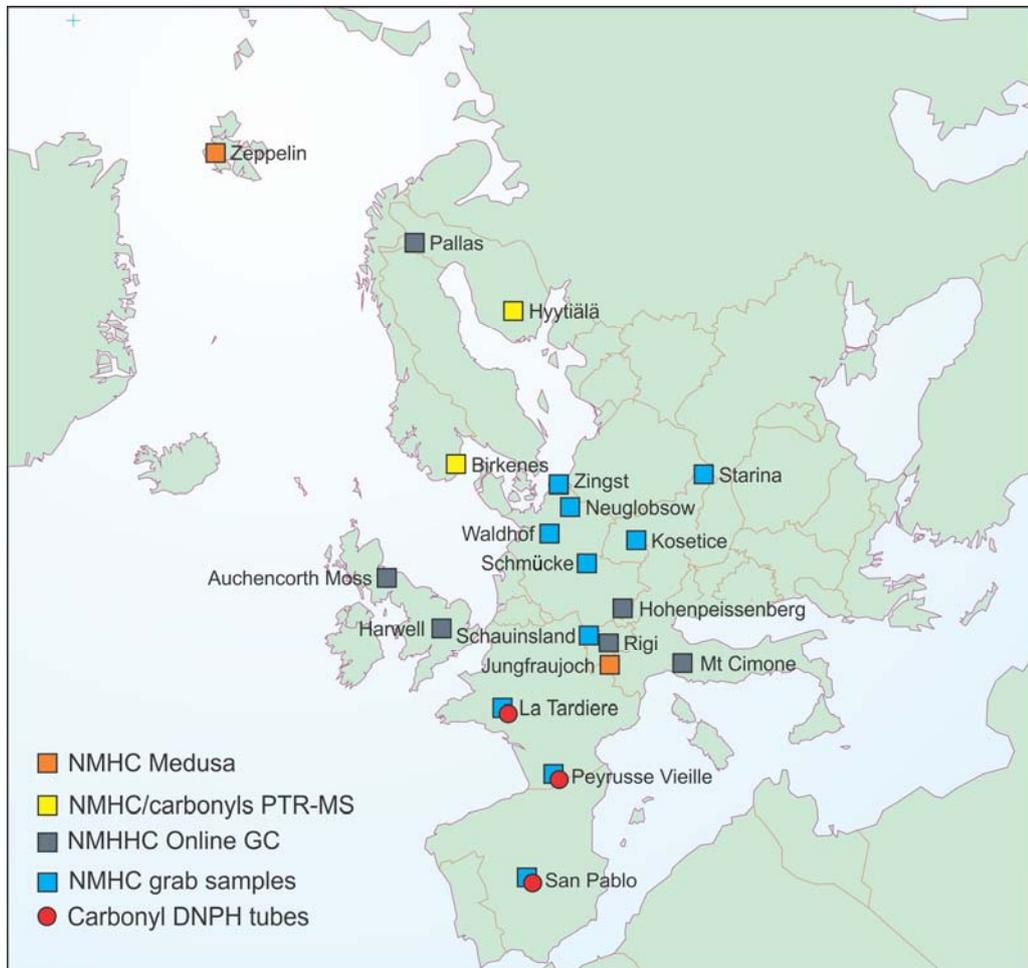


VOC measurements 2012 - 2013

Sverre Solberg, Corinne Hörger, Anja Claude, Christian Plass-Dülmer, Stefan Reimann, Stéphane Sauvage



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

VOC measurements 2012 - 2013

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Christian Plass-Dülmer, Stefan Reimann, Stéphane Sauvage**



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Summary

This report presents VOC measurements carried out during 2012-2013 at EMEP monitoring sites. Such monitoring was carried out at 20 EMEP sites these two years. The VOC monitoring has become more and more diverse with time. Starting in the early 1990s with standardized methods based on manual sampling in steel canisters for NMHCs and collection in DNPH tubes for carbonyls with subsequent lab analyses, the methods now consist of a variety of instruments and measurement principles, including both automated continuous monitors and manual flask samples.

The reported EMEP VOC data for the winter half year 2012-2013 show generally highest concentration levels in central Europe and lower levels in the north and at high mountain sites. Downward trends in the long-term measured concentrations of NMHC are documented in many regions except for ethane and propane showing relatively stable levels. For Northern Finland, however, the long-term data indicate significant declines only in ethyne, reflecting stronger source influence from eastern parts.

Within the EU FP7 infrastructure project ACTRIS which ended in 2015, data quality issues related to measurements of VOCs were important topics. 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. Many of the institutions providing VOC data to EMEP participated in the ACTRIS project, and also in a round-robin intercomparison for NMHC.

The intercomparison showed the best results for a gas mixture in N₂ whereas the results were clearly poorer for a whole air sample. C₄-C₅ alkenes and C₇-C₈ species (alkanes and aromats) turned out to be the most problematic species to measure. For all species/laboratories, almost 62 % of the results from the N₂ 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.

VOC measurements 2012 - 2013

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.

The measurements of VOC within EMEP started with the collection of grab samples of light hydrocarbons in the middle of 1992 and measurements of carbonyls in 1993. In the beginning five stations were included in the monitoring programme, Rucava (LV10), Košetice (CZ03), Waldhof (DE02), Tänikon (CH32) and Donon (FR08). Since then the number and selection of VOC measurement sites have changed several times.

The EMEP VOC measurements are reported annually, and officially made public by the Steering Body of EMEP. 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). Highlights and findings from the EMEP VOC programme have also been presented in a number of scientific papers (Lindskog et al., 1995; Solberg et al., 1996; Hov et al., 1997; Solberg et al., 2001; Borbon et al., 2004; Hakola et al., 2006).

In 2014 no EMEP data report was published for VOCs for various reasons: The release of a new EMEP data base in May 2014 combined with extensive on-going quality assurance work within ACTRIS for the VOC monitoring data from 2012 made it impossible to report the data at that stage. Thus, the present report documents the VOC measurements from both years, 2012-2013.

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: sulphur, 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 sulphur 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 limit values 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. A main 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. Harmonisation 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. 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. These compounds would be of interest to include in the EMEP monitoring as well, but require other sampling methods and instrumentations than presently used for the hydrocarbons and carbonyls.

In the new EMEP Monitoring Strategy for 2010-2019 (ECE/EB.AIR/GE.1/2009/15), which hydrocarbons and carbonyls to measure have not been specified, but it is clearly stated that it is necessary to harmonise 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. The project lasted from 1 April 2011 to 31 March 2015 and included a large number of partners with experience in VOC monitoring, including most of the 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.

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

	EMEP required	EMEP desirable	GAW priority ¹		ACTRIS priority ²	
			accuracy	precision	uncert.	repeat.
Alkanes						
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%		
Acetaldehyde	X					
Propionaldehyde		X				
Acetone	X		20%	15%		
Methylethylketone		X				
Methylvinylketone		X				
Other						
Monoterpenes			20%	15%		
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 2012-2013

As mentioned in the introduction, no EMEP VOC data report was published in 2014 and thus results from the two years 2012-2013 are documented in the following.

2.1 The station network

The location of the EMEP monitoring sites for VOC in 2012-2013 is shown in Figure 1 and an overview of the measurement programme and the responsible laboratories is given in Table 2. Totally 20 measurement sites which have done VOC monitoring are included in the list. For some of the sites, the data values are not included in this report since they are still regarded preliminary either due to data format technicalities or due to unresolved questions to the data quality and the data filtering (flagging local influences).

All the sites do NMHC monitoring while carbonyls are only measured regularly at a few sites; two sites in France and one in Spain. In addition, PTR-MS instruments at Birkenes in Norway and Hyytiälä in Finland have been in operation also measuring a number of carbonyls, but only for short campaigns at Birkenes, and for Hyytiälä, the data are not yet ready.

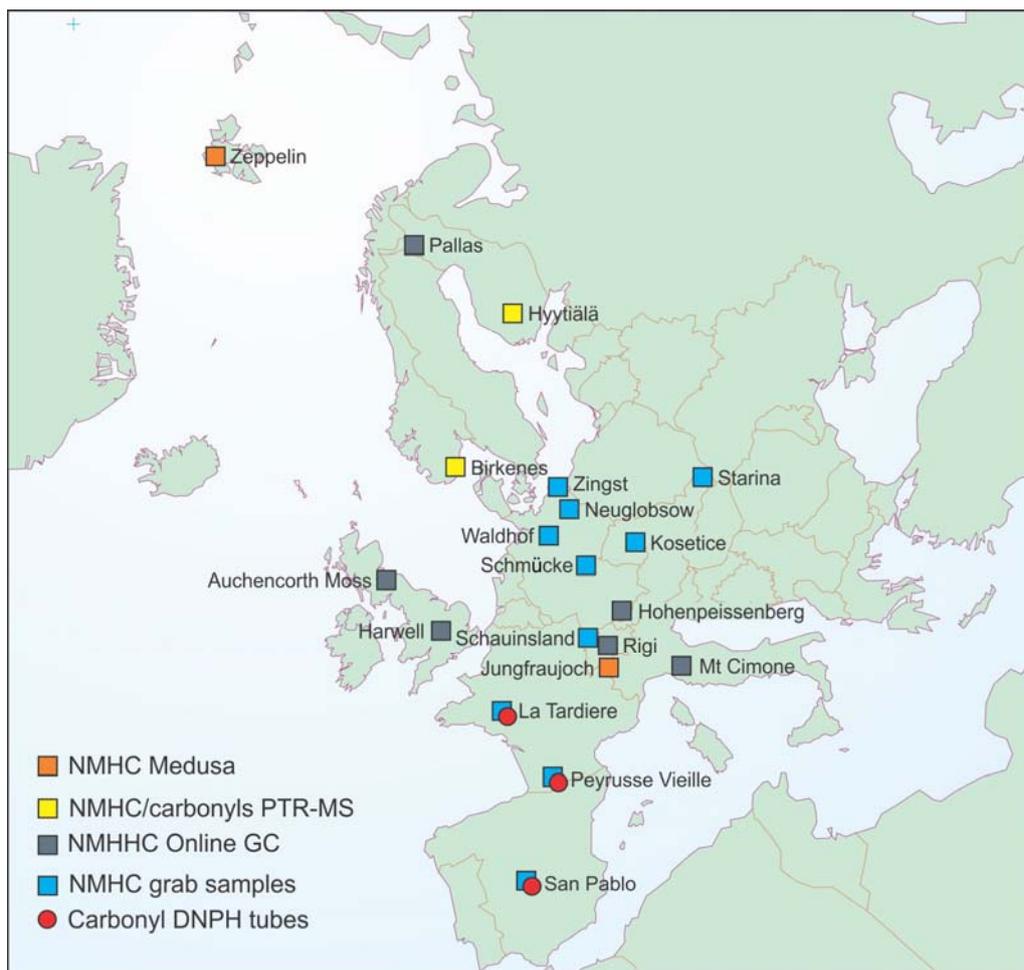


Figure 1: Monitoring sites for VOC in 2012-2013.

The VOC monitoring at EMEP sites has become more and more diverse with time. Starting in the early 1990s with standardized methods based on manual sampling in steel canisters for NMHCs and DNPH tubes for carbonyls and subsequent lab analyses, the methods now comprise a variety of instruments and measurement principles.

The development of the EMEP NMHC monitoring network with time is illustrated in Figure 2. Although a substantial number of sites has contributed to the 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 VOCs at European background sites. Additionally, shifts in instrumentation, as marked in black in Figure 2, 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.

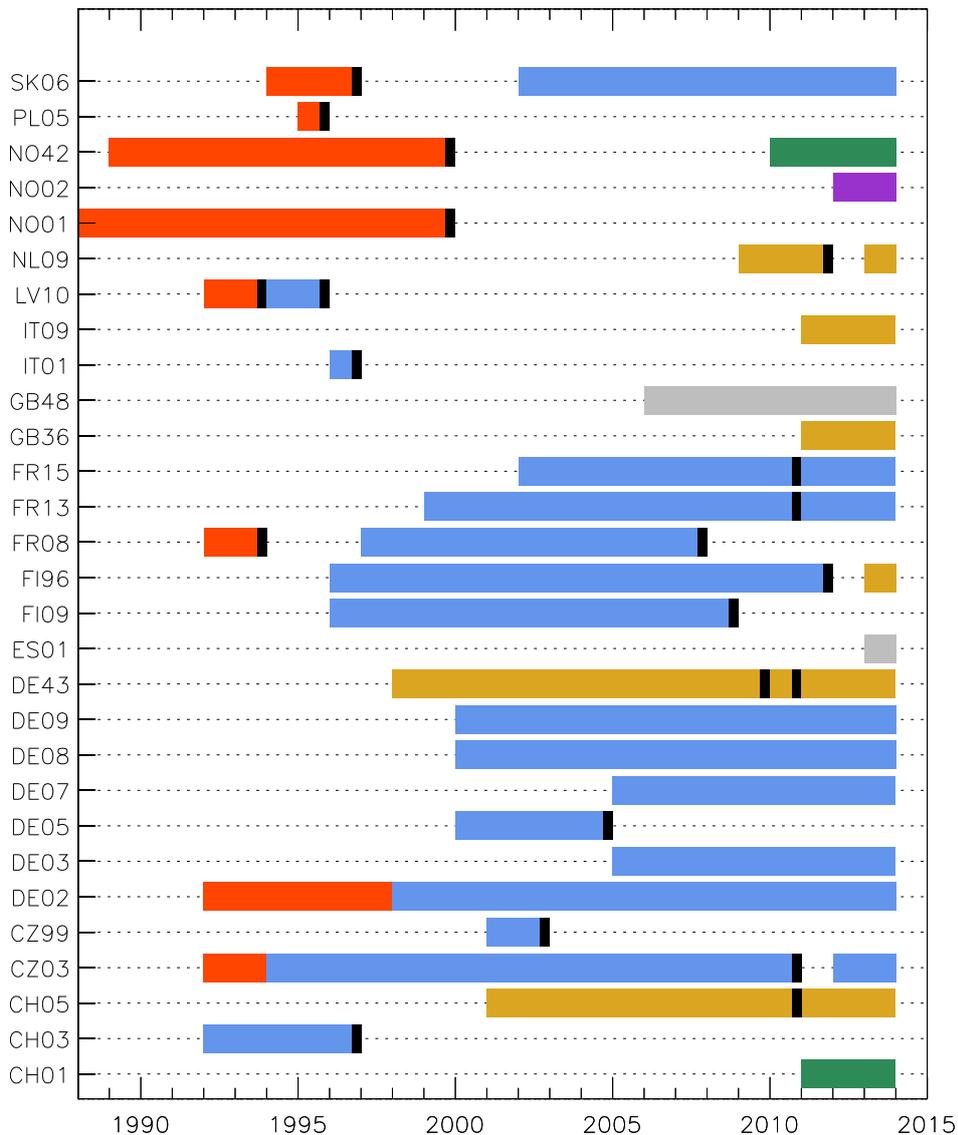


Figure 2: Development of the EMEP NMHC monitoring with time. All sites contributing with data from EMEP stations are included and the colors mark the various methods: Red = sampling in steel canisters followed by analyses by GC/FID at NILU's lab; Blue = sampling in steel canisters followed by analyses by GC at local labs; Brown = automated online GC; Green = Online MEDUSA; Violet = Online PTR-MS. Black bars mark breaks in the monitoring due to shifts in instruments etc. Grey marks data that are still considered preliminary and unsettled.

Table 2: VOC monitoring at EMEP sites in 2012-2013. The columns give the station names, site code, and the sampling frequencies for hydrocarbons (HC) and carbonyl compounds (Carb). The laboratory responsible for the chemical analyses is also given.

Station	Code	HC ¹⁾	Lab. ²⁾	Carb ¹⁾	Comment
Zeppelin Mtn.	NO42	Cont.	NILU	-	MEDUSA
Birkenes II	NO02	Scat.	NILU	Scat.	Campaign periods with PTR-MS
Pallas	FI96	Cont.	FMI	-	Changed from canister sampling to online GC/FID in 2012
Hyytiälä	FI50	-	UHel	-	PTR-MS. Data not final
Auchencorth Moss	GB48	Cont.	CEH	-	Online GC/MS. Data awaits filtering
Harwell	GB36	Cont.	AEA	-	Online GC/MS
Waldhof	DE02	Reg.	UBA	-	Flask samples 2/week. New GC Instrument in 2012
Schauinsland	DE03	Reg.	UBA	-	"
Neuglobsow	DE07	Reg.	UBA	-	"
Schmücke	DE08	Reg.	UBA	-	"
Zingst	DE09	Reg.	UBA	-	"
Hohenpeissenberg	DE43	Daily	DWD	-	2/day (noon, midnight)
Košetice	CZ03	Reg.	CHMI	-	Flask samples 2/week
Starina	SK06	Scat.	SMHI	-	Flask samples
Jungfrauoch	CH01	Cont.	EMPA	-	MEDUSA
Rigi	CH05	Cont.	EMPA	-	Online GC
Peyrusse Vieille	FR13	Reg.	EMD	Reg.	Flask samples NMHC 2/week DNPH samples Carb. 1/week (carb. data for 2013 not yet available)
La Tardière	FR15	Reg.	EMD	Reg.	"
Mt. Cimone	IT09	Cont.	UU	-	Online GC/MS
San Pablo	ES01	Reg.	MMA	Reg.	Flask samples NMHC 2/week (data status not settled) DNPH samples Carb. 2/week

1) Reg. = regularly, Scat. = scattered, n.m. = not measured., n.a. = not yet analysed, cont. = Continuous

- 2) CHMI = Czech Hydrometeorological Institute
DWD = Deutscher Wetterdienst
EMD = Ecole des Mines de Douai (France)
EMPA = Swiss Federal Lab. for Materials Testing and Research
FMI = Finnish Meteorological Institute
UHel = Univ. Helsinki
AEA = AEA Technology
UBA = Umweltbundesamt (Germany)
UU = University of Urbino
MMA = Ministerio de Medio Ambiente

2.2 Analytical procedures, quality control and intercomparisons

Quality control of the VOC measurements includes QA procedures at all stages from sampling to chemical analyses and integration. QA procedures are described in the EMEP manual (EMEP/CCC, 1995) and are the laboratories' responsibility to follow up. In addition, data received from the individual laboratories are inspected by use of various statistical tools before being accepted by EMEP/CCC. Dialogues between EMEP/CCC and the data providers are essential in this work.

Furthermore, the ACTRIS consortium as mentioned above also took a central role in the quality control of the laboratories' reported data from the regular monitoring for institutes participating in that project. A comprehensive Standard Operation Procedures (SOP) manual for VOCs has been developed in the project.

NMHC data from ACTRIS-stations were presented by the representatives and discussed in detail at dedicated workshops. Then, based on various common statistical tools, potential outliers and errors in the data were discussed, and recommendations for data base flagging were provided by the workshop. 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 3.

VOC data from the EMEP network have been published and documented e.g. in Hellen et al. (2015), Hoerger et al. (2015), Malley et al. (2015), Solberg, S. (2013), Tørseth et al. (2012), Worton et al. (2012), Hakola et al. (2006), Sauvage et al. (2009), Plass-Dülmer et al. (2009), Plass-Dülmer et al. (2006), Solberg et al. (2001), Solberg et al. (1996).

Data flow of VOCs within ACTRIS/EMEP

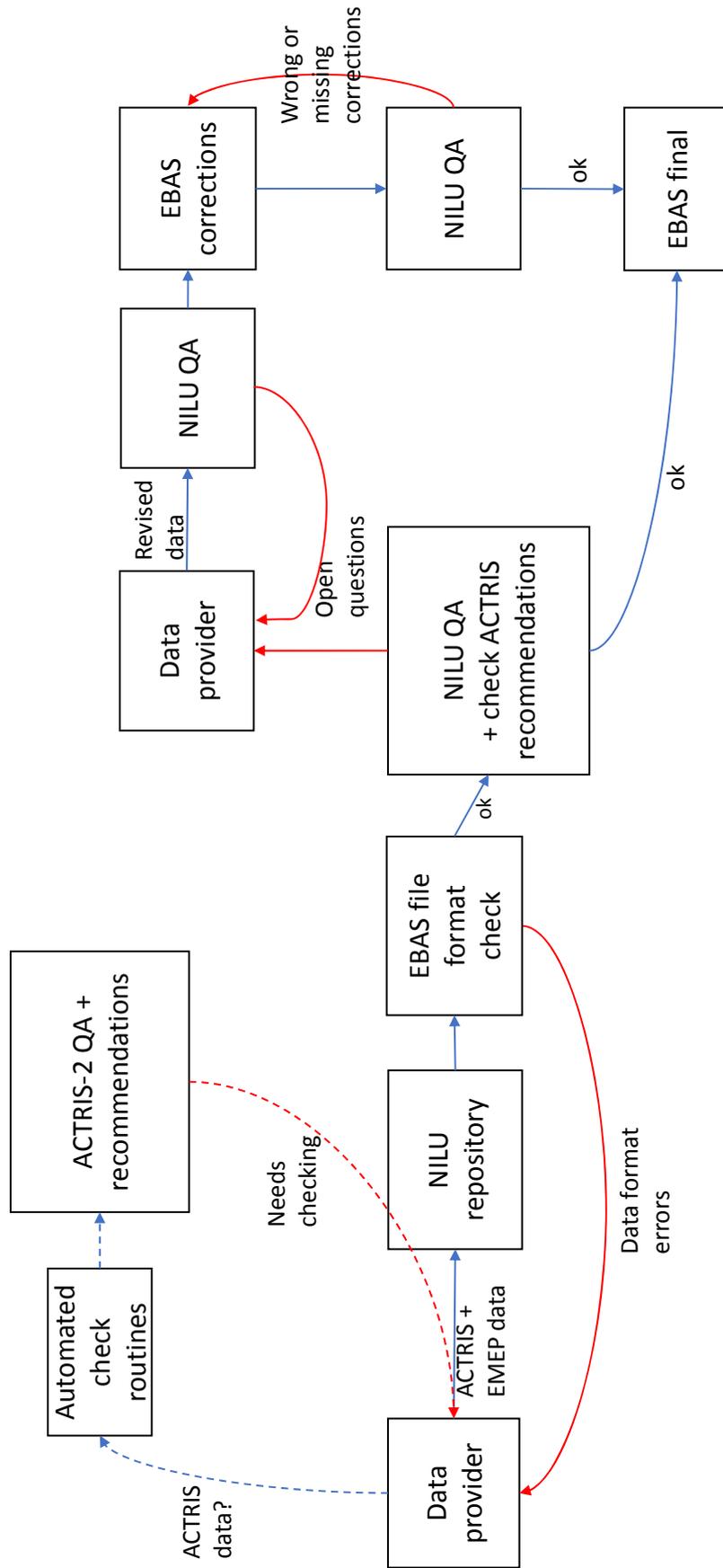


Figure 3: Flow diagram for the VOC data submitted within ACTRIS/EMEP.

The first laboratory intercomparison of light hydrocarbons in EMEP was organised already in 1993 (Romero, 1995). The variation or relative deviation among the laboratories was in a range $\pm 25\%$ from the median. The exercise showed that the majority of the participating laboratories had the required analytical technique to correctly analyse a wide range of NMHC within an accuracy of $\pm 10\text{--}15\%$. Furthermore, the results showed no substantial differences whether the air samples were analysed immediately after collection or after a period up to 2 months (for C₂–C₅ hydrocarbons).

Since then, various intercomparisons for VOCs have been carried out, e.g. through the projects 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., 2003) with participation from a large number of laboratories in Europe and elsewhere. A major part of the AMOHA project was to organize four annual intercomparisons starting in 1997 and ending in 2000. The results showed that except for a few laboratories the agreement was within $\pm 25\%$ of the median for the lighter alkanes. For some aromatics and unsaturated hydrocarbons as well as the C₆–C₇ alkanes a large spread in the values were seen, indicating measurement difficulties with these compounds. The spread in the results were, however, much less for laboratories using a 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.

The ACTRIS project also included an intercomparison for NMHCs in which 18 laboratories with 23 different GC instruments participated and the results were recently published (Hoerger et al., 2015). In addition, a side-by-side intercomparison for OVOCs (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.

Details of the ACTRIS NMHC intercomparison can be found in Hoerger et al. (2015). The intercomparison covered a list of 34 NMHCs, including C₂–C₈ alkanes, C₂–C₅ alkenes, five aromatics and two alkynes. One canister with a mixture of 30 NMHCs at 1 ppb level in N₂ and one canister with whole air sampled in an suburban area (Dübendorf, Switzerland) was distributed to all participating laboratories for analyses. For calibration, the laboratories were asked to use their own certified multicomponent standards, which should be traceable to the GAW scale. Three laboratories served as reference labs, analyzing the mother cylinders before and after the exercise: The WCC-VOC (World Calibration Centre for VOC, Karlsruhe Institute of Technology, Garmisch-Partenkirchen), DWD (Deutsche Wetterdienst at Hohenpeissenberg) and EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland.

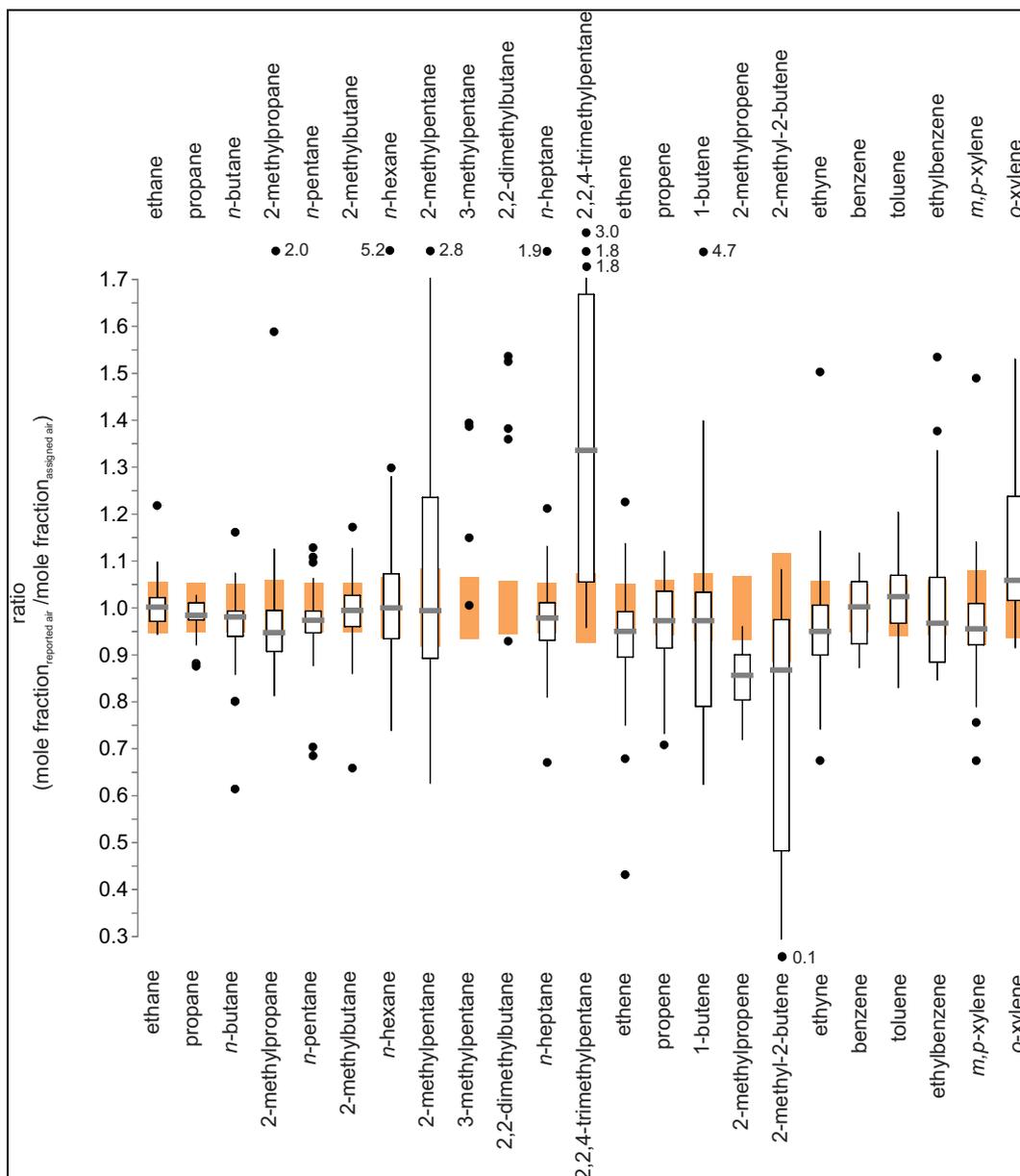


Figure 4: Boxplot of the results from the ACTRIS intercomparison for NMHCs in whole air (above 0.1 ppb) as analysed by 18 laboratories relative to the assigned reference values. White box shows 25-and 75 percentile with the median inside. Whiskers show the min and max or at most 1.5 times the interquartile range. Outliers lower or higher than 1.5 times the interquartile range are shown separately by dots. Orange box indicates the ACTRIS data quality objective (5 % class). The figure is adopted with courtesy from Hoerger et al. (2015).

The intercomparison showed the best results for the gas mixture in N₂ and for the lighter alkanes. In comparison, the results were clearly poorer for the whole air sample (Figure 4). C₄-C₅ alkenes and C₇-C₈ species (alkanes and aromatics) turned out to be the most problematic species to measure. For all species/laboratories, almost 62 % of the results from the N₂ 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 C₇-C₈ 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 reasonably good results although not among the best ones. 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 to the intercomparison for NMHCs 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 2012-2013

3.1 General

Time series of the diurnal means of all compounds during 2012-2013 are given in the Appendix. A comparison of the seasonal mean and percentile concentrations of hydrocarbons in four winter months (Jan., Feb., Nov., Dec.) measured at the different stations is given in Figure 5. Note that for isoprene, the plot shows the values for three summer months (June-August). The stations are arranged from north to south. Considering that the sites span a wide area from Southern Europe to the most northern part of the continent, the hydrocarbon winter mean levels are fairly uniform. A systematic pattern is seen though, with generally lower levels in the north (Zeppelin, Pallas) and at the high mountain sites (Jungfraujoch and Mt Cimone). For several species a generally higher mean and maximum level are seen at Harwell (GB36) and the German sites with steel canister data (DE02, DE03, DE07, DE08 and DE09). That regards in particular toluene and the butenes.

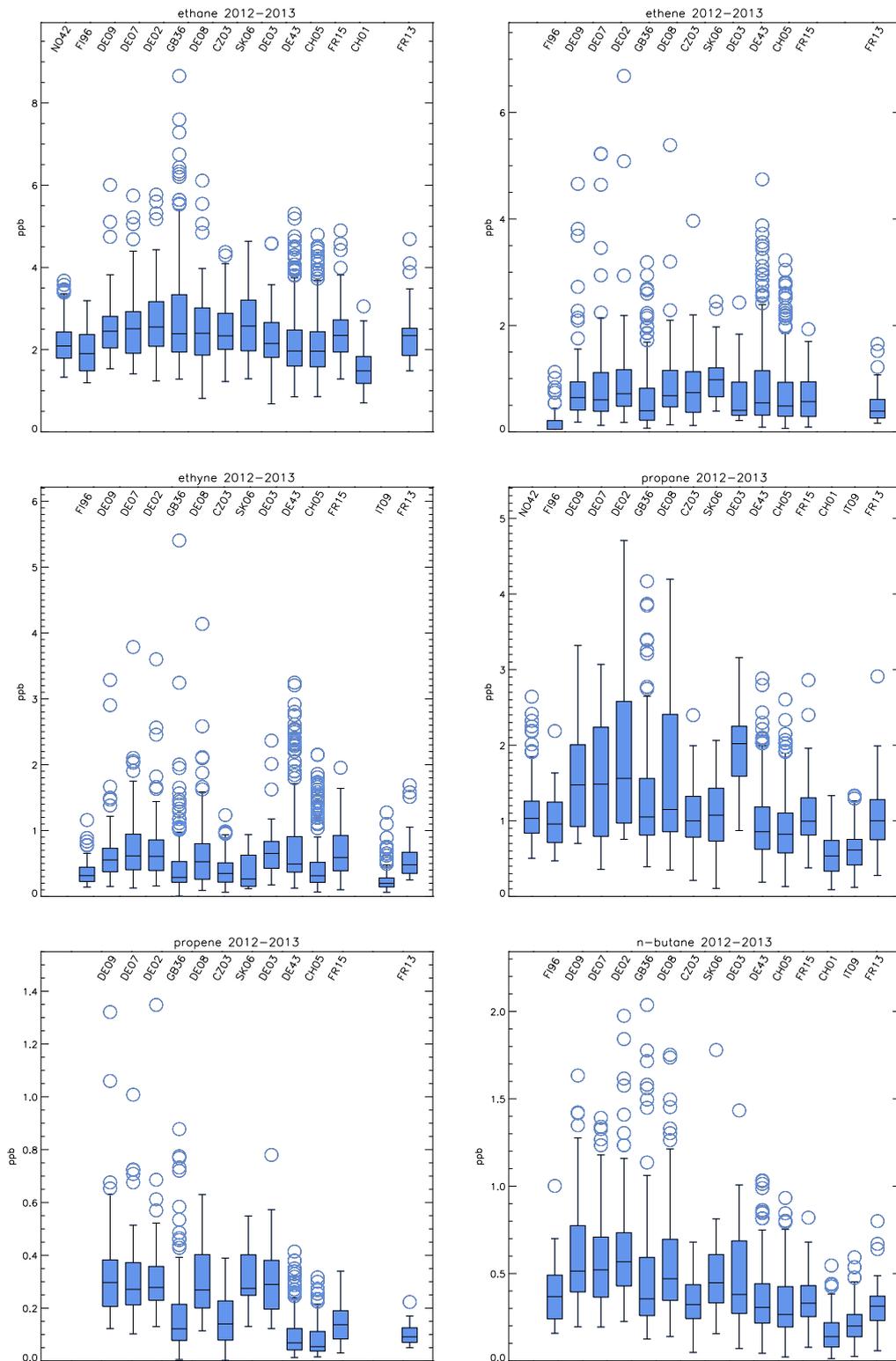


Figure 5: Box- and whisker-diagrams for hydrocarbons during winter months in 2012-2013 (Jan., Feb., Nov., Dec.). The boxes enclose the 25- and 75-percentile with the median marked inside. The whiskers extend out to the max or min value, or to the 1.5 times of the 25p or 75p if there is data beyond this range. Outliers are identified with small circles.

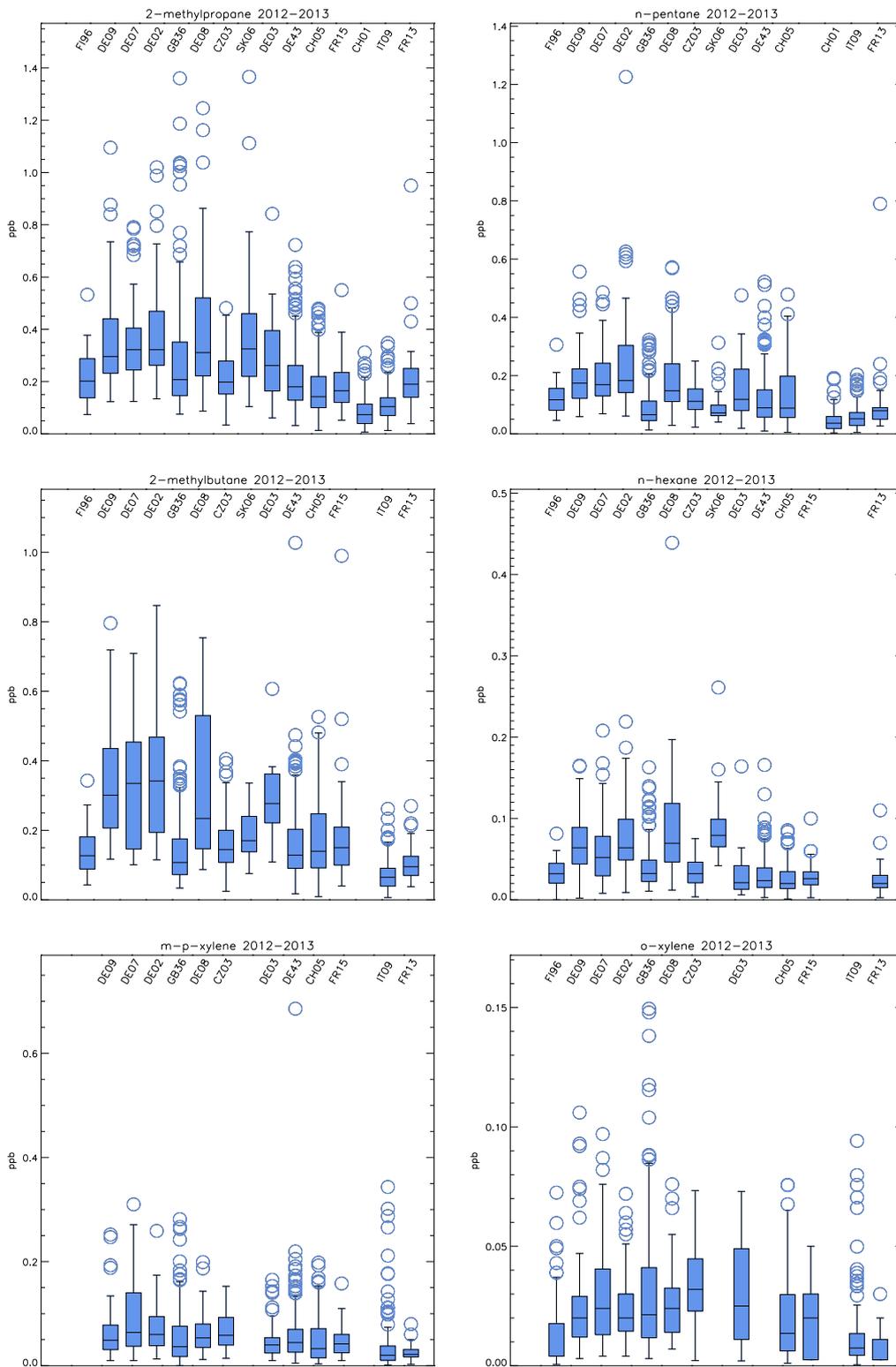


Figure 5. (contd)

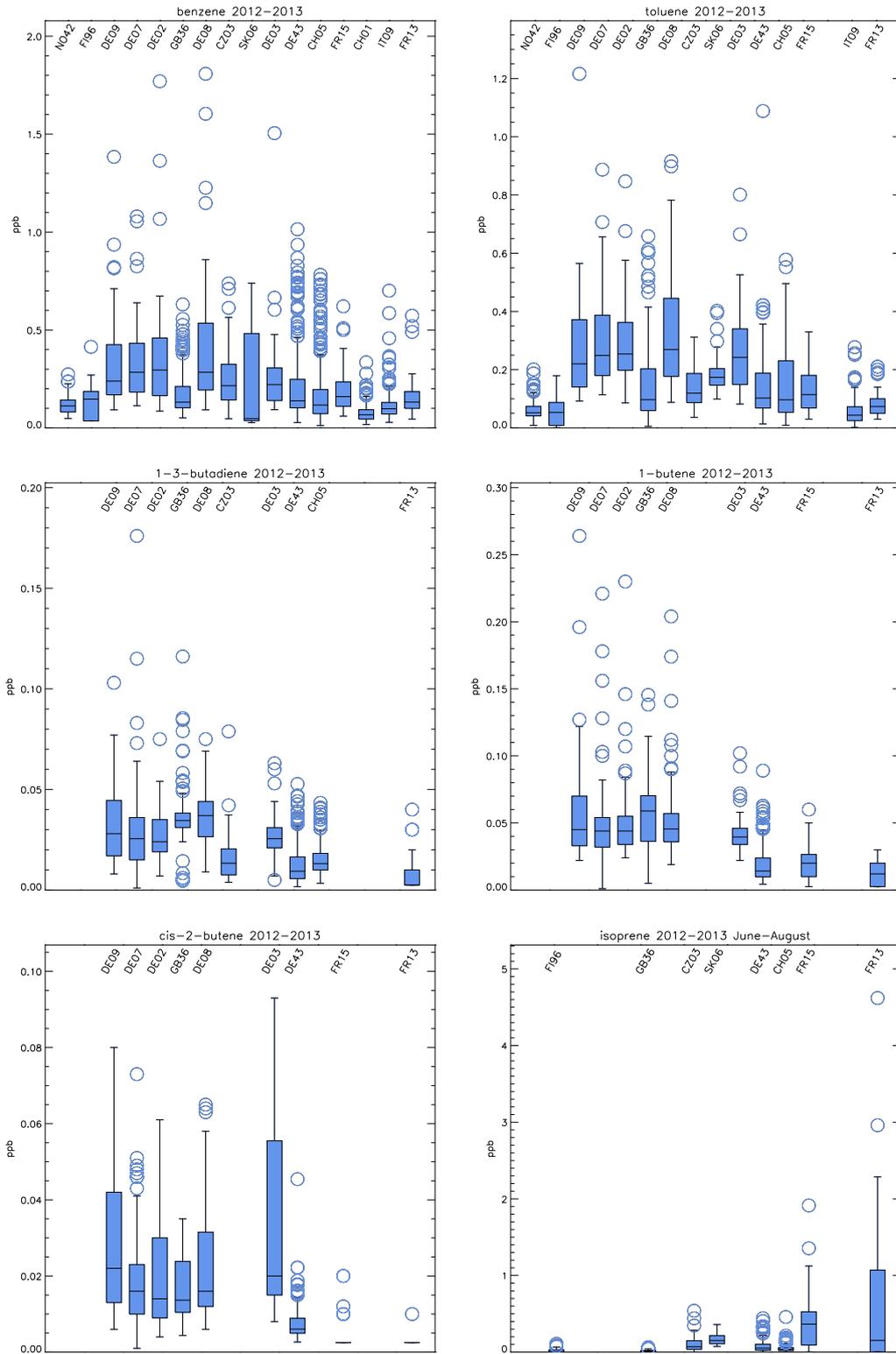


Figure 5. (contd)

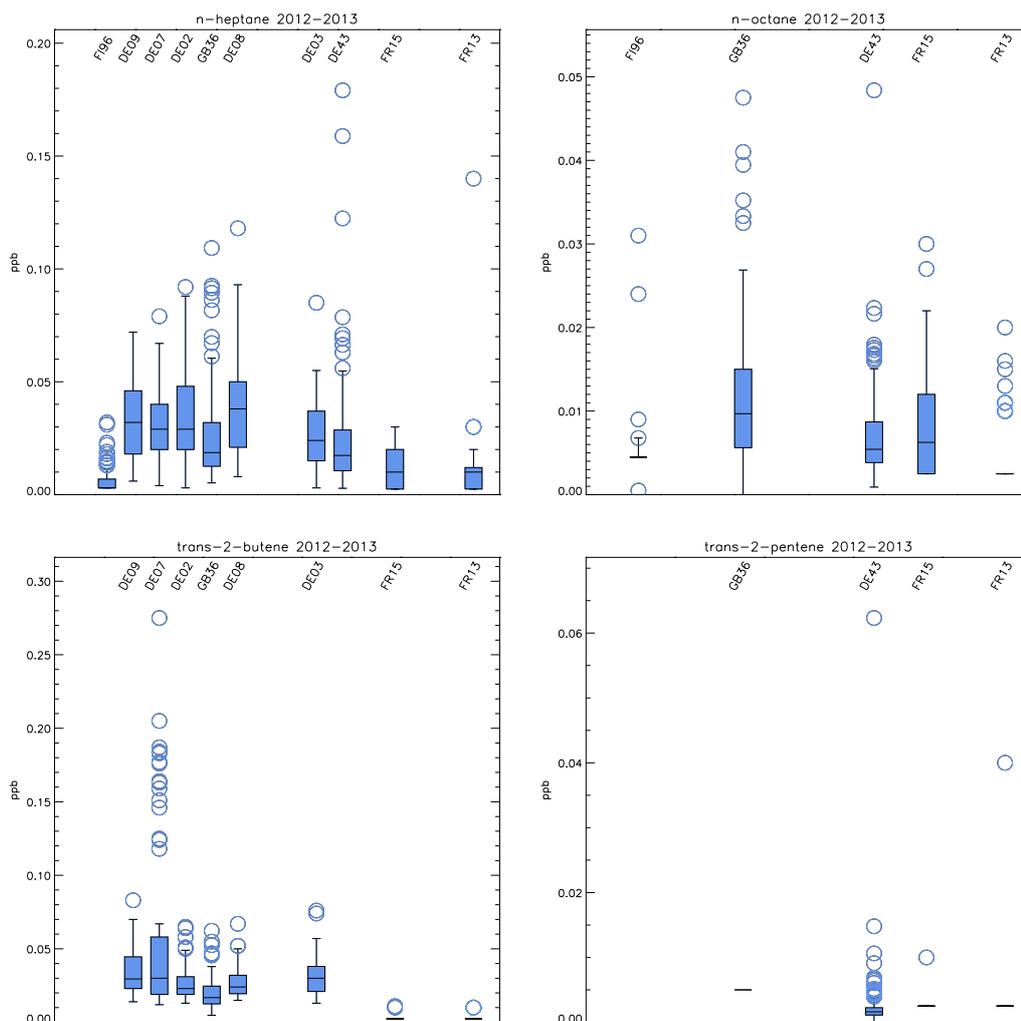


Figure 5. (contd)

3.2 Regional distribution of VOC

Figure 6 shows maps with the stations' median concentrations of light hydrocarbons for the winter half year (October-March) in 2012 and 2013 taken together (summer months June-August for isoprene). 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. This is particularly true for isoprene which has a strong diurnal cycle due to the dominant biogenic emissions. A bias for other species is also likely at a varying extent. The mountain stations (Hohenpeissenberg and Mt Cimone) are influenced by the diurnal venting of the planetary boundary layer, and will receive upslope polluted air masses at daytime and cleaner free tropospheric air at night. The site at Harwell, although rural, is surrounded by nearby emission sources and will experience a diurnal cycle in pollutants determined by the combined effect of planetary boundary height and emission variation through the day.

Similar figures for three carbonyl species for the summer months May-August 2012-2013 are given in Figure 7. Note that the carbonyl data at this stage consist

only of data from ES01 in 2013 and from the two French sites (FR13 and FR15) in 2012.

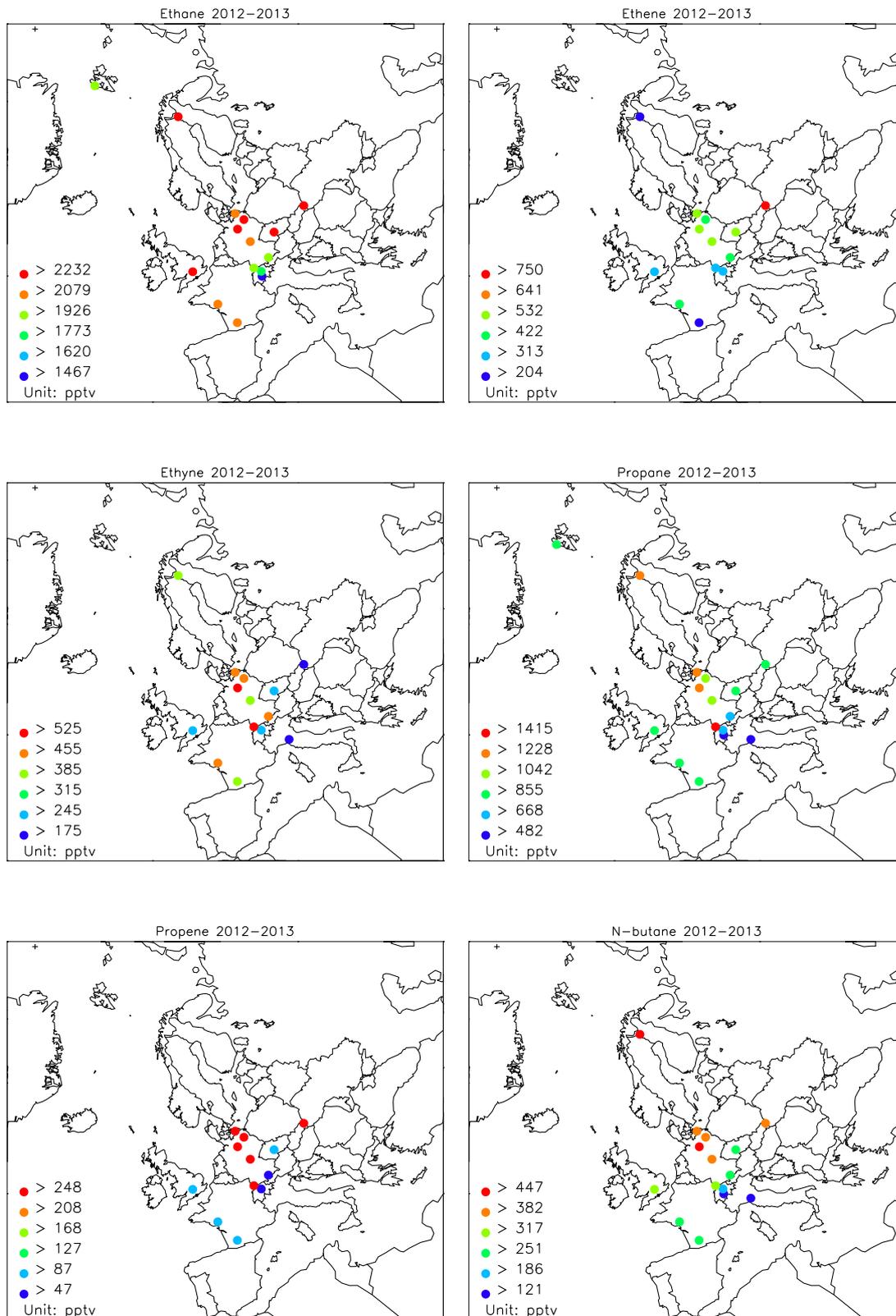


Figure 6: Median concentration of NMHCs in the winter half years (Oct-Mar) 2012-2013 taken together.

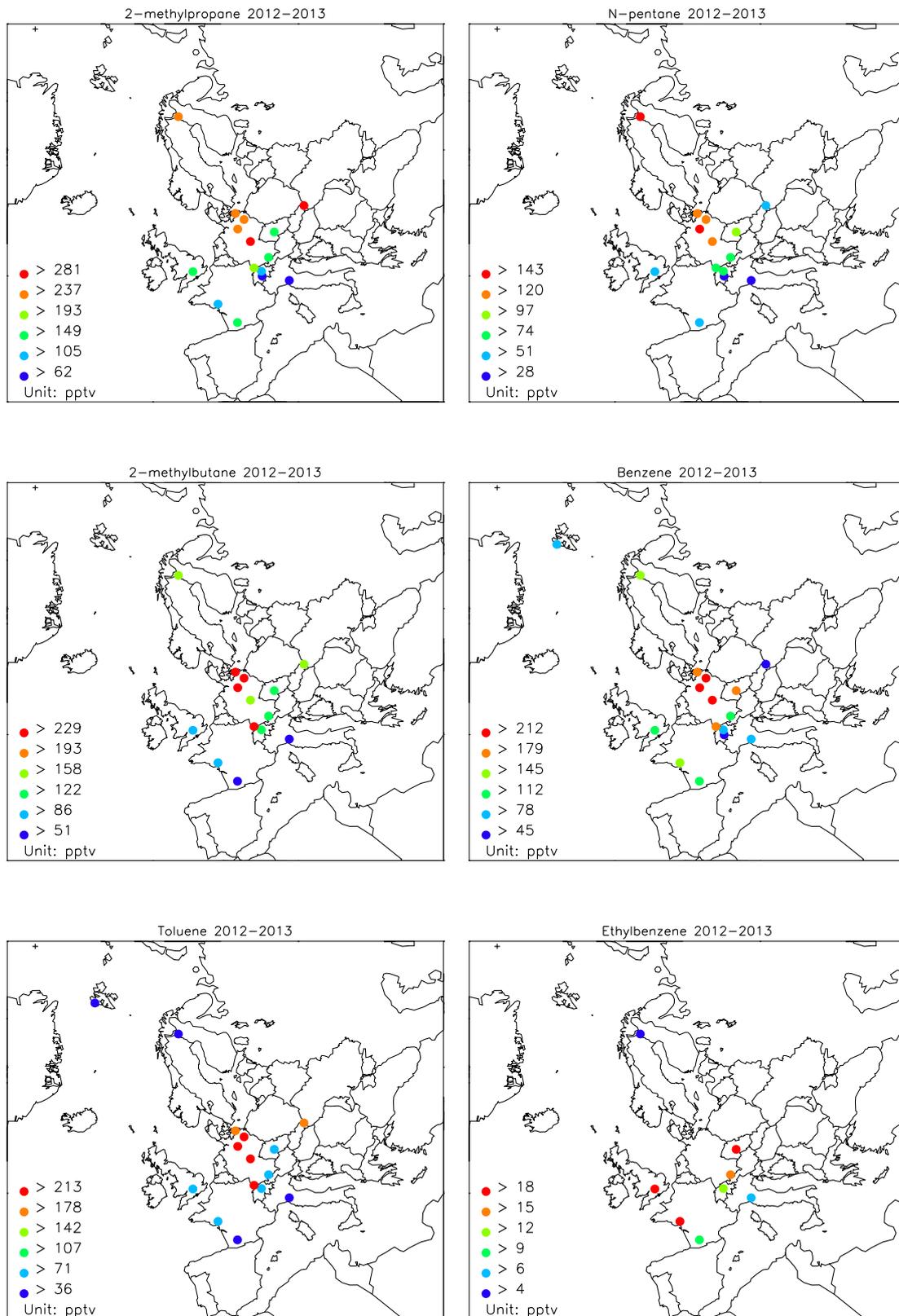


Figure 6 (contd.).

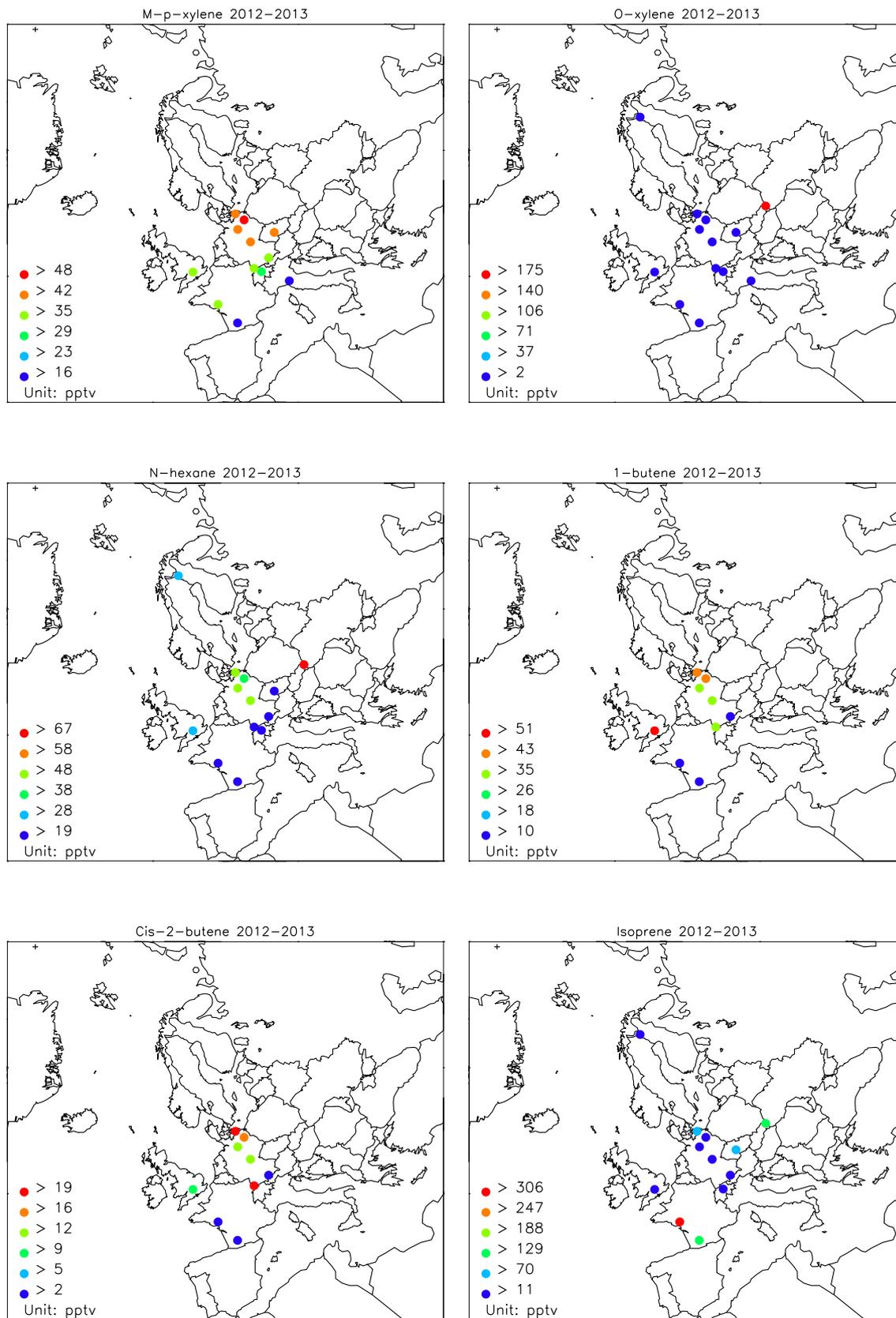


Figure 6 (contd.). For isoprene, the plot shows the median for the summer months June, July and August 2012-2013 taken together.

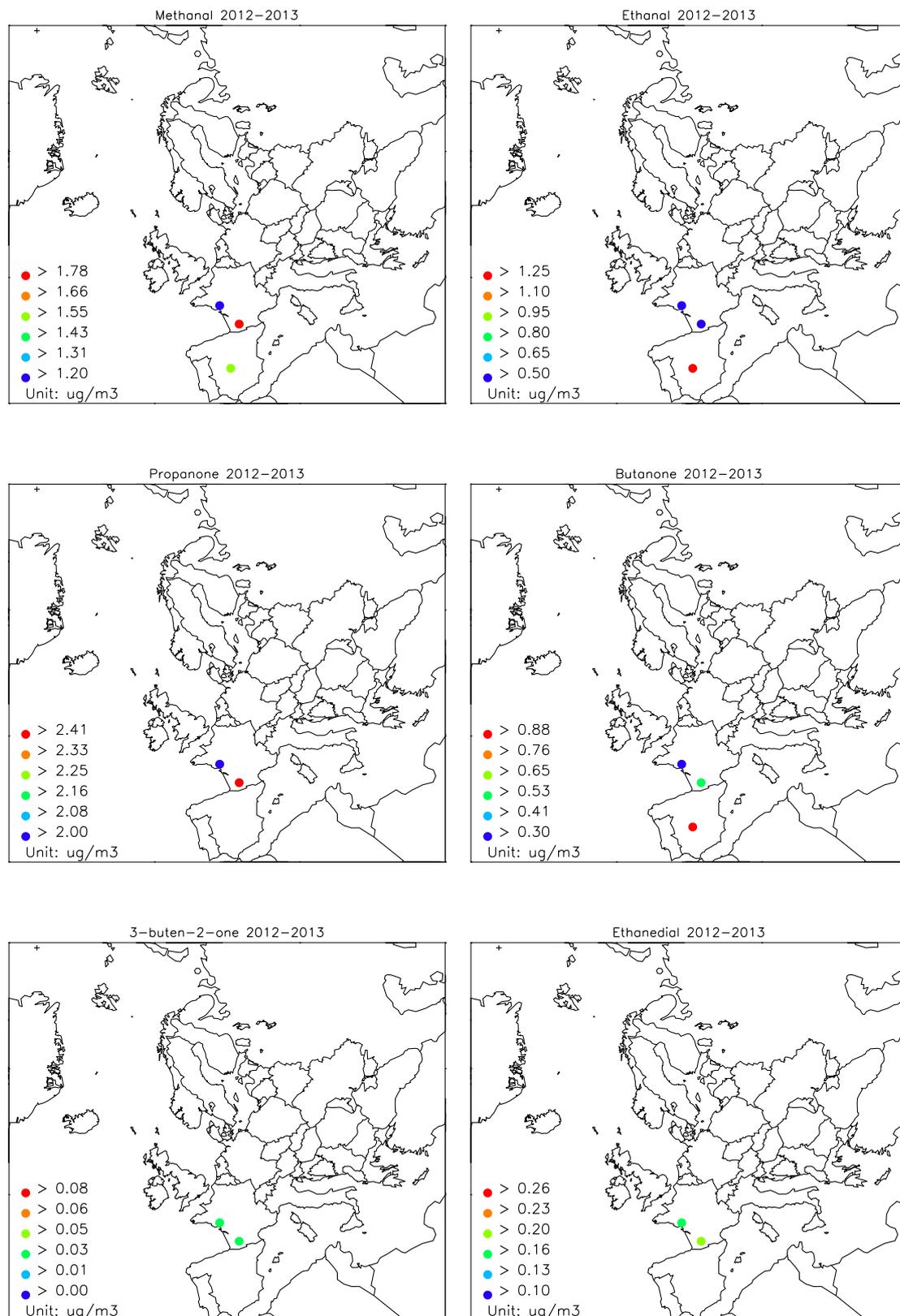


Figure 7: Median concentration of carbonyls in the summer half years (Apr-Sept) 2012-2013 taken together.

4. Long-term trends in VOC

According to the official emission data, there have been substantial reductions in the anthropogenic emissions of VOCs the last two decades, of the order of 40-50 % from 1990 to 2013 and 20-25 % from 2000 to 2013 for the EMEP region as a whole. There are, however, large regional differences in these numbers with strong reductions in some countries/areas and only minor changes in others.

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 C₂-C₈ 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. They also found a marked difference between ethane and propane on one hand, showing relatively stable levels and other alkanes showing pronounced declines on the other hand.

Long-term monitoring data from an urban network in Switzerland (Hüglin, pers. comm.) also shows strong declines in the concentration levels of NMHCs and OVOCs from the start of the 1990s to present.

Various trend studies have been carried out for VOC data from EMEP rural sites as well. Sauvage et al. (2009) found clear decreases at the French EMEP sites of most NMHCs. Ethane was an exception to this and showed more stable levels. Figure 8 shows the results for the French sites (FR08, FR13 and FR15) using the non-parametric Mann-Kendall method with Sen's slope estimates (Sauvage, 2015). Significant declines in concentration are seen for many species, most prominently for aromatics, ethene and iso-pentane. For the lightest NMHCs, ethane and propane, the estimated trends are, however, not significant.

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 was the main source region for high concentration levels at Pallas.

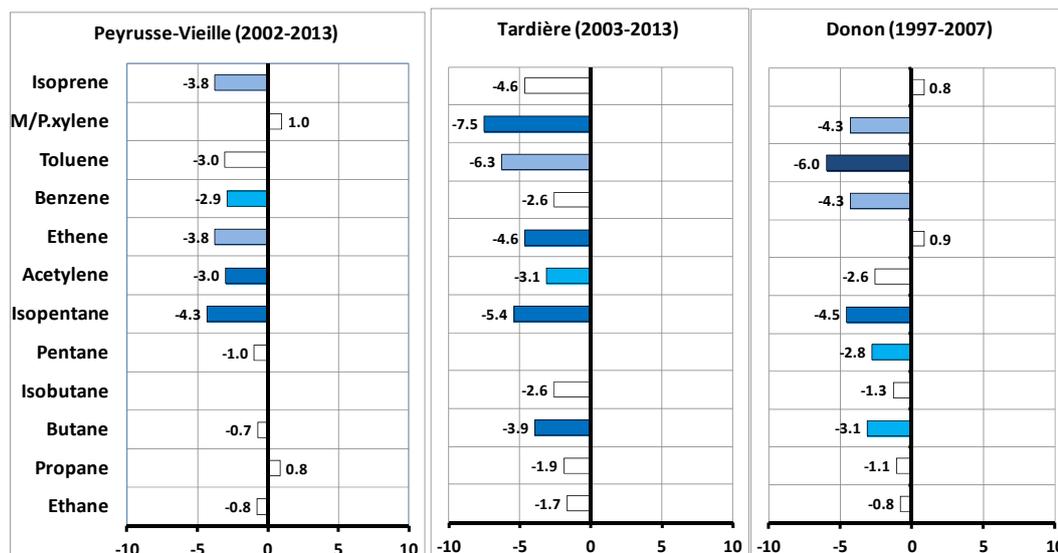


Figure 8: Mann-Kendall trends with Sen's slope estimates for NMHCs measured at French EMEP sites (Sauvage, 2015). Bars without color means not statistically significant values. For the colored bars, the significance is proportional to the darkness of the blue color.

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Appendix

Time series of daily means of VOC measured in 2012 and 2013

