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# Variability-lifetime relationship of VOCs observed at the Sonnblick Observatory 1999—estimation of HO-densities

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## Abstract

An extensive dataset of VOC measurements was collected at the Sonnblick Observatory, Austria (3106 m) in Fall/Winter 1999/2000, showing high mixing ratios of anthropogenic and biogenic VOCs at this high altitude site due to upward mixing of air masses (Geophys. Res. Lett. 2F (2001) 507). Here we give an interpretation of proton-transfer-reaction (PTR-MS) mass scans obtained in November 1999 based on fragmentation data, GC-PTR-MS analysis and the variability-lifetime relationship, described by the power law,  $\sigma(\ln(x)) = A\tau^{-b}$ . The variability-lifetime plot of anthropogenic VOCs gave a proportionality factor  $A$  of 1.40 and  $a, b$  exponent (sink term) of 0.44 and allowed an estimate of average HO-densities on the order of  $(1.5 \pm 0.4) \times 10^5$  molecules  $\text{cm}^{-3}$ . Additionally we were able to indirectly determine a diurnal HO-profile with peak values of  $(1.3 \pm 0.5) \times 10^6$  molecules  $\text{cm}^{-3}$  around midday. HO-reaction rate coefficients for higher aldehydes (heptanal to nonanal) were estimated due to photochemical losses during a stagnant air episode (27 November) and from the variability-lifetime relationship. Combining long term PTR-MS analysis of VOCs and the variability-lifetime method provides a valuable tool for assessing the dominant cause of the variability in VOC concentrations. This information is essential in understanding the sources and photochemical processing of VOCs detected in ambient air at field measurement sites. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

We have recently observed high anthropogenic and biogenic VOC mixing ratios at the Sonnblick Observatory (3106 m) situated on the main ridge of the Alps (Karl et al., 2001). A proton-transfer-reaction mass spectrometer (PTR-MS) system continuously monitored

VOC concentrations from mid-October 1999 until March 2000. The experiment showed a big variation of VOC mixing ratios resulting from various different meteorological situations (Karl et al., 2001). Part of the biogenic VOC mixture came from senescing and freezing vegetation after the first hard freeze in November 1999 (Fall et al., 2001). These VOCs were occasionally transported to the Sonnblick due to upward mixing. Vertical transport processes of this type are well known in the Alps (Prévôt et al., 2000; Wotawa et al., 2000). Thus such a high altitude site, mostly located in the free troposphere, helps to assess the influence of biogenic

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<sup>1</sup>This paper is dedicated to the memory of Werner Lindinger.

VOCs in the late season. In addition these measurements would allow determination of VOC patterns over substantial regions of the European Alps as a result of long range transport of VOCs.

VOC measurements at the Sonnblick not only allowed analysis of VOC sources, but provided a unique opportunity to determine photochemistry of VOCs in the free troposphere. This was possible because a strong inversion layer prohibited upward mixing during late November 1999 and cut off all major source contributions from the lower troposphere and polluted boundary layer. These circumstances designated the sampling site for monitoring photochemical loss processes.

According to Junge's relationship (1974) the reactivity of species, which can be considered to be in steady state with respect to global production and loss terms, inversely affects their variability, and thus the standard deviation of their mixing ratios. He formulated an inverse relationship between this standard deviation and atmospheric lifetime. This empirical formula was primarily related to long-lived species with lifetimes in the order of years. Only recently a similar approach for short-lived compounds, which are not in steady state, such as alkanes, alkenes and aromatics, was applied by Jobson et al. (1999). The authors proposed a variability-lifetime relationship according to theoretical considerations of Jaenicke (1982) and Slinn (1988) in the form:

$$\sigma(\ln(x)) = A\tau^{-b}, \quad (1)$$

where  $\sigma(\ln(x))$  is the relative standard deviation of the natural logarithm of mixing ratios,  $\tau$  is the atmospheric lifetime and  $A$  and  $b$  are empirical fitting parameters.

Jobson et al. (1998) applied this approach to hydrocarbon datasets obtained at various sampling locations including the NARE 1993 dataset. They observed that for remote areas (no significant influence by nearby sources) (1) should give a reasonable linear fit with  $b$  exponents in the range of 0.28–0.56. Ehhalt et al. (1998) presented three-dimensional tracer model studies and found a similar relationship. Their model results predicted much weaker lifetime dependence than Junge's inverse relationship and showed a smaller exponent for continental areas varying with geographical location. They also pointed out that by knowing a lifetime—rate constant relationship it is possible to estimate HO-densities from experimental VOC data sets.

Variability-lifetime plots can be used for checking data set quality and give an estimate on the remoteness of the sampling location (Jobson et al., 1994, 1998, 1999). In addition Williams et al. (2000) showed that relation (1) can also be used to estimate average HO-densities along the back trajectory. VOC measurements obtained on research flights during LBA-Claire (Crutzen et al., 2000) were subjected to a variability treatment,

from which Williams et al. (2000) estimated average HO-densities in the range of  $2 \times 10^5$  molecules  $\text{cm}^{-3}$ .

Here, we report the results of variability-lifetime analysis of the Sonnblick VOC data set for November 1999. This analysis and complementary data contribute to an understanding of the sources and photochemical processing of VOCs detected in ambient air at this remote site.

## 2. Experimental

For monitoring air masses surrounding this high altitude site we used a conventional PTR-MS system, which is described in detail elsewhere (Lindinger et al., 1998; www.ptrms.com). The system was housed in the main building at the top of the Sonnblick Observatory (3106 m, 47.05°N, 12.3°E). The inlet of the mass spectrometer was an 1/8" Teflon tube (flow rate ca. 16 STP  $\text{cm}^3 \text{min}^{-1}$ ) bypassed by a 3 m line (i.d. 1/8") taking in outside air at a flow rate of 300 STP  $\text{cm}^3 \text{min}^{-1}$ . The instrument was operated in a selective ion mode including only a few masses until 11 November 1999 at which time additional masses such as 83, 85, 107 (xylenes, ethylbenzene), 121 ( $\text{C}_9$  benzenes) and 135 ( $\text{C}_{10}$  benzenes) were added; a full mass scan mode was applied from 26 November on. Concentrations of VOCs were calculated as described in Lindinger et al. (1998). On occasions cartridge samples of ambient air were taken and analyzed by GC-PTR-MS (Fall et al., 2001; Karl et al., 2001). Several GC runs showed for example that acetone and methyl ethyl ketone (MEK) contributed to most of the signal observed on masses  $59^+$  and  $73^+$ , respectively. In many cases the proton-transfer reactions are nondissociative (Lindinger et al., 1998), however in the present case, where emissions of various  $n$ -aldehydes, pentenol, hexenal and hexenol family compounds were investigated, dissociation can occur during the proton transfer. Using standard compounds that were available commercially, we examined the fragmentation patterns of each under PTR-MS conditions that were identical to that used in leaf wound volatile analysis (Fall et al., 1999).

The assignments of the protonated ions  $83^+$ ,  $97^+$ ,  $101^+$ ,  $111^+$ ,  $115^+$ ,  $125^+$ ,  $129^+$  and  $143^+$  to  $n$ -aldehydes come from several arguments. Isotopic ratios ( $\text{C}^{13}/\text{C}^{12}$ ) suggest  $\text{C}_6$ ,  $\text{C}_7$ ,  $\text{C}_8$  and  $\text{C}_9$ -compounds on masses  $101^+$ ,  $115^+$ ,  $129^+$  and  $143^+$ , respectively; these masses correspond to the empirical formulas,  $\text{C}_6\text{H}_{12}\text{O}$ ,  $\text{C}_7\text{H}_{14}\text{O}$ ,  $\text{C}_8\text{H}_{16}\text{O}$  and  $\text{C}_9\text{H}_{18}\text{O}$ . The dominant correlation between  $97^+$  and  $115^+$ ,  $111^+$  and  $129^+$  and  $125^+$  and  $143^+$ , each separated by 18 amu, clearly shows that these pairs represent fragment and parent ions. Comparison of the observed to the measured fragmentation of heptanal, octanal and nonanal standards showed very similar breakup patterns. As long as one

distinct ion (such as the parent ion) can be identified it is possible to reconstruct the original concentration and iteratively subtract interfering fragments appearing at lower masses. It is well known that protonated aldehydes tend to dehydrate more than ketones and less than alcohols. Thus under certain circumstances like those described here it is possible to distinguish different carboxyls using the PTR-MS technique (Lindinger et al., 1998). We were also able to identify major VOCs in a GC-cartridge filled on 26 November. In this cartridge hexanal was the major compound contributing to mass  $83^+$  (Karl et al., 2001; Fall et al., 2001).

The origin of these normal-chain aldehydes (*n*-aldehydes) in ambient air is uncertain. Several investigators have detected a series of *n*-aldehydes in air at remote and rural sites (Yokouchi et al., 1990; Ciccioli et al., 1993; McClenny et al., 1998; Wedel et al., 1998), and suggest that they are derived from biogenic sources. Some of these aldehydes may be artifacts of analysis, arising from reactions of organics with ozone in the sampling stream (Pires and Carvalho, 1998), or from organic aerosols collected during sampling VOCs (Greenberg et al., 1996). Whether biogenic *n*-aldehydes are directly released from vegetation, or are derived from the oxidative breakdown of leaf materials is still somewhat uncertain (Possanzini et al., 2000). Small amounts of *n*-aldehydes have been observed to be released from a variety of plant species (König et al., 1995; Kirstine et al., 1998); the *n*-hexanal detected in these experiments is most likely derived from leaf linoleic acid peroxidation as reviewed by Hatanaka (1993). Since VOC analysis with PTR-MS does not require any presampling or trapping procedures and the residence time of air in sampling lines is usually on the order of a few seconds, it is highly unlikely that the *n*-aldehydes observed here are due to artifacts.

The sensitivity of the PTR-MS instrument during this study was typically on the order of 50 Hz/ppbv (counts per second per ppbv) for acetone and 35 Hz/ppbv for methanol at 2.3 mbar buffer gas pressure with a reaction time of 110  $\mu$ s and 2 MHz  $H_3O^+$  ions. The detection limit was around 10 pptv for a 10 s integration time with a signal/noise ratio of 40%. At 100 pptv the signal/noise ratio with a 10 s integration time was 14%. The lowest observed ambient concentrations for most compounds were above the detection limit. A fraction of the toluene (17%) and of the  $C_8$ -benzenes (14%) data were below 20 pptv close to their detection limit and were discarded. All biogenic VOCs present in concentrations above 30 pptv were included in the variability analysis. The obtained dataset was filtered with a SYMLET 4 level 3 wavelet (linear phase filter), which basically removed the frequency part mostly associated with the instrument's noise. This denoising method left the low frequency variation unchanged and assured that the observed standard deviation was mainly caused by atmospheric

variability. Reference measurements were taken through a catalytic converter (platinum wool at 430°C). It is noted that the variability—lifetime approach is not sensitive to background issues, since the standard deviation of a constant is zero. The sampling rate (5–10 s integration time per mass) was around 2 min in the selective ion mode and 11 min in the scan mode (up to 145 amu).

Meteorological data and various other atmospheric measurements were available from continuous measurements being made at the Sonnblick station. Back trajectories for the mean model topography (2250 m) surrounding the Sonnblick station (3106 m) and for 700 hPa (3106 m) were calculated from the global ECMWF model with analysis data of wind, temperature and geopotential height.

### 3. Results

#### 3.1. Meteorology and VOC measurements

The last week of November 1999 was dominated by a high pressure region above central Europe. This synoptic pattern was also reflected in the backward trajectories calculated for the mean model topography height of 2250 m from 25 to 30 November at 12.00 UTC and shown in Fig. 1. As a consequence, late November was characterized by strong inversion layers with temperatures on top of the Sonnblick (3106 m a.s.l.) around freezing and in the nearby valleys (ca. 1000 m a.s.l.) between 0°C at noon and –12°C during the night. Local wind systems over complex terrain, such as mountain, valley and slope winds, which are usually superimposed on the large-scale synoptic wind field (Doran et al., 1990; Prévôt et al., 2000), can cause distinct diurnal patterns even at high altitude sites. Dominant diurnal variations of both anthropogenic and biogenic VOCs were seen from the beginning of November until 25 November (Karl et al., 2001). The meteorological situation from 25 November on changed significantly, since inversion layers between 1700 and 2200 m prohibited upward mixing of polluted boundary layer air. The height of the mixed layer is in most cases coupled to the height of the valley wind system; thus with inversion layers typically above the tree line (1800–2000 m), slope and valley winds could not transport local biogenic VOCs up to 3100 m from 25 November on. VOCs originating from the lower troposphere were thus isolated from their sources and subjected to photochemical destruction and losses due to mixing.

An estimate of the average photochemical age of anthropogenic pollutants was obtained by assuming that both benzene and toluene are mainly removed by HO-radicals. As long as no additional traffic emissions are admixed, the [toluene]/[benzene] ratio in air changes as a

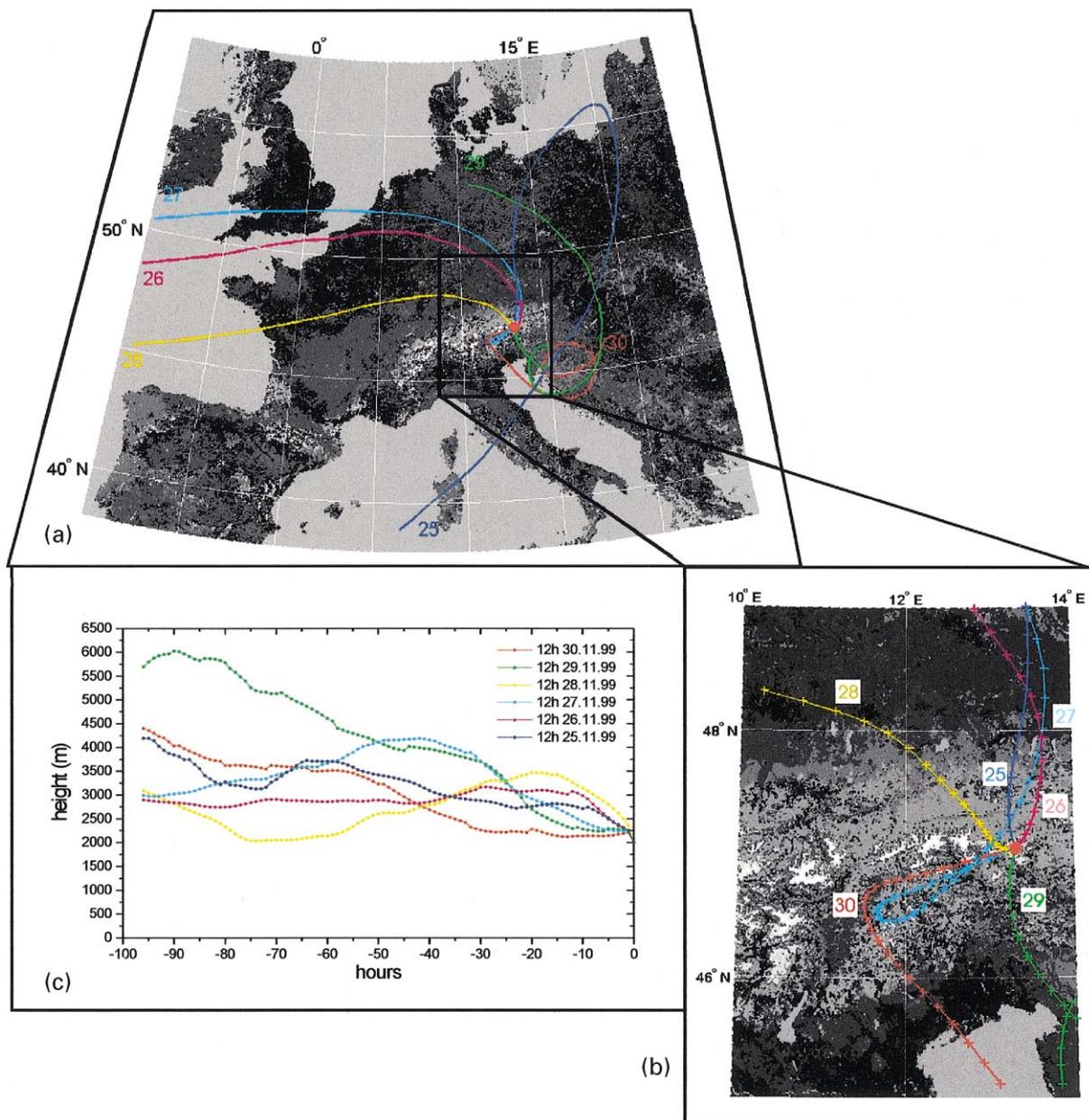


Fig. 1. (a) Backward trajectories for the mean model topography from 25 to 30 November at 1200 UTC; (b) zoomed frame: each cross represents a 1 h step back; (c) meteorological height section along back trajectories.

function of time due to the different reaction rate coefficients of benzene and toluene with HO radicals (Volz-Thomas and Kolahgar, 2000). Volz-Thomas and Kolahgar (2000) reported an initial [toluene]/[benzene] fraction of 2.0 for the European continent. Taking reaction rate coefficients with HO for toluene ( $6.64 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ) and benzene ( $1.16 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ) (Atkinson et al., 1997) and an average HO-density of

$1.5 \times 10^5 \text{ molecules cm}^{-3}$  as obtained in this work for November 1999, we estimated the average photochemical age of anthropogenic pollutants around  $(18 \pm 5)$  days. These observations suggest that older, anthropogenically-polluted boundary layer air parcels were mixed together with air containing reactive biogenic VOCs when passing over large forested areas surrounding the Sonnblick. Until 25 November these air masses

were transported up to the station mostly following the diurnal variation of the slope wind system. Only on one occasion, 11 November, anthropogenic pollutants were transported up to the Sonnblick by the large scale synoptic pattern (Karl et al., 2001), that caused a rapid increase of the concentration of these pollutants over a two day period with [toluene]/[benzene] ratios around 1.8 close to the original emitted fraction of  $\sim 2.0$  (Volz-Thomas and Kolahgar, 2000).

The back trajectory on 27 November (Fig. 1(b)) is consistent with meteorological observations on the Sonnblick showing very little horizontal movement of air masses at the top level with winds of  $1\text{--}5\text{ m s}^{-1}$  from varying directions. Concentrations of reactive VOCs on that day rapidly decreased during daytime (9:00–15:00). The quantile plots (Fig. 2) show a significant concentration shift for these compounds. Longer-lived species such as methanol, acetaldehyde, acetonitrile and benzene on the other hand did not show such drastic changes in their ambient concentrations (Fig 2). The interquartile ranges normalized to mean concentrations (rel iqr) for methanol, acetonitrile, acetaldehyde and benzene for example were 16%, 9%, 2% and 7%, respectively. Ozone concentrations were constant around 50 ppbv (rel iqr = 5%). Thus the sharp decline of reactive VOC concentrations (30–50%) on 27 November cannot be explained by losses mainly due to mixing. Taking these observations, we conclude that neither a stratospheric intrusion with enhanced ozone and reduced VOC concentrations nor local transport of air masses from low elevations with reduced ozone and elevated VOC concentrations influenced the chemical composition of air masses circling around the station on 27 November. The variability lifetime relationship allowed us to assess the influence of photochemistry directly during the last week of November 1999.

### 3.2. Variability-lifetime analysis

Jobson et al. (1999) described several important features of the variability-lifetime concept. Here, we will briefly summarize the basic relations involved and explore some of the resulting implications by using the VOC dataset collected between 25 and 30 November 1999. The standard deviation of the natural logarithm of the concentration  $x$  is defined as

$$\sigma(\ln(x)) = \sqrt{\frac{\sum_n \ln(x)^2 - 1/n (\sum_n \ln(x))^2}{n-1}}. \quad (2)$$

If two species ( $x_i$ ,  $x_j$ ) with common sources and sinks can be related by

$$\ln(x_i) = c + m \ln(x_j), \quad (3)$$

one can derive the direct relationship between  $\sigma(\ln(x_{i,j}))$  and the ratio of atmospheric lifetimes by

combining (1)–(3):

$$\begin{aligned} \sigma(\ln(x_i)) &= m \sigma(\ln(x_j)) = \left(\frac{\tau_j}{\tau_i}\right)^b \sigma(\ln(x_j)) \\ &\xrightarrow{k=1/\tau} \left(\frac{k_i}{k_j}\right)^b \sigma(\ln(x_j)) \xrightarrow{b=1} \left(\frac{k_i}{k_j}\right) \sigma(\ln(x_j)). \end{aligned} \quad (4)$$

The basic underlying principle of the variability-lifetime relation implies that investigated VOCs have common sources and are therefore removed from the same air mass. The  $b$  factor basically describes the influence of the source contribution. Thus, when sampling close to a source,  $b$  will approach zero and the variability lifetime relation will be 'weaker'. In the extreme case of  $b = 0$  the variability will not depend on the atmospheric lifetime anymore, but will reflect the variability of the emission source. On the other hand the more distant to potential sources the higher the  $b$  factor will be. In remote areas  $b$  will approach 1. Stratospheric data for several halogens for example have shown a  $b$  factor approaching one (Jobson et al., 1999). In the case where  $b$  is close to one, the observed variability will mainly depend on atmospheric lifetimes.

Under the assumption that the observed VOCs have common sources, a consistent variability trend can be used to check atmospheric lifetimes. By knowing the removal rate (e.g. reaction rate with HO) of two compounds, it is in principle possible to estimate the reaction rate of a third compound. The variability—lifetime relation can therefore be used to estimate atmospheric losses of VOCs and obtain reaction rates with HO. In the next sections, we use the variability approach to estimate HO radicals based on the observed anthropogenic trend, show that losses of reactive VOCs on 27 November were mostly due to photochemistry and estimate reaction rates with HO radicals for some short-lived biogenic compounds.

### 3.3. Anthropogenic VOC trends and HO density estimate

The variability trend can also be used to estimate radical densities, which has been demonstrated by Jobson et al. (1999) and Williams et al. (2000). In order to estimate radical densities Williams et al. (2000) considered the reaction with HO radicals and photolysis. The photolysis rates of acetone and MEK constrained the linear trend in the variability plot. It should be noted that the variability-lifetime approach for deriving HO-densities implies that no significant photochemical sources in the atmosphere contribute to the variability of each compound. However for acetone, butanone, and especially the sum of methacrolein (MAC) plus methyl vinyl ketone (MVK), potential sources in the atmosphere can not be excluded a priori. Photochemical production reduces the effective loss rate of these

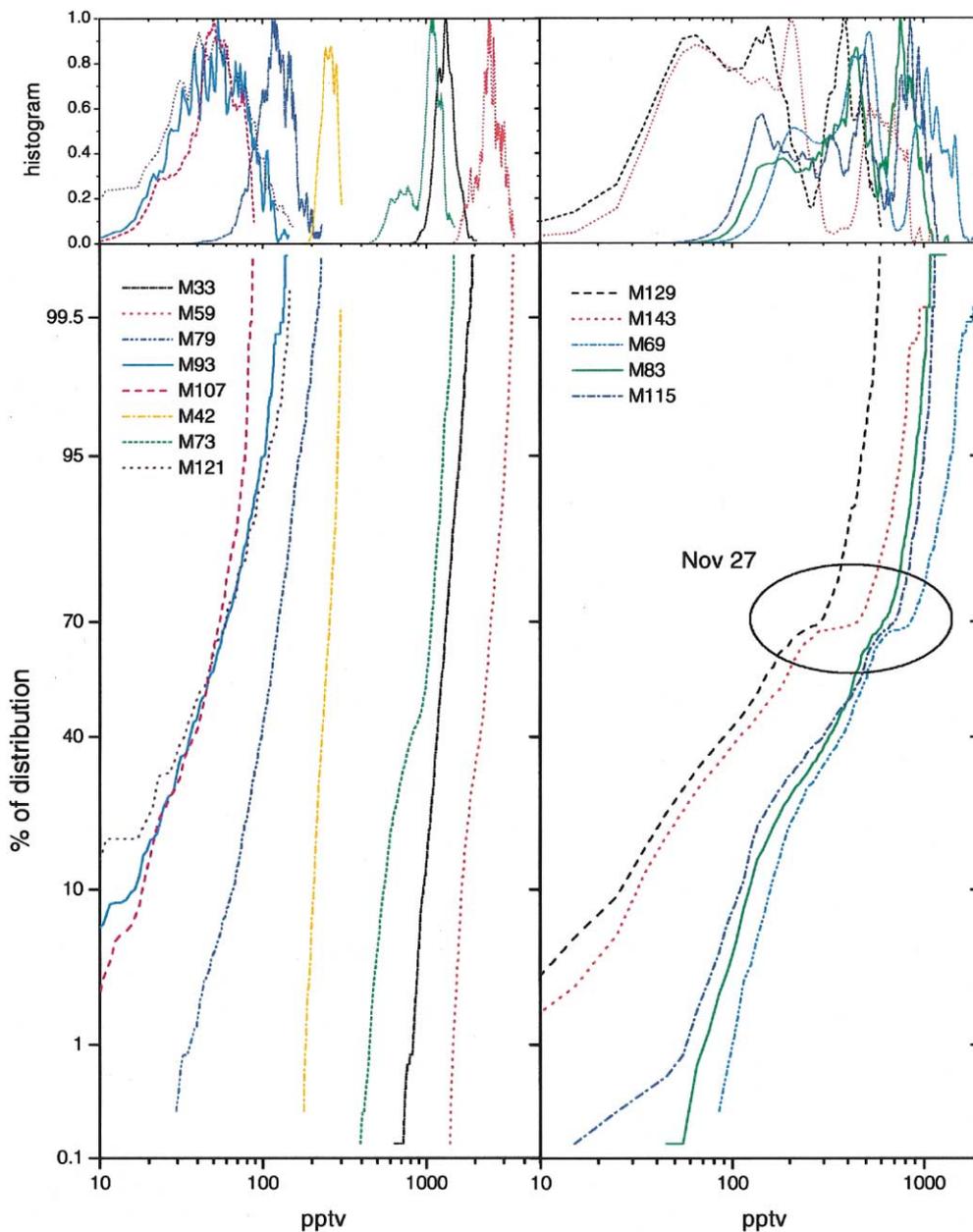


Fig. 2. Cumulative distribution plots of anthropogenic and biogenic VOCs—methanol (M33), acetone (M59), benzene (M79), toluene (M93), xylenes (M107), C<sub>9</sub>-benzenes (M121), acetonitrile (M42), MEK (M73), hexanal (M83), pentenols + 3-methyl-butanol (M69), heptanal (M115), octanal (M129) and nonanal (M143)—considered in the variability lifetime relation.

compounds; as pointed out by Williams et al. (2000) the calculated HO-density doubles if the effective loss rates of butanone and acetone are two times lower. The estimated average HO-density from the variability-lifetime relationship will therefore represent a lower limit.

The variability-lifetime relationship of the biogenic and anthropogenic trend was performed for selected compounds, where reaction rate coefficients with HO and ozone were reliable, potential photochemical sources could be excluded, and the accuracy of the measured concentration and the selectivity of the

Table 1

Reaction rate coefficients with OH, ozone and photolysis rates for 3000 m as used in the variability lifetime plot. VOCs associated with the biogenic trend are labeled with numbers (1)–(8) according to their order in Fig. 3(a)

Protonated mass	Compounds	HO-rate constant ( $\text{cm}^3 \text{s}^{-1}$ )	O <sub>3</sub> -rate constant ( $\text{cm}^3 \text{s}^{-1}$ )	Photolysis rate (3000 m) 12:00 ( $\text{s}^{-1}$ )
<i>Anthropogenic trend</i>				
M33	Methanol	8.19E-13	0	0
M59	Acetone	1.93E-13	0	3.60E-07
M73	Butanone	1.10E-12	0	3.60E-07
M79	Benzene	1.16E-12	0	0
M93	Toluene	6.64E-12	2.76E-22	0
M107	C <sub>9</sub> -benzenes	1.11E-11	0	0
M121	C <sub>10</sub> -benzenes	5.86E-12	0	0
M42	Acetonitrile	2.40E-14	1.0E-22*	0
<i>Biogenic trend</i>				
M83 (1)	Hexanal	3.20E-11	0	0
M115 (2)	Heptanal	3.32E-11	0	0
M129 (3)	Octanal	3.78E-11	0	0
M143 (4)	Nonanal	4.56E-11	0	0
M69 (5)	Methylbutanal	2.52E-11	0	0
	Pentenols	8.00E-11	0	0
M99 (6)	Hexanals	2.80E-11	2.0E-18	0
M85 (7)	EVK	3.50E-11	0	0
M71 (8)	MVK + MAC	2.85E-11	2.95E-18	1.80E-06
	Pentenenes	3.00E-11	1.00E-17	0

\*Orlando, personal communication.

measured compound were satisfactory. In this work we also include losses due to ozonolysis (average O<sub>3</sub> density in November 1999: 30–50 ppbv), which can affect the lifetime of some compounds (e.g. toluene). Photolysis rates at 3000 m a.s.l. for clear skies were calculated according to the model of Madronich (Madronich and Flocke, 1999; <http://acd.ucar.edu/models/TUV>). Values for butanone (mass 73<sup>+</sup>), MVK plus MACR (mass 71<sup>+</sup>) were taken from Williams et al. (2000) and rescaled for the current altitude. All photolysis rates were averaged (~1/4 of the noon time value) in order to get a mean value. Most reaction rate coefficients were taken from Atkinson (1997) except those for pentenols, which were from Orlando et al. (2001). Table 1 summarizes all kinetic data needed for and obtained from the variability-lifetime calculation. In cases where several isomers (e.g. C<sub>9</sub>-benzenes) contributed to the observed mass we took a mean average value of all isomers. The HO-rate assignment for C<sub>8</sub>-benzenes was based on cartridge samples and GC analysis, which showed mainly a mixture of p&m-xylenes and o-xylene.

Fig. 3(a) shows a plot of  $\sigma(\ln(\gamma))$  versus lifetime for two groups of VOCs. The first group includes anthropogenic species, and the trend for the period of 25 November until 30 November was obtained from several long lived species and aromatic compounds as listed in Table 1. It was used to determine the average HO concentration similar as described by Williams et al. (2000). The trend is constrained by photolysis rates,

reaction rate coefficients with ozone and the slope of the linear fit through all data points. Thus the problem of finding the average HO-radical density can be solved by a simple linear programming routine as follows. By varying the HO density between 10<sup>3</sup> to 10<sup>8</sup> molecules cm<sup>-3</sup> it is possible to estimate an average lifetime and iteratively find the optimal value for [HO]<sub>average</sub>, yielding either the maximum correlation coefficient *R* or the minimum squared 2-norm of the residual as shown in Fig. 3(b). The accuracy of the calculated HO-density is mainly dependent on photolysis rates. Higher photolysis rates give higher values for [HO]. The same applies for  $k_{\text{O}_3} \times [\text{O}_3]$ ; higher values result in increased HO-densities. However, it is noted that the HO-calculation is much more sensitive to photolysis than to ozonolysis. The best fit (*R* = 0.983) gives an average HO-density of  $(1.5 \pm 0.5) \times 10^5$  molecules cm<sup>-3</sup>, an A factor of 1.44 and a b exponent of 0.44. This comes close to values obtained from other remote datasets such as ABLE 3B, TRACE-A and PEM-West B showing b exponents of 0.46, 0.52 and 0.53, respectively (Jobson et al., 1999). Williams et al. (2000) claimed that most of the anthropogenic VOCs seen during LBA-Claire originated from Europe and were transported towards Surinam by the northeast trade winds. Consistently they saw a strong decline in the variability trend with a *b* value of 0.65 supporting their interpretation of the abundance of old-aged anthropogenic air masses. Warneke (personal

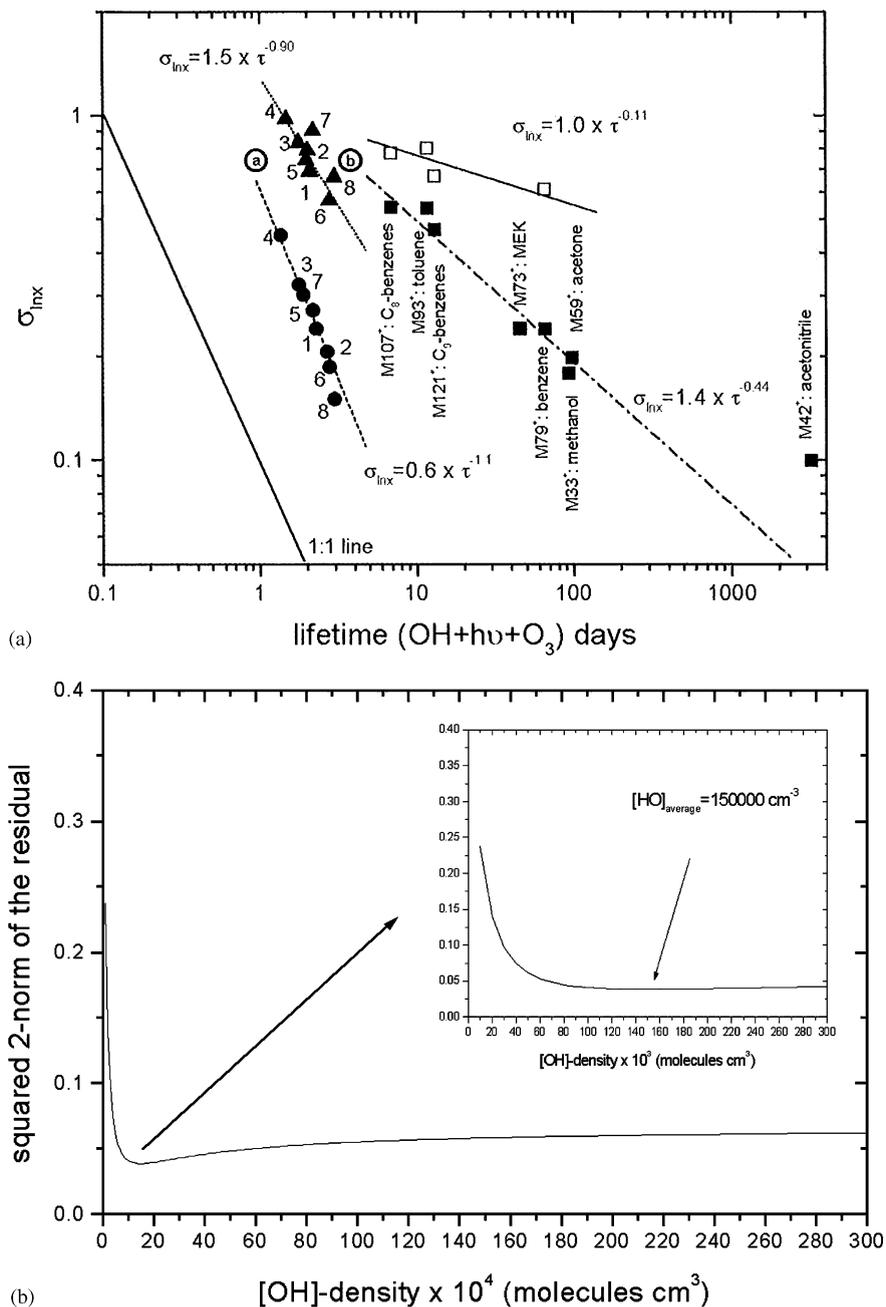


Fig. 3. (a) Variability versus lifetime; the anthropogenic trend is represented by squares, open squares indicate the variability lifetime plot for the beginning of November, closed squares from 25 to 30 November; closed triangles show the biogenic trend from 25 to 30 November, closed circles for a subset on 27 November, numbers 1–8 correspond to VOCs following the biogenic trend as assigned in Table 1; the two different conditions for mass 69<sup>+</sup> are indicated by open symbols (pentenol (a), 3-methylbutanal (b)), (b) the squared 2-norm of the residual as a function of the HO-density; the minimum yields the optimal HO-density of  $(1.5 \pm 0.5) \times 10^5$  molecules cm<sup>-3</sup>.

communication) calculated a *b* factor of 0.4 for various VOCs measured on a cruise through the Western Indian Ocean during the INDOEX field study. This is similar to the value obtained in this work for the end of

November. For comparison open squares show the variability dependence of aromatic compounds between 7 and 17 November. Strong diurnal variations (Karl et al., 2001) caused a much smaller *b* factor of 0.11,

showing that during this time the site was clearly influenced by nearby anthropogenic sources.

Acetonitrile ( $M42^+$ ) can be regarded as an ‘outlier’ in the variability trend. This is not surprising, as this compound is thought to be almost exclusively released by biomass burning and wood fires (Holzinger et al., 1999). It is common practice in the Alps to heat houses with wood fires throughout the winter. This might substantially contribute to the variability of this long lived compound seen at the Sonnblick Observatory.

### 3.4. Short-lived biogenic VOCs

Reactive VOCs from biogenic sources on the other hand give a different picture. The variability trend during the end of November 1999, when strong inversion layers cut off the site from nearby sources, approaches the case where it is mainly affected by atmospheric loss processes. The  $b$  exponent between 25 and 30 November is  $\sim 0.9$  (Fig. 3, triangles); a subset of the same dataset for 27 November gives a  $b$  factor of  $\sim 1.1$  (circles). These high  $b$  values suggest that reaction with HO radicals accounted for most of the observed VOC decline. Under the assumption that VOCs during the daytime on 27 November were mainly removed by photochemistry, one would also expect the ratio of the  $\sigma(\ln(x_{i,j}))$  to be directly proportional to the reaction rates according to (4). Indeed the ratio between

$\sigma(\ln(\text{toluene}))/\sigma(\ln(\text{benzene}))$  was around  $(6.2 \pm 2.0)$  which is comparable to the ratio of their reaction rates  $(5.9 \pm 1.3)$ . Since we could not find reaction rates with HO radicals for higher aldehydes ( $> C_7$ ) an approximation of these rates was based on values obtained from the “structure-activity” relationship proposed by Kwok and Atkinson (1995). Under the assumption that most of the reactive VOC loss on 27 November was caused by the removal with HO-radicals we used the known reaction rate of hexanal  $(3.20 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} @ 295 \text{ K})$  (Papagni et al., 2000; Thévenet et al., 2000) and extrapolated the reaction rates for heptanal, octanal and nonanal by comparing different declines of VOC concentrations on this specific day. These values were finally used in Fig. 3. If the variability lifetime trend is known, relations (3) and (4) can also be used to estimate reaction rates of VOCs. In our case the biogenic trend from 25 November until 30 November (triangles) can be fixed by hexanal and hexenals (mass  $99^+$ ) (Fall et al., 1999), where reaction rates with HO-radicals have been reported by Atkinson et al. (1995, 1997). By knowing the  $b$  factor (0.9) we can plot  $\ln(x_i)$  versus  $\ln(x_{\text{hexanal}})$  and relate the reaction rate of compound  $i$  with the rate of hexanal (or hexenals). Fig. 4 shows the concentrations of  $C_7$ – $C_9$  aldehydes plotted versus hexanal. The slope is defined by  $(k_i/k_{\text{hexanal}})^b$ . Rates obtained by this approach for heptanal,  $(3.7 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , octanal  $(3.9 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , and nonanal,  $(4.8 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$   $\times$

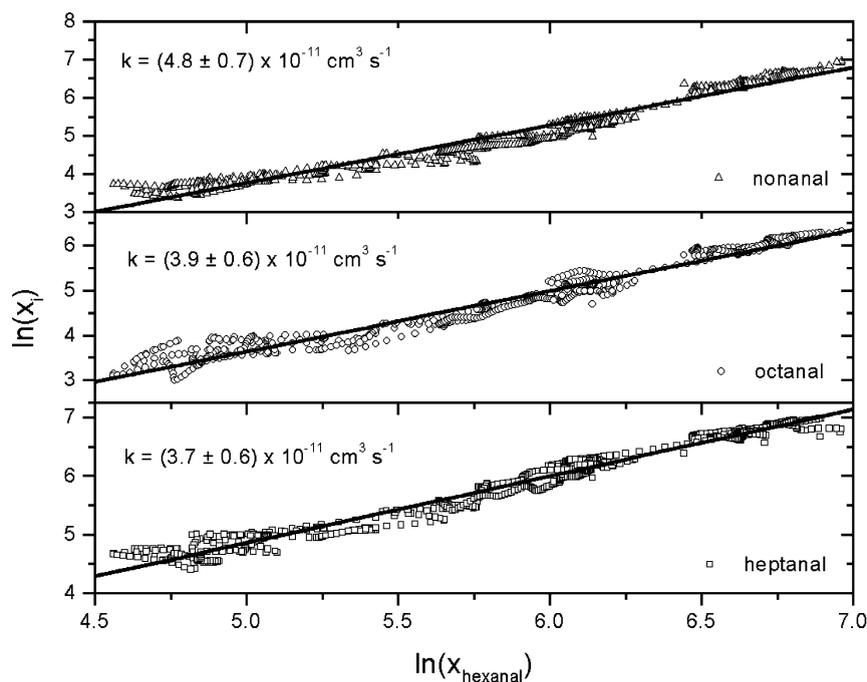


Fig. 4. Natural logarithms of ambient concentrations of heptanal, octanal and nonanal plotted versus hexanal. Slopes are proportional to reaction rates by relation (4).

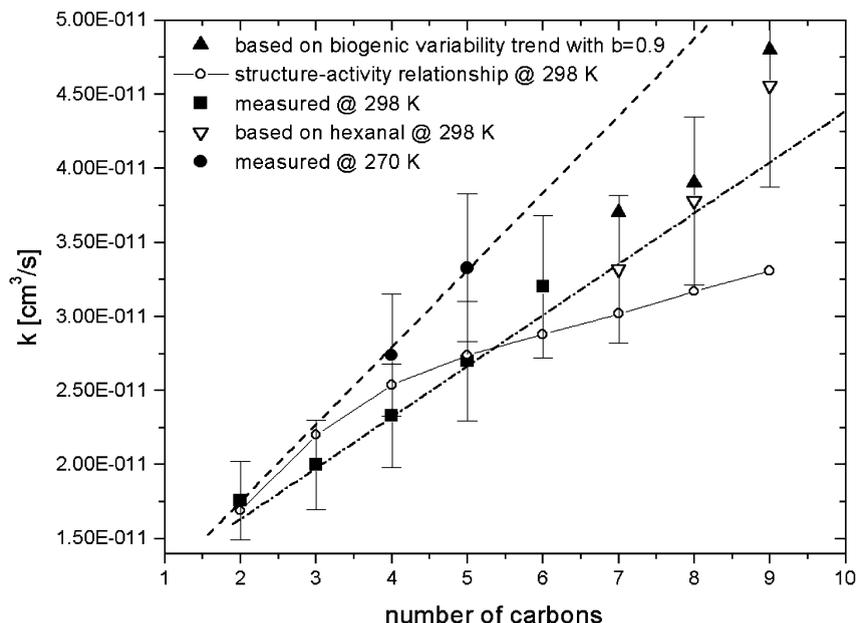


Fig. 5. Reaction rates for aldehydes with HO as a function of chain length (number of carbons) as obtained on 27 November 1999 and from the variability lifetime. Values are compared to predictions from the “structure-activity” relationship.

$10^{-11} \text{ cm}^3 \text{ s}^{-1}$  are in good agreement with reaction rates for heptanal,  $(3.32 \pm 0.50) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , octanal  $(3.78 \pm 0.56) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , and nonanal,  $(4.56 \pm 0.67) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , estimated on 27 November.

Fig. 5 compares reaction rates for *n*-aldehydes as a function of the number of carbons in the aldehyde. Unfortunately no measured reaction rates for long chained aldehydes could be found. It can be seen that the “structure activity” relationship predicts a weaker increase of the reactivity with higher carbon number than our observed estimates. This discrepancy could reflect the fact that for long chained aldehydes, such as nonanal, other loss processes might be important. Photolysis and ozonolysis can play a role for the removal of these compounds. However, we also want to draw attention to possible aerosol formation, which could significantly effect the removal rate of semivolatile compounds such as nonanal.

### 3.5. Interpretation of other ions

We know from laboratory experiments that wounded plants produce a mixture of VOCs exhibiting mass  $69^+$  in the PTR-MS instrument (Fall et al., 2001). As observed in GC-PTR-MS analysis of several laboratory experiments mostly methylbutanals and pentenols (mainly 1-penten-3-ol) contributed to the observed mass  $69^+$ . Thus we can exclude compounds such as isoprene. This argument is also strengthened by the fact, that the general abundance of isoprene-emitting plants through-

out the Alps is rather low (Simpson et al., 1999) and plants would not produce significant amounts of isoprene in November (Guenther et al., 1995). We can use the biogenic variability trend to find the best fit of the methylbutanals and pentenols mixture. This was done under three different conditions (Fig. 3a). The first fit assumed that mainly 3-methylbutanal (open symbol (b)) contributed to protonated mass  $69^+$  ( $R = 0.80$ ), the second fit assumed a mixture of 70% 3-methylbutanal and of 30% pentenols (triangle) ( $R = 0.98$ ), and the third fit considered mainly pentenols (open circle (a)) for protonated mass  $69^+$  ( $R = 0.79$ ). By varying the relative pentenol to 3-methylbutanal fraction it is possible to estimate the best mixture. In our case a 70/30 mixture gave the best correlation coefficient. The fact that we see a mixture of these compounds is in agreement with the GC-sample drawn on the Sonnblick on 26 November suggesting that about 48% of 3-methylbutanal and 52% of pentenols explained the total signal on mass  $69^+$  (Karl et al., 2001). Mass  $85^+$  is known to be released from vegetation (Fall et al., 2001). In laboratory experiments with freezing vegetation more than 90% of the observed signal could be assigned to mainly ethyl vinyl ketone (EVK) and only a minor part came from pentenals. Assuming that EVK contributes to mass  $85^+$ , we can estimate the lifetime by fitting it to the observed biogenic trend (Fig. 3 triangles, circles) yielding a lifetime around 2.2 days ( $k \sim 3.5\text{E-}11 \text{ cm}^3 \text{ s}^{-1}$ ). The parent ion  $71^+$  can originate from MVK, MACR or several pentene isomers. Since no significant amounts of

isoprene were present in late November, MACR and MVK derived from isoprene oxidation are highly unlikely. However, MVK can also be emitted from plants directly (König et al., 1995) and cannot be excluded completely in our analysis. On the other hand, pentene isomers could also be released from vegetation (Isidorov, 1990). Pentene isomers have reaction rates with HO similar to MVK, but ozonolysis also plays an important role for their lifetimes. By calculating the mean atmospheric lifetime of 1-pentene, 2-pentene, 3-methyl-1-butene, 2-methyl-1-butene and 2-methyl-2-butene ( $t \sim 0.24$  days) (Atkinson, 1997) it seems the assumption of mass 71<sup>+</sup> originating from MVK ( $t \sim 3.2$  days) fits the biogenic trend best and is therefore the most reasonable interpretation.

### 3.6. Photochemical losses of VOCs and HO density calculation

As concluded above, on 27 November the main atmospheric loss mechanism for VOCs at the Sonnblick was due to reaction with HO, allowing a calculation of the HO density. Taking the known rate constants  $k$  for hexanal ( $3.20 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ) (Papagni et al., 2000; Thévenet et al., 2000) and the estimated rate constant for a mixture of 3-methylbutanal plus pentenols ( $4.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ) it is possible to calculate the diurnal HO-density on 27 November according to:

$$[\text{HO}] = \frac{1}{kC} \frac{\partial C}{\partial t},$$

with  $C$  being the VOC concentration,  $t$  the time and  $k$  the reaction constant. Fig. 6 shows the HO-profile together with UVB fluxes which we use as a surrogate for the diurnal cycle of photolysis rates. The calculated HO-density started increasing at 09:00 local time and peaked around midday with maximal values around  $(1.3 \pm 0.5) \times 10^6 \text{ molecules cm}^{-3}$ . Thereafter, HO-densities decreased rapidly and were below the detection limit after 15:00 local time. The calculated HO-densities followed UVB quite closely as expected, also supporting the idea that on this day mainly photochemistry caused the observed concentration profiles of reactive VOCs. Integration over the diurnal HO-profile in Fig. 6 gives an averaged density of  $176000 \pm 50000 \text{ molecules cm}^{-3}$  on 27 November. Comparison with the average HO-density obtained from the variability-lifetime relation shows good agreement.

## 4. Summary and conclusions

We used the variability-lifetime relationship of VOCs to estimate average HO-densities at the Sonnblick Observatory (3106 m a.s.l.) in late November 1999, giving an average value of  $(1.5 \pm 0.5) \times 10^5 \text{ molecules cm}^{-3}$ . The photochemical destruction of short-lived compounds at this site allowed two other determinations. First, we independently verified the HO concentration using a diurnal HO-profile with a maximum value around  $(1.3 \pm 0.5) \times 10^6 \text{ molecules cm}^{-3}$ ; this

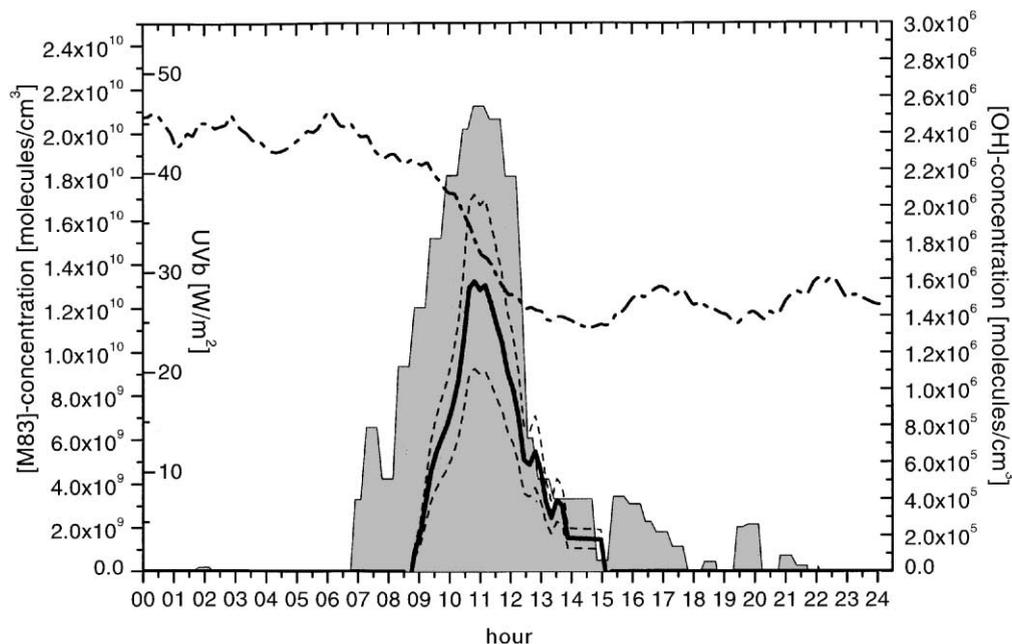


Fig. 6. Diurnal HO-density (solid line) plus estimated errors (thin dashed lines) derived from photochemical destruction of hexanal (mass 83<sup>+</sup>) (dash dotted line) together with the diurnal UVB cycle (gray area) on 27 November 1999.

is equal to an average value of  $\sim(1.7 \pm 0.5) \times 10^5$  molecules  $\text{cm}^{-3}$ . Second, based on the reaction rate constant of hexanal ( $3.20 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  @ 295 K) (Papagni et al., 2000; Thévenet et al., 2000) we estimated the reaction rate coefficients for heptanal ( $3.32 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ), octanal ( $3.78 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ) and nonanal ( $4.56 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ). The obtained values generally fit well to a linear trend of known reaction rate coefficients of shorter chain aldehydes with HO; comparison with values obtained from the “structure-activity” relationship shows higher reaction rate constants with HO than predicted, which could be due to other loss processes for semivolatile aldehydes such as aerosol formation.

Due to potential photochemical sources for acetone and butanone the variability-lifetime approach will give a lower limit for the [HO]-density. In contrast the derived [HO]-density from photochemical destruction of short lived compounds as obtained on 27 November will result in an upper limit for [HO] since losses due to mixing were neglected. It is reasonable to assume that the actual average [HO]-density has to lie between both values. The good agreement between the calculated average [HO]-densities suggests that potential interferences for both estimates played a minor role. The variability-lifetime approach also allowed a check on data quality, such as the estimate of the ratio of 3-methylbutanal and pentenols, both fragmenting to give protonated mass  $69^+$ . We showed that if a variability trend can be fixed by at least two compounds it is in principle possible to estimate reaction rate constants of other VOCs following the same trend. This allowed an estimate of the reaction rate constants for  $C_7$ ,  $C_8$  and  $C_9$  aldehydes and compare these values with reaction rates obtained independently on 27 November. The lifetime for EVK was estimated to be 2.2 days ( $k \sim 3.5 \text{ e-}11 \text{ cm}^3 \text{ s}^{-1}$ ), we also reasoned that MVK contributes mostly to the protonated signal on mass  $71^+$ . The biogenic  $b$  exponent, which is considered to be a sink term in the regional variability budget, being close to 1, suggests that the observed rapid decline of ambient concentrations of short-lived biogenic VOCs during the end of November was mainly caused by photochemical destruction with HO-radicals. On the other hand the  $b$  exponent for the anthropogenic trend was lower around 0.44 close to values observed during ABLE 3B (0.46), TRACE-A (0.52), PEM-West B (0.53) and INDOEX (0.4). (Jobson et al., 1999, Warneke et al., 2001). This suggests that under certain circumstances the Sonnblick Observatory ( $47.05^\circ\text{N}$ ,  $13.3^\circ\text{E}$ ), which is located on the central ridge of the Austrian Alps, can be considered a remote sampling site on the European continent. The somehow lower  $b$  value for the anthropogenic trend probably reflects Ehhalt's model results (Ehhalt et al., 1998) which showed a smaller  $b$  value for continental air masses.

The A factor in Eq. (1) can be interpreted as a range factor for sampled air mass ages. The observed values of 0.6, 1, 1.4 and 1.5 for all four variability trends in Fig. 3a are comparable to that measured in a hydrocarbon data set at the Harvard forest site (0.99) (Jobson et al., 1998) and indicate a rather small age range of sampled pollutants. Values for the LBA-Claire and PEM-West B campaigns were reported to be in the order of 4.3–4.63 (Williams et al., 2000). The observation of a rather small A factor is not surprising, since shortlived compounds such as reactive biogenic VOCs were mainly removed by reaction with HO radicals from similar air masses and not diluted by mixing and longerlived anthropogenic compounds showed an average photochemical age of  $(18 \pm 5) d$  of photochemical exposure.

We conclude that the measurements performed on the Sonnblick between October 1999 and March 2000 under a wide range of different meteorological situations allowed us to distinguish various VOC source-receptor relationships. Further investigation at this site should help evaluate atmospheric chemistry and transport models and help understand processes controlling oxidants in the Alps.

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