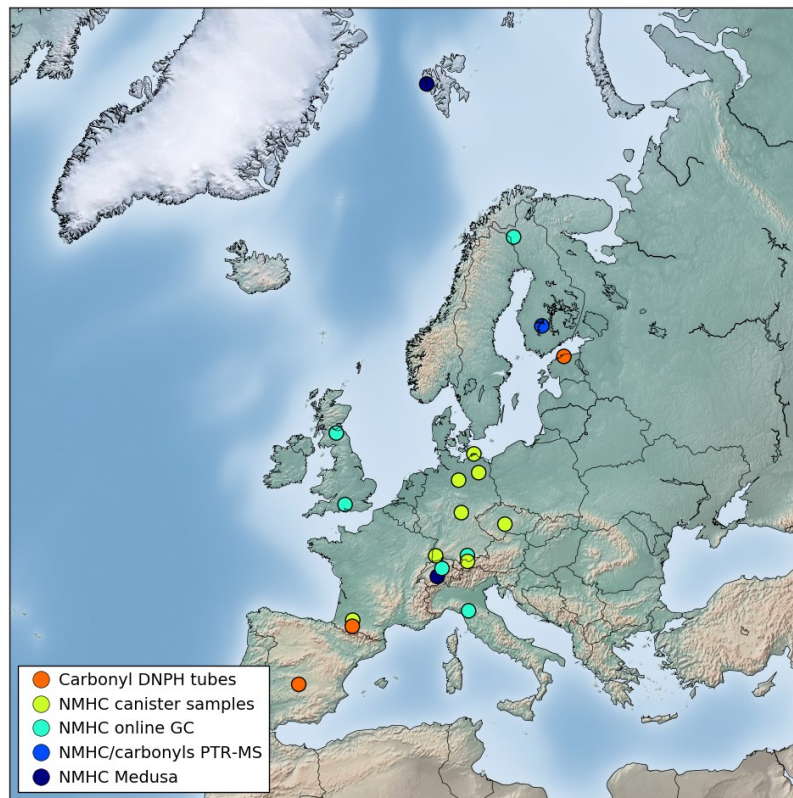


## VOC measurements 2019

Sverre Solberg, Anja Claude, Stefan Reimann and Stéphane Sauvage





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

**VOC measurements 2019**

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## Summary

This report presents VOC (volatile organic compound) measurements carried out during 2019 at EMEP monitoring sites. In total, 19 sites reported VOC-data from EMEP VOC sites this year. Some of the data-sets 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 2019 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 2000-2019 period at five sites by three independent statistical methods. All three methods gave comparable estimates of the trends, although the Mann-Kendall method based on annual data (compared to daily data for the other two methods) found fewer significant trends.

These estimates indicate marked differences in the long-term trends for the individual species. Small or non-significant trends were found for ethane during 2000-2019. Propane also showed fairly small reductions. On the other hand, components linked to road traffic (ethene, ethyne and benzene) showed the strongest drop in mean concentrations, up to 60-80% at some stations.

# VOC measurements 2019

## 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, 2013 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.

In the current EMEP Monitoring Strategy for 2010-2019 (ECE/EB.AIR/GE.1/ 2009/15), hydrocarbons and carbonyls have not been specified to be measured, but it is clearly stated that it is necessary to harmonize the EMEP Monitoring Strategy with the WMO GAW programme.

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 2019

### 2.1 The station network

The locations of the EMEP monitoring sites for VOC in 2019 are shown in Figure 1 and an overview of the measurement programme and the responsible laboratories is given in Table 2. In total, 19 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 except Lahemaa in Estonia, whereas OVOC are measured at fewer sites.

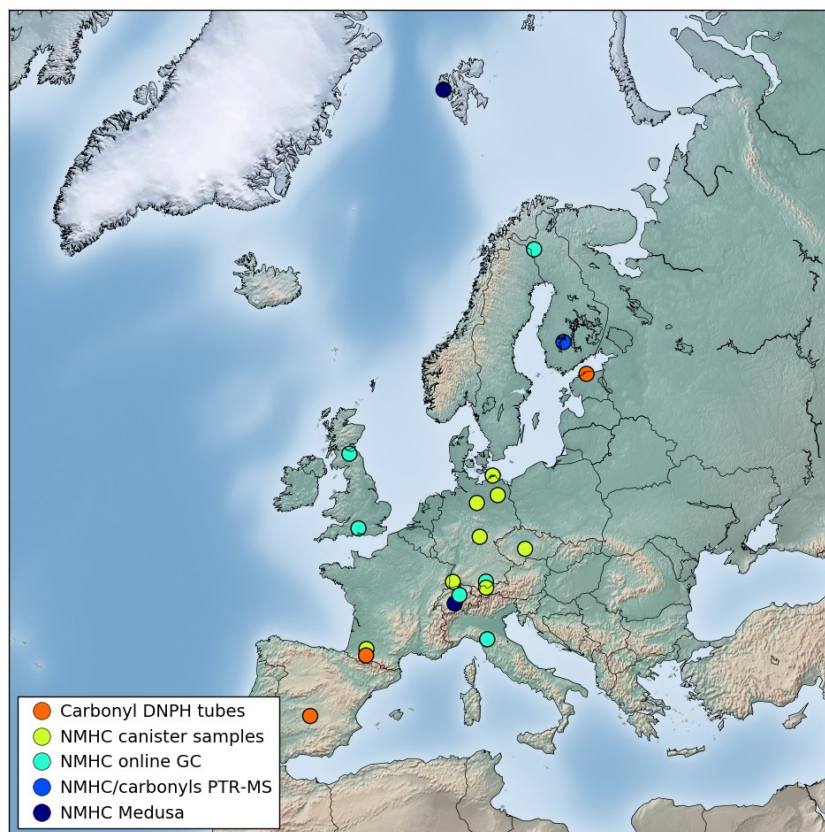


Figure 1: Monitoring sites for VOC in 2019.

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, Spain and Estonia. 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 ongoing 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 N and NE, 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 2019 as in the two 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.

**Table 2:** VOC monitoring at EMEP sites in 2019. 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	
Lahemaa	EE0009	-	EERC	Reg.	DNPH tubes	n	Very few valid data
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
Jungfraujoch	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  
 EERC = Estonian Environmental Research Centre  
 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

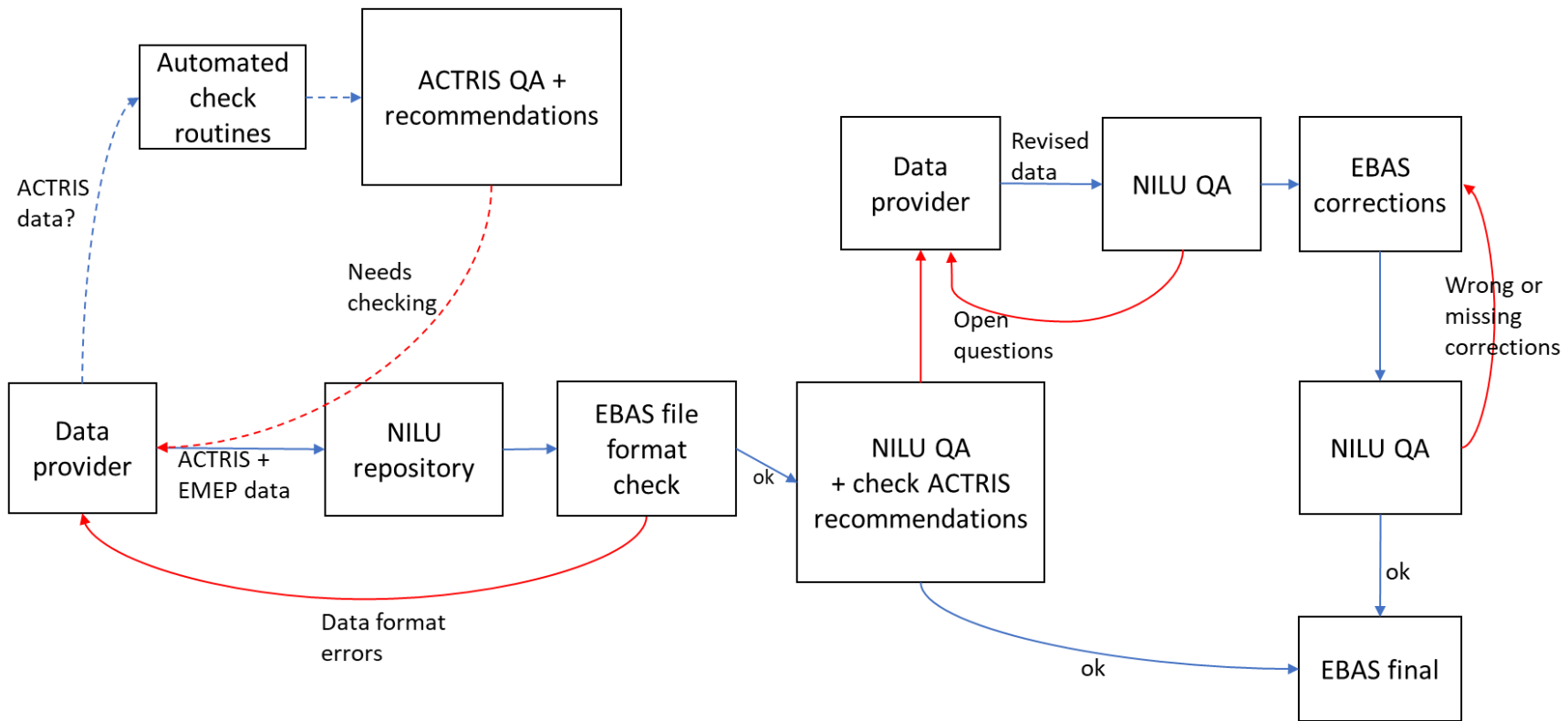


Figure 2: Flow diagram for the VOC data submitted within ACTRIS/EMEP.



### 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, a side-by-side intercomparison 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.

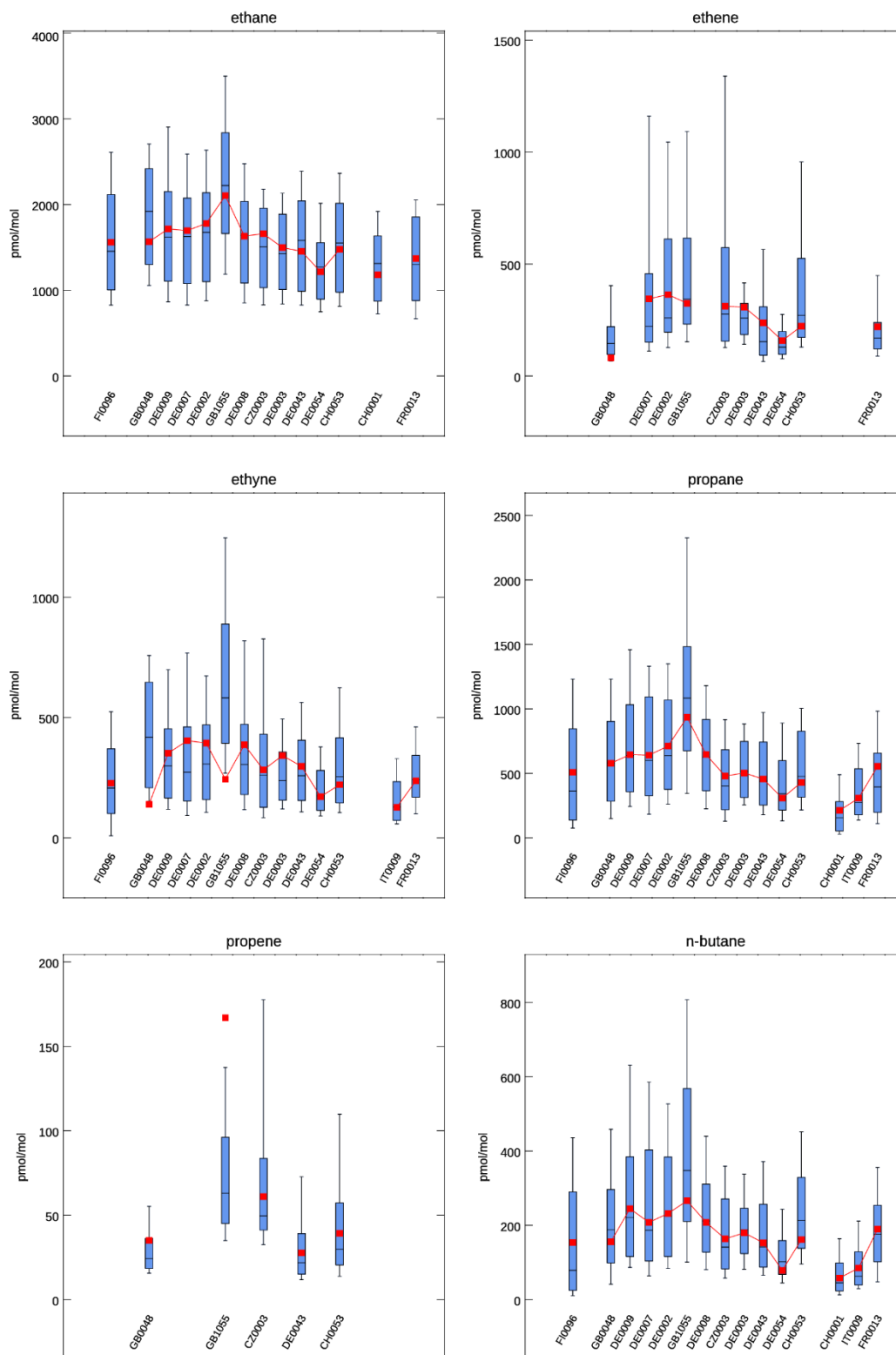
In addition to the intercomparison for NMHC discussed above, a side-by-side intercomparison for oxygenated VOC (OVOC) was carried out within ACTRIS at Hohenpeissenberg, with synthetic test mixtures and ambient air. The results of this exercise are, however, not yet published.

### **3. VOC concentrations in 2019**

#### **3.1 General levels**

Time series of the diurnal means of all compounds at all stations during 2019 are given in the Appendix. Figure 3 shows the spread of data values for each station and NMHC species in 2019 in box and whisker plots, and the annual median values based on the previous 10 years of data (2009-2018) 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 2019 concentration levels relative to the previous 10 years climatology as well as the spread in 2019 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 2019 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 2009-2018 period that presumably are not real. For other species, the differences between the 2019 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 2019. 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 (2009-2018).

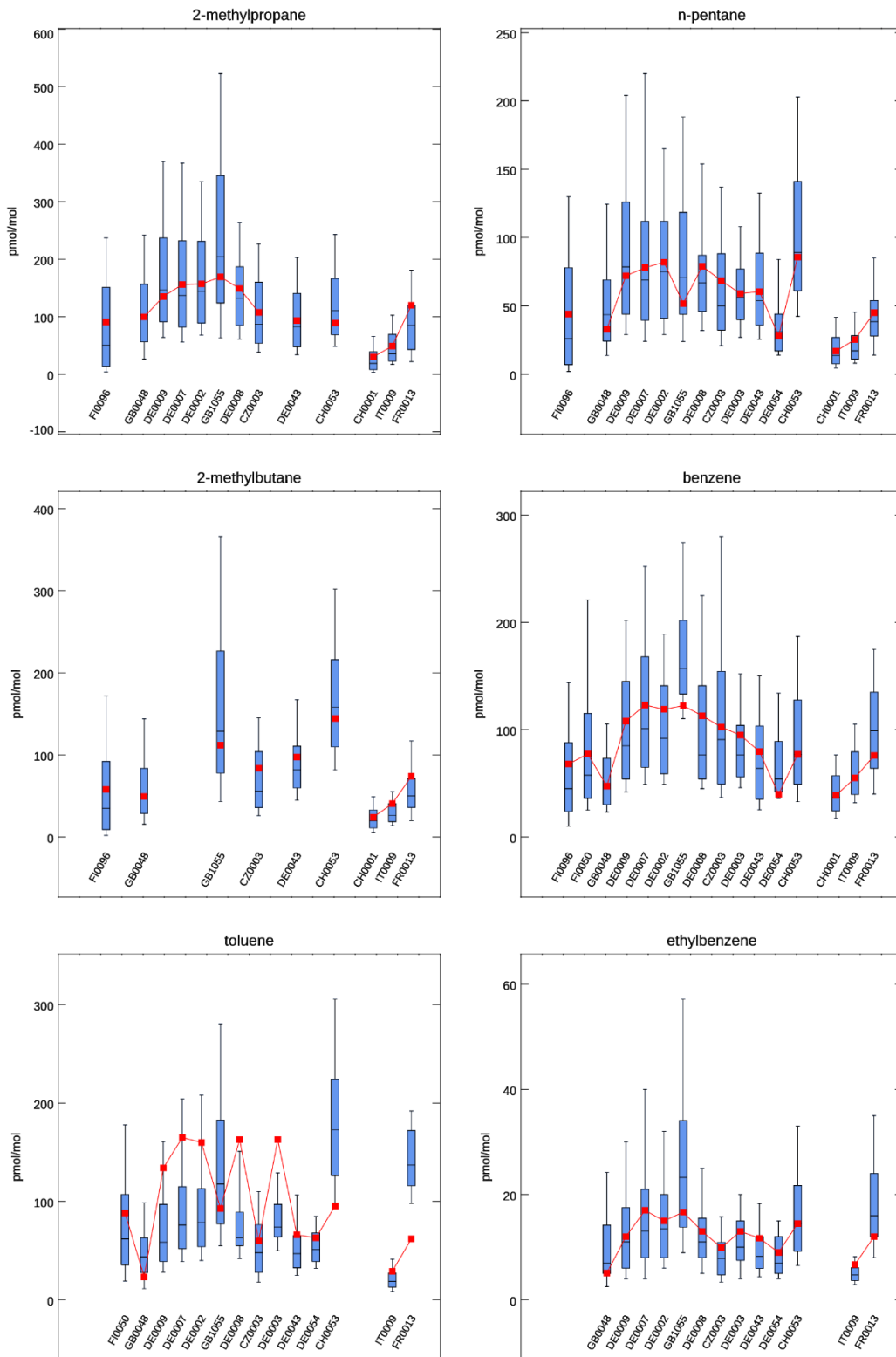


Figure 3 (cont.)

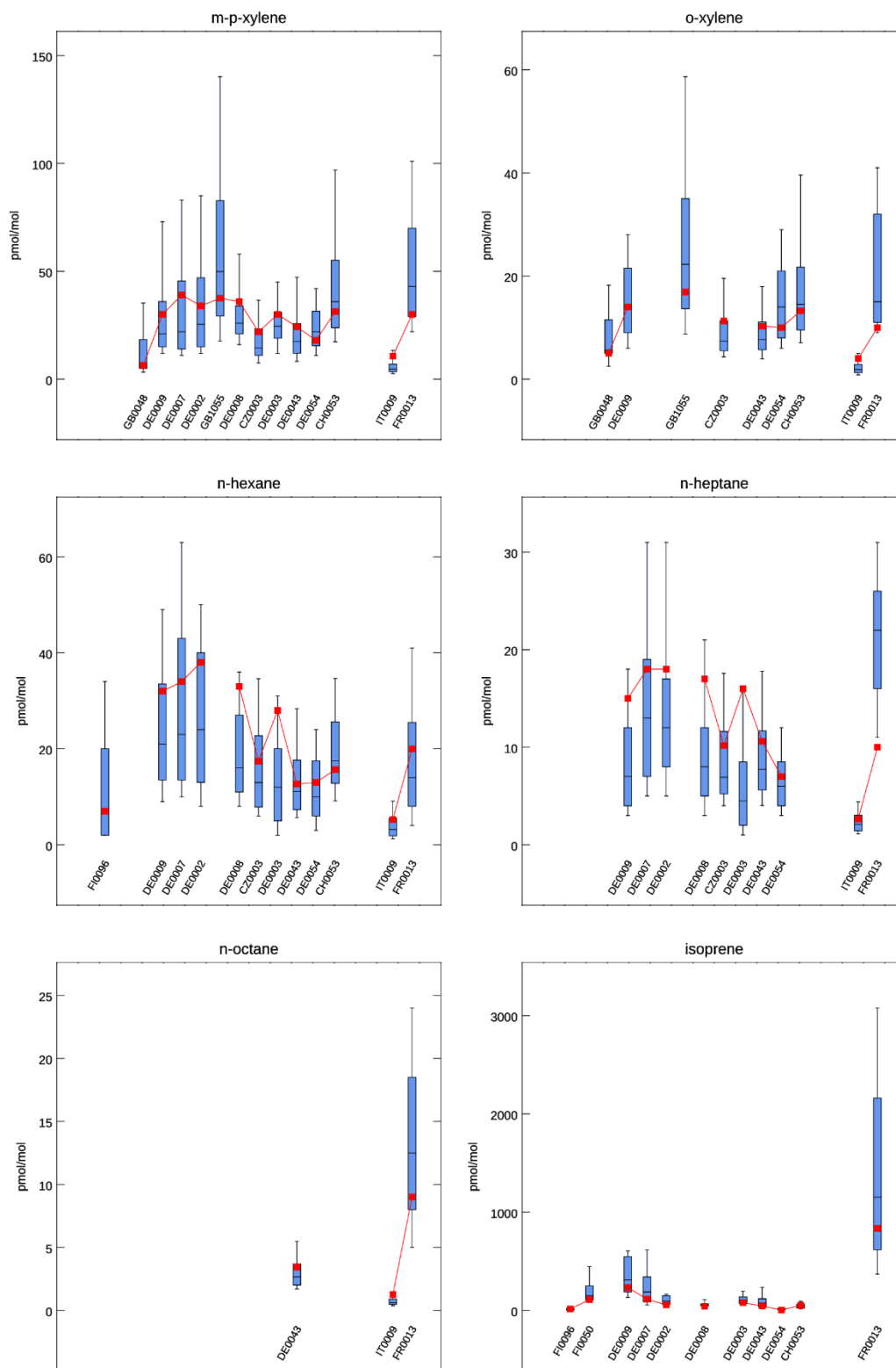
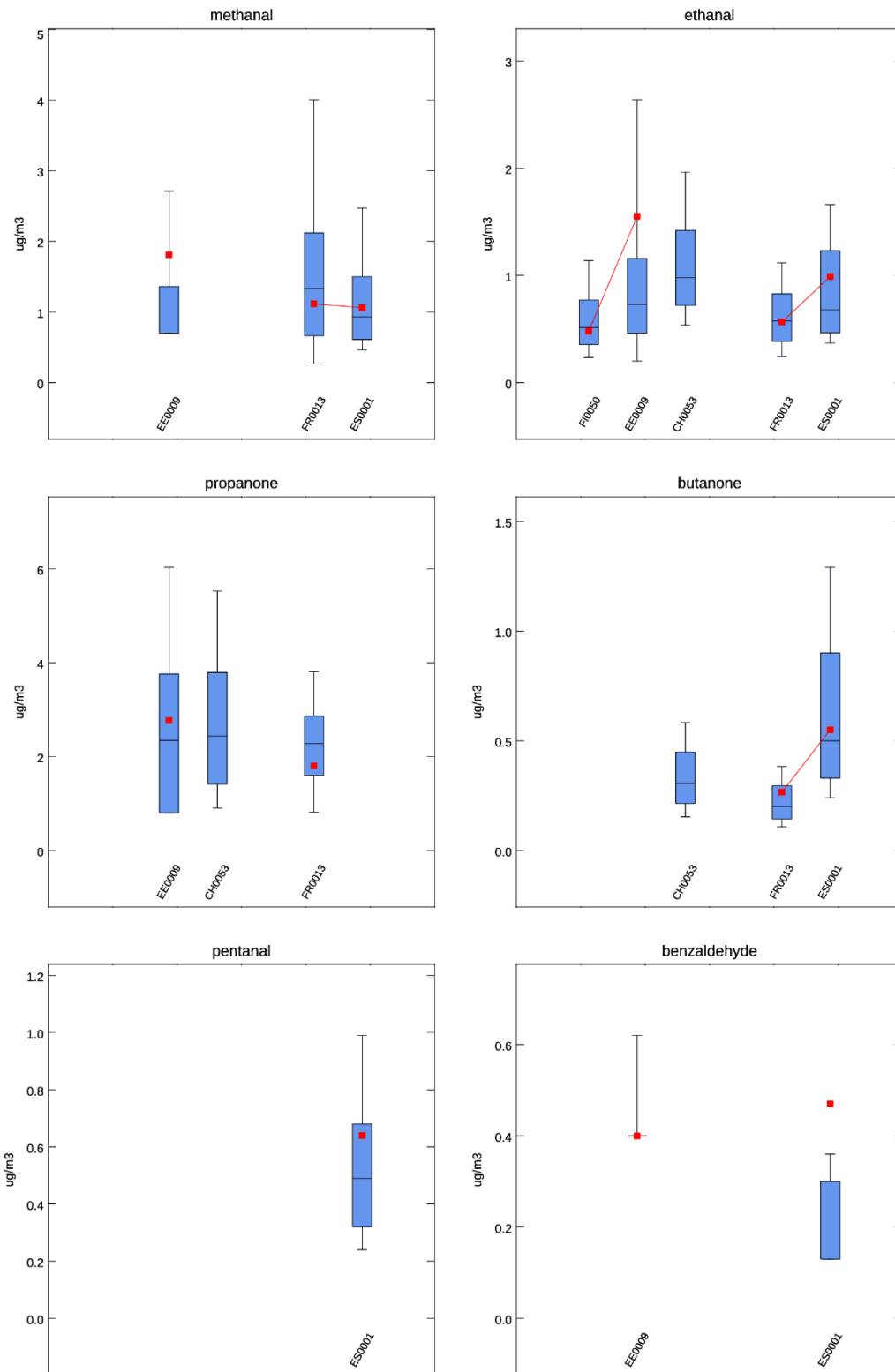


Figure 3 (cont.). Note that for isoprene only data for June-August (whole day) were used.



**Figure 4:** Box- and whisker-diagrams for carbonyls based on all measurements in 2019. 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 (2009-2018).

### 3.2 Regional distribution of VOC

Figure 5 shows maps with the stations' annual median concentrations of light hydrocarbons in 2019. 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. Particularly poor data coverage was seen at the site in Estonia (Lahemaa) and thus the annual medians calculated in Figure 6 were based on just a very few values.

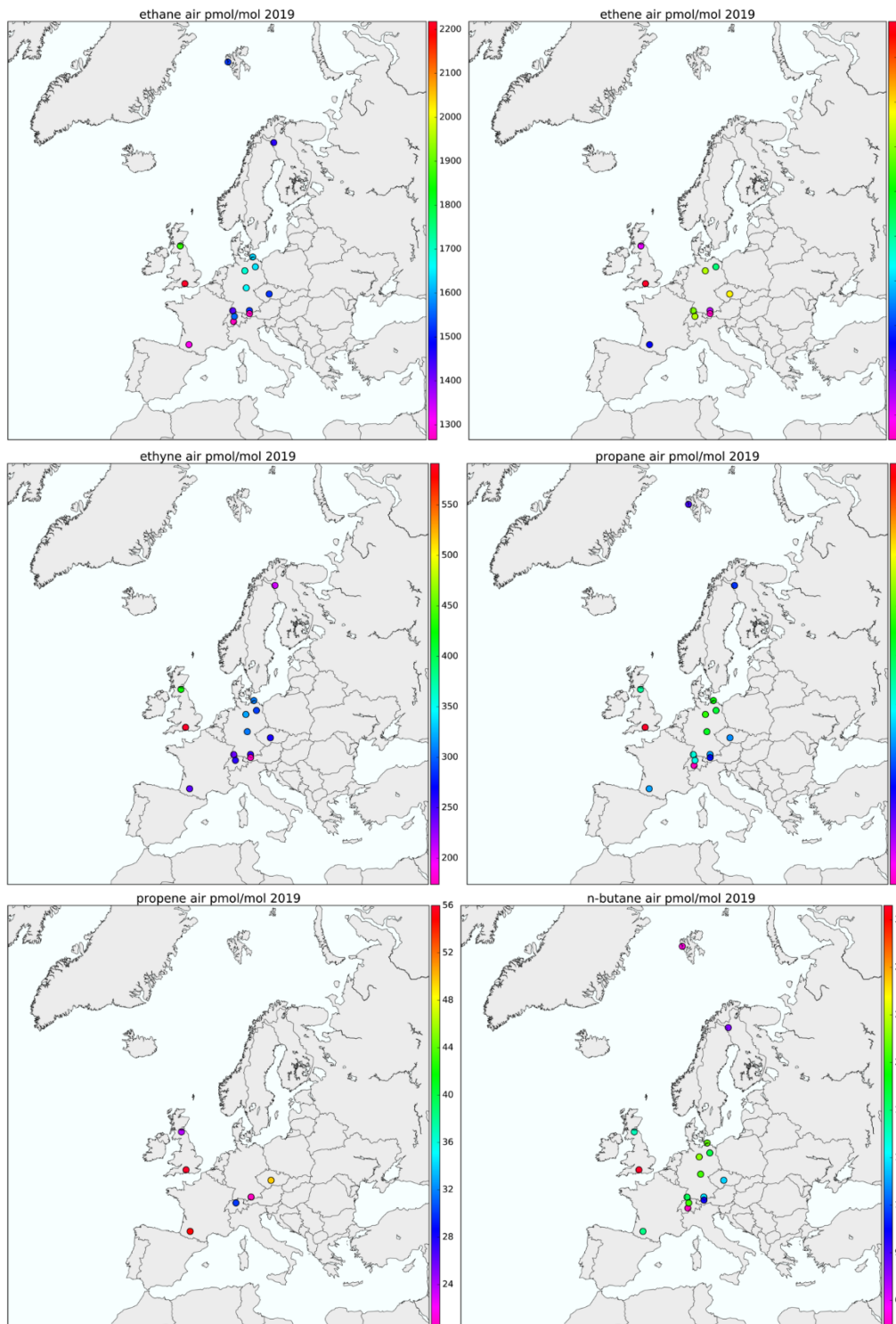


Figure 5: Annual median concentration of NMHCs in 2019. Unit: pmol/mol.



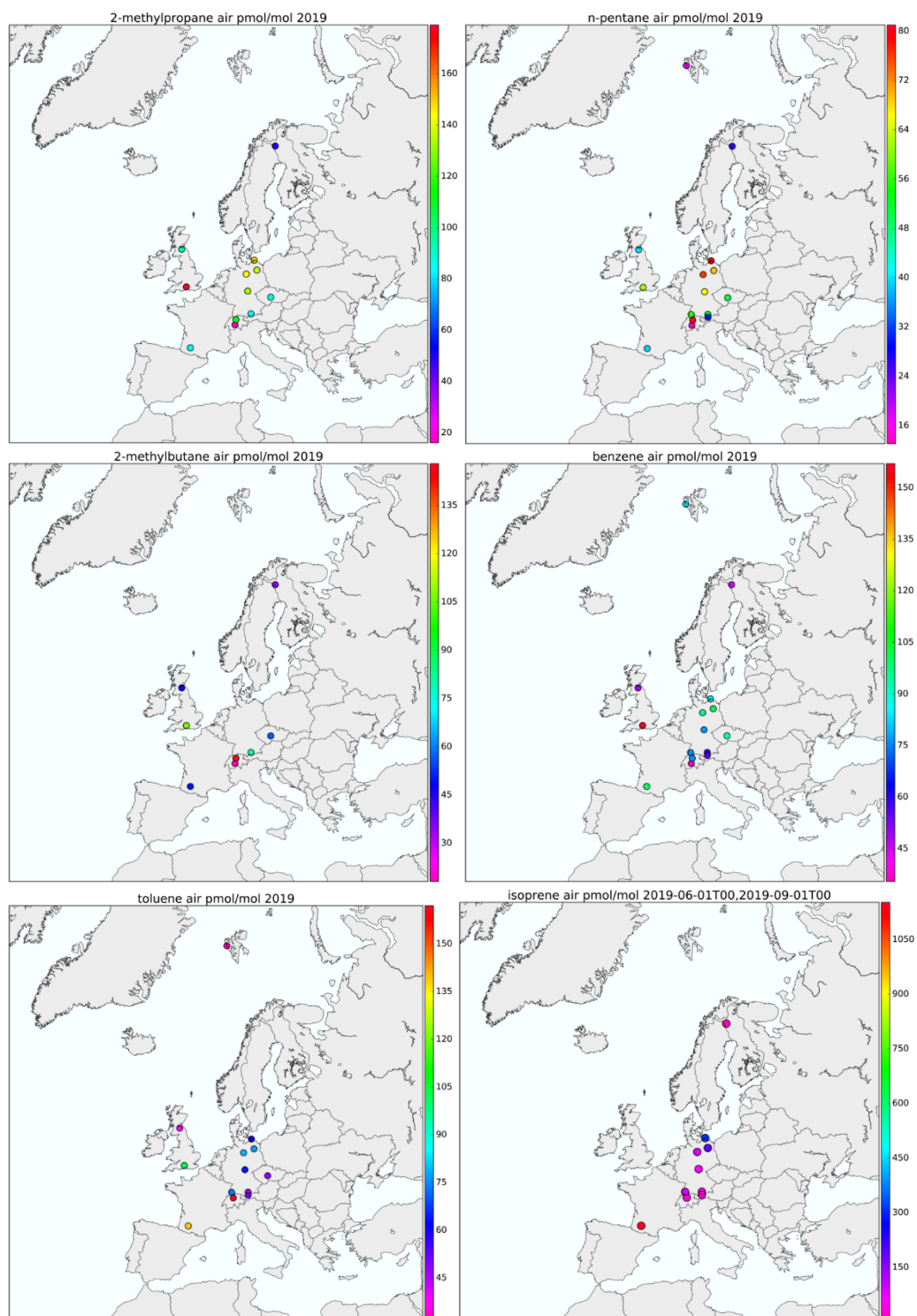


Figure 5 (contd.). Note that for isoprene the summer median (Jun-Aug) is shown.

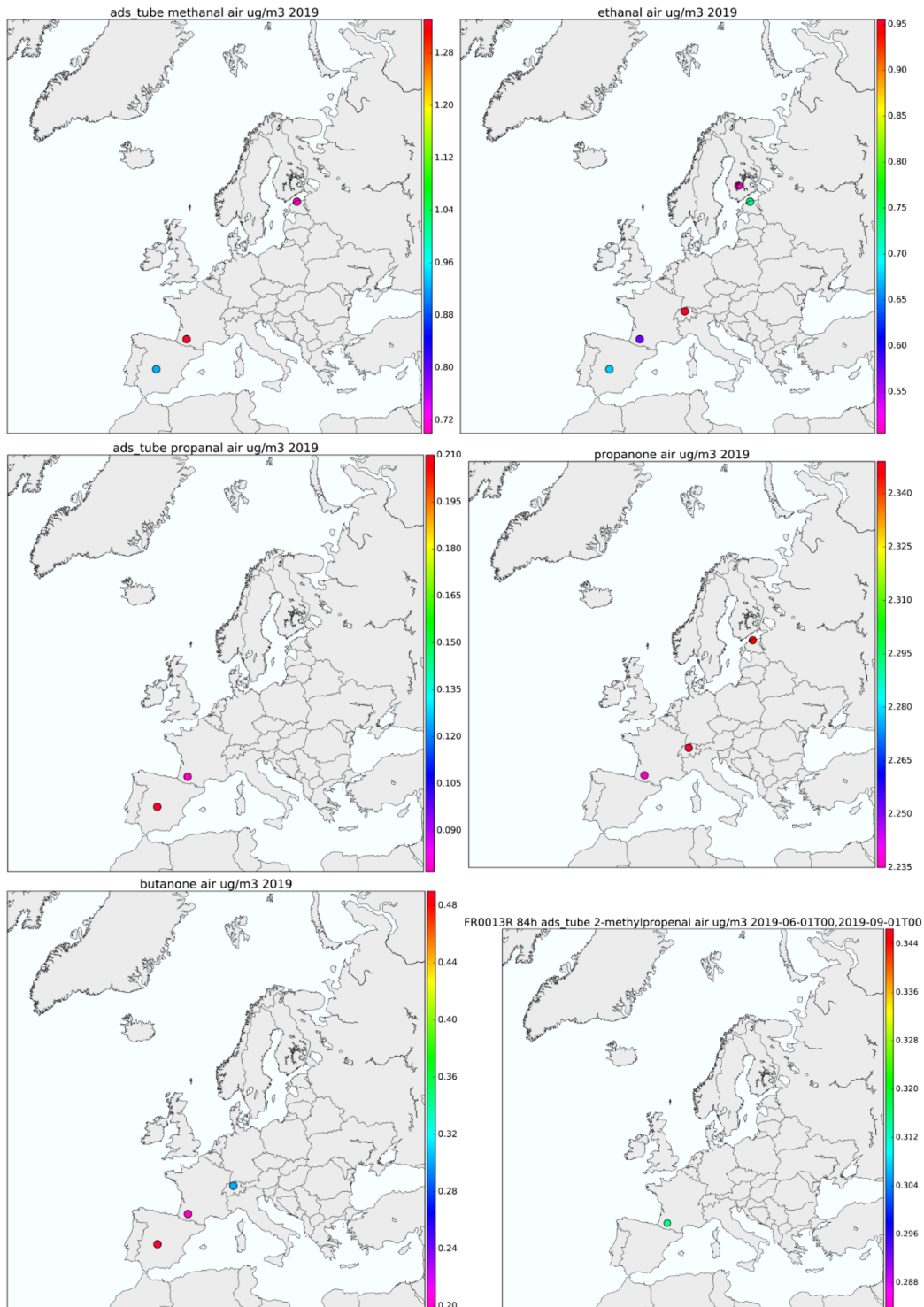


Figure 6: Annual median concentration of carbonyls in 2019. Note that for 2-methylpropanal the summer median (Jun-Aug) is shown. Unit:  $\mu\text{g}/\text{m}^3$ .



#### 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 however, substantial differences in the emission trends between countries and regions. For the area defined as “EMEP-West” there is an overall reduction in VOC emissions of the order of 40 % since 2000 (Fagerli et al., 2019) and for larger countries as Germany, France, UK, Italy, Spain and Poland the reductions are 35%, 63%, 51%, 42%, 34% and 6%, respectively. For the area defined as “EMEP-East” the emission data including so-called gap-filling indicate an increase of more than 50 % from 2000 to 2017. As stated in the EMEP Status report (Fagerli et al., 2019), the emission estimates for EMEP-East are 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 present 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 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, however, 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 though. Interannual variations in atmospheric transport patterns, vertical mixing, photochemical oxidation as well as spatial differences in emission reductions complicates the analyses.

Furthermore, various methods used for trend analyses in terms of mathematical method, selection of time periods and stations etc. could give different results. In the following we have looked at daily measurements of selected VOCs at five EMEP sites with long term data over the period 2000-2019. Based on these data, best-fit seasonal trend curves were calculated by a non-linear least squares fit method by use of a standard statistical package (Markwardt, 2009) to the following equation:

Eq. 1:

$$c(t) = [a_0 + a_1(\sin(2\pi(t - a_2)))] \exp[a_3(t - t_0)]$$

where

$$\begin{aligned} c(t) &= \text{value at time } t \text{ measured in years} \\ t_0 &= 2000 \end{aligned}$$

and the coefficients  $a_0$ ,  $a_1$ ,  $a_2$ ,  $a_3$  were determined by the non-linear least squares fit using the iterative algorithm by Markwardt, 2009. It turned out that Eq. 1 converged for all our cases with less than 10 iterations, even when using very strict tolerance criteria for the iterations. In addition to best fit values for the coefficients  $a_0$ ,  $a_1$ ,  $a_2$ ,  $a_3$ , the algorithm also provided confidence intervals for each of the coefficients.

Eq. 1 represents a simple seasonal cycle with a mean level  $a_0$ , amplitude  $a_1$  and seasonal phase displacement  $a_2$  that change exponentially over time with the  $a_3$  coefficient defining the rate of either a growth ( $a_3 > 0$ ), a decline ( $a_3 < 0$ ) or no trend ( $a_3 = 0$ ).

To ensure positive solutions, the least squares fit was applied to log-transformed data, i.e. in Eq. 1 we defined  $c(t) = \log(cc(t))$ , where  $cc(t)$  is the actual daily observed mixing ratio in  $\text{pmol mol}^{-1}$ . This also implies a weighting of the data, increasing the weight of the low-level concentrations relative to the high-level ones since the data follow a right tailed distribution. Without such a weighting, the least squares fit would be strongly determined by the highest concentration values that are mostly observed in winter.

For comparison, we included a best fit of the daily data (not log-transformed) to a linear polynomial function as presented by Simmonds et al (2006) for AGAGE trace gases:

Eq. 2:

$$\begin{aligned} f(t) = & a + b \cdot N \cdot P_1\left(\frac{t}{N} - 1\right) + \frac{1}{3} \cdot d \cdot N^2 \cdot P_2\left(\frac{t}{N} - 1\right) \\ & + c_1 \cdot \cos(2\pi t) + s_1 \sin(2\pi t) + c_2 \cos(4\pi t) + s_2 \sin(4\pi t) \end{aligned}$$

where  $P_1$  and  $P_2$  are the Legendre polynomials of order 1 and 2,  $t$  is time measured in years ( $t = 0$  for year 2000) and  $2N$  is the total number of years. The coefficient  $a$  defines the average mole fraction, while coefficients  $b$  and  $d$  define the linear trend and the acceleration in trend, respectively. The coefficients  $c$  and  $s$  define the annual cycle in concentration. We note that the polynomial function in Eq. 2 could lead to negative values for species that are observed at low concentration levels, and that is indeed seen in the results below.

Figure 7 - Figure 13 shows the daily concentrations (blue marks) together with the curves fitted to Eq. 1 in red and to Eq. 2 in black for six selected sites: Pallas, Kosetice, Hohenpeissenberg, Rigi/Beromünster, and Peyrusse Vielle. The trend part of the AGAGE function, i.e. the linear and acceleration terms without the seasonal components are marked as a thick green line in the plots. At Beromünster the VOC monitoring started in 2018 and data from Rigi was used for the earlier years. The Beromünster/Rigi data therefore don't constitute one consistent time series since the station locations differ by around 40 km, but assuming that both are background rural stations, we expect small differences in the overall levels which was also seen when comparing the data. For toluene (not included in the trend calculations) there were larger differences in the concentration levels at the two sites, though.

For the time series where a statistically significant trend was found by *Eq. 1*, the percentage change (as given by *Eq. 1*) from 2000 to 2019 using 2000 as a reference year is given in the title. We assumed significant trends if  $|a_3| > 2\sigma$ , where  $\sigma$  is the confidence interval as mentioned above. The change in concentrations during the period as calculated by the trend part (green curve) of AGAGE equation (*Eq. 2*) is given in the title for comparison.

In addition to these two methods that both were based on a functional fit to the daily measured values, the Mann-Kendall/Theil-Sen's slope methodology (MK) was applied to the annual median concentrations (Bronaugh and Werner, 2019; Sen, 1968). This method implies that the Mann-Kendall test is first applied to the data to see if there is a statistical significant trend ( $p=0.05$ ) and if this is found, the actual trend is calculated by the Theil-Sen's slope.

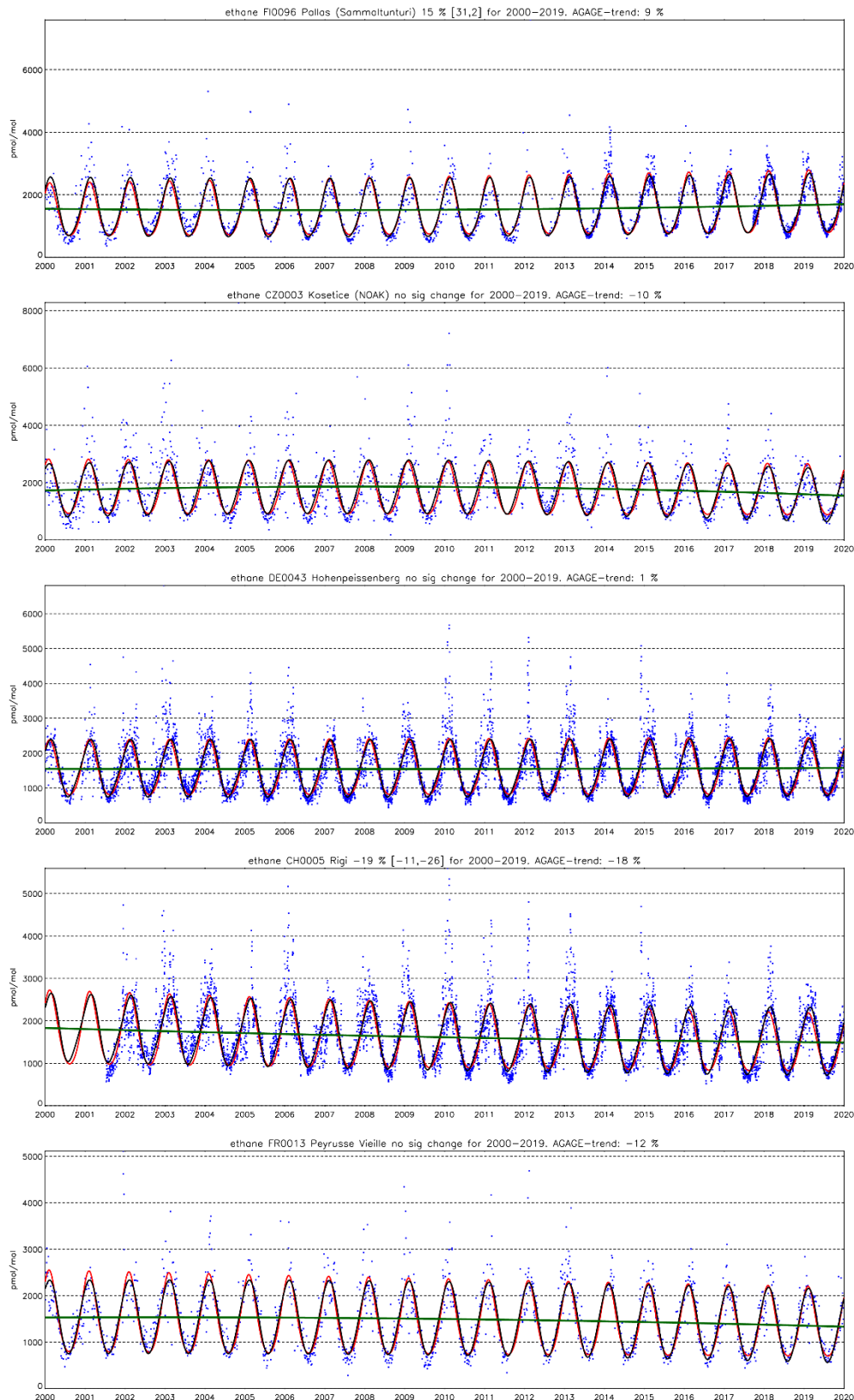
Table 3 lists the percentage reductions of these species from 2000 to 2019 as estimated by *Eq. 1*, *Eq. 2*, and the MK method, respectively. We calculated the total reductions over the 2000-2019 period based on the annual mean values in 2000 and 2019 as calculated directly from *Eq. 1* and from *Eq. 2*, respectively. For *Eq. 1* the reductions were not calculated if  $|a_3| < 2\sigma$ , and similarly for *Eq. 2* ( $|b| < 2\sigma$ ).

The results in Figure 7 - Figure 13 and in Table 3 indicate marked differences in the long-term trends between the individual species. The smallest percentage changes, or most frequent non-significant trends, are seen for ethane and propane. The largest reductions are found for ethene, ethyne and benzene (depending on site). Furthermore, fairly similar reductions are found with *Eq. 1* and *Eq. 2* overall although there are differences for certain sites/species. In general, the polynomial fit (*Eq. 2*) gave somewhat smaller confidence intervals than the non-linear fit (*Eq. 1*) and thus more significant values. The results from the MK method also agree fairly well with the two other methods although the number of statistically significant trends are found to be less with the MK approach.

These results indicate that the European background levels of light hydrocarbons have experienced a substantial reduction since 2000 amounting up to 60-80% in the annual means. The species with the strongest reductions are all linked to emissions from combustion and this likely reflects strong reductions in emissions from road traffic in Europe.

Ethane on the other hand shows either no significant trend or only small changes since 2000, and fairly small changes are found for propane as well. This indicates that emissions linked to the exploration and use of natural gas have not dropped significantly over this period. It should be said that these species also have a long chemical lifetime in the atmosphere, making them significantly dependent on emissions from other continents in the northern hemisphere. For n-butane we estimate a reduction of the order of 20-50% from 2000 to 2019, which is a number in between the number found for the natural gas tracers and the tracers of road traffic emissions.

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 however, not be done since the EMEP emission data are given for NMHC as a whole and not for individual substances. The fact that the strongest decline is seen in the more reactive species compared to no change in ethane and propane is important for the level of secondary pollutants as O<sub>3</sub> and PM. Since the potential for ozone (and PM) formation generally increases with chemical reactivity of the hydrocarbons, one would expect that the overall potential for formation of secondary pollutants will be even larger than the emission reduction of the sum of NMHC.



**Figure 7:** Daily mean ethane concentrations (blue) at six EMEP sites during 2000-2019 together with the estimated seasonal trend curve in red. Significant trends are given with confidence intervals in the header as percentage change from 2000 to 2019. The black curve shows the curve fit using the AGAGE polynomial function. Thick green line indicates the AGAGE trend term.



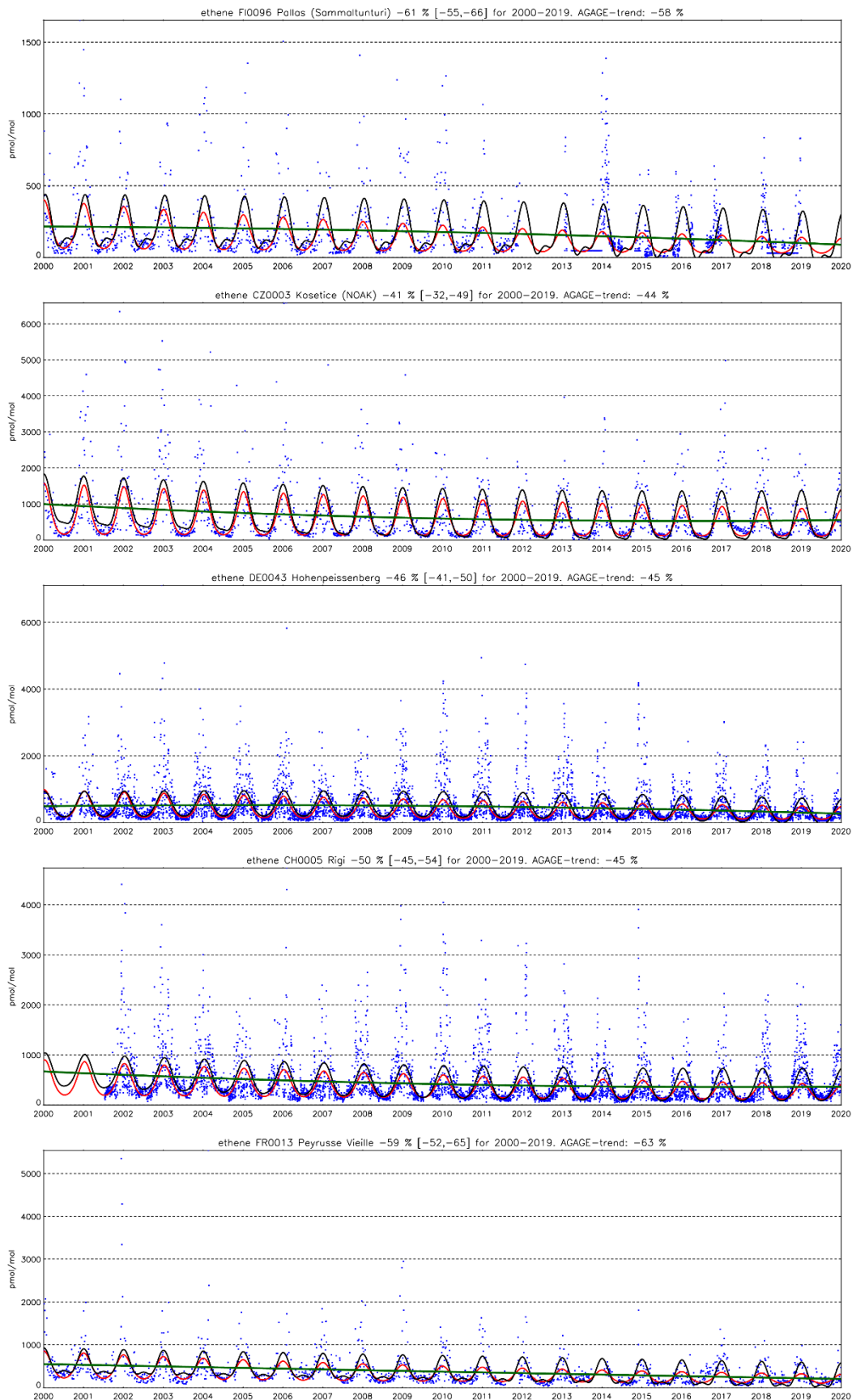


Figure 8: Same as Figure 7 for ethene.

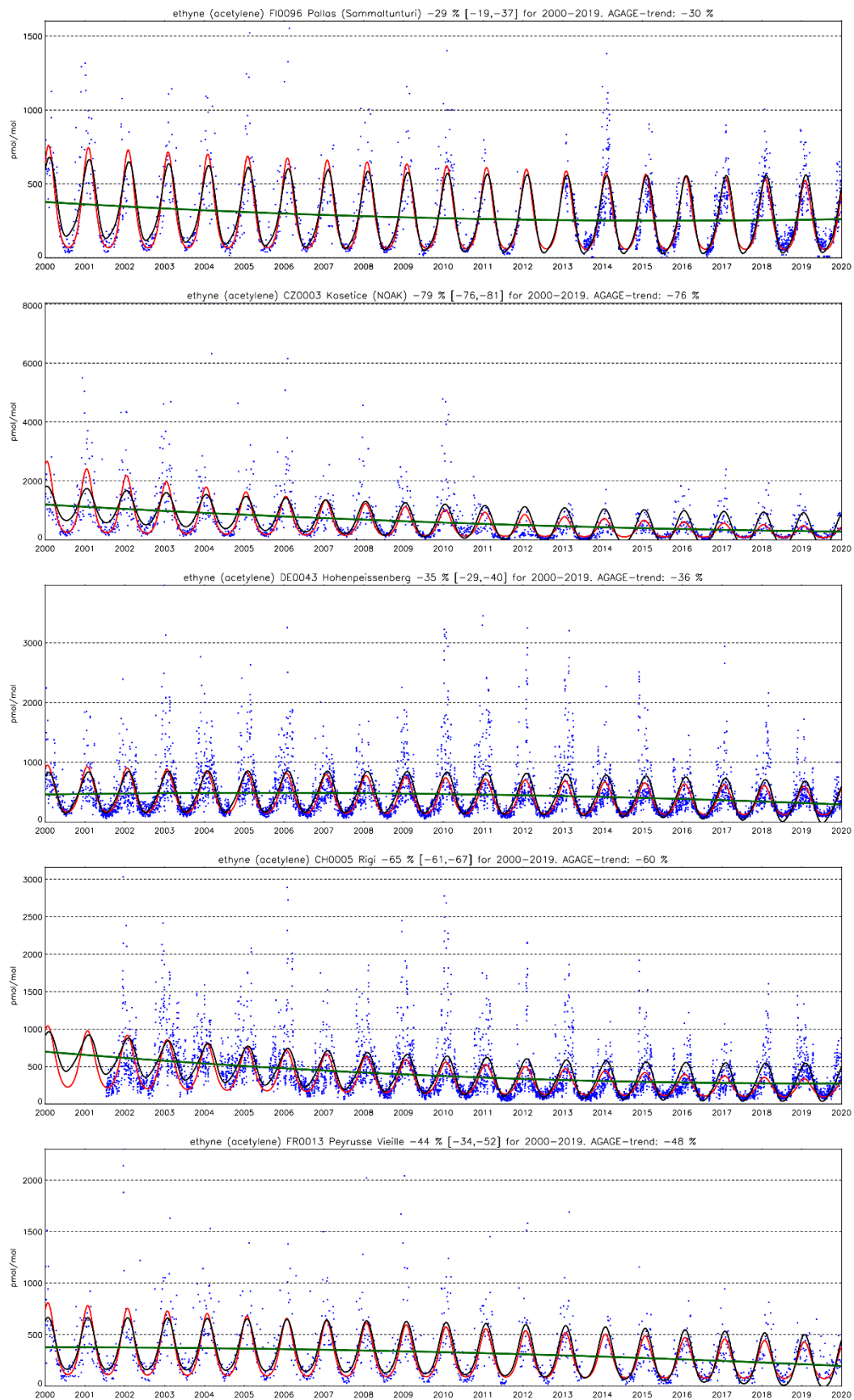


Figure 9: Same as Figure 7 for ethyne.

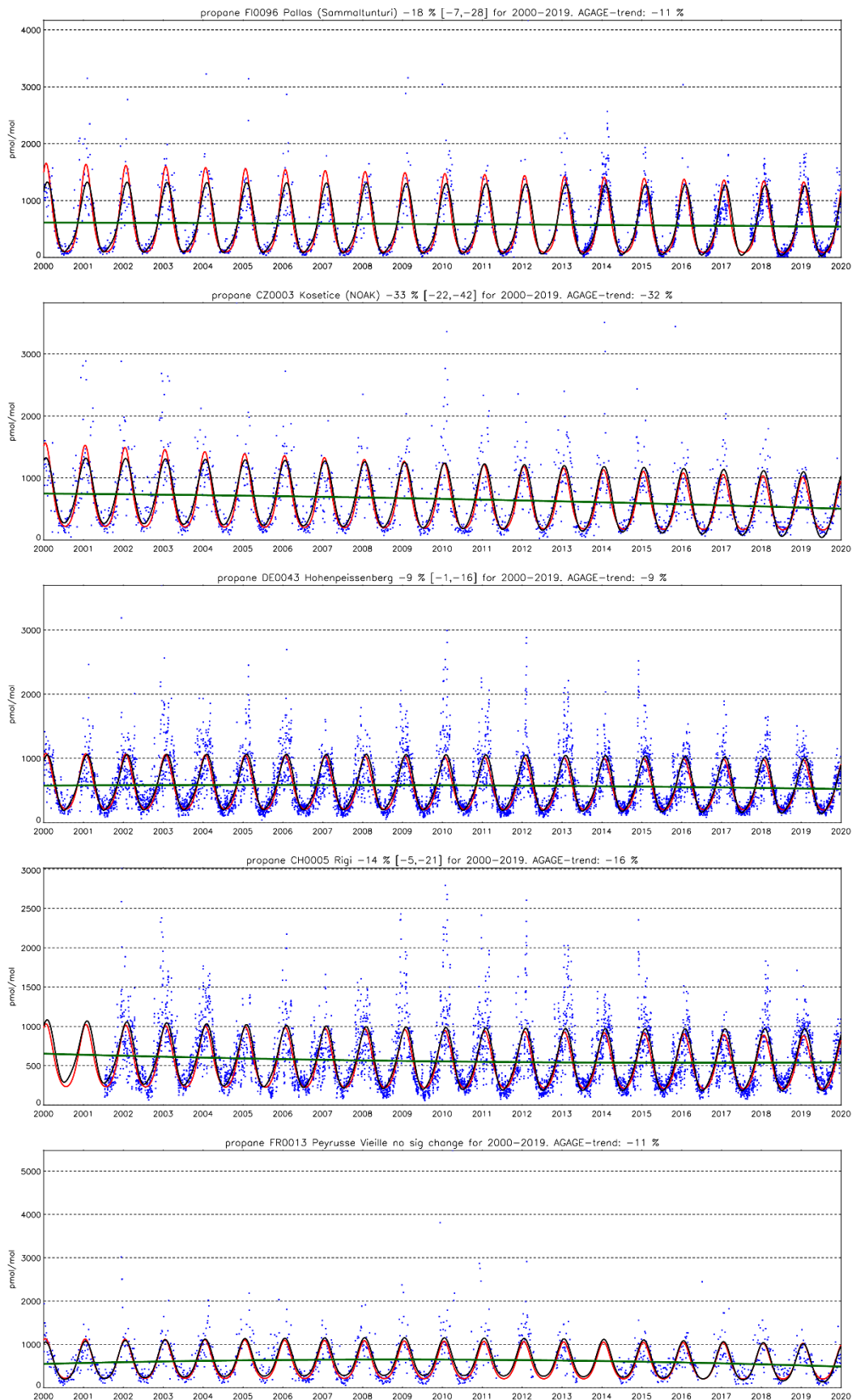


Figure 10: Same as Figure 7 for propane.

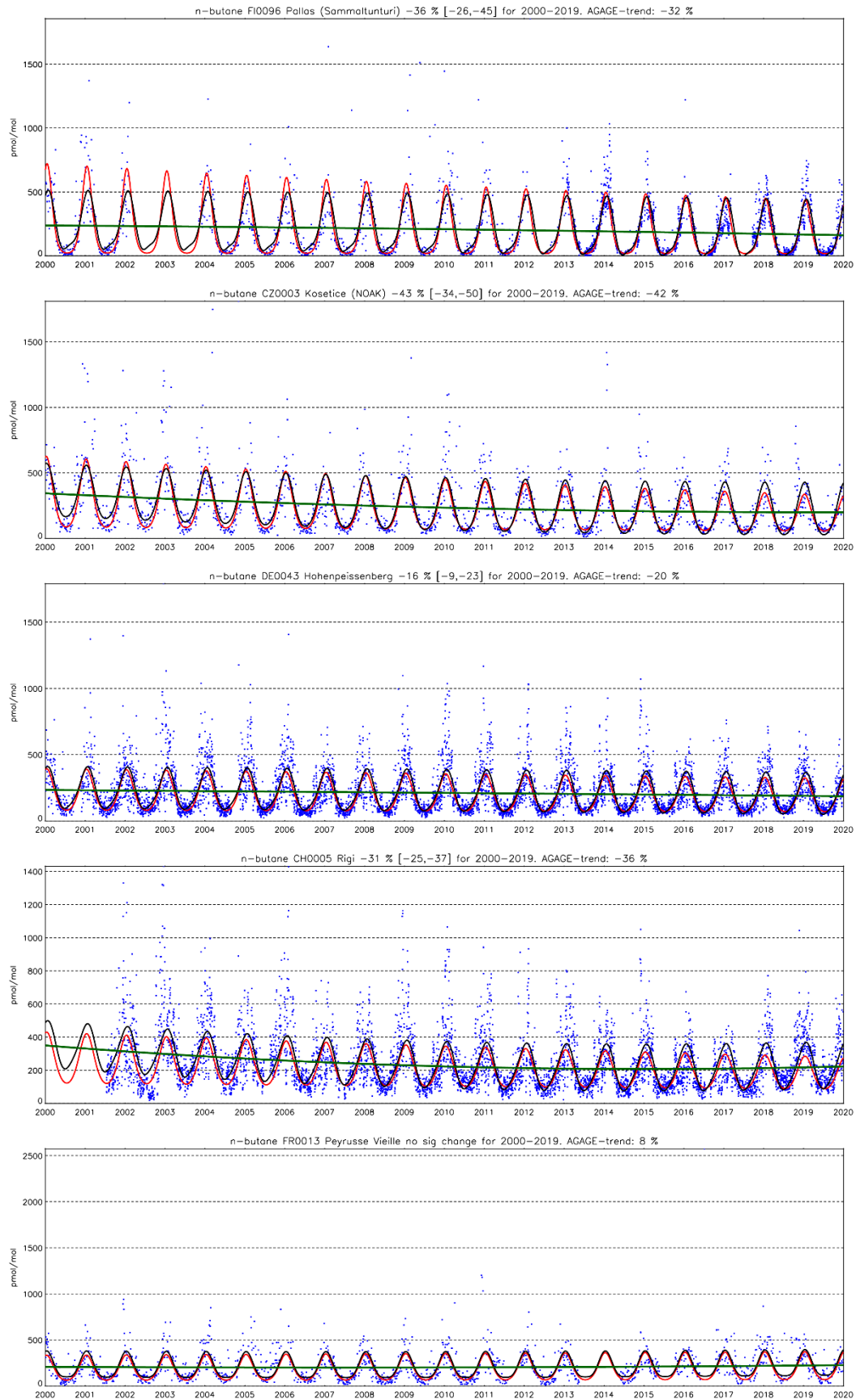


Figure 11: Same as Figure 7 for n-butane.

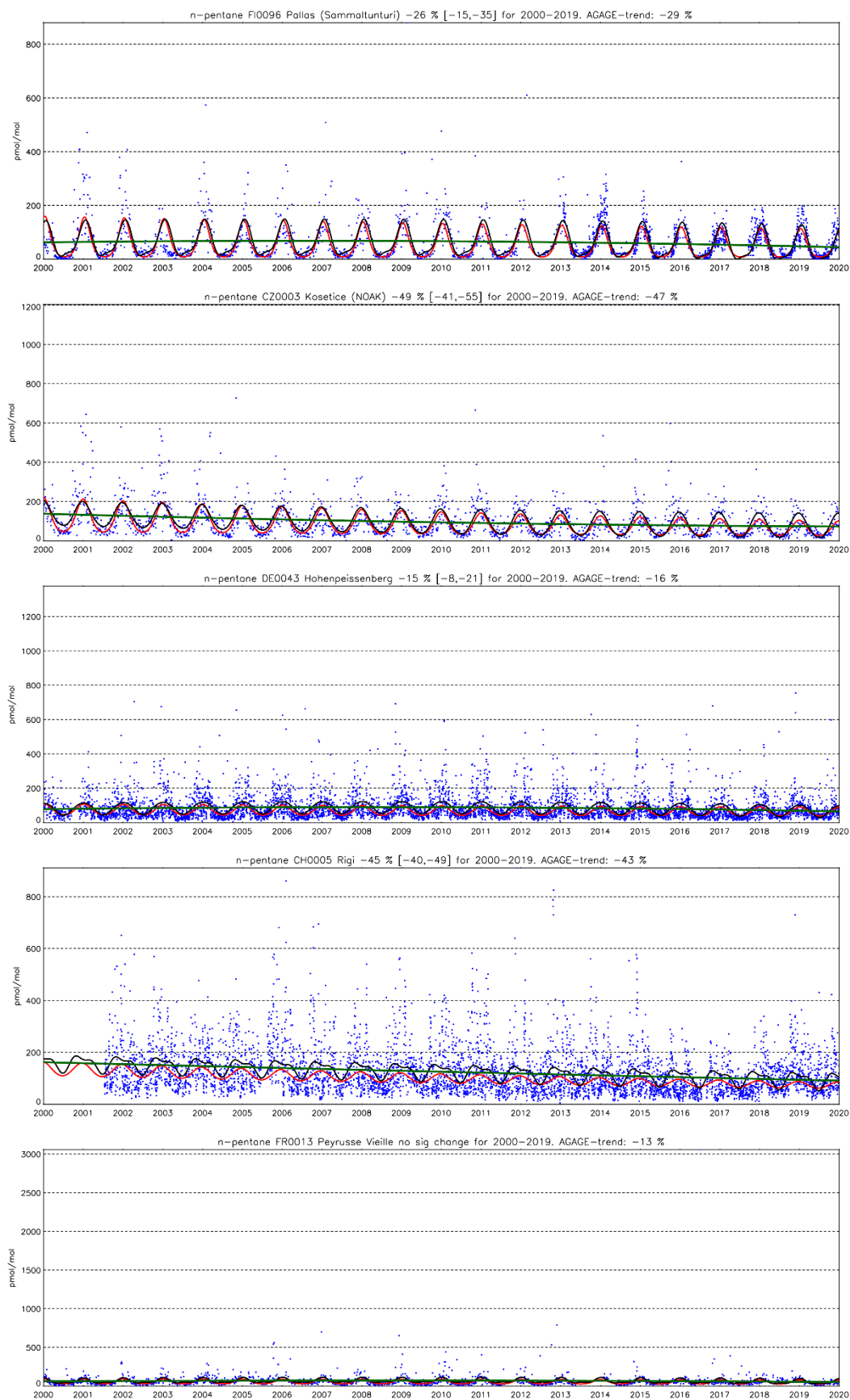


Figure 12: Same as Figure 7 for n-pentane.

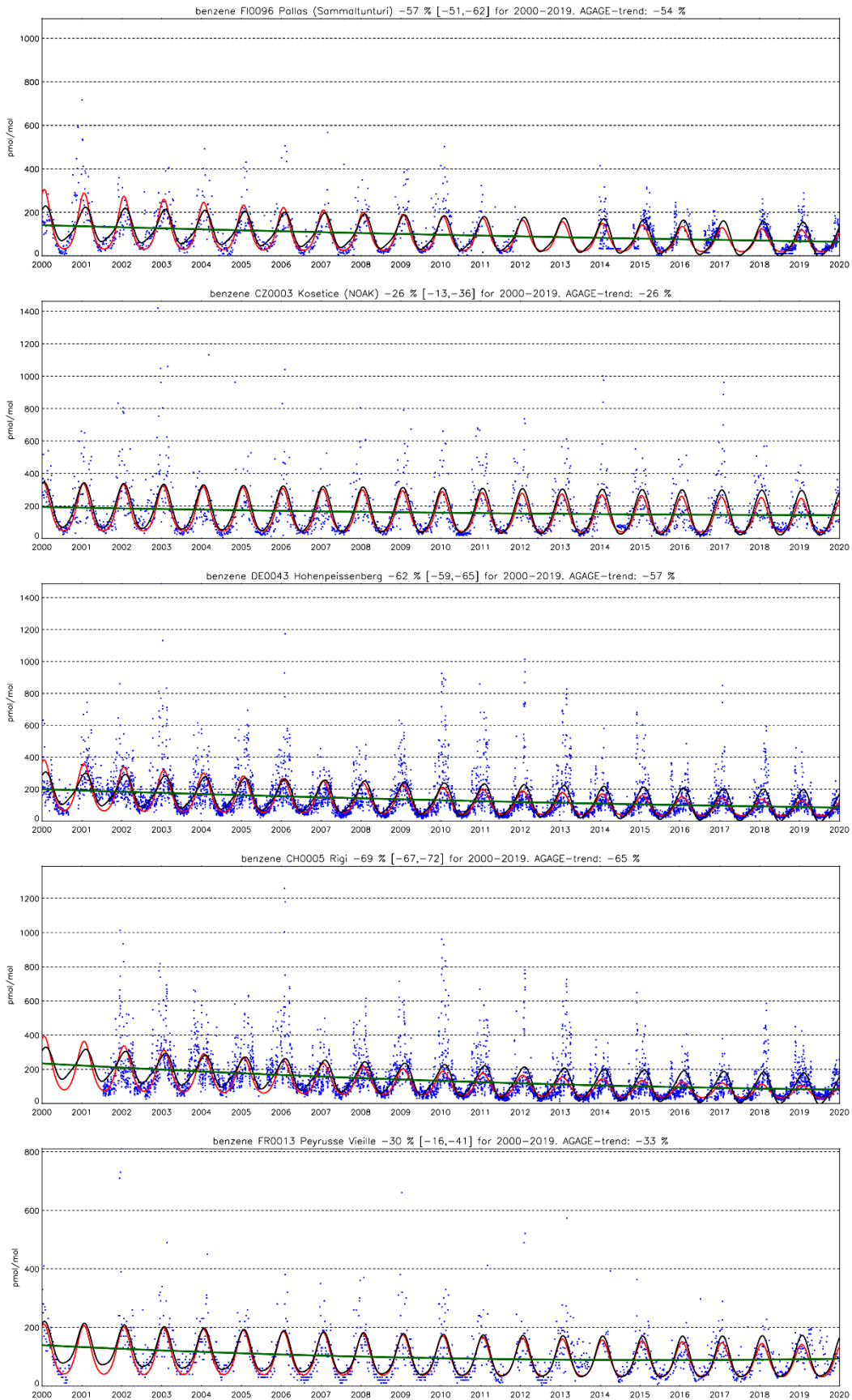


Figure 13: Same as Figure 7 for benzene.

Table 3: The percentage reduction in measured hydrocarbons over the period 2000-2019 relative to 2000 as the base year estimated from Eq 1 and Eq 2, respectively. The percentage reduction calculated by the Mann-Kendall/Theil-Sen's slope method is also included (MK). '-' implies that no significant trend was found. The stations are: Pallas (PAL), Kosetice (KOS), Hohenpeissenberg (HPB), Rigi/Beromünster (RIG), and Peyrusse Vieille (PEY).

	<b>PAL</b>			<b>KOS</b>			<b>HPB</b>			<b>RIG</b>			<b>PEY</b>		
	<b>Eq 1</b>	<b>Eq 2</b>	<b>MK</b>	<b>Eq 1</b>	<b>Eq 2</b>	<b>MK</b>	<b>Eq 1</b>	<b>Eq 2</b>	<b>MK</b>	<b>Eq 1</b>	<b>Eq 2</b>	<b>MK</b>	<b>Eq 1</b>	<b>Eq 2</b>	<b>MK</b>
Ethane	15	9	-	-	10	-	-	1	-	19	18	-	-	12	
Ethene	61	58	-	41	44	48	46	45	49	50	45	62	59	63	62
Ethyne	29	30	-	79	76	80	35	36	39	65	60	71	44	48	-
Propane	18	11	-	33	32	30	9	9	13	14	16	-	-	11	-
n-butane	36	32	-	43	42	43	16	20	22	31	36	42	-	+8	92
n-Pentane	26	29	-	49	47	50	15	16	18	45	43	51	-	13	-
Benzene	57	54	58	26	26	33	62	57	63	69	65	71	30	33	-

## 5. Acknowledgement

Data originators for individual datasets can be found as part of the metadata by visiting <http://ebas.nilu.no>. Special thanks to the extensive effort and contribution provided by all participants through the ACTRIS-2 project including long-lasting detailed discussions on individual data values.

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## **Appendix 1**

### **Time series of daily means of VOCs measured in 2019 listed from north to south**



