

The influence of small aerosol particles on the properties of water and ice clouds

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In this paper, results are presented of the influence of small organic- and soot-containing particles on the formation of water and ice clouds. There is strong evidence that these particles have grown from nano particle seeds produced by the combustion of oil products. Two series of field experiments are selected to represent the observations made. The first is the CLOUD-Aerosol Characterisation Experiment (CLACE) series of experiments performed at a high Alpine site (Jungfraujoch), where cloud was in contact with the ground and the measuring station. Both water and ice clouds were examined at different times of the year. The second series of experiments is the CLOUD Processing of regional Air Pollution advecting over land and sea (CLOPAP) series, where ageing pollution aerosol from UK cities was observed, from an airborne platform, to interact with warm stratocumulus cloud in a cloud-capped atmospheric boundary layer. Combining the results it is shown that aged pollution aerosol consists of an internal mixture of organics, sulfate, nitrate and ammonium, the organic component is dominated by highly oxidized secondary material. The relative contributions and absolute loadings of the components vary with location and season. However, these aerosols act as Cloud Condensation Nuclei (CCN) and much of the organic material, along with the other species, is incorporated into cloud droplets. In ice and mixed phase cloud, it is observed that very sharp transitions (extending over just a few metres) are present between highly glaciated regions and regions consisting of supercooled water. This is a unique finding; however, aircraft observations in cumulus suggest that this kind of structure may be found in these cloud types too. It is suggested that this sharp transition is caused by ice nucleation initiated by oxidised organic aerosol coated with sulfate in more polluted regions of cloud, sometimes enhanced by secondary ice particle production in these regions.

Introduction

The last Intergovernmental Panel on Climate Change (IPCC) scientific assessment (IPCC, 2001) showed that the largest source of uncertainty in radiative forcing

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estimates arises from clouds *via* the first aerosol indirect effects. It is generally assumed that this tends to offset global warming but the magnitude is very uncertain. Mixed phase and ice clouds are very important in the atmosphere but little progress has been made in understanding the aerosol indirect effects in these clouds. To improve these models, a much clearer understanding of the role of ice nuclei in ice formation is required. It is clear from recent projects, such as INCA studying cirrus clouds in the Northern and Southern Hemisphere, that anthropogenic effects on Chamber studies such as those carried out at AIDA are providing a better understanding of how and under what conditions various materials, *e.g.*, these clouds, are substantial. Desert dust and soot are able to act as ice nuclei. Recent airborne studies have suggested that in many mixed phase clouds, concentrations of Ice Nuclei (IN) are orders of magnitude too small to explain the numbers of ice particles observed, implying ice multiplication processes are important. The Hallett–Mossop process is the only multiplication mechanism that has been well quantified; it operates at temperatures between -3 and -9 °C. There is also the possibility of splinter production associated with droplet freezing and, at colder temperatures, ice crystal fragmentation during evaporation has been identified as a possible mechanism of secondary ice particle production. The role of ice nuclei, which operate in water subsaturated but ice supersaturated conditions, needs to be investigated. Many of the studies designed to investigate these processes have been performed from aircraft, although ground-based mountain cloud studies provide the opportunity for more detailed study over longer periods.

In this paper, we investigate the role of small organic particles, generally found to be internally mixed with soluble inorganic material as both cloud droplet and ice particle nuclei. These particles are thought to originate from the burning of oil products in industry and motor vehicles, where they are emitted as organic particles a few tens of nanometre in size or smaller. The primary material has a large fraction of black elemental carbon and has associated organic carbon. The majority of the organic carbon observed in the experiments reported here is secondary in nature. The role and fate of these mixed organic particles in the atmosphere is largely unknown.

The CLACE experiments

Several CLOUD-Aerosol Characterisation Experiments (CLACE) have been performed in both summer and winter within international collaborations at the high alpine research station Jungfraujoch (JFJ, 3580 m asl; 46.55 °N, 7.98 °E), Switzerland. The experiments are designed to investigate the chemical composition of aerosol particles, their hygroscopic properties and their interaction with clouds. The presented results are based on findings from CLACE 2, CLACE 3 and CLACE 4 and were carried out in July 2002, February and March 2004 and February to March 2005 respectively.

Description of Jungfraujoch (JFJ)

Due to its exposed location on a mountain col, the JFJ experiences a high frequency of clouds (annual mean cloud frequency of 37%, [Baltensperger *et al.*, 1998¹]) and has been the subject of many cloud scavenging experiments. The high alpine site is influenced by remote continental/marine air masses from the free troposphere, and on occasion from the convective boundary layer due to local convection. The observation of cloud and aerosol parameters at the JFJ allows measurements to be conducted under a wide range of anthropogenically-influenced conditions yielding very different variable aerosol concentrations and compositions. Such measurements have been carried out since 1988 and have established the site to be suitable for the long-term monitoring of Free Tropospheric (FT) background aerosol [Baltensperger *et al.*, 1997²], (Henning *et al.* 2002³ and 2003⁴). The station is part

Table 1 Current Jungfraujoch aerosol/cloud measurement program

Instrument	Measured parameter	Time resolution	Inlet system/sampling technique		
			Total aerosol	Interstitial aerosol	No inlet <i>i.e.</i> , <i>in situ</i>
Condensation particle Counter (TSI 3010)	Aerosol number conc $d \sim 0.010\text{--}1 \mu\text{m}$	1 min	✗		
Aethalometer (AE-31)	Aerosol BC mass conc.	10 min	✗		
	Aerosol absorption coefficient at 7 different wavelengths 350–950 nm				
Nephelometer (TSI 3563)	Aerosol scat. coeff. 450, 550, 700 nm	30 min	✗		
Filters packs	Aerosol major ionic composition PM1 and TSP	1 d every 6th d	✗		

of the Swiss National Monitoring Network for Air Pollution (NABEL) and the Swiss Meteorological Institute (SMI). Many of the cloud and aerosol parameters recommended by the WMO for measurement at GAW baseline stations are already being measured at the JFJ and are indicated in Table 1.

Instrumentation and inlets

The large suite of instruments deployed during these experiments sampled from the free stream or utilised a combination of three well characterised inlets that will sample the total residual particulate, the interstitial (unactivated) particulate within the cloud, and the ice crystal residuals within the cloud.

The Institut für Troposphärische Research (IfT) operated a Counterflow Virtual Impactor (CVI), which has been successfully employed in artificially seeded mixed phase clouds (*e.g.* Mertes *et al.*, 2001⁵ and 2006⁶). The CVI was part of a new prototype sampling system (Ice-CVI) that allows for the separation of small ice particles from large ice crystals, cloud droplets and interstitial aerosol particles. The extracted ice particles are dried airborne in the system and the remaining residual particles that correspond to the former ice nuclei are analysed with a variety of different instruments (Table 2). Initial separation of cloud droplets, ice crystals and non-activated aerosol particles is performed under ambient conditions. In addition, the total aerosol is sampled with a heated inlet designed to evaporate all activated cloud droplets and ice crystals smaller than 30 μm at an early stage of the sampling process [Weingartner *et al.*, 1999⁷]. An interstitial inlet sampled the non-activated or interstitial aerosol particles by the removal of larger cloud particles during cloudy events. Ice particle residues may be complex if the crystal is heavily rimed as the residue would be a mixture of IN and CCN from the frozen droplets. The degree of riming was quantified using the Manchester Cloud Particle Imager (CPI) and formvar replicas.

The sampled air from the three different inlet systems was then brought into the laboratory, where aerosol measurements were performed at low Relative Humidities (RH < 20%). By duplicating and/or triplicating identical measurements for the total aerosol, the interstitial aerosol and the residual aerosol particles, cloud activation and heterogeneous ice nucleation properties are derived by differencing. Finally, other instruments were used to characterize cloud droplets *in situ* (Table 2).

The main cloud physics instruments are the Cloud Particle Imager (CPI), the Aerosol Droplet Analyser (ADA), a Knollenberg 2D probe, and the Forward Scattering Spectrometer Probe (FSSP). The CPI, manufactured by Stratton Park

Table 2 Additional instrumentation deployed during the campaigns. Note that duplication of measurements using the different inlets will allow cloud droplet properties to be derived by differencing

Instrument	Measured parameter	Availability		Inlet system/sampling technique						
		2004	2005	Time resol	Flow rate lpm	Responsible person/institute	Ice CVI	Total aerosol	Interstitial aerosol	No inlet <i>i.e., in situ</i>
Aerosol mass spectrometer AMS	Chemical aerosol composition	Y	Y	1 min	0.12	MPI Mainz	✗			
SPLAT (Single Particle Laser Ablation Time-of-flight mass spectrometer)	Single Particle Analysis	Y	Y				✗			
Aerosol mass spectrometer AMS	Chemical aerosol composition	Y	Y	1 min	0.12	Manchester		✗	✗	
Forward Scattering Spectrometer	Cloud and aerosol number	Y	Y	1 min		Manchester				✗
Probe PMS FSSP-100	Spectra $d = 2-44 \mu\text{m}$	Y	Y	1 min		Manchester				✗
Phase doppler anemometry system (ADA)	Liquid droplet number size distribution	Y	Y	1 min		Manchester				✗
Cloud particle imager (CPI) and 2-D probe	Ice Crystal imaging ($> 10 \mu\text{m}$)	Y	Y	40 s^{-1}		Manchester				✗
Formvar replicas	Cloud LWC, PSA Effective droplet diameter	Y	Y	1 min		ETH Zürich				✗
Gerber PVM-100	CCN concentration	Y	Y			PSI/Uni Copenhagen				✗
Cloud condensation nuclei counter (parallel plate type)	CCN concentration	Y	Y			Uni Copenhagen		✗		
Cloud condensation nuclei counter (expansion type)	CCN concentration	Y	Y	5 min		PSI		✗		
HTDMA	Hygroscopicity at ambient temperature ($T \sim -10 \text{ }^\circ\text{C}$)	Y	Y	10 min		PSI			✗	
SMPS	Aerosol number spectra $d = 15-800 \text{ nm}$	Y	Y	5 min	0.3	PSI		✗		✗
SMPS	Aerosol number spectra $d = 15-800 \text{ nm}$	Y	Y	5 min	0.3	PSI			✗	

Table 2 (continued)

Instrument	Measured parameter	Availability		Time resol	Flow rate lpm	Inlet system/sampling technique			
		2004	2005			Responsible person/institute	Ice CVI	Total aerosol	Interstitial aerosol
OPC (Grimm)	Aerosol number spectra $d = \sim 0.3\text{--}7.5\mu\text{m}$	Y	Y	1 min	1	Manchester		✗	✗
OPC (Grimm)	Aerosol number spectra $d = \sim 0.3\text{--}7.5\mu\text{m}$	Y	Y	1 min	1	PSI	✗		
Aethalometer (AE-31)	Aerosol BC mass conc. Aerosol absorption coefficient at 7 different wavelengths $\lambda = 350\text{--}950\text{ nm}$	Y	Y	10 min		PSI			✗
Filter samples	Major ions	Y	Y	h	2.3	IFT	✗	✗	✗
PSAP	IN BC concentration	Y	Y	3 min	2	IFT	✗		
CPC 3010	Residual number concentration	Y	Y	1 min	1	IFT	✗		
Ly-alpha hygrometer	condensed water content	Y	Y	1 min	0.1	IFT	✗		
Impactor for environmental scanning electron microscopy (ESEM) and electron microscopy	Ice nucleation on residual particles, Particle morphology, Elemental composition	Y	Y		4	Manchester TUD	✗	✗	✗

Engineering, images ice particles larger than 10 μm onto a CCD chip at a rate of 40 images per second. The instrument is designed for aircraft use and the Manchester group have successfully deployed the instrument on the ARA Egrett aircraft for studying the crystal habits of cirrus clouds during the NERC Clouds, Water Vapour and Climate programme funded EMERALD experiments (Choularton *et al.*, 2002⁸). The CPI was adapted to ground-based operation by fitting it with a high volume aspirator, a method previously adopted by Lawson *et al.*, 2001.⁹ The images produced by the CPI are far more detailed than has previously been possible and lead to a more reliable and better resolved classification of ice crystals at higher temporal resolution. This enabled us to obtain information on the origin of the crystals and the growth regimes that the crystals have been subject to, as the growth habit is a strong function of temperature and supersaturation with respect to ice. In addition, any riming of the crystals can be resolved using this instrument. This was operated alongside a Knollenberg 2D probe owned by Manchester, which provided absolute number concentrations of crystals at around 200 μm to correct the CPI sample volume. Precipitation may significantly affect the results, a present weather sensor was used to identify such periods.

The Airborne Droplet Analyser (ADA), manufactured by TSI Inc., is based on phase Doppler anemometry. It utilises an Argon Ion laser to generate two cross-directed laser beams with a small sample volume in the interfering region. The interference fringes are modified by the presence of cloud droplets and the size and velocity of the droplet can be determined. The technique can discriminate between spherical droplets and aspherical particles and so is capable of rejecting the small ice crystals in the cloud. In addition, changes in refractive index can be measured and used to reject non-liquid water particles. The ADA has a much larger size range than the FSSP and were operated with approximately 200 channels ranging from 1–200 μm .

The FSSP, modified by DMT to provide faster electronics, improved size binning and better rejection of multiple counting, measures the number size distribution of both liquid droplets and ice crystals and cannot discriminate between them. In principle, the three instruments allow number closure between the liquid and ice phases to be achieved.

The Paul Scherrer Institute provided measurements of aerosol size distributions alternately through the total and interstitial inlets using a combination of Scanning Mobility Particle Sizers (SMPSs) and Optical Particle Counter (OPC). This allows a comparison of the number of activated droplets and particles in a cloud with the activated droplet and ice spectra derived from the Manchester instruments (Verheggen *et al.*, 2007¹⁰). The particle number concentrations and size distributions provide sound measures of the anthropogenic pollution observed during the cloud event. These measurements, coupled with those of black carbon and CO, NO, NO_x and ozone, serve to identify the extent to which the air mass is influenced by anthropogenic effects.

Manchester deployed an Aerodyne Aerosol Mass Spectrometer (AMS) (Allan *et al.*, 2003¹¹). The AMS measures the mass of volatile and semi-volatile components of submicron aerosol particles in real time as a function of their size. This information makes it possible to link the chemistry of aerosol particles with the gas phase, and particle microphysical measurements at a time resolution that is higher than changes in air mass occur. This has not been possible in the past using filter or impactor technology and helps to resolve current uncertainties in long range transport, phase partitioning of organic material, the direct aerosol radiative effect and aerosol–cloud interactions at the heart of the indirect effect. The Manchester and Mainz AMS instruments were used to sample from all three inlets throughout the experiment, allowing discrimination of the mass spectra, mass loadings and mass size distributions of organics, sulfate, nitrate and ammonium from ice crystal residuals, total cloud particle residuals and interstitial particles at a time resolution of around 6 min. The MPI Mainz single particle laser ablation system was in other

CLACE experiments used to sample the residuals of ice crystals selected by the CVI. The instrument delivers mass spectra of single particles but is unable to deliver mass loadings due to the single stage ablation/ionisation process being non-reproducible. It is able, however, to deliver a mass spectral fingerprint of the residuals of the ice crystals measured. The instrument is sensitive to metals, crustal material and inorganic salts but tends to significantly fragment the organic fraction of the particles.

Aircraft observations in an urban plume

The interaction of pollution from urban areas with stratocumulus cloud is important both for understanding the fate of gases and particulate emitted in the urban environment and for understanding the aerosol indirect effect of ageing mixed organic and inorganic particulate. In this paper, results will be presented from an airborne study to investigate these processes, known as CLOud Processing of regional Air Pollution advecting over land and sea (CLOPAP).

The interaction of ageing aerosol emitted from urban areas of the UK was investigated as the plumes advected away from the area over the sea in a stratocumulus-capped boundary layer. Detailed measurements of the size distribution and chemical composition of the aerosol were made on the Facility for Airborne Atmospheric Measurements (FAAM), the UK community's new BAe 146 research aircraft. These measurements were complemented by detailed measurements of the atmospheric liquid water content and cloud microphysics. Detailed measurements of precursor trace gases were also made by colleagues from the University of York and the University of East Anglia.

Methodology of CLOPAP

During a typical sortie, the aircraft would fly to a region immediately downwind of the urban source in conditions with a well marked boundary layer capped by stratocumulus cloud. The aircraft made a series of horizontal passes perpendicular to the line of the plume below cloud, within the cloud deck and above the cloud top. This series of passes was repeated at 50 km intervals moving downwind from the source (Fig. 1). Within cloud, an airborne CVI was used to separately measure the droplet residual aerosol components to investigate the nucleation scavenging of the particulate.

A key measurement of the aerosol composition was made using an Aerodyne Aerosol Mass Spectrometer (Jayne *et al.*, 2000¹², Allan *et al.*, 2004¹³). This

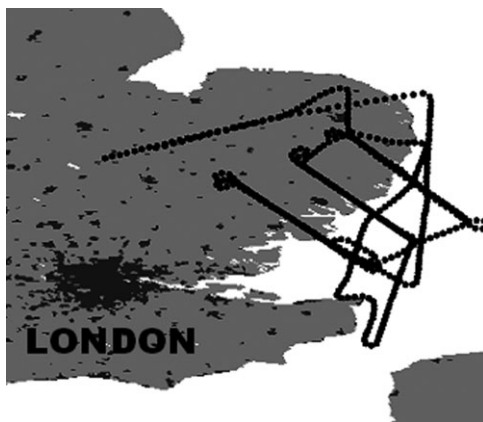


Fig. 1 An example of a typical sortie, in this case studying the London plume as it advects east.

instrument is able to provide size resolved information of the semi-volatile components of the aerosol, including major ions and organic material. Some information is available on the main functional groups in the organic material and the state of oxidation. Cloud and aerosol microphysical measurements were made using a series of outboard optical scattering probes to measure the size range 0.05 to 50 μm . These included particles that were nucleation scavenged and particles that remained interstitial to the cloud droplets.

Results from the CLACE experiments

It was found, from the AMS, that the aerosol consisted of a mixture of sulfate, organic and nitrate distributed as shown in Fig. 2. The similarity of the size distribution for all the species suggests that the particles are internally mixed. For the winter project, Fig. 2b (CLACE-3), the aerosol was mostly long range, transported from source regions over Europe and did not show a clear diurnal variation. Nevertheless, measurements of CO concentration on a 10-min timescale did show fluctuations and day-to-day variations as air from polluted sources and plumes arrived at the site. The influence of these variations in the amount of pollution aerosol on the cloud microphysics is discussed below. A similar result was found for warm clouds during CLACE 2, performed during the summer months, except that the composition of the aerosol was dominated by organic material that was internally mixed with sulfate and nitrate. There were marked variations in the loadings of these species on a diurnal basis and this could be attributed to boundary layer air being transported to the summit by convection during the day.

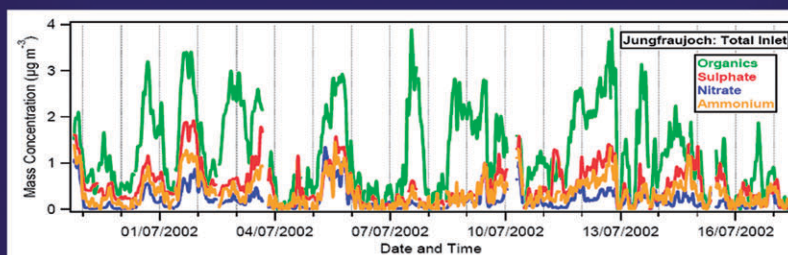
Composition of the organic fraction

The AMS delivers a mass spectrum of the aerosol ensemble as a function of time based on standard 70 eV ionisation after vaporization at 500 °C. The fragmentation pattern of the inorganic ions can be identified easily and signals due to air can be accounted for by referencing to the nitrogen ion signal at m/z 28 or the oxygen ion at m/z 32. Allan *et al.*, (2004)¹⁴ have developed a method for accounting for such signatures and so are able to obtain a mass spectrum composed only of the organic mass. Major ion peaks in this spectrum occur at 41, 43, 55, 57, 69, 71 and at higher mass, separated by 14 mass units. These peaks represent alkyl chain fragments and are dominant when the particles are composed of aliphatic-rich compounds typically found in motor vehicle exhaust aerosol. Alfarra *et al.*, (2004)¹⁵ have shown that after some distance from the source, mass fragments due to oxygenated ions become dominant. The main oxygenated peaks occur at m/z 43 ($\text{C}_2\text{H}_3\text{O}^+$) and m/z 55 ($\text{C}_3\text{H}_3\text{O}^+$), which occur commonly from a number of carbonyl functionalities, and m/z 44 (CO_2^+), which indicates mainly di- and multifunctional acids, as these undergo decarboxylation on the vaporizer forming neutral CO_2 , which is ionised directly.

Mass fragments 44 and 43 dominate the mass spectrum, indicating that the organic fraction is mainly composed of highly oxygenated compounds of secondary nature, such as carbonyls and dicarboxylic and poly acids. The mass fragment 44, the AMS signature of oxidised organic compounds and humic-like substances, accounts, on average, for about 14% of the total organic mass at Jungfrauoch. The dominance of mass fragments 44 and 43 in the accumulation mode and the lack of significant contributions of mass fragments 57 and 43 in the small mode indicate that the aerosol organic fraction at Jungfrauoch is largely composed of highly oxidized compounds and that secondary organic aerosols are more significant than primary compounds during the sampling period. These results are supported by a previous report of oxygen-to-carbon atomic ratio of 0.55 at Jungfrauoch, which

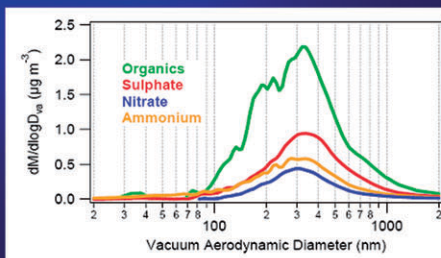
(a)

AMS Aerosol Composition from the Total Inlet (CLACE-2)



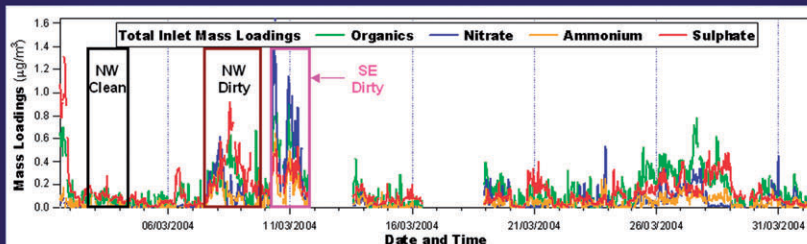
Summertime Summary:

- Dominated by Organic loading
- Diurnal cycle as BL top ascends towards JFJ level during day
- Size distribution of components consistent with internally mixed aerosols



(b)

AMS Aerosol Composition from the Total Inlet (CLACE-3)



Wintertime Summary:

- No diurnal cycle – Long range transported/source dominated
- Lower loadings than in summer
- Size distribution of components still consistent with internally mixed aerosols

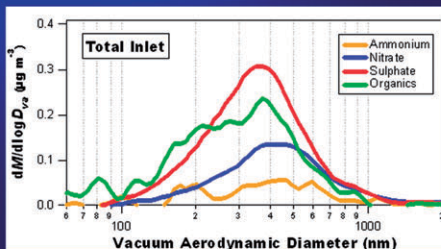


Fig. 2 A comparison between the Aerosol Mass spectrometer data in the (a) summer (CLACE-2) and (b) winter (CLACE-3).

implies that the organic compounds are highly oxygenated at this location (Krivacny *et al.*, 2001¹⁶).

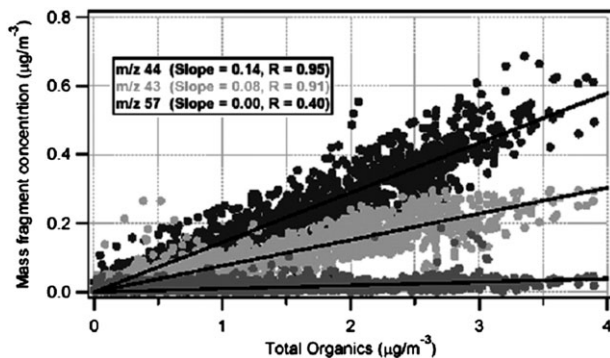


Fig. 3 A scatter plot of the mass concentration of the organic mass fragments 43, 44 and 57 versus the total organic mass concentration for the entire CLACE2 set.

These conclusions are emphasised in Fig. 3, where the mass concentrations of the three mass fragments discussed above are scatter-plotted against the total organic concentration for the entire sampling period. The slopes and Pearson's r values of the correlation of each mass fragment with the total organic mass are summarised in the figure. Results show that m/z 44 followed by m/z 43 have the highest slope and Pearson's r values, while mass concentration of m/z 57 does not appear to increase with increasing total organic mass. Hence, it would appear that the aerosol has grown by the deposition of oxidized secondary organic material on a seed of aliphatic material.

Aerosol scavenging in liquid clouds in CLACE

In both seasons, it was found by comparing data on the total and interstitial inlets that a large fraction of all the species were incorporated into cloud droplets in liquid dominated clouds. Results show that all four chemical components, including organics, appear to be scavenged by cloud droplets. Within the same in-cloud event, the scavenging ratios of the different components were found to be of similar values. However, variable mass scavenging ratios ranging between 0.3 and ~ 1 were observed for the same chemical species in different cloud events. This result is discussed further below, where we examine the scavenging of organic aerosol by cloud in flights over the UK.

The ice phase

During CLACE-3, temperatures were below freezing throughout and the cloud consisted of a mixture of supercooled water and ice crystals. It was observed, however, that rapid fluctuations occurred between cloud dominated by liquid water and ice crystals, often on timescales of tens of seconds. On some occasions it was found that ice and water co-existed in the same cloud at the same time, and at others there were rapid fluctuations between cloud regions consisting almost entirely of supercooled water and almost entirely of ice. Fig. 4 shows an example of this behaviour in a cloud at a temperature of -11 °C. In this figure, the CPI data shows large numbers of small spherical particles in the high liquid water content regions and smaller numbers of irregular particles in the regions dominated by ice crystals, note that the ice crystals are both larger (second panel) and less numerous than the water droplets. The third panel shows the number concentration of small droplets measured by the FSSP; again, these are much higher in the liquid water-dominated regions than the ice-dominated regions. Fig. 5 shows an example of the sharp

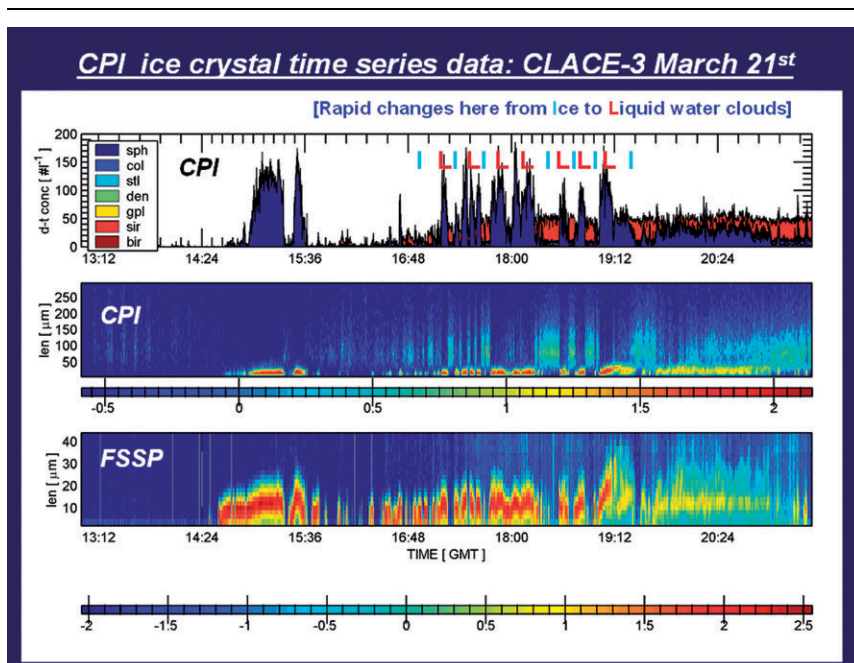


Fig. 4 Time histories of particle number concentration divided according to habit from the CPI (top panel), particle length from the CPI (middle panel), particle size and number concentration from the FSSP (lower panel) for 1 d during the CLACE-3 winter campaign.

transition between the ice- and water-dominated regions with examples of the images close to the interface.

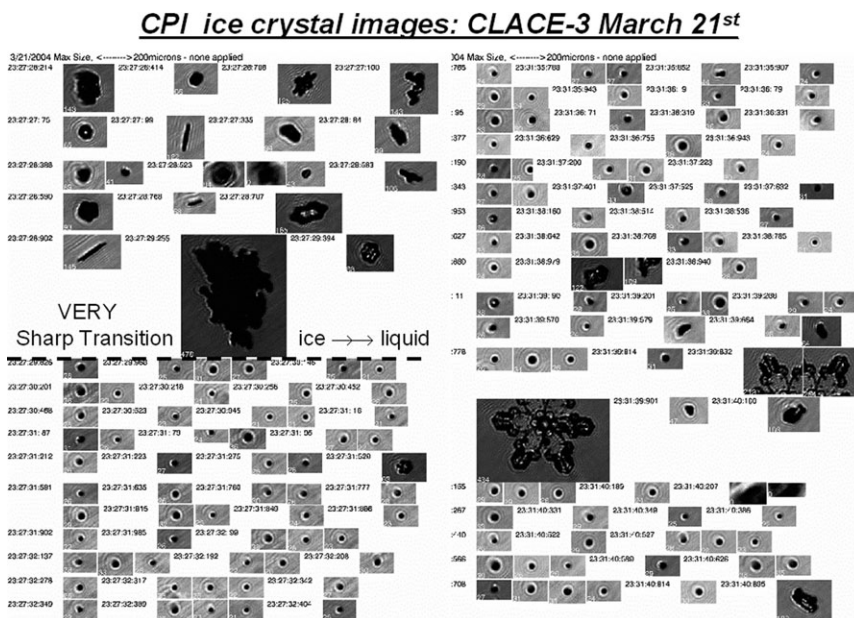


Fig. 5 Particle images recorded by the CPI showing the very sharp transition between water- and ice-dominated cloud.

The liquid water content in the cloud can be deduced from the PVM and the ice water content from the CPI images using the method described by Connolly *et al.* 2007.¹⁷ The Ice Mass Fraction (IMF) is defined by

$$\text{IMF} = \frac{\text{IWC}_{\text{CPI}}}{\text{IWC}_{\text{CPI}} + \text{LWC}_{\text{PVM}}}$$

where IWC is the Ice Water Content from the CPI, and LWC is liquid water content from the FSSP. When liquid water content from the PVM and droplet number concentration from the FSSP, for the whole of CLACE-3, are plotted against ice mass fraction it can be seen both the liquid water content and droplet number concentration fall with increasing ice water fraction Fig. 6. This can be readily explained by the fact that ice particles, which are fewer in number than the cloud droplets, are thermodynamically favoured at temperatures below 0 °C and so these grow rapidly in the cloud, at the expense of the cloud droplets and rapidly deplete the cloud droplets.

This process is likely to explain the rapid glaciation of parts of the cloud. It does not, however, account for the observation that ice particles are only observed in some parts of the cloud at the same temperature.¹⁸

The origin of the ice phase

It is not possible to use the AMS data to look at the short-term fluctuations in the ice content of the cloud as the resolution is not good enough. However, conditional sampling was carried out based on the presence of ice in the cloud. The result is shown in Fig. 7. It can be seen that regions containing ice have higher loadings, particularly of sulfate. The likely origin of this organic material, particularly in winter, is from combustion confirmed by its association with higher levels of sulfate and nitrate (from the AMS) and black carbon. At Jungfraujoch, it was found that ice crystal residues from the ice CVI consisted of black carbon and mineral particles (Walter *et al.*, 2007,¹⁹ Cozic *et al.*, 2007¹⁰). The question that arises is whether these carbon-rich aerosols are likely to act as good ice nuclei. Work has been conducted in the AIDA chamber to investigate the role of black carbon and organic material as an ice nucleus (Möhler *et al.*, 2005²⁰). It was found that black carbon could act as a deposition nucleus at low temperatures but organic coatings inhibited this. However, it was shown that sulfate coatings considerably increased the effectiveness of the ice nuclei at water saturation when they first acted as CCN, then causing the droplets to freeze. In these circumstances, the carbon particles were effective as ice nuclei at –20 °C. Further recent work carried out at the chamber has shown that the presence of highly oxidized organic material (as observed at Jungfraujoch) can further enhance the effectiveness of the immersion nuclei. It is, therefore, possible that the source of the ice is emersion freezing by organic/carbon particles being carried to Jungfraujoch in plumes of polluted air. This would explain the very inhomogeneous glaciations of the cloud as these plumes arrive at the observation site.

A possible role for secondary ice particle production

A feature of the data presented above is that when ice is present there is sometimes a truly mixed phase cloud and at others it is purely an ice cloud. This does not seem to be clearly related to temperature. A likely explanation for this is the presence or absence of secondary ice particle production referred to in the introduction to this paper. As discussed above, the presence of ice will deplete the liquid water for thermodynamic reasons and this will tend to leave behind a relatively small number of larger ice particles, each ice particle being nucleated by an ice-forming nucleus. It is known, however, that at temperatures between –3 °C and –9 °C, a powerful process of secondary ice particle production by riming and splintering occurs called the Hallett–Mossop process. In a mixed phase cloud, ice particles will sweep up

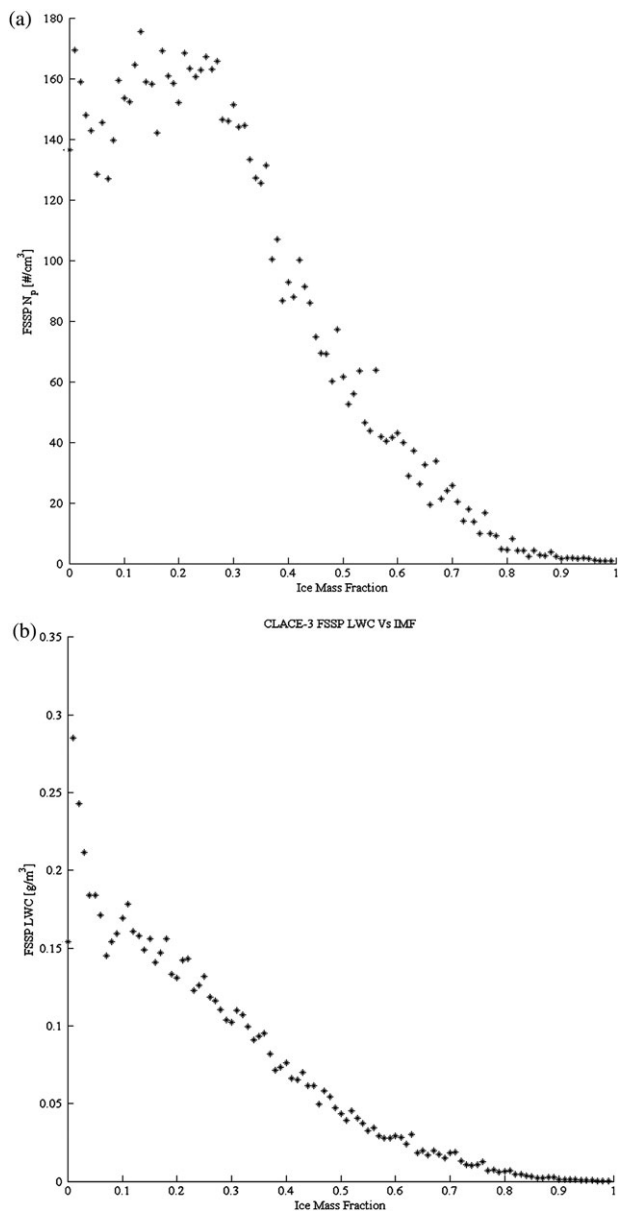


Fig. 6 (a) FSSP droplet number concentration plotted against ice mass fraction. (b) A comparison of the cloud droplet number concentration and cloud liquid water content measured by the FSSP with ice mass fraction.

supercooled cloud droplets, which will freeze on contact. As they freeze they throw off ice splinters which are then able to grow rapidly by vapour diffusion. This process could contribute to the relatively high concentrations of ice particles observed at $-11\text{ }^\circ\text{C}$ on 21 March (Fig. 4) as the cloud undoubtedly filled this temperature range between the summit site and the lower, warmer cloud base. Data from the ice CVI may help us to quantify this, as each ice particle should leave behind one ice-forming nucleus, whereas particles that were formed on secondary splinters may leave no residue. This work is not completed. As mentioned in the introduction, other, less

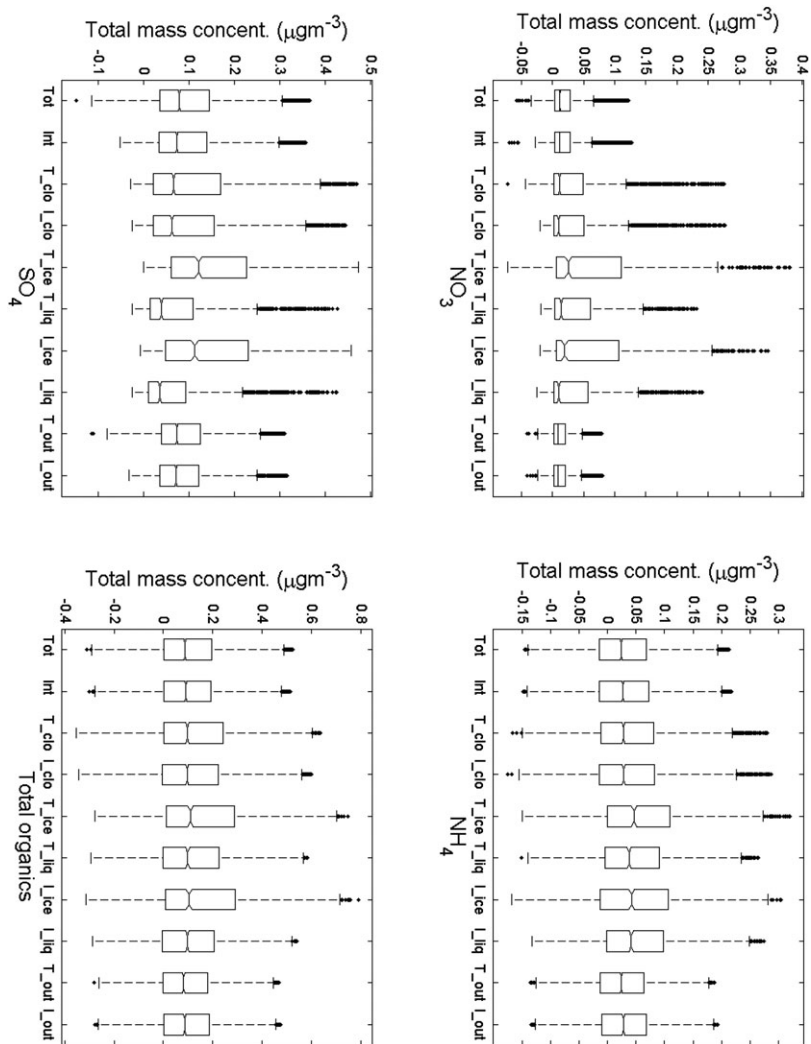


Fig. 7 Conditionally sampled AMS loading of major species showing higher values of sulfate, nitrate and organics in ice cloud than water cloud. Tot: All data (in and out of cloud) from total inlet. Int: All data (in and out of cloud) from Interstitial inlet. T_clo: Data from all cloud events, regardless of cloud phase (Total inlet). I_clo: Data from all cloud events, regardless of cloud phase. (Interstitial inlet). T_ice: Data from ICE cloud events (Total inlet). T_liq: Data from LIQUID cloud events (Total inlet). I_ice: Data from ICE cloud events (Interstitial inlet). I_liq: Data from LIQUID cloud events (Interstitial inlet). T_out: Data out of cloud (Total inlet). I_out: Data out of cloud (Interstitial inlet).

powerful secondary ice processes may operate at other temperatures, however, this remains to be quantified.

Results from the CLOPAP experiments in stratocumulus cloud

Several sorties took place during the summer of 2005, studying the plumes of several eastern UK cities as they evolved, as they were transported east. The changes in the chemical composition, size distribution and nucleation properties of the aerosol will be presented as a function of plume age for the different case studies.

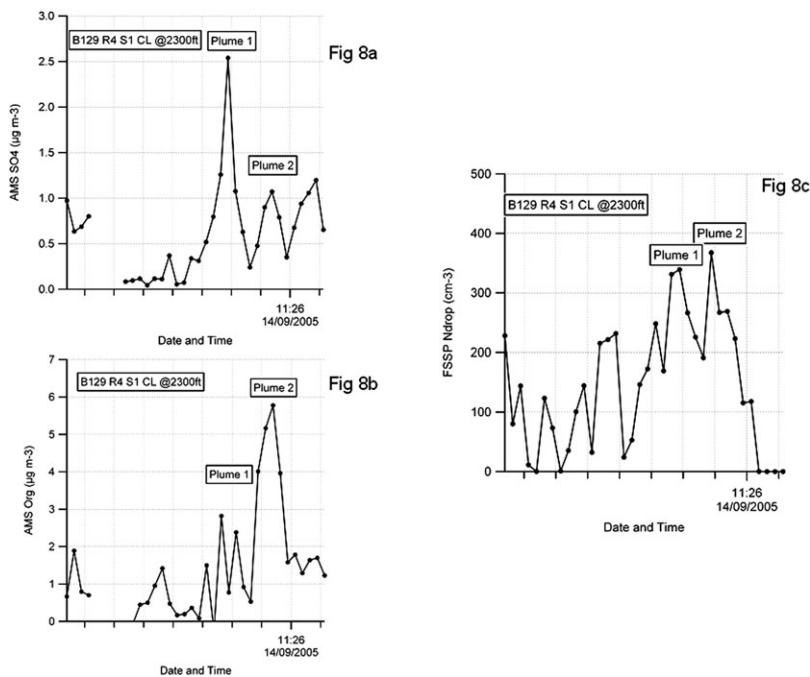


Fig. 8 CLOPAP case study from flight B129. Plume 1 contains predominantly sulfate aerosol internally mixed with some organic material, whereas plume 2 contains predominantly organic aerosol internally mixed with some sulfate (parts a and b). Part c shows that both aerosol plumes are effective as CCN increasing the droplet number in the cloud.

The compositions of cloud drop residuals were successfully measured with the AMS and shown to be composed mainly of a mixture of ammonium, sulfate, organics and nitrate. Changes as a function of age were noted, including the relative mass concentrations of inorganics to organics and the amount of oxidation in the organic fraction. The overall level of organic oxidation was higher than is typically seen in urban environments, and similar to that found in the winter CLACE experiments described above. A total of 12 case studies were flown around the UK. In this paper, we will concentrate on the results of one case study flown on 14 September 2005 over Kent and the Thames Estuary. The results in Fig. 8 show a transect through stratocumulus cloud about 100 km from London. The results presented are droplet residuals sampled through a CVI mounted on the aircraft and fed to an aerodyne AMS. It can be seen that one plume contained predominantly sulfate aerosol internally mixed with a small amount of organic material, whilst a neighbouring plume consisted of predominantly organic material internally mixed with sulfate. The organic material sampled shows evidence of being highly oxidised, with 10% m/z 44 fragments, similar to CLACE-2. Both plumes resulted in increased droplet number in the cloud to roughly the same degree. This confirms the picture from the CLACE experiments of aged organic aerosol acting as an excellent CCN, but much closer to the source. The likely scenario for the two plumes is that they had rather different sources. The following process probably formed plume 1: organic seeds of hydrophilic hydrocarbons produced from engine exhausts in the urban environment with a size of about 30 nm. Such particles are widely observed on urban areas. These would grow as additional oxidised secondary organic material was added. This would cause the particles to be weakly hydrophilic. At this point, nitric acid and then sulfuric acid would be deposited to the particles, the sulfuric acid tending to displace the nitric acid. Plume 2 probably formed in a similar way but

evolved in a much more organic-rich environment, hence deposition of secondary organic material dominated. In this case, the atmospheric boundary layer was stratocumulus-capped throughout and hence it is not clear how much of a role cloud processing played in the evolution of the plume. Other flights in cloud free conditions did show plumes of similar composition at a similar distance for urban sources.

Discussion

In this paper, results have been presented of the influence of atmospheric aerosol particles in the size range 50 nm and upwards on the formation of water and ice clouds. Two series of field experiments were selected to represent the observations made. The first is the CLACE series of experiments performed at a high Alpine site (Jungfraujoch), where cloud was in contact with the ground and the measuring station. Both water, ice and mixed phase clouds were examined at different times of the year. The second series of experiments is the CLOPAP series where ageing pollution aerosol from UK cities was observed, from an airborne platform—the UK FAAM BAE146 aircraft—to interact with warm stratocumulus cloud in a cloud-capped atmospheric boundary layer.

It has been shown that aged pollution aerosol consists of an internal mixture of organics, sulfate, nitrate ammonium; the organic component is dominated by highly oxidized secondary material. The relative contributions and absolute loadings of the components vary with location and season. For example, during CLACE-2 in the summer at Jungfraujoch, it was observed that organic material dominated the aerosol, whereas during the CLOPAP experiments the observations were made much closer to sources, and hence the plumes had marked structure with very different aerosol composition in different parts of the plume. It was found, however, that most of the aerosols act as cloud condensation nuclei, irrespective of their composition and the ratio of the species found in the cloud droplets were very similar to those found in the total aerosol, confirming that the particles were internally mixed. Hence, much of the organic material along with the other species is incorporated into cloud droplets. It was observed, in CLOPAP, that by 100 km down wind of London the urban aerosol produced from that area has this characteristic internally mixed structure and was a good CCN. This is an important result, as the lifetime of organic aerosol will be limited, as by being incorporated into cloud droplets it will be readily removed by rainout and wet deposition. Further, however, it means that urban-produced aerosol will modify cloud structure only a short distance downwind of the urban environment.

In ice and mixed phase cloud, it is observed that very sharp transitions (just a few meters in horizontal extent) are present between highly glaciated regions and regions consisting of supercooled water. This is a unique finding, although unpublished results from aircraft observations in cumulus clouds suggest that a similar structure may exist. This observation is very important in understanding the structure of mixed phase clouds. Precipitation particles grow rapidly when ice and supercooled water are intimately mixed in cloud both by growth of the ice particles from the vapour and by the riming process. However, if the phases are separated on small scales then these processes will be inhibited.

It is suggested that this transition is caused by ice nucleation initiated by oxidised organic aerosol coated with sulfate in more polluted regions of cloud. This suggestion is supported by conditional sampling of the aerosol data, which shows that glaciated regions of cloud contain higher loadings of the major ions and organic material than regions dominated by supercooled water. The possible explanation of the glaciated regions often being short and intermittent is that they form as more polluted air is intermittently transported upwards from the atmospheric boundary layer below. Studies performed in the AIDA chamber have suggested that sulfate-coated organic material acts as an efficient condensation, freezing ice nuclei at

temperatures encountered in these clouds in CLACE-3. Very recent results have suggested that the process is further enhanced if the organic material is highly oxidized. This interpretation is tentative at the present time, and further discussion and investigation is needed. This process does not necessarily explain the presence of completely glaciated regions of cloud at temperatures as high as $-11\text{ }^{\circ}\text{C}$. Once ice is formed, it will grow rapidly by vapour diffusion at the expense of the supercooled water droplets that will tend to evaporate. However, a powerful mechanism of secondary ice particle production (the Hallett–Mossop process), which occurs at temperatures between $-3\text{ }^{\circ}\text{C}$ and $-9\text{ }^{\circ}\text{C}$, may be playing an important role in completing the glaciation of the cloud at relatively high temperatures.

These results are potentially very important for understanding the role of man-made aerosol on the microphysics of mixed phase cloud and hence their interaction with solar radiation. These particles can also affect the precipitation production and lifetime of such clouds.

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