

VOC measurements 2006

Sverre Solberg



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

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

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Sverre Solberg



Norwegian Institute for Air Research
P.O. Box 100, N-2027 Kjeller, Norway

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Summary

This report presents measurements of VOC carried out during 2006 at EMEP monitoring sites. VOC measurements are reported for a total of 15 sites, and 7 of these with carbonyls. All the VOC measurements are made by grab samples of light hydrocarbons in canisters and by 8-hours samples of carbonyls by DNPH adsorption tubes.

This year was characterized by a number of technical problems with the VOC monitoring. Thus the amount of valid measurement data was lower in 2006 than in previous years and this affected the number of carbonyl data in particular.

Fairly uniform mean concentration levels of alkanes were seen in winter, indicating that these compounds become well mixed in the dark season without effective chemical loss mechanisms, although the data from the Slovak station Starina was an exception and showed elevated concentrations of many compounds. Larger regional differences were seen for the alkenes consistent with the fact these compounds undergo chemical oxidation also in winter through the reaction with ozone.

The winter median concentration of the hydrocarbons, used as a proxy for the European emission source strength, was of the same order as seen in the last few years for several components (ethane, propane, pentane). However, some compounds, as acetylene and ethene was higher than in previous years at certain stations (in the Czech Republic and Germany). Toluene and the toluene:benzene ratio was substantially higher at the German EMEP sites compared to previous years, possibly reflecting improved analytical sensitivity of a new GC instrument at the responsible laboratory.

The trend in hydrocarbon concentrations based on the 12 years winter median values for the period 1995-2006 show a mixed picture. For toluene the data do show a strong decline in the concentrations through the whole period whereas for other compounds there are signs of a concentration level levelling off or even increasing during the last few years. Modelling studies are needed to separate the effect of changes in emissions from those of changing meteorology from year to year.

Inspecting the ratio of individual components vs. acetylene reveal a long-term trend in the hydrocarbon speciation. At three sites with sufficient amount of data (Utö, Donon and Košetice) the measurements indicate that ethane and propane increase relative to acetylene, possibly reflecting a larger reduction in traffic related emissions (acetylene) compared to emissions from natural gas. A strong decline in the toluene:acetylene ratio is also found, and the reason for this is not clear.

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1. Introduction

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.

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 at each station centred at 12 noon GMT. 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. A list of required and desirable compounds was defined and is shown in Table 1.

Certain additional remarks at the Workshop were underlined in the proceedings report (EMEP/CCC, 1990). The need for more information on VOC concentrations close to the emission sources for modelling purposes was raised. Harmonisation with national urban measurement programmes was recommended as well as the assembling of VOC emission inventories. Furthermore, the importance of concurrent measurements of oxides of nitrogen was strongly emphasised.

At the Lindau Workshop it was also recommended that during the starting period the analyses of the VOC samples should be made by the CCC and that other laboratories should be included later on.

Table 1: List of volatile organic compounds that are “required” or “desirable” to measure within the EMEP programme as defined at the EMEP Workshop in Lindau, 1989 (EMEP/CCC, 1990).

	required	desirable
Alkanes	ethane	hexane
	propane	branched hexanes
	i-butane	heptane
	n-butane	branched heptanes
	i-pentane	octane
	n-pentane	
Alkenes	ethene	butenes
	propene	pentenes
	isoprene	
Alkynes	acetylene	
Aromatics	benzene	styrene
	toluene	propylbenzenes
	o-xylene	ethyltoluenes
	m,p-xylene	
	ethylbenzene	
	trimethylbenzenes	
Aldehydes	formaldehyde	propionaldehyde
	acetaldehyde	
Ketones	acetone	methylethylketone
		methylvinylketone

The measurements of VOC within EMEP started with the collection of grab samples of light hydrocarbons in the middle of 1992, whereas measurements of carbonyls started 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 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).

In the EU FP5 project AMOHA (Accurate Measurements of Hydrocarbons in the Atmosphere) a large number of laboratories in Europe participated in parallel sampling and analyses of hydrocarbons in ambient air (Slemer et al., 2002). A major part of the 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 may be 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 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, 2007). 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).

An initiative has been taken to increase the cooperation and exchange of VOC data between GAW (Global Atmospheric Watch) and EMEP. At the EMEP TFMM workshop in Oslo in November 2004, on the implementation of the EMEP monitoring strategy, a closer harmonisation between the VOC monitoring in EMEP and GAW was discussed. Minutes and conclusions from the workshop is given elsewhere (EMEP/CCC, 2005). Harmonisation of data quality objectives (DQOs) and using a common audit questionnaire was recommended, and it is 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).

A revision and extension of the species recommended to measure was also discussed at the Oslo TFMM workshop. One starting point for such a revision is the VOC speciated emissions provided by UK's National Atmospheric Emissions Inventory (NAEI) as reported by Dore et al. (2004). Table 2, adopted from Dore et al. (2004), shows the photochemical ozone creation potential (POCP) for the top 50 VOCs (with respect to POCP) for the UK. The POCP identifies, on a relative basis, the ozone creation potential for each NMVOC compound through modelling studies. The creation potentials are then normalised by defining ethene

as a creation potential of 1. Many of the components in Table 2 are not measured by the present EMEP VOC program due to limitations by the methods presently used, as e.g. alcohols, chlorinated compounds and long-chained alkanes. An extension to include these compounds in the monitoring program will require additional sampling devices as e.g. adsorption tubes.

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 proposed species are: Ethane, propane, acetylene, isoprene, formaldehyde, terpenes, acetonitrile, methanol, ethanol, acetone, DMS, benzene, toluene, iso- and n-butane, iso- and n-pentane. Most of these compounds are already part of the EMEP VOC programme with some exceptions. 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.

2. Status of the measurement programme in 2006

2.1 The station network

The location of the monitoring sites for VOC presented in this report is shown in Figure 1 and an overview of the measurement programme and the responsible laboratories in 2006 is given in Table 3. Totally 15 measurement sites reported VOC data to CCC in 2006. Carbonyls were sampled at 7 of these sites but due to technical problems the data from Utö and Košetice could not yet be analysed in the laboratory. Furthermore, hydrocarbon data from Campisábalos were provided for the last half year of 2006 only and as the data needed more inspection they are still considered preliminary. Carbonyl data from Campisábalos were delivered for the whole year, but the data values for formaldehyde and acetaldehyde for the period January to July were very low and flagged as invalid. Further inspection should be carried out on these data.

In 2006 there were problems with the VOC analyses at the German lab at UBA and the old GC was replaced by a new one. The new analytical method was somewhat different from the old one. It used a different column and cooling was with liquid CO₂ instead of liquid N₂. Many peaks changed order in the chromatograms making it difficult to identify the peaks as the results was not always reproducible. Due to operational restrictions, it was not possible to run both methods in parallel to make detailed comparisons. In general, the new method seems to be more sensitive for C₇- and higher VOCs.

VOC data were also reported from NL09, Kollumerward, for 3 months of 2006, July – September. These data are included in EMEP's database ebas, but due to the short period with data they are not included in this report.

Table 4 gives the number of valid (daily) samples of hydrocarbons and carbonyls (after inspection and removal of outliers). According to EMEP's recommendations, the samples should be taken at least twice a week, implying that 104 samples per year correspond to 100% data cover.

A 90% data completeness, i.e. 94 samples pr year, of daily values is given as data quality objective according to the EMEP manual (EMEP/CCC, 1996). The data capture was lower than this for many sites in 2006. Carbonyls are only measured once per week in France giving a data capture of the order of 50%. Only Pallas, Utö, Košetice and La Tardière had a sufficient data capture of hydrocarbons, i.e. 94 samples or more, in addition to the sites with daily/continuous monitoring, Hohenpeissenberg and Rigi. None of the stations measuring carbonyls had a data completeness fulfilling the criteria of 90%.

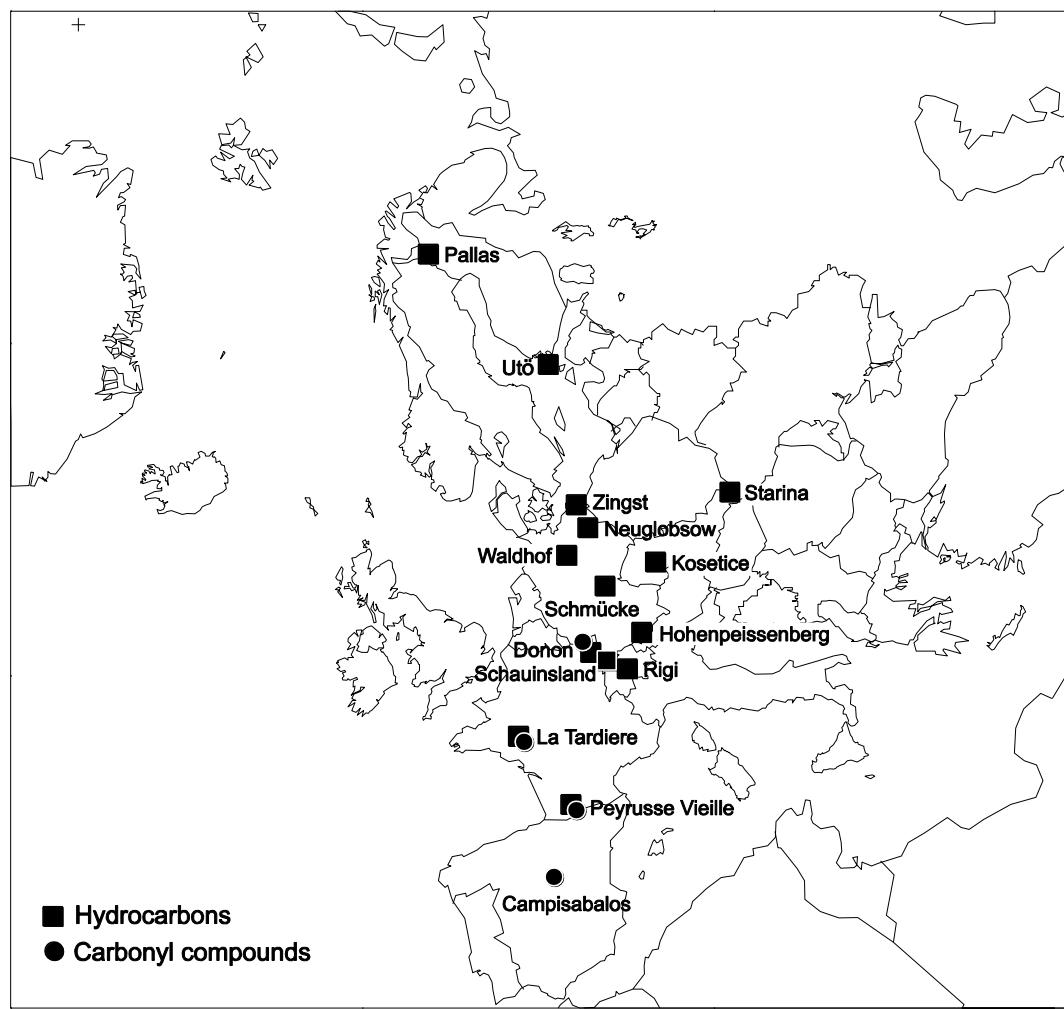


Figure 1: Monitoring sites for VOC in 2006.

Table 3: Status of the VOC monitoring programme in 2006. 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⁾	Lab. ²⁾	Comments
Pallas	FI96	Reg.	FMI	n.m.	-	
Utö	FI09	Reg.	FMI	n.a.	NILU	Samples not yet analysed in the lab due to technical problems
Waldhof	DE02	Reg.	UBA	n.m.	-	
Schauinsland	DE03	Reg.	UBA	n.m.	-	
Neuglobsow	DE07	Reg.	UBA	n.m.	-	
Schmücke	DE08	Reg.	UBA	n.m.	-	
Zingst	DE09	Reg.	UBA	n.m.	-	
Hohenpeissenberg	DE43	Daily	DWD	n.m.	-	GAW station
Košetice	CZ03	Reg.	CHMI	n.a.	NILU	Samples not yet analysed in the lab due to technical problems
Starina	SK06	Reg.	SHMI	n.m.	-	
Rigi	CH05	Cont.	EMPA	n.m.	-	
Donon	FR08	Reg.	EMD	Reg.	EMD	
Peyrusse Vieille	FR13	Reg.	EMD	Reg.	EMD	
La Tardière	FR15	Reg.	EMD	Reg.	EMD	
Campusábalos	ES09	(Reg.)	MMA	Reg.	MMA	Hydrocarbons for the last half year are reported but are considered preliminary

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

MMA = Ministerio de Medio Ambiente (Spain)

NILU = Norwegian Institute for Air Research

SHMI = Hydrometeorological Institute in Slovakia

UBA = Umweltbundesamt (Germany)

Table 4: The number of valid samples of hydrocarbons (HC) and carbonyls (Carb) in 2006.

Station	Number of samples HC ²⁾	Carb ³⁾
Pallas	96	-
Utö	97	-
Waldhof	77	-
Schauinsland	77	-
Neuglobsow	78	-
Schmücke	79	-
Zingst	79	-
Hohenpeissenberg ¹⁾	356	-
Košetice	103	-
Starina	90	-
Rigi ¹⁾	309	-
Donon	93	51
Peyrusse Vieille	76	49
La Tardière	100	47
Campusábalos	-	42

¹⁾ Refers to days with monitoring data

²⁾ Refers to ethane (may differ for other HCs)

³⁾ Refers to formaldehyde (may differ for other carbonyls)

2.2 Analytical procedures and quality control

The procedures for sampling and chemical analyses were similar in 2006 as in previous years, and are not discussed in this report. A detailed description of the procedures used by NILU is given in the EMEP manual (EMEP/CCC, 1996). The technical procedures for the sampling and analysis of hydrocarbons by FMI at the two Finnish stations, as well as a site description and data interpretation, are given by Laurila and Hakola (1996). A presentation of the sampling and analyses performed by the laboratories at EMD (France), EMPA (Switzerland), CHMI (Czech Republic), MMA (Spain), SHMI (Slovakia) and UBA (Germany) has been given in previous annual reports and by Solberg et al. (1996) and is not repeated here. The instrumentation and methods applied by DWD at Hohenpeissenberg have been successfully tested in two international intercomparison experiments (NOMHICE, AMOHA) and have been documented by Plass-Dülmer et al. (2002).

For the EMEP VOC measurements in general, the quality control of the VOC measurements includes QA procedures at all stages from sampling to chemical analyses and integration. The QA procedures are described in the EMEP manual (EMEP/CCC, 1996) and are the laboratories' responsibility to follow up. In addition, data received from the individual laboratories are inspected before classified as valid or invalid by the EMEP/CCC.

A few notes about the measurements are given in the following. The concentrations of 3-buten-2-one, 2-methylpropenal, 2-butanone and butanal have for many years been difficult to interpret. No systematic and explainable pattern has been found and inter-laboratory comparisons between EMD, UBA and NILU have indicated analytical problems. Laboratory studies at CCC indicate that unsaturated carbonyl compounds are not chemically stable in the prepared sample solution. Furthermore, LC/MS studies indicate possibilities of chromatographic interference in the C₄ carbonyl compound range. Thus, a revision of the monitoring procedures for these carbonyls is needed.

3. VOC concentrations in 2006

3.1 General

Monthly mean and median concentrations of the individual hydrocarbons and carbonyls for 2006 are tabulated in Appendix A. The monthly statistics were not calculated for sample numbers less than 4. Time series of all compounds during 2006 are given in Appendix B. For the continuous monitor data from CH05 Rigi the average of two 2-hourly values around noon were used in the calculations whilst the sample taken around noon at Hohenpeissenberg were used (samples from noon and midnight were reported). Based on previous experience there is not much difference in the anthropogenic HC concentrations at noon and at midnight at Hohenpeissenberg (pers. comm., Christian Plass-Dülmer). For isoprene the difference is substantial as this is a reactive biogenic compound, emitted during daytime, with low concentrations during night.

A comparison of the seasonal mean and percentile concentrations of hydrocarbons in winter (Jan., Feb., Nov., Dec.) and carbonyls in summer (May, June, July, Aug.) measured at the different stations is given in Figure 2 and Figure 3. 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 for the alkanes but some systematic differences are seen. Highest concentrations are seen at Starina for many of the hydrocarbons while high peak values are also seen for some compounds at Neuglobsow (DE07). Low concentration levels are seen at the two Finnish sites, Pallas and Utö, and the two German mountain sites, Schauinsland (1205 m asl) and Hohenpeissenberg (985 m asl).

For the alkenes, ethene and propene, the differences among the sites are larger reflecting an efficient chemical loss in the atmosphere also during winter through the reaction with O₃. The ratio between the peak values (90 percentiles) and the mean are generally largest for propene of all the compounds.

The amount of carbonyl data for 2006 is too low to allow any statements about geographical or latitudinal patterns. Furthermore, at the French sites the sampling frequency is once per week, making the seasonal statistics more uncertain. In addition, the Spanish "seasonal" statistics for formaldehyde and acetaldehyde shown in Figure 3 is based on data from August only, as data for the first 7 months were taken out of the data set as mentioned above.

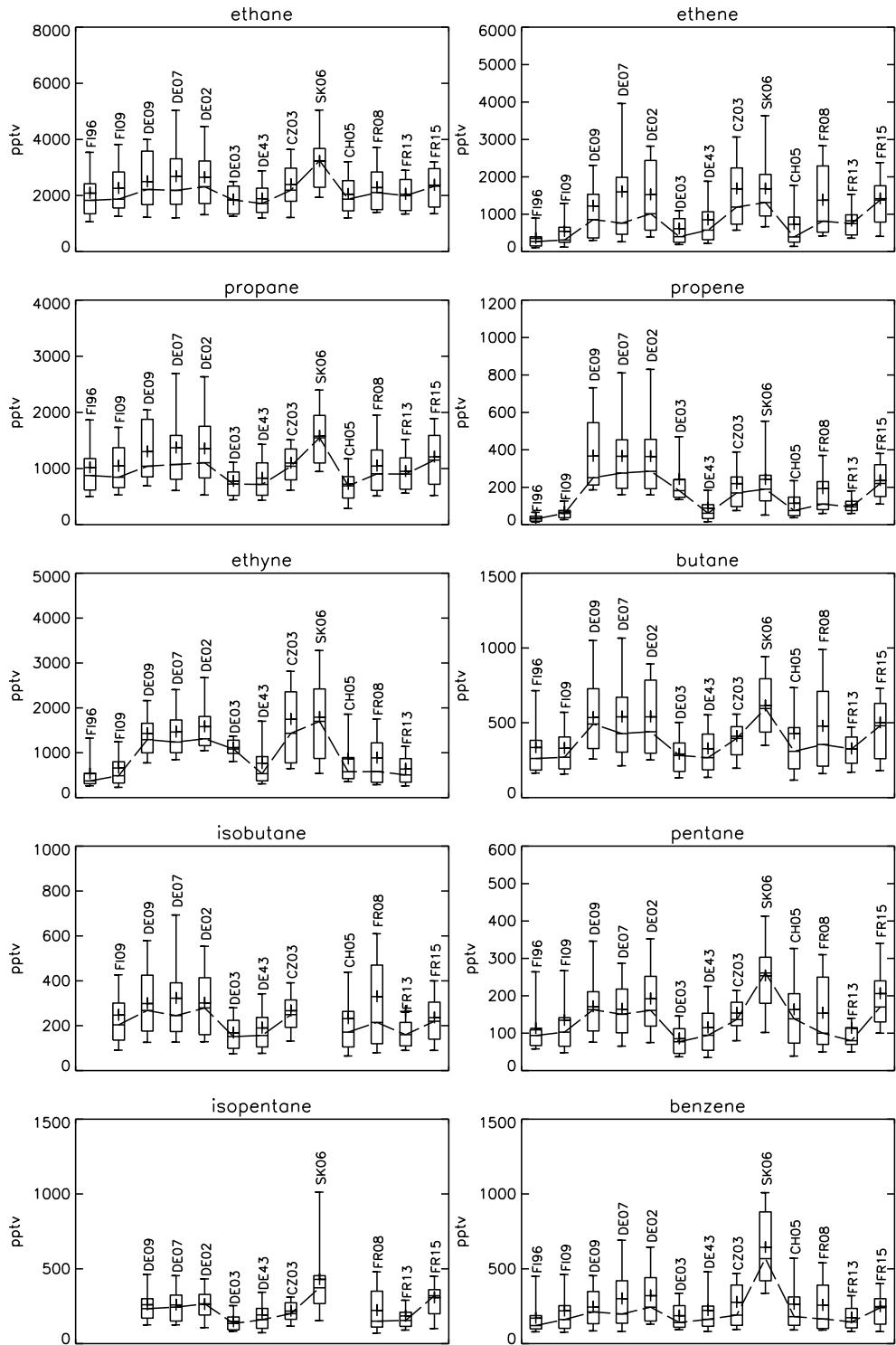


Figure 2: Box- and whisker-diagrams for hydrocarbons during winter 2006 (Jan., Feb., Nov., Dec.). The markers indicate the 10-, 25-, 50-, 75- and 90-percentiles. Mean values are indicated by a cross. The dashed line connects the median values for clarity.

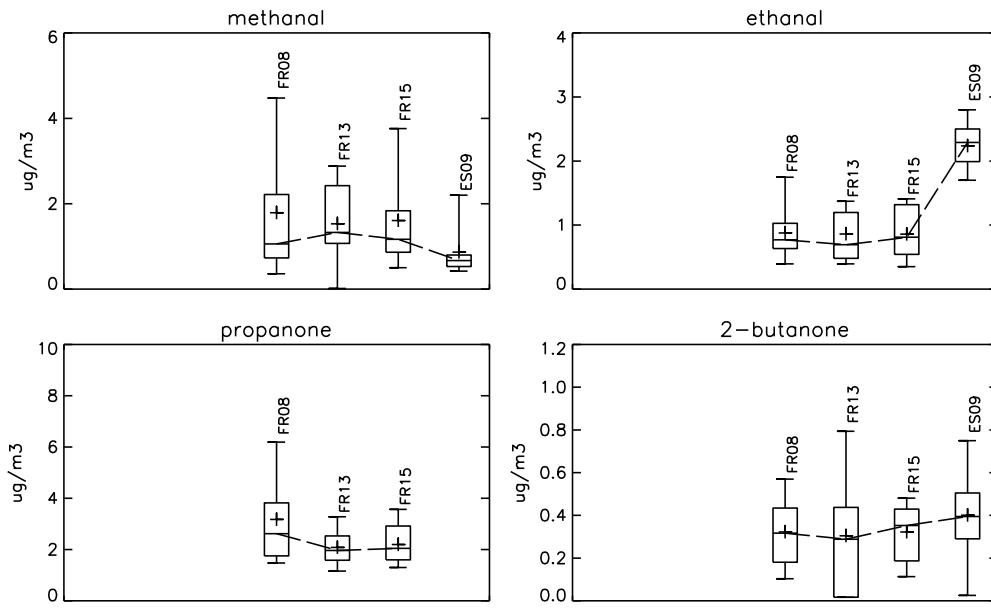


Figure 3: Box- and whisker-diagrams for carbonyls during summer 2006 (May, June, July, August). The markers indicate the 10-, 25-, 50-, 75- and 90-percentiles. Mean values are indicated by a cross. Note that the values for methanal and ethanal at ES09 are based on August only.

3.2 Regional distribution of VOC

Figure 4–Figure 13 show maps with the stations' median concentrations of 10 light hydrocarbons for the winter months January, February, November and December in 2006 taken together. These medians are based on the average of the two 2-hourly values around noon at Rigi and on the day-time values at Hohenpeissenberg.

Although the number of sites obviously is too low to give a picture of the regional background distribution of hydrocarbons in Europe, some characteristics are indicated by these results. Similar figures for three carbonyls for the summer months May-August 2006 are given in Figure 14–Figure 16.

As noted in previous reports, the measurements indicate that hydrocarbons become fairly well mixed in Europe in winter. Components with a long chemical lifetime in winter, such as ethane and propane, show less geographical variations except for the results from Starina, SK06, which show generally higher levels. For benzene the median winter concentrations at Starina are twice as high as measured at the other sites.

Certain characteristics are seen in the 2006 though. For acetylene, propene and i-butane particularly high winter median concentrations are seen at the three German sites in the north (Zingst, Waldhof and Neuglobsow). Also at Košetice the acetylene and i-butane median concentrations are elevated.

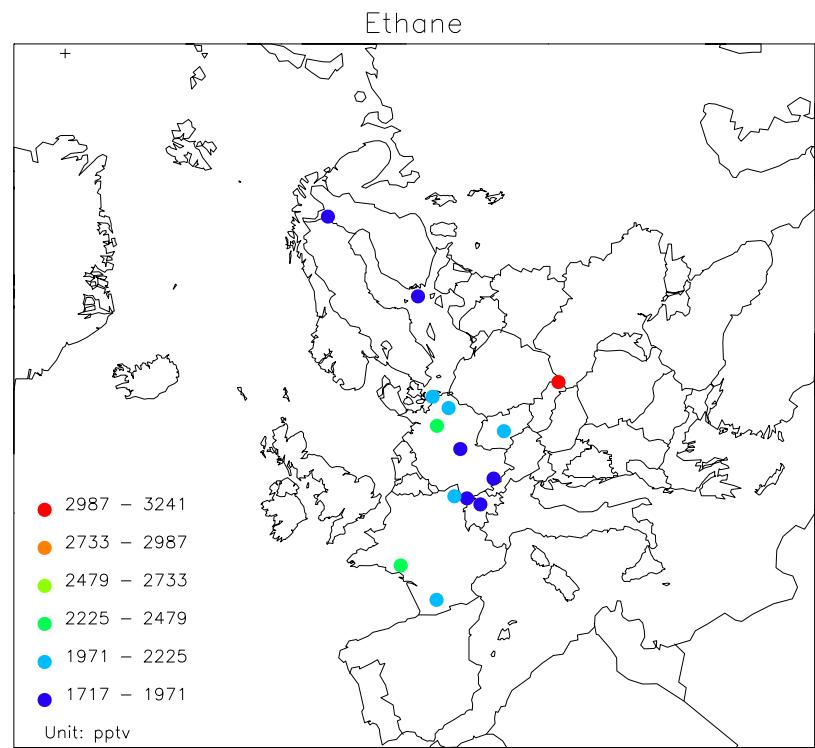


Figure 4: Median concentration of ethane at EMEP sites in the winter months November, December, January and February 2006 taken together.

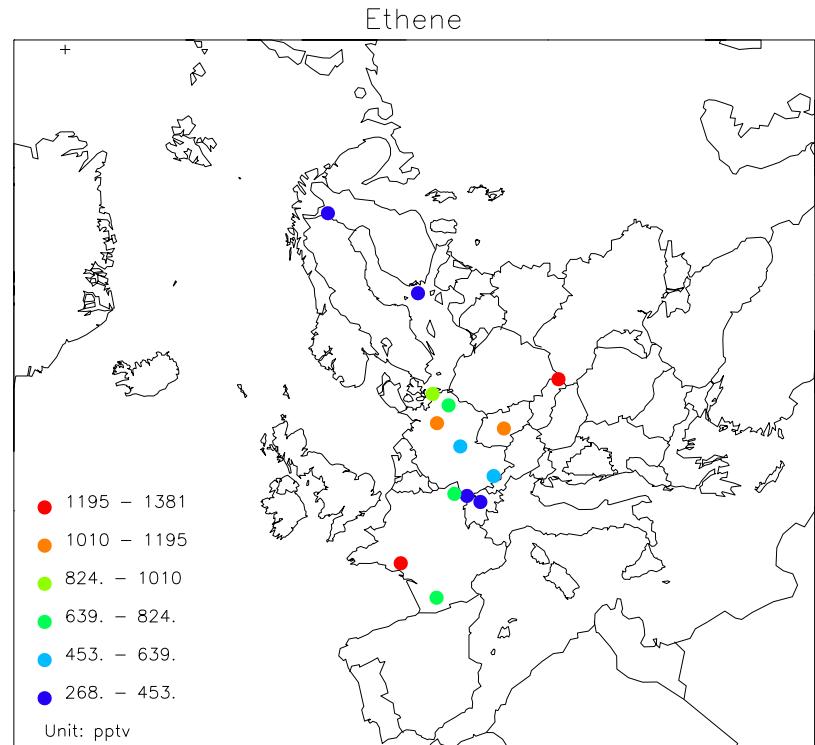


Figure 5: Median concentration of ethene at EMEP sites in the winter months November, December, January and February 2006 taken together.

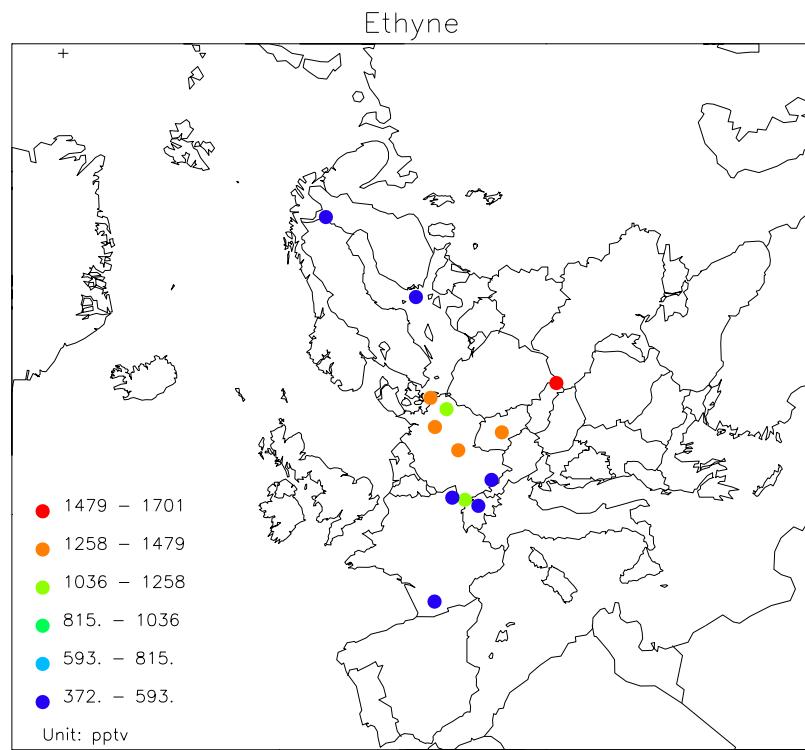


Figure 6: Median concentration of acetylene at EMEP sites in the winter months November, December, January and February 2006 taken together.

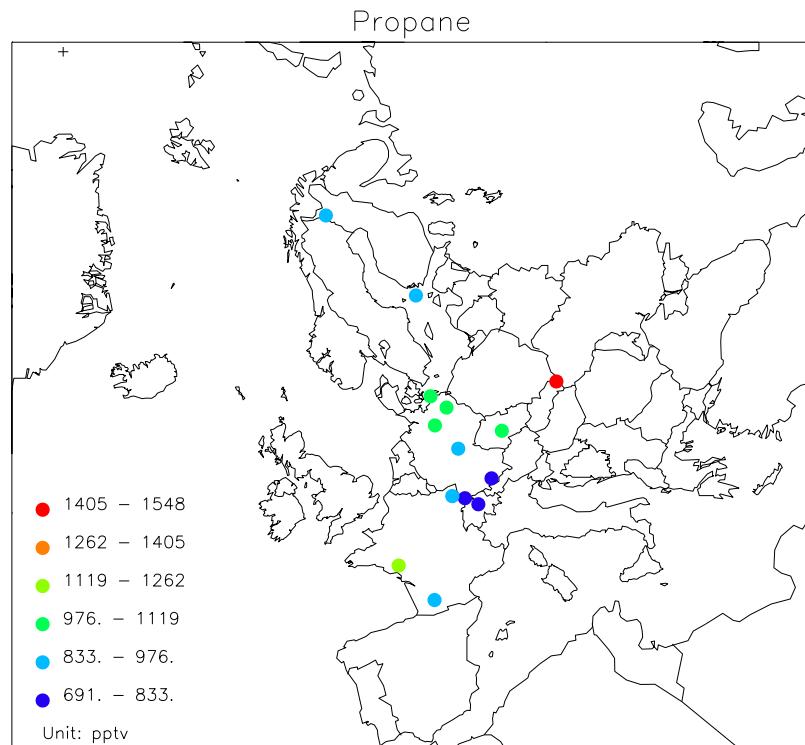


Figure 7: Median concentration of propane at EMEP sites in the winter months November, December, January and February 2006 taken together.

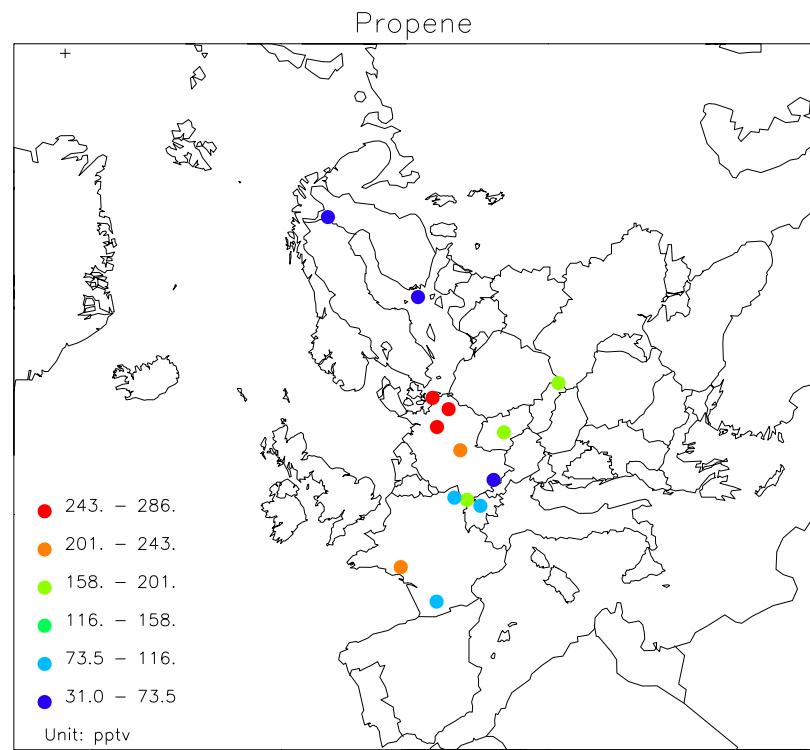


Figure 8: Median concentration of propene at EMEP sites in the winter months November, December, January and February 2006 taken together.

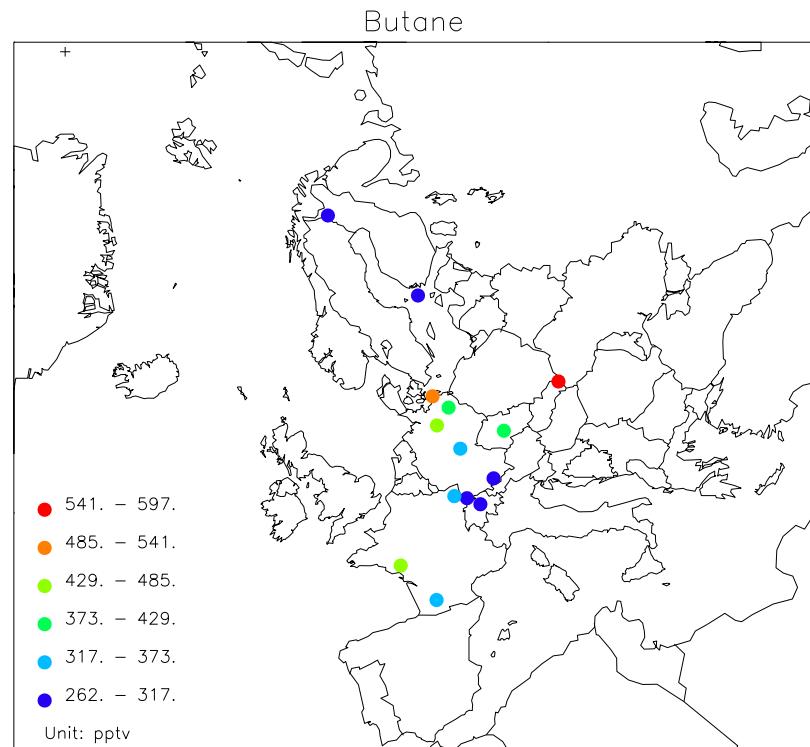
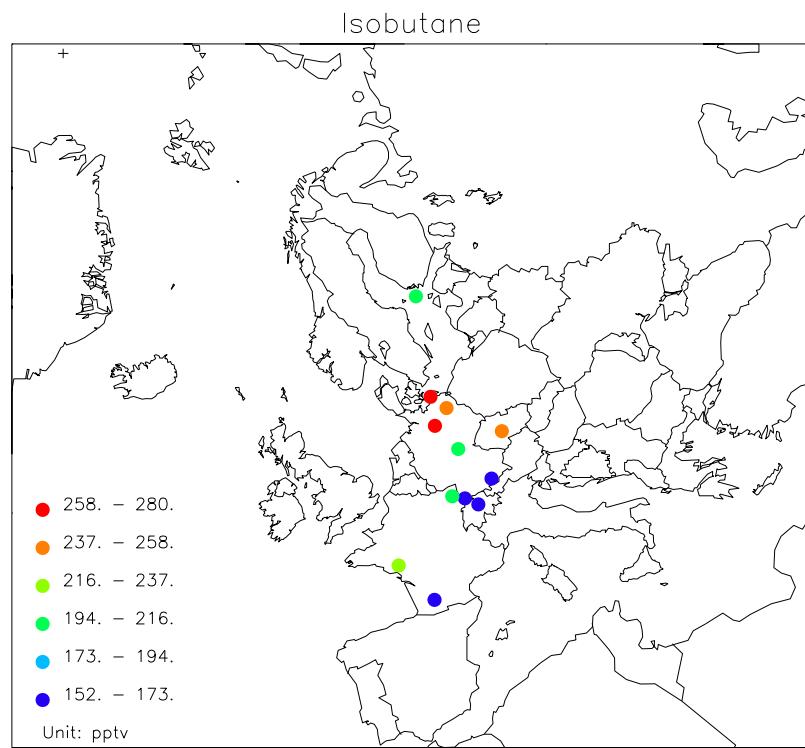
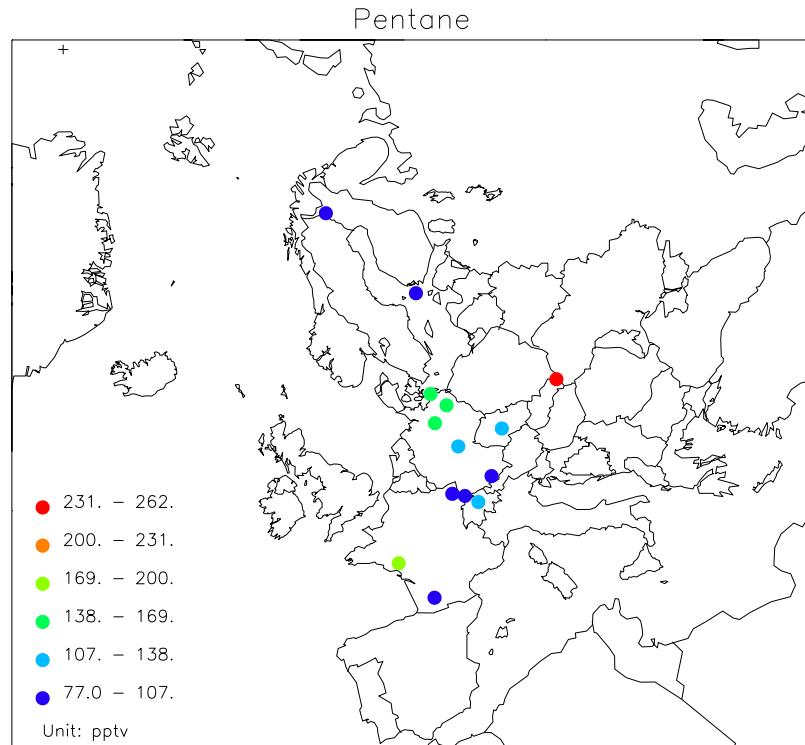


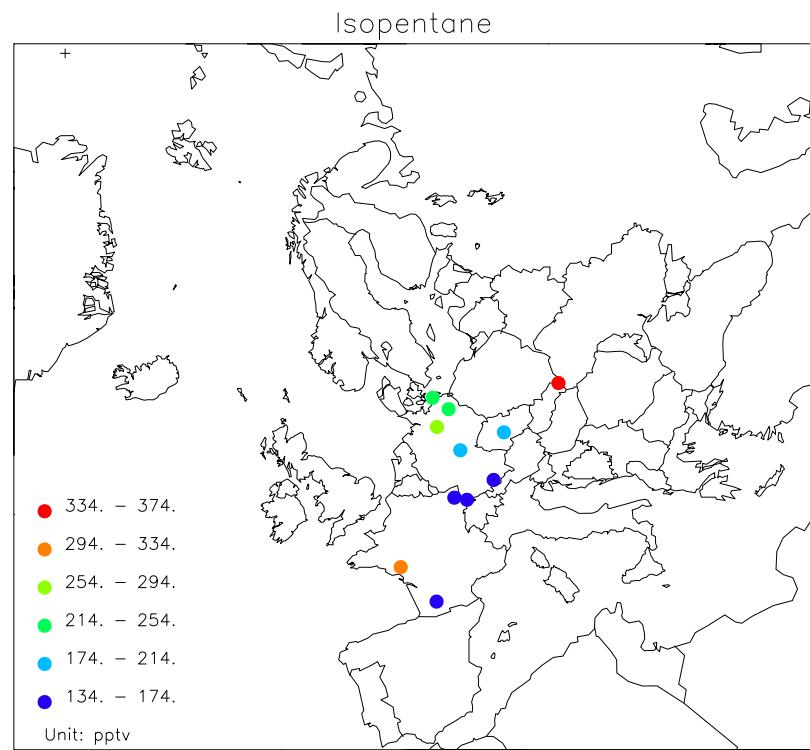
Figure 9: Median concentration of n-butane at EMEP sites in the winter months November, December, January and February 2006 taken together.



*Figure 10: Median concentration of *i*-butane at EMEP sites in the winter months November, December, January and February 2006 taken together.*



*Figure 11: Median concentration of *n*-pentane at EMEP sites in the winter months November, December, January and February 2006 taken together.*



*Figure 12: Median concentration of *i*-pentane at EMEP sites in the winter months November, December, January and February 2006 taken together.*

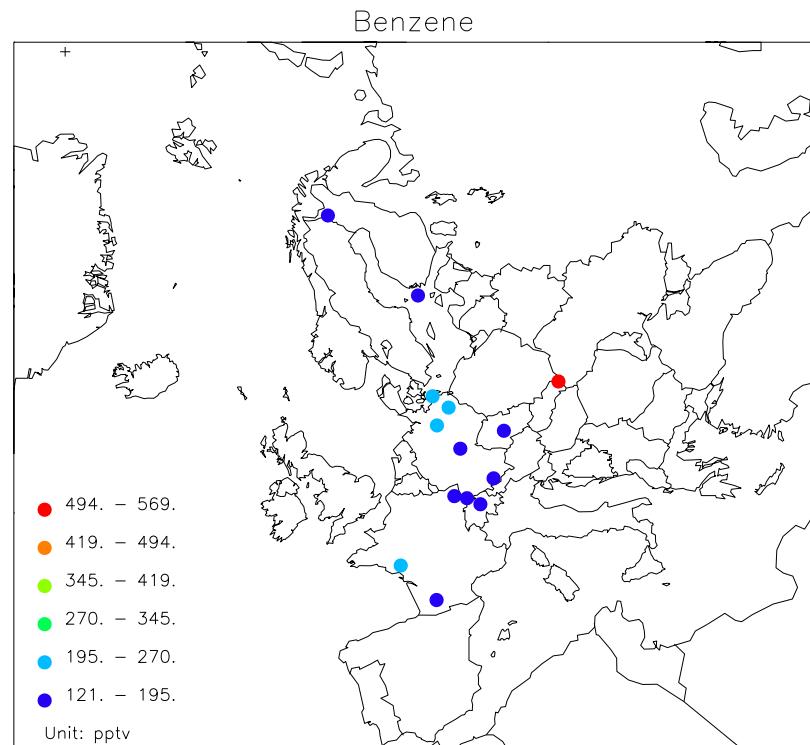


Figure 13: Median concentration of benzene at EMEP sites in the winter months November, December, January and February 2006 taken together.

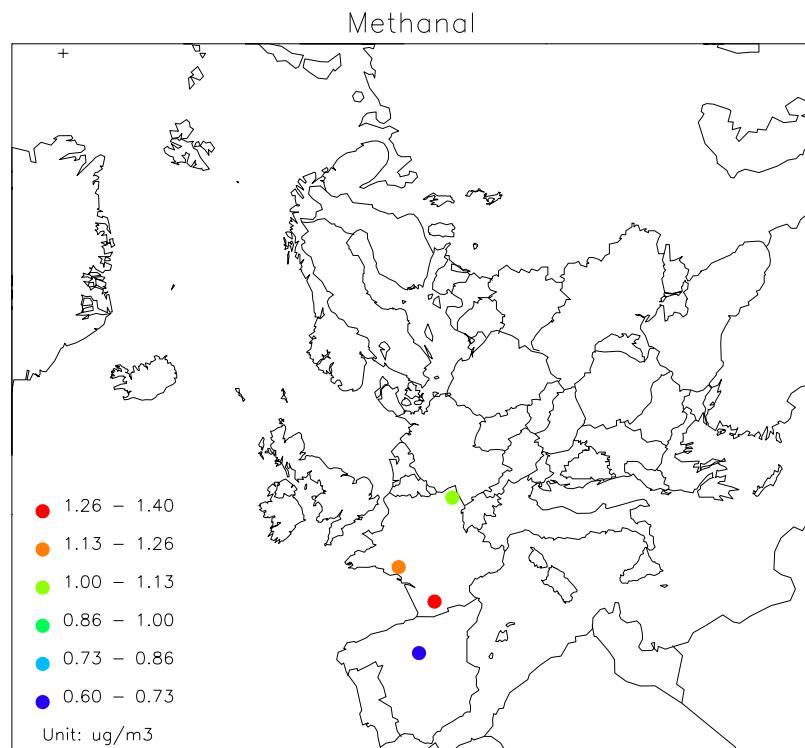


Figure 14: Median concentration of formaldehyde at EMEP sites in the summer months May, June, July and August 2006 taken together. Note that the values for ES09 are based on data for August only.

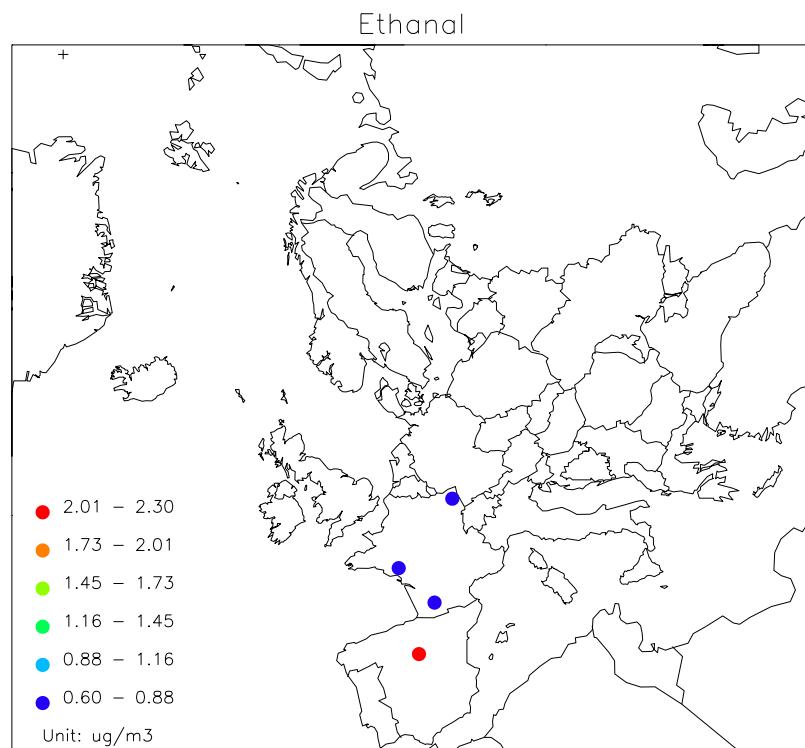


Figure 15: Median concentration of acetaldehyde at EMEP sites in the summer months May, June, July and August 2006 taken together. Note that the values for ES09 are based on data for August only.

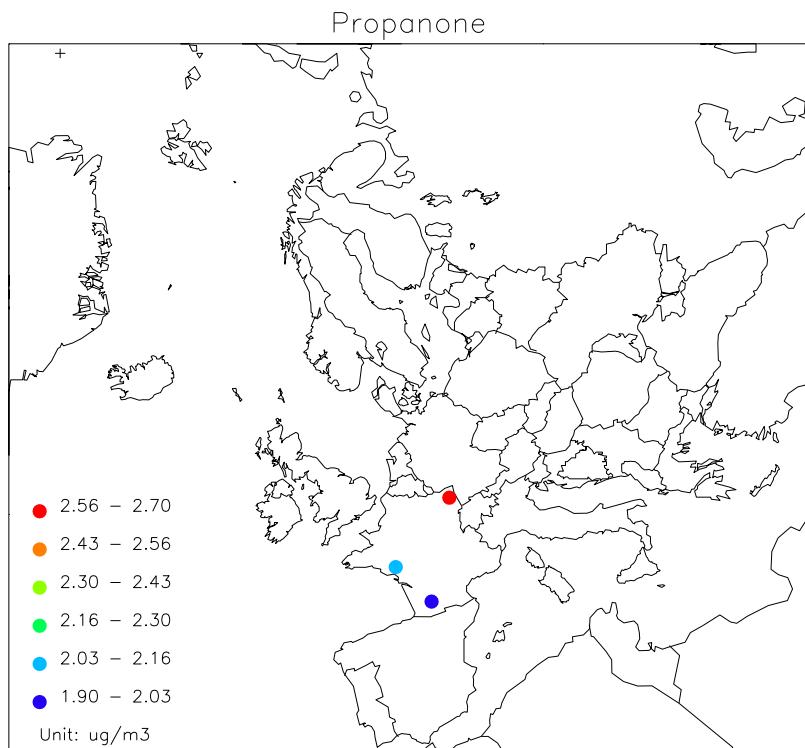


Figure 16: Median concentration of acetone at EMEP sites in the summer months May, June, July and August 2006 taken together.

4. Long-term trends in VOC

The 12 year's trend in the measured VOC from 1995 is indicated in Figure 17 showing the winter medians at Pallas (FI96), Utö (FI09), Waldhof (DE02), Schmücke (DE08), Košetice (CZ03) and Donon (FR08) of selected hydrocarbons.

In addition to the emission source strength, these long-term trends or variations will be largely controlled by inter-annual changes in weather conditions and atmospheric stability. Furthermore, the changes in chemical analysing laboratory may also have a significant impact on the median concentrations and this is marked in the Figures. Note that the parallel sampling and analyses has not necessarily been carried out during the whole season. Thus, large differences between two laboratories for the same year may give a false impression of the laboratory differences.

The 12 year's trend, or variations, in the winter medians varies for the various hydrocarbons as indicated by Figure 17 and no overall picture is seen. For some compounds, like toluene, the results do indicate a long-term reduction in the winter median concentration level, whereas for other compounds, there are signs of a concentration levelling off or even increasing during the last few years. Relative to the other components, the level of acetylene at Košetice and the German sites were higher in 2006 than compared to the last previous years.

The German sites DE02 and DE08 show substantially higher concentrations of toluene in 2006 compared to previous years and the reason for this is unclear. An

inspection of the long-term trend in the toluene:benzene ratio showed that after a 2-months gap in the time series in 2006 this ratio became significantly higher than seen in the years before that period. Thus, one should rule out the possibility of systematic changes in the toluene (and benzene) concentrations due to changes in sampling and analyses before making further conclusions.

To separate the sole effect of changes in European VOC emissions on the observed concentrations trends in Figure 17 requires a number of detailed model calculations. Furthermore, due to the large scatter in data values from year to year, a linear trend is of little value to assign.

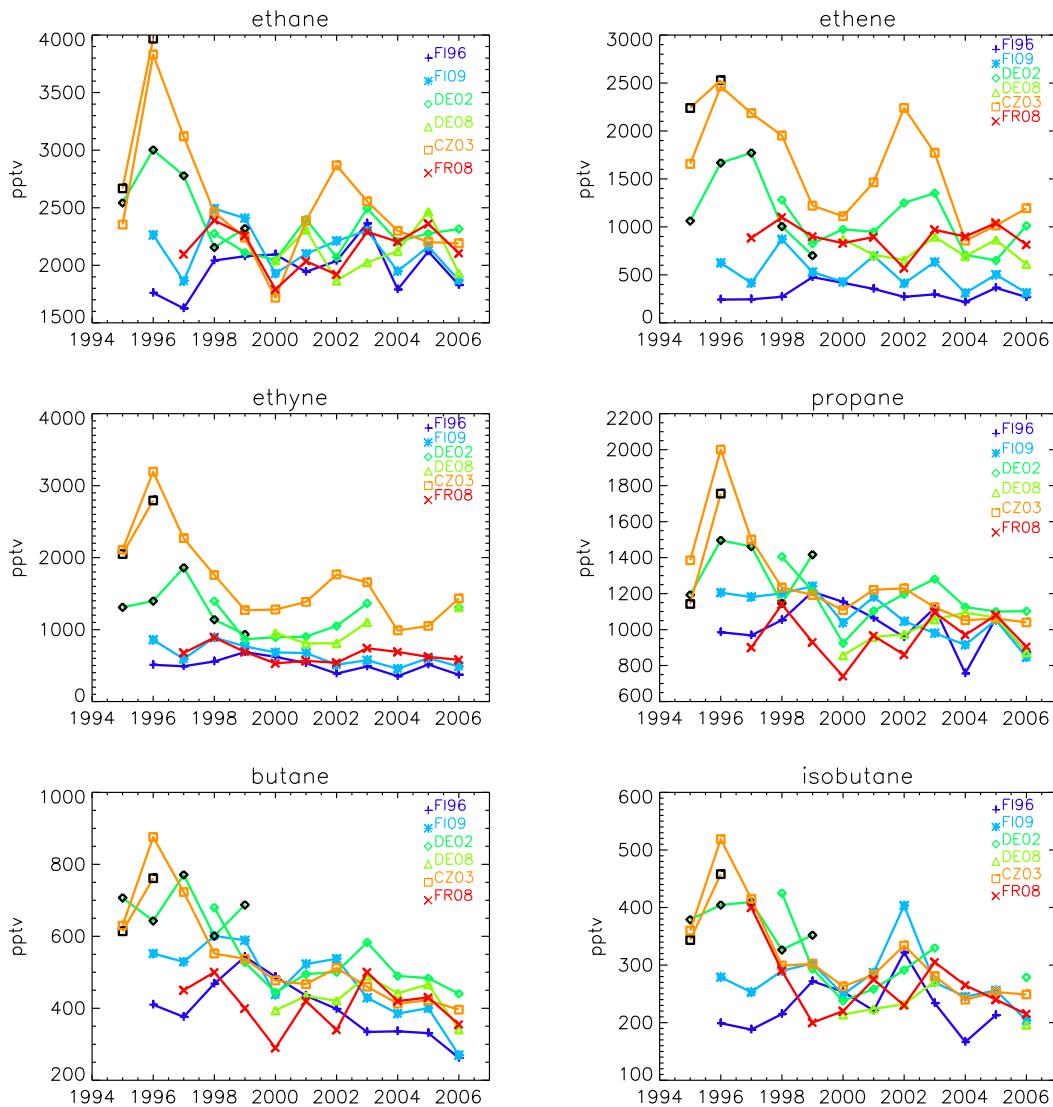


Figure 17: Annual winter (Jan., Feb., Nov., Dec.) median concentrations of hydrocarbons at Košetice (CZ03), Waldhof (DE02), Donon (FR08), Peyrusse Vieille (FR13), Utö (FI09) and Pallas (FI96). Black symbols mark analyses from NILU's lab., coloured symbols mark the national lab.

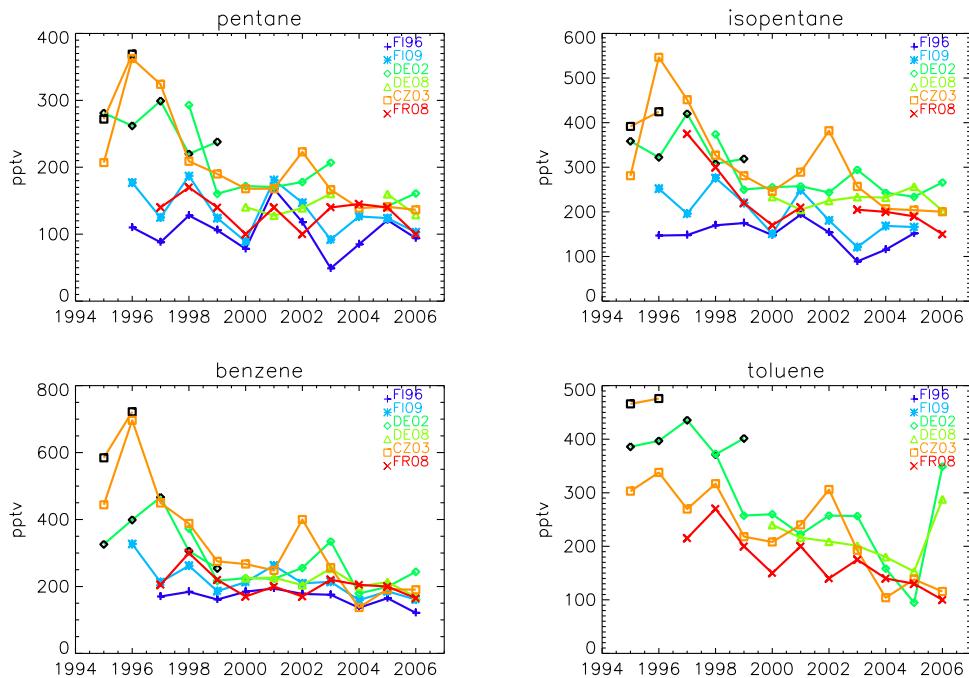


Figure 17, cont.

While the trend in absolute concentrations could be more difficult to interpret due to the large natural variability and the changing influence from large scale meteorology and dispersion, the individual components tend to fluctuate in parallel. Various studies have looked at concentrations relative to acetylene, as this component is regarded to be 100% anthropogenic origin, mainly stemming from combustion processes and thus a tracer of road and ship transport.

The results for three stations Utö (FI09), Donon (FR08) and Košetice (CZ03) are given in Table 5. The Table shows the long term trend of the concentration ratios based on winter-time data (Oct.-March) for the years 1998-2006 together with the linear correlation coefficients (r^2) for the same concentration pair. The trend was calculated from a robust linear regression, less sensitive to outliers and the slope was divided by the median concentration to obtain the "% year⁻¹" value shown in Table 5.

The results show a similarity between data from Donon and Košetice while the data from Utö differs somewhat. Ethene is found to increase significantly relative to acetylene at both Donon and Košetice at the same time as a very good correlation is found. The reason for this increase is yet unclear. One reason could be changes in the general emission from road traffic e.g. connected to a larger fleet of diesel powered vehicles, but more investigations are needed to look at this. Then, an considerable increase in ethane and propane relative to acetylene is found at all three sites, possibly indicating that the emissions of road traffic are dropping faster than the emissions of natural gas (source of the lightest alkanes). Furthermore, the largest downward trend vs. acetylene is found for toluene and also benzene at Donon and Košetice.

Table 5. The long-term trend (1998-2006) in the concentration ratio between individual hydrocarbons and acetylene. The square of the linear correlation coefficients (component vs. acetylene) are also given. Only data from winter (October-March) were used.

	Utö		Donon		Košetice	
	trend (% year ⁻¹)	r ²	trend (% year ⁻¹)	r ²	trend (% year ⁻¹)	r ²
Ethane	+5.56	0.58	+1.40	0.64	+4.09	0.61
Ethene	-0.29	0.71	+4.38	0.77	+1.75	0.82
Propane	+1.49	0.62	+1.75	0.69	+2.41	0.63
Propene	+5.35	0.31	+0.31	0.53	-1.18	0.47
n-butane	-2.22	0.46	-0.35	0.46	+0.68	0.61
i-butane	+0.53	0.52	+1.28	0.25	+2.33	0.44
n-pentane	+3.69	0.52	+2.15	0.66	-0.31	0.56
i-pentane	+2.50	0.54	-2.46	0.28	-1.64	0.54
benzene	+2.20	0.62	-2.07	0.94	-3.67	0.74
toluene	n.m.	n.m.	-4.56	0.71	-7.46	0.47

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Appendix A

Monthly mean and median concentrations of hydrocarbons and carbonyls in 2006

**Monthly mean and median concentrations
(first and second line, respectively)
of hydrocarbons (pptv)**

	PROPANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	1168 1093	1749 1865	891 796	472 484	211 210	127 104	65 60	180 191	295 287	349 344	535 535	851 875
Utö	1333 1371	1499 1275	1145 1130	636 562	344 284	173 131	133 112	245 269	296 266	351 334	553 536	784 767
Zingst	1787 1590	1559 1876	1315 1279	- -	- -	255 257	249 247	311 299	526 615	654 555	706 693	1094 920
Neuglobsow	2196 2166	1361 1158	1439 1427	- -	- -	319 319	399 306	352 320	559 517	1048 1028	731 690	890 818
Waldhof	2124 2262	- -	1068 853	- -	- -	321 320	267 249	428 381	705 523	665 604	729 705	1109 915
Schmücke	1146 1103	1026 1042	1086 1015	- -	- -	367 346	346 243	369 351	441 394	514 515	650 727	1065 942
Schauinsland	943 973	1021 899	923 993	- -	- -	284 225	292 271	239 235	392 369	540 373	496 488	672 636
Hohenpeissenberg	979 917	1132 1037	945 922	501 408	320 265	251 239	230 229	191 170	349 304	421 372	517 517	702 708
Starina	1551 1523	1754 1779	1410 1333	763 704	476 375	325 313	343 287	365 341	513 440	816 507	1446 1464	1531 1492
Košetice	1532 1399	1199 1189	1049 1109	687 596	429 377	236 226	253 173	222 207	456 537	590 467	716 751	944 989
Rigi	842 758	1104 870	759 666	438 357	280 247	326 308	283 261	232 219	582 527	596 520	572 527	583 617
La Tardière	1604 1390	1334 1170	872 890	555 455	269 280	300 310	241 220	136 120	271 290	493 450	614 620	1229 1245
Donon	1500 1330	1254 995	883 970	705 685	314 310	393 350	300 310	221 210	377 330	450 370	588 560	845 775
Peyrusse Vieille	- -	1191 1190	702 630	438 435	- -	301 305	211 180	186 190	279 300	438 445	629 630	1029 1005
	PROPENE											
	JAN 38 30	FEB 50 47	MAR 19 17	APR 22 21	MAY 18 20	JUN 24 18	JUL 24 23	AUG 51 49	SEP 24 25	OCT 20 18	NOV 31 30	DEC 24 19
Utö	78 63	75 56	53 45	46 34	38 34	41 33	32 29	45 40	33 26	46 51	49 48	68 57
Zingst	474 489	467 445	142 144	- -	- -	94 91	109 103	176 177	153 131	210 189	236 223	293 225
Neuglobsow	650 697	307 277	236 217	- -	- -	115 110	147 134	171 184	168 161	345 336	245 246	205 188
Waldhof	583 472	- -	147 142	- -	- -	113 101	100 99	149 142	161 139	213 214	259 226	264 196
Schmücke	274 233	335 206	176 170	- -	- -	91 85	84 79	150 153	128 122	175 163	231 209	235 207
Schauinsland	257 228	358 239	138 130	- -	- -	131 141	115 113	185 176	178 174	234 225	217 202	155 143
Hohenpeissenberg	72 31	98 47	42 25	40 30	25 20	24 21	18 14	20 17	29 21	46 33	79 55	100 74
Starina	188 97	156 161	97 99	65 66	47 30	54 41	50 48	79 78	38 24	90 74	301 178	304 237
Košetice	350 336	223 164	107 75	64 49	30 32	42 34	31 30	58 21	36 38	56 69	121 113	178 176
Rigi	121 82	264 167	92 69	71 56	76 72	63 59	49 45	45 40	59 47	84 65	96 70	108 78
La Tardière	278 280	223 170	86 70	85 80	76 70	91 100	108 100	74 80	129 100	121 110	140 125	299 340
Donon	293 230	194 95	94 90	121 105	78 60	180 110	127 130	100 110	101 100	113 80	137 100	141 120
Peyrusse Vieille	- -	84 80	68 60	55 55	- -	120 120	120 130	86 80	83 70	86 50	105 90	129 105

	ETHYNE (ACETYLENE)											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	506 440	1124 1326	429 439	380 365	197 181	107 94	65 65	107 108	114 101	152 142	328 314	379 337
Utö	798 724	1103 959	831 820	564 463	339 221	171 149	94 93	142 130	161 104	218 161	282 247	471 401
Zingst	1706 1236	1466 1655	1571 1317	- -	- -	630 653	537 523	726 720	733 680	1176 1151	1108 1025	1431 1388
Neuglobsow	2150 1891	1454 1468	1767 1370	- -	- -	593 588	541 534	697 707	688 673	1205 1027	1049 1008	1160 1166
Waldhof	2157 2014	- -	1182 982	- -	- -	618 601	574 574	721 756	672 677	951 781	1288 1157	1155 1164
Schmücke	1402 1152	1412 1306	1264 1268	- -	- -	607 629	566 564	727 710	674 650	843 840	1268 1253	1531 1404
Schauinsland	997 878	1288 1280	1257 1277	- -	- -	668 626	609 611	719 725	679 683	808 809	1071 1048	1119 1095
Hohenpeissenberg	918 721	1150 916	898 705	413 383	289 240	190 167	176 158	139 123	280 253	379 385	435 363	578 535
Starina	2085 1824	2477 2365	1579 1576	784 824	382 308	305 219	166 178	147 119	164 182	355 319	1342 827	1350 1300
Košetice	2638 2383	2474 2189	1353 1200	704 550	431 388	252 240	206 189	228 174	429 447	671 683	809 723	1063 926
Rigi	1143 727	1814 1249	1114 590	522 490	408 358	550 479	486 480	304 270	554 474	746 604	645 549	506 415
La Tardiére	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Donon	1508 1520	1030 670	641 550	433 425	264 275	208 190	171 190	140 150	259 240	322 210	411 310	571 525
Peyrusse Vieille	- -	871 870	384 370	468 345	- -	140 145	110 120	223 110	170 150	278 245	316 315	723 600
	BUTANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	392 340	580 573	304 237	217 166	65 50	44 26	13 10	47 50	86 88	100 96	170 168	275 252
Utö	442 435	461 376	378 424	183 146	101 108	43 32	39 29	72 72	138 123	108 105	173 170	256 273
Zingst	683 552	670 659	510 479	- -	- -	87 74	98 91	114 122	181 211	267 217	316 273	461 347
Neuglobsow	863 946	543 521	565 595	- -	- -	99 102	118 85	126 110	217 208	497 471	297 264	336 320
Waldhof	817 792	- -	402 326	- -	- -	109 105	104 108	167 168	248 205	284 270	323 302	444 391
Schmücke	447 418	428 436	429 468	- -	- -	110 106	85 83	143 121	136 128	170 179	265 249	428 379
Schauinsland	360 315	405 365	322 363	- -	- -	115 85	161 127	103 93	166 126	218 126	178 157	235 238
Hohenpeissenberg	372 349	458 407	324 327	158 136	99 85	92 79	84 75	76 70	144 117	179 134	219 192	266 264
Starina	602 607	656 663	486 478	270 226	192 177	123 118	147 141	177 152	220 209	278 218	580 574	609 573
Košetice	565 552	434 425	345 373	205 194	108 97	80 75	80 64	85 72	182 200	222 171	273 257	366 389
Rigi	468 410	630 446	350 290	216 201	138 113	158 154	138 128	97 83	232 190	285 238	248 209	418 256
La Tardiére	733 660	489 445	298 350	179 180	100 70	130 110	109 100	66 65	125 135	236 230	255 230	496 555
Donon	733 720	583 370	343 330	258 220	119 100	140 130	147 150	90 90	187 150	200 120	251 210	340 305
Peyrusse Vieille	- -	396 375	216 180	113 110	- -	103 100	76 75	64 60	104 110	138 135	226 225	358 325

	ISOBUTANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Utö	307 301	369 289	246 274	119 96	68 52	29 24	27 19	57 47	68 62	72 76	143 99	166 177
Zingst	396 425	367 353	293 309	-	-	41 41	50 43	64 68	98 82	163 124	161 149	263 190
Neuglobsow	509 611	317 300	357 346	-	-	78 70	72 44	85 67	147 143	431 408	201 155	191 189
Waldhof	452 444	- -	226 161	-	-	63 55	58 52	104 85	177 160	171 145	191 160	238 216
Schmücke	265 271	245 258	249 262	-	-	55 52	47 42	87 75	82 85	94 100	155 135	238 212
Schauinsland	202 179	219 204	188 204	-	-	61 44	79 61	51 52	94 72	223 73	107 85	152 131
Hohenpeissenberg	214 186	259 235	195 194	94 83	63 50	60 53	62 57	47 43	97 77	119 90	136 118	159 146
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	383 353	267 268	221 218	139 122	71 60	54 50	56 50	56 48	123 129	150 124	189 175	222 241
Rigi	267 229	373 263	211 167	122 112	74 62	83 78	79 73	64 60	105 102	177 143	150 123	204 150
La Tardière	318 305	268 230	166 170	438 120	38 30	53 50	44 30	25 25	99 70	123 90	126 130	233 260
Donon	527 510	429 220	230 180	176 125	78 45	95 85	100 110	59 60	154 90	154 80	159 110	201 200
Peyrusse Vieille	-	220 215	122 110	158 80	-	61 60	35 35	32 30	150 60	80 70	120 115	451 175
	BUTENES											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Neuglobsow	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Schauinsland	-	-	-	-	-	-	-	-	-	-	-	-
Hohenpeissenberg	-	-	-	-	-	-	-	-	-	-	-	-
Starina	63 59	64 65	54 54	42 43	39 38	32 33	32 32	44 44	40 38	40 38	80 79	63 59
Košetice	119 94	82 72	58 53	45 37	42 32	37 36	27 26	37 24	45 33	36 34	48 49	71 73
Rigi	-	-	-	-	-	-	-	-	-	-	-	-
La Tardière	-	-	-	-	-	-	-	-	-	-	-	-
Donon	-	-	-	-	-	-	-	-	-	-	-	-
Peyrusse Vieille	-	-	-	-	-	-	-	-	-	-	-	-

	BUT_1_ENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	8 7	11 10	4 3	13 7	5 5	5 3	6 6	11 11	6 7	5 4	5 5	5 5
Utö	11 7	12 10	10 8	10 9	9 8	9 7	7 7	11 10	7 6	7 6	10 10	13 11
Zingst	48 38	-	-	-	-	-	-	-	-	-	-	-
Neuglobsow	63 65	-	-	-	-	-	-	-	-	-	-	-
Waldhof	55 56	-	-	-	-	-	-	-	-	-	-	-
Schmücke	38 40	-	-	-	-	-	-	-	-	-	-	-
Schauinsland	33 27	-	-	-	-	-	-	-	-	-	-	-
Hohenpeissenberg	15 11	19 10	11 9	10 9	8 7	7 6	7 7	7 6	8 8	12 10	18 13	20 16
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	-	-	-	-	-	-	-	-	-	-	-	-
Rigi	-	-	-	-	-	-	-	-	-	-	-	-
La Tardiére	48 50	43 40	21 20	23 20	23 20	26 30	30 30	26 25	56 30	31 30	34 30	56 55
Donon	47 40	33 20	23 20	29 30	21 20	33 35	36 40	31 30	30 30	30 30	32 30	29 30
Peyrusse Vieille	-	17 20	15 10	14 15	-	33 30	31 30	23 20	20 20	23 20	19 20	26 25
	TRANS_2_BUTENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	7 5	5 3	5 3	14 4	8 8	5 3	3 3	9 10	6 6	3 3	4 3	5 3
Utö	16 17	3	3	5 3	7 6	3	5 5	3 3	4 3	3 3	4 3	5 3
Zingst	6 6	-	-	-	-	-	-	-	-	-	-	-
Neuglobsow	8 7	-	-	-	-	-	-	-	-	-	-	-
Waldhof	5 6	-	-	-	-	-	-	-	-	-	-	-
Schmücke	8 7	-	-	-	-	-	-	-	-	-	-	-
Schauinsland	8 7	-	-	-	-	-	-	-	-	-	-	-
Hohenpeissenberg	-	-	-	-	-	-	-	-	-	-	-	-
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	-	-	-	-	-	-	-	-	-	-	-	-
Rigi	-	-	-	-	-	-	-	-	-	-	-	-
La Tardiére	-	-	-	-	-	-	-	-	-	-	-	-
Donon	-	-	-	-	-	-	-	-	-	-	-	-
Peyrusse Vieille	-	-	-	-	-	-	-	-	-	-	-	-

	CIS_2-BUTENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	3 3	5 3	4 3	8 3	3 3	3 3	3 3	3 3	3 3	3 3	3 3	3 3
Utö	6 3	3 3	3 3	3 3	3 3	4 3	3 3	3 3	3 3	3 3	3 3	3 3
Zingst	6 6	-	-	-	-	-	-	-	-	-	-	-
Neuglobsow	8 7	-	-	-	-	-	-	-	-	-	-	-
Waldhof	7 7	-	-	-	-	-	-	-	-	-	-	-
Schmücke	7 5	-	-	-	-	-	-	-	-	-	-	-
Schauinsland	7 5	-	-	-	-	-	-	-	-	-	-	-
Hohenpeissenberg	6 5	7 5	6 6	5 4	4 4	3 3	4 4	3 3	4 4	5 4	6 4	6 6
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	-	-	-	-	-	-	-	-	-	-	-	-
Rigi	-	-	-	-	-	-	-	-	-	-	-	-
La Tardière	-	-	-	-	-	-	-	-	-	-	-	-
Donon	-	-	-	-	-	-	-	-	-	-	-	-
Peyrusse Vieille	-	-	-	-	-	-	-	-	-	-	-	-
	PENTANE											
	JAN 114 98	FEB 205 188	MAR 93 81	APR 59 67	MAY 16 18	JUN 15 10	JUL 8 10	AUG 26 25	SEP 34 35	OCT 38 36	NOV 67 68	DEC 100 88
Utö	156 133	229 170	159 156	76 58	41 33	22 15	19 10	43 42	62 42	50 34	65 63	93 100
Zingst	177 163	198 192	158 138	-	-	33 24	48 30	43 47	69 77	123 90	146 159	168 122
Neuglobsow	223 240	164 176	173 180	-	-	41 44	42 30	61 53	106 102	302 280	125 102	122 131
Waldhof	246 242	- 103	128 103	-	-	58 50	53 55	94 74	125 119	146 160	152 137	183 151
Schmücke	142 121	128 139	140 153	-	-	66 54	50 46	66 64	84 87	91 91	106 101	162 160
Schauinsland	85 73	113 99	94 103	-	-	55 32	85 63	45 38	81 80	192 49	85 48	61 60
Hohenpeissenberg	116 101	145 123	100 92	62 49	46 33	65 48	60 46	41 34	98 76	103 73	100 67	98 80
Starina	268 278	247 237	172 167	118 106	151 76	70 46	82 71	113 95	113 109	150 142	215 216	287 264
Košetice	212 183	144 140	119 115	72 61	54 47	50 41	45 41	46 38	92 88	112 97	118 112	138 136
Rigi	162 125	310 185	157 101	117 89	79 59	131 102	126 99	73 48	217 135	231 148	160 93	114 102
La Tardière	251 180	170 150	120 140	171 125	137 140	167 180	228 240	119 110	173 170	223 220	138 130	260 255
Donon	223 160	165 115	94 90	104 70	64 45	75 70	76 80	38 40	83 80	92 80	94 70	130 100
Peyrusse Vieille	-	108 100	108 50	48 50	-	56 60	41 40	36 30	49 40	46 45	60 65	173 100

	ISOPENTANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	267 270	291 279	206 179	-	-	57 40	67 67	109 105	138 149	213 179	244 229	242 185
Neuglobsow	357 324	244 268	235 239	-	-	88 83	102 97	147 114	186 186	402 467	194 151	206 194
Waldhof	331 318	- 169	172 169	-	-	86 100	87 87	143 132	181 162	234 230	216 205	238 196
Schmücke	203 201	191 209	186 203	-	-	103 102	87 76	124 130	150 151	191 174	187 167	256 227
Schauinsland	144 124	170 139	141 161	-	-	77 65	145 118	125 100	186 182	127 104	150 109	130 126
Hohenpeissenberg	189 162	260 198	170 165	112 97	98 81	115 101	122 108	91 77	188 163	193 160	160 129	160 144
Starina	318 340	311 312	238 241	157 136	191 174	110 74	125 142	305 304	225 216	264 234	544 410	504 374
Košetice	296 289	209 200	156 147	106 92	71 81	65 62	70 64	80 67	153 136	148 152	161 159	201 191
Rigi	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
La Tardiére	423 350	270 225	162 180	165 150	94 90	119 100	138 140	86 90	180 190	254 240	195 165	328 345
Donon	340 290	230 155	149 120	150 100	94 65	98 95	130 130	84 90	154 160	130 90	140 110	173 155
Peyrusse Vieille	- -	204 215	218 90	108 95	-	76 75	63 60	66 60	116 90	93 105	119 135	231 175
	HEXANE											
	JAN 40 34	FEB 69 60	MAR 25 21	APR 14 15	MAY 4 3	JUN 4 3	JUL 3 3	AUG 6 7	SEP 10 9	OCT 11 11	NOV 20 19	DEC 30 26
Utö	52 38	78 55	47 42	19 13	12 8	6 7	5 3	17 15	10 9	13 10	22 19	35 32
Zingst	78 65	103 74	84 69	-	-	40 30	39 39	38 36	110 48	76 72	113 73	102 72
Neuglobsow	92 90	95 99	102 106	-	-	41 42	54 48	78 45	53 56	128 131	74 69	95 73
Waldhof	94 91	- -63	75 63	-	-	58 62	37 41	59 54	117 55	73 74	73 76	95 87
Schmücke	53 48	76 85	76 79	-	-	49 46	40 43	95 54	47 49	90 74	105 83	96 86
Schauinsland	35 31	63 64	61 68	-	-	49 41	68 56	49 43	56 52	146 43	56 44	89 55
Hohenpeissenberg	30 27	37 30	25 22	13 11	10 8	11 9	11 9	9 8	18 16	19 15	19 16	23 21
Starina	188 198	117 96	71 72	90 85	63 37	43 23	59 38	76 51	53 43	66 53	109 113	138 118
Košetice	68 61	46 39	28 22	22 19	16 13	13 11	11 9	14 10	22 22	26 19	28 27	42 45
Rigi	47 39	68 44	32 25	22 18	21 18	33 31	29 27	22 19	46 40	44 39	35 30	30 30
La Tardiére	79 70	54 40	25 30	23 20	24 20	38 40	26 30	16 20	35 30	39 30	31 35	61 60
Donon	80 60	63 45	34 30	61 40	36 30	33 30	34 30	33 30	43 30	30 25	40 30	43 40
Peyrusse Vieille	- -	40 30	21 20	23 20	-	49 40	39 35	29 30	31 20	34 35	24 20	44 40

	ISOPRENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	7 4	4 4	5 4	4 4	10 4	19 20	54 45	50 48	16 13	4 4	4 4	4 4
Utö	4 4	4 4	12 4	4 4	14 4	12 4	28 19	42 32	8 4	4 4	6 4	7 4
Zingst	33 18	12 12	5 4	-	-	107 34	515 539	283 240	147 184	33 26	13 7	6 4
Neuglobsow	20 21	10 6	8 5	-	-	130 121	411 364	150 107	163 152	51 40	11 8	11 8
Waldhof	11 7	- -	6 6	-	-	40 28	115 109	52 50	80 57	39 30	8 8	8 8
Schmücke	13 10	7 6	5 5	-	-	59 40	69 60	28 27	27 27	13 13	6 5	6 5
Schauinsland	123 37	20 15	5 4	-	-	99 66	200 141	56 56	102 102	32 30	16 15	6 7
Hohenpeissenberg	4 4	4 3	3 2	8 4	23 12	73 17	124 46	18 10	43 15	18 10	8 4	6 5
Starina	13 9	9 9	10 9	14 9	30 23	222 46	558 403	140 67	145 150	25 19	25 25	18 15
Košetice	9 4	6 4	5 4	32 11	35 22	83 66	122 119	51 35	53 44	15 11	10 9	10 4
Rigi	15 15	20 21	13 11	13 12	37 23	107 37	195 126	57 31	86 35	48 35	27 19	14 12
La Tardiére	10 10	9 5	9 5	8 5	63 50	340 300	718 740	316 345	306 300	69 70	10 8	12 10
Donon	46 20	29 30	24 10	64 60	176 155	1130 750	2610 2570	599 440	707 560	313 210	76 60	58 35
Peyrusse Vieille	- -	5 5	38 10	58 50	-	1158 965	2019 1900	741 780	589 290	278 295	42 35	10 5
	BENZENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	181 137	348 433	144 150	118 120	52 56	27 27	14 14	53 42	37 33	41 39	97 93	114 100
Utö	297 250	335 279	242 212	152 132	93 67	41 36	38 38	65 52	69 57	62 49	97 85	143 136
Zingst	311 301	377 419	377 289	-	-	56 57	54 56	66 63	97 95	167 104	122 115	184 133
Neuglobsow	526 448	377 350	456 309	-	-	59 56	60 53	68 68	110 103	235 195	121 125	143 139
Waldhof	532 491	- -	249 188	-	-	64 62	54 53	76 75	103 105	168 116	159 148	190 171
Schmücke	360 267	315 326	262 260	-	-	69 63	52 50	69 68	83 66	107 83	131 131	207 185
Schauinsland	224 206	302 276	261 254	-	-	68 56	72 64	66 71	85 79	112 83	121 108	114 117
Hohenpeissenberg	267 212	340 281	273 229	143 132	101 88	73 68	66 61	58 53	94 86	116 92	121 102	169 156
Starina	670 682	660 608	403 414	296 282	130 120	112 89	128 118	140 139	172 127	212 199	607 423	645 624
Košetice	402 392	374 293	206 176	163 154	88 73	50 46	47 39	51 41	83 90	116 111	128 122	204 168
Rigi	354 238	548 396	317 246	184 179	112 100	123 118	89 85	72 67	128 115	155 126	149 125	167 141
La Tardiére	328 300	279 265	176 150	96 80	52 50	56 50	46 40	34 35	54 50	97 90	111 110	261 255
Donon	438 430	295 180	174 150	116 120	59 55	55 50	50 50	50 40	70 70	91 60	118 90	170 160
Peyrusse Vieille	- -	231 225	100 100	65 60	-	46 50	26 30	30 30	49 40	69 65	98 95	190 165

	TOLUENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	190 147	348 253	252 252	-	-	251 175	454 311	291 332	424 428	461 439	347 335	321 293
Neuglobsow	340 261	294 276	279 269	-	-	282 292	353 300	396 331	379 342	606 610	348 341	380 400
Waldhof	290 285	- 203	227 203	-	-	455 452	394 209	485 560	422 369	508 446	424 390	412 391
Schmücke	157 98	288 292	237 213	-	-	430 404	294 225	304 325	377 334	274 225	329 290	355 353
Schauinsland	121 101	302 348	207 207	-	-	166 170	555 643	290 256	624 572	483 516	561 621	286 235
Hohenpeissenberg	144 104	227 165	132 111	81 71	68 56	64 57	62 54	60 52	119 103	136 112	132 98	132 115
Starina	139 142	54 25	21 22	83 75	42 18	31 15	43 21	28 18	31 17	30 23	23 18	42 33
Košetice	179 178	150 134	82 62	67 54	30 33	28 26	23 19	42 24	72 49	75 64	87 78	114 96
Rigi	217 130	395 229	234 150	165 130	192 156	144 134	150 128	122 91	287 263	356 296	227 163	174 133
La Tardiére	452 450	265 205	130 100	88 90	69 70	93 70	114 100	61 65	191 140	367 340	166 120	335 310
Donon	276 280	183 90	94 70	104 80	51 35	55 55	66 70	60 60	100 80	92 70	103 60	116 90
Peyrusse Vieille	- -	146 160	68 50	58 60	-	79 70	51 45	42 40	120 90	68 60	96 110	200 145
ETHYLBENZENE												
Pallas	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Neuglobsow	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Schauinsland	-	-	-	-	-	-	-	-	-	-	-	-
Hohenpeissenberg	23 16	38 25	22 20	14 11	11 9	10 8	10 8	10 8	19 17	22 18	23 19	22 19
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	33 29	33 31	15 13	15 9	6 5	9 6	12 7	10 6	11 10	14 12	16 15	18 17
Rigi	29 21	55 29	27 16	34 31	46 45	42 49	20 17	18 15	38 29	46 38	36 25	28 23
La Tardiére	62 60	42 40	29 20	31 30	28 30	31 30	41 40	24 20	49 35	91 60	36 30	51 55
Donon	49 50	31 10	19 10	28 25	23 20	15 15	23 20	18 20	23 20	19 20	20 20	23 20
Peyrusse Vieille	-	19 20	10 10	10 8	-	29 25	30 30	20 20	30 20	19 20	23 20	34 30

	m+p-XYLENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	-	104	34	-	-	65	22	17	35	44	50	56
	-	118	31	-	-	50	21	16	30	35	53	39
Neuglobsow	-	65	52	-	-	41	29	28	31	131	52	52
	-	46	53	-	-	25	20	23	28	112	33	42
Waldhof	-	-	43	-	-	33	17	29	49	60	67	59
	-	-	21	-	-	37	14	23	33	51	74	44
Schmücke	-	73	59	-	-	33	23	26	28	42	48	72
	-	58	60	-	-	31	21	27	24	42	50	74
Schauinsland	-	56	38	-	-	57	35	28	-	30	42	30
	-	51	33	-	-	58	36	16	-	26	30	27
Hohenpeissenberg	49	83	42	29	25	22	20	21	39	49	60	57
	38	55	35	21	18	14	14	18	31	36	40	39
Starina	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	66	57	31	36	16	18	36	29	17	31	35	42
	52	32	25	27	12	11	8	17	15	26	34	40
Rigi	64	129	72	114	73	79	40	36	78	98	94	74
	42	52	31	105	63	71	32	29	54	74	60	59
La Tardiére	174	104	76	104	111	108	134	76	166	300	121	160
	150	105	70	125	120	100	130	80	140	190	110	160
Donon	112	64	34	69	51	53	53	47	51	42	59	61
	80	35	30	60	50	50	50	50	40	40	40	55
Peyrusse Vieille	-	31	26	29	-	91	84	69	77	45	68	84
	-	35	20	20	-	90	75	70	50	45	55	65
	o-XYLENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	-	42	15	-	-	11	7	11	15	21	22	23
	-	44	14	-	-	8	7	10	13	21	23	17
Neuglobsow	-	28	22	-	-	11	9	21	16	43	27	25
	-	22	21	-	-	9	9	17	15	50	17	21
Waldhof	-	-	17	-	-	10	10	14	14	30	31	25
	-	-	14	-	-	9	9	13	13	27	26	19
Schmücke	-	28	22	-	-	12	14	17	14	18	20	29
	-	20	22	-	-	12	13	16	13	17	22	25
Schauinsland	-	27	15	-	-	13	18	15	-	16	18	13
	-	20	13	-	-	11	18	12	-	14	13	12
Hohenpeissenberg	19	31	16	11	10	9	9	9	18	21	22	22
	15	20	13	9	9	8	8	8	16	16	14	19
Starina	404	317	196	234	137	146	171	199	167	211	388	469
	473	302	188	226	141	105	143	193	160	166	304	389
Košetice	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
Rigi	27	54	35	39	-	23	21	18	47	45	38	32
	19	26	28	34	-	22	18	14	37	38	24	26
La Tardiére	58	29	18	18	17	15	17	10	33	64	28	48
	50	30	10	20	20	10	20	10	25	50	25	45
Donon	39	24	12	21	8	8	5	5	12	11	16	19
	30	8	5	15	8	8	5	5	10	5	5	15
Peyrusse Vieille	-	9	-	24	-	25	8	8	21	6	16	24
	-	10	-	25	-	20	10	5	10	5	10	20

**Monthly mean and median concentrations
(first and second line, respectively)
of carbonyls ($\mu\text{g m}^{-3}$)**

Appendix B

Time series of VOC measured in 2006

Explanations and synonyms to component names

ethyne:	acetylene
butane:	n-butane
isobutane:	i-butane
pentane:	n-pentane
isopentane:	i-pentane
hexane:	n-hexane
methanal:	formaldehyde
ethanal:	acetaldehyde
propanone:	acetone
N2propenal:	2-propenal (acrolein)
N2butanone:	2-butanone (methyl ethyl ketone)
N3buten2one:	3-buten-2-one (methyl vinyl ketone)
N2methylpropenal:	2-methyl propenal (methacrolein)
benzenecarbaldehyde:	benzaldehyde
ethanodial:	glyoxal
N2oxoproanal:	2-oxopropanal (methyl glyoxal)

