

Deployment of a ground-based CIMS apparatus for the detection of organic gases in the boreal forest during the QUEST campaign

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Abstract. Measurements of atmospheric volatile organic compounds were performed in the Finnish Boreal forest atmosphere during spring 2003, as part of the project QUEST (Quantification of Aerosol Nucleation in the European Boundary Layer), using a ground-based Chemical Ionization Mass Spectrometer (CIMS) instrument. Based on the study of their hydrate distribution, methanol, acetonitrile, acetaldehyde, dimethyl amine (DMA), ethanol/formic acid, acetone, trimethyl amine (TMA), propanol/acetic acid, isoprene, methyl vinyl ketone (MVK) and metacrolein (MaCR), monoterpenes and monoterpene oxidation product (MTO) are proposed as candidates for masses 32, 41, 44, 45, 46, 58, 59, 60, 68, 70, 136, and 168 amu, respectively. It would be, to our knowledge, the first time DMA, TMA and MTO are measured with this method. Most compounds show a clear diurnal variation with a maximum in the early night, corresponding to the onset of the nocturnal inversion and in agreement with independent measurements of CO. Biogenic compounds are highly correlated with each other and the ratio monoterpene/oxidation product shows a typical daily pattern of nighttime maxima. However, because isoprene mixing ratios are also maximum during the early night, it is likely that it suffers of the interference from another unidentified biogenic compound. Hence mass 68 amu is identified as isoprene+compound X.

drocarbons (NMHC) are estimated to be higher than those of anthropogenic NMHC (Guenther et al., 1995), and their oxidation products may be the greatest natural continental source of fine particles. Hoffman et al. (1997) suggested that at night the products from ozonolysis of pinene were of sufficiently low vapor pressures to condense freely on existing particles or possibly homogeneously nucleate, which makes daily variations studies important. Also, high resolution time series of biogenic gases concentrations bring new information for the understanding of how NMHC are oxidized in a natural atmosphere and how their ambient concentrations are driven by the dynamic of the boundary layer.

In this paper, we present the results of measurements of atmospheric volatile organic compounds (VOC) in the Finnish Boreal forest atmosphere during spring 2003, as part of the project QUEST (Quantification of Aerosol Nucleation in the European Boundary Layer), using a ground-based Chemical Ionization Mass Spectrometer (CIMS) instrument. Monoterpenes have already been measured at the site by means of adsorbent cartridges and GC-FID (Hakola et al., 2000) or GC-MS (Spirig et al., 2003). The advantages of the CIMS instrument over cartridge sampling associated to gas chromatographic analysis is the fast time response of a few seconds and the online detection of reactive species that might be modified otherwise. If integrated over several minutes, which still allow for the study of relatively fast changing atmospheric concentrations, a low detection limit down to less than 10 ppt for some trace gases can also be achieved. CIMS has been previously used for the air-borne measurements of organic gases (Arnold et al., 1997; Wohlfrom et al., 1999; Schröder et al., 2003). The ground-based adaptation of the CIMS apparatus for the measurement of organic gases provides a set of on-line data over extended periods of time, and enables the study of high time resolution daily variations. The chemical ionization (CI) technique involved in the CIMS instrument uses ion-molecule reactions which cause much less fragmentation than electron impact or photoionization.

1 Introduction

Vast quantities of biogenic hydrocarbons are emitted to the atmosphere by vegetation, having an impact both on the atmospheric chemistry at local, regional and global scale, and on atmospheric processes such as new particle formation and growth. The amount of emissions of natural nonmethane hy-

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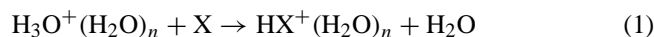
However, ion identification is still a problem when the ionized molecules are hydrated with several water clusters. The goal of this paper is mainly to address all atmospheric candidates for the gases detected during the Quest campaign with CIMS. Furthermore, daily variation of the measured species are observed, and used as a validation tool for the consistency of the data set. Hence, we report mixing ratios time variation of a large variety of species (some of them being measured for the first time with this technique) as the result of the first ground-based CIMS operated for measurement of organic gases.

2 Site and Instrumental deployment

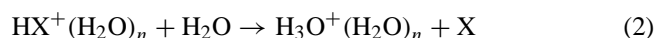
The SMEAR experimental station (Station for Measuring Forest Ecosystem-Atmosphere Relations) located in Hyytiälä, southern Finland (61°51' N, 24°17' E, 181 m above sea level) is representative of the boreal coniferous forest. A complete description of the site can be found elsewhere (Kulmala et al., 2001). Data presented in this paper are based on samplings achieved during 2 weeks: from 17 to 29 March 2003. Gas measurements have been sampled from an adapted measuring container located 50 m south-west of the SMEAR station, at 2.5 m above the ground. The comparison of water vapor measurements obtained with the CIMS set up with the water vapor measured at the station (4.2 m) show excellent agreement (less than 5% disagreement). This indicates that the location of the measurement container is suitable for comparison of the CIMS results with the SMEAR data set. In order to avoid wall effects and sampling of fine particles, the measuring container was equipped with a large diameter-high velocity inlet, in which the sampling line was installed perpendicularly to the inlet flux (Hanke et al., 2003). The inlet protrudes about 1 m above the roof of the container, so that the air should not have encountered any surface before being drawn into the sampling line.

Measurements were performed using a Chemical Ionization Mass Spectrometer (CIMS) instrumental set-up, based on ion-molecule reaction for the detection of trace gases. The instrument, which was designed by the MPIK-Heidelberg, is composed of (a) the high velocity inlet mentioned above (b) a sampling line equipped with a critical orifice and thermostatted at ~30°C, (c) an ion source, generating $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ educt ions (d) a flow tube reactor, also thermostatted at ~30°C, in which educt ions react with the atmospheric gases to be analyzed (e) a quadrupole mass spectrometer for the detection of ionized gas molecules (Fig. 1). A similar experimental set-up has been used by MPIK-HD for previous atmospheric trace gas measurements and is described in detail elsewhere (Hanke et al., 2003). Briefly, atmospheric air enters the critical orifice, which assures a constant flow rate of about 10 slpm (also measured with two anemometers further in the sampling line) and a pressure of 10 mbars, created by using two oil-free SCROLL vac-

uum pumps. Educt ions H_3O^+ are produced by a high-frequency glow-discharge capillary-tube ion source (CIS) and a 2 slm O_2 source gas flow: O_2^+ ions produced from the CIS rapidly react with the more abundant atmospheric H_2O to give H_3O^+ . Hydration of the H_3O^+ reactant ions occurs by association with water vapor in the main flow tube, leading to a distribution of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ions, with n from 0 to 6, of which the ions with $n=3$ are most abundant. Then, as a first approximation of the complex chemistry involved, it is calculated that atmospheric gases X with proton affinities larger than that of H_2O (166.5 kcal mol⁻¹) react in the flow tube reactor with educt ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ via:



Thus, also the product ions are hydrated with up to 6 water molecules. Depending on the number of water ligands and on the molecule X proton affinity (PA), also a backward reaction is possible (Viggiano et al., 1988):



The lower the PA of molecule X, the more important the reverse reaction. In our experimental set-up, we intentionally lowered the total gas pressure in the flow tube reactor to 10 mbar (compared to the previous use of 50 mbar), in order to reduce the occurrence of reverse reactions, which will specifically be addressed later. The residence time in the flow tube reactor is much longer than the reaction time for a collision rate ($2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), allowing the atmospheric gases to react during traveling in the flow tube reactor. Both products and excess educt ions enter the quadrupole mass spectrometer where they are selected according to their mass. One mass scan (for ion masses from 10 to 200 amu) lasts 3.2 s. For improving the detection limit of organic trace gases, an integration time of 100 to 200 successive scans has been chosen, leading to a time resolution of 320 to 640 s.

The concentration of the atmospheric gas X_i is obtained from the count rate of X_i , the count rate of the educt ion H_3O^+ and of the sum of all product ions $\sum \text{X}_j$, the measured reaction time τ between the ion source and the detector, and the collision rate constant k ($2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) of the ion-molecule reaction (parallel Acims-formula) according to:

$$[\text{X}_i] = (k * \tau)^{-1} \text{X}_i(\text{H}_2\text{O})_n / \sum \text{X}_j(\text{H}_2\text{O})_n * \ln[1 + \sum \text{X}_j(\text{H}_2\text{O})_n / \text{H}_3\text{O}^+(\text{H}_2\text{O})_n] \quad (3)$$

Where $\text{X}_i(\text{H}_2\text{O})_n$, $\text{X}_j(\text{H}_2\text{O})_n$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ are the sum of count rates of all hydrates from $n=1$ to $n=5$ when possible (see Sect. 3). How many hydrates are taken into account will be discussed for each compound in Sect. 3. This mixing ratio calculation does not take into account diffusion and sticking of gases onto the sampling tube walls, reverse reactions and mass discrimination in the mass spectrometer. In order to take those parameters, as well as uncertainties on reaction rate constants into account, in-situ calibrations were performed for acetonitrile, acetaldehyde, methanol, isoprene

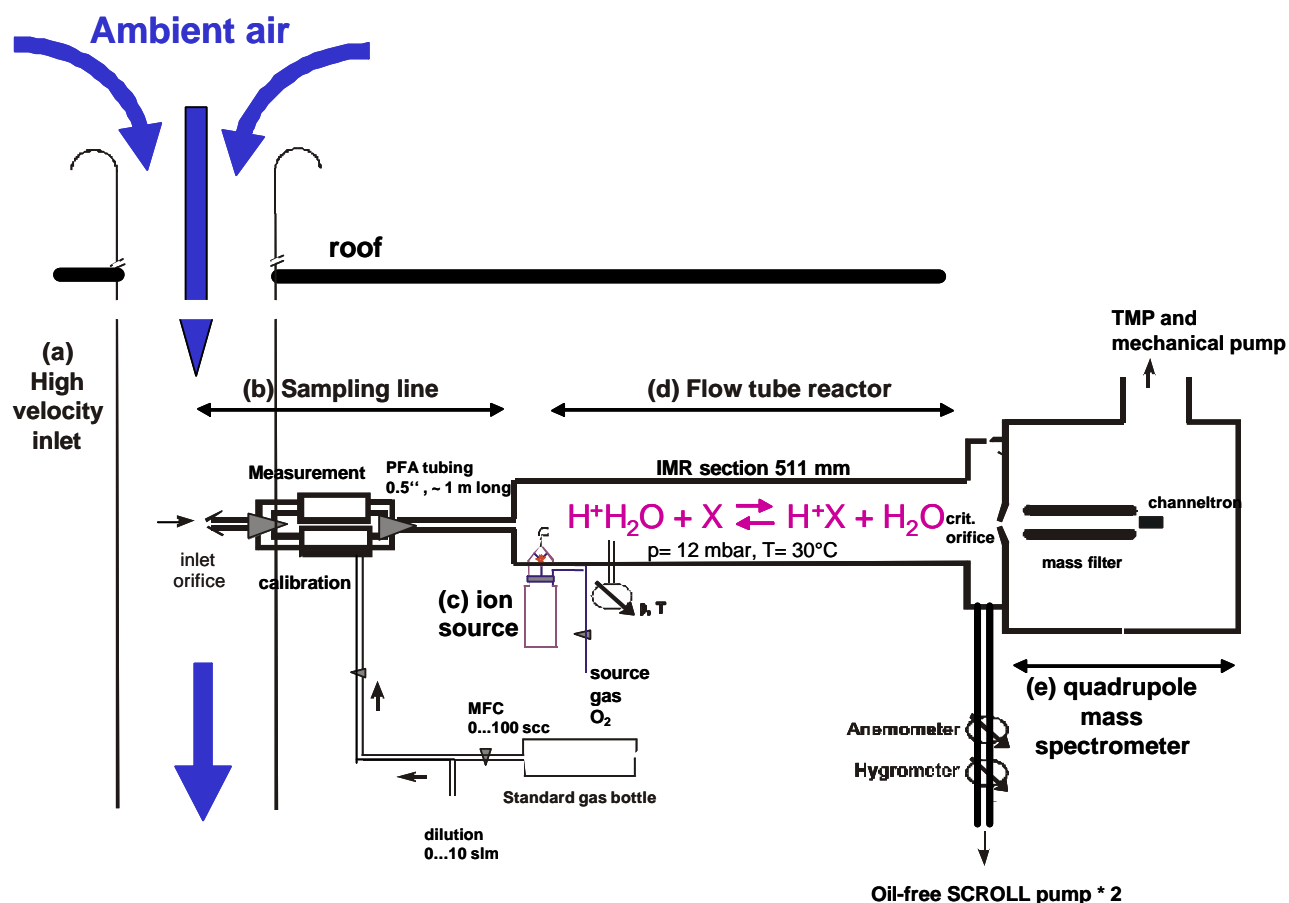


Fig. 1. Experimental set up: schematic view of the CIMS instrument. (a) high velocity inlet (b) critical orifice and sampling line (c) ion source, generating $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ educt ions (d) flow tube reactor (e) quadrupole mass spectrometer.

and DMA. Calibrations were performed on-line during measurements using gas bottle standards (one standard gas bottle contained a mixture of acetonitrile, acetaldehyde, methanol, isoprene, while another one contained DMA), both in zero air and in atmospheric air in order to evaluate the influence of other atmospheric gases on the calibration. Zero air levels are obtained using a commercial zero air generator (Breitfuss GmbH) by passing atmospheric air through a catalyst at 450°C and quenching the water, with a frequency of about an hour per two days.

3 Ion identification

An example of the mass spectra obtained during the campaign is shown Fig. 2. The sensitivity of the instrument was raised to the maximum in order to obtain the best detection limit within our experimental set up. However, a high sensitivity induced a lower mass resolution. This can be seen on Fig. 2 in the proximity of the educt ion peaks (especially 73 ($\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$) and 91 amu ($\text{H}_3\text{O}^+(\text{H}_2\text{O})_4$)). Peaks from ions 1 amu smaller or larger than the educt ions and hydrates

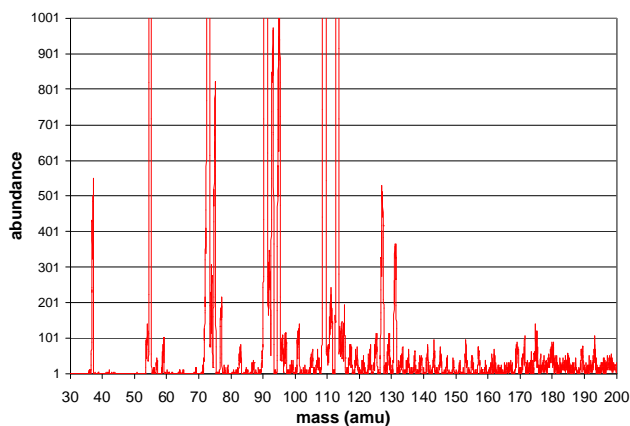


Fig. 2. Example of the mass spectra obtained during the atmospheric measurements.

could not always be reliably separated from the educt ions peaks. This is the case for masses 72, 90, and 108.

Table 1. Monitored mass numbers of ions X, sorted by hydrate families in the form of $\text{HX}^+(\text{H}_2\text{O})_n$. between brackets are the ions which peaks have not always been correctly separated from the reactant peaks. Underlined are the masses for which the count rate was maximum within the peak family.

Core ion HX^+	$\text{HX}^+(\text{H}_2\text{O})$	$\text{HX}^+(\text{H}_2\text{O})_2$	$\text{HX}^+(\text{H}_2\text{O})_3$	$\text{HX}^+(\text{H}_2\text{O})_4$	$\text{HX}^+(\text{H}_2\text{O})_5$	$\text{HX}^+(\text{H}_2\text{O})_6$	$\text{HX}^+(\text{H}_2\text{O})_7$	$\text{HX}^+(\text{H}_2\text{O})_8$
18	36	54	(72)	(90)	(108)	126	144	162
19	37	55	<u>73</u>	91	109	127	145	163
33	51	<u>69</u>	87	105	123	<u>141</u>	159	<u>177</u>
42	60	78	96	<u>114</u>	132	150	168	<u>186</u>
45	<u>63</u>	81	99	117	135	153	<u>171</u>	189
46	<u>64</u>	82	100	118	136	154	<u>172</u>	
47	65	<u>83</u>	101	119	137	155	<u>173</u>	
49	67	85	103	<u>121</u>	139	<u>157</u>	<u>175</u>	
59	77	<u>95</u>	<u>113</u>	131	149	<u>167</u>	185	
61	79	<u>97</u>	115	133	151	<u>169</u>	187	
71	89	107	<u>125</u>	<u>143</u>	161	<u>179</u>		

Table 2. Some chemical and physical properties of measured compounds; sulfuric acid and NH_3 properties are also indicated for comparison. Ref: Handbook of Chemistry and Physics for proton affinities. Life time order of magnitude, Williams et al. (2000) for acetone, acetonitrile, acetaldehyde, isoprene, methan, using $\text{OH}=5 \times 10^5$ molecules cm^{-3} and Atkinson (1994) for pinene, MVK and MACR using $\text{OH}=1 \times 10^6$ molecules cm^{-3} and ozone =40 ppbv.

Compound	Molecular Mass Number	Proton affinity kcal mol^{-1}	Structure	Order magnitude Life time (/OH+hv)
acetone	58	188	CH_3COCH_3	1 month
acetonitrile	41	186	CH_3CN	3 years
acetaldehyde	44	185	CH_3CHO	1 day
isoprene	68	197	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	6 hours
methanol	32	180	CH_3OH	1 month
DMA	45	218-225	$\text{CH}_3\text{-NH-CH}_3$	–
TMA	59	222-230	$\text{CH}_3\text{-N}(\text{CH}_3)\text{-CH}_3$	–
ethanol	46	185.5	$\text{CH}_3\text{CH}_2\text{OH}$	–
formic acid	46	178	H-COOH	–
propanol	60	189.4	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{OH}$	–
acetic acid	60	188	$\text{CH}_3\text{-COOH}$	–
pinonaldehyde	168	–	$\text{C}_{10}\text{H}_{16}\text{O}_2$	–
methyl vinyl ketone/ methacrolein	70	199/193	$\text{CH}_2=\text{CH-CO-CH}_3/\text{CH}_2=\text{C}(\text{CH}_3)\text{-CH=O}$	vsOH=15/8 hours vsO ₃ =62/248 hours
α -pinene/ β -pinene	136	–	$\text{C}_{10}\text{H}_{16}$	vsOH=5/3.5 hours vsO ₃ =3/19 hours

We monitored the acquisition of the ion masses summarized in Table 1, sorted by peak families: as already mentioned, core ions XH^+ can be hydrated with several water molecules and thus be detected at masses higher by several multiples of 18 amu than their original core ion mass. Consequently, at one mass, there can be a contribution of the types XH^+ , $\text{Y}(\text{H}_2\text{O})\text{H}^+$, or $\text{Z}(\text{H}_2\text{O})_2\text{H}^+$ etc. Therefore, one mass can be the signature, not only of different compounds having the same mass as X (isomeres), but also of compound having the mass of Y, Z, etc. In order to distinguish one compound from the other, the count rates of clusters versus the

number of hydrates associated to the core mass are studied. Distributions obtained are shown Fig. 3 for the driest and the wettest day of the campaign (20/03/2003 with a water vapor mole fraction of 2000–2500 ppm and 23/03/2003 with 6500 ppm), as well as for the calibration tests when available (i.e. for DMA, acetonitrile, acetaldehyde, methanol and isoprene). For the reactant ion H_3O^+ , the maximum count rate is observed for $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ clusters with $n=3$. Because hydronium ions have hydration enthalpies larger than any other ion species (Keese et al., 1986), and H_2O exchange reactions are fast compared to the ion-molecule reactions with

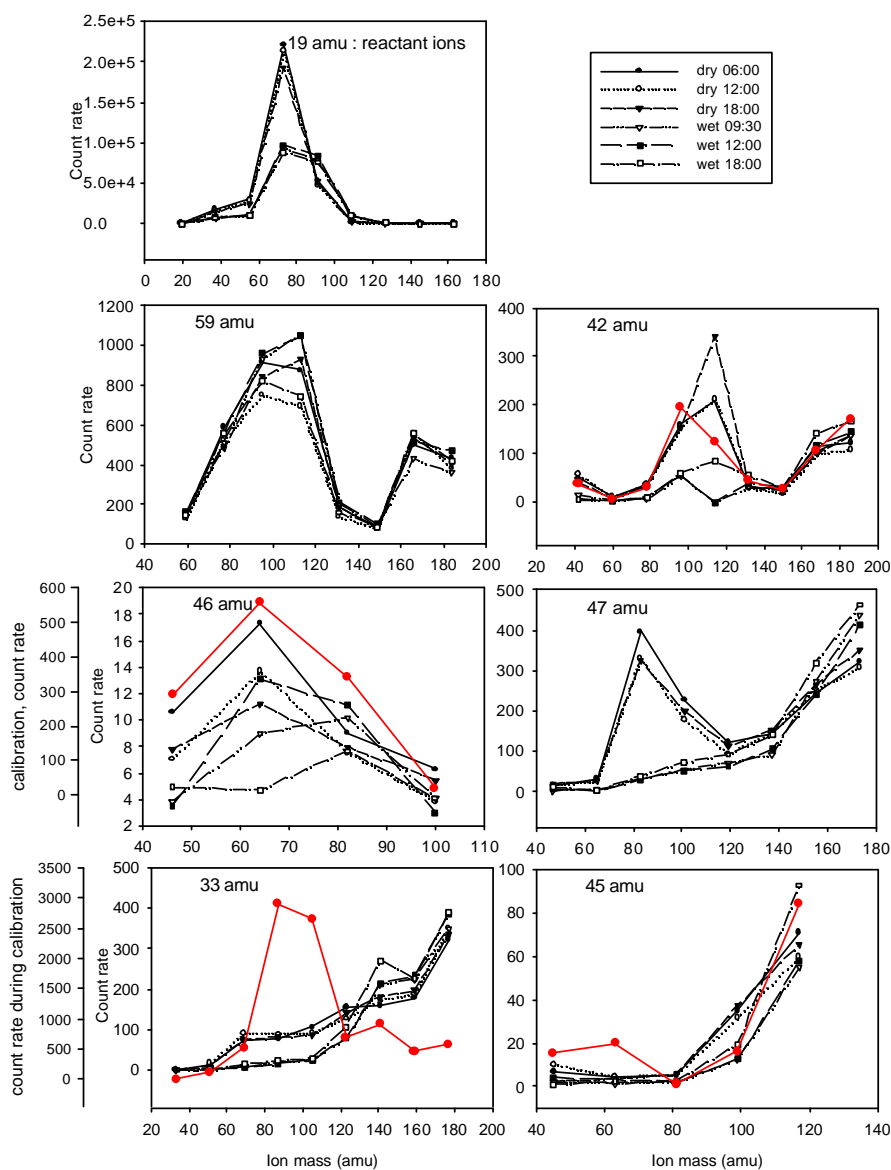


Fig. 3. Count rates plotted against the increasing hydration states of the core ions, averaged over different times in the day for the driest and wettest days of the campaign. Red curves are for calibrations with standard bottles when possible.

trace gases of interest (Wohlfrom, 2000), maximum count rates for other species than H_3O^+ are observed for n equal to or lower than 3. This observation is confirmed during calibrations of acetonitrile, acetaldehyde, methanol, isoprene and DMA, when the count rates show a maximum for $n=3, 1, 3, 2$ and 1 respectively in a 4000 ppm water content air, and also for acetone which shows a maximum count rate for $n=2$ or 3 depending on humidity.

Because 33 amu, 42 amu, 45 amu, and 46 amu are relatively low molecular masses, atmospheric compounds which are a combination of C, O, N and H with a higher proton affinity than the one of water (Table 2), which are candidates for these masses are of limited number. For these four

masses, candidates are respectively protonated methanol, acetonitrile, acetaldehyde and DMA, and we did not find any other compound with the required characteristics mentioned above that could interfere at the same masses.

Atmospheric hydrate distributions of the peak families corresponding to mass 33 amu show a maximum count rate plateau on masses 69, 87 and 105 amu. During calibration of methanol and isoprene with a ratio of 1:1, we also observed a maximum for masses 87 and 105. These masses would correspond to $(\text{H}^+\text{methanol}(\text{H}_2\text{O})_{3,4})$ or to $\text{H}^+\text{isoprene}(\text{H}_2\text{O})_{1,2}$. Thus masses 69 and 87 amu are expected to be mostly representative of methanol, and mass 105 amu is expected to be mostly representative of Isoprene.

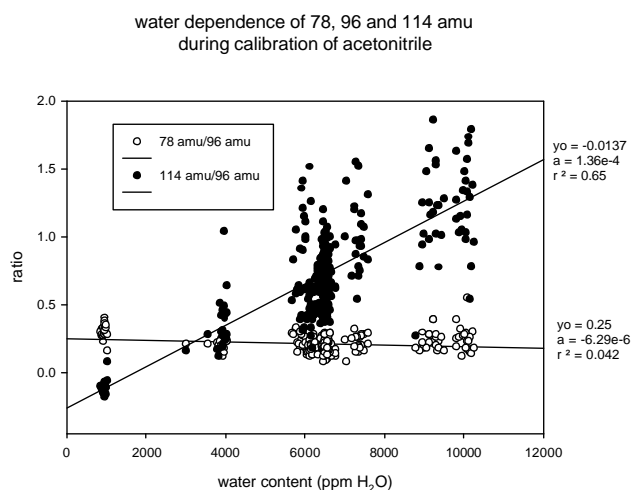


Fig. 4. Ratios of 96/114 and 96/78 amu versus water content of the analyzed air mass during calibration of acetonitrile.

Consequently, calculation of the methanol concentration will be based on masses 51, 69, and 87 amu, while isoprene concentrations will be calculated on the basis of masses 105, 123 and 141 (Table 3). In fact, mass 141 is occasionally also a maximum count rate in this peak family, and it would stand for H^+ isoprene(H_2O)₄, which should be smaller than H^+ isoprene(H_2O)₃. Another candidate in this peak family is 2-methyl-3-buten-2-ol (hereafter referred as MBO) which protonated mass is 87, and that could contribute to the same masses as isoprene. MBO is also a biogenic hydrocarbon that has already been measured in the ambient air of a pine forests (Goldan et al., 1993; Spaulding et al., 2003) and in a subalpine forest by Karl et al. (2002). Measurements of MBO interfere with measurements of isoprene in the PTRMS method as well (Karl et al., 2002). However, the pine species found in Hyytiala are not MBO-emitting species and MBO will not be considered to contribute to the mass 69 amu mixing ratios.

Atmospheric hydrate distributions of the peak families corresponding to mass 42 amu (acetonitrile, CH_3CN) show a maximum count rate at 114 amu, which would correspond to $(\text{H}^+\text{acetonitrile}(\text{H}_2\text{O})_4)$. During calibration of acetonitrile though, a maximum count rate is observed for 96 amu, corresponding to $\text{H}^+\text{acetonitrile}(\text{H}_2\text{O})_3$. This would indicate that a compound with a mass of the type $41+x18$ amu (where x could be 1, 2 or 3) is actually measured in the atmosphere and overlapping acetonitrile hydrate distribution. The protonated compound X which would give a maximum count rate at 114 amu in atmospheric air for $n=3$ (i.e. in the form $\text{H}^+\text{X}(\text{H}_2\text{O})_3$) would have the mass 60 amu. The candidate for this mass is trimethyl amine (TMA). Once respectively protonated and hydrated, TMA (59 amu) and acetonitrile (41 amu) have both a signature at 60 amu, and furthermore at 78 amu and 96 amu. For the calculation of their re-

spective mixing ratio, we have, during calibration of acetonitrile in zero air (where TMA mixing ratios were less than 10 ppt), calculated the ratio of $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_3$ (mass 96) to $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_2$ (mass 78) and $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_4$ (mass 114) for different water vapor contents. We obtain a “shape” of clustering hydrate distribution of CH_3CN for different relative humidity. Ratios of mass 96 to masses 114 and 78 amu are proportional to the water content, as shown Fig. 4. Thus, for calculation of respectively acetonitrile and TMA mixing ratio in atmospheric air, the shape clustering hydrate distribution of CH_3CN for different relative humidity is assumed to be the same as for calibrations. Then, the contribution of acetonitrile to mass 96 amu is calculated from the count rate ratio mass78/mass96 (Fig. 4) measured during calibrations of acetonitrile, 78 amu presumably all due to acetonitrile. Once calculated, the contribution of acetonitrile to mass 96 is subtracted from the measured count rate of mass 96 in order to obtain the contribution from TMA to this mass. The same procedure is applied for mass 114 amu. After calculation, we did not find any correlation or anti-correlation between acetonitrile and TMA or acetonitrile and H_2O or TMA and H_2O , indicating that there was no bias in the calculation and that both compounds are clearly distinct from each other.

Atmospheric hydrate distributions of the peak families corresponding to mass 45 amu do not show a clear maximum count rate in atmospheric air, but do show a maximum count rate during calibration of acetaldehyde for 63 amu, corresponding to $\text{H}^+\text{acetaldehyde}(\text{H}_2\text{O})$. Count rates raise again after mass 81 amu (Fig. 3), indicating that a compound different from acetaldehyde is responsible for these count rates, and only masses 45, 63 and 81 were taken into account in the acetaldehyde mixing ratio calculation.

Atmospheric hydrate distributions of mass 46 amu (DMA) show a maximum count rate for mass 64 amu, which corresponds to $(\text{DMA}(\text{H}_2\text{O}))$, in agreement with the hydrate distributions of calibrated DMA.

Both protonated ethanol and formic acid are candidates for mass 47 amu. Respective proton affinities of ethanol and formic acid are 185.5 and 178 kcal mol⁻¹ (Table 3), which are similar. Thus it is difficult to distinguish between the two compounds from their hydration, which shows a maximum count rate at $n=2$. Also Lindinger et al. (1998) found both compounds with a signature 47 amu. Similarly, protonated propanol or acetic acid are candidates for mass 61 amu, with respective proton affinities of 189.4 and 188 kcal mol⁻¹. However, Lindinger et al. (1998) found that while acetic acid has a signature at 61 amu (in the regular protonated form HX^+), Propan-1-ol and Propan-2-ol have a signature at 43 amu, corresponding to the loss of a molecule of H_2O . In this study, hydrate distributions in atmospheric air show a maximum count rate at $m=97$ amu which would stand for propanol(H_3O^+)₂ or acetic acid(H_3O^+)₂.

Possible contributors to mass 59 amu include acetone, propanal and glyoxal. Propanal have been excluded by PIT-

Table 3. Masses taken into account for MR calculation.

	acetone	acetonitrile	acetal	TMA	DMA	methanol	ethanol/formic acid
Masses (amu)	59; 77; 95; 113; 131	42; 60; 78 ;min(96, 96 _{calc}); min(114, 114 _{calc})	45; 63; 81	96-min(96,96 _{calc}) 114-min(114,114 _{calc}) 132	46; 64; 82; 100	51; 69; 87	47; 65; 83 101; 119
	propanol/acetic acid	isoprene	MVK/MACR (70)	monoterpenes (136)	MTOPI (168)		
Masses (amu)	61; 79; 97; 115	105; 123; 141 125; 143	71; 89; 107 173	137; 155	169; 187		

MAS studies in aircraft-based atmospheric measurements (Shröder et al., 2003). Glyoxal has a short atmospheric lifetime due to rapid photolysis, and the variability of the signal associated to mass 59 amu shows a lifetime close to the lifetime of acetone. Hydrate distribution of the peak serie of mass 59 shows a maximum count rate for $n=2$ clusters for the driest day, and for $n=3$ clusters for the wettest day. Consequently, count rates of masses 59, 77, 95, 113 and 131 amu are taken into account to calculate the acetone concentration according to Eq. (3).

Possible contributors to mass 69 include protonated isoprene, cyclopentene, and furan. Candidates for mass 71 amu are protonated methyl vinyl ketone and methacrolein, hereafter referred as MVK/MaCR, which are both oxidation products from isoprene (Williams et al., 2000). Correlation between mass 69 amu and mass 71 amu are highly significant during the QUEST campaign (Fig. 5a). Good correlation was also observed between isoprene and MVK+MACR with an airborne PTR-MS (Warneke et al., 2001). Consequently, at this stage, we propose isoprene as a candidate for mass 69 amu, and the sum of MVK and MaCR, as oxidation products of isoprene for mass 71 amu.

A maximum count rate is observed for mass 169 amu, leading to high mixing ratios for the compound contributing to this mass. The contribution to mass 169 amu can be of the types XH^+ , $Y(H_2O)H^+$ or $Z(H_2O)_2H^+$, where Z is 132 amu, Y is 150 amu and X is 168 amu. For each of the compounds X, Y and Z, a candidate was investigated:

- A possible contributor for 132 amu is glutaric acid. With a molecular structure containing to carboxyl groups, glutaric acid has a high potential to form hydrogen bonds. However, there is little information on the proton affinity of this compound. We tested its capacity to be measured with the CIMS instrument by injecting vapours of a 1% aqueous solution of glutaric acid into a proton transfer instrument (PITMAS). No signature of glutaric vapours was found in the PITMAS spectra, indicating that its proton affinity is not high enough to be measured with this method.

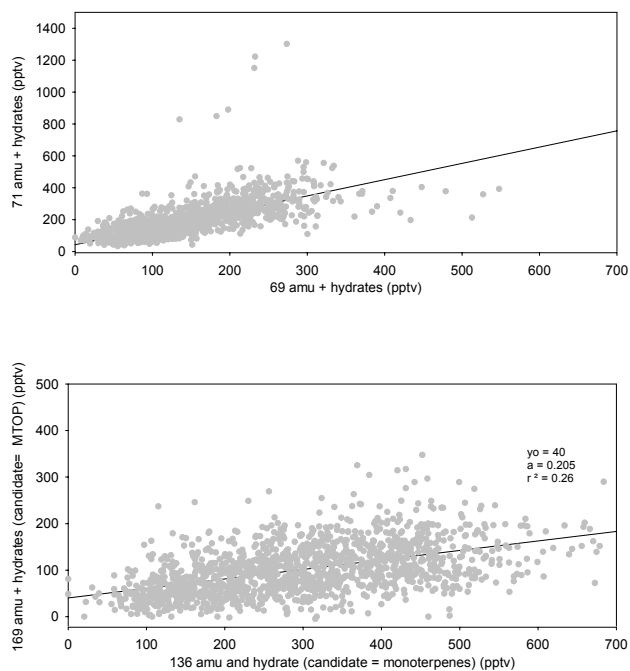


Fig. 5. (a) Correlation between the total count rate of mass 69 amu and hydrates (candidate is isoprene) and mass 71 amu and hydrates (candidates are MVK and MaCR) (b) Correlation between the total count rate of mass 137 amu and hydrates (candidate is monoterpenes) and mass 169 amu and hydrates (candidates are pinonaldehyde and other monoterpene oxidation products MTOPI).

- We did not find any combination of C, O, N, H which could be an atmospheric compound of mass 150 amu with a proton affinity larger than water.
- One contributor to mass 169 amu can be pinonaldehyde. This compound has been identified as a major oxidation product of pinene (Hakola et al., 1994; Yu et al., 1999). Other oxidation products of monoterpenes (MTOPI) such as 3-carene, limonene and terpinolene can also contribute to the mass of 169 amu (Hakola et al., 1994). If mass 169 amu is composed of XH^+

with X being pinonaldehyde or another MTOP, it implies that pinonaldehyde is poorly hydrated, the $n=1$ hydrate (mass 187 amu) being less abundant than the $n=0$ hydrate (mass 169 amu) (Fig. 3). This is consistent with the fact that a similar poor hydration was observed during the calibrations of the other aldehyde (acetaldehyde), which maximum count rate was for the clusters containing only one molecule of water, and with previous observations of poor hydration of saturated aldehydes (Spanel et al., 2002).

Consequently, the most likely candidate compounds contributing to mass 169 amu are MTOP. Moreover, a maximum count rate is observed for mass 173 amu (peak family 47 amu), with a possible contribution of the type $Z(\text{H}_2\text{O})_2\text{H}^+$, with Z being mass 136 amu, representative of α -pinene and other monoterpenes. Mass 136 has already been reported to be an indicator for monoterpenes at forest sites (Helmig et al., 1998; Wisthaler, 2001). Also, selected ion flow tube studies have shown that monoterpenes M (α -pinene, β -pinene, limonene, Δ^3 -carene, myrcene and camphene) react with H_3O^+ via proton transfer at the collisional rate and result in the protonated MH^+ with mass $m/z=137$ amu (Schoon et al., 2003). Correlation between the proposed candidates monoterpenes and MTOP are fairly good (Fig. 5b), confirming our hypothesis.

4 Calibration factors and Reverse reactions (water dependence)

Calibrations have been performed using standard gases bottle (DMA, acetonitrile, acetaldehyde, isoprene and methanol). The intensity of reverse reactions (Eq. 2) can be evaluated from the dependence of calibration factors on the water vapor mixing ratio. For DMA and isoprene, the water dependence of the calibration factor is less than a factor 1.5 between 2000 and 6500 ppm H_2O (range of water content during the campaign). For methanol and acetaldehyde though, a clear dependence of the calibration factor on the water content is observed with a high increase up to 25 times less methanol measured than injected at 6000 ppm. For acetonitrile, no water dependence is observed below 6000 ppm H_2O ; an abrupt rise is measured for higher water contents but water contents were not higher than 6500 ppm during the QUEST campaign. These observations are in agreement with the theory already mentioned, that the closer is the PA of the measured compounds to the PA of water, the more efficient will be the reverse reaction.

Acetone has been calibrated and reverse reactions with water studied with the CIMS apparatus in previous work (Wohlfrom et al., 1999). Calibration factors and water dependence were found to be very similar to the ones found for acetonitrile (in agreement with their similar PAs).

For other un-calibrated compounds, it is necessary to evaluate if a reverse reaction is possible and significant. From the

known PA of compounds studied in this work, we can elaborate a scale of reverse reaction rate coefficients relative to the reverse reactions measured for calibrated compounds. Starting from isoprene (PA of 197), the water dependence is negligible in the range of 3000–6000 ppm of water. Thus also a low reverse reaction is found for DMA (PA of 218–225) and no reverse reaction is expected from compounds such as TMA and MVK+MaCR. However, for ethanol/formic acid (respective PAs of 185.5 and 178) and propanol/acetic acid (respective PAs of 189.4 and 188), a reverse reaction with water can occur and is not taken into account, leading to an underestimation of the mixing ratios calculated in this work. For these compounds, we will only be able to give a lower limit of the concentrations measured in the boreal forest atmosphere. According to the correction applied on calibrated species of equivalent PAs, the uncertainty on the mixing ratios measured for ethanol/formic acid, propanol/acetic acid, can be estimated to be up to a factor 4 for ethanol and high water contents. The lack of data on the PA of pinonaldehyde, other MTOP and monoterpenes make it difficult to evaluate the uncertainty on the mixing ratios calculated in this work, and they have to be considered as lower limits.

5 Concentrations and daily variations

Atmospheric trace gas mixing ratios are presented in Table 4, as well as the detection limits calculated as twice the standard deviation on the zero air levels. All compounds but DMA are above the detection limit, the highest mixing ratio is found for acetone, closely followed by mass 168 amu (candidate: MTOP). Variability of the daily variation can be seen on Fig. 6a, on which all data are plotted according to the time of the day; a smoothing procedure over 9 data points has been applied to make the features clearer. A median diurnal variation has been calculated over the two weeks measuring period as well (Fig. 6b). Two outstanding days are varying significantly from the median concentration (27 and 28 March), these days have been highlighted in Fig. 6a.

Background mixing ratios of acetone range between 200 pptv in the southern atmosphere and 500 pptv in the Northern atmosphere (Singh et al., 1995). The average mixing ratios measured during the Quest campaign are clearly above background levels, and varied from 1 to 3.5 ppbv. Acetone has been measured at similar mixing ratios (1–2 ppbv) over the rain forest (Pöschl et al., 2001), in rural areas in Eastern Canada (around 3 ppbv) (Biesenthal et al., 1998) but also in the upper troposphere (Wohlfrom et al., 1999) and at much higher mixing ratios in urban areas (1–18 ppbv from the Fraser valley, O'Brien et al., 1997). Acetone has both direct emission and secondary photochemical sources in the atmosphere. The major secondary source for acetone in the lower troposphere is the photochemical reaction of the OH radical and propane (Singh, 1994) and also monoterpenes (Wisthaler et al., 2001). Direct emission sources for acetone

Table 4. Detection limits calculated as twice the standard deviation of zero air level, and statistics on mixing ratios over the 2-weeks measurements.

(ppt)	acetone	acetonitrile	acetaldehyde	TMA	DMA	methanol	ethanol/formic acid	propanol/acetic acid
Zero air level	47	7.1	5.6	8.1	29.5	8.8	26.5	36.5
Detection limit	35	4.0	6.6	6.2	32.4	8.6	11	18
Mean	1495	75	36	59	12.2	334	318	107
Stdev	596	33	31	35.5	7.7	143	926	104
25ile	1091	51	15	34	7	229	73	34
75ile	1655	97	50	79	17	424	259	146
median	1370	66	33	55	12	330	135	85

compound X (68 amu)	isoprene/ compound Y (70 amu)	MVK/MACR/ (136 amu)	monoterpenes (168 amu)	MTOP
Zero air level	28.0	41	181	288
Detection limit (ppt)	12.0	11.6	87	86
Mean	140	185	301	603
Stdev	73	125	139	345
25ile	88	104	192	323
75ile	185	237	401	839
median	120	165	300	605

include anthropogenic and biogenic emissions, including direct emission from vegetation, decaying organic material, biomass burning (Singh et al., 1994) and possibly an oceanic source (Jacob, 2002). Acetone is removed from the atmosphere by photolysis, the reaction with OH radicals and wet and dry deposition (Jacob, 2002). The acetone diurnal variations show one peak during the morning between 10:00 and 12:00 and one peak during the early night with a maximum around 21:00. As most organic trace gases diurnal profile show a maximum around 21:00, it is believed that the onset of a nocturnal inversion is responsible for their accumulation close to the ground, including acetone. The morning peak can be ascribed to a strong photochemical source (thus related to the radiation diurnal profile), as well as it can be due to direct emissions from vegetation and soil (thus related to the temperature profile).

Isoprene is released to the atmosphere by forest areas in high quantities (i.e. 44% of the total VOC emissions by vegetation, Guenther et al., 1995). It is highly reactive, its oxidation products being methyl vinyl ketone (MVK) and methacrolein (MaCR) as the highest yield. In Hyytiälä, low concentrations are expected because of the type of vegetation, which is composed of poor isoprene emitters (Scots pine and Norway spruce) (Hakola et al., 2003). Isoprene has been reported to have a high seasonal variability, with a maximum during the growing season (from mid-June to mid-September in the boreal zone) (Hakola et al., 2000; Hakola et al., 2003) while its oxidation products MVK and MaCR remained constant through the year. Isoprene mix-

ing ratios reached 6.5 ppbv over the tropical rain forest in March (Warneke et al., 2001) and (isoprene+MBO) 8 ppbv over a Northern American temperate forest in July (Helmig et al., 1998), while the typical mixing ratios of isoprene and (MVK+MACR) measured during Quest were, as expected, much lower: roughly between 100 and 200 pptv. In fact, these mixing ratios are higher than previous measurements of isoprene on the site of Hyytiälä (average 41 ppt in August (Spirig et al., 2003) and average 10 pptv in May (Hakola et al., 2000)). This discrepancy can either be due to differences of analytical techniques, or to a contribution of another compound, to the masses selected for the analysis of isoprene. Our MVK+MACR mixing ratios are the same levels as the mass 68 amu mixing ratios (median 165 ppt). MVK and MaCR have been previously measured with the same level of concentration than isoprene during March 2001 at the SMEAR station (Hakola et al., 2003). Due to its sources and high reactivity with NO₃ at night (lifetime/NO₃ is 0.8 h, Seinfeld and Pandis 1998), isoprene is usually measured in the literature with a diurnal profile showing a maximum at 18:00 LT (Goldan, 1995; Lindinger, 1998; Biesenthal, 1998; Warneke et al., 2001). During the Quest campaign, isoprene showed a diurnal profile with three peaks: one in the morning around 8:00, one in the afternoon around 14:00 and the most important one around 21:00 starting around 18:00. The fact that isoprene reaches a maximum in the first part of the night is in contradiction with the late afternoon peak which is usually observed. For the increase of isoprene up to 21:00 to be ascribed to the onset of the

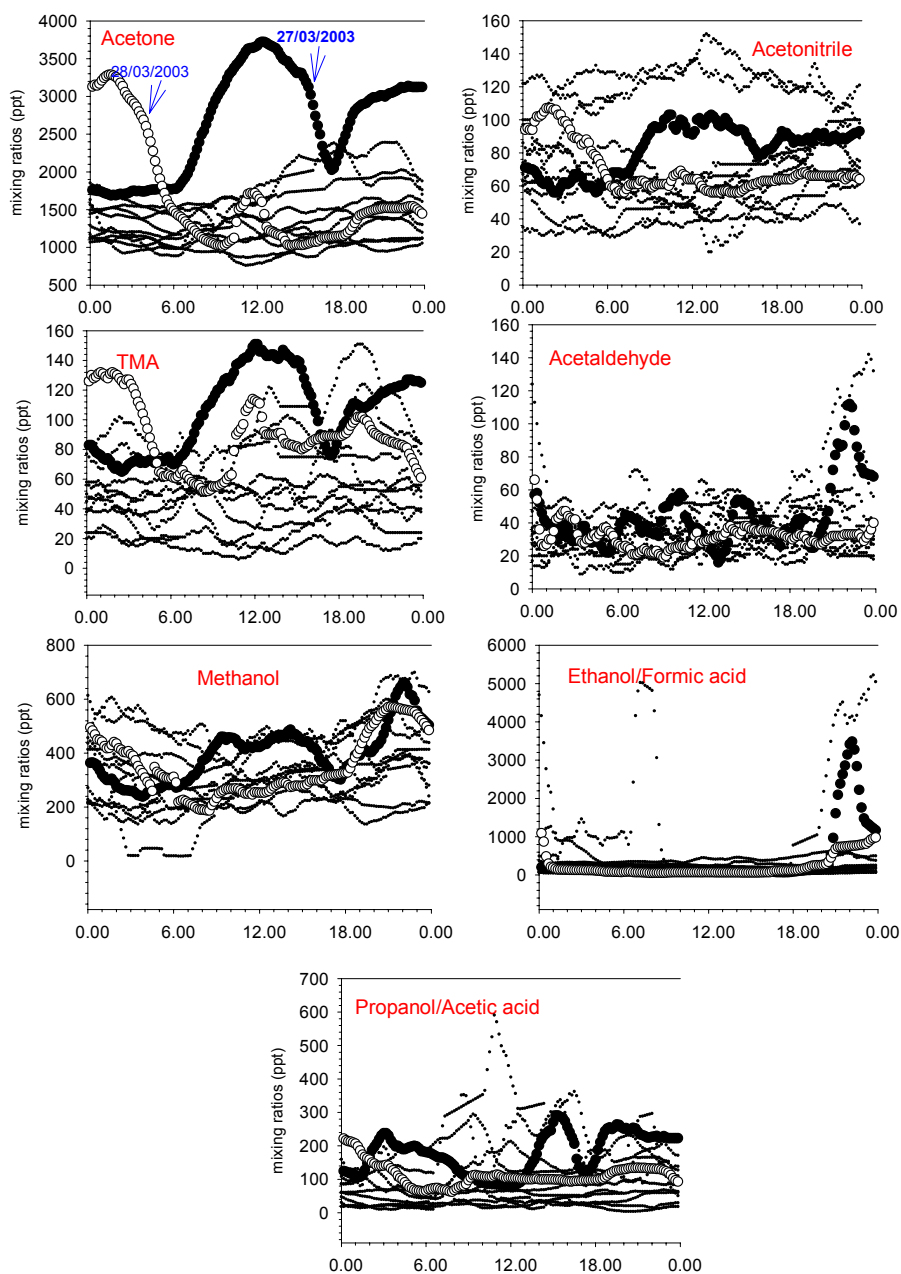


Fig. 6a. (a) Daily variation of mixing ratios for the whole measurement period.

nocturnal inversion layer, the source of isoprene has to be still active until two hours after sunset, which is improbable. MVK+MACR shows the same pattern as the daily pattern of isoprene, with a more pronounced morning and afternoon peaks and a broader night peak. Because of the level of its mixing ratios, which are high compared to previous measurements on the same site, and because of its diurnal variation, mass 68 amu+hydrates might contain the contribution of another compound than isoprene, night time emitted. However, we do not have any other candidate for this mass, which seems to be correlated to other biogenic compounds

(monoterpenes, MTOP and MVK+MaCR), and hence has probably a biogenic source. It is possible that at night, when isoprene mixing ratios are close to 0, the contribution from methanol on peak 105 is not negligible. Consequently, we will refer hereafter to mass 68 amu as isoprene+compound X, and, for the same reasons, mass 70 amu+hydrates will be referred to as MVK+MaCR+compound Y.

Mass 136 amu mixing ratios (candidate: monoterpenes) shows a median mixing ratio of 300 ppt. Similarly to isoprene, the total monoterpene concentrations usually have a high seasonal variability with a maximum in summer.

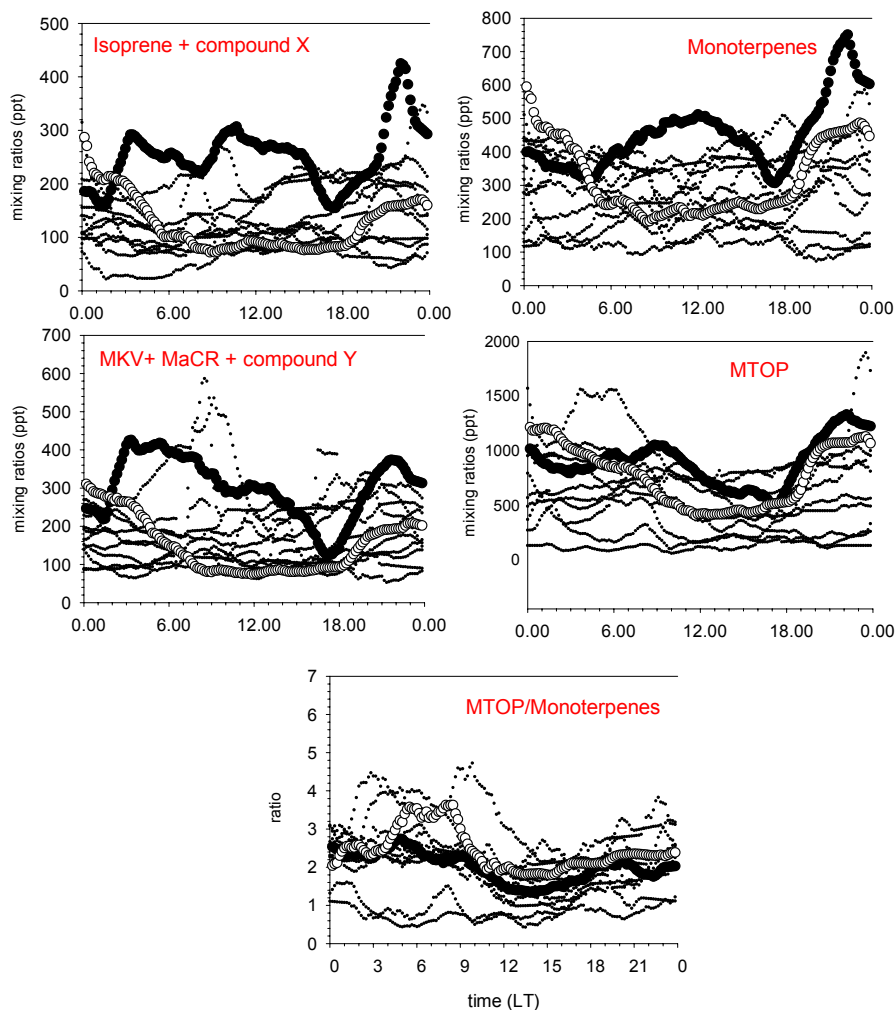


Fig. 6a. Continued.

Typical mixing ratios of around 500 ppt have been measured in April in the boreal forest (Hakola et al., 2000) and 360 ppt have been detected at 18 m above the ground during BIOFOR2 (Spanke et al., 2001), which lies within the range of our measurements. Spanke et al. (2001) previously measured in Hyytiälä a monoterpene daily variation showing a nighttime maximum and daytime minimum. We also measure a nighttime maximum although our daily variation is a little bit more complex with also two daily secondary maxima (Fig. 6b).

The MTOP mixing ratios measured in Hyytiälä were in the range 320–840 pptv, which are the highest mixing ratios measured after acetone. We choose Pinonaldehyde as a representative of those MTOP, as it is a main oxidation product of α -pinene, itself main monoterpene detected in the boreal atmosphere (Hakola et al., 2000; Spanke et al., 2003). The main production path of pinonaldehyde is the oxidation of monoterpenes with O_3 (Yu et al., 1999) or

OH radicals. Measured primary yields of pinonaldehyde from the reaction between α -pinene and OH radicals during chamber experiments were higher than the yields of acetone (respectively 30% and 12%, Wisthaler et al., 2001) and hence, high mixing ratios of pinonaldehyde are expected at the Hyytiälä site. However, to our knowledge, atmospheric measurements of MTOP are very scarce and comparison with other sites is difficult. Pinonaldehyde has been measured on the Hyytiälä site with maximum concentrations of 140 ppt, which indicate that other monoterpene oxidation products comprise a non-negligible part of the MTOP measured with CIMS. As already shown in Fig. 5b, MTOP and monoterpenes are correlated. Figure 6a shows that monoterpenes and MTOP have a similar diurnal variation, also very comparable to “isoprene+compound X” and “MVK+MaCR+compound Y” showing maximum concentrations early at night. This nighttime maximum of monoterpenes has previously been observed by Lindinger

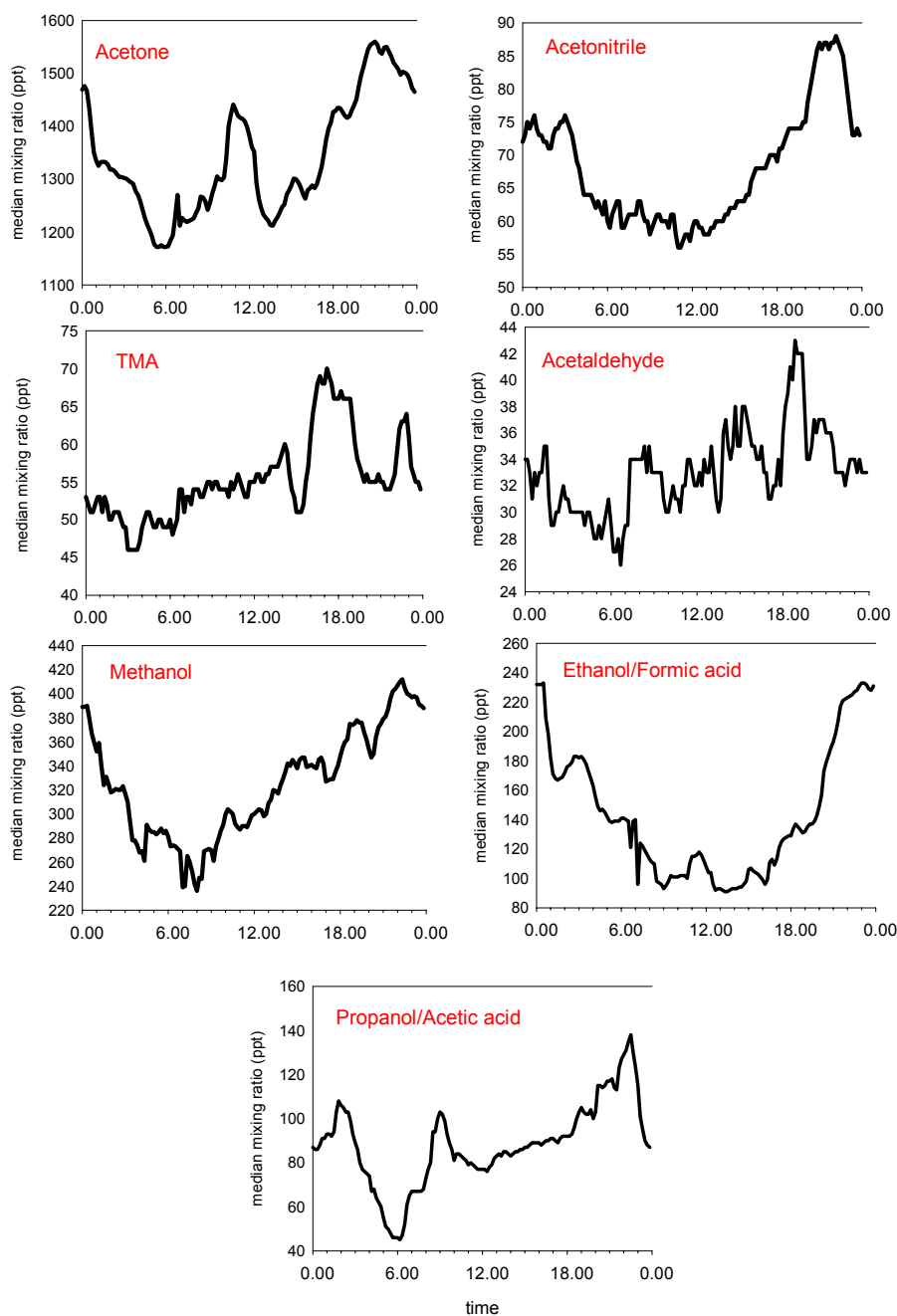


Fig. 6b. (b) Median daily variation of mixing ratios after smoothing procedure (ppt).

at al. (1998) and attributed to emissions by the wood during the day and during the night, but effective dissociation during the day. Monoterpenes nighttime maxima have also been observed by Hakola et al. (2000) and attributed to trapping of the emitted compounds in a nocturnal inversion layer. Hakola et al. (2000) do not measure any daytime peak, and explain this with a high OH radical sink and dilution by vertical transport. From our data set, daytime peaks are observed with the same covariation for isoprene+compound X,

monoterpenes, MVK+MaCR+compound Y and CO, with a mid-morning decrease of about 3 h. The yield of pinonaldehyde from monoterpenes was estimated to be 48%, and the yield of CO from pinonaldehyde was estimated to be 13.4% (Hatakeyma et al., 1991). However, the contribution of the oxidation of other organic compounds should be necessary to explain the change of several tens of ppb in the CO concentration. Hence, co-variations between CO and monoterpenes and MTOP are more likely due to dynamics-driven

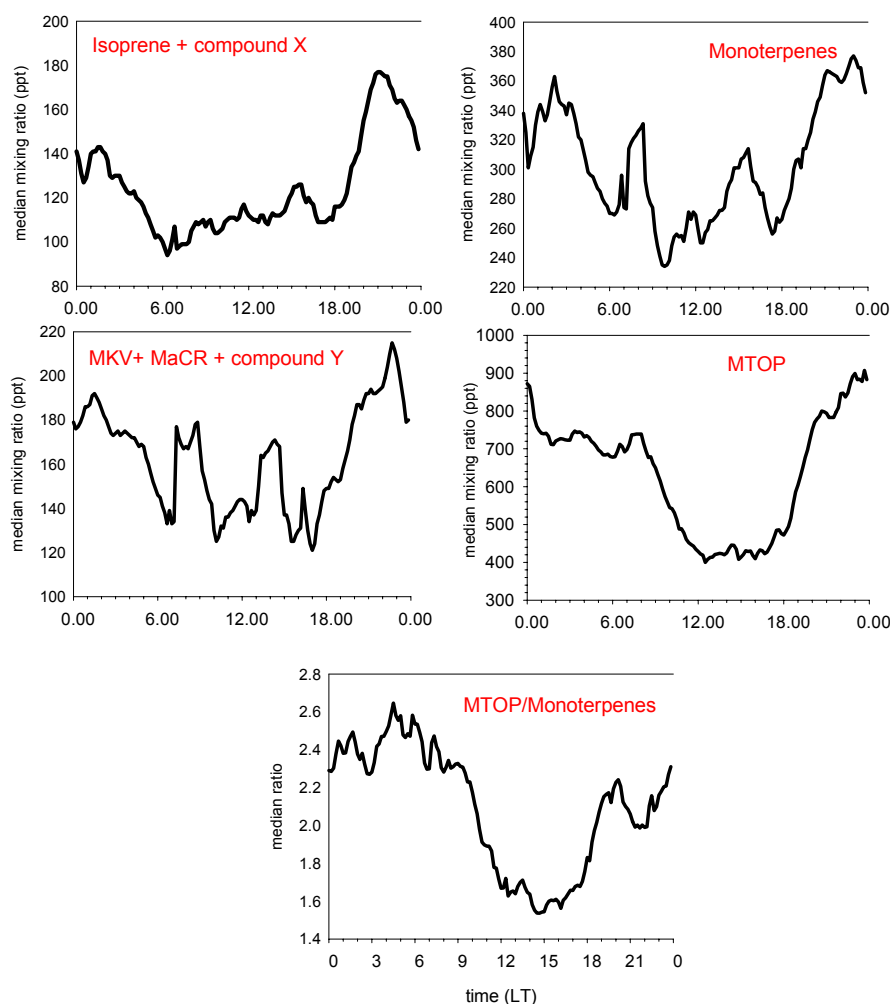


Fig. 6b. Continued.

variations of the concentrations. The daytime peaks of isoprene+compound X, and monoterpenes, are consistent with the diurnal variation of the emissions, which are temperature dependant. Compared to MVK+MaCR+compound Y, MTOP rarely shows a daytime peak though, and might be more rapidly removed in the presence of light. According to Glasius et al. (1997), pinonaldehyde reacts twice as fast as α -pinene with OH radical which would explain the low daytime mixing ratios of MTOP. Highest concentrations of BVOC oxidation products (and among them pinonaldehyde) have previously been observed to occur in the early morning hours (Spanke et al., 2001). The mid-day depletion is unexplained by photochemistry or dynamics, it is correlated with the increase of acetone, and with the appearance of the particle nucleation burst.

The diurnal variations of the ratio MTOP/monoterpenes show maximum values at night and a sharp morning decrease (Fig. 6a). This is in agreement with the higher reactivity to OH of pinonaldehyde compared to pinene, as mentioned above.

In the literature, emission rates of methanol were calculated to be larger than those of isoprene, methanol having a major biogenic source (Lamanna and Goldstein, 1999). Our measurements show mixing ratios varying between 230 and 425 pptv. These ratios are indeed two times higher than the mixing ratios of isoprene+compound X in Hyytiälä. However, methanol has been reported to be an ubiquitous compound in the atmosphere which levels in remote conditions are around 1 ppbv (de Gouw et al., 2003), which is twice as high as what we measured. Although the high water dependence of methanol due to non negligible reverse reactions has been taken into account with calibrations, the uncertainty on the mixing ratios of this compound are slightly higher than for other compounds, because of the additional uncertainty of the water vapor measurements and of the dependence of the calibration factor. Ethanol/Formic acid and propanol/acetic acid are respectively two and four times lower than methanol. Ethanol/Formic acid concentrations show a high variability (Fig. 6b), and there are indications of a contaminating source in the vicinity of the measurement

station. However, the contaminations are easily detected and can be excluded. Its median daily variations are similar to the ones of methanol with nighttime maximum and daytime minimum. Propanol/acetic acid do not show the same daily pattern as acetone on the particularly highly concentrated days (27 and 28 March, Fig. 6a), but show a similar median daily pattern then acetone (Fig. 6b), with a mid-day peak and a nighttime maximum.

In remote areas, acetonitrile has been found with mixing ratios of 100–150 pptv (Sprung et al., 2001). The mean mixing ratio found during QUEST is 75 pptv, with concentrations main variations between 50 and 100 pptv (25ile and 75ile). The major source of acetonitrile seems to be biomass burning (Holzinger et al., 1999), while anthropogenic fuel burning plays only a minor role (Holzinger et al., 2001). Acetonitrile may therefore serve as a tracer for biomass burning activity. Sinks of acetonitrile are the chemical reaction with OH radicals, dry or wet deposition. Lifetime against the reaction of OH and photolysis is of the order of magnitude of 1–3 years, thus much higher than the time scale of the condensing process. The mixing ratios of acetonitrile measured during Quest, found to be lower than mixing ratios in remote areas, would indicate that it is not locally produced. With such a long life time and without any local source, acetonitrile should be rather stable during the day. However, as for methanol and ethanol/formic acid, acetonitrile shows maximum mixing ratios at night and minimum mixing ratios during the day (Fig. 6b). Nighttime maxima of acetonitrile and ethanol can, as for acetone, be explained by the onset of a nocturnal inversion, together with higher destruction processes during day compared to night.

Mixing ratios of acetaldehyde measured during the campaign range between 15 and 50 pptv (25ile and 75ile). Acetaldehyde is a common photo-oxidation product of many organic compounds in the atmosphere, and itself a precursor of peroxyacetyl nitrate (PAN, $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) in polluted air. Acetaldehyde has one of the shortest day-lifetime of all analyzed compound (after isoprene) and is also destroyed at night by its reaction with NO_3 , but at a slower rate (night-lifetime/ NO_3 is 17days, Seinfeld and Pandis, 1998). Our daily variation of acetaldehyde are not very pronounced, which, together with the low mixing ratio measured at the site, indicate either the lack of a local source of this compound at the measurement site, or its immediate destruction. From Fig. 6a, there are indications that the contamination source producing ethanol also contained acetaldehyde.

DMA mixing ratios are below the detection limit of 32 pptv, and TMA mixing ratios vary between 34 and 80 pptv. TMA has a late afternoon peak which is not seen in any other compound measured at the site with this technique.

6 Summary and conclusions

The goal of this study was to address the different organic compounds measured with the CIMS method during the QUEST campaign. We proposed candidates for the masses observed in the spectra measured in the Boreal atmosphere. Based on the study of their hydrate distribution, methanol, acetonitrile, acetaldehyde, DMA, ethanol/formic acid, acetone, TMA, propanol/acetic acid, isoprene, MVK/MaCR, monoterpenes and MTOP are proposed in a first step as candidates for masses 32, 41, 44, 45, 46, 58, 59, 60, 68 70, 136 and 168 amu, respectively.

Concentrations of acetone are in the range of the concentrations found in the literature in forest areas, and acetonitrile in the range of concentrations found in remote areas. Methanol is measured with mixing ratios two times higher than in the remote regions, ethanol/formic acid and propanol/acetic acid are measured with concentrations respectively two and four times lower than methanol. Amines are found with the lowest concentrations.

However, the high hydration level of the analyzed compounds makes interferences with other compounds more likely. While monoterpenes have been measured with similar mixing ratios than previously found at the same site and same season, isoprene concentrations were about an order of magnitude higher and their daily variations do not show the usual pattern of a late afternoon maximum. Hence, most probably, isoprene is measured with the interference of a yet unknown biogenic, night-emitted compound X.

In fact, all of the measured organic trace gases but TMA show higher mixing ratios at night, in agreement with measurements of independent measurements of CO (Sellegri et al., this issue). This is ascribed to the onset of a nocturnal inversion, coupled with continuous emission by the forest into the night and higher dissociation during the day. In particular, oxidation products of monoterpenes and isoprene+compound X are significantly higher at night, implying that an active NO_3 chemistry is also taking place. In fact, the ratio MTOP/monoterpenes are higher at night by a factor 1.5. Daytime peaks are observed with the same covariation for isoprene+compound X, monoterpenes, MVK/MaCR and CO, with a mid-morning decrease of about 3 hours. The covariance may be indicative of a local important production of CO, or may be indicative that the dynamics of the boundary layer are the main factor influencing the organic concentrations on the site. The mid-day depletion may be indicative of a condensing process coinciding with the appearance of nucleation bursts.

This paper is preparing for further discussions on the implications that the detection of these species have on the atmospheric physics and particularly on the formation or growth of new particles in the boreal forest atmosphere. This matter is addressed in a companion paper (Sellegri et al., this issue).

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