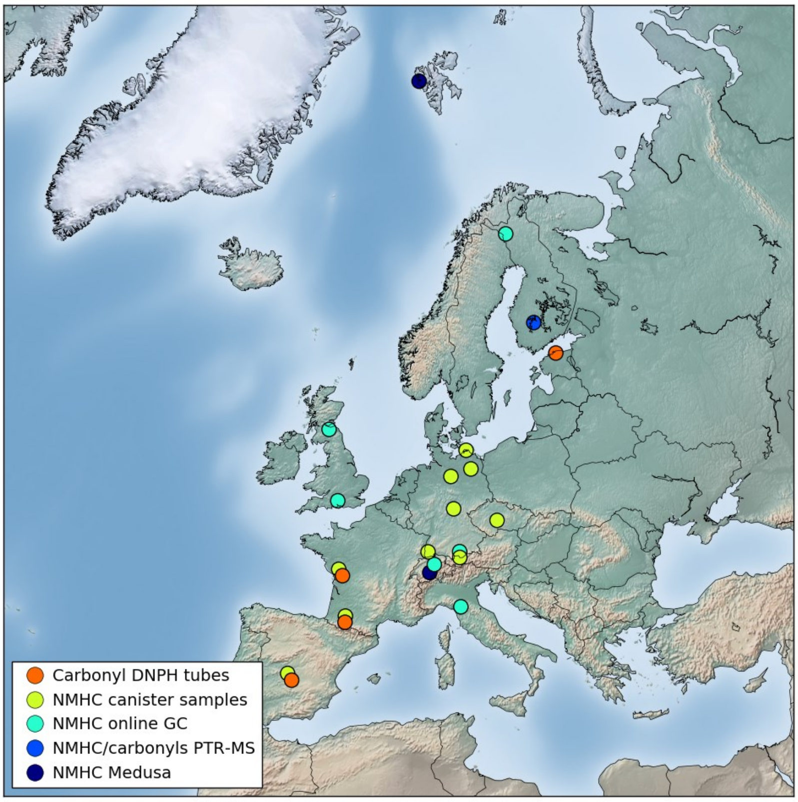
EMEP
Co-operative Programme for Monitoring and Evaluation
of the Long-Range Transmission of Air Pollutants in Europe

VOC measurements 2018

Sverre Solberg, Anja Claude, Stefan Reimann and Stéphane Sauvage



NILU
Norwegian Institute for Air Research
PO Box 100, NO-2027 Kjeller, Norway
Chemical Co-ordinator Centre of EMEP (CCC)

NILU	:	EMEP/CCC-Report 4/2020
REFERENCE	:	O-7726
DATE	:	SEPTEMBER 2020
ISBN	:	978-82-425-3015-8
ISSN	:	2464-3920

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

VOC measurements 2018

Sverre Solberg[1], Anja Claude[2], Stefan Reimann[3] and Stéphane Sauvage[4]

1) NILU – Norwegian Institute for Air Research, Kjeller, Norway
2) Deutscher Wetterdienst, Hohenpeissenberg, Germany
3) Swiss Federal Laboratories for Materials Science and Technology (Empa), Dübendorf, Switzerland
4) Institut Mines Telecom Lille Douai, Douai, France

NILU – Norwegian Institute for Air Research
PO Box 100, NO-2027 Kjeller, Norway

Contents

Summary

This report presents VOC (volatile organic compound) measurements carried out during 2018 at EMEP monitoring sites. In total, 20 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 NMHC (non-methane hydrocarbons) 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 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. For oxygenated VOCs (OVOCs), sampling in DNPH-tubes with subsequent lab-analyses is still the only method in use at EMEP sites.

Within the EU infrastructure project ACTRIS-2, data quality issues related to measurements of VOC have been an important topic. Many of the institutions providing VOC-data to EMEP have participated in the ACTRIS-2 project, either as formal partners or on a voluntary basis. Participation in ACTRIS-2 has meant 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 and has led to improved data quality in general.

Comparison between median levels in 2018 and the medians of the previous 10-years period, revealed a similar north-to-south pattern for several species.

Changes in instrumentation, procedures, station network etc. during the last two decades 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 long-term trends in NMHC over the 2000-2018 period at six sites by two independent statistical methods. These estimates indicate marked differences in the trends for the individual species. Small or non-significant trends were found for ethane over this period followed by propane which 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.

The persistent heatwave in summer 2018 in northern and central Europe lead to higher isoprene-levels than normal. The data indicate a clear relationship between isoprene and afternoon temperature at the sites. An exponential fit is seen to be well suited for the relationship between isoprene and temperature.

VOC measurements 2018

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 17th May 2005 the Protocol entered into force. The Protocol sets emission ceilings for 2010 for four pollutants:SO_2, NO_x, 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_2 emissions should be cut by at least 63%, its NO_x 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, $PM_{2.5}$ 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 present data report, we do however include monitoring data of terpenes and alcohols for the first time. These are measurements done at the Swiss site Beromünster and (for methanol) at the Finnish site Hyytiälä.

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 EU FP7 infrastructure project ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure), data quality issues related to measurements of VOCs were 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.

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**[1]		**ACTRIS target**[2]	
Alkanes			accuracy	precision	uncert.	repeat.
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%
Alkenes					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%
Alkynes					5%	2%
Acetylene	X		15%	5%	5%	2%
Propyne					5%	2%
Styrene		X			5%	2%
Aromatics					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%
Carbonyls					5%	2%
Formaldehyde	X		20%	15%	10%	5%
Acetaldehyde	X					
Propionaldehyde		X				
Acetone	X		20%	15%	10%	5%
Methylethylketone		X				
Methylvinylketone		X				
Other						
Monoterpenes			20%	15%	10%	5%
Acetonitrile			20%	15%		
Methanol			20%	15%		
DMS			20%	15%		

---

[1] Accuracy = 20 ppt, Precision = 15 ppt if level < 0.1 ppb

[2] Uncertainty = 5 ppt, Repeatability = 2 ppt if level < 0.1 ppb

2. Status of the measurement programme in 2018

2.1 The station network

The locations of the EMEP monitoring sites for VOC in 2018 are shown in Figure 1 and an overview of the measurement programme and the responsible laboratories is given in Table 2. In total, 20 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.

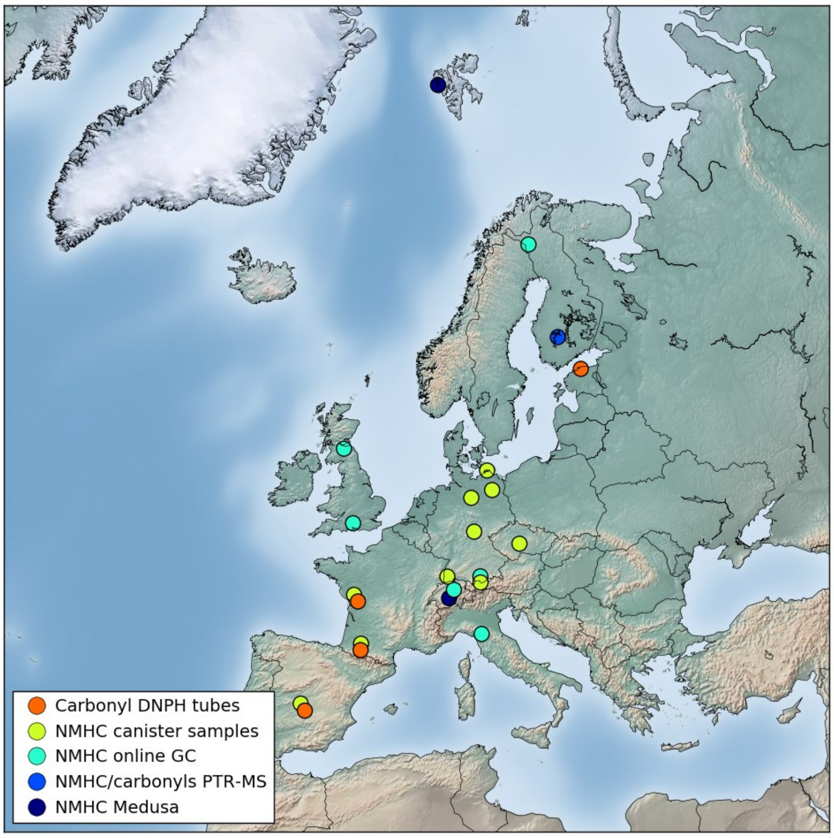


Figure 1: Monitoring sites for VOC in 2018.

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 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 as described below.

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 certain NMHCs; e.g. an annual mean level of n-hexane being almost two orders of magnitude larger than at the other sites whereas the annual mean of ethyne is only 10% of that seen at the other sites. There has been a dialogue between NILU and the data provider in Spain on this issue and the status of the data is still regarded unsettled and hence the data are not included in this report.

The data from Chilbolton observatory, located in southern England, clearly 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 3 or more C-atoms (propene and higher) as well as 2-methylbutane (iso-pentane) were reported for all sites from UBA in Germany, i.e. Waldhof, Schauinsland, Neuglobsow, Schmücke, Zingst, and Zugspitze in 2018 as in 2017. Since these levels were substantially higher than in previous years and no similar change were seen at the other EMEP sites, all 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 2018. 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	HC1)	Institute2)	Carb1)	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	Extreme spikes in data. Need further evaluation
Chilbolton Obs.	GB1055	Cont.	Ricardo	-	GC/MS	y	Strong local influences
Waldhof	DE0002	Reg.	UBA	-	Canister samples	y3)	Twice//week
Schauinsland	DE0003	Reg.	UBA	-	“	y3)	“
Neuglobsow	DE0007	Reg.	UBA	-	“	y3)	“
Schmücke	DE0008	Reg.	UBA	-	“	y3)	“
Zingst	DE0009	Reg.	UBA	-	“	y3)	“
Zugspitze	DE0054	Reg.	UBA	-	“	y3)	“
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/MS	y	
Peyrusse Vieille	FR0013	Reg.	IMT LD	Reg.	Canister/DNPH samples	y	NMHC 2/week. OVOC 1/week
La Tardière	FR0015	Reg.	IMT LD	Reg.	“	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, Scat. = scattered, n.m. = not measured., n.a. = not yet analysed, cont. = Continuous

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 = Minestrio de Medio Ambiente

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

2.2 Quasi-on-line in-situ measurements of NMHC and OVOC at Beromünster Switzerland

The NMHC monitoring at the Swiss site Rigi was ended in 2017 whereas the EMEP site Beromünster located 40 km to the northwest took over and started monitoring with a new system in 2018. At Beromünster, NMHC and OVOC are measured every hour, using 2-dimensional gas chromatography equipped with two flame ionization detectors (GC-GC FID/FID). In view of the ever growing importance of OVOC versus the NMHC, this system has the advantage that it is not only measuring one of these groups but allows for concurrent analysis of both NMHC and OVOC. As this instrument is not commercially available, it is described below.

First, humidity is removed from the airflow by a home built cold trap at -42 °C. Then, NMHC and OVOC are sampled from 500 ml of air by a Markes Unity –2 system, equipped with a Ozone Precursor Trap (Markes) at -30 °C. This is followed by thermal desorption at 300 °C with helium as carrier gas for transferring the substances into the GC.

Both NMHC and OVOC are initially injected onto the first analytical column (GS-OxyPlot, 30 m, 0.53 mm ID, 10 µm layer). OVOC and low volatile aromatic NMHC are separated already on the first column, whereas the high volatile NMHC are not retained by this column and are flushed through to the second analytical column (CP-Al_2O_3 Na_2SO_4 deactivated, 50 m × 0.53 mm ID, 10 µm layer).

Just before the aromatic NMHC would leave the first column, both columns are detached from each other by a so-called Deans switch and are then separately analysed by two FIDs.

For the calibration of NMHC a 30-component NPL 4 ppb mixture in nitrogen is used. For the calibration of the OVOC the FID-response factors related to NPL mixture and the effective carbon number concept are used.

2.3 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 and the subsequent ACTRIS-2 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-2 partners are invited to take part in this, and UBA (Umweltbundesamt) in Germany has used this opportunity.

Based on statistical tools developed within ACTRIS and ACTRIS-2, 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-2 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.

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 and ACTRIS-2 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-2 and EMPA in particular, has meant a significant improvement in the general data quality. Hopefully, these procedures and routines will incorporated into the parts of the EMEP VOC program and stations that are not formally part of ACTRIS-2.

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.

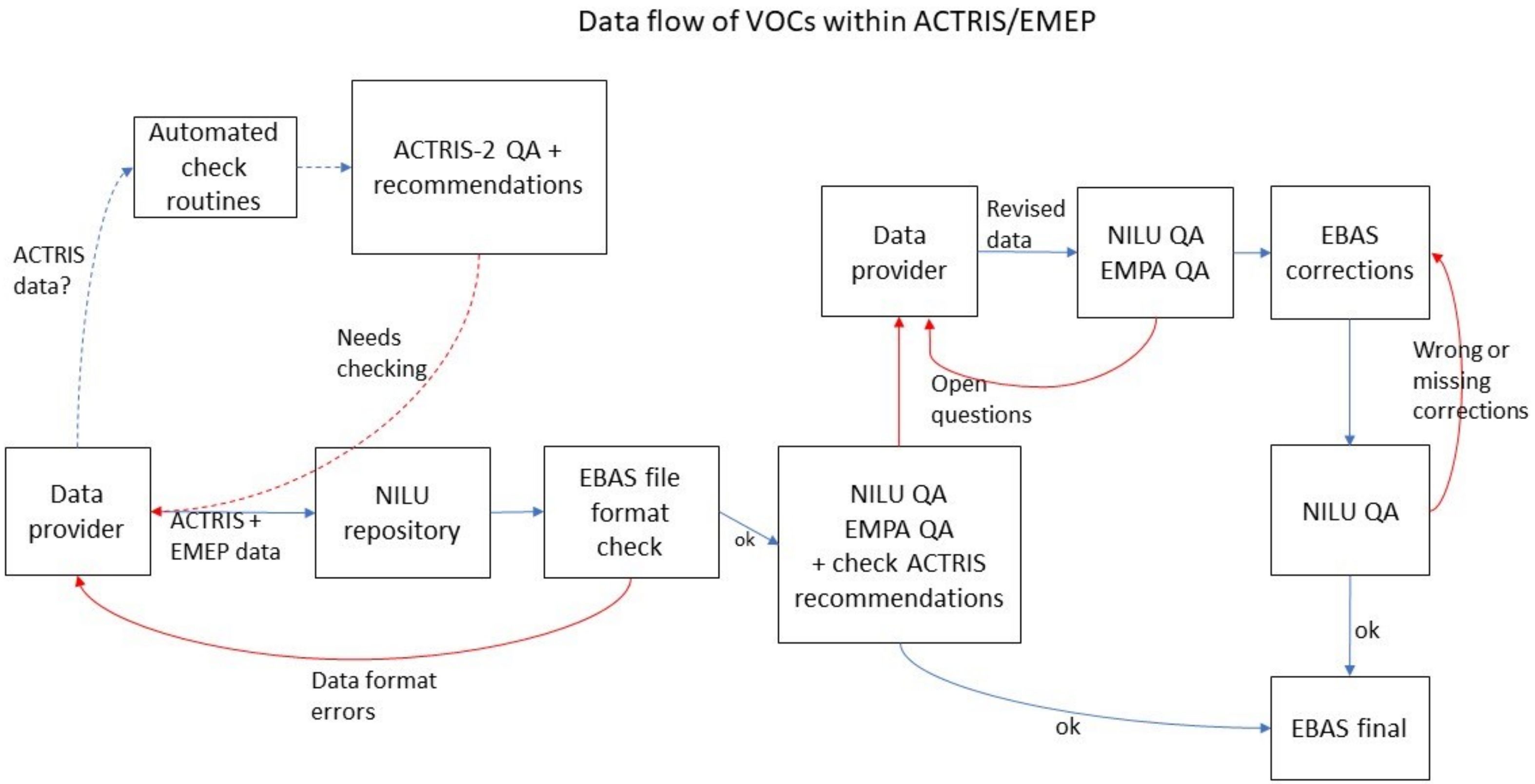


Figure 2: Flow diagram for the VOC data submitted within ACTRIS/EMEP.

2.3.1 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 ±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 ±10–15%. 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–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 ±25% of the median for the lighter alkanes. For some aromatics and unsaturated hydrocarbons as well as the C_6-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-C_8 alkanes, C_2-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 an 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-C_5 alkenes and C_7-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_7-C_8 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 2018

3.1 General levels

Time series of the diurnal means of all compounds at all stations during 2018 are given in the Appendix. Figure 3 shows the spread of data values for each station and NMHC species in 2018 in box and whisker plots, and the annual median values based on the previous 10 years of data (2008-2017) 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 2018 concentration levels relative to the previous 10 years climatology as well as the spread in 2018 data at each site separately.

For C_2–C_5 hydrocarbons there is a striking similarity between the variation in median values in 2018 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 2008-2017 period that presumably are not real. For other species, the differences between the 2018 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.

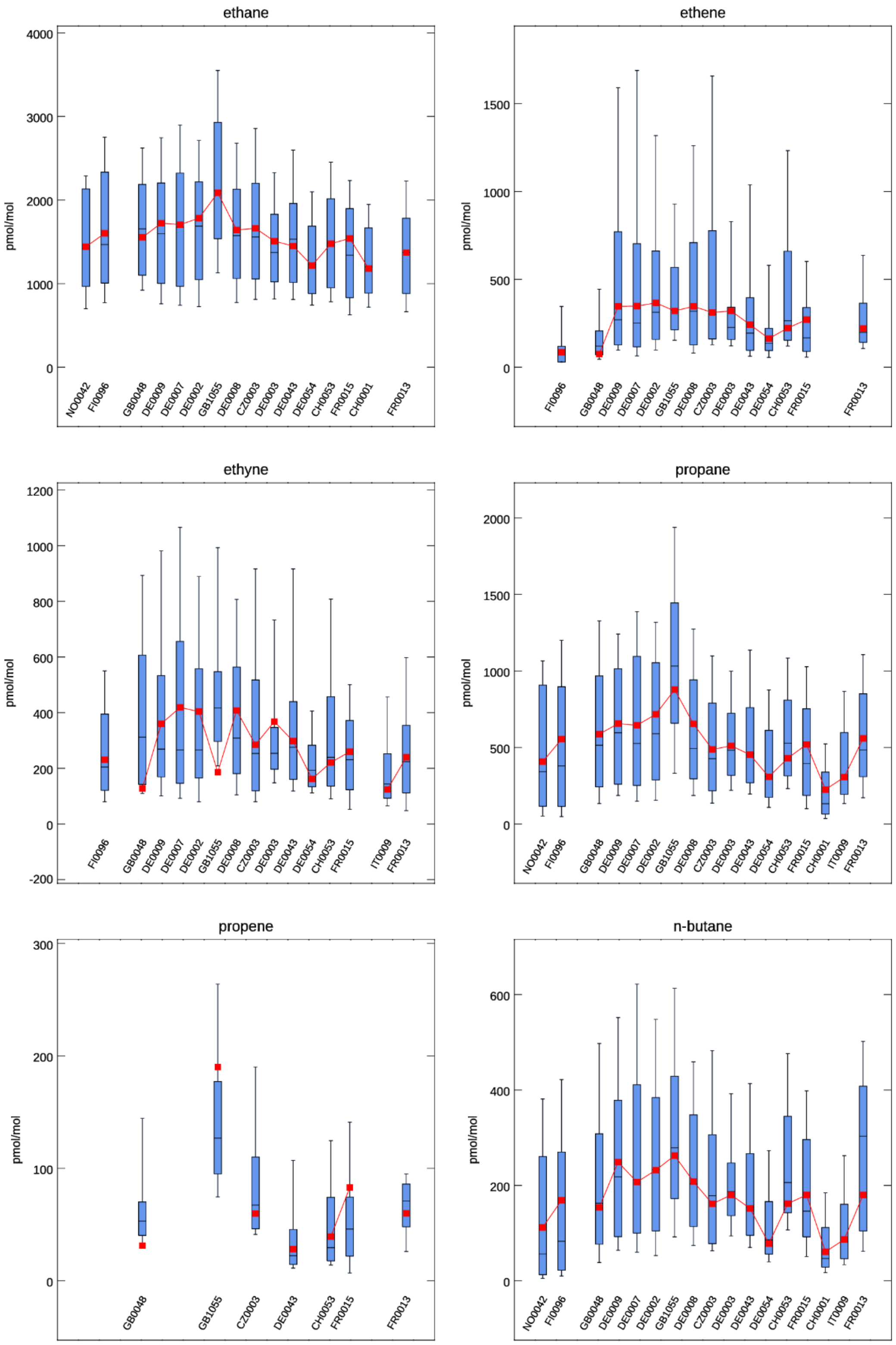


Figure 3: Box- and whisker-diagrams for light hydrocarbons based on all measurements in 2018. The boxes enclose the 25- and 75-percentile with the median marked inside. The whiskers extend out to the 9th and 91th percentile. The red squares connected with a red line mark the medians based on all data for the previous 10 years (2008-2017).

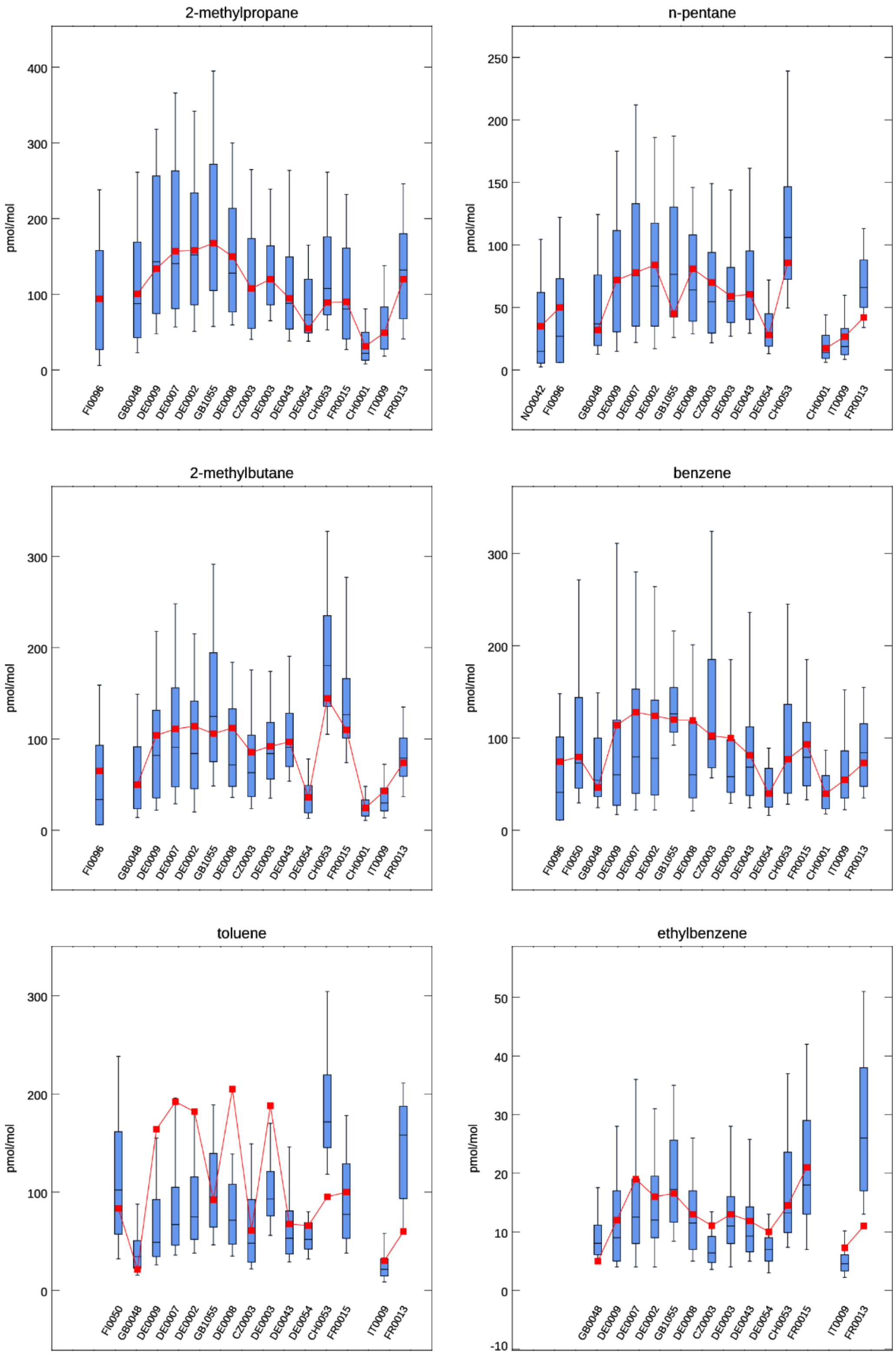


Figure 3. (cont.)

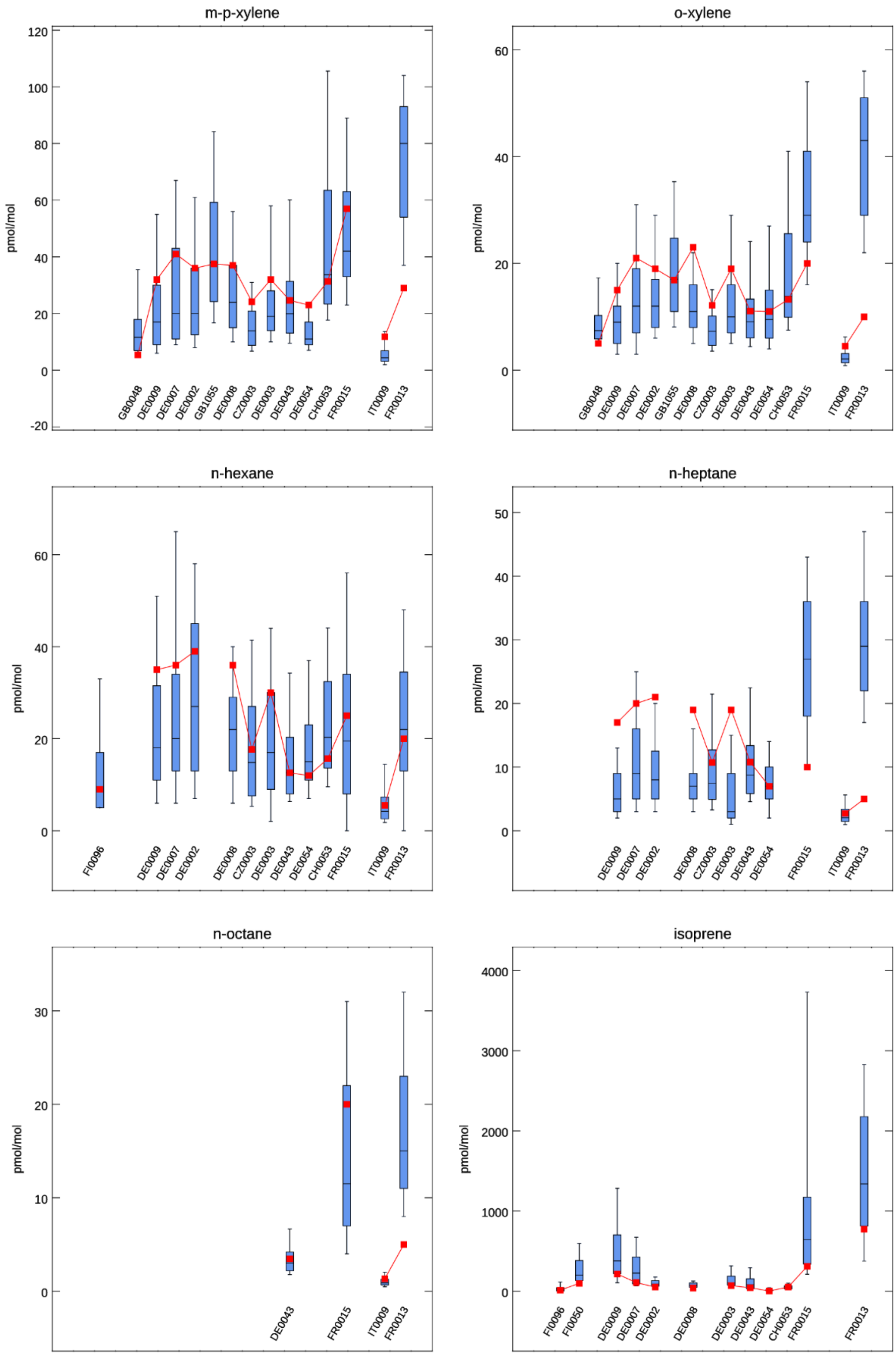


Figure 3. (cont.). Note that for isoprene only data for June-August (whole day) were used.

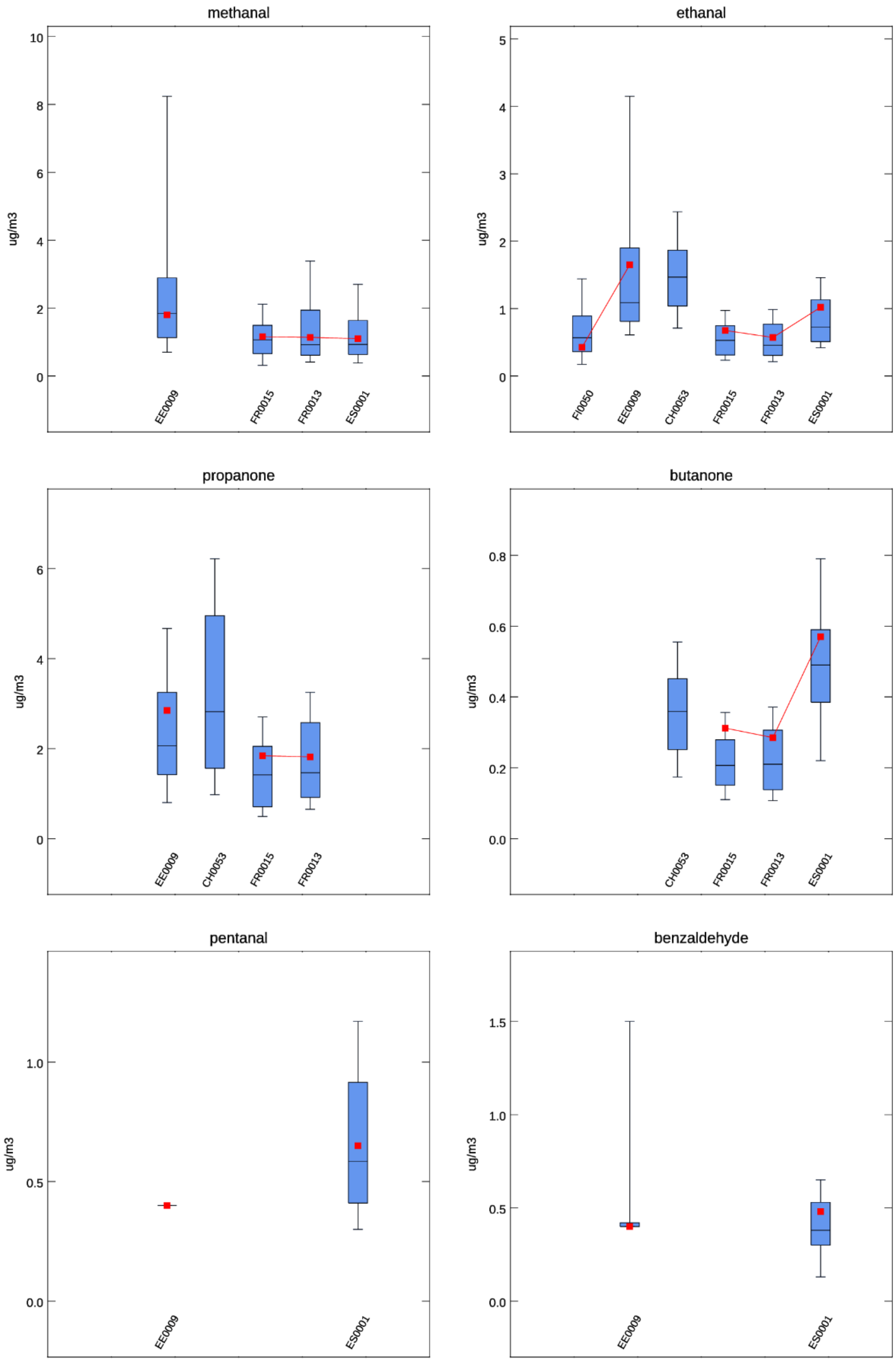


Figure 4: Box- and whisker-diagrams for carbonyls based on all measurements in 2018. The boxes enclose the 25- and 75-percentile with the median marked inside. The whiskers extend out to the 9th and 91st percentile. The red squares connected with a red line mark the medians based on all data for the previous 10 years (2008-2017).

3.2 Regional distribution of VOC

Figure 5 shows maps with the stations' annual median concentrations of light hydrocarbons in 2018. 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.

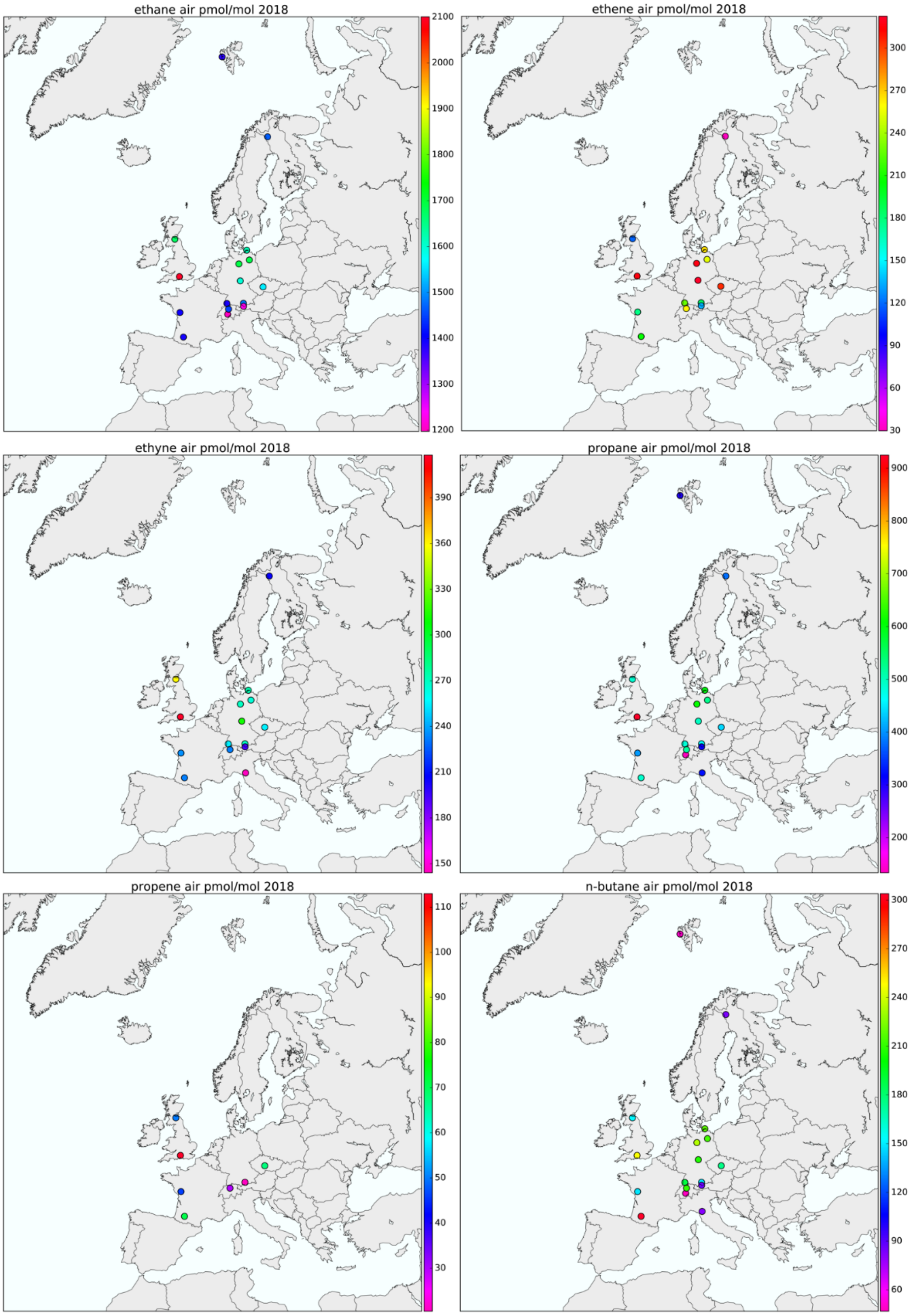


Figure 5: Annual median concentration of NMHCs in 2018. Unit: pmol/mol.

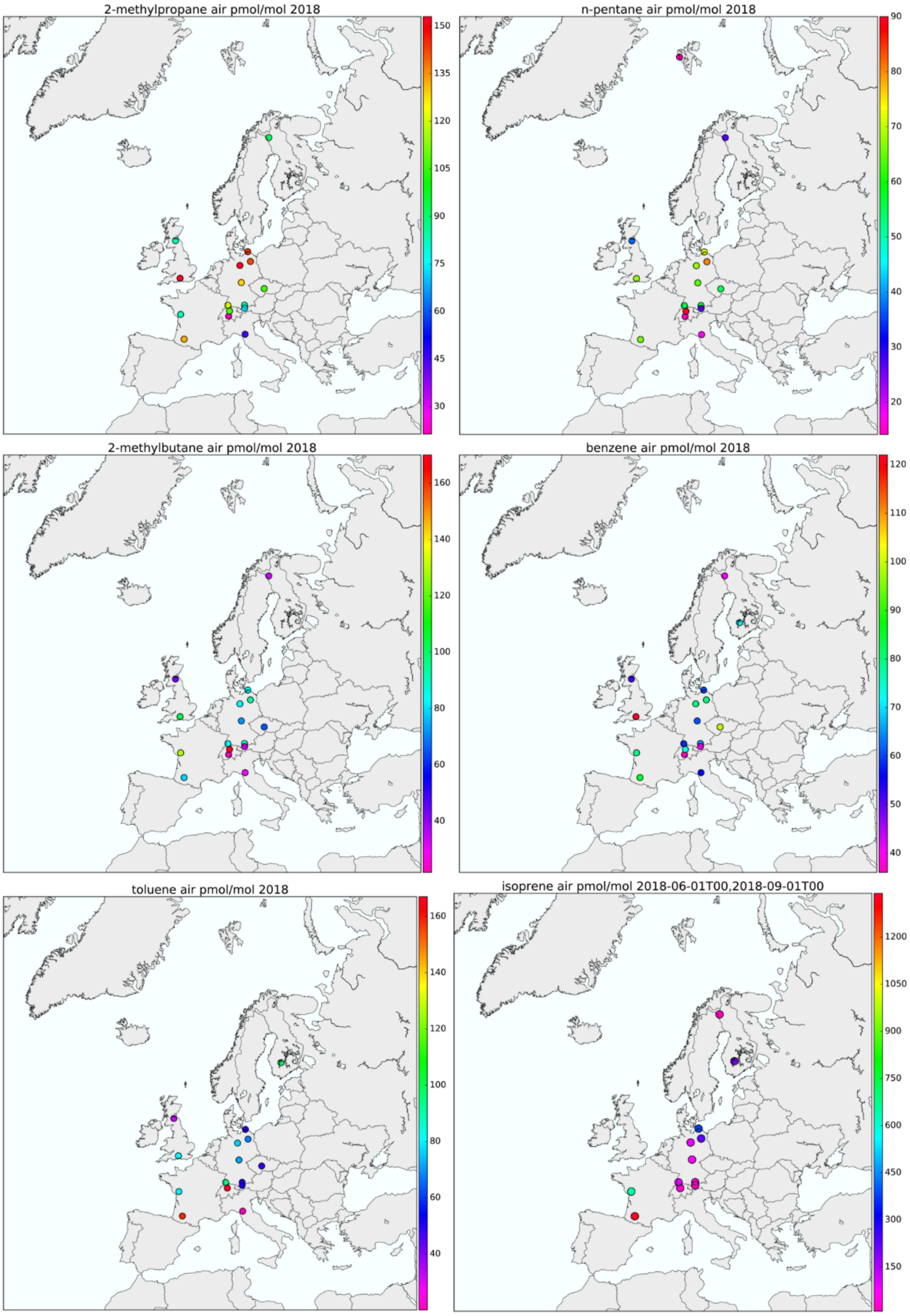


Figure 5 (contd.). Note that for isoprene the summer median (Jun-Aug) is shown.

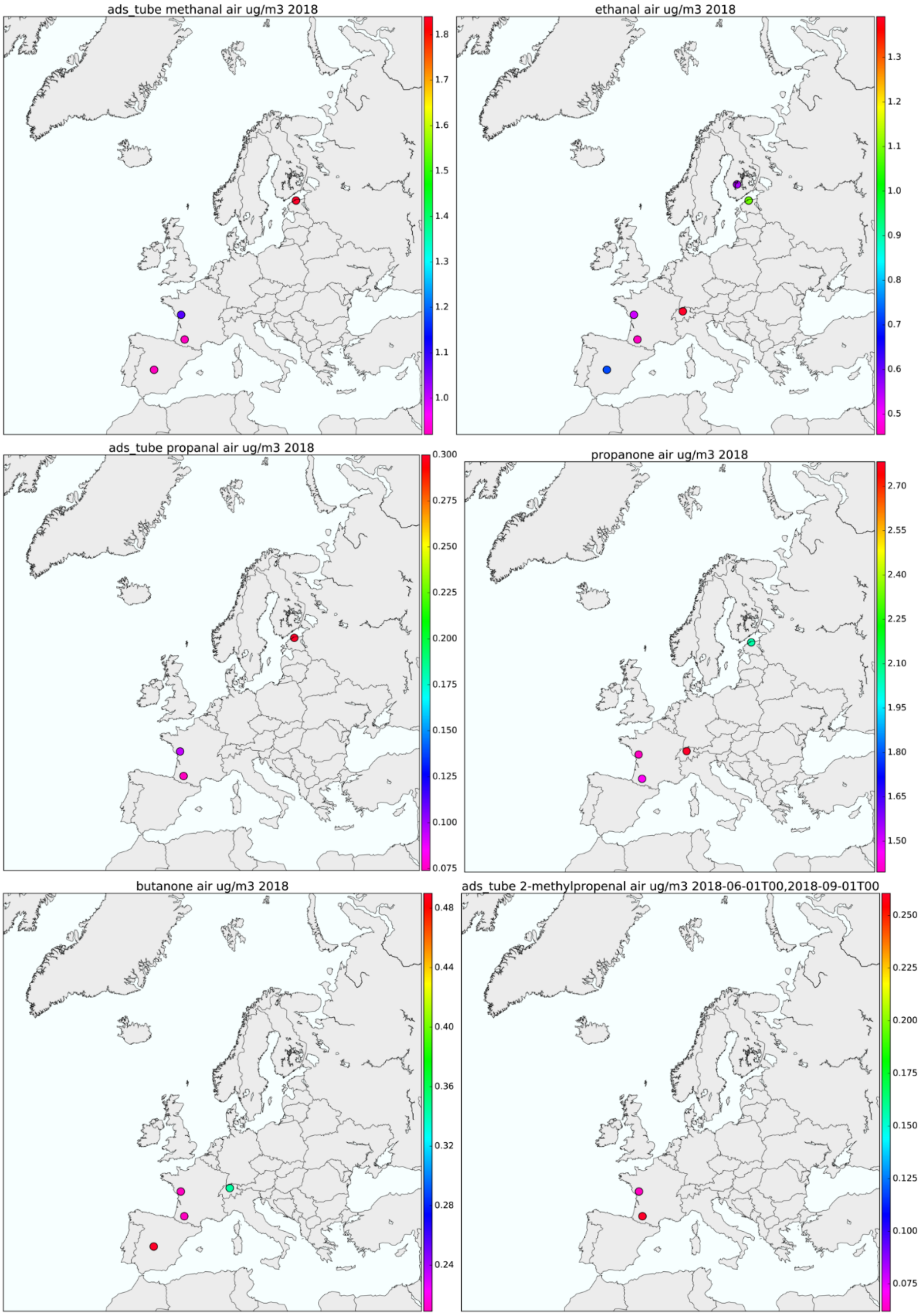


Figure 6: *Annual median concentration of carbonyls in 2018.* Note that for 2-methylpropenal the summer median (Jun-Aug) is shown. Unit: μg/m3.

4. Isoprene during the 2018 summer heat wave

Northern and central parts of Europe experienced a persistent heatwave during April-August 2018. This is discussed in more detail in Fagerli et al., 2020. The heatwave was associated with elevated concentrations of surface ozone and also isoprene. Figure 7 (from Fagerli et al., 2020) shows the dependency between surface temperature (as retrieved from the ECMWF data) and measured isoprene at four EMEP sites during May-August 2018. This shows a clear relationship between temperature and isoprene, which is as expected since the isoprene emissions depend on ambient temperature and solar radiation. An exponential fit is applied to the data giving fairly similar results for the stations FI0050 and DE0043 although they are located very far apart and presumably in fairly different environments. The data from the two French sites show much higher isoprene levels but have significantly less data since they are based on two grab samples per week taken in the afternoon between 12 and 16 UTC. Further details about isoprene during the 2018 heatwave can be found in Fagerli et al., 2020.

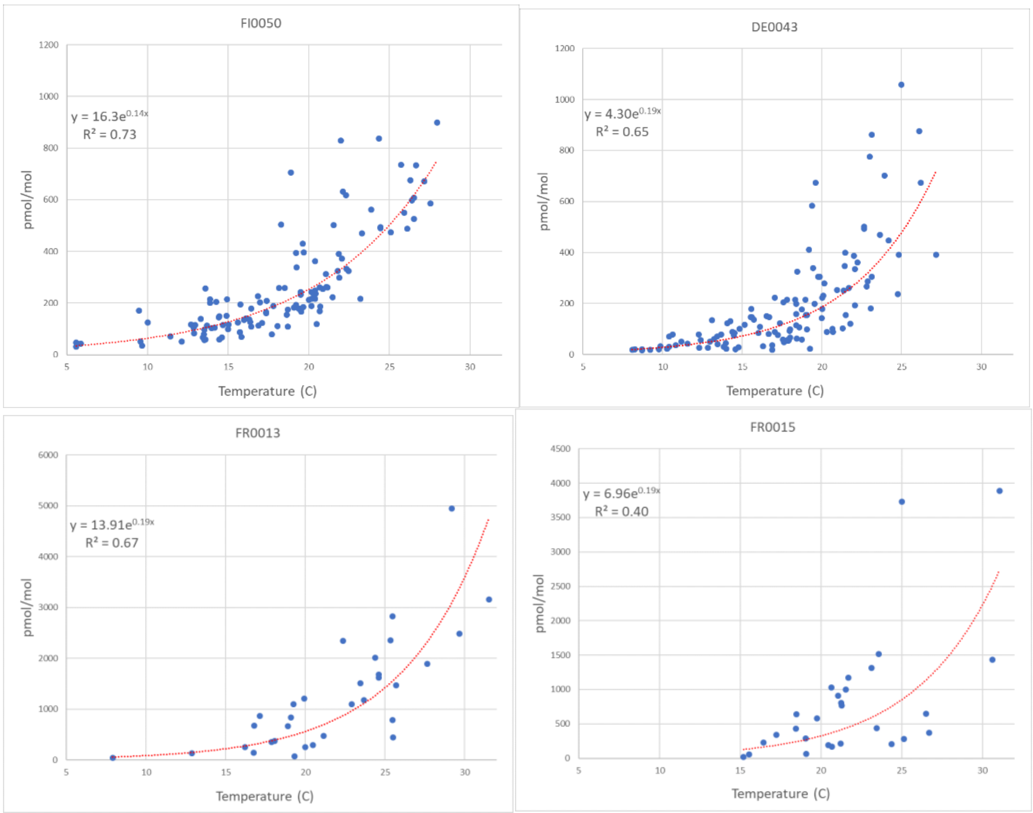


Figure 7. Scatter plots of measured daytime mean isoprene levels during May-August 2018 vs afternoon 2m temperature at 18 UTC as retrieved from gridded ECMWF data.

5. 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_2-C_8 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^{-1} to -22% y^{-1} 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 six EMEP sites with long term data over the period 2000-2018. 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:

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

where

c(t) = value at time *t* measured in years
t_0 = 2000

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 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:

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

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 8 - Figure 14 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, Beromünster, La Tardiere 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 2018 using 2000 as a reference year is given in the title. We assumed significant trends if $|a_3| > 2\sigma$, where σ 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.

Table 3 lists the percentage reductions of these species from 2000 to 2018 as estimated by *Eq. 1* and *Eq. 2,* respectively. We calculated the total reductions over the 2000-2018 period based on the annual mean values in 2000 and 2018 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 8 - Figure 14 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 both methods 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.

These results indicate that the European background levels of light hydrocarbons have experienced a substantial reduction since 2000 amounting up to 50-80% 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 2018, 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_3 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.

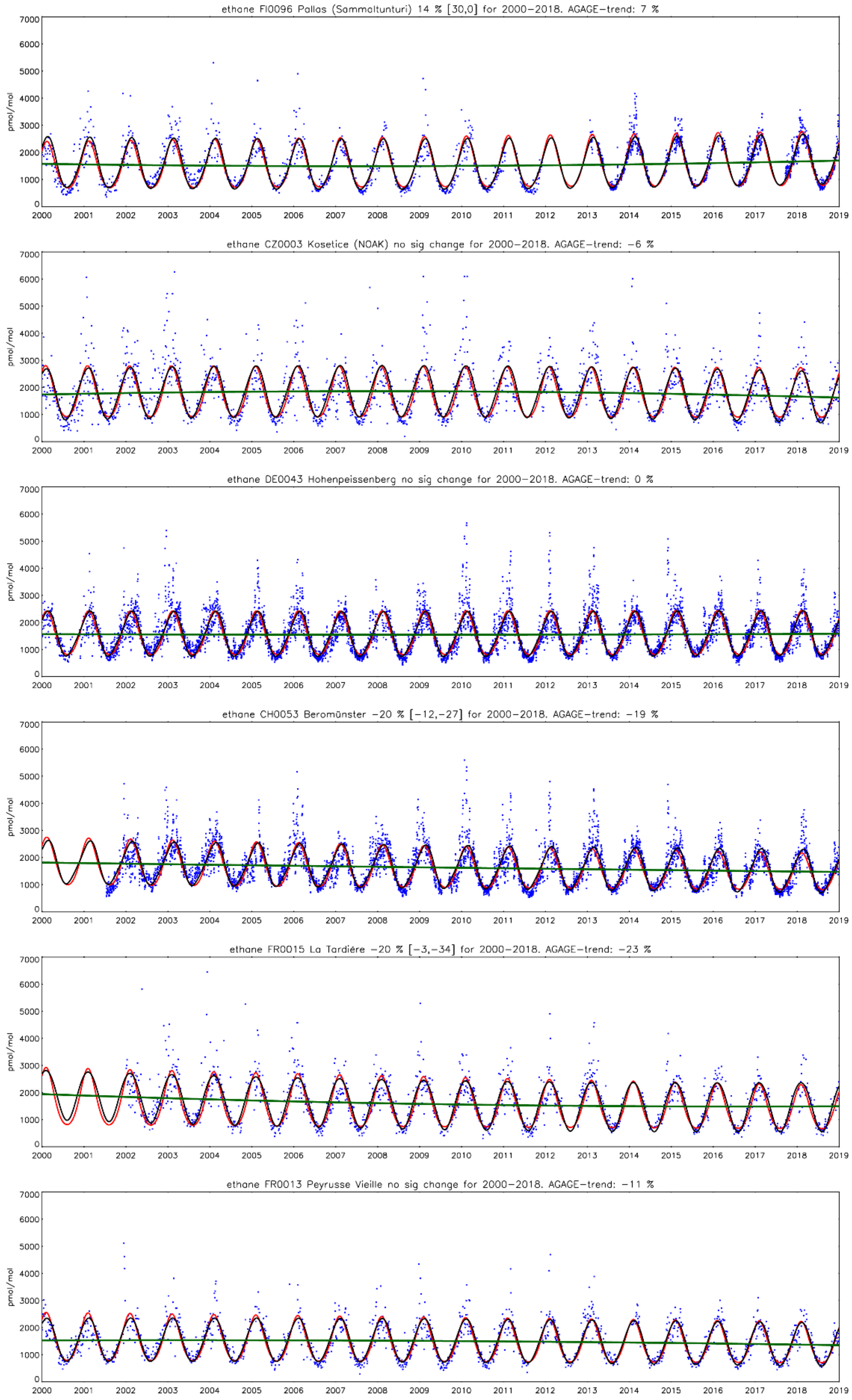


Figure 8: Daily mean ethane concentrations (blue) at six EMEP sites during 2000-2018 together with the estimated seasonal trend curve in red. Significant trends are given with confidence intervals in the header as percentage change from 2000 to 2018.The black curve shows the curve fit using the AGAGE polynomial function. Thick green line indicates the AGAGE trend term.

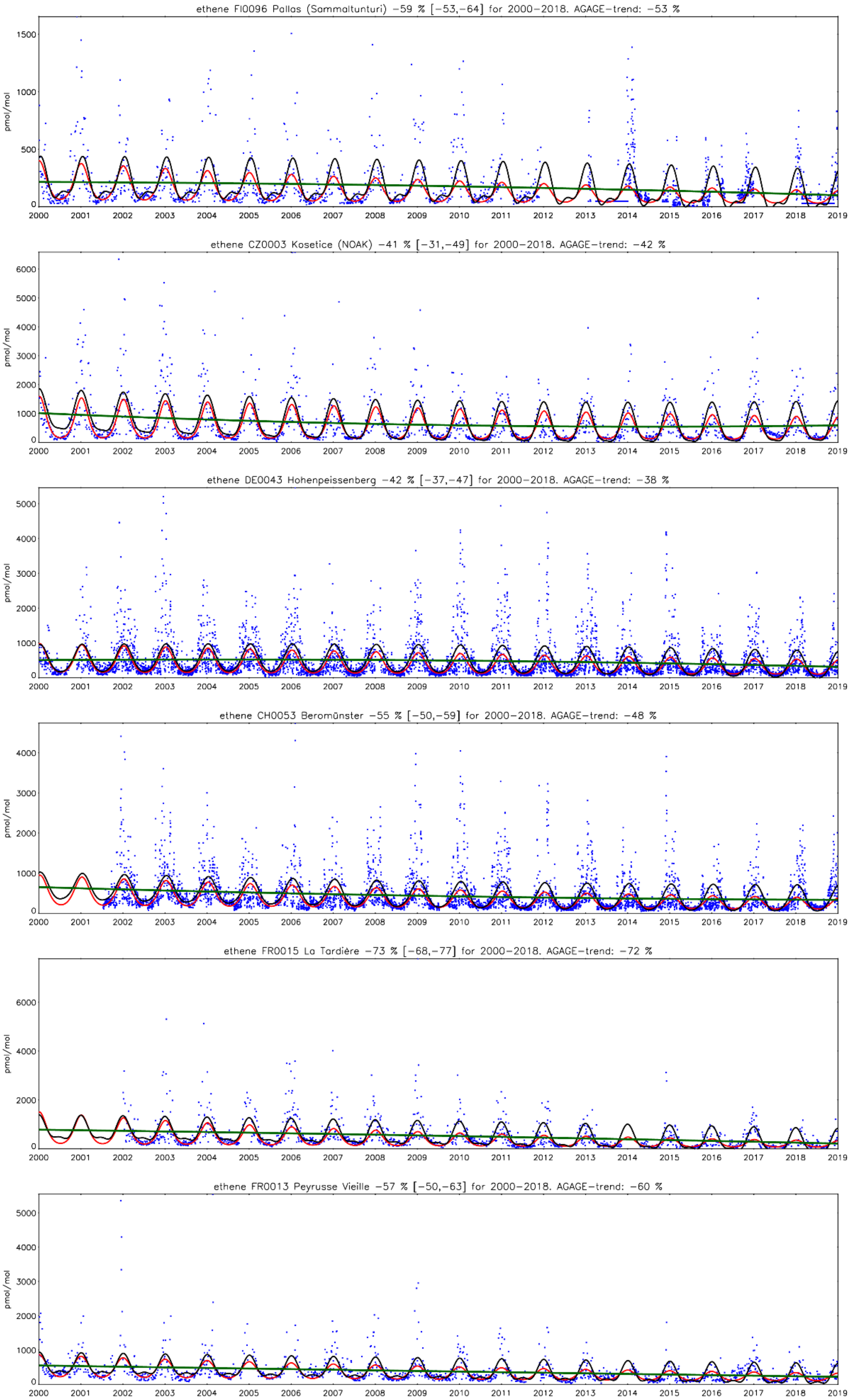
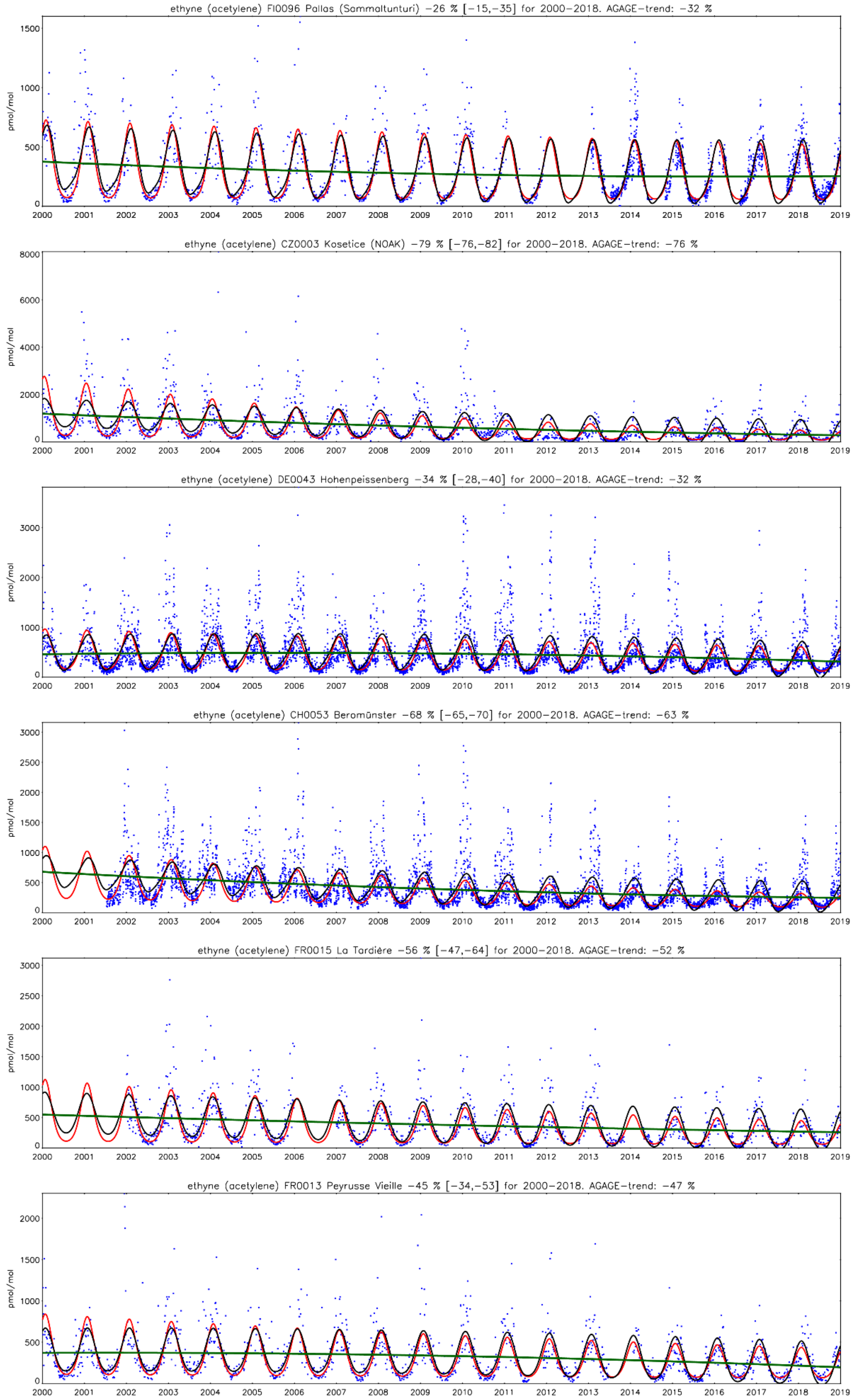


Figure 9. Same as Figure 8 for ethene.



ethyne (acetylene) FI0096 Pallas (Sammaltunturi) −26 % [−15,−35] for 2000−2018. AGAGE−trend: −32 %

ethyne (acetylene) CZ0003 Kosetice (NOAK) −79 % [−76,−82] for 2000−2018. AGAGE−trend: −76 %

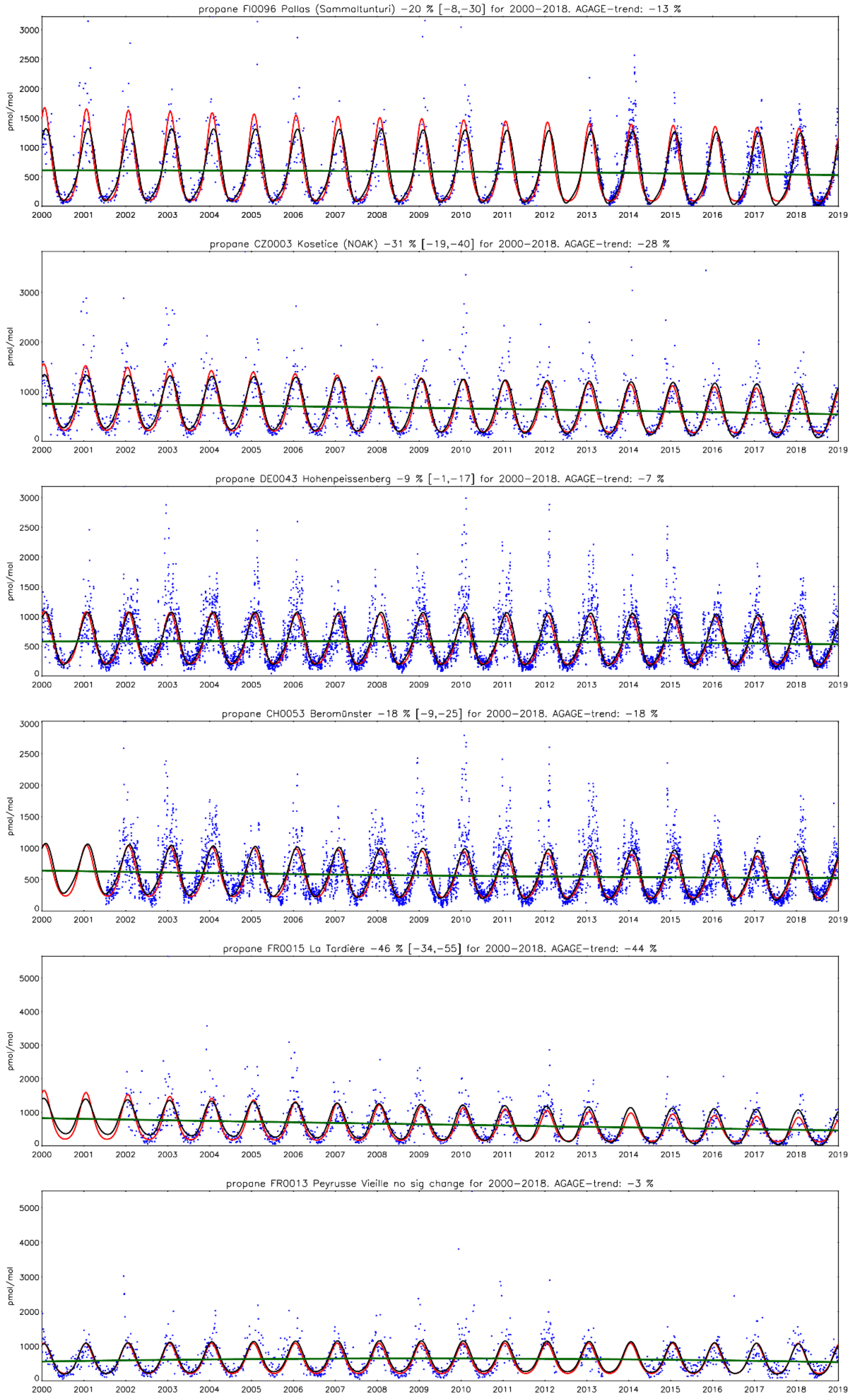
ethyne (acetylene) DE0043 Hohenpeissenberg −34 % [−28,−40] for 2000−2018. AGAGE−trend: −32 %

ethyne (acetylene) CH0053 Beromünster −68 % [−65,−70] for 2000−2018. AGAGE−trend: −63 %

ethyne (acetylene) FR0015 La Tardière −56 % [−47,−64] for 2000−2018. AGAGE−trend: −52 %

ethyne (acetylene) FR0013 Peyrusse Vieille −45 % [−34,−53] for 2000−2018. AGAGE−trend: −47 %

Figure 10. Same as Figure 8 for ethyne.



propane FI0096 Pallas (Sammaltunturi) -20 % [-8,-30] for 2000-2018. AGAGE-trend: -13 %

propane CZ0003 Kosetice (NOAK) -31 % [-19,-40] for 2000-2018. AGAGE-trend: -28 %

propane DE0043 Hohenpeissenberg -9 % [-1,-17] for 2000-2018. AGAGE-trend: -7 %

propane CH0053 Beromünster -18 % [-9,-25] for 2000-2018. AGAGE-trend: -18 %

propane FR0015 La Tardière -46 % [-34,-55] for 2000-2018. AGAGE-trend: -44 %

propane FR0013 Peyrusse Vieille no sig change for 2000-2018. AGAGE-trend: -3 %

Figure 11. Same as Figure 8 for propane.

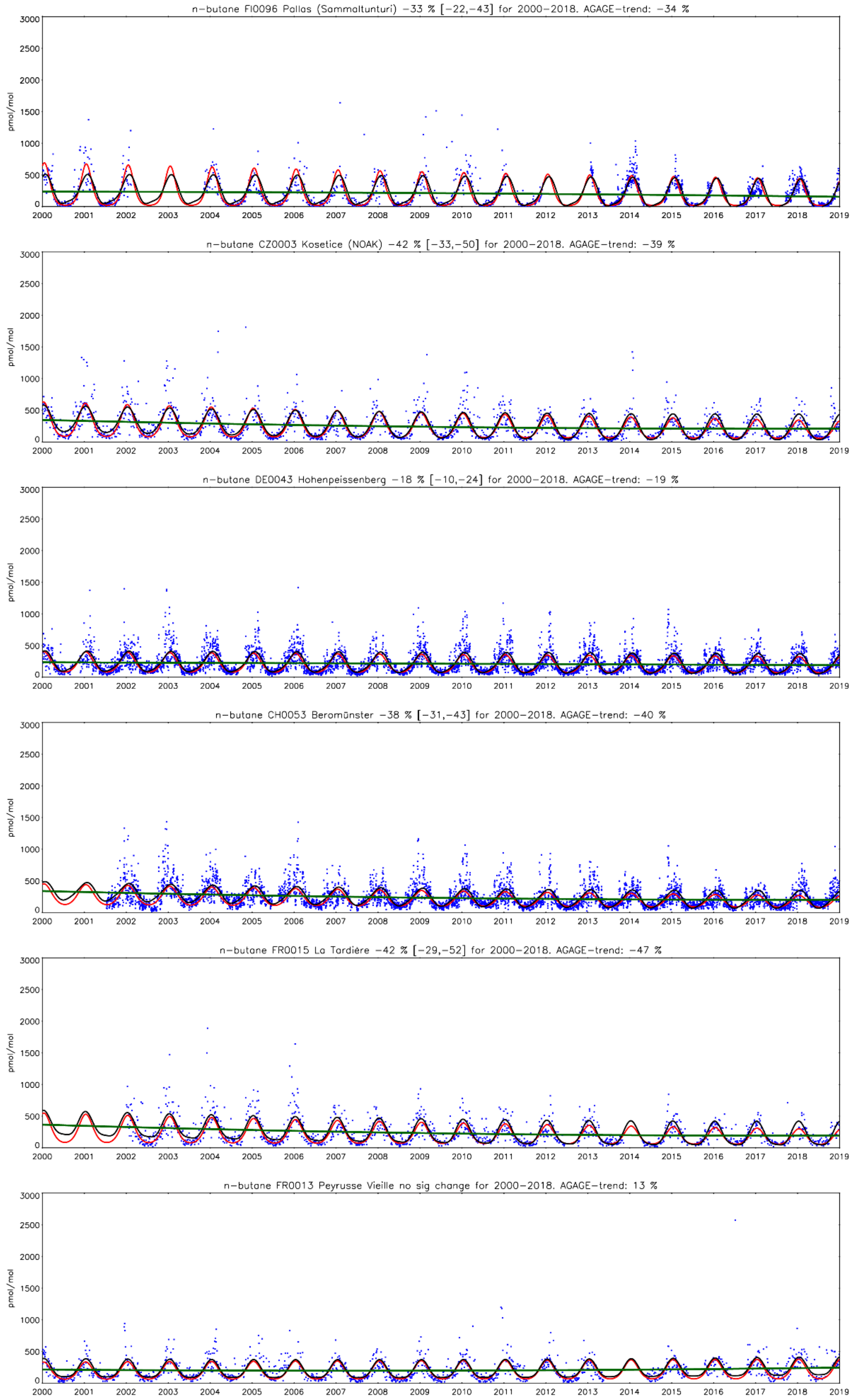


Figure 12. Same as Figure 8 for n-butane.

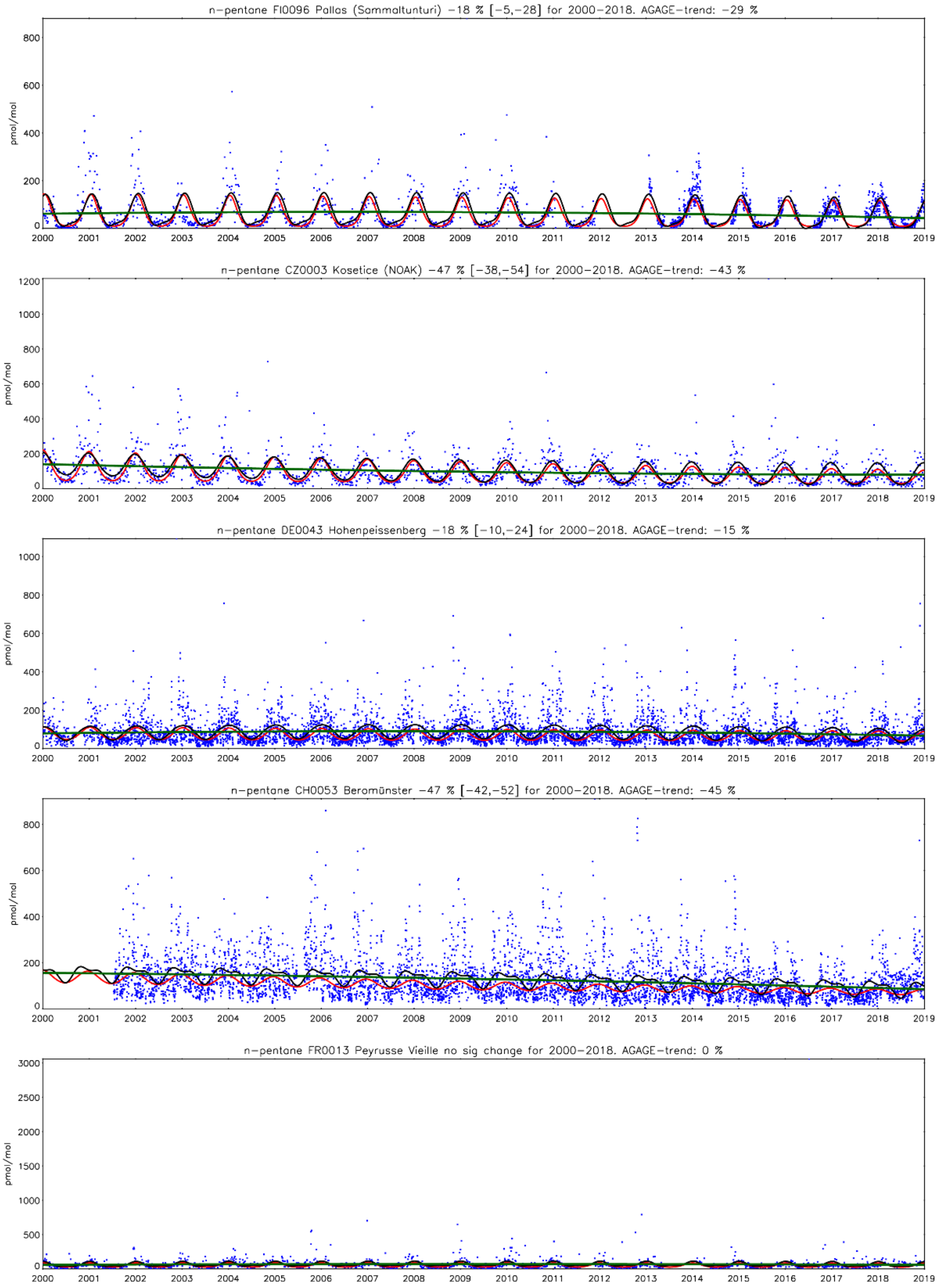


Figure 13. Same as Figure 8 for n-pentane. The station FR0015 (La Tardiere) was not included due to lack of data in some years.

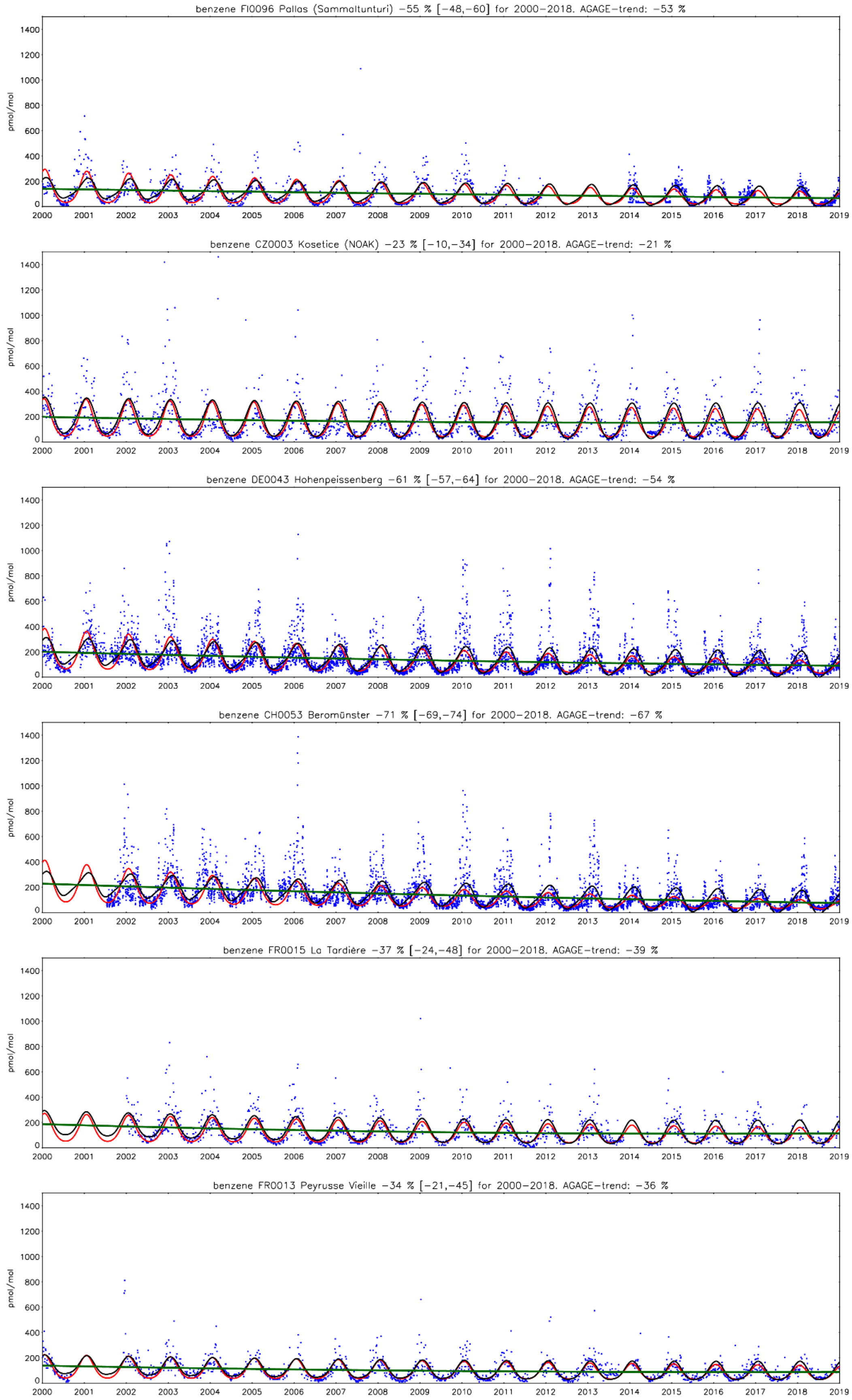


Figure 14. Same as Figure 8 for benzene.

Table 3. The percentage reduction in measured hydrocarbons over the period 2000-2018 relative to 2000 as the base year estimated from Eq 1 and Eq 2, respectively. 'ns' implies that no significant trend was found. The stations are: Pallas (PAL), Kosetice (KOS), Hohenpeissenberg (HPB), Rigi (RIG), La Tardiere (LTA) and Peyrusse Vieille (PEY).

	PAL		KOS		HPB		BER		LTA		PEY	
	Eq 1	***Eq 2***	***Eq 1***	***Eq 2***	***Eq 1***	***Eq 2***	***Eq 1***	***Eq 2***	***Eq 1***	***Eq 2***	***Eq 1***	***Eq 2***
Ethane	14	7	*ns*	6	*ns*	*ns*	20	19	20	23	*ns*	11
Ethene	59	53	41	42	42	38	55	48	73	72	57	60
Ethyne	26	32	79	76	34	32	68	63	56	52	45	47
Propane	20	13	31	28	9	7	18	18	46	44	*ns*	3
n-butane	33	34	42	39	18	19	38	40	42	47	*ns*	13
n-Pentane	18	29	47	43	18	15	47	45	-	-	*ns*	*ns*
Benzene	55	53	23	21	61	54	71	67	37	39	34	36

6. 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.

7. References

Aas, W., Hjellbrekke, A. G., Schaug, J., Solberg, S. (2001) Data quality 1999, quality assurance and field comparisons. Kjeller, NILU (EMEP/CCC Report 6/2001).

Apel, E. C., Calvert, J. G., Gilpin, T. M., Fehsenfeld, F., Lonneman, W. A. (2003) Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Task 4, ambient air. *J. Geophys. Res., 108D, 4300,* doi:10.1029/2002jd002936.

Derwent, R. G., Dernie, J. I. R., Dollard, G. J., Dumitrean, P., Mitchell, R. F., Murrells, T. P., Telling, S. P., Field, R. A. (2014) Twenty years of continuous high time resolution volatile organic compound monitoring in the United Kingdom from 1993 to 2012. *Atmos. Environ., 99*, 239-247.

EMEP/CCC (1990) EMEP workshop on measurement of hydrocarbons/VOC. Lindau, Federal Republic of Germany. Lillestrøm, NILU (EMEP/CCC Report 3/90).

EMEP/CCC (2014) Manual for sampling and chemical analysis. Kjeller, NILU (EMEP/CCC-Report 1/2014).

Fagerli, H., Tsyro, S., Denby, B.R., Nyíri, A., Gauss, M., Simpson, D., Wind, P., Benedictow, A., Jonson, J.E., Klein, H., Schultz, M., Griesfeller, J., Aas, W., Hjellbrekke, A.-G., Solberg, S., Platt, S.M., Fiebig, M., Yttri, K.E., Rud, R.O., Tørseth, K., Mareckova, K., Pinterits, M., Tista, M., Ullrich, B., Wankmüller, R., Posch, M., Bergström, R., Imhof, H., Minguillón, M.C., Putaud, J.-P., Cavalli, F., Poulain, L., Schlag, P., Heikkinen, L.M., Swietlicki, E., Martinsson, J., Vana, M., Smejkalova, A.H., Kouvarakis, G., Mihalopoulos, N. (2017) Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components. EMEP Status Report 2017. Oslo, Norwegian Meteorological Institute - MSC-W (EMEP Report 1/2017).

Fagerli, H., Tsyro, S., Jonson, J.E., Nyíri, A., Gauss, M., Simpson, D., Wind, P., Benedictow, A., Valdebenito, A., Klein, H., Schultz, M., Mortier, A., Aas, W., Hjellbrekke, A.-G., Solberg, S., Platt, S.M., Yttri, K.E., Rud, R.O., Tørseth, K., Mareckova, K., Matthews, B., Tista, M., Wankmüller, R., Posch, M., Bergström, R., Lazzeri, P., Pandolfi, M., Luoma, K., Aurela, M., Lenartz, F., Bergmans, B., Pittavino. S., Tombolato, I. (2018) Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components. EMEP Status Report 2018. Oslo, Norwegian Meteorological Institute - MSC-W (EMEP Report 1/2018).

Fagerli, H., Tsyro, S., Jonson, J.E., Nyíri, Á., Gauss, M., Simpson, D., Wind, P., Benedictow, A., Klein, H., Mortier, A., Aas, W., Hjellbrekke, A.-G., Solberg, S., Platt, S.M., Yttri, K.E., Tørseth, K., Gaisbauer, S., Mareckova, K., Matthews, B., Schindlbacher, S., Sosa, C., Tista, M., Ullrich, B., Wankmüller, R., Scheuschner, T., Bergström, R., Johanson, L., Jalkanen, J-P., Metzger, S., Denier van der Gon, H. A.C., Kuenen, J. J.P., Visschedijk, A. J.H., Barregård, L., Molnár, P., Stockfelt, L. (2019) "Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components". Joint MSC-W & CCC & CEIP Report. Oslo, Norwegian Meteorological Institute. EMEP Status Report 1/2019.

Hilde Fagerli, Svetlana Tsyro, Jan Eiof Jonson, Ágnes Nyíri, David Simpson, Peter Wind, Anna Benedictow, Heiko Klein, Qing Mu, Bruce Rolstad Denby, Eivind Grøtting Wærsted, Wenche Aas, Sabine Eckhardt, Anne Hjellbrekke, Sverre Solberg, Stephen Matthew Platt, Karl Espen Yttri, Kjetil Tørseth, Katarina Mareckova, Bradley Matthews, Sabine Schindlbacher, Bernhard Ullrich, Robert Wankmüller, Thomas Scheuschner, Robert Bergström, Hugo A.C. Denier van der Gon, Jeroen J.P. Kuenen, Antoon J.H. Visschedijk, Stefan Reimann, Matthias Hill, Claude, A. (2020) Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components. ". Joint MSC-W & CCC & CEIP Report. Oslo, Norwegian Meteorological Institute. EMEP Status Report 1/2020.

Hakola, H., Hellén, H., Laurila, T. (2006) Ten years of light hydrocarbons (C_2-C_6) concentration measurements in background air in Finland. *Atmos. Environ., 40*, 3621-3630.

Hellén, H., Kouznetsov, R., Anttila, P., Hakol, H. (2015) Increasing influence of easterly air masses on NMHC concentrations at the Pallas-Sodankylä GAW station. *Boreal Env. Res., 20*, 542-552.

Hjellbrekke, A.-G., Solberg, S. (2020) Ozone measurements 2018. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 2/2020).

Hoerger, C. C., Claude, A., Plass-Duelmer, C., Reimann, S., Eckart, E., Steinbrecher, R., Aalto, J., Arduini, J., Bonnaire, N., Cape, J. N., Colomb, A., Connolly, R., Diskova, J., Dumitrean, P., Ehlers, C., Gros, V., Hakola, H., Hill, M., Hopkins, J. R., Jaeger, J., Junek, R., Kajos, M. K., Klemp, D., Leuchner, M., Lewis, A. C., Locoge, N., Maione, M., Martin,D., Michl, K., Nemitz, E., O'Doherty, S., Perez Ballesta, P., Ruuskanen, T. M., Sauvage, S., Schmidbauer, N., Spain, T. G., Straube, E., Vana, M., Vollmer, M. K., Wegener, R., Wenger, A. (2015). ACTRIS non-methane hydrocarbon intercomparison experiment in Europe to support WMO GAW and EMEP observation networks. *Atmos. Meas. Tech., 8,* 2715-2736, doi:10.5194/amt-8-2715-2015.

Laurila, T., Hakola, H. (1996) Seasonal cycle of C2-C5 hydrocarbons over the Baltic Sea and Northern Finland. *Atmos. Environ., 30,* 1597-1607.

Malley, C. S. Braban, C. F., Dumitrean, P., Cape, J. N., Heal, M. R. (2015) The impact of speciated VOCs on regional ozone increment derived from measurements at the UK EMEP supersites between 1999 and 2012. *Atmos. Chem. Phys., 15*, 8361-8380, doi:10.5194/acp-15-8361-2015.

Markwardt, C. B. (2009) Non-linear least squares fitting in IDL with MPFIT. In: *Astronomical Data Analysis Software and Systems XVIII. Proceedings of a workshop held at Hotel Loews Le Concorde, Quebec City, QC, Canada, 2-5 November 2008.* Ed. by: Bohlender, D., Dowler, P. & Durand, D. San Francisco, Astronomical Society of the Pacific (ASP Conference Series, Vol. 411). pp. 251-254.

Plass-Dülmer, C., Michl, K., Ruf, R., Berresheim, H. (2002) C_2-C_8 hydrocarbon measurement and quality control procedures at the Global Atmosphere Watch Observatory Hohenpeissenberg. *J. Chromatogr., 953*, 175-197.

Plass-Dülmer, C., Schmidbauer, N., Slemr, J., Slemr, F., D'Souza, H. (2006) European hydrocarbon intercomparison experiment AMOHA part 4: Canister sampling of ambient air. *J. Geophys. Res., 111D, 4306,* doi:10.1029/2005jd006351.

Prinn, R. G., Weiss, R. F., Arduini, J., Arnold, T., DeWitt, H. L., Fraser, P. J., Ganesan, A. L., Gasore, J., Harth, C. M., Hermansen, O., Kim, J., Krummel, P. B., Li, S., Loh, Z. M., Lunder, C. R., Maione, M., Manning, A. J., Miller, B. R., Mitrevski, B., Mühle, J., O'Doherty, S., Park, S., Reimann, S., Rigby, M., Saito, T., Salameh, P. K., Schmidt, R., Simmonds, P. G., Steele, L. P., Vollmer, M. K., Wang, R. H., Yao, B., Yokouchi, Y., Young, D., and Zhou, L.: History of chemically and radiatively important atmospheric gases from the Advanced Global Atmospheric Gases Experiment (AGAGE). *Earth Syst. Sci. Data, 10,* 985-1018, doi:10.5194/essd-10-985-2018.

Romero, R. (1995) The first laboratory intercomparison of light hydrocarbons in EMEP. Kjeller, Stockholm University, Institute of Applied Environmental Research, Air Pollution Laboratory/Norwegian Institute for Air Research (EMEP/CCC Report 2/95).

Sauvage S., Plaisance, H, Locoge, N., Wroblewski, A., Coddeville, P., Galloo, J. (2009) Long term measurement and source apportionment of non-methane hydrocarbons in three French rural areas. *Atmos. Environ*., *43*, 2430-2441.

Sauvage, S., Waked, A., Locoge, N., Pascaud, A. Coddeville, P. (2015) What can we learn from 15 years of VOC measurements in France? Presentation at the 16th EMEP/TFMM workshop Krakow, May 2015.

Simmonds, P. G., Manning, A. J., Cunnold, D. M., McCulloch, A., O'Doherty, S., Derwent, R. G., Krummel, P. B., Fraser, P. J., Dunse, B., Porter, L. W., Wang, R. H. J., Greally, B. R., Miller, B. R., Salameh, P., Weiss, R. F., and Prinn, R. G.: Global trends, seasonal cycles, and European emissions of dichloromethane, trichloroethene, and tetrachloroethene from the AGAGE observations at Mace Head, Ireland, and Cape Grim, Tasmania, *J. Geophys. Res., 111,* D18304, doi:10.1029/2006JD007082, 2006.

Slemr, J., Slemr, F., Partridge, R., D'Souza, H., Schmidbauer, N. (2002) Accurate measurements of hydrocarbons in the atmosphere (AMOHA): Three European intercomparisons. *J. Geophys. Res., 107D,* 4409, doi:10.1029/2001JD001357.

Solberg, S., Dye, C., Schmidbauer, N., Herzog, A., Gehrig, R. (1996) Carbonyls and nonmethane hydrocarbons at rural European sites from the Mediterranean to the Arctic. *J. Atmos. Chem., 25,* 33-66.

Solberg, S., Dye, C., Walker, S.-E., Simpson, D. (2001) Long-term measurements and model calculations of formaldehyde at rural European monitoring sites. *Atmos. Environ., 35*, 195-207.

Solberg, S. (2013). EMEP VOC measurements 2011. Kjeller, NILU (EMEP/CCC, 05/2013).

Tørseth, K., Aas,W., Breivik, K., Fjæraa, A.M., Fiebig, M., Hjellbrekke, A. G., LundMyhre, C., Solberg, S., Yttri, K. E. (2012) Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009. *Atmos. Chem. Phys., 12,* 5447-5481, doi:10.5194/acp-12-5447-2012.

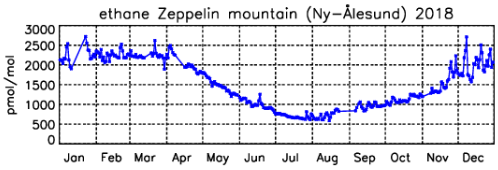
Waked, A., Sauvage, S., Borbon, A., Gauduin, J., Pallares, C., Vagnot, M. P., Thierry, L., and Locoge, N. (2016) Multi-year levels and trends of non-methane hydrocarbon concentrations observed in ambient air in France. *Atmos. Environ., 141,* 263-275, doi:10.1016/j.atmosenv.2016.06.059.

WMO (2007) A WMO/GAW expert workshop on global long-term measurements of volatile organic compounds (VOCs). Geneva, World Meteorological Organization (WMO TD No. 1373).

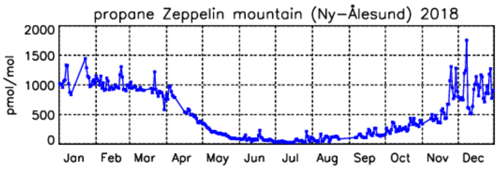
Worton, D. R., Sturges, W. T., Reeves, C. E., Newland, M. J., Penkett, S. A, Atlas, E., Stroud, V., Johnson, K., Schmidbauer, N., Solberg, S. (2012) Evidence from firn air for recent decreases in non-methane hydrocarbons and a 20th century increase in nitrogen oxides in the northern hemisphere *Atmos. Environ., 54*, 592-602.

Appendix 1

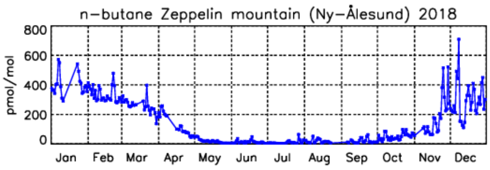
Time series of daily means of VOCs measured in 2018 listed from north to south



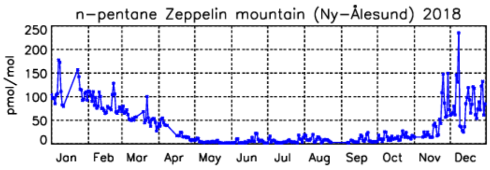
ethane Zeppelin mountain (Ny−Ålesund) 2018



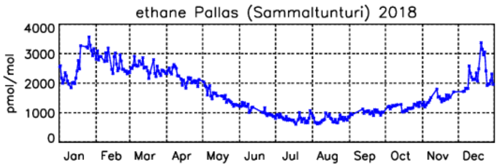
propane Zeppelin mountain (Ny−Ålesund) 2018

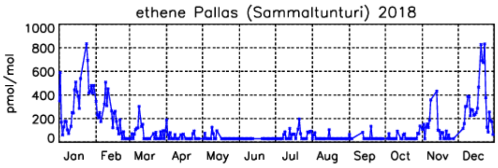


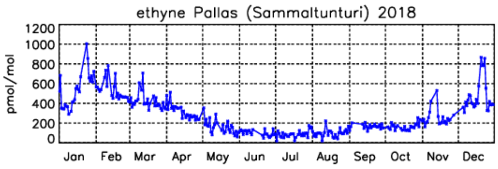
n−butane Zeppelin mountain (Ny−Ålesund) 2018

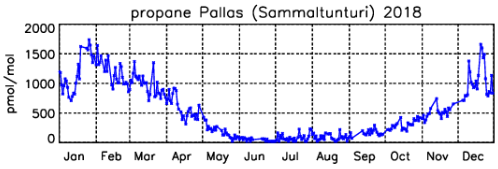


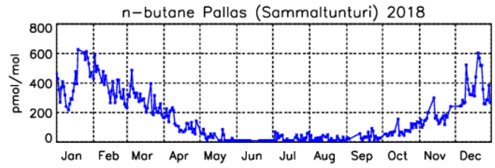
n−pentane Zeppelin mountain (Ny−Ålesund) 2018

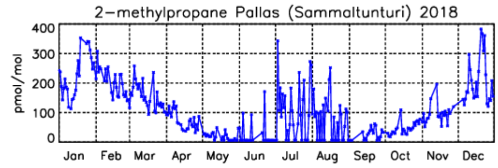

ethane Pallas (Sammaltunturi) 2018

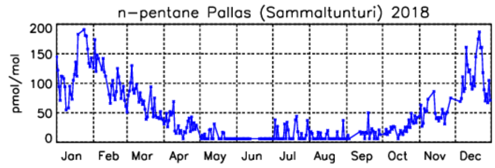

ethene Pallas (Sammaltunturi) 2018

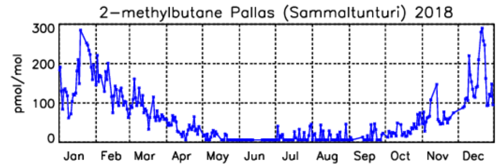

ethyne Pallas (Sammaltunturi) 2018

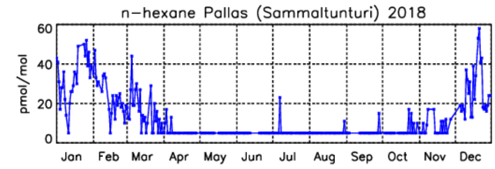

propane Pallas (Sammaltunturi) 2018

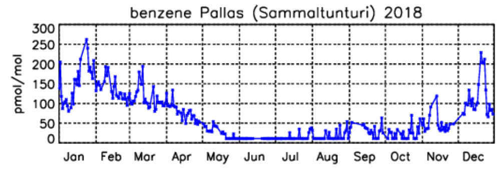

n−butane Pallas (Sammaltunturi) 2018

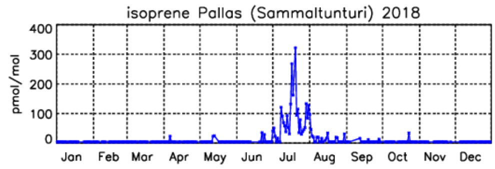

2−methylpropane Pallas (Sammaltunturi) 2018

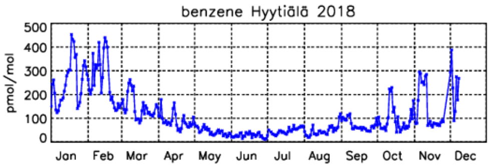

n−pentane Pallas (Sammaltunturi) 2018


2−methylbutane Pallas (Sammaltunturi) 2018

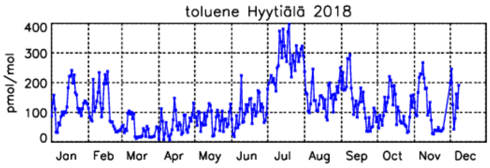

n−hexane Pallas (Sammaltunturi) 2018


benzene Pallas (Sammaltunturi) 2018

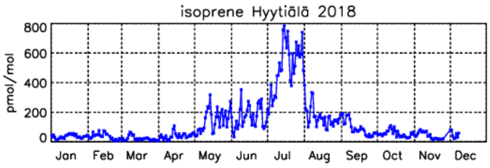

isoprene Pallas (Sammaltunturi) 2018



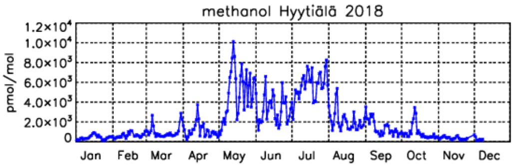
benzene Hyytiälä 2018



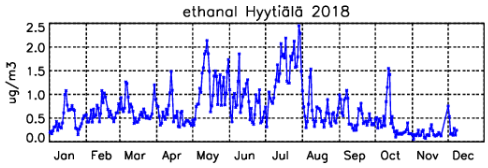
toluene Hyytiälä 2018



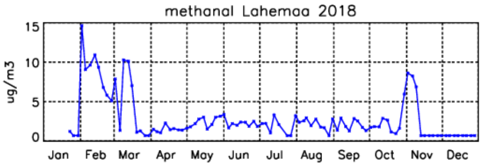
isoprene Hyytiälä 2018

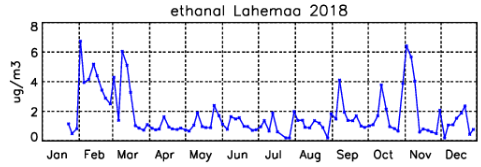


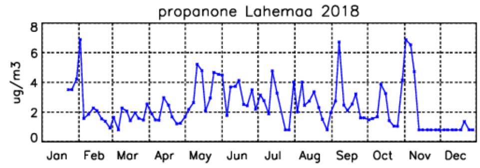
methanol Hyytiälä 2018

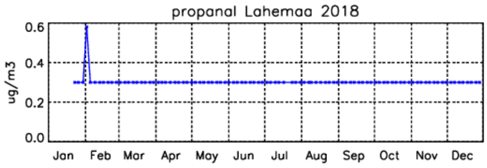


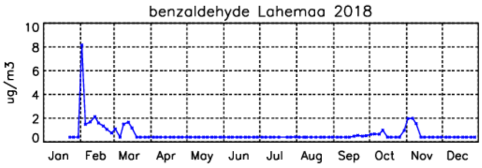
ethanal Hyytiälä 2018

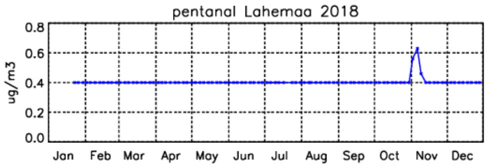

methanal Lahemaa 2018
ug/m3
0
5
10
15
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

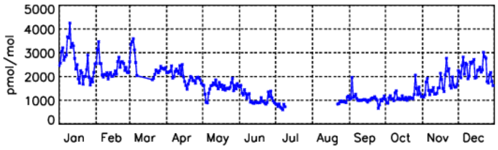

ethanal Lahemaa 2018
ug/m3
0
2
4
6
8
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

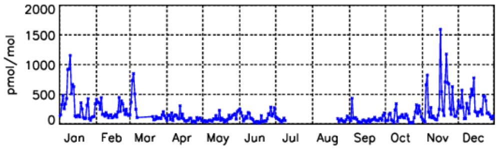

propanone Lahemaa 2018
ug/m3
0
2
4
6
8
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

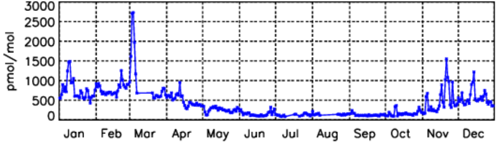

propanal Lahemaa 2018
ug/m3
0.0
0.2
0.4
0.6
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

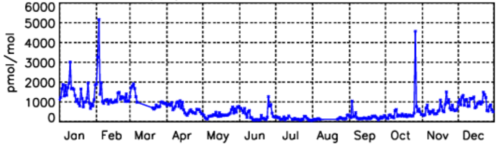

benzaldehyde Lahemaa 2018
ug/m3
0
2
4
6
8
10
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

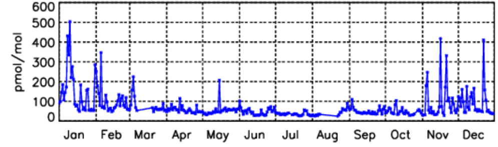

pentanal Lahemaa 2018
ug/m3
0.0
0.2
0.4
0.6
0.8
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

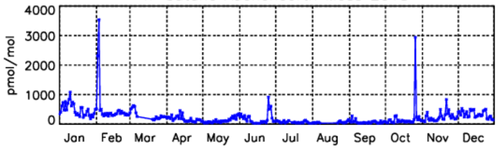

ethane Auchencorth Moss 2018

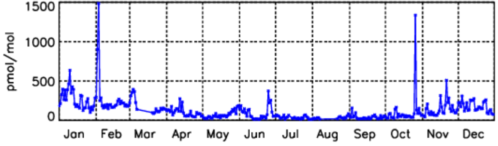

ethene Auchencorth Moss 2018

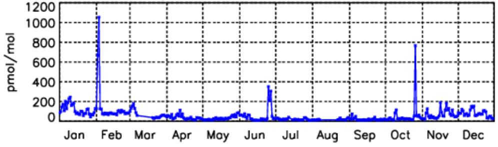

ethyne Auchencorth Moss 2018

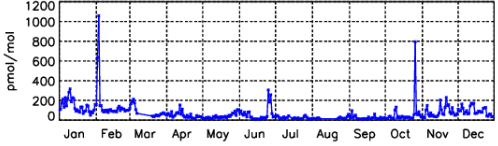

propane Auchencorth Moss 2018

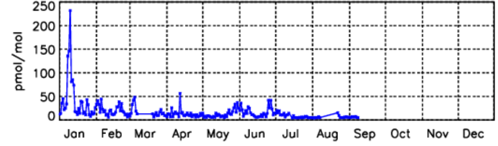

propene Auchencorth Moss 2018

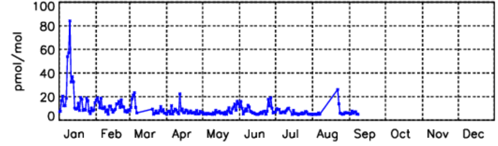

n−butane Auchencorth Moss 2018

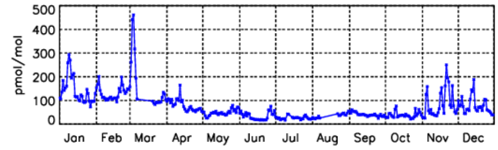

2−methylpropane Auchencorth Moss 2018

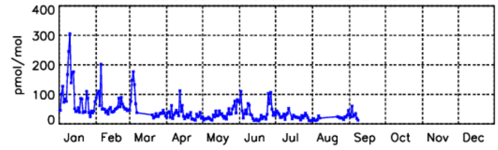

n−pentane Auchencorth Moss 2018

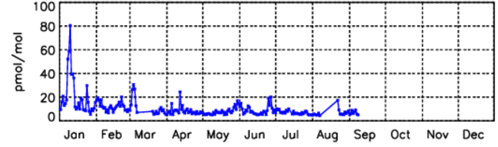

2−methylbutane Auchencorth Moss 2018

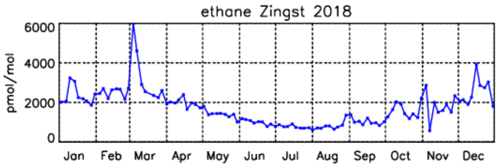

m−p−xylene Auchencorth Moss 2018

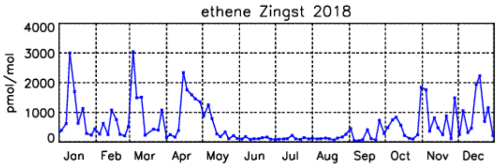

o−xylene Auchencorth Moss 2018

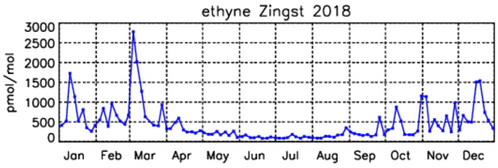

benzene Auchencorth Moss 2018

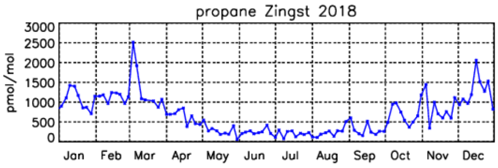

toluene Auchencorth Moss 2018

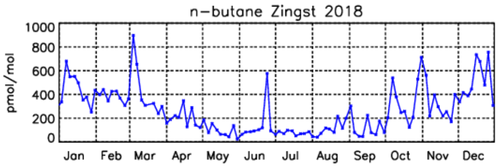

ethylbenzene Auchencorth Moss 2018

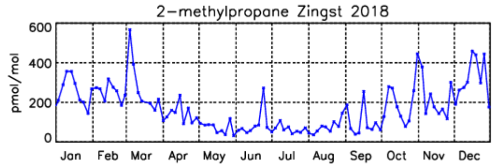

ethane Zingst 2018
pmol/mol
6000
4000
2000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

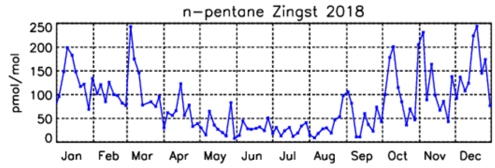

ethene Zingst 2018
pmol/mol
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

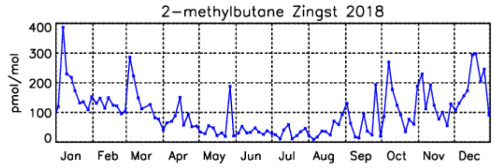

ethyne Zingst 2018
pmol/mol
3000
2500
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

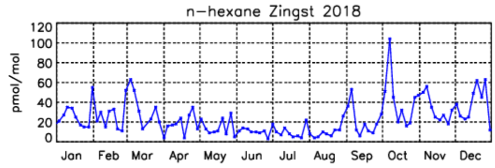

propane Zingst 2018
pmol/mol
3000
2500
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

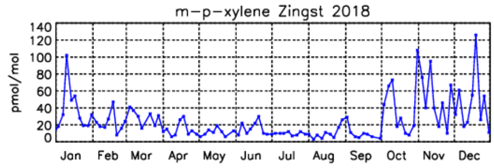

n−butane Zingst 2018
pmol/mol
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

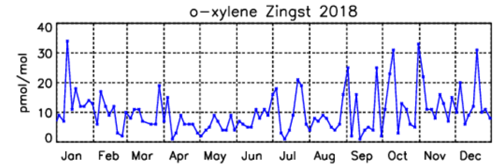

2−methylpropane Zingst 2018
pmol/mol
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

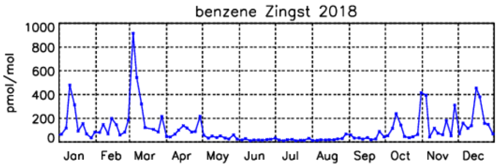

n−pentane Zingst 2018
pmol/mol
250
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

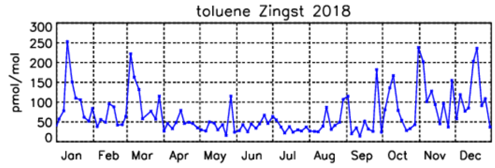

2−methylbutane Zingst 2018
pmol/mol
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

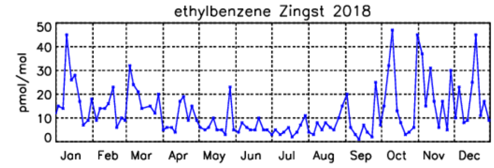

n−hexane Zingst 2018
pmol/mol
120
100
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

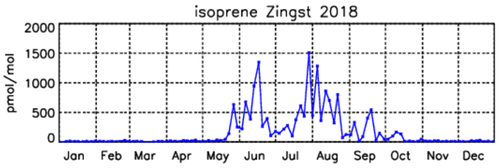

m−p−xylene Zingst 2018
pmol/mol
140
120
100
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

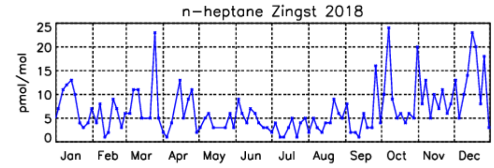

o−xylene Zingst 2018
pmol/mol
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

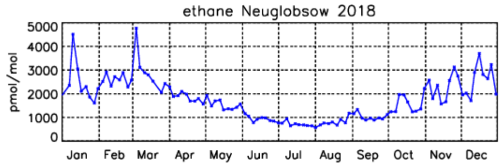

benzene Zingst 2018
pmol/mol
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

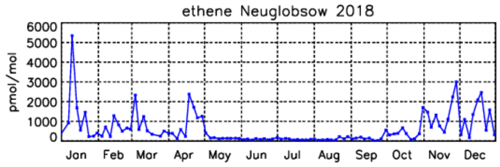

toluene Zingst 2018
pmol/mol
300
250
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

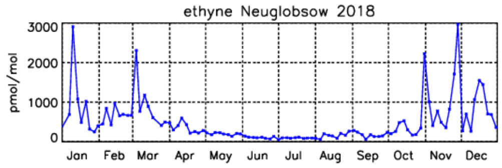

ethylbenzene Zingst 2018
pmol/mol
50
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

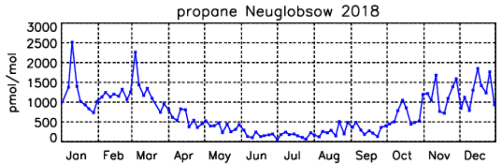

isoprene Zingst 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

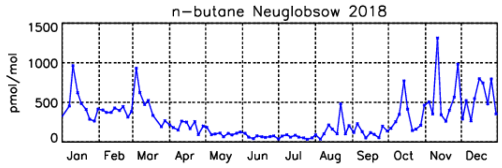

n−heptane Zingst 2018
pmol/mol
25
20
15
10
5
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

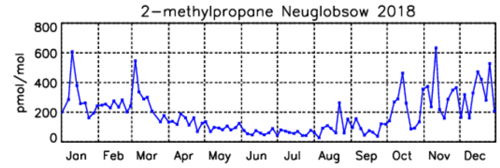

ethane Neuglobsow 2018
pmol/mol
5000
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

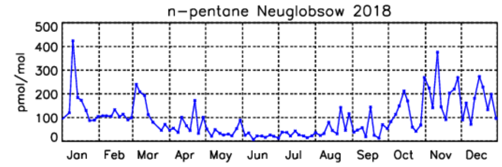

ethene Neuglobsow 2018
pmol/mol
6000
5000
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

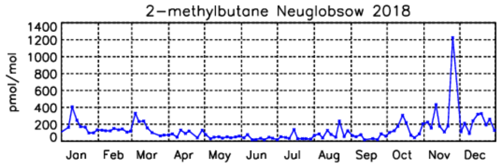

ethyne Neuglobsow 2018
pmol/mol
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

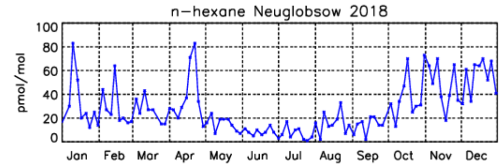

propane Neuglobsow 2018
pmol/mol
3000
2500
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

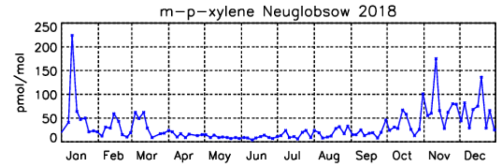

n−butane Neuglobsow 2018
pmol/mol
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

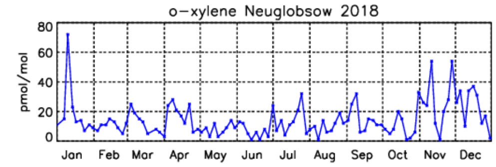

2−methylpropane Neuglobsow 2018
pmol/mol
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

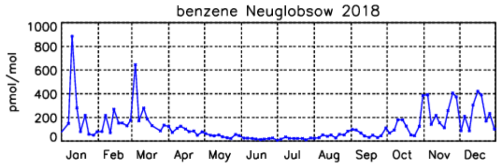

n−pentane Neuglobsow 2018
pmol/mol
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

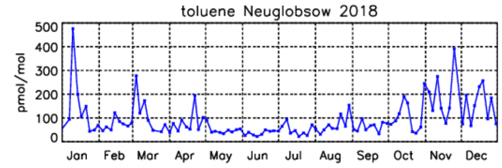

2−methylbutane Neuglobsow 2018
pmol/mol
1400
1200
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

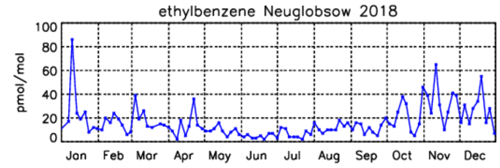

n−hexane Neuglobsow 2018
pmol/mol
100
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

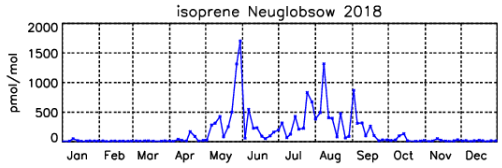

m−p−xylene Neuglobsow 2018
pmol/mol
250
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

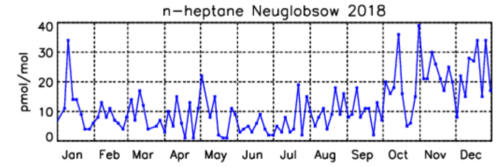

o−xylene Neuglobsow 2018
pmol/mol
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

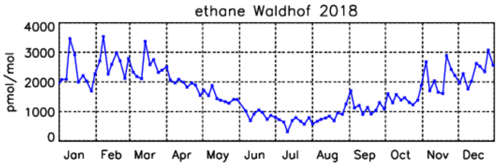

benzene Neuglobsow 2018
pmol/mol
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

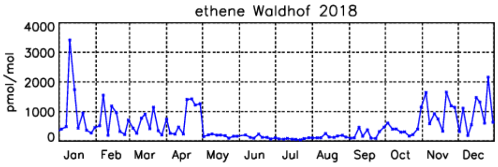

toluene Neuglobsow 2018
pmol/mol
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

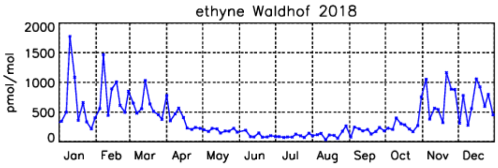

ethylbenzene Neuglobsow 2018
pmol/mol
100
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

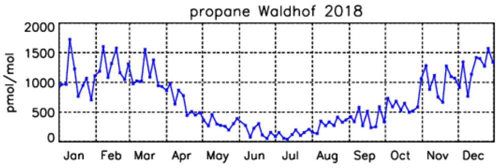

isoprene Neuglobsow 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

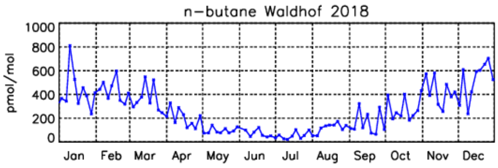

n−heptane Neuglobsow 2018
pmol/mol
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

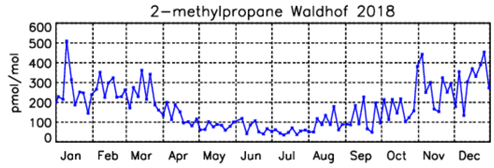

ethane Waldhof 2018
pmol/mol
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

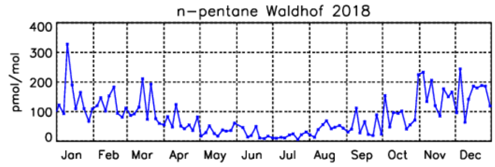

ethene Waldhof 2018
pmol/mol
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

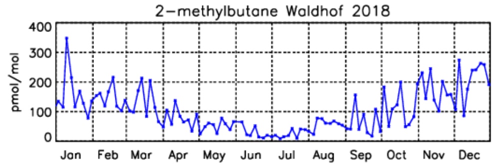

ethyne Waldhof 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

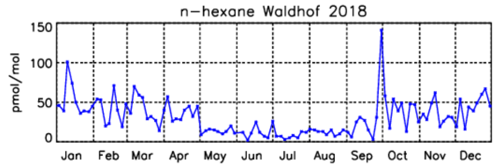

propane Waldhof 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

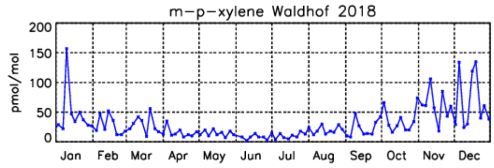

n–butane Waldhof 2018
pmol/mol
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

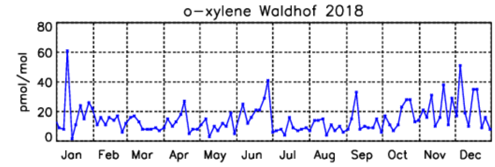

2–methylpropane Waldhof 2018
pmol/mol
600
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

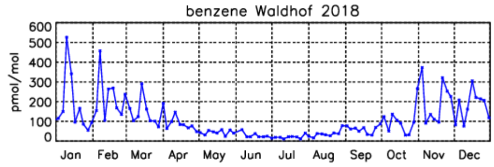

n–pentane Waldhof 2018
pmol/mol
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

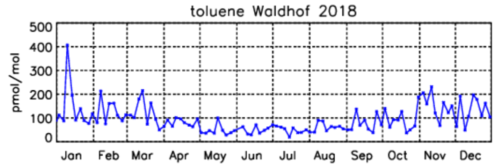

2–methylbutane Waldhof 2018
pmol/mol
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

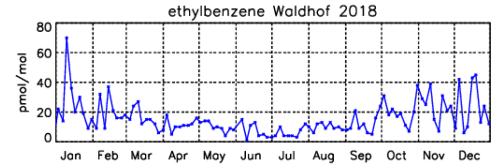

n–hexane Waldhof 2018
pmol/mol
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

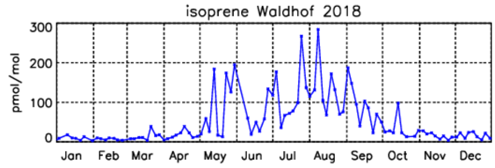

m–p–xylene Waldhof 2018
pmol/mol
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

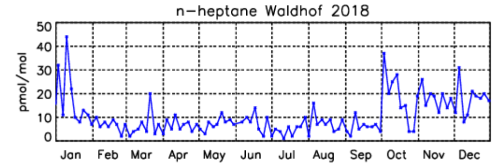

o–xylene Waldhof 2018
pmol/mol
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

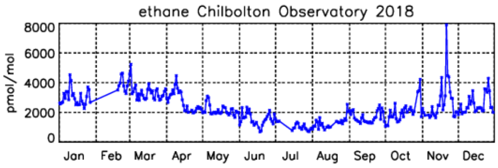

benzene Waldhof 2018
pmol/mol
600
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

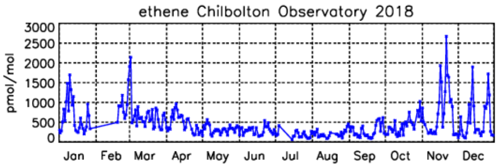

toluene Waldhof 2018
pmol/mol
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

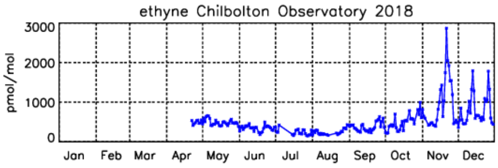

ethylbenzene Waldhof 2018
pmol/mol
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

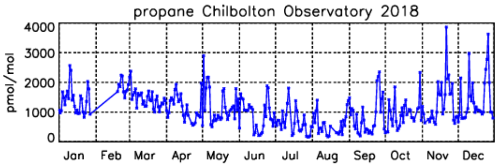

isoprene Waldhof 2018
pmol/mol
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

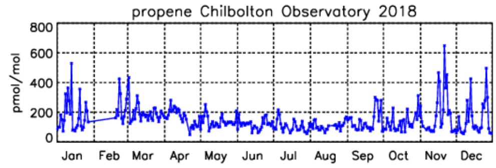

n–heptane Waldhof 2018
pmol/mol
50
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

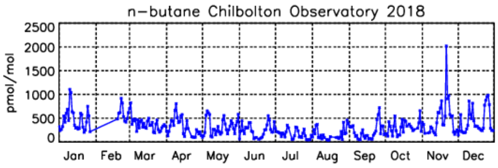

ethane Chilbolton Observatory 2018

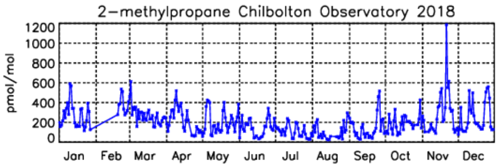

ethene Chilbolton Observatory 2018

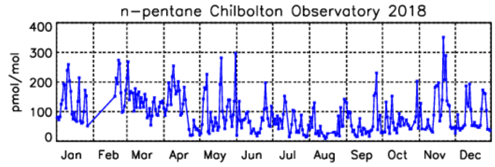

ethyne Chilbolton Observatory 2018

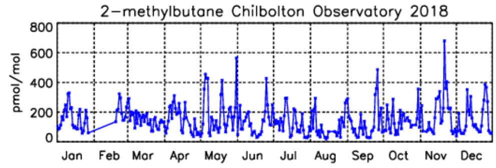

propane Chilbolton Observatory 2018

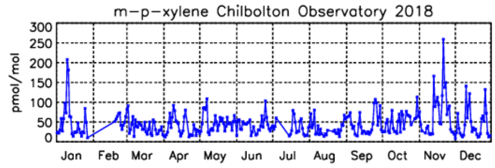

propene Chilbolton Observatory 2018

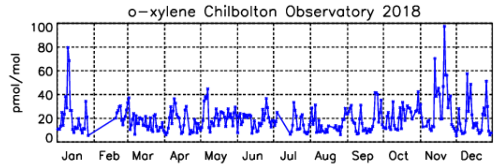

n−butane Chilbolton Observatory 2018

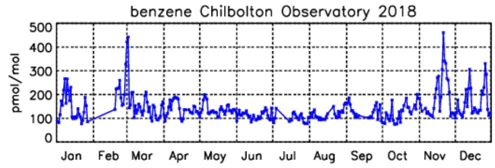

2−methylpropane Chilbolton Observatory 2018

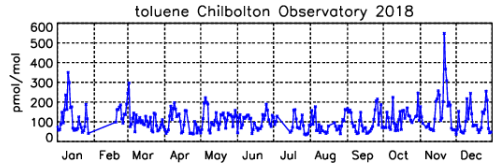

n−pentane Chilbolton Observatory 2018

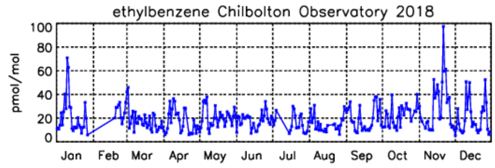

2−methylbutane Chilbolton Observatory 2018

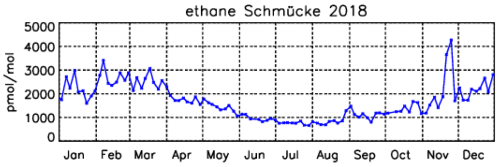

m−p−xylene Chilbolton Observatory 2018

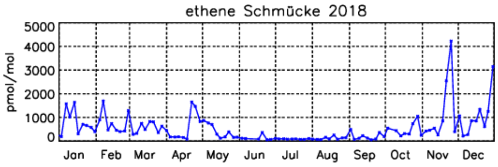

o−xylene Chilbolton Observatory 2018

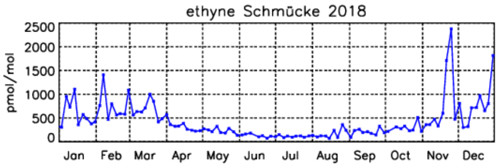

benzene Chilbolton Observatory 2018

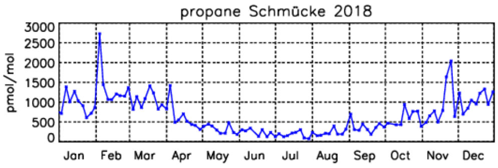

toluene Chilbolton Observatory 2018

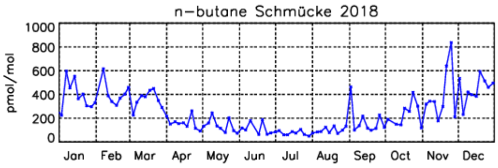

ethylbenzene Chilbolton Observatory 2018

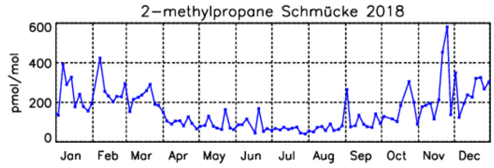

ethane Schmücke 2018

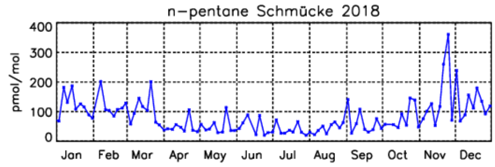

ethene Schmücke 2018

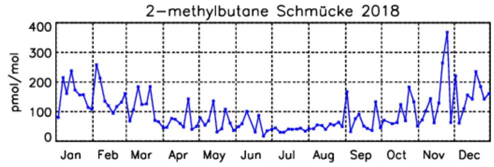

ethyne Schmücke 2018

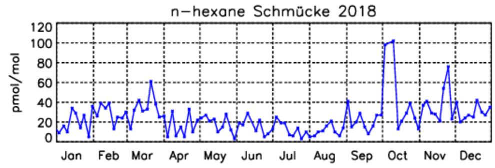

propane Schmücke 2018

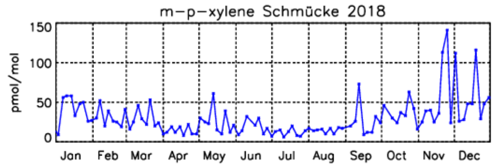

n−butane Schmücke 2018

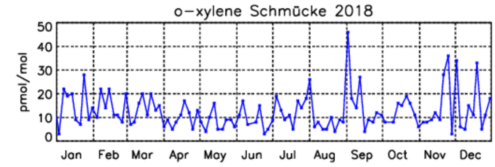

2−methylpropane Schmücke 2018

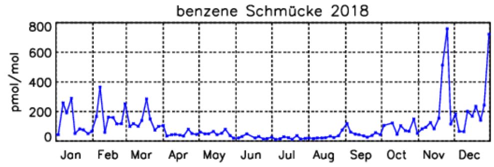

n−pentane Schmücke 2018

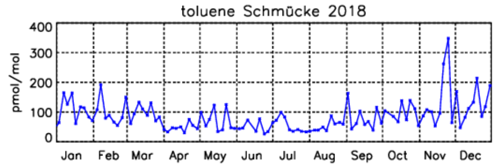

2−methylbutane Schmücke 2018

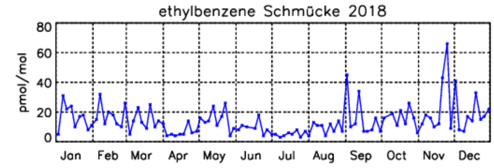

n−hexane Schmücke 2018

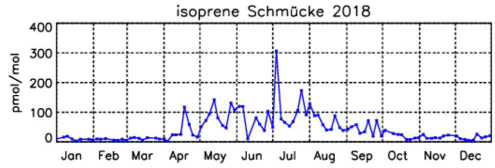

m−p−xylene Schmücke 2018

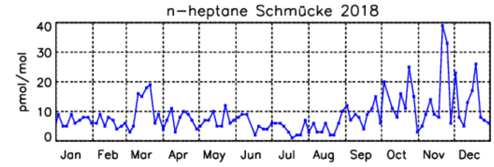

o−xylene Schmücke 2018

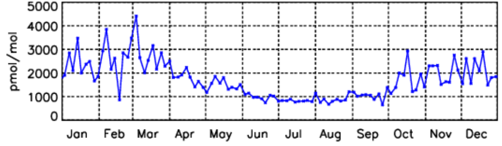

benzene Schmücke 2018

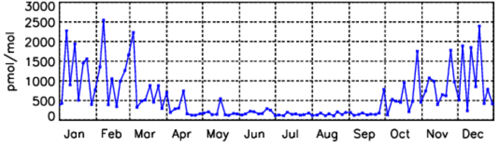

toluene Schmücke 2018

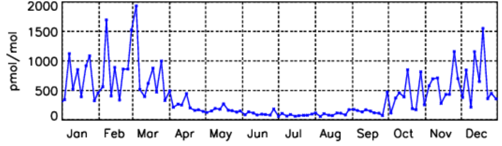

ethylbenzene Schmücke 2018

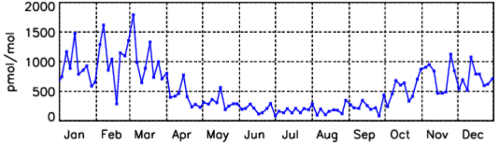

isoprene Schmücke 2018

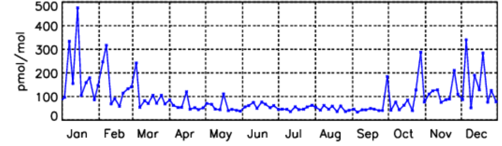

n−heptane Schmücke 2018

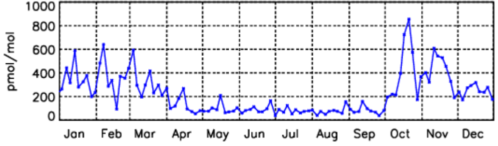

ethane Kosetice (NOAK) 2018

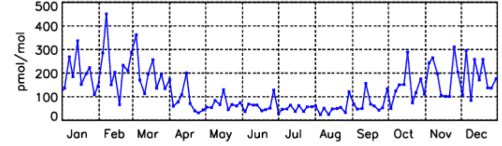

ethene Kosetice (NOAK) 2018

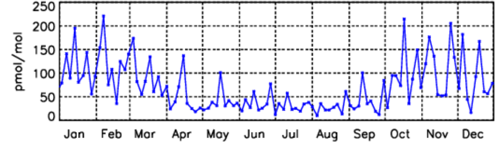

ethyne Kosetice (NOAK) 2018

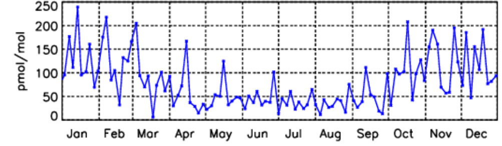

propane Kosetice (NOAK) 2018

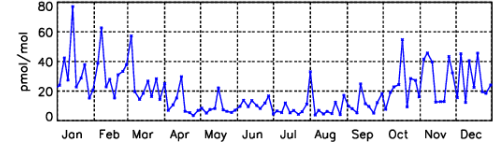

propene Kosetice (NOAK) 2018

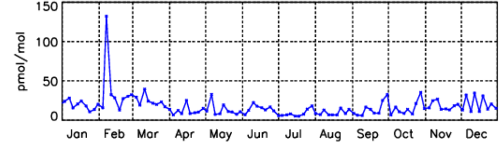

n–butane Kosetice (NOAK) 2018

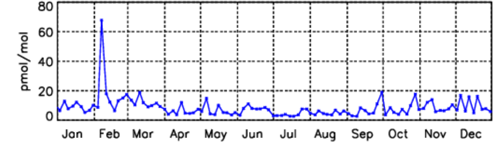

2–methylpropane Kosetice (NOAK) 2018

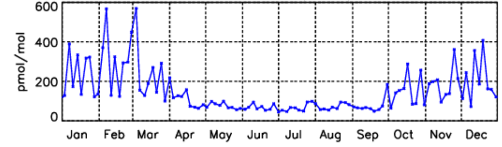

n–pentane Kosetice (NOAK) 2018

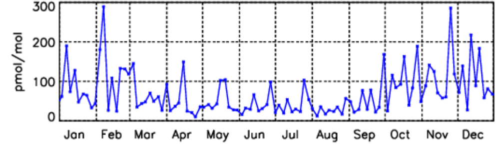

2–methylbutane Kosetice (NOAK) 2018

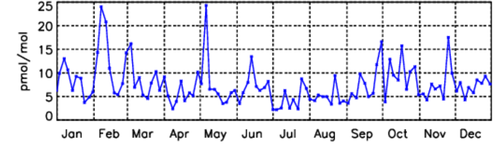

n–hexane Kosetice (NOAK) 2018

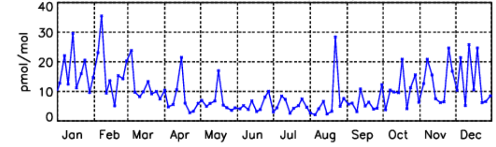

m–p–xylene Kosetice (NOAK) 2018

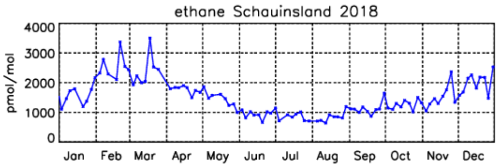

o–xylene Kosetice (NOAK) 2018

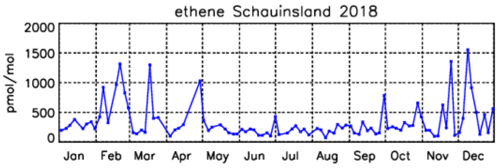

benzene Kosetice (NOAK) 2018

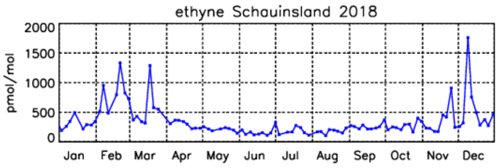

toluene Kosetice (NOAK) 2018

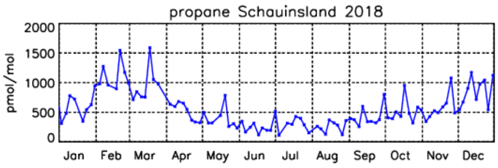

ethylbenzene Kosetice (NOAK) 2018

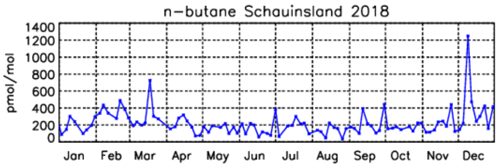

n–heptane Kosetice (NOAK) 2018

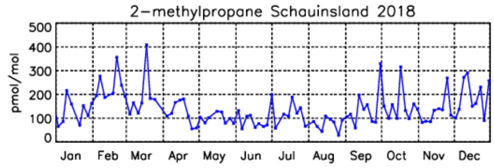

ethane Schauinsland 2018
pmol/mol
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

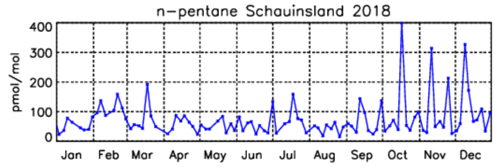

ethene Schauinsland 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

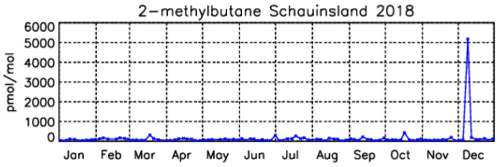

ethyne Schauinsland 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

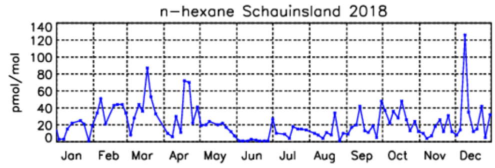

propane Schauinsland 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

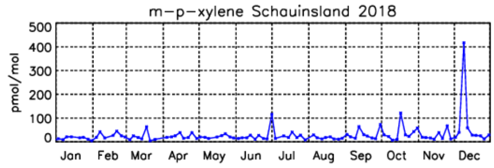

n−butane Schauinsland 2018
pmol/mol
1400
1200
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

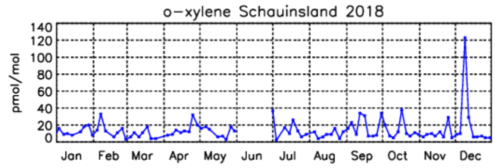

2−methylpropane Schauinsland 2018
pmol/mol
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

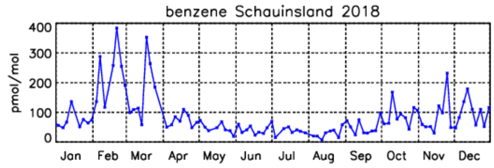

n−pentane Schauinsland 2018
pmol/mol
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

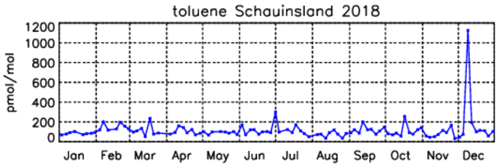

2−methylbutane Schauinsland 2018
pmol/mol
6000
5000
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

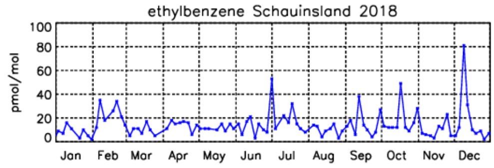

n−hexane Schauinsland 2018
pmol/mol
140
120
100
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

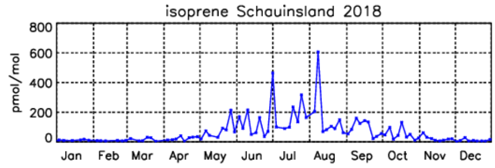

m−p−xylene Schauinsland 2018
pmol/mol
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

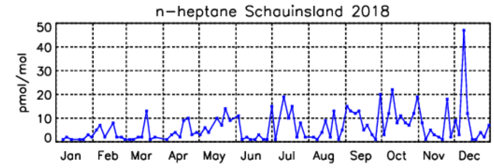

o−xylene Schauinsland 2018
pmol/mol
140
120
100
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

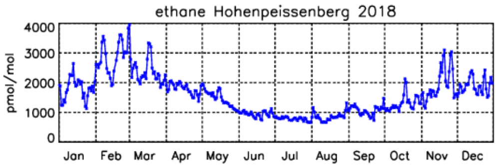

benzene Schauinsland 2018
pmol/mol
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

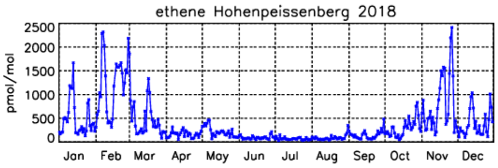

toluene Schauinsland 2018
pmol/mol
1200
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

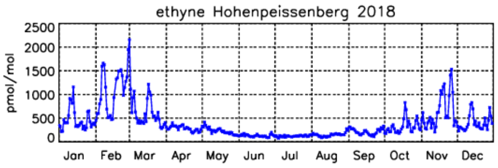

ethylbenzene Schauinsland 2018
pmol/mol
100
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

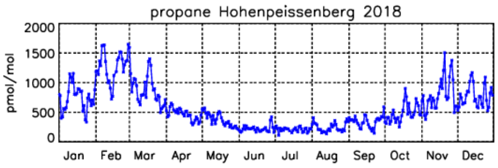

isoprene Schauinsland 2018
pmol/mol
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

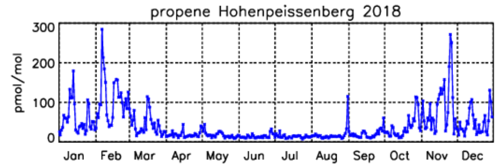

n−heptane Schauinsland 2018
pmol/mol
50
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

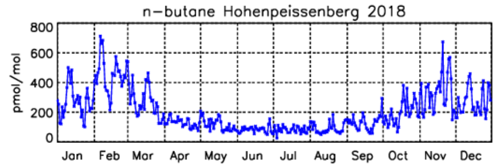

ethane Hohenpeissenberg 2018
pmol/mol
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

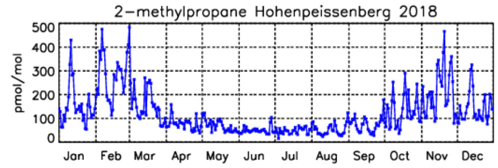

ethene Hohenpeissenberg 2018
pmol/mol
2500
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

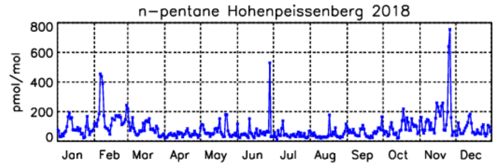

ethyne Hohenpeissenberg 2018
pmol/mol
2500
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

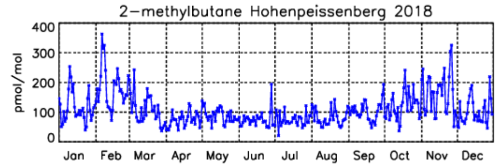

propane Hohenpeissenberg 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

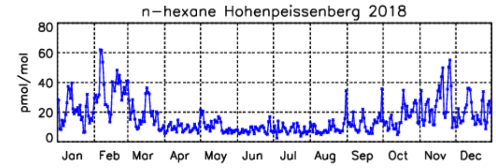

propene Hohenpeissenberg 2018
pmol/mol
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

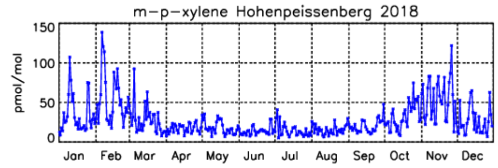

n−butane Hohenpeissenberg 2018
pmol/mol
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

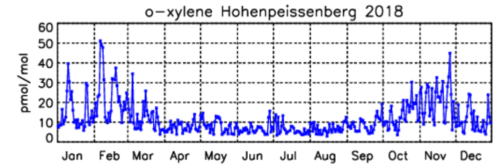

2−methylpropane Hohenpeissenberg 2018
pmol/mol
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

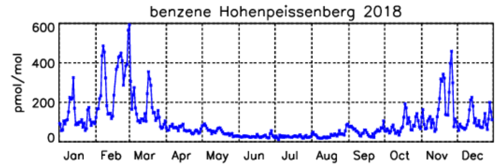

n−pentane Hohenpeissenberg 2018
pmol/mol
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

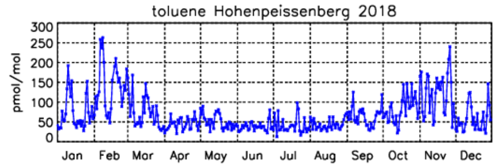

2−methylbutane Hohenpeissenberg 2018
pmol/mol
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

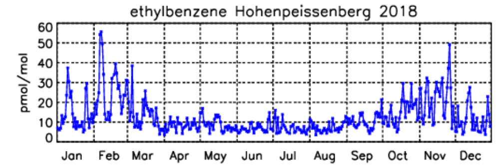

n−hexane Hohenpeissenberg 2018
pmol/mol
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

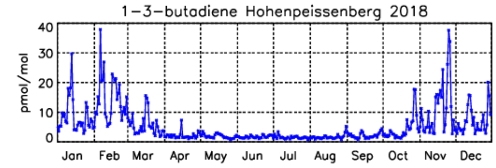

m−p−xylene Hohenpeissenberg 2018
pmol/mol
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

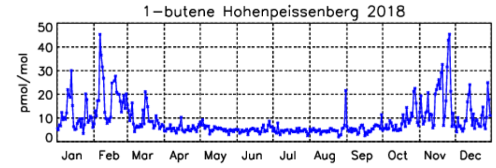

o−xylene Hohenpeissenberg 2018
pmol/mol
60
50
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

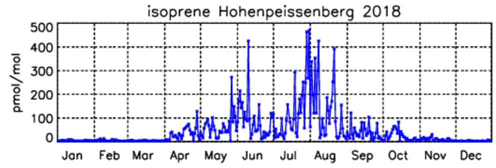

benzene Hohenpeissenberg 2018
pmol/mol
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

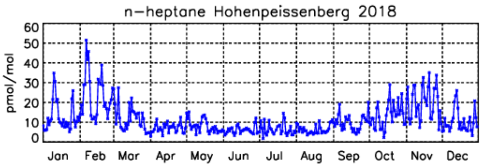

toluene Hohenpeissenberg 2018
pmol/mol
300
250
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

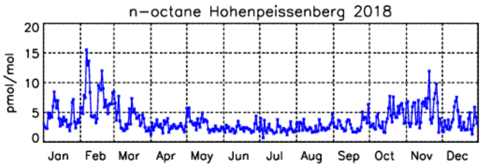

ethylbenzene Hohenpeissenberg 2018
pmol/mol
60
50
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

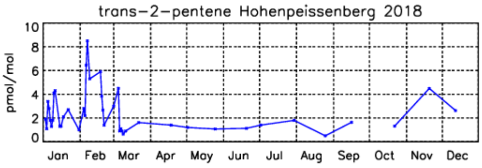

1−3−butadiene Hohenpeissenberg 2018
pmol/mol
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

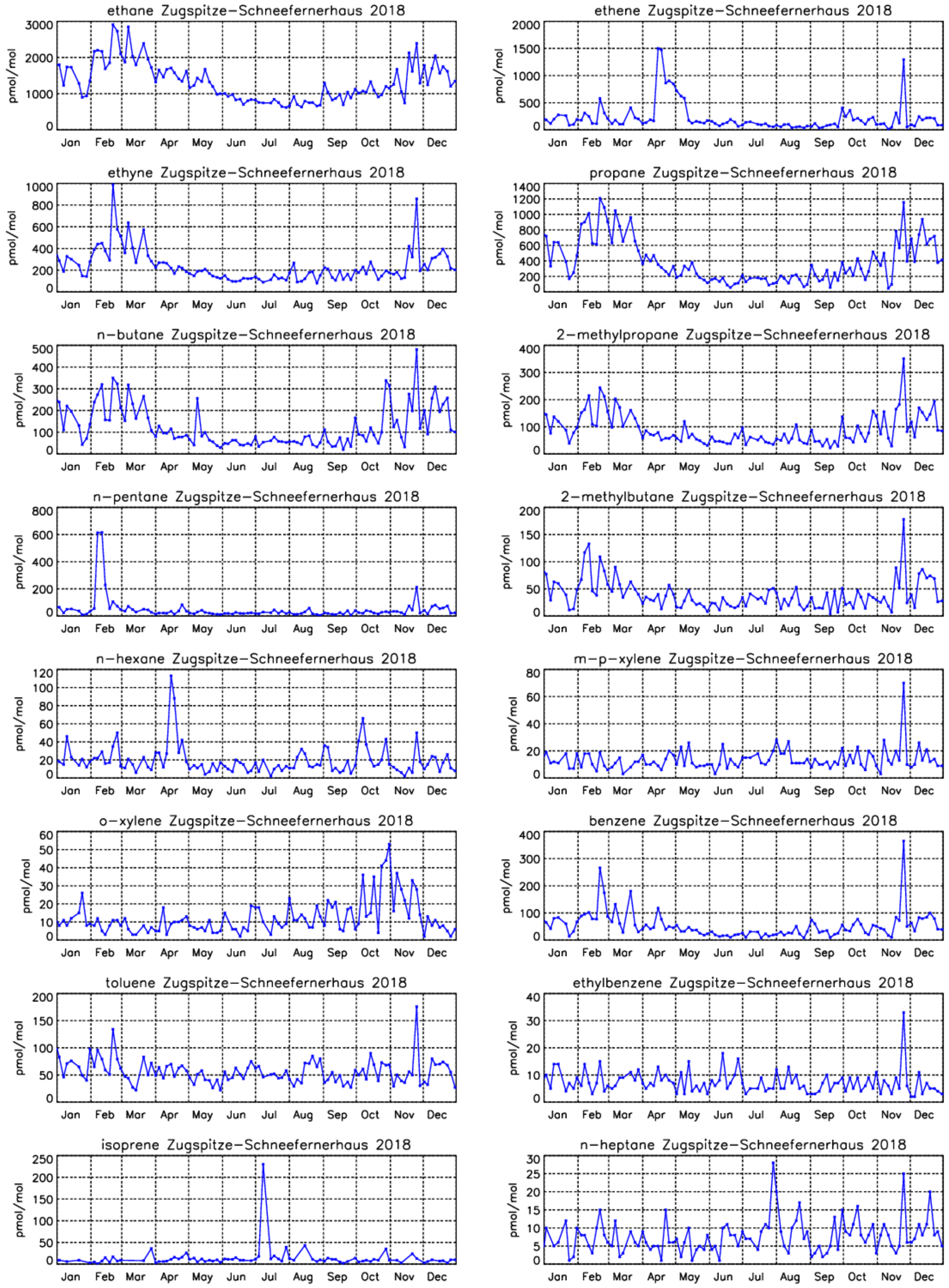

1−butene Hohenpeissenberg 2018
pmol/mol
50
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

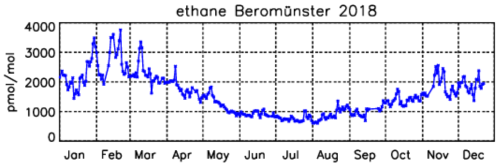

isoprene Hohenpeissenberg 2018
pmol/mol
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

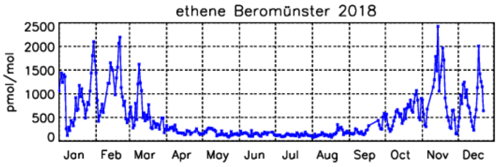

n−heptane Hohenpeissenberg 2018
pmol/mol
0
10
20
30
40
50
60
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

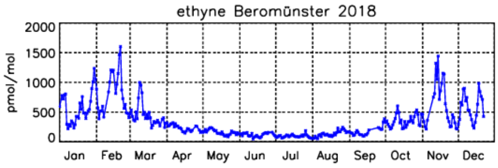

n−octane Hohenpeissenberg 2018
pmol/mol
0
5
10
15
20
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

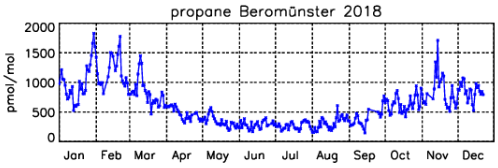

trans−2−pentene Hohenpeissenberg 2018
pmol/mol
0
2
4
6
8
10
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

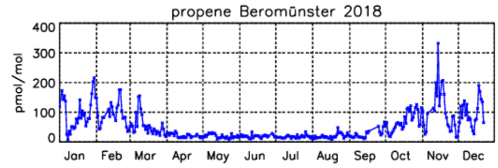

ethane Zugspitze−Schneefernerhaus 2018
pmol/mol
0
1000
2000
3000
ethene Zugspitze−Schneefernerhaus 2018
0
500
1000
1500
2000
ethyne Zugspitze−Schneefernerhaus 2018
0
200
400
600
800
1000
propane Zugspitze−Schneefernerhaus 2018
0
200
400
600
800
1000
1200
1400
n−butane Zugspitze−Schneefernerhaus 2018
0
100
200
300
400
500
2−methylpropane Zugspitze−Schneefernerhaus 2018
0
100
200
300
400
n−pentane Zugspitze−Schneefernerhaus 2018
0
200
400
600
800
2−methylbutane Zugspitze−Schneefernerhaus 2018
0
50
100
150
200
n−hexane Zugspitze−Schneefernerhaus 2018
0
20
40
60
80
100
120
m−p−xylene Zugspitze−Schneefernerhaus 2018
0
20
40
60
80
o−xylene Zugspitze−Schneefernerhaus 2018
0
10
20
30
40
50
60
benzene Zugspitze−Schneefernerhaus 2018
0
100
200
300
400
toluene Zugspitze−Schneefernerhaus 2018
0
50
100
150
200
ethylbenzene Zugspitze−Schneefernerhaus 2018
0
10
20
30
40
isoprene Zugspitze−Schneefernerhaus 2018
0
50
100
150
200
250
n−heptane Zugspitze−Schneefernerhaus 2018
0
5
10
15
20
25
30
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

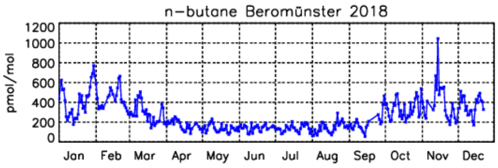

ethane Beromünster 2018
pmol/mol
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

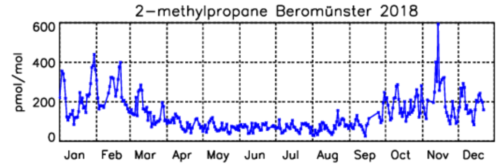

ethene Beromünster 2018
pmol/mol
2500
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

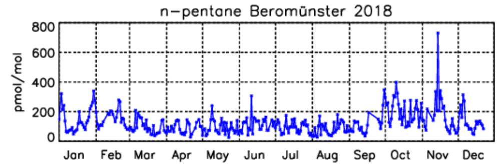

ethyne Beromünster 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

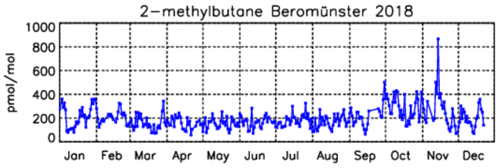

propane Beromünster 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

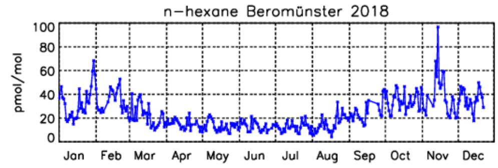

propene Beromünster 2018
pmol/mol
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

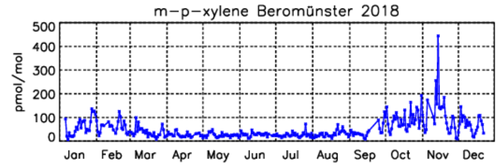

n−butane Beromünster 2018
pmol/mol
1200
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

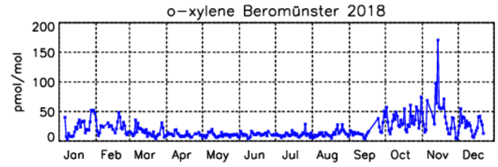

2−methylpropane Beromünster 2018
pmol/mol
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

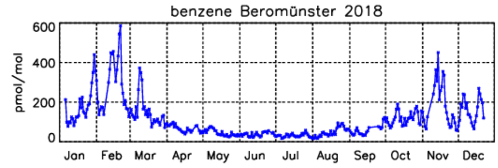

n−pentane Beromünster 2018
pmol/mol
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

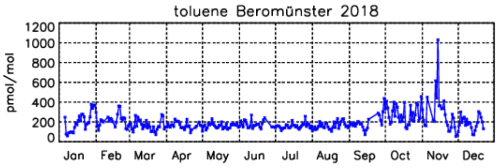

2−methylbutane Beromünster 2018
pmol/mol
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

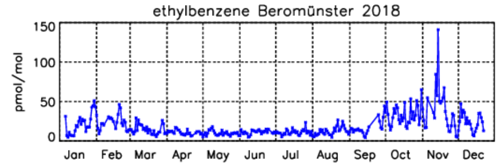

n−hexane Beromünster 2018
pmol/mol
100
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

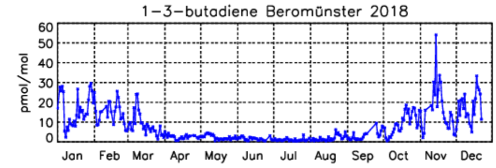

m−p−xylene Beromünster 2018
pmol/mol
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

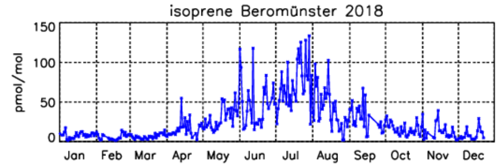

o−xylene Beromünster 2018
pmol/mol
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

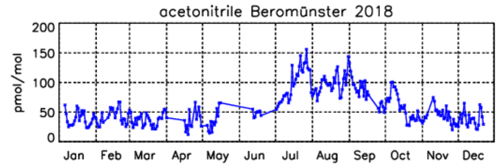

benzene Beromünster 2018
pmol/mol
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

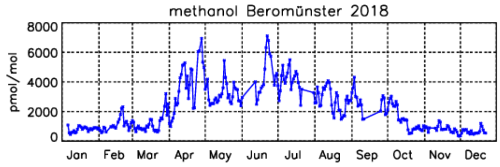

toluene Beromünster 2018
pmol/mol
1200
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

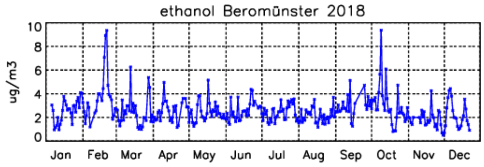

ethylbenzene Beromünster 2018
pmol/mol
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

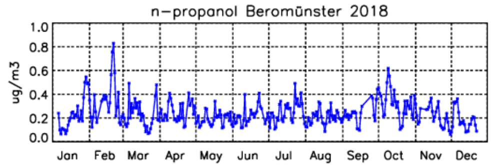

1−3−butadiene Beromünster 2018
pmol/mol
60
50
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

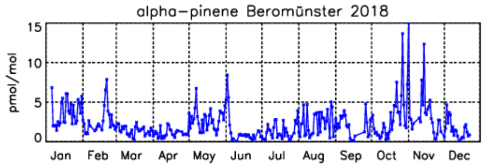

isoprene Beromünster 2018
pmol/mol
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

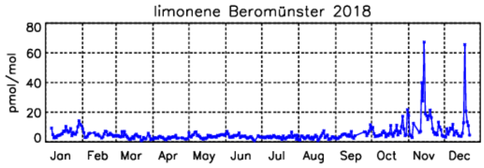

acetonitrile Beromünster 2018
pmol/mol
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

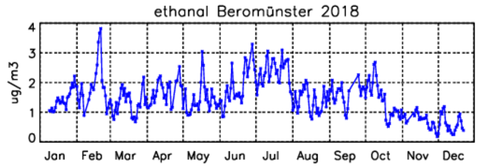

methanol Beromünster 2018
pmol/mol
8000
6000
4000
2000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

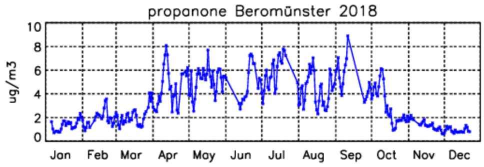

ethanol Beromünster 2018
ug/m3
10
8
6
4
2
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

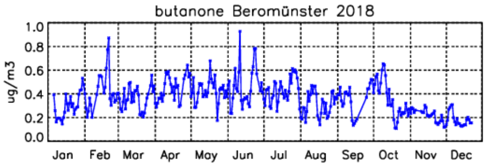

n−propanol Beromünster 2018
ug/m3
1.0
0.8
0.6
0.4
0.2
0.0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec


alpha−pinene Beromünster 2018
pmol/mol
15
10
5
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

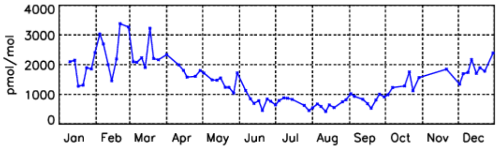

limonene Beromünster 2018
pmol/mol
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec


ethanal Beromünster 2018
ug/m3
4
3
2
1
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

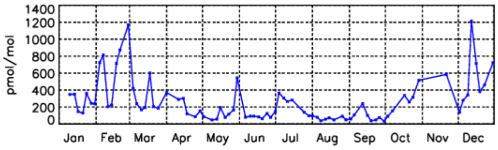

propanone Beromünster 2018
ug/m3
10
8
6
4
2
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec


butanone Beromünster 2018
ug/m3
1.0
0.8
0.6
0.4
0.2
0.0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

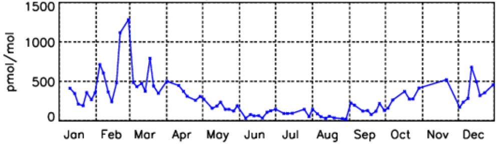
ethane La Tardière 2018



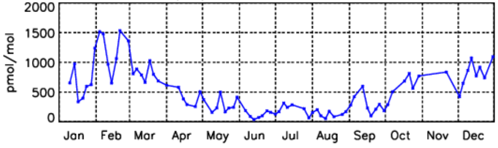
ethene La Tardière 2018



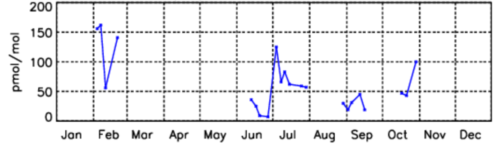
ethyne La Tardière 2018



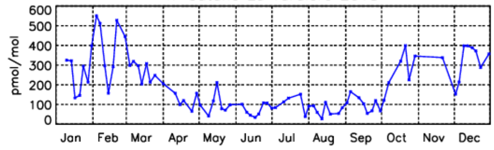
propane La Tardière 2018



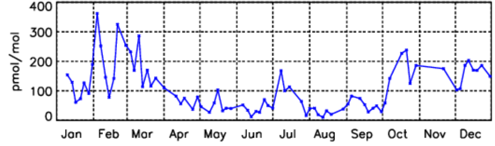
propene La Tardière 2018



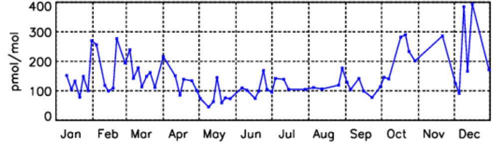
n−butane La Tardière 2018



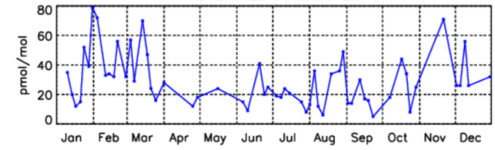
2−methylpropane La Tardière 2018



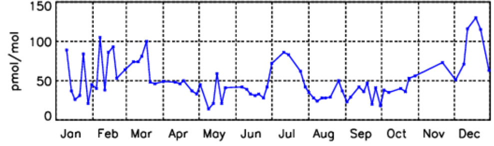
2−methylbutane La Tardière 2018



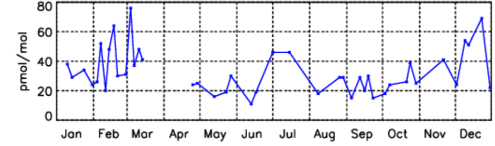
n−hexane La Tardière 2018



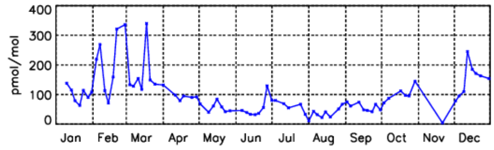
m−p−xylene La Tardière 2018



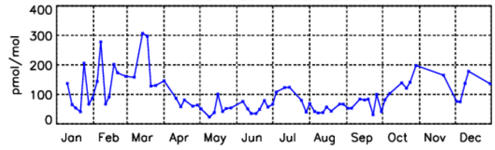
o−xylene La Tardière 2018



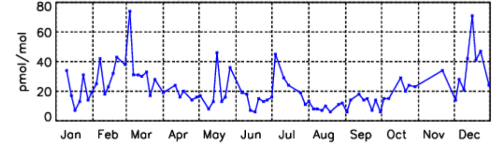
benzene La Tardière 2018



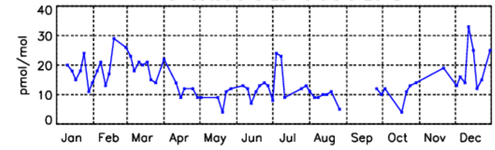
toluene La Tardière 2018



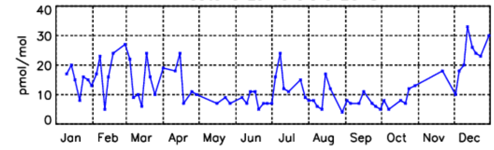
ethylbenzene La Tardière 2018



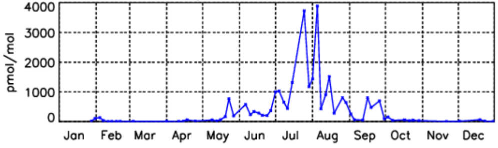
1−3−butadiene La Tardière 2018



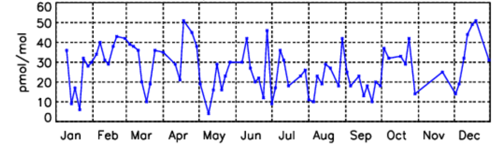
1−butene La Tardière 2018

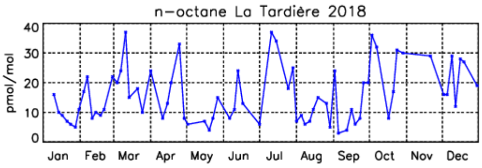


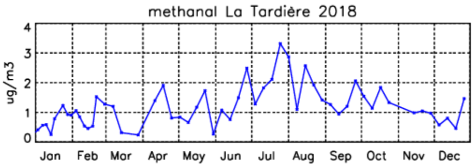
isoprene La Tardière 2018

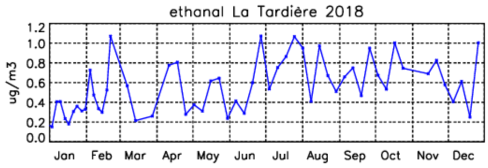


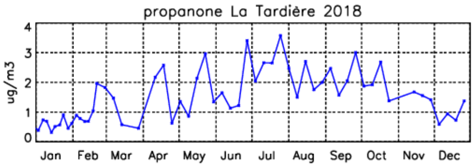
n−heptane La Tardière 2018

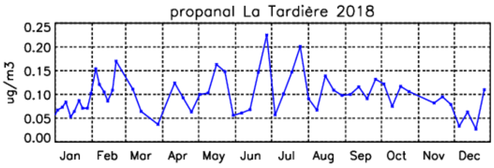


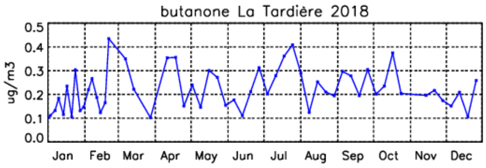

n–octane La Tardière 2018
pmol/mol
0
10
20
30
40
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

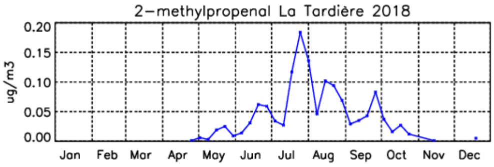

methanal La Tardière 2018
ug/m3
0
1
2
3
4
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

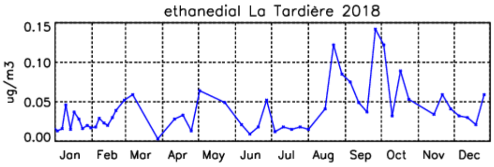

ethanal La Tardière 2018
ug/m3
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

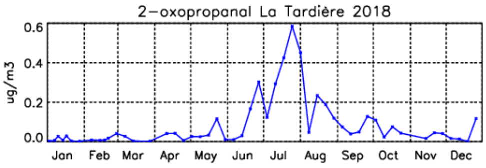

propanone La Tardière 2018
ug/m3
0
1
2
3
4
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

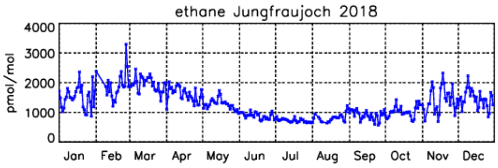

propanal La Tardière 2018
ug/m3
0.00
0.05
0.10
0.15
0.20
0.25
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

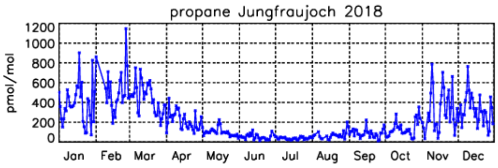

butanone La Tardière 2018
ug/m3
0.0
0.1
0.2
0.3
0.4
0.5
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

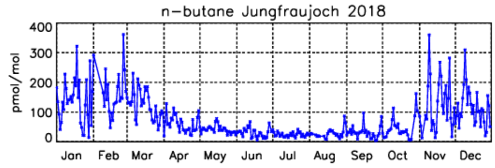

2–methylpropenal La Tardière 2018
ug/m3
0.00
0.05
0.10
0.15
0.20
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

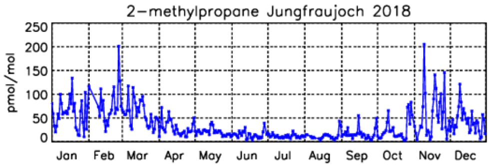

ethanedial La Tardière 2018
ug/m3
0.00
0.05
0.10
0.15
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

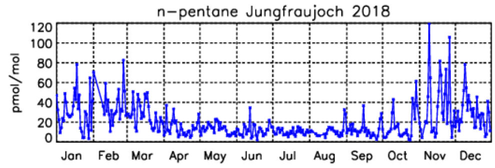

2–oxopropanal La Tardière 2018
ug/m3
0.0
0.2
0.4
0.6
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

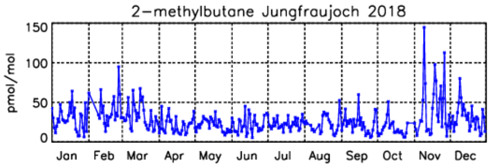

ethane Jungfraujoch 2018
pmol/mol
4000
3000
2000
1000
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

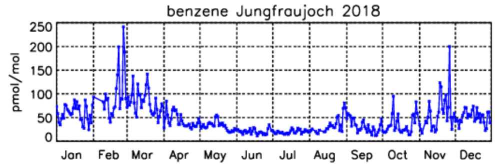

propane Jungfraujoch 2018
pmol/mol
1200
1000
800
600
400
200
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

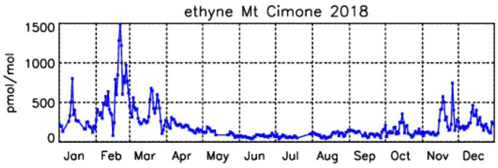

n–butane Jungfraujoch 2018
pmol/mol
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

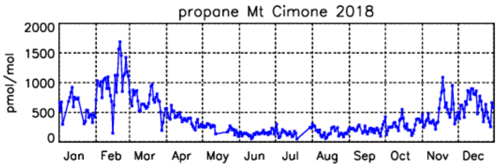

2–methylpropane Jungfraujoch 2018
pmol/mol
250
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

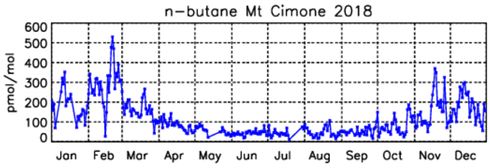

n–pentane Jungfraujoch 2018
pmol/mol
120
100
80
60
40
20
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

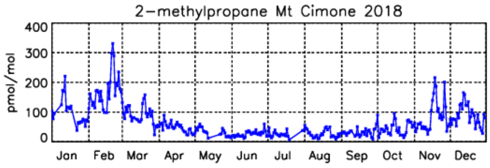

2–methylbutane Jungfraujoch 2018
pmol/mol
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

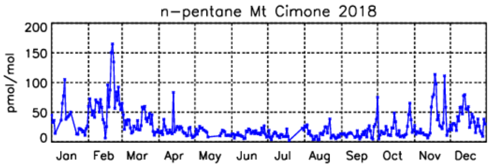

benzene Jungfraujoch 2018
pmol/mol
250
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

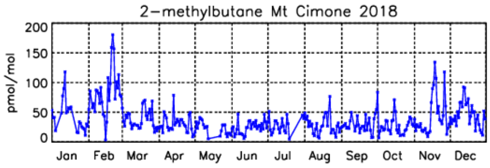

ethyne Mt Cimone 2018
pmol/mol
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

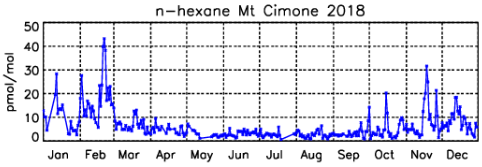

propane Mt Cimone 2018
pmol/mol
2000
1500
1000
500
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

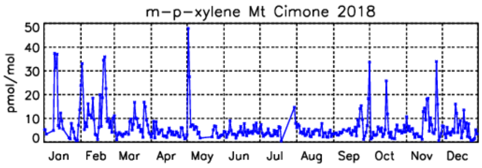

n−butane Mt Cimone 2018
pmol/mol
600
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

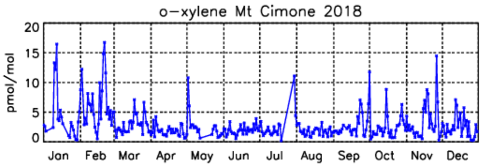

2−methylpropane Mt Cimone 2018
pmol/mol
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

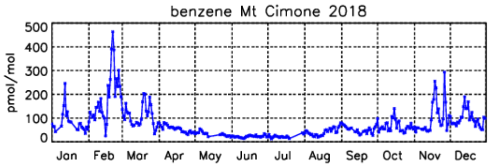

n−pentane Mt Cimone 2018
pmol/mol
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

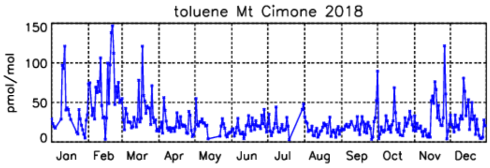

2−methylbutane Mt Cimone 2018
pmol/mol
200
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

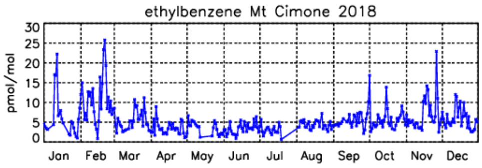

n−hexane Mt Cimone 2018
pmol/mol
50
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

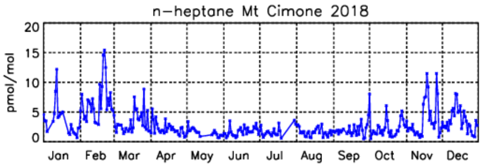

m−p−xylene Mt Cimone 2018
pmol/mol
50
40
30
20
10
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

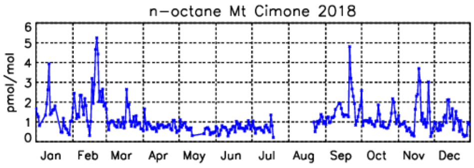

o−xylene Mt Cimone 2018
pmol/mol
20
15
10
5
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

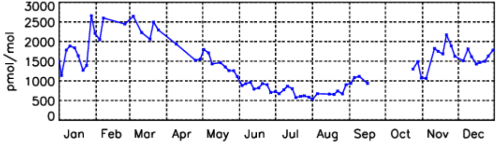

benzene Mt Cimone 2018
pmol/mol
500
400
300
200
100
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

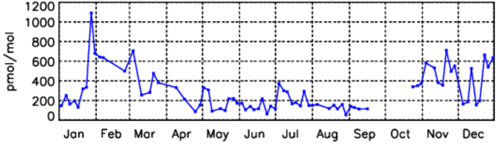

toluene Mt Cimone 2018
pmol/mol
150
100
50
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

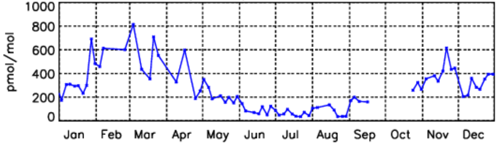

ethylbenzene Mt Cimone 2018
pmol/mol
30
25
20
15
10
5
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

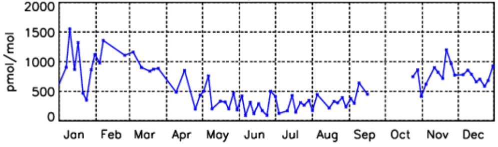

n−heptane Mt Cimone 2018
pmol/mol
20
15
10
5
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

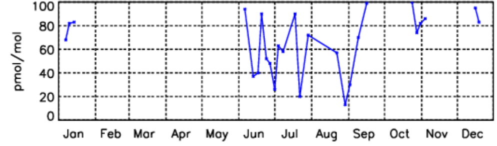

n−octane Mt Cimone 2018
pmol/mol
6
5
4
3
2
1
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

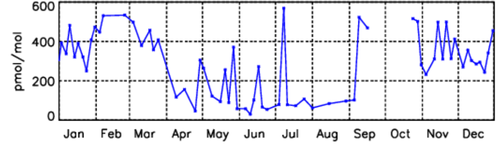

ethane Peyrusse Vieille 2018

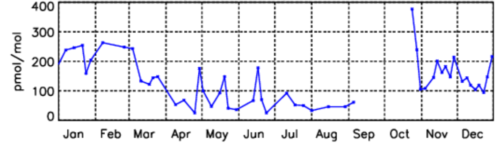

ethene Peyrusse Vieille 2018

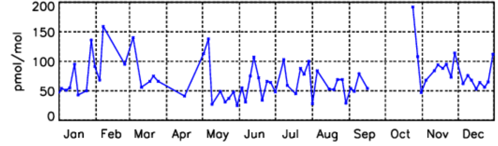

ethyne Peyrusse Vieille 2018

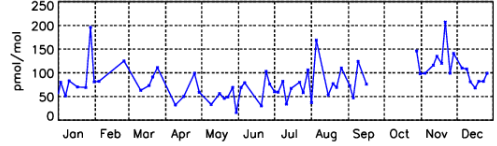

propane Peyrusse Vieille 2018

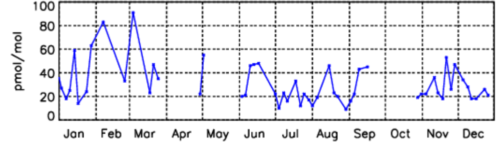

propene Peyrusse Vieille 2018

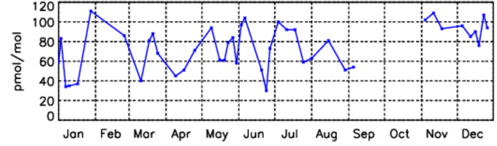

n–butane Peyrusse Vieille 2018

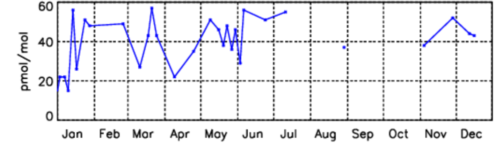

2–methylpropane Peyrusse Vieille 2018

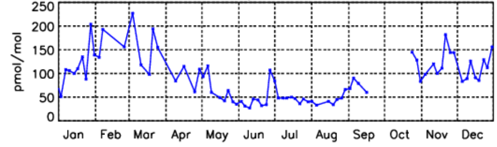

n–pentane Peyrusse Vieille 2018

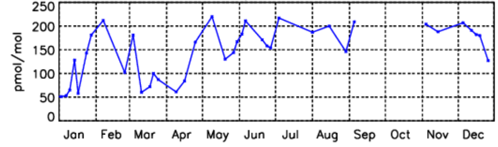

2–methylbutane Peyrusse Vieille 2018

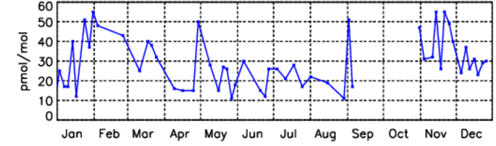

n–hexane Peyrusse Vieille 2018

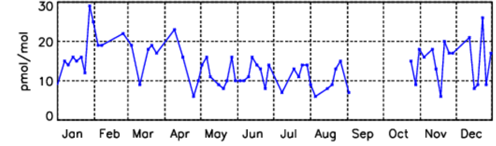

m–p–xylene Peyrusse Vieille 2018

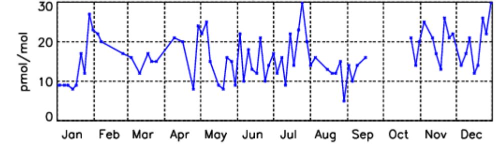

o–xylene Peyrusse Vieille 2018

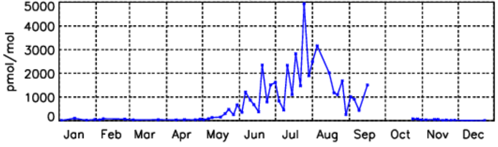

benzene Peyrusse Vieille 2018

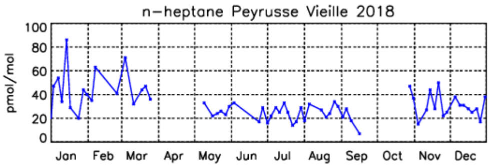

toluene Peyrusse Vieille 2018

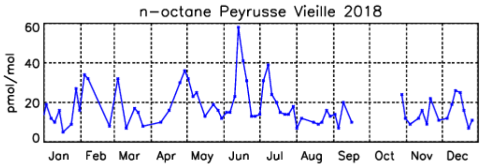

ethylbenzene Peyrusse Vieille 2018

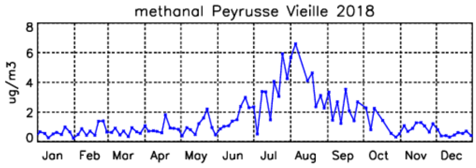

1–3–butadiene Peyrusse Vieille 2018

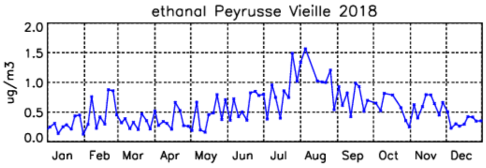

1–butene Peyrusse Vieille 2018

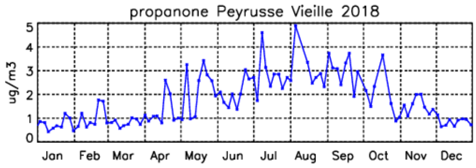

isoprene Peyrusse Vieille 2018

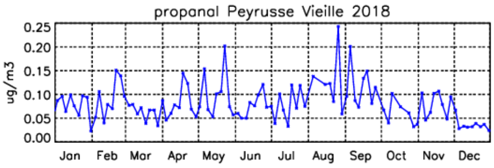

n−heptane Peyrusse Vieille 2018

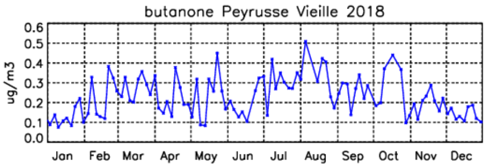

n−octane Peyrusse Vieille 2018

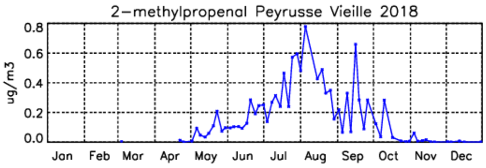

methanal Peyrusse Vieille 2018

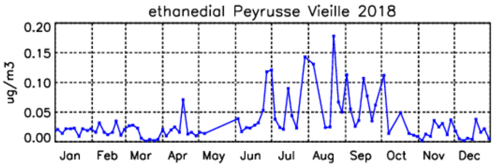

ethanal Peyrusse Vieille 2018

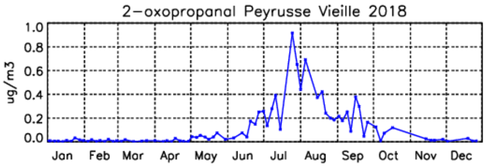

propanone Peyrusse Vieille 2018

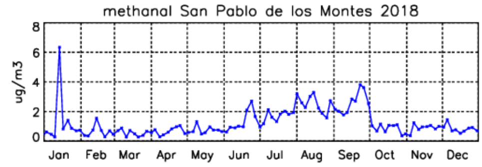

propanal Peyrusse Vieille 2018

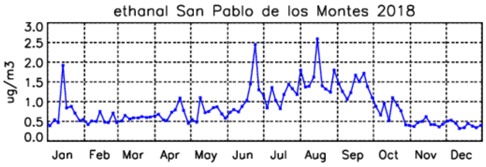

butanone Peyrusse Vieille 2018

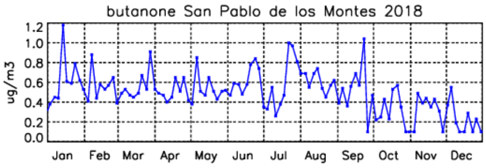

2−methylpropenal Peyrusse Vieille 2018

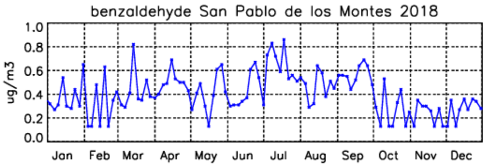

ethanedial Peyrusse Vieille 2018

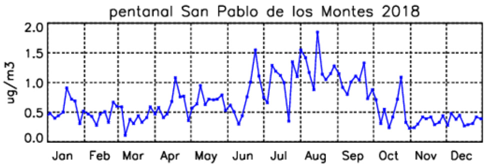

2−oxopropanal Peyrusse Vieille 2018

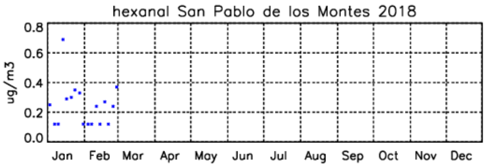

methanal San Pablo de los Montes 2018


ethanal San Pablo de los Montes 2018


butanone San Pablo de los Montes 2018


benzaldehyde San Pablo de los Montes 2018


pentanal San Pablo de los Montes 2018


hexanal San Pablo de los Montes 2018