**Atmospheric
Chemistry
and Physics**

In-situ measurement of reactive hydrocarbons at Hohenpeissenberg with comprehensive two-dimensional gas chromatography (GC×GC-FID): use in estimating HO and NO$_3$

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Abstract. During a field campaign at the Meteorological Observatory Hohenpeissenberg (MOHp) in July 2004, volatile organic compounds (VOCs) were measured using comprehensive two-dimensional gas chromatography (GC×GC). Comparison to routinely made gas chromatography mass spectrometry (GC-MS) measurements showed good agreement for a variety of anthropogenic and biogenic ambient VOCs ranging in concentration from below the detection limit (0.1 pmol mol^{-1}) to 180 pmol mol^{-1}. Pronounced diurnal cycles were found for both the biogenic and anthropogenic compounds, driven for the most part by the daily rise and fall of the boundary layer over the station. For the reactive compounds (lifetimes <2 days), a significant, non-zero dependency of the variability on lifetime was found, indicating that chemistry (as opposed to transport alone) was playing a role in determining the ambient VOC concentrations. The relationship was exploited using a single-variate analysis to derive a daytime mean value of HO (5.3±1.4×10^6 molecules cm^{-3}), which compares well to that measured at the site, 3.2±2.3×10^6 molecules cm^{-3}. The analysis was extended to the night time data to estimate concentrations for NO$_3$ (1.47±0.2×10^8 molecules cm^{-3}), which is not measured at the site. The feasibility of this approach for environments dominated by emissions of short-lived VOCs to estimate ambient levels of radical species is discussed.

1 Introduction

Volatile organic compounds (VOCs) play an important role in tropospheric air chemistry and are emitted to the atmosphere from a variety of anthropogenic and biogenic sources (Williams, 2004, and references therein). Some of these compounds can have a direct impact on human health and the environment (Fenger, 1999), while further VOC species can have an indirect impact by undergoing a series of atmospheric oxidation reactions in the presence of NO$_x$ (NO and NO$_2$) to produce O$_3$ which is toxic to both humans and plants (Jacobson, 2002). Removal of VOCs from the atmosphere is mainly initiated by reaction with an HO radical, although reactions with O$_3$ and NO$_3$ may also be significant for certain species under certain conditions. Through oxidation, the VOCs are converted into more polar and hydrophilic forms, which make these photooxidation products more susceptible to wet removal by rain, formation of secondary organic aerosol or dry deposition on surfaces. The combined efficiency of the physical and chemical removal processes define the atmospheric residence time τ, i.e. the time needed for a compound's initial concentration in the atmosphere to be reduced to 1/e times the initial concentration (Finlayson-Pitts and Pitts, 2000).

To investigate the emission, distribution, and oxidation of VOCs in the atmosphere it is essential that accurate measurements of their concentrations are made. In this study we have applied a comprehensive two-dimensional gas chromatography flame ionisation detection (GC×GC-FID) system to determine ambient mixing ratios of VOCs at the Meteorological Observatory Hohenpeissenberg (MOHp), Germany, also member in the Global Atmosphere Watch (GAW) network (http://www.dwd.de/gaw). The relatively new technique of

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GC×GC has been shown previously to provide superior separation power and improved detection limits compared to standard gas chromatographic methods (one-dimensional gas chromatography or GC) in the analysis of complex oil or flavour samples (Beens et al., 2000; Blomberg et al., 1997; Marriott et al., 2000). More recently, GC×GC has also been successfully applied to the analysis of C_5–C_{15} VOCs in air samples (Lewis et al., 2000; Xu et al., 2003a and b). In this study a GC×GC-FID system was operated in parallel with a conventional gas chromatography mass spectrometry (GC-MS) system at Hohenpeissenberg during July 2004, and the results for selected anthropogenic and biogenic VOCs compared. The temporal trends and diurnal cycles of these VOCs will be presented and discussed in terms of sources and local meteorology.

The atmospheric variability of the VOCs measured by the GC×GC system was also examined as a function of their chemical residence time. Many previous studies have demonstrated the utility of this approach in assessing data quality as well as garnering valuable information on VOC sources and sinks (Junge, 1974; Jobson et al., 1998, 1999; Williams et al., 2000). We expect a high variability from species that are most rapidly removed from the atmosphere. In contrast, long-lived species are relatively insensitive to transport time differences between their source and point of measurement, and hence exhibit smaller ranges in measured concentration (i.e. variability). Thus an approximate inverse relationship would be expected between variability and residence time for VOC species, provided the source and sink distributions are similar. It has been found empirically that for studies of VOCs with lifetimes between a few days to a few months, the expression (1) below gives tractable results (Jobson et al., 1998). Here variability is expressed as the standard deviation σ of the natural logarithm of all concentrations X in a dataset i.e. σ ln(X); τ is the chemical lifetime; and A and b empirical fitting parameters.

$$\sigma \ln(X) = A\tau^{-b} \qquad (1)$$

It has been further shown that the exponent b indicates the proximity of the measurement to the source region; b=0 indicates a nearby source and no dependence of variability on chemistry; whereas b=0.5 indicates a remote source, where the variability is significantly influenced by the chemistry. Several groups have used this relationship to derive estimates of the ambient HO radical concentration (Williams et al., 2000, 2001; Karl et al., 2001). Since the HO radical is highly reactive and ambient concentrations are small, (typically of the order of 1×10^6 molecules cm^{-3} or 0.04 pmol mol^{-1}), HO concentrations are difficult to measure. Hohenpeissenberg where the present study was performed is the only station in the world presently measuring HO on a routine basis (e.g. Berresheim et al., 2000; Rohrer and Berresheim, 2006). Although HO concentrations and seasonal dependencies derived through the variability analysis have been shown

to be reasonably accurate (Williams et al., 2000, 2001; Karl et al., 2001), such estimates have never previously been compared with an in-situ measurement. The interpretation of a variability derived HO value is also not easy to comprehend. Previously such HO values have been interpreted as the average HO acting on the air parcel along the back trajectory. However, just how far back along the back trajectory should be considered is not clear since the HO values are derived from VOCs with a wider range of lifetimes and hence regions of influence. To clarify the interpretation and to examine the method we have applied the variability analysis to short-lived compounds (0–2 days), for which the effects of the sources and sinks are local. We then compare the variability derived HO value with the HO measured in-situ. An extension of the method to determine the nocturnal oxidant NO$_3$ is also explored.

2 Experimental

2.1 Site description and meteorology

The field campaign (HOHenpeissenberg Photochemistry EXperiment) was conducted in July 2004 at the Meteorological Observatory Hohenpeissenberg (MOHp), southern Germany (47°48′ N, 11°01′ E). This station is operated by the German Weather Service (Deutscher Wetterdienst, DWD). As part of its Global Atmosphere Watch programme long-term measurements of VOCs (Plass-Dülmer et al., 2002) and HO (Berresheim et al., 2000) are conducted and complemented by campaign studies focussing on particle and oxidant formation processes (e.g. Acker et al., 2006; Handisides et al., 2003; Birmili et al., 2002, 2000). The site is located on a hilltop (elevation of 980 m a.s.l.) in a rural agricultural and forested area, approximately 40 km north of the Alps. It surmounts the adjacent countryside by approximately 300–400 m with the slopes mostly covered by coniferous forest and grassland dominating in the valley below. In the north-to-south foothills the village of Hohenpeissenberg is located with typical country road traffic. The nearest major city is Munich, at a distance of about 70 km to the northeast. Main wind direction was south to southwest.

During HOHPEX, VOC concentrations at the Hohenpeissenberg station were strongly influenced by the diurnal variation in height of the atmospheric boundary layer (BL) and atmospheric turbulence (e.g. Handisides et al., 2003). During the night the boundary layer often formed below the measurement station, isolating the station from nocturnal emissions in the boundary layer and leaving it in the residual layer under the influence of air masses from the previous day (before 10 July and after 17 July). However, on average higher wind speeds during the middle part of the campaign may have prevented the nocturnal inversion layer developing, thus night time VOC mixing ratios were higher and fluctuating (between 11 July and 16 July). After sunrise the BL
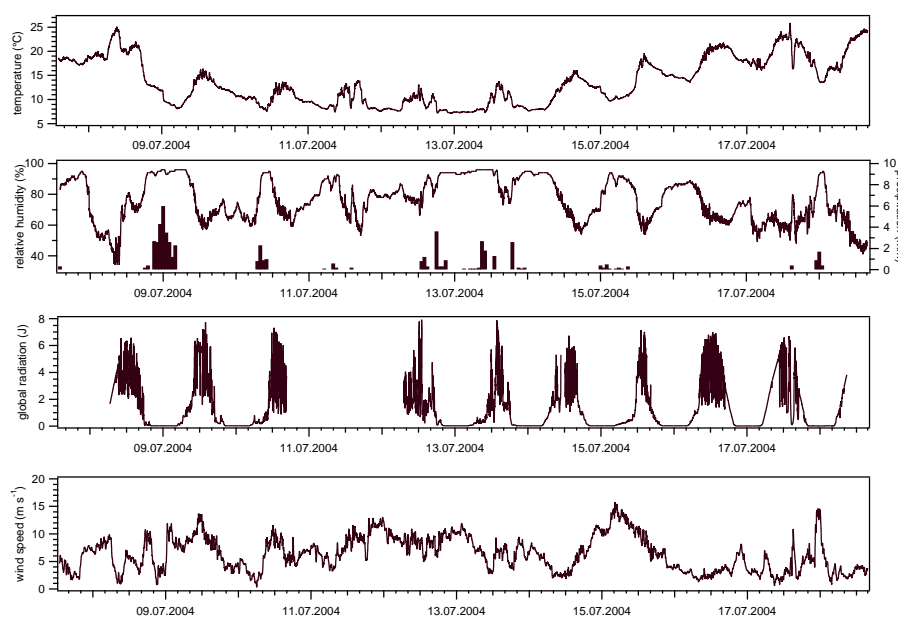
Fig. 1. Selected meteorological parameters for Hohenpeissenberg during the measurement period.

was rising and reached the station at mid-morning hours with significant advection of VOCs from both anthropogenic and biogenic emissions. Between about noon and 16:00 CEST (Central European Summer Time), Hohenpeissenberg was situated in the well-mixed BL, and during this time transport processes played an important role for VOCs measured at the station.

Weather conditions during the campaign ranged from warm and sunny in the beginning to cold and rainy for the main part before reverting to warmer conditions at the end. A selection of meteorological parameters is shown in Fig. 1. The highest temperature measured was around 25°C; the lowest, 7°C, was reached at night during the middle section of the campaign. The cooler days between the 11 and 14 July showed temperatures mostly below 15°C, and the weather was generally foggy, with short rain showers and an overcast sky.

2.2 Gas chromatographic systems

The in-situ GC×GC-FID measurement system used during the campaign includes a gas chromatograph (GC6890, Agilent, Wilmington, USA) equipped with a flame ionisation detector (FID) and a jet-modulator (Zoex, Lincoln, USA); a flow controller and a thermal desorber (Markes Int., Pontyclun, UK). The system has been described in detail elsewhere (Xu et al., 2003b).

In GC×GC, two columns with different selectivity, in this case produced by a non-polar and a polar stationary phase, respectively, are connected in series. The entire sample undergoes separation in both dimensions unlike heartcut-GC, where only parts of the sample are subjected to further sep-

aration on a second column. The sample is separated on the first column based on volatility, small fractions of the effluent are retained in the modulation part at the end of this column. After short periods of accumulation in the modulator, usually a few seconds, the retained effluent is completely transferred to the second column while the original separation is preserved. Following the injection into the second column the compounds are quickly separated based on their polarity and subsequently detected. From this description it is clear that the detector will record a series of high-speed second-column chromatograms with narrow peaks. Fast detectors with high frequency (0.1–1.0 Hz) like the micro electron-capture detector (μ-ECD), time-of-flight-mass spectrometer (ToF-MS) or FID are required for reliable data acquisition. Visualisation of the data is achieved by stacking the short second-dimension chromatograms side by side to form a two-dimensional chromatogram. One dimension represents the retention time on the first column, the other the retention time on the short second column.

Since the invention of GC×GC in the early 1990's, several different types of modulators have been designed. The first modulators successfully applied were dual-stage thermal desorption modulators with a thick-film modulator column coated with a thin conductive metal film. By passing electrical current pulses through this metal film, the retained fraction is heated and injected into the second dimension (Liu and Phillips, 1991; Venkatramani and Phillips, 1993). Another modulator type, termed "Sweeper", consists of a heater element rotating over a small part of thick-film capillary column. While doing this, a hot spot travels along the modulation column, focussing, accelerating and injecting

**Table 1.** Sampling, desorption and analysis data for the GC×GC-FID.

Sampling and desorption		
Sampling	Flow:	50 ml min⁻¹
	Duration:	60 min
	Volume:	3 L
	Cold trap:	25°C trapping,
		Tenax TA/Carbograph I
Desorption	Prepurge:	10 min
	Desorption:	200°C, 5 min
	Flow Path:	140°C
Analysis		
First column	DB-5, 30 m, 0.25 mm I.D., 1 μm film	
	40°C, 100°/min to 50°C, 3°/min to 140°C,	
	2.5°/min to 170°C, 3.5°/min to 200°C	
Second column	BPX-50, 3 m, 0.1 mm I.D., 0.1 μm film	
	30°C, 3°/min to 120°C, 2.5°/min to 150°C,	
	3.5°/min to 180°C	
Analysis time	50 min	
Modulation	5 sec, four-jet system, nitrogen-cooled	

Table 2. Sampling, desorption and analysis data for the GC-MS (MOHp).

Sampling and desorption		
Preconcentration	Flow:	75 ml min⁻¹
	Duration:	20 min
	Volume:	1.5 L
	Cold trap:	Tenax TA/Carboxen
	Temperature:	30°C
	Desorption:	190°C
Refocussing	Cold trap:	FS Capillary (0.25 mm I.D., 20 cm)
	Temperature:	−196°C (liq. N₂)
	Desorption:	180°C
Analysis		
Column	BPX-5, 50 m, 0.22 mm I.D., 1 μm film (SGE, Germany)	
	10°C, hold 10 min, 6°/min to 240°C	
Analysis time	48 min	

the effluent into the second column (Blomberg et al., 1997; Phillips et al., 1999). The most commonly used modulators apply cryogenic means to focus. With the longitudinally modulated cryogenic system (LCMS) approach, a CO₂-cooled trap moves back and forth along the column. The trapped eluent is released by moving the cooling trap away from the cold spot to expose it to the oven temperature (Marriott and Kinghorn, 1997; Kinghorn and Marriott, 1998). During the past few years, efforts have been made to reduce the risk of breaking columns by minimising moving parts. A practical solution is the use of stationary cooling and heating

jets, as was done in this study. The modulator consists of either one pair or two orthogonally to each other fixed pairs of jets. Liquid nitrogen or CO₂ is used as cooling agent. The first cryojet upstream is turned on, trapping the sample eluting from the primary column in its cold spot. When the cold spot is heated up, either by turning off this cryojet or using a hot jet, the focussed sample is released onto the second column. Meanwhile the second cryojet upstream is switched on to prevent interference of the material eluting from the first column with the re-injected fraction. The first cryojet is then switched on again and the next modulation cycle starts
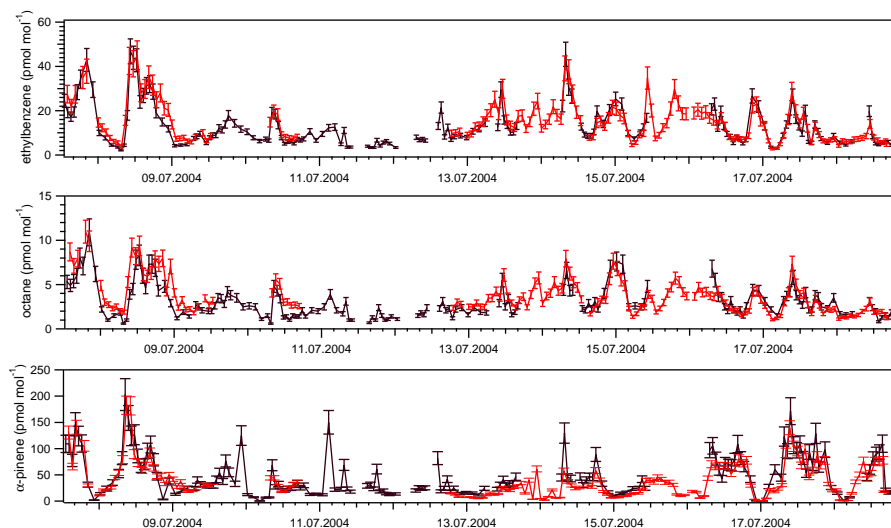
Fig. 2. VOCs measured from 7 to 18 July during HOHPEX. The black line illustrates GC-MS measurements (MOHp), the red line GC×GC-FID (MPI-C). The bars represent the total measurement uncertainty.

(Beens et al., 2001; Ledford and Billesbach, 2000). The latest development made in this area is the single-jet loop modulator where the two-stage modulation is effected by looping a segment of the column or uncoated capillary twice through the path of the jet nozzles (Harynuk and Gorecki, 2003; Ledford et al., 2004). For more details on GC×GC and its applications see Dallüge et al., 2003 or Xu et al., 2003a.

An approximately 15 m long, 12.7 mm diameter Teflon inlet line was attached to a railing on the top of the measurement platform (1000 m a.s.l.). The line itself was shielded from sunlight inside an opaque tube, leading from the platform along the outside wall to the laboratory. The volume flow through the main inlet was set to 3.2 L min^{-1}, resulting in a residence time of circa 20 s. Ambient air was drawn from the fast flow into the cold trap through a 3.2 mm Teflon line at a rate of 50 ml min^{-1} using a membrane pump (KNF Laboport, Germany). The pertinent sampling and analysis parameters are summarised in Table 1. Blanks were conducted by focussing helium 6.0 (Messer-Griesheim, Germany) on the cold trap with the same parameters as shown for ambient air. The adsorbent trap temperature was set to 25°C, as the weather was generally humid throughout the campaign and condensation of water vapour inside the trap had to be strictly avoided. Breakthrough from the sampling trap at such temperatures prohibits measurement of compounds of lower mass than hexane (Markes Ltd. – technical datasheet), therefore this was assumed not to affect measurements of monoterpenes. After the sample was accumulated, the trap was purged with helium for 10 min to remove traces of water vapour, then heated up to 200°C to inject the focussed compounds onto the column. For complete desorption, this temperature was maintained for 5 min. The column set used during the field campaign was a non-polar DB-5 (Agilent, Wald-

bronn, Germany) in the first dimension and a polar BPX-50 (SGE Deutschland, Darmstadt, Germany) in the second dimension. Calibration was achieved based on a 74 compound VOC standard (Apel-Riemer, CT, USA). A similar standard from the same company is routinely used in the Hohenpeissenberg GAW VOC programme. Laboratory multi-point calibrations were accomplished earlier and revealed for all VOCs a good linear dependency of peak area to the respective compound mass. Based on this stability, a one-point calibration of 200 ml standard was carried out every second day throughout the rainy period, whereas the sunny period of four days towards the end of the campaign was only disrupted for blanks. Blanks were taken every third day and showed no high levels for the compounds discussed. Commercially available software for peak detection and integration was found to be slow and unsuitable. An integration procedure was written within IgorPro 4.0 software (WaveMetrics Inc., USA) to calculate the volume of each peak and allow semi-automatic data analysis processing of selected substances.

Continuous daily GC-MS measurements were conducted at the observatory within the GAW programme at 1 h time resolution and 20 min sampling integration. The sampling for the GC-MS measurements of the MOHp was done from a permanently installed 10 m×40 mm I.D. glass tube flushed with ambient air at a rate of 1 m^3 min^{-1}. The sample was accumulated from this glass tube by means of a 1 m, 1/8″ silcosteel tube for 20 min at 75 ml min^{-1}. The sampling and analysis details are given in Table 2. The measurement uncertainties ranged between 6%–10% for the GC×GC-FID and between 11%–34% for the GC-MS. The limits of detection ranged from 0.1 pmol mol^{-1} to 2.8 pmol mol^{-1} for the GC×GC-FID and 0.5 and 2.6 pmol mol^{-1} for the GC-MS.

Table 3. Correlation parameters slope and coefficient of variation (r^2) of VOCs measured by GC-MS and GC×GC-FID.

VOC	slope	r^2
Hexane	1.09±0.05	0.69
Heptane	1.28±0.05	0.77
Octane	1.10±0.06	0.69
Nonane	1.97±0.10	0.41
Ethylbenzene	1.08±0.04	0.86
o-Xylene	1.62±0.07	0.72
p/m-Xylene	1.10±0.03	0.85
α-Pinene	0.87±0.02	0.83
β-Pinene	0.96±0.02	0.74
3-Carene	0.73±0.02	0.77
Camphene	0.69±0.03	0.81
Eucalyptol	1.20±0.11	0.88

The atmospheric HO was measured using the selected ion/chemical ionisation mass spectrometer (SI/CIMS) described by Berresheim et al. (2000). O$_3$ was determined with a UV absorption instrument (Thermo Env., USA).

3 Results

3.1 Comparison of GC×GC-FID and GC-MS measurements

During the campaign, from 7 July to 18 July 2004, the GC×GC-FID measurements were intercompared with the concurrent GC-MS measurements. A total of 162 and 130 measurements were made with the GC-MS and the GC×GC-FID, respectively. Included in the comparison were the anthropogenic compounds hexane, heptane, octane, nonane, ethylbenzene, the co-eluting p-/m-xylene and o-xylene as well as the biogenic compounds α- and β-pinene, 3-carene, camphene and eucalyptol. Figure 2 shows a time series of ethylbenzene, octane and α-pinene for both instruments (red points GC×GC-FID and black points GC-MS). The markers represent the middle of the sampling time, the upper and lower bars the total measurement uncertainty for the depicted VOC.

Generally there was good agreement between measured VOC concentrations. Slight differences could be attributed to the different sampling periods of the two instruments: the GC-MS sampled for 20 min, while air was collected for 60 min in the GC×GC-FID system. There is generally good agreement for the reactive biogenic VOC measurements (see e.g. α-pinene), although no O$_3$ scrubber was applied for GC×GC sampling but a Na$_2$S$_2$O$_3$ impregnated filter was used in the GC-MS sampling line. According to a study, the sampling of reactive terpenes on Tenax in presence of O$_3$ leads to losses if no O$_3$ scrubber is used (Calogirou et

al., 1996). However, the terpenes discussed here are only slightly or not at all affected, although it should be noted that the most reactive terpenes towards O$_3$, e.g. terpinolene are not included.

The data from both systems were correlated using orthogonal distance regression (ODR) instead of the standard linear regression (SLR). With this method, all data points are assumed to have an equal weight and the orthogonal distance between the fitted line and the individual data points is minimised, whereas in the SLR only the distance in y-direction is optimised. Good correlations were found for the examined compounds, with the exception of nonane which was caused by low concentrations close to the detection limit, see Table 3.

3.2 Diel cycles

Average diel cycles of the GC×GC-FID measured VOCs α-pinene and sabinene (biogenic); and octane and ethylbenzene (anthropogenic), are shown in Fig. 3. The black line illustrates the hourly mean mixing ratio, the lower and upper bars represent the minimum and maximum measured values respectively, and the dotted line the median value. The effects of the diurnally changing boundary layer height described in Sect. 2.1 can be observed in the mean values for all measured VOCs in the late morning around 09:00 CEST, when the ascending BL reaches the station. In the night, the usually low BL and the stations' isolation from the ground based sources leads to lower mean VOC levels.
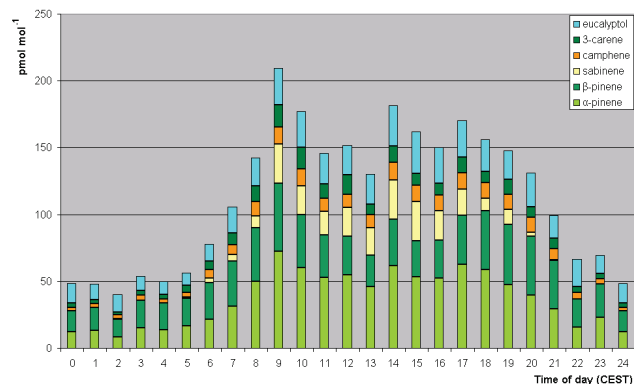
Biogenically emitted compounds followed a diurnal profile similar to that of α-pinene. The mixing ratios for all biogenic VOCs measured with GC×GC-FID are shown in Fig. 4. For biogenic species the mean mixing ratios increased slowly after sunrise, and abruptly as the BL reached the elevation of the site. An additional maximum around 14:00 CEST was also observed for α- and β-pinene later in the afternoon, whereas the other measured terpenes remain at a constant high level or decrease slowly. Different from the other monoterpenes shown, sabinene concentrations are close to zero at night. The diurnal cycles are driven by the dependence of the emission on insolation and temperature. With mostly mixed spruce forest surrounding the station, the most abundant biogenic compounds were α- and β-pinene. These VOCs, along with camphene and 3-carene, are known to be emitted by spruce trees (Street et al., 1996; Fulton et al., 1998). Continuous elevated mixing ratios for these terpenes have been detected on some of the cooler nights, indicating a constant release from the storage pools in the needles (Fuentes et al., 2000) although α-pinene seems to have a larger diurnal dependence than β-pinene, with significantly higher mixing ratios during daytime. In contrast, sabinene has been reported to be mainly emitted by beech and other deciduous trees (Tollsten et al., 1996). At Hohenpeissenberg, sabinene is almost only observed during daytime, suggesting that the emission was strongly light dependent. This
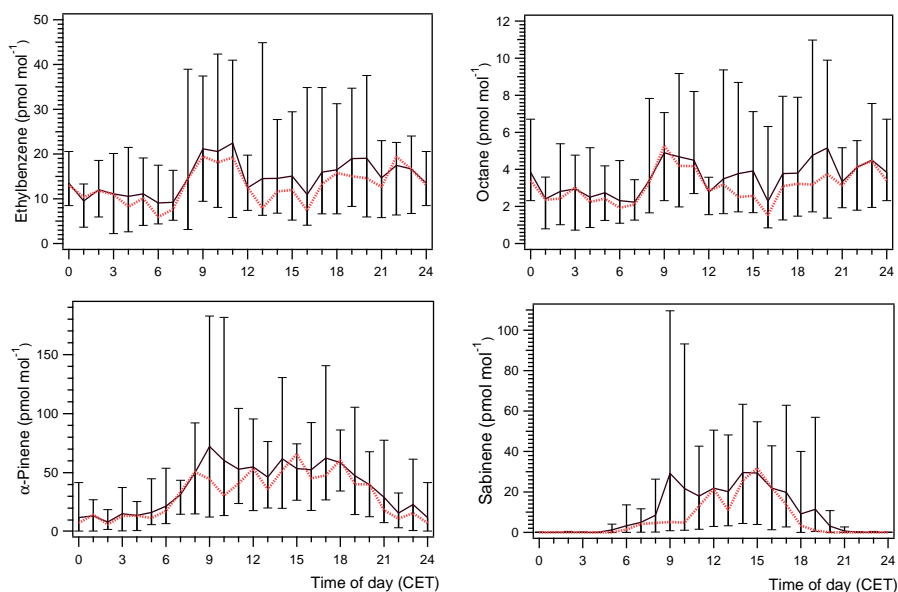
Fig. 3. Hourly averaged diurnal cycles of the VOCs ethylbenzene, octane, α-pinene, and sabinene as measured by GC×GC-FID. The black line shows mean values, upper and lower bars the maximum and minimum measured value, the red dotted line shows the median value. All times are CEST (GMT+2 h).

phenomenon has been observed in earlier studies (Staudt et al., 1997; Bertin et al., 1997) and was also reported for beech and birch leaves, where emission in the dark gradually decreased for all measured monoterpenes at a constant temperature (Hakola et al., 2001). Eucalyptol also makes up a significant proportion of the total monoterpenes (Plass-Dülmer and Berresheim[1]). Previous studies have indicated that it is emitted from various plants such as rape, birch, spruce, hornbeam and grassland (König et al., 1995; Hakola et al., 2003; Kirstine et al., 1998). The emission from grassland is reported to be particularly strong at elevated temperatures and after mowing (König et al., 1995). Short-term increases in mixing ratios for all monoterpenes have been detected occasionally during the night, mainly in the cold, windy and rainy phase of the field campaign. This indicates a turbulent atmosphere without the development of the nocturnal inversion, thus no decoupling between the boundary layer and the measurement point occurred and the station was still influenced by emissions at ground level or aged residual layer air through vertical and horizontal transport processes. Additionally, relative humidity and rainfall can exert positive influence on the emission of monoterpenes from pine trees (Schade et al., 1999), a further study proposed a connection between contact stimulation and stronger emission of terpenes in Japanese cypresses (Yatagai et al., 1995). Both hypotheses might also be relevant for nocturnal emissions originating from the mixed spruce forest around the Hohen-
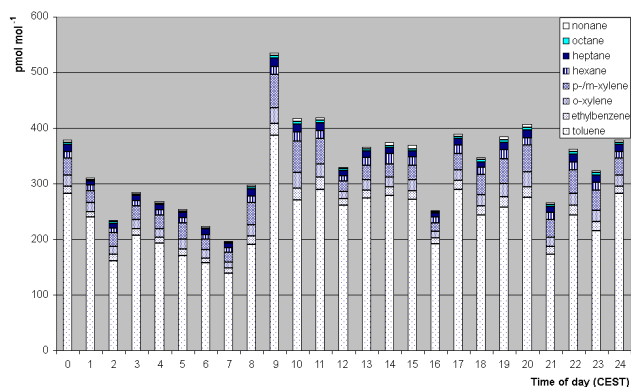

Fig. 4. Sum and contribution of the measured biogenic VOCs to the diurnal biogenic concentrations.

peissenberg, as the observed wind speed during these nights was mostly higher than $8\,\mathrm{m\,s^{-1}}$, the humidity was very high and precipitation occurred frequently.

The anthropogenic compounds show a slightly different diurnal cycle to the biogenic VOCs, the sum and the fractional contributions are shown in Fig. 5. Main sources for these species can be found in automobile exhaust, gasoline evaporation or solvents. Just as the biogenic compounds, the mean atmospheric mixing ratios for anthropogenic VOCs also peak between 09:00 and 10:00 CEST (with the arrival of the boundary layer at the site), but remain approximately constant at this level until around noon, when the boundary layer is well-mixed. The fluctuating course of the mixing

[1]Plass-Dülmer, C. and Berresheim, H.: On-line GC measurements of atmospheric monoterpenes at the Global Atmosphere Watch observatory Hohenpeissenberg, in preparation, 2006.

Fig. 5. Sum and contribution of the measured alkanes and aromatics to the diurnal anthropogenic concentrations.

Fig. 6. Logarithmic graph showing the variability of measured short-lived VOCs. The black line is a fit through all VOCs, the dotted line with biogenically emitted compounds only. Assumed concentration for HO is 1.7×10^6 molecules cm^{-3} (0.071 pmol mol^{-1}) and for O$_3$ 1.0×10^{12} molecules cm^{-3} (42.0 nmol mol^{-1}).

ratios throughout the rest of the day is probably driven by variations in anthropogenic emissions and/or a changing fetch area. The development of a shallow nocturnal BL between 22:00 and 01:00 CEST was accompanied by an almost steady or decreasing level of anthropogenic VOCs during the night, until the BL ascended over the station again the following morning. Like for the biogenic VOCs, fluctuating anthropogenic nighttime mixing ratios were occasionally measured (13 to 16 July, see Fig. 2), when the nocturnal BL did not develop as a result of the turbulent atmosphere.

3.3 Lifetime-variability dependence of VOCs

In Sects. 2.1 and 3.2 we have shown that in addition to synoptic scale horizontal air mass advection the Hohenpeissenberg site was influenced by diurnal changes in boundary layer height with local air influence prevailing by day and aged local air by night. Since the biogenic compounds are emitted from the nearby forest and the sources for the anthropogenic VOCs are also close, we can expect a weak or negligible influence of chemistry on the variability-lifetime relationship. The atmospheric lifetimes of the VOCs during daytime are mainly dependent on HO and O$_3$. Both of these species were measured at Hohenpeissenberg and the mean values $(1.7\times10^6$ molecules cm^{-3} (0.071 pmol mol^{-1}) HO and 1.0×10^{12} molecules cm^{-3} (42.0 nmol mol^{-1}) O$_3$ were taken for the plot shown in Fig. 6. These averages were determined over the period when all three instruments were operating, from 7 July to 16 July (Table 4).

The variability of the measured species was obtained according to Jobson et al. (1998), as described in Sect. 1. A relatively high variability can be observed in all biogenic compounds, particularly sabinene (see Fig. 6). The higher variability for sabinene as compared to the other terpenes is possibly caused by it being predominately emitted from deciduous trees (e.g. beech) which exhibit mostly light-dependent emission (Tollsten et al., 1996), in contrast to the conifers which generally emit as a function of temperature and light
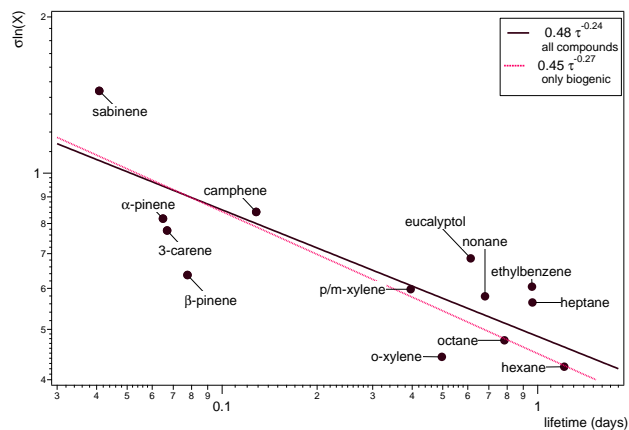
(Street et al., 1996; Fulton et al., 1998). However, both tree types are found mixed throughout the Hohenpeissenberg forest, therefore we assume that the source location and distribution of all terpenes is sufficiently similar to permit the variability analysis. Moreover in the subsequent more detailed variability analysis we segregate the data into day (high temperature and light) and night (low temperature and no light) to minimise any effect of different source terms as well as of different radical chemistry on the analysis. It is also interesting to note that eucalyptol and β-pinene exhibit approximately the same variability although they have longer lifetimes than the other terpenes analysed, especially at night. Eucalyptol appears to be more variable than expected, possibly indicating an additional sink. Since eucalyptol contains an oxygen atom and is therefore more polar than the other monoterpenes, one may speculate that wet removal or deposition of this compound has occurred. The anthropogenic species, which in this case have relatively long lifetimes, show less variability in their measured concentration. The lifetimes were calculated using the reaction rate coefficients from Atkinson (1997), Atkinson et al. (1986, 1990), Corchnoy and Aktinson (1990) and the average measured O$_3$ and HO concentration, the data was fitted to the previously described function $\sigma\ln(X){=}A\tau^{-b}$. The coefficients derived for all compounds are $A{=}0.48{\pm}0.06$ and $b{=}0.24{\pm}0.06$. If only the biogenically emitted compounds are considered, $A{=}0.45{\pm}0.24$, and $b{=}0.27{\pm}0.20$. For only the biogenic VOCs reacting rapidly with both O$_3$ and HO (lifetime $<$6 h), b increases to $0.75{\pm}0.33$.

Interestingly, the exponent $b{=}0.24$ for all VOCs indicates that there is a significant, non-zero dependency of the variability on lifetime for these species at the measurement site, and therefore that chemistry (as opposed to transport alone)

Table 4. Comparison of measured and calculated mean HO at the mean O$_3$ concentration. Period 1 represents the measurements between 7 July and 16 July 2004, when both GC×GC-FID and the HO instrument were operating. Period 1a represents the whole time period of the GC×GC-FID measurements (7 July to 18 July 2004).

|	avg. O$_3$ measured (x 10^{12} molec cm^{-3})	avg. HO measured (x 10^6 molec cm^{-3})	avg. HO calculated (x 10^6 molec cm^{-3})	
			anthropogenic and biogenic VOCs	Short-lived biogenic VOCs
Day and night				
Period 1	1.0	1.7±2.2	1.07±0.1	2.9±1.2
Period 1a	1.0		0.64±0.1	1.96±0.7
Day (10:00–19:30 CEST)				
Period 1	1.0	3.2±2.3	–	5.3±1.4
Period 1a	1.1		0.92±0.1	4.6±1.2

is playing some role in determining the ambient concentrations. At first this result may seem surprising as previous studies have shown that sources of alkane emissions near to a point of measurement tend to generate variability in a dataset that is not connected with chemistry and hence reduce the coefficient b ($b \approx 0$) (Jobson et al., 1998). In the case of Hohenpeissenberg the site is surrounded by mixed forest (the source of the biogenic compounds) on all sides. A low value ($b=0.18$) was found for a VOC dataset, albeit with somewhat longer lifetimes ranging from 1 to 500 days, taken over Harvard forest (Jobson et al., 1999). We interpret this finding as showing that the species measured in the present study are sufficiently reactive to be oxidised on such short temporal and spatial scales that a significant variability-lifetime relationship can develop.

The measured HO and O$_3$, and the derived NO$_3$ can also be used to obtain variability-lifetime plots for the dataset separated into day and night. During the day we obtained for the complete dataset the coefficients $A=0.48\pm0.1$ and $b=0.14\pm0.07$; if the dataset is split into anthropogenic and biogenic compounds the coefficients $A=0.46\pm0.12$, $b=0.20\pm0.17$, and $A=0.25\pm0.27$, $b=0.33\pm0.31$, respectively, are obtained. During the night we get for all compounds the coefficients $A=0.73\pm0.03$ and $b=0.099\pm0.01$. The anthropogenic amount to $A=0.77\pm0.43$ and $b=0.11\pm0.23$, the biogenic VOCs to $A=0.66\pm0.04$ and $b=0.13\pm0.02$. By night the b factor is significantly less, in particular when only biogenic species are considered. We attribute this to weaker chemical processing by night.

3.4 Estimation of HO radical concentrations

As described previously, VOCs can be removed from the atmosphere by HO, NO$_3$ and O$_3$. Several studies have demonstrated that when a significant variability-lifetime relationship exists for a suite of VOCs, it can be used to estimate the HO radical concentration in the atmosphere (e.g. Jobson et al., 1999; Williams et al., 2000; Karl et al., 2001). The general principle is: if measured VOCs react with more than one oxidant (e.g. HO and O$_3$) and the atmospheric concentration of either one is known (e.g. O$_3$), it is possible to estimate the concentrations of the other reactant(s), assuming that all reaction rates are known. From the Hohenpeissenberg data set both HO and O$_3$ measurements are available presenting the unique opportunity to test this approach in a rural continental environment. Assuming the level of one oxidant (here O$_3$) is known, its concentration is kept constant while that of the "unknown" oxidant species (here HO) is varied. The distribution of the data points on the variability-lifetime plot thus varies as a function of the assumed HO radical concentration and fits with varying degrees are obtained. The goodness of a fit is expressed by the χ^2 (chi squared) value, which evaluates the correlation of the least squares fit and indicates the discrepancy between the fitting function and the data. A lower χ^2 indicates a better fit to the data. The assumed concentration of the oxidant that gives the best fit to the data is interpreted as the average concentration of the oxidant that has affected the airmass. The standard deviation of the gradient b (Eq. 1) is then used to express the uncertainty in the HO estimate. To illustrate the method, Fig. 7 shows the variability-lifetime relationship for the measured VOCs in the presence of different atmospheric HO concentrations and the measured average O$_3$. Open circles show the atmospheric lifetime at 1.0×10^6 molecules cm^{-3} (0.04 pmol mol^{-1}) HO, the red line is the respective fit, and open triangles show the atmospheric lifetime in presence of 1.5×10^6 molecules cm^{-3} (0.06 pmol mol^{-1}) HO, the black dotted line the respective fit and open squares with the green dashed line the fit in presence of 2.0×10^6 molecules cm^{-3}
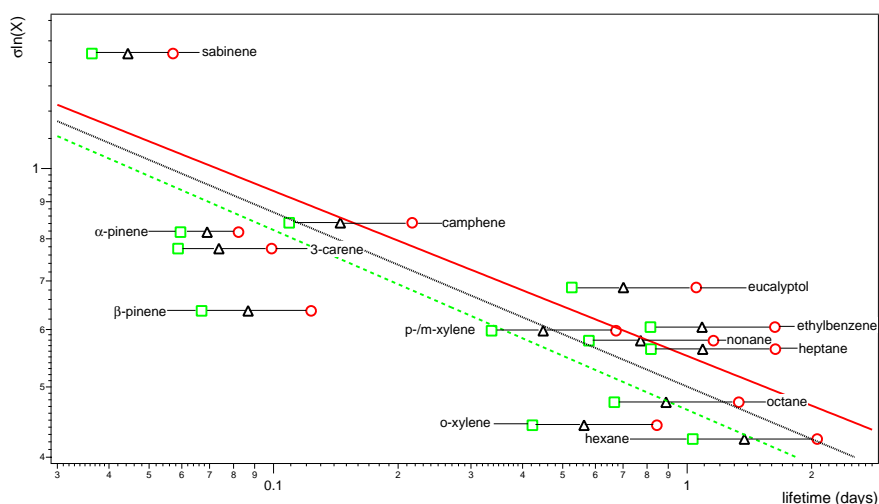
Fig. 7. Logarithmic graph illustrating the procedure to estimate the HO concentration. The open red circles show the compounds in presence of the measured O$_3$ (1.0×10^{12} molecules cm^{-3}, 42.0 nmol mol^{-1}) and 1.0×10^6 molecules cm^{-3} (0.04 pmol mol^{-1}) HO, the red line is the fit. The black open triangles and the black dotted line show the compounds and the fit in presence of 1.5×10^6 molecules cm^{-3} (0.06 pmol mol^{-1}) HO. The green open squares with the green dashed line show the compounds in presence of 2.0×10^6 molecules cm^{-3} (0.08 pmol mol^{-1}) HO.

(0.06 pmol mol^{-1}) HO. Each fitting procedure results in a value for χ^2, the HO concentration resulting in the lowest χ^2 is the optimum concentration.

This method was applied here first to all VOCs anthropogenic and biogenic, and in a second step to the short-lived VOCs, since both have shown a significant variability-lifetime dependence, despite being close to the sources. An advantage of using short-lived species is that the HO calculated should be comparable to the in-situ HO measurements made during the HOHPEX field campaign. This is because the radical chemistry that gives rise to the variability-lifetime dependency must be occurring locally. To investigate this further, two strategies were tested. First the O$_3$ concentration was kept constant at the daytime average of 1.0×10^{12} molecules cm^{-3} (42.0 nmol mol^{-1}) and the HO concentration was varied. This simulates the common situation where O$_3$ is measured but HO is not. Secondly we varied O$_3$ and HO simultaneously to determine whether the VOC variability-lifetime relationship yields reasonable values for both oxidants without assuming a measured value.

To calculate the daytime OH mixing ratio with a minimised influence of changes in the boundary layer height, the dataset was divided according to time in two sections (10:00 and 19:30 CEST day; 22:00 and 05:30 CEST night). For comparison it should also be recalled that when both GC×GC-FID and the HO instrument were operational, the average measured daytime HO was found to be $3.2\pm2.3\times10^6$ molecules cm^{-3} (0.13±0.097 pmol mol^{-1}). When O$_3$ is held at the average daytime mixing ratio and only HO is varied, for all the measured biogenic and anthropogenic VOCs no best fit (i.e lowest χ^2) can

be calculated, see Table 4. However, if only the highly reactive biogenic VOCs with similar sources, i.e. the forest surrounding the station, and atmospheric lifetimes lower than 6 h are considered, the calculated average daytime HO concentration is $5.3\pm1.4\times10^6$ HO molecules cm^{-3} (0.22±0.06 pmol mol^{-1}), which is at the upper limit of the HO actually measured. This shows the analysis to be highly sensitive to which species are used in the fitting procedure. In particular, VOC species emitted by the same spatial and temporal source pattern must be used. However, there remain some uncertainties since the fit results strongly depend on the sabinene data point, which, as outlined above, originates from deciduous trees with potentially a different source-variability (light dependent) as compared to the other terpenes analysed here, which originate from coniferous trees (light and temperature dependent). Sabinene is the most variable of the monoterpenes measured, an observation which is consistent with its reaction rate with OH, O$_3$, and NO$_3$. Both sabinene and camphene exert important influences on the regression. We note that the analysis of the short lived biogenic compounds (excluding camphene) results in a derived HO of 1.6×10^6 molecules cm^{-3} which is close to the average measured value 1.7×10^6 molecules cm^{-3}. However if sabinene is excluded no significant slope can be generated. It is not possible to determine from this dataset whether such effects are attributable to 1) different source characteristics for certain terpenes, 2) erroneous rate coefficients with O$_3$, HO or NO$_3$, or 3) some form of measurement artefact. It is therefore prudent to include as many terpene compounds as possible with a wide reactivity spectrum in future studies of this kind. The calculated average HO concentration for the
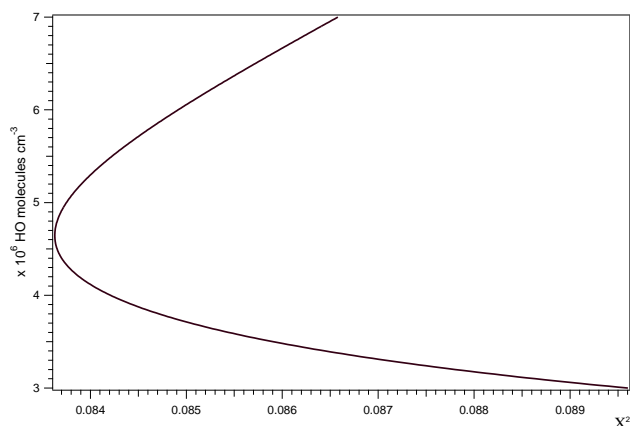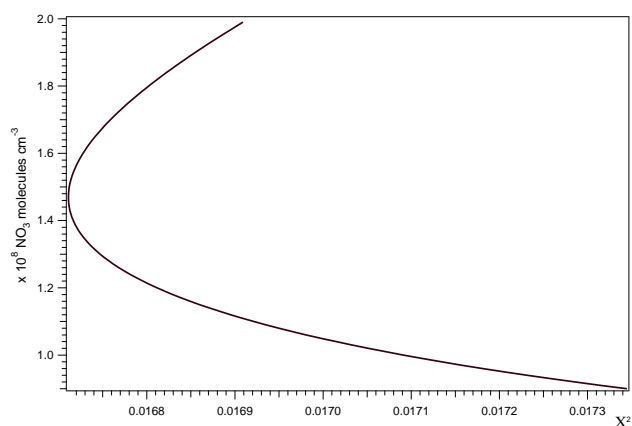
Fig. 8a. Variation of the HO concentration versus χ^2 or the diurnal short-lived biogenic GC×GC-FID data. At the measured mean O$_3$, the calculated HO is $4.6\pm1.2\times10^6$ molecules cm^{-3} (0.19 ± 0.05 pmol mol^{-1}).

Fig. 8b. Variation of the NO$_3$ concentration versus χ^2 or the nocturnal GC×GC-FID short-lived biogenic data. At the measured mean O$_3$, the calculated NO$_3$ is $1.47\pm0.2\times10^8$ molecules cm^{-3} (6.2 ± 0.8 pmol mol^{-1}).

whole diurnal GC×GC biogenic VOC dataset, which, unlike the HO instrument, was also operating during rainy periods, yields an average of $4.6\pm1.2\times10^6$ HO molecules cm^{-3} (0.19 ± 0.05 pmol mol^{-1}), see Fig. 8a. Table 4 additionally shows the results for the average day and night HO concentration as calculated from all VOCs and the short-lived biogenic VOCs, respectively. During the period in which both HO instrument and GC×GC-FID measured, $1.07\pm0.1\times10^6$ HO molecules cm^{-3} (0.05 ± 0.004 pmol mol^{-1}) were obtained for all compounds and $2.9\pm1.2\times10^6$ HO molecules cm^{-3} (0.12 ± 0.05 pmol mol^{-1}) for the biogenic VOCs only. The actually measured average HO amounted to $1.7\pm2.2\times10^6$ HO molecules cm^{-3} (0.07 ± 0.09 pmol mol^{-1}). For the period in which only the GC×GC was in operation, the average HO concentration was calculated to be $0.64\pm0.1\times10^6$ HO molecules cm^{-3} (0.03 ± 0.004 pmol mol^{-1}) for all VOCs and $1.96\pm0.7\times10^6$ HO molecules cm^{-3} (0.08 ± 0.03 pmol mol^{-1}) for only the biogenic compounds.

For the simultaneous variation of both O$_3$ and HO no distinct O$_3$/HO optimum was obtained for the biogenic dataset, instead a ridge of "best guess" HO values for each O$_3$ concentration is generated. The HO concentration based on the measured O$_3$ with $\pm1\sigma$ uncertainty ($1.0\pm0.2\times10^{12}$ molecules cm^{-3}, 42.0 ± 8.4 nmol mol^{-1}) was between 4.1 ± 1.6 and $6.5\pm2.6\times10^6$ molecules cm^{-3} (0.17 to 0.27 pmol mol^{-1}).

From the in-situ measurements at MOHp, an average daytime HO concentration of $3.2\pm2.3\times10^6$ molecules cm^{-3} (0.13 ± 0.1 pmol mol^{-1}) was obtained, whereas for the HO estimated from the combined biogenic and anthropogenic VOCs no concentration could be calculated. This is very likely caused by the differences in sources for the individual species (which generate variability unrelated to chemistry) as

well as the low reactivity of O$_3$ with the anthropogenic VOCs as compared to the biogenic (Ehhalt et al., 1998). To obtain an estimate for the local concentration of an oxidant, compounds should be selected which are emitted from similar source types and have generally short atmospheric lifetimes, but a sufficient span of reactivity to define the variability-lifetime plot. We should consider, however, the possibility that the agreement found between measured and estimated HO could be coincidental. This would mean that the variability of the selected terpenes is driven by processes other than HO (i.e. source variability or distribution) and the constellation of variabilities fortunately co-incides with the measured HO when this method is applied. To test this requires further studies, ideally where high time resolution measurements of terpenes and HO are made over large homogeneous tracts of vegetation. Large areas of monocultures such as the vast oil palm plantations of Malaysia would be one possibility as these would emit the same species in the same source profile. Another interesting possibility would be the tropical rainforest, if large areas are covered with airborne measurements. A future possibility to achieve atmospheric monoterpene measurements at high frequency could be the Proton-Transfer Reaction-TOFMS (PTR-TOFMS) instrumentation, provided the monoterpenes can be specifically fragmented and hence identified. However, to date the reported detection limits of this system (ppb level) are unsuitable for such remote measurements (Blake et al., 2004; Inomata et al., 2006).

3.5 Estimation of NO$_3$ radical concentrations

By day VOC oxidation proceeds mainly through reaction of HO and O$_3$. However, by night NO$_3$ and O$_3$ are understood to be the most important oxidising species since the main source of HO, photolysis, becomes negligible. Unlike

HO, NO$_3$ was not measured at Hohenpeissenberg, therefore it is particularly interesting to use the VOC data to extract an estimate of the NO$_3$ concentration. To investigate the levels of NO$_3$, the variability analysis was applied as before but on the night time data only (from 22:00 to 05:30 CEST). Alas, for this dataset no optimum was found when either O$_3$ was fixed at the measured value or when both O$_3$ and NO$_3$ were varied simultaneously. On the other hand, when an HO value was specified (as measured) and the O$_3$ and NO$_3$ radical values varied, a χ^2 surface could be generated with a maximum for the different O$_3$ concentrations, but, as with the O$_3$/HO calculation, without a distinct O$_3$/NO$_3$ maximum. Taking the biogenic data only (since the station was mostly cut off from anthropogenic sources by night) and adopting the average measured O$_3$ and HO value by night (1.0×10^{12} molecules cm^{-3} and 0.1×10^{6} molecules cm^{-3}, respectively) we find a calculated NO$_3$ value of $1.47 \pm 1.0 \times 10^{8}$ molecules cm^{-3} (6.2 ± 4.2 pmol mol^{-1}), see Fig. 8b.

A recent study of Handisides et al. (2003) during HOPE2000 considered the production and loss rates of NO$_3$ and assumed an average nocturnal NO$_3$ concentration of 6 pmol mol^{-1} at Hohenpeissenberg. This value and the value derived in the work presented here is also in general agreement with measurements conducted in the continental boundary layer near Berlin, Germany, which revealed a nocturnal average of 4.6 pmol mol^{-1} (Geyer et al., 2001).

4 Conclusions

During the field campaign HOHPEX at the Meteorological Observatory Hohenpeissenberg (MOHp) in July 2004, anthropogenic and biogenic VOCs were successfully measured using GC×GC-FID. Comparison to routinely conducted GC-MS measurements at MOHp during the same period showed that good agreement was obtained for a variety of ambient VOCs ranging in concentration from zero to 180 pmol mol^{-1}.

Pronounced diel cycles were found for both the biogenic and anthropogenic compounds, driven for the most part by the daily rise and fall of the boundary layer over the station. The mixing ratios of the biogenic species (e.g α- and β-pinene, sabinene, 3-carene, camphene and eucalyptol) were strongly influenced by emissions from the forest in the vicinity of the station. In agreement with previous studies, cool and cloudy days showed generally less terpene emission than warm and sunny days. Diel cycles for the anthropogenic (aromatic and aliphatic) compounds were also found, but with different characteristics to those of the biogenic species. The highest mixing ratios for all VOCs were measured in the morning when the boundary layer rose over the station.

The variability-lifetime relationship of the short-lived VOCs has been examined for the first time. The weak but significant b dependence of the measured compounds

showed that although the VOC sources are relatively close, chemistry was playing a significant role in determining their concentration. The relationship was exploited to estimate the atmospheric mean HO concentration from the GC×GC-FID VOC measurements for comparison with measured HO. The mean daytime HO concentration thus derived is $5.3 \pm 1.4 \times 10^{6}$ molecules cm^{-3} (0.22 ± 0.06 pmol mol^{-1}), slightly higher compared to the mean HO measured at MOHp. No distinct optimum for HO and O$_3$ are found when both O$_3$ and HO are co-varied to estimate oxidant levels. By extending the analysis to the night time data, the mean NO$_3$ radical concentration is estimated to be $1.47 \pm 0.2 \times 10^{8}$ molecules cm^{-3} (6.2 ± 0.8 pmol mol^{-1}). This appears to represent the limit of what can be extracted from this dataset with its limited temporal resolution and suite of compounds. However, this study indicates the potential to determine the ambient radical concentrations of HO and NO$_3$ by analysing measured VOC mixing ratios at rural sites surrounded by homogeneous vegetation and unaffected by major pollution. This possibility should be further explored in future studies including fast reacting biogenic species and in-situ HO measurements over a large scale homogeneous ecosystem. Particularly suitable in this regard would be monoterpene measurements over a tropical rainforest.

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