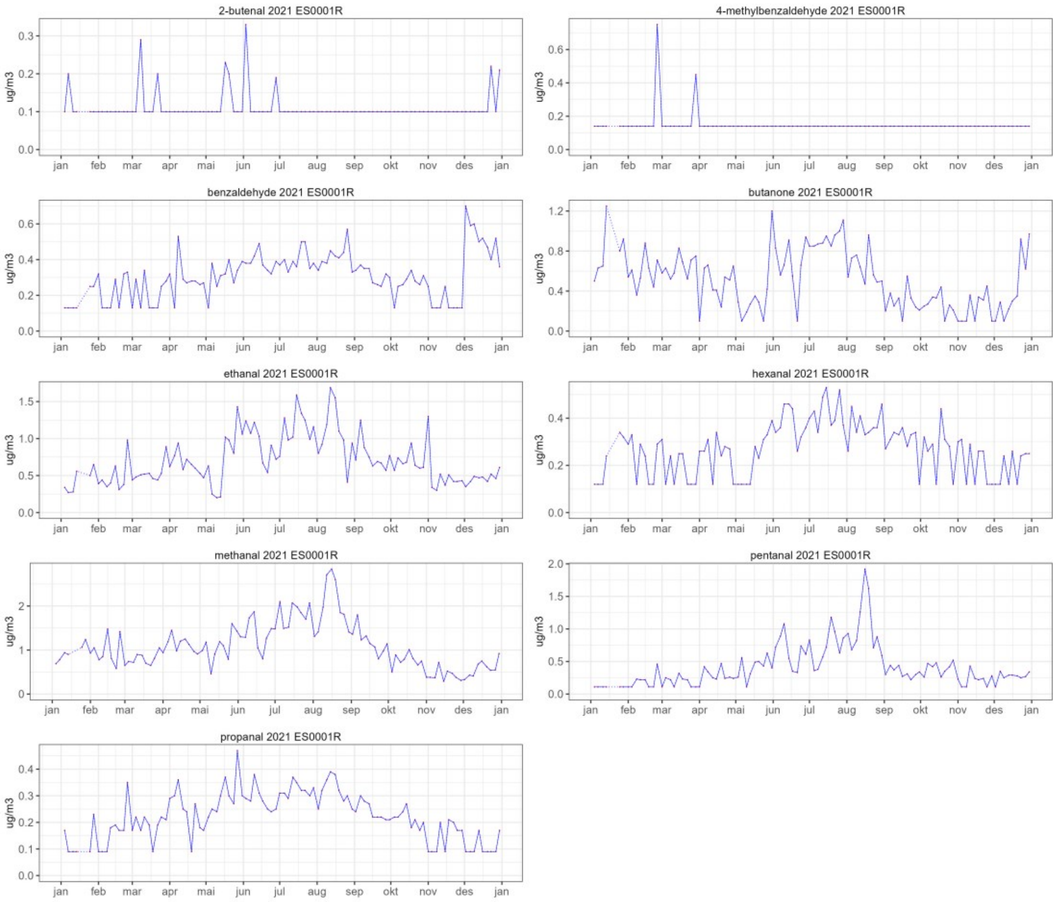
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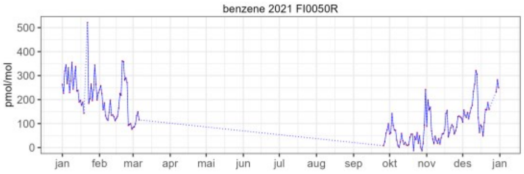
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pmol/mol
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toluene 2021 FI0050R
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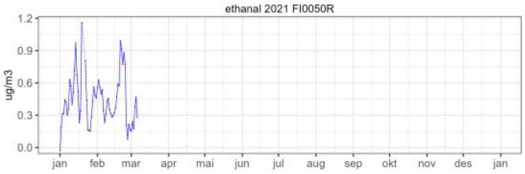
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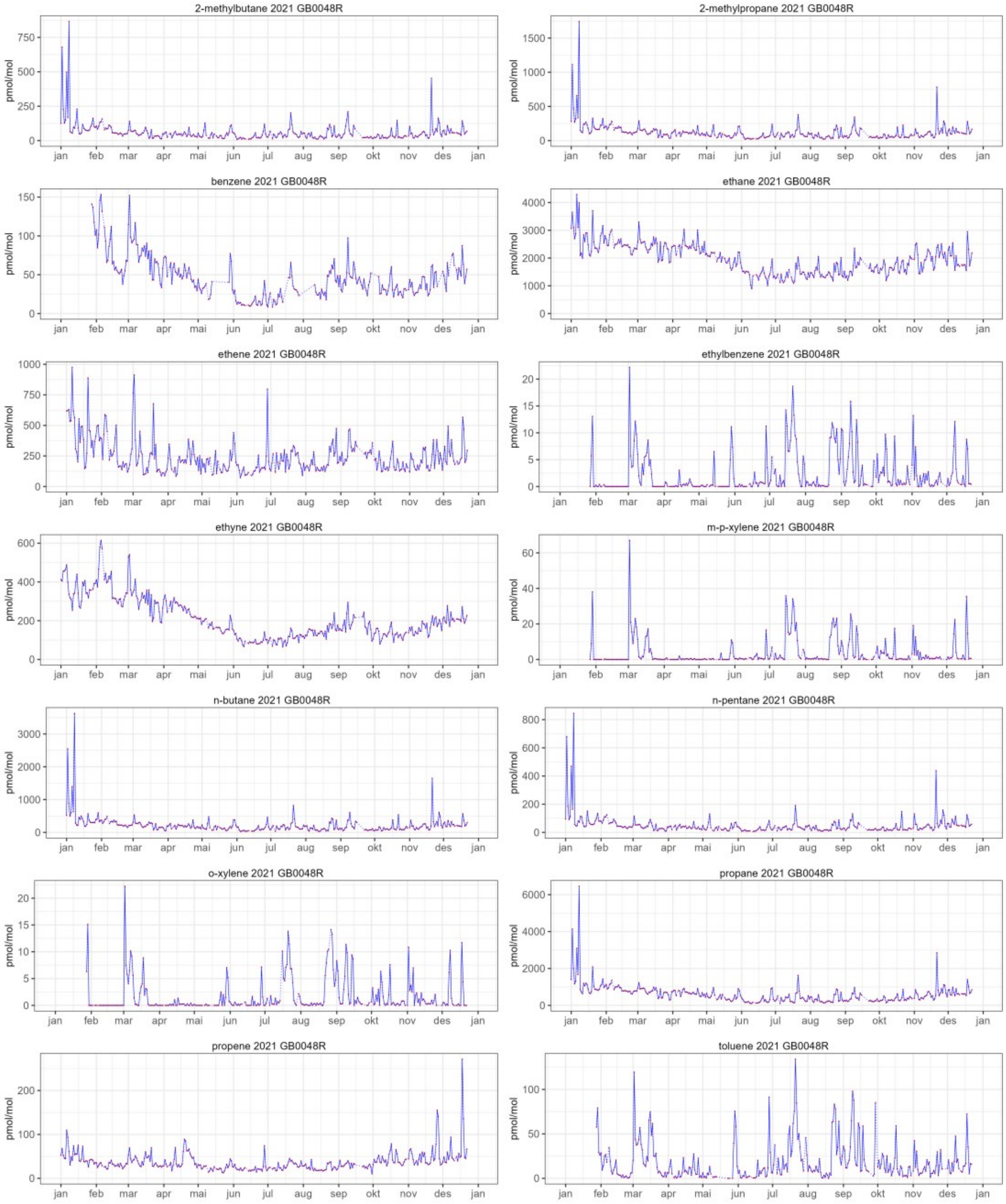
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m-p-xylene 2021 GB0048R
n-butane 2021 GB0048R
n-pentane 2021 GB0048R
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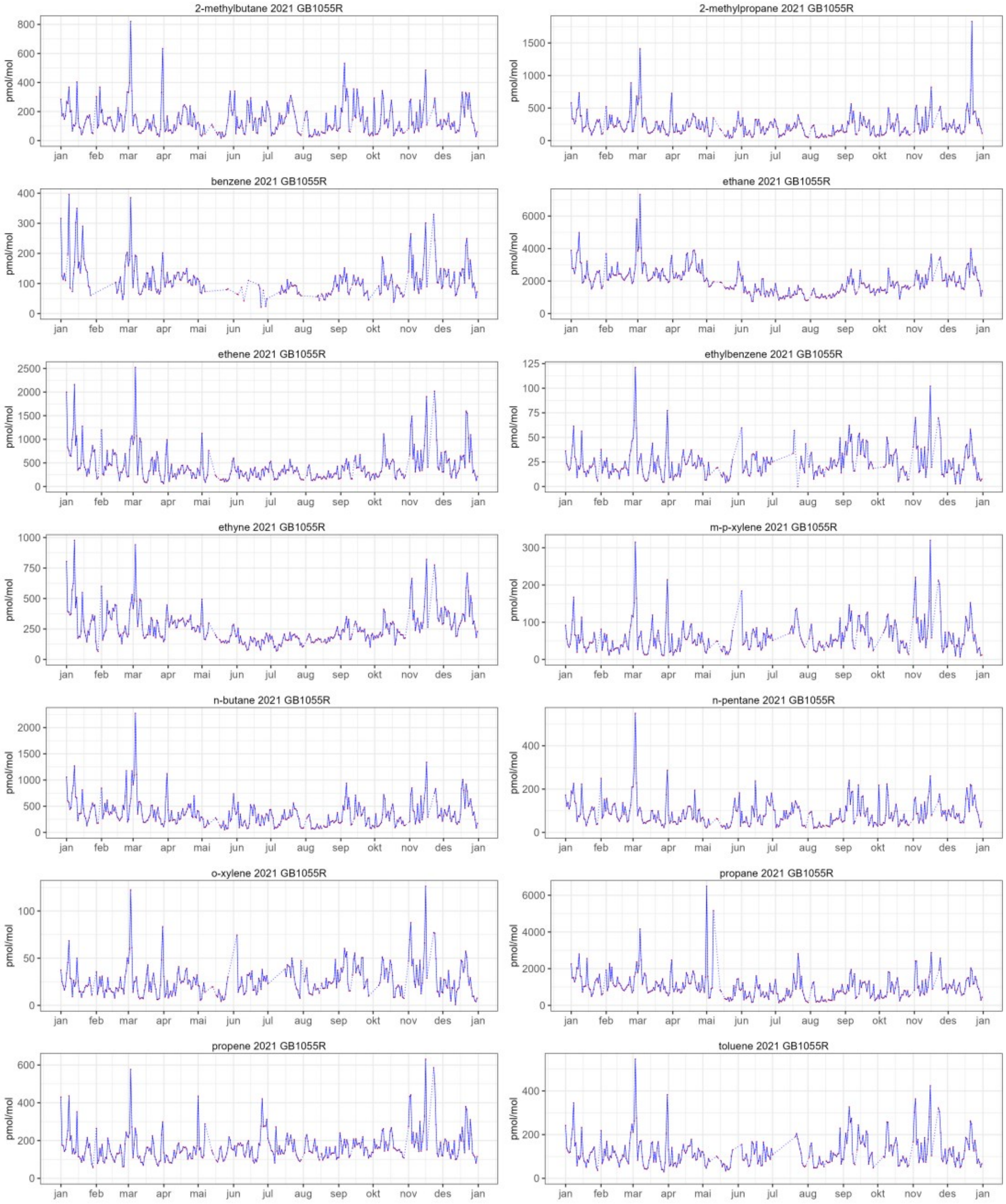
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ethyne 2021 GB1055R
m-p-xylene 2021 GB1055R
n-butane 2021 GB1055R
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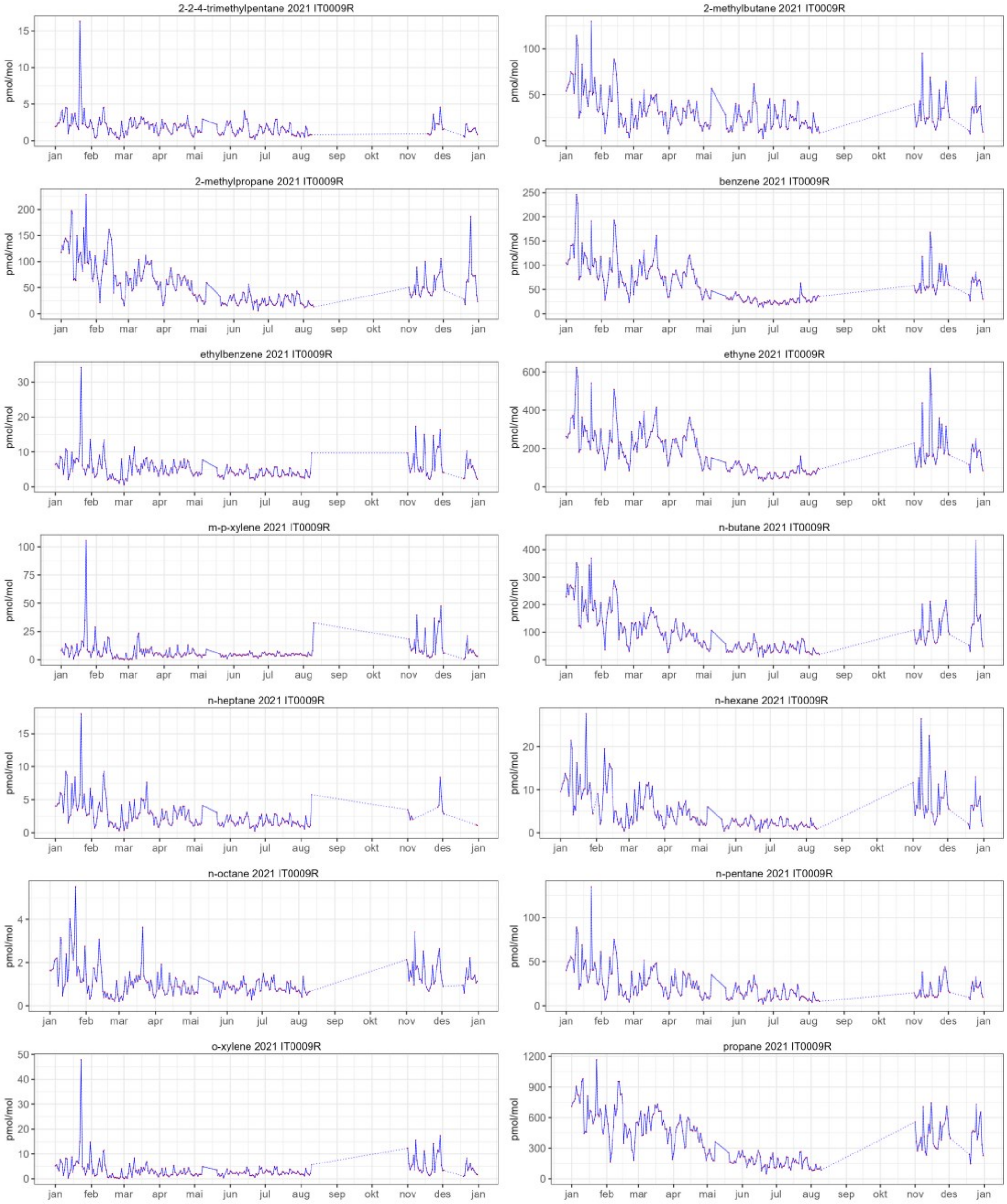
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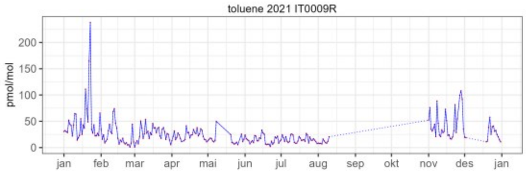
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