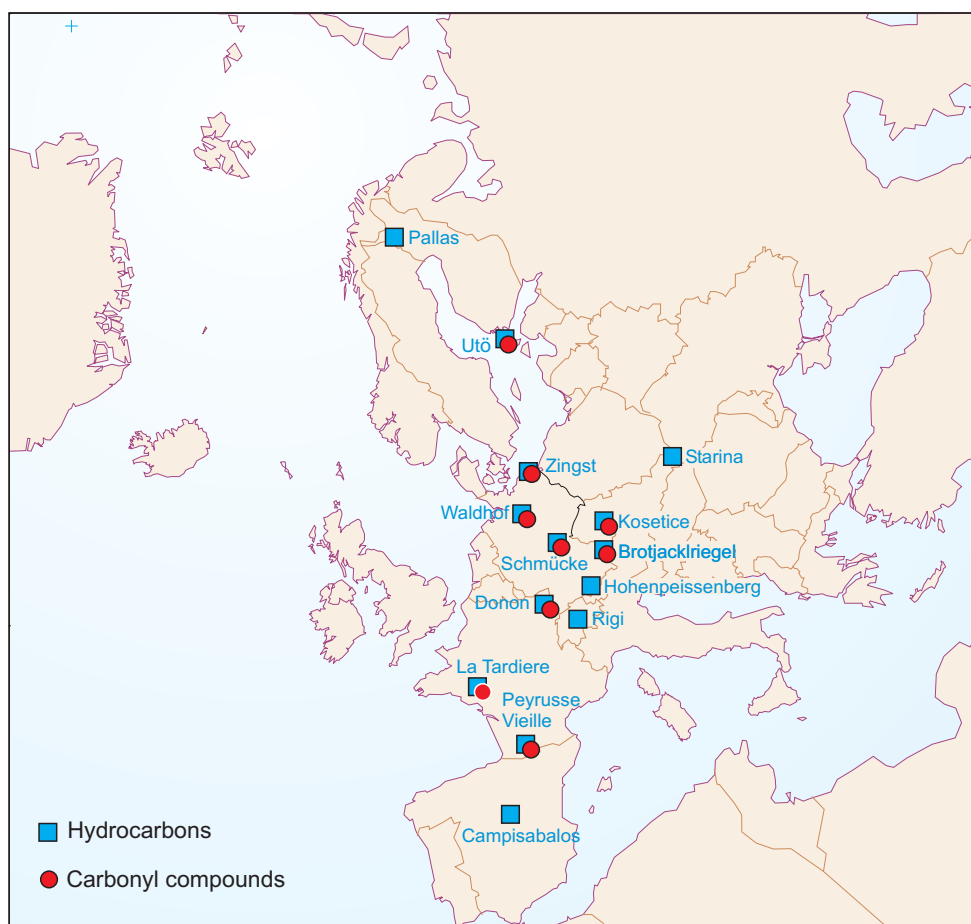


# VOC measurements 2003

Sverre Solberg





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

**VOC measurements 2003**

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## Summary

This report presents measurements of VOC carried out during 2003 at EMEP monitoring sites. VOC measurements are reported for a total of 14 sites and 9 of these with carbonyls. All the VOC measurements are made by grab samples of light hydrocarbons in canisters and 8-h samples of carbonyls by DNPH adsorption tubes.

The carbonyl samples from Germany and France were analysed by the national laboratories. For the light hydrocarbons the national laboratories in the respective countries carried out their own chemical analyses. No parallel sampling of hydrocarbons or carbonyls were carried out in 2003.

Europe experienced extreme weather conditions in the summer half year of 2003 with several heat waves, the most pronounced in August. Overall the European summer was probably the warmest since year 1500. The measured concentration of the VOCs, however, don't indicate anomalous concentration in either direction. Isoprene is an exception to this and showed about twice as high concentrations in summer than compared to previous years at Donon in France whilst not at any of the other sites. This is an indication of increased biogenic emissions caused by the elevated temperature and enhanced solar radiation reaching the surface during the heat waves.

The long-term changes in the winter medians of hydrocarbons indicate a marked decline from 1993 to 2000 and a levelling off or even increase after that. The reduction is particularly evident for benzene, butane and isobutane and somewhat less for ethene and acetylene. To what extent these effects are explained by changes in European, anthropogenic emissions or by changes in meteorological conditions are not possible to quantify without long-term detailed transport model calculations.

For the summer medians in carbonyls the trends are less clear, presumably reflecting that inter-annual variations in photo-oxidation are controlling these species.





# VOC measurements 2003

## 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 17<sup>th</sup> May 2005 the Protocol entered into force. The Protocol sets emission ceilings for 2010 for four pollutants: sulphur, NO<sub>x</sub>, VOCs and ammonia. These ceilings were negotiated on the basis of scientific assessments of pollution effects and abatement options. Parties whose emissions have a more severe environmental or health impact and whose emissions are relatively cheap to reduce will have to make the biggest cuts. According to the Protocol, Europe's sulphur emissions should be cut by at least 63%, its NO<sub>x</sub> emissions by 41%, its VOC emissions by 40% and its ammonia emissions by 17% compared to 1990. The Protocol also sets tight 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).*

	<b>required</b>	<b>desirable</b>
<b>Alkanes</b>	ethane	hexane
	propane	branched hexanes
	i-butane	heptane
	n-butane	branched heptanes
	i-pentane	octane
	n-pentane	
<b>Alkenes</b>	ethene	butenes
	propene	pentenes
	isoprene	
<b>Alkynes</b>	acetylene	
<b>Aromatics</b>	benzene	styrene
	toluene	propylbenzenes
	o-xylene	ethyltoluenes
	m,p-xylene	
	ethylbenzene	
	trimethylbenzenes	
<b>Aldehydes</b>	formaldehyde	propionaldehyde
	acetaldehyde	
<b>Ketones</b>	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 (Langenbrügge) (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  $C_2\text{--}C_5$  hydrocarbons).

The 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, 2004). 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).

Lately, 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.

Table 2: POCP Weighted NMVOC emissions (adopted from UK's NAEI emissions reported by Dore et al., 2004).

	POCP	code	Stationary Combustion	Production Processes	Extraction and Distrib_ Fossil Fuels	Solvent Use	Road Transport	Other Transport	Waste Treatment	TOTAL (Mass Emission)	TOTAL (POCP Weighted)	TOTAL (POCP Weighted %)	
butane	35.2	a	4.37	4.52	70.21	19.61	13.30	0.47	0.02	112	40	7.2%	
ethanol	39.9	a	1.39	53.56		40.27			0.27	95	38	6.9%	
ethylene	100.0	a	3.29	5.65	0.03		14.22	3.55	1.07	28	28	5.0%	
toluene	63.7	a	2.03	4.06	0.24		11.44	16.95	3.10	0.16	38	24	4.4%
m-xylene	110.8	a	0.75	2.14	0.09		10.90	5.04	0.70	0.07	20	22	3.9%
propylene	112.3	a	1.65	6.01	0.02		0.00	6.80	1.37	0.06	16	18	3.2%
pentane	39.5	a	2.66	2.00	28.93	0.41	8.64	0.29	0.02	43	17	3.1%	
hexane	48.2	a	0.51	4.39	14.93	2.32	7.92	0.20	0.10	30	15	2.7%	
1,2,4-trimethylbenzene	127.8	a	0.00	0.52	0.01		5.44	4.69	0.51		11	14	2.6%
2-methylbutane	40.5	a	3.48	1.08	11.11		0.04	17.74	0.77	0.01	34	14	2.5%
formaldehyde	51.9	a	9.05	0.38	0.21		0.03	6.26	1.50	3.40	21	11	2.0%
o-xylene	105.3	a	0.25	0.75	0.04		2.74	5.05	0.80	0.04	10	10	1.8%
heptane	49.4	a	0.77	0.30	15.07		1.26	1.61	0.09		19	9	1.7%
propane	17.6	a	3.22	2.26	36.90	3.81	1.18	0.38	5.11	53	9	1.7%	
ethylbenzene	73.0	a	0.24	1.75	0.03		4.17	4.93	0.77	0.12	12	9	1.6%
p-xylene	101.0	a	0.19	0.92	0.02		2.92	3.90	0.54	0.06	9	9	1.6%
ethane	12.3	a	5.84	1.46	49.57		0.00	3.15	0.57	5.44	66	8	1.5%
octane	45.3	a	0.06	0.18	13.27		1.10	0.77	0.09		15	7	1.3%
2-methylpropane	30.7	a	1.01	0.24	13.24		0.89	5.96	0.22	0.01	22	7	1.2%
trichloroethene	32.5	a		0.87			18.97			0.06	20	6	1.2%
1,3,5-trimethylbenzene	138.1	a	0.00	0.19			1.82	1.85	0.24		4	6	1.0%
2-butene	113.9	a	0.60	0.14	0.81		2.67	0.21	0.02		4	5	0.9%
2-methylpropene	62.7	a	0.15	0.68	0.26		5.23	1.03	0.00		7	5	0.8%
2-butanone	37.3	a		0.68			11.38	0.24	0.02	0.01	12	5	0.8%
1,2,3-trimethylbenzene	126.7	a	0.00	0.18			1.84	1.07	0.15		3	4	0.7%
methanol	14.0	a		2.01	0.00		26.09			0.07	28	4	0.7%
2-pentene	111.9	a	0.34	0.01	1.41		1.57	0.04	0.00		3	4	0.7%
decane	38.4	a	0.03	0.84	0.03		7.38	0.92	0.47		10	4	0.7%
1,3-butadiene	85.1	a	0.00	0.29	0.01		2.74	0.61	0.01		4	3	0.6%
butyl acetate	26.9	a		0.19			11.19			0.02	11	3	0.6%
1-butanol	62.0	a		0.23			4.58			0.01	5	3	0.5%
methylethylbenzene	94.1	c		0.23			2.91				3	3	0.5%
benzene	21.8	a	3.88	1.41	0.84		0.00	5.06	1.44	0.89	14	3	0.5%
4-methyl-2-pentanone	49.0	a		0.65			5.07				6	3	0.5%
acetaldehyde	64.1	a	0.00	0.75				2.86	0.67		4	3	0.5%
ethylmethylbenzene	132.0	c		0.11			1.98				2	3	0.5%
1-butene	107.9	a	0.34	0.62	0.23		0.00	1.21	0.12	0.01	3	3	0.5%
naphthalene	97.7	b	0.48	0.02			1.43		0.01		2	2	0.3%
nonane	41.4	a	0.05	0.52	0.08		4.44	0.21	0.11		5	2	0.4%
2-butoxyethanol	48.3	a		0.10			4.48				5	2	0.4%
dipentene	74.5	b		0.01			2.84				3	2	0.4%
1-propanol	56.1	a		0.06			3.29			0.04	3	2	0.3%
acetone	9.4	a	0.19	1.93			17.04	0.81	0.08	0.00	20	2	0.3%
2-methylpentane	42.0	a	0.03	0.99	2.17		1.09		0.01	0.05	4	2	0.3%
2-propanol	18.8	a	0.01	0.73			8.92			0.02	10	2	0.3%
ethyl acetate	20.9	a		1.31			6.98			0.02	8	2	0.3%
undecane	38.4	a	0.00	0.44			3.85		0.19		4	2	0.3%
1-pentene	97.7	a	0.14	0.06	0.29			0.93	0.04	0.00	1	1	0.3%
3-methylpentane	47.9	a	0.02	0.67	1.21		0.86			0.03	3	1	0.2%
1,2,3,5-tetramethylbenzene	136.0	b		0.06			0.84				1	1	0.2%
<b>Total Top 50 (POCP)</b>			<b>47</b>	<b>109</b>	<b>261</b>	<b>257</b>	<b>155</b>	<b>21</b>	<b>17</b>	<b>868</b>	<b>399</b>	<b>72.3%</b>	
unspeciated	51.3	c	1.86	32.11	1.20		7.06	1.22	0.36		44	22	4.1%
other grouped species			0.72	23.31	9.51		6.69	34.54	32.53	1.13	108	68	12.3%
other VOC			1.50	29.87	1.80		106.06	19.80	4.44	1.78	165	62	11.3%
<b>Total VOC</b>			<b>51</b>	<b>194</b>	<b>274</b>	<b>376</b>	<b>211</b>	<b>59</b>	<b>20</b>	<b>1186</b>	<b>552</b>	<b>100%</b>	

## 2. Status of the measurement programme in 2003

### 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 2003 is given in Table 3. Totally 14 measurement sites reported VOC data to CCC in 2003, 9 of these with carbonyls.

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 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) and that is fulfilled at most of the VOC sites but not all. The data capture of the hydrocarbons was lower than 90% at Starina and at Peyrusse Vieille. The data capture of the carbonyls was particularly low at the three French sites, as it was around 50% for all these sites due to lack of an automatic sampler with a good quality of sampling.

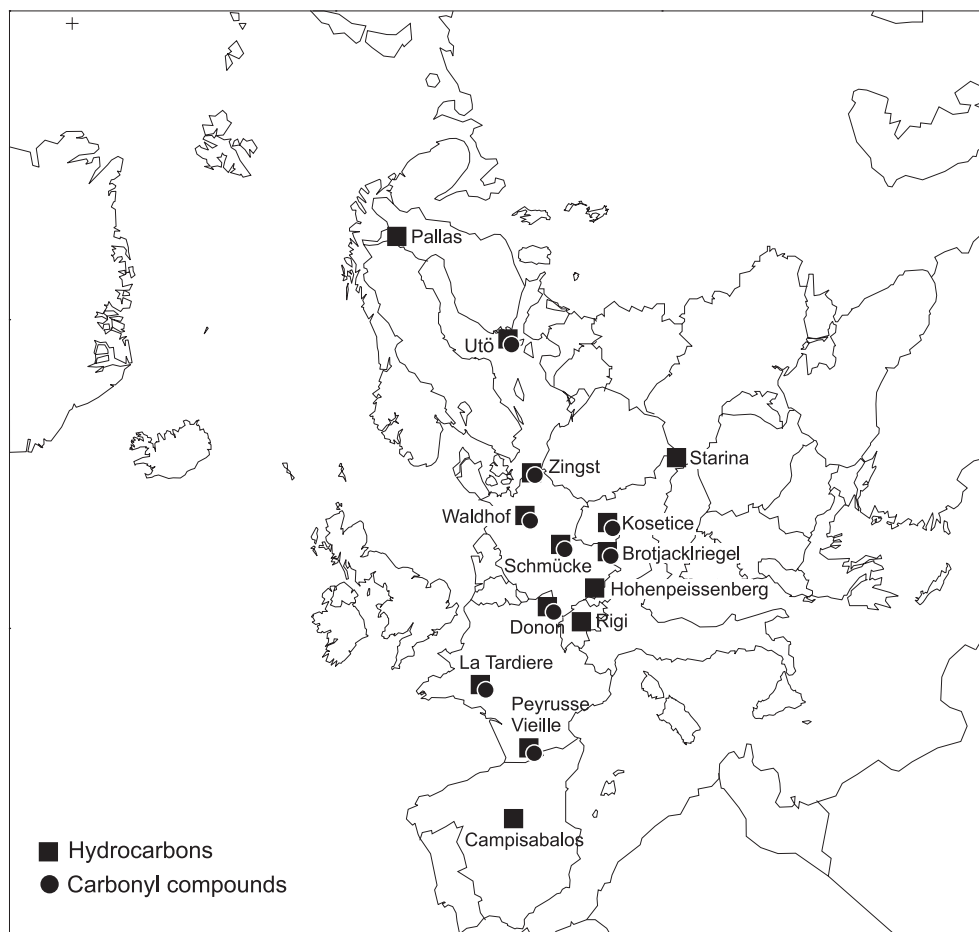


Figure 1: Monitoring sites for VOC in 2003.

*Table 3: Status of the VOC monitoring programme in 2003. 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 <sup>1)</sup>	Lab. <sup>2)</sup>	Carb <sup>1)</sup>	Lab. <sup>2)</sup>	Comments
Pallas	FI96	Reg.	FMI	n.m.	-	
Utö	FI09	Reg.	FMI	Reg.	NILU	
Waldhof	DE02	Reg.	UBA	Reg.	UBA	
Schmücke	DE08	Reg.	UBA	Reg.	UBA	
Zingst	DE09	Reg.	UBA	Reg.	UBA	
Brotjacklriegel	DE05	Reg.	UBA	Reg.	UBA	
Hohenpeissenberg	DE43	Daily	DWD	n.m.	-	GAW station
Košetice	CZ03	Reg.	CHMI	Reg.	NILU	
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 Tardiere	FR15	Reg.	EMD	Reg.	EMD	
Campisábalos	ES09	Reg.	MMA	Reg.	EMD	Monitoring of carbonyls started in May 2003. Data will be reported when the results from a parallel campaign is ready.

1) Reg. = regularly, Scat. = scattered, n.m. = not measured., 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 samples of hydrocarbons (HC) and carbonyls (Carb) in 2003.*

Station	Number of samples	
	HC	Carb
Pallas	94	-
Utö	98	97
Zingst	100	104
Waldhof	100	103
Schmücke	98	103
Brotjacklriegel	102	104
Hohenpeissenberg <sup>1)</sup>	329	-
Košetice	104	102
Starina	87	-
Rigi <sup>1)</sup>	287	-
Donon	101	47
Peyrusse Vieille	86	45
La Tardiere	101	47
Campisábalos	97	-

<sup>1)</sup> Refer to days with monitoring data

## 2.2 Analytical procedures and quality control

The procedures for sampling and chemical analyses were similar in 2003 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) and were presented in the last annual report (Solberg, 2004).

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 chemical stable in the prepared sample solution. Furthermore, LC/MS studies indicate possibilities of chromatographic interference in the C<sub>4</sub> carbonyl compound range. Thus, a revision of the monitoring procedures for carbonyls is needed.

## 2.3 Revised parallel data of carbonyl compounds at Waldhof

The results of previous parallel sampling of carbonyls at Waldhof have been reported by Solberg et al. (2002) and Solberg (2003). However, since then UBA's data have been revised as the blank values were not subtracted previously. Figure 2 shows the revised results of the parallel time series of methanal, ethanal and propanone (formaldehyde, acetaldehyde and acetone) at Waldhof from NILU's and UBA's laboratories for all parallel data during 1999-2001. A statistical summary of the parallel analysis is given in Table 5. The statistical parameters include the medians of the data from NILU and UBA and the median differences as well as the modified median absolute difference estimator, M.MAD, as described in the EMEP manual (EMEP/CCC, 1996) and the coefficient of variation, CoV, defined as  $CoV=(M.MAD)/(NILU's\ median)$ . The analyses from the laboratory at NILU were regarded the reference in these calculations.

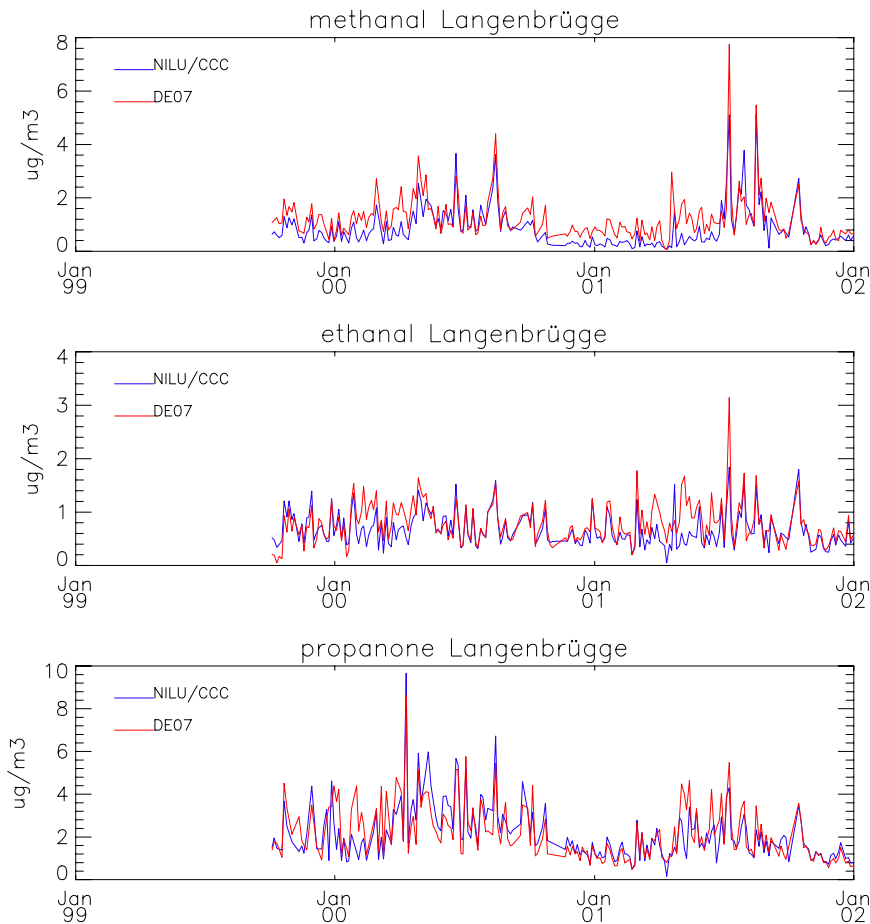


Figure 2: Revised results of parallel sampling and analyses of carbonyl compounds at Waldhof by NILU (blue line) and UBA (red line) during 1999-2001.

Table 5: Revised results from parallel sampling and analyses of carbonyl compounds at DE02, Waldhof during 1999-2001. The columns give the median of all samples as analysed by NILU and UBA, respectively, as well as the median difference, the modified median absolute difference estimator (M.MAD), the coefficient of variation (CoV) and the linear correlation coefficient ( $r$ ). Unit:  $\mu\text{g m}^{-3}$ .

	median NILU	median UBA	median difference	M.MAD	CoV	$r$
methanal	0.630	1.010	0.390	0.329	0.522	0.829
ethanal	0.570	0.705	0.073	0.176	0.310	0.751
propanone	1.795	1.752	-0.115	0.523	0.292	0.812

M.MAD expresses the spread of the data and equals the standard deviation if the population has a normal distribution. CoV expresses the relative spread of the data, and, similar to the M.MAD, approaches the relative standard deviation for a normal distributed population. Both parameters are non-parametric statistics that make them particularly useful for trace gas measurements that normally show a non-normal distribution in the data.



The revised data show a generally better agreement between the two time series than before. The most pronounced change is for ethanal (acetaldehyde) for which the subtraction of the blank values has significantly reduced the values and differences with NILU's data.

### 3. VOC concentrations in 2003

#### 3.1 General

Monthly mean and median concentrations of the individual hydrocarbons and carbonyls for 2003 are tabulated in Appendix A. The monthly statistics were not calculated for sample numbers less than 4. Time series of all compounds during 2003 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 day-time and night-time data from Hohenpeissenberg were used. 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, however, the difference is large.

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 3 and Figure 4. This shows that the hydrocarbon concentrations at SK06, Starina, and, to a less extent CZ03, Košetice, were high for many of the hydrocarbons. Furthermore, a number of very high concentrations of isobutane and butane in January 2003 are the reason for the high values at FR08, Donon. At the Finnish sites there were problems with the blank values for butane, thus most of these data had to be deleted.

The hydrocarbon concentrations at ES09, Campisábalos, were substantially lower than at the other sites, particularly for the most lightweight components. In winter ethane, propane and many other hydrocarbons are chemically stable and the results from previous years have indicated well-mixed concentrations of these species in Europe during winter. The monitoring results from Campisábalos are thus surprisingly low and parallel sampling and analyses with other laboratories have been recommended. In November 2004 representatives from NILU/CCC visited Campisábalos and the Spanish laboratory and made parallel samples. The result of this exercise and the Spanish carbonyl data will be reported when the evaluation is finished.

The summer seasonal means and percentiles for four selected carbonyls, formaldehyde, acetaldehyde, acetone and butanone, are given in Figure 4. This shows particularly low concentrations at DE05, Brotjacklriegel, probably reflecting the altitude of the monitoring site (approx. 1000 m asl.) and at Utö, located further north than the other sites. The formaldehyde (methanal) concentrations were highest at Donon, while acetaldehyde (ethanal) were highest at Košetice. A likely explanation for this is biogenic formation of formaldehyde from the degradation of isoprene at Donon as the isoprene concentrations at Donon are substantially higher than at the other sites. Acetaldehyde, on the other hand is to a larger extent a primary or secondary product of anthropogenic emissions.

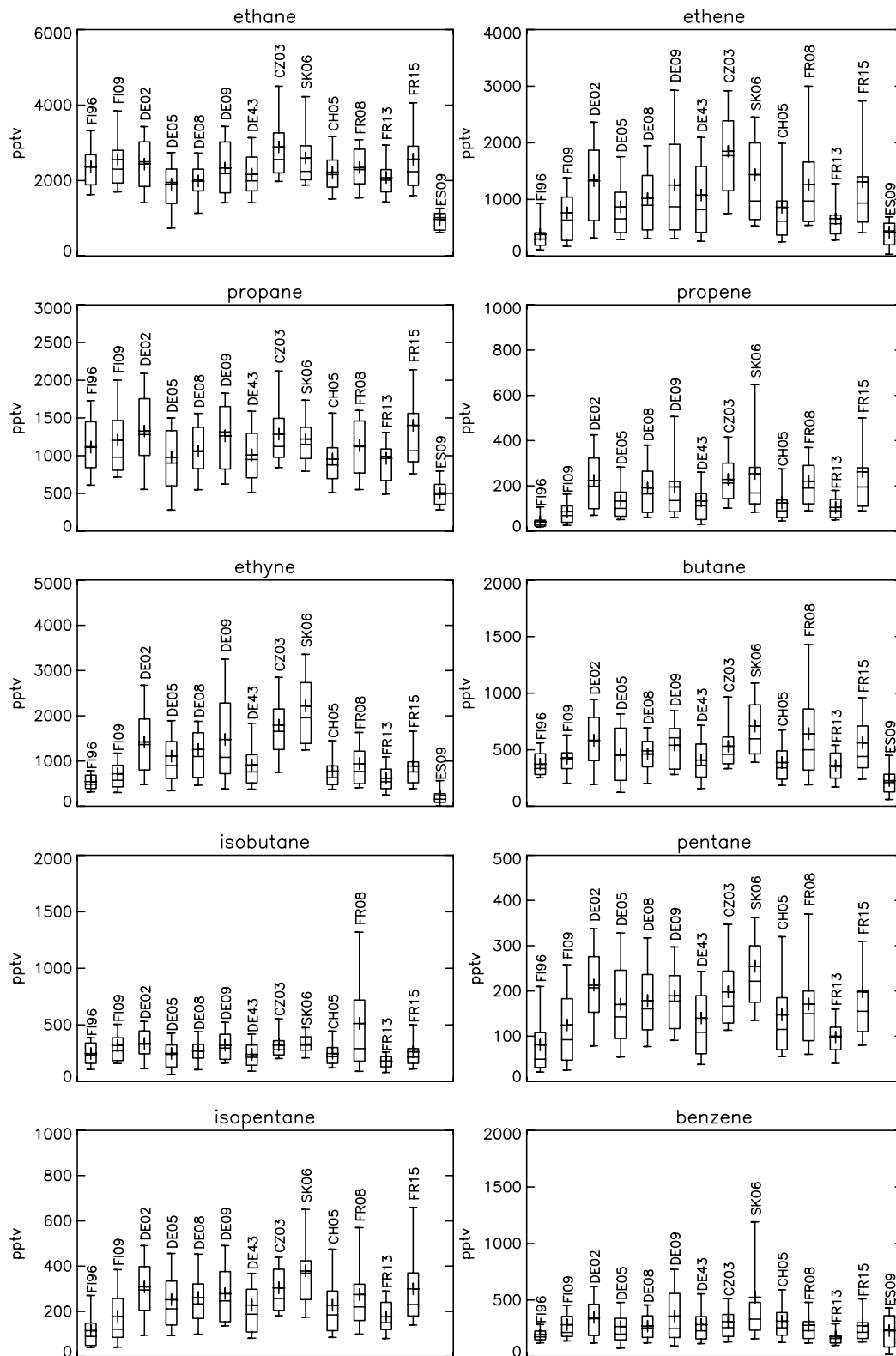


Figure 3: Box- and whisker-diagrams for hydrocarbons during winter 2003 (Jan., Feb., Nov., Dec.). The markers indicate the 10-, 25-, 50-, 75- and 90-percentiles. Mean values are indicated by a cross.

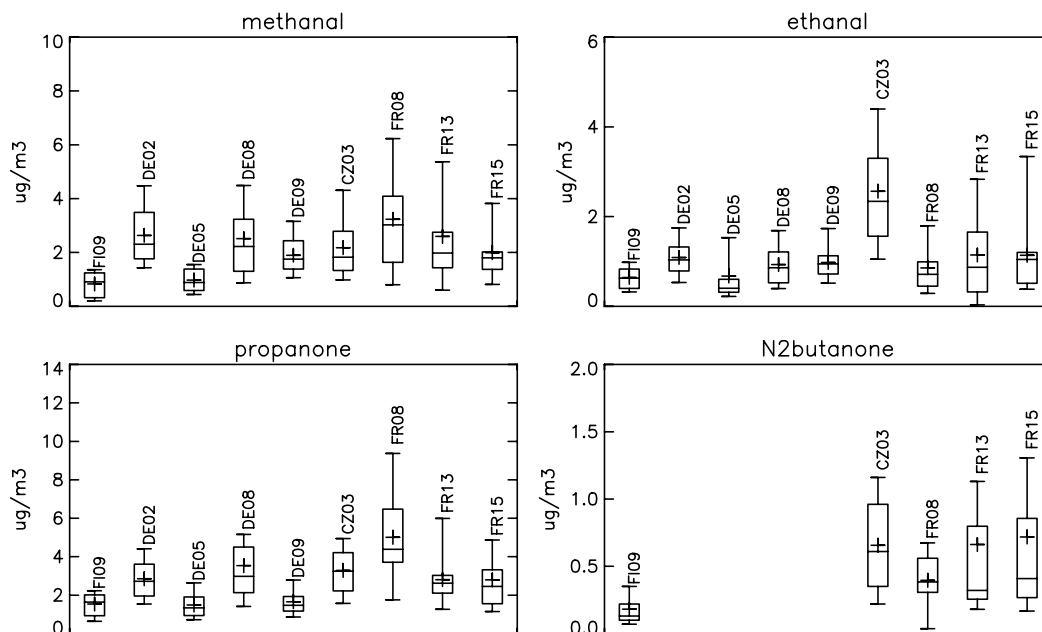


Figure 4: Box- and whisker-diagrams for carbonyls during summer 2003 (May, June, July, August). The markers indicate the 10-, 25-, 50-, 75- and 90-percentiles. Mean values are indicated by a cross.

The weather conditions were extreme in Europe in the summer half year of 2003 and the continent experienced several heat waves, most pronounced in August. The meteorological conditions have been extensively described in other studies (e.g. Fink et al., 2004). Luterbacher et al. (2004) concluded that the summer of 2003 was very likely warmer than any other summer back to 1500. Over Europe, persistent anticyclonic anomalies, warm temperatures and a series of intense heat waves characterised the summer (Schär et al., 2004; Stott et al., 2004).

As argued by Solberg et al. (2005) the anomalous weather conditions likely lead to a number of side effects, as e.g. increased biogenic emissions due to the elevated temperature and increased sunshine during the heat waves. As shown by Figure 5 the summer concentrations of isoprene at Donon were clearly elevated in summer 2003 compared to previous years indicating increased emissions. There was no corresponding increase in the other anthropogenic VOCs. For the German and Czech sites there was not a similar enhancement in summer isoprene in 2003 compared to previous years. This is surprising as the heat waves affected large regions of central Europe. One possible reason could be if the other VOC sites to a less extent reflects the biogenic emissions. Donon is located inside a forest and normally shows considerably higher isoprene concentrations than the other sites (e.g. Solberg, 2004). If the other sites are located further away from the area of biogenic emission than Donon the isoprene concentrations measured at these sites will to a larger degree reflect the photochemical breakdown and to a less degree the emissions. However, many other factors could also contribute, as e.g. changes in vertical exchange and in OH concentration. Thus, without more detailed analyses we can't really conclude why a marked isoprene increase was seen at Donon and not at the other sites during the extreme summer 2003.

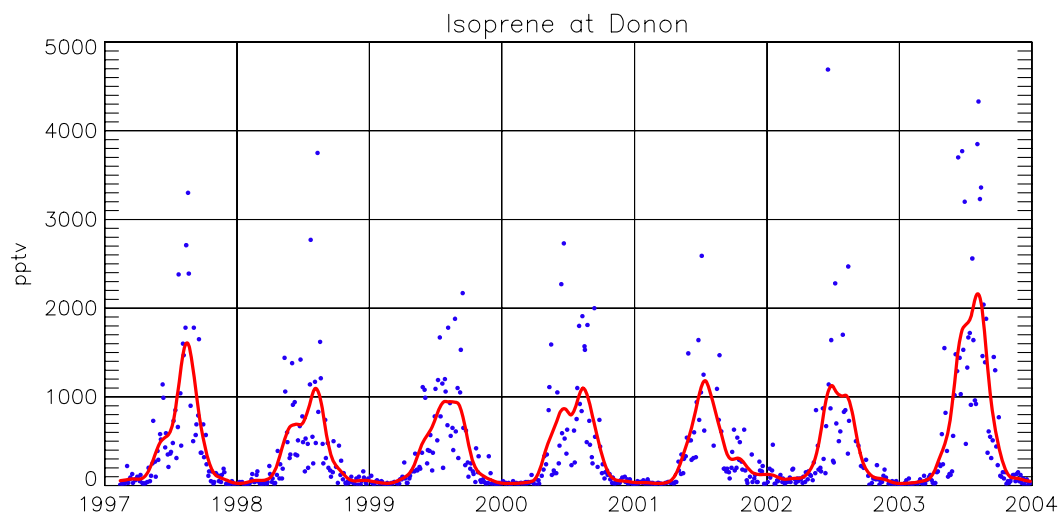


Figure 5: *Isoprene measurements at Donon during 1997-2003. Individual samples (twice a week) are shown as blue marks and the corresponding smoothed running average as a red curve (adopted from Solberg et al., 2005).*

### 3.2 Regional distribution of VOC

Figure 6–Figure 15 shows maps with the stations' median concentrations of 10 light hydrocarbons for the winter months January, February, November and December in 2003 taken together. These medians are based on the average of the two 2-hourly values around noon at Rigi and on both the day-time and night-time values at Hohenpeissenberg.

Although the number of sites obviously is too low to give a clear 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 2003 are given in Figure 16–Figure 18.

As noted in previous reports, the measurements indicate that hydrocarbons become fairly well mixed in Europe in winter. Components indicative of natural gas emissions, ethane and propane, were higher in north and east, whereas e.g. ethene, propene and acetylene were higher in central and eastern parts of the continent. n- and i-butane that stems from a number of different emissions sources also show high concentrations to the north.

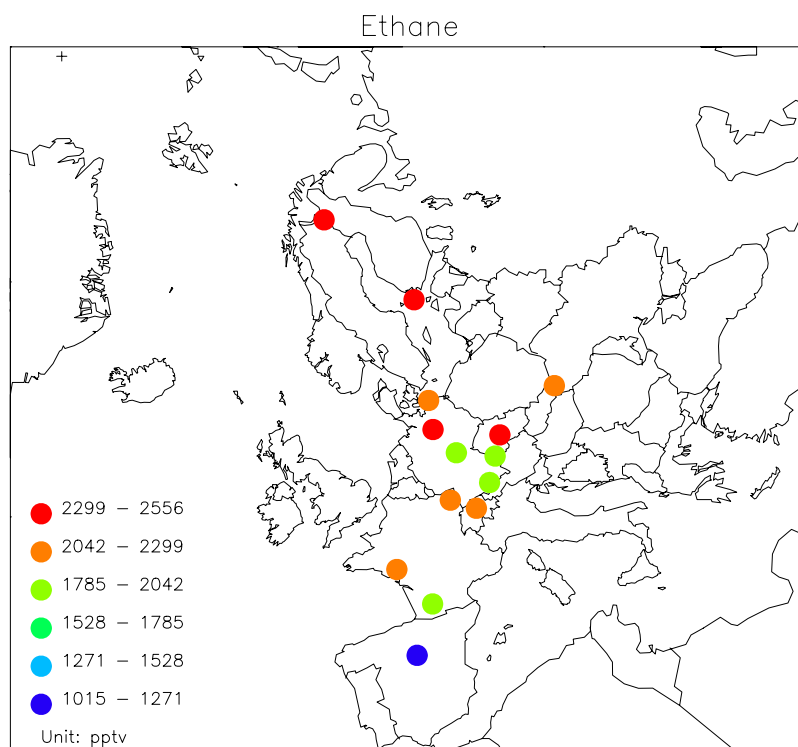


Figure 6: Median concentration of ethane at EMEP sites in the winter months November, December, January and February 2003 taken together.

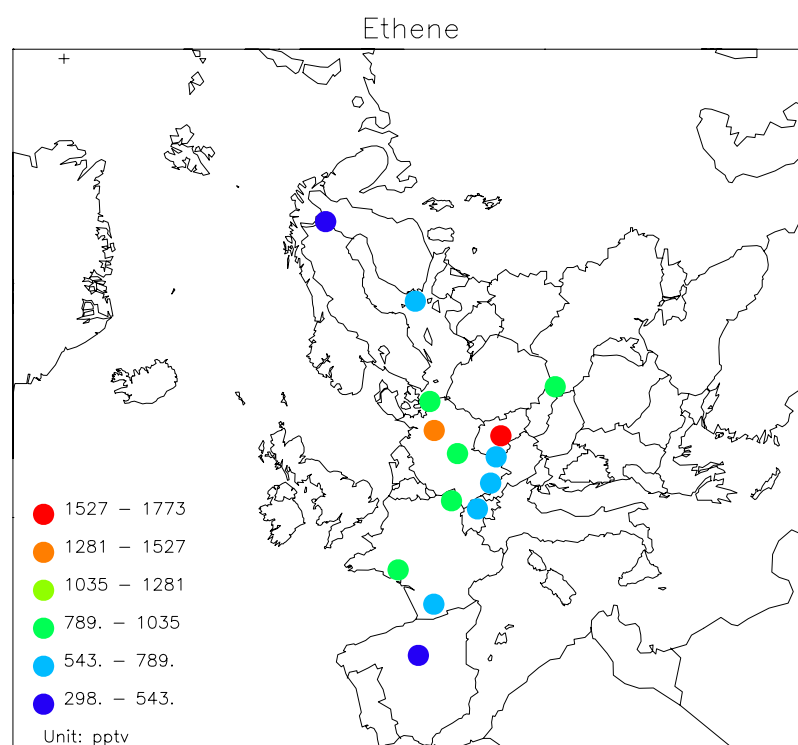
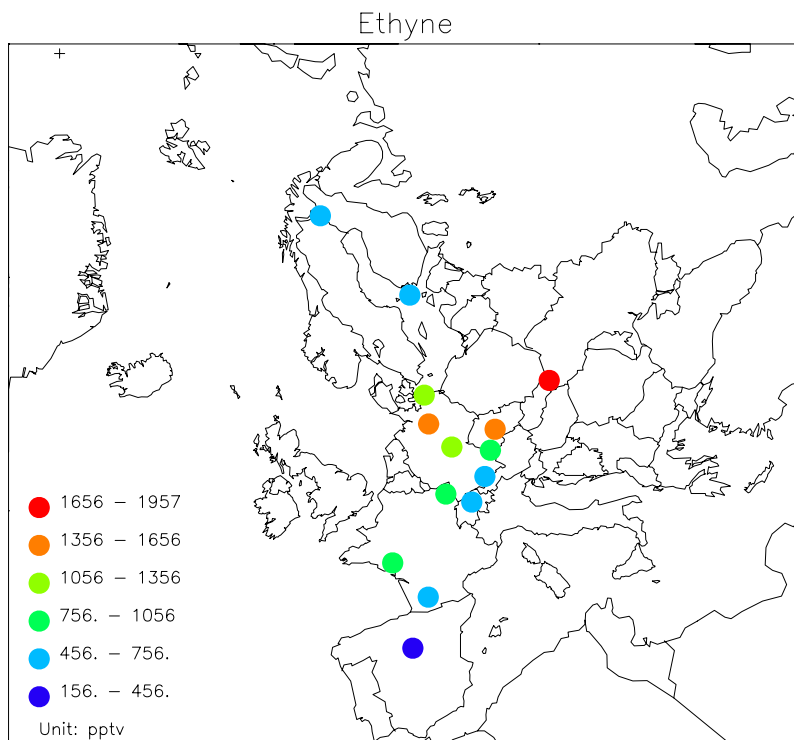
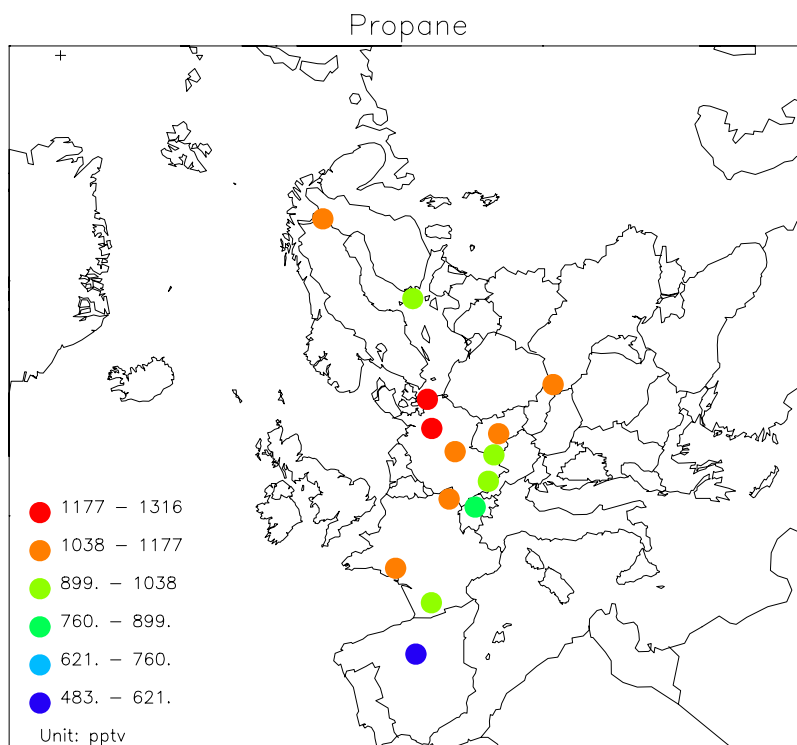


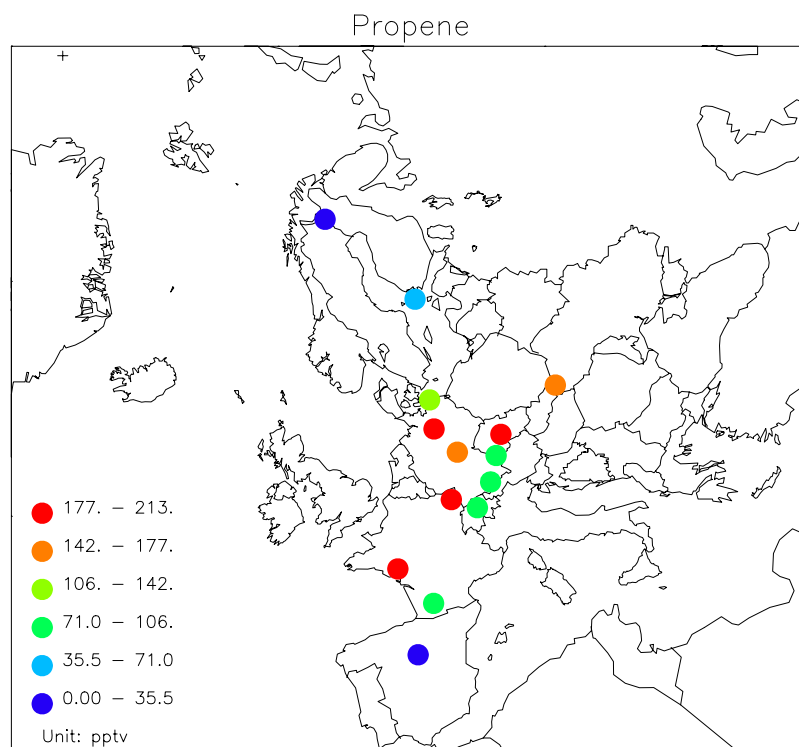
Figure 7: Median concentration of ethene at EMEP sites in the winter months November, December, January and February 2003 taken together.



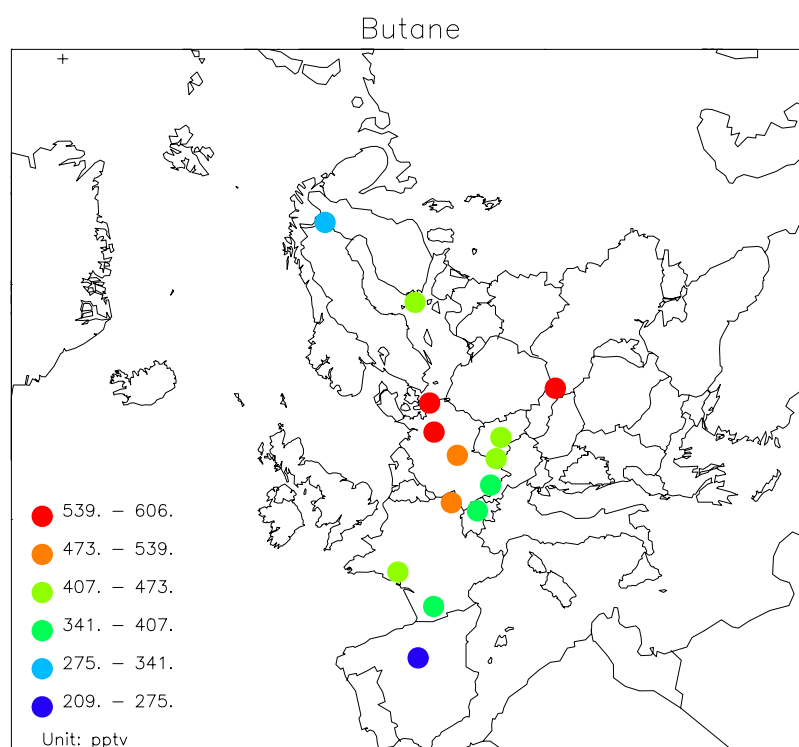
*Figure 8: Median concentration of acetylene at EMEP sites in the winter months November, December, January and February 2003 taken together.*



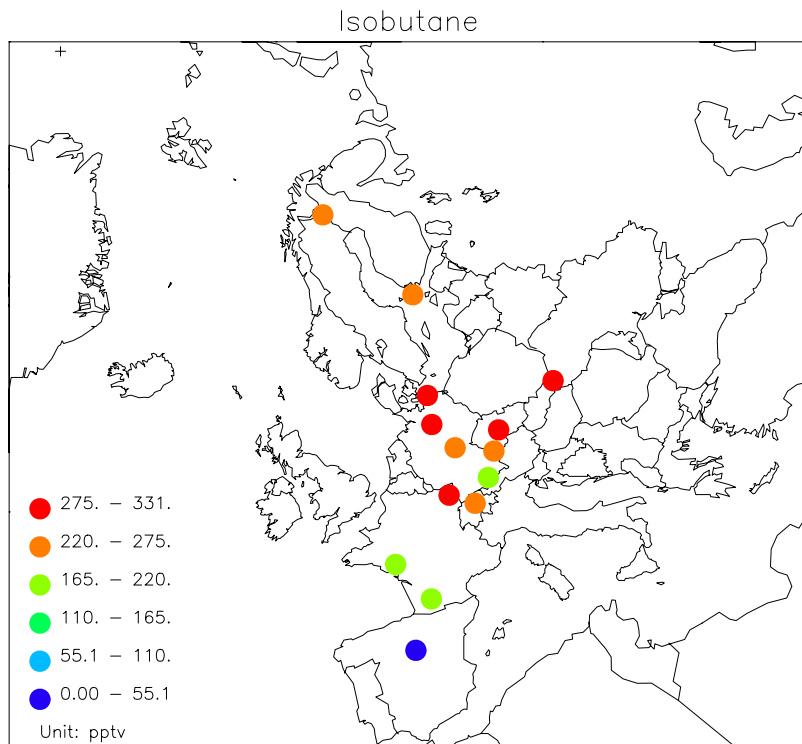
*Figure 9: Median concentration of propane at EMEP sites in the winter months November, December, January and February 2003 taken together.*



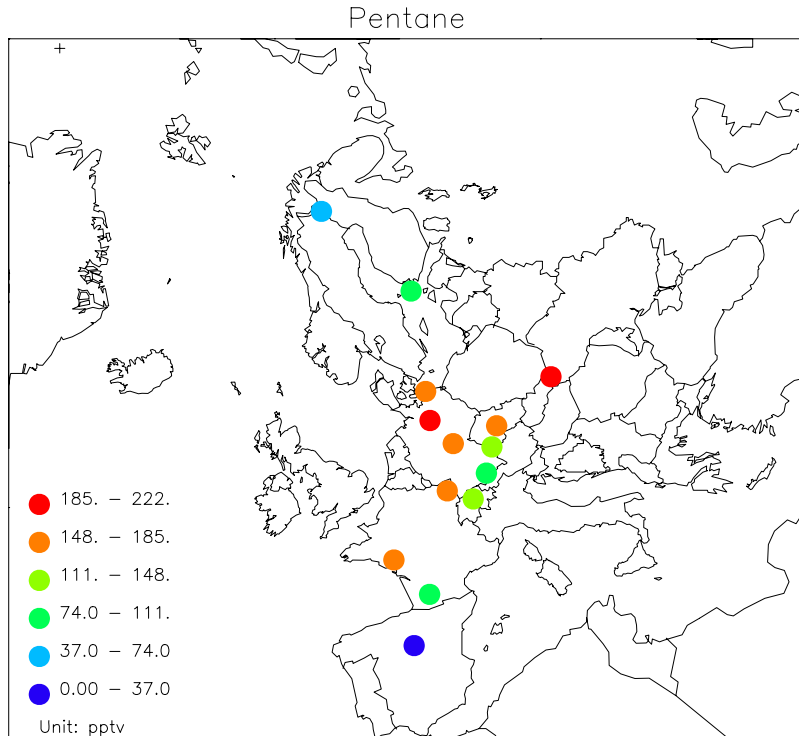
*Figure 10: Median concentration of propene at EMEP sites in the winter months November, December, January and February 2003 taken together.*



*Figure 11: Median concentration of n-butane at EMEP sites in the winter months November, December, January and February 2003 taken together.*

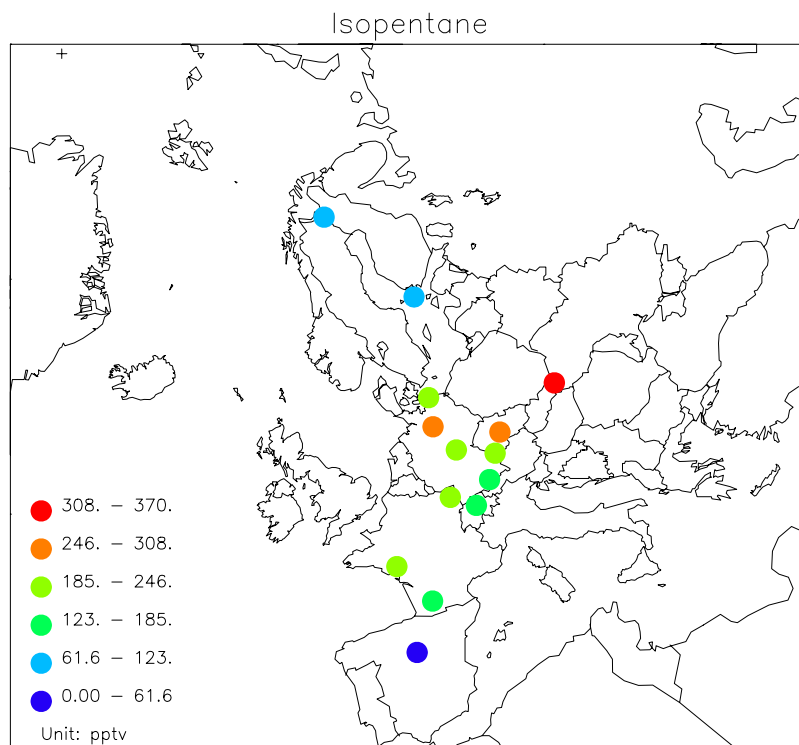


*Figure 12: Median concentration of i-butane at EMEP sites in the winter months November, December, January and February 2003 taken together.*

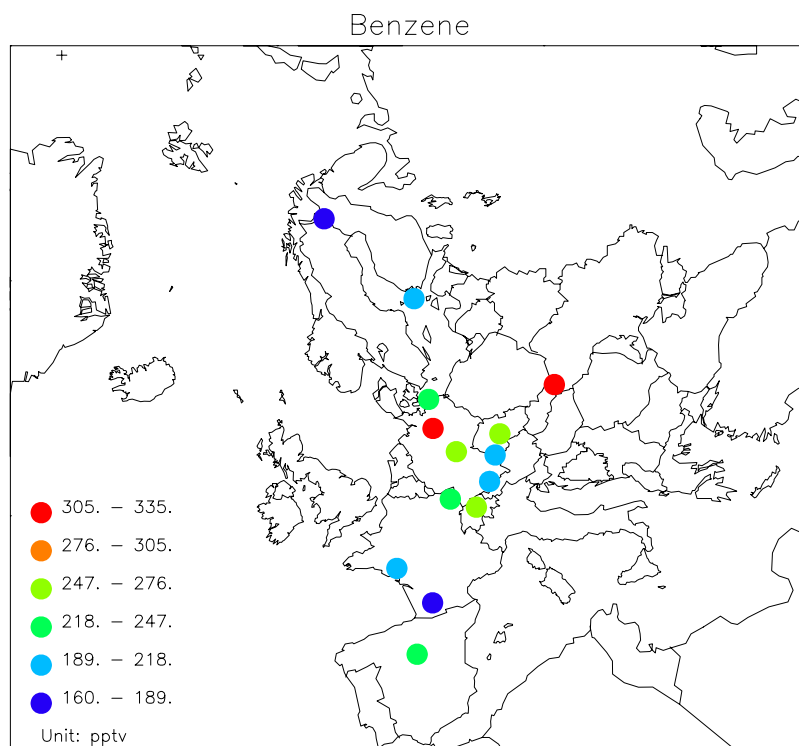


*Figure 13: Median concentration of n-pentane at EMEP sites in the winter months November, December, January and February 2003 taken together.*

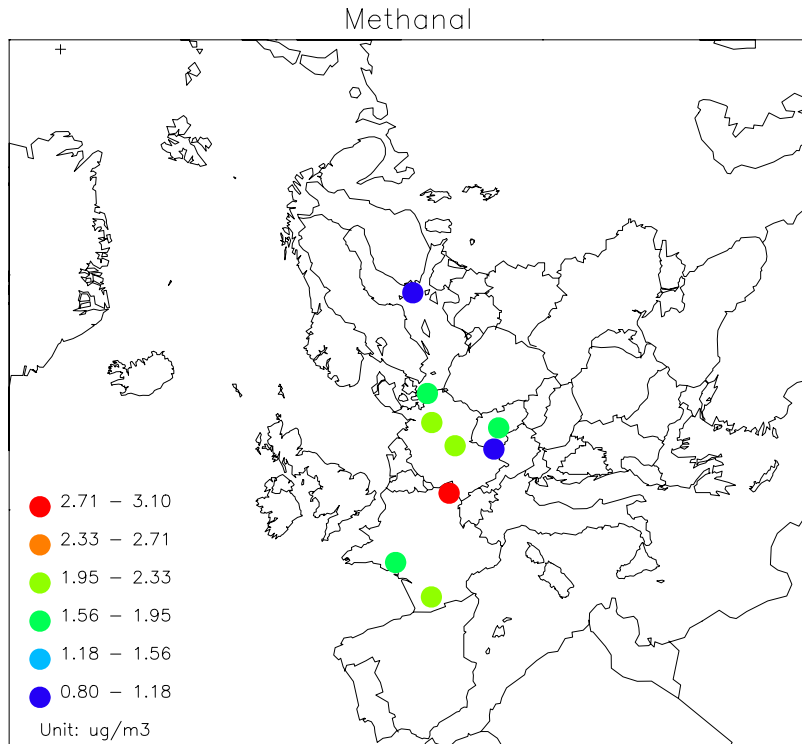




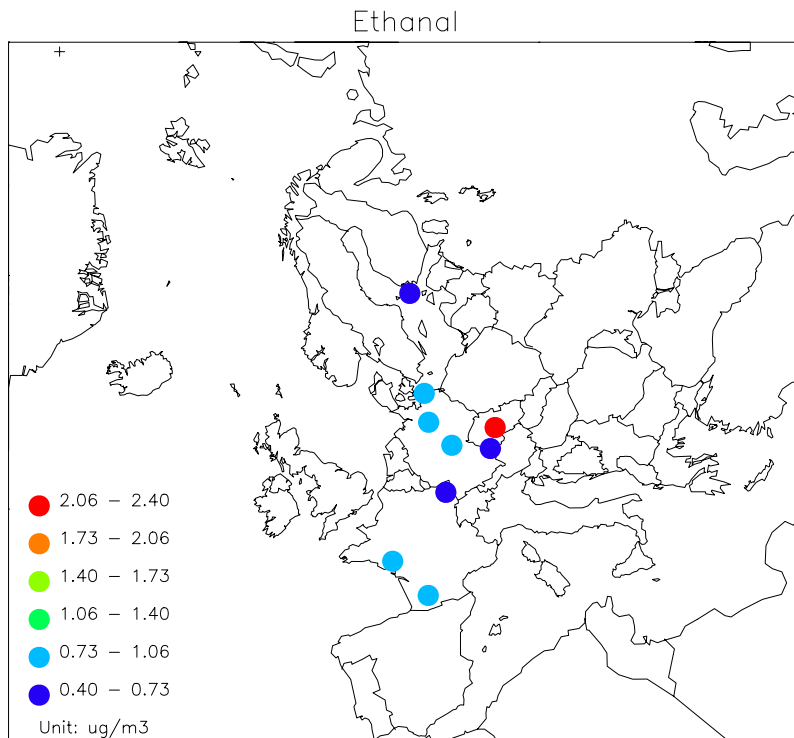
*Figure 14: Median concentration of i-pentane at EMEP sites in the winter months November, December, January and February 2003 taken together.*



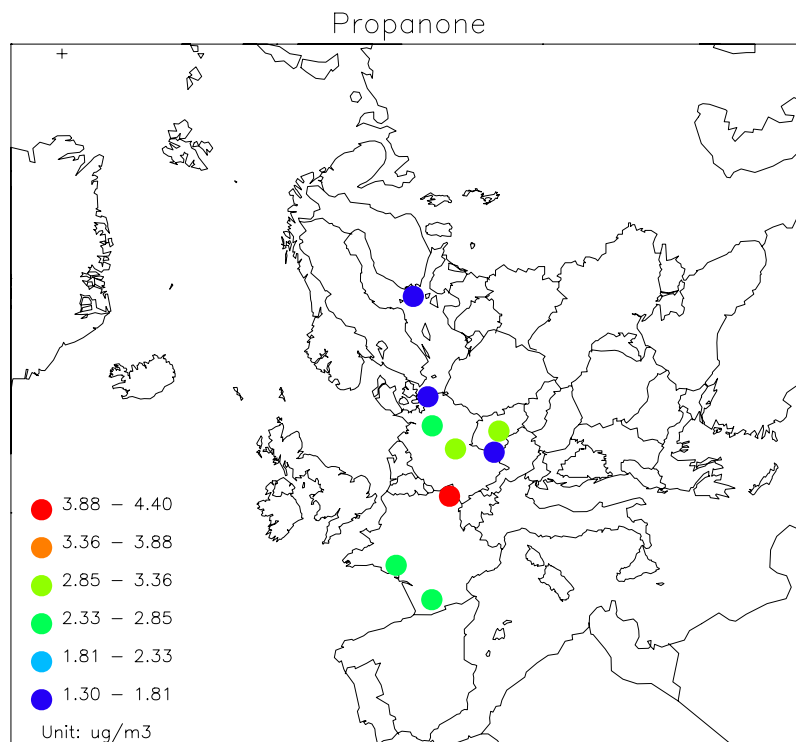
*Figure 15: Median concentration of benzene at EMEP sites in the winter months November, December, January and February 2003 taken together.*



*Figure 16: Median concentration of formaldehyde at EMEP sites in the summer months May, June, July and August 2003 taken together.*



*Figure 17: Median concentration of acetaldehyde at EMEP sites in the summer months May, June, July and August 2003 taken together.*



*Figure 18: Median concentration of acetone at EMEP sites in the summer months May, June, July and August 2003 taken together.*

#### 4. Long-term trends in VOC

The long-term trend in the measured VOC from 1993 is indicated in Figure 19 and Figure 20 showing the seasonal medians at Waldhof (DE02), Košetice (CZ03), Donon (FR08) and Peyrusse Vieille (FR13) of selected hydrocarbons (winter) and carbonyls (summer), respectively.

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.

A marked decline in the winter medians of several hydrocarbons is indicated by Figure 19. To separate the sole effect of changes in European VOC emissions on the observed concentrations trends in Figure 19 and Figure 20 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.

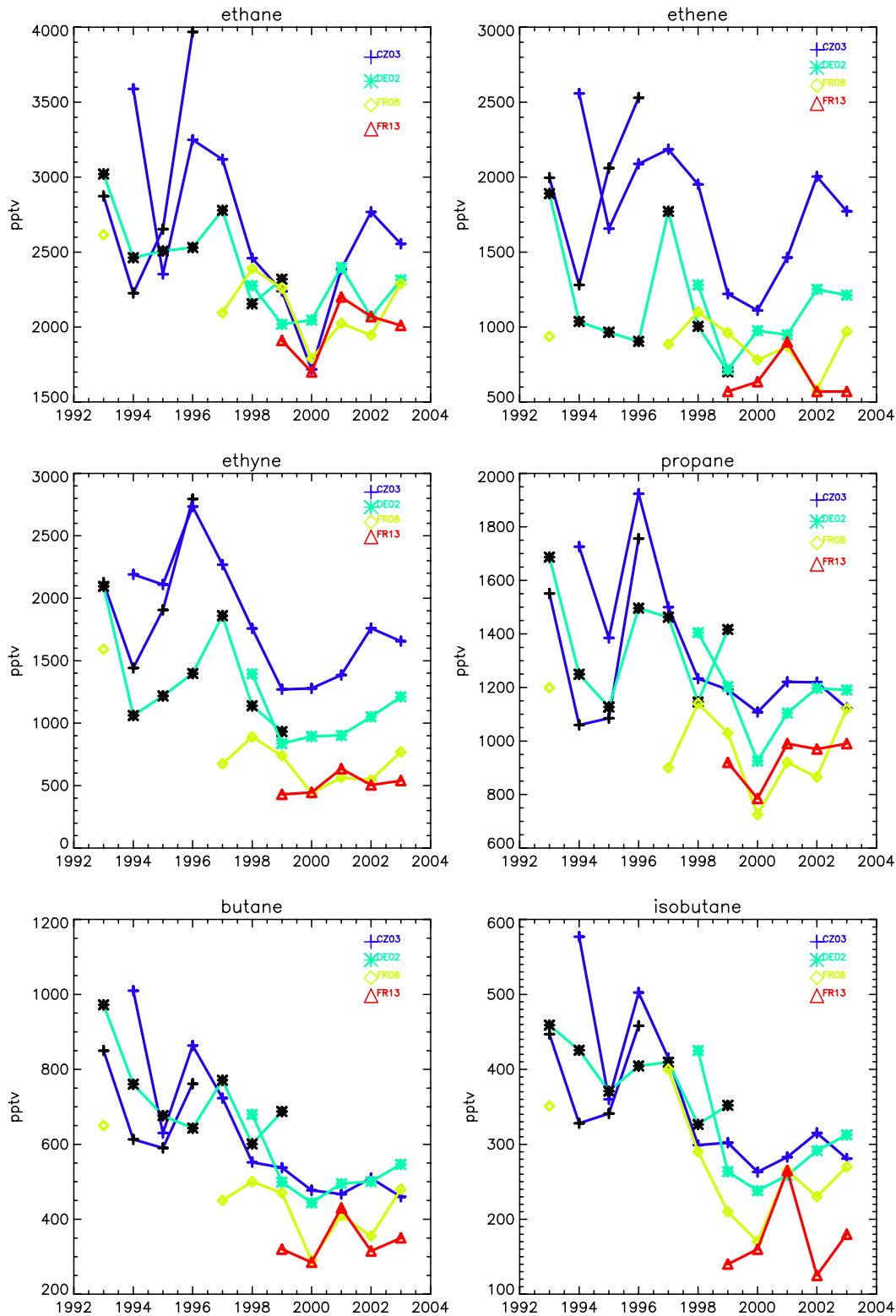


Figure 19: Annual winter (Jan., Feb., Nov., Dec.) median concentrations of hydrocarbons at Košetice (CZ03), Waldhof (DE02), Donon (FR08) and Peyrusse Vieille (FR13). Black symbols mark analyses from NILU's lab., coloured symbols mark the national lab.

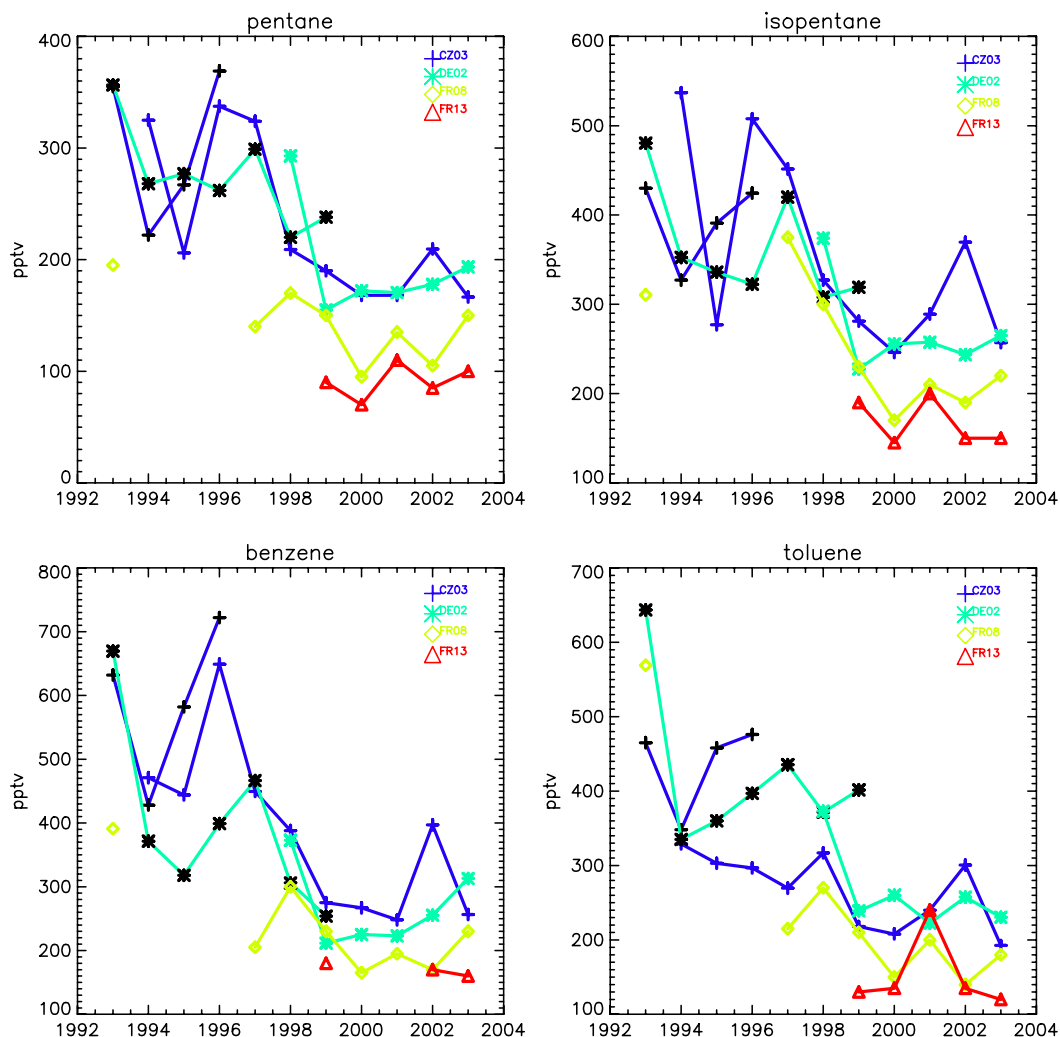


Figure 19, cont.

Particularly strong reductions are indicated for benzene, butane and isobutane and somewhat less for ethane and ethyne (acetylene). The hydrocarbon data suggest that the median concentrations dropped markedly until 2000 and that the trends then have levelled off or even increased after that. To what extent this is explained by meteorological variability or by an actual increase in European VOC emissions after 2000 is not possible to answer without transport model calculations.

For the summer median concentrations of carbonyls (formaldehyde, acetaldehyde, acetone and butanone) the trends are less clear, probably because these compounds are determined by secondary photochemical formation in summer, and thus even more controlled by the inter-annual meteorological conditions than the primary hydrocarbons.

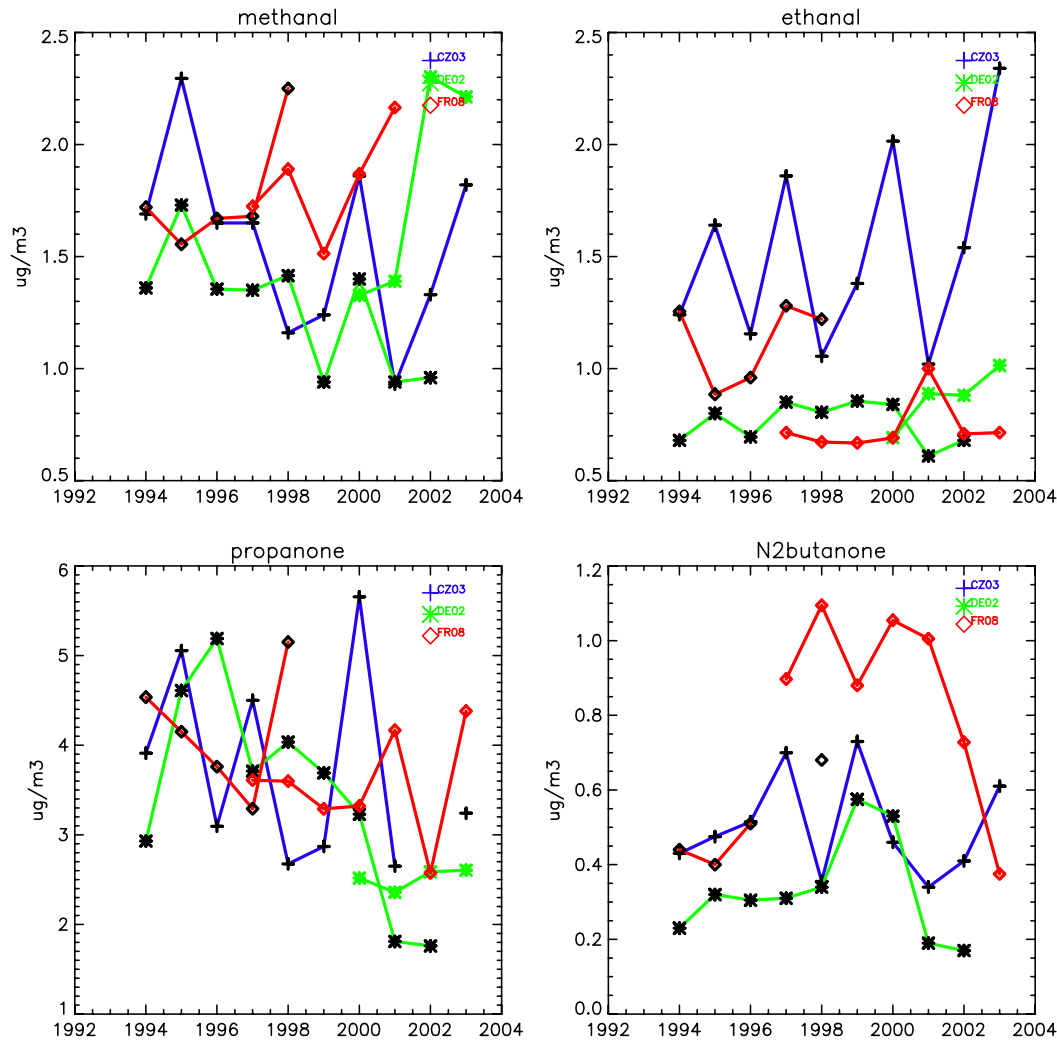


Figure 20: Annual summer (May, June, July, Aug.) median concentrations of carbonyls at Koštice (CZ03), Waldhof (DE02) and Donon (FR08). Black symbols mark analyses from NILU's lab., coloured symbols mark the national lab.

## 5. Acknowledgement

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## **Appendix A**

### **Monthly mean and median concentrations of hydrocarbons and carbonyls in 2003**



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



	ETHANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	2837 2623	2492 2288	2629 2505	2536 2473	1706 1666	1285 1261	936 941	977 981	1059 1055	1321 1349	1661 1651	2092 1886
Utö	3057 2801	2769 2570	2859 2521	2635 2587	1570 1594	1394 1385	1137 1095	1125 1051	1441 1422	1523 1463	1901 1919	2451 2063
Zingst	2498 2596	2743 2879	2513 2218	2110 2171	1404 1451	1231 1221	1028 993	957 917	1109 1161	1158 1160	2135 1785	1749 1773
Waldhof	2537 2797	2702 2567	2505 2339	1877 1840	1384 1398	1170 1132	1082 1099	997 986	1278 1212	1467 1387	1864 1838	2736 2583
Schmücke	2224 2229	2173 2046	2077 2028	1909 1930	1433 1444	1049 1066	954 982	1048 987	1175 1197	1457 1440	1860 1792	1742 1952
Brotjacklriegel	2241 2224	2377 2083	2155 2047	1963 1994	1178 1238	1051 1057	916 900	928 868	1050 1110	1199 1185	1440 1289	1554 1820
Hohenpeissenberg	2451 2273	2648 2583	2435 2383	2251 2300	1490 1544	1085 1077	990 979	937 910	1196 1196	1446 1486	1868 1828	1866 1774
Starina	3247 2922	2999 2853	3383 3322	2298 2255	1669 1584	1185 1238	1168 1014	714 740	1581 1525	1706 1427	2107 2057	2009 2021
Košetice	2800 2685	3759 3353	2703 2554	2428 2452	1452 1535	1101 1099	944 924	940 944	1258 1323	1665 1354	2347 2365	2689 2390
Rigi	2287 2220	2641 2565	2607 2510	2186 2160	1724 1660	1415 1390	1268 1260	1342 1320	1509 1490	1813 1800	1925 1850	2108 2040
La Tardiere	2759 2310	2595 2580	2674 2785	2128 2140	1461 1435	1117 1120	935 880	974 950	1172 1160	1677 1570	1975 1810	2863 2160
Donon	2543 2480	2762 2750	2488 2380	2368 2265	1542 1580	1122 1080	989 890	1121 1065	1599 1340	1619 1550	1864 1765	2280 2220
Peyrusse Vieille	2184 2210	2833 2615	2121 2250	2070 2110	1509 1515	1160 1160	918 920	846 825	1176 1120	1303 1260	1721 1730	1937 1950
Campisábalos	1036 1064	1223 1174	1014 969	1046 1034	765 772	636 549	547 429	631 560	586 570	747 740	760 685	856 875
	ETHENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	359 335	430 172	204 71	116 66	60 59	62 59	92 96	116 141	104 94	127 110	357 320	359 260
Utö	589 429	726 859	297 174	282 257	170 147	179 178	283 259	152 155	287 250	354 248	854 853	878 372
Zingst	1190 843	1234 1299	671 447	277 263	226 176	205 194	285 238	189 161	224 201	357 236	1515 902	1063 678
Waldhof	1127 1249	1298 1334	793 526	225 194	265 279	265 254	212 194	183 191	312 243	571 338	1334 1299	1733 1783
Schmücke	1174 1186	1023 781	453 430	340 192	217 212	170 176	160 169	140 144	243 178	616 611	1052 1080	839 426
Brotjacklriegel	1337 1260	714 569	608 570	314 287	248 203	258 248	229 230	243 202	313 248	538 440	840 528	555 534
Hohenpeissenberg	1252 810	1149 929	570 477	430 354	257 195	185 161	185 131	180 135	295 270	659 533	1031 853	790 574
Starina	1963 1257	994 850	1939 1491	2183 2142	265 283	217 244	276 228	219 125	329 385	1027 614	2002 1954	808 562
Košetice	1847 1680	1909 1874	945 694	424 345	195 184	172 143	231 169	159 144	265 212	803 317	1850 1816	1796 1771
Rigi	753 660	1099 835	681 560	446 350	460 340	325 300	281 245	242 220	407 350	791 555	829 670	806 570
La Tardiere	1694 1010	965 685	781 645	308 280	210 210	239 250	201 220	325 295	373 370	902 780	1108 880	1416 1030
Donon	1204 970	1422 1295	539 490	451 305	301 280	279 300	256 240	339 295	424 350	916 870	974 735	1491 1070
Peyrusse Vieille	590 520	1020 905	286 300	246 225	166 135	184 210	158 105	230 230	276 260	393 385	553 430	634 570
Campisábalos	457 348	549 525	470 344	433 419	293 290	431 397	465 391	548 440	499 445	507 540	312 250	351 400

	PROPANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	1415 1358	1119 935	1077 1033	941 1001	348 339	114 104	158 108	217 203	204 151	435 440	635 609	1059 906
Utö	1552 1475	1231 980	1163 1054	947 976	345 284	281 228	268 242	208 207	458 469	521 469	824 798	1176 942
Zingst	1456 1565	1444 1542	1165 1010	869 914	721 569	326 315	348 308	210 224	386 381	420 379	1114 1007	904 813
Waldhof	1442 1578	1447 1397	1157 1105	877 847	438 441	319 308	294 264	303 277	518 498	665 525	1032 1008	1398 1284
Schmücke	1345 1471	1097 1026	932 920	789 907	486 453	396 273	312 306	352 318	463 449	667 652	930 828	902 1009
Brotjackriegel	1298 1333	1247 1183	914 884	701 688	370 380	282 238	212 201	284 243	367 365	462 405	658 532	704 757
Hohenpeissenberg	1176 1036	1164 1208	920 852	738 739	350 316	273 254	249 213	285 261	439 437	591 597	833 792	836 761
Starina	1178 1220	1574 1557	1932 1909	1107 1234	591 601	409 405	393 317	255 259	617 700	1015 874	1090 1050	1069 1105
Košetice	1289 1168	1631 1398	1037 1003	835 883	348 348	235 213	230 193	241 257	420 417	663 484	1016 1022	1210 1072
Rigi	1025 1010	1195 1150	942 910	672 630	443 360	291 270	270 250	393 350	507 510	747 730	787 730	899 830
La Tardiere	1866 1350	1214 1235	998 975	709 645	308 260	239 240	206 175	349 260	368 390	740 710	971 940	1489 1000
Donon	1263 1120	1408 1315	872 830	799 815	350 350	264 250	206 180	370 310	591 370	743 840	779 665	1133 1085
Peyrusse Vieille	1010 1090	1320 1190	677 750	638 620	323 275	329 290	249 250	256 245	394 360	488 480	756 660	930 990
Campisábalos	536 547	642 638	399 325	532 375	362 192	298 249	238 199	285 220	431 160	371 330	351 330	485 505
	PROPENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	37 29	52 25	23 18	31 31	29 29	34 31	41 40	55 49	48 41	38 36	35 42	39 27
Utö	64 45	55 46	36 31	87 61	47 45	73 69	60 62	72 70	93 79	80 71	106 97	113 39
Zingst	204 148	122 106	89 91	66 69	74 73	60 59	80 73	56 50	60 57	90 80	268 149	195 125
Waldhof	224 164	145 155	103 78	48 39	77 68	63 65	55 52	55 53	74 66	121 97	234 268	334 277
Schmücke	247 262	169 111	71 57	50 42	58 56	50 50	44 44	36 33	60 48	148 128	216 164	135 63
Brotjackriegel	215 202	85 75	90 83	66 66	82 66	71 70	66 61	54 49	75 53	110 82	133 88	92 87
Hohenpeissenberg	146 121	102 121	61 55	49 43	35 28	33 31	30 27	30 29	38 33	82 67	148 105	109 72
Starina	402 374	126 134	124 133	308 170	84 90	91 76	88 101	48 42	118 150	192 189	232 179	218 127
Košetice	231 247	167 148	128 62	85 26	28 28	34 29	70 41	27 27	51 34	113 39	264 220	251 251
Rigi	122 100	117 90	82 70	67 60	62 60	44 40	41 30	38 30	73 50	113 90	129 90	156 100
La Tardiere	349 260	164 135	144 85	68 60	53 50	70 70	64 60	78 70	98 90	178 150	204 175	313 200
Donon	273 230	185 190	89 80	74 65	51 50	60 60	47 50	69 70	80 60	137 130	146 115	261 195
Peyrusse Vieille	127 120	128 95	31 40	36 35	33 40	37 40	45 35	54 60	59 60	53 55	76 60	99 90
Campisábalos	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -

	ETHYNE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	641 663	619 466	576 468	455 393	196 184	118 123	75 65	114 93	124 119	193 169	383 324	453 397
Utö	613 630	918 1030	661 502	611 573	222 212	174 159	154 166	103 101	242 208	291 235	662 630	700 456
Zingst	1442 1106	1961 1931	1370 1061	745 718	287 263	220 211	253 254	195 192	341 357	432 328	1465 883	895 664
Waldhof	1171 1155	1919 1925	1377 987	779 831	303 301	240 234	196 187	226 204	388 396	628 419	1211 1033	1419 1444
Schmücke	1153 1094	1999 1575	929 858	730 651	401 372	245 220	208 203	262 248	370 340	630 655	1165 855	847 668
Brotjacklriegel	1522 1423	1402 1015	1140 1106	781 788	350 353	300 288	224 226	303 298	391 377	601 490	831 529	679 652
Hohenpeissenberg	975 691	1114 848	682 638	513 498	266 251	201 192	157 150	184 189	310 308	535 510	838 755	742 585
Starina	- 1923	1944 1846	3790 3620	2987 2930	570 614	397 466	502 457	408 269	808 681	1908 1489	2739 2674	1574 1389
Košetice	1801 1577	2480 2367	1284 1060	842 854	402 404	271 260	237 249	265 252	405 337	857 452	1363 1446	1548 1642
Rigi	872 805	998 880	676 620	654 530	603 510	415 380	403 310	276 260	479 420	880 765	687 630	701 600
La Tardiere	1124 850	936 870	793 770	469 465	231 215	177 180	149 165	286 210	294 270	591 500	669 550	801 710
Donon	978 830	1278 1040	629 600	533 500	328 270	262 190	166 150	255 225	326 240	648 600	666 455	919 765
Peyrusse Vieille	611 600	1045 955	557 650	484 415	233 210	186 180	158 135	185 155	281 220	367 270	443 260	569 530
Campisábalos	191 164	280 278	269 177	181 178	152 158	241 311	251 199	239 110	193 180	103 5	229 95	232 105
	n-BUTANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	372 353	372 315
Utö	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	431 448	417 358
Zingst	652 672	553 605	430 389	285 284	246 116	113 117	174 166	74 62	142 143	178 201	486 428	418 347
Waldhof	620 639	555 552	440 456	261 267	118 117	123 114	112 102	130 105	219 187	270 267	517 494	661 657
Schmücke	593 574	465 414	318 298	243 292	159 134	106 99	106 108	138 130	162 155	267 249	424 420	376 424
Brotjacklriegel	661 726	488 472	328 358	209 187	113 118	114 101	104 104	122 91	157 129	227 206	308 269	344 314
Hohenpeissenberg	479 430	435 474	313 288	213 212	106 80	105 100	86 78	102 88	147 136	216 212	356 310	331 305
Starina	1097 1038	630 605	1118 1099	423 415	237 244	164 195	200 169	151 141	264 315	480 426	623 512	459 463
Košetice	532 463	622 511	367 371	250 260	119 116	97 85	108 86	92 87	192 187	275 165	443 435	527 441
Rigi	394 380	464 460	388 370	243 210	195 140	182 170	147 130	208 160	225 210	329 300	374 330	395 350
La Tardiere	639 570	468 465	391 340	278 255	105 80	114 90	89 85	174 120	161 160	306 290	373 345	731 460
Donon	696 580	688 605	359 380	298 290	126 90	137 120	92 70	190 150	283 150	362 390	478 285	720 490
Peyrusse Vieille	367 380	465 450	221 240	189 175	83 85	109 90	111 95	91 80	114 120	153 150	269 250	379 380
Campisábalos	313 275	255 220	191 133	200 171	136 90	183 153	122 96	185 135	99 80	257 180	121 90	215 225

	i-BUTANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	288	237	180	148	41	19	23	36	35	83	146	273
	282	167	162	169	42	13	14	38	24	82	136	234
Utö	409	258	189	162	55	60	68	40	115	161	290	308
	321	190	165	164	44	46	46	38	101	113	267	258
Zingst	367	329	263	176	134	67	99	41	82	96	297	257
	355	357	248	171	74	66	90	37	79	79	259	215
Waldhof	351	330	265	159	71	68	68	70	131	151	293	378
	357	318	285	158	72	67	54	61	120	142	283	339
Schmücke	342	261	196	145	87	80	71	72	92	148	252	223
	328	251	181	165	77	56	54	65	95	132	240	248
Brotjacklriegel	365	277	212	127	80	64	74	79	92	110	173	170
	363	251	230	122	73	51	48	56	71	101	121	184
Hohenpeissenberg	266	268	184	127	62	60	52	62	92	138	216	192
	227	285	171	128	47	57	48	58	88	128	192	174
Starina	415	329	527	238	136	138	127	83	163	276	307	264
	415	341	549	235	134	119	106	88	173	261	310	276
Košetice	317	369	226	152	93	64	72	60	121	175	278	322
	301	298	218	160	80	53	48	58	108	98	269	277
Rigi	233	284	221	130	101	114	79	102	132	192	223	281
	240	280	210	120	80	120	70	90	130	170	190	250
La Tardiere	308	243	219	144	46	46	43	81	67	161	163	320
	250	240	180	130	40	30	30	50	70	150	160	220
Donon	551	530	219	171	68	69	47	138	161	240	364	610
	350	390	200	155	40	50	40	85	90	240	180	335
Peyrusse Vieille	184	238	121	105	109	47	63	44	56	80	130	184
	190	225	130	100	40	40	30	40	50	85	140	180
Campisábalos	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-
SUM OF BUTENES												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Brotjacklriegel	-	-	-	-	-	-	-	-	-	-	-	-
Hohenpeissenberg	-	-	-	-	-	-	-	-	-	-	-	-
Starina	121	144	153	-	114	142	82	33	58	60	-	653
	125	146	165	-	114	117	68	30	57	62	-	628
Košetice	144	121	214	59	101	259	158	45	454	191	145	213
	130	107	113	66	26	70	93	38	75	45	123	171
Rigi	161	127	96	118	53	35	55	62	102	172	167	146
	145	140	90	110	50	30	50	60	100	150	140	120
La Tardiere	-	-	-	-	-	-	-	-	-	-	-	-
Donon	-	-	-	-	-	-	-	-	-	-	-	-
Peyrusse Vieille	-	-	-	-	-	-	-	-	-	-	-	-
Campisábalos	-	-	-	-	-	-	-	-	-	-	-	-



	BUT-1-ENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	39 29	28 27	23 23	17 16	13 15	16 17	24 17	17 17	19 16	25 26	47 34	37 26
Waldhof	45 37	32 34	24 21	12 12	21 21	18 17	15 14	16 16	17 16	26 26	45 50	52 51
Schmücke	46 50	38 29	19 19	21 13	16 16	17 19	19 15	14 14	17 15	29 25	43 35	32 26
Brotjacklriegel	45 44	24 24	25 23	21 20	21 21	19 17	19 19	18 17	19 19	27 23	30 25	23 25
Hohenpeissenberg	26 21	20 23	14 14	9 10	8 7	8 8	8 7	8 8	7 7	13 11	26 18	21 14
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	-	-	-	-	-	-	-	-	-	-	-	-
Rigi	-	-	-	-	-	-	-	-	-	-	-	-
La Tardiere	53 40	40 40	43 35	29 30	24 20	22 20	21 20	25 20	27 30	36 40	40 35	68 40
Donon	266 50	45 45	38 30	23 25	16 20	20 20	19 20	24 25	17 20	23 20	24 20	43 30
Peyrusse Vieille	17 20	25 20	17 20	20 20	16 15	17 20	16 20	18 20	12 10	11 10	7 5	23 20
Campisábalos	75 57	87 88	83 70	75 70	51 45	83 72	78 69	76 65	80 80	103 90	56 40	55 65
	TRANS-2-BUTENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	6 6	7 7	6 6	7 7	5 5	6 5	8 6	4 4	4 4	5 4	6 6	10 5
Waldhof	7 7	5 5	7 8	5 5	5 4	5 5	4 4	5 5	4 4	6 5	8 5	7 6
Schmücke	9 9	15 8	5 5	6 7	9 5	5 5	4 4	4 4	5 5	6 6	11 7	5 5
Brotjacklriegel	12 11	8 8	9 9	7 6	5 5	6 5	7 7	4 4	5 5	6 5	7 6	7 7
Hohenpeissenberg	9 9	8 8	7 7	7 7	7 7	7 7	7 7	7 7	6 5	9 7	10 6	9 6
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	-	-	-	-	-	-	-	-	-	-	-	-
Rigi	-	-	-	-	-	-	-	-	-	-	-	-
La Tardiere	18 20	14 10	12 10	9 8	6 5	11 10	10 10	9 10	8 5	7 5	8 5	19 10
Donon	178 40	13 10	21 10	9 8	8 5	11 10	8 10	9 8	5 5	5 5	7 5	10 5
Peyrusse Vieille	-	-	-	-	-	-	-	-	-	-	-	-
Campisábalos	23 16	24 25	20 16	22 18	14 11	20 17	19 14	16 10	18 10	38 30	14 10	16 20

	CIS-2-BUTENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	9 7	11 10	9 7	11 11	7 5	5 6	11 8	5 4	3 3	4 5	10 10	8 5
Waldhof	8 5	9 9	11 11	6 6	6 6	6 6	5 4	5 5	6 6	6 5	11 7	8 5
Schmücke	13 14	18 14	7 5	8 9	10 7	4 3	7 5	6 5	6 5	7 7	11 9	6 5
Brotjacklriegel	16 15	9 7	14 14	8 8	6 5	5 4	7 6	6 5	6 6	6 5	9 7	6 5
Hohenpeissenberg	5 5	6 6	7 7	7 6	5 5	5 4	4 4	4 4	3 3	5 5	9 6	7 5
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	-	-	-	-	-	-	-	-	-	-	-	-
Rigi	-	-	-	-	-	-	-	-	-	-	-	-
La Tardiere	11 5	9 10	9 8	6 5	5 5	7 5	6 5	5 5	7 5	7 5	7 5	14 10
Donon	122 30	13 10	18 10	8 5	6 5	9 10	7 5	6 5	6 5	5 5	7 5	10 5
Peyrusse Vieille	5 5	5 5	5 5	5 5	5 5	5 5	9 5	5 5	5 5	5 5	5 5	5 5
Campisábalos	186 110	136 88	148 48	165 73	99 26	178 183	137 100	199 155	61 30	241 200	140 75	190 185
	n-PENTANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	38 38	36 25	19 17	12 13	22 20	21 19	18 14	25 25	25 18	52 51	102 81	172 134
Utö	82 60	31 25	19 17	21 18	49 41	72 57	101 71	55 55	107 81	115 112	181 175	190 137
Zingst	220 216	172 178	134 114	95 84	103 42	43 43	93 101	32 33	63 58	78 65	190 146	165 131
Waldhof	204 210	184 180	144 153	81 72	50 39	63 55	60 51	71 51	119 84	115 79	221 198	260 245
Schmücke	179 179	172 153	110 103	92 87	88 72	112 106	92 77	103 60	82 92	135 124	167 155	194 228
Brotjacklriegel	217 197	155 132	155 145	98 73	77 80	68 66	95 70	87 63	97 85	91 87	196 144	115 119
Hohenpeissenberg	129 96	140 134	81 74	69 56	47 29	47 42	51 31	51 38	72 70	91 75	154 130	114 90
Starina	348 333	241 230	1260 981	485 358	136 155	128 107	145 111	58 57	129 143	207 178	244 234	180 175
Košetice	188 178	212 166	104 121	82 83	61 49	49 44	58 47	46 43	90 84	125 76	195 210	198 149
Rigi	136 120	182 160	150 120	114 90	118 70	100 80	114 80	111 80	177 140	177 150	164 130	135 110
La Tardiere	200 180	159 165	149 135	205 120	141 105	178 120	113 90	156 125	119 110	141 100	134 115	288 150
Donon	168 130	180 170	109 100	110 100	53 30	56 50	39 30	86 55	127 80	163 180	141 80	198 165
Peyrusse Vieille	113 100	118 115	56 60	53 50	34 30	47 40	58 40	24 20	40 40	52 50	73 60	98 100
Campisábalos	-	-	-	-	-	-	-	-	-	-	-	-

	i-PENTANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	70 71	79 48	42 40	37 38	25 26	25 26	- -	- 70	31 24	80 74	129 104	203 195
Utö	121 97	63 42	39 38	114 66	60 56	371 393	359 308	- 274	244 152	241 176	252 238	255 313
Zingst	329 281	250 261	200 181	186 130	156 72	92 83	167 157	72 73	105 85	113 85	295 247	222 168
Waldhof	300 300	268 256	208 210	106 95	77 85	85 85	87 82	112 84	167 106	168 125	316 292	377 358
Schmücke	287 279	283 221	154 156	129 122	180 113	107 91	96 95	115 99	126 136	199 165	276 234	208 190
Brotjackriegel	392 357	220 208	227 218	112 99	127 105	120 112	334 153	183 134	169 134	149 163	200 138	184 188
Hohenpeissenberg	199 171	210 206	150 139	107 104	98 64	111 104	95 86	127 110	148 153	175 140	256 215	193 172
Starina	447 390	394 361	1694 1438	991 802	758 408	486 373	312 223	170 113	207 182	902 458	393 408	285 252
Košetice	300 330	307 244	187 209	111 113	125 95	104 115	129 95	97 86	197 145	189 126	310 338	297 241
Rigi	226 200	305 280	259 240	216 180	207 140	197 180	189 170	227 200	267 250	269 250	258 210	210 170
La Tardiere	296 270	229 215	214 210	160 165	78 70	108 70	79 75	163 110	236 160	251 190	268 205	393 230
Donon	241 190	303 265	160 150	161 150	107 120	102 100	89 70	188 120	216 130	251 230	260 155	305 220
Peyrusse Vieille	171 150	215 210	117 130	90 75	51 45	80 70	151 60	81 75	91 90	103 115	149 120	184 180
Campisábalos	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
	n-HEXANE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	65 61	45 41	38 34	15 14	6 3	4 3	4 3	9 9	17 20	18 18	25 21	50 43
Utö	56 58	40 40	36 33	22 18	14 12	19 15	29 25	15 15	29 24	33 25	53 46	55 40
Zingst	76 76	57 52	44 38	35 31	- 98	- 18	44 35	14 15	21 20	24 23	69 80	60 51
Waldhof	78 77	62 59	44 45	23 20	15 16	18 19	17 14	21 21	28 20	35 28	66 57	95 90
Schmücke	68 75	57 40	31 27	21 20	- 16	19 21	16 15	16 15	24 23	41 37	55 48	51 59
Brotjackriegel	79 80	48 43	40 36	21 21	- 21	22 18	39 21	29 21	34 20	32 25	43 23	40 39
Hohenpeissenberg	52 46	52 55	32 31	21 21	17 15	16 15	15 14	17 14	19 17	26 22	45 37	38 32
Starina	190 131	196 164	87 86	153 146	177 84	612 102	75 41	18 18	64 63	87 64	231 202	507 449
Košetice	73 69	68 50	36 39	25 24	23 24	25 18	23 13	14 10	29 20	39 20	70 66	77 51
Rigi	44 40	50 50	35 30	24 20	15 10	14 10	16 10	21 20	37 30	74 70	65 60	40 30
La Tardiere	53 50	38 35	- 20	25 25	5 5	13 10	21 15	28 25	23 20	41 30	35 30	120 50
Donon	45 50	33 25	28 25	29 13	15 5	8 5	26 20	39 30	48 20	43 50	48 30	69 60
Peyrusse Vieille	36 30	- 20	- -	14 10	33 20	14 5	83 25	16 15	18 20	23 20	33 30	43 30
Campisábalos	1171 291	2348 214	516 275	1299 902	643 295	2212 2205	2476 2540	2664 920	1366 1225	1216 380	1119 420	1392 280

	ISOPRENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	4 4	4 4	4 4	4 4	23 23	25 18	77 67	54 42	10 4	33 39	4 4	6 4
Utö	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Zingst	10 9	10 9	14 11	40 34	- 26	- 222	609 467	650 617	225 285	81 41	24 19	16 13
Waldhof	13 12	11 11	6 6	6 5	10 9	70 64	71 77	84 65	44 29	64 30	72 27	19 17
Schmücke	16 16	18 12	8 7	10 10	- 9	63 47	70 58	59 45	19 20	24 26	27 26	16 15
Brotjacklriegel	24 16	14 13	21 13	33 31	- 564	383 523	510 346	715 756	129 126	262 39	63 59	21 18
Hohenpeissenberg	7 6	5 4	6 5	14 5	40 15	81 36	50 16	74 17	23 6	8 5	9 6	7 4
Starina	- -	- 224	64 50	- 23	192 123	220 202	182 147	107 110	171 48	131 71	- -	26 26
Košetice	16 16	14 11	19 9	13 9	44 24	161 94	97 62	97 92	40 35	11 7	15 10	35 8
Rigi	23 20	12 10	19 10	29 20	39 20	87 50	112 55	173 90	44 20	31 20	20 20	16 10
La Tardiere	13 5	9 8	13 10	29 20	130 70	402 340	470 320	898 600	237 190	63 40	20 15	11 5
Donon	24 10	32 20	66 60	179 155	452 240	2051 1480	1353 1330	2693 2635	641 510	162 100	95 105	51 45
Peyrusse Vieille	8 5	13 10	49 40	121 100	468 205	1334 1190	986 880	2048 1565	757 590	317 140	45 40	7 5
Campisábalos	183 18	16 10	64 9	22 13	94 51	113 122	187 96	135 140	45 40	34 5	43 10	36 15
	BENZENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	202 192	215 197	218 178	179 164	92 78	42 41	41 38	60 64	63 61	79 72	158 135	182 164
Utö	257 213	314 345	244 195	214 193	115 106	80 70	65 54	37 37	114 119	152 141	276 294	288 208
Zingst	359 282	470 462	326 232	177 162	72 56	56 60	81 67	61 58	110 105	109 90	344 223	225 155
Waldhof	297 322	474 469	330 237	178 176	70 69	61 61	53 51	64 52	105 111	160 107	272 241	352 349
Schmücke	287 260	368 335	207 203	170 151	88 87	62 51	57 63	74 76	95 95	175 168	230 212	212 171
Brotjacklriegel	362 323	335 246	264 256	173 168	79 89	71 65	63 59	77 73	98 92	149 124	202 142	166 167
Hohenpeissenberg	337 242	387 281	226 216	190 193	104 100	74 71	61 59	70 69	136 133	185 168	228 205	202 176
Starina	1047 941	361 362	514 464	263 273	169 155	247 123	127 111	75 76	167 157	250 210	170 207	446 338
Košetice	321 295	481 401	298 225	159 155	50 56	47 34	41 36	53 53	78 78	140 104	204 181	239 237
Rigi	295 270	397 355	226 210	175 150	126 110	88 90	73 70	116 110	215 190	394 350	362 330	216 180
La Tardiere	347 220	294 265	248 250	174 170	88 85	73 80	54 55	99 95	93 90	178 160	204 170	247 200
Donon	277 230	397 385	186 180	179 160	97 100	78 80	57 50	103 85	100 100	193 190	193 140	273 220
Peyrusse Vieille	189 180	280 240	156 160	139 140	79 65	63 70	61 50	76 70	74 70	90 90	134 120	153 150
Campisábalos	354 301	379 362	318 286	465 265	265 244	254 185	193 164	138 115	105 80	164 140	101 100	53 40

	TOLUENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	233 184	210 245	147 137	70 66	93 56	51 47	128 88	70 78	75 76	77 59	249 158	188 129
Waldhof	257 213	237 231	178 178	70 53	55 52	102 76	143 59	98 65	125 73	171 111	295 276	332 281
Schmücke	273 289	285 197	136 132	87 76	85 75	76 65	87 85	81 72	100 104	190 150	237 191	164 110
Brotjacklriegel	553 465	181 193	173 165	75 78	125 88	87 76	226 110	94 84	103 98	125 116	153 105	144 150
Hohenpeissenberg	234 212	228 231	141 137	96 87	90 69	81 68	69 63	78 67	130 126	167 141	249 208	153 110
Starina	- 71	120 62	44 29	84 87	- 18	38 11	48 24	- 4	66 47	84 86	69 19	53 24
Kosetice	237 229	278 224	199 176	85 81	75 45	102 42	86 73	43 38	92 81	119 100	236 220	158 130
Rigi	330 260	342 270	243 210	211 160	210 130	153 120	194 160	210 180	371 320	408 340	365 280	249 160
La Tardiere	466 340	310 320	340 330	226 210	153 140	168 170	134 110	211 140	376 210	559 420	589 340	399 270
Donon	226 180	295 240	142 130	115 90	78 80	84 80	44 40	96 60	133 80	196 190	223 130	239 185
Peyrusse Vieille	143 120	245 230	91 100	84 80	68 75	80 70	121 40	48 50	76 60	93 95	151 100	183 160
Campisábalos	1013 695	770 711	632 421	539 491	828 403	829 678	654 559	921 795	581 490	768 810	655 495	490 475

	ETHYLBENZENE											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Brotjacklriegel	-	-	-	-	-	-	-	-	-	-	-	-
Hohenpeissenberg	37 35	40 39	25 24	17 16	16 14	12 11	11 10	11 9	17 17	24 22	40 27	24 16
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Kosetice	44 43	44 39	28 27	14 11	18 18	12 8	18 17	12 11	19 14	24 16	44 47	37 33
Rigi	52 40	58 50	35 30	32 30	- -	- -	- -	- -	- -	102 100	114 90	76 50
La Tardiere	66 40	51 60	70 45	34 35	25 25	30 30	21 20	28 20	58 40	62 50	78 50	62 30
Donon	38 30	60 50	26 20	23 20	18 20	17 20	7 5	18 10	22 10	33 30	39 20	41 30
Peyrusse Vieille	19 20	35 35	12 10	13 15	9 8	9 5	23 5	6 5	8 10	15 20	31 10	23 20
Campisábalos	-	-	-	-	-	-	-	-	-	-	-	-

	<b>m+p-XYLENE</b>											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	69 59	46 51	29 32	68 24	17 5	13 5	52 43	31 24	28 28	39 34	124 130	51 30
Waldhof	92 60	50 53	42 50	42 34	38 5	15 5	29 29	16 19	36 35	74 44	146 81	87 99
Schmücke	116 124	113 56	40 34	79 87	5 5	20 22	43 42	44 40	53 57	93 67	105 86	58 37
Brotjacklriegel	215 187	41 30	51 42	33 25	41 5	20 18	63 41	25 22	40 28	47 45	62 48	49 47
Hohenpeissenberg	87 70	78 79	47 40	33 29	29 19	26 22	24 20	25 21	31 27	56 43	104 58	61 35
Starina	-	-	-	-	-	-	-	-	-	-	-	-
Kosetice	107 104	97 93	64 56	31 26	26 22	26 17	36 27	17 17	38 27	59 34	103 109	71 69
Rigi	155 130	176 130	63 50	53 45	-	-	-	-	-	220 230	229 180	147 85
La Tardiere	211 160	163 185	218 95	91 70	76 65	101 90	81 60	69 55	197 130	187 150	274 140	179 100
Donon	109 90	130 110	54 50	45 35	48 50	37 40	17 20	30 20	38 20	73 60	96 50	100 70
Peyrusse Vieille	54 50	70 65	21 20	24 20	31 30	33 30	58 15	16 15	21 20	27 25	83 20	54 40
Campisábalos	-	-	-	-	-	-	-	-	-	-	-	-
	<b>o-XYLENE</b>											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Pallas	-	-	-	-	-	-	-	-	-	-	-	-
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	26 14	15 16	11 10	21 5	5 5	5 5	14 6	6 5	5 5	24 21	25 26	15 5
Waldhof	30 23	24 22	16 18	11 9	5 5	5 5	5 5	5 5	5 5	20 13	40 16	34 24
Schmücke	36 33	49 28	13 10	24 20	10 5	5 5	7 5	8 5	5 5	21 5	26 25	19 5
Brotjacklriegel	65 55	18 15	15 11	15 12	14 5	5 5	19 5	5 5	5 5	27 25	25 23	17 14
Hohenpeissenberg	32 26	32 33	19 19	13 13	13 9	15 11	12 10	15 12	14 13	22 18	39 26	24 16
Starina	421 346	420 376	475 400	306 275	407 291	267 220	223 235	383 182	578 437	829 406	376 402	363 323
Kosetice	39 38	34 32	27 20	11 10	15 11	17 10	23 21	8 7	13 9	18 13	37 38	31 30
Rigi	25 10	58 50	31 20	24 20	-	-	-	-	-	111 105	103 80	63 40
La Tardiere	83 90	65 70	83 50	34 35	26 30	36 30	20 20	18 10	63 40	42 40	81 55	73 50
Donon	59 50	58 50	33 30	30 20	17 20	19 20	6 5	20 15	23 10	31 30	39 30	46 40
Peyrusse Vieille	59 50	50 50	39 40	33 25	23 25	20 20	24 10	21 15	7 5	15 10	34 10	33 30
Campisábalos	-	-	-	-	-	-	-	-	-	-	-	-

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





<b>METHANAL (FORMALDEHYDE)</b>												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.236 0.255	0.326 0.285	0.411 0.180	0.294 0.230	0.291 0.230	0.646 0.630	1.408 1.270	1.063 1.135	1.022 0.940	0.578 0.280	0.418 0.390	0.498 0.345
Zingst	0.574 0.496	1.242 0.862	1.139 0.951	1.289 1.314	1.627 1.251	1.778 1.664	2.250 2.436	1.926 1.978	1.750 1.212	0.669 0.571	0.676 0.548	0.578 0.400
Waldhof	0.562 0.507	1.508 1.817	1.417 1.485	1.575 1.680	1.812 1.547	2.612 2.086	2.866 3.299	3.316 3.103	2.402 1.511	1.026 0.717	0.711 0.610	0.640 0.595
Schmücke	0.532 0.486	1.007 1.108	1.102 1.180	1.346 1.411	1.592 1.097	2.277 2.154	2.306 2.212	4.008 3.706	1.807 1.176	0.892 0.914	0.877 0.911	0.602 0.506
Brotjacklriegel	0.434 0.448	0.622 0.582	0.688 0.644	0.581 0.700	0.856 0.758	1.210 1.300	0.972 0.928	0.838 0.639	0.436 0.417	0.317 0.297	0.222 0.197	0.342 0.351
Košetice	0.872 0.670	1.381 1.310	1.310 0.940	0.836 0.700	1.347 1.120	1.760 1.630	2.010 1.730	3.560 3.650	1.880 1.480	0.926 0.840	0.927 0.980	0.917 0.780
La Tardiere	- -	- -	1.540 1.694	1.779 1.867	1.098 0.816	1.938 1.854	1.458 1.592	3.607 3.411	2.143 2.132	0.962 1.050	0.941 0.923	1.024 0.903
Donon	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Peyrusse Vieille	- -	- -	- -	1.436 1.432	1.494 1.701	2.680 1.960	1.461 1.249	5.032 4.400	1.904 1.890	1.333 1.204	1.424 0.966	0.887 0.800
<b>ETHANAL (ACETALDEHYDE)</b>												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.633 0.650	0.771 0.640	0.701 0.450	0.668 0.470	0.352 0.330	0.567 0.520	0.857 0.835	0.845 0.810	0.872 0.910	0.683 0.420	0.368 0.345	0.491 0.455
Zingst	0.501 0.414	1.087 0.779	0.952 0.769	0.761 0.812	0.898 0.816	0.910 0.946	1.129 1.202	0.965 0.954	0.949 0.791	0.637 0.522	0.638 0.597	0.708 0.576
Waldhof	0.637 0.435	1.234 1.398	1.077 1.109	0.886 1.040	0.845 0.787	1.098 0.965	1.037 0.925	1.410 1.271	1.182 0.710	0.707 0.698	0.635 0.598	0.760 0.651
Schmücke	0.475 0.353	0.813 0.953	0.822 0.877	0.756 0.835	0.736 0.624	0.738 0.759	0.814 0.858	1.496 1.412	0.895 0.744	0.690 0.692	0.640 0.688	0.585 0.458
Brotjacklriegel	0.388 0.348	0.457 0.411	0.520 0.508	0.333 0.347	0.371 0.347	0.420 0.469	0.439 0.330	1.565 1.417	1.286 1.411	0.991 0.510	0.390 0.337	0.372 0.417
Košetice	1.085 0.990	1.926 1.995	1.277 1.130	1.277 1.075	1.867 1.580	2.556 2.000	2.544 1.800	3.211 3.230	2.055 1.760	0.945 0.970	1.105 1.070	1.153 1.130
La Tardiere	- -	- -	1.437 1.258	0.644 0.586	0.590 0.462	1.014 0.944	0.671 0.672	2.386 2.484	1.681 2.129	0.762 0.825	0.648 0.647	0.758 0.672
Donon	0.579 0.505	- -	1.311 1.277	1.046 0.992	0.502 0.483	1.019 0.967	1.047 0.714	0.814 0.536	1.675 1.593	0.837 1.021	0.557 0.531	0.627 0.510
Peyrusse Vieille	0.855 0.834	- -	- -	0.803 0.815	0.993 0.298	0.638 0.467	0.936 0.869	2.058 2.060	1.388 1.717	0.686 0.646	0.687 0.538	0.542 0.605
<b>PROPANONE (ACETONE)</b>												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.753 0.810	1.188 1.060	2.282 1.055	1.792 1.600	0.952 0.840	1.666 1.640	1.423 1.465	2.150 2.020	1.723 1.850	1.892 1.260	0.783 0.830	1.005 0.965
Zingst	0.605 0.735	1.180 0.934	1.528 2.029	1.733 1.647	1.667 1.473	1.412 1.328	1.698 1.789	1.866 1.574	1.916 1.543	0.912 0.843	0.699 0.694	0.731 0.476
Waldhof	0.747 0.645	1.600 1.591	2.177 1.893	2.613 2.720	2.366 1.837	2.410 2.129	3.032 2.595	3.628 3.461	3.312 2.024	1.475 1.300	1.068 1.017	0.912 0.867
Schmücke	0.712 0.551	1.347 1.174	1.924 1.777	2.504 2.801	2.384 1.782	2.716 2.898	3.434 2.837	5.759 5.124	3.418 3.237	1.372 1.227	1.331 1.124	0.877 0.812
Brotjacklriegel	0.530 0.542	0.651 0.586	0.937 0.955	0.931 0.983	1.323 1.297	1.796 1.527	1.328 1.302	1.485 1.317	0.760 0.804	0.242 0.214	0.312 0.312	0.219 0.148
Košetice	1.190 1.175	2.813 2.865	2.841 3.060	3.363 4.145	2.588 2.300	2.474 2.220	3.483 3.980	4.576 4.550	3.647 3.300	2.157 2.120	2.033 2.040	1.735 1.660
La Tardiere	- -	- -	2.508 2.687	3.304 3.221	1.819 1.532	3.043 3.251	2.665 2.451	3.668 3.257	3.515 3.398	2.107 1.788	1.530 1.557	1.680 1.625
Donon	- -	- -	3.142 3.690	3.763 4.027	2.946 2.969	5.691 5.811	4.729 4.381	6.735 6.791	3.951 3.602	2.400 2.533	1.399 1.222	1.161 0.977
Peyrusse Vieille	1.436 1.397	- -	- -	3.087 2.948	- -	2.890 2.968	2.840 2.656	3.120 2.106	2.547 2.454	2.159 2.138	2.162 1.838	3.812 1.454

<b>PROPANAL</b>												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.193 0.160	0.145 0.105	0.181 0.110	0.116 0.080	0.030 0.020	0.094 0.100	0.163 0.150	0.143 0.145	0.148 0.165	0.100 0.060	0.058 0.060	0.066 0.060
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Brotjackriegel	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	0.178 0.170	0.322 0.285	0.205 0.180	0.196 0.135	0.245 0.190	0.430 0.350	0.460 0.280	0.537 0.520	0.402 0.400	0.190 0.200	0.180 0.180	0.183 0.160
La Tardiere	-	-	0.173 0.143	0.134 0.152	0.851 0.110	3.089 3.297	0.076 0.049	0.298 0.307	0.172 0.187	0.113 0.120	0.114 0.120	0.127 0.113
Donon	0.101 0.107	-	0.222 0.170	0.134 0.117	0.084 0.080	2.826 2.215	0.102 0.073	0.119 0.130	0.167 0.146	0.152 0.183	0.095 0.095	0.108 0.094
Peyrusse Vieille	0.165 0.144	0.128 0.156	-	0.152 0.151	0.144 0.114	0.308 0.125	0.113 0.108	0.239 0.237	0.133 0.140	0.126 0.132	0.114 0.080	0.097 0.093
<b>2-PROPENAL (ACROLEIN)</b>												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.022 0.020	0.020 0.020	0.026 0.020	0.017 0.015	0.022 0.020	-	0.095 0.050	-	-	-	0.020	0.030
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Brotjackriegel	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	0.068 0.045	0.028 0.030	0.026 0.030	0.013 0.010	0.017 0.010	0.020 0.010	0.036 0.035	0.058 0.055	0.084 0.080	-	0.062 0.065	0.056 0.050
La Tardiere	0.045 0.015	0.040 0.015	0.035 0.035	0.015 0.016	0.015 0.015	-	0.016 0.015	0.015 0.015	0.023 0.015	0.015 0.015	0.015 0.015	0.017 0.017
Donon	0.015 0.015	-	-	0.015 0.015	0.015 0.015	-	-	0.023 0.023	0.027 0.015	0.015 0.015	0.015 0.015	0.016 0.017
Peyrusse Vieille	0.015 0.015	0.015 0.015	-	0.015 0.015	0.015 0.015	-	0.020 0.017	0.034 0.030	0.076 0.016	-	-	0.016 0.017
<b>2-BUTANONE (METHYL ETHYL KETONE)</b>												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.281 0.285	0.506 0.455	0.271 0.300	0.231 0.230	0.082 0.090	0.158 0.160	0.346 0.340	0.151 0.140	0.325 0.285	0.205 0.190	0.156 0.140	0.248 0.260
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Brotjackriegel	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	0.404 0.360	0.713 0.655	0.546 0.540	0.581 0.720	0.391 0.330	0.423 0.370	0.841 0.700	0.942 1.020	0.703 0.580	0.521 0.510	0.562 0.570	0.536 0.520
La Tardiere	2.237 1.258	0.411 0.298	0.619 0.575	0.730 0.711	0.416 0.338	0.514 0.490	0.979 0.254	0.894 0.984	0.832 0.640	0.648 0.461	0.399 0.400	0.887 0.799
Donon	0.162 0.057	-	0.365 0.360	0.847 0.533	0.180 0.171	0.542 0.557	0.350 0.386	0.510 0.514	0.452 0.411	0.390 0.448	0.292 0.264	0.306 0.225
Peyrusse Vieille	2.206 2.464	0.116 0.015	-	0.460 0.448	0.510 0.385	0.405 0.320	1.205 0.535	0.525 0.355	0.323 0.375	0.325 0.297	0.280 0.273	0.431 0.289

<b>3-BUTEN-2-ONE (METHYL VINYL KETONE)</b>												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	-	-	-	-	-	-	-	-	-	-	-	-
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Brotjacklriegel	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	0.048 0.025	-	-	-	-	-	-	-	-	-	-	-
La Tardiere	-	-	-	-	-	-	-	-	-	-	-	-
Donon	-	-	-	-	-	-	-	-	-	-	-	-
Peyrusse Vieille	-	-	-	-	-	-	-	-	-	-	-	-

<b>2-METHYLPROPENAL (METHACROLEIN)</b>												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	-	-	-	-	0.046 0.035	-	-	-	-	-	-	-
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Brotjacklriegel	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	0.010 0.010	-	-	-	-	0.042 0.020	-	0.070 0.065	0.033 0.035	-	-	-
La Tardiere	0.022 0.011	0.018 0.017	0.011 0.011	0.014 0.012	0.017 0.011	0.263 0.191	0.472 0.262	0.781 0.562	0.111 0.120	0.052 0.043	0.023 0.019	0.016 0.013
Donon	0.020 0.019	-	0.050 0.056	0.085 0.080	0.175 0.064	0.965 0.991	0.895 0.569	0.893 0.883	0.263 0.206	0.040 0.047	0.029 0.027	0.012 0.012
Peyrusse Vieille	0.011 0.011	0.011 0.012	-	0.024 0.018	0.092 0.090	0.794 0.676	0.495 0.499	1.445 1.481	0.325 0.292	0.057 0.060	0.041 0.027	0.015 0.013

<b>BENZENECARBALDEHYDE (BENZALDEHYDE)</b>												
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	-	0.065 0.070	0.052 0.055	-	-	-	0.086 0.080	-	-	-	0.035 0.035	-
Zingst	-	-	-	-	-	-	-	-	-	-	-	-
Waldhof	-	-	-	-	-	-	-	-	-	-	-	-
Schmücke	-	-	-	-	-	-	-	-	-	-	-	-
Brotjacklriegel	-	-	-	-	-	-	-	-	-	-	-	-
Košetice	0.040 0.030	0.084 0.100	0.050 0.050	-	0.046 0.020	0.024 0.020	-	-	0.032 0.030	-	0.054 0.050	0.045 0.050
La Tardiere	0.091 0.073	0.097 0.091	0.085 0.090	0.057 0.063	0.069 0.064	0.125 0.132	0.056 0.063	0.112 0.095	0.069 0.066	0.062 0.050	0.088 0.087	0.049 0.057
Donon	0.027 0.015	-	0.056 0.052	0.057 0.050	0.044 0.038	0.063 0.065	0.045 0.015	0.062 0.062	0.212 0.084	0.037 0.030	0.015 0.015	0.028 0.019
Peyrusse Vieille	0.034 0.015	0.015 0.015	-	0.058 0.061	0.043 0.050	0.046 0.050	0.051 0.031	0.084 0.072	0.028 0.016	0.029 0.016	0.026 0.016	0.021 0.017

	PENTANAL											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.180 0.190	0.090 0.080	0.072 0.040	- -	- -	- -	0.074 0.080	- -	- -	0.057 0.030	0.042 0.040	0.033 0.030
Zingst	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Waldhof	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Schmücke	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Brotjacklriegel	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Košetice	0.045 0.050	0.115 0.110	0.068 0.055	0.080 0.045	0.068 0.060	0.194 0.150	0.215 0.190	0.241 0.250	0.142 0.125	- -	0.085 0.080	0.067 0.060
La Tardiere	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Donon	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Peyrusse Vieille	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
	ETHANEDIAL (GLYOXAL)											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.045 0.050	0.112 0.095	0.163 0.145	0.051 0.050	- -	0.057 0.050	0.077 0.090	- -	0.037 0.035	0.040 0.030	0.021 0.020	0.036 0.020
Zingst	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Waldhof	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Schmücke	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Brotjacklriegel	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Košetice	0.053 0.030	0.320 0.290	0.113 0.100	0.143 0.140	0.075 0.020	0.154 0.120	0.091 0.030	0.166 0.160	0.134 0.090	0.078 0.070	0.052 0.055	0.067 0.065
La Tardiere	0.035 0.011	0.025 0.011	0.011 0.011	0.016 0.012	0.042 0.026	0.011 0.011	0.011 0.011	0.011 0.012	0.020 0.017	0.011 0.011	0.011 0.011	0.013 0.013
Donon	0.011 0.011	- -	0.071 0.077	0.033 0.011	0.045 0.011	0.041 0.040	0.045 0.031	0.262 0.166	0.024 0.011	0.011 0.011	0.011 0.011	0.012 0.012
Peyrusse Vieille	0.011 0.011	0.011 0.012	- -	0.011 0.011	0.028 0.019	0.010 0.011	0.014 0.012	0.011 0.011	0.033 0.012	0.012 0.011	0.012 0.012	0.012 0.013
	HEXANAL											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.075 0.070	0.073 0.075	0.150 0.065	0.147 0.060	- -	0.104 0.130	0.128 0.130	0.107 0.105	0.116 0.130	0.118 0.030	0.036 0.035	0.051 0.050
Zingst	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Waldhof	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Schmücke	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Brotjacklriegel	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Košetice	0.071 0.070	0.131 0.120	0.063 0.060	0.090 0.055	0.128 0.110	0.180 0.130	0.172 0.160	0.273 0.235	0.164 0.130	0.100 0.100	0.082 0.080	0.088 0.080
La Tardiere	0.067 0.038	0.029 0.023	0.052 0.052	0.091 0.086	0.058 0.049	0.070 0.068	0.065 0.055	0.145 0.142	0.069 0.070	0.029 0.028	0.019 0.015	0.017 0.017
Donon	0.045 0.041	- -	0.105 0.085	0.215 0.197	0.159 0.121	0.148 0.152	0.122 0.092	0.207 0.207	0.260 0.078	0.035 0.033	0.015 0.015	0.020 0.018
Peyrusse Vieille	0.100 0.076	0.058 0.062	- -	0.220 0.178	0.567 0.334	0.124 0.091	0.245 0.195	0.224 0.218	0.069 0.077	0.174 0.065	0.272 0.032	0.204 0.067

	2-OXOPROPANAL (METHYL GLYOXAL)											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Utö	0.055 0.050	0.091 0.095	0.243 0.100	0.088 0.100	0.065 0.050	0.108 0.090	0.102 0.085	- -	0.077 0.085	0.058 0.050	- -	- -
Zingst	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Waldhof	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Schmücke	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Brotjacklriegel	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Košetice	0.046 0.030	0.230 0.220	0.100 0.075	0.168 0.140	0.117 0.050	0.316 0.180	0.190 0.100	0.352 0.350	0.198 0.170	0.097 0.105	0.022 0.020	0.050 0.035
La Tardiere	0.081 0.025	0.074 0.044	0.077 0.072	0.033 0.016	0.038 0.015	0.042 0.035	0.064 0.031	0.313 0.304	0.070 0.064	0.026 0.015	- -	0.017 0.017
Donon	0.015 0.015	- -	0.124 0.121	0.099 0.081	0.084 0.068	0.182 0.146	0.140 0.107	0.462 0.363	0.077 0.081	0.015 0.015	0.015 0.015	0.016 0.017
Peyrusse Vieille	0.022 0.015	0.020 0.016	- -	0.051 0.055	0.057 0.015	0.213 0.198	0.107 0.074	0.384 0.229	0.228 0.054	0.016 0.015	0.016 0.016	0.016 0.017



## **Appendix B**

### **Time series of VOC measured in 2003**





**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
ethanedial:	glyoxal
N2oxoproanal:	2-oxopropanal (methyl glyoxal)



