

Physical and chemical properties of aerosol particles and cloud residuals on Mt. Åreskutan in Central Sweden during summer 2014

By EMELIE LINNÉA GRAHAM¹, PAUL ZIEGER¹, CLAUDIA MOHR¹, ULLA WIDEQVIST¹, TABEA HENNIG¹, ANNICA M. L. EKMAN², RADOVAN KREJCI¹, JOHAN STRÖM¹, AND ILONA RIIPINEN^{1*}, ¹*Department of Environmental Science (ACES) and Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden;* ²*Department of Meteorology (MISU) and Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden*

(Manuscript Received 4 December 2019; in final form 17 May 2020)

ABSTRACT

The size distribution, volatility and hygroscopicity of ambient aerosols and cloud residuals were measured with a differential mobility particle sizer (DMPS) and a volatility–hygroscopicity tandem differential mobility analyser (VHTDMA) coupled to a counterflow virtual impactor (CVI) inlet during the Cloud and Aerosol Experiment at Åre (CAEsAR) campaign at Mt. Åreskutan during summer 2014. The chemical composition of particulate matter (PM) and cloud water were analysed offline using thermo-optical OC/EC analysis and ion chromatography. The importance of aerosol particle size for cloud droplet activation and subsequent particle scavenging was clearly visible in the measured size distributions. Cloud residuals were shifted towards larger sizes compared to ambient aerosol, and the cloud events were followed by a size distribution dominated by smaller particles. Organics dominated both PM (62% organic mass fraction) and cloud water (63% organic mass fraction) composition. The volatility and hygroscopicity of the ambient aerosols were representative of homogeneous aged aerosol with contributions from biogenic secondary organics, with median volume fraction remaining (VFR) of 0.04–0.05, and median hygroscopicity parameter κ of 0.16–0.24 for 100–300 nm particles. The corresponding VFR and κ for the cloud residuals were 0.03–0.04 and 0.18–0.20. The chemical composition, hygroscopicity and volatility measurements thus showed no major differences between the ambient aerosol particles and cloud residuals. The VFR and κ values predicted based on the chemical composition measurements agreed well with the VHTDMA measurements, indicating the bulk chemical composition to be a reasonable approximation throughout the size distribution. There were indications, however, of some more subtle changes in time scales not achievable by the offline chemical analysis applied here. Further, online observations of aerosol and cloud residual chemical composition are therefore warranted.

List of abbreviations: AS: ammonium sulphate; BC: black carbon; CAEsAR: cloud and aerosol experiment at Åre; CCN: cloud condensation nucleus; CPC: condensation particle counter; CVI: counterflow virtual impactor; DMPS: differential mobility particle sizer; EC: elemental carbon; EF: enrichment factor (in CVI measurements); ELVOC: extremely low volatile organic compound; EM: elemental mass (an estimate of BC mass from the EC concentration); GF: growth factor; IC: ion chromatography; IM: inorganic mass; IPCC: Intergovernmental Panel on Climate Change; LVOC: low volatile organic compound; MAAP: multi-angle absorption photometer; NPF: new particle formation; NPOC: non-purgeable organic carbon; OC: organic carbon; OM: organic mass; PBL: planetary boundary layer; PM: particulate matter; RH: relative humidity; SOA: secondary organic aerosol; TD: thermodenuder; TOC: total organic carbon; TOT: thermo-optical transmission; VFR: volume fraction remaining; VHTDMA: volatility–hygroscopicity tandem differential mobility analyser; WSOC: water-soluble organic carbon; WSOM: water-soluble organic mass; WINSOC: water-insoluble organic carbon; WINSOM: water-insoluble organic mass

Keywords: aerosol, cloud residual, chemical composition, volatility, hygroscopicity, thermodynamic modelling

*Corresponding author. e-mail: ilona.riipinen@aces.su.se

1. Introduction

Aerosol particles are ubiquitous in the atmosphere and important for the Earth radiative balance. They interact directly with radiation through scattering and absorption, and indirectly by acting as cloud condensation nuclei (CCN). The indirect aerosol radiative effect, through cloud formation, generally cools the Earth system, but can also cause local heating. According to the Intergovernmental Panel on Climate Change (IPCC, 2013), aerosol-cloud interactions currently represent the largest uncertainty in estimates of the anthropogenic perturbation of the Earth's radiative budget. Removal by clouds and precipitation is also the major sink of atmospheric aerosol particles and therefore an important factor influencing regional scale air quality and aerosol climate effect (Theobald et al., 2019). To quantify aerosol indirect effects on climate and to better constrain the wet deposition mechanisms of particulate matter (PM), the complex interactions between atmospheric aerosol particles, clouds and precipitation need to be better understood (e.g. Ervens, 2015 and references therein).

The ability of an aerosol particle to act as CCN depends, in favourable meteorological conditions, on the size and chemical composition of the particle (Köhler, 1936; Hobbs, 1993; Seinfeld and Pandis, 2006; Ervens, 2015; Lowe et al., 2019). Therefore, the fraction of particles acting as CCN at a certain supersaturation and thus also taken up by clouds and precipitation can be predicted if the atmospheric aerosol size distribution and composition are known. Owing to the multitude of atmospheric aerosol sources, the aerosol population in the atmosphere is generally a mixture of particles with different sizes between a few nm and up to several μm with varying chemical composition. The chemical complexity is a particular challenge for the atmospheric aerosol organic fraction, as it contains thousands of different compounds with various molecular properties (Goldstein and Galbally, 2007; Jimenez et al., 2009). To develop general approaches for describing aerosol-cloud interactions in various climate or air quality applications, we need to systematically investigate the roles of the size-dependent chemical composition of aerosol particles and their number size distribution (e.g. Dusek et al., 2006), and simplify them accordingly without losing any necessary level of detail.

The scientific understanding of aerosol-cloud interactions is still limited by the lack of direct observational data on aerosol and cloud properties with sufficient resolution. This is true also for simultaneous observations of aerosol particle and cloud residual size distributions and chemical compositions. Besides, direct and simultaneous chemical characterisation of aerosol particles and cloud residuals, observations of volatility (see e.g. Häkkinen et al., 2012 and references therein) and hygroscopicity (see e.g. Rissler et al., 2006 and references therein) are useful in this regard. Besides being a proxy for particle

composition, the volatility of aerosol constituents (related to saturation vapour pressure or -concentrations) governs phase transitions and condensational growth and is therefore needed in descriptions of the evolution of the size distribution of aerosol particles (Mohr et al., 2019). The hygroscopicity described by the parameter κ (Rissler et al., 2006; Petters and Kreidenweis, 2007), on the other hand, is a direct proxy of the ability of a given particle (or particle population) to take up water and act as CCN. Previous studies with simultaneous measurements of aerosol chemical composition, size distribution, volatility and hygroscopicity in- and out-of-cloud exist (e.g. Seifert et al., 2004; Drewnick et al., 2006; Ditas et al., 2012; Hao et al., 2013; Hammer et al., 2014; Kruger et al., 2014; Väisänen et al., 2016), and have generally demonstrated the importance of particle size in CCN activation: the size distributions of ambient aerosols contain generally more and on average larger particles than those observed in the interstitial aerosol. In particular, closure studies of particle number size distributions in- and out-of-cloud, including measurements of the cloud residuals, have provided as a valuable means to estimate water supersaturation conditions within clouds where direct measurements are extremely challenging. We are not, however, aware of any measurements coupling direct measurements of the volatility and hygroscopicity of atmospheric aerosol particles and cloud residuals (particles remaining after evaporating the cloud water) to corresponding observations of the ambient and residual size distribution and chemical composition. Such measurements can, however, shed light on the processes and properties governing (1) aerosol particle uptake by clouds; (2) transport and scavenging of chemical species via clouds and rain; (3) the potential aqueous phase processing of the species present in the particles (Targino et al., 2007).

Here we present simultaneous observations of the key physical and chemical properties of ambient aerosol and cloud residuals during the Cloud and Aerosol Experiment at Åre (CAEsAR 2014) campaign, which took place between summer and early autumn 2014 at a remote site on a mountaintop in central Sweden. We combine simultaneous (with time resolution of about 12 min or less) observations of aerosol particle size distributions, volatility, hygroscopicity and black carbon (BC) content with sampling and chemical analysis of the bulk PM and cloud water over much longer time scales. Using the collected data sets, we investigate the similarities and differences in the chemical composition, volatility and hygroscopicity of the aerosol particles and the cloud residuals, along with the influence of the clouds on the ambient particle size distribution. Finally, we compare the volatility and hygroscopicity estimated based on the bulk chemical compositions to those directly observed with the online techniques. This comparison is used to discuss the level

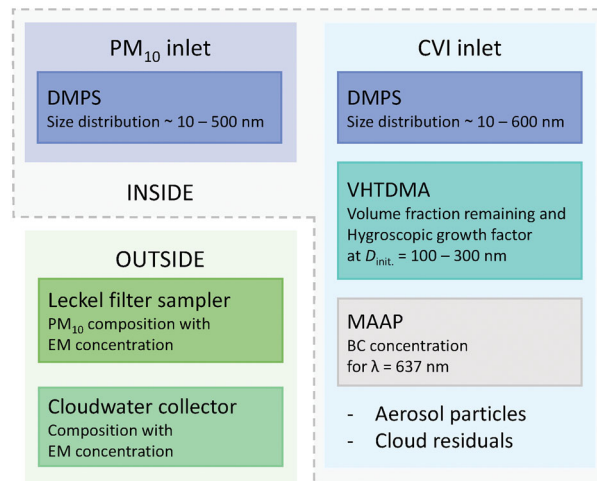


Fig. 1. Inlet system and instrumental setup during the CAEsAR campaign. PM_{10} refers to particulate matter with aerodynamic diameters smaller than $10\mu m$ and CVI to counterflow virtual impactor, which were the two main aerosol inlets. DMPS refers to differential mobility particle sizer, VHTDMA to volatility and hygroscopicity tandem differential mobility analyser, measuring at the initial diameter (D_{init}), MAAP to multi-angle absorption photometer, measuring the black carbon (BC) content at the wavelength (λ), and EM to elemental mass (an estimate of BC derived from EC).

of detail in aerosol size distribution and composition representations that is needed to reproduce the ability of aerosol particles to interact with clouds at a remote boreal site like Mt. Åreskutan.

2. Method

2.1. The CAEsAR campaign at Mt. Åreskutan

Mount Åreskutan, Sweden ($63^{\circ}26'N$ and $13^{\circ}6'E$), is located in central Scandinavia, surrounded primarily by the boreal vegetation zone with no major cities nearby. It provides an opportunity to study aerosols of various origins as the station is located at an intersection of e.g. marine, boreal, polar and continental air masses (Ogren and Rodhe, 1986; Drewnick et al., 2006; Franke et al., 2017). At an elevation of 1250 m a.s.l., the station is most of the time located within the planetary boundary layer (PBL) but it is frequently encompassed in clouds (Franke et al., 2017). The closest potential source of PM and related precursors is the village of Åre down in the valley (~ 400 m a.s.l.) with approximately 1500 inhabitants during the summer.

The CAEsAR campaign took place at Mt. Åreskutan from 27 June to 10 October 2014 (Franke et al., 2017; Vega et al., 2019). Aerosol particle size distributions of the ambient aerosol and cloud residuals were continually measured during the entire campaign, PM filter samples were collected 27 June–10 October (Franke et al., 2017) and cloud water samples 4 July–12 September (Vega et al., 2019). Additionally, the volatility (8–26 July) and

hygroscopicity (1 August–21 September) of the ambient aerosol particles were measured with a VHTDMA (volatility–hygroscopicity tandem differential mobility analyser) system. Further details of the measurements used in this study are provided below.

2.2. Sampling setup and in-situ measurements

Figure 1 presents an overview of the experimental setup, with the two main aerosol inlets (the CVI [counterflow virtual impactor] with variable cut-off diameters as described below and the PM_{10} inlet with an aerodynamic particle cut-off diameter of $10\mu m$) along with the PM filter (with a cut-off diameter of $10\mu m$) and cloud water samplers. Hereafter, ambient aerosol and cloud residuals refer to atmospheric particulate phases sampled *in-situ* behind the CVI. The material collected on the filters and the cloud water samples were analysed offline in the laboratory, and are referred to as PM and cloud water. This is important to keep in mind since the CVI and PM_{10} inlets have different cut-off sizes and hence collect different parts of the atmospheric aerosol population.

A ground-based CVI (Bretchel Inc., GCVI, model 1205) was used to collect cloud residuals for size distribution measurements and *in-situ* volatility and hygroscopicity analysis. The CVI allows separation of aerosols and cloud elements by their inertia (Noone et al., 1988). In this experiment the aerodynamic particle cut-off diameter was $6.3 \pm 0.8\mu m$ (mean $\pm$ standard deviation) when the CVI was on, hence sampling hydrometeors and aerosol particles larger than this diameter. The measurements

were corrected with a setting-dependent enrichment factor of $EF = 8.5 \pm 1.2$ (see e.g. Shingler et al., 2012). After collection, the hydrometeors were quickly evaporated in the dry particle-free carrier air and transported to various instruments operating downstream of the CVI inlet. The CVI was controlled via a visibility sensor and turned on automatically during periods with visibilities below 1 km. During periods with visibilities above 1 km, the CVI inlet was operated as a normal total aerosol inlet, sampling the majority of the ambient aerosol population.

Size distributions of 10–600 nm ambient aerosol and cloud residual particles were measured with a time resolution of about 6 min using a differential mobility particle sizer (DMPS) located downstream the CVI. The sample flow was dried to relative humidity (RH) = $20.4 \pm 9.6\%$ using a combination of dried pressurised air and Nafion dryers (Perma Pure, model MD-110-12S-4), and brought to charge equilibrium using a Ni-63 source before entering the DMPS. The DMPS consists of a custom-built Vienna-type differential mobility analyser (DMA) operated at RH = $9.8 \pm 2.9\%$ (using Nafion dryers, Perma Pure, model PD-100T-12MSS), and a condensation particle counter (CPC; TSI, model 3010). The ambient aerosol particles and cloud residuals were also characterised for their BC content using a multi-angle absorption photometer (MAAP, Thermo Fisher Scientific Inc., model 5012). The MAAP measures the intensity of attenuated and scattered light (wavelength $\lambda = 637$ nm; Müller et al., 2011) by particles deposited on a glass micro-fibre filter, and derives the equivalent BC (hereafter referred to as BC) mass concentration using a fixed mass absorption coefficient with a time resolution of about 1 min. The ambient aerosol size distributions 10–500 nm were simultaneously sampled through a PM₁₀ inlet with a second DMPS system, with a time resolution of about 10 min (see Franke et al., 2017 for a more detailed description). Size distributions measured with both DMPS systems were corrected for multiple charge effects and diffusion losses using the Particle Loss Calculator developed by von der Weiden et al. (2009). All measurements used in this study are given at ambient conditions.

Particulate matter (PM₁₀) was also collected over intervals of 72 h on micro-quartz fibre filters (Munktell and Filtrak GmbH, model T293, 47 mm, heated at 800 °C for 12 h before sampling) using a low-volume reference sampler (Leckel GmbH, model LVS3 Small Filter Device). The substrates were stored at +4 °C until chemical analysis was performed (Franke et al., 2017). Cloud water samples were collected using a custom-built single-stage Caltech Active Strand Cloudwater Collector (see e.g. Demoz et al., 1996; Vega et al., 2019). At RH > 80%, a fan was turned on causing a flow through the system trapping cloud droplets on Teflon strings through inertial

impaction. The cloud droplets were then collected in pre-cleaned glass bottles (Vega et al., 2019), and the collected cloud water was further filtered into glass bottles through micro-quartz fibre filters and stored at −20 °C until chemical analysis. The sampling periods varied between 23 and 395 h depending on the amount of collected water.

2.3. Chemical analysis of PM and cloud water samples

The chemical composition of the PM₁₀ filter samples was characterised using a combination of a thermo-optical transmission (TOT) method (Sunset Laboratory B.V, see Birch and Cary, 1996; Wallén et al., 2010 for more detailed descriptions) and ion chromatography (IC, Thermo Scientific, model Dionex ICS-2000) to determine the organic carbon (OC) and elemental carbon (EC) content and inorganic mass (IM, here the sum of the dominant inorganic ions; Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺, Cl[−], NO₃[−], SO₄^{2−}), respectively. The chemical composition measurement and analysis of the PM filters are described in detail by Franke et al. (2017). The PM characterised by the TOT and IC corresponded to about 80% of the total PM₁₀ mass, the rest being likely mineral dust from local sources (Franke et al., 2017).

The cloud water samples were filtrated through micro-quartz fibre filters to separate the water-soluble organic carbon (WSOC) from the water-insoluble organic carbon (WINSOC) and EC. The filtrates were analysed for WSOC using a total OC analyser (Shimadzu, model TOC-LCPH), which determines the non-purgeable organic carbon (NPOC) with infrared gas detection after acidification, sparging and high-temperature catalytic combustion (Campos et al., 2007). The IM (here the sum of the dominant inorganic ions; Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺, Cl[−], NO₃[−], SO₄^{2−}) was analysed using IC (Metrohm, model ProfIC850, Vega et al., 2019). The material left on the filters was considered to solely consist of WINSOC and EC, whose concentrations were determined using the TOT.

The OC and EC concentrations of the PM₁₀ and cloud water samples were converted to total organic mass (OM) and elemental mass (EM) (the latter of which is an estimate of BC based on the EC concentration) and added to IM to determine the total analysed mass and the corresponding mass fractions of the analysed species. Concentrations were multiplied with the following conversion factors to account for atoms other than carbon, where water-soluble organic mass (WSOM) was assumed to contain more heteroatoms than water-insoluble organic mass (WINSOM): $EM = 1.05 \times EC$, $WINSOM = 1.3 \times WINSOC$, $TOM = 1.8 \times TOC$ and $WSOM =$

2.1 $\times$ WSOC (Turpin and Lim, 2001; Franke et al., 2017). The EM concentration determined from the chemical analysis might be representative of somewhat different material than the BC measured using the MAAP which can, for instance, include also non-elemental absorbing material (Andreae and Gelencser, 2006).

2.4. Volatility and hygroscopicity tandem DMA

The tandem differential mobility analyser (TDMA, first introduced by Liu et al., 1978), is a commonly used technique for measuring a change in particle size due to physical or chemical processes. The custom-built TDMA used in this work combines evaporation and humidification to characterise particle volatility and hygroscopicity (VHTDMA, see e.g. Tritscher et al., 2011) and was measuring ambient aerosols and cloud residuals downstream of the CVI (see Fig. 1). Before the sample flow entered the VHTDMA system, the particles were brought into charge equilibrium using a Ni-63 source. The first DMA selected a monodisperse aerosol at $RH = 11.7 \pm 2.7\%$ (using Nafion driers, Perma Pure, Model PD-100T-12MSS), with a time resolution of 12 min and the median electrical mobility diameter set to either 100, 200 and 300 nm, hereafter referred to as D_{100} , D_{200} , D_{300} , respectively. The monodisperse aerosol was then either heated to $300 \pm 3^\circ\text{C}$ in a 30 cm long custom-built thermodenuder (TD) with a residence time of 1.6 s, or humidified to $RH = 80\text{--}95\%$ using a custom-built humidifier combining Gore-tex tubing and Nafion driers (Perma Pure, model PD-100T-12MSS). The resulting size distribution was measured using a second DMPS system (one for volatility and one for hygroscopicity each). From the change in particle diameter, distributions of the aerosol volume fraction remaining (VFR) or hygroscopic growth factor (GF) were obtained as:

$$\text{VFR}(D, T, D_{\text{init}}) = \frac{D(T)^3}{D_{\text{init}}^3} \quad (1)$$

$$\text{GF}(D, RH, D_{\text{init}}) = \frac{D(RH)}{D_{\text{init}}} \quad (2)$$

where D_{init} is the initial diameter, and $D(T)$ and $D(RH)$ are the measured and humidified particle diameters. The RH in the HTDMA was calibrated using ammonium sulphate (AS) particles (Topping et al., 2005). The geometric mean mode diameters of the heated and humidified size distributions were estimated by using a bimodal lognormal fit function, and used for the VFR and GF calculations as values representative of the whole heated or humidified size distribution.

Quantitative estimates of the volatility of the PM were obtained using a kinetic model that simulates the evaporation of monodisperse aerosol particles in a TD (Riipinen

et al., 2010; Häkkinen et al., 2012; Hong et al., 2017). The analysed PM and cloud water composition along with the initial particle diameters D_{100} , D_{200} and D_{300} were used as the model inputs. The saturation concentration c^* (in $\mu\text{g m}^{-3}$) of the organic fraction was then estimated by matching the measured and calculated VFR, assuming AS to represent the inorganic components present in the mixture (see Franke et al., 2017) with its c^* estimated in the same manner as in Hong et al. (2017). EM was assumed to be completely non-volatile.

The measured GF was used to determine the hygroscopicity parameter κ (Petters and Kreidenweis, 2007):

$$\kappa = \frac{(\text{GF}^3 - 1)(1 - S)}{S} \exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D_d}\right) \quad (3)$$

where $\sigma_{s/a}$ is the surface tension of the surface/air interface, M_w is the molecular weight of water, R is the universal gas constant, T is the temperature, ρ_w is the density of water, D_d is the droplet diameter and saturation ratio $S = RH/100\%$. The exponential Kelvin term can be omitted for diameters larger than about 100 nm and was not included in the present analysis. Using the determined κ values, the HTDMA scans (with $RH = 80\text{--}95\%$) were then converted back to $RH = 90\%$ for comparisons. The hygroscopicity of the PM and cloud residuals was also estimated using the analysed chemical composition of the PM and cloud water samples. The total hygroscopicity was estimated for each sample as

$$\kappa = \sum_i \varepsilon_i \kappa_i \quad (4)$$

where ε_i and κ_i are the mass fraction and hygroscopicity parameter of each chemical component i . The IM fraction of aerosol particle- and cloud water samples was dominated by AS, so $\kappa_{\text{AS}} = 0.53$ was used to represent the IM hygroscopicity parameter (Franke et al., 2017). The OM and EM were represented by $\kappa_{\text{org.}} = 0.01\text{--}0.3$ and $\kappa_{\text{EM}} = 0$, respectively (Petters and Kreidenweis, 2007).

3. Results and discussion

3.1. Physical and chemical properties of aerosol particles, PM and cloud water during the CAEsAR campaign

An overview of the physical and chemical properties of the aerosol particles and cloud water during the CAEsAR campaign is presented in Fig. 2, together with information on when the station was engulfed in clouds as well as the data availability from the VHTDMA. The total particle number concentrations for particles with diameter above 10 nm were $342\text{--}817\text{ cm}^{-3}$ (quartiles) with a median concentration of 584 cm^{-3} . The size distributions generally consisted of accumulation and/or Aitken modes,

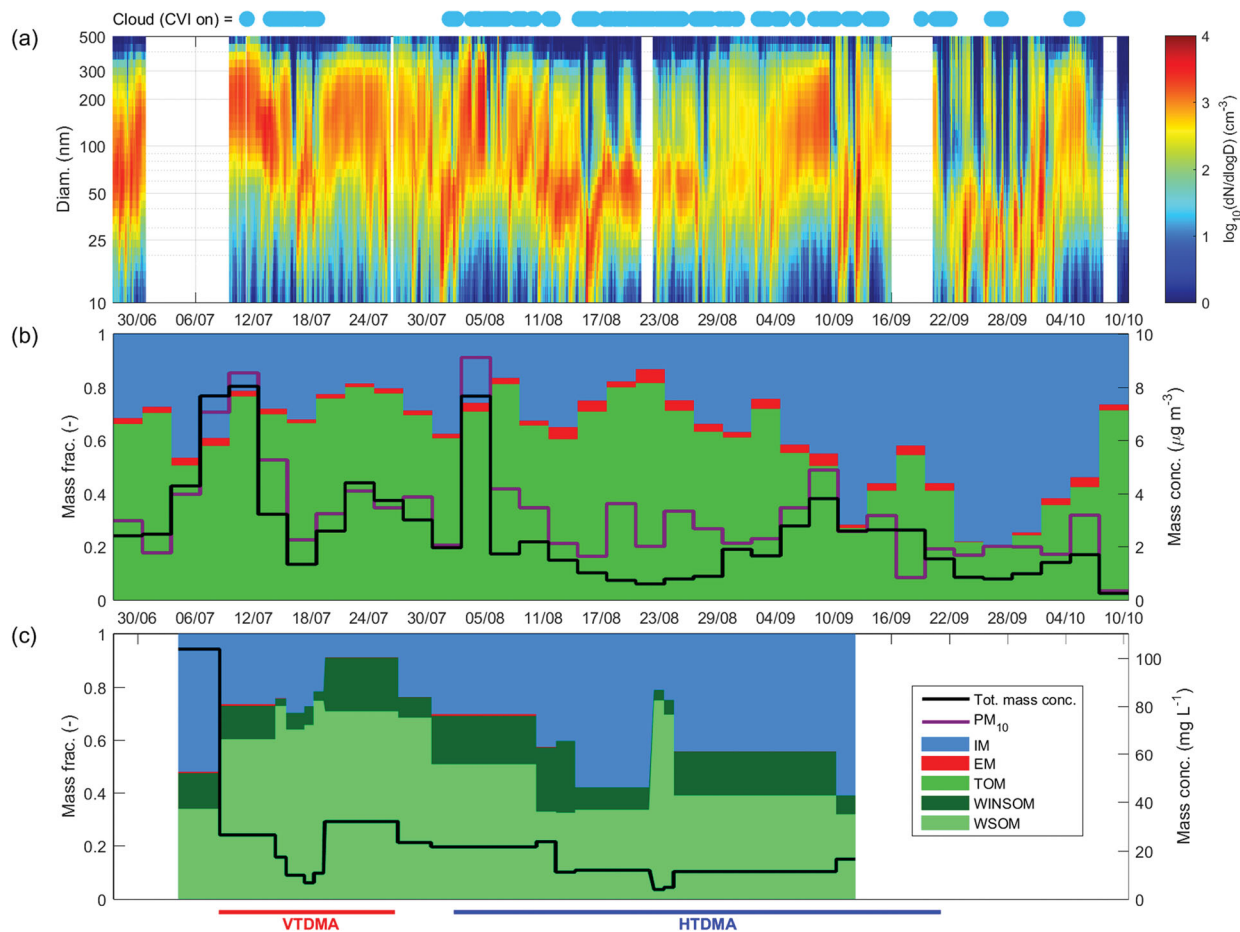


Fig. 2. Overview of the ambient particle size distribution and chemical composition of PM_{10} and cloud water during the CAEsAR campaign. (a) Ambient size distribution measured behind the PM_{10} inlet; (b) and (c) the chemical composition of the analysed fraction of PM_{10} (indicated by the black lines, see below) and cloud water, respectively. The analysed chemical composition is comprised of total organic mass (TOM, with water-soluble and water-insoluble OM for the liquid phase), elemental mass (EM) and inorganic mass (IM). The black lines represent the total mass concentrations inferred from the sum of analysed chemical species, and the purple line the total (sub- $10\text{ }\mu\text{m}$) PM mass inferred from the particle size distribution measurements assuming a particle density of 1500 kg m^{-3} . Blue circles above panel (a) mark the times when the station engulfed in cloud and the CVI inlet was on. The red and blue lines below panel (c) mark the times when the VHTDMA was running in volatility and hygroscopicity mode, respectively.

with occasions of nucleation mode linked to new particle formation (NPF) events (on e.g. 17 August, see Fig. 2a).

The average total PM concentration analysed from the filter samples during the CAeSAR campaign was $2.5 \pm 1.9\text{ }\mu\text{g m}^{-3}$, and OM dominated the aerosol composition with the exception of the period at the end of the campaign when IM was a major aerosol component (Fig. 2b, Table 1). Franke et al. (2017) used back trajectories to identify several pollution events during which air masses arrived from central Europe, such as 3–12 July. The second highest mass concentration measured during the campaign, 2–5 August, originated from a major wildfire outbreak in the county of Västmanland (Lidskog and Sjödin, 2016). During 22–28 September, the air masses originated over the Atlantic ocean, bringing emissions

from the degassing of the Bardarbunga volcano on Iceland (Grahn et al., 2015) and coinciding with a dominant Aitken mode (Fig. 2a) and distinct NPF events as a result of the increased sulphuric acid concentrations (Olenius et al., 2018).

The cloud water composition follows the temporal variation of the analysed PM composition. Overall, there is little difference in the bulk chemical composition between PM and cloud water (Fig. 2 and Table 1), in line with earlier studies at Mt. Åreskutan (Drewnick et al., 2006), except for EM, which is enriched in the PM. This is in agreement with the general low hygroscopicity of EM (Liu et al., 2013), but could also indicate an enrichment of EC in the Aitken mode. The small differences in the chemical composition indicate that (a) the average

Table 1. Mean chemical composition ($\pm$ standard deviation) of PM₁₀ and cloud water, based on 37 and 16 samples collected during 2520 and 1682 h, respectively.

Aerosol particles	TOM		EM	IM
Conc. ($\mu\text{g m}^{-3}$)	1.56 ± 1.40		0.07 ± 0.06	0.88 ± 0.64
Mass frac. (–)	0.62		0.03	0.35
Cloud water	WSOM	WINSOM	EM	IM
Conc. (mg L^{-1})	10.20 ± 8.46	2.80 ± 3.46	0.06 ± 0.12	7.87 ± 12.23
Mass frac. (–)	0.49	0.13	<0.01	0.38

aerosol particle chemical composition represents also the average chemical composition of the cloud residuals, and therefore is also related to the composition of particles acting as CCN; (b) most of the analysed particulate mass can be taken up and scavenged by clouds and thereafter potentially also deposited by precipitation. The similarity of the chemical signature of the cloud water and the ambient particles is most likely linked to the remote nature of the measurement site and hence the aerosol being relatively aged and therefore e.g. subject to previous cloud processing.

Interestingly, WINSOM is present in a significant proportion in the cloud water (Table 1), indicating that even compounds with extremely low water solubility can enter the cloud phase. This observation could be explained by recent results on phase separation behaviour (Rastak et al., 2017) and surface activity (e.g. Ruehl et al., 2016) of secondary organic aerosol (SOA) from monoterpene oxidation, which show that compounds of low solubility can be present on the droplet surfaces, hence lowering the surface tension and enhancing CCN activation (e.g. Ruehl et al., 2016; Ovadnevaite et al., 2017). Monoterpene oxidation products are expected to be the dominant SOA compounds present at the Åre station (Tunved et al., 2006). In general, the organic fraction can be deemed representative of a boreal background station, albeit with influence from anthropogenic activities, marine air and even forest fires and volcanic emissions in the overall chemical composition (Jimenez et al., 2009; Grahn et al., 2015; Lidskog and Sjödin, 2016; Hong et al., 2017).

3.2. Aerosol particle and cloud residual number size distributions

The change in the ambient aerosol size distributions as a result of presence of clouds at the station during 8 July–22 September is presented in Fig. 3. The figure also includes the size distribution of cloud residuals, based on in total 197 h of in-cloud measurements behind the CVI.

The overall median size distribution (the black dotted distribution in Fig. 3) was generally monodisperse with the mode around 100 nm, based on a total of 823 h

sampling time (8232 DMPS scans). Before the cloud events, the aerosol particle size distribution (green line in Fig. 3a) resembled the average ambient aerosol particle size distribution (dotted lines in Fig. 3) with also comparable total number concentration of particles. After the cloud events, the ambient aerosol size distribution changed shape towards a bimodal distribution with an Aitken mode around 50 nm and an accumulation mode around 100 nm, in line with the expected size dependence of CCN activation and previous measurements at Mt. Åreskutan (Drewnick et al., 2006). The appearance of the distinct Aitken mode after cloud cover may, however, also be related to the ability of clouds to clean the air from larger particles and hence enhance the effect of NPF along the trajectory of the air mass arriving at the station. As expected for size-limited CCN activation, the measured size distribution of the cloud residuals is shifted towards larger particle sizes as compared with the average ambient distribution (Fig. 3c). The results are qualitatively consistent with previous literature reporting measurements of aerosol particle size distributions in- and out-of-cloud at a number of European background sites (e.g. Ditas et al., 2012; Hammer et al., 2014; Kruger et al., 2014). While these studies have investigated interstitial aerosol instead of direct measurements of cloud residuals, they also show the enrichment of smaller particles in the interstitial aerosol as compared with the overall particle population, and report average CCN activation diameters between roughly 50–150 nm depending on conditions – which is also generally consistent with our observed cloud residual size distributions (see Fig. 3c). We observe, however, a small contribution of very small (<50 nm in diameter) Aitken mode particles in the cloud residual size distribution. Aitken-mode particles within cloud residuals have been observed previously by e.g. Schwarzenboeck et al. (2000) and are also theoretically confirmed to be plausible CCN at low particle concentrations or high updrafts (e.g. G  r  my et al., 2000; Korhonen et al., 2008). At Mt Åreskutan, Targino et al. (2007) also previously observed cloud residuals smaller than 25 nm which were believed to originate from biogenic organic aerosol sources.

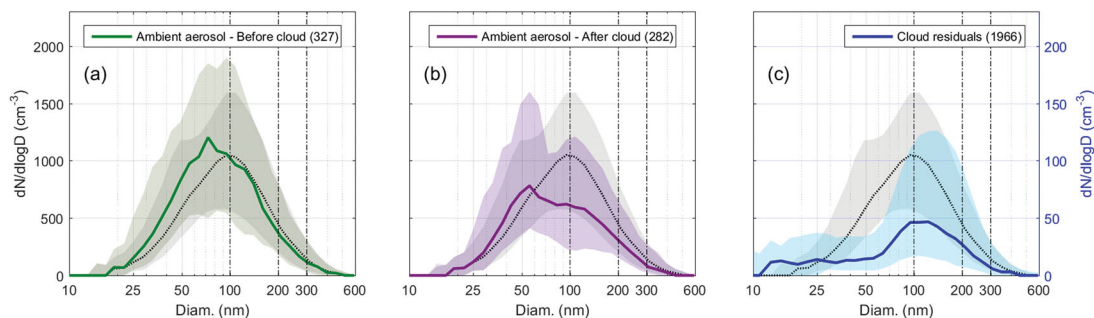


Fig. 3. Median size distributions, with shaded areas presenting the quartiles, of the ambient aerosol (a) 2 h before and (b) 2 h after cloud events together with (c) the median size distribution of the cloud residuals (rightmost y-axis, marked in blue) measured behind the CVI. The overall median ambient aerosol particle size distribution is presented as the dotted line in all three panels. Numbers in parentheses mark the number of DMPS scans included in each median and the black dash-dotted lines mark the diameters analysed in the VHTDMA.

3.3. Volatility of ambient aerosol particles and cloud residuals

The temporal evolution of the volatility of ambient aerosols and cloud residuals is presented in Fig. 4. The VFR distributions for D_{100} , D_{200} , D_{300} (Fig. 4a–c) generally displayed a monomodal shape, indicating internal mixing of the particles. The median VFR values corresponding to the fitted mode diameters were 0.036–0.053 for the ambient aerosol populations and 0.036–0.046 for the cloud residuals (Table 2). VFR increased, hence volatility decreased, with increasing D_{init} for the ambient aerosols. In contrast, the average VFR of the cloud residuals slightly decreased for increasing D_{init} . Both of these trends, however, are within the standard deviations of the recorded VFR values. The temporal variation in the VFR of the ambient aerosols was relatively small (see black lines in Fig. 4), and consistent among the three diameters. The VFR never dropped below 0.01 and exhibited less variability with increasing particle size, indicating some contribution from essentially non-volatile material (e.g. BC, Fig. 4d) throughout the campaign. One clear bimodal event was identified in the early morning on 13 July. The event appeared simultaneously for all D_{init} and coincided with a brief bimodal event in the ambient size distribution (not visible in Fig. 2a due to the time resolution), indicating externally mixed aerosols due to a shift in the local wind direction. The observed values of the VFR are in a reasonable agreement with the studies by Häkkinen et al. (2012) and Hong et al. (2014), which report a VFR of about 0.05–0.09 for boreal forest summer aerosol for a comparable BC fraction of about 0.04 but somewhat lower TD temperature of 280 °C.

In general, only few cloud events took place at the measuring site during the month of July. However, one long-lasting stratiform cloud event occurred on the 14 July. During 22 h, the station was covered in clouds the measured VFR of the cloud residuals decreased simultaneously for all D_{init} , by

52%, 50% and 59% for D_{100} , D_{200} and D_{300} , respectively. There are several potential explanations for the increasing volatility for the cloud residuals during this cloud event. The most likely explanation is the decreasing fraction of BC in the cloud residuals during the cloud event, coinciding with the drop in the VFR. Other potential explanations are increased evaporation rates due to fragmentation as a result of heterogeneous chemistry in the cloud droplet (Romonosky et al., 2017), or co-condensation of semi-volatile vapours during the evolution of the cloud (Topping et al., 2013), or that the more volatile fraction is more efficiently taken up by the clouds due to e.g. size-dependent chemical composition. It is unclear however why this would result in the time-dependent change in the volatility instead of a consistent difference between cloud residuals and ambient aerosols.

Figure 5 presents the VFR calculated from the PM composition as a function of D_{init} and fitted c^* (see Section 2.4) together with the measured VFR. The measured and calculated VFR are systematically higher than the EM mass fraction throughout the period, indicating that while EM is an important component explaining the fraction remaining after the TD, it does not account for all of the non-volatile material. Since the inorganics in the submicron fraction are expected to evaporate at temperatures lower than used in this experiment (e.g. ammonium nitrate and AS are reported to fully evaporate at 60 and 180 °C, respectively, Villani et al., 2007), the remaining part is assigned to organics. The temporal evolution of the VFR predicted from the PM composition captures the measured decreasing trend during the first half of the period remarkably well, while it slightly overestimates VFR in the end of the period, indicating that the overall volatility of the organic fraction decreased somewhat over the course of the measurement period. The organic saturation concentrations corresponding to the measured VFR were $c^*(D_{100}) = 1.9 \times 10^{-4} \mu\text{g m}^{-3}$, $c^*(D_{200}) = 4.1 \times 10^{-4} \mu\text{g m}^{-3}$ and $c^*(D_{300}) = 6.5 \times 10^{-4} \mu\text{g m}^{-3}$. These values correspond to

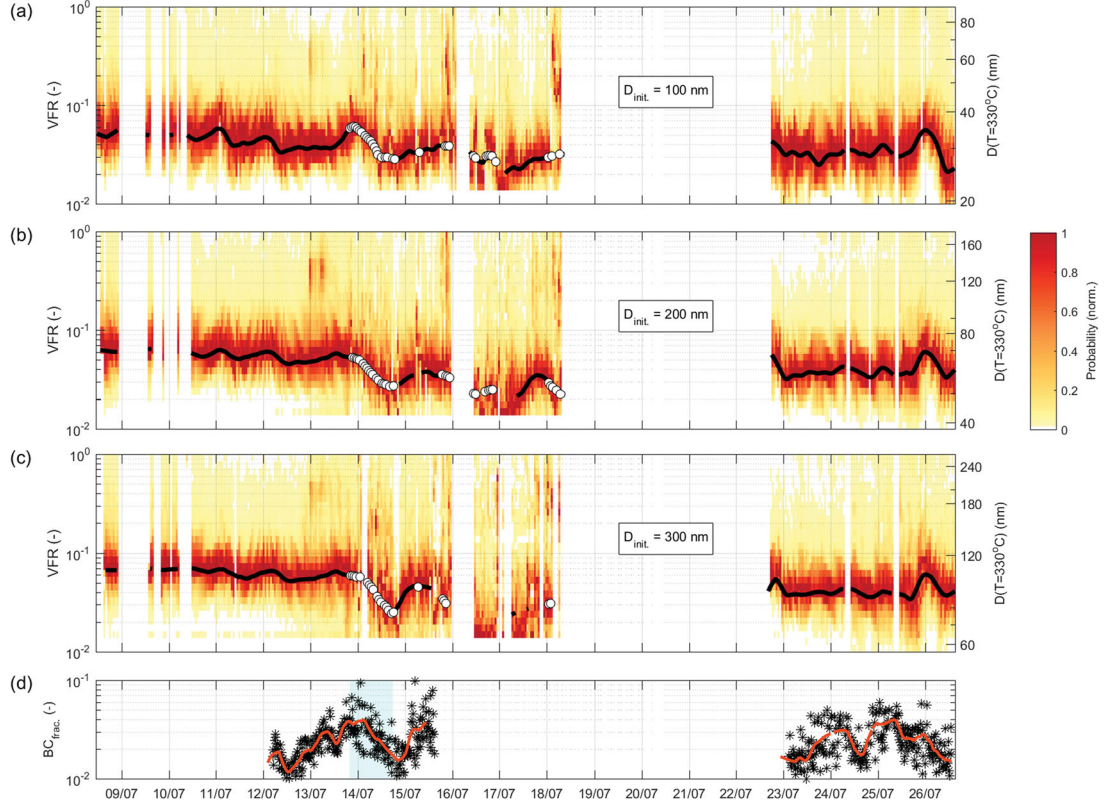


Fig. 4. Measured VFR distributions as a function of time and D_{init} . (a–c) together with the (d) BC mass fraction from the MAAP. The black lines represent the median VFR and the white circles mark cloud events (CVI in operation, VFR of cloud residuals). BC fraction of the cloud residuals during the longer cloud event are marked with a blue rectangle in panel d.

Table 2. Mean and median measured VFR, together with the standard deviation and quartiles, of the ambient aerosols and cloud residuals, with total sampling times of 194 and 33 h, together with the estimated organic c^* ($\mu\text{g m}^{-3}$) and the predicted VFR of the PM, based on 7 filter samples.

	Ambient aerosols					Cloud residuals				
	VFR _{meas.} $\times 10^2$ (–)					VFR _{meas.} $\times 10^2$ (–)				
	Mean	Std.	25%	Median	75%	Mean	Std.	25%	Median	75%
D_{100}	3.7	1.0	2.9	3.6	4.4	4.2	1.5	3.1	4.0	5.1
D_{200}	4.5	1.2	3.5	4.6	5.5	3.2	1.1	2.4	2.9	3.9
D_{300}	5.1	1.2	3.9	5.3	6.1	3.9	1.4	1.4	3.3	5.1
	VFR _{PM} $\times 10^{-2}$ (–)					c^* ($\mu\text{g m}^{-3}$)				
	Mean	Std.	25%	Median	75%					
D_{100}	3.9	0.5	3.9	3.9	4.4	1.9×10^{-4}				
D_{200}	4.5	0.6	4.2	4.5	5.1	4.1×10^{-4}				
D_{300}	5.1	0.8	4.6	5.3	5.9	6.5×10^{-4}				

those of extremely low volatile organic compounds (ELVOC) and low volatile organic compounds (LVOC), expected to originate from boreal forests (Mohr et al., 2019). During 22 h, cloud event on 14 July the change in the VFR was equal to, or even smaller than, the change in BC – suggesting that the observed trend in VFR could result from a corresponding trend in BC.

3.4. Hygroscopicity of ambient aerosol particles and cloud residuals

The temporal evolution of the hygroscopic GF of the ambient aerosols and cloud residuals for D_{100} , D_{200} and D_{300} is presented in Fig. 6, with the mean and median GF and κ values given in Table 3. The GF distributions were

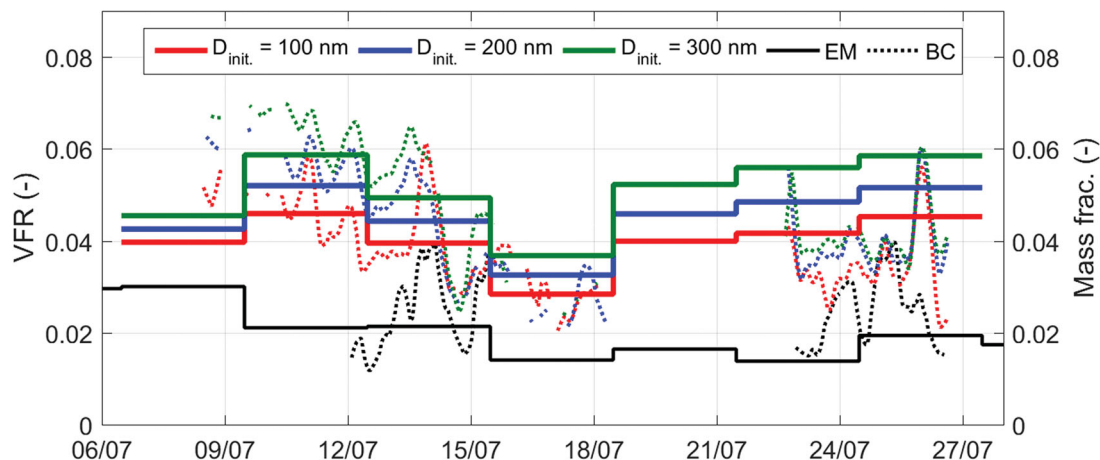


Fig. 5. Predicted VFR as a function of time and D_{init} . Dashed lines represent the measured VFR as a function of time and D_{init} . The black line illustrates the EM mass fraction in the PM_{10} and the dashed black line the BC mass fraction behind the CVI.

generally monomodal, indicating internally mixed aerosol populations, with median ambient aerosol GF and corresponding κ value ranging 1.35–1.47 and 0.16–0.24. The hygroscopicity of the cloud residuals falls within the same GF- and κ -ranges (Table 3). The hygroscopicity is slightly higher in cloud residuals compared to the ambient aerosols for D_{100} , but lower in cloud residuals for D_{200} and identical for D_{300} (see Table 3). These results could support the idea that chemical composition and hygroscopicity play a more important role for the activation of smaller particles as compared with the more CCN-active larger particles (Fig. 3 and e.g. Dusek et al., 2006). However, all values are within the standard deviation for both the measured GF and κ values, indicating the differences between the cloud residuals and ambient aerosol particles to be small – much like the differences between the chemical composition of the PM and cloud water (Table 1).

The overall temporal evolution of GF reveals no clear trends, apart from a few specific events. For instance, the GF was lower than average (around 1.2 for all sizes) on 7 August, when the station was influenced by the fire plume, and higher than average (around 1.5–1.6) on 10–16 September, when IM concentrations increased as a result of the volcanic emissions.

The average κ values of the ambient aerosols, $\kappa(D_{100}) = 0.18$, $\kappa(D_{200}) = 0.26$ and $\kappa(D_{300}) = 0.24$ (see Table 3), agree relatively well with a study in the boreal forest in Hyytiälä, Finland, performed by Hong et al. (2014) who report κ values of 0.17, 0.28 and 0.22 for 70, 102 and 203 nm. The results are also at least qualitatively consistent with the study by Väisänen et al. (2016), who infer the hygroscopicity of the cloud residuals based on the difference between the hygroscopicity of ambient aerosol (out-of-cloud) and interstitial aerosol at a semi-urban site at Puijo, Eastern Finland. While we observe primarily monomodal aerosol

size and hygroscopicity distributions, Väisänen et al. (2016) report the presence of a more and a less hygroscopic mode, assigning the less hygroscopic particles to local anthropogenic influence. While our aerosol is somewhat less hygroscopic (with median κ values of 0.16–0.24 for 100–200 nm particles, see Table 3) than the hygroscopic mode observed by Väisänen et al. (2016) who report typical κ values of about 0.3–0.4 for 120–150 nm particles, both studies observe only minor differences in the hygroscopicity of ambient aerosols and cloud residuals.

Figure 7 presents the time series of κ values predicted from the PM and cloud water chemical composition (Equation (4)) together with the κ values calculated from the measured GF(D_{init}) of the ambient aerosol and cloud residuals. The measured κ values are independent of D_{init} , at the beginning of the period, indicating relatively homogeneous hygroscopicity with particle size. After the 17 August, the hygroscopicity becomes different for D_{100} resulting in lower κ values, lasting for the rest of the period. Overall, the κ values calculated from the PM composition capture the trend in the measured κ values rather well, hence corroborating the assumption that the organic fraction is representative of aged boreal forest SOA – in line with what was observed with the volatility as well. The chemical composition of the cloud water resulted in slightly higher κ values compared to the values derived from the PM. This is due to the lower EM but mainly due to higher IM fractions compared to the aerosol particles (see Table 1). On the 14 August, the predicted κ values of the particle samples decreased while the predicted κ value of the cloud sample remained high, suggesting that the more hygroscopic material (IM) was scavenged by the cloud leaving the less hygroscopic fraction (OM and EM) in the particle phase. This was a period of persistent cloud cover at the measurement station (see Figs. 2b,c).

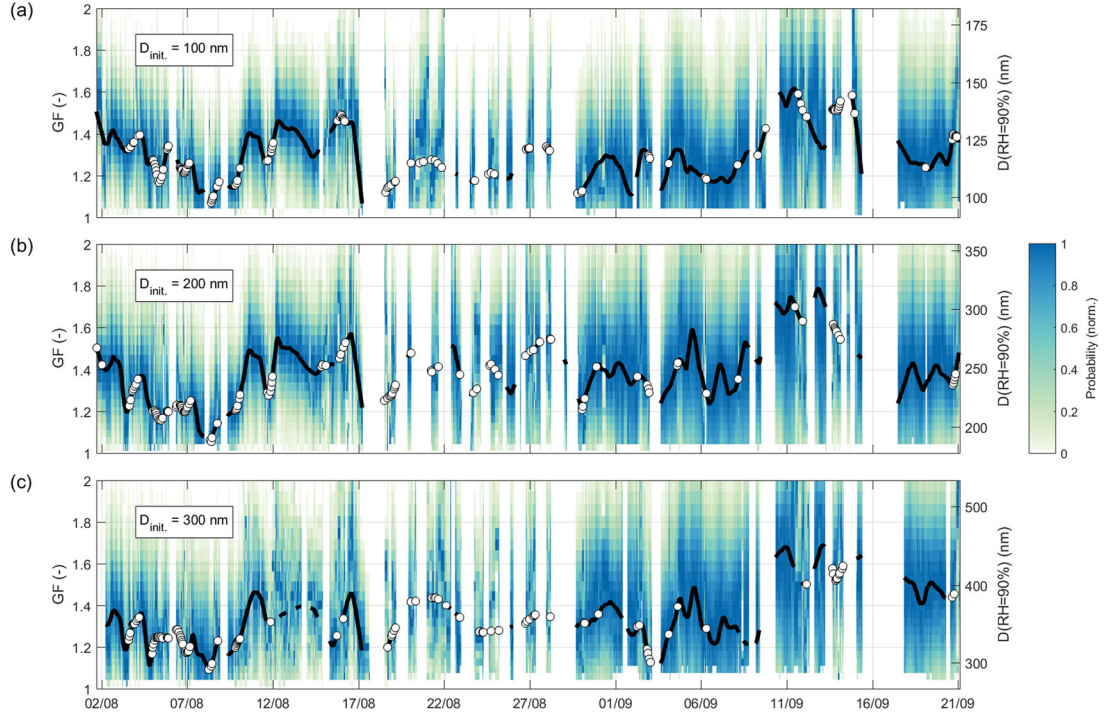


Fig. 6. Measured hygroscopic GF as a function of time and D_{init} . (a–c). The black line represents the median GF and the white circles mark the cloud events (CVI in operation, GF of cloud residuals).

Table 3. Mean and median measured GF and corresponding hygroscopicity parameter, κ , (together with the standard deviation and quartiles) for ambient aerosols and cloud residuals, with total sampling times of 235 and 87 h, respectively, presented together with the predicted κ values of the aerosol particles and cloud water, based on 19 filter samples and 7 water samples.

	Ambient aerosols					Cloud residuals				
	GF (–)					GF (–)				
	Mean	Std.	25%	Median	75%	Mean	Std.	25%	Median	75%
D_{100}	1.35	0.18	1.22	1.35	1.47	1.39	0.19	1.27	1.38	1.49
D_{200}	1.47	0.19	1.33	1.47	1.59	1.42	0.20	1.27	1.40	1.55
D_{300}	1.43	0.23	1.27	1.40	1.58	1.43	0.23	1.28	1.40	1.52
$\kappa_{\text{meas.}} (-)$										
	Mean	Std.	25%	Median	75%	Mean	Std.	25%	Median	75%
D_{100}	0.18	0.13	0.09	0.16	0.24	0.20	0.13	0.12	0.18	0.25
D_{200}	0.26	0.15	0.15	0.24	0.34	0.23	0.15	0.12	0.19	0.30
D_{300}	0.24	0.21	0.11	0.19	0.32	0.24	0.23	0.12	0.20	0.28
$\kappa_{\text{pred.}} (-)$										
	Mean	Std.	25%	Median	75%	Mean	Std.	25%	Median	75%
	0.20	0.08	0.14	0.19	0.24	0.22	0.08	0.15	0.23	0.29

3.5. Comparing the observed VFR and κ values to those predicted from PM and cloud water composition

A comparison of measured VFR and κ values with those predicted from the PM (for VFR and κ) and cloud water

(for κ only) composition (Table 1) are presented in Fig. 8. The measured κ value was derived from the observed GF. A weak to intermediate linear correlation between predicted and measured volatility and hygroscopicity is observed (cf. Figs. 4 and 7), with $R^2 = 0.27$ for VFR, R^2

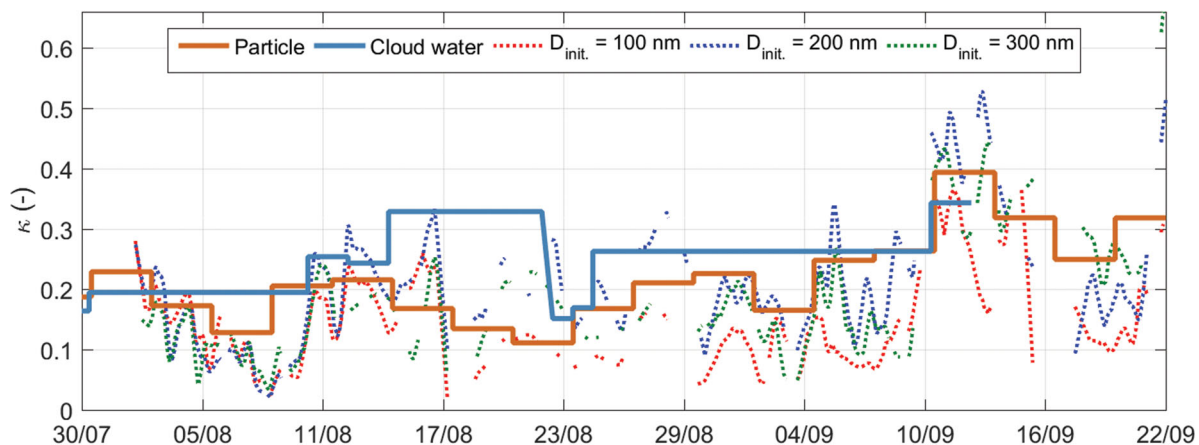


Fig. 7. Hygroscopicity parameter, κ , determined from measured GF as a function time and D_{init} . (red, blue and green dashed lines for D_{100} , D_{200} and D_{300} , respectively) together with the κ values predicted with Equation (4) based on the chemical composition of the PM_{10} and cloud water samples (orange and grey solid lines, respectively).

$= 0.39$ for κ (ambient aerosol vs. PM) and $R^2 = 0.60$ for κ (cloud residuals vs. cloud water).

The volatility displayed a systematic change in predicted VFR with time (Figs. 5 and 8a), changing from over- to underestimation in the volatility from the beginning to the end of the period, suggesting a change in the chemical composition. However, if this change was to be explained by a changing volatility of the organic PM fraction, the corresponding difference turns out to be $c^*(D_{100}) = 1.7\text{--}2.0 \times 10^{-4} \mu\text{g m}^{-3}$, $c^*(D_{200}) = 3.6\text{--}4.4 \times 10^{-4} \mu\text{g m}^{-3}$, $c^*(D_{300}) = 5.6\text{--}7.1 \times 10^{-4} \mu\text{g m}^{-3}$, which still remains in the ELVOC range (vertical error bars in Fig. 8a). No significant changes in the IM composition were evident either (see Franke et al., 2017).

Figure 8b reveals a general overestimation in the hygroscopicity derived from the chemical composition as compared with the measured κ value. The most plausible explanation to these discrepancies is probably an uncertainty in the pure component hygroscopicity and the different time resolution between the chemical sampling and the VHTDMA measurement. The least well-known component of the PM composition is the organic matter, which can contain species with highly varying water solubility. The expected κ_{org} at Mt. Åreskutan could range from about 0.05 (corresponding to e.g. monoterpene SOA in sub-saturated conditions) up to as high as 0.2 (see e.g. Mikhailov et al., 2013; Pajunoja et al., 2015; Rastak et al., 2017). However, uncertainty in κ_{org} is not likely to explain the overprediction – as the κ_{org} values required to match the observations would be well below 0.05 assuming the composition of the PM. Uncertainty in the IM hygroscopicity is also an unlikely explanation to the missing low-hygroscopicity material, as the IM throughout the campaign was dominated by AS (Franke

et al., 2017), whose hygroscopicity is well known. A plausible explanation for the missing low-hygroscopicity material could be an enrichment of the EM (or the OM) in the submicron particle range as compared with the larger particles, therefore resulting in larger insoluble mass fractions at the size range covered by the VHTDMA than in the bulk sample. Another potential explanation could be mineral dust, which has been shown to likely to contribute to the overall undetermined fraction of the total particulate composition (Koehler et al., 2009; Franke et al., 2017).

As a summary, the general agreement between the measured VFR and κ and the values derived from bulk chemical composition measurements is promising. There is, however, still room for improvement in (1) understanding the exact properties of the various chemical components; (2) measuring the chemical composition of the aerosol particles and cloud hydrometeors – especially on time resolutions higher than achievable here.

4. Summary and conclusions

The size distributions, volatility and hygroscopicity of ambient aerosol particles and cloud residuals have been characterised as part of the CAEsAR campaign, performed at Mt. Åreskutan during summer to early autumn in 2014. These observations were compared with chemical analysis of PM filter samples and cloud water collected at the same site. Located in central Scandinavia, the measurement site is a good representation of the remote boreal background, albeit with some influence of airmasses of various origins. This was manifested in e.g. organic compounds dominating the chemical composition and a monomodal average size, volatility and hygroscopicity

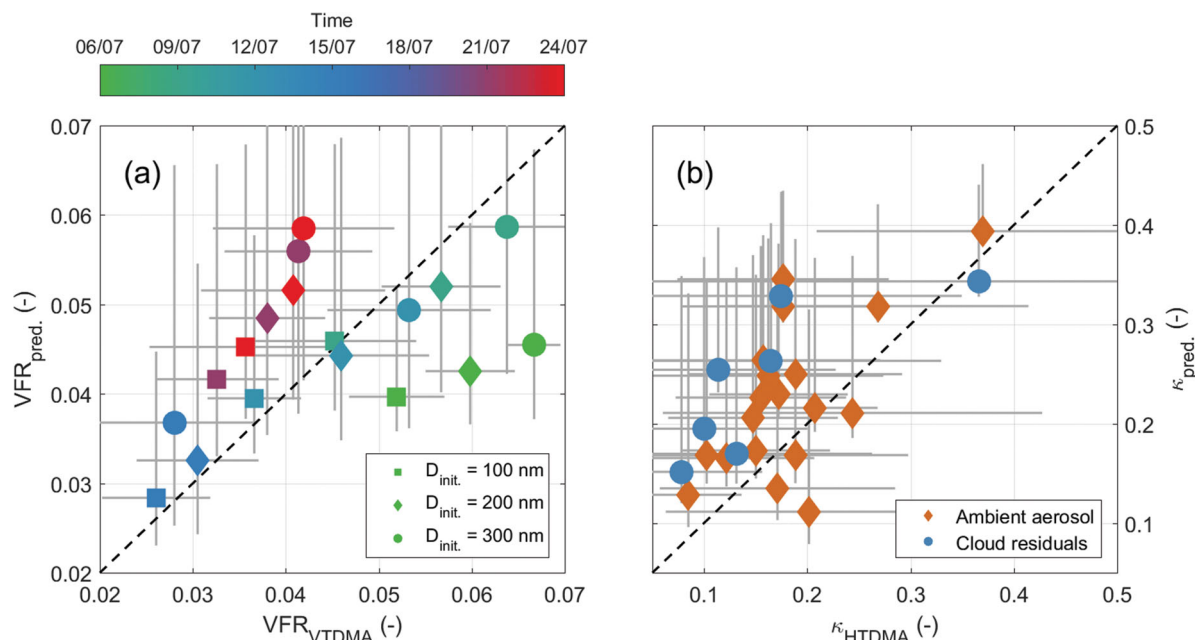


Fig. 8. (a) Predicted versus measured VFR, separated by $D_{\text{init.}}$ and coloured according to time of observation (see legend), where the error bars present the variability in the measurements and uncertainty of the predicted c^* . (b) Predicted versus measurement-based κ value, separated in ambient aerosols and cloud residuals, where the error bars represent the variability of $\kappa_{\text{org.}} = 0.01\text{--}0.3$. Dashed lines display the 1:1 line.

distributions, which were interpreted as a sign of internally mixed aerosol that had been subjected to atmospheric aging. The volatility and hygroscopicity of the organic aerosol fraction were representative of biogenic SOA found in the boreal region.

The station was frequently covered in clouds, which was followed by a shift in the ambient size distributions towards smaller particle sizes, with the larger particles being more efficiently scavenged to cloud droplets. However, also Aitken-mode particles were frequently observed as cloud residuals. The composition of the cloud water, however, was very similar to the composition of the PM mass, apart from a slight EM enrichment in the latter. Interestingly, a significant portion of WINSOC was present in the cloud water, indicating that also compounds with very low water solubility can enter the cloud phase. The average volatility and hygroscopicity of 100–300 nm ambient aerosol particles and cloud residuals were also very similar with only subtle differences, in line with the observed similar compositions. EC could explain a large part of the non-volatile fraction of the ambient aerosol, while the remaining fraction was found to be consistent with ELVOC and LVOC known to be present in the boreal SOA. While a clear effect of the clouds on the aerosol number size distributions was observed, our results do not show indications of the importance of size-dependent chemical composition for CCN activation nor

significant cloud-phase chemical processing at Mt. Åreskutan in the time scales captured.

Our results indicate that in environments with aged homogeneous aerosol such as Mt. Åreskutan, relatively simple approximations of aerosol composition based on the overall aerosol mass and only a few chemical species are sufficient to capture the volatility and hygroscopicity of the particles. Furthermore, the chemical composition of the PM seems to be representative of the chemical composition of the cloud residuals. The number size distribution and the influence of cloud processing on it, however, needs to be represented with more detail to capture the evolution of aerosol particle populations, CCN and eventually cloud droplet numbers. The overall magnitude and trends in volatility and hygroscopicity could be captured relatively well with the simple approach of assuming bulk composition for the whole aerosol population. Higher resolution observations (both temporally but also chemically) of the chemical composition are, however, warranted to investigate processes taking place on shorter time- and smaller size scales. Such future studies might reveal unexpected subtleties in the processes taking place in the aerosol-cloud continuum.

Acknowledgements

We thank the Department of Environmental Science (ACES) at Stockholm University for providing access to

the Åreskutan sampling facility. Lars ‘Lumpan’ Lundberg and the team at Skistar Åre are acknowledged for their extensive support during the CAEsAR campaign. Finally, we thank Birgitta Noone, Zahra Hamzavi, Vera Franke, Matthias Tesche, Sebastian Arnoldt, Samuel Lowe, Therese Gadd, Peggy Achtert, Dan Partridge and Leif Bäcklin for their help in setting up the campaign, collection of the data and fruitful discussions.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

We acknowledge financial support from Knut and Alice Wallenberg foundation (WAF projects AtmoRemove 2015.0162 and CLOUDFORM 2017.0165), Vetenskapsrådet (project 2011-04340), Swiss national science foundation (project P300P2_147776), European Commission (ERC-CoG project INTEGRATE GA N:o 865799 and H2020 project FORCeS GA N:o 821205) and Formas (project 2015-00748).

References

- Andreae, M. O. and Gelencser, A. 2006. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. *Atmos. Chem. Phys.* **6**, 3131–3148. doi:10.5194/acp-6-3131-2006
- Birch, M. E. and Cary, R. A. 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol.* **25**, 221–241. doi:10.1080/02786829608965393
- Campos, M. L. A. M., Nogueira, R. F. P., Dametto, P. R., Francisco, J. G. and Coelho, C. H. 2007. Dissolved organic carbon in rainwater: glassware decontamination and sample preservation and volatile organic carbon. *Atmos. Environ.* **41**, 8924–8931. doi:10.1016/j.atmosenv.2007.08.017
- Demoz, B. B., Collett, J. L. and Daube, B. C. 1996. On the caltech active strand cloudwater collectors. *Atmos. Res.* **41**, 47–62. doi:10.1016/0169-8095(95)00044-5
- Ditas, F., Shaw, R. A., Siebert, H., Simmel, M., Wehner, B. and co-authors. 2012. Aerosols-cloud microphysics-thermodynamics-turbulence: evaluating supersaturation in a marine stratocumulus cloud. *Atmos. Chem. Phys.* **12**, 2459–2468. doi:10.5194/acp-12-2459-2012
- Drewnick, F., Schneider, J., Hings, S. S., Hock, N., Noone, K. and co-authors. 2006. Measurement of ambient, interstitial, and residual aerosol particles on a mountaintop site in central Sweden using an aerosol mass spectrometer and a CVI. *J. Atmos. Chem.* **56**, 1–20. doi:10.1007/s10874-006-9036-8
- Dusek, U., Frank, G. P., Hildebrandt, L., Curtius, J., Schneider, J. and co-authors. 2006. Size matters more than chemistry for cloud-nucleating ability of aerosol particles. *Science* **312**, 1375–1378. doi:10.1126/science.1125261
- Ervens, B. 2015. Modeling the processing of aerosol and trace gases in clouds and fogs. *Chem. Rev.* **115**, 4157–4198. doi:10.1021/cr5005887
- Franke, V., Zieger, P., Wideqvist, U., Navarro, J. C. A., Leck, C. and co-authors. 2017. Chemical composition and source analysis of carbonaceous aerosol particles at a mountaintop site in central Sweden. *Tellus B: Chem. Phys. Meteorol.* **69**, 1353387. doi:10.1080/16000889.2017.1353387
- Gérémy, G., Wobrock, W., Flossmann, A. I., Schwarzenböck, A. and Mertes, S. 2000. A modelling study on the activation of small Aitken-mode aerosol particles during CIME 97. *Tellus B: Chem. Phys. Meteorol.* **52**, 959–979.
- Goldstein, A. H. and Galbally, I. E. 2007. Known and unknown organic constituents in the Earth’s atmosphere. *Environ. Sci. Technol.* **41**, 1514–1521. doi:10.1021/es072476p
- Grahn, H., von Schoenberg, P. and Brännström, N. 2015. What’s that smell? Hydrogen sulphide transport from Bardarbunga to Scandinavia. *J. Volcanol. Geotherm. Res.* **303**, 187–192. doi:10.1016/j.jvolgeores.2015.07.006
- Hammer, E., Bukowiecki, N., Gysel, M., Jurányi, Z., Hoyle, C. R. and co-authors. 2014. Investigation of the effective peak supersaturation for liquid-phase clouds at the high-alpine site Jungfraujoch, Switzerland (3580 m a.s.l.). *Atmos. Chem. Phys.* **14**, 1123–1139. doi:10.5194/acp-14-1123-2014
- Häkkinen, S. A. K., Äijälä, M., Lehtipalo, K., Junninen, H., Backman, J. and co-authors. 2012. Long-term volatility measurements of submicron atmospheric aerosol in Hyytiälä, Finland. *Atmos. Chem. Phys.* **12**, 10771–10786. doi:10.5194/acp-12-10771-2012
- Hao, L., Romakkaniemi, S., Kortelainen, A., Jaatinen, A., Portin, H. and co-authors. 2013. Aerosol chemical composition in cloud events by high resolution time-of-flight aerosol mass spectrometry. *Environ. Sci. Technol.* **47**, 2645–2653. doi:10.1021/es302889w
- Hobbs, P. V. 1993. Chapter 2: Aerosol-cloud interactions. In: *International Geophysics* (ed. P. V. Hobbs). Elsevier, Amsterdam, pp. 33–73.
- Hong, J., Äijälä, M., Häme, S. A. K., Hao, L., Duplissy, J. and co-authors. 2017. Estimates of the organic aerosol volatility in a boreal forest using two independent methods. *Atmos. Chem. Phys.* **17**, 4387–4399. doi:10.5194/acp-17-4387-2017
- Hong, J., Häkkinen, S. A. K., Paramonov, M., Äijälä, M., Hakala, J. and co-authors. 2014. Hygroscopicity, CCN and volatility properties of submicron atmospheric aerosol in a boreal forest environment during the summer of 2010. *Atmos. Chem. Phys.* **14**, 4733–4748. doi:10.5194/acp-14-4733-2014
- IPCC. 2013. *Climate change 2013: the physical science basis, Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK and New York, NY, USA.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q. and co-authors. 2009. Evolution of

- organic aerosols in the atmosphere. *Science* **326**, 1525–1529. doi:10.1126/science.1180353
- Köhler, H. 1936. The nucleus in and the growth of hygroscopic droplets. *Trans. Faraday Soc.* **32**, 1152–1161. doi:10.1039/TF9363201152
- Koehler, K. A., Kreidenweis, S. M., DeMott, P. J., Petters, M. D., Prenni, A. J. and co-authors. 2009. Hygroscopicity and cloud droplet activation of mineral dust aerosol. *Geophys. Res. Lett.* **36**, L08805. doi:10.1029/2009GL037348
- Korhonen, H., Carslaw, K. S., Spracklen, D. V., Ridley, D. A. and Ström, J. 2008. A global model study of processes controlling aerosol size distributions in the Arctic spring and summer. *J. Geophys. Res.* **113**, 1–20.
- Kruger, M. L., Mertes, S., Klimach, T., Cheng, Y. F., Su, H. and co-authors. 2014. Assessment of cloud supersaturation by size-resolved aerosol particle and cloud condensation nuclei (CCN) measurements. *Atmos. Meas. Tech.* **7**, 2615–2629. doi:10.5194/amt-7-2615-2014
- Lidskog, R. and Sjödin, D. 2016. Extreme events and climate change: the post-disaster dynamics of forest fires and forest storms in Sweden. *Scand. J. For. Res.* **31**, 148–155. doi:10.1080/02827581.2015.1113308
- Liu, B. Y. H., Pui, D. Y. H., Whitby, K. T., Kittelson, D. B., Kousaka, Y. and co-authors. 1978. The aerosol mobility chromatograph: a new detector for sulfuric acid aerosols. In: *Sulfur in the Atmosphere – Proceedings of the International Symposium, Dubrovnik, Yugoslavia*, pp. 99–104.
- Liu, D., Allan, J., Whitehead, J., Young, D., Flynn, M. and co-authors. 2013. Ambient black carbon particle hygroscopic properties controlled by mixing state and composition. *Atmos. Chem. Phys.* **13**, 2015–2029. doi:10.5194/acp-13-2015-2013
- Lowe, S. J., Partridge, D. G., Davies, J. F., Wilson, K. R., Topping, D. and co-authors. 2019. Key drivers of cloud response to surface-active organics. *Nat. Commun.* **10**, 5214. doi:10.1038/s41467-019-12982-0
- Mikhailov, E., Vlasenko, S., Rose, D. and Pöschl, U. 2013. Mass-based hygroscopicity parameter interaction model and measurement of atmospheric aerosol water uptake. *Atmos. Chem. Phys.* **13**, 717–740. doi:10.5194/acp-13-717-2013
- Mohr, C., Thornton, J. A., Heitto, A., Lopez-Hilfiker, F. D., Lutz, A. and co-authors. 2019. Molecular identification of organic vapors driving atmospheric nanoparticle growth. *Nat. Commun.* **10**, 4442. doi:10.1038/s41467-019-12473-2
- Müller, T., Henzing, J. S., de Leeuw, G., Wiedensohler, A., Alastuey, A. and co-authors. 2011. Characterization and intercomparison of aerosol absorption photometers: result of two intercomparison workshops. *Atmos. Meas. Tech.* **4**, 245–268. doi:10.5194/amt-4-245-2011
- Noone, K. J., Ogren, J. A., Heintzenberg, J., Charlson, R. J. and Covert, D. S. 1988. Design and calibration of a counterflow virtual impactor for sampling of atmospheric fog and cloud droplets. *Aerosol Sci. Technol.* **8**, 235–244. doi:10.1080/02786828808959186
- Ogren, J. and Rodhe, H. 1986. Measurements of the chemical composition of cloudwater at a clean air site in central Scandinavia. *Tellus B: Chem. Phys. Meteorol.* **38B**, 190–196. doi:10.1111/j.1600-0889.1986.tb00186.x
- Olenius, T., Yli-Juuti, T., Elm, J., Kontkanen, J. and Riipinen, I. 2018. New particle formation and growth. In: *Physical Chemistry of Gas-Liquid Interfaces* (eds. J. Faust and J. House). Elsevier, Amsterdam, pp. 315–352.
- Ovadnevaite, J., Zuend, A., Laaksonen, A., Sanchez, K. J., Roberts, G. and co-authors. 2017. Surface tension prevails over solute effect in organic-influenced cloud droplet activation. *Nature* **546**, 637–641. doi:10.1038/nature22806
- Pajunoja, A., Lambe, A. T., Hakala, J., Rastak, N., Cummings, M. J. and co-authors. 2015. Adsorptive uptake of water by semisolid secondary organic aerosols: water uptake of SOA. *Geophys. Res. Lett.* **42**, 3063–3068. doi:10.1002/2015GL063142
- Petters, M. D. and Kreidenweis, S. M. 2007. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmos. Chem. Phys.* **7**, 1961–1971. doi:10.5194/acp-7-1961-2007
- Rastak, N., Pajunoja, A., Acosta Navarro, J. C., Ma, J., Song, M. and co-authors. 2017. Microphysical explanation of the RH-dependent water affinity of biogenic organic aerosol and its importance for climate. *Geophys. Res. Lett.* **44**, 5167–5177. doi:10.1002/2017GL073056
- Riipinen, I., Pierce, J. R., Donahue, N. M. and Pandis, S. N. 2010. Equilibration time scales of organic aerosol inside thermodenuders: evaporation kinetics versus thermodynamics. *Atmos. Environ.* **44**, 597–607. doi:10.1016/j.atmosenv.2009.11.022
- Rissler, J., Vestin, A., Swietlicki, E., Fisch, G., Zhou, J. and co-authors. 2006. Size distribution and hygroscopic properties of aerosol particles from dry-season biomass burning in Amazonia. *Atmos. Chem. Phys.* **6**, 471–491. doi:10.5194/acp-6-471-2006
- Romonosky, D. E., Li, Y., Shiraiwa, M., Laskin, A., Laskin, J. and co-authors. 2017. Aqueous photochemistry of secondary organic aerosol of α -pinene and α -humulene oxidized with ozone, hydroxyl radical, and nitrate radical. *J. Phys. Chem. A* **121**, 1298–1309. doi:10.1021/acs.jpca.6b10900
- Ruehl, C. R., Davies, J. F. and Wilson, K. R. 2016. An interfacial mechanism for cloud droplet formation on organic aerosols. *Science* **351**, 1447–1450. doi:10.1126/science.aad4889
- Schwarzenboeck, A., Heintzenberg, J. and Mertes, S. 2000. Incorporation of aerosol particles between 25 and 850 nm into cloud elements: measurements with a new complementary sampling system. *Atmos. Res.* **52**, 241–260. doi:10.1016/S0169-8095(99)00034-4
- Seifert, M., Ström, J., Krejci, R., Minikin, A., Petzold, A. and co-authors. 2004. Thermal stability analysis of particles incorporated in cirrus crystals and of non-activated particles in between the cirrus crystals: comparing clean and polluted air masses. *Atmos. Chem. Phys.* **4**, 1343–1353. doi:10.5194/acp-4-1343-2004
- Seinfeld, J. H. and Pandis, S. N. 2006. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. 2nd ed. John Wiley & Sons, Hoboken, NJ.
- Shingler, T., Dey, S., Sorooshian, A., Brechtel, F. J., Wang, Z. and co-authors. 2012. Characterisation and airborne deployment of a new counterflow virtual impactor inlet. *Atmos. Meas. Tech.* **5**, 1259–1269. doi:10.5194/amt-5-1259-2012
- Targino, A. C., Noone, K. J., Drewnick, F., Schneider, J., Krejci, R. and co-authors. 2007. Microphysical and chemical

- characteristics of cloud droplet residuals and interstitial particles in continental stratocumulus clouds. *Atmos. Res.* **86**, 225–240. doi:[10.1016/j.atmosres.2007.05.001](https://doi.org/10.1016/j.atmosres.2007.05.001)
- Theobald, M. R., Vivanco, M. G., Aas, W., Andersson, C., Ciarelli, G. and co-authors. 2019. An evaluation of European nitrogen and sulfur wet deposition and their trends estimated by six chemistry transport models for the period 1990–2010. *Atmos. Chem. Phys.* **19**, 379–405. doi:[10.5194/acp-19-379-2019](https://doi.org/10.5194/acp-19-379-2019)
- Topping, D., Connolly, P. and McFiggans, G. 2013. Cloud droplet number enhanced by co-condensation of organic vapours. *Nat. Geosci.* **6**, 443–446. doi:[10.1038/ngeo1809](https://doi.org/10.1038/ngeo1809)
- Topping, D. O., McFiggans, G. B. and Coe, H. 2005. A curved multi-component aerosol hygroscopicity model framework: Part 1 – inorganic compounds. *Atmos. Chem. Phys.* **5**, 1205–1222. doi:[10.5194/acp-5-1205-2005](https://doi.org/10.5194/acp-5-1205-2005)
- Tritscher, T., Dommen, J., Decarlo, P. F., Gysel, M., Barmet, P. B. and co-authors. 2011. Volatility and hygroscopicity of aging secondary organic aerosol in a smog chamber. *Atmos. Chem. Phys.* **11**, 11477–11496. doi:[10.5194/acp-11-11477-2011](https://doi.org/10.5194/acp-11-11477-2011)
- Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Maso, M. D. and co-authors. 2006. High natural aerosol loading over boreal forests. *Science* **312**, 261–263. doi:[10.1126/science.1123052](https://doi.org/10.1126/science.1123052)
- Turpin, B. J. and Lim, H.-J. 2001. Species contributions to PM_{2.5} mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Sci. Technol.* **35**, 602–610. doi:[10.1080/02786820119445](https://doi.org/10.1080/02786820119445)
- Väisänen, O., Ruuskanen, A., Ylisirniö, A., Miettinen, P., Portin, H. and co-authors. 2016. In-cloud measurements highlight the role of aerosol hygroscopicity in cloud droplet formation. *Atmos. Chem. Phys.* **16**, 10385–10398. doi:[10.5194/acp-16-10385-2016](https://doi.org/10.5194/acp-16-10385-2016)
- Vega, C. P., Mårtensson, E. M., Wideqvist, U., Kaiser, J., Zieger, P. and co-authors. 2019. Composition, isotopic fingerprint and source attribution of nitrate deposition from rain and fog at a Sub-Arctic Mountain site in Central Sweden (Mt Åreskutan). *Tellus B: Chem. Phys. Meteorol.* **71**, 1559398–1559319. doi:[10.1080/16000889.2018.1559398](https://doi.org/10.1080/16000889.2018.1559398)
- Villani, P., Picard, D., Marchand, N. and Laj, P. 2007. Design and validation of a 6-volatility tandem differential mobility analyzer (VTDMA). *Aerosol Sci. Technol.* **41**, 898–906. doi:[10.1080/02786820701534593](https://doi.org/10.1080/02786820701534593)
- von der Weiden, S.-L., Drewnick, F. and Borrmann, S. 2009. Particle loss calculator – a new software tool for the assessment of the performance of aerosol inlet systems.pdf. *Atmos. Meas. Tech.* **2**, 479–494. doi:[10.5194/amt-2-479-2009](https://doi.org/10.5194/amt-2-479-2009)
- Wallén, A., Lidén, G. and Hansson, H.-C. 2010. Measured elemental carbon by thermo-optical transmittance analysis in water-soluble extracts from diesel exhaust, woodsmoke, and ambient particulate samples. *J. Occup. Environ. Hyg.* **7**, 35–45.