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Measurements of organic gases during aerosol formation events in the boreal forest atmosphere during QUEST

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Abstract

Biogenic VOCs are important in the growth and possibly also in the formation of atmospheric aerosol particles. In this work, we present 10 min-time resolution measurements of organic trace gases at Hyytiälä, Finland during March 2002. The measurements were part of the project QUEST (Quantification of Aerosol Nucleation in the European Boundary Layer) and took place during a two-week period when nucleation events occurred with various intensities nearly every day. Using a ground-based Chemical Ionization Mass Spectrometer (CIMS) instrument, the following trace gases were detected: acetone, TMA, DMA, mass 68 amu (candidate=isoprene), monoterpenes, Methyl Vinyl Ketone (MVK) and Methacrolein (MaCR), cis-3-hexenyl acetate and MonoTerpene Oxidation Products (MTOP). For all of them except for the amines, we present daily variations during different classes of event days, and non-event days. Isoprene, monoterpenes, MVK+MaCR, cis-3-hexenyl acetate and MTOP are found to show significant correlations with the condensational sink (CS), which indicates that a fraction of these compounds are participating to the growth of the nucleated particles and generally secondary organic aerosol formation. Moreover, the terpene oxidation products (TOP) (MVK, MaCR and MTOP) show a higher ratio to the CS on event days compared to non-event days, indicating that their abundance relative to the surface of aerosol available is higher on nucleation days.

1. Introduction

Organic molecules have been found to be important constituents of atmospheric aerosols in many air masses (Novakov et al., 1997; Sellegri et al., 2003), and are often present together with sulfate and other inorganic species in a single aerosol particle (Murphy et al., 1998). However, the chemical composition of particles at an early stage of their formation (nano-particles) is still an open question, as the aerosol mass available for analysis is not sufficient. We know now that "atmospheric oxidation of biogenic hydrocarbons, such as monoterpenes, is estimated to be a significant source of global aerosol" (Yu et al., 1999), as established by several laboratory studies (Hoffmann et al., 1997; Griffin et al., 1999; Koch et al., 2000; Gao et al., 2001) and field studies (Leaitch et al., 1999; Kavouras et al., 1999). The important question related to the ability of organic gases to form secondary aerosol particles, i.e. when and how they are incorporated into the particulate phase, can be alternatively studied from the gaseous point of view.

Smog chamber experiments showed that very low organic-ozone reactant levels as precursor for the formation of new sub-μm aerosols were needed (Gao et al., 2001). In the boreal forest, frequent formation of new particles has been observed (Kulmala et al., 2001a), and VOCs (Volatile Organic Compounds) have been studied in relation to this new particle formation in different manners. Seasonal and diurnal variation of terpenes have been measured, using Tenax tubes (Hakola et al., 2000), emission fluxes of monoterpenes have been studied using Tenax tubes as well with a 2 h resolution (Janson et al., 2001), and vertical profiles of monoterpenes have been measured using tethered balloons and adsorbent cartridges (Spirig et al., 2003). However, high time resolution measurements of terpenes and particularly of their oxidation products, which are candidates for condensation, are missing to address the possibility of organic-induced nucleation.

VOCs are released from a wide variety of sources, and their mixing ratios measured at one point can be either dominated by a remote source or, in our case, by the local biogenic source or even a local pollution source. Most VOCs react with hydroxyl radicals (OH); some can be photolyzed, react with ozone, or at night with nitrate radicals (NO_3). In this work, we present measurements of organic gases with a high time resolution on the Hyytiala SMEAR II station site, using a ground-based CIMS instrument developed by MPI-K Heidelberg. Both the fast time response and the extended periods of measurements allow the study of the variability of mixing ratios, hence giving indications on the proximity of their sources/sinks. This paper aims to present the atmospheric time evolution of volatile organic gases in relation to nucleation events.

Dimethylamine (DMA), trimethylamine (TMA), the sum of Methyl Vinyl Ketone (MVK) and methacrolein (MaCR), cis-3-hexenyl acetate and pinonaldehyde are studied as organic candidates, or representative of organic candidates for nucleation and/or growth of the newly formed particles. Isoprene and the sum of monoterpenes are also reported as precursors of condensing species, and acetone are reported as indicators of biogenic degradation products as a whole.

2. Site and sampling characteristics

2.1. Site characteristics

The SMEAR II 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. Meteorological parameters including wind speed and direction, temperature, pressure, relative humidity, and global radiation are measured at different levels above the ground, using a 72-m-high mast on a permanent basis (Kulmala et al., 2001a). Gas measurements using the CIMS instrument presented in this work have been performed from a container located in the vicinity of the SMEAR II station, i.e. 50 m south-west, 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). Thus our trace gas measurements can be considered to have taken place in the same air masses as the SMEAR II station measurements. Meteorological conditions together with aerosol size distributions over the measurement period are summarized in Fig. 1.

Data presented in this paper are based on samplings achieved during 12 days: from 17 to 29 March 2001.

2.2. Instrumental

The Chemical Ionization Mass Spectrometer (CIMS) method is based on ion-molecule reactions involving gaseous ions and atmospheric trace gas molecules. An atmospheric gas X which has a proton affinity larger than that of H_2O (166.5 kcal mol^{-1}) reacts in the flow tube reactor with the reactant ions $H_3O^+(H_2O)_n$ (produced by an external high frequency glow-discharge ion source) via:

$$H_3O^+(H_2O)_n + X \rightarrow HX^+(H_2O)_n + H_2O. \qquad (1)$$

The residence time in the flow tube reactor is 3.2 s, allowing some fraction of X to react during traveling in the flow tube reactor. The X-concentration is determined. by measuring the abundance ratio of product and reactant ions. The scanning time for the mass range 1 to 200 amu is 40 ms.

Because the detection of organic gases with the CIMS technique used here allows only to determine the mass number of X, the exact chemical identification of X remains somewhat ambiguous (i.e. several different compounds might have the same mass), mixing ratios presented in this work, namely acetone, DMA, TMA, isoprene, MVK/MaCR, monoterpenes, cis-3-hexenyl acetate and MTOP are only the most likely candidates. Detailed analytical procedures, assumptions, calibrations and measurement problems are discussed in Sellegri et al. (accepted, 2004).

The routine measurements performed with commercial instruments at the SMEAR II station such as the meteorological data and CO concentrations are reported, as well as the measurements relevant to aerosol nucleation events performed as part of the QUEST campaign, such total number concentrations, and Condensational Sink (CS) (Kulmala et al., 2001b).

3. Results

3.1. Detected species relevant to particle nucleation in the boreal forest atmosphere

Isoprene and the sum of monoterpenes could be detected by CIMS, as well as, for the first time with this technique, some of their oxidation product with a 10 min resolution. We have to be cautious with isoprene concentrations, as the level of its mixing ratios and diurnal variations are not similar to what is usually found at the SMEAR II station. Methyl Vinyl Ketone (MVK) and Methacrolein (MaCR), both oxidation products from isoprene, and pinonaldehyde (major oxidation product of α-pinene), and other monoterpene oxidation products (hereafter referred as MTOP), were identified and measured with a 10 min resolution as well. Although monoteprenes, MTOP and MVK/MaCR calibrations could not be performed during the QUEST campaign, the CIMS instrument provides lower limits of mixing ratios (because all artifacts are leading to an underestimation of the concentrations: wall losses, water content dependant back reactions, use of the collision rate reaction constant)(Sellegri et al., accepted, 2004).

Pinenes are among the most abundant monoterpenes, and isoprene, α-pinene and Δ^3-carene were found to be the most abundant compounds among light hydrocarbon and monoterpene in the boreal forest (Hakola et al., 2000; Spanke et al., 2001). Our concentrations during the QUEST campaign ranged between 90 and 185 pptv (25 and 75iles) for isoprene, and 190 and 400 pptv for the sum of monoterpenes. Those concentrations are higher than previous measurements on the same site for isoprene (Hakola et al., 2000; Spirig et al., 2003). The sum of monoterpenes has been detected above the boreal forest canopy with concentrations of 360 ppt (Spanke et al., 2001), which lies within the range of our measurements.

Ozonolysis of α- and β-pinene can give aerosol carbon yields of 14–18% and oxidation of α- and β-pinene by OH can give carbon yields of 40–60% (Hatakeyama et al., 1989, 1991). According to the work of Yu et al. (1999), the major oxidation products of the reaction between O_3 and pinene or carene are usually aldehydes (pinonaldehyde for α-pinene and caronaldehyde for carene), showing that they are good tracers for the oxidation product of terpenes. It is those aldehydes which are detected by CIMS on mass 168 amu. Pinonaldehyde has been detected in the gas and aerosol phase after introduction of pinene and O_3 in a cloud chamber, showing that it is a condensable gas (Yu et al., 1999; Kavouras et al., 1999). Although the partionning of pinonaldehyde is only 1% in the aerosol phase, this compound is also representative for the other terpene oxidation products which have lower vapor pressures and can not be detected by the CIMS method (mostly dicarboxylic acids, Gao et al., 2001). Moreover, MTOP mixing ratios measured by CIMS in Hyytiälä were in the range 320–840 pptv, hence it is the second most abundant compound family measured with CIMS after acetone (Sellegri et al., accepted, 2004). Pinonaldehyde has been measured on the Hyytiälä site with maximum concentrations of 140 ppt. Other monoterpene oxidation products may comprise a large part of the MTOP that we measured with our technique but also, it is a considerable advantage to measure them online, compared to the classic cartridge measurement type which might imply several pre-analysis artifacts. The sum of MVK+MaCR was measured with ratios varying between 100 and 240 pptv (25 and 75iles), in agreement with our isoprene mixing ratios and previous measurement performed on the Hyytiala site (Hakola et al., 2003).

Dimethyl amine (DMA) and trimethyl amine (TMA) have also been found in atmospheric aerosols, and especially in aerosols with small sizes (Kulmala et al., 2001a). Thus they are integrated in the condensed phase either by dry condensation, either by dissolution in partially liquefied aerosols at higher relative humidity. DMA and TMA could be measured with CIMS for the first time. Vapor pressures for these two species are relatively high (respectively 203 and 215 kPa mol^{-1}), thus unary condensation is unlikely. However, DMA and TMA are highly soluble; a wet deposition on aerosol surfaces is expected. DMA mixing ratios are below the detection limit of 32 pptv, and TMA mixing ratios vary between 34 and 80 pptv. Both compounds are either poorly produced or efficiently removed from the boreal forest atmosphere. DMA and TMA are derivative of ammonia in which two or three of the hydrogen have been replaced by methyl groups. In the presence of TMA, measuring DMA mixing ratio lower than the detection limit would indicate that it has been produced and destructed by an efficient sink. Although DMA and TMA can not be excluded from condensing on newly formed particles during nucleation events, the low mixing ratios they showed during the campaign do not allow us to study further their times series.

3.2. Time series

For a large time scale overview of the evolution of mixing ratios during the measurement campaign, we applied a 9 data point box smoothing procedure to the 10 min resolution mixing ratios, and plotted the sum of them together with global radiation, condensational sink and independent measurements of CO (Fig. 2).

The beginning of the measurement period is characterized by northern clean air masses, until 21 March (Fig. 1, and also air mass back trajectories, low CO, NO and NO_x levels, Keronen, personal communication). Particle formation occurred every day under these clean-northern conditions (Period 1). West-Southern winds follow this period, with higher levels of pollution until 23 March. Nucleation is not observed on 22 March and very weak on 23 March (Period 2). From 23 to 26 March, Northern winds favoring nucleation are observed again, similar to the Period 1, even though the air mass origin is West. On 27 March, air masses are similar to the Period 2.

In general, the particle number rise due to nucleation is starting at mid-day and is slowly increasing further into the night, also followed by an increase of the CS generally showing a maximum during the night. Day and night, the sum of organics are clearly correlated with the Condensational Sink (CS) (Fig. 3), but not to the particle number concentration, indicating that concentrations of organics increase in parallel to the growth of particles freshly nucleated. Marti et al. (1997) have previously found that calculated oxidized organics were correlated to the CS in a remote continental site. Independent measurements of CO is also correlated to the condensational sink (Fig. 3) and to the sum of organic gases measured at the station. Oxidation products of terpenes have been previously found to be correlated to CO above a pine plantation (Spauling et al, 2003) and 40% of the estimated total emission of CO from the oxidation of natural hydrocarbons is accounted by oxidation of terpenes (Hatakeyama et al., 1991). Although both night-time increases can be due to the onset of a nocturnal inversion, the day-time covariance of VOC mixing ratios and CS are also observed, and indicate a possible cause-to-consequence link between VOCs and CS variations, i.e. VOCs are likely to condense on nucleated particle and participate to their growth to sizes relevant for CCN and radiative properties. If this is the case, obviously, the sum of organics measured by CIMS are not consumed efficiently by the condensation process, although it is difficult to conclude on the sink without estimating what the source term of these compounds are. In order to overcome this problem, we will hereafter study the event to non-event behavior of VOCs.

3.3. Average daily variations for event and non-event days

From 17 to 29 March, 10 nucleation events occurred (every day but for 22 and 27 March). Nucleation events were of various intensities and have been classified into three classes, from class 1 events (high intensity) to class 3 events (poor intensity) (Fig. 1, Miikka Dal Maso, personal communication). A mean daily variation is calculated for each of the event class and for non-event class (Fig. 4). 28 March was excluded, as part of the day was still non-event.

On both event and non-event days, ozone has a very similar daily pattern. Class 1 event days are characterized by a lower amount of water vapor and a lower temperature than other classes of event days and than non-event days. The particle total number concentration is rapidly increasing from 10:00 to 14:00 on class 1 and class 2 event days (from 2000 to 10 000 cm^{-3}) while it stays rather stable on class 3 event days and non-event days (between 1000 and 4500 # cm^{-3}). Going from class 1 to class 3, the mid-day peak of particle number is decreasing, while for all cases (all class event and non-event), a secondary late evening-early night peak is observed with the similar intensities.

Concentrations of all organic gases, as well as the CS, are higher on non-event days. In all cases (event and non-event days), acetone, isoprene, monoterpenes, MTOP, MVK+MaCR and cis-3-hexenyl acetate show the same pattern than the CS: a main night peak showing a maximum between 21:00 and midnight, and a mid-day peak, more or less pronounced and more or less early, depending on the specie. For class 1, class 2 and class 3 event days, the dawn peak is emphasized for the terpene oxidation products (MVK+MaCR and MTOP).

Covariance between terpene oxidation products (TOP), i.e. MVK and MTOP, and the CS can be further investigated by observing the correlation between their mixing ratios and CS on different event cases and on non-event days (Figs. 5a and 5b). When separating correlation plots day by day, we observe that the compound-to-CS ratio for class 1 and 2 event days is very different from the non-event and poor event days (class 3) ratio. While the TOP mixing ratios show little variations with CS changes during non-event days, the increase TOP/CS is 3 to 4 times higher for the event days. For MVK+MaCR, its behavior with increasing CS is the same for all event days, while it is different for MTOP. It is interesting to note that for 28 March, for which part of the day has the same characteristics then the non-event 27 of March and the other part of the day has the same characteristics than 29 March (event), MTOP/CS shows a mixture of event and non-event behavior (Fig. 5b). Consequently, although the representatives of TOP are measured with atmospheric mixing ratios lower during event days than non-event days, their ratio to the condensational sink are higher on event days. Hence TOP are, relatively to the condensing surface available, more abundant on nucleation days. This can also be seen on Fig. 6, showing TOP/CS ratio daily variation for class 1 and 2 events on one hand, and class 3 and non-event days on another hand. The TOP/CS ratio is rather stable through the diurnal variation and night-time maxima are not observed; there is a tendency of an early morning to mid-day increase of MVK+MaCR/CS during event days.

Variations of TOPs relative to their precursors can be studied (Fig. 7). On class 1nucleation days, MTOPs are either less produced, or more condensing/destroyed on nucleation days as shown by the MTOP/Monoterpene ratios on event and non event days. Ratios between monoterpenes and their oxidation products are in favor of the oxidation product on non-event days compared to the event days. This “depletion” of TOP during class1 nucleation days can be related to a higher light related reactivity (class1 event days are overall sunny, class 2, 3 and non event days are overall more cloudy), but also could indicate that, in comparison to the non-condensing terpenes, their sink by condensation is higher on class1 nucleation days. The difference between event and non-event days is higher for the ratio MTOP/monoterpenes than for the ratio MVK+MaCR/isoprene, in agreement with the lower vapor pressure of MTOP such as pinonaldehyde compared to MVK or MaCR, but also in agreement with the high OH reactivity of pinonaldehyde compared to Momoterpenes such as pinene (Glasius et al., 1997) .

4. Discussion

Results from the BIOFOR campaign (BIOgeic aerosol FORmation in the boreal forest), which took place on the Hyytiala sampling site during spring in the years 1998 and 1999 gave little support for the hypothesis that terpene oxidation products were the precursors to the observed new particle formation. They were however not excluded from taking an active part in the growth of the new particles (Janson et al., 2001). The reasons for these conclusions were that (1) SOC (Secondary Organic compounds) were higher at night when no nucleation occurred, and (2) SOC were not significantly higher during event days compared to non-event days.

There are similarities and discrepancies between our data set and the data set from the BIOFOR campaign:

- Mixing ratios were of similar order of magnitude during both field measurement campaigns.
- In both field measurement campaigns terpenes and their oxidation products have been found to be higher at night with a maximum between 21:00 and midnight.

- While a poorly significant enhancement of monoterpenes and of the calculated source terms for secondary organic compounds were found during event days compared to non-event days during BIOFOR, our QUEST data revealed an enhancement of organic compounds including terpenes during non-event days compared to event days.

Together with the fact that a strong correlation is found between the CS and biogenic organic compounds, our observations would lead to the same conclusion than during BIOFOR: a condensing rather than nucleating role of organics.

However, the parameter SOC/CS might be of higher significance to the nucleation processes than the only SOC mixing ratio absolute values. Then, based on the fact that the SOC/CS ratio is higher on event days than on non-event days, and that the aldehydes measured by CIMS, as monoterpene oxidation products, are representative of low vapor compounds not detected by CIMS, such as diacids., we can not exclude organics from being candidates for the new particle formation. Actually, also among the MTOPs measured with CIMS, some can have a relatively low vapor pressure. For example, pinonaldehyde has a vapor pressure of $4.4\ 10^{-2}$ kPa at 25°C, to be compared with the $2.7\ 10^{-6}$ at 25°C of sulfuric acid. Since MTOP were found with mixing ratios up to 10^4 higher than sulfuric acid mixing ratios (between 40 and 600 ppq, F. Arnold, personal communication), and pinonaldehyde is the most abundant representative of MTOP, it is probable that it condenses at a some stage of particle formation. In fact, the comparison of TOP/CS behavior between MVK+MaCR and MTOP shows a difference that could be due to an additional sink by condensation for the MTOP, compared to MVK+MaCR. Indeed, correlation plot for event days of MTOP vs. CS show negative MTOP mixing ratios when extrapoling to low CS, which could be an indication of the condensing process at the very early stage of particle formation.

5. Summary and conclusions

Measurements of volatile organic gases were performed with a 10 min resolution in the boreal forest atmosphere, using a ground-based CIMS instrument, as part of the QUEST project. Acetone, TMA, DMA, isoprene, monoterpenes, MVK+MaCR, cis-3-hexenyl acetate and pinonaldehyde were selected to study the relationship between biogenic gaseous emissions and nucleation and growth of new particles.

Mass 68 amu (candidate=Isoprene), monoterpenes, MVK+MaCR, cis-3-hexenyl acetate and MTOP are measured with a higher mixing ratio at night than during the day (maximum between 21:00 and midnight). The onset of a nocturnal stable surface layer is presumably trapping the night-produced VOCs (but also acetone and CO). These five biogenic organic species show a clear correlation with the condensational sink (CS), indicating that their concentration is increasing while particles grow. Most of these species do not have a sufficiently low vapor pressure to actively participate to the growth of the nucleated particles. However, they are representative of other terpene oxidation products (TOP) which are candidates for condensation. Also some of MTOP measured with CIMS, such as pinonaldehyde (amongst MTOP) have a relatively low vapor pressure and they are likely to condense on nucleated particle and participate to their growth to sizes relevant for CCN and radiative properties. As a whole though, the sum of the MTOP analyzed with the CIMS method are not consumed efficiently by the condensation process, i.e. their source is higher than their sink. In order to further study the possibility that some of the MTOP are candidates for nucleation, we have studied the event to non-event behavior of the TOPs detectable by CIMS. While always correlated to the CS, TOPs show a different co-variance with the CS on event and non event days. First, the ratio of TOP/CS is higher on event days than on non-event days. If the amount of condensing gas, corrected from the condensing surface available is indicative of the probability of nucleation (i.e. TOP/CS), then this probability is higher on nucleation days. Second, mixing ratios of TOP increase with CS by a factor 3 to 4 compared to non-event days. Moreover, the MTOP mixing ratios measured by CIMS in

Hyytiälä were in the range 320–840 pptv, which makes MTOP the second most abundant compounds measured with CIMS after acetone, and, considering the low vapor pressure of some of them, possible candidates for nucleation.

Amines were measured with the lowest mixing ratios, presumably because of their high solubility and high reactivity. The low concentrations of DMA and TMA prevented us from a reliable daily variability study and work must be continued to lower the detection limit of such species with the CIMS method.

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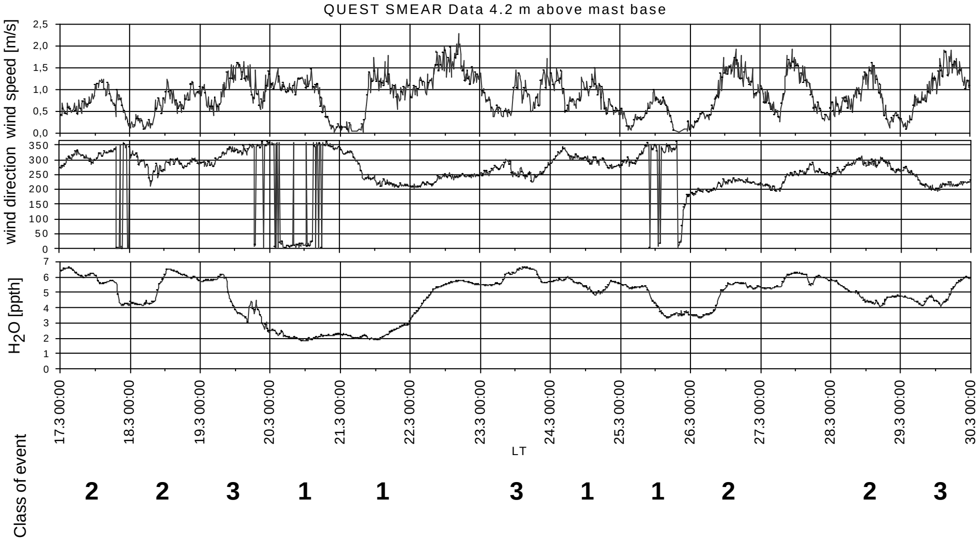

Fig. 1. Meteorological conditions (temperature, H_2O, wind speed and direction, radiation) during the two weeks measurement period. During this period, particle formation event occurred every day but on 22 and 27 March. Particle formation events are classified into three classes according to their strength, with decreasing strength from 1 to 3.

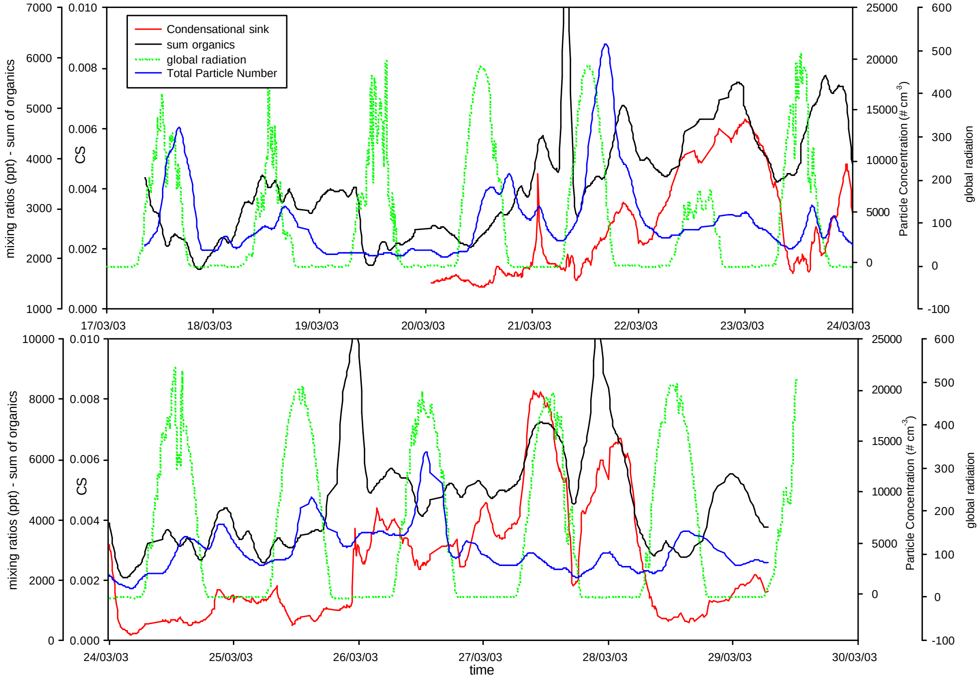

Fig. 2. Total organic gases measured with the CIMS technique, total particle number, condensational sink and radiation versus UTC time. A good co-variation is observed between the sum of detected organic gases and the condensational sink (calculated form the surface of particles available for condensation).

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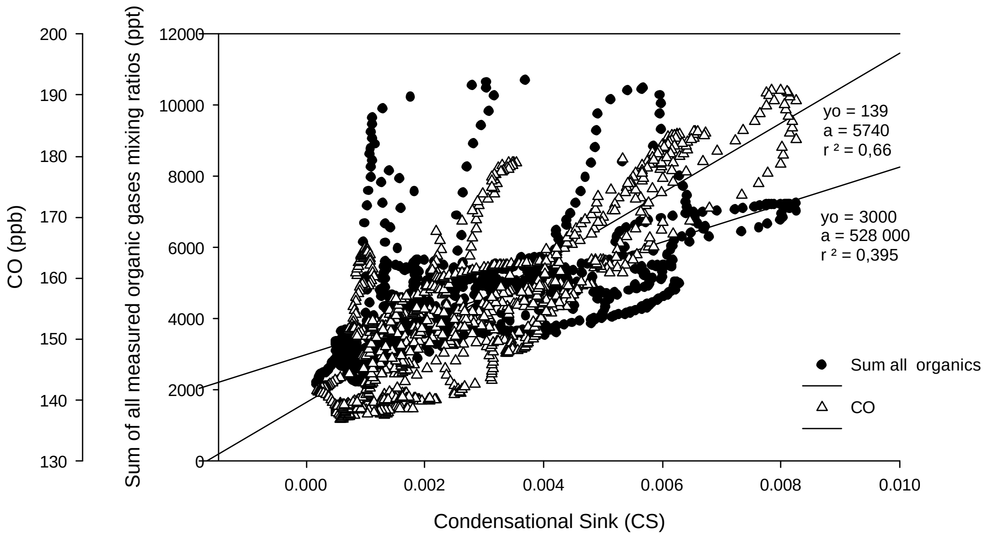

Fig. 3. Correlations plot between the sum of detected organic gases, CO, and the condensational sink (CS) including all data points. Significant correlations are observed between the sum of detected organics and CS, but also between independent measurements of CO and CS.

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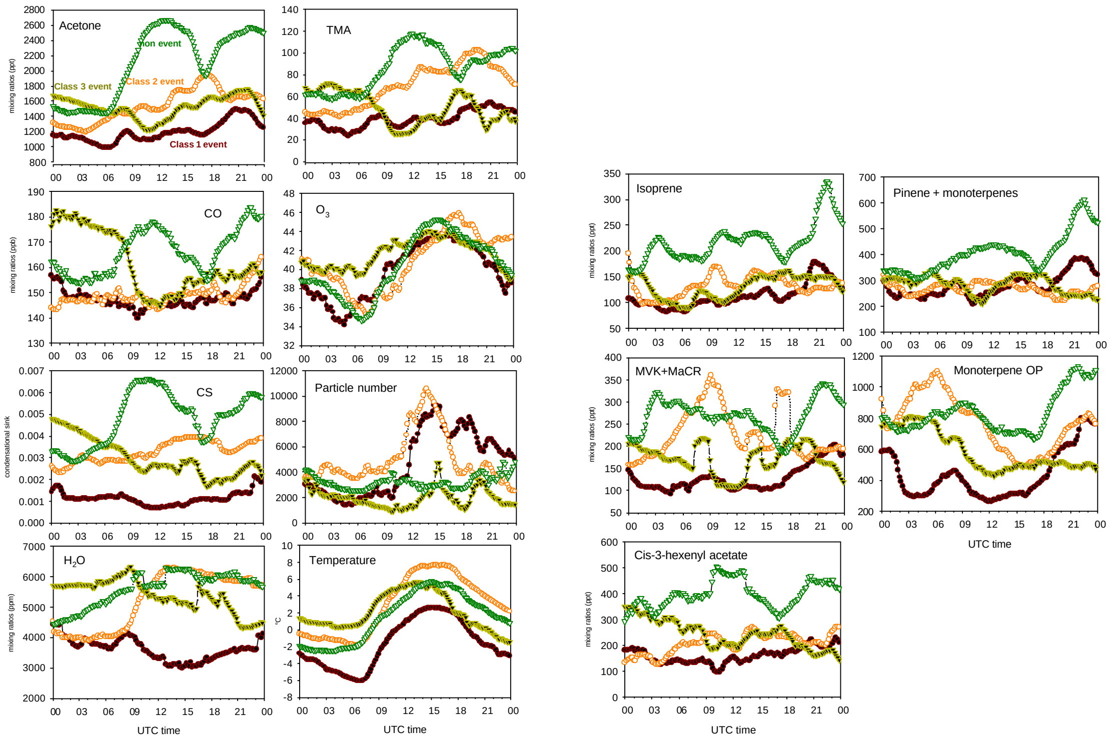

Fig. 4. Daily median concentrations of organic gases, ozone, H_2O, particle number, and CS class 1 event days (brown), class 2 (orange), class 3 (yellow) and non-event days (green). On non-event days, the condensational sink and most organic gases concentrations are higher than on event days.

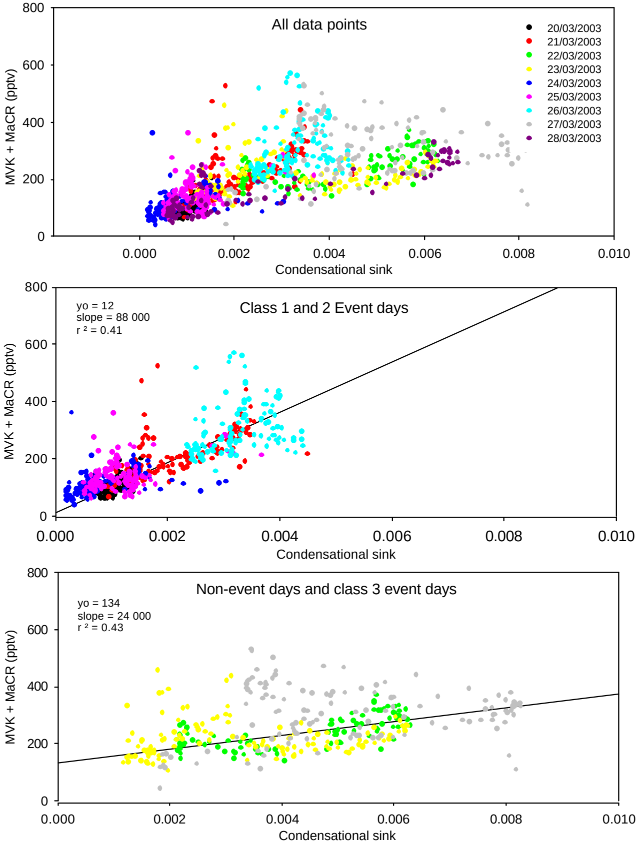

Fig. 5. (a) Correlations between the terpenes oxidation products MVK+MaCR and the Condensational sink for all data points (upper panel), for class 1 and class 2 event days (middle panel), and for class 3 and non event days (lower panel). **(b)** Same than Fig. 5a, but with the Monoterpenes Oxidation Products (MTOP). For both oxidation products, correlations are different on class 1+2 event days than on class 3 and non-event days.

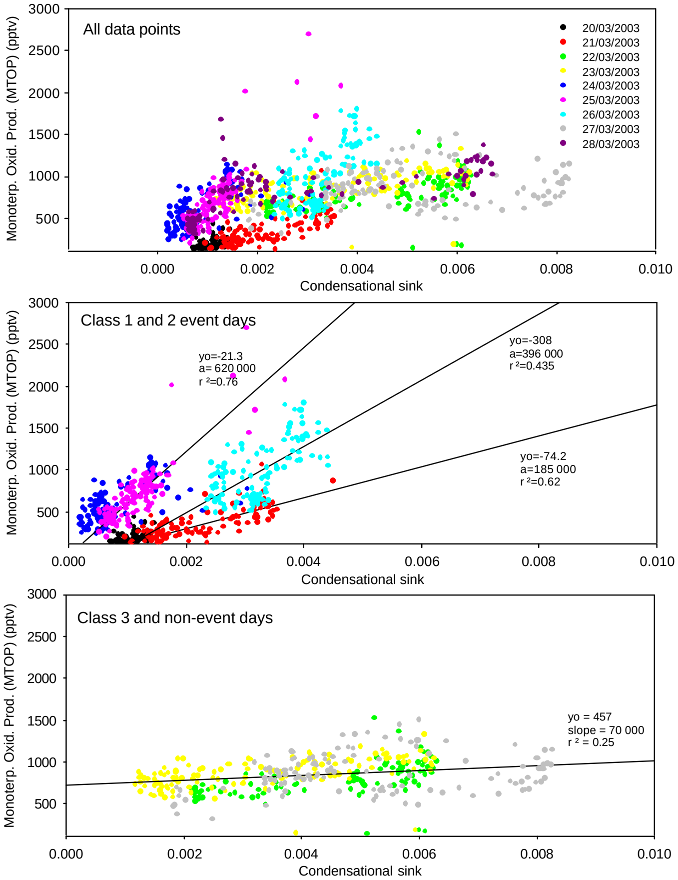

Fig. 5. Continued.

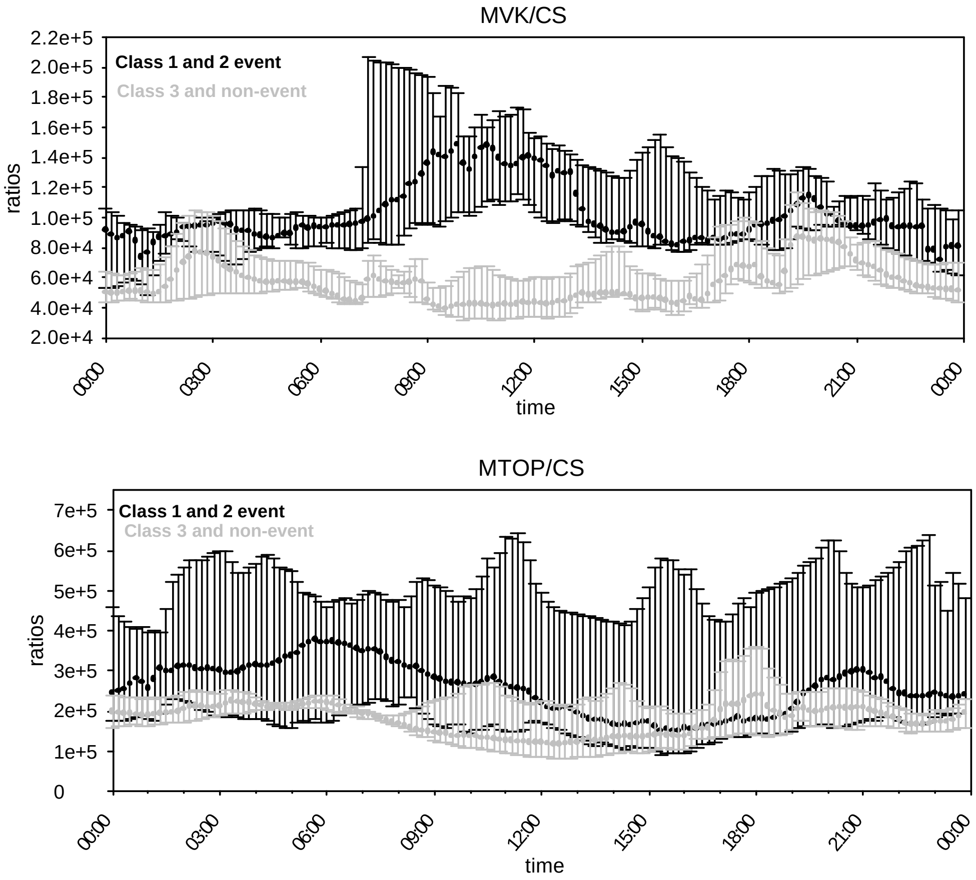

Fig. 6. Daily median ratios (MVK+MaCR)/CS (upper panel) and MTOP/CS (lower panel) during class 1 and 2 event days (black) and class 3 and non-event days (grey). Error bars are calculated from percentiles 25% and 75%. The ratio of MVK+MaCR to the condensational sink is higher on class 1 and 2 event days, and maximum during the day.

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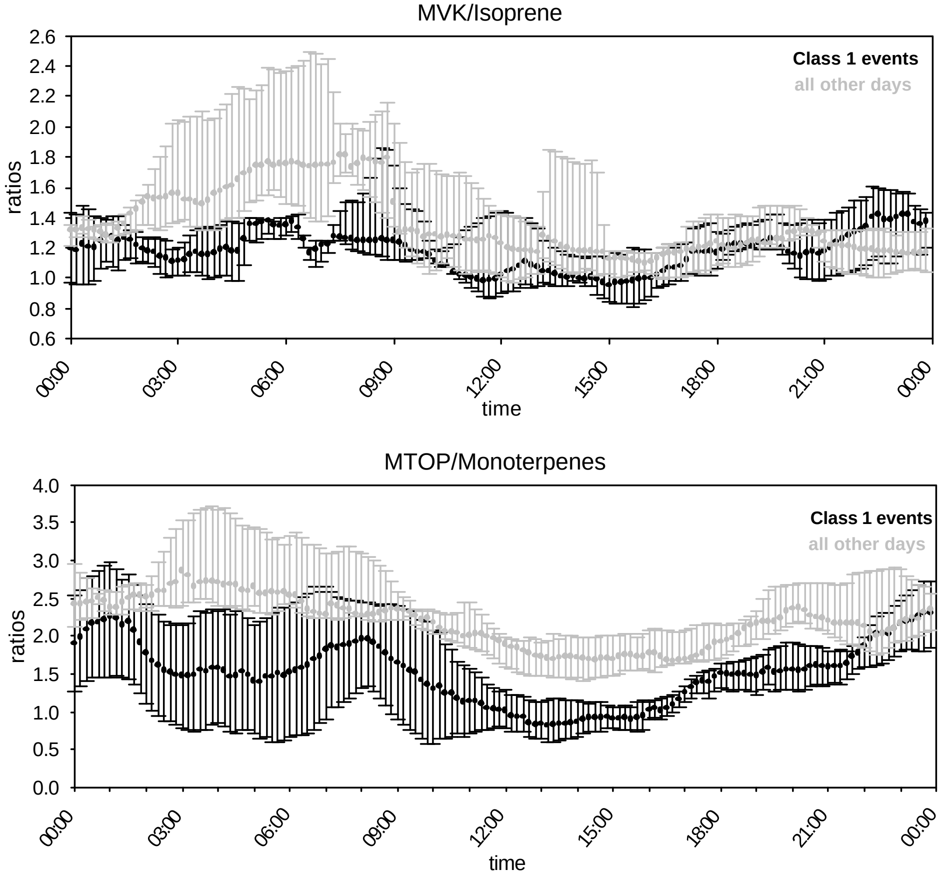

Fig. 7. Daily median ratios MVK+MaCR/isoprene (upper panel) and MTOP/monoterpenes (lower panel) during class 1 event days (black) and during all other cases (grey). Error bars are calculated from percentiles 25% and 75%. The ratios are in favor of the Monoterpenes Oxidation Products during class1 nucleation days compared to other cases.