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Chapter 3

Preparation of Simulation Chambers for Experiments



David Bell, Jean-François Doussin, and Thorsten Hohaus

Abstract When setting up a simulation chamber experiment it is essential, in order to ensure meaningful results, to start with a well-controlled chemical system. Coming after the chapter dealing with the requested careful characterization of the simulation chamber, the present chapter describes the preparation of the chamber before running an experiment. It includes various chamber cleaning protocols, the preparation of a clean chamber atmosphere (the reacting mixture) and a series of protocols for blank experiments. Indeed, having a clean atmosphere in a simulation chamber, as free as possible from both particulate and gaseous impurities, is essential to ensure high quality experimental results. As it may not be possible to have a perfectly clean chamber, blank experiments are crucial to both assess chamber cleanliness, account for impurities and establish uncertainties of the observed phenomena. In the present chapter, various cleaning protocols which involve the oxidation of the impurities, dilution, temperature degradation/evaporation, but the evacuation or manual cleaning are described as well. The various techniques to generate clean gas mixture—mostly clean O₂, N₂ or water vapor, are discussed. Finally, complementarily to the reference experiments proposed in Chap. 2, blank experiments to characterize walls chemical inertia, chamber-dependent radical sources or the presence of water-soluble species are also described.

Having a clean atmosphere in a simulation chamber, as free from both particulate and gaseous impurities as possible is essential to ensure high quality experimental results that have a meaningful impact. It may not be practical or possible to

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have a perfectly clean chamber and therefore blank experiments are crucial to both assess chamber cleanliness and account for impurities. Hence, cleaning processes and regular blank experiments are required to have a chamber that can generate meaningful and reproducible results.

The goal of chamber cleaning is to recreate the state of the chamber at the beginning of the previous experiment and to remove all unwanted species that were formed or injected over the course of a previous experiment. When operating in a batch mode, the chamber needs to be cleaned prior to each experiment in order to start in a state where there are minimal particles or gas phase species present. The goal is obviously to eliminate species from previous experiments down to levels that will not affect the consecution of the planned experiment. However, when operating in a continuous flow mode (where all reactants are continually added), then chamber cleaning should occur on a systematic cycle to verify that no build-up of unwanted contaminants is occurring.

The goal of blank experiments is to assess if a chamber is sufficiently clean or not and, if during a campaign, chamber cleanliness is an issue hampering the interpretation of results. The simplest blank experiment is certainly exposing a chamber only filled with clean air to the source of light and carefully monitor compounds build-up coming out directly from walls release or indirectly from the decomposition of sticky compounds trapped on the walls. A complementary typical blank experiment proceeds by conducting an experiment, but only with the addition of oxidant i.e., without the addition of a volatile organic compound (VOC). This makes possible to evaluate if a chamber artefact/contaminant is reacting with the oxidant rather than the VOC as desired. If this is the case, and there is significant production of low-volatility material then organic aerosol can be formed and observed.

3.1 Chamber Cleaning Protocols

Each chamber has its own chamber cleaning techniques that has been specially developed for its unique setup and may vary depending on the specific requirements of the coming experiments. Despite significant differences between the setup of each chamber, their desired studies, and their volume (1–270 m³), the principles of chamber cleaning are similar across all facilities. The steps for cleaning a chamber typically include:

- Creating an oxidative environment via O₃ and/or OH radicals.
- Dilution of gases and particles with a source of clean air.
- Creating a humid environment, as it has been shown that competitive adsorption of water allow the release of stuck species when chambers are exposed to high RH clean air.
- Proceed until all relevant VOCs, oxidants, inorganic compounds, and particle number concentration are below specifically set thresholds (e.g., 1 ppb, limit of detection, 1–10 #/cc).

- If unsuccessful, physically clean the chamber or replace the chamber (last resort).

As a result, typical measurements required during the course of chamber cleaning include: relevant gas monitors, a VOC detector such as a proton transfer reaction mass spectrometer (PTR-MS) or GC-FID, scanning mobility particle sizers (SMPS), and/or a condensation particle counter (CPC).

3.2 Chamber Cleaning Concepts

General non-invasive chamber cleaning methods rely upon using temperature, dilution, and oxidation to remove unwanted species from the chamber environment. The three aspects of the chamber that need to be cleaned are the air inside of the chamber, the walls of the chambers, and any leftover material on the sampling lines.

3.2.1 Oxidation

Oxidation of unwanted species present in the chamber is primarily used to turn heavy molecule stuck on the walls into smaller molecules (including CO and CO₂) through molecular fragmentation that can be easily eliminated thanks to their higher volatility. If the contamination is not that severe then one or two cleaning cycles should be sufficient to remove the contamination from the system. Of course, the evaluation of the level of cleanliness of the chamber requires well defined test or blank experiments to decide whether to continue or stop the cleaning process, which will be discussed below.

Oxidation typically proceeds by addition of O₃ or H₂O₂ in large quantities, which is photolyzed to produce OH radicals that rapidly react with most volatile organic compounds (VOCs), and produce molecules with lower volatility. Lower volatility species will condense on pre-existing particles, form new particles, or stick to the walls of the chamber. If the molecules have sufficiently low-volatility then they will be effectively removed from the chamber assuming they remain relatively unreactive on the walls of the chamber, or are removed from the chamber via dilution.

Ozonolysis of the remaining chamber contaminants is probably the most common procedure. It is nevertheless not without any drawbacks. First, whilst ozone will react with most unsaturated species, compounds such as aromatics and saturated hydrocarbons will remain unaffected. Second, ozonolysis may also lead to lower volatility products (Atkinson 2000) which may contribute to the organic contaminants burden of the chamber.

In order to favor the fragmentation of the contaminant carbon skeleton, and so to lead to lighter products that will be eliminated from chamber atmosphere, the exposure to oxidizing gases such as ozone can be further completed in the case of indoor chamber by switching on the irradiation system or exposing to the sun

for outdoor chambers. In particular, the photolysis of ozone in large concentration in the presence of water produce a series of oxidizing radicals such as OH, $O(^3P)$, $O(^1D)$ that are extremely reactive toward most contaminants in the chamber (Atkinson 2000). Direct photolysis of contaminants carrying chromophores (e.g., aldehydes and ketones) also leads to fragmentation and the production of lighter products, which will contribute to the chamber cleaning.

3.2.2 Dilution

Dilution is the other process used to clean the chamber. For an inflatable chamber, this process is achieved by continually flushing the chamber with purified air (see Sect. 3.4) in order to remove contaminants/particles. Removal of particles is directly related to their wall loss lifetime and the lifetime of chamber dilution. Depending on the volume of the chamber, the chamber dilution lifetime may or may not be shorter than the wall loss lifetime of the chamber. Generally, smaller chambers can be cleaned more quickly via dilution than larger chambers because the flows required to clean large chambers are substantial. For instance, a 8 m^3 collapsible chamber at the Paul Scherrer Institute (PSI) can be cleaned from particles after flushing for 6 h, and this can be observed in Fig. 3.1 which shows how the particle number concentration changes as a function of time. In this demonstration, the chamber volume had been reduced to $\sim 4\text{ m}^3$. The red line corresponds to the smoothed particle concentration over a 20 min. window. Over the duration of cleaning, shown in Fig. 3.2 the particle number concentration reached near background levels ($5\text{ \#}/\text{cc}$) at $\sim 24:00$.

Regarding the gas phase, a typical non-linear rate at EUPHORE is a removal of half of the concentration in 30 min. Some gases can be particularly tricky to clean from the chamber due to their “stickiness”. These include some small molecules, such

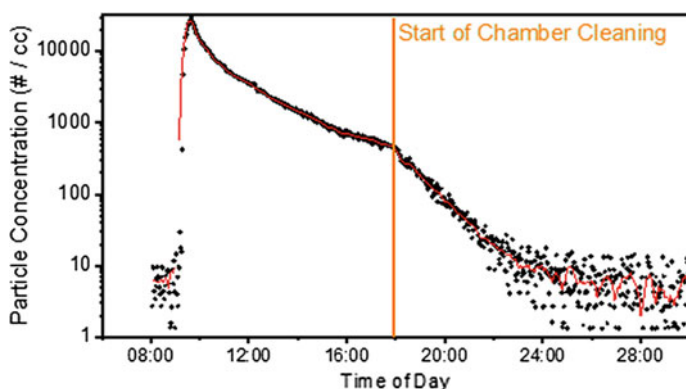


Fig. 3.1 Particle number concentration from an experiment with NH_4SO_4 seeds during photo-oxidation of Toluene +OH in the 8 m^3 chamber at the Paul Scherrer Institute

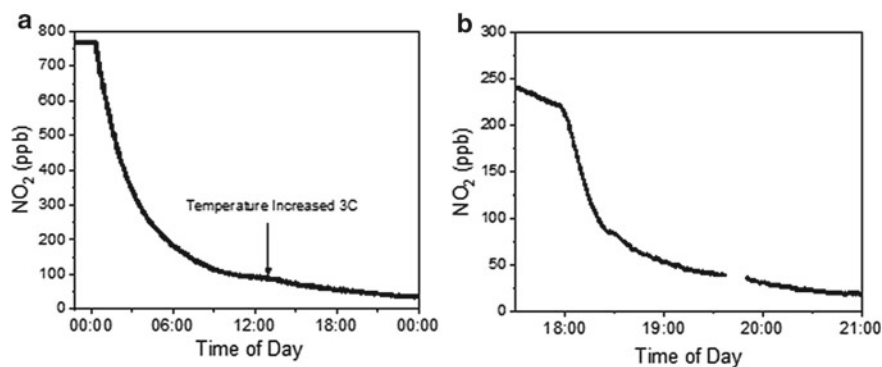


Fig. 3.2 **a** An experiment where 770 ppb of NO₂ had been added to the chamber, and chamber dilution at 18–21 °C over the course of 24 h. **b** Chamber dilution of NO₂ during a temperature ramp from 15 to 33 °C

as: NO₂, HCl, formic acid, ammonia, amines, etc. When different types of “sticky” VOCs are used (or formed) in the chamber it will be necessary to spend time to troubleshoot how to best clean the chamber after such experiments. For instance, in preliminary experiments performed in the PSI 8m³ chamber, with a crystalline N₂O₅ source, large amounts of NO₂ and HNO₃ were formed. This results from the reactions: $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$ and $\text{N}_2\text{O}_5 + 2 \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$. In some initial experiments, large quantities of N₂O₅ were added to the chamber resulting in significant concentrations of NO₂. Figure 3.2a shows the NO₂ concentrations during the cleaning cycle. In the example described here, the temperature of the chamber enclosure was initially 18 °C and was increased to 21 °C. Over 24 h of chamber flushing the NO₂ concentration never decreased below 50 ppb, and continued cleaning was required as a result. In subsequent experiments, the temperature was increased to 30 °C overnight to drive NO_y off the chamber walls and into the gas phase. Figure 3.2b shows cleaning of NO₂ with dilution taking place alongside a temperature ramp from 15 to 33 °C. Here NO₂ is efficiently cleaned out overnight and reaches reasonable concentrations after 3 h of dilution. The initial loss of NO₂ is due to expanding the chamber from ~3 to ~6 m³.

For evacuable chambers, dilution cleaning is often achieved by pumping the chamber down to high vacuum by mean of oil-free pumping systems involving combination of special rotary pumps, roots pump and/or turbomolecular pumps (Barnes et al. 1994; Doussin et al. 1997; Wang et al. 2011). Sometime the systems are completed with series of sorption pumps (De Haan et al. 1999). In comparison to dilution, evacuating the chamber does not only allow the possibility to quickly replace potentially contaminated air with clean air, but also by reducing the total pressure in the chamber, it helps evaporating the low volatility species adsorbed on the walls. This advantage is nevertheless somewhat limited by the fact that the saturating vapor pressure of the species involved in SOA formation are often orders of

magnitude lower than the best vacuum achieved in simulation chambers (Schervish and Donahue 2020).

3.2.3 *Baking*

As seen with in the “oxidation” section, cleaning a chamber generally means combining dilution with a process aiming at pushing the gas-wall partitioning of contaminants towards the gas phase. Raising the chamber temperature can increase that partitioning into the gas phase. Some chambers have the possibility to increase their wall temperature, for example the CESAM chamber (Créteil, France) where the walls are raised to 60 °C for several hours during the cleaning/pumping procedure. The NIES chamber (Tsukuba, Japan) has the capability to reach 200 °C and so to efficiently evaporate semi-volatile species on the surface of the walls. The benefit of raising chamber wall temperature has been more thoroughly described by Schnitzhofer et al. (2014) during the first runs of the CLOUD chamber (CERN). The CLOUD chamber was filled with synthetic air and was heated to 100 °C for 2 days at atmospheric pressure. No significant difference appears between 100 and 5 °C as total VOCs concentration measurements remain in the 1 ppbv range. These authors recognize, nevertheless, that the chamber cleanliness benefited from a heating cycle, when a specific VOC had been added to the chamber for experimental reasons. From this last protocol, it can be recommended that a baking procedure when possible should be coupled with a low pressure evacuation of the chamber for a greater efficiency of low volatility species adsorbed on the wall.

3.2.4 *Manual Cleaning*

The above-described protocols have shown their efficiency in many instances. Nevertheless, in some cases such as the first use of a rigid chamber or after particularly dirty experiments (e.g., soot or mineral dust use, high concentration experiment, bio-aerosol study...) or before a particularly sensitive experiments, it is often needed to physically enter the chamber to manually clean it before applying a more common cleaning procedure. Indeed, some contaminants (dust, soots, bio-aerosol) may exhibit such a low vapor pressure that evacuation or dilution or baking would have a very limited cleaning efficiency. The presence of machining grease on the new material or heavy adsorbed chemicals arising from oxidation experiments may lead to similar issues.

Generally, the manual cleaning of chambers involves the use of significant quantities of both organic solvents and ultrapure water in order to remove both organic and ionic contaminants. Due to the fact that staff will be exposed to the chemical used, the toxicity of the chosen cleaning agent has to be minimized—often absolute ethanol is used. Safety should be considered carefully in manual cleaning processes,

Fig. 3.3 Manual cleaning of an indoor evacuable stainless steel chamber. © LISA-CNRS



for example check that chamber and laboratory are well ventilated, do not allow lone working, ensure appropriate personal protection equipment (PPE) (see Fig. 3.3). Appropriate PPE will also prevent contamination of the chamber by human material (hair, cells...), the proper personal protection equipment has to be used. Ultra clean lint free tissues must be employed. Do not be tempted to take short-cuts; always remove or protect internal fittings such as White cell mirrors!

The benefit of this procedure being mostly to remove low- to non-volatile species, after a manual cleaning, the chamber must be considered as heavily contaminated by the solvent used. Generally, the solvent will be a volatile chemical and will be eliminated through flushing or pumping with or without baking the chamber. Traces of the cleaning solvent must then be systematically sought for, in blank experiments following manual cleaning.

Another possibility is to clean the chamber by applying hot pressurized water steam directly on the walls with a vaporizer to facilitate the removal of sticky contaminants. On a second step, milli-Q grade water is sprayed to help drag dirty water from the walls.

3.3 Preparation of a Clean Chamber Atmosphere

Producing a well-controlled environment not only implies working in a clean chamber but also to be able to fill this reactor with well-controlled matrix i.e., to fill the chamber with clean air. Again, various technological set-up are currently in operation. They mostly depend on the required clean air flow and so of volume of the chamber or the type of experiment (i.e., batch flow operation requires more clean air than static chamber operation).

In one of the biggest chambers in the world, the EUPHORE chamber, a high-volume clean air set-up has successfully been in operation for several decades. The EUPHORE facility comprises of two 200 m³ chambers. Each chamber can be filled with air from a separate air purification system. For pressurizing the filter system

to ca. 6 bar, a screw compressor (Mannesmann, Type Ralley 110 AS) is used. This type of compressor is suitable for continuous operation. After the compressor the air is passed through a condensate trap to separate oil and water from the air. The emulsion is separated in an oil/water separator. Two pressure tanks with a volume of 1 m^3 each are used as a buffer reservoir to reduce the switch frequency of the compressor. The air is dried in adsorption driers (Zander, Type HEA 1400) with an air throughput of ca. $500\text{ m}^3/\text{h}$. These driers are filled with a molecular sieve type 4A (ECO 30%, MOL 70%). With this, a pressure dew point of $-70\text{ }^\circ\text{C}$ is reached and the CO_2 content is reduced significantly. With the help of a charcoal adsorber, NO is eliminated and oil vapor as well as non-methane hydrocarbons are reduced, e.g., benzene and toluene are below the detection limits of the instruments, 70 ppt and 40 ppt (3 standard deviations), respectively. The air inlets are located in the center of the chambers. After passing a pressure reduction valve the clean air is blown into the chamber via silencers of bespoke design. Due to its dimension and the noise when in operation, this device is located in a dedicated room located next to the smog chamber laboratories.

At the SAPHIR chamber, another large ($>270\text{ m}^3$) outdoor chamber, synthetic air is produced by mixing evaporated liquid nitrogen and liquid oxygen (Linde, purity $>99.9999\%$). Mixing is done with flow-controllers to ensure specific mixing ratios of oxygen and nitrogen. A metal tank of several cubic meter serves as reservoir for the consumption of the chamber, but also instruments. It is filled with the mixed synthetic air with a two-point pressure control loop. A similar route toward synthetic air production is used to produce the clean chamber environment found at the Cosmics Leaving Outdoor Droplets (CLOUD) chamber at CERN (Duplissy et al. 2010).

At the CESAM chamber (Wang et al. 2011), synthetic air produced from the mixture of high purity O_2 originating from commercial cylinder (Air Liquide®, Alphagaz® class 1) and nitrogen produced from the evaporation of a pressurized liquid nitrogen tank. Similar to the SAPHIR process, this nitrogen source is cost-effective and free from trace gas such as VOCs or NO_x , but it exhibits a contamination of ca. 200 ppb of carbon monoxide (± 100 ppb depending on pressure service or delivery lot). However, due to its low reactivity compared to atmospheric processes and its very high vapor pressure this was not considered as a major inconvenience either for ozone production studies or for aerosol chemistry studies. Further, blank reactivity experiments (see below) account for the consequences of such a contamination.

The chambers at the Paul Scherrer Institute ($8\text{--}27\text{ m}^3$) utilize an AADCO 250 series (AADCO Instruments, Inc. USA) air purifiers coupled to high pressure air lines. This air purification system provides zero air with background of trace gases including: $\text{O}_3 < 1$ ppb, $\text{CO} < 6$ ppb, $\text{NO}_x < 100$ ppt, organic contamination ~ 4 ppb (Paulsen et al. 2005). These contamination levels are sufficient to study SOA formation, but not clean enough for new particle formation studies such as that mentioned above in CLOUD.

In some specific cases, special care to the cleanliness of the background air must be taken. It is especially the case for experiments involving nucleation event studies where results may be extremely sensitive to H_2SO_4 , NH_3 and Extremely Low

Volatility OC (ELVOC) background concentrations. When relevant these species must be targeted by the analytical techniques involved in the background characterization. These techniques must be extremely sensitive as their target must be monitored in the sub-ppt range to avoid any impact on the results. This is particularly the case for NH_3 background blanks. Bianchi et al. (2012) and Brégonzio-Rozier et al. (2016) have shown that ammonia contamination in the ppt range were not uncommon in simulation chamber. Being ubiquitous at these low concentrations, prone to permeation because of its small size and possibly formed by reduction at the wall of the stainless chamber, ammonia elimination from chamber atmosphere is a particular challenge. Ammonia has been discussed as having a dramatic impact on the nucleation rate (Ball et al. 1999; Benson et al. 2011; Korhonen et al. 1999). It can also play a role on condensation growth if there is an attempt to use low or modest amounts of acidic seeds. Similarly, previous wall HNO_3 contamination can rapidly lead to nitrate buildup in particles.

When humidifying the chamber, significant quantities of water vapor have to be injected to adjust the relative humidity of the simulated atmosphere. As an example, saturating with water a 20 °C atmosphere requires more than 17 g-per-cubic-meter of water which make water the most abundant gas right after nitrogen (N_2) and oxygen (O_2) in most of the atmospheric simulation experiment. In consequence, using the highest purity water is often desirable as soluble species can often be introduced during water evaporation.

3.4 Control and Blank Experiments

Similar to the chamber cleaning protocols, the protocols for blank experiments are specifically developed for each chamber. However, certain procedures are observed by most of the chamber protocols which can be used as a general guideline on how to check for the cleanliness and status of a chamber. Overall, to ensure a basic understanding of the status of a chamber prior to an experiment, most chambers are monitoring the following conditions while oxidants are introduced and/or produced in the chamber:

- Concentration of oxidants (typically O_3 and/or OH)
- Concentration of inorganic compounds (typically NO , NO_2 , SO_2)
- Concentration of volatile organic compounds (VOCs)
- Aerosol number concentrations and size distribution.

In general, the chamber is regarded as clean when the concentration of most of the compounds measured falls below the detection limit of the monitoring instrument. Aside from the direct measurement of contaminant concentration after a cleaning procedure, more dynamic protocols take advantage from the atmospheric processes themselves to characterize invisible (or unmeasured) contamination. Indeed, even if an initial characterization of the chamber state through measurements remains a

clear prerequisite for any simulation run, major contamination affecting the results of the planned experiments are often not detectable.

As an example, in spite of very high cleanliness levels, it was observed at the CLOUD chamber from CERN (Duplissy et al. 2010) that a small rise of wall temperature over a short time interval almost always gave rise to a spontaneous burst of freshly nucleated particles. This effect most probably due to trace vapors (sulfur dioxide, sulfuric acid and/or organic compounds) previously below the instruments detection limits and who, when released from the walls of the chamber, contributed to nucleation.

“Blank” or “control” experiments are hence critical part of the experimental strategy to such an extent that they need to be carefully analyzed and stored together with the experiments themselves. Similarly, to the chamber cleaning protocols, the protocols for blank experiments may be specific to a chamber but they are always tightly related to the objectives of the experiments. There is certainly a significant diversity. However, certain procedures are observed by most of the chamber protocols for a common type of experiment and can be used as a general guideline on how to check for the state of a chamber.

3.4.1 Walls Chemical Inertia

The walls of a chamber are a vital aspect of any experiment taking place. The walls represent a large surface area which facilitates interfacial reactions and consequently can be a reactive sink or source of any gas phase species. Therefore, characterizing the walls’ oxidative or reductive potential represents a fundamental task in any chamber blank experiment. Adding chemically sensitive species (e.g., O₃, NO, NO₂, etc....) to the chamber and following their time series can be a useful blank experiment to determine the role the chamber walls are playing. The lifetime of sensitive species such as ozone or NO, in a ‘clean’ chamber filled with air is often considered as indicators of the chemical inertia of the chamber walls. (Leskinen et al. 2015; Wang et al. 2011). The clean-air and NO_x system has been studied in Teflon chambers in a number of studies (Bloss et al. 2005; Metzger et al. 2008; Wang et al. 2014). It has been proven as a very sensitive system to detect the release of NO_y species from the wall or unknown radical sources. As these processes are often related to wall cleanliness, these blank experiments provide useful insight on chamber walls physico-chemical behavior. Moreover, as the NO_x/air/light chemical system lies in the heart of tropospheric chemistry oxidation scheme, it is now promoted, in addition, as reference experiments that need to be carried out regularly not only to check for chamber contamination but also to set the chamber auxiliary mechanism parameters. Protocols are hence recommended in Chap. 2.

3.4.2 Chamber Dependent Radical Sources

The history of the chamber is also important when considering the chemical inertia of the walls. Indeed, walls are not only sinks for reactive species or products, they are also well known sources for species that can more or less directly affect the radical balance of a simulation experiments. In particular, HONO and HCHO are among the most common wall emitted species that will give rise to OH radical through photolysis. For low NO_x experiment, irradiating a mixture of a reactive VOC (such as propene) and air while checking that ozone formation remain negligible is a good diagnostic. Another option could be being able to model the production of O₃ in high NO_x experiments with a reactive VOC (e.g., propene) (refer to protocol provided in Chap. 2).

To characterize an invisible organic reactivity of the chamber background, one can photolyse a “clean air” atmosphere (Hynes et al. 2005) and control for the formation of any relevant species (see Sect. 2.4, Chap. 2). This procedure must be carried out under typical relative humidity conditions as humidity is known to affect release of some adsorbed contaminants. Ozone is certainly a good target for such a blank experiment due to the amplification of the ozone production through radical cycle. HCHO or formic acid as termination products of oxidation processes are also common species arising under such conditions.

Aside from gas phase processes, an undetected organic reactivity of the chamber background can also affect aerosol formation. These blank experiments are especially important to carry out when focusing on weak secondary aerosol producers such as isoprene. As experiments are performed semi-volatile and low volatility oxygenated organics can build up on the chamber walls changing their effect on experiments. These species coming off the walls can act as a source of reactivity with O₃ or OH thereby resulting in the formation of SOA. Therefore, it is necessary to conduct blank experiments on a regular basis. Proper blank experiments are performed in the presence of an oxidation source (OH or O₃) and seed aerosol, which provides a surface for low-volatility species to condense. For example, after a series of experiments in the PSI chamber where a polymer-mix was injected into the chamber, it was necessary to check the cleanliness of the chamber.

Sources of VOC contaminations can also result from the presence of undesired components of the chamber itself. In experiments at the CLOUD chamber in CERN, plastic material used in both sampling lines and the O₃ generator itself were responsible for the production VOCs that correlated with the presence of O₃ (CLOUD3 and 4 in Fig. 3.4). Likely from the reaction of O₃ with the material itself. Once the plastic parts were removed from the chamber and a new O₃ generator was built out of quartz and stainless steel then the production of VOCs was minimized and there was no longer a strong correlation with the presence of O₃.

Similarly, when studying SOA formation from VOC oxidation, it is often recommended to set-up the oxidation process (e.g., ozonolysis or OH oxidation) in the presence of seeds aerosol, absence of any VOC and to monitor, as a background formation, the aerosol formation and growth. (Leskinen et al. 2015).

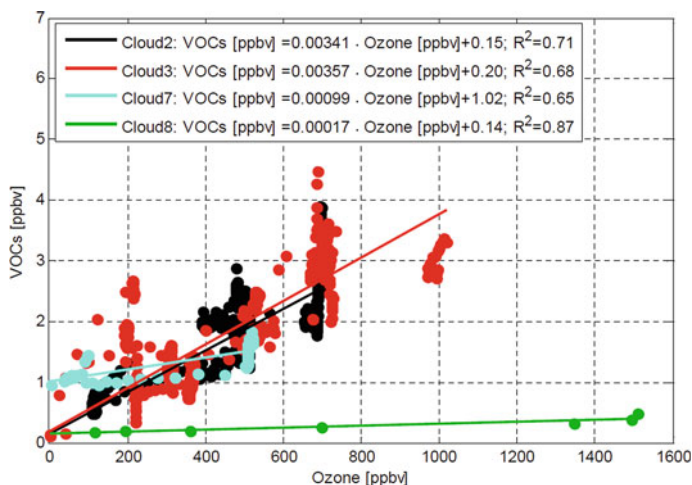


Fig. 3.4 Correlation between VOCs (C1-C3) measured by the PTR-MS. In CLOUD 2 and 3 there were plastic parts present on the ozone generator and other instruments around the chamber. After their replacement, the contamination was significantly diminished. (Reused with permission from Schnitzhofer et al. 2014 Open access under a CC BY 3.0 license, <https://creativecommons.org/licenses/by/3.0/>)

3.4.3 Soluble Species Affecting Potential Aqueous SOA Formation

The scope of simulation chamber use has been extended to the investigation of cloud assisted aerosol formation (Ervens et al. 2011). Cloud assisted SOA formation is extremely difficult to control and is a very sensitive process to potential water-soluble contaminants. Brégonzio-Rozier et al. (2016) found out that it was necessary to perform a thorough manual cleaning involving the use ultrapure ethanol, followed by bathing the walls with large quantities of ultrapure water, and completed by baking the wall to 60 °C and overnight pumping at a secondary vacuum. They also implemented an experimental sequence including, before each experiment, a cleaning session followed by a “blank” experiment. Considering that the overall goal of their study was to quantify aqSOA formation trigger by a cloud event, these “blank” experiments consisted of triggering cloud formation events in the ‘clean’ chamber only filled up with ultrapure air at RH close to 100% (Brégonzio-Rozier et al. 2016). An example of these tests aiming at quantifying a potential background aqSOA formation is given in Fig. 3.5. It can be seen that even if the cleaning protocol was not able to totally suppress the formation of particles through cloud processing of impurities, it was able to reduce its extent by a factor of ca. 5 and to bring it close to the instrument detection limits. The authors organized the curation of their experiments, together with the related “blank” experiments, in order to take into account this artifact in their data analysis.

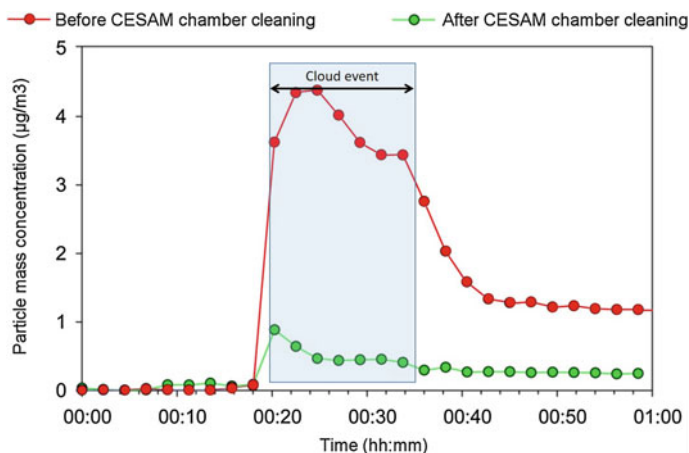


Fig. 3.5 Effect of cleaning a cloud chamber on background aqueous SOA formation during a cloud event (adapted from Brégonzio-Rozier thesis 2013). The mass concentration is deduced from SMPS measurement assuming spherical particle and a density of 1. The particles are dried to below 30% RH before injection in the differential mobility analyzer

Finally, protocols for preparing the chambers differ strongly with regard to chambers (material, size, specialization of each chamber) and even more with regard to the scientific objective of the planned experiments. Cleaning procedure must take this into account as well as the experiments that were previously carried out. Every time it is possible, the experiments themselves must be accompanied with control/blank experiments aiming at evaluating the cleanliness and status of the chambers as well as the chemical background reactivity of the reactive mixture (bath gas, purity of water, of precursors...).

Preparing a chamber for conducting robust atmospheric simulation experiments, is not only about applying carefully standard cleaning protocols and reactive mixture recipes, but also about implementing the full traceability of the experimental conditions, that implies the curation of blank experiments datasets, together with the precise preparation protocol applied.

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