

European VOC Emission Estimates Evaluated by Measurements and Model Calculations

ØYSTEIN HOV^{1,2}, ASGEIR SORTEBERG¹, NORBERT SCHMIDBAUER²,
SVERRE SOLBERG², FRODE STORDAL², DAVID SIMPSON³,
ANNE LINDSKOG⁴, HANS ARESKOUG⁵, PEDRO OYOLA⁵,
HEIKKI LÄTTILÄ⁶ and NIELS Z. HEIDAM⁷

¹*Geophysical Institute, University of Bergen, N-5007 Bergen, Norway*

²*NILU, PO Box 100, N-2007 Kjeller, Norway*

³*DNMI, PO Box 43, N-0113 Oslo, Norway*

⁴*IVL, Box 47086, S-40258 Göteborg, Sweden*

⁵*ITMI, University of Stockholm, S-10691 Stockholm, Sweden*

⁶*FMI, Sahaajankatu 22E, SF-00810 Helsinki, Finland*

⁷*DMU, FOLU, Frederiksborgvej 399, DK-4000 Roskilde, Denmark*

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Abstract. Observations and model calculations of the concentration of hydrocarbons at five Scandinavian rural sites during March–June 1993 are reported. Decreasing concentrations from March to June are observed at all sites. The highest concentrations of hydrocarbons were found in air masses coming in from the southwest to southeast, indicating that long range transport from continental Europe and the U.K. is important in pollution episodes. An episode of elevated concentrations of hydrocarbons observed at three of the sites in the middle of March is described and discussed in relation to the synoptic situation and the presence of other chemical compounds (NO₂, PAN, total nitrate and ozone). A Lagrangian numerical model is used to calculate the concentrations of the individual hydrocarbons at the five sites and comparison with observations is made. The calculated concentrations for nonmethane hydrocarbons with quite long chemical lifetimes agree well with the observations. For the sum of observed and calculated hydrocarbons the correlation coefficients are in the range of 0.65–0.88 for the five sites and the ratio between calculated and measured concentrations was 0.72–0.97, indicating that the European VOC emission inventory is quite well estimated.

Key words: volatile hydrocarbons, observations and computer modelling, tropospheric concentrations, long range transport, emission validation.

1. Introduction

Field studies have shown that yields of agricultural crops decrease as tropospheric ozone increases with reductions of 6–8% per 10 ppb of O₃ (Heck *et al.*, 1982). There is concern that ozone may have contributed to the observed forest decline in Europe and eastern United States (Skärby and Sellén, 1984; Woodman and Cowling, 1987). Elevated O₃ levels is also believed to be harmful to animals and humans (Hanst *et al.*, 1980; Folinsbee *et al.*, 1988).

Model studies by, e.g., Hov *et al.* (1978) and Isaksen *et al.* (1978) showed that O₃ may build up to values of 100–180 ppb in a few days in rural air subject

to emission of NO_x and hydrocarbons. O_3 produced in this way may persist for several days, permitting long range transport (Eliassen *et al.*, 1982). Other and more recent studies have confirmed the importance of NMHC species in tropospheric ozone formation (e.g. Liu *et al.*, 1987), and in the photochemical production of CO (Chameides and Cicerone, 1978; Greenberg and Zimmermann, 1984), in acid precipitation through the formation of PAN and through the influence of NMHC on OH, H_2O_2 as well as O_3 and for global warming through the influence of NMHC on greenhouse gases (Isaksen and Hov, 1987).

NMHC together with NO_x control the episodic occurrence of elevated ozone concentrations found over Europe (Grennfelt and Schjoldager, 1984; Derwent and Jenkin, 1990).

In this paper observations of individual nonmethane hydrocarbons during spring 1993 (March–June) at five Scandinavian rural sites (Figure 1) are presented. At Rørvik and Aspvreten measurements of VOCs have been carried out for several years during the EUROTRAC subproject TOR (Tropospheric Ozone Research) and their variability and composition have been investigated (Lindskog and Moldanova, 1994; Mowrer and Lindskog, 1991; Lindskog *et al.*, 1992; Oyola and Areskoug, 1991, 1992). At the Norwegian TOR sites Birkenes and Ny Ålesund, air samples taken 3–7 times/week have been analysed for NMHCs since 1989 at Ny Ålesund and 1987 at Birkenes, which is the longest continuous record of individual hydrocarbons in Europe. Measurements and model interpretations have been reported in Hov *et al.* (1989, 1991, 1997), Isaksen *et al.* (1985), Solberg *et al.* (1993a, 1993b, 1994) and Hov and Schmidbauer (1992). VOCs and several other compounds have been measured at Utø during the 1990s (Laurila *et al.*, 1992, 1993; Hakola *et al.*, 1991). In this paper NMHC measurements from the spring of 1993 are presented together with detailed photochemical long range transport model calculations. The purpose of the investigation was to see whether the emission inventory for NMHC as well as the speciation of emissions, are supported by the observations.

2. Measurement Sites and Experimental Methods

The measurement campaign during the spring of 1993 was carried out at five Scandinavian rural sites (Figure 1): at Aspvreten on the east coast of Sweden south of Stockholm, at Birkenes in a forested area 30 km from the southern coast of Norway, on the Zeppelin mountain at the west coast of Svalbard near Ny Ålesund, at Rørvik on the west coast of Sweden and on Utø which is a small island off the southwest coast of Finland. A more detailed description of the sites is given in Cvitas and Kley (1994). The observations at Rørvik were done every 4 hour, at Utø every second day while the other sites had daily measurements (spot samples with typically 15 min. sampling time).

At Birkenes and Ny Ålesund pressurized air samples were taken manually in stainless steel bottles with subsequent analysis of NMHC at Norwegian Institute for Air Research (NILU) using gas chromatography and a flame ionization detec-

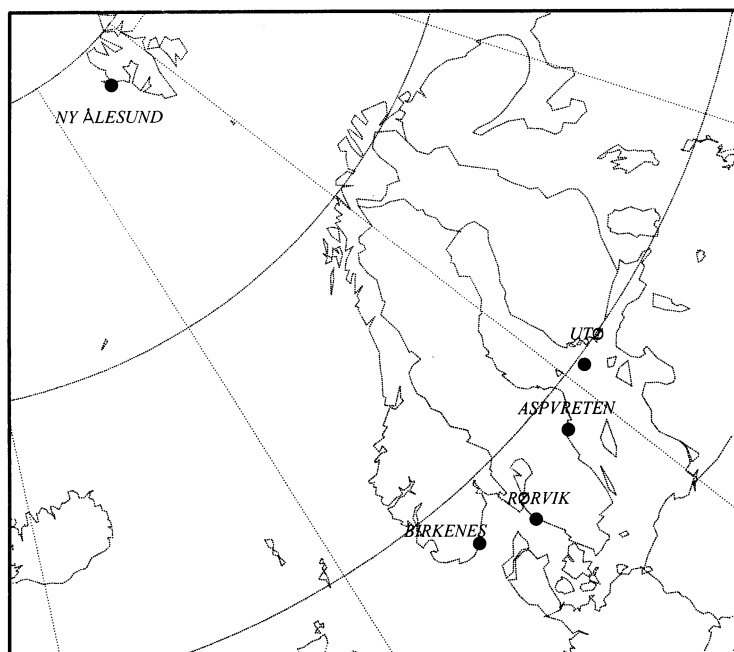


Figure 1. The location of the five Scandinavian measuring sites.

tor. A detailed description of the hydrocarbon sampling technique and analytical method is given by Schmidbauer and Oehme (1986). A NIST (National Institute of Standards and Technology) certified standard gas mixture containing 10 ppb *n*-butane and benzene was used for calibration and a response factor calculated for 1 ppbC together with the carbon number applied to all hydrocarbons. The analytical technique together with this type of calibration was used in the intercalibration organized by Joint Research Center Ispra (De Saeger and Tsani-Bazaka, 1992) with good results (Hov *et al.*, 1997).

At Utø and Aspvreten an identical method is being used for pressurized air samples taken every second day and every day, respectively (Laurila *et al.*, 1993; Oyola and Areskog, 1992) using the same analytical procedure as NILU.

At Rørvik air was sampled every four hours with a sampling time of 20 minutes and analysed using an automatic gas chromatographic system (Mowrer and Lindskog, 1991). The method is based on adsorption of hydrocarbons onto an active charcoal based adsorbent, desorption/cryofocusing onto a capillary trap and analysed using capillary gas chromatography with a flame ionization detector. The method was tested in the nonmethane hydrocarbon intercomparison experiment (Apel *et al.*, 1994).

3. Observed VOC Concentrations

Table I gives the average concentrations of observed VOCs at the measuring sites and the sum of observed alkanes, alkenes and aromatics at the different sites. The sums are not directly comparable since the air samples were not analysed for the same set of individual species at all sites. Birkenes and Ny Ålesund had identical analysis programs. Seven compounds were measured at all sites (ethane, propane, *n*-butane, *n*-pentane, ethene, propene and acetylene) and the average sum of these seven species (denoted ΣVOC^*) over the measurement period was 11.4 and 7.7 ppbC at Birkenes and Ny Ålesund, as the highest and lowest value among the sites.

All sites have a quite similar distribution of the hydrocarbons with ethane being by far the largest contributor, followed by propane and acetylene. This is not surprising since the sites are receiving most of their VOC concentrations from long range transport, which means that the short lived species are depleted during the transport before the air masses arrive at the sites. The local influence seems to be small. A pattern of decreasing concentrations from March to June for species with long and moderate lifetimes (Figure 2) is also evident at all stations. This is a well established feature from several other studies of hydrocarbons and is due to the seasonal cycle of the OH radical, which peaks in concentration during summer and is controlling the lifetime of the hydrocarbons. Also a more stably stratified atmosphere during winter will trap the anthropogenic emissions in a shallower surface layer than in summer and thereby contribute to the winter maximum. The annual variation in the emissions of VOCs is probably small. In Figure 2 it is seen that the concentration of ethane drops later in the spring than the concentration of *n*-butane. This is probably due to long lifetime of ethane compared to *n*-butane, which means that an imbalance between the sources and sinks (mainly OH-reaction) will last longer into the spring in the case of ethane. For ethene and propene which have chemical lifetimes of the order of 1 day or less, the concentrations are more variable than for the light alkanes, and the concentrations at Ny Ålesund are generally very low.

For reactive compounds like propene no significant change in concentrations was observed throughout the measuring period.

From Table I it can be seen that for relatively short-lived species like ethene and propene Aspvreten has the largest concentrations which indicate that there can be sources of petrol exhaust near the site. It should be noted that the site may be somewhat influenced by Stockholm 100 km to the NE under certain meteorological conditions. On the other hand Utø and Ny Ålesund have the lowest concentrations of the most reactive compounds, indicating longer transport times to these sites from the sources.

The average VOC values do not differ significantly from measurements reported by Lindskog *et al.* (1992), Laurila *et al.* (1992) and Solberg *et al.* (1993b).

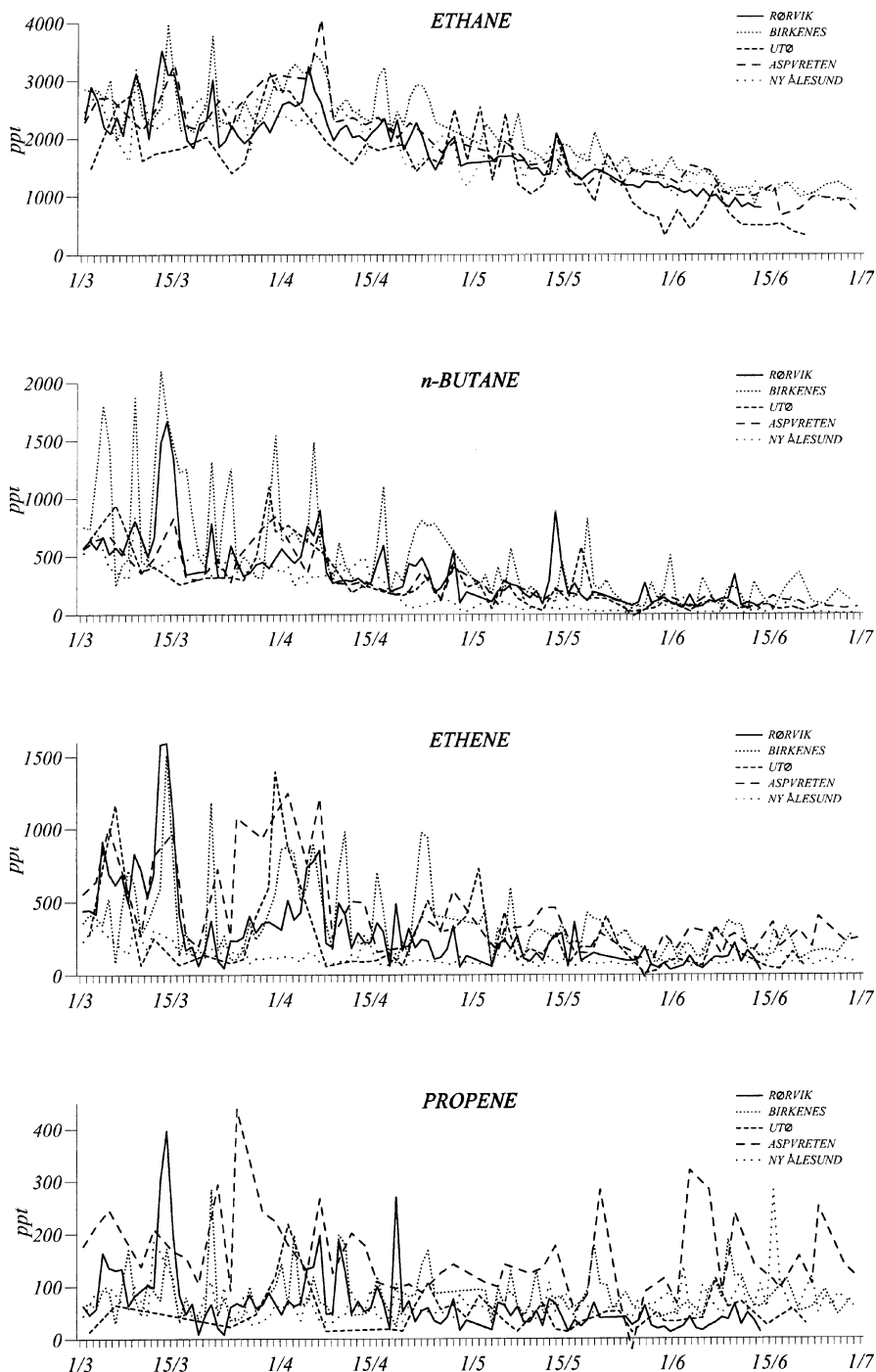


Figure 2. Time series of individual observation of highly reactive, moderately reactive and slowly reactive volatile organic gases at five Scandinavian rural sites March–June 1993.

Table I. Average values of observed NMHCs (ppt) at the different Scandinavian sites during March–June 1993. Σ VOC* is the sum of the VOCs measured at all sites (ethane, propane, *n*-butane, *n*-pentane, ethene, propene, acetylene). The number of observations is given in parentheses

Species	Birkenes		Rørvik		Ny Ålesund		Aspvreten		Utø	
Ethane	2103	(103)	1916	(466)	1809	(100)	1864	(51)	1503	(50)
Propane	784	(103)	887	(466)	570	(100)	626	(51)	662	(50)
2-Methylpropane							115	(50)		
<i>n</i> -Butane	488	(102)	384	(466)	201	(100)	277	(50)	275	(47)
<i>i</i> -Butane	258	(103)	211	(466)	103	(100)				
<i>n</i> -Pentane	121	(103)	125	(466)	53	(100)	109	(43)	128	(42)
<i>i</i> -Pentane	205	(103)	212	(466)	63	(99)				
<i>i</i> -Hexane	134	(103)			70	(99)				
<i>n</i> -Hexane	85	(103)	37	(466)	67	(99)			64	(28)
<i>n</i> -Heptane	53	(103)			44	(98)				
<i>i</i> -Heptane	99	(103)			72	(99)				
Ethene	351	(103)	318	(466)	124	(100)	430	(50)	256	(50)
Propene	82	(103)	70	(466)	67	(100)	160	(50)	50	(38)
2-Methylpropene							194	(40)		
Butenes	108	(103)			115	(100)				
1-Butene			13	(466)			50	(17)	24	(10)
Pentenes	34	(103)			39	(100)				
cycl-Pentene	18	(89)			11	(100)				
2,2-Dimethyl- propene	3	(93)			3	(85)				
Benzene	254	(103)	255	(466)	194	(98)	375	(42)		
Toulene	277	(103)	174	(466)	165	(98)	311	(36)		
<i>o</i> -xylene	31	(103)			25	(93)				
<i>m, p</i> -xylene	95	(103)			64	(95)				
Ethylbenzene	32	(103)			17	(95)				
Acetylene	692	(103)	479	(466)	435	(100)	533	(51)	521	(50)
Propyne	12	(102)	13	(466)	4	(83)				
1,3-Butadiene	5	(103)			4	(88)	66	(4)		
c6-Unres	92	(103)			66	(97)				
Isoprene	25	(103)			5	(99)				
Σ Alkanes	13550		10780		8758		7719		7116	
Σ Alkenes	1655		898		1174		2316		758	
Σ Aromatics	4727		2748		3167		4427			
Σ VOC	22049		15423		14418		15792		8916	
Σ VOC*	11447		10478		7716		9665		8436	

3.1. EPISODE

The concentration of VOCs is controlled by a combination of physical and chemical factors; e.g. the synoptic system determines the air flow to the station, the intensity of the UV radiation is important for the photooxidant formation and the temperature is important for the reaction rates. In this section a pollution episode

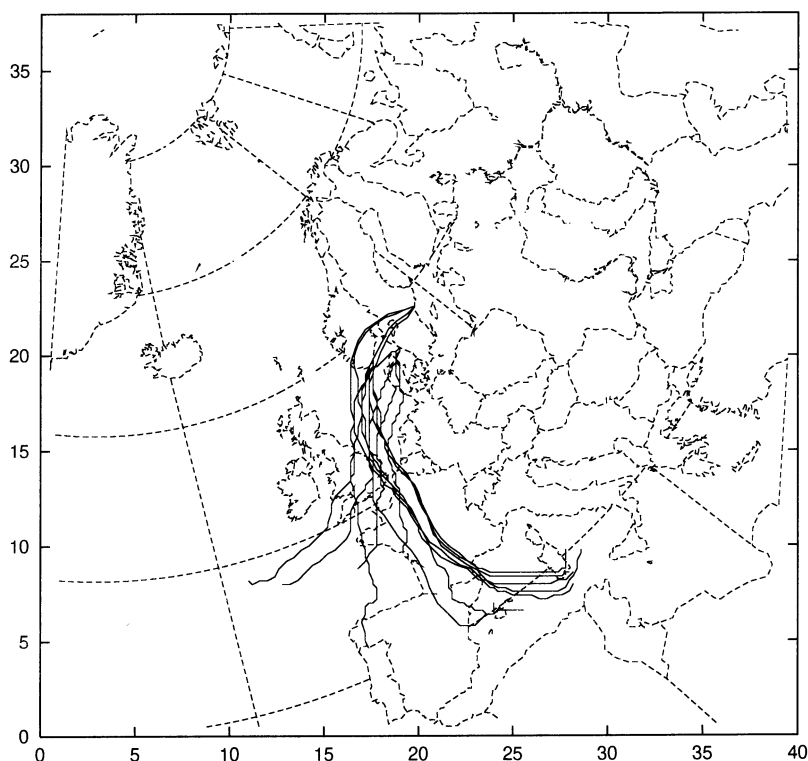


Figure 3. Calculated 4 days back trajectories arriving at Rørvik on 13 March, Birkenes on 14 March, Aspvreten on 15 March 1993 at 0, 6, 12 and 18 UTC. 925 hPa winds were used.

with particularly high concentrations at three of the Scandinavian stations is studied and related to the synoptic weather situation and the presence of other chemical compounds (NO_2 , PAN, total nitrate ($\text{NO}_3^- + \text{HNO}_3$) and O_3).

The weather system between 13 and 15 March 1993 was characterized by a low pressure west of the UK giving southwesterly winds towards Scandinavia. From 8 to 15 March a high pressure system was located over Europe giving warm and sunny weather with temperatures exceeding 15°C daily from 11 to 15 March over wide areas of southern U.K. The episode was terminated by the passage of a cold front from the west across northern Europe on 16 March.

Trajectories were calculated to Rørvik, Birkenes and Aspvreten on 13, 14 and 15 March, respectively (Figure 3). The trajectories arriving at Rørvik passed over the western coast of France 4 days earlier and over England and the North Sea before arriving at Rørvik on 13 March. The highest concentrations of hydrocarbons were observed on the 13th and the following day with the sum of the VOCs which were analysed at all sites (ΣVOC^*) being equal to 30.1 ppbC. This is about twice the average concentration for March.

Table II. Observed concentrations of NMHCs (ppt), sum of observed NMHCs at all sites (ppbC), O₃ and N-compounds (ppb) at the three Scandinavian sites influenced by the March episode in 1993, and the monthly average concentrations in March

Species	Rørvik		Birkenes		Aspvreten	
	13.3	March	14.3	March	15.3	March
Ethane	3530 ^a	2418	3962 ^a	2589	3296 ^a	2581
Propane	2340 ^b	1392	2052 ^b	1194	1566	1195
<i>n</i> -Butane	1483	618	1695 ^b	904	825	537
<i>n</i> -Pentane	440 ^b	184	365	179	214	166
Ethene	1584 ^b	522	1512 ^a	393	974	679
Propene	301 ^b	98	172	80	166	208
Acetylene	1898 ^a	795	2319 ^a	1002	1607 ^a	889
Benzene	894 ^a	386	645 ^a	328	691 ^a	424
ΣVOC*	30.1	15.3	30.9	16.3	21.3	15.5
PAN (max)	–	–	–	–	1.1 ^a	0.6
NO ₂ (max)	18.1 ^b	7.3	2.1	0.9	3.1	3.2
ΣNO ₃	17.8 ^a	2.4	6.3 ^b	0.9	5.1 ^a	0.9
O ₃ (max)	21	39.6	54 ^a	41.1	60 ^a	40.7

^a The highest observed value that month.

^b The second highest value, with the highest recorded the day before or after.

ΣVOC* is the sum of the VOCs that are measured at all the sites (ethane, propane, *n*-butane, *n*-pentane, ethene, propene, acetylene).

ΣNO₃ = NO₃⁻ + HNO₃. (max) indicates that the maximum hourly value of the diurnal cycle is taken in the analysis whenever the measurements were continuous.

Table II shows observed concentrations of hydrocarbons, NO₂, PAN, total nitrate and ozone during the episode and the average concentrations in March 1993. The elevated VOC concentrations were accompanied by very high NO₂ and total nitrate concentrations of 18.1 and 17.8 ppb, respectively, at Rørvik. This is probably a result of photochemical formation of NO₂ through



followed by



where RO₂ is a peroxy radical and RO an alkoxy radical.

The lowest daily maximum of O₃ on an hourly basis during the campaign was also recorded that day (21 ppb) at Rørvik. This is perhaps surprising bearing in mind the high amount of total nitrate observed. The global radiation during the episode was low, not higher than 74, 182 and 78 Wm⁻² on the 12, 13 and 14 March, respectively, which means that the photolysis of NO₂ was slow. Ozone was transformed quickly to NO₂ in:



and the $\text{NO}_2 + \text{O}_3$ concentration was about 40 ppb. This is not very different from the monthly average value for Rørvik in March (47 ppb). If no photochemical generation of O_3 or loss of NO_x take place in an air mass, $\text{NO}_2 + \text{O}_3$ is a conserved quantity.

Birkenes and Aspvreten were both affected by much the same air masses as Rørvik, but with 0.925 sigma level (approximately 925 hPa) trajectories which four days earlier were over the Mediterranean with transport over France and southern England where the VOC emissions are high (Figure 3). The episode was most pronounced at Birkenes with especially high ethene values probably emitted from the southern parts of the U.K. 1–2 days earlier. The total VOC concentration (ΣVOC^*) was 30.9 ppbC on 14 March and a daily O_3 maximum of 54 ppb was recorded together with a high total nitrate concentration (6.3 ppb). At Aspvreten the composition of VOCs was slightly different from that at Birkenes, with the less reactive species like ethane and acetylene being more pronounced, while more reactive compounds like ethene and propene did not exceed their normal values, indicating that the air had been exposed to photochemical activity for some time. This is supported by elevated concentrations of PAN, total nitrate and O_3 during the episode.

4. Model Calculations and Comparison with Measurements

4.1. MODEL DESCRIPTION

The EMEP photooxidant model (Simpson, 1992, 1993, 1995) is used in the theoretical analysis of the observed hydrocarbons at the Scandinavian sites in the spring of 1993. The model is a single-layer Lagrangian model covering Europe. Analyzed meteorological data fields are used as input every six hour on the 0.925 sigma level surface (approximately 925 hPa) with a grid resolution of $150 \times 150 \text{ km}^2$ at 60° N and the concentrations of 70 trace constituents are calculated along 96 hour back trajectories to the measuring sites every 6 hour (4 per day). To apply the model results in the analysis of the NMHC measurements changes were made in the handling of emission data. Emission data are available in the UN ECE-CORINAIR cooperation on a $50 \times 50 \text{ km}^2$ grid compatible with the EMEP model grid for each of 11 source categories for nonmethane hydrocarbons. Based on the CORINAIR data a NMHC model inventory was derived. More information about this is given in Solberg *et al.* (1995).

The assimilation procedure (Simpson, 1993) was used to initialize all the trajectory calculations. This means that the initial concentrations are equal to the results of the model calculations that started 96 hour earlier than the new trajectory start time as long as the new trajectory starts over the European continent.

The EMEP photooxidant model distributes the total VOC emissions on 11 different VOC species, which then represent a lumped set of individual components (e.g. the *n*-butane concentration in the model is representing a number of reactive alkanes). The modelled concentrations of these species are not directly comparable

to the observed concentrations of individual hydrocarbons. The simulation of specific hydrocarbons was therefore done by adding a large number of individual hydrocarbons to the main model with emissions assumed to have the same composition as the detailed VOC emission inventory for the U.K. (PORG, 1993) as described in Solberg *et al.* (1994, 1995). Fifty-seven individual VOCs were calculated by using the OH, O₃ and NO₃ (nitrate radical) concentrations calculated in the lumped chemical scheme in the complete EMEP model. Reaction rate coefficients were taken from international recommendations of kinetic data (Atkinson, 1990; Atkinson *et al.*, 1992). As mentioned above an emission estimate for each of these 57 compounds for the 11 source categories of the CORINAIR data set was given by using the fractional emission of each VOC specie given in the individual VOC specified emission inventory for the United Kingdom (PORG, 1993) and applied in every grid square. The CORINAIR source categories do not match exactly the PORG categories, and a subjective regrouping was done into the PORG report categories (see Solberg *et al.* (1995) for detail).

The initialization of the additional hydrocarbons was similar to the procedure for initializing the main model components, and depended on location and time of the trajectory starting point. Outside the assimilation area a set of background concentrations was used.

The background values are a seasonal least-squares fit to the two lowest concentrations each month measured at Rucava in Latvia (Solberg *et al.*, 1994)

$$c = c_0 + c_1 \sin \left(\frac{2\pi}{365}(t - c_2) \right), \quad (4)$$

where t is the day number. The coefficients c_0 , c_1 and c_2 were calculated by the least-square method and represent the mean, amplitude and day number of the maximum value, respectively.

Inside the assimilation area the initial values of the additional components were based on assimilated lumped components in the main model by

$$c_i = ac_{\text{lumped}} + b, \quad (5)$$

where c_i is the concentration of the individual hydrocarbon, c_{lumped} is the concentration of the lumped compound which compound i is a part of in the main model and a and b are calculated by linear regression between the observed individual hydrocarbons at Waldhof (Solberg *et al.*, 1994) and the calculated concentrations of the lumped specie. Initial and background concentrations of formaldehyde, acetaldehyde and acetone were set to 200, 200, and 400 ppt, respectively. For compounds not measured at Rucava the initial and background values were set to zero.

The individual VOC measurements at the Scandinavian sites are used here both to validate the performance of the model and to analyse the accuracy of the European VOC emission inventory, including the speciation.

4.2. COMPARISON OF MODEL RESULTS WITH MEASUREMENTS

The model was run for the four months period, March–June 1993, to the Scandinavian sites. The observed hydrocarbons are normally analysed in air samples taken around noon. To compare measurements and calculations, the average of the calculated concentrations for 6, 12 and 18 UTC was compared to measurements. The measurements should in some respects be more comparable to the modelled concentration at 12 UTC than other hours of the day, but for longer averaging times (e.g. 6 + 12 + 18 UTC values) the role of sub-grid concentration variations not resolved by the model, is smaller than when instantaneous or 1 h averaged measured and calculated concentrations are compared. Solberg *et al.* (1995) showed that the agreement between observed and modelled 12 UTC concentration was in fact slightly poorer than for the 6 + 12 + 18 UTC average.

For Rørvik where measurements were done every 4 hours, the daily observed mean is compared with the calculated average based on the 6, 12, 18 and 0 UTC values.

The model simulates the longest lived compounds quite well (Tables III–VII), both with respect to correlations and absolute levels. One exception here is the poor correlation for benzene at Aspvreten (0.33) which is due to episodes in May and June which were not reproduced by the model.

The good correlation for ethane, propane and acetylene is to a large extent due to the seasonal cycle assumed for the initial concentrations. Solberg *et al.* (1995) calculated the fraction of the initial concentrations which remained after 4 days of chemical decomposition to be 0.97 for ethane, 0.84 for propane and 0.88 for acetylene in average conditions for spring. The good correlation for these species therefore confirms that the seasonal cycle assumed in the initial concentrations is realistic. The model seems to give higher modelled to observed ratios from May and onwards than before May, however, indicating that a steeper decrease in the initial concentrations during spring should be introduced.

The compounds that are best suited for comparison and evaluation of the description of the chemistry and transport in the model should have lifetimes comparable to the length of the integration (4 days). Hence, the correlation between modelled and observed C₄–C₇ alkanes and toluene should give an indication of the performance of the model. The model results are quite satisfactory even for these compounds. In Figure 4 is shown the observed and average calculated *n*-butane concentrations as open boxes where the error bars mark the lowest and highest of the concentrations calculated at 06, 12 and 18 UTC each day (for Rørvik also 00 UTC). The correlations range from 0.69 to 0.89 for this compound, which have a lifetime of approximately 10 days during spring. The modelled to observed ratios range from 0.67–1.08, with the lowest value at Birkenes, where in several episodes with elevated concentrations, too low concentrations were calculated. It should be noted that the errorbars are large during the episodes and that the averaging of the modelled values instead of using the 12 UTC value results in lower calculated concentrations.

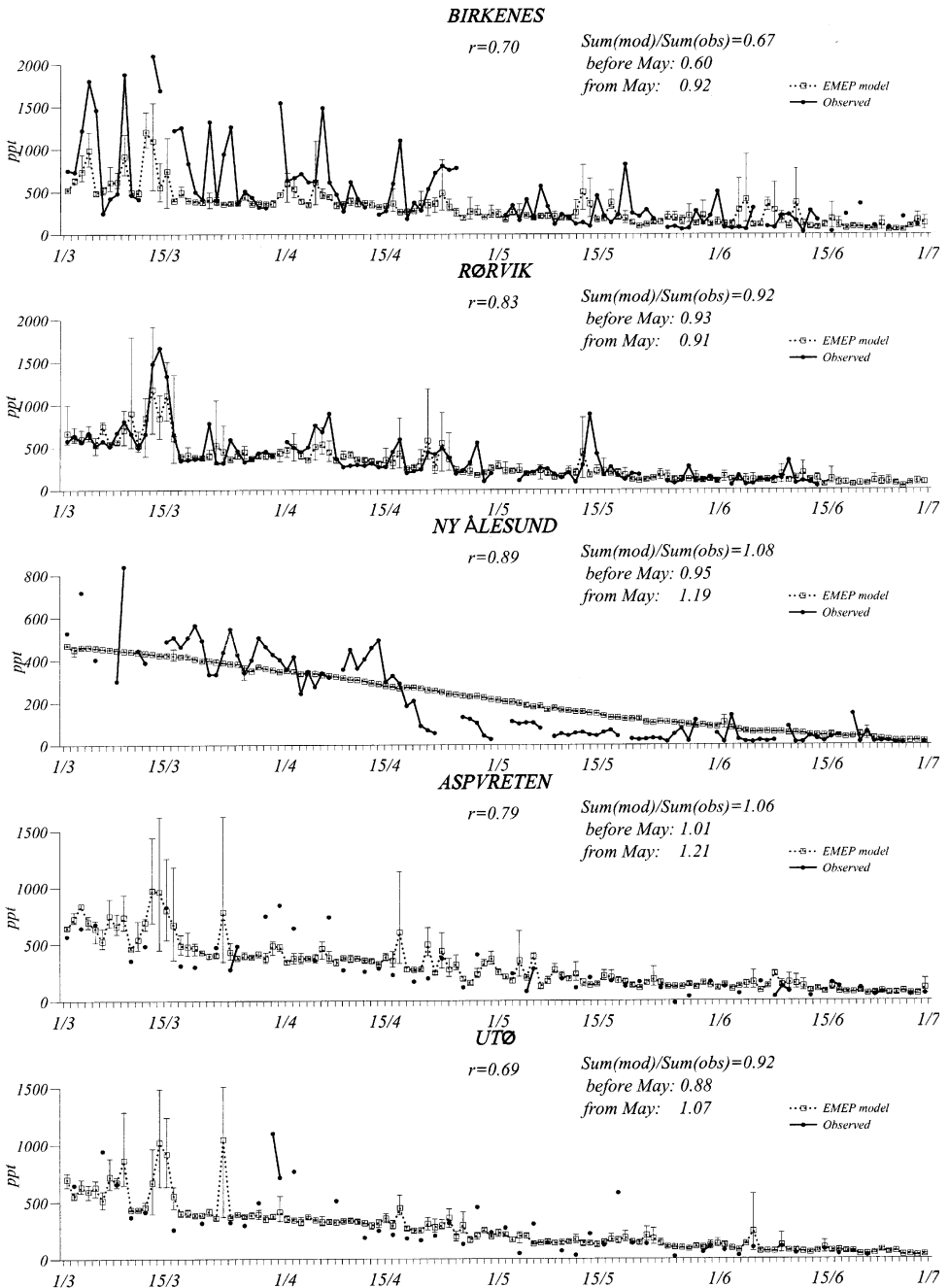


Figure 4. Observed and modelled concentrations for *n*-butane, March–June 1993. The open boxes mark the average of the calculated values, and the error bars mark the highest and lowest of the concentrations calculated each day (for 06, 12 and 18 UTC (also 00 at Rørvik)).

Table III. Modelled and observed concentrations averaged over the days with measurements in ppt (Σ VOC is the sum of observed NMHC at the site in ppbC), the linear correlation coefficient between modelled and measured hydrocarbons and the ratio between modelled and observed concentrations for Birkenes

Species	Birkenes					
	Mod.	Obs.	Corr.	Mod./obs.	Bef. May	From May
Ethane	1901	2103	0.82	0.90	0.86	0.99
Propane	539	784	0.79	0.69	0.68	0.71
<i>n</i> -Butane	325	488	0.70	0.67	0.60	0.92
<i>i</i> -Butane	200	258	0.71	0.77	0.67	1.20
<i>n</i> -Pentane	95	121	0.65	0.79	0.79	0.80
<i>i</i> -Pentane	135	205	0.55	0.66	0.63	0.72
<i>n</i> -Hexane	49	75	0.33	0.65	0.80	0.45
<i>i</i> -Hexane	75	123	0.42	0.61	0.70	0.47
<i>n</i> -Heptane	19	53	0.16	0.37	0.53	0.13
<i>i</i> -Heptane	54	99	0.14	0.54	0.74	0.26
Acetylene	743	692	0.78	1.07	0.99	1.33
Benzene	250	254	0.66	0.98	1.02	0.92
Ethene	329	351	0.41	0.94	1.14	0.55
Toluene	168	277	0.20	0.61	0.85	0.30
<i>o</i> -Xylene	27	31	0.10	0.88	1.21	0.43
Ethyl benzene	24	32	0.31	0.74	0.88	0.50
Propene	35	82	0.12	0.43	0.67	0.16
Σ VOC	15.7	21.8	0.65	0.72	0.76	0.64

For Ny Ålesund the calculated *n*-butane concentration reflects the initial concentration. The fluctuations in the observed concentrations were not reproduced in the calculations even though the correlation is quite high. The correlation and modelled to observed ratio at Rørvik is very good and at this site the underestimation of modelled concentrations during episodes is less pronounced, perhaps due to continuous measurements every four hours so that the average daily measured concentration at this site has less of a noon-time bias which may be present in the measurements of VOC at the other sites.

In Tables III–VII a summary is given of the comparison of measured and calculated VOCs at each site. Compounds with shorter lifetimes than four days (ethene, propene and *o*-xylene) do not compare well. This can in parts be due to the requirements that an accurate calculation of these species put on the accuracy and resolution in time and space of emissions and description of chemical and physical processes, and also other sources than anthropogenic ones can be important in particular for light alkenes (marine emissions, terrestrial emissions). The ratio of modelled to observed concentrations is mostly lower than 1 for the most reactive species. These compounds seem to be even more underestimated during the last months of the measuring campaign than in the beginning. On average for the

Table IV. Modelled and observed concentrations averaged over the days with measurements in ppt (Σ VOC is the sum of observed NMHC at the site in ppbC), the linear correlation coefficient between modelled and measured hydrocarbons and the ratio between modelled and observed concentrations for Ny Ålesund

Species	Ny Ålesund					
	Mod.	Obs.	Corr.	Mod./obs.	Bef. May	From May
Ethane	1715	1818	0.90	0.94	0.91	0.99
Propane	498	575	0.90	0.87	0.80	1.19
<i>n</i> -Butane	218	203	0.89	1.08	0.95	2.06
<i>i</i> -Butane	118	104	0.90	1.13	0.94	3.14
<i>n</i> -Pentane	54	54	0.82	0.99	0.88	1.76
<i>i</i> -Pentane	77	63	0.87	1.23	1.01	3.49
<i>n</i> -hexane	47	61	0.23	0.78	0.88	0.62
<i>i</i> -hexane	57	69	0.38	0.82	0.93	0.63
<i>n</i> -Heptane	32	44	0.64	0.71	0.85	0.47
<i>i</i> -Heptane	61	72	0.64	0.85	0.95	0.65
Ethene	134	125	0.52	1.08	1.57	0.35
Propene	13	67	-0.01	0.20	0.42	0.01
Acetylene	507	438	0.91	1.16	1.07	1.42
Benzene	183	195	0.70	0.94	0.99	0.86
Toluene	132	166	0.27	0.80	0.97	0.50
<i>o</i> -Xylene	8	25	0.56	0.33	0.35	0.24
Σ VOC	11.8	14.1	0.88	0.84	0.86	0.79

Table V. Modelled and observed concentrations averaged over the days with measurements in ppt (Σ VOC is the sum of observed NMHC at the site in ppbC), the linear correlation coefficient between modelled and measured hydrocarbons and the ratio between modelled and observed concentrations for Aspvetren

Species	Aspvetren					
	Mod.	Obs.	Corr.	Mod./obs.	Bef. May	From May
Ethane	1933	1864	0.85	1.04	0.94	1.21
Propane	537	626	0.90	0.86	0.80	1.08
<i>n</i> -Butane	293	277	0.79	1.06	1.01	1.21
<i>n</i> -Pentane	127	109	0.46	1.17	1.19	1.12
Ethene	433	430	0.33	1.01	1.05	0.90
Propene	75	160	0.16	0.47	0.64	0.26
Acetylene	698	533	0.78	1.31	1.16	1.78
Benzene	255	375	0.33	0.68	0.78	0.50
Σ VOC	12.2	14.5	0.74	0.84	0.82	0.88

stations the modelled to observed ethene ratio was 1.26 before May and 0.76 from May, while for propene the values were 0.76 and 0.25. The chemical lifetimes for ethene and propene are very short in the spring and summer (much less than one

Table VI. Modelled and observed concentrations averaged over the days with measurements in ppt (Σ VOC is the sum of observed NMHC at the site in ppbC), the linear correlation coefficient between modelled and measured hydrocarbons and the ratio between modelled and observed concentrations for Utø

Species	Utø					
	Mod.	Obs.	Corr.	Mod./obs.	Bef. May	From May
Ethane	1825	1504	0.77	1.21	1.09	1.42
Propane	531	662	0.82	0.80	0.80	0.81
<i>n</i> -Butane	252	275	0.69	0.92	0.88	1.07
<i>n</i> -Pentane	83	128	0.31	0.65	0.62	0.75
Ethene	215	256	0.21	0.84	0.94	0.65
Propene	14	50	-0.09	0.29	0.48	0.12
Acetylene	642	521	0.68	1.23	1.13	1.49
Σ VOC	9.0	9.4	0.71	0.96	0.90	1.12

Table VII. Modelled and observed concentrations averaged over the days with measurements in ppt (Σ VOC is the sum of observed NMHC at the site in ppbC), the linear correlation coefficient between modelled and measured hydrocarbons and the ratio between modelled and observed concentrations for Rørvik

Species	Rørvik					
	Mod.	Obs.	Corr.	Mod./obs.	Bef. May	From May
Ethane	2055	1888	0.87	1.09	1.03	1.25
Propane	627	865	0.87	0.72	0.73	0.71
<i>n</i> -Butane	343	371	0.83	0.92	0.93	0.91
<i>i</i> -Butane	230	204	0.82	1.13	1.13	1.12
<i>n</i> -Pentane	121	122	0.75	1.00	1.02	0.90
<i>i</i> -Pentane	151	205	0.72	0.74	0.80	0.59
Ethene	475	305	0.71	1.55	1.60	1.35
Propene	69	67	0.43	1.03	1.12	0.71
Acetylene	832	463	0.82	1.80	1.59	2.97
Benzene	276	246	0.80	1.12	1.02	1.66
Toluene	201	168	0.57	1.20	1.36	0.64
Σ VOC	14.7	15.1	0.84	0.97	0.95	1.05

day), which means that the distance between the sources and the receptor sites is only of the order of 100 km. An accurate calculation of ethene and propene therefore depends on an accurate knowledge of the emissions nearby as well as of the subgrid scale dispersion processes. It should be recalled that the measurements are virtually instantaneous.

There is no clear under- or overestimation of any compound with the exception of propane and acetylene which are underestimated by 13–29% and overestimated by 7–80%, respectively, depending on the individual site. The underestimation of

propane is also reported by Solberg *et al.* (1994, 1995) indicating that the emission rates are too low to balance the photochemical loss of this compound.

4.3. SUM OF VOCs

Figure 5 shows the sum of the individual hydrocarbons given in Table I for every site on a C-atom basis. The sums are not directly comparable between the different sites since the set of compounds that was analyzed, is not the same at each site, except for Birkenes and Ny Ålesund where the values can be compared. The modelled sum of VOC given in Figure 5 is the sum of the compounds that were measured at each site. In Figure 6 is shown for each site the calculated sum of the 57 individual VOCs that together made up the composition of the VOC emissions in the model.

The agreement between modelled and observed sums is good, with the highest correlation at Ny Ålesund and Rørvik ($r = 0.88$ and 0.84 , respectively). The model underestimates the sums of the concentrations of VOCs at all sites and on the average by 13%.

At Birkenes the difference between the model results and the observations is mainly due to differences in episodes in the late spring, when the model underestimated the concentrations compared to the measurement. Also at Utø a marked episode in March was not reproduced properly by the model.

We conclude that the correlation and ratio between calculated and measured VOCs indicate that the VOC emission inventory and speciation used for Europe in these calculations seem to be a reasonable estimate of the VOC composition and amount emitted, with an indication that the total anthropogenic VOC emissions are underestimated by 15–20%. Certain episodes are not reproduced by the model however, and in particular these episodes should be investigated further with respect to wind directions to find out more about the most important sources. A more advanced model approach using a Eulerian type model may also provide more accurate determination of the most important terms in the continuity equation for each VOC. It can be recalled that in the calculations, the annual emission figures for VOC are translated into daily (or instantaneous) emission fluxes without taking into account that emission factors may vary with season, day of the week, temperature and other parameters. The only variability included in the calculations is that the daytime VOC emissions (06-18 local time) are 1.5 times the diurnal mean, and the nighttime VOC emissions (18-06 local time) are 0.5 times the diurnal mean. The composition of VOC emissions is also fixed regardless of the grid square of emissions. This is a considerable simplification compared to the real situation where different source categories with quite different speciation characteristics, contribute to the total amount of VOCs in each grid square (see e.g. Henry *et al.*, 1994; Goldan *et al.*, 1995).

The high correlation coefficients at Ny Ålesund indicate that the initial and background values used are quite close to reality and give a good estimate of background levels in the Arctic, but the relatively small variations observed in

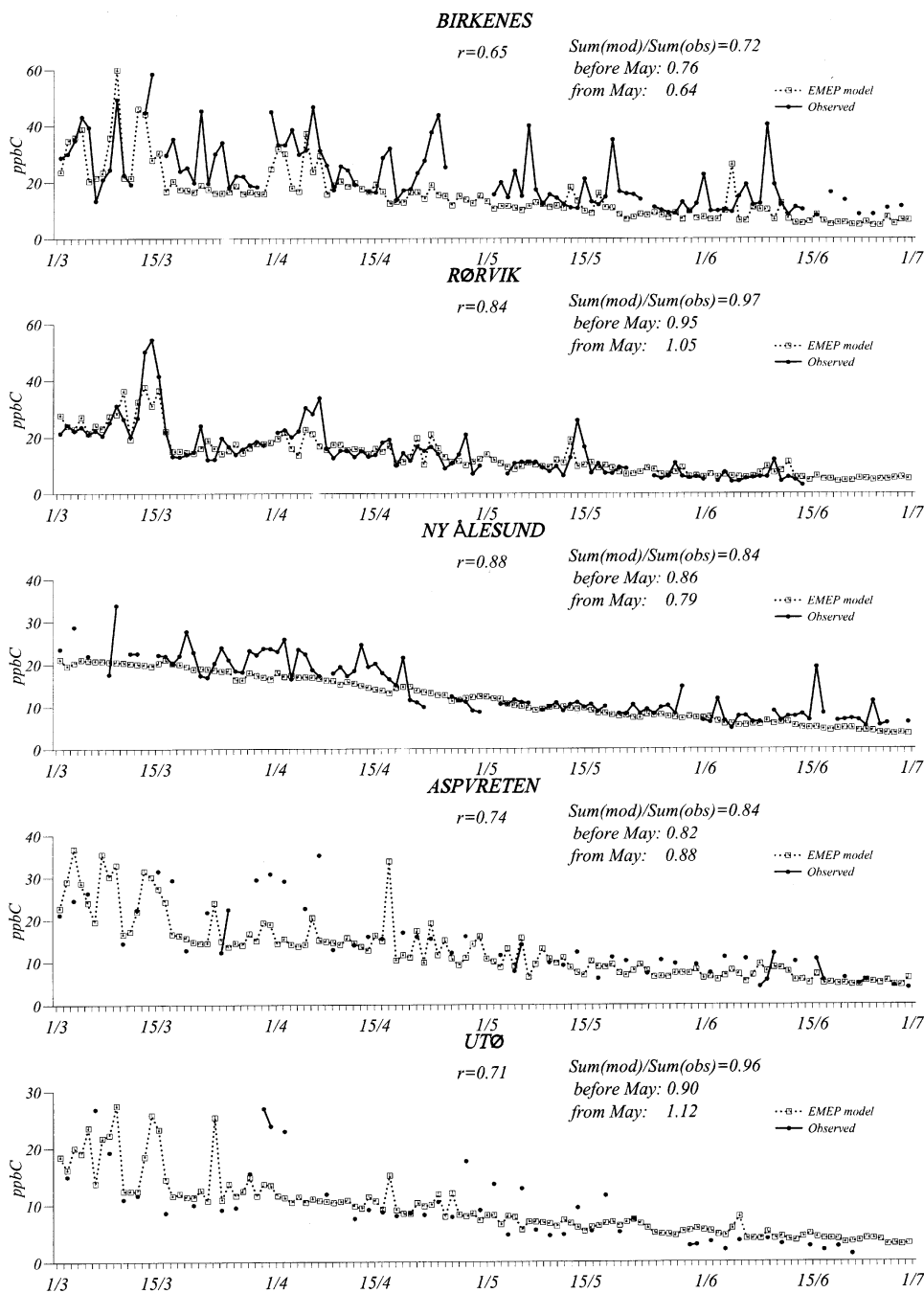


Figure 5. Observed and modelled concentrations for the sum hydrocarbons, March–June 1993. The sums are not directly comparable because the set of compounds which was analysed was different from site to site, except for Birkenes and Ny Ålesund where the same analysis programme was applied.

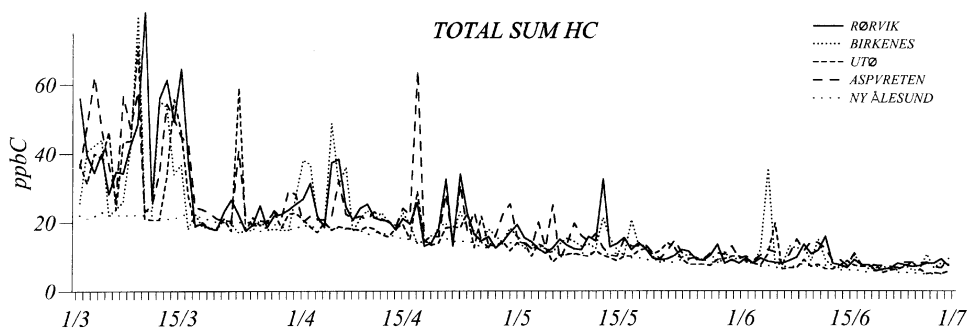


Figure 6. Modelled concentrations of the sum of the 57 individual volatile organic compounds (in ppbC).

the VOC concentrations at Ny Ålesund are not reproduced or seen in the model calculations.

It is seen that there is a stronger reduction in the measured slowly reactive alkanes towards the summer than in the calculated concentrations. This may indicate that there is a seasonal variation in the main sources of these compounds with a lower emission in the summer. On the other hand, aromatics and $> C_5$ alkanes are calculated to decline faster in concentration towards the summer than that shown by the observations. Therefore the mod/obs ratio for Σ VOC before and from May changes less than the mod/obs ratio for most of the individual hydrocarbons. The drop in the mod/obs ratio for $> C_5$ alkanes and aromatics from May is seen at Birkenes and Ny Ålesund, while $> C_5$ compounds were not analysed at Aspvangen or Utø while only toluene and benzene were analysed at Rørvik. The mod/obs ratio for benzene at Rørvik increased towards the summer, while for toluene the ratio changed in the same direction as at Birkenes and Ny Ålesund. It may therefore be concluded that there is a seasonal variability in the $> C_5$ emissions.

The use of spot samples of air in the VOC analysis introduces a bias when compared with calculated concentrations which are averages over several hours. For short sampling times the rate of spread of the emissions is important, while for longer sampling times (e.g. 24 h) the swinging of the trajectories which is due to changes in the large scale, or synoptic, advection dominates. The small scale dispersion of puffs is not resolved in the model calculations, while synoptic scale changes in advection are resolved in the meteorological data used.

If significant sources are located less than 24 hours transport time upwind of a site, concentration in spot samples of air will in general not be comparable to calculated concentrations with the present model resolution in time and space.

5. Conclusion

The high correlation found between measured and calculated concentrations of ethane, propane and acetylene is to a large extent due to the seasonal cycle assumed

for the initial concentrations. The compounds that are best suited for comparison and evaluation of the description of the chemistry and transport in the model are those with lifetimes comparable to the length of the integration (4 days). The model results are quite satisfactory for these. Compounds with shorter lifetimes than four days (ethene, propene and *o*-xylene) do not compare well. The ratio of modelled to observed concentrations is mostly lower than 1 for the reactive species, and these compounds are even more underestimated in the calculations during the last months of the measuring campaign than in the beginning. On average for the stations the modelled to observed ethene ratio was 1.26 before May and 0.76 from May, while for propene the values were 0.76 and 0.25. An accurate calculation of ethene and propene therefore depends on an accurate knowledge of the emissions nearby as well as of the subgrid scale dispersion processes. There is no clear under- or overestimation of any compound with the exception of propane and acetylene which are underestimated by 13–29% and overestimated by 7–80%, respectively, depending on the individual site.

The agreement between modelled and observed sums of VOCs is good, with the highest correlation at Ny Ålesund and Rørvik ($r = 0.88$ and 0.84 , respectively). The model underestimates the sums of the concentrations of VOCs at all sites and on the average by 13%. The correlation and ratio between calculated and measured VOCs indicate that the VOC emission inventory and speciation used for Europe in these calculations are reasonable estimates of the VOC composition and amount emitted, with an indication that the total anthropogenic VOC emissions are underestimated by 15–20%. The study reported here should be extended, however, by including more measurement sites and data from several seasons in order to reduce the uncertainties in the calculations. Also, alternative model interpretation based on Eulerian type models should be carried out to establish the contribution of European emissions, background concentrations and the role of OH, O₃ and NO₃ radical oxidation, to the concentration distribution of each individual hydrocarbon.

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References

- Apel, E. C., Calvert, J. G., and Fehsenfeld, F. C., 1994: The nonmethane hydrocarbon intercomparison experiment (NOMHICE): Task 1 and 2, *J. Geophys. Res.* **99**, 16651–16664.
- Atkinson, R., 1990: Gas phase tropospheric chemistry of organic compounds: A review, *Atmos. Environ.* **24**, 1–41.
- Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Kerr, J. A., and Troe, J., 1992: Evaluated kinetic and photochemical data for atmospheric chemistry, Supplement IV, *J. Phys. Chem. Ref. Data* **21**, 1125–1568.

- Chameides, W. L., Cicerone, R. J., 1978: Effects of nonmethane hydrocarbons in the atmosphere, *J. Geophys. Res.* **83**, 947–952.
- Cvitaš, T. and Kley, D. (eds), 1994: *The TOR Network*, EUROTRAC International Scientific Secretariat, Garmish-Partenkirchen, Germany, 182 p.
- De Saeger, E. and Tsani-Bazaca, E., 1992: *EC Intercomparison of VOC Measurements*, Environmental Institute, Joint Research Center, Ispra, Italy.
- Derwent, R. G. and Jenkin, M. E., 1990: *Hydrocarbon Involvement in Photochemical Ozone Formation in Europe*, AERE R13736, Her Majesty's Stationery Office, London.
- Derwent, R. G. and Jenkin, M. E., 1991: Hydrocarbons and the long range transport of ozone and PAN across Europe, *Atmos. Environ.* **25A**, 1661–1678.
- Eliassen, A., Hov, Ø., Isaksen, I. S. A., Saltbones, J., and Stordal, F., 1982: A Lagrangian long range transport model with atmospheric boundary layer chemistry, *J. Appl. Met.* **21**, 1645–1661.
- Folinsbee, L. J., McDonnell, W. F., and Horstman, D. H., 1988: Pulmonary function and symptom responses after 6.6 hour exposure to 0.12 ppm ozone with moderate exercise, *J. Air Pollut. Control Assoc.* **38**, 28–35.
- Goldan, P. D., Trainer, M., Kuster, W. C., Parrish, D. D., Carpenter, J., Roberts, J. M., Yee, J. E., and Fehsenfeld, F. C., 1995: Measurements of hydrocarbons, oxygenated hydrocarbons, carbon monoxide and nitrogen oxides in an urban basin in Colorado: Implications for emission inventories, *J. Geophys. Res.* **100**, 22771–22784.
- Greenberg, J. P. and Zimmermann, P. R., 1984: Nonmethane hydrocarbons in remote tropical, continental and marine atmospheres, *J. Geophys. Res.* **89**, 4767–4778.
- Hakola, H. S., Joffe, S. M., Lähtilä, H., and Taalas, P., 1991: Transport, formation and sink processes behind surface ozone variability in north European conditions, *Atmos. Environ.* **25A** (8), 1437–1447.
- Hanst, P. L., Spence, W., and Edney, E. O., 1980: Carbon monoxide production in photo-oxidation of organic molecules in the air, *Atmos. Environ.* **14**, 1077–1088.
- Grennfelt, P. and Schjoldager, J., 1984: Photochemical oxidants in the troposphere: A mounting menace, *Ambio* **13**, 61–67.
- Heck, W. W., Taylor, O. C., Adams, R., Bingham, G., Miller, J., Preston, E., and Weinstein, L., 1982: Assessment of crop loss from ozone, *J. Air Pollut. Control Assoc.* **32**, 353–361.
- Henry, R. C., Lewis, C. W., and Collins, J. F., 1994: Vehicle – related hydrocarbon source composition from ambient data: The GRACE/SAFER method, *Environ. Sci. Technol.* **28**, 823–832.
- Hov, Ø., Hesstvedt, E., and Isaksen, I. S. A., 1978: Long range transport of tropospheric ozone, *Nature* **273**, 341–344.
- Hov, Ø., Schmidbauer, N., and Oehme, M., 1989: Light hydrocarbons in the Norwegian Arctic, *Atmos. Environ.* **23**, 2471–2482.
- Hov, Ø., Schmidbauer, N., and Oehme, M., 1991: C₂–C₅ hydrocarbons in rural south Norway, *Atmos. Environ.* **25A**, 1981–1999.
- Hov, Ø. and Schmidbauer, N., 1992: Atmospheric concentrations of nonmethane hydrocarbons at a North European coastal site, *J. Atmos. Chem.* **14**, 515–526.
- Hov, Ø., Flatøy, F., Krognes, T., Schmidbauer, N., Heidam, N. Z., Manscher, O. H., Lähtilä, H., Areskoug, H., Ferm, M., and Lindskog, A., 1997: The relationship between ozone, PAN and precursors in long range transport of photooxidants to Scandinavia, *Atmos. Environ.* (in press).
- Isaksen, I. S. A., Hov, Ø., and Hesstvedt, E., 1978: Ozone generation over rural areas, *Environ. Sci. Technol.* **12**, 1279–1284.
- Isaksen, I. S. A., Hov, Ø., Penkett, S. A., and Semb, A., 1985: Model analyses of measured concentrations of organic gases in the Norwegian Arctic, *J. Atmos. Chem.* **3**, 3–27.
- Isaksen, I. S. A. and Hov, Ø., 1987: Calculations of trends of tropospheric concentrations of O₃, OH, CO, CH₄ and NO_x, *Tellus* **39B**, 271–285.
- Laurila, T., Joffe, S. M., Lähtilä, H., Koskinen, T., and Boij, H., 1992: *Ozone Variability in Northern Maritime Conditions*, EUROTRAC Annual Report 1991, Part 9, TOR, EUROTRAC International Scientific Secretariat, Garmish-Partenkirchen, pp. 54–58.
- Laurila, T., Joffe, S. M., Lähtilä, H., Koskinen, T., Boij, H., and Hakola, H. S., 1993: *Ozone Precursors in Northern Maritime Conditions*, EUROTRAC Annual Report 1992, Part 9, TOR, EUROTRAC International Scientific Secretariat, Garmish-Partenkirchen, pp. 86–89.

- Lindskog, A., 1991: *Results from the IVL TOR Station Rørvik, Sweden*, EUROTRAC Annual Report 1990, Part 9, TOR, EUROTRAC International Scientific Secretariat, Garmish-Partenkirchen, pp. 141–150.
- Lindskog, A., Andersson-Sköld, Y., Grennfelt, P., and Mowrer, J., 1992: Concentration profiles of hydrocarbons during episodes in relation to emission pattern, model calculations and oxidants, *J. Atmos. Chem.* **14**, 425–438.
- Lindskog, A. and Moldanova J., 1994: The influence of the origin, season and time of the day on the distribution of individual NMHC measured at Rørvik, Sweden, *Atmos. Environ.* **28A**, 2383–2398.
- Liu, S. C., Trainer, M., Fehsenfeld, F. C., Parrish, D. D., Williams, E. J., Fahey, D. W., Hübler, G., and Murphy, P. C., 1987: Ozone production in the rural troposphere and implications for regional and global ozone distributions, *J. Geophys. Res.* **92**, 4191–4207.
- Mowrer, J. and Lindskog, A., 1991: Automated unattended sampling and analysis of background levels of C₂-C₅ hydrocarbons, *Atmos. Environ.* **25A**, 1971–1979.
- Oyola, P. and Areskou, H., 1991: *Measurements and Intercalibrations of Ozone and Related Precursors*, EUROTRAC Annual Report 1990, Part 9, TOR, EUROTRAC International Scientific Secretariat, Garmish-Partenkirchen, pp. 141–150.
- Oyola, P. and Areskou, H., 1992: *Measurements and Intercalibrations of Ozone and Related Precursors*, EUROTRAC Annual Report 1991, Part 9, TOR, EUROTRAC International Scientific Secretariat, Garmish-Partenkirchen, pp. 164–170.
- PORG, 1993: In: D. Fowler (ed), *U.K. Photochemical Oxidant Review Group*, U.K. Ministry of Environment, London.
- Schmidbauer, N. and Oehme, M., 1986: Improvement of a cryogenic preconcentration unit for C₂-C₅ hydrocarbons in ambient air at ppt levels, *J. High Res. Chromatogr. Chromatogr. Commun.* **9**, 502–505.
- Simpson, D., 1992: Long period modelling of photochemical oxidants in Europe. Model calculations for July 1985, *Atmos. Environ.* **26**, 1609–1634.
- Simpson, D., 1993: Photochemical oxidant calculations over Europe for two extended summer periods: 1985 and 1989. Model results and comparison with observations, *Atmos. Environ.* **27A**, 921–943.
- Simpson, D., Andersson-Sköld, Y., and Jenkin, M. E., 1993: *Updating the Chemical Scheme for the EMEP MSC-W Oxidant Model: Current Status*, EMEP MSC-W Note 2/93, The Norwegian Meteorological Institute, P.O. Box 43 Blindern, N-0131 Oslo, Norway, 31 p.
- Simpson, D., 1995: Biogenic emissions in Europe. Part II: Implications for ozone control strategies, *J. Geophys. Res.* **100**, 22891–22906.
- Skärby, L. and Selldén, G., 1984: The effects of ozone on crops and forests, *Ambio* **13**, 68–72.
- Solberg, S., Schmidbauer, N., Dye, C., Pedersen, U., and Schaug, J., 1993a: *VOC Measurements August 1992–June 1993*, EMEP/CCC-Report 6/93, Kjeller, Norwegian Institute for Air Research.
- Solberg, S., Stordal, F., Schmidbauer, N., and Hov, Ø., 1993b: *Non-Methane Hydrocarbons (NMHC) at Birkenes in South Norway, 1988–1993*, EMEP/CCC-Report 7/93, Kjeller, Norwegian Institute for Air Research, submitted to *Atmos. Environ.*
- Solberg, S, Dye, C., and Schmidbauer, N., 1994: *VOC Measurements 1993*, EMEP MSC-W Report 3/94, Kjeller, Norwegian Institute for Air Research.
- Solberg, S., Dye, C., Schmidbauer, N., and Simpson, D., 1995: *Evaluation of the VOC Measurement Programme within EMEP*, EMEP MSC-W Report 5/95, Kjeller, Norwegian Institute for Air Research.
- Woodman, J. N. and Cowling, E. B., 1987: Airborne chemicals and forest health, *Environ. Sci. Technol.* **21**, 120–126.