Atmospheric
Measurement
Techniques
Open Access

Discussions

Characterisation of organic contaminants in the CLOUD chamber at CERN

R. Schnitzhofer[1], A. Metzger[2], M. Breitenlechner[1], W. Jud[1], M. Heinritzi[1], L.-P. De Menezes[3], J. Duplissy[3,5], R. Guida[3], S. Haider[3], J. Kirkby[3], S. Mathot[3], P. Minginette[3], A. Onnela[3], H. Walther[4], A. Wasem[3], A. Hansel[1,2], and the CLOUD Team[3]

[1]Institute of Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria
[2]Ionicon Analytik, Innsbruck, Austria
[3]CERN, Geneva, Switzerland
[4]Paul Scherrer Institute, Villigen, Switzerland
[5]Department of Physics, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland

Correspondence to: A. Hansel (armin.hansel@uibk.ac.at)

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

AMTD

6, 7709–7734, 2013

Cloud: VOC background characterisation

R. Schnitzhofer et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

The CLOUD experiment (Cosmics Leaving OUtdoor Droplets) investigates the nucleation of new particles and how this process is influenced by galactic cosmic rays in an electro-polished, stainless-steel environmental chamber at CERN (European Organization for Nuclear Research). Since volatile organic compounds (VOCs) can act as precursor gases for nucleation and growth of particles, great efforts have been made to keep their unwanted background levels as low as possible and to quantify them. In order to be able to measure a great set of VOCs simultaneously in the low parts per trillion (pptv) range, proton-transfer-reaction mass spectrometry (PTR-MS) was used. Initially the total VOC background concentration strongly correlated with ozone in the chamber and ranged from 0.1 to 7 parts per billion (ppbv). Plastic used as sealing material in the ozone generator was found to be a major VOC source. Especially oxygen-containing VOCs were generated together with ozone. These parts were replaced by stainless steel from CLOUD4 (June 2011) on, which strongly reduced the total VOC background. An additional ozone induced VOC source is surface assisted reactions at the electropolished stainless steel walls. The change in relative humidity (RH) from very dry to humid conditions increases background VOCs released from the chamber walls. This effect is especially pronounced when the RH is increased for the first time in a campaign. Also the dead volume of inlet tubes for trace gases that were not continuously flushed were found to be a short but strong VOC contamination source. For the later CLOUD campaigns lower ozone levels (below 100 ppbv) were used. During these conditions the total VOC contamination was usually below 1 ppbv and therewith considerably cleaner than a comparable Teflon chamber. On average more than 80 % of the total VOCs are coming from only 5 exact masses (tentatively assigned as formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid), which have a rather high vapour pressure and are therefore not important for nucleation and growth of particles.

1   Introduction

According to the IPCC 2007 report (Solomon et al., 2007) aerosols and clouds represent the largest uncertainties in global climate models and their estimated significant influence on the observed global warming remains poorly understood. The aim of the initial CLOUD (Cosmics Leaving OUtdoor Droplets) experiments at CERN (European Organization for Nuclear Research) is to thoroughly investigate the first crucial steps of cloud formation i.e. the nucleation of condensable vapors and how galactic cosmic rays (GCR) may enhance this process by ion-induced nucleation (Carslaw et al., 2002). The first results from CLOUD (Kirkby et al., 2011) showed that the enhancement due to ions and ammonia was insufficient to account for the nucleation of sulphuric acid particles in the lower atmosphere, indicating that organic ternary vapours are required. Organic trace vapours initiate the nucleation process together with sulphuric acid and are fundamentally involved in the subsequent growth of the initial cluster to gain the crucial size when water starts to condense and cloud droplets form (Metzger et al., 2010; Kulmala et al., 2013).

In the CLOUD experiments great efforts have been made to control the chamber conditions, including the introduced gases. Since organic vapours are expected to impact nucleation and growth of particles their background-levels need to be kept small. Despite a considerable number of similar experiments in various environmental chambers around the world, reports about background organic contamination are rare. Wisthaler et al. (2008) report an increase of formaldehyde and other C_2 to C_{10} aldehydes when ozone is inserted into the Teflon SAPHIR chamber (Jülich, Germany). Total organic contamination are given for the Teflon chambers EUPHORE $< 0.3\,\mu g\,m^{-3}$ (Bloss et al., 2005), PSI 4 ppbv (Paulsen et al., 2005), and Caltech Indoor Chamber Facility below limit of detection (Cocker et al., 2001).

In order to be able to measure a large set of different organic compounds the PTR-technique has been chosen to monitor the background concentration of organics in the chamber. The aim of CLOUD was to study first the effect of GCR on binary sulfuric

Back   Close

Full Screen / Esc

acid water nucleation and subsequently to investigate more complex systems such as the ternary sulphuric acid–ammonia–water system (Kirkby et al., 2011). Later on the impact of amines (dimethylamine, DMA) and organic compounds (Pinanediol, PD) on new particle formation and growth was studied (Almeida et al., 2013; Schobesberger et al., 2013; Keskinen et al., 2012). The first CLOUD chamber experiment (CLOUD1) was conducted during November–December 2009. So far 7 campaigns have been carried out, each one lasted between 1 and 3 months. Here we present data from CLOUD1-3 and CLOUD7.

2 Experimental

2.1 The CLOUD chamber

A $26\,\text{m}^3$ electro-polished stainless-steel cylinder is the central part of the CLOUD experiment. It can be temperature controlled over the whole range of atmospheric relevant temperatures (-65 to $100\,°C$), with an accuracy of $0.1\,°C$. The chamber can be evacuated from 1200 to 1000 hPa over any chosen time interval above 10 s, in order to simulate the adiabatic cooling in ascending air masses and form clouds. In addition, an adjustable π^+ beam from the CERN Proton Synchroton can simulate cosmic rays (for details see Duplissy et al., 2010, and Kirkby et al., 2011). A schematic drawing of the CLOUD chamber is shown in Fig. 1.

A crucial part of the chamber is the gas supply system. The CLOUD atmosphere consists of 79 % nitrogen (N_2) and 21 % oxygen (O_2), and a varying amount of trace gases like water-vapour, ozone (O_3, 0–1000 ppbv), sulfur dioxide (SO_2, 0–60 ppbv), ammonia (NH_3, < 0.35–2 ppbv, Bianchi et al., 2012), pinanediol (PD, $C_{10}H_{18}O_2$, 0–21 ppbv, Schobesberger et al., 2013), dimethylamine (DMA, 0–100 pptv, C_2H_7N, Praplan et al., 2012; Almeida et al., 2013), and α-pinene ($C_{10}H_{16}$, 0–1600 pptv). All these gases and their injection into the chamber pose potential sources of organic impurities and are therefore treated with particular care. Synthetic air is provided by evaporation

from cryogenic liquid N_2 and O_2, mixed in the gas phase in ratio 79 : 21. A continuous flow into the chamber of 100–160 standard liter per minute (slpm) of humidified synthetic air mixed with trace gases compensates for air extracted by the analysing instruments.

5　Water vapour concentration can be controlled over 6 orders of magnitude with a deviation of 1 % relative humidity (RH). Water is purified by circulation through a bank of Millipore Super-Q filters (MQ-water), de-ionised and added to the N_2–O_2 gas stream via a Nafion humidifier.

One of the essential gases for nucleation is sulphuric acid. In the CLOUD chamber
10　it is produced by photo-dissociation of ozone in the presence of SO_2, water vapour, O_2 and N_2. To avoid heat load from the light source, a fibre optic system is installed that produces an uniform illumination (240–750 nm) in the chamber and therefore a uniform sulphuric acid production. The temperature increase in the chamber is smaller than 0.005 °C at full illumination (Kupc et al., 2011).

15　The trace gases are supplied in concentrated form and then highly diluted with synthetic air to ensure minimum contamination from the supply.

Ozone is generated by a low pressure mercury lamp (CLOUD1–CLOUD3). The plastic sealings of this device was suspicious as a potential source of organic impurities during exposure of very high ozone levels. Therefore it was replaced by a CERN de-
20　signed and built all stainless steel and quartz ozone generator from CLOUD4 on.

The gases are injected at the bottom of the chamber close to one of the two mixing fans in order to quickly, and uniformly distribute them throughout the whole chamber. This is important to rapidly reach newly adjusted levels of trace gases (Voigtlaeander et al., 2012).

25　There are 16 ports installed in the mid-plane of the chamber, to which sampling probes are mounted. The inner tips of the sampling probes project into the chamber a distance of 50 cm (CLOUD1–3) or 35 cm (CLOUD4 and later). The pressure in the chamber is maintained at least 5 hPa above ambient. Accidental low pressure in the chamber bears the danger of back-flow through the various instruments to the chamber

and contamination with e.g. butanol from the Condensation Particle Counters (CPCs). Therefore an independent fail-safe system has been implemented to ensure a 5 hPa above ambient pressure in the chamber.

2.2 PTR-MS

To be able to quantitatively monitor a great set of volatile organic compounds (VOCs) in the low pptv range in real-time and to identify the individual species, the PTR-technique has been chosen. Proton transfer reaction mass spectrometry (PTR-MS; Hansel et al., 1995) is a chemical ionisation method for real-time measurements of VOCs. H_3O^+-ions, produced from pure water vapour in a glow discharge ion source are injected into a drift tube which is continuously flushed with sampling air. H_3O^+ ions transfer protons, at every collision, to compounds that have a higher proton affinity than water (691 kJ mol^{-1}; i.e. most VOCs except alkanes). The protonated VOCs are then detected and quantitatively analysed by a quadrupole (CLOUD1) or a time-of-flight (ToF; CLOUD2, CLOUD3, CLOUD4, and CLOUD7) mass spectrometer. In contrast to the PTR-quadrupole system (PTR-Q-MS), the PTR-ToF-MS provides full mass scans within a fraction of a second. In addition, the high mass resolving power (about 5000 full width at half maximum – FWHM), combined with the high mass accuracy (2.5 ppm) allows for unambiguous sum formula identification (Graus et al., 2010).

2.3 Inlet system and background correction

The inlet system has been especially designed in order to minimize inlet wall losses and ozone surface induced reactions. A combination of high flow and heated inlet tubes should guide the VOCs most efficiently to the instruments. Fig. 2 shows a schematic drawing of the whole PTR-MS inlet system. A 3/8″ OD (7 mm ID) sulfinert coated stainless steel tube projects 50 cm (CLOUD1–3) to 35 cm (CLOUD4 and later) into the CLOUD chamber to draw the air sample into the PTR instruments. Through this tube sample air is continuously drawn between 8 and 11 slpm (resulting in a Reynolds

number of 2300) depending on the temperature of the chamber air. After an additional 15 cm section of 3/8″ stainless steel tube, a 1/16″ Silcosteel capillary extracts about 1 slpm sample air from its center. From this point on, all surfaces which are in contact with the sample air are heated to 60 °C. The capillary (as short as possible; 25 cm) has two more T-connections. One of them is used to periodically introduce purified air to perform instrumental background measurements and the other one to have a pressure controlled inlet. Finally, only 0.011 slpm enter the drift-tube of the PTR-instruments.

Measurements close to the limit of detection (LOD) require an accurate and continuous determination of the instrumental background. During the CLOUD campaigns background measurements have usually been performed 4–5 times per day with different duration (1/2 h to several hours). For these measurements 3 slpm of chamber air were purified using two Pd-Pt catalytic converters (EnviCat®, VOC 5538, Süd-Chemie AG, Germany) arranged in series. The purified gas stream was injected into the 1/16″ capillary. Then 1 slpm of this air was pumped to the instrument and the rest was displaced to the 3/8″ tube and pumped away. The inlet system was slightly different at each CLOUD campaign. For example during CLOUD3 another PTR-MS, modified to measure ammonia, sampled chamber air in the same way from the same 3/8″ stainless steel tube. During CLOUD7 the zero air flow to the T-connection was inadvertently set too low so the "zero air" contained 25 % chamber air for the first two weeks of the campaign. However, these data could subsequently be corrected since all flows were recorded.

2.4 Calibration

The PTR-instruments were calibrated about 5 times during each campaign, using gas standards (Apel-Riemer Inc., Denver, CO, USA). The gas standards contained a set of pure and oxygenated hydrocarbons, which were dynamically diluted into purified air and fed to the PTR-instruments. Based on these calibrations we estimated a total accuracy of the instruments of < 13 % at 1 ppbv for the compounds included in the gas standard. This is due to uncertainties given for the calibration gas and the di-

Cloud: VOC background characterisation

R. Schnitzhofer et al.

lution system (5.2 %) and the precision of the counting system 12 % (for acetone at 1 ppbv). Formaldehyde (HCOH) also included in the gas standard shows a water dependent sensitivity, because its proton affinity is only slightly higher than that of water and therefore there is a backward reaction (Hansel et al., 1997). The amount of the backward reaction depends on the ambient humidity, which adds to the water coming from the ion source (for details see Vlasenko et al., 2010). The relative distribution of the H_3O^+ (mass to charge ratio (m/z) 19) and $H_2OH_3O^+$ (m/z 37) ions detected is also dependent on ambient humidity with a higher relative amount of m/z 37 during humid conditions. Due to high amount of water ions they can only be counted correctly at the natural isotopes $H_3^{18}O^+$ (m/z 21) and $H_2^{18}OH_3O^+$ (m/z 39). Having various calibrations at constant instrument conditions (i.e. a constant water stream from the ion source into the drift tube, a constant drift tube temperature, and a constant E/N in the drift tube) and at different ambient humidities (see Fig. 3) we can give a humidity dependent sensitivity of

$$\varepsilon_{(HCOH)} = 105 \cdot ncps_{(m/z\ 39)}^{-0.7} \tag{1}$$

using $H_2^{18}OH_3O^+$ (m/z 39) as a reference for humidity of the air sample. Similar water dependent formaldehyde sensitivities have been found during laboratory- and in-flight calibrations by Warneke et al. (2011).

Due to the lower overall sensitivity the total accuracy for formaldehyde at 1 ppbv is between 25 % (dry) and 50 % (humid).

For compounds that were not included in the gas standard we used the sensitivity derived from calibrated oxygenated and pure hydrocarbons (compare Mueller et al., 2012). The sensitivities could be cross-checked using the formula

$$\varepsilon_{(R)} = 10^{-3} \frac{kL}{\mu_0 N_0} \cdot \frac{N^2}{E} \cdot \frac{T(RH^+)}{T(H_3O^+)} \tag{2}$$

given by de Gouw et al. (2003) and reaction rate constants given by Cappellin et al. (2012). Here R represents the individual VOCs, k is the reaction rate constant, L the

length of the drift tube, μ_0 the reduced ion mobility, N the gas number density, N_0 the gas number density at standard pressure and temperature, E the electric field strength, and T the transmission of the individual ions.

The LOD of the individual compounds is determined from the 2σ uncertainty from the background measurements (compare Table 1).

Since PTR-ToF-MS provides sum formula identification we could insert a oxygenated hydrocarbon sensitivity or a pure hydrocarbon sensitivity for every compound above the LOD not explicitly calibrated. Therefore, the overall amount of PTR detectable VOCs (total VOCs) in the chamber can be calculated in parts per billion by volume (ppbv). Multiplying the individual compounds by their carbon atom number and adding up all compounds gives the total carbon mole fraction detected in the chamber (parts per billion by volume of carbon; ppbvC). When accounting for the uncertainty of the calibration and the counting system the average number of total VOCs can be given with an uncertainty of 40 %.

3 Results

The measurement principle of the PTR technique does not require sample preparation and therefore data can be acquired in real time. Although these real time data do not pass several quality checks, they can provide a first glance at the experiment. During CLOUD these data provided a first estimation of the chamber cleanliness.

The inlet system was designed with particular care in order to keep the artificial loss or gain of VOCs on the inlet surfaces as low as possible. However for some sticky compounds (particularly for acetic acid) the response time (switching between chamber measurements and zero calibration) was close to one hour. Consequently zero calibrations had to be elongated until a constant level was reached and data from the transition period had to be excluded. Due to a higher flow rate of the sample air through the drift tube the response time was strongly improved during CLOUD7.

A total of 36 different VOCs above their individual LOD could be detected. The most predominant compounds, which account for > 80 % of the total VOCs are listed in Table 1.

On average, CH_2OH^+ (e.g. formaldehyde) and $CH_2O_2H^+$ (e.g. formic acid) account for 50 % of total VOCs. Other important impurities are $C_2H_4O_2H^+$ (e.g. acetic acid), $C_2H_4OH^+$ (e.g. acetaldehyde), and $C_3H_6OH^+$ (e.g. acetone/propanal). Those compounds have a rather high vapour pressure and are therefore not important for nucleation and growth (compare Kroll et al., 2005).

Although CH_2OH^+ and $CH_2O_2H^+$ are treated as formaldehyde and formic acid in this work an interference with fragments from methyl hydroperoxide and hydroxy methyl hydroperoxide, with considerable lower vapour pressure (Kroll and Seinfeld, 2008), cannot be ruled out.

Figure 4 shows a summary of measurements made at the start of several CLOUD campaigns, before intentional addition of any organic vapours. In panel e the sum of all detected VOCs is plotted. Panel f shows the sum of the detected VOCs on a carbon basis. In parallel the gases ozone (panel d), SO_2 (panel c) and the physical properties (temperature – panel b, and relative humidity – panel a) that potentially impact the detected VOCs are shown. The longest time series concerning the background contamination of the chamber is available for CLOUD3 (about 35 days). Instrumental problems shortened the time series for CLOUD2 to about 12 days. Only a short time series is available for CLOUD7 since DMA was added to the chamber early in the campaign.

Although the measured equilibrium organic contaminant levels are around a factor 10 lower than the PSI teflon smog chamber which is of comparable size, the contamination was higher than expected and variable. At the beginning of the campaigns a burst of VOCs (up to 7 ppbv total VOCs) was detected as soon as water vapour, ozone, or SO_2 were added (CLOUD3 and CLOUD7 in Fig. 4). This is in agreement with Wisthaler et al. (2008) who report an increase of formaldehyde and other C_2–C_{10} aldehydes during the first hour after ozone addition to the atmosphere simulation chamber SAPHIR

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

(Jülich, Germany). After some hours the VOC concentration decays although the injected gases remain at a constant level. After this "chamber-startup-burst", the VOC contamination tends to decrease. This indicates that impurities on the chamber walls and the inlet tubes of the gas supply system are gradually removed.

The most obvious source of the contamination is the gas injection system of the chamber. Nitrogen and oxygen are evaporated from cryogenic liquids and injected into the chamber at a constant rate of about 160 slpm. When only these gases were added to the chamber, total VOCs were below 150 pptv (400 pptvC; compare Fig. 4).

In order to estimate possible contamination through the humidifying system, the purity of the water was checked using liquid chromatography. The total organic carbon (TOC) content was found to be < 7 ppbv, which could explain < 70 pptvC in humid air at 20 °C and 40 % RH. However, organics may be subsequently introduced by the Nafion humidifier.

Another source might be adsorption, followed by desorption from the chamber wall depending on internal temperature. However, no significant influence on the VOC concentration was found during the heating cycles shown in Figs. 4 and 7. Instead, the desorption of organics seems to be triggered by water vapour (compare CLOUD3 in Fig. 4).

Figure 5 shows a full mass scan measured during CLOUD1 at 0 and at 600 ppbv O_3. As before, only a few compounds are responsible for the overall VOC contamination. Most of the masses above the LOD increase when ozone is added to the chamber. Consequently, ozone was found to correlate with total VOCs, as shown in Fig. 6. An increase of 300 ppbv ozone resulted in an increase of total VOCs by 1 ppbv, but less than 0.25 ppbv during CLOUD7 (data from the "chamber-startup-bursts" have been excluded here). This can be attributed to the replacement of the ozone generator after CLOUD3 with an all-metal/quartz construction. On the other hand, the ozone effect could be an artifact caused by surface assisted reactions in the instruments inlets. To evaluate this, the inlet flow was varied at 600 ppbv ozone between 0.4 and 2 slpm during CLOUD1, but no significant difference was found.

During the experiments H_2SO_4 was produced from photo oxidation of SO_2. The OH radical involved in this process, produced from ozone and H_2O in the presence of UV, potentially produces oxygenated VOCs. However, no connection between UV intensity and total or individual background VOCs could be found.

5   To better quantify the different contamination sources, an experiment was conducted at the beginning of CLOUD7 (see Fig. 7). After the chamber was filled with the synthetic air, it was heated to 100 °C for 2 days. No significant difference in total VOCs appears between 100 °C (30 September 2012) and 5 °C (2 October 2012) before H_2O, SO_2 and ozone were added sequentially (Fig. 7b). Total VOCs were constant at about 1000 pptv

10 except in the afternoon of 30 September when the signal increased to 2500 pptv for a few hours. This can be related to the first introduction of ozone. Since many sensors (including the ozone analyzer) have been disconnected from the chamber during the heating cycle, no measured data are available and the ozone concentration can only be estimated from the mass flow controller settings. The intention was to reach

15 200 ppbv ozone from 30 September 17:40 UTC on. At 20:30 UTC on the same day ozone was set to zero again. Due to the thermal contraction of the chamber during cooling to 5 °C, the inflexible PTR-TOF inlet developed a leak, resulting in loss of data for 1 day. After recovery of the PTR-TOF, gases were sequentially added to the chamber. Injection of 100 ppbv ozone produced a step increase of total VOCs from 1000

20 to 1900 pptv. After 4 h, the total VOCs declined to 1400 pptv. On 2 October at 09:00 UTC, SO_2 was added to chamber and increased over the next 10 h to a constant level around 50 ppbv. In contrast to the slowly increasing SO_2 signal, total VOCs increased to 3500 pptv within 15 min of first opening the SO_2 inlet valve. This is interpreted as contamination in the SO_2 inlet line, which was flushed for the first time in several months

25 during this event. About 90 % of this increase can be attributed to formaldehyde (see Fig. 7b). In the next step ozone was increased from 100 ppbv (11:45 UTC, 2 October) to 500 ppbv (15:00 UTC). The corresponding VOC increase was rather slow and followed the ozone concentration. The most abundant individual compound during this event was acetic acid (Fig. 7b). No VOC information is available during the short dip

Cloud: VOC background characterisation

R. Schnitzhofer et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄   ►|

◄   ►

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

(2 h) seen in ozone and SO_2 since the PTR-TOF background was being measured at that time. Until 4 October 03:00 UTC (i.e. 18 h) the ozone and SO_2 were constant arround 515, and 55 ppbv, respectively. Total VOCs reached their maximum level of 4500 pptv on 2 October 15:00 UTC, when ozone and SO_2 obtained their set points.

5 However, the total VOC peak lasted only a few hours and the signal slowly declined, reaching 1000 pptv by 4 October. Afterwards ozone was set to 15 ppbv and nucleation experiments started.

Data from this experiment show that flushing the whole gas inlet system and a water vapour/ozone cleaning cycle washes off a large amount of organic contaminants from

10 metal surfaces, and reduces their equilibrium concentrations during the subsequent nucleation experiments.

4 Conclusions

Total organic impurities in the CLOUD chamber were found between 0.1 and 7 ppbv, and 0.4 and 12 ppbv C, respectively. The organic impurities are dominated by light C_1–

15 C_3 organics of high vapour pressure, which are not important for particle nucleation and growth. A correlation between ozone and total background VOCs was found. After replacing all plastic parts of the ozone generator with stainless-steel and quartz, the ozone effect decreased by more than a factor of 4. After CLOUD3, the ozone concentration for the nucleation experiments was always below 100 ppbv. During these

20 rather low ozone levels the total VOC contamination was usually below 1 ppbv. Therefore, the CLOUD chamber was found to be considerable cleaner than a comparable Teflon chamber. Beside the ozone-generator effect, ozone yields to VOC formation by heterogeneous reactions on the chamber walls. In addition, water vapour appears to release organic compounds from the chamber walls, especially when introduced for

25 the first time after completely dry conditions. A significant contamination source – but of short time duration – is the dead volume of the various trace gas tubes connected to the chamber; this can be avoided by careful flushing before starting the experiments.

Cloud: VOC background characterisation

R. Schnitzhofer et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A comprehensive cleaning cycle would include a heating cycle (100 °C), together with high ozone concentrated and humidified air, and flushing of all gas inlet tubes.

References

Almeida, J., Schobesberger, S., Kuerten, A., Ortega, I. K., Kupiainen, O., Praplan, A. P., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Jokinen, T., Junninen, H., Kajos, M., Keskinen, H., Kupc, A., Kurten, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppae, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petaejae, T., Riccobono, F., Riipinen, I., Rondo, L., Ruuskanen, T., Santos, F. D., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilae, M., Stozhkov, Y., Stratmann, F., Tome, A., Troestl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D.: Molecular

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

understanding of amine-sulphuric acid particle nucleation in the atmosphere, in revision, 2013. 7712

Bianchi, F., Dommen, J., Mathot, S., and Baltensperger, U.: On-line determination of ammonia at low pptv mixing ratios in the CLOUD chamber, Atmos. Meas. Tech., 5, 1719–1725, doi:10.5194/amt-5-1719-2012, 2012. 7712

Bloss, C., Wagner, V., Bonzanini, A., Jenkin, M. E., Wirtz, K., Martin-Reviejo, M., and Pilling, M. J.: Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data, Atmos. Chem. Phys., 5, 623–639, doi:10.5194/acp-5-623-2005, 2005. 7711

Cappellin, L., Karl, T., Probst, M., Ismailova, O., Winkler, P. M., Soukoulis, C., Aprea, E., Maerk, T. D., Gasperi, F., and Biasioli, F.: On quantitative determination of volatile organic compound concentrations using proton transfer reaction time-of-flight mass spectrometry, Environ. Sci. Technol., 46, 2283–2290, doi:10.1021/es203985t, 2012. 7716

Carslaw, K., Harrison, R., and Kirkby, J.: Cosmic rays, clouds, and climate, Science, 298, 1732–1737, doi:10.1126/science.1076964, 2002. 7711

Cocker, D., Flagan, R., and Seinfeld, J.: State-of-the-art chamber facility for studying atmospheric aerosol chemistry, Environ. Sci. Technol., 35, 2594–2601, doi:10.1021/es0019169, 2001. 7711

de Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., and Fall, R.: Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, Int. J. Mass Spectrom., 223, 365–382, 2003. 7716

Duplissy, J., Enghoff, M. B., Aplin, K. L., Arnold, F., Aufmhoff, H., Avngaard, M., Baltensperger, U., Bondo, T., Bingham, R., Carslaw, K., Curtius, J., David, A., Fastrup, B., Gagné, S., Hahn, F., Harrison, R. G., Kellett, B., Kirkby, J., Kulmala, M., Laakso, L., Laaksonen, A., Lillestol, E., Lockwood, M., Mäkelä, J., Makhmutov, V., Marsh, N. D., Nieminen, T., Onnela, A., Pedersen, E., Pedersen, J. O. P., Polny, J., Reichl, U., Seinfeld, J. H., Sipilä, M., Stozhkov, Y., Stratmann, F., Svensmark, H., Svensmark, J., Veenhof, R., Verheggen, B., Viisanen, Y., Wagner, P. E., Wehrle, G., Weingartner, E., Wex, H., Wilhelmsson, M., and Winkler, P. M.: Results from the CERN pilot CLOUD experiment, Atmos. Chem. Phys., 10, 1635–1647, doi:10.5194/acp-10-1635-2010, 2010. 7712

Graus, M., Mueller, M., and Hansel, A.: High resolution PTR-TOF: quantification and formula confirmation of VOC in real time, J. Am. Soc. Mass Spectr., 21, 1037–1044, doi:10.1016/j.jasms.2010.02.006, 2010. 7714

Cloud: VOC background characterisation

R. Schnitzhofer et al.

Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., and Lindinger, W.: Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level, Int. J. Mass. Spectrom., 149, 609–619, 1995. 7714

Hansel, A., Singer, W., Wisthaler, A., Schwarzmann, M., and Lindinger, W.: Energy dependencies of the proton transfer reactions $H_3O^+ + CH_2O$ double left right arrow $CH_2OH^+ + H_2O$, Int. J. Mass Spectrom., 167, 697–703, doi:10.1016/S0168-1176(97)00128-6, 1997. 7716

Keskinen, H., Virtanen, A., Joutsensaari, J., Tsagkogeorgas, G., Duplissy, J., Schobesberger, S., Gysel, M., Riccobono, F., Slowik, J. G., Bianchi, F., Yli-Juuti, T., Lehtipalo, K., Rondo, L., Breitenlechner, M., Kupc, A., Almeida, J., Amorim, A., Dunne, E. M., Downard, A. J., Ehrhart, S., Franchin, A., Kajos, M.K., Kirkby, J., Kürten, A., Nieminen, T., Makhmutov, V., Mathot, S., Miettinen, P., Onnela, A., Petäjä, T., Praplan, A., Santos, F. D., Schallhart, S., Sipilä, M., Stozhkov, Y., Tomé, A., Vaattovaara, P., Wimmer, D., Prevot, A., Dommen, J., Donahue, N. M., Flagan, R.C., Weingartner, E., Viisanen, Y., Riipinen, I., Hansel, A., Curtius, J., Kulmala, M., Worsnop, D. R., Baltensperger, U., Wex, H., Stratmann, F., and Laaksonen, A.: Evolution of particle composition in CLOUD nucleation experiments, Atmos. Chem. Phys., 13, 5587–5600, doi:10.5194/acp-13-5587-2013, 2013. 7712

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagne, S., Ickes, L., Kuerten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkila, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petaja, T., Schnitzhofer, R., Seinfeld, J. H., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429–433, doi:10.1038/nature10343, 2011. 7712, 7728

Kroll, J. and Seinfeld, J.: Representation of secondary organic aerosol laboratory chamber data for the interpretation of mechanisms of particle growth, Environ. Sci. Technol., 39, 4159–4165, doi:10.1021/es048292h, 2005. 7727

Kroll, J. H. and Seinfeld, J. H.: Chemistry of secondary organic aerosol: formation and evolution of low-volatility organics in the atmosphere, Atmos. Environ., 42, 3593–3624, doi:10.1016/j.atmosenv.2008.01.003, 2008. 7718

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Kroll, J., Ng, N., Murphy, S., Varutbangkul, V., Flagan, R., and Seinfeld, J.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, J. Geophys. Res.-Atmos., 110, D23207, doi:10.1029/2005JD006004, 2005. 7718

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petaja, T., Sipila, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Jarvinen, E., Aijala, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkila, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin III, R. L., Duplissy, J., Vehkamaki, H., Back, J., Kortelainen, A., Riipinen, I., Kurten, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation, Science, 339, 943–946, doi:10.1126/science.1227385, 2013. 7711

Kupc, A., Amorim, A., Curtius, J., Danielczok, A., Duplissy, J., Ehrhart, S., Walther, H., Ickes, L., Kirkby, J., Kuerten, A., Lima, J. M., Mathot, S., Minginette, P., Onnela, A., Rondo, L., and Wagner, P. E.: A fibre-optic UV system for H2SO4 production in aerosol chambers causing minimal thermal effects, J. Aerosol Sci., 42, 532–543, doi:10.1016/j.jaerosci.2011.05.001, 2011. 7713

Metzger, A., Verheggen, B., Dommen, J., Duplissy, J., Prevot, A. S. H., Weingartner, E., Riipinen, I., Kulmala, M., Spracklen, D. V., Carslaw, K. S., and Baltensperger, U.: Evidence for the role of organics in aerosol particle formation under atmospheric conditions, P. Natl. Acad. Sci. USA, 107, 6646–6651, doi:10.1073/pnas.0911330107, 2010. 7711

Müller, M., Graus, M., Wisthaler, A., Hansel, A., Metzger, A., Dommen, J., and Baltensperger, U.: Analysis of high mass resolution PTR-TOF mass spectra from 1,3,5-trimethylbenzene (TMB) environmental chamber experiments, Atmos. Chem. Phys., 12, 829–843, doi:10.5194/acp-12-829-2012, 2012. 7716

Paulsen, D., Dommen, J., Kalberer, M., Prevot, A., Richter, R., Sax, M., Steinbacher, M., Weingartner, E., and Baltensperger, U.: Secondary organic aerosol formation by irradiation of 1,3,5-trimethylbenzene-NO$_x$-H$_2$O in a new reaction chamber for atmospheric chemistry and physics, Environ. Sci. Technol., 39, 2668–2678, doi:10.1021/es0489137, 2005. 7711

Praplan, A. P., Bianchi, F., Dommen, J., and Baltensperger, U.: Dimethylamine and ammonia measurements with ion chromatography during the CLOUD4 campaign, Atmos. Meas. Tech., 5, 2161–2167, doi:10.5194/amt-5-2161-2012, 2012. 7712

Schobesberger, S., Junninen, H., Bianchi, F., Lönn, G., Ehn, M., Lehtipalo, K., Dommen, J., Ehrhart, S., Ortega, I. K., Franchin, A., Nieminen, T., Riccobono, F., Hutterli, M., Duplissy, J.,

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Almeida, J., Amorime, A., Breitenlechner, M., Downard, A., Dunne, E. M., Flagan, R. C., Kajos, M., Keskinen, H., Kirkby, J., Kupc, A., Kürten, A., Kurtén, T., Laaksonen, A., Mathot, S., Onnela, A., Praplan, A. P., Rondo, L., Santos, F. D., Schallhart, S., Schnitzhofer, R., Sipilää, M., Tomée, A., Tsagkogeorgas, G., Vehkamäki, H., Wimmer, D., Baltensperger, U., Carslaw, K. S., Curtius, J., Hansel, A., Petäjä, T., Kulmala, M., Donahue, N. M., and Worsnop, D. R.: Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules, in revision, 2013. 7712

Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K., Tignor, M., and Miller, H. e.: IPCC, 2007: Summary for policymakers, in: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, 2007. 7711

Vlasenko, A., Macdonald, A .M., Sjostedt, S. J., and Abbatt, J. P. D.: Formaldehyde measurements by Proton transfer reaction – Mass Spectrometry (PTR-MS): correction for humidity effects, Atmos. Meas. Tech., 3, 1055–1062, doi:10.5194/amt-3-1055-2010, 2010. 7716

Voigtländer, J., Duplissy, J., Rondo, L., Kürten, A., and Stratmann, F.: Numerical simulations of mixing conditions and aerosol dynamics in the CERN CLOUD chamber, Atmos. Chem. Phys., 12, 2205–2214, doi:10.5194/acp-12-2205-2012, 2012. 7713

Warneke, C., Veres, P., Holloway, J. S., Stutz, J., Tsai, C., Alvarez, S., Rappenglueck, B., Fehsenfeld, F. C., Graus, M., Gilman, J. B., and de Gouw, J. A.: Airborne formaldehyde measurements using PTR-MS: calibration, humidity dependence, inter-comparison and initial results, Atmos. Meas. Tech., 4, 2345–2358, doi:10.5194/amt-4-2345-2011, 2011. 7716

Wisthaler, A., Apel, E. C., Bossmeyer, J., Hansel, A., Junkermann, W., Koppmann, R., Meier, R., Müller, K., Solomon, S. J., Steinbrecher, R., Tillmann, R., and Brauers, T.: Technical Note: Intercomparison of formaldehyde measurements at the atmosphere simulation chamber SAPHIR, Atmos. Chem. Phys., 8, 2189–2200, doi:10.5194/acp-8-2189-2008, 2008. 7711, 7718

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Vapour pressure (from http://www.chemspider.com, Kroll and Seinfeld, 2005), individual abundance, limit of detection (LOD), and sensitivity of the most predominant (> 80 % of the total VOC volume mixing ratio) peaks detected by PTR-ToF during CLOUD3.

exact mass	sumformula	compound (e.g.)	vapour pressure (mmHg at 25 °C)	relative abundance [%]	LOD [pptv]	sensitivity [ncps ppbv^{-1}]
31.018	CH_2OH^+	formaldehyde	23–26	33	97	1.6–3.25
45.034	$C_2H_4OH^+$	acetaldehyde	965	9	17	18.6
47.013	$CH_2O_2H^+$	formic acid	41	21	43	19.5
59.049	$C_3H_6OH^+$	acetone/propanal	348/300	5	9	19.5
61.029	$C_2H_4O_2H^+$	acetic acid	14	14	61	13
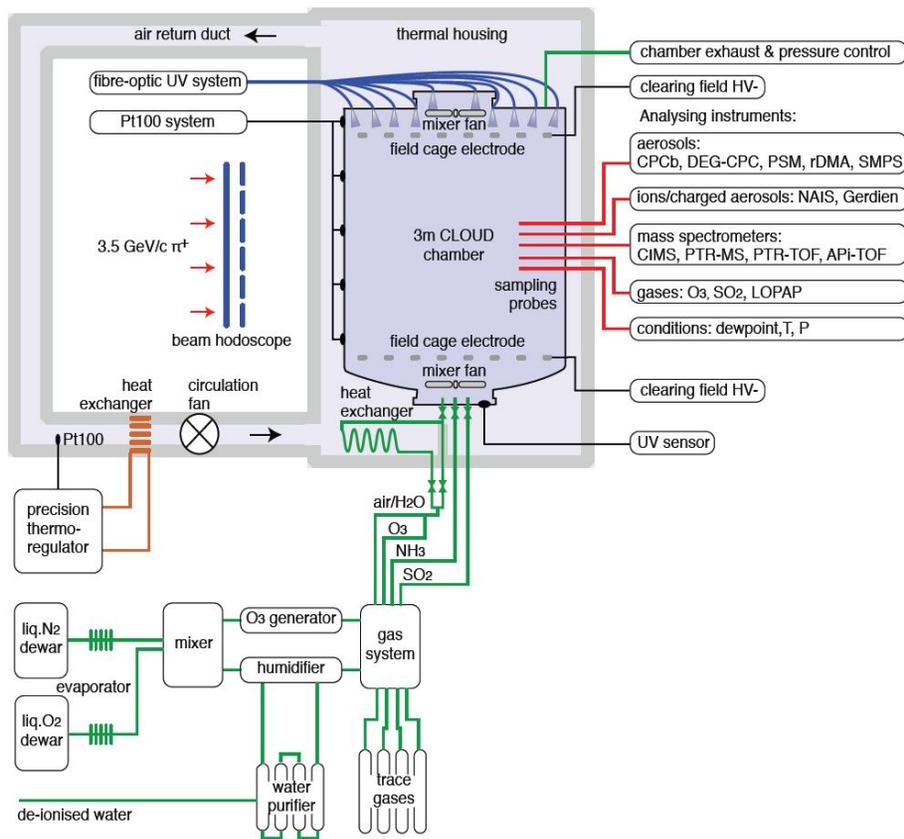
Fig. 1. Schematic drawing of the CLOUD chamber, the gas system and the connected instruments (Kirkby et al., 2011).
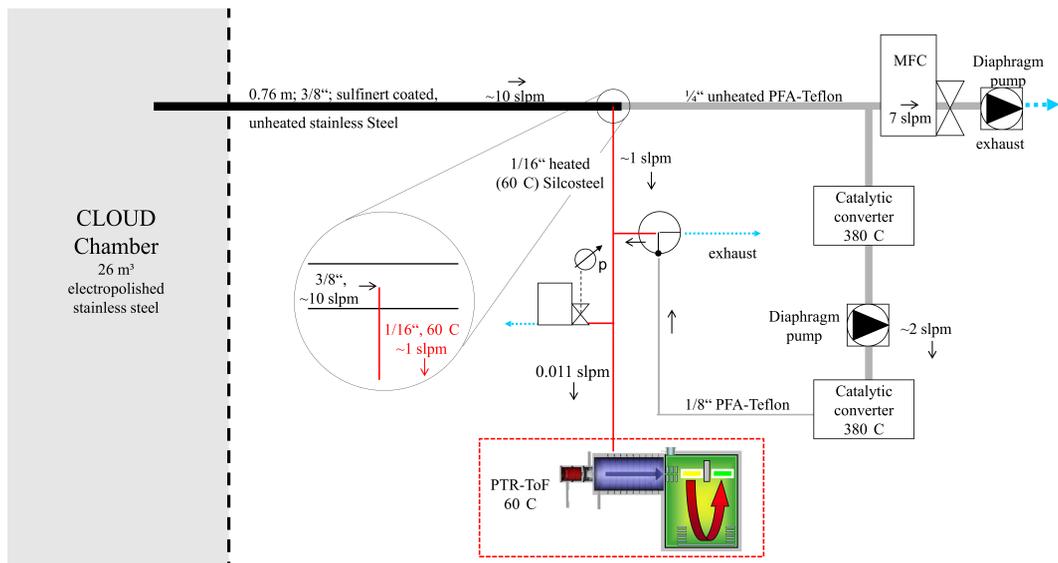
Fig. 2. Schematic drawing of the PTR-Q-MS/PTR-ToF-MS inlet system during the various CLOUD campaigns.
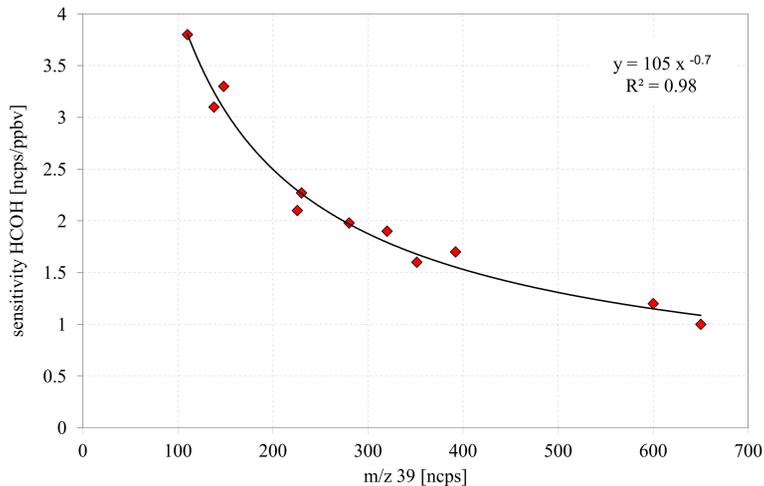
Fig. 3. Scatter plot of formaldehyde sensitivities vs. $H_2^{18}OH_3O^+$ (m/z 39) as a reference for the absolute humidity in the drift tube.
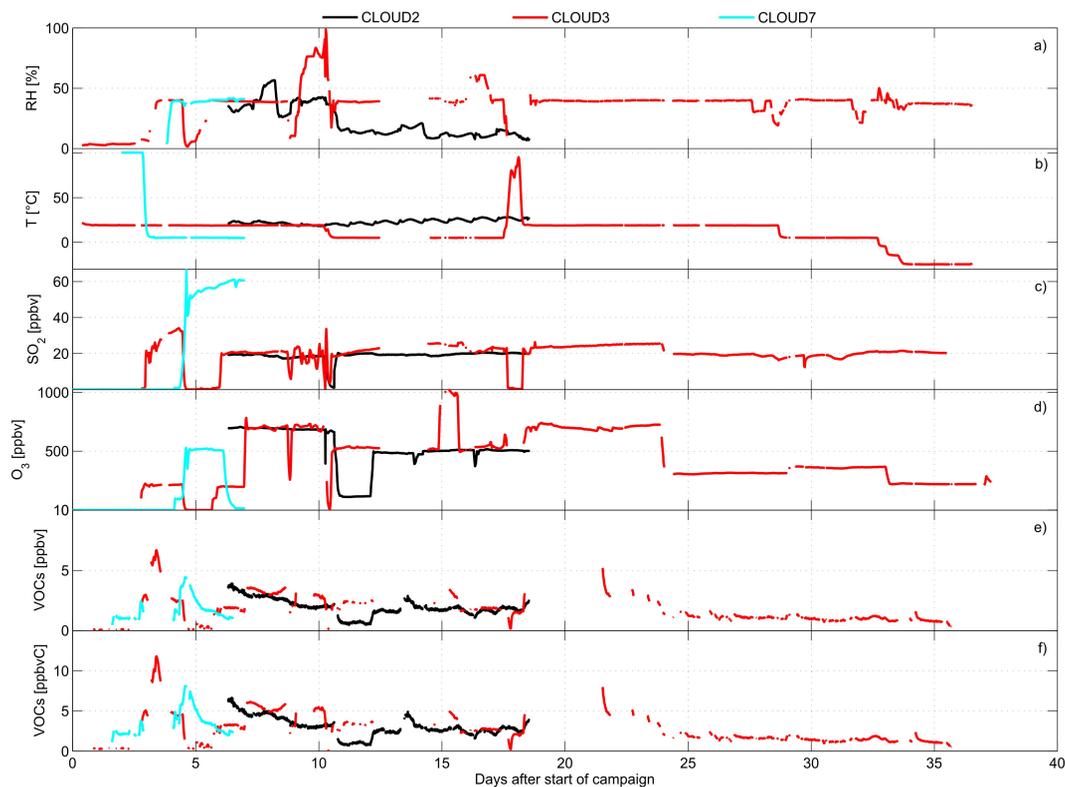
Fig. 4. Temporal evolution of relative humidity **(a)**, temperature **(b)**, SO$_2$ **(c)**, ozone **(d)**, total VOCs **(e)**, and total VOCs on a carbon basis **(f)** during CLOUD2, CLOUD3, and CLOUD7.
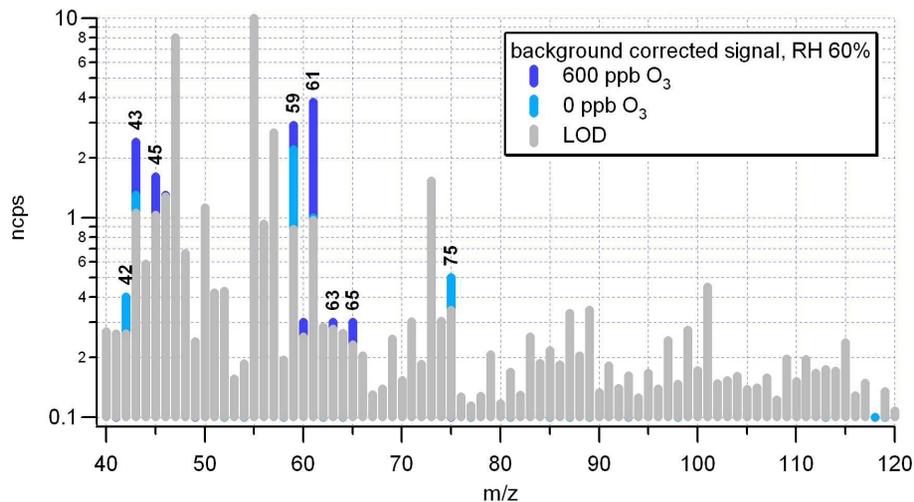
Fig. 5. Comparison of mass spectra of the background VOC in the CLOUD chamber during CLOUD1. All spectra are averaged for two hours and background corrected. The gray bars at the bottom of individual mass fragments are the associated LOD.
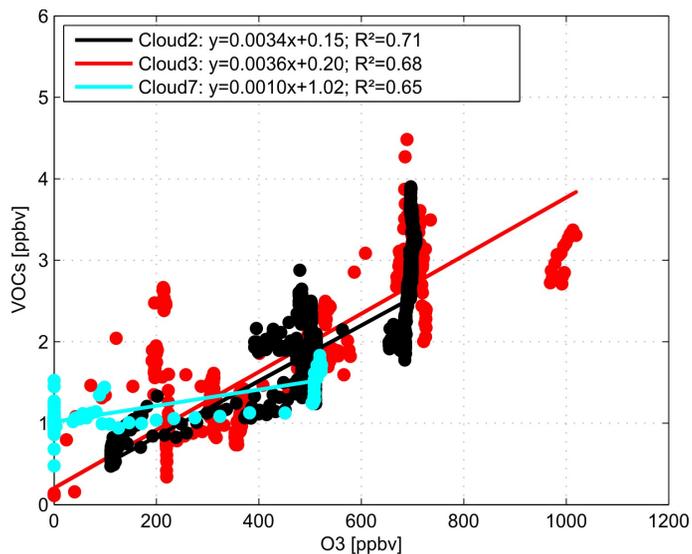
Fig. 6. Scatter plot of ozone vs. total VOCs for CLOUD2, CLOUD3, and CLOUD7.
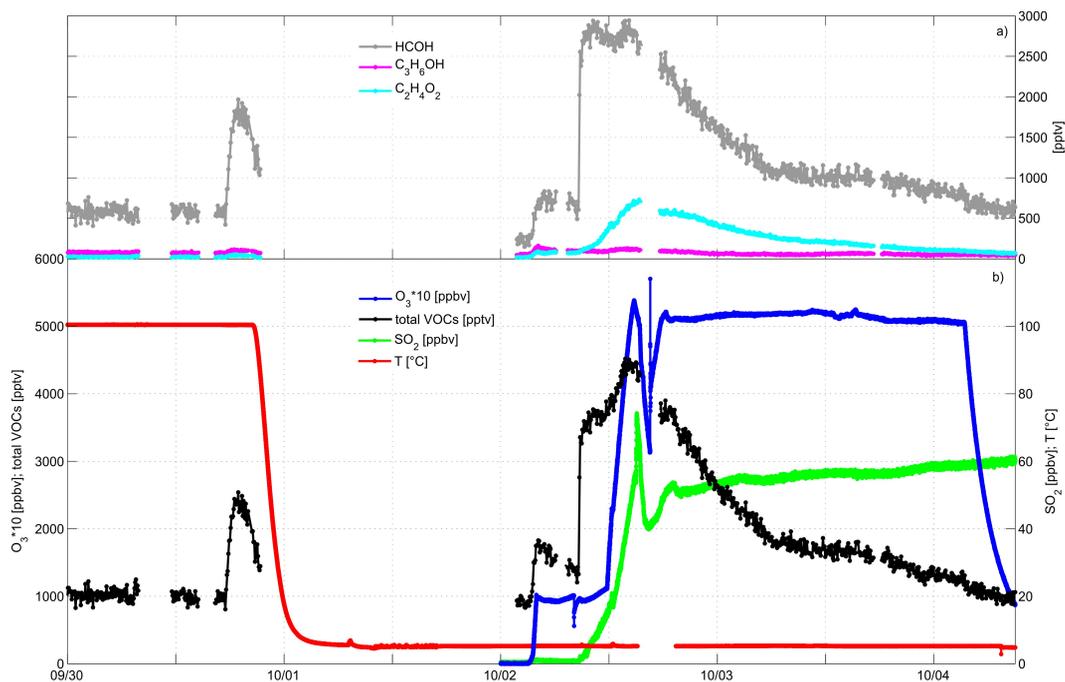
Fig. 7. Total **(b)** and individual VOCs **(a)** at the beginning of CLOUD7, when following a heating cycle, ozone and SO$_2$ were sequentially added to the chamber.