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CLOUD STATUS & LONG-TERM PLANS

CLOUD Collaboration

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Abstract

The CLOUD experiment (PS215, CLOUD 2000, 2006) started operation in November 2009 and has since collected data during eight runs at the CERN PS for periods from 4 to 12 weeks duration (Table A1). The primary goal is to understand the influence of galactic cosmic rays (GCRs) on aerosols and clouds, and their implications for climate. Atmospheric aerosols and their effect on clouds are poorly understood and yet important for climate. Indeed, they are recognised by the Intergovernmental Panel on Climate Change (IPCC 2013) as the largest source of uncertainty in present radiative forcing and in climate projections over the 21st century. Although its design is optimised to address the cosmic ray question, CLOUD is the first experiment to reach the demanding technological performance and ultra-low contaminant levels necessary to be able to measure aerosol nucleation and growth under controlled conditions in the laboratory. Consequently CLOUD has become the world's leading laboratory experiment to address not only the influence of cosmic rays on aerosol-cloud processes but also more general and equally poorly understood aspects.

This has been reflected by two papers in Nature (Kirkby 2011, Almeida 2013), one in the Proceedings of the National Academy of Sciences (Schobesberger 2013) and one in Science (Riccobono 2014) that, together, have established the vapours responsible for atmospheric nucleation and measured the particle formation rates and the influence of ions from galactic cosmic rays. Although these vapours (sulphuric acid, ammonia, amines and oxidised biogenic vapours) are likely to explain a large fraction of atmospheric nucleation, CLOUD has yet to explore all the conditions – vapour concentrations, vapour combinations, temperature, etc. – and so there are many important measurements remaining.

CLOUD measurements are repeated under three conditions in order to isolate and measure the influence of ions: "neutral" (ion-free, i.e. with the chamber's electric clearing field present), GCR (without beam) and then pion beam conditions (variable ion pair concentrations equivalent to between ground level and the top of the atmosphere). Ions are found to significantly enhance the formation rate of aerosol particles under certain conditions, and the climatic effects are being evaluated with the University of Leeds' global aerosol model, GLOMAP.

More recently, CLOUD has expanded its scientific reach to study direct ion effects on liquid and ice clouds themselves. Here, clouds are formed by adiabatic pressure reductions, as in a classical Wilson cloud chamber. Once more, there are a large number of cloud processes where CLOUD can make significant contributions, beyond the influence of ions, that are important for climate and yet poorly understood.

The purpose of this document is to take stock of what has been learnt in the first five year's operation of CLOUD and to use this experience to foresee how the scientific programme and the experimental apparatus may evolve over the next few years. So far CLOUD has in a very real sense been in a discovery mode, which has opened up many more questions than it has settled. So the experimental programme outlined in this document should be considered as representative rather than definitive since we can expect to find more surprises in future. Furthermore, it is important to appreciate that the nature of our laboratory studies in atmospheric science does not allow precise projections to be made of the required beam time as is customary (and feasible) for particle physics experiments.

The CLOUD collaboration is inter-disciplinary and very large by the standards of atmospheric science experiments. Thus, as well as being a state-of-the-art research facility, the experiment has proved a fruitful "trading zone" for the exchange of ideas and methods between scientific communities and between global and process modellers and experimentalists working both in the laboratory and in the field. In this way the virtuous circle of experimental work with CLOUD, modelling of the atmospheric implications, field measurements, and further experimental work guided by model results is efficiently perpetuated and can continue for the foreseeable future.

With these considerations – and based on our first five years' experience – we estimate that CLOUD will need a further ten years' operation at the CERN PS to carry out the important experimental and modelling programme described here and represented schematically in Fig. A1. We consider this to be a conservative estimate since it does not take into account either further scientific discoveries or technical advances that could open new experimental windows on ion-aerosol-cloud-climate interactions.

Table A1: CLOUD experimental campaigns at the CERN PS.

Run	Month	Year	Aim
CLOUD1	Nov–Dec	2009	Commissioning
CLOUD2	Jun–Jul	2010	Binary H_2SO_4 and NH_3 ternary nucleation
CLOUD3	Oct–Nov	2010	Binary H_2SO_4 and NH_3 ternary nucleation
CLOUD4	Jun–Jul	2011	Dimethylamine & pinanediol ternary nucleation
CLOUD5	Oct–Nov	2011	Free tropospheric binary H_2SO_4 & NH_3 ternary nucleation
CLOUD6	Jun	2012	Initial cloud formation (cloudy) experiments
CLOUD7	Oct–Dec	2012	NH_3, dimethylamine & alpha-pinene ternary nucleation & growth
CLOUD8	Oct-Dec	2013	Low H_2SO_4 nucleation & cloudy expts. (aqueous phase & ice, with GCRs – PS off)
CLOUD9	Sep-Nov	2014	Cloudy experiments (aqueous phase & ice) & small ion studies

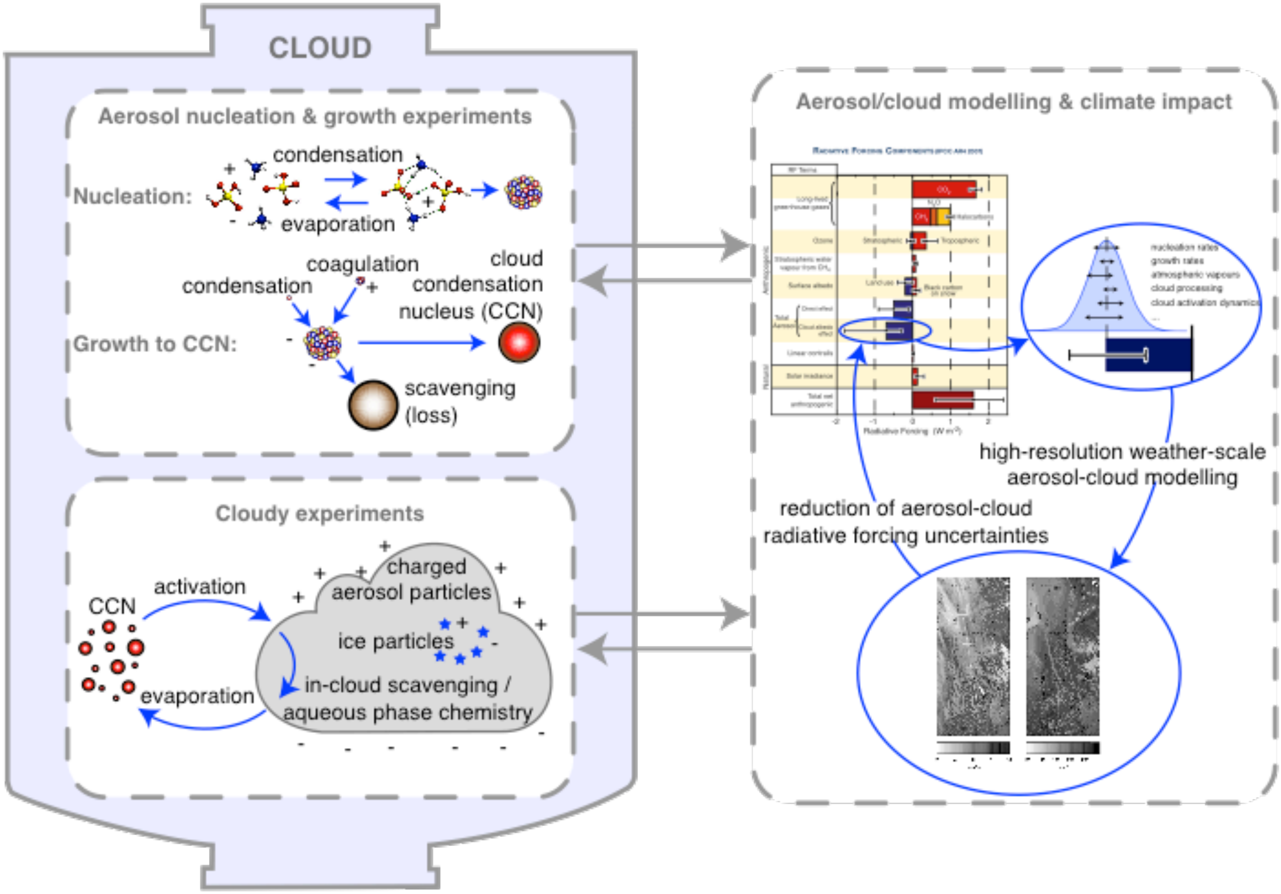

Fig. A1: Schematic representation of the planned CLOUD experiments and modelling.

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1. INTRODUCTION

1.1 Climate change

Climate change is one of the most important issues facing society in the 21st century. The Intergovernmental Panel on Climate Change estimates that by the end of this century Earth will likely be warmer than at the beginning by 2.6-4.8^{o}C (5-95% model range) [1, 2]. However, our ability to accurately forecast long-term climate change is clouded by uncertainty in how aerosol and cloud physics may have changed between the pre-industrial era and the present, and how it may continue to change in the future.

The influence of fine particles and atmospheric ions from galactic cosmic rays (GCRs) on clouds, and how that influence may have changed over time, is the central focus of the Cosmics Leaving OUtdoor Droplets (CLOUD) experiment at CERN. CLOUD combines exceptional cleanliness; precise control and measurement of condensable vapours and tiny particles at extremely low concentrations; sufficient chamber size for lifetimes of vapours and molecular clusters to match those in the atmosphere; control over ion production rate from zero to high rates characteristic of the upper atmosphere, using the CERN PS beam; precise and uniform control of "sunlight" from a UV fibre-optic system; and highly stable operation at any temperature found in the troposphere. This unique equipment enables the study of chemistry associated with new-particle formation and growth literally molecule by molecule as clusters form and grow. Control over ion formation and removal enables complete differentiation of neutral from charged processes, while parallel control over relative humidity coupled with adiabatic expansion enables exploration of water and ice formation, and any associated effects of atmospheric ionisation on ice formation and charge separation in glaciated clouds.

The "climate forcing" of CO_2 and other greenhouse gases is well understood. Climate forcing is the effective increase in energy flux on Earth's surface for a specified change in the radiative system, such as the increase of a greenhouse gas, since a pre-industrial baseline, which by convention is taken to be 1750. The total estimated forcing from greenhouse gases is about 3 Wm^{-2}, compared with an average incident solar flux of 241 Wm^{-2} (solar irradiance averaged over Earth is 345 Wm^{-2} but about 30% is reflected back to space because of Earth's albedo) [1]. The forcing from long-lived greenhouse gases is easy to calculate because the radiative transfer physics is well understood and we have accurate data on most of the important greenhouse gas concentrations over time.

The climate problem is often split between this forcing term and a "climate sensitivity," which is the global average temperature change for a given forcing. Conventionally, a forcing equivalent to doubling of CO_2 from the pre-industrial 280 ppmv to 560 ppmv is used as a reference for climate models since this could be reached by the end of the present century. The climate sensitivity has been stubbornly uncertain over the years, with best-guess estimates remaining between 2K and 5K from the seminal 1979 "Charney" report of the US National Academy of Sciences until the current IPCC AR5 [1] One reason for this persistent uncertainty is that the climate sensitivity includes complex feedbacks that are not well understood. This underscores the importance of a precise determination of the net forcing since that can be used with the observed temperature rise to experimentally determine the climate sensitivity.

1.2 Radiative forcings from aerosols and clouds

Central to the uncertainty in forcing and hence sensitivity is the albedo mentioned above. Roughly half of the albedo is due to reflection from clouds. Clouds are not uniformly white; they are reflective because of multiple scattering from refractive droplets, and so cloud whiteness is a function of the cloud-water surface area. Because cloud-water volume is fixed by the amount of water vapour in air, cloud-droplet number governs cloud albedo. Cloud-droplet number is in turn controlled by a subset of particles known as cloud condensation nuclei (CCN). To a good approximation, CCN are soluble particles larger than about 50-100 nm diameter.

They require a sufficient number of water-soluble molecules (roughly 10^6) to allow nascent water droplets to overcome a free-energy maximum associated with high surface curvature (the Kelvin effect) and Raoult's-law (suppression of vapour pressure by solute molecules). Thus cloud-droplet number concentrations are highly correlated with the number concentrations of particles larger than about 50-100 nm [4].

Aerosol particles thus influence climate through the indirect aerosol effect, known as the Twomey effect [5]. They also influence climate through a direct effect simply by scattering light. The aerosol-climate effects are especially strong where CCN numbers are low (because the effect saturates) and over dark surfaces (because the contrast with white clouds is high). The oceans, where CCN numbers are low and contrast is high (since oceans have low albedo), are thus thought to be most sensitive to aerosol-climate effects.

A climate effect is not a climate forcing; the effect influences Earth's energy balance, but the forcing is the change in that effect between some date and the reference date (1750). The climate forcing from the indirect aerosol effect is highly uncertain because the pre-industrial number of CCN is unknown; furthermore, the indirect effect of CCN number saturates strongly, so that a given incremental change in CCN has a much larger forcing at low CCN than at high CCN number [6]. The current estimate of indirect aerosol forcing ranges from roughly -1.5 to 0 $\mathrm{Wm^{-2}}$ with a best estimate of -0.5 $\mathrm{Wm^{-2}}$ [1]. The forcing is negative because the CCN number has increased due to pollution in the industrial era. However, while it is obvious that the mass of fine-particle pollution has increased since pre-industrial times (witness the fine-particle haze over any city, especially in the developing world), the budget for particle number is far less certain, and this applies to CCN number as well.

1.3 Aerosol particle nucleation and growth to cloud condensation nuclei (CCN)

Most particles are ultrafine – diameters between 1 and 50 nm. Most CCN are formed by the condensational growth of those ultrafine particles [7], as opposed to direct emission of CCN via mechanisms like sea spray or combustion. Ultrafine particles have two sources: nucleation, where particles are formed from supersaturated condensable vapours at roughly 1 nm in diameter, and ultrafine emission, often from combustion in a broad mode between 10 and 30 nm. However, because of their high Brownian diffusivity, all ultrafine particles are also lost efficiently to larger particles forming the "background condensation sink." The coagulation loss rate is a maximum when the particles are in the few nm size range. Thus a key to understanding CCN number is to understand the survival probability of particles – specifically the likelihood that they will grow to CCN size from any given starting size [8]. Depending on their growth rate and the ambient condensation sink, nucleated particles may have survival probabilities as high as between 0.01 and 0.08 (and sometimes much less), while larger combustion emissions have correspondingly larger survival probabilities of around 0.20 [7,8]. Because high nucleation rates often mean high production rates of condensable vapours, and the condensable vapours also cause the background particle surface area to grow, there is a strong negative feedback of the nucleation rate which dampens the sensitivity of CCN to the nucleation rate [8-10].

In spite of the low survival probability and negative feedbacks, roughly half of the CCN worldwide appear to arise from new-particle formation [7, 9, 10]. The most dramatic manifestation is the now common daily observations of "bananas" in the atmosphere showing bursts of new particles forming in the atmosphere. Banana plots show the time progression of the particle number size distribution between 1 and 100 nm, which typically reveal emergence of new particles shortly after the onset of intense photochemistry from sunlight, followed by steady growth toward 50-100 nm over the course of the day [11-15]. In many locations, particle formation events occur frequently, between 20% and 50% of the days, and often with pronounced seasonal cycle peaking in spring and autumn [12, 13]. Ambient observations also indicate that sulphuric acid is involved in the majority of nucleation events [16–20], but that in most cases condensation of something other than sulphuric acid (probably organic vapours) drives the subsequent growth [21–23]. However, while most observations are confined to the continental boundary layer, global model simulations indicate that much of the nucleation may occur in the free troposphere (the atmosphere below 10-15 km but above the boundary layer of about 1 km thickness) [9, 24, 25]. Much less is known about this, as observations are difficult, and experiments must reach the low temperatures and concentrations of the free troposphere. Particle nucleation and growth in the free troposphere is an area where CLOUD can provide valuable information that is extremely hard to obtain in the atmosphere.

1.4 Changes of CCN in the industrial era

Because sulphuric acid and organic vapours are involved in nucleation and growth, it is highly probable that CCN production from nucleation has increased during the industrial era, and thus that there is a negative climate forcing (a cooling) associated with these changes. Critical to determining the forcing is to determine the magnitude of the aerosol indirect effect in the pre-industrial era, because of the nonlinearity of the indirect effect. If CCN numbers were relatively high in the pre-industrial era, then the forcing due to anthropogenic changes in CCN would be modest; on the other hand if pre-industrial CCN levels were low, then the forcing due to anthropogenic changes would be high [26].

CCN-related aerosol effects can also occur independent of human activity. One such effect was proposed in the 1980s as a negative feedback mechanism within the climate system (a thermostat would reduce climate sensitivity to a given forcing). Named the "CLAW" hypothesis after the authors' initials, the conjecture was that sulphuric acid derived from marine dimethyl sulphide (DMS) emissions might increase in a warmer climate if DMS production in the surface ocean increased with warming. This could cause an increase in CCN and a corresponding cooling via the indirect effect on clouds [27]. A similar negative feedback may also occur with trees, which emit more monoterpenes and other biogenic vapours when stressed by higher temperature or too much sunlight. CLOUD has recently shown that oxidised vapours derived from these monoterpenes form new particles with sulphuric acid [31].

Another natural driver of CCN variability could be the variation in ionisation due to short-term and long-term fluctuations in solar activity and the solar wind, which modulates the galactic cosmic ray flux, causing variations in the ion-pair formation rate throughout the atmosphere [6, 28]. Typical variations of the cosmic ray flux over the solar cycle are around 20% at 3 km altitude in high latitudes. It is thought that the GCR flux was around 40% higher during the Little Ice Age (1645-1715) compared with today's minima during the solar cycle [28]. It has been proposed that GCR variations could explain a substantial fraction of long-term climate variability and, indeed, it is a central goal of CLOUD to address this question and settle it with quantitative measurements. Here it is likely that the pre-industrial climate would have been more sensitive to any putative cosmic ray influence since the CCN number concentrations were lower.

Pre-industrial CCN concentrations are important because they define the baseline from which the present-day aerosol-cloud forcing is calculated. However, because they cannot be measured, pre-industrial CCN concentrations and their global distribution must be determined using global aerosol models. Thus there is a critical need to establish nucleation and growth mechanisms via laboratory experiments such as CLOUD and to embed them in climate models. Ambient measurements are crucial as well but alone they cannot constrain the aerosol-climate effects; to establish the baseline of the non-linear aerosol-climate response curve, laboratory experiments and global models are essential. For this reason CLOUD was established with precise control over the hypothesized chemical and physical drivers of nucleation, including levels of sulphur, base vapours, and organics, temperature, relative humidity, and ionisation rate. The consortium was established with a tight linkage to global aerosol modelling and climate modelling so that the global effects of the laboratory measurements could be assessed and, furthermore, so that the models could guide the experimental measurements to ensure that robust parametrisations can be made with the experimental data covering the full range of ambient conditions.

1.5 CLOUD results so far

CLOUD has published 2 articles in Nature [29, 30], one in Science [31], one in PNAS [32] and one in ACP [33] along with another 3 under review in PNAS [34], EST [35] and ACP [36], and one about to be submitted to Science [37]. In addition, there have been 7 CLOUD papers describing technical developments of instruments and analysis methods. Experiments have systematically measured new-particle formation and growth rates along with particle composition for a sequence of systems thought to be important in the atmosphere. The experiments have explored a wide range of vapour concentrations, ion pair production rates, and temperatures encountered in the troposphere.

The first CLOUD campaigns have addressed nucleation mechanisms involving sulphuric acid and various stabilising agents including ions, ammonia, dimethylamine, and oxidised organic vapours. For the first time, a laboratory experiment has observed nucleation rates that match those observed in the atmosphere [30, 31]. Concurrent measurements of cluster molecular composition provide an additional important constraint for atmospheric comparisons [32]. To match the atmosphere, nucleation in the laboratory must occur at the correct rate and also produce particles of the correct molecular composition.

Broadly, the initial campaigns revealed that sulphuric acid can nucleate at rates observed in the lower atmosphere, but only with a stabilising agent. Sulphuric acid nucleation alone (known as binary homogeneous nucleation because water vapour is believe to be involved in all cases) is many orders of magnitude too slow to explain atmospheric observations [29]. The stabilising agent can be charge [29], a weak base (ammonia) and charge [29], a strong base (dimethylamine) [30], or organics [31, 32]. In all cases, nucleation is enhanced by charge from cosmic rays when the nucleation rates are low. The collective findings are influential, as indicated by the number of high-impact publications [29, 30, 31]. Reference 29 has already been cited 179 times and is in the 97th percentile of articles of a similar age in Nature (ranked 21st out of 863 tracked articles).

Two essential features of the CLOUD experiment are apparent. Firstly, composition measurement of molecular clusters is essential [29-32]. This is because extremely low levels of contaminants such as ammonia can appear in emerging clusters when they contain only a few molecules [29]. Secondly, with measurement of the contaminants and scrupulous control of materials and conditions, it is possible to drive contaminant condensable vapours down to levels well below 1 part in 1 trillion where they are not influential and then systematically introduce them to explore their role over the range of levels observed in the atmosphere [29, 30]. A corollary to this finding is that experiments that do not measure cluster composition and lack such control cannot claim to be free of these contaminants. In parallel, the control over ionisation has revealed that essentially in all cases where nucleation is slow, the presence of charge enhances the nucleation rate [29–31]. However, when nucleation is too slow, then the particle growth is also likely to be slow, and then particle survival probability will be very low [38, 39]. Nevertheless, there are conditions – especially in the free troposphere - where relatively slow nucleation, slow growth, and low ambient aerosol particle backgrounds mean that slow but persistent nucleation and growth is a significant source of CCN. A major finding of the CLOUD campaigns is that organic compounds can participate in nucleation from the very first molecular steps [31, 32]. This is consistent with a few earlier experiments [40, 41], as well as theoretical expectations, [38], but the CLOUD experiments were the first to control the sulphuric acid and organic concentrations independently and measure the molecular composition of the embryonic clusters [31]. Furthermore, the essential role of the global modelling was made clear, as implementing the new ternary biogenic nucleation mechanism based on the CLOUD experimental findings into a global model improved the seasonal predictions at numerous continental measurement sites in ways strictly outside of the variance range of prior predictions [26, 31]. Given the emerging importance of organics, it is thus clear that future experiments will need to explore and constrain the role that variations in atmospheric oxidation chemistry play in changing the rate of nucleation associated with these vapours. Although biogenic vapours arise predominantly from natural sources (trees), human activity changes the oxidation chemistry of the atmosphere by adding further organic compounds and by changing the way in which these vapours are (most notably by changing the relative levels of oxidants: OH radicals, ozone, and NO_3 radicals).

Given the rapid progress by CLOUD experiments and modelling, by field experiments and by quantum chemistry, there is reason for optimism that, within the decade, experiments, observations and theory will be able to converge on an understanding of aerosol particle nucleation and growth in the atmosphere, and the influence of ions. Future CLOUD campaigns will drive that convergence by systematically exploring a range of potentially important organic compounds and by pushing the state-of-the-art for characterising the oxidation chemistry. Given the ubiquity of bases (ammonia and amines) in the atmosphere, the acid-base and hydrogen bonding acid-oxidised organic pathways will then be more fully explored as a coupled “cocktail” system. However, an arguably more important objective over the coming decade will be to combine CLOUD experiments with global modelling in order to constrain the nucleation rates and CCN concentrations in the pre-industrial area. Successful experiments and modelling of current ambient observations will be an essential element, but modelling for pre-industrial conditions, coupled with experimental constraints on the likely ranges for key controlling species during that era, has the strong potential to greatly improve our understanding of aerosol climate forcing and, in so doing, to improve the precision of our understanding of Earth’s climate sensitivity and, in turn, reduce the uncertainty of climate projections over the 21st century.

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2. AEROSOL NUCLEATION AND GROWTH EXPERIMENTS

2.1 Current understanding prior to CLOUD

Over the past decades the formation of new aerosol particles in the atmosphere, as well as the growth of these particles, have been subject of intense investigation. Aerosol nucleation was found to occur at various regions in the atmosphere and under a wide range of conditions. Nucleation was identified in the upper free troposphere [Brock et al., 1995; Lee et al., 2003], in the mid troposphere [Clarke et al., 1999; Weber et al., 2001] and in the planetary boundary layer [Kerminen et al., 2010]. It was found to occur in pollution plumes, urban, rural, forested and pristine arctic conditions, in continental, coastal, and marine environments (for an overview see e.g., [Curtius, 2006; Kerminen et al., 2010; Kulmala et al., 2004]). Aerosol nucleation plays a decisive role for the number concentration of aerosol particles in the atmosphere. Results from the Leeds global aerosol model GLOMAP show that about half the global cloud condensation nuclei (CCN) originate from nucleation [Merikanto et al., 2009]. Aerosol nucleation is therefore regarded as a key process for understanding clouds and climate. Despite several hundred individual studies on atmospheric observations of aerosol nucleation, a fundamental understanding is still lacking. In particular, before the start of CLOUD we had yet to:

- identify and quantify the chemical species participating in atmospheric nucleation,
- quantify the production of the nucleating species from their gas phase precursors,
- identify the nucleation mechanism (e.g. neutral vs. ion-induced nucleation),
- quantify competing loss processes such as loss of nucleating and condensable species on pre-existing aerosol and on other surfaces such as trees,
- determine the growth rates between the critical size and particle sizes of ~3nm.
- determine the species that contribute to the growth of the particles up to CCN sizes (>50 nm).

Due to these unknowns it remained impossible to predict when and where nucleation would happen, how many particles would form and how fast the particles would grow.

For many years it was assumed that the binary nucleation of sulphuric acid and water is the most important nucleating system in the atmosphere [Curtius, 2006]. But even for this comparatively simple system, and despite large experimental efforts, broad disagreement and confusion existed on the experimentally-measured nucleation rates as a function of sulphuric acid concentration (see e.g. [Benson et al., 2008; Laaksonen et al., 2008; Sipila et al., 2010; Zollner et al., 2012]. More than four orders of magnitude difference in sulphuric acid concentration were measured to produce the same value of the nucleation rate, J ($cm^{-3}s^{-1}$). Similarly, power dependencies between 1.5 and 10 (and even up to 20) were reported for the slope of ln (J) as a function of ln ($[H_2SO_4]$). According to the first nucleation theorem, this slope should indicate the number of molecules of the nucleating substance in the critical cluster (the cluster where the evaporation rate equals the growth rate). A similar situation existed for other chemical systems; the influence of ammonia, amines, and organics on J and growth rate was unclear. Some laboratory studies found an enhancement of the nucleation rate of sulphuric acid in the presence of organics while others did not [Zhang et al., 2004, 2009; Berndt et al., 2005]. However, these experiments were performed under very high concentrations of sulphuric acid not representative of the atmosphere. Although Metzger et al. [2010] found nucleation rates of sulphuric acid and organics typical for ambient conditions, many questions remained. In that study the concentrations of sulphuric acid and the nucleating organics were modelled from the precursor decay, and a potential influence of impurities in the Teflon bag smog chamber could not be ruled out. Moreover, the experiment could not distinguish between an enhancement of the growth rate due to organics and an enhancement of the nucleation rate. In addition, the influence of ions in nucleation cannot be studied in Teflon bag chambers since the plastic material is an efficient scavenger of charged molecules and clusters due to static electric fields. Furthermore, reliable laboratory studies for the dependence of J and growth rate on temperature and relative humidity are still missing.

In most atmospheric observations, sulphuric acid concentrations have been shown to be insufficient for driving the observed growth rates of aerosol particles even in the initial size range of few nanometres (see e.g. Paasonen et al. [2010]. It has been suggested that organic vapours having low enough volatilities for condensing on these freshly formed particles could be responsible for this unexplained growth (e.g. Riipinen et al. [2013]). Previously, the oxidation pathway leading to an oxidation state high enough for the required low volatilities has been unclear, since it was assumed that several oxidation steps by reactions with oxidizers such as ozone or hydroxyl radical were needed. However, recently Crounse et al. [2013] and Ehn et al. [2014] showed in their laboratory experiments that extremely low volatility organic compounds (ELVOCs) can form in a fast auto-oxidation process at levels sufficient for explaining the high growth rates. In this process, the initial ozonolysis of an organic vapour starts a chain reaction that oxidizes the vapours further by repeated collisions with oxygen molecules on the same initial organic molecule. Due to the abundance of oxygen molecules in atmosphere, this process is very fast and converts a high fraction (several per cent) of ozone-vapours to ELVOCs.

2.2 CLOUD's contribution

The CLOUD facility combines several decisive advantages over previous laboratory nucleation experiments:

- The large 26 m^3 reactor allows nucleation experiments at atmospheric levels of the participating vapours (ppqv-pptv), involving extremely slow molecular arrival rates on the growing clusters.
- Despite the large size of the reactor, very low levels of contaminant substances are achieved. Contaminant species are continuously monitored with a suite of highly sensitive instrumentation.
- The large size of the reactor allows simultaneous operation of a comprehensive suite of instruments with high sample flow rates to reduce sampling line losses of condensable gases and small particles.
- CLOUD combines a large number of partly redundant state-of-the-art instrumentation to cover the full range of measurements of precursor gases, nucleating gases, ions, cluster concentration, cluster chemical composition, and aerosol particle number concentration and size.
- A highly flexible, state-of-art gas supply system provides the chamber with humidified synthetic air from cryogenic liquids and delivers precise amounts of ozone and selected trace gases at pptv-ppbv levels.
- The CLOUD aerosol chamber is homogeneously mixed and precisely temperature-stabilised over the full range of atmospheric conditions (-70 to +40°C).
- Photochemical processes are studied with precise control of the UV intensity and without introducing any additional heat load inside the chamber, by means of a unique UV fibre optic illumination system.
- Operation with the CERN pion beam or with the electric clearing field allows direct quantitative comparison of the neutral and ion-induced nucleation processes (Fig. 2.1 shows an example event).
- Nucleation rates and growth rates are determined with high precision directly from the measurements.
- Experiments are highly reproducible.
- Measurements are supported by detailed process modelling at the molecular level.
- The experimental data are tightly integrated with a global aerosol/cloud model (GLOMAP), ensuring that a) the climatic effects of the experimental measurements are evaluated and b) the global model can guide experimental measurements to be carried out at the most important atmospheric conditions.

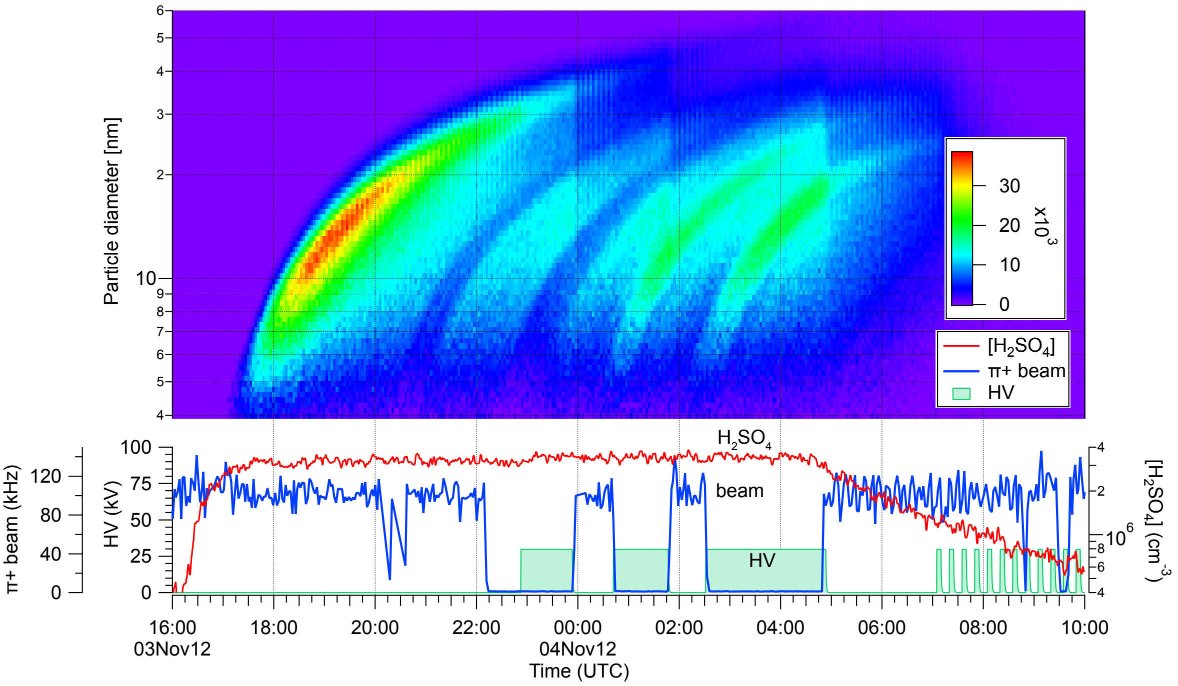

Figure 2.1: Example of ion-induced particle formation during the CLOUD7 campaign. a) The run started at 16:11, 3 November 2012, when the fibre-optic UV system was turned on to establish 4 10^6 cm^{-3} [H_2SO_4] in the chamber. The UV is turned off at 04:49, 4 November 2012, and the chamber cleared of aerosol particles in preparation for the next run. During the run, only the ionisation conditions were varied in the CLOUD chamber, by adjustments of the beam intensity and/or high voltage clearing field, as indicated. b) The variations of ionisation produced a strong response in the rate of nucleation of new particles, as shown by nucleation bursts (banana-shaped events) recorded in the scanning mobility particle sizer (SMPS).

These advantages allow us to perform atmospheric aerosol nucleation and growth experiments of much higher quality and confidence than previous experiments. So far, the following chemical systems were studied:

- H_2SO_4-H_2O (binary sulphuric acid-water system)
- NH_3- H_2SO_4-H_2O (ammonia ternary system)
- $(CH_3)_2NH$- H_2SO_4-H_2O (dimethylamine ternary system)
- Pinanediol oxidation products- H_2SO_4-H_2O
- α-pinene oxidation products-H_2SO_4-H_2O
- α-pinene oxidation products-H_2O at very low H_2SO_4

All of these systems were studied with and without ions present in the chamber.

For some of these systems, experiments were conducted over a broad temperature range (H_2SO_4-H_2O and NH_3- H_2SO_4-H_2O), down to 208 K, a range not previously accessible to nucleation studies. Furthermore, novel mass spectrometers were operated at the CLOUD chamber, in particular the Atmospheric Pressure Interface Time-of-Flight Mass Spectrometer, both without and with a chemical ionisation source (APi-TOF and CI-APi-TOF). These techniques allowed for the first time the highly sensitive detection of ions and charged clusters as well as neutral clusters, and a precise chemical identification of the molecular composition became possible. The measurements are accompanied by detailed process modelling. The experimental data allow evaluation of thermodynamic aerosol models as well as process modelling of evaporation and condensation for systems including acid/base molecules and larger organic molecules. Furthermore the data are currently parametrised and the new parametrisations are included in the global model GLOMAP (developed by the CLOUD partner, Univ. Leeds). Therefore the CLOUD experimental results serve as direct input for global aerosol, cloud and climate modelling, allowing an assessment of the impact of aerosol particle nucleation and growth on global cloud formation and climate based, for the first time, on experimentally-determined vapours and reaction rates.

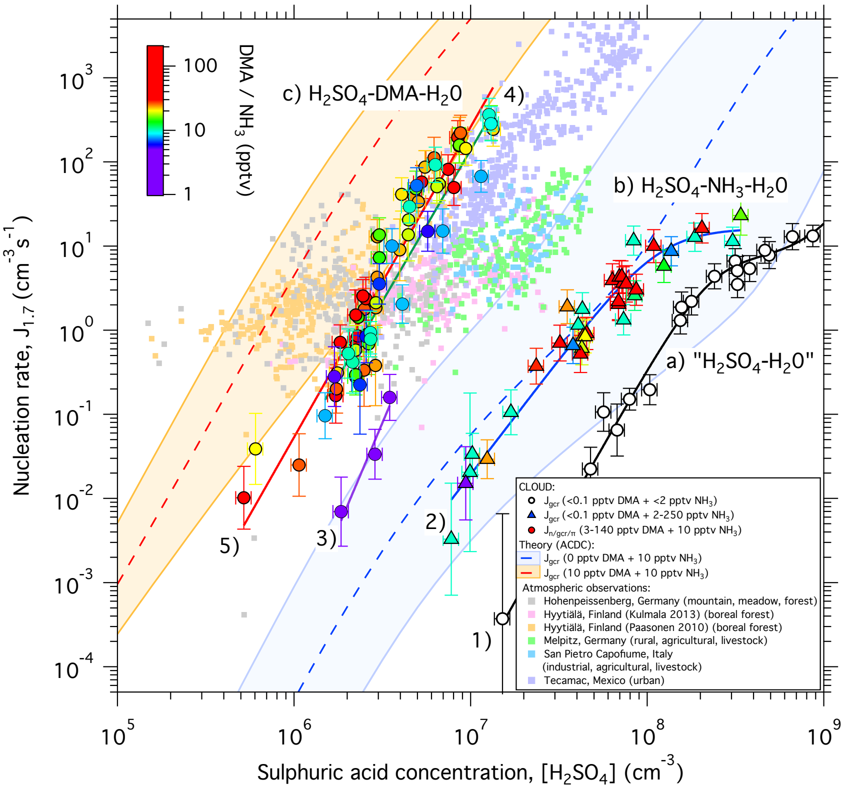

Fig.2.2: Comparison of nucleation rates measured by CLOUD with atmospheric observations and quantum chemical calculations (Almeida et al, 2013). The CLOUD curves show binary (H_2SO_4-H_2O), ammonia ternary (H_2SO_4-NH_3-H_2O) and dimethylamine ternary (H_2SO_4-C_2H_5N-H_2O) nucleation rates versus sulphuric acid concentration.

Numerous new findings in the area of aerosol nucleation and growth have resulted from the CLOUD studies on aerosol nucleation and growth. Here we briefly summarise the key findings of the most important studies:

- Kirkby et al. [2011] present aerosol nucleation rates for binary H_2SO_4-H_2O and ternary NH_3- H_2SO_4-H_2O that were measured at temperatures of 258, 278 and 292 K. It is demonstrated that ammonia mixing ratios of less than 100 pptv increase the nucleation rate of sulphuric acid particles by 2-3 orders of magnitude. The ammonia increases the nucleation rate due to an efficient base-stabilisation mechanism. Ions increase the nucleation rate by an additional factor 2-10. Ion-induced binary nucleation of H_2SO_4-H_2O can occur in the mid troposphere but is negligible in the boundary layer. However, atmospheric concentrations of ammonia and sulphuric acid are insufficient to account for observed boundary-layer nucleation events.
- Almeida et al. [2013] (Fig. 2.2) find that dimethylamine (DMA) mixing ratios above 3 pptv enhance particle formation rates more than 1,000-fold compared with NH_3-H_2SO_4-H_2O, and these nucleation rates are sufficient to account for the particle formation rates observed in the planetary boundary layer. Cluster evaporation is strongly reduced by an efficient-acid-base stabilisation mechanism. It is found that the ion-induced contribution for this chemical system is small [reflecting the high stability of $(CH_3)_2NH$-H_2SO_4-H_2O clusters], but increases at the lowest nucleation rates (Fig. 2.3).

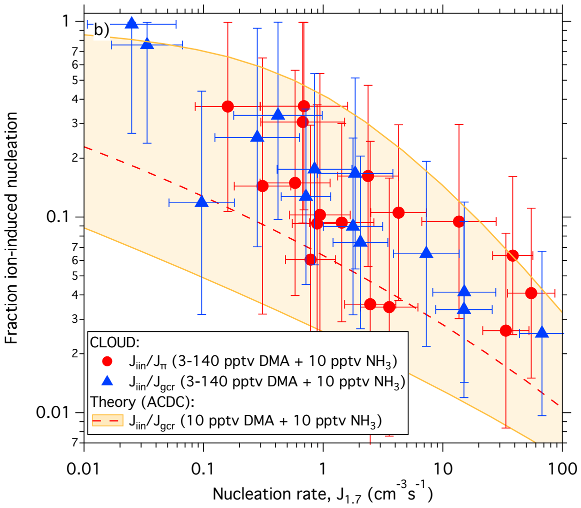

Fig. 2.3: Contribution of ion-induced nucleation to formation of sulphuric acid-dimethylamine particles, and comparison with quantum chemical calculations (Almeida et al, 2013).

- Schobesberger et al. [2013] present high-resolution mass spectra of ion clusters observed during new particle formation for experiments involving sulphuric acid vapour and different stabilising species, including ammonia, dimethylamine, and oxidation products of pinanediol (a first generation oxidation product of alpha-pinene). The mass spectra from the pinanediol closely resemble ambient data obtained during new particle formation events in boreal forests (Fig. 2.4). Large organic compounds from the oxidation of monoterpenes cluster directly with sulphuric acid molecules. Some of the observed organics are remarkably highly oxidised (up to 12 oxygen atoms in the molecule, and oxygen-to-carbon ratios up to 1.2). The measurements connect oxidised organics directly with the very first steps of new particle formation and growth between 1 and 2 nm. The experiments demonstrate that oxidised organics are involved in both the formation and growth of particles under ambient conditions. Figure 2.4 shows a mass defect plot of the ion clusters detected with the APi-TOF. It can be seen that several hundred different cluster ions are detected. It will be a challenge for future work at CLOUD to identify these compounds and to discern which compounds actively participate in nucleation and which ones are rather spectator ions that do not grow into aerosol particles.

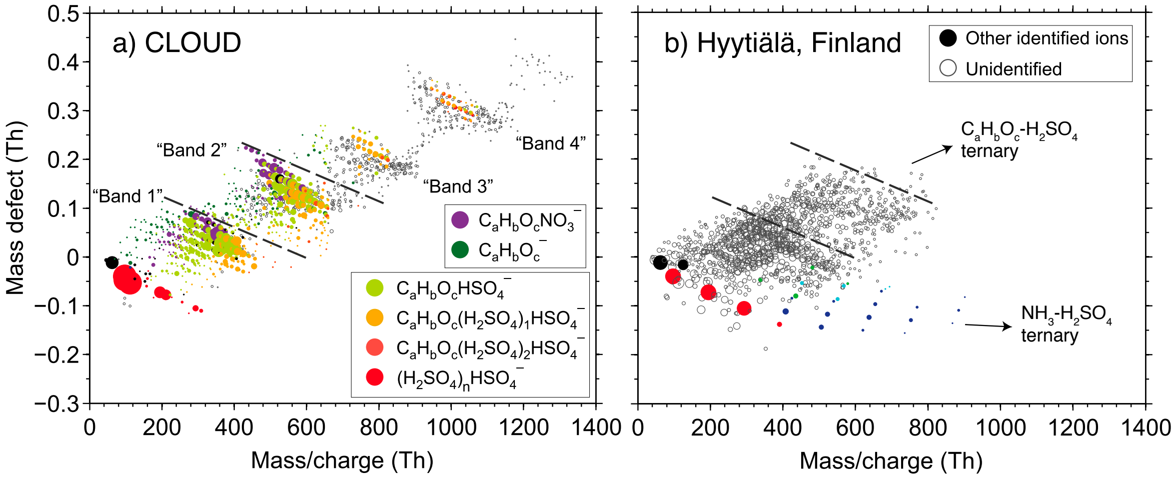

Fig. 2.4: Molecular composition of nucleating clusters seen a) in CLOUD when oxidised biogenic vapours and sulphuric acid are present at atmospheric concentrations [Schobesberger et al., 2013] and b) at Hyytiälä, Finland (boreal forest)

- Riccobono et al. [2014] demonstrate that sulphuric acid and oxidised organic vapours at atmospheric concentrations reproduce particle nucleation rates observed in the lower atmosphere (Fig. 2.5). The experiments reveal a nucleation mechanism involving the formation of clusters containing sulphuric acid and organic molecules from the very first step. Inclusion of this mechanism in a global aerosol model yields a photochemically- and biologically-driven seasonal cycle of particle concentrations in the continental boundary layer, in good agreement with observations.

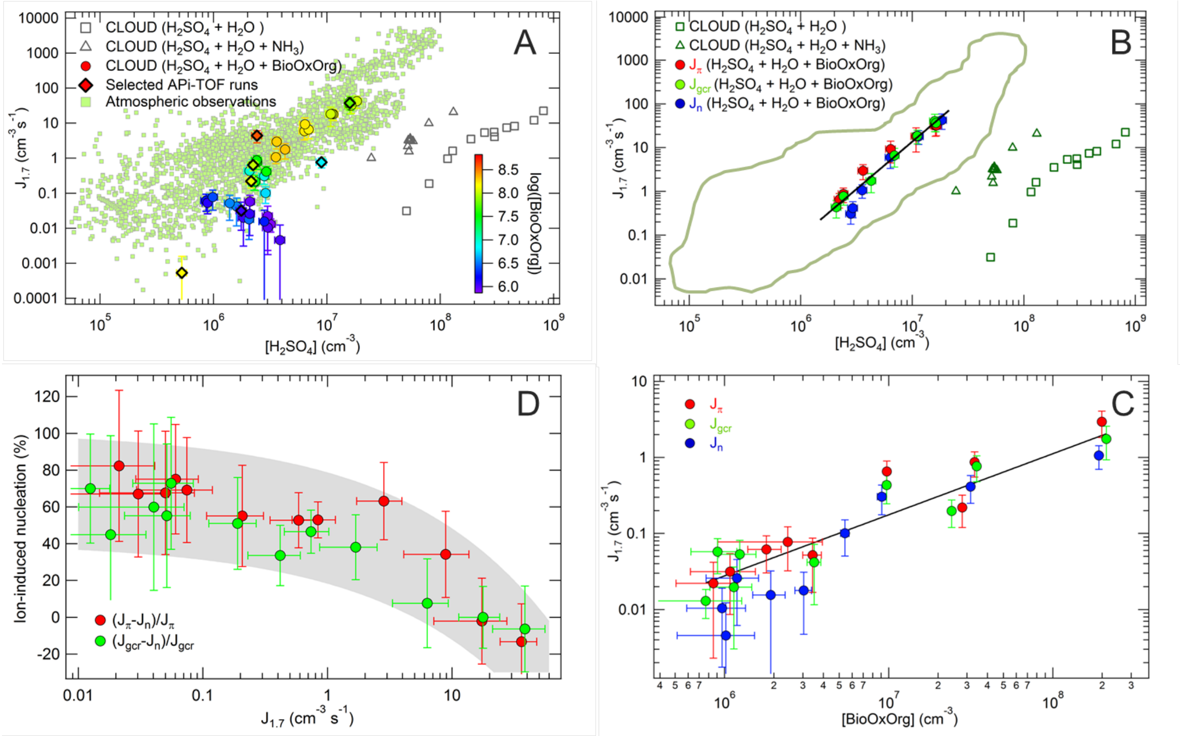

Fig. 2.5: Ternary nucleation of biogenic oxidised organics (BioOxOrg) with sulphuric acid: a) J vs. [H_2SO_4] over wide range of BioOxOrg, b) J vs. [H_2SO_4] with BioOxOrg restricted to be near 4 pptv, c) J vs. BioOxOrg with [H_2SO_4] restricted to be near 0.1 pptv (2 10^6 cm^{-3}), and d) ion-induced fraction vs. total nucleation rate [Riccobono et al., 2014].

- Kürten et al. [PNAS, submitted 2014] report the concentration and molecular composition of the neutral (uncharged) clusters during nucleation for the dimethylamine-sulphuric acid-water system (DMA- H_2SO_4-H2O) for neutral particles containing up to 14 H_2SO_4 and 16 DMA molecules under atmospheric conditions. The measurements bridge the gap between the molecular and particle perspectives of nucleation and reveal the fundamental processes involved in particle formation and growth. The neutral clusters are found to form at or close to the kinetic limit, where particle formation is limited only by the collision rate of H_2SO_4 molecules. Though the neutral particles are stable against evaporation from the H_2SO_4 dimer onwards, the formation rates of particles at 1.7 nm size, which contain about 10 H_2SO_4 molecules, are as much as 4 orders of magnitude smaller compared to those of the dimer, due to coagulation and wall loss of particles before they reach 1.7 nm in diameter. This demonstrates that neither the atmospheric particle formation rate, nor its dependence on H_2SO_4 can simply be interpreted in terms of cluster evaporation or the molecular composition of the critical nucleus [Ehrhart & Curtius, 2013].
- Further scientific findings as well as detailed technical descriptions of the CLOUD facility and various research instruments used at CLOUD are presented in [Bianchi et al., 2012; Bianchi et al., 2014; Keskinen et al., 2013; Schobesberger et al. 2014; Kupc et al., 2011; Praplan et al., 2012; Voigtlander et al., 2012; Wimmer et al., 2013; Schnitzhofer et al. 2013].
- Unpublished CLOUD data reveal further key findings that will be published shortly.

2.3 CLOUD's future scientific strategy

Our aim is to reach a detailed scientific understanding at the molecular level for all important atmospheric nucleation and growth processes, to determine the chemical composition of the nucleating and growing clusters and to quantify the nucleation and growth rates as a function of all relevant variables, including ions from galactic cosmic rays. This includes the dependence on the concentrations of the nucleating species for numerous combinations of precursor gases, and the dependence on temperature, relative humidity and condensation sink. Since the reactions of volatile organics by different oxidants like O_3, OH or NO_3 radicals produces different oxidation products with different functionalities and varying degrees of volatility, it is crucial to develop an in-depth analysis of the identity of the various products, their O:C ratio, and their ability to participate in the nucleation and growth process. As rather complex chemistry is involved, producing easily several hundred compounds, it will be an extensive and challenging programme for several years to identify the most important nucleating species and growth processes.

CLOUD is uniquely positioned to carry out this important experimental programme that goes to the heart of the main issues underlying the uncertainties in current climate change. CLOUD’s unique capabilities to precisely measure the nucleation and growth rates are based on its high cleanliness and precise control of all process parameters, including ions; the ability to observe the processes with complementary and redundant instrumentation; the reproducibility of the experimental results; and the accompanying process and global modelling. The broad goals include:

- Role of organics in global nucleation and growth.
- Role of ions from galactic cosmic rays.
- Role of humidity.
- Role of NO_x.
- Role of temperature.
- Role of condensation sink for nucleation rates.
- Nucleation with barrier vs. barrierless nucleation.
- Role of nucleation and growth for clouds and climate.
- Role of terpenes, monoterpenes, sesquiterpenes, anthropogenic organics, iodine oxides, different amines, etc.
- Role of nucleation cocktails: organic vapours, ammonia, various amine species and sulphuric acid.
- Nucleation in ultra-cold regions of the stratosphere and mesosphere (noctilucent clouds and polar stratospheric clouds)

A list of specific experiments (Table 2.1) to study atmospheric nucleation and growth at CLOUD in the coming years includes:

- Nucleation and growth of terpene oxidation products. Here different terpenes will be used as precursors (e.g. α-pinene, β-pinene, limonene, further cyclic, bicyclic or acyclic terpenes).
- Nucleation and growth of sesquiterpene oxidation products. Different acyclic, monocyclic or polycyclic sesquiterpenes will be used as precursors.
- Nucleation and growth of oxidation products from volatile organic carbons of anthropogenic origin such as toluene, xylene and 1,3,5 trimethylbenzene as precursors.
- Different oxidation mechanisms will be studied in order to distinguish between atmospheric daytime vs. nighttime chemistry, this includes addition/production of different radicals in the chamber, especially OH, O_3, NO_3, and peroxide radicals, RO_2. The reaction pathways will be studied for the different radicals alone (e.g. by use of OH scavengers) as well as for representative combinations of these radicals. Besides representing typical present day oxidation a focus will also be put on simulation of pre-industrial conditions (low NO_x, low SO_2, etc.).

- The above as a function of H_2SO_4, down to very low concentrations.
- Nucleation with and without NO_x.
- Besides the early growth in the size range 1-5 nm, also further growth to CCN sizes (>50 nm) will be studied.
- Further terpene oxidation experiments. Structure dependence (acyclic, mono- and bicyclic monoterpenes).
- 2nd generation alpha-pinene oxidation products vs. H_2SO_4, T, RH.
- Sesquiterpenes (acyclic, mono- and polycyclic sesquiterpenes).
- Anthropogenic organics (aromatics, long chain alkanes).
- Further amine experiments: MEA, MMA, TMA, …, T dependence, RH dependence.
- Combination of H_2SO_4/ELVOC/NH_3/DMA/H_2O 4-5 component 'cocktail' nucleation.
- Oxidised iodine nucleation: OIO nucleation and growth, J, GR, as function of T, RH, neutral vs. IIN.
- Dimethyl sulphide studies (primary natural and marine source of SO_2, from phytoplankton).

Table 2.1: Run conditions for aerosol nucleation and growth rate experiments.

Campaign	**Chemical species**	**Relative humidity, T**	**Comments**
CLOUD10 (2015)	Monoterpene and isoprene oxidation products: day vs. night-time chemistry, pre-industrial vs. present day chemistry, O_3 vs. OH oxidation, night time chemistry: role of NO_3 w/ & w/o H_2SO_4, w/ & w/o NO_x, w/ & w/o isoprene, size-dependent growth to CCN size, T dependence	RH: 5-80% 278 and 293 K	Determine J and GR of terpene oxidation products vs [OH], [O_3], [NO_3]. [H_2SO_4], [NO_x], [C_5H_8], T, RH; identify terpene oxidation products
CLOUD12 (2016)	Sesqui-terpene oxidation; Anthropogenic organics (trimethylbenzene, TMB). Further amines (MEA, MMA, and TMA)?	RH: 5-90% 278 and 293 K	Identify low volatility oxidation products participating in nucleation and growth, determine J and GR.
CLOUD14 (2017)	Oceanic and coastal nucleation: DMS oxidation, potential nucleation and growth; iodine oxidation, OIO nucleation and growth experiments	RH: 70-90% 278 and 293 K	

Regarding beam requirements, all planned experiments on aerosol nucleation and growth will be done as a sequence of neutral conditions (with clearing field on and without pion beam), natural galactic cosmic ray conditions (clearing field off and without pion beam) and with additional pion beam ionisation of selected intensities to simulate stronger ionisation conditions characteristic of the upper atmosphere. This allows us to quantitatively study the effect of ions on all processes under study (nucleation rate, growth rate, etc.). This procedure has been established over the previous experiments and proved to be successful and efficient – and capable of revealing surprising effects where not expected *a priori*. Beam time (3 spills per supercycle provides suitable maximum intensity) is therefore required for the full duration of the experimental campaigns (typically 6-8 weeks).

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3. CLOUDY EXPERIMENTS: ICE PARTICLES

3.1 Current understanding

Cloud microphysical processes involving the ice phase in tropospheric clouds are still among the major uncertainties for cloud, weather and climate models (IPCC 2013). Among these processes, which are only poorly or incompletely formulated in models up to now, are (1) primary ice formation by homogeneous and heterogeneous ice nucleation (Hoose and Möhler, 2012; Murray et al., 2012), (2) secondary ice processes like ice multiplication by the Hallett-Mossop effect or riming in mixed-phase clouds and splintering or aggregation in cirrus clouds, (3) the impact of growth and evaporation conditions on the morphology of ice crystals (Connolly 2005, Saunders 1969, Latham 1964, Latham 1970a and 1970b, Crowther 1973, Saunders 1975) and (4) the influence of heterogeneous chemistry on both the ice crystal growth or evaporation, and the trace gas budgets in the upper troposphere.

Some of the above processes like primary ice formation, aggregation or ice habit growth may also be influenced by ambient ions or charged particles as hypothesized in previous work. However, experimental evidence or accurate results are still missing in many cases in order to better formulate and assess the impact of ions and charged particles on ice processes in tropospheric, stratospheric and mesospheric clouds (Gavet 2012).

Another area of interest for CLOUD is noctilucent clouds (NLCs) (Friedrich 2009). Three formation pathways for NLCs in the polar summer mesosphere region have been hypothesised: a) ice forming on meteoric smoke particles (nucleation and re-condensation of evaporated meteoroids when entering the mesosphere leads to nano-sized meteor smoke particles, ice forms heterogeneously on these particles) or b) ion-induced nucleation: ice forms around (positive) ions ($H_3O^+(H_2O)_n$ clusters form), or c) homogeneous nucleation of ice from the gas phase at the very low summer polar mesopause temperatures. It would be feasible to study these processes in CLOUD provided the thermal system can be extended down to temperatures of -120 to -130°C.

As mentioned above, homogeneous and heterogeneous ice nucleation are the two primary ice formation processes taking place in the atmosphere (e.g. Pruppacher and Klett, 1997). Both processes represent phase transitions from gaseous or liquid water to ice and therefore require overcoming of an energy barrier to form a critical cluster that is capable of growing to an ice crystal. In the case of heterogeneous ice nucleation, this energy barrier is reduced by the presence of a foreign ice nucleus (IN). Four different mechanisms of heterogeneous ice nucleation are known, i.e., deposition nucleation, immersion, condensation, and contact freezing. Some ice nuclei are already known, for example mineral dust (e.g. Murray et al., 2012) and organic (e.g. glassy, e.g. Baustian et al., 2013; Wilson et al., 2012) aerosol particles, and biological macro-molecules (e.g. Augustin et al., 2013; Hartmann et al, 2013). Both homogeneous and heterogeneous ice nucleation have been extensively investigated in the past. However, despite these significant research efforts, a fundamental quantitative understanding of homogeneous and heterogeneous ice nucleation is lacking. This applies especially where the influence of ions on these processes is concerned. A possible influence of ions could be the reduction of the energy barrier for both homogeneous and heterogeneous ice nucleation. There is evidence that even high amounts of electrical charges on droplets are not influencing their freezing (Rzesanke et al., 2012). However that does not necessarily imply that ions could not influence processes such as the formation of ice clusters from water vapour at very low temperatures and/or the deposition nucleation of ice on heterogeneous IN.

Secondary ice particle production during riming is a well-known process (the Hallett-Mossop process) and occurs between -3C and -9C. It has been observed in a wide range of cloud types including convective, frontal and arctic stratus. The power of the process is partly due to the very low numbers of heterogeneous ice nuclei that operate in the same temperature range. Key factors determining the number of splinters produced in a given time are the riming rate and the capture of ice splinters by supercooled water droplets (see for example Crawford et al 2012). It is proposed to use the CERN chamber to examine the effects of particle charging and electric fields on these two key steps in the process.

Ice crystal aggregation is another area that may be enhanced by electric fields. It has been shown in several field studies that strong updraughts in deep convective clouds systems can initiate rapid homogeneous nucleation at -36 to -38 °C, transporting very high concentrations of very small ice particles (< 50 μm) to the upper tropospheric/lower stratospheric region. These high concentrations can lead to strong depletion of water vapour, limiting any further nucleation in this region. These small ice crystals may also contribute significantly to the radiative budget of these clouds whose outflow regions can cover many hundreds of kilometres. Observations have also shown many of the ice crystals in these environments are composed of unusually long, linear chain aggregates (Connolly et al. 2005). The mechanism leading to the formation of these agregates is unknown although it has been hypothesised that strong electric fields could be responsible. This suggests there is an additional, strong aggregation enhancement mechanism that may significantly contribute to the microphysical evolution and radiative properties of clouds in these regions, (Connolly et al. 2012).

Ice particles nucleate and develop in the polar summer mesopause environment, observed as noctilucent clouds or polar mesospheric clouds (NLC/PMC). There has been renewed interest in these ice clouds since it has been speculated that they are extremely sensitive to small changes of water vapor and planetary background temperature. It has been suggested therefore that their presence, frequency of occurrence and properties can act as an important indicator of changes in Earth's climate in response to radiative forcing. However the underlying causes for these changes are not understood and, due to the difficulty of reproducing conditions in this region, there are very few experimental data with which to understand the microphysical and nucleation processes involved.

It is thought, for example, that heterogeneous nucleation on meteoric smoke particles may be the key nucleation mechanism, but while there is some experimental evidence to support this, solid evidence is lacking and recent rocket studies of flash current and day-night MSP ice crystal charging phenomena combined with high charge densities in this region cast doubt on the accepted nucleation mechanisms (Rapp et al. 2010/2011). Recent model studies suggest ice particle nucleation sizes from 20-140 nm diameter, and concentrations of around 90 cm^{-3} at altitudes of 90 km. These then grow and sediment into the lower mesosphere (Baumgarten et al. 2008). However, challenging these models with quantifiable laboratory measurements remains one of the most difficult challenges in cloud physics to date.

The aggregation of ice crystals to form snow is a fundamental precipitation process that influences the lifetime of clouds and, hence, their radiative properties, but recent observations in the tropics suggest that the efficiency of the aggregation process is much higher than previously thought (Gallagher et al, 2012). Latham and Saunders (1964, 1970); Saunders (1969); Crowther (1972); Crower and Saunders (1973); Saunders and Wahab (1975) and Wahab (1974) found that the electric field influences the efficiency by which ice particles aggregate together. Electric field strengths as low as $5\mathrm{x}10^4$ V m^{-1} were sufficient to increase the aggregation efficiency of ice crystals, whereas the crystals were torn apart for field strengths higher than 10^5 V m^{-1}. Electric field magnitudes of $\sim 10^4$ kV/m are known to be present within thunderstorm outflows (Dye et al. 2007). Although, typically small ice crystals carry a positive charge, it is known that, for typical charge distributions, two like-charged particles can still experience a force of attraction under the action of an applied electric field (Davis, 1964). Thus we aim to study ice-ice aggregation in the CLOUD chamber at different temperatures and a possible ice multiplication process.

Ice particle microscopic structures, like surface roughness, are key parameters that determine the optical parameters of cirrus clouds, and are required for modelling the effect of cirrus clouds on climate. Based on laboratory and modelling studies (Yi et al., 2013; Ulanowski et al., 2006) it has been concluded that rough ice crystals reflect more light in the backward hemisphere and thus have a more negative radiative effect compared to smooth ice crystals. Charges and ions may possibly influence the surface roughness of ice crystals (Nielsen et al., 2011) and therefore influence the radiative properties of cirrus clouds.

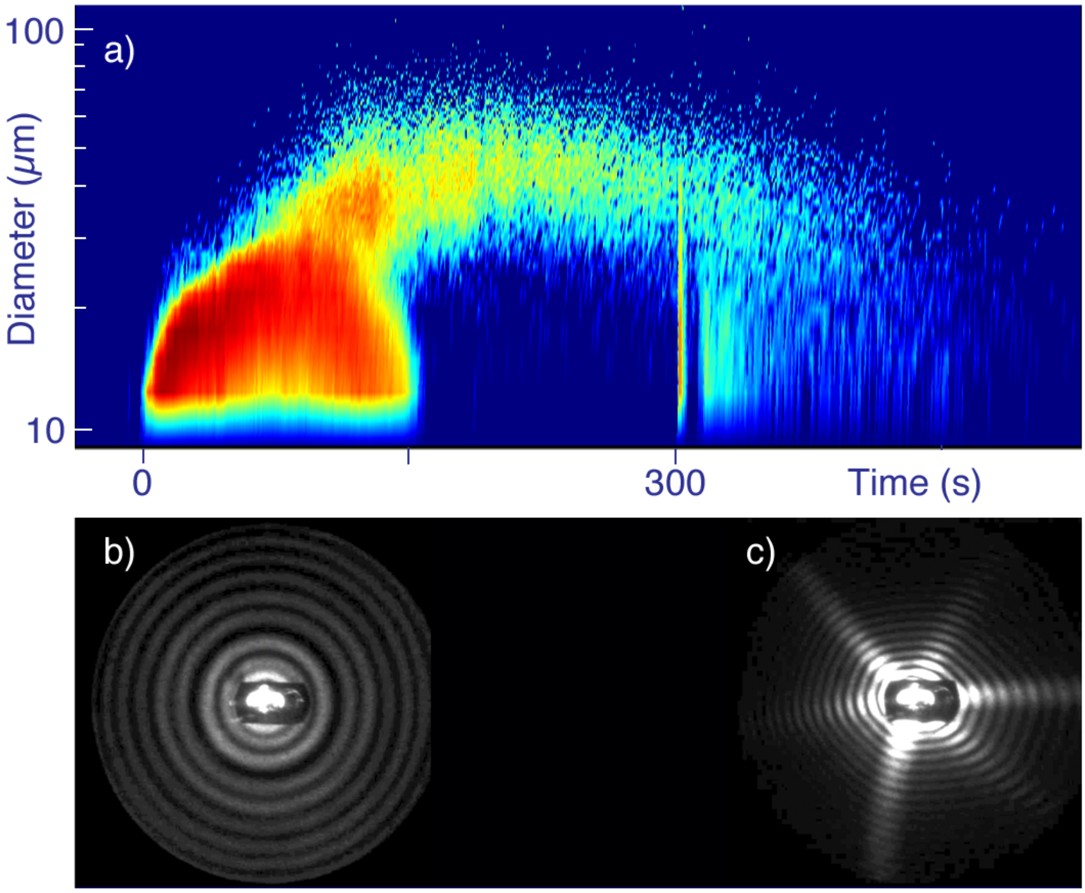

Fig. 3.1: Example cloud during the CLOUD8 campaign. Panel a) shows the cloud particle size as a function of time during an adiabatic expansion in the CLOUD chamber (the colour scale indicates the concentration, red being denser). Liquid droplets start to form at time zero. About 100 s later, some droplets freeze and rapidly grow bigger. Then, the remaining liquid droplets (everything smaller than 30 microns) evaporate, leaving a pure ice cloud - exactly as happens when ice forms in natural clouds. At 300 seconds, air is re-injected into the chamber, terminating the cloud. The lower panels show optical images from this same cloud of a single b) liquid droplet and c) hexagonal ice plate, made with the PPD instrument.

3.2 CLOUD's contributions so far

During the CLOUD6 and CLOUD8 campaigns, the expansion system was tested and used at first for a series of cloud simulation experiments investigating the homogeneous freezing rates of supercooled cloud droplets and the properties of frozen droplets and ice crystals (example measurements are shown in Fig. 3.1). The initial droplet freezing experiments were proof-of-concept runs for further CLOUD experiments investigating and quantifying ice nucleation rates, in particular those involving ions and charged particles. First results of homogenous droplet freezing rate coefficients are shown in Fig. 3.2. Within experimental uncertainty, the CLOUD results are in good agreement with previous AIDA cloud chamber results (Benz et al., 2005) and the parameterisation of Pruppacher (1995).

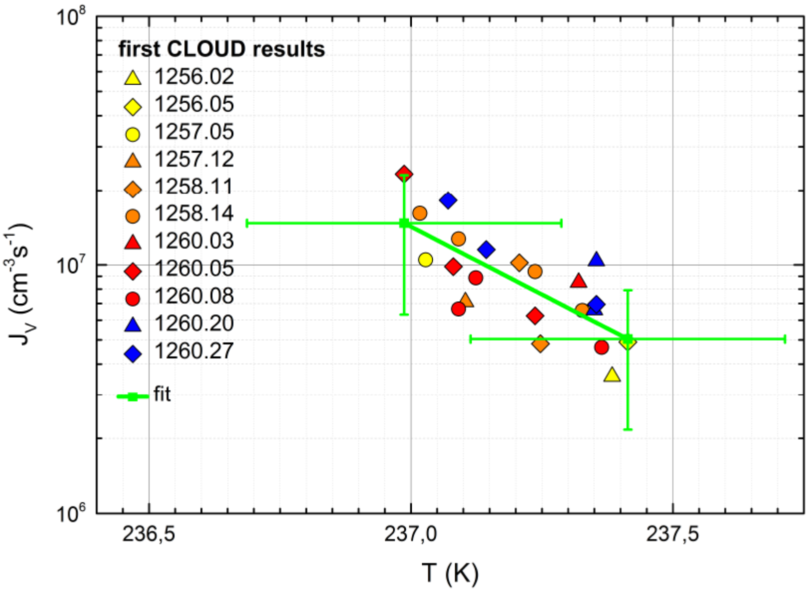

Fig. 3.2: First CLOUD results for the nucleation rate, J_V, of pure supercooled cloud droplets as a function of temperature T.

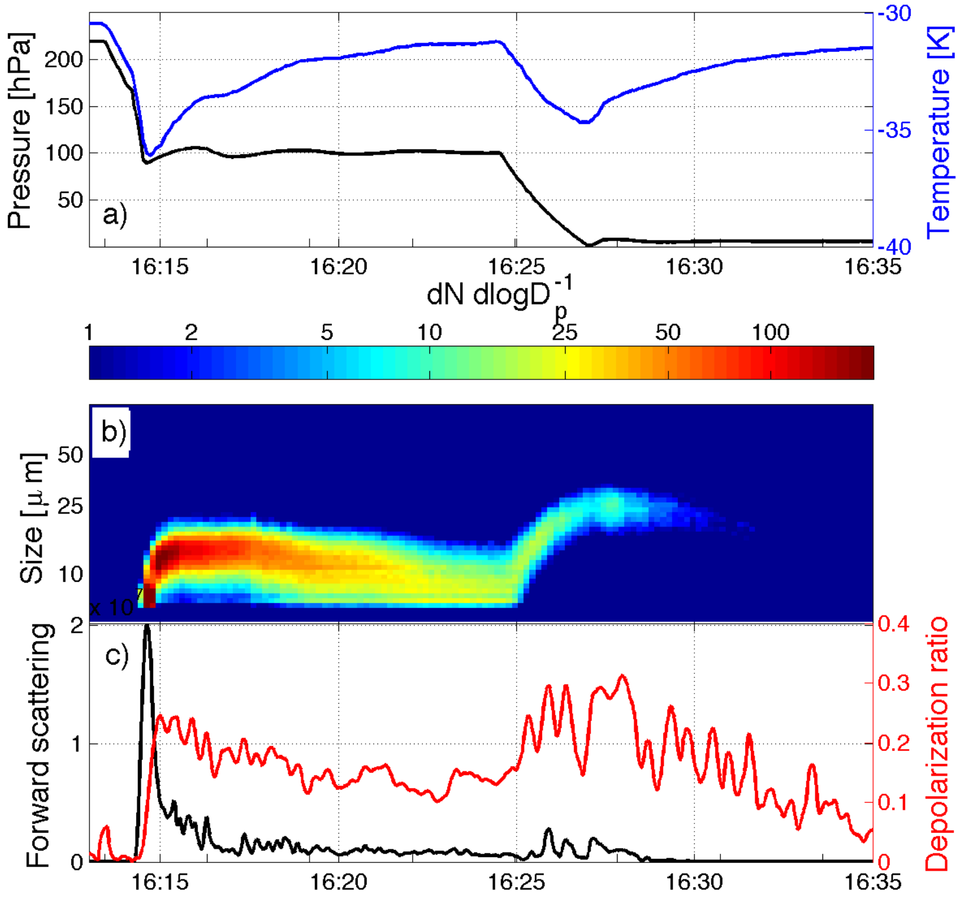

Fig. 3.3: Homogeneous nucleation of frozen droplets during CLOUD8. Two successive pure ice clouds are formed by stepped pressure reductions and adiabatic coolings (Järvinen et al., in preparation).

The behaviour of ice crystals in the cirrus temperature regime was studied for the first time in the CLOUD8 campaign. The aim was to resolve whether ions would have an effect of the microphysical properties of ice. Ice crystals were nucleated homogeneously and their growth and sublimation were simulated in ice sub- and supersaturated conditions, respectively (Fig. 3.3). An effect of ions or charged particles on the ice surface properties during growth has not yet observed, mainly because it was not possible until now to maintain and control very low ice supersaturation conditions during ice crystal growth. Only under such slow growth conditions, will ice crystals develop clear facets and smooth surfaces. The presence of ions or charged particles during such condition could then affect the crystal growth encouraging crystal roughness and formation of irregularities. This will be investigated in future CLOUD campaigns with an improved expansion system and an additional in situ precision measurement of the relative humidity.

The CLOUD chamber offers the opportunity of producing fast cooling rates and thus simulating the relevant convection speeds observed in deep convective clouds. Therefore, droplet-freezing experiments were performed at fast expansion conditions to simulate the production of frozen droplets that are a prominent ice particle type in anvils of convective cloud systems, which contribute significantly to the hydration of the upper tropospheric/lower stratospheric region. First results show a significant difference in the surface properties of the frozen droplets in the different life cycles of the anvil cirrus.

3.3 CLOUD's future broad scientific strategy

Future droplet and ice cloud experiments will take advantage of CLOUD’s capabilities of fast expansion control, a variable electric field setting and various ways to generate and control the amount of ions and charged particles. An important aspect for addressing new and important scientific objectives in future CLOUD experiments is the comprehensive set of instruments and methods provided by the CLOUD partners, covering a broad range of high quality measurements for thermodynamic parameters like temperature and relative humidity, trace gases, charges, aerosols, droplets and ice crystals. With this strong collaborative effort, the CLOUD consortium can address and answer important open questions on aerosol-cloud-climate interactions.

Science objectives to be addressed in future CLOUD campaigns will include:

- formation of glassy aerosols and their ice nucleation behaviour,
- photochemical and nucleation processes in the vicinity of evaporating clouds,
- ion-mediated particle and ice nucleation in cold and supercooled environments,
- influence of ions, charged particles and co-condensing trace gases on the morphology of growing ice crystals,
- impact of charges and electric fields on the aggregation rate of ice crystals, and
- heterogeneous chemistry and photochemistry in ice clouds.

The experiments on the ice nucleation properties of glassy aerosols, as well as the photochemistry or nucleation during or after cloud evaporation, will be closely linked with the aqueous-phase chemistry experiments described in section 4. The idea behind these experiments is that volatile or semi-volatile compounds accumulated by droplets during the cloud lifetime may instantly be released into the gas-phase upon droplet evaporation, and therefore locally influence photochemical or nucleation processes at comparatively elevated concentrations.

Experiments on the nucleation of ice at very low temperatures could elucidate the formation mechanisms of so-called noctilucent clouds (NLCs) in the extremely cold polar summer mesopause region. The important open question whether ion-mediated nucleation contributes to NLC formation could be addressed with CLOUD, but would require an extension of the cooling system for operation the CLOUD chamber at temperatures as low as about 150 K.

Ambient ions or charged particles may also play a role in ice growth and ice crystal agglomeration, particularly at high altitude clouds. The presence of charges may induce more ice crystal irregularities and surface roughness, which would modify ice clouds by an enhanced forward scattering component and therefore a stronger contribution to global warming. Charged ice crystals or strong electric fields could lead to faster ice crystal agglomeration, which modifies the crystal fall speed and thereby cirrus cloud properties and life-cycles. Furthermore, enhanced collision rates between ice crystals and supercooled droplets due to charges and electric fields could contribute to faster secondary ice formation and thereby faster glaciation in mixed-phase clouds.

To achieve these goals, the CLOUD chamber will be upgraded for fast-response and more accurate temperature measurements, a better expansion control, a faster internal mixing to achieve homogeneous conditions also during fast expansion experiments, and a tuneable diode laser system (TDL) for fast *in situ* water vapour and relative humidity measurements.

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4. CLOUDY EXPERIMENTS: AQUEOUS PHASE CHEMISTRY

Recent research shows that the aqueous phase production of secondary organic aerosol (SOA) can be of a similar magnitude to the traditional gas-to-particle partitioning. However this mechanism is poorly understood and existing model parameterisations are rather basic. The CLOUD experiment is in a unique position to make a substantial contribution to quantifying the major processes in this field, due to the possibility to control conditions in the CLOUD chamber with unprecedented accuracy. Furthermore, the huge array of instrumentation that is brought together for each campaign enables the characterisation of chemical and physical processes in the gas and aerosol at a level of detail that has not hitherto been possible.

4.1 Current state of research

The influence of aqueous phase processes on inorganic aerosol species has been the subject of research for more than 30 years (Sievering et al., 1992; Hoppel et al., 1994a; Hering and Friedlander, 1982; Meng and Seinfeld, 1994). However, it was not until relatively recently that a review of atmospheric measurements and laboratory based experimental data led (Blando and Turpin, 2000) to hypothesize that the aqueous phase may be responsible for a significant fraction of secondary organic aerosol mass.

Atmospheric observations in a number of locations indicate the important role of aqueous phase organic chemistry. Similarly to the inorganic studies, observations of organic composition of aerosol as a function of the aerosol size have shown more oxidised compounds to be enhanced in the droplet mode, i.e. the mode of the aerosol size distribution that results from cloud processing (Pickle et al., 1990;Blando et al., 1998). Measurements of glyoxal in Mexico City during the Mexico City Metropolitan Area Field Campaign (MCMA-2003) were found to be far lower than predicted, leading (Volkamer et al., 2007) to speculate that uptake into cloud droplets and subsequent reaction to form less volatile compounds may act as an additional sink. Indeed, they found that the timing of unexplained SOA formation correlated with the timing of the discrepancy between measured and predicted glyoxal concentrations. Aircraft based observations over the eastern Pacific, the Gulf of Mexico and the Huston area show aerosols above clouds to be enhanced in organic acid relative to below cloud aerosols, consistent with a cloud processing source of these acids (Sorooshian et al., 2007).

A further indication of the role of aqueous phase chemistry is that the ratio of oxygen to carbon atoms in molecules comprising organic aerosol has been found to be higher in atmospheric measurements than in chamber experiments (Aiken et al., 2008). Relatively large organic molecules become semi-volatile and condense on aerosol after only a few oxidation steps, thus retaining an O:C ratio of around 0.4 (Lim et al., 2010). More highly branched carbon chains undergo fragmentation, which increases their volatility, inhibiting condensation to aerosol (Lim et al., 2010;Lim and Ziemann, 2009). In contrast, shorter chain organic molecules will partition to the aqueous phase more easily, where, upon oxidation, they will exhibit relatively high O:C ratios (of around 1 or 2) (Lim et al., 2010;Ervens et al., 2011). Indeed, aqueous phase oxidation experiments of methylglyoxal, for example, result in products with O:C ratios of between 1 and 4 (Altieri et al., 2008). Further, (Bateman et al., 2011) performed photolysis experiments on the products of the dark oxidation of limonene by O_3, and found that exposure of extracts from a particle-into-liquid sampler (PILS) to UV light lead to higher O:C ratios than when the dry products are exposed to UV. They suggest this as another possible mechanism for the higher O:C ratios observed in ambient aerosols relative to dry chamber experiments.

Several modelling studies have suggested that the amount of SOA attributable to aqueous phase reactions in clouds is similar in magnitude to that formed via gas phase oxidation and subsequent condensation. Using box model simulations, (Chen et al., 2007) report a 27% increase in SOA formation was found for rural conditions, with high monoterpene emissions, and a 9% increase in SOA formation for urban conditions where aromatic emissions are high. They also report a domain-average increase in SOA production of 9% for three dimensional model simulations over eastern North America. In a comparison of aircraft based organic aerosol measurements with modelled values, (Carlton et al., 2008) found that both the model bias and the correlation with measurements was improved when aqueous phase chemistry was accounted for, with aqueous phase chemistry accounting for around half of the SOA. Modelling studies by (Fu et al., 2009) found that including aqueous phase processing of dicarbonyl gases such as glyoxal and methylglyoxal effectively doubled the water soluble SOA yield.

Aqueous phase reactions can be divided between two regimes: those occurring in hydrated aerosol under sub-saturated conditions, and those occurring in cloud droplets. The reactions that take place in hydrated aerosol occur in a concentrated aerosol mixture, and likely form oligomers or other high molecular weight compounds. In the more dilute conditions of cloud droplets, organic acids such as oxalate are more likely to form (Lim et al., 2010).

Given the large potential role of aqueous phase processes in the formation of secondary organic aerosol, a number of previous laboratory experiments have been performed to measure aerosol growth rates, aqueous phase reaction rates and yields of aqueous phase products in both hydrated aerosol and cloud droplets. The great majority of the aerosol chamber based experiments performed so far have been restricted to studying hydrated aerosol at relative humidities below about 80%. Investigations of reactions occurring in cloud droplets have been performed, for the most part, in bulk liquid solutions, with volumes of up to 1 Litre, negating the possibility of studying exchange processes between the gas and aqueous phases, or the effects of chemistry on droplet surfaces. Both the hydrated aerosol and the bulk phase experiments have generally been performed at temperatures above zero Celsius, while in the atmosphere, a large fraction of the relevant gas phase oxidation reactions and aqueous phase chemistry will be occurring at temperatures below zero Celsius, and in super-cooled cloud droplets, or on the surface of ice particles.

The CLOUD facility is the unique experiment in the world that combines where high relative humidities can be maintained in a stable fashion, where reactions can be observed over the full range of tropospheric temperatures, where CCN can be grown from trace vapours at atmospheric concentrations, where ion concentration can be precisely adjusted over the atmospheric range and where clouds consisting of super-cooled water droplets or ice particles can be created, and aqueous phase reactions can be studied in an environment that closely reproduces the conditions in the atmosphere.

Below we detail a number of the previous experiments, and show where the CLOUD experiment can improve upon and extend this work.

4.1.1 Effect of relative humidity (RH)

Relative humidity can influence the type and amount of precursors available for heterogeneous reactions, and it can influence the type of reactions that occur.

In the absorptive partitioning framework (Chacon-Madrid et al., 2013), the amount of pre-existing organic aerosol mass determines the fraction of organic species in the gas and condensed phases. In aqueous phase chemistry it is the water content of the aerosol or cloud droplet that determines how much of the water soluble species will reside in the gas phase or in the particles. In addition to semi-volatile water-soluble species, compounds that would normally be too volatile to be found in aerosol particles (for example glyoxal, methylglyoxal or small organic acids) will dissolve in the condensed water, and be available for aqueous phase reactions (Volkamer et al., 2007; Loeffler et al., 2006). During summer in Atlanta, (Hennigan et al., 2008) find a significant increase in the mass of water soluble organic carbon (WSOC) in aerosol particles, at RH greater than about 70%. They did not however study the fate of this organic carbon once the water evaporates from the particles, and were therefore unable to reach conclusions about the reversibility of this process. An increase in particle phase pinonaldehyde that correlated with increased RH was found by (Zhao et al. 2013) in ambient measurements.

The formation of SOA from the OH-initiated oxidation of acetylene (which forms glyoxal as the highest yield product) was studied by (Volkamer et al., 2009), in the RH range from 10% to 90%, under UV lights and dark conditions. They found that the SOA yield increased linearly with the water content of the aerosol, and attribute this to the increased volume available for reaction at higher humidities.

The products of aqueous phase reactions occurring in cloud droplets and aerosol particles depend on the concentration of the solutions. The reactive uptake of glyoxal (via aqueous phase oxidation by the OH radical) was studied by (Kroll et al., 2006), who found that at dilute, cloud-relevant concentrations, the main product was oxalic acid. At higher concentrations (i.e. lower aerosol/droplet water contents), the yield of oxalic acid was lower, and instead, oligomers and other higher molecular weight compounds form. Similar findings were reported by (Guenther et al., 2006) for experiments with methylglyoxal. They suggest that at cloud relevant concentrations, small carboxylic acids are the main products, while at higher concentrations, the formation of larger carboxylic acids (more than 4 carbon atoms) and oligomers are favoured. The formation of not just oxalic acid, but also high molecular weight compounds, in dilute (similar to cloud droplet concentrations) aqueous phase glyoxal oxidation (via OH radical) experiments was reported by Carlton et al. (2007).

As water evaporates from the aerosol, and as aqueous phase reactions increase the organic content of the particles, they become more viscous, eventually reaching a state where diffusion from the surface into the particle volume has slowed to such an extent that the further reactions are slowed or inhibited (Ervens et al., 2011;Virtanen et al., 2010). Further, Loeffler et al. (2006) found that glyoxal itself may form oligomers as the aerosol droplets become more concentrated as water evaporates, through acid catalysed reactions. It was shown by (De Haan et al., 2009) that the reaction of glyoxal with amino acids in evaporating droplets leads to the formation of imidazoles, causing the growth of aerosols. A study by Noziere et al. (2009) showed that the ammonium catalysed reactive uptake of glyoxal via the iminium pathway was strongly dependent on the activity of the ammonium ions in the solutions studied. Sulphate ions have been shown to enhance the effective Henry's law coefficient of glyoxal, shifting the hydration equilibrium more towards the hydrated form of the carbonyl (Yu et al., 2011). The partitioning of glyoxal between the particle and gas phase was studied by Kampf et al. (2013), who found the solubility of glyoxal to increase exponentially with increasing ammonium sulphate concentration, due to a salting-in effect

Aqueous phase photolysis was found to produce similar products (for example carboxylic acids) to photolysis of dry limonene SOA, but higher yields (Bateman et al., 2011).

Aerosol chamber experiments involving the oxidation of isoprene by NOx were performed at 20°C by (Kroll et al., 2005), in the absence of seed particles, at RH ranging between 0% and 85%. They found that the volatility of the products (measured after heating the samples) increased with increasing RH. However the yield of SOA was relatively constant, regardless of the RH. The reasons for this were not clear.

CLOUD is uniquely suited to studying the effects of high relative humidities on aerosol chemistry, since a high and stable RH can be maintained within the chamber, with a good degree of precision. Furthermore, several cloud cycles can be performed during each experiment, allowing insights into the different chemistry taking place during each stage of cloud formation and evaporation, and the effects of the cloud processing history of the aerosol measured on its composition and its ability to act as a CCN.

4.1.2 Effect of temperature

Reaction rates are often strongly temperature dependent, and since the temperature dependence differs between different reactions, a change in temperature may not only change the rate of formation of SOA, but also its composition. Furthermore, the partitioning of semi-volatile species between the gas phase and aerosol phase is also temperature dependent. Temperature changes are likely to influence aerosol and droplet processes in different ways, while an increase in temperature will shift the partitioning of semi volatile species into the gas phase, it will also likely increase the rate of aqueous phase reactions, possibly leading to increased aerosol mass (Ervens et al., 2011). A study by von Hessberg et al. (2009) showed that under dry conditions the yield of SOA from the ozonolysis of beta-pinene decreases with increasing temperature, however at higher humidities up to 68%, the yield increased with increasing temperature.

The vast majority of laboratory studies of the aqueous phase chemistry relevant for atmospheric aerosol have been performed at temperatures between approximately 20°C and 30°C (Altieri et al., 2006; Lim et al., 2013; Carlton et al., 2007; Liu et al., 2012; Perri et al., 2009; Sun et al., 2010). Exceptions include (Chen et al., 2008), who studied the bulk aqueous phase ozonolysis of methacrolein (MAC) and methyl vinyl ketone (MVK), at temperatures between 4°C and 40°C, finding almost no influence of temperature on the relative product yields. Also (Kameel et al., 2013) investigated the aqueous reaction of isoprene with the OH radical, at 10°C. However they did not perform experiments at other temperatures, and so it was not possible to evaluate the effect of temperature. Bulk aqueous phase ozonolysis experiments were performed with alpha- and beta-pinene at temperatures ranging from 4°C to 25°C, by (Zhang et al., 2009), who found no significant temperature effect on the composition of the reaction products.

The studies described above were all bulk aqueous phase experiments, and while the limited results available show no significant effect of temperature on the relative yields of the products, bulk aqueous phase experiments are subject to some limitations. To model aerosol growth, it is important to know the yield and rate of aqueous phase reactions relative to the gas phase concentrations of the participating species. Bulk experiments such as those performed in the studies above cannot provide this information since they cannot account for temperature-related changes in solubility and partitioning rates. Furthermore, different products may form during the evaporation of droplets, as the solution becomes more concentrated (Ervens et al., 2011). As evaporation may proceed rapidly, temperature related changes in reaction rates may be important in this process. Again, this can only be determined in a cloud chamber experiment.

Very few aerosol chambers exist where experiments at temperatures approaching 0°C or lower are possible (Hallquist et al., 2009) in combination with the ability to perform experiments at supersaturated conditions, where cloud or fog droplets are formed. This makes the CLOUD chamber a powerful tool for investigating the temperature dependence of aqueous phase reactions.

4.1.3 Effect of galactic cosmic rays

The effect of GCR on organic molecules and on the partitioning of organic mass between the gas and aqueous phase is uncertain, and to the best of our knowledge no experimental research exists on this topic. During the first aqueous phase campaign, CLOUD8, the PS beam was not available, and so no optimised experiments on this topic have been possible so far in CLOUD. During future campaigns, we intend to perform dedicated experiments to investigate the possible presence and quantification of such effects. These are detailed in the run plan below.

4.1.4 Effect of NOx

The amount of NO and NO_2 (together known as NOx) has a large impact on the yield of organic aerosol formed via gas phase reactions (Hoyle et al., 2011). The amount of NOx is usually defined as the ratio of the mixing ratio of the volatile organic compound being oxidised, and the mixing ratio of NOx, the VOC:NOx ratio. The dependence of the yield of isoprene SOA, for example, on the VOC:NOx ratio is complex. Kroll et al. (2006), for example, found that the yield of isoprene increased with increasing NOx between VOC:NOx ratios of more than 2.25:1, reaches a plateau between ratios of 2.25:1 and 0.75:1, and decreases at higher NOx concentrations. Dommen et al. (2006) also report low yields for VOC:NOx ratios of between 25:1 and 10.5:1, with high yields for ratios between 10.5:1 and 7:1. This NOx dependent change in aerosol yield from the gas phase reactions is consistent with a change in the volatility of the oxidation products, with more volatile products being formed at the limits of high and low VOC:NOx ratios, while the yield of lower volatility products reaches its maximum at intermediate VOC:NOx ratios. The yields of low volatility products from the oxidation of other organic precursor molecules also display a dependence on the NOx concentrations (Hoyle et al., 2011).

At low NOx concentrations (Ng et al., 2007) found the oxidation products of toluene to be essentially non-volatile, however at higher NOx concentrations, the formation of more volatile carbonyl products such as glyoxal and methylglyoxal is favoured (Ervens et al., 2011). Because of the potential for these products to undergo aqueous phase reactions, the role of aqueous phase chemistry in forming organic aerosol from toluene oxidation products is likely to be greater when the oxidation occurred under high NOx conditions.

Due to the expected differences in the significance of aqueous phase chemistry for aerosol growth at different NOx concentrations, CLOUD experiments will be performed under high NOx as well as low NOx conditions.

4.2 Current contributions of CLOUD

During the CLOUD8 campaign in November-December 2013, the first two series of comprehensive aqueous phase chemistry experiments were performed, examining aerosol growth due to aqueous phase reactions of sulphur dioxide, and of isoprene oxidation products.

4.2.1 Sulphur dioxide

There were several objectives for the SO_2 experiments performed during CLOUD8. The aqueous phase oxidation of SO_2 and its hydrolysis products has been extensively studied in the past [e.g. Maahs, 1983, Seinfeld and Pandis, 2006], which made this an ideal experiment to test the experimental set up of the CLOUD chamber and instrumentation. Rates have been determined for these reactions from bulk phase experiments [Seinfeld and Pandis, 2006], and we can calculate the reaction rates leading to the observed aerosol growth in the CLOUD chamber, and compare these to the commonly accepted values. Previous cloud chamber experiments that measured the oxidation reaction rates in droplets found significantly higher aerosol growth and therefore reaction rates (Caffrey et al., 2001; Hoppel et al., 1994b). They speculate that this discrepancy may be due to contamination by ammonium in the aerosol, but as ammonium concentrations were not measured, they were unable to prove this. In CLOUD, the aerosol ammonium concentrations are measured with an aerosol mass spectrometer (AMS), therefore we can determine if the oxidation rates observed in cloud droplets match the bulk reaction rates, and we can show that the experiments were contaminant free. The experiments were performed at temperatures of +10°C, -10°C and -30.5°C, enabling us to investigate the reaction rates at atmospherically relevant temperatures that are lower than has previously been achieved. The relative humidity was approximately 95% during the sub-saturated phases of the experiments. Each experiment began with the injection of SO_2 into the chamber, until the desired concentration was reached (approximately 20 ppbv). Then a seed aerosol was added, to provide a volume for the aqueous phase reactions to take place, and to act as condensation nuclei for the formation of cloud droplets. Experiments were performed with acidic seed (sulphuric acid) and semi- or fully-neutralised seed (ammonia was added to the chamber, which partitioned to the sulphuric acid seed, forming ammonium sulphate in the fully neutralised case). After the seed number concentrations stabilised at around 4000 particles per cubic centimetre, O_3 was added, up to a concentration of approximately 100 ppbv. The aerosol size distributions were measured to determine if any growth occurred at subsaturation, and then the chamber pressure was rapidly reduced to produce an adiabatic cooling, resulting in a supersaturation, and cloud formation. From the aerosol growth rates during the supersaturated period, the rate of oxidation of SO_2 in the aqueous phase can be determined. The results of these experiments are currently being evaluated. Figure 4.1 shows the growth of the aerosol size distributions from three experiments at temperatures of 10°C, -10°C and -30.5°C, with ammonium sulphate seed particles. The finite but reduced growth at lower temperatures is clearly visible.

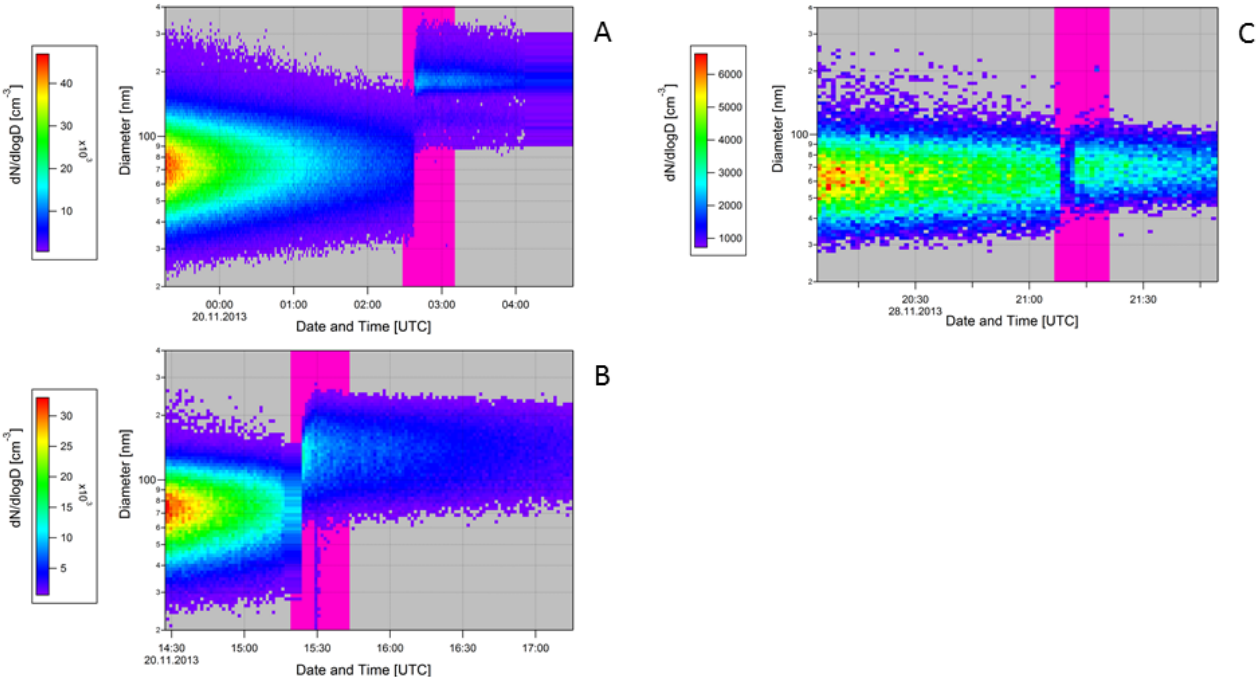

Fig. 4.1: Growth of the aerosol size distribution due to reactive uptake of SO_2 on ammonium sulphate seed aerosol, at 10°C (panel A), -10°C (panel B), and -30.5°C (panel C). The super-saturated period is indicated by the purple band.

4.2.2 Isoprene

During the CLOUD8 campaign, experiments were also performed to examine the influence of cloud processing on the mass of aerosol formed from isoprene oxidation products. Although bulk aqueous phase experiments have been performed in the past with isoprene and its oxidation products, the experiments during CLOUD8 are, to our knowledge, the first that have ever been performed in an artificial cloud created in an aerosol chamber, realistically representing the processes that occur in a natural cloud cycle in the atmosphere. These experiments were performed under the same temperature, RH and seed aerosol conditions as the SO_2 experiments. The isoprene mixing ratios were approximately 40 ppbv, and the oxidant was O_3 again at a mixing ratio of around 100 ppbv. Substantial growth of the aerosol was observed under sub-saturated and super-saturated conditions, particularly at warmer temperatures. Figure 4.2 shows the growth of aerosol particles during an experiment with sulphuric acid seed at a temperature of 10°C. The mode diameter of the particle size distribution, indicated by the white dots increases steadily during the sub-saturated period, and increases more rapidly during the super-saturated period (indicated by the purple stripe). At least some of the products appear to partition back into the gas phase subsequently, as a small decrease in the mode diameter is evident before growth resumes again.

The results of these experiments are currently being analysed to determine if different species are being produced in the aerosol particles/cloud droplets at sub-saturated and super-saturated conditions, and to quantify the products and growth rates at the different temperatures and different seed types.

4.3 CLOUD's broad future strategy

The future strategy of the aqueous phase chemistry experiments in CLOUD will be to explore the role of the condensed phase (hydrated aerosol, cloud droplets and ice particles) in determining the chemical and physical properties of aerosol, as well as the composition of the gas phase. Further, the importance of the condensed phase relative to gas phase processes will be assessed. The experiments will be designed such that they are of direct use in building new numerical parameterisations of the studied processes, in order to improve global atmospheric chemistry and climate models.

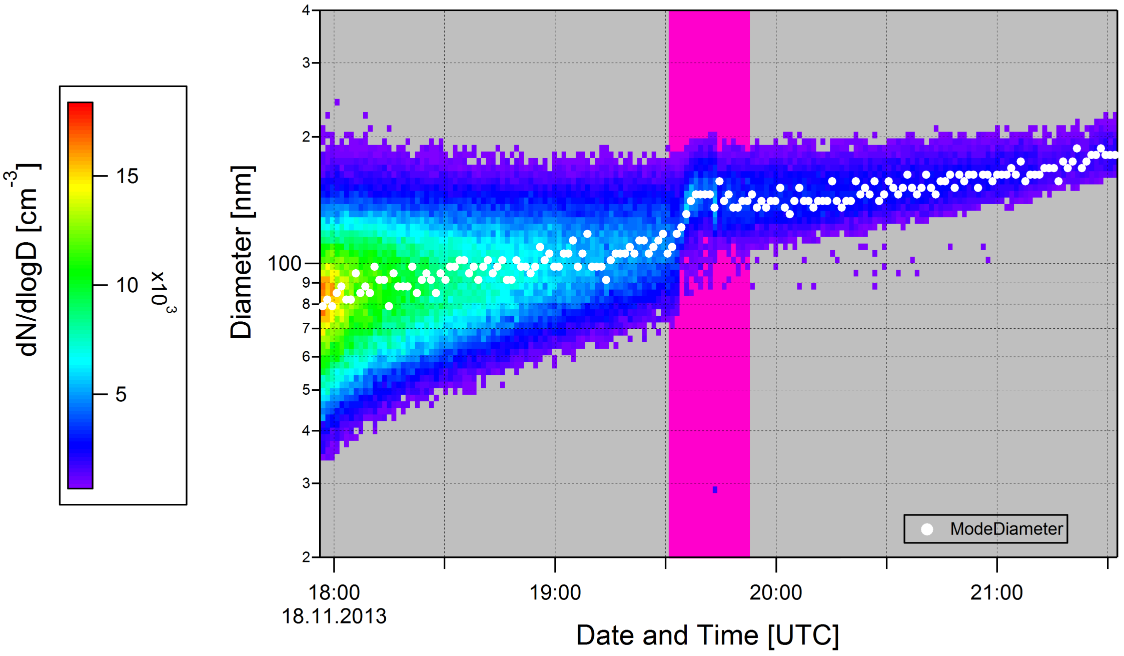

Fig. 4.2: Growth of the aerosol size distribution as a function of time, due to reactive uptake of isoprene oxidation products. The supersaturated (cloud) period is indicated by the purple band.

Specific goals are:

- Determination of the most important aqueous phase reactions that control the growth of aerosol particles. Quantification of the corresponding reaction rates.
- Quantification of the dependence of these rates on aerosol composition, on relative humidity, on temperature and on pH.
- Determination of the influence of GCR on these reactions, especially through the modification of gas phase compounds and therefore alteration of the partitioning of reactive compounds between the gas and condensed phases.
- Identification of product compounds in the aqueous phase reactions that can be used as markers, which, when found in the atmosphere, will show that the reactions observed in the chamber also occur in the atmosphere.

4.4 Future isoprene experiments

4.4.1 Aims and general background

The aims are:

- To determine the growth rates and limitations of isoprene secondary organic aerosol (SOA) under sub-saturated and supersaturated conditions. This will give insights into the role of cloud processing on the growth of SOA. Oxidants will be O_3 and NO_3; the latter may be important for nighttime SOA production.
- To determine the temperature effect on SOA yields, accounting for sub-zero temperatures.

Global emissions of isoprene are estimated to be between 440 and 660 Tg C yr^{-1} (Guenther et al., 2006), comprising approximately 40% of the global volatile organic compound (VOC) budget (Hallquist et al., 2009). Atmospheric concentrations of isoprene are approximately 0.3 to 10 ppbv (Lee and Wang (2006); Rasmussen and Khalil, 1988; Wiedinmyer et al., 2001). Because isoprene is a relatively small molecule in comparison with other VOC from which secondary organic aerosol (SOA) can form (isoprene contains five carbon atoms compared with, for example, ten carbon atoms for monoterpenes), it was long thought that isoprene oxidation products would not lead to extensive SOA formation. However, studies including the laboratory experiments of (Kroll et al., 2006, 2005) showed that SOA could indeed form from isoprene, although the SOA yields via gas phase oxidation and condensation onto aerosol particles are low (of the order of 1-10% (Kleindienst et al., 2007; Xu et al., 2014)). Despite the small yields of low volatility compounds, the high global isoprene emissions makes gas phase oxidation of isoprene a very important source of SOA. It is also the magnitude of these emissions that makes the aqueous phase chemistry of the isoprene oxidation products such an important area of research. Any mechanism that could further reduce the volatility of those species that are too volatile to form SOA via the gas phase pathway could have an enormous impact on the global estimates of isoprene-related SOA. In fact many of the second generation oxidation products of isoprene, such as glyoxal, methylglyoxal and glycolaldehyde are soluble, and participate in aqueous phase reactions (Carlton et al., 2009).

As described above, factors such as RH, temperature, and the VOC:NOx ratio may play a role in determining the products and yields from isoprene oxidation. Furthermore, oxidation by NO_3 may be an important sink of isoprene during nighttime, when NO_3 concentrations are higher (Kwan et al., 2012). These factors will be assessed in the proposed aqueous phase isoprene experiments.

The basic procedure of each experiment is as follows:

- The chamber temperature and RH conditions will be set, and the chamber pressurised to 1.2 atm.
- Isoprene will be injected into the chamber to establish the desired equilibrium mixing ratio.
- The seed aerosol will be injected.
- The conditions in the chamber will be observed for a period of 15-30 minutes to show that no reactions are occurring in the absence of oxidants.
- The oxidant will be injected and the reaction will begin. During this time the RH will be ramped up from 70% to 95%, so that the effect of different RH can be examined.
- Once 95% RH is reached, the first adiabatic pressure reduction will be made, forming cloud droplets.
- When 1 atm pressure has been reached, the conditions in the chamber will be allowed to stabilise for 15 min before raising the pressure once more to 1.2 atm.
- Up to three adiabatic pressure reductions will be performed for each run so that aqueous phase reactions can be observed across multiple cloud cycles progressively changing the chemical and physical nature of the CCN.

The mixing fans will be kept on during all stages of the experiment to ensure a well-mixed and homogeneous environment.

4.4.2 Proposed isoprene experiments

- The first set of experiments will complete the work done during CLOUD8. These experiments will involve the oxidation of isoprene with O_3 in the dark (i.e. the UV lights will be off). Acidic seed aerosol (sulphuric acid) as well as neutral or semi-neutral seed aerosol will be used (ammonium sulphate), to examine the effect of seed composition on products. Temperatures will be 20°C, -5°C, and -20°C. Isoprene concentrations will be similar to those found in the atmosphere (1 to 10 ppbv), and O_3 concentrations will be up to around 1 ppm. An important consideration is that enough organic mass be created that the aerosol mass spectrometer can see the particle phase organic products (the

AMS has a detection limit of around 0.1 µg/m^3). The number concentration of the seed concentrations will be varied between 15,000 cm^{-3} and 4,000 cm^{-3}, to provide varying volumes in which the aqueous phase reactions will occur. This will also allow us to assess the influence of reactant concentration on the products. The total number of runs will be approximately 10-15, to allow for different combinations of temperature, seed composition and seed concentration.

- A series of experiments will be performed to assess the effect of ionisation from the PS pion beam on the products of isoprene oxidation. Similarly to above, experiments will be performed with O_3 as an oxidant, with the UV lights off, and at temperatures of 20°C, -5°C, and -20°C. We will use neutral ammonium sulphate seed for these experiments, and the PS beam will be used. This will require a further set of experiments.
- A series of 10-15 experiments, analogous to those with O_3 will be carried out with NO_3 as the oxidant.
- The pion beam experiments will be repeated to determine the effect of ionisation on the NO_3 oxidation experiments.
- A further series of experiments analogous to those with O_3 will be performed, except the UV lights will be turned on 15 min before the first addition of O_3 to the chamber, and then left on for the duration of the experiment. Any changes in chemistry or size of the aerosols before the O_3 is injected will be observed, and the results will allow us to determine the effect of the UV radiation on the aqueous phase chemistry.
- Once again, these experiments will be repeated with the pion beam present.

4.5 Future toluene experiments

4.5.1 Aims and general background

The aims are:

- To investigate the effect of cloud processing on the growth of SOA from an anthropogenic precursor - toluene - by measuring growth of SOA under sub- and super-saturated conditions.
- To investigate the influence of temperature (in particular sub-zero temperatures), RH, VOC:NOx ratio and pH on toluene SOA yield.

Toluene is one of the major anthropogenic contributors to SOA, and can comprise 20-40% of the total aromatics in urban environments (Parikh et al., 2011). Atmospheric concentrations of toluene are around 0.1-0.7 ppb (Lee and Wang, 2006), measured at the rural perimeter of London. It is likely that substantially higher mixing ratios will be needed in the chamber experiments in order to generate enough organic mass for precise measurements.

Previous work has found that the SOA yield from OH radical oxidation of toluene at high VOC:NOx ratios is essentially constant, at around 30%, (Ng et al., 2007), indicating that the products are basically non-volatile. At lower VOC:NOx ratios (high NOx conditions), the yield depends on the amount of aerosol available for absorptive partitioning of the semi-volatile products. Both the high NOx and the low NOx cases would be interesting to study, as there is significant potential for the SOA yield to be enhanced through aqueous phase reactions. Indeed, under high NOx conditions, the oxidation leads to enhanced production of water soluble carbonyls such as glyoxal and methyl glyoxal (Ervens et al., 2011).

It was found by (Parikh et al., 2011) that the role of the aqueous phase in toluene related SOA formation is greatest under low initial seed conditions (such that the assumption of equilibrium partitioning of SVOC between gas and particle is not valid) and when the RH is high. Therefore a range of seed aerosol concentrations will be used.

The basic procedure for the experiments will be analogous to that of the isoprene experiments. All experiments will be performed at temperatures of 20°C, -5°C and -20°C.

4.5.2 Proposed toluene experiments

- A set of low NOx, OH-initiated oxidation experiments. The OH precursor will be H_2O_2 in combination with UV lights. The seed aerosol will be ammonium sulphate. Toluene mixing ratios of around 50 ppbv will be used; these may be increased if the oxidation does not proceed fast enough to produce measurable organic mass. Seed concentrations of between 15000 and 4000 cm^{-3} will be used.
- The experiments above will be repeated under high NOx conditions, with up to 500 ppbv NOx. HONO will be the OH precursor in this case, in combination with UV lights.
- The previous experiments will be repeated with sulphuric acid seed aerosol.
- Both the high NOx and low NOx experiments will be repeated with the PS pion beam on, to determine the effects of ionisation on the chemistry.
- A set of dark oxidation experiments will be performed, with NO_3 as the oxidant. These will be performed with sulphuric acid seed aerosol.

4.6 Future alpha-pinene experiments

4.6.1 Aims and general background

The aims are:

- To investigate the effect of cloud processing on SOA from a common BVOC precursor (alpha-pinene), as a supplement to the isoprene experiments. The SOA yield from alpha-pinene oxidation products is much higher than that of isoprene. Therefore we expect a less marked effect of cloud processing. However since alpha-pinene is a common precursor, it is important for it to be investigated.
- It is of considerable interest to measure how well alpha-pinene can be carried up to high altitudes by deep convective clouds where it can participate in new particle formation and growth in the free troposphere.
- We will further investigate the effect of temperature on SOA yields, in particular in the sub-zero range.
- We will also determine the differences of NO_3 as the oxidant, compared with O_3.

Alpha-pinene concentrations in the atmosphere are in the range of about 0.02ppbv to 0.7ppbv (Yu et al., 1999). Previous chamber experiments have shown that the yield is higher with more acidic seed aerosol, i.e. water activity also plays a role (Liggio and Li, 2006;Gao et al., 2004). A further study performed at an outdoor site in California by (Zhao et al., 2013), found that the yield of pinonaldehyde increased with increasing RH.

4.6.2 Proposed alpha-pinene experiments

The basic procedure for the experiments will be analogous to that of the isoprene experiments. All experiments will be performed at temperatures of 20°C, -5°C and -20°C.

- A set of dark oxidation experiments will be performed with O_3 (ca. 50 ppbv) as the oxidant. The seed aerosol will be ammonium sulphate, at concentrations of 15,000 to 4,000 cm^{-3}. The alpha-pinene mixing ratio will be around 1 ppbv.
- The experiments above will be repeated, with sulphuric acid seed aerosol.

- A set of dark oxidation experiments will be performed with approximately 10 pptv NO_3 as oxidant. The seed aerosol will be ammonium sulphate, at concentrations of 15,000 to 4,000cm^{-3}. The alpha-pinene mixing ratio will be around 1ppbv.
- The experiments above will be repeated, with sulphuric acid seed aerosol.
- All experiments will be repeated with the PS pion beam on to determine the effect of GCR ionisation on the chemistry.

4.7 Future experiments on ageing of aerosol by GCR

Ageing experiments will be performed using pinonaldehyde (Chacon-Madrid et al., 2013) or a similar first or second generation oxidation product of alpha-pinene. Ammonium sulphate aerosol will be injected into the chamber, and then the pinonaldehyde, or similar species will be added until partitioning between the particle and gas phase has been achieved and the desired gas phase concentration has been reached and is stable. The PS beam will then be directed at the chamber, and any changes in the aerosol composition, mass or partitioning between the gas phase and particles will be observed. Experiments will be conducted at 20°C, -5°C and -20°C. Experiments will be conducted at 95% RH, and 2-3 depressurisations will be performed to create cloud droplets. A second set of identical experiments conducted with the beam off will act as control (neutral) experiments.

4.8 Total experimental time

Each experiment is expected to take approximately 8 hours, assuming the chamber is at the correct initial temperature and RH conditions at the beginning of the experiment. The experimental time includes time for reactions to proceed during the sub-saturated phase, as well as the time taken to re-pressurise the chamber between each one of up to three cloud formation events. The table below lists the required experimental times, but does not include chamber preparation times to establish the desired gas mixtures, concentrations and temperatures, nor time for unexpected delays.

Table 4.1: Estimate of required beam time for the next round of aqueous phase experiments.

Experiment/VOC	**Time with beam (hr)**	**Total time (hr)**
Isoprene	408	816
Toluene	120	240
Alpha-pinene	96	192
Ageing experiments	24	48
Total time	648	1296

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5. PROCESS MODELLING

5.1 Interaction of CLOUD measurements with process models

Process models in the CLOUD chamber treat various processes, such as nucleation, growth, chemical reactions or the transport of ions, gases and aerosol particles inside the chamber. The models interact with the measurements in several ways. Some models describe processes based on parameterisations of older experiments. These models place the results of the CLOUD chamber measurements into the context of existing measurements and can help to define a baseline for new effects, a discovery or major revision of current understanding in various aspects of atmospheric physics and chemistry. These comparisons with CLOUD data are also important since the same models are being used for studying atmospheric implications. Some models help to understand the fundamental physical processes underlying the measurements and are used to evaluate the influence on the measurements of characteristic features of the instruments. Models that include very detailed microphysics with few fit parameters can be adjusted to reproduce the CLOUD measurements and interpolate the phase space for regions with little or even no experimental data. Newly adjusted models are used to evaluate the atmospheric implications of the CLOUD findings on a small scale before the results are implemented into global models to evaluate the climate impact.

In addition, microphysical models allow a more fundamental understanding of the underlying physics of CLOUD measurements. Some questions that have to be answered by a combination of process modelling and state of the art measurements in CLOUD are:

- How stable are small neutral and charged clusters?
- How does the experimental set up influence the observation?
- How do instrument response functions affect the measured values?
- How do acid-base clusters affect the particle growth, and can the observed growth rates be reproduced by models?
- What is the volatility of the organic vapours that condense on ultrafine particles?
- How large is the Kelvin (curvature) effect on these nanometre-sized clusters?
- Does the growth rate vary with particle diameter due to the Kelvin effect?
- At what rates do chemical reactions in the CLOUD chamber occur? And which pathways do they take?
- How do reactions in the condensed aerosol phase affect the chemical composition of air?
- How comparable are CLOUD measurements to atmospheric long-term measurements?
- How many ion-pairs are generated by cosmic rays and what is their chemical and physical development with time under different ambient conditions (trace gas concentrations, temperature, humidity, etc.)?

5.2 Current model results

A variety of models have been compared and fitted to the CLOUD results. These comparisons were done mainly with nucleation rates and either have been published or are in preparation for publication. Comparisons that have been published already include the comparison between the PARNUC steady state model (Kazil & Lovejoy 2007) for ion-induced nucleation of sulphuric acid and water (Kirkby et al 2011). The PARNUC model has been used in previous publications as input for global climate models. It was found that the PARNUC model adapted to the CLOUD results provided a lower limit for the nucleation rate since nucleation rates in Kirkby et al 2011 are enhanced by the contribution of contaminant ammonia. The Almeida et al 2013 results were compared with the ACDC H_2SO_4-DMA model. This model is based on quantum chemical calculations of cluster energies and allows detailed comparisons with the CLOUD experimental data. The data from the model and the experimental data indicate an almost kinetically-limited nucleation, i.e. the nucleation is not limited by an energy barrier due to evaporation of small clusters. Ehrhart & Curtius 2013 showed with a model calculation that a kinetically-limited nucleation in an environment with losses to pre-existing particles (like in the atmosphere) or walls (like in the CLOUD chamber) would behave similar to a system with an energy barrier. This similarity is with respect to the first nucleation theorem that relates the number of particles in a critical cluster to the sensitivity of the nucleation rates to the concentration of condensable vapour. A CLOUD publication that provides experimental proof of this using CLOUD data of the H_2SO_4-DMA system has recently submitted to PNAS.

Three publications are currently in preparation for the comparison of ion-induced and neutral binary and ternary nucleation over a wide range of atmospherically relevant temperatures (-65°C to 20°C).

- A paper using the Binary Homogenous Nucleation (BHN) model fitted to the latest CLOUD results is currently in preparation. The original version of the BHN model is already used in global models, and so the intercomparison gives an important estimate of the uncertainties in present global models.
- The Sulphuric Acid Water NUCleation (SAWNUC) model concerns ion-induced binary sulphuric acid water nucleation. SAWNUC includes measurements from previous experiments made with ion trap mass spectrometers to determine evaporation rates of small charged clusters. Evaporation rates of neutral clusters were adjusted to fit nucleation experiments by Ball et al 1999. Thus the comparison with this model provides a useful comparison to older experiments with complementary techniques. The comparison with SAWNUC also includes a study that evaluates uncertainties that arise from the counting efficiency curves of the condensation particle counters.
- The third publication compares the ACDC sulphuric acid-ammonia model with CLOUD nucleation rates.

Aerosol particle growth rates have a strong influence on the survival probability for nucleated particles to reach CCN sizes (>50 nm). The most critical range is at small sizes around a few nm since here the particles have high mobility and are rapidly lost by coagulation (scavenging) onto pre-existing large aerosol particles. The measured growth rates from CLOUD experiments have been compared with existing growth rate models.

- Model predictions of 1-3 nm particles for binary H_2SO_4-H_2O experiments at the kinetic limit using the parametrisation by Niemienen et al. (2010) give growth rates approximately equal or slightly higher than observed in the CLOUD chamber for the binary system, indicating that some sulphuric acid may evaporate from the 1-3 nm particles.
- When DMA and NH_3 are present, the kinetic contribution from acid-base clusters needs to be included in model predictions for the growth of these 1-3 nm particles. To assess the importance of acid-base clusters in the growth of nanoparticles, a set of model simulations were performed with the dynamical atmospheric cluster model (DACM) (Kulmala, 2010) and the SAWNUC (Lovejoy et al 2004) model under the assumption of kinetic-limited nucleation. The growth rate when H_2SO_4 is allowed to cluster with DMA is substantially higher than the growth rate from the kinetic model by Nieminen et al. (2010), which allows only monomers to condense on a growing particle. Therefore, under conditions in which the cluster concentration is non-negligible compared to the monomer concentration, cluster collisions also contribute to the growth and have to be considered when comparing measured and modeled particle growth rates (publication in preparation).
- The growth of particles larger than 3 nm is being investigated using the model MABNAG (Yli-Juuti et al., 2013) for the H_2SO_4-NH_3-DMA system. The first results indicate that MABNAG underpredicts the growth when DMA and NH_3 are present for particles larger than 3 nm. This is likely a result of clusters contributing to the growth, similar to what was observed for particles smaller than 3 nm. The impact of these clusters for the growth of particles >3 nm is currently being investigated.

A major contribution of modelling to the design of the chamber was a simulation of the turbulence and transport of tracers inside the chamber (Voigtländer et al 2010). The aim of that model was to determine the improvement in mixing the chamber by two fans and to determine the typical time a tracer needs to be mixed in the chamber. The fluid dynamic modelling indicated that the mixing time of a tracer in the chamber is around 60 s. The CLOUD chamber mixing fans are currently being upgraded to operate at a factor 3.5 higher speeds.

5.3 Broad process modelling strategy

Currently most process models are developed individually in the CLOUD partner institutes. Although this approach has the advantage that it provides diversity and in some aspects redundancy, the disadvantage remains that these models include only a subset of the microphysics in the CLOUD chamber. An example of this is the relation between models describing the chemical kinetics of vapours and the modelling of nucleation processes with these vapours. Another example is that currently the production of ion pairs and their transport by convection and diffusion is not directly coupled to any model. The ion balance equation are solved on a single spatial grid point. While this is in some cases, especially slow processes, a reasonable approximation, it becomes increasingly inaccurate for fast processes. Some models that describe the microphysics or aerosol processes are considered to be the reference standard but are not easily available for everyone in CLOUD. Model does not necessarily mean a code that is available to provide numerical solutions. Various implementations can exist that are not freely available. One main goal of future modelling is therefore to provide an interface or library for the atmospheric and climate communities for some of the most basic atmospherically-relevant microphysical processes measured and parameterised by CLOUD. Such a library would increase the rate at which results from CLOUD are used by the atmospheric and climate modelling communities.

5.4 Detailed modelling plans for process models

5.4.1 Large scale chamber model

The physical interpretation of the data that comes from the instruments connected to the chamber requires different layers of modelling. Since instruments only sample from specific points inside the chamber, the results have to be corrected to describe what is happening inside the full chamber volume and what would be the corresponding values in a free atmosphere. The significant values may be masked by existing processes in the chamber, and instrument data has to be corrected to achieve the final results. There is a need for a thorough understanding of each of the processes taking place inside the chamber, including (but not limited to):

- Transport processes - including turbulent transport.
- Processes during expansion experiments.
- Wall reaction processes.
- Ion mixing and charged transport processes.

The processes discussed above require expertise in both physics and chemistry and thus a close cooperation between experts in both fields is mandatory (indeed, the CLOUD consortium is strongly represented by chemists as well as physicists). Also, the study of these processes demands that experimental data be cross-checked with simulation results so that mutual validation implies a good fundamental understanding.

The transport of particles inside the chamber can occur in different ways. The existence of two fans, at the top and bottom of the chamber, make this system challenging to simulate. The need for a well-mixed chamber is of paramount importance for any experiment carried out in CLOUD. This means that during each experiment (be it nucleation or ice/aqueous phase chemistry) the chamber must ensure mixing of the different components in a time frame that is short relative to the processes under study for that experiment. That being said, many different components exist in the chamber air mixture (aerosols, ions, droplets, CCN) and each has its own unique underlying physics and chemistry that influence the transport. A good understanding of the transport processes and how these affect and/or are affected by sensor/instrument readings is required. For instance, if a thermal gradient exists in the chamber, processes that are sensitive to temperature (such as ice nucleation, new particle formation, etc.) show a different behaviour in parts of the chamber and thus the measured quantities can be different. Furthermore the existence of turbulence could help increase the mixing in the chamber, or if near the walls, could increase the wall loss rates. In addition, the existence of charged particles changes the transport properties (ambipolar transport).

All of the processes discussed above are usually handled by different groups and the results are usually available as individual (single cell) models of the different processes. The models are the result of microphysical and/or microchemical analysis and thus computationally heavy to expand into a full scale model of the CLOUD chamber. In order to handle all of the different processes, a CLOUD chamber large scale model is proposed to act as an 'integrator' of these model results. A Computational Fluid Dynamics (CFD) model of the chamber is proposed using the appropriate modelling tools that will simulate large scale development of specific quantities (i.e. fluid velocities and densities). All the different processes are to be inputs to this model proving a microscopical description that is lacking in the current CFD model. The small scale single cell models should be able to return their output into the large scale model so that it can predict large scale changes in the chamber. The large scale model should be exible to handle the incorporation of different parametrisations (be it simulation results or instrument data). A proposed set of initial processes to be incorporated are those enumerated above.

5.4.2 Modelling of nucleation and growth

Existing models that include the microphysics of nucleation and growth will be refined by adjusting them to fit the most recent CLOUD results. This includes further development of MABNAG to conform with the growth rates observed in the CLOUD chamber, as well as nucleation models that include the full Becker-Döring kinetics. With such nucleation models adjusted to the CLOUD measurements, valuable presently-unknown information on the stability of small clusters can be derived. Also the influence of condensation sinks or chamber walls will be quantified in more detail for the actual nucleating system.

5.4.3 Modelling of chemical kinetics

Modelling gas phase chemistry has become increasingly important in the light of recent CLOUD measurements of nucleation with oxidised organic vapours. These vapours are produced from biogenic precursor molecules inside the CLOUD chamber by oxidation with O_3 and OH radicals. The end product of this oxidation is a complex mixture of hundreds of organic compounds, many of which were previously inaccessible to any experiment other than in the gas phase at ultra-low vapour concentrations characteristic of the atmosphere. In addition to the direct measurements of these oxidised organics, a model incorporating the chemical kinetics of their formation provides additional input and makes the results transferable to measurements with different starting or background conditions, such as ambient data. To facilitate the modelling of chemical kinetics inside the CLOUD chamber, the Kinetic PreProcessor (KPP) (Sandu & Sander 2006), a model originally intended to be used for atmospheric modelling, is adapted to the CLOUD chamber. These adaptions include the replacement of sunlight and zenith angle by the CLOUD UV system, the implementation of wall loss parameterisations, and the implementation of processes on aerosol surfaces or within the condensed aerosol phase. The actual rate constants of the chemical reactions used for KPP come from the ASAD (Carver et al 1997) and MCM (Jenkin et al 1997, Saunders et al 2003) models already used widely in atmospheric science and climate models. The effects on the chemistry due to ionising radiation from the PS pion beam or GCRs will also be included in this modelling, i.e. the chemical fate of the primary ions produced by the ionising particles will be followed through to the cluster ions and charged aerosol particles.

5.4.4 Modelling of ion pair production

The production of primary ions, i.e. nitrate and oxygen ions will be modelled with particle physics standard tools to understand the ionisation process in detail. These standard tools include for example HEED (Smirnov 2005) or FLUKA (Battistoni et al 2007). In order to understand the convective transport of ions inside the chamber, a fluid dynamic model will be used. The induced chemical reactions will then be treated by the kinetic chemistry modelling described above.

5.4.5 Comparison with atmospheric observations

The ultimate aim of incorporating CLOUD data into models is to improve the ability of global climate models to evaluate the effects of aerosol particle nucleation and growth on climate. To facilitate this goal the CLOUD measurements must be compared with long-term atmospheric observations from various sites. Some of these sites are operated by the CLOUD partner institutes. In particular, the Hyytiälä atmospheric observatory sited in a boreal forest in Finland provides the world's most comprehensive time series of atmospheric observations. The modelling strategy approaches this goal in two ways. Firstly, the nucleation and growth rates and associated chemical species are measured by CLOUD, parametrised, and then compared with ambient data. This serves to verify the atmospheric relevance of the CLOUD measurements, and also clarifies the atmospheric observations, which include large backgrounds of "spectator" molecules and clusters that do not participate in the nucleation or growth processes. The new information is then included in global models. Secondly, the CLOUD measurements offer a unique possibility for improving comprehensive previously box models e.g. for particle growth rate. By improving the capability of these models to capture the behaviour in the CLOUD chamber, they provide an ideal tool to compare CLOUD results with ambient observations and can in future be directly used in global models.

The incorporation of CLOUD measurements into global models will be conducted in four steps:

- First, nucleation and growth rate parameterisations in terms of vapour concentrations, ionisation and meteorological conditions will be derived from the data. Data from all CLOUD campaigns will be used in deriving the general parameterisations. This work will be done at the University of Helsinki by following previous practices for parametrising atmospheric neutral (Paasonen et al., 2010) and charged (Nieminen et al., 2011) new particle formation rates.
- In the second stage, the parameterisations will be applied in process models in order to test how well they represent the CLOUD experiments. If there are discrepancies between the experiments and the modelled evolution within the chamber, the parameterisations will be revised in order to reproduce the experimental measurements quantitatively.
- Next, the parameterisations will be compared with ambient measurement data and with box models that have been set to approximate the local atmospheric measurements. At this stage we can evaluate how well the CLOUD chamber measurements represent the ambient situation. Where differences emerge, we can analyse under which conditions the parameterisations need further improvement.
- After achieving good agreement between the CLOUD-based parameterisations and ambient measurements, the parameterisations will be applied in global models and the climate effects evaluated.

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6. GLOBAL MODELLING

6.1 Current status

The status of global models. Despite the importance of nucleation as a globally extensive source of aerosol, a quantitative understanding of the process has not yet been reached. This is in stark contrast to the situation for many gas phase chemical and photochemical rates, which have been defined in models based on laboratory experimental measurements for decades. Fundamental questions concerning the source of global aerosol have therefore driven the design of CLOUD experiments to deliver data to models.

Firstly, it is not known whether particle formation is predominantly a neutral process or whether atmospheric ions are important. Most global models assume that particle formation is a neutral process but other models and observations suggest that ion-induced nucleation may dominate. Secondly, it is not known whether nucleation involves predominantly inorganic molecules (sulphuric acid and ammonia being primary candidate molecules) or whether organic molecules enhance the rates throughout the atmosphere.

In CLOUD we have used experimental measurements of nucleation rates to develop parameterisations suitable for incorporation in global models. We have then run these models and compared the predictions against observations to begin to understand how well these mechanisms can account for global measured particle concentrations. Our progress towards understanding the complete atmospheric aerosol system is only just beginning, but we have made two important steps, described below.

Global neutral and charged inorganic nucleation. Measurements made in the CLOUD chamber of neutral and ion-induced nucleation involving sulphuric acid and ammonia between 208 and 292 K have been parameterised and included in the GLOMAP global aerosol model. Global model simulations incorporating the measurements show that inorganic nucleation rates are consistent with observed particle concentrations above the planetary boundary layer (Fig. 6.1), with ion-induced nucleation accounting for about one-third of the formed particles. By making laboratory nucleation rate measurements as close as technically feasible to atmospheric conditions and using the data in models, we have made considerable progress in understanding the origin of global aerosol.

Based on these simulations we have shown that the response of global cloud droplet concentrations and cloud radiative properties to changes in the cosmic ray ionisation rate is likely to be weak where inorganic nucleation is concerned. However, we recognise that firm statements on the role of cosmic rays in modulating aerosols and climate will require (i) a more complete mechanism of nucleation incorporating more species, and (ii) a closer investigation of aerosol-cloud interaction that resolves cloud-scale processes and local charge generation processes. Both of these form part of our plan for modelling in the next phase of CLOUD.

Role of biosphere emissions in controlling global particle concentrations. CLOUD experiments show that organic compounds emitted by the biosphere can strongly influence the nucleation mechanism (Schoebesberger et al., 2013) and rate (Riccobono et al., 2014). We used the GLOMAP global aerosol model (Mann et al., 2010) to show that these rates may explain observed nucleation rates and variations in particle concentrations in the planetary boundary layer. Figure 6.2 shows the seasonal cycle in simulated and observed particle number concentrations across 19 locations in the northern hemisphere continental boundary layer (Riccobono et al., 2014). Model simulations based on the assumption that only H_2SO_4 controls nucleation in the boundary layer (as commonly used in other global models) tend to predict peak particle concentrations in early spring and autumn. The CLOUD parameterization (dark green line in Fig. 6.2) improves both the simulated magnitude and the seasonal variation of particle concentrations. This difference in seasonality is particularly apparent at sites located in or near forests (the new mechanism can explain about 50% of the temporal variability in particle concentrations but sulphuric acid nucleation can explain only 12%). The new

CLOUD mechanism involving biogenic vapours also explains the spatial distribution of observed particle concentrations (Fig. 6.3) driven by the availability of organic compounds emitted by vegetation.

These results show, for the first time, how the biosphere can influence global particle concentrations, and that the biospheric effects may be suppressed in more polluted regions. We don't yet know the implications for climate, but a strong biological control of aerosol suggests that we are now beginning to understand how aerosols may have behaved prior to industrial emissions. This is an important advance because new research shows that the pre-industrial atmosphere has a substantial bearing on the magnitude of anthropogenic forcing of climate (Carslaw et al., 2013; see section 4).

Limitations of existing modelling. The modelling so far in CLOUD has answered some important questions about the role of nucleation in the budget of particles in the global atmosphere. Nevertheless, there are some important open questions. We highlight these questions in the next section.

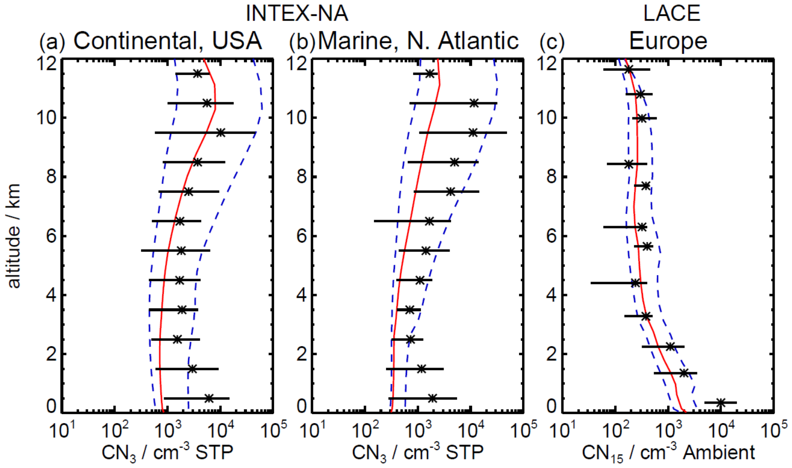

Fig. 6.1: Comparison of modelled aerosol vertical profile, based on CLOUD measurements, with atmospheric observations. a) Concentration of all particles larger than 3 nm diameter (N3) from the INTEX-NA campaign in summer 2004 over thecontinental USA; b) N3 from the INTEX-NA campaign summer 2004 over the North Atlantic; c) concentration of all particles larger than 15 nm diameter (N15) from the LACE campaign over Europe in summer 1998. Black symbols represent measurements; error bars show the 25% and 75% quartiles of the data; red lines represent a simulation at solar minimum (high ionisation), with dashed blue lines giving the uncertainty based on a factor 10 change in sulphuric acid concentration in the nucleation process only.

6.2 Science challenges to be solved using models

As described in the introduction, the effect of aerosols on clouds is one of the largest uncertainties in understanding the causes of global climate change over the industrial period. Future CLOUD measurements will be used in models to help reduce this uncertainty.

Although we can determine with reasonable accuracy the change in global mean temperature (ΔT) over the industrial period, the radiative forcing (ΔF, the energy imbalance at the top of the atmosphere) that caused the change is highly uncertain. This means that the sensitivity of climate to future forcing ($\Delta T/\Delta F$) is uncertain. Thus, understanding past radiative forcing is a critical step towards being able to accurately predict how future climate will change as the forcing due to greenhouse gases increases.

The main source of uncertainty in historical radiative forcing is the interaction of aerosols with clouds (Boucher et al., 2014). The modelling programme in CLOUD will therefore focus on understanding the sources of cloud-forming aerosol (cloud condensation nuclei, CCN), understanding the physical processes of aerosol-cloud interaction, and demonstrating that the models have an improved ability to reproduce global aerosol measurements.

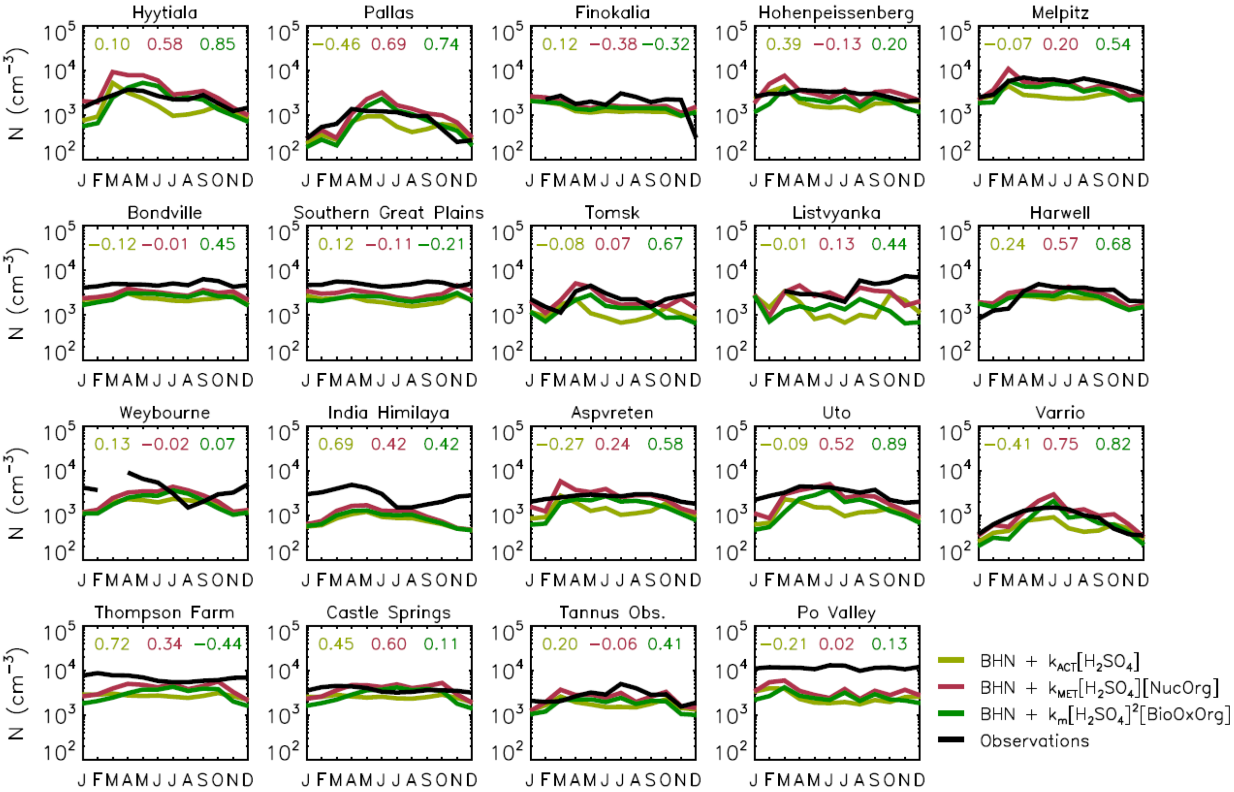

Fig. 6.2: Simulated and observed monthly mean total particle number concentration across 19 northern hemisphere continental boundary layer locations. Multi-annual observations, represented by the black line, are derived from measurements with minimum cut-off diameters ranging from 3 nm to 14 nm. Simulations using three different nucleation mechanisms are shown as coloured lines: light green – binary homogeneous nucleation (BHN) plus activation boundary layer nucleation (BHN + k[H2SO4]); dark green – BHN plus the new mechanism in the boundary layer based on CLOUD measurements, Riccobono et al. (2014); red – BHN plus Metzger et al. (2011) in the boundary layer.

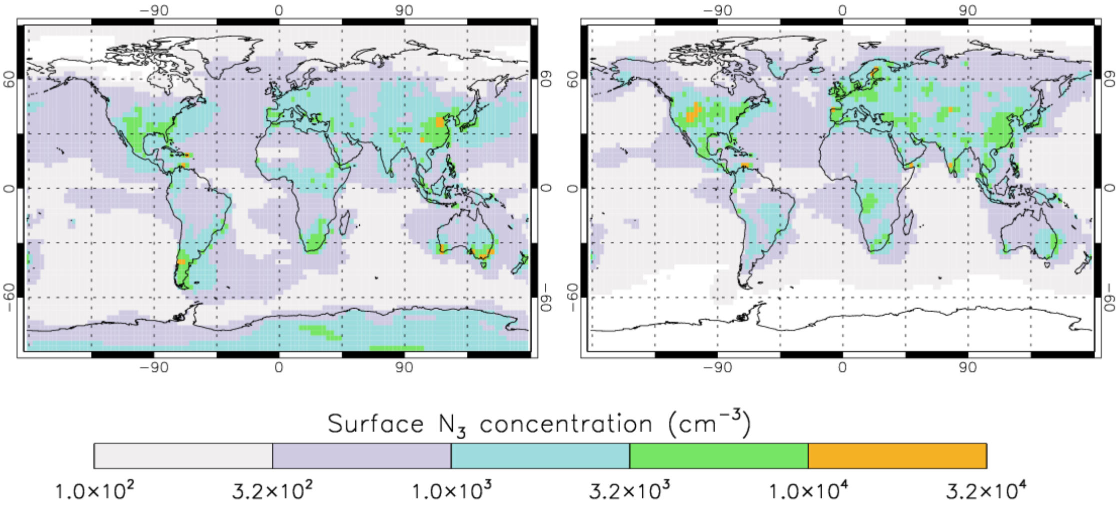

Fig. 6.3: Simulated monthly mean particle number concentrations (diameter greater than 3 nm) per cm^3 for January (left) and June (right), when the parameterized nucleation rate involving organics occurs throughout the atmosphere.

The major challenges in the next phase of CLOUD are as follows:

a) Understanding aerosol sources in the pristine pre-industrial atmosphere.

Our recent research has shown that nearly half the uncertainty in the aerosol forcing of clouds can be attributed to lack of knowledge of the pre-industrial atmosphere (Fig. 6.4, Carslaw et al., 2013). The radiative forcings (of greenhouse gases, aerosols and other factors) are calculated relative to a pre-industrial baseline because at this time all anthropogenic forcings are assumed to be zero and the climate system is assumed to have been in energy balance. The large contribution of baseline aerosols to the forcing uncertainty arises because the cloud albedo depends far more sensitively on aerosol concentrations when concentrations are low (Twomey 1977).

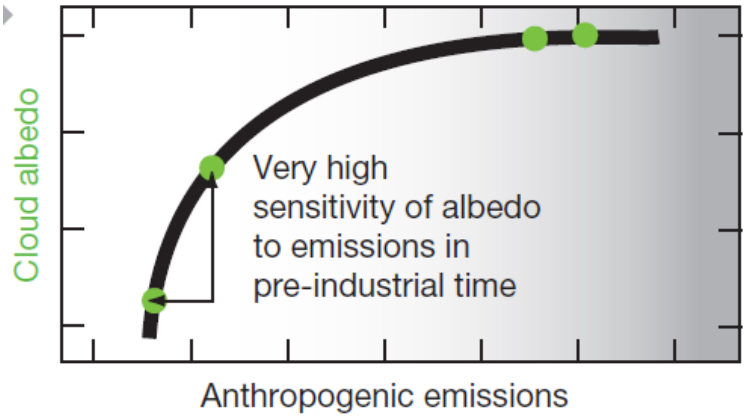

Fig. 6.4: Schematic showing why the radiative forcing due to aerosol-cloud interaction is very sensitive to the properties of aerosol in the pristine pre-industrial atmosphere. Cloud albedo (reflectivity) depends non-linearly on aerosol, so small uncertainties in the pre-industrial aerosol state cause large uncertainties in the change in albedo over the industrial period. From Carslaw et al. (2013).

Understanding the properties and behaviour of pre-industrial aerosols is a new and significant challenge that is very well suited to CLOUD. In particular, very few regions of the world are sufficiently pristine to be good analogues of the pre-industrial atmosphere, so there are significant observational challenges. Thus, well-designed and controlled chamber experiments can provide important information about aerosol processes in such environments.

The modelling will address the following specific questions:

- What is the effect of terrestrial biogenic compounds on particle formation in the global atmosphere and how does it affect the baseline pre-industrial aerosol? We will include new chemical mechanisms as well as nucleation and particle growth rate data from CLOUD in GLOMAP and run the model under pre-industrial and present-day conditions to calculate the effect of "natural nucleation" on aerosol concentrations, cloud properties and radiative forcing.
- Is the atmosphere more sensitive to ionisation rates in the pristine pre-industrial atmosphere than today? How does this affect the role of cosmic ray ionisation in climate change under present-day and under historical conditions? Our current work shows that in the present-day atmosphere particle concentrations are not very sensitive to ionisation rates. Sensitivity may be higher in the pristine atmosphere in which a much larger fraction of particles derive from nucleation, and particle loss rates are lower. We will use new CLOUD data under neutral and ionised conditions to simulate both processes separately in the global model.

b) Understanding the formation and growth of aerosols in cloudy environments.

So far, global model simulations have been run at a resolution of ~200km. Thus, the model does not resolve the behaviour of individual clouds. Although a global model is needed for climate prediction, progress needs to be made in understanding the fine-scale interactions of aerosols and clouds, which lead to the radiative forcing. Figure 6.5 shows results from the UK Met Office Large Eddy Model (LEM), which will be further developed in CLOUD to incorporate nucleation and growth processes. We will explore how nucleation of new particles can sustain concentrations in such cloudy environments, and how this process affects how air pollution affects the cloud drop concentration and cloud albedo.

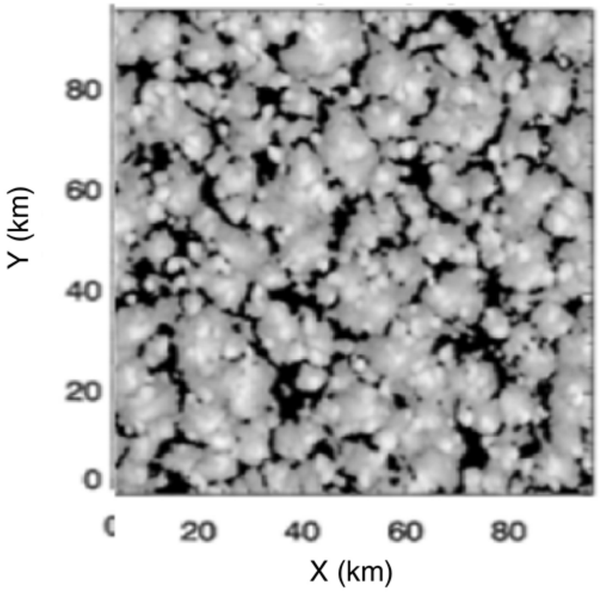

Fig. 6.5: Large Eddy simulation of stratocumulus clouds using the Met Office LEM. Simulations at this scale can resolve the fine-scale interactions between aerosols and clouds. An important question is how cloud condensation nuclei concentrations are maintained in precipitating cloudy environments. Nucleation may occur in these environments, particularly when high concentrations of sulphuric acid and organic compounds are present.

The major challenge for CLOUD in this research will be to approach the extreme conditions that exist in such near-cloud environments. The model, together with ambient measurements, will need to be used to inform the experimental programme in terms of concentrations of nucleating vapours and relative humidity. These are likely to vary substantially on small scales, and it may be that nucleation occurs only under very high humidity conditions near evaporating clouds.

c) Developing a comprehensive nucleation and growth model for the global atmosphere.

In the real atmosphere there are likely to be multiple nucleation mechanisms operating simultaneously, with different mechanisms perhaps dominating in specific environments. In the next phase of CLOUD, a significant challenge will be to develop model mechanisms that can account for multiple nucleation pathways. At present, we have explored the NH_3/H_2SO_4 system, the pinanediol/H_2SO_4 system, the amine-H_2SO_4 system and the alpha-pinene-H_2SO_4 system. A mechanism is needed that transitions between these separate systems, which will also need to account for competition between the different pathways (e.g., for available trace vapours and ions). This is a very large parameter space to cover in the CLOUD chamber experiments. The model will be used to test how such a 'master mechanism' can explain particle concentration variability in the real atmosphere (see next item).

d) Evaluation of CLOUD discoveries against real-world measurements.

Using models to make predictions is only useful if the model has been carefully evaluated against ambient measurements. As CLOUD aerosol mechanisms are incorporated in the models, a significant challenge will be to show that the models have an improved fidelity – or realism – when judged against ambient measurements. The challenge is very substantial because of the very wide range of environments of interest and the temporal and spatial sparseness of the measurements. We have used CLOUD measurements to great effect in Riccobono et al. 2014 (Fig. 6.2) and in our study of the NH_3/H_2SO_4 system (Fig. 6.1).

In the next phase of CLOUD we will substantially enhance our ability to evaluate model simulations against measurements on a range of space and time scales. To do this we will make use of an extensive synthesis of *in situ* aerosol measurements being compiled by the University of Leeds in their Global Aerosol Synthesis and Science Project (GASSP http://gassp.org.uk). GASSP, a UK project led by Leeds, is collating all relevant aerosol microphysical measurements (particle concentrations, chemical compositions, CCN, etc.) made from ground stations, ships and aircraft. In CLOUD, we will exploit these measurements to test our improved models, focusing on evidence for particle formation.

Our evaluations of models against ambient measurements will make extensive use of model uncertainty analysis to avoid drawing conclusions that are not supported by the uncertainty in other model processes. For example, work at Leeds has enabled uncertainty ranges to be placed on the model predictions using emulators and Monte Carlo simulation (see below), which enabled us to conclude that a biogenically-driven nucleation mechanism was needed to explain seasonal variations in particle concentrations, which lie outside the model uncertainty range (Riccobono et al., 2014).

6.3 Overall modelling strategy

The continuing success of CLOUD over the next few years requires significant advances in computer models of the atmosphere and climate system as well as a closer synergy between the experimental programme and models. The main developments over the next few years will be:

- An extension of the atmospheric modelling down to much finer spatial and temporal scales to capture regional processes and aerosol-cloud interaction at the scales of individual clouds and cloud systems. A nested model from global to cloud scale will be used so that the experimental measurements of processes can be incorporated and tested, while still allowing the global cycling of aerosols to be simulated. This approach will overcome the fundamental limitation of many previous studies that the majority of processes measured in the laboratory have no direct analogue in low resolution (>100 km) global models.
- New techniques of model uncertainty and sensitivity analysis will be used so that the impacts of uncertain aerosol processes on aerosols, clouds and climate can be quantified and the reduction in uncertainty can be estimated through the project.
- New approaches using models to dictate the design of the CLOUD experiments will be developed based on quantified uncertainties and gaps in understanding. We will exploit the improved process measurements, and identify new experiments in the light of progress towards the goal of reducing overall uncertainty. Such synergy has not been achievable in previous projects in which the modelling tends to follow the experimental work, with no flexibility to refine the experiments and models as the science dictates. This method of combining models and experiments to specifically quantify and reduce uncertainty will provide a new way forward in other areas of climate science. For the first time, atmospheric models will be fully integrated with a laboratory experiment uniquely capable of realistically simulating atmospheric aerosol-cloud processes.

Figures 6.6 and 6.7 summarise the concept:

- The uncertainty analysis of a global-to-regional cloud-resolving model will be used to identify the key uncertain processes and their effects on overall uncertainty.
- The important processes will be studied by CLOUD and provide new data for the models.
- The model simulations and uncertainty analysis will be repeated and a new estimate of uncertainty made, enabling the effect of the laboratory experimental data to be quantified.
- This process will be repeated continuously through the project, carrying out the model simulations in a range of cloudy environments and aerosol regimes so that a near-global picture of aerosol-cloud interaction uncertainty can be obtained. CLOUD experiments will continually be focused on the most uncertain processes and environmental conditions.

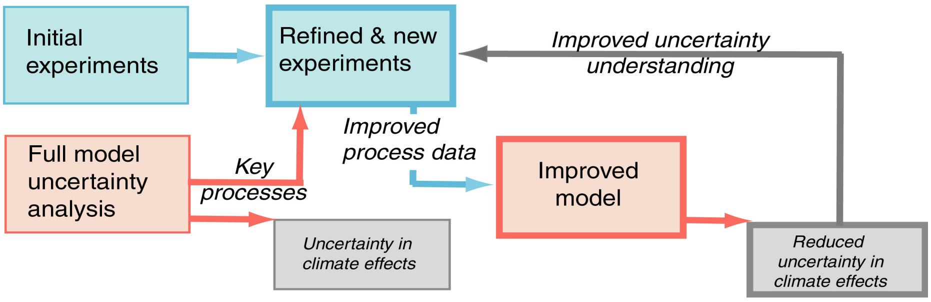

Fig. 6.6: Coupled use of laboratory experiments, model simulations and uncertainty analyses in the next phase of CLOUD.

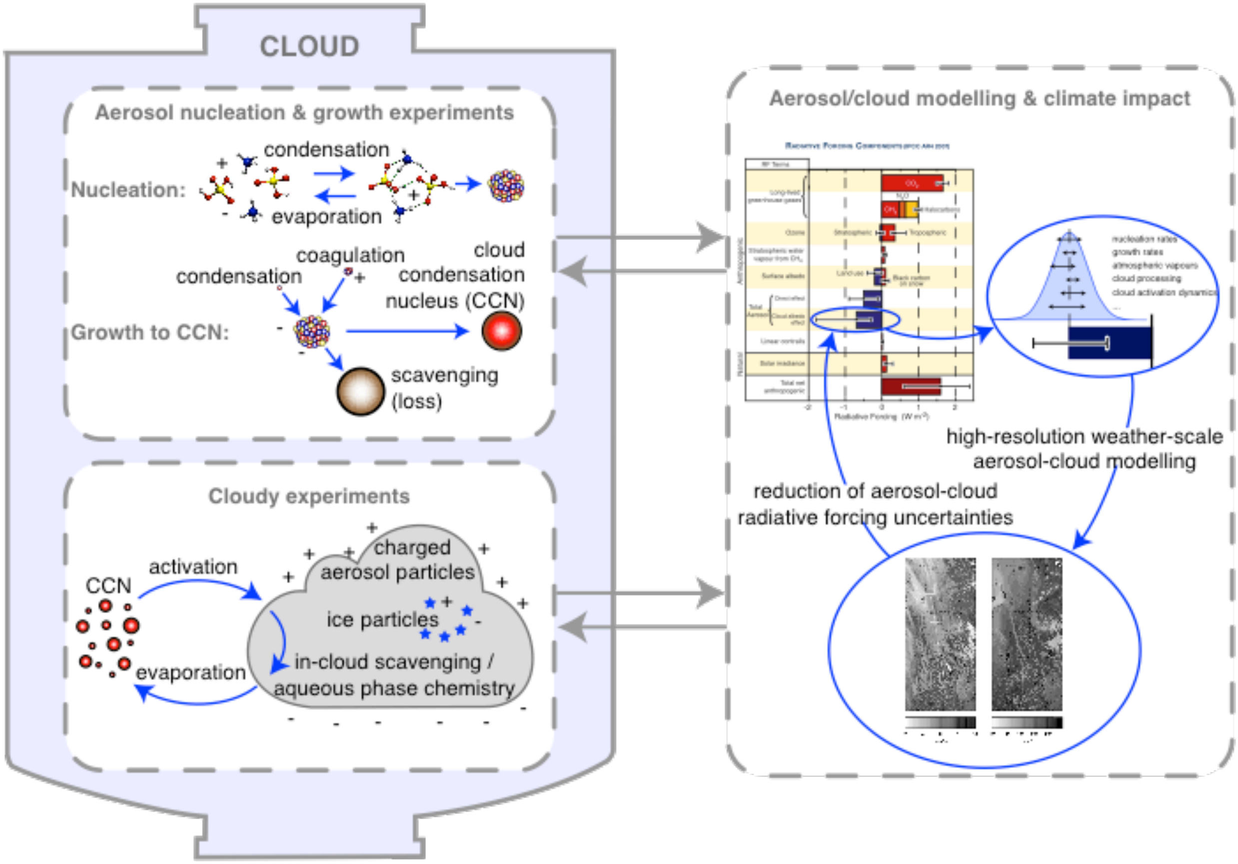

Fig. 6.7: The future modelling strategy in CLOUD will be to establish a much closer synergy between the experimental results and their impact on model simulations of the real world. The models will provide important information about how the experimental results are helping to reduce uncertainty in climate models and how they are helping to reduce discrepancies between models and ambient observations.

A key step in building an improved global model is the development of parameterisations: simplified but realistic computer algorithms that reproduce what is observed in the chamber and contain enough physics to be extrapolated reliably to other atmospheric conditions. Where possible, the parameterisations of aerosol processes derived from CLOUD data are influenced by the process models CLOUD has developed (Sec. 5) as well as directly from laboratory data. The global model results must also be compared with field measurements to ensure that the model faithfully replicates the situation in the atmosphere. Once these detailed checks are performed, the results can be used to plan the next round of experiments in the CLOUD chamber to maximise the impact of CLOUD measurements on our understanding of the atmosphere and climate.

6.4 New modelling technology

There are two principal model developments foreseen during the next phase of CLOUD that will enable us to understand better how the experimental results are helping to reduce uncertainty in climate prediction models. The first is to develop and apply much higher resolution models that can resolve processes occurring at the scale of individual clouds. Currently we have used low-resolution global models with grid spacings of ~100-200 km. In future we will increasingly use models with grid spacings of ~100 m or less so that aerosol-cloud interaction processes can be captured. Secondly, we will increasingly use emerging techniques of model uncertainty analysis so that the impact of CLOUD discoveries can be put into context with other uncertain model processes when evaluating the model skill against ambient measurements.

6.4.1 Aerosol-cloud interaction model simulation

We will use a modelling system that is capable of resolving the cloud-scale processes being measured in the CLOUD chamber, while also simulating the large-scale behaviour of aerosols and clouds required to quantify climate effects. Two new and highly advanced models will be used:

- *The UK Met Office Unified Model (UM).* The UM is a global weather and climate model capable of being nested down to regional domains (e.g. a few hundred km) with a spatial resolution of ~100 x 100 m^2. The UM can simulate real meteorological situations, such as in Fig. 6.8, so the inner domain can be moved to any location on the globe to study particular real cloud systems, with the 3-D aerosol fields nesting down from the global scale so that climate impacts of transported aerosol can be studied.
- *The Met Office Large Eddy Model (LEM)* (Fig. 6.5) can simulate cloud-scale processes down to the scale of metres. It can run in idealised controlled environments, such as typical stratocumulus regions, to provide a highly detailed three-dimensional picture of aerosol-cloud interaction down to the scale of individual updraughts and downdraughts.

Each model will be substantially developed in synergy with the CERN experimental programme to couple them with the advanced aerosol chemistry and physics model GLOMAP developed at Leeds (Mann et al., 2011). GLOMAP is capable of representing the nucleation, growth, activation and cloud interaction processes studied in the laboratory.

These model simulations will generate the essential information about the effect of uncertain aerosol processes on climate-relevant model outputs: for example, cloud drop concentrations, cloud albedo, liquid water path, precipitation intensity and distribution, diurnal cycle, etc. The models will be run for periods of a few days over a wide range of meteorological situations and in different environments (different stratocumulus regions and aerosol regimes). Information about the effect of the processes under investigation will be obtained from ensembles of perturbed parameter runs as described below.

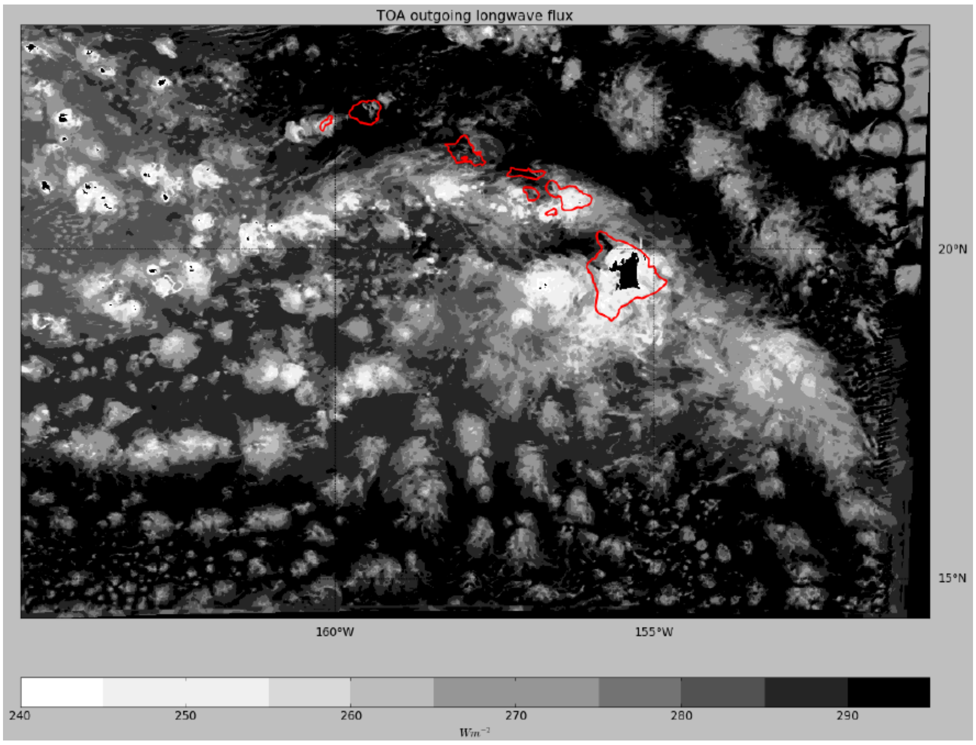

Fig. 6.8: UK Met Office Unified Model output at 12:00 17/07/2008 at 1 km resolution showing the top of the atmosphere outgoing longwave radiation over Hawaii. The model has been nested down from the global scale so that large-scale aerosol can influence the high-resolution cloud field in one region on the model. Using this more advanced model in the next phase of CLOUD will enable a much more realistic simulation of how global aerosols affect clouds and climate. Courtesy A. Hodgson (University of Leeds).

6.4.2 Uncertainty quantification – testing the robustness of CLOUD findings

The combination of advanced model uncertainty analysis techniques with an experimental programme is a unique and challenging way to quantify and reduce the magnitude of uncertainty in aerosol-cloud interaction. Typically, in short-term collaborative projects a range of interesting experiments are identified, which then deliver new data to models. The models are then used to show how the new processes affect the atmosphere. However, this approach, in which the models are de-coupled from experiments and at the end of the research chain, does not enable quantification of the effect of the new processes on the reduction in uncertainty. That is the main challenge to be overcome in the field of aerosol-cloud effects on climate.

The most innovative aspect of global modelling in the next phase of CLOUD will be a rigorous assessment of uncertainty using a range of models from the global climate scale (~100 km resolution) to eddy-resolving scale (~10-100 m resolution). Although these advanced models are needed to study the processes of interest, one drawback is their computational expense. This limits the number of simulations that can be performed, and in the past has meant that simulations with similar models have been limited to case studies. But to fully characterise the causes of uncertainty typically requires a prohibitively large number of model simulations in which the uncertain processes are perturbed. In CLOUD we propose to use statistical techniques pioneered at Leeds (Lee et al., 2011; 2012; 2013; Carslaw et al., 2013) to extract the maximum information about model uncertainty from a manageable number of model simulations.

The techniques we plan to use go well beyond normal model sensitivity studies. To fully characterise the model sensitivity and uncertainty based on a manageable number of model simulations we will use a Bayesian Gaussian Process emulator approach (Fig. 6.9). This approach enables a Monte Carlo-type sampling of the model uncertainty space to be performed based on a reasonably small ensemble of perturbed parameter model runs, which are used to train the emulator. The statistical data then allow a full variance-based sensitivity analysis of the model outputs to be performed. This approach generates probability density functions of any model output (e.g., mean cloud albedo), from which the variance (i.e., measure of overall uncertainty) and variance contributions of the uncertain parameters (i.e., causes of uncertainty) can be computed. The variance analysis quantifies the effect that uncertain processes have on the spread of model predictions, allowing the sensitivity to one process to be isolated as well as to understand how processes interact. In principle, this approach can be used to quantify the uncertainty in the state of the system (e.g. cloud albedo) or the change in state in response to a change in aerosol (i.e. albedo radiative forcing).

We have demonstrated the applicability of this approach to global aerosol uncertainty in recent papers (Lee et al., 2011; 2012b; 2013; Carslaw et al., 2013), but in CLOUD it will be a significant challenge to adapt the approach to a fully coupled non-linear aerosol-cloud model in which the cloud response to aerosol changes is likely to be small compared with meteorological variability. The Leeds team will comprise both aerosol scientists and statisticians with expertise in this emerging area of statistical analysis. We fully expect to have to develop new emulator approaches and to identify novel ways of designing computer simulations in order to generate the required information.

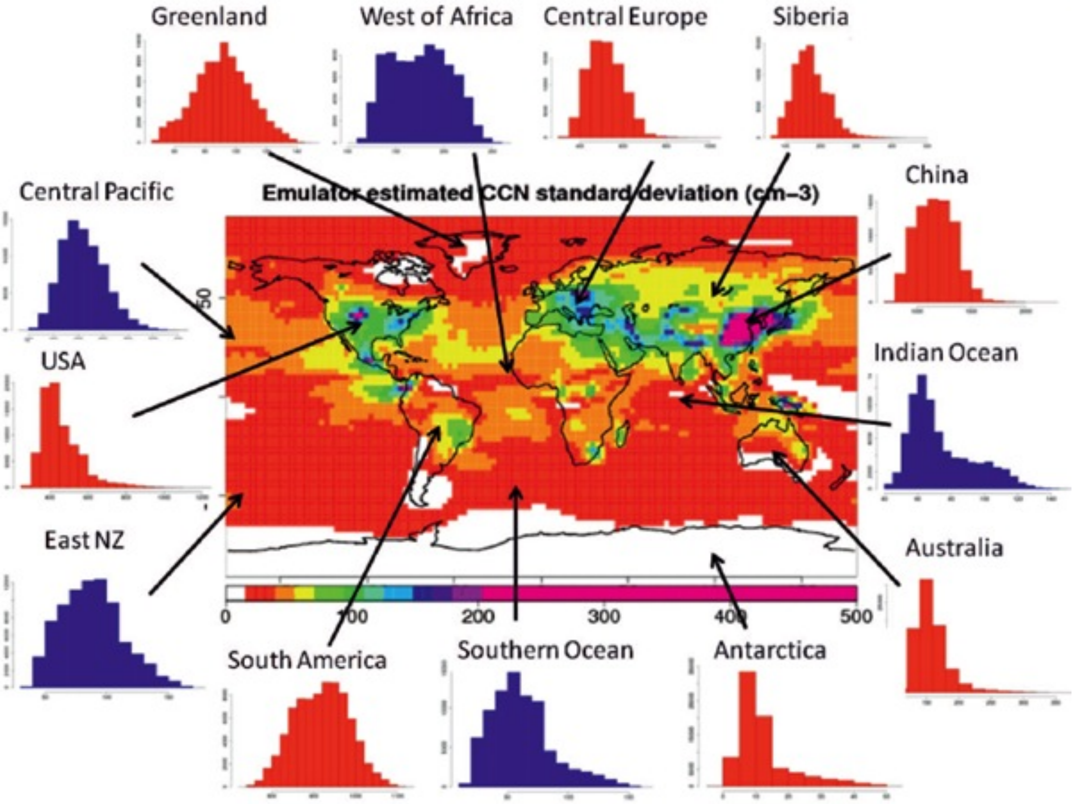

Fig. 6.9: Probability density functions of global cloud condensation nuclei (CCN) concentrations generated using the emulator approach. The Monte Carlo-level of information for 28 uncertain model parameters was generated based on just 168 model simulations and a Gaussian Process emulator in each grid cell of the model. By applying this technique to high-resolution aerosol-cloud models, CLOUD aims to generate unprecedented information about uncertainty in aerosol-cloud effects on climate. From Lee et al. (2013).

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7. CLOUD FACILITY

7.1 Current status

The central component of the CLOUD facility (Figs. 7.1, and 7.2, and Table 7.1) is a 3 m-diameter electropolished stainless steel cylinder (26.1 m^3). The large size allows nucleation and growth processes to be studied at atmospheric concentrations, which are characterised by slow collision rates and cluster growth rates. Manhole covers of 1 m diameter are located at the top and bottom of the chamber to allow internal access. The chamber is equipped with numerous ports to allow installation of electrical/optical feedthroughs and sampling probes to extract air samples. Two transparent electrodes operating at voltages up to +/-30 kV are installed inside the chamber to simulate an ion-free environment. The contents of the chamber can be irradiated by ultra violet (UV) light in the range 250-400 nm. The UV is introduced via 240 optical fibre vacuum feedthroughs installed on the top plate of the chamber. These provide a uniform UV irradiation inside the chamber for photolytic reactions, without any parasitic heat load. All materials and procedures used for the chamber are chosen to suppress contaminant vapours at the technological limit.

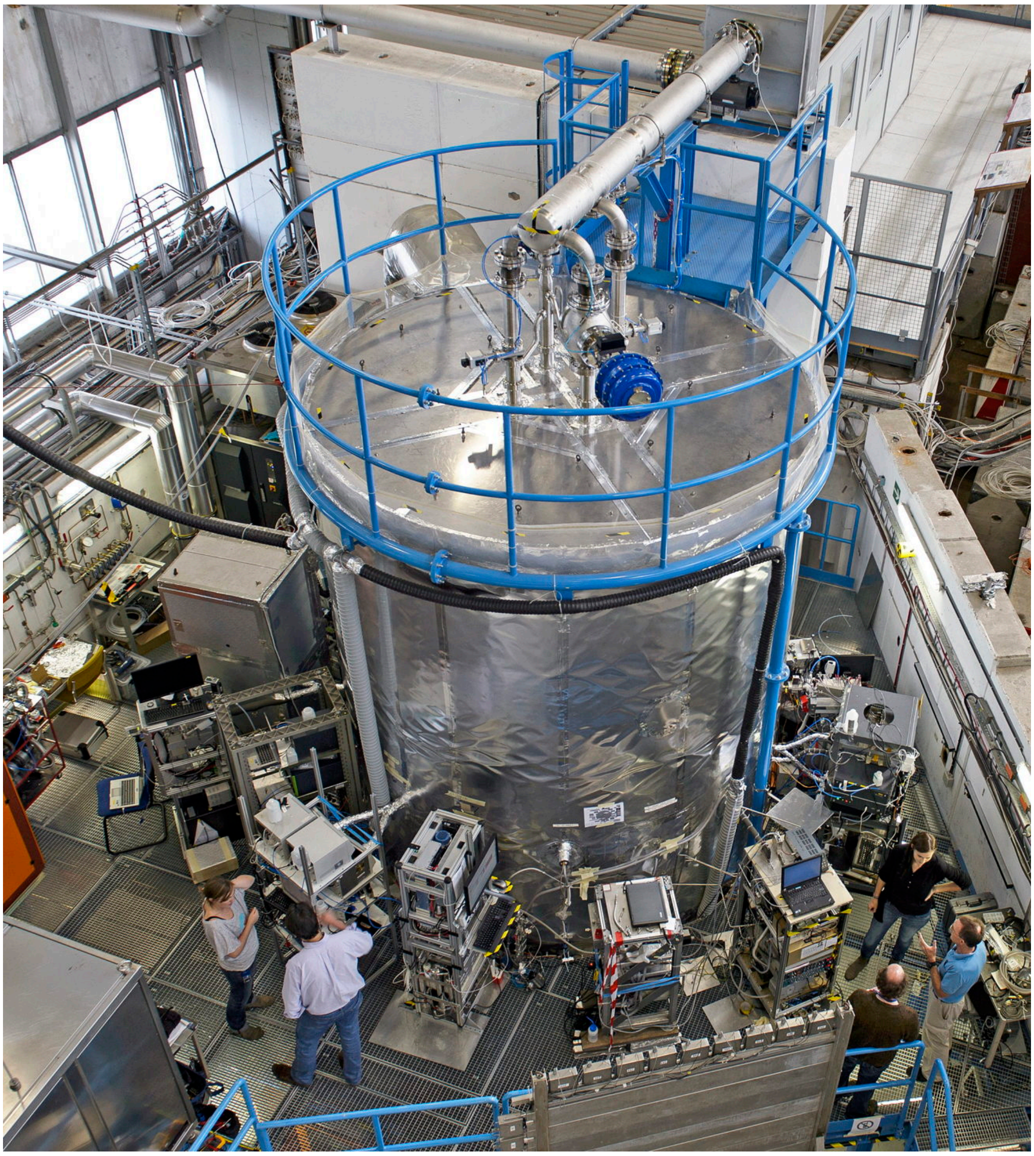

Fig. 7.1: CLOUD in the T11 zone of the East Hall during CLOUD8, October 2013.

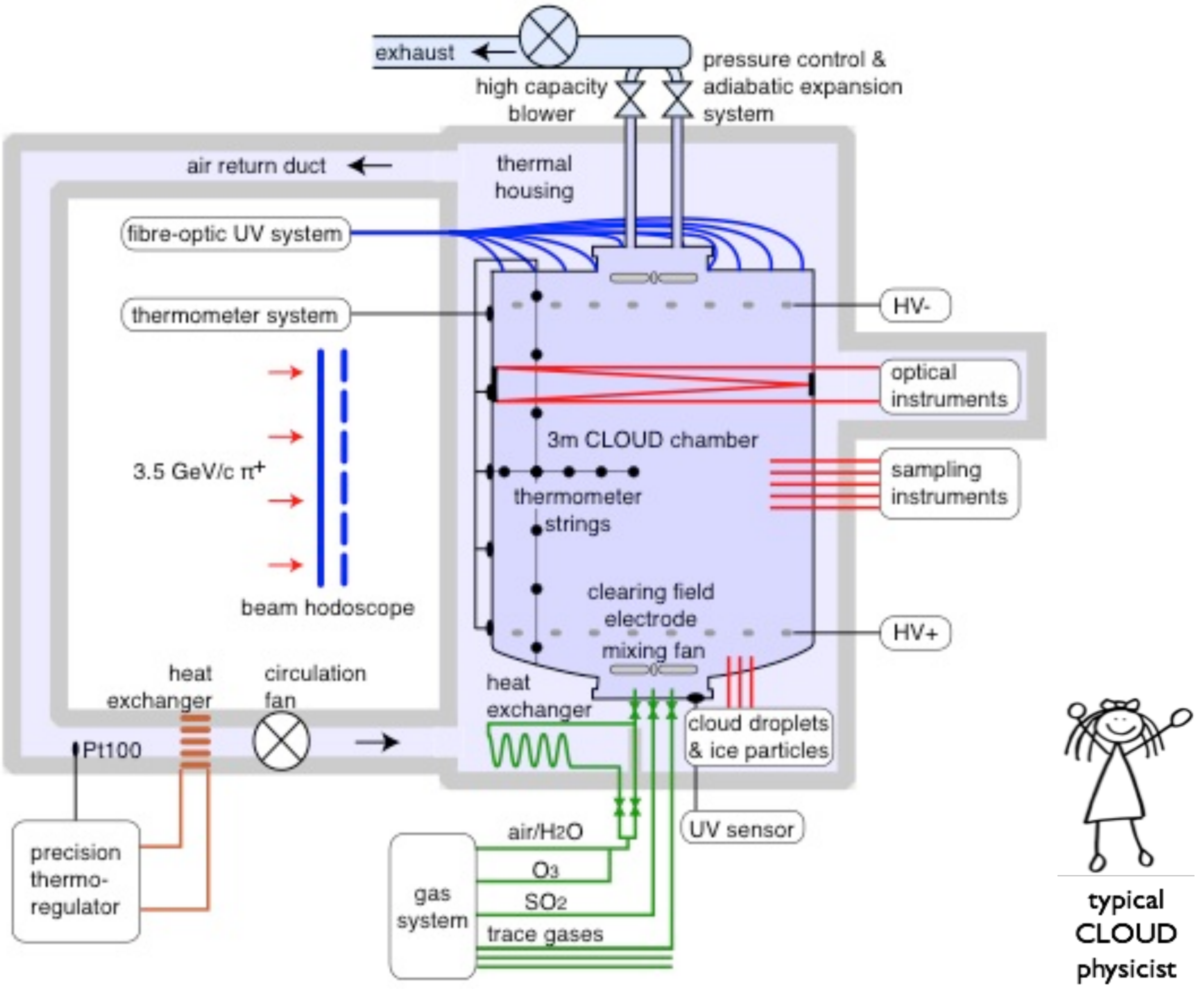

Fig. 7.2: Schematic of the CLOUD experiment.

An insulated thermal housing surrounds the chamber. The temperature is controlled by precisely regulating the temperature of the air circulating in the space between the chamber and the thermal housing. Experimental runs can be performed at highly stable temperatures (near $0.01\,^{\circ}$C) between +40 $^{\circ}$C and -70 $^{\circ}$C. In addition, the chamber can be raised to 100 $^{\circ}$C for bakeout. The chamber is exposed to a 3.5 GeV/c secondary $\pi+$ beam from the CERN PS, corresponding to the characteristic energies and ionisation densities of cosmic ray muons in the lower troposphere. The beam intensity can be adjusted to generate an ion-pair concentration in the chamber spanning the atmospheric range from ground level to the stratosphere. A comprehensive array of state-of-the-art instruments continuously samples and analyses the contents of the chamber (Sec. 8). The instrumentation is changed during each CLOUD run at the CERN PS according to the physics goals.

Ultra-pure synthetic air is obtained from the evaporation of cryogenic liquid N_2 and liquid O_2, mixed in the ratio 79:21, respectively. The air is humidified using ultra-pure water from a filtered re-circulation system. Ozone is added to the chamber by UV irradiation of a small inlet flow of dry air. Each trace gas delivered to the chamber has a dedicated line and isolation valve located at the chamber entrance, under the lower manhole cover. Magnetically coupled stainless steel fans on both manhole covers serve to mix the fresh gases and beam ions, and ensure uniformity inside the chamber. Volatile trace gases such as SO_2 or NH_3 are supplied from concentrated gas cylinders pressurised with N_2 carrier gas. The trace gas mixtures are highly diluted using synthetic air before injection into the chamber. Less volatile trace gases such as alpha-pinene ($C_{10}H_{16}$) or pinanediol ($C_{10}H_{18}O_2$) are supplied from temperature-controlled stainless steel evaporators using ultrapure N_2 carrier gas. Chemically-produced trace vapours such as nitrous acid (HONO) are supplied from custom-built stainless steel reactors. In order to compensate for sampling losses, there is a continuous flow of fresh gases into the chamber of about 150 l/min, resulting in a dilution lifetime of about 3 h. The chamber normally operates at +5 mbar relative to atmospheric pressure. However the chamber and gas system are designed to operate at up to +200 mbar relative pressure and to make controlled adiabatic expansions down to +5 mbar. In this way, starting from relative humidities near 100%, the chamber can be operated as a classical Wilson cloud chamber for studies of ion-aerosol interactions with cloud droplets and ice particles.

Table 7.1: CLOUD facility systems and instruments.

Item	**System/instruments**
Gas system:	
Ultrapure air	Cryogenic N_2 and O_2 systems
Ultrapure water	Re-circulating Milli-Q water purification system
Ultrapure synthetic water (under development)	Combustion of electrolytically-produced hydrogen in pure oxygen
O_3	Ozone generator (inox/quartz)
Volatile trace gases (SO_2, NH_3, DMA, isoprene, H_2, etc.)	Delivery system from bottles
Low volatility trace gases (pinanediol, alpha-pinene)	Evaporators (x2)
Other trace gases (eg. HONO)	Custom-designed reactors
Cloud condensation nuclei, CCN (H_2SO_4, oxalic acid…)	CCN generators (x3)
Internal gas mixing	Magnetically-coupled mixing fans (x2)
Air pressure	Pressure gauges (x3)
Air pressure failsafe	Independent air backup system (UPS)
Liquid/ice cloud activation	Pressure control system (gate valves, regulation valves, high-volume blower, software control system)
Gas control system	Highly flexible software control system & GUI
UV system:	
UV 250-400 nm	UV fibre-optic system (Hg-Xe lamps)
UV 254 nm	UV sabre
UV 254 nm (under development)	Excimer laser source for UV fibre-optic system
UV intensity	UV photodiodes
Thermal system:	
Chamber temperature	Thermal control system and thermal housing
Air temperature uniformity (radial)	Pt100 string; thermocouple string
Air temperature uniformity (vertical)	GaAs optical thermometer string
Beam/ion system:	
Electric clearing field	Transparent HV electrodes (+/-30 kV)
Unipolar ion generator	Corona ion generator for atmospheric research (CIGAR)
Beam counter	B12 counter (plastic scintillator)
Beam horizontal and vertical profile	VH hodoscope (plastic scintillator)
Cosmic ray intensity	Cosmic ray telescope (240 Geiger counters)
Data acquisition system:	
Data acquisition system	On-line data collection, storage and real-time analysis
Data server system	Off-line data server and GUI for easy data access

7.2 Planned upgrades of the CLOUD facility

There is an essential difference between particle physics detectors and CLOUD. Particle physics detectors are assembled, brought into operation and then maintained in a relatively stable experimental configuration for several years duration while sufficient data statistics are accumulated. CLOUD, on the other hand, is completely re-configured for each experimental run at the CERN PS according to the physics goals. Furthermore, the physics goals for each campaign are largely shaped by new experimental and modelling results that often only emerged a few months earlier. Hence CLOUD campaigns are typically planned with only a one-year lead-time.

As a result of the rapid developments in this field, not only the analysing instruments but also the CLOUD facility itself has been in a continual state of development since the first run in November 2009, substantially advancing its performance. This work has considerably extended the physics reach of the experiment over the last 5 years – and it is a process likely to continue as more discoveries are made and more demands are made on the performance of CLOUD. It is a credit to the CERN team that designed CLOUD and its gas system that the apparatus has proved itself highly flexible and adaptable to these new requirements. Nevertheless, the modifications and new equipment often require highly specialised design and engineering, and so it is vital for CLOUD to be able to count on the participation of CERN technical experts to ensure the continuing success of the experiment.

Foreseen upgrades of the CLOUD facility over the next few years include:

- ***Increased UV intensity:*** The unique UV fibre optic system has proved very successful. It provides precisely-adjustable, uniform UV illumination in the chamber without any parasitic heat load. However the maximum intensity is only a few % of atmospheric actinic UV fluxes. We therefore plan to replace the current lamps (Hamamatsu low pressure Hg-Xe lamps) with an excimer laser system at 254 nm. Our calculations indicate this will give a large increase in UV intensity below 310 nm (the threshold for photolytic dissociation of ozone), providing at least a factor 100 higher OH radical concentrations in the chamber, and comfortably reaching peak atmospheric OH levels of around $5\ 10^6$ cm^{-3}. Once more, the fibre optic system will prevent parasitic heating of the chamber and ensure uniform illumination. Furthermore the UV intensity will be precisely controllable by reducing the laser repletion rate below its 2 kHz maximum rate.
- ***Thermal uniformity:*** Cloud activation is sensitive to temperature changes of around 0.1°C. Although the CLOUD chamber has excellent thermal stability (near 0.01°C), there is an inevitable vertical temperature gradient in the chamber due to heat entering through the thermal housing into the circulating thermal air. We have prepared a conceptual design that could reduce the vertical temperature gradient by a factor 5 or so, and we plan to implement this upgrade to the thermal system.
- ***Precision temperature scale:*** In order to determine freezing temperatures of supercooled liquid clouds, we need to calibrate the vertical and horizontal thermometer strings that measure the internal air temperature. The required absolute precision is better than 0.1°C at all CLOUD chamber temperatures above -70°C. This will require construction of calibrated Pt100 strings that can be temporarily mounted alongside the present optical and thermocouple temperature strings inside the CLOUD chamber during dedicated thermal calibration campaigns.
- ***Improved internal mixing:*** The rotation speed of the two magnetically-coupled fans is being increased by a factor 3.5 to improve the internal air mixing and uniformity.
- ***Operation of the chamber at polar stratospheric temperatures:*** The current thermal system can operate the chamber at temperatures down to -70°C. We aim to study freezing processes and the effect of ions in polar stratospheric clouds (nacreous clouds), for which temperatures in the range -90°C to -100°C are required. To do this we will add a liquid nitrogen booster cooler to the thermal system to provide further cooling capacity during these studies.
- ***Ion generator for unipolar charges:*** We have designed and built a corona ion generator for atmospheric research (CIGAR). The aim is to use this to generate high unipolar charges in the chamber to simulate high space charge conditions existing at the top and bottom of stratified clouds.
- ***Synthetic water:*** The present water has a residual contamination from light (C_1-C_3) organics and ammonia (about 5 pptv at 5°C), even after many passages through a state-of-art re-circulating Milli-Q filtration system. We have therefore developed a synthetic ultra-pure water system involving the combustion of electrolytic hydrogen in pure oxygen. There is one remaining technical challenge,

involving an efficient heat removal system from the quartz burner (about 5 kW in a small volume). After taking care of this remaining challenge, we plan to implement the synthetic water system for CLOUD.

- ***Ultra-clean humidifier:*** The present humidifier uses a special synthetic fluoropolymer (Nafion) which has ionic properties and is highly permeable to water. We plan to replace this with an all-metal (inox) custom designed humidifier to reduce possible chamber contamination from the Nafion.
- ***New trace gases:*** Each CLOUD run makes demands on the gas system for new trace gases, either from bottles or evaporators, and also, for the cloudy experiments, new requirements for CCN generators involving different chemical compositions.

7.3. Data acquisition system

The data acquisition, distribution and analysis support system developed for the CLOUD experiment is currently managing all the instruments and users involved in the CLOUD experiments. The overall system is working in a stable manner for data taking during the CLOUD campaigns at CERN and for serving CLOUD data to the CLOUD users for their analyses. It provides a rather unique environment for the development of more ambitious solutions that would address the main user requirements in a simpler and more effective way.

The present system includes several components with different levels of potential for future development:

- *The data collection agents*, connected to the central database infrastructure at CERN, are successfully running on a wide number of heterogeneous platforms associated with different instruments attached to the CLOUD chamber. It is based on local caching of data, making the system very robust to possible central infrastructure or network downtime. The data gatherers are highly configurable and are able to cope with the many different forms and operations involved in collecting the data from a highly diverse set of instruments. These individual systems are synchronised by precise UTC clocks.
- *The central database system* and the data collection mechanism achieve high performance, and their open nature has already allowed the development of optimised solutions for different instruments. Similar procedures can be readily implemented in the future.
- *The replication infrastructure* forwards raw data and databases from the instrument-protected intranet to publicly available services maintained at the University of Lisbon. Similar replication mechanisms are being implemented at other sites involved in the CLOUD data analysis.
- *Universal access to data* is performed through a specially-developed user application, which has integrated the most important plotting capabilities and data copying to the local computer file system. A web interface to data is also available.

7.3.1 DAQ future plans

A computing cloud system to manage a distributed file-system of raw data has proven to be highly beneficial in similar collaboration environments. Further requirements of the CLOUD data analysis community can be addressed by the CLOUD to the power of cloud DAQ project ($\text{CLOUD}^{\text{cloud}}$).

The new system will:

- directly enable the incorporation of user data that results from re-calibration and new alignment processing,
- provide the raw and user-generated files to the community with different file-sharing privileges,
- manage data processing jobs that require large amounts of computing power, enabled by a distributed broker that allocates jobs to idle servers,

- implement a decentralised data collection procedure into the databases alongside a file sharing mechanism; this will replace the more complex data administrator procedures that are currently used to ingest newly calibrated data in the databases, and
- extend the central CLOUD data analysis application, be computing cloud aware by enabling indiscriminate access and visualisation to the central database data and shared user files.

We now have considerable experience running the CLOUD DAQ system and interacting with a large user community, sharing the same data and addressing the same type of problems. This experience will ensure the optimal development and required functionality of the new CLOUD$^{\mathrm{cloud}}$ DAQ system.

8. CLOUD ANALYSING INSTRUMENTS

8.1 Current status

The research conducted at the CLOUD chamber so far would not have been possible without the use of state-of-the-art and even beyond-state-of-the-art instruments (Fig. 8.1). Table 8.1 lists the instrumentation that has been used at CLOUD for analysis of gases, ions, clusters, aerosol particles, cloud elements and physical parameters. These instruments need to be capable to trace the transition of molecules to the size of cloud condensation nuclei (CCN of ~50 nm in size). This transition includes the formation of clusters and the partitioning of reaction products from the gas phase to the particle phase. Additionally, the role of ions in all the processes involved needs to be studied. It is therefore mandatory to deploy a suite of different instruments that can measure the concentration of trace gases (like SO_2, O_3, H_2SO_4, NH_3, dimethylamine, volatile organic compounds, etc.), as well as particle and ion concentrations. One of the main breakthroughs at CLOUD has been the measurement of the chemical composition of charged clusters at sizes below 2 nm. The evolution of these clusters directly showed how ions (HSO_4^-) are transformed into particles by the stepwise accretion of molecules. These kinds of measurement were for the first time applied to a controlled-chamber study at CLOUD and gave new insights into the formation of particles at the molecular level (Kirkby et al., 2011; Almeida et al., 2013).

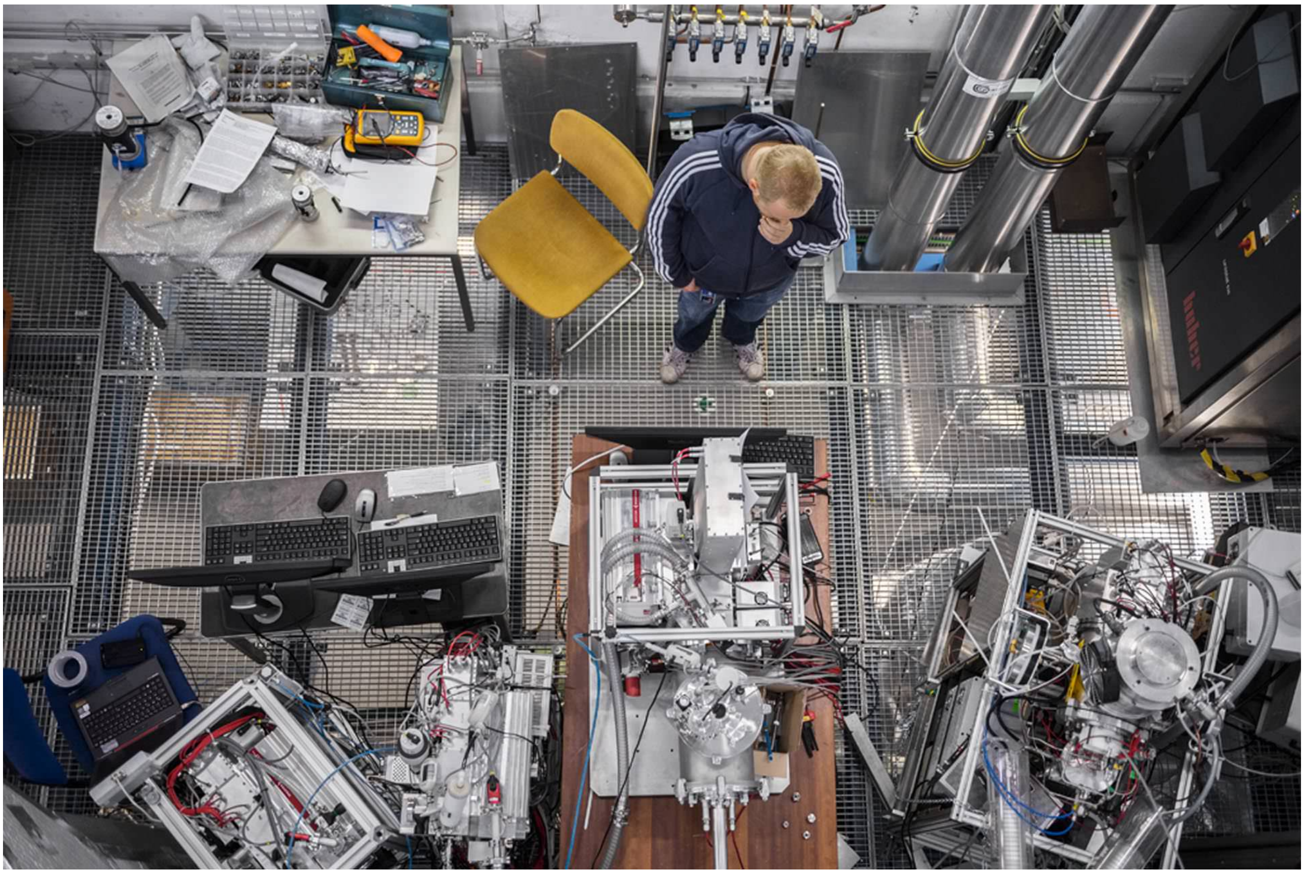

Fig. 8.1 Four of the nine mass spectrometers attached to CLOUD during the CLOUD7 run, November 2012 (left-to-right: APi-TOF+, APi-TOF-, IMS-TOF, Alexey Adamov, TD-CIMS). [Photo: Andri Pol.]

During the five years since the first CLOUD campaign in 2009, several new measurement techniques have been developed and been deployed at the CLOUD chamber. Indeed, their development was to an appreciable extent driven by the CLOUD project. The new techniques include the Particle Size Magnifier (PSM) for

Table 8.1: CLOUD analysing instruments.

Measurement	**Instrument**
Gases:	
O_3	Ozone monitor
SO_2	SO_2 monitor
H_2O	Dew point/frost point mirror
NH_3, amines	Long path absorption photometer (LOPAP)
NH_3, amines	Ion chromatograph (IC)
Volatile organic compounds (VOCs), NH_3, amines	Proton transfer reaction mass spectrometer (PTR-TOF)
H_2SO_4	Chemical ionisation mass spectrometer (CIMS)
H_2SO_4, extremely low volatility organic compounds (ELVOCs)	Chemical ionisation - atmospheric pressure interface - time of flight - mass spectrometer (CI-APi-TOF)
Neutral Clusters:	
Molecular composition up to 2 nm	CI-APi-TOF
Aerosol hygroscopicity >10 nm	Hygroscopic tandem differential mobility analyser (HTDMA)
Aerosol organic composition > 10 nm	Organic tandem differential mobility analyser (OTDMA)
Chemical composition of clusters down to 5 nm	Thermal desorption chemical ionisation mass spectrometer (TD-CIMS)
Size-resolved chemical composition of clusters, 20-1000 nm	Aerosol mass spectrometer (AMS)
Charged clusters:	
Molecular composition of positive ions and clusters up to 2nm	Atmospheric pressure interface - time of flight - mass spectrometer (APi-TOF+)
Molecular composition of negative ions and clusters up to 2nm	APi-TOF-
Mobility diameter and molecular composition of negative ions and clusters up to 2nm	Ion mobility spectrometer – time of flight – mass spectrometer (IMS-TOF)
Ion and charged cluster spectra 0-40 nm	Neutral and air ion spectrometer (NAIS)
Total ion/charged cluster concentration 0-40 nm	Gerdien condenser
Aerosol particles:	
Particle concentration >1.5 nm	Particle size magnifier (PSM)
Particle concentration >3 nm	Condensation particle counter, butanol-based (CPC)
Particle concentration >2.1 nm	Condensation particle counter, diethyleneglycol-based (DEG-CPC)
Particle size spectra, 1-5 nm	Radial differential mobility analyser (rDMA)
Particle size spectra, 5-200 nm	Scanning mobility particle sizer (SMPS)
Clouds:	
Interstitial aerosol particle spectra, 10-400 nm	Cyclone probe + SMPS
Activated (CCN) particle spectra, 10-400 nm	Pumped counter-flow virtual impactor (PCVI) + SMPS
Total aerosol particle spectra, 10-400 nm	Heated vertical probe + SMPS
Fast CCN particle spectra, 50-1000 nm	Ultra high sensitivity aerosol spectrometer (UHSAS)
Cloud condensation nucleus (CCN) concentration	Cloud condensation nucleus counter (CCNC)
Ice nucleus (IN) concentration	Spectrometer for ice nuclei (SPIN)
Droplet/ice particle size spectra, 1-100 µm	Mie scattering spectrometer (WELAS)
Droplet/ice particle size spectra, 1-100 µm	Cloud aerosol spectrometer (CAS-DPOL)
Droplet/ice particle size spectra, 1-100 µm	Laser scattering & depolarisation spectrum. (SIMONE)
Individual cloud particle optical scattering images, >1 µm	3 view cloud particle imager (3V-CPI)
Individual cloud particle optical scattering images, >1 µm	Small ice detector (SID-3)
Individual cloud particle optical scattering images, >1 µm	Particle phase discriminator (PPD)
Cloud droplet/ice particle concentration & dynamics	CCD camera (x3) (CCDCAM)

measurement of the particle number density down to 1.2 nm in size (Vanhanen et al., 2011), the Diethylene Glycol-Condensation Particle Counter (DEG-CPC) for particle number density measurement down to 1.7 nm in size (Iida, Stolzenburg and McMurry, 2009), the Atmospheric Pressure interface-Time Of Flight (APi-TOF) mass spectrometer for the measurement of ions and cluster ions (Junninen et al., 2010), the Chemical Ionisation APi-TOF (CI-APi-TOF) for measuring neutral clusters up to 2 nm in size (Jokinen et al., 2012) and the LOng Path Absorption Photometer (LOPAP) for ammonia measurements as well as the Ion Chromatograph (IC) for ammonia and dimethylamine measurements (Bianchi et al., 2012; Praplan et al., 2012). The publication of the CLOUD results in high-impact journals (Kirkby et al., 2011; Schobesberger et al., 2013; Almeida et al., 2013; Riccobono et al., 2014) was made possible through the application of some or several of these new techniques, brought together with a unique chamber facility.

It is therefore expected that further instrument development will continue to be vital for CLOUD. One of the main challenges in the future will be acquiring a detailed understanding of the mechanisms involved in the formation of new particles from organic compounds, what compounds and mechanisms drive their subsequent growth to CCN sizes and what role ions have in these processes. To get the full picture of these mechanisms and their relative importance in different environments it will be necessary to measure atmospheric oxidants like OH and NO_3, which are currently not directly measured at CLOUD. Furthermore, to understand the chemistry behind these processes it will be necessary to measure peroxy radicals, organic acids and other organic compounds (Ehn et al., 2014). The measurement of Extremely Low Volatility Organic Compounds (ELVOCs) and neutral clusters will be made with the newly developed Chemical Ionisation-Atmospheric Pressure interface-Time Of Flight (CI-APi-TOF) mass spectrometer (Jokinen et al., 2012). This instrument can be coupled to a high sensitivity Ion Mobility Spectrometer (IMS) – one of the latest developments from the CLOUD partner, TOFWERK – to gain further information on the chemical structure and functionality of molecules and clusters and whether these can fragment during the analysis. Characterising the chemical composition of nano-particles will help to understand how these particles can reach CCN sizes. Such analysis is extremely challenging due to the tiny mass of these particles, and techniques such as the Thermal Desorption-Chemical Ionisation Mass Spectrometer (TD-CIMS) need to be deployed (Voisin et al., 2003). The quantification of ammonia and amines in real time at sub-pptv levels is necessary to better understand the relative importance of organics and base molecules when nucleating with sulphuric acid. Instruments capable of measuring such tiny concentrations in real time are highly desirable and are needed at the CLOUD chamber. The most important instruments required for such analyses are outlined below.

8.2 Measurement of OH and HO_2

The hydroxyl radical OH is the most important oxidant in the atmosphere and reacts with many trace gases (Rohrer and Berresheim, 2006). The OH radical can be measured by (a) Chemical Ionisation Mass Spectrometry (CIMS) (Eisele and Tanner, 1991; Mauldin, Tanner, Eisele, 1999), (b) Laser Induced Fluorescence (LIF) (Heard, 2006) or (c) Differential Optical Absorption Spectroscopy (DOAS) (Dorn, Neuroth, Hofzumahaus, 1995). The methods (a) and (b) have about the same detection limit ($\sim 1 \times 10^5$ molecule cm^{-3}) and sensitivity. However, application of the CIMS method (a) at CLOUD seems to be favourable as experience with CIMS instruments exists within the CLOUD collaboration (U-HEL, U-FRA and PSI) and OH measurements have been performed by one of the collaboration members (U-HEL, Petäjä et al., 2009). OH can be measured by injecting isotopically-labelled $^{34}SO_2$ in front of the CIMS inlet, the sulphur dioxide will be converted to $H_2{}^{34}SO_4$ and subsequently be measured by nitrate (NO_3^-) ion chemistry. One challenge will be the rather high wall loss rate, e.g. for a tube with a length of 1 m, a flow rate of 10 litre/min and a diffusion coefficient of 0.215 cm^2/s for OH (Ivanov et al., 2007) only ~19 % of the OH will be detected. However, calibration of the CIMS instrument and the lines losses is possible and therefore high precision measurement of OH at low detection limits will be possible. Regarding OH experiments it is also important to upgrade the UV light system of the CLOUD chamber to produce higher OH levels. Currently, the maximum UV light intensity to produce OH radicals photolytically is only a few per cent of the mid-day atmospheric levels. A UV upgrade is planned (see Section 7.2).

Peroxy radicals, HO_2 and RO_2, can be formed from the reaction of OH with volatile organic compounds (VOCs) and are e.g. responsible for the formation of photochemical smog (Monks, 2005). More importantly, a recent study suggests that the formation of Extremely Low Volatility Organic Compounds (ELVOCs) is driven by organic peroxy radical (RO_2) chemistry (Ehn et al., 2014). The exact formation pathways of the ELVOCs remain to be studied; therefore application of a HO_2/RO_2 measurement technique is desirable. HO_2 measurement by CIMS can be realised in a similar way than the measurement of OH; adding NO to the sample flow converts HO_2 to OH, which can subsequently be titrated to H_2SO_4. RO_2 can be converted to HO_2 by reaction with NO and subsequently be measured the same way as HO_2 (Edwards et al., 2003). Detection limits for HO_2/RO_2 reached with this method are around $1x10^7$ cm^{-3}.

8.3 Measurement of NO_3

The nitrate radical (NO_3) is the most important oxidant in tropospheric nighttime chemistry. It is produced by the reaction of NO_2 with O_3. During day, NO_3 has a very short lifetime (about 5 s) because it absorbs strongly in the visible region (maximum absorption at 662 nm) and dissociates (Orlando et al., 1993). In order to distinguish between the different oxidation schemes (OH and O_3 during the day vs. NO_3 and O_3 during the night) the role of the nitrate radical with respect to the oxidation of organic compounds needs to be studied in the CLOUD chamber. For chamber experiments, NO_3 can be produced by thermal decomposition of N_2O_5. Reaction of NO, NO_2 and O_3 can produce N_2O_5, which can be cryogenically trapped in an acetone dry-ice bath at -80°C and evaporated into the chamber (Ng et al., 2008). The measurement of NO_3 can be performed by DOAS (Allan et al., 2000, JGR), cavity ring-down spectroscopy (Brown et al., 2003) or CIMS (using I^- primary ions, Slusher et al., 2004). The optical measurement of NO_3 seems to be favourable over the CIMS technique as it detects both NO_3 and N_2O_5 at the same product ion signal (i.e. at m/z 62, NO_3^-) and therefore cannot easily distinguish between the NO_3 and its precursor. Cavity ring-down spectroscopy seems to be a desirable technique to be applied at CLOUD since it is capable of measuring both NO_3 and N_2O_5 simultaneously at detection limits in the pptv range (Brown et al., 2003). Cavity ring-down spectroscopy has also been applied for the measurement of other trace gases (Wagner et al., 2011; Wang and Zhang, 2000).

8.4 Chemical Ionisation Mass Spectrometry (CIMS)

CIMS is a powerful technique that allows a suite of atmospherically relevant compounds to be measured at high time resolution and low detection limits (Huey, 2007). At the moment CLOUD uses H_3O^+ (Proton Transfer Mass Spectrometry, PTR-MS in positive ion mode for detection of organic compounds), NO_3^- (Nitrate-CIMS, negative ion mode for detection of sulphuric acid and ELVOCs) and CO_3^- (negative ion mode for the measurement of SO_2). However, other primary ions can be used to detect a larger variety of trace gases (see also above regarding the measurement of OH, HO_2, RO_2 and NO_3^-) and would essentially only require the upgrade of the ion sources (and the ion reaction zones) of the mass spectrometers, which are already in use at the CLOUD chamber. However, if other compounds besides the ones being measured already want to be targeted simultaneously, more mass spectrometers would be required. An alternative method would be the development of ions sources that can rapidly switch between different reagent ions (primary ions). Candidates for other primary ions to be used are (a) I^- ions (iodide), which can be used for the measurement of N_2O_5 and NO_3 (Huey, 2007) and organic compounds (Aljawhary, Lee, Abbatt, 2013; see also below), (b) CF_3O^- ions for the measurement of HOOH and $CH_3C(O)OOH$ (Crounse et al., 2006), HNO_3, N_2O_5, SO_2 (Huey et al., 1996), organic acids (Amelynck et al., 2000) and products of isoprene oxidation chemistry (Paulot et al., 2009), (c) $CH_3C(O)O^-$ ions (acetate) to measure inorganic acids (Roberts et al., 2010) and organic acids (Veres et al., 2008), (d) HSO_4^- ions (bisulphate) can be used to measure HNO_3 because it efficiently clusters with nitric acid to from $HNO_3 \bullet HSO_4^-$ (Mauldin, Tanner, Eisele, 1998), and (e) SF_6^- ions which are e.g. suitable for measuring HNO_3 and SO_2 (Huey et al., 2007). A recent publication (Aljawhary, Lee, Abbatt, 2013) reports on the analysis of water-soluble organic compounds from secondary organic aerosol by using CIMS with three different reagent ions (H_3O^+, $CH_3C(O)O^-$ and I^-). The results show that H_3O^+ reagent ions have a higher selectivity towards the more reduced organic compounds, while $CH_3C(O)O^-$ and I^- allow for the detection of more highly oxygenated compounds, with I^- being more selective to multifunctional compounds.

In general, it seems that during alpha-pinene oxidation experiments only the compounds that are highly oxidised are capable to cluster with NO_3^- and will therefore be detectable with a nitrate-CIMS (or nitrate CI-API-TOF). Therefore, an iodide and/or acetate CIMS will extend the range of compounds to be detected towards the lower components.

8.5 Ammonia/Amine measurement by PTR-MS

Highly sensitive measurement of NH_3 and amines in real-time is a major challenge. Proton Transfer Reaction Mass Spectrometry (PTR-MS) allows the quantitative measurement of substances that have a higher proton affinity (PA) than water (691 kJ/mol). There are many substances that fulfil this requirement; therefore PTR-MS is a versatile but generally not a very selective method. The proton affinities of NH_3 (853.6 kJ/mol) and amines (e.g. dimethylamine 929.5 kJ/mol, trimethylamine 948.9 kJ/mol) are considerably higher than the proton affinity of water (691 kJ/mol). Clusters of water have much higher PAs than the monomer of water, e.g. the dimer ($(H_2O)_2$) has a PA of 808 kJ/mol. Therefore, a lot of compounds will not react with the protonated dimer and the larger water cluster ions, but ammonia and amines will react. This principle can be used for the selective ionisation of base molecules at ambient pressure. With this method detection limits of sub-pptv levels are reported for certain amines and high time resolution measurement is feasible (Hanson et al., 2011).

8.6 Measurement of particle chemical composition

Whether freshly nucleated nano-particles (<1.7 nm diameter) eventually survive to become cloud condensation nuclei (CCN) of ~50 nm diameter depends strongly on their growth rates. It is therefore important to characterise which compounds partition into the aerosol phase, at what sizes these compounds are capable of doing so and what mechanisms (e.g. heterogeneous reactions) are important. Therefore the gas phase composition does not provide the full picture, and the particle chemical composition needs to be studied also. For this discussion particle size can be divided into three categories (i) clusters below ~2 nm in diameter, (ii) nano-particle size between ~2 and 30 nm (iii) particles in the CCN size range (> ~ 30 nm in diameter).

The smallest clusters/particles (i) can be analysed with the Chemical Ionisation-Atmospheric Pressure interface-Time Of Flight (CI-APi-TOF) mass spectrometer (MS). It has been shown that this method allows the sensitive measurement of neutral clusters up to ~ 2 nm in mobility diameter for particles consisting of sulphuric acid and dimethylamine (Kürten et al., 2014).

Chemical analysis of particles in the intermediate size range (ii) is challenging due to the tiny mass of the particles. Currently there are very few instruments in the world that can do this. The analysis requires collection of the nano-particles on a substrate, and their subsequent evaporation and chemical analysis. The Thermal Desorption-Chemical Ionisation Mass Spectrometer (TD-CIMS) can analyse particles larger than about 5 nm (Voisin et al., 2003) and has been deployed at the CLOUD chamber during the CLOUD7 campaign. There also exist developments similar to the TD-CIMS, e.g. the Chemical Analyser for Charged Ultrafine Particles (CAChUP, Gonser and Held, 2013). Future developments should aim to enable the size-resolved chemical analysis of nano-particles and combine the collection and evaporation methods used in the TD-CIMS or the CAChUP with the gas phase analytical techniques mentioned above (see CIMS section) to allow the measurement of a wide range of different substances.

The larger particles above ~30 nm (iii) can be analysed by several methods; e.g. the Aerosol Mass Spectrometer (AMS, Jayne et al., 2000; Drewnick et al., 2005), which is used at CLOUD. Other methods have not yet been deployed at the CLOUD chamber but have the future potential. These include the TAG-GC (Thermal Desorption Aerosol GC/MS) method which collects particles after inertial impaction, and analyses their composition with gas chromatography and mass spectrometry after evaporation (Williams et al., 2006). There is also the FIGAERO (Filter Inlet for Gases and AEROsols) which collects particles on a Teflon filter, evaporates them by flowing hot gas over the filter, and allows the identification and quantification of evaporated material (Lopez-Hilfiker et al., 2014).

Quantification and speciation of particulate material will be an important topic in future CLOUD campaigns and a great deal of effort will continue to go into the development of new techniques.

8.7 Physical properties of particles

The measurement of the particle number concentration and their variation with time is the key to derive the formation rates of new particles. Condensation Particle Counters (CPC) are widely used for this task. Deriving the formation rates requires exact knowledge of the detection efficiency of a CPC with respect to the size, chemical composition and charging state (whether it is a neutral or positively/negatively charged). The detection efficiency also depends on the chemical composition of the condensing vapour, e.g. it has been shown that secondary organic aerosol from the oxidation of limonene is not detected as efficiently as other commonly-used particles for CPC calibration (like ammonium sulphate, sodium chloride or tungsten oxide) (Kangasluoma et al., 2014). Therefore more work is required to characterise and to optimise CPC response functions for the different chemical systems to be studied at CLOUD. Another parameter that has not been explored extensively is the influence of the chamber temperature on the CPC response functions. All available CPCs are not operated isothermally and therefore temperature gradients between the environment where the particles are sampled from and that of the instrument could lead to the evaporation (or shrinkage) of particles. Development of isothermally operating CPCs is intended, and CLOUD offers the optimal environment for testing such devices.

Another challenge is to measure aerosol size distributions down to diameters as small as the freshly nucleated particles. Several state-of-the-art instruments such as the neutral air ion spectrometer (NAIS, Manninen et al. 2009), nano scanning mobility particle sizer (nano-SMPS), radial DMA (rDMA, Zhang et al. 1995) and scanning mobility particle sizer (SMPS, Wang and Flagan 1990) have been already used to determine size distributions covering diameters from 0.8 to several 100 nm. Such size distributions are needed to determine aerosol growth rates and aerosol uptake of condensable vapour species but also to determine loss terms for freshly nucleated particles. Current aerosol sizing instrumentation have a time resolution of typically 60 s or higher. New particle formation events and early growth show very high dynamics and therefore reducing the scan time is desired. Recent studies have shown that aerosol size distribution measured by the nano-SMPS can be precisely measured (Tröstl et al. in preparation in collaboration with CLOUD partners) with scan times as low as 5 s. This is especially important for recent cloud formation experiments conducted at CERN. Typical cloud durations were in the order of minutes. With systems taking 60 s to determine one size distribution, decreasing the scan time can substantially improve current measurements.

8.8 Other topics

Calibration of instruments like the CI-APi-TOF is important to reliably quantify different compounds. While calibration for sulphuric acid monomers is straightforward, it is much more challenging to do this e.g. for clusters of sulphuric acid and dimethylamine or ELVOCs. Currently no calibration techniques are available to calibrate for these substances and more work is required to develop new ideas.

The interpretation of mass spectra from experiments involving organic compounds is extremely complex. To some extent this is due to the limitations of the best mass resolving power that can be reached by current time of flight mass spectrometers. These reach a mass resolution no higher than about 7000 $m/\Delta m$ which is not sufficient to unambiguously identify all organic molecules having the same integer mass but different exact mass. In addition, the mass spectra deliver only the elemental composition but not the chemical structure of the detected ions/molecules. Therefore, coupling an Ion Mobility Spectrometer (IMS) with an APi-TOF or an CI-APi-TOF adds another parameter to the observed mass spectra and can help to identify the elemental as well as the molecular composition or functionality of the observed species.

Increasing the mass resolving power of the analysing mass spectrometer will also help in unambiguously identifying the elemental composition of even the largest organic molecules. The Orbitrap reaches a mass resolving power up to several times 100,000 (Zubarev and Makarov, 2013). At present it has been applied to the analysis of organic aerosol from filter samples (e.g. Laskin et al., 2010) but it could also potentially be used for the on-line measurements of gas phase, cluster or particle chemical composition if detection limits are sufficient.

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9. T11 BEAMLINE AND INFRASTRUCTURE

The CLOUD experimental apparatus consists of two parts: 1) a central facility and 2) a set of analysing instruments.

The CLOUD facility (Sec. 7) comprises the fixed infrastructure located in the T11 zone: aerosol chamber, field cage, UV system, mixing fans, thermal housing and thermal control system, cryogenic synthetic air system, gas system, adiabatic expansion system, beam counters, cosmic ray monitor, platform structure and data acquisition system. The aerosol chamber is equipped with sampling probes, optical ports, UV fibre optic feedthroughs, electrical ports, gas inlet and exhaust pipes, manholes, circulation fans and isolation valves, and instrumented with temperature and pressure sensors.

The analysing instruments (Sec. 8) are mostly mounted outside the aerosol chamber on the CLOUD platform and analyse its contents via sampling probes or optical ports. Some droplet and ice particle analysers are mounted underneath the chamber, using vertical sampling probes. The configuration of analysing instruments for each beam run changes according to the specific physics goals.

9.1 CLOUD in the PS T11 beamline

The CLOUD facility is installed in the CERN PS East Hall T11 beam area (Fig. 9.1). The counting room is in close proximity, behind shielding blocks. Gas and cryogenic supplies are located outside the building, at about 10 meters distance from T11.

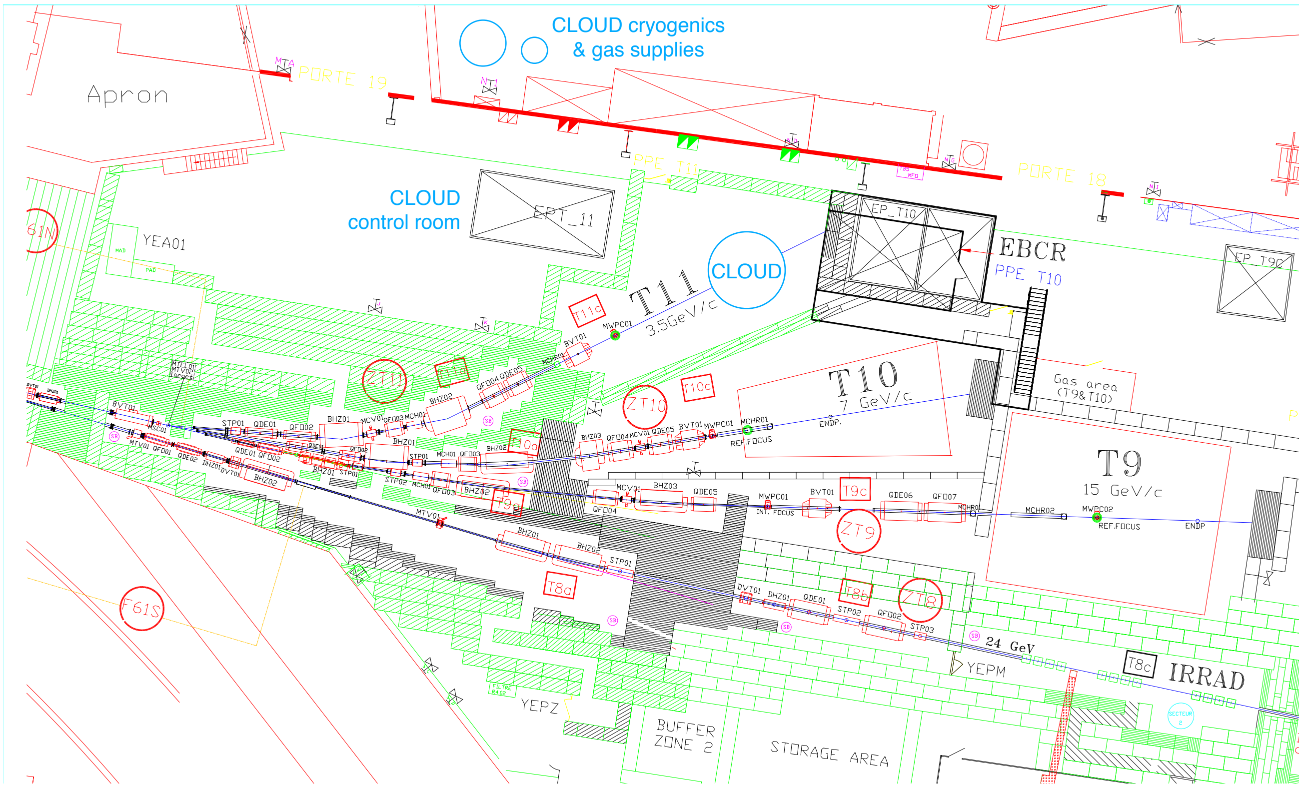

Fig. 9.2: Layout of the PS East Hall and CLOUD in 2014.

The 3.5 GeV/c pion beam available in the present T11 is well suited for CLOUD. To uniformly ionise the gases inside the aerosol chamber, CLOUD needs a beam with a large cross-sectional area. For this reason the aperture of the last beam-guiding dipole magnet has been enlarged and special beam optics settings are used to provide a beam of ~ 1.5 m x 1.5 m cross-section at the aerosol chamber. The beam-dump in T11 has been increased in width and in height to match the enlarged beam.

To minimise losses along the sampling-lines, CLOUD's analysing instruments are located as close as possible to the aerosol chamber. Most of the instruments are located on a platform that provides instrument access at the mid-plane of the aerosol chamber. Some instruments are located directly below or above the chamber – such as those analysing water droplet and ice particles, which would sediment out of horizontal sampling probes.

Currently very few of the CLOUD analysing instruments stay permanently at CERN. Most of the instruments are transported from the collaborating institutes at the start of each measurement campaign and are then shipped back at the end of the campaign. The same instruments are also used in field and other campaigns where their measurements can be directly compared with CLOUD's. In this way there is an important synergy between the laboratory and field measurements; on the one hand CLOUD needs the guidance of field measurements to identify potentially interesting vapours for study and, on the other hand, CLOUD can definitively measure selected vapours and quantify their ability to nucleate and grow atmospheric aerosol particles, and quantify the influence of ions.

9.2. Future requirements for experimental zone and infrastructure

The highest priorities for CLOUD in future are a) the availability and flexibility of beam time, and b) open access to the experimental area during non-beam periods so that the chamber and support systems can be upgraded and developed. The scientific potential of CLOUD has proven to be very high and the field of studies still ahead is large. To best exploit this potential, the CLOUD facility and instruments are re-configured and extended for each new measurement campaign. These modifications are done during non-beam time, and require continual free access to the beam area.

The above-mentioned requirements are well met in the present T11, which should be preserved for CLOUD's use in the future. The currently beam size and energy are perfectly satisfactory for CLOUD.

The T11 experimental zone is small, but well suited for CLOUD. In planning future beam-line modifications, it would be extremely valuable if the T11 area could be slightly enlarged - even by one or two metres - in the direction towards the current T10 beam area. The space available on that side of the CLOUD aerosol chamber is tight, leading to difficulties in placing measurement instruments and in maintaining the necessary access paths around the chamber.

The currently available space outside building 157 for storing liquid nitrogen and liquid oxygen, as well as trace gases, is also well adapted for CLOUD's future needs. These storage areas are close to the T11 beam area, properly fenced and accessible by trucks for gas deliveries.

A material transit area is needed next to T11 to receive the instruments for each measurement campaign and to allow their return packing and transport back from CERN. This is generally available (although occupied at present with concrete shielding blocks). The open loading/unloading space should be preserved in future.

The currently available storage space in the East Hall needs to be preserved for CLOUD instruments racks and other equipment used frequently in the beam area. Radiation protection and safety issues are minimized as the equipment does not need to leave the radiation-controlled building, and equipment can be lifted using the hall crane.

CLOUD needs a dedicated open office space and meeting room for its daily run coordination meetings, for use of the experimenters at CERN (which number up to 30 or more during runs at the PS) and external experimenters via audio-visual link. For radiation protection reasons this open office/meeting room cannot be inside the East Hall. However it needs to be close to the T11 experimental zone where all the work takes place. The CLOUD run team is required to do daily setup, calibration and modification work continually throughout the measurement campaigns. The meeting room needs adequate video-conferencing equipment to allow for on-line participation in the run coordination meetings by CLOUD people outside CERN. A study is currently underway in the CERN GS Department to find a technical solution for such a room. The current proposal is to locate the open office/meeting room (bat. 657, christened CORE, the "CLOUD office room extension") in a pre-fabricated building to be installed next to building 352 (Fig. 9.2). CORE would be a multi-purpose room serving the following functions:

- Daily data analysis and run planning meetings during campaigns at the CERN PS.
- Weekly technical planning and physics meetings for the CERN team throughout the year, including audio-visual communications with the CLOUD Analysis Working Group members in other institutes.
- An open office for the CERN CLOUD team (numbering 6 fellows and graduate students - who are presently using temporary offices loaned from PH-DT).
- Open office space for CLOUD experimenters during campaigns at CERN and at other times (at present the only "office space" available to experimenters is in the CLOUD control room in the East Hall, which cannot be used for radiation protection reasons).

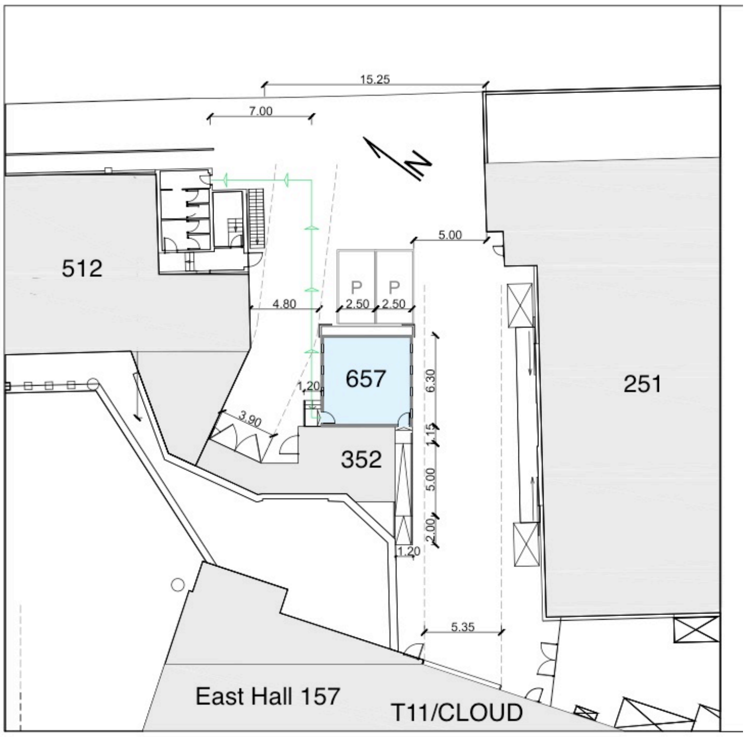

Fig. 9.3: Bat. 657 (the CLOUD office room extension, CORE) - the open office for the CERN CLOUD team and CLOUD experimenters, and the CLOUD daily meeting/planning room during experimental campaigns, under study by CERN GS.