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1 CLOUD - THE FIRST 10 YEARS

1.1 Introduction

CLOUD is studying, under controlled conditions in the laboratory, how aerosol particles form and grow from trace atmospheric vapours, and how these processes are affected by ions from galactic cosmic rays [1, 2, 3]. The experiment involves a large chamber whose contents are continuously sampled and analysed by a suite of mass spectrometers and other instruments. A 3.5 GeV/c π^+ beam from the CERN PS simulates galactic cosmic ray (GCR) ionisation in the chamber corresponding to any chosen altitude in the troposphere. CLOUD is also studying the effects of ions and aerosols on cloud microphysics, using adiabatic pressure reductions to form liquid or ice clouds in the chamber and also with sampling instruments that measure the liquid droplet or ice particle activation properties of the aerosol particles.

We simulate conditions in the CLOUD chamber corresponding to specific regions of the atmosphere, with the goal of improving the fundamental understanding of aerosols and ions, and their impact

on air quality, cloud formation, and climate. CLOUD is the world's first—and, so far, unique—laboratory experiment to reach the demanding technical performance required to measure aerosol particle formation under controlled atmospheric conditions, which requires a large atmospheric-pressure chamber with extremely low contaminants (well below 1 molecule per trillion). Other notable features of CLOUD are a) experiments are performed under atmospheric conditions (vapour concentrations, oxidant levels, temperature, relative humidity, ion concentrations, etc.), b) the chamber operates over the full temperature range of the troposphere (-65°C $\rightarrow$ +30°C), c) there is highly stable control of all experimental parameters, including UV illumination and cosmic ray ionisation and d) a comprehensive array of state-of-the-art instruments analyses the contents of the chamber.

Since starting data collection in 2009, CLOUD has helped reach an unprecedented understanding of atmospheric nucleation and growth at the molecular and mechanistic level in a series of major advances reported in high-impact journals (5 in *Nature*, 3 in *Science*, 1 in *Nature Comm.*, 2 in *Science Adv.*, and 4 in *Proc. Nat. Acad. Sci.*). During 2019–2021 CLOUD has published 15 papers so far [4]–[18], including one in *Nature* [6] and one in *Science* [15]. Four more papers are under review [19]–[22]. In recognition of CLOUD's scientific contributions, Kirkby received the 2019 Benjamin Y.H. Liu Award of the American Association for Aerosol Research (AAAR) for *"outstanding contributions to aerosol instrumentation and experimental techniques that have significantly advanced the science and technology of aerosols"*.

1.2 Atmospheric aerosol particle formation and growth

Aerosol particle formation and growth is important for climate change. It is also a major health issue as the dominant source of particle pollution in urban environments, which ranks fifth in risk factors for mortality worldwide. More than half of all cloud droplets are formed on cloud condensation nuclei (CCN) that originate from the clustering of trace atmospheric molecules (known as new particle formation) rather than being directly emitted into the atmosphere, like sea spray particles, desert dust or biomass burning (Gordon *et al., J. Geophys. Res.,* 2017 [23]). Increased CCN make clouds brighter and suppress precipitation, thereby cooling the climate.

According to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), Earth's mean temperature is predicted to rise by between 1.5–4.5°C for a doubling of carbon dioxide in the atmosphere, which is expected to occur by the second half of this century. One of the main reasons for this large range in the projected warming, which makes it difficult for society to know how best to act against climate change, is a poor understanding of aerosol particles in the atmosphere and their effects on clouds. CCN and clouds have increased since pre-industrial times, which has offset a significant but poorly known fraction of the warming due to greenhouse gases; it may be as much as one half or as little as none. This large uncertainty in aerosol-cloud radiative forcing has stubbornly remained unchanged through all IPCC assessment reports since 1995.

When CLOUD was designed, new particle formation had been observed in many regions of the atmosphere and was clearly associated with sulphuric acid, albeit with a wide scatter of the observed particle formation rates versus acid concentration (red and green points in Fig. 1). Theoretical estimates suggested that nucleation by sulphuric acid and water vapour alone (known as 'binary' nucleation) was too slow to explain atmospheric observations. On the other hand, laboratory experiments to measure binary sulphuric acid nucleation disagreed by up to a factor 1000 in the concentration of sulphuric acid required to produce 1 particle $cm^{-3}s^{-1}$, with some claiming it could account for atmospheric observations but others not (lines in Fig. 1). The most recent laboratory measurements at the time suggested that binary nucleation did indeed account for atmospheric observations.

Figure 1 encapsulates the understanding of atmospheric new particle formation when CLOUD started measurements. Experiments and observations up to that point had almost entirely been based on particle counters (measuring number and mass concentrations) together with gas-phase measurements. The chemical composition of nucleating particles was unmeasured. Since then, in its first ten years of operation, CLOUD has reached a molecular and mechanistic understanding of atmospheric particle

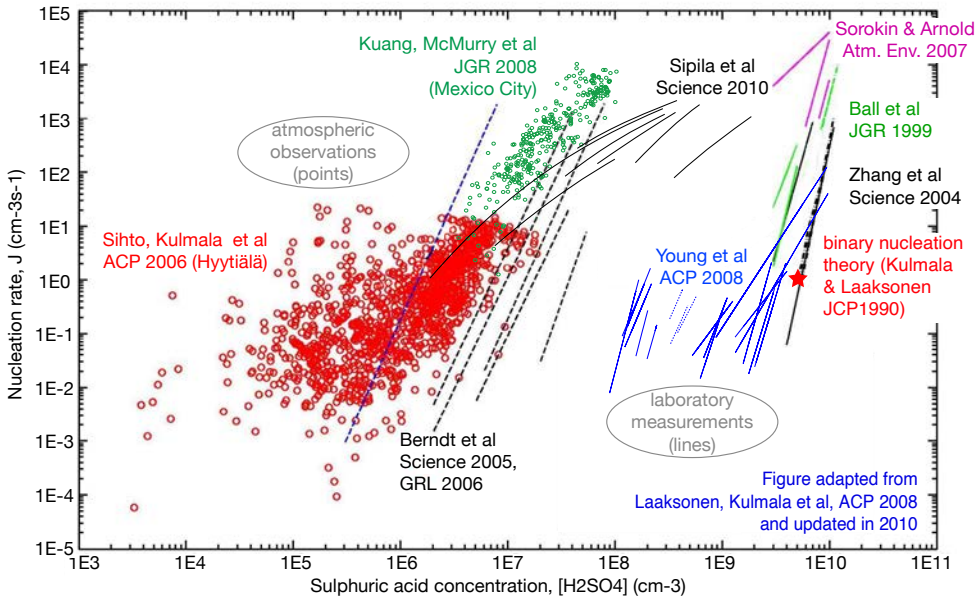

Fig. 1: Understanding of atmospheric aerosol formation before CLOUD. Particle nucleation rates in the boundary layer (red and green points) were known to depend of sulphuric acid but laboratory experiments of binary H_2SO_4-H_2O nucleation (lines) disagreed whether or not it could explain the atmospheric observations. The current understanding in 2010 was that binary H_2SO_4-H_2O nucleation *could* account for atmospheric observations. The first results from CLOUD (Kirkby *et al., Nature,* 2011 [24]) showed it was too slow by about a factor one million.

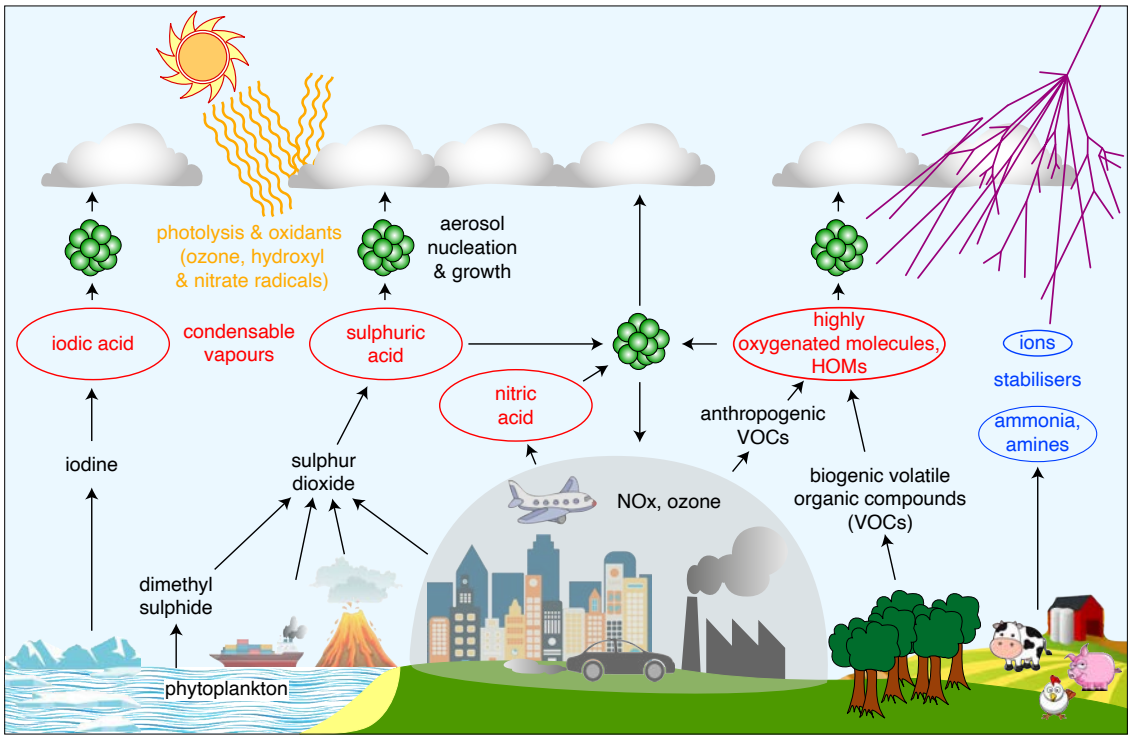

Fig. 2: CLOUD's contributions to the understanding of atmospheric aerosol formation. The molecular and mechanistic understanding of atmospheric aerosol particle formation from CLOUD's first ten years of operation. Condensable vapours are indicated in red circles; stabilisers, which reduce evaporation of embryonic molecular clusters, are in blue circles. Atmospheric oxidants—especially hydroxyl radicals and ozone—transform volatile precursors such as sulphur dioxide, organic compounds or iodine into extremely low volatility vapours.

formation, represented schematically in Fig. 2. Sulphuric acid remains the most important atmospheric vapour for aerosol particle formation but it is joined by at least two additional classes of extremely low volatility vapours that can condense to form particles: organic highly oxygenated molecules (HOMs) and iodic acid. To stabilise the embryonic molecular clusters against evaporation, these vapours generally require the presence of base vapours such as ammonia or amines, or else ions from galactic cosmic rays. Ammonia is also able to stabilise nucleation of the volatile but ubiquitous nitric acid, to form semi-volatile particulate ammonium nitrate. Iodic acid nucleates without needing base vapours, although ions greatly accelerate the particle formation rates. Once formed, particle growth in the boundary layer is largely driven by HOMs. Particle growth in the upper troposphere depends on these same low volatility vapours but their abundances are poorly known at present due to the scarcity of atmospheric measurements at the required part-per-trillion sensitivity.

Upon starting its first experiments at the end of 2009, CLOUD found that binary nucleation of sulphuric acid was around one million times too slow to account for observed rates of particle formation in the warm boundary layer (red and green points in Fig. 1). CLOUD showed that stabilisers such as base vapours (ammonia or amines) or ions from galactic cosmic rays play a crucial role in suppressing evaporation of the newly-formed sulphuric acid particles (Kirkby *et al., Nature,* 2011 [24]). Concentrations of amines as low as a few parts per trillion by volume are sufficient to allow sulfuric acid particles to form at the kinetic limit (Almeida *et al., Nature,* 2013 [25]); Kürten *et al., Proc. Nat. Acad. Sci.,* 2014 [26]). Although sulphuric acid-amine nucleation had not been observed in the atmosphere at the time of CLOUD's publication in 2013 [25], recent observations suggest it is the primary mechanism responsible for forming smog particles in polluted Chinese megacities.

Up to 2016, global climate models had largely used relatively simple parameterisations for aerosol production that were not based on experimental data. However, in 2016 CLOUD published the first global model results based solely on laboratory measurements (Dunne *et al., Science,* 2016 [27]; Kürten et al., *et al., J. Geophys. Res.,*, 2016 [28]). These results established the importance of ammonia and ions for sulphuric acid nucleation throughout the troposphere. CLOUD's experimental parameterisations are helping to narrow the variations among different models in their projected global temperature rise this century. Global emissions of ammonia are predominantly due to agricultural activities, namely livestock and over-use of fertilizers, so the CLOUD findings have implications for air quality control.

CLOUD went on to discover that highly oxygenated molecules (HOMs) from atmospheric oxidation of biogenic monoterpenes such as α-pinene are able to generate aerosol particles even in the absence of sulphuric acid (Kirkby *et al., Nature,* 2016 [29]). CLOUD had already shown that HOMs greatly enhanced the formation rate of sulphuric acid particles (Schobesberger *et al., Proc. Nat. Acad. Sci.,* 2013 [30]; Riccobono *et al., Science,* 2014 [31]; Lehtipalo *et al., Science Adv.,* 2018 [32]). However it had been thought that sulphuric acid—which largely arises from sulphur dioxide emitted by fossil fuels—was essential to initiate particle formation. The CLOUD studies of pure biogenic nucleation were later extended over a wide temperature range, -50°C – +25°C, showing that the slower oxidation rate at lower temperatures is almost exactly compensated by the reduced volatility of the HOMs (Simon *et al., Atmos. Chem. Phys.,* 2020 [11]). Consequently, pure biogenic nucleation remains an efficient process for new particle formation and growth at all temperatures and altitudes, depending on the ambient vapour concentrations. Monoterpenes ($C_{10}H_{16}$ hydrocarbons) are abundantly produced by trees. Many trees also emit isoprene (C_5H_8) and, indeed, global isoprene emissions are 10 times higher than monoterpenes. However, atmospheric observations have found that isoprene reduces new particle formation and growth from HOMs. CLOUD revealed the detailed chemical mechanism responsible for this (Heinritzi *et al., Atmos. Chem. Phys.,* 2020 [14]).

CLOUD recently reported the particle formation and growth rates from a second pure biogenic source—iodic acid—under conditions found at coastal mid-latitude and polar sites (He *et al., Science,* 2021 [15]). The particle formation rates from iodic acid are extremely rapid, even exceeding those of sulfuric acid-ammonia under similar conditions. Below +10°C, ion-induced nucleation of iodic acid pro-

ceeds at the kinetic limit (limited only by the molecular collision rate). Contemporaneous measurements on the Swedish icebreaker, Oden, drifting with the Arctic pack ice confirmed the importance of iodic acid for new particle formation and cloud condensation nuclei over the Arctic.

The CLOUD findings imply the presence of ubiquitous sources of biogenically-driven aerosols alongside the largely anthropogenically-driven aerosols with sulphuric acid. Pure biogenic nucleation has a much larger relative effect on CCN concentrations in the pristine pre-industrial atmosphere than today because of the lower aerosol concentrations in earlier times. The effect is to raise the baseline aerosol state of the pre-industrial atmosphere and reduce estimates of anthropogenic aerosol radiative forcing and their uncertainties. CLOUD estimates that the magnitude of annual global mean radiative forcing caused by changes of cloud albedo since 1750 is reduced by 0.22 W m^{-2} (27 %) to -0.60 W m^{-2} after including nucleation of biogenic organic vapours (Gordon *et al., Proc. Nat. Acad. Sci.,* 2016 [33]).

CLOUD has also studied the growth of freshly-formed particles near 1 nm up to sizes above 50 nm, where they constitute cloud condensation nuclei. At small sizes, below around 3 nm, aerosol growth in the atmospheric boundary layer is often mainly due sulphuric acid (Lehtipalo *et al., Nature Comm.,* 2016 [34]; Stolzenburg *et al., Atmos. Chem. Phys.,* 2020 [10]). However, CLOUD showed that extremely low volatility organic compounds (HOMs) can drive rapid particle growth directly from molecular clusters up to CCN sizes (Tröstl *et al., Nature,* 2016 [35]; Stolzenburg *et al., Proc. Nat. Acad. Sci.,* 2018 [36]).

More recently, CLOUD has broadened its studies to include the formation of urban smog (Xiao *et al., Atmos. Chem. Phys.,* 2021 [18]). CLOUD discovered that ammonia and nitric acid at urban concentrations can drive the growth rates of newly formed particles up to more than 100 times faster than seen before, but only in short spurts that have previously escaped detection (Wang *et al., Nature,* 2020 [6]). This can explain puzzling observations of bursts of new particles that form and grow under highly polluted urban conditions, leading to winter smog episodes. The high loading of pre-existing haze particles would be expected to efficiently scavenge new particles. However, the high growth rates are sufficient to shepherd the particles rapidly to larger sizes where they are less sensitive to scavenging losses. An accompanying *News & Views* [37] in Nature on the CLOUD paper states, *"This work provides key knowledge that will inform air-quality policy as the chemical composition of urban atmospheres changes in the future."*

1.3 Cosmic ray-cloud-climate mechanism

CLOUD experiments have shown that ions from galactic cosmic rays help to stabilise nucleating clusters against evaporation and, for otherwise weakly bound clusters, that ions can enhance nucleation rates by a factor 10-100, depending on conditions (Kirkby *et al., Nature,* 2011 [24]; Riccobono *et al., Science,* 2014 [31]; Kirkby *et al., Nature,* 2016 [29]; Dunne *et al., Science,* 2016 [27]; Kürten *et al., J. Geophys. Res.,* 2016 [28]); He *et al., Science,* 2021 [15]). The influence of ions is strongest for nucleation of biogenic species (organics and iodic acid) which were especially important during pristine pre-industrial times, suggesting a possible higher sensitivity to solar variations in the past. However, model simulations using CLOUD measurements show very little sensitivity of present-day global CCN to solar-cycle variations of ionisation (Gordon *et al., Proc. Nat. Acad. Sci.,* 2016 [33]; Gordon *et al., J. Geophys. Res.,* 2017 [23]).

The CLOUD results on GCR-climate forcing are now informing the IPCC, which writes in its recent climate assessment report, AR6 (Climate Change 2021 - The Physical Science Basis, section 7.3.4.5): *"Since AR5, the link between GCR and new particle formation has been more thoroughly studied, particularly by experiments in the CERN CLOUD chamber (Cosmics Leaving OUtdoor Droplets) (Dunne et al., 2016 [27]; Kirkby et al., 2016 [29]; Pierce, 2017 [38]). By linking the GCR-induced new particle formation from CLOUD experiments to CCN, Gordon et al., 2017 [23], found the CCN concentration for low clouds to differ by 0.2% to 0.3% between solar maximum and solar minimum of the solar cycle. ... it is therefore unlikely that cosmic ray intensity affects present day climate via nucleation. ... There is high confidence that GCRs contribute a negligible effective radiative forcing over the period 1750 to 2019."*

Does this mean the GCR-cloud-climate question is settled? No, what CLOUD has shown is that *global* CCN in the present-day atmosphere are insensitive to the ion-induced nucleation rate. Although ions strongly affect the formation rate of small particles, the change in CCN is muted because less vapour is available to grow the particles and so their scavenging losses by pre-existing aerosol increase. However, CLOUD has not yet studied the effect of ions in climate-sensitive *regions*, e.g. polar regions or the upper free troposphere, or with new chemical systems such as iodic acid. Furthermore, CLOUD has barely investigated direct effects of cosmic ray ions on cloud microphysics—the so-called "ion-aerosol near cloud effect" related to the global electric circuit [39].

Fig. 3: CLOUD's scientific goals. CLOUD's scientific goals comprise 1. settling the cosmic ray-cloud-climate question, 2. sharpening the understanding of anthropogenic aerosol-cloud radiative forcing, and c) understanding what drives urban smog formation.

2 CLOUD - THE NEXT 10 YEARS

2.1 Scientific goals and open questions

The overall goals of the CLOUD experiment (Fig. 3) are to:

1. Settle the cosmic ray-cloud-climate question. Answer whether or not cosmic rays provide a physical mechanism for solar-climate variability .

2. Reduce the uncertainties of anthropogenic aerosol-cloud radiative forcing. Anthropogenic radiative forcing requires knowledge of the baseline aerosol state of the pristine pre-industrial atmosphere. This will require global model simulations based on a firm empirical foundation of aerosol formation and growth rates from both biogenic and anthropogenic sources. Reduced uncertainties of aerosol-cloud radiative forcing will lead to improved estimates of Earth's climate sensitivity and, in turn, sharpen climate model predictions of expected warming in the 21st century. Improved knowledge of biogenic aerosol is also important to assess how far aerosol cooling may weaken as anthropogenic emissions of polluting vapours are reduced.

3. Understand what drives urban smog formation. This will provide the scientific basis for informed public-health policy decisions to reduce urban pollution.

In its first 10 years, CLOUD has largely solved atmospheric aerosol particle formation at the level of the molecules responsible and their mechanisms. CLOUD has also shown that ion-induced nucleation is an important atmospheric process, but that solar-induced variations of cosmic rays have a negligible effect on *global* cloud condensation nuclei (CCN). However, major challenges and open questions remain for CLOUD to address in the next decade, including:

1. Simulation and understanding of new particle formation and growth for all distinct regions and altitudes across the globe.

2. Simulation and understanding of the transport of precursor vapours in convective clouds from the boundary layer to the upper troposphere.

3. Parameterisations for global climate models of aerosol particle formation and growth for all chemical systems and ambient conditions (precursor vapour concentrations, oxidant concentrations, temperature, relative humidity, and ionisation).

4. Do cosmic rays affect the number of CCN in climatically-sensitive regions?

5. Do cosmic rays directly affect cloud microphysics ("ion-aerosol near cloud effect")?

6. Which vapours and mechanisms are driving smog formation in polluted cities?

2.2 CLOUD experiments

2.2.1 Aerosol particle formation and growth experiments

CLOUD measures particle nucleation rates under neutral (J_n), galactic cosmic ray (GCR; J_{gcr}) and π^+ beam (J_π) conditions, corresponding to ion pair concentrations of around 0, 700 and up to 3000 cm^{-3}, respectively. This spans atmospheric ion concentrations between ground level and 15 km altitude. The nucleation rate J_n describes the neutral rate alone, whereas J_{gcr} and J_π describe the sum of the neutral and ion-induced rates, $J_n + J_{iin}$. The nucleation rate J_n is measured in the presence of 20 $\mathrm{kV\,m}^{-1}$ electric field, which sweeps all ions from the chamber in under 1 s.

So far, CLOUD experiments have largely focused on *chemical systems* in order to identify the vapours and mechanisms responsible for atmospheric particle formation and growth. However, future CLOUD experiments will focus more on simulating *specific regions* of the globe such as:

Upper free troposphere: Amazon, Asian monsoon, tropical oceans, mid latitudes. Recent aircraft campaigns have shown that the upper free troposphere is a major global source of new aerosol particles. Despite low precursor concentrations, particle formation and survival is enhanced by the low temperatures and extremely low condensation sinks of pre-existing larger particles. These particles influence cirrus clouds, which are important for Earth's radiation balance. Furthermore, subsequent large-scale descending air circulation can carry these particles to lower altitudes where they may provide an important source of CCN for pristine regions such as the open ocean. The chemical systems driving upper tropospheric nucleation are poorly known (although CLOUD institutes are currently planning aircraft campaigns to measure them). However, simulating the upper troposphere will likely involve biogenic organic vapours (isoprene, monoterpenes, sesquiterpenes) for the Amazon; sulphur dioxide, nitric acid, ammonia and amines for the Asian monsoon region; and iodine, dimethyl sulphide (DMS), methanesulphonic acid (MSA) and amines for marine regions.

Although CLOUD has already carried out preliminary studies of these chemical systems, the experimental phase space explored so far is insufficient to provide robust paramaterisations for global climate models. Moreover, CLOUD's instrumentation has dramatically improved since the original experiments. For example, CLOUD's published data on global $\mathrm{H_2SO_4}-\mathrm{NH_3}-\mathrm{H_2O}$ nucleation (Dunne *et al., Science,* 2016 [27]; Kürten et al., *et al., J. Geophys. Res.,*, 2016 [28]) involved instruments with around 10–35 pptv limits-of-detection (LoD) for $\mathrm{NH_3}$ for 1–3 h sampling time (Bianchi *et al., Atmos. Meas. Tech.,* 2012 [40]; Praplan *et al., Atmos. Meas. Tech.,*[41]). CLOUD has now developed a mass spectrometer for $\mathrm{NH_3}$ with a LoD of 0.5 pptv for 1 s sampling time (Pfeifer *et al., Atmos. Meas. Tech.,* 2020 [7]). This is one example of how rapidly CLOUD instrumentation is advancing—and will continue to do so in future.

Polar regions: coastal sites, Arctic ice pack, Antarctic. The polar regions are especially sensitive to new particle formation since they constitute pristine regions with very low aerosol number concentrations. Increased clouds in these regions have a warming effect since they strongly reduce longwave radiative losses. The chemical systems involved in forming particles in these regions include SO_2, NH_3, amines, I_2, DMS, MSA, and marine organics.

Open ocean: tropics, mid latitudes, Southern Ocean. Two-thirds of Earth's surface is covered by oceans and yet very little is known about particle formation over the open ocean. Important chemical systems are likely to be I_2, DMS, MSA, NH_3, amines, and organics. CLOUD will also study marine particle growth by reactive uptake of volatile organics such as glyoxal (CHOCHO) which is ubiquitous in the marine boundary layer at levels around 10 pptv.

Boreal forest and continental northern hemisphere. Around 30% of the world's forests are northern boreal forests, dominated by coniferous trees and covering one sixth of Earth's surface. Particle formation in boreal forests has been characterised over the last two decades at the Hyytiälä site in Finland, led by the University of Helsinki CLOUD partner. CLOUD will extend its initial simulation of the boreal forest (Lehtipalo *et al., Science Adv.,* 2018 [32]) with new instrumentation and advances in the performance of the CLOUD facility. The chemical systems include SO_2, NH_3, amines (di-, tri-methyl amine and diamines), biogenic organics and NO_x.

Urban sites: Asian, European/US cities. New particle formation is generally responsible for the majority of aerosol particle *number* concentrations in polluted urban environments. Once formed, these particles can grow rapidly by condensation of anthropogenic HOMs. Simulating polluted urban environments requires quite different conditions in the chamber than those typical for CLOUD, notably involving anthropogenic organic vapours and much higher particle loadings to simulate high condensation sink conditions (few $\mu g\,m^{-3}$ rather than $ng\,m^{-3}$). The chemical systems to be studied include SO_2, NH_3, amines, anthropogenic organics (toluene, trimethylbenzene, cresol and naphthalene) and NO_x.

Our approach to focus future CLOUD experiments on simulating specific regions of the global atmosphere reinforces a key principle of CLOUD, namely that the experiments are closely linked with the real atmosphere. CLOUD collaborating institutes are actively studying the atmosphere from ground-based observatories and from ships, research aircraft and satellites. Examples include the Hyytiälä SMEAR site (Station for Measuring Ecosytem-Atmosphere Relations; University of Helsinki); the High Altitude Research Station, Jungfraujoch (PSI), the High Altitude and Long Range Research Aircraft, HALO (Goethe University Frankfurt, MPIC), and the German and Swedish research ice breakers, Polarstern and Oden, respectively (University of Helsinki, PSI, Tropos). The exact same instruments attached to CLOUD during a run at the PS are also used for these atmospheric observations. The observations flag interesting vapours and then CLOUD reveals which vapours are important and measures their associated particle nucleation and growth rates, as well as the underlying physical and chemical mechanisms. Through this symbiotic relationship CLOUD identifies and measures the atmospheric vapours and processes driving aerosol particle formation, and parameterises the associated nucleation and growth rates for global climate models.

2.2.2 Cloudy experiments

So far, CLOUD has studied ion-aerosol-cloud interactions by two methods First, in "cloudy" experiments which use controlled gradual adiabatic pressure reductions in the chamber from around 220 mbar above atmospheric pressure down to the normal operating level of 5 mbar. When the initial relative humidity in the chamber is high (>90%) this creates liquid or ice clouds in the chamber, depending on the starting temperature. However, due to the non thermal equilibrium of the air with respect to the walls of the chamber, the lifetime of the cloud is limited to 5–10 minutes. This is, nevertheless, sufficient to measure a wide

range of ion-aerosol-cloud interactions. Second, we can attach CCN counters and ice nucleation instruments to the chamber via sampling probes and measure the liquid- or ice-forming characteristics of the aerosol externally, with precisely-controlled water vapour supersaturations and temperatures characteristic of clouds in the troposphere. In CLOUD14, four ice nucleation sampling instruments were attached to the chamber and both these methods were used in different experiments. In future a third method for cloudy experiments will become possible with the addition of the FLOw TUbe System (FLOTUS), currently under construction (§6.2). FLOTUS will allow slightly warmer, more humid air to be injected from a port on the upper manhole of the CLOUD chamber. The resulting cloud is rapidly mixed within the chamber by fans, maintaining a liquid or ice cloud continuously.

Future cloudy experiments will address questions such as:

Are there direct effects of ions/charge on cloud microphysics? There are very few established fair weather ion/charge effects on cloud microphysics, so these are highly speculative experiments. (Here, "fair-weather" distinguishes from experiments that have studied charge-separation mechanisms for generating lightning.) Laboratory experiments measuring single falling droplets have shown that (relatively large) charges enhance the collision rate of aerosols with sedimenting cloud droplets (enhanced aerosol-droplet scavenging), but ion/charge experiments with aerosol and cloud ensembles under fair weather (small charge) conditions have to our knowledge never been performed outside CLOUD. Initial experiments were performed in CLOUD14 with multiply-charged aerosol from an electrospray CHarged AeRosol GEnerator (CHARGE) (§ 3). Based on the experience gained in CLOUD14, a more advanced instrument (CHARGE-2) is currently being designed and will be used together with the π beam for future ion-aerosol-cloud studies in CLOUD. The experiments will investigate ion-related processes such as enhanced (or suppressed) scavenging of interstitial aerosol particles by cloud droplets, aggregation (or repulsion) of water droplets or ice particles, droplet activation at lower water vapour supersaturation, or higher freezing points of supercooled water droplets.

What are the activation (CCN) and ice nucleating properties of secondary aerosol particles? Clouds contain a great deal of supercooled water between 273 K and the homogeneous freezing point of water, 235 K. Ice nucleation is important because it originates rain from mixed-phase clouds via the Wegener-Bergeron-Findeisen process (rapid growth of ice particles in a cloud at the expense of liquid droplets). It is also important for the formation of cirrus clouds, composed entirely of ice, which regulate the amount of long-wave radiation emitted to space. However ice nuclei in the atmosphere are rare and poorly understood. During CLOUD14 we began studies of the efficiency of secondary aerosol particles to provide ice nuclei, and these studies will be extended in future.

How are vapours transported from the boundary layer to the upper troposphere in convective clouds? As noted in §2.2.1, the upper troposphere is an important global source of aerosol particles. Essentially all vapours that contribute to upper tropospheric new particle formation and growth have been convected from the boundary layer. However the rate at which the vapours are transported aloft is poorly understood since it is not known how effectively deep convective clouds scavenge the vapours. To model such processes reliably requires knowledge of Henry's Law (solubility) constants for vapours in supercooled water. These have not yet been measured but will be measured by CLOUD in cloudy experiments. Ammonia is of particular importance since it greatly accelerates upper tropospheric particle formation involving sulphuric or nitric acids. Ammonia is highly soluble so it is rapidly taken up by liquid droplets in a cloud. However, theoretical studies suggest it is released back into the gas phase when the droplets freeze. CLOUD will measure this.

How important is the reactive uptake of vapours? Cloud droplets constitute miniature reactors where fast chemical processing can take place. This aqueous-phase processing transforms both the mass and physico-chemical properties of the CCN released upon evaporation of the cloud. These processes will be studied in future cloudy experiments.

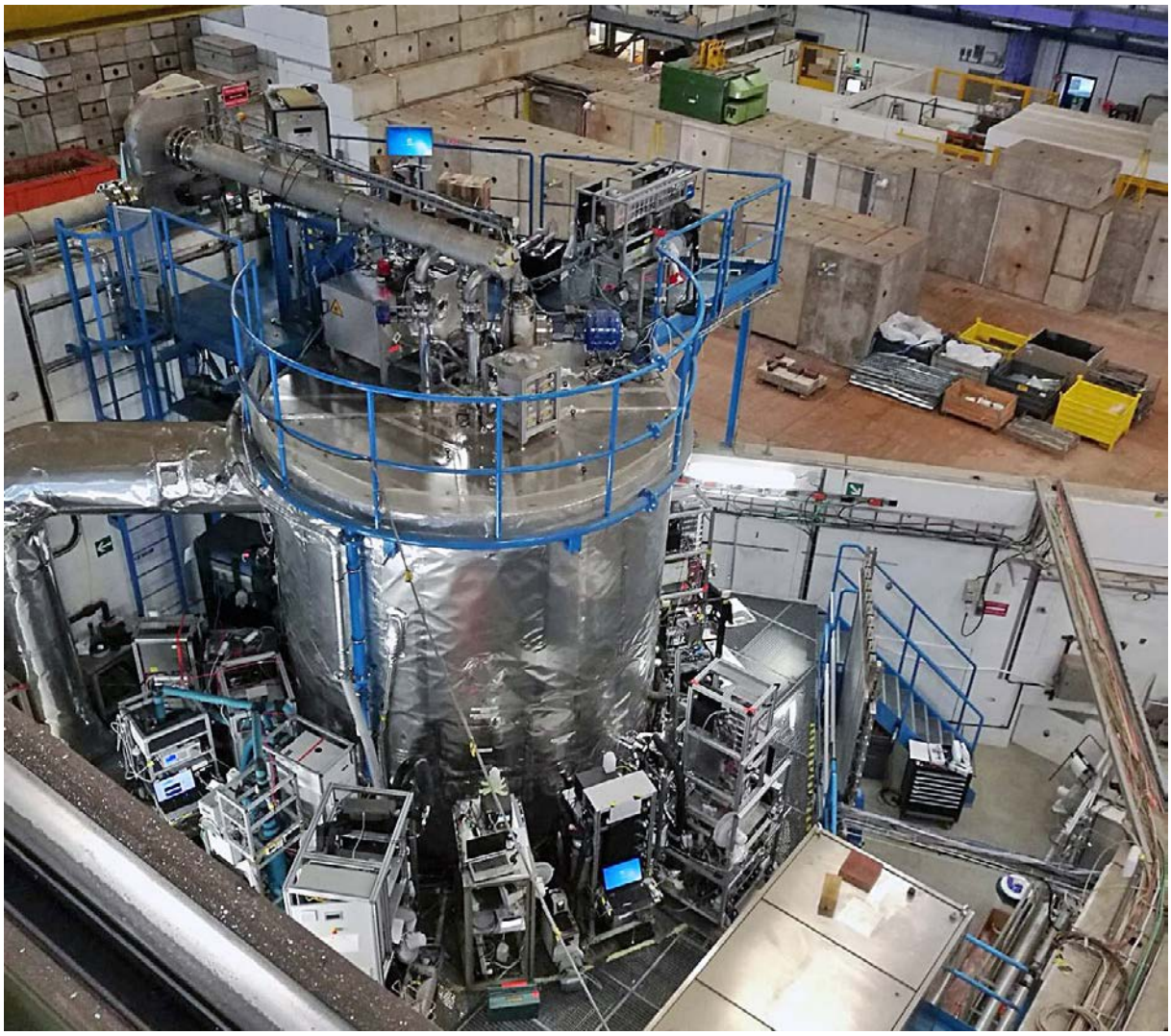

Fig. 4: CLOUD14 cosmic ray run (23 Sep - 27 Nov 2019). CLOUD with its analysing instruments in the East Hall during the CLOUD14 cosmic ray run, Oct 2019.

3 CLOUD14 COSMIC RAY RUN (23 Sep – 27 Nov 2019)

The CLOUD14 cosmic ray run took place 23 Sep – 27 Nov 2019, during the East Area Renovation, when all CERN accelerators were off for Long Shutdown 2 (LS2). Around 30 analysing instruments were attached to the chamber, including 7 mass spectrometers, 4 ice particle counters and 1 CCN counter (Figs. 4, 5, 6). This was the first time that an Orbitrap mass spectrometer (from IRCE Lyon) has been used at the CLOUD chamber. The highest resolution mass spectrometers used previously (so-called LTOFs) have a resolution ($m/\Delta m$) of around 10,000; the resolution of the Orbitrap is 1,000,000. The higher resolution greatly aids identification of multiple organic species lying at the same integer mass.

The CLOUD14 experiments included the following:

1. **Activation properties of secondary aerosol for cloud droplets and ice particles:** A wide range of secondary aerosol were nucleated and grown in the CLOUD chamber under various conditions (chemical species, relative humidity, temperature, and ion concentration). The chemical systems included biogenic (α-pinene, isoprene) and anthropogenic (naphthalene) organics as well as iodic acid, sulphuric acid, nitric acid and ammonia. An example measurement of the onset of ice nu-

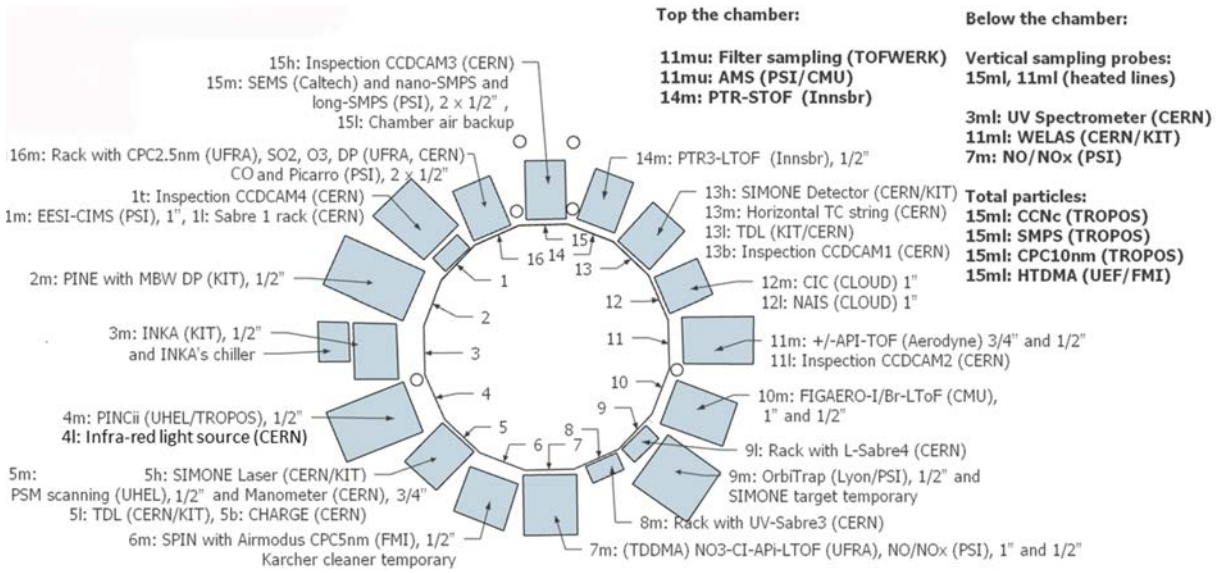

Fig. 5: CLOUD14 instrument layout. Layout of the analysing instruments around the chamber during CLOUD14 cosmic ray run.

MID-PLANE

Port #	Measured parameter for CLOUD14	Instrument for CLOUD14	Sampling probe for CLOUD14
1 m	HOMs and Nitric acid in gas and particle phase	EESI-CIMS (PSI)	1"
1 l	Diiodomethane photolysis to I·	UV L-Sabre1 (254 nm, not adjustable)	UV L-Sabre1
2 m	IPN concentration with expansion	PINE with DP MBW (KIT)	1/2"
3 m	IPN concentration	INKA (KIT)	1/2"
3 l	EMPTY	EMPTY	EMPTY
4 m	Ice nuclei number and phase	PINCii (=SPIN) (UHEL/TROPOS)	1/2"
4 l	Light chamber for cameras	Infra-red light source	EMPTY
5 h	Droplet size distributions and ice formation rates	SIMONE laser	Optical window
5 m	Sub 3nm number size distributions and J-rates	Scanning PSM (UHEL) and chamber pressure sensor	1/2" + 1/2" DSP
5 l	In-situ measurement of water vapour	TDL Hygrometer	TDL, optical window
6 m	Ice nuclei counter for ice and water particles (0.5 – 15 µm)	SPIN (FMI); Also for Karcher cleaner (temp); SIMONE camera	1/2"
7 m	HOMs, Sulfuric acid, DMA, DMA-SA clusters in gas and particle phase	NO3-CI-APITOF + NO/NO2 (CAPS)	1/2" + 1" DSP
8 m	NO2 photolysis to NO, and HONO photolysis to OH·	UV L-Sabre3 (Blue, 385 nm)	L-Sabre3
9 m	Mass spectrometer; Droplet size distributions and ice formation rates	Orbitrap; Also used for SIMONE targer (temp)	1/2", SIMONE target
9 l	I2 photolysis to I·	UV L-Sabre4 (Green, 528 nm)	L-Sabre4
10 m	Uncounted organics in gas and particle phase	FIGAERO (CMU)	1" + 1/2" DSP
11 m	Small ion mass spectrum	APITOF (Aerodyne/UHEL)	1/2" + 3/4" DSP
11 l	Inspection camera	CCDCAM2	Optical window
12 m	Small ion number	CIC	1"
12 l	Small ion number size distribution	NAIS	1"
13 h	Droplet size distributions and ice formation rates	SIMONE detector	Optical window
13 m	Temperature profile	Horizontal TC string	Horizontal TC string
13 l	In-situ measurement of water vapour	TDL Hygrometer	TDL, optical window
14 m	VOCs and SVOCs	PTR3 LTOF	1/2"
15 h	Inspection camera	CCDCAM3	Optical window
15 m	Total/intertitial particle number size distribution	SEMS (Caltech) + nanoSMPS + longSMPS (PSI)	1/2" + 1/2" DSP
15 l	Chamber operation	Air backup + 2 x P gauge	Air backup
16 m	J2.5nm, ammonia, and trace gases	CPC2.5nm and SO2, O3, DP, CO, PICARRO	1/2" + 1/2" DSP

TOP-PLANE

Port #	Measured parameter for CLOUD14	Instruments for CLOUD14	Sampling probe for CLOUD14
1t	Inspection camera	CCDCAM4	Optical window
5 t	EMPTY	EMPTY	EMPTY
9 t	EMPTY	EMPTY	EMPTY
13 t	EMPTY	EMPTY	EMPTY
15 t	HV clearing field on/off	HV- feedthrough	HV- feedthrough
5 tp	EMPTY	EMPTY	EMPTY
1 mu	Chamber operation	DN25 regulation valve	n/a
3 mu	EMPTY	EMPTY	EMPTY
5 mu	Chamber operation	DN40 expansion valve #1	n/a
9 mu	Chamber operation	DN150 regulation valve	n/a
11mu	Electron-microscope analysis and molecular structure	AMS (PSI/CMU), Filter sampling (PSI,TOFWERK)	1/4"
13 mu	Chamber operation	DN40 expansion valve #2	n/a
15 mu	O3 photolysis to OH·	UVX; UV laser (248 nm, adjustable)	UVX

BOTTOM-PLANE

Port #	Measured parameter for CLOUD14	Instruments for CLOUD14	Sampling probe for CLOUD14
5 b	Generation of highly charged CCN and space charge	CHARGE generator	CHARGE generator with X-ray sources
13 b	Inspection camera	CCDCAM1	Optical window
15 b	HV clearing field on/off	HV+ feedthrough	HV+ feedthrough
3 ml	Check O3 photolysis to OH·, and broad spectrum photolysis	UV photdiodes and UV spectrometer	Fibre-optic readout, Quartz window
11ml	Hydrometeor number size distribution (<10 µm)	WELAS	1/2" WELAS-type, Vertical probe
15ml	Total particle properties (activated and not-activated)	Total particles: SMPS, CCNc, CPC10nm (TROPOS), HTDMA (UEF)	Vertical probe with evaporator (heated line)

h, m, l = high, mid
t, b = top, bottom
mu, ml = upper/lower manhole
tp = top plate

Fig. 6: CLOUD14 instrument descriptions. Explanation of the instrument acronyms used in Fig. 6.

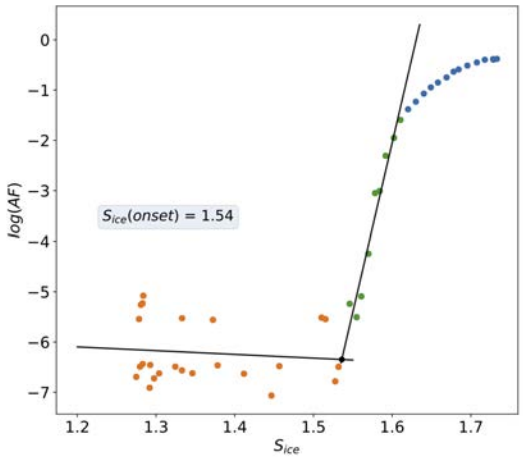

Fig. 7: Ice nucleation during CLOUD14. Example measurement of the onset of ice nucleation with the mINKA instrument. The vertical axis shows the $\log_{10}$ fraction of aerosol particles that nucleated ice and the horizontal axis shows the water vapour supersaturation over ice.

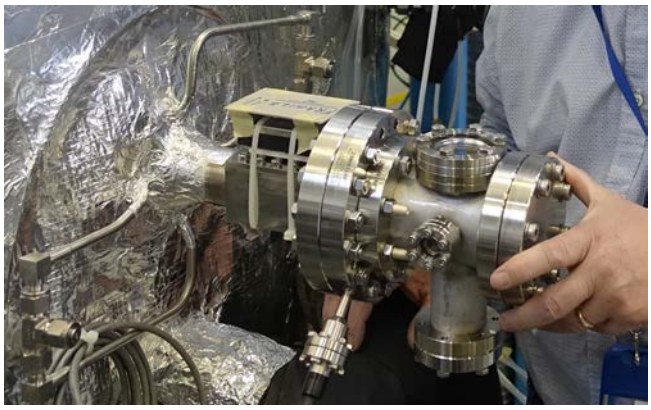

Fig. 8: The CHarged AeRosol GEnerator (CHARGE) at CLOUD14, Nov 2019. CHARGE comprises an electrospray charged aerosol source followed by an X-ray section before entering the CLOUD chamber. The aerosol particles are neutralised when the X-ray source is switched on, allowing an experimental comparison to be made between charged and uncharged aerosol particles. Optical ports on CHARGE allow visual confirmation of proper operation of the electrospray tip.

cleation is shown in Fig. 7. Under upper tropospheric conditions, ammonium nitrate particles with very small molar addition of sulphate were found to be highly efficient ice nuclei for cirrus clouds, comparable to desert dust [22].

2. **Nucleation and growth of inorganic, marine, pure biogenic, multicomponent and urban particles:** The secondary aerosol for item 1 were nucleated and grown from vapours in the CLOUD chamber under a variety of experimental conditions and temperatures. These experiments extended previous nucleation and growth studies made during CLOUD13.

3. **Effect of charge on cloud microphysics:** A new charged aerosol generator was developed to produce multiply-charged aerosol particles (Fig. 8). The collisional properties of these multiply-charged aerosol particles were studied and compared with uncharged or singly-charged particles. The data are currently under analysis and a manuscript is in preparation reporting the first measurements ever made of the ion-aerosol particle attachment rate coefficients versus aerosol particle charge in the range 1–9 e.

4 CLOUD MEETINGS, 2019–2021

The following CLOUD Collaboration meetings and data workshops were held in 2019–2021:

CLOUD13 data workshop, U Stockholm, Sweden, 11–15 Feb 2019. Analysis of data from CLOUD10–13, discussion of CLOUD manuscripts and planning for CLOUD14.

CLOUD-MOTION mass spectrometer workshop, U Wuppertal, Germany, 25–28 Mar 2019. Theory and practice of chemical ionisation mass spectrometers for atmospheric research.

CLOUD-MOTION summer school and CLOUD collaboration meeting, Wengen, Switzerland, 14–20 June 2019. Summer school on climate modelling, clouds, ice particles, aerosol-cloud interactions, atmospheric chemistry, and urban particle formation, together with practical sessions on scientific writing. Planning for CLOUD manuscripts and CLOUD14 experiments.

CLOUD14 status and CLOUD collaboration meeting, CERN, 29 Oct – 1 Nov 2019. Assessment of the CLOUD14 GCR run in progress, followed by a CLOUD collaboration meeting and Finance Review Committee meeting FRC8.

CLOUD14 data workshop, Sofia Cultural Center, Helsinki, 24–28 Feb 2020. Initial results from CLOUD14, instrument developments, CLOUD modelling and planning for CLOUD15T/15. This was the last physical meeting before the start of covid-19 restrictions.

CLOUD-MOTION summer school (zoom), originally Paphos, Cyprus, 21-25 Sep 2020. Summer school on aerosol nucleation, marine aerosol, cloud dynamics, aerosol optics and aircraft measurements, together with practical sessions on scientific writing.

CLOUD collaboration meeting and data workshop (zoom), originally Paphos, Cyprus, 29 Sep - 2 Oct 2020. Analysis of data from CLOUD14, preparation of papers and planning for CLOUD15T/15.

CLOUD Finance Review Committee meeting FRC9 (zoom), 30 Oct 2020.

CLOUD collaboration meeting (zoom), 16-18 Feb 2021. Results from CLOUD14, preparation of papers and planning for CLOUD15T.

CLOUD-MOTION final workshop (zoom), originally Vienna, Austria, 20-23 Apr 2-21. Presentation of results by CLOUD-MOTION fellows, and invited presentations from leading international aerosol scientists on their latest results.

CLOUD modelling workshop (zoom), originally Stockholm, Sweden, 19-20 & 26-27 May 2021. Presentation of the modelling activities underway in the CLOUD collaboration and discussion of future CLOUD modelling needs and how to optimise the links between the experimental and modelling activities.

"CLOUD Fridays" (zoom). During 2021 the normal biannual physical collaboration meetings have been replaced by zoom meetings held on Friday afternoons approximately twice per month, with draft agenda prepared beforehand on specific science results or experimental planning.

5 NEW MEMBERS OF THE CLOUD COLLABORATION

During 2020/2021 three institutes joined the CLOUD Collaboration, which greatly strengthen our modelling and instrumental expertise, as well as our links to atmospheric observations:

The Cyprus Institute, Climate & Atmosphere Research Centre, Nicosia, Cyprus (team leader: Theodoros Christoudias). The special expertise and interests include atmospheric, climate and air quality modelling of the CLOUD data with the global EMAC model, and comparisons of the CLOUD data with those obtained in field campaigns in the tropics, marine and urban regions.

Max Planck Institute for Chemistry, Department of Atmospheric Chemistry, Mainz, Germany (team leaders: Hartwig Harder, Jos Lelieveld). The special expertise and interests include a) measurements of gas-phase oxidants in CLOUD (OH, HO_2, NO_3 and related gases NO_2, N_2O_5) as well as organic species that contribute to particle growth, b) comparison of CLOUD measurements with those obtained in future ground-based, ship and aircraft campaigns (eg. the HALO missions CAFE-Pacific and CAFE-Brazil), in addition to previous field campaigns of MPIC, and c)

atmospheric and climate modelling of the CLOUD data using the EMAC global model, from the process level to regional and global climate, and health impacts.

The University of Tartu, Laboratory of Environmental Physics, Tartu, Estonia (team leaders: Heikki Junninen, Sander Mirme). The special expertise and interests include new particle formation; air ion chemical composition and its role in new particle formation; and development of next-generation ion mobility spectrometers.

6 DEVELOPMENTS OF THE T11 BEAMLINE AND CLOUD

6.1 T11 beam and experimental zone

As part of the East Area Renovation, the T11 beamline has been completely rebuilt with new magnets, power supplies and optics. The T11 experimental zone has also been re-configured (Fig. 9), which will provide substantially better access for instruments around the CLOUD chamber (compare Figs. 4 and 10). All the experimental control rooms for the East Area beamlines have also been replaced. CLOUD has added an additional chemicals room (including a fume hood) adjacent to the new T11 control room to handle the wide range of chemicals required to operate the facility and its instruments (Fig. 9). This work was previously carried out in the CERN EP Chemistry Lab.

6.2 CLOUD facility and analysing instruments

The East Area Renovation necessitated the dismantling and rebuilding of almost all the CLOUD facility infrastructure including, in particular, the gas supply and distribution system. The gas distribution system is being rebuilt in a consolidated area of the T11 experimental zone, underneath the platform (Fig. 9). Trace gases for the chamber are provided either from bottles (for volatile vapours) or from evaporators (for chemicals that are liquid or solid at room temperature). The bottles are located in temperature-controlled cabinets outside the East Hall, adjacent to CLOUD's liquid nitrogen and liquid oxygen dewars. The gas supply cabinets and their pipework, valves, etc. are being completely rebuilt. The evaporators are installed in temperature-controlled water baths in the gas rack area of the T11 zone.

In addition to the rebuilt systems, we are adding two major new components to CLOUD in 2022 to extend its scientific reach:

HO_x radical measurements - HORUS: The most important measurement that CLOUD has lacked so far is HO_x, namely the hydroxyl (OH) radical and the hydroperoxyl (HO_2) radical. The most abundant oxidants in the atmosphere are O_2 and O_3 but these have large bond energies, leaving OH as the primary oxidising species in the atmosphere. For example, OH concentrations in the atmosphere determine the 12-year lifetime of the important greenhouse gas, methane. HO_x radicals also have a major influence on the chemical pathways that transform volatile vapours in the atmosphere into extremely low volatility vapours that drive particle nucleation and growth. However, measurements of OH are extremely challenging because daytime atmospheric levels are around 0.1 pptv and the OH lifetime is 1 s or less. Nevertheless, MPIC Mainz has developed a sensitive instrument for measurement of HO_x named the HydrOxyl Radical measurement Unit based on fluorescence Spectroscopy (HORUS) using Laser Induced Fluorescence (LIF). HORUS is currently being adapted for CLOUD and it will have its first tests at the chamber during CLOUD15T (§7).

Pre-ageing of organic vapours - FLOTUS: CLOUD can study rapid gas phase oxidation of organic precursor vapours on timescales of about an hour, limited by the wall loss lifetime of vapours and particles. At present, CLOUD is blind to a broad class of oxidation processes that are occurring in the real atmosphere on longer timescales, involving repeated independent oxidation steps. However, from 2022 onwards, CLOUD will be able to study aerosol particle formation and growth

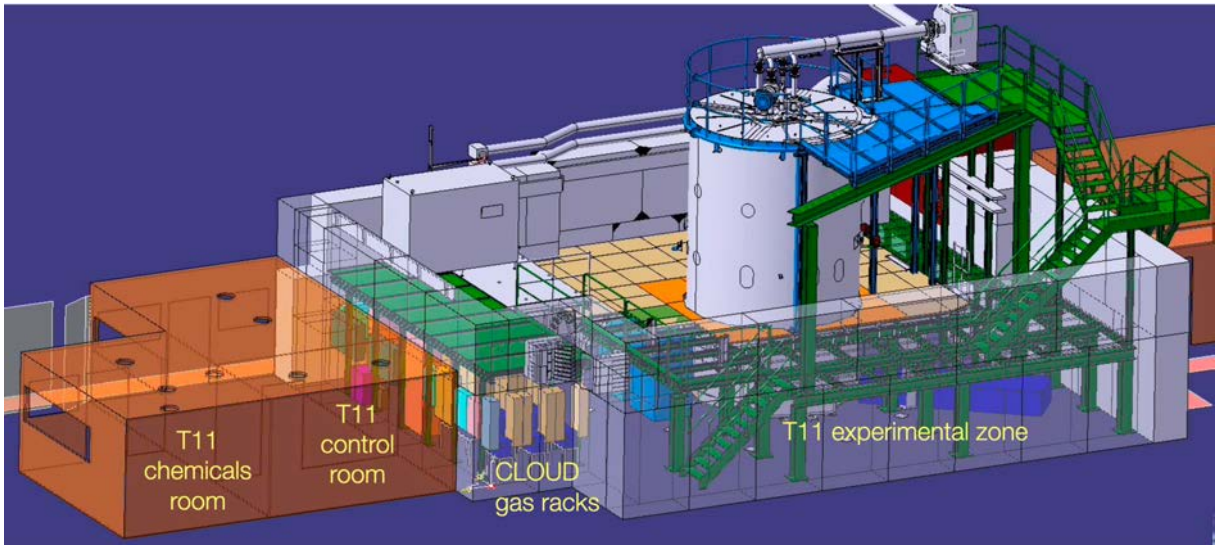

Fig. 9: Model drawing of the East Area T11 zone and CLOUD facility when completed. Model drawing of CLOUD in the T11 experimental zone at the CERN Proton Synchrotron after completion of the East Area renovation, 2019–2021. In addition to the new T11 beamline, essentially the entire CLOUD facility infrastructure, gas system and controls systems will have been rebuilt by the end of 2021.

Fig. 10: Present status of the East Area T11 experimental zone, 30 Sep 2021. The main platform is installed and a large fraction of the CLOUD gas system under the platform (not visible) has been rebuilt. The remaining work for the T11 experimental zone, the exterior gas supply racks, the T11 control room and the T11 chemicals room is expected to be completed before the end of 2021. This includes the upper platform, gas supply and distribution systems, electricity, lighting, cooling & ventilation, IT network, and CLOUD facility systems such as beam counters, thermal, Pt100 sensors, mixing fans, high voltage, UV, slow control and DAQ.

Fig. 11: FLOTUS (FLOw TUbe System) at CLOUD. FLOTUS is a 3 m laminar-flow quartz drift tube in which organic and other vapours receive hydroxyl radical exposures corresponding to several days in the real atmosphere. The outflow from FLOTUS is directed into the CLOUD chamber for studies of "aged" organics. All the operating conditions of FLOTUS (gases, UV irradiation, relative humidity and temperature) are controlled independently of the CLOUD chamber.

from these "aged" organic vapours using the FLOw TUbe System, FLOTUS, attached to the chamber (Fig. 11). FLOTUS is currently being designed and constructed at CERN and will become a permanent part of the CLOUD facility. It is a laminar-flow quartz drift tube of 3 m length and 20 cm diameter, with gas occupancy times of a few minutes. In the presence of ozone and intense UV light, FLOTUS simulates hydroxyl radical oxidative exposures of organic vapours equivalent to several days in the atmosphere. The output of FLOTUS is transferred to the CLOUD chamber where the full power of its instrumentation will be used to study particle formation and growth with aged organics. The first operation of FLOTUS will be at CLOUD15 in fall 2022 (§7).

7 BEAM REQUESTS

The CLOUD15T run ("T" signifies "Technical") has been postponed from the originally-planned dates (Oct-Nov 2021) due to the lack of basic infrastructure in the T11 zone, especially the lack of electricity in the T11 control room, which has had a knock-on effect with many other CLOUD tasks. We are therefore requesting two runs in 2022, as follows.

7.1 CLOUD15T beam request (Apr 2022)

CLOUD requests 4 weeks beam when the PS starts up in 2022 (the date is not yet fixed but we understand it is likely to be April 2022). The aims of the CLOUD15T are as follows:

1. (Re-)commission CLOUD facility.
2. Characterise the new T11 beam (π flux, μ backgrounds, transverse profile, etc.).
3. Instrument development (HORUS).
4. Physics (exploratory studies):
   (a) Carbon closure (accounting for all organic sources and end products).
   (b) Marine nucleation with methanesulphonic acid (MSA) and ammonia.
   (c) Upper tropospheric nucleation with iodic acid.

7.2 CLOUD15 beam request (Sep - Nov 2022)

CLOUD requests 9 weeks beam in fall 2022 (Sep/Oct/Nov). The science goals are to be finalised during discussions within the CLOUD collaboration over the coming weeks, but are likely to include full studies of the three physics topics above plus biogenic nucleation with aged vapours (FLOTUS).

8 SUMMARY

In its first 10 years, CLOUD has provided a molecular-level understanding of atmospheric aerosol particle formation and growth, and identified the main vapours and mechanisms involved. CLOUD measurements and model results show that, although ion-induced nucleation is responsible for a large fraction of global particle formation, there is very little sensitivity of present-day global cloud condensation nuclei to solar-cycle variations of ionisation. However, major questions remain. Do cosmic rays affect cloud condensation nuclei in climatically-sensitive regions, or else directly affect cloud microphysics? What are the sources of aerosol particles over the open ocean? What is driving upper tropospheric particle formation and growth? How are vapours transported aloft in deep convective clouds? What was the baseline aerosol state of the pristine pre-industrial atmosphere, from which anthropogenic aerosol forcing is evaluated? Which vapours and mechanisms are driving smog formation in polluted cities? The Collaboration is committed to providing answers to these and other important questions with CLOUD over the next 10 years.

Acknowledgements

The CLOUD Collaboration wishes to thank the East Area Renovation team (project leader, Sebastien Evrard /EN-EA-AC) for maintaining essential CLOUD services (access, crane use, electricity, de-ionised water, chilled water, counting room, etc.) to allow the CLOUD14 run to take place in fall 2019. We would also like to thank CERN EP-DT, EN-MME, Michael Lazzaroni, Barbara Holzer (SPS/PS Coordinator) and the CERN PS machine team for their support of CLOUD.

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