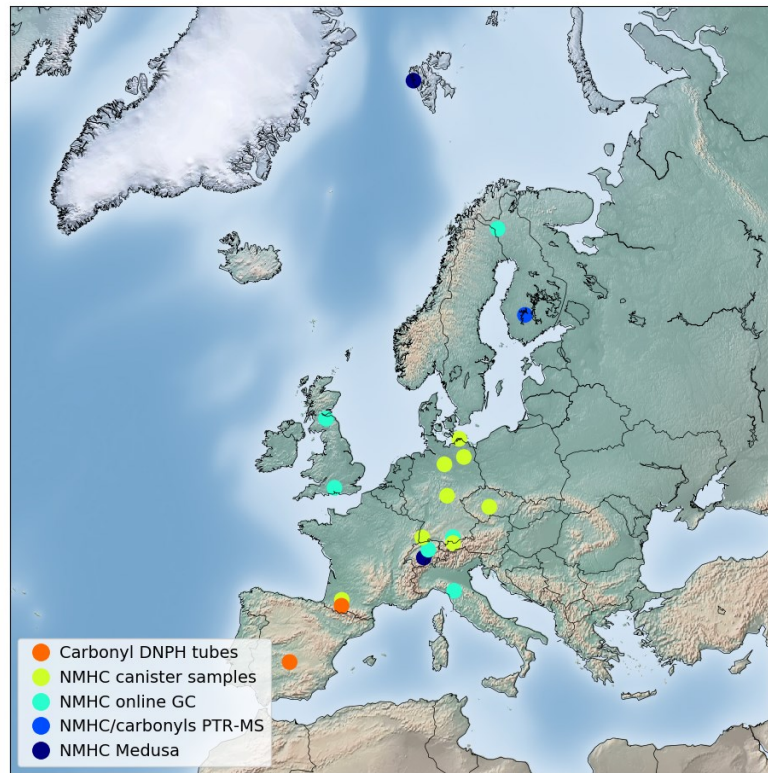


## VOC measurements 2020

Sverre Solberg, Anja Claude, Stefan Reimann, Stéphane Sauvage, and Sam-Erik Walker





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

**VOC measurements 2020**

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## Summary

This report presents VOC (volatile organic compound) measurements carried out during 2020 at EMEP monitoring sites. In total, 19 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 an important topic. Many 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.

Comparison between median levels in 2020 and the medians of the previous 10-years period, revealed similar geographical patterns as in the previous years. Changes in instrumentation, procedures and station network with time make it difficult though 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 NMHC over the 2001-2020 period using a newly developed method, a so-called GAM (generalized additive model) that includes the possibility of removing the effect of anomalies in the meteorology.

These estimates indicate marked differences in the long-term trends for the individual species. No trend was found for ethane during 2001-2020. Propane also showed a small reduction. On the other hand, components linked to road traffic (ethene and benzene) showed the strongest drop in mean concentrations, indicating their levels have been halved during the period.

# VOC measurements 2020

## 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, 2021a 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), Solberg (2013), Tørseth et al. (2012), Worton et al. (2012), Sauvage et al. (2009), Plass-Dülmer et al. (2009), Plass-Dülmer et al. (2006), Hakola et al. (2006), Borbon et al. (2004), Solberg et al. (2001), Solberg et al. (1996).

### 1.2 Underlying protocols for VOC

The Geneva Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes was adopted in November 1991. It entered into force on 29 September 1997. Three options for emission reduction targets are specified by the Protocol:

- (i) 30% reduction in emissions of VOC by 1999 using a year between 1984 and 1990 as a basis;



- (ii) The same reduction as for (i) within a Tropospheric Ozone Management Area (TOMA) and ensuring that by 1999 total national emissions do not exceed 1988 levels;
- (iii) Finally, where emissions in 1988 did not exceed certain specified levels, Parties may opt for a stabilization at that level of emission by 1999.

In 1999 the Gothenburg protocol to Abate Acidification, Eutrophication and Ground-level Ozone was adopted by the Executive Body of UN-ECE, and on the 17<sup>th</sup> May 2005 the Protocol entered into force. The Protocol sets emission ceilings for 2010 for four pollutants: SO<sub>2</sub>, NO<sub>x</sub>, VOCs and ammonia. These ceilings were negotiated on the basis of scientific assessments of pollution effects and abatement options. Parties whose emissions have a more severe environmental or health impact and whose emissions are relatively cheap to reduce will have to make the biggest cuts. According to the Protocol, Europe's SO<sub>2</sub> emissions should be cut by at least 63%, its NO<sub>x</sub> emissions by 41%, its VOC emissions by 40% and its ammonia emissions by 17% compared to 1990. The Protocol also sets tight limits for specific emission sources (e.g. combustion plant, electricity production, dry cleaning, cars and lorries) and requires best available techniques to be used to keep emissions down. VOC emissions from such products as paints or aerosols will also have to be cut.

In 2012 a revised Gothenburg protocol was adopted. An important difference from the previous protocol is that the emission ceilings now are given as percentage reductions from 2005 to 2020 and thereafter. Furthermore, PM<sub>2.5</sub> and BC (black carbon) is now included in the protocol. According to the revised protocol, the VOC emissions from the Parties to the Convention must be cut by 28% as an average for all the parties in 2020 compared to the 2005 emissions, with national commitments ranging from 8% (the Netherlands) to 54% (Greece).

### **1.3 Cooperation with other bodies – GAW and ACTRIS**

At some stage, initiatives were taken to increase the cooperation and exchange of VOC data between GAW (Global Atmospheric Watch) and EMEP. Harmonization of data quality objectives (DQOs) and using a common audit questionnaire were recommended, and it was also a wish to arrange common GAW/EMEP training course and to further increase the exchange of VOC monitoring data between EMEP, GAW and WDCGG (World Data Centre of Greenhouse Gases).

In 2006 a WMO/GAW workshop on global measurements of VOCs (WMO, 2007) proposed a list of species to be measured based on current and future possibilities and needs of GAW. The GAW species and their DQOs are given in Table 1 together with the original list of so-called required and desirable compounds within EMEP as defined at the Lindau workshop in 1989 (EMEP/CCC, 1990). Table 1 also lists the ACTRIS species and their DQOs, as explained below.

Most of the GAW compounds are already part of the EMEP VOC programme with some exceptions: Alcohols, terpenes, DMS (dimethyl sulfide) and acetonitrile are not part of the original EMEP VOC programme. In addition to being important biogenic compounds, the alcohols (methanol and ethanol) are likely to become more important in the future due to increased use of biofuels in vehicles. Furthermore, terpenes are important as precursors for secondary organic aerosols. Acetonitrile and DMS would be good to include

in the monitoring due to their role as tracers for biomass burning and oceanic emissions, respectively.

Within the infrastructure project ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure), data quality issues related to measurements of VOCs are important topics. ACTRIS, the European Research Infrastructure for the observation of Aerosol, Clouds, and Trace gases was launched as a EU FP7 project in 2011 and includes a large number of partners with experience in VOC monitoring, including most of EMEP laboratories. The aim was to evaluate the performance, repeatability and uncertainty of the present NMHC monitoring, as well as to develop guidelines and data quality objectives for the monitoring. Highly ambitious DQOs were defined for a number of individual species as shown in Table 1. ACTRIS is progressing to a long-term ERIC and future EMEP labelled data will continue to profit from the related quality assurance.

Furthermore, GAW are in the process of adopting the ACTRIS DQOs and are introducing the terminologies “GAW basic performance” and “GAW target performance”, the latter corresponding to the ACTRIS DQOs as given in Table 1.

Table 1: Original list of required and desirable VOCs within EMEP. The GAW priority species with required accuracy/precision and the targeted list for ACTRIS with required uncertainty/repeatability are also listed.

	EMEP required	EMEP desirable	GAW priority <sup>1</sup>		ACTRIS target <sup>2</sup>	
			accuracy	precision	uncert.	repeat.
<b>Alkanes</b>						
Ethane	X		10%	5%	5%	2%
Propane	X		10%	5%	5%	2%
n-butane	X		10%	5%	5%	2%
i-butane	X		10%	5%	5%	2%
n-pentane	X		10%	5%	5%	2%
i-pentane	X		10%	5%	5%	2%
n-hexane		X			5%	2%
i-hexanes		X			5%	2%
n-heptane		X			5%	2%
i-heptanes		X			5%	2%
n-octane		X			5%	2%
i-octanes					5%	2%
Cyclohexane					5%	2%
<b>Alkenes</b>					5%	2%
Ethene	X				5%	2%
Propene	X				5%	2%
butenes		X			5%	2%
pentenes		X			5%	2%
1,3-butadiene					5%	2%
Isoprene	X		20%	15%	5%	2%
<b>Alkynes</b>					5%	2%
Acetylene	X		15%	5%	5%	2%
Propyne					5%	2%
Styrene		X			5%	2%
<b>Aromatics</b>					5%	2%
Benzene	X		15%	10%	5%	2%
Toluene	X		15%	10%	5%	2%
o-xylene	X				5%	2%
m,p-xylene	X				5%	2%
Ethylbenzene	X				5%	2%
trimethylbenzenes	X				5%	2%
propylbenzenes		X			5%	2%
Ethyltoluenes		X			5%	2%
<b>Carbonyls</b>					5%	2%
Formaldehyde	X		20%	15%	10%	5%
Acetaldehyde	X					
Propionaldehyde		X				
Acetone	X		20%	15%	10%	5%
Methylethylketone		X				
Methylvinylketone		X				
<b>Other</b>						
Monoterpenes			20%	15%	10%	5%
Acetonitrile			20%	15%		
Methanol			20%	15%		
DMS			20%	15%		

<sup>1</sup> Accuracy = 20 ppt, Precision = 15 ppt if level < 0.1 ppb

<sup>2</sup> Uncertainty = 5 ppt, Repeatability = 2 ppt if level < 0.1 ppb

## 2. Status of the measurement programme in 2020

### 2.1 The station network

The locations of the EMEP monitoring sites for VOC in 2020 are shown in Figure 1 and an overview of the measurement programme and the responsible laboratories is given in Table 2. In total, 18 measurement sites 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 and filtering (flagging local influences).

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.

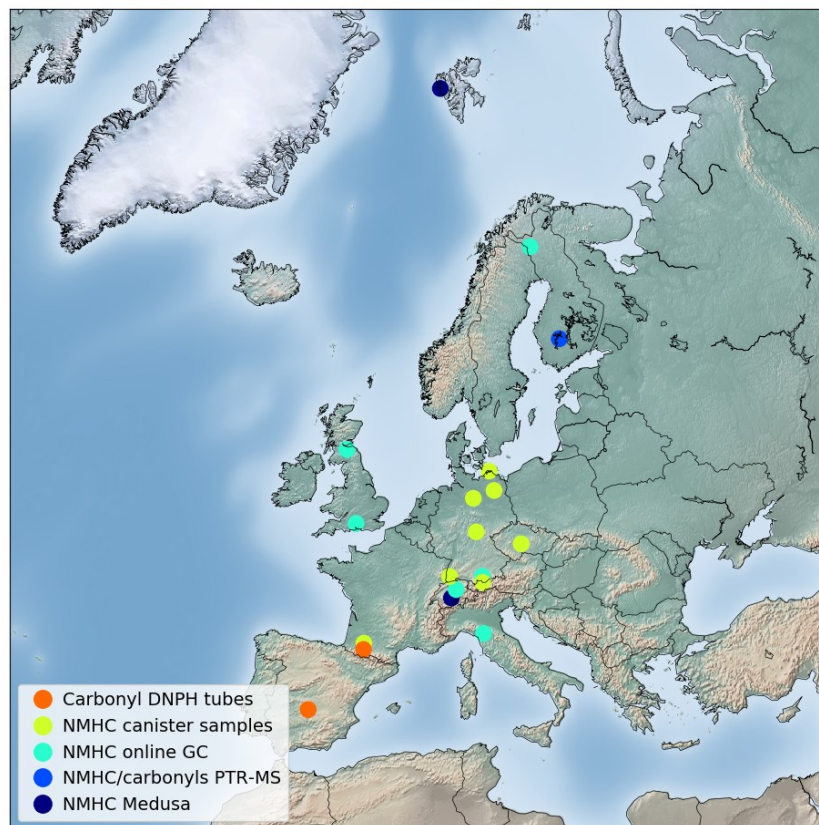


Figure 1: Monitoring sites for VOC in 2020.

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 (Hyttiälä), Medusa

monitors (Zeppelin Mountain and Jungfrauoch) 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 the sites in France and Spain. 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 a substantial number of sites has contributed to the EMEP VOC programme since the early 1990s, very few sites have long and continuous time series. This poses a 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.

As given in Table 2, 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. Highly deviating ratios compared to what is seen at other sites and reported in the literature is a sign that something could be wrong. There is a dialogue between EMEP-CCC/NILU and the data provider in Spain on this issue but the pandemic has made it difficult to carry out the planned field visits.

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.

The NMHC data from Auchencorth Moss in Scotland, a rural location around 20 km south of Edinburgh also show very spiky time series with peak levels of propane, n-butane and other species resembling what is seen at street level in major cities. 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.

Very high levels of alkenes with three or more C-atoms (propene and higher) were reported for all sites from UBA in Germany, i.e. Waldhof, Schauinsland, Neuglobsow, Schmücke, Zingst, and Zugspitze for 2020 as in previous years. As in the preceding reports, these data were flagged invalid and regarded erroneous and not used further. This flagging was according to the recommendations from ACTRIS-2.

A large fraction of OVOC data reported for the site Lahemaa (EE0009) were below detection limit making it difficult to evaluate the performance of the monitoring and the data were thus flagged as preliminary.

**Table 2:** VOC monitoring at EMEP sites in 2020. 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 <sup>1)</sup>	Institute <sup>2)</sup>	Carb <sup>1)</sup>	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 <sup>3)</sup>	Twice/week
Schauinsland	DE0003	Reg.	UBA	-	"	y <sup>3)</sup>	"
Neuglobsow	DE0007	Reg.	UBA	-	"	y <sup>3)</sup>	"
Schmücke	DE0008	Reg.	UBA	-	"	y <sup>3)</sup>	"
Zingst	DE0009	Reg.	UBA	-	"	y <sup>3)</sup>	"
Zugspitze	DE0054	Reg.	UBA	-	"	y <sup>3)</sup>	"
Hohenpeissenberg	DE0043	Daily	DWD	-	GC/FID	y	2/day (noon, midnight)
Košetice	CZ0003	Reg.	CHMI	-	Canister samples	y	Twice/week
Jungfrauoch	CH0001	Cont.	EMPA	-	MEDUSA	y	
Beromünster	CH0053	Cont.	EMPA	-	GC/FID	y	
Peyrusse Vieille	FR0013	Reg.	IMT LD	Reg.	Canister/DNPH samples	y	NMHC 2/week. OVOC 1/week
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 = Ministerio de Medio Ambiente

3) Participated voluntarily in ACTRIS-2 without being a formal partner

## 2.2 Analytical procedures, quality control and intercomparisons

Quality control of the VOC measurements includes QA/QC procedures at all stages from sampling to chemical analyses and integration. The QA procedures for the original EMEP methods (manual sampling of NMHC in stainless steel canisters and OVOC in DNPH adsorption tubes with subsequent analyses in the lab) are described in the EMEP manual (EMEP/CCC, 2014) and are more or less identical to the original manual description given in EMEP/CCC 1995.

Measurement guidelines for the original EMEP method based on manual sampling of NMHCs has furthermore been provided in detail by GAW (GAW, 2012). A review of the various methods for VOC monitoring within GAW has also been prepared based on a GAW expert workshop in 2006 (WMO/GAW, 2006).

As mentioned, the ACTRIS consortium played a central role in the quality control of data from the regular monitoring by the laboratories of the participating institutes. A comprehensive Standard Operation Procedures (SOP) manual for VOCs has also been developed as part of the project.

VOC data from ACTRIS-stations are presented by representatives from each institution and discussed in detail at dedicated workshops annually (normally in May the following year). Associated institutions not being formal ACTRIS partners are invited to take part in this, and UBA (Umweltbundesamt) in Germany has used this opportunity.

Based on statistical tools developed within ACTRIS, potential outliers and errors in the data were discussed, and recommendations for database flagging were agreed on through discussion at the workshop. EMPA, the ACTRIS task leader for VOC, had a key role in this process. Detailed inspection of the data has furthermore been done by NILU in parallel with the tools developed at EMPA. Dialogue between EMPA, NILU and the data providers has been essential in this work and a web based issue tracker has been developed and used in the process. This task will be taken over in the future by CiGAS of ACTRIS (Centre for Reactive Trace Gases In Situ Measurements).

The whole QA/QC process has become fairly complex and demanding but is now “on track” and goes much more smoothly than in the first years. The procedures developed within ACTRIS follow somewhat in the footsteps of the AGAGE project for greenhouse gases and ozone depleting substances (e.g. Prinn et al., 2018). The elaborate QA work on VOC provided by ACTRIS-in particular, has meant a significant improvement in the general data quality. Hopefully, these procedures and routines will be incorporated into the parts of the EMEP VOC program and stations that are not formally part of ACTRIS.

In conjunction with EBAS, the templates for data submission were further developed to the requirements of GAW, EMEP and WIGOS. The data flow for VOC data collected at EMEP/ACTRIS stations are shown in Figure 2.

## Data flow of VOCs within ACTRIS/EMEP

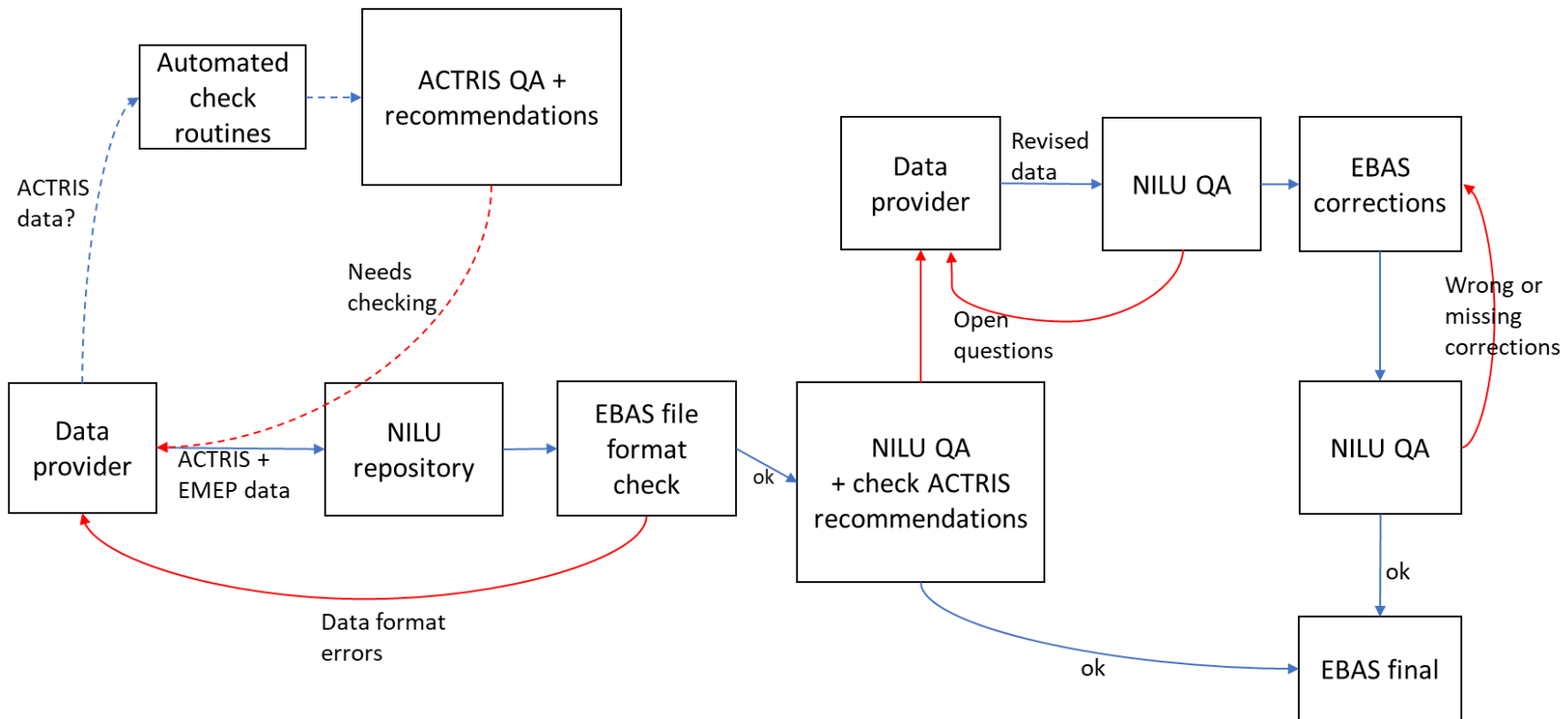


Figure 2: Flow diagram for the VOC data submitted within ACTRIS/EMEP.



### 2.2.1 Intercomparisons

The first laboratory intercomparison of light hydrocarbons in EMEP was organized in 1993 (Romero, 1995). The variation or relative deviation among the laboratories was in the range  $\pm 25\%$  from the median. The exercise showed that the majority of participating laboratories had the required analytical technique to correctly analyze a wide range of NMHC within an accuracy of  $\pm 10\text{--}15\%$ . Furthermore, the results showed no substantial differences, regardless of whether the air samples were analysed immediately after collection or after a period up to 2 months (for  $C_2\text{--}C_5$  hydrocarbons).

Since then, various intercomparisons for VOC have been carried out, e.g. through the NOMHICE (Nonmethane Hydrocarbon Intercomparison Experiment) (Apel, 2003, and references therein) and AMOHA (Accurate Measurements of Hydrocarbons in the Atmosphere) (Slemr et al., 2002; Plass-Duelmer et al., 2006) projects, with participation from a large number of laboratories in Europe and elsewhere. A major part of the AMOHA project was to organize four annual intercomparisons starting in 1997 and ending in 2000. The results showed that except for a few laboratories the agreement was within  $\pm 25\%$  of the median for the lighter alkanes. For some aromatics and unsaturated hydrocarbons as well as the  $C_6\text{--}C_7$  alkanes a large spread in the values was seen, indicating measurement difficulties with these compounds. The spread in the results was, however, much less for those laboratories using an NPL standard for calibration (Aas et al., 2001). Thus, it was concluded that a large part of the differences seen among the laboratories reflected the use of different calibration gases. When using the same NPL standard the results from this intercomparison were very satisfactory.

Details of the ACTRIS NMHC intercomparison can be found in Hoerger et al. (2015). The intercomparison covered a list of 34 NMHC, including  $C_2\text{--}C_8$  alkanes,  $C_2\text{--}C_5$  alkenes, five aromatics and two alkynes. One canister with a mixture of 30 NMHC at 1 ppb level in  $N_2$  and one canister with whole air sampled in a suburban area (Dübendorf, Switzerland) were distributed to all participating laboratories for analysis. For calibration, the laboratories were asked to use their own certified multicomponent standards, traceable to the GAW scale. Three laboratories served as reference labs, analyzing the starting cylinders before and after the exercise: The WCC-VOC (World Calibration Centre for VOC, Karlsruhe Institute of Technology, Garmisch-Partenkirchen), DWD (Deutscher Wetterdienst at Hohenpeissenberg) and EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland.

The intercomparison showed the best results for the gas mixture in  $N_2$  and for the lighter alkanes. In comparison, the results were clearly poorer for the whole air sample.  $C_4\text{--}C_5$  alkenes and  $C_7\text{--}C_8$  species (alkanes and aromatics) were the most problematic species. For all species/laboratories, almost 62% of the results from the  $N_2$  canisters fell within the 5% DQO and 90% within the former 10% DQO of GAW. For the real air samples, larger and more frequent deviations were found. Only 50% of the results were within the ACTRIS 5% DQO and 79% within the 10% group

As seen in previous intercomparison studies (e.g. AMOHA, Plass-Duelmer et al. (2006)), the type of calibration standard is important for the performance of the laboratory. In the ACTRIS study, it turned out that systems based on direct calibrations with standards in the ppb-range performed better than those based on a two-step calibration using more concentrated standards. Furthermore, ethyne was a problem in several systems, and direct calibration of ethyne turned out to be essential for the result. Additionally, almost

all the participating laboratories/instruments showed indications of losses of the C<sub>7</sub>-C<sub>8</sub> aromatics, most probably due to adsorption effects.

In general, the best results were provided by GC-FID instruments. GC-MS systems also delivered good results; however, they require more frequent calibrations since they are less stable. The only commercially available system, the Perkin Elmer Online Ozone Precursor Analyzer, provided reasonable results although not among the best. A main conclusion from the ACTRIS study is that the very ambitious ACTRIS DQOs for NMHCs could be met. It will, however, require experienced personnel, well-characterized instrumentation and detailed procedures for quality control at all stages.

In addition, two intercomparisons for OVOC (aldehydes and ketones) was carried out within ACTRIS at Hohenpeissenberg, with synthetic test mixtures and ambient air. The results of this exercise are, however, not yet published.

### **3. VOC concentrations in 2020**

#### **3.1 General levels**

Time series of the diurnal means of all compounds at all stations during 2020 are given in the Appendix. Figure 3 shows the spread of data values for each station and NMHC species in 2020 in box and whisker plots, and the annual median values based on the previous 10 years of data (2010-2019) are included for comparison for stations that had such data. The sites are arranged from north to south going from left to right in the panels. Thus, the panels in Figure 3 indicate both the north-to-south differences, the deviation of the 2020 concentration levels relative to the previous 10 years climatology as well as the spread in 2020 data at each site separately.

For C<sub>2</sub>-C<sub>5</sub> hydrocarbons there is a striking similarity between the variation in median values in 2020 compared to the 10-year climatology whereas for heavier compounds there are larger differences. The previous monitoring problems at UBA's sites in Germany explain parts of this – most evident for toluene showing very high median levels for the 2010-2019 period that presumably are not real. For other species, the differences between the 2020 and the historical data reflect that the number of measurements are fewer and therefore show a larger spread in concentration levels. Similar box and whisker plots for a number of OVOC are shown in Figure 4.

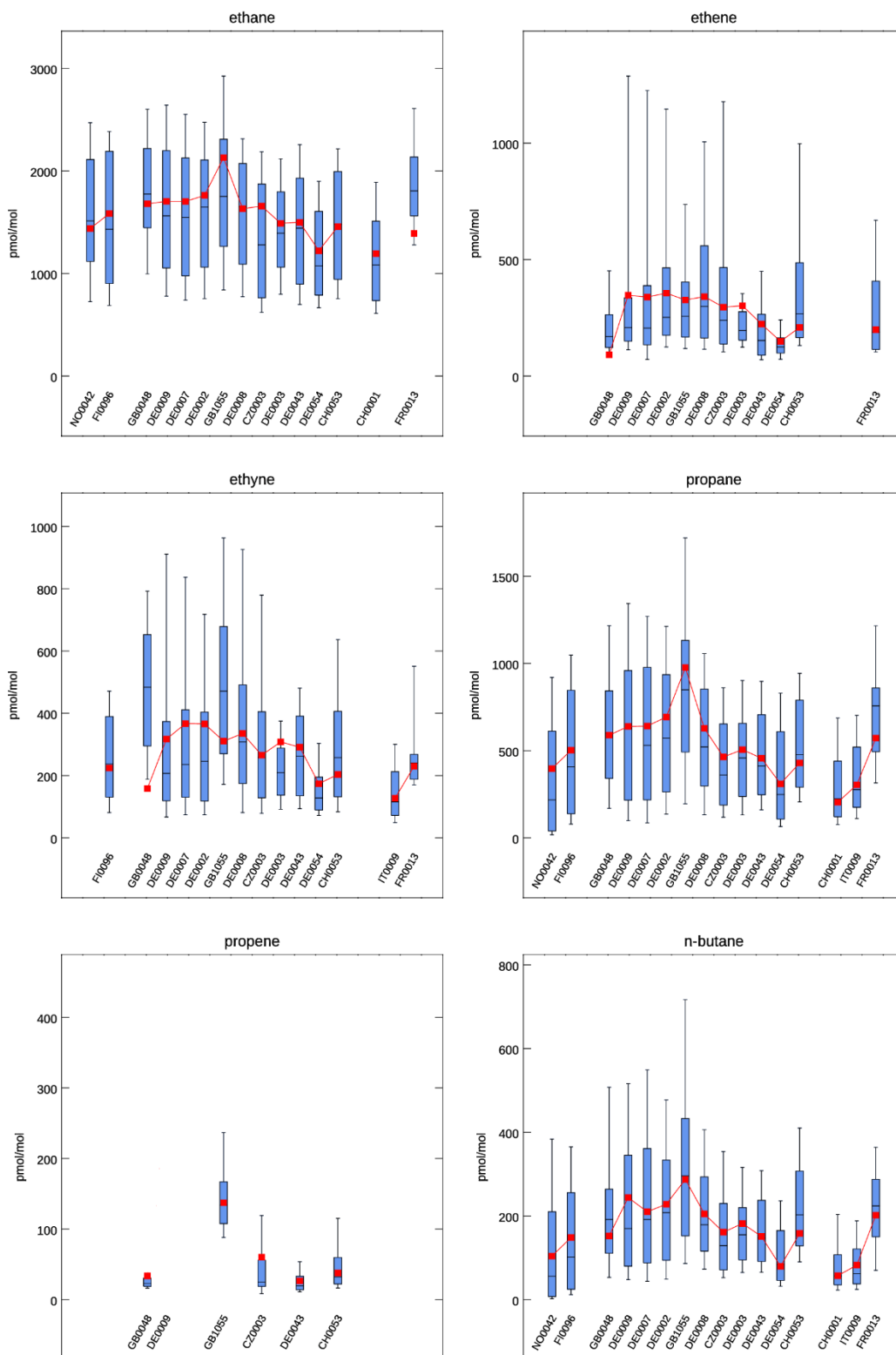


Figure 3: Box- and whisker-diagrams for light hydrocarbons based on all measurements in 2020. The boxes enclose the 25- and 75-percentile with the median marked inside. The whiskers extend out to the 9<sup>th</sup> and 91<sup>th</sup> percentile. The red squares connected with a red line mark the medians based on all data for the previous 10 years (2010-2019).

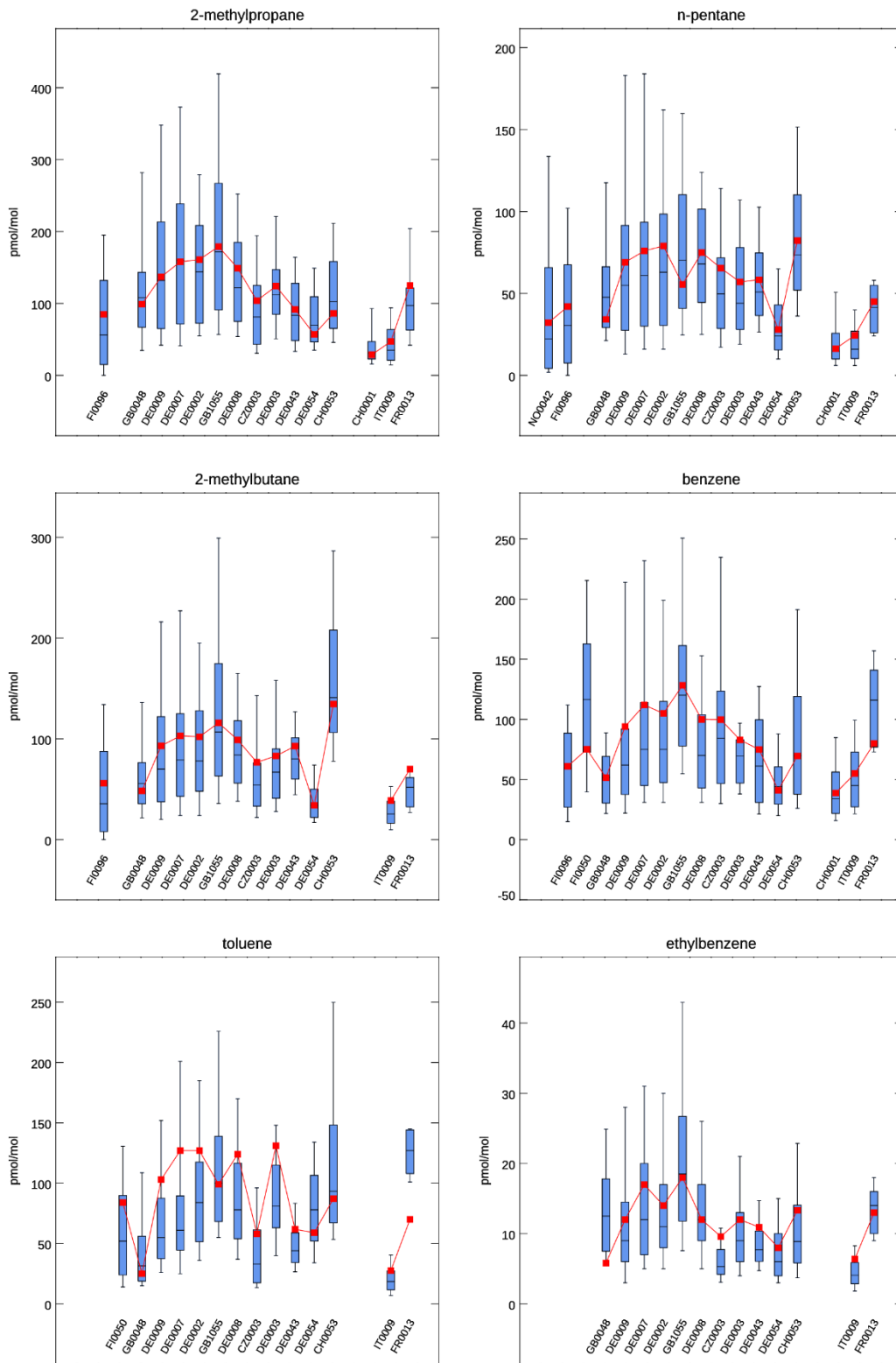


Figure 3 (cont.).

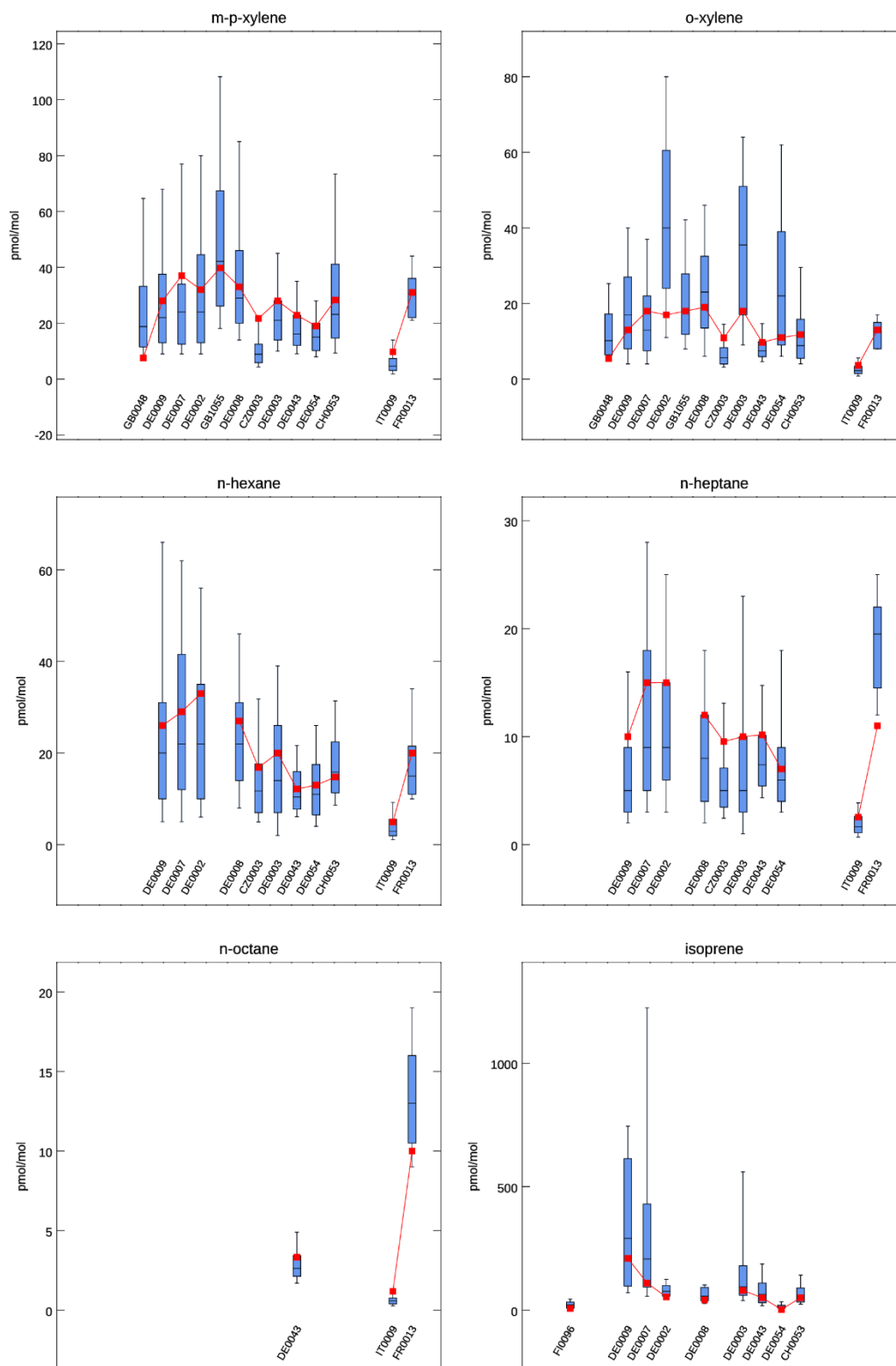
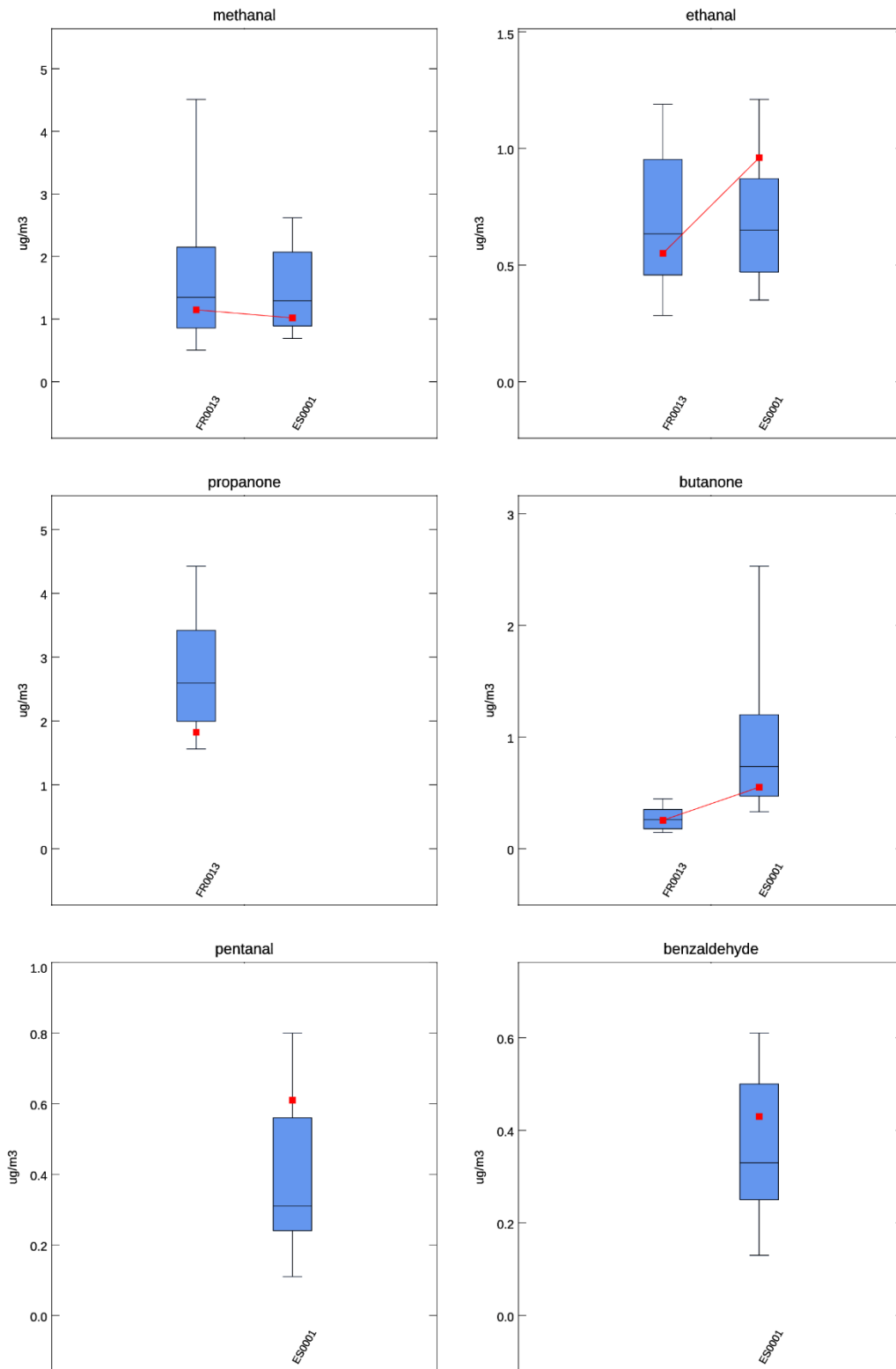


Figure 3 (cont.).

Note that for isoprene only data for June-August (whole day) were used.



**Figure 4:** Box- and whisker-diagrams for carbonyls based on all measurements in 2020. The boxes enclose the 25- and 75-percentile with the median marked inside. The whiskers extend out to the 9<sup>th</sup> and 91<sup>st</sup> percentile. The red squares connected with a red line mark the medians based on all data for the previous 10 years (2010-2019).

### 3.2 Regional distribution of VOC

Figure 5 shows maps with the stations' annual median concentrations of light hydrocarbons in 2020. 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.

Similar maps for selected carbonyl species based on data from the whole year are given in Figure 6. The number of monitoring sites for carbonyls are much less than for NMHC and the sampling frequency is in general somewhat poorer.

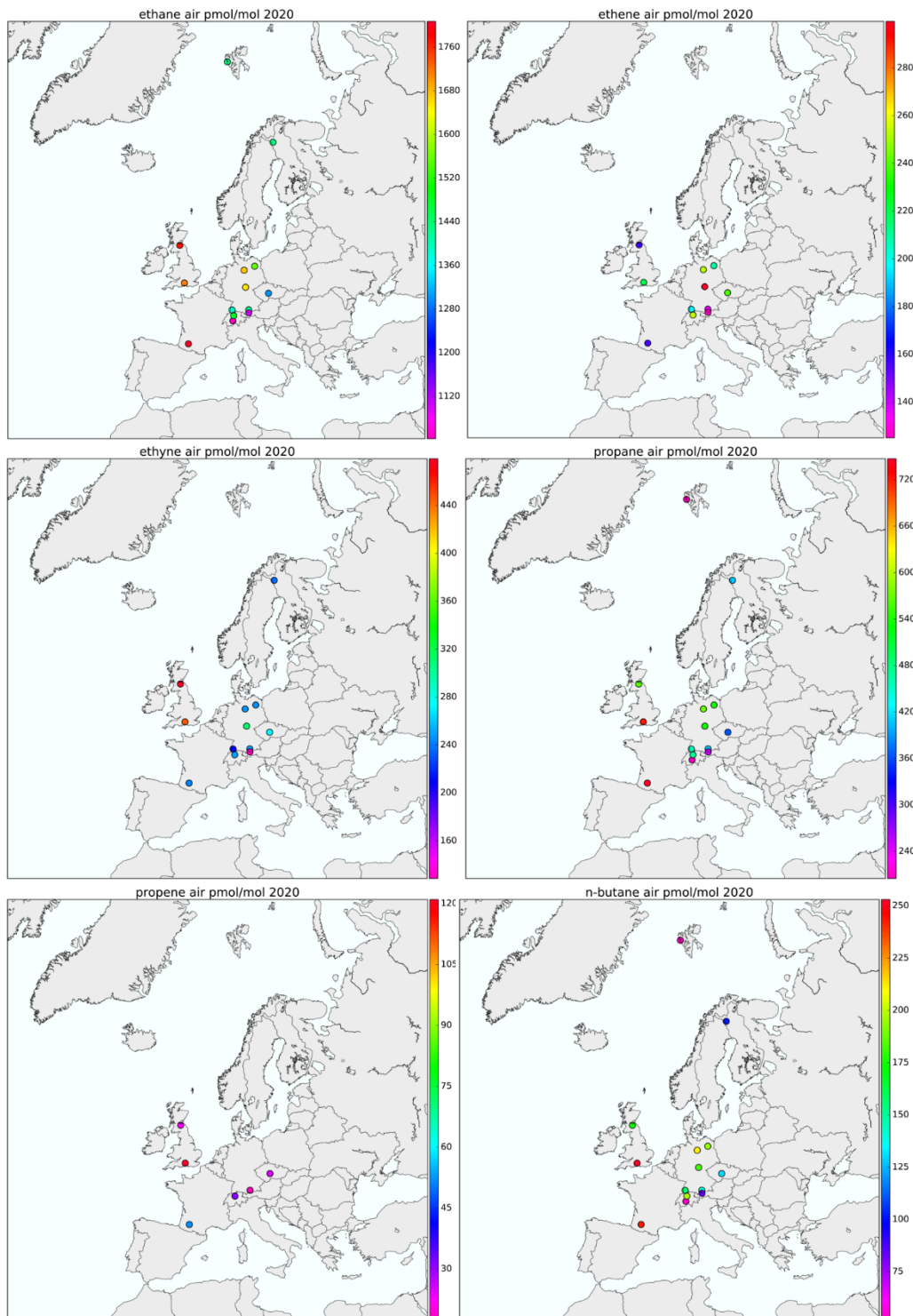


Figure 5: Annual median concentration of NMHCs in 2020. Unit: pmol/mol.



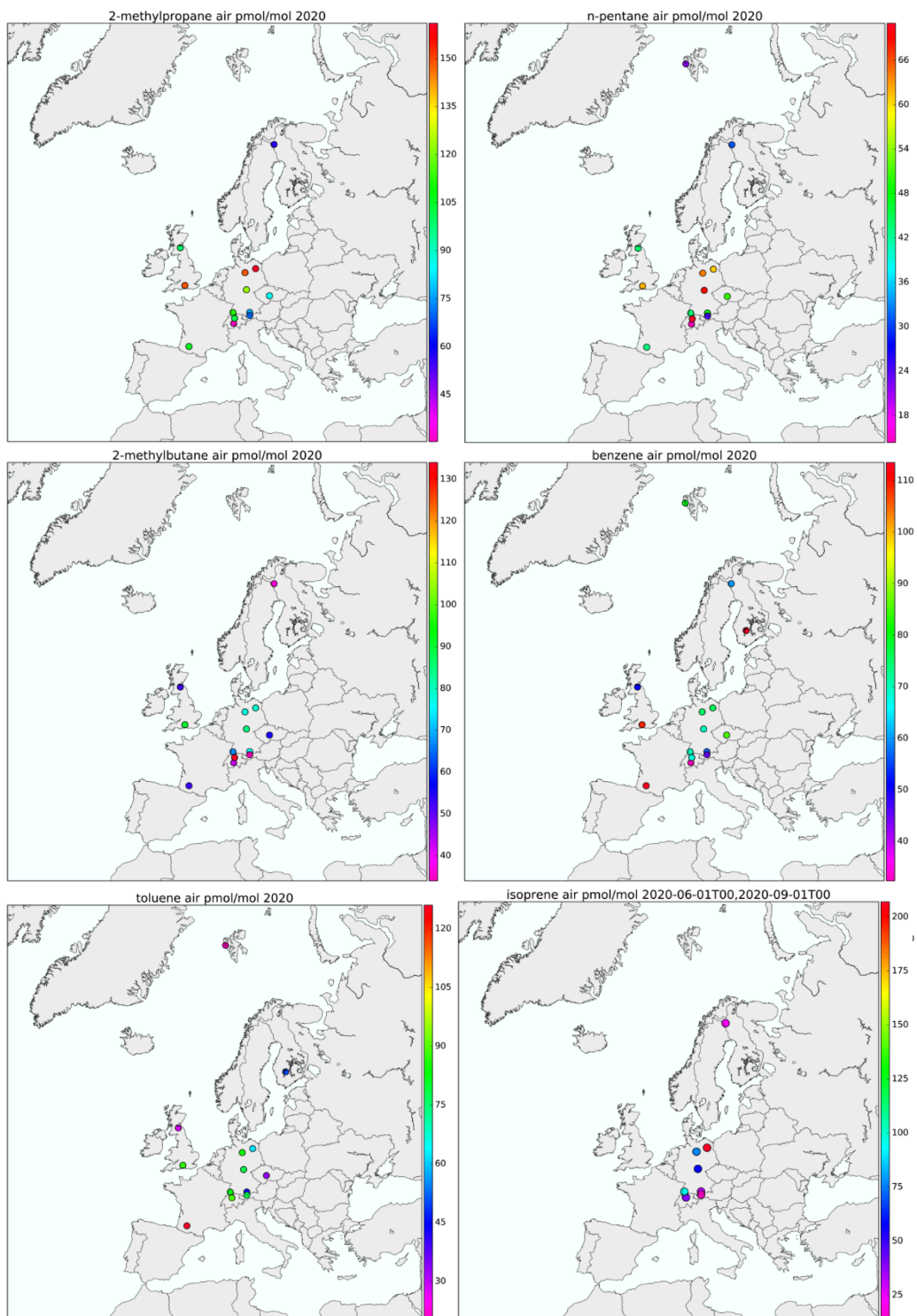
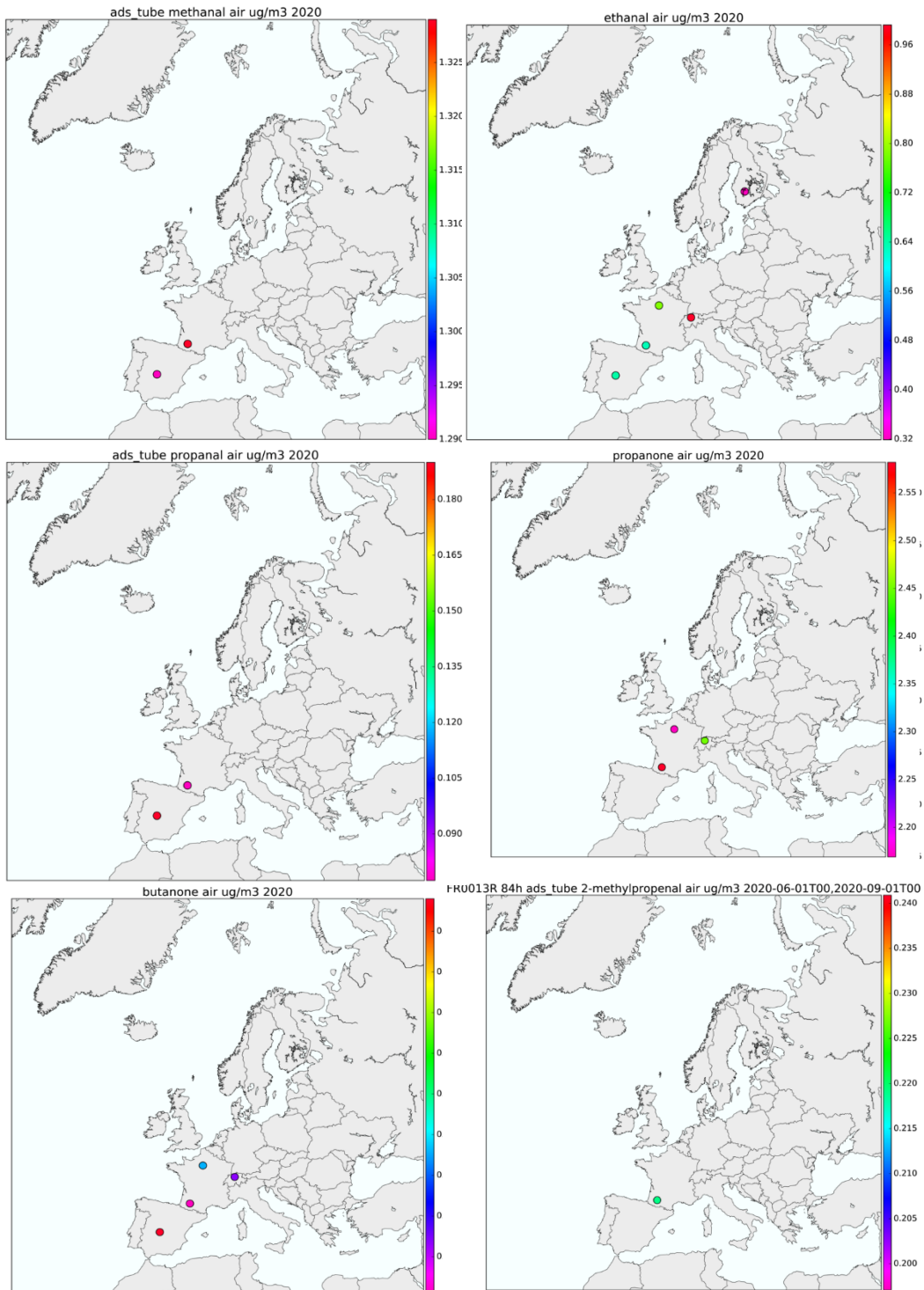


Figure 5 (contd.).

Note that for isoprene the summer median (Jun-Aug) is shown.



**Figure 6:** Annual median concentration of carbonyls in 2020.  
 Note that for 2- methylpropanal the summer median (Jun-Aug) is shown.  
 Unit:  $\mu\text{g}/\text{m}^3$ .

## 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 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<sub>2</sub>-C<sub>8</sub> 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<sup>-1</sup> to -22% y<sup>-1</sup> 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 complicates 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., 2021a) 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., 2022). 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 7 hydrocarbons measured at Hohenpeissenberg (DE0043) 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. (2022). The same model set-up as used for NO<sub>2</sub> (Walker et al., 2022) 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.

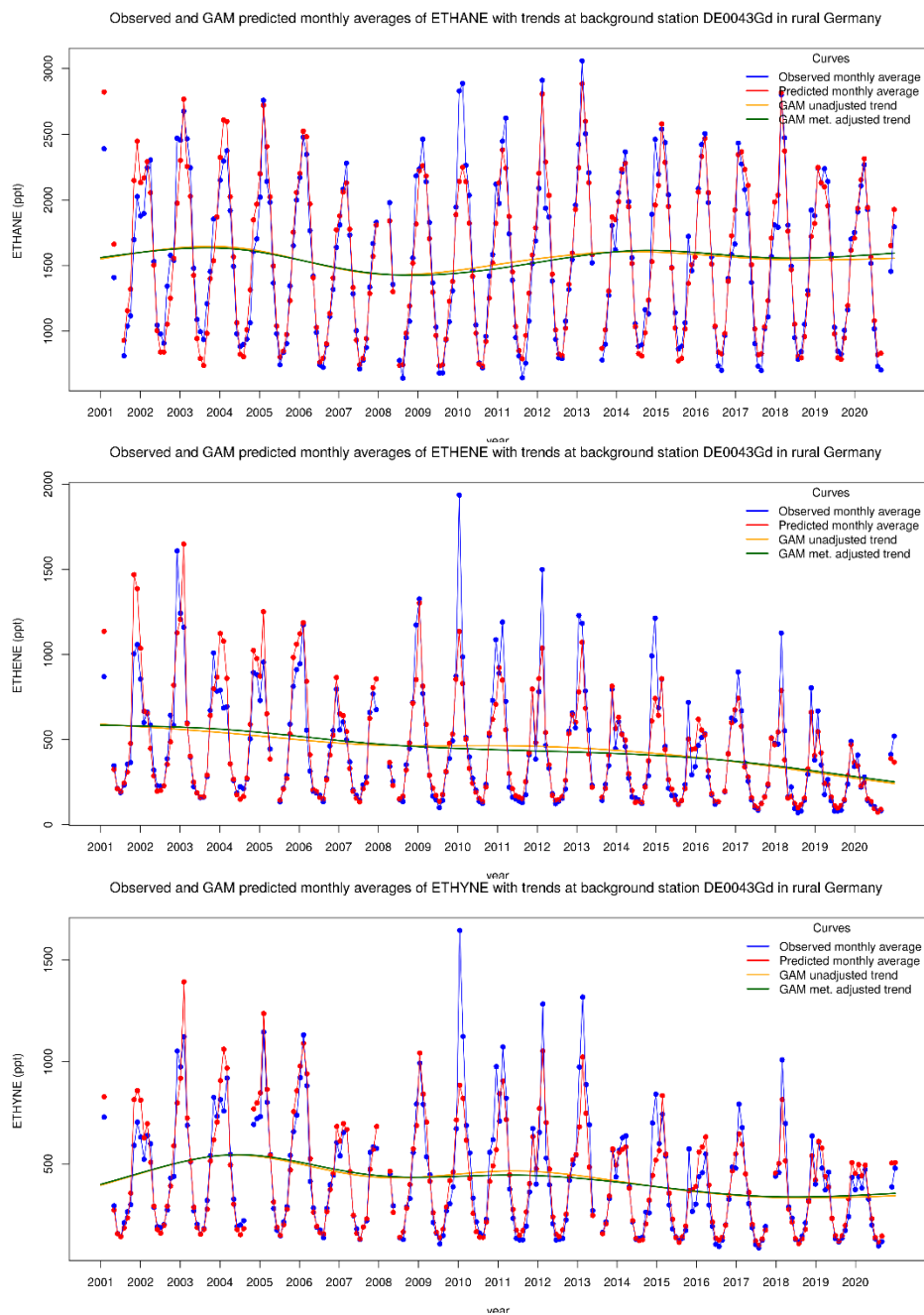
The observed and modelled monthly mean values during 2001-2020 are presented in Figure 7 together with the estimated trend curves when corrected for the varying meteorological data and in uncorrected way. The results show a close agreement between observed and predicted monthly values although some spikes in the observed data are not reproduced by AirGAM. These data include the "Covid-year" 2020 which required that the lockdown periods in the individual countries were considered as described in Solberg et al (2021b).

The time series and trend curves shown in Figure 7 indicate very small differences in the meteorologically adjusted and the unadjusted trends. The meteorologically adjusted trends implies that that the effect of anomalies in the day-to-day variation in weather conditions (wind, temperature, humidity and mixing) is "removed" so that the adjusted trend is not biased by such anomalies during the 2001-2020 period.

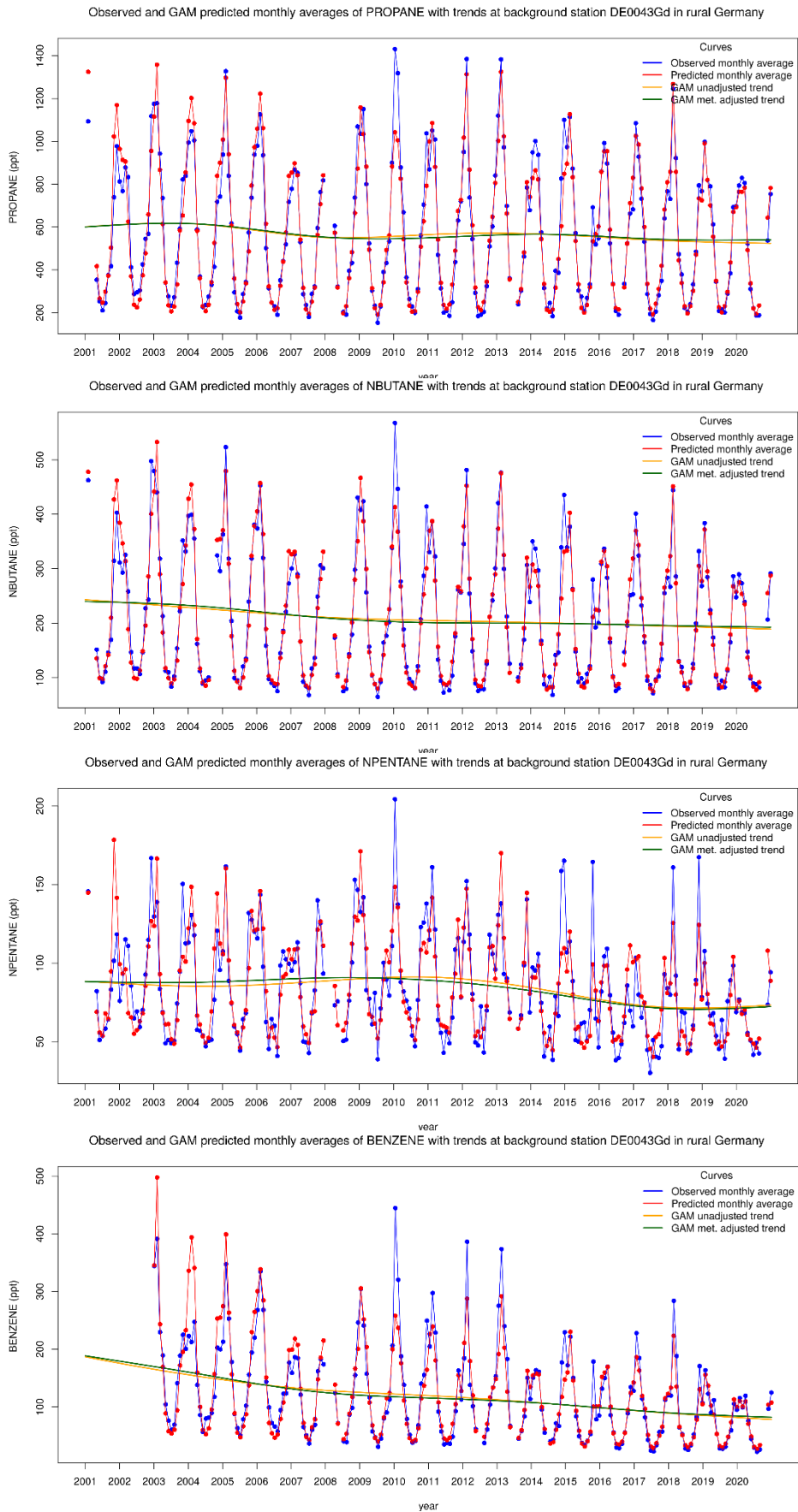
The results when applying a linear trend approach (on the log-transformed measurement data) in AirGAM are given in Table 3 together with the estimated downward trends as shown in the previous year's VOC report for comparison (Solberg et al., 2021a). The type of trend during the 2001-2020 period is also indicated.

These results show a close agreement between the long-term changes as estimated by AirGAM for 2001-2010 compared to the trends calculated in the previous year's report for 2000-2019. Furthermore, marked differences are seen for the individual species. Strongest reductions are found for benzene and ethene which are approximately halved since 2001. These species are tracers of traffic emissions. On the other side, there is no change in ethane and just a minor reduction in propane, both tracers of natural gas.

These marked reductions in observed NMHC levels in Europe since 2000 is 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.



**Figure 7:** Monthly mean concentrations of selected NMHC as observed (blue) and modelled by AirGAM (red) at Hohenpeissenberg during 2001-2020 together with the estimated trend curves based on unadjusted and met-adjusted daily data.

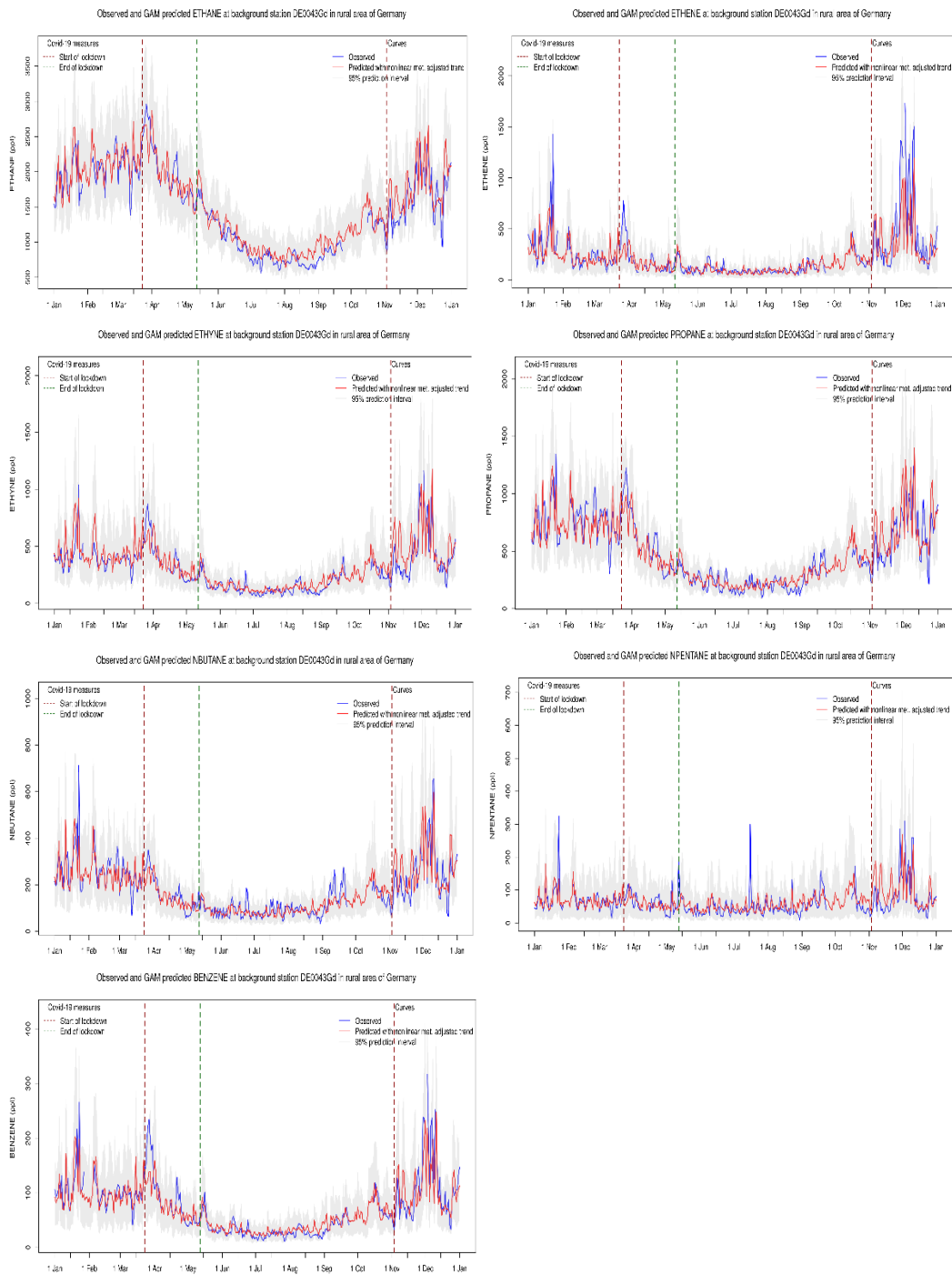


*Table 3: The percentage reduction in measured hydrocarbons at Hohenpeissenberg (DE0043) as presented in the previous year's report (Solberg et al., 2021a) for the period 2000-2019 and as calculated now by AirGAM for 2001-2020 relative to 2001 as the base year.*

	2000-2019 <sup>1)</sup>	AirGAM (2001-2020)	
	Range of downward trends (%)	Percentage change (%)	Trend type
Ethane	0-1	<1	Variable
Ethene	45-49	-49	Straight
Ethyne	35-39	-35	Variable
Propane	9-13	-12	Variable
n-butane	16-22	-20	Straight
n-Pentane	15-18	-23	Smooth
Benzene	57-63	-53	Straight

1) Based on three methods for trend estimation (Solberg et al., 2021a).

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 8 show the observed daily levels of 7 NMHCs at Hohenpeissenberg during 2020 together with the levels predicted by AirGAM as well as the start and end of the lockdown periods in Germany. These results indicate that the concentration of these species at Hohenpeissenberg were not significantly affected by the lockdown in Germany.



**Figure 8:** Daily concentrations of selected NMHC as observed (blue) and modelled by AirGAM (red) at Hohenpeissenberg in 2020. The start and end of lockdown periods in Germany is indicated by dashed vertical lines.



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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), Tovo Truuts (EERC), Jitka Privoznikova (CHMI), James Dernie (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  
2020 listed from north to south**



