Cloud response to co-condensation of water and organic vapors over the boreal forest

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Abstract

Accounting for the condensation of organic vapors along with water vapor (co-condensation) has been shown in adiabatic cloud parcel model (CPM) simulations to enhance the number of aerosol particles that activate to form cloud droplets. The boreal forest is an important source of biogenic organic vapors, but the role of these vapors in co-condensation has not been systematically investigated. In this work, the environmental conditions under which strong co-condensation-driven cloud droplet number enhancements would be expected over the boreal biome are identified. Recent measurement technology, specifically the Filter Inlet for Gases and AEROsols (FIGAERO) coupled to an iodide-adduct Chemical Ionization Mass Spectrometer (I-CIMS), is utilized to construct a volatility distribution of the boreal atmospheric organics. Then, a suite of CPM simulations initialized with a comprehensive set of concurrent aerosol observations collected in the boreal forest of Finland during Spring 2014 is performed.

The degree to which co-condensation impacts droplet formation in the model is shown to be dependent on the initialization of the updraft velocity, aerosol size distribution, organic vapor concentration and the volatility distribution. The predicted median enhancement in cloud droplet number concentration (CDNC) due to accounting for the co-condensation of water and organics is 20% (interquartile range 29–14%). This corresponds to activating particles 12–16 nm smaller in dry diameter, that would otherwise remain as interstitial aerosol. The highest CDNC enhancements (ΔCDNC) are predicted in the presence of a nascent ultrafine aerosol mode with a geometric mean diameter of ~40 nm and no clear Hoppel minimum, indicative of pristine environments with a source of ultrafine particles (e.g., via new particle formation processes). Such aerosol size distributions are observed 30–40% of the time in the studied boreal forest environment in spring and fall when new particle formation frequency is the highest (six years of statistics). Five years of UK Earth System Model (UKESM1) simulations are further used to evaluate the frequencies to which such distributions are experienced by an Earth System Model over the whole boreal biome. The frequencies are substantially lower than those observed at the boreal forest measurement site (<6% of the time) and the positive values, peaking in spring, are modeled only over Fennoscandia and western parts of Siberia. For the aerosol size distribution regime simulated by UKESM1, offline simulations with the adiabatic parcel model reveal the ΔCDNC to be sensitive to the concentrations of semi-volatile and some intermediate-volatility organic compounds (SVOCs and IVOCs). The magnitudes of ΔCDNC remain less affected by the more volatile vapors such as formic acid and extremely low and low volatility organic compounds (ELVOCs and LVOCs) in the CPM simulations. The reasons for this are that most volatile organic vapors condense inefficiently due to their high volatility below cloud base and the concentrations of LVOCs and ELVOCs are too low to gain significant concentrations of soluble mass to reduce critical
supersaturations needed for droplet activation. Suppression of the critical supersaturation caused by organic condensation is the main driver of the modeled ΔCDNC. The results highlight the potential significance of co-condensation in pristine boreal environments close to sources of fresh ultrafine particles. For accurate predictions of co-condensation effects on CDNC, the representation of the aerosol size distribution is of essence. Further studies targeted at finding observational evidence and constraints for co-condensation in the field are encouraged.

1 Introduction

Boreal forests emit significant quantities of volatile organic compounds (VOCs, Guenther et al., 1995; Artaxo et al., 2022), such as monoterpenes, that undergo oxidation in the atmosphere. The condensable oxidation products contribute considerably to the secondary organic aerosol (SOA) mass concentrations in the boreal forest air (e.g., Tunved et al., 2006; Artaxo et al., 2022). The emissions of monoterpenes are strongly temperature-dependent, which leads – together with the higher oxidative potential in the sunlit months – to highest biogenic SOA concentrations in summer (Paasonen et al., 2013; Heikkilä et al., 2020; Mikhailov et al., 2017). This has recently been shown to have implications for cloud properties above the boreal forest through the availability of more cloud condensation nuclei (CCN; Yli-Juuti et al., 2021; Petäjä et al., 2022). Under constant meteorological conditions, an increase in aerosol concentration typically results in an increase in CDNC and smaller average droplet size for a given liquid water content (Yli-Juuti et al., 2021). These effects alter the cloud brightness making clouds scatter incoming solar radiation more efficiently (Twomey effect; Twomey, 1974, 1977). The relationships between the number of aerosol particles, cloud droplet number concentration (CDNC), and their effects on climate are non-linear and complex, which makes aerosol-cloud interactions the largest source of uncertainty in radiative forcing estimates from climate models (e.g., Lohmann and Feichter, 2005; Carslaw et al., 2013; Bellouin et al., 2020). The development of “bottom-up” predictive models is needed for providing accurate, yet robust, simplifications of key processes involved in aerosol-cloud interactions – eventually for inclusion in climate models in computationally efficient parameterizations.

Numerous studies have been carried out to understand the role of condensable organic vapors in SOA formation (e.g., Hallquist et al., 2009; Shrivastava et al., 2017) and hence the concentrations of CCN (i.e. particles of at least 50–100 nm in diameter for the water vapor supersaturations typical of the boreal environments; Cerully et al., 2011; Sihto et al., 2011; Paramonov et al., 2013; Hong et al., 2014; Paramonov et al., 2015). The yields of volatile, intermediate-volatility or semi-volatile organic compounds (VOCs, IVOCs, or SVOCs) from monoliterene oxidation, such as those of pinonaldehyde, formic acid, or acetic acid, are generally much higher than those of the readily condensable lower-volatility vapors (low-volatility organic compounds, LVOCs and extremely low volatility organic compounds, ELVOCs). The above-mentioned volatility classes are determined based on the volatilities of individual compounds binned into a volatility basis set (VBS; Donahue et al., 2006): VOCs have a saturation vapor concentration ($C^*$; given in units of μg m$^{-3}$ throughout the paper) of at least 10$^7$ μg m$^{-3}$, IVOCs are distributed in the $C^*$ range of [10$^1$, 10$^3$] μg m$^{-3}$, SVOCs of [1, 100], LVOCs of [10$^{-1}$, 10$^1$] and ELVOCs have a $C^*$ below 10$^4$ μg m$^{-3}$ (e.g., Donahue et al., 2011). While VOCs, IVOCs, and some SVOCs are unlikely to produce significant concentrations of SOA at ground level without additional oxidation steps or reactive uptake, some of them can condense at higher altitudes if transported aloft (e.g., Murphy et al., 2015). This
work focuses on the role of SVOCs and IVOCs in warm cloud microphysics due to their high abundance in tropospheric air and co-condensation potential.

Warm (liquid) clouds can form when air rises and cools, eventually leading to the air being supersaturated with water vapor. The excess water vapor condenses onto aerosol particles, rapidly growing them into cloud droplets. While water vapor represents the most abundant vapor in the atmosphere, other trace species can influence the cloud droplet activation process as the cooling of the rising air triggers also their condensation. As the trace vapors condense, the molar fraction of water in the swelling droplets increases slower than in the absence of co-condensation, which in turn leads to the condensation of additional water by the time the air parcel reaches lifting condensation level. The co-condensation of water with other vapors eventually leads to a reduction in critical supersaturation (s*) required for droplet activation of the particles due to an increased amount of organic solute (Topping and McFiggans, 2012) as described by Köhler theory (Köhler, 1936). Topping et al. (2013) studied the impact of organic co-condensation on CDNC using a cloud parcel model (CPM) initialized with a suite of realistic conditions describing the aerosol particle number size distribution (PNSD), composition, and organic aerosol (OA) volatility distribution. They showed significant enhancements in CDNC (ΔCDNC up to roughly 50%) when comparing simulations with organic condensation (CC) to simulations without (noCC). In addition to co-condensing organics and water, also co-condensation of nitric acid and ammonia together with water has been suggested to enhance CDNC in earlier process modeling studies (e.g., Kulmala et al., 1993; Korhonen et al., 1996; Hegg, 2000; Romakkaniemi et al., 2005). Direct experimental studies of co-condensation remain challenging, however, as aerosol particles are typically dried during the sampling process and the loss of liquid water may lead to evaporation of co-condensed organics, too. While direct observational evidence of organic co-condensation in the atmosphere is still lacking, recent laboratory studies show significant water uptake due to co-condensation of propylene glycol and water onto ammonium sulfate particles (Hu et al., 2018).

The cloud response to co-condensation in the form of ΔCDNC is the result of a complex interplay between updraft velocity, PNSD and organic compound volatility distribution (Topping et al., 2013). For the same amount of organic vapor, Topping et al. (2013) modelled a non-linear updraft response of ΔCDNC. The highest ΔCDNC were obtained when updrafts were below 1 m s⁻¹, but the peak ΔCDNC was dependent on the initial PNSD characteristics. Under higher updrafts, the modelled ΔCDNC was found to decrease exponentially as a function of updraft, but the asymptote of the curve depended on the initial PNSD – although the dependence on the exact parameters describing multimodal PNSD were not extensively explored. If assumed representative of the global continents, ΔCDNC values of tens of percent could impose a significant impact on predictions of cloud albedo and the Earth’s radiative budget. In fact, Topping et al. (2013) suggest accounting for co-condensation could result in up to 2.5% increase in cloud albedo (corresponding to global ΔCDNC = 40%). This albedo increase would translate into a ~1.8 W m⁻² change in the global cloud radiative effect over land. Topping et al. (2013) stress, however, that the impacts of co-condensation will be spatially heterogeneous because of variable surface albedo and variation in VOC sources. For comparison, one should note that the net radiative effect of clouds is approximately ~20 W m⁻² (Boucher et al., 2013). The recent best estimate of the effective radiative forcing from aerosol-cloud interactions is, on the other hand, ~1.0 [-1.7 to –0.3] W m⁻² (Forster et al., 2021). The potential contribution of co-condensation to estimates on aerosol forcing or to future cloud radiative effects remains unclear.

Boreal forests make up about one third of the Earth’s forested area, which makes it an important source of biogenic vapors that could affect droplet activation in warm clouds through co-condensation. ΔCDNC due to
co-condensation over the boreal forest could reduce the albedo over the dark boreal forest canopy. In a warming climate, temperature-dependent biogenic terpene emissions (Guenther et al., 1993) are expected to rise (e.g., Turnock et al., 2020). These increasing emissions enrich the ambient pool of organics available for condensation in rising air. As suggested in Topping et al. (2013), through the effects organic co-condensation poses on CDNC, co-condensation could enhance the proposed negative climate feedback mechanism associated with the biogenic SOA (Kulmala et al., 2004; Spracklen et al., 2008; Kulmala et al., 2014; Yli-Juuti et al., 2021), the magnitude of which is currently highly uncertain (Thorhill et al., 2021; Sporre et al., 2019; Scott et al., 2018; Paasonen et al., 2013; Sporre et al., 2020).

Since the publication of the Topping et al. (2013) study, improved constraints of the effective volatilities of organic aerosol (e.g., Thornton et al., 2020) can be placed through the application of chemical ionization mass spectrometers (CIMS) providing molecular level information on gas- and particle-phase composition in near-real time. With the up-to-date volatility parameterizations using the molecular formulae retrieved from CIMS data, volatility distributions can be calculated along a volatility scale ranging from ELVOCs to VOCs, while previous techniques could not enable constraints on volatilities exceeding $C^* = 1000 \mu g m^{-3}$ (SVOC) (Cappa and Jimenez, 2010). This means that a notable amount of semi- and intermediate volatility vapors with high co-condensation potential were not included in the early organic co-condensation work (Topping et al., 2013; Crooks et al., 2018). The recent methodological developments motivate revisiting work of Topping et al. (2013), as potentially large concentrations of condensable organic vapors have been so far neglected.

In this study, the cloud response to the co-condensation of organic vapors over the boreal forest of Finland is investigated using a CPM. Measurements and parameterization techniques involving FIGAERO-I-CIMS data are utilized to constrain the volatility distribution of organics for these simulations. In addition, to ensure realistic modeling scenarios, simultaneously recorded measurements of PNSD and chemical composition from the Aerosol Chemical Speciation Monitor (ACSM) are used for the CPM initialization. 97 CPM simulations initialized with conditions from boreal spring and early summer following measurement time series recorded during the Biogenic Aerosols – Effects on Clouds and Climate (BAECC) campaign at the Station Measuring Atmosphere–Ecosystem Relationships (SMEAR) II (Hari and Kulmala, 2005) in Finland (Petäjä et al., 2016) are performed, and sensitivity to updraft velocity is studied. These simulations are then used to characterize the environmental conditions (with respect to the size distribution and organic aerosol volatility distribution characteristics) that promote co-condensation-driven CDNC enhancements in the boreal atmosphere. The frequencies to which a strong cloud response to co-condensation can be expected and its spatiotemporal variability over the boreal biome is further investigated using long-term measurements from SMEAR II station and UK Earth System Model (UKESM1) simulations.

### 2 Methods and Data

#### 2.1 The adiabatic cloud parcel model (ICPM)

The CPM chosen for this study is the Institute for Marine and Atmospheric research Utrecht (IMAU) entrained pseudo-adiabatic CPM (ICPM, Roelofs and Jongen, 2004). ICPM was further developed so that it could perform simulation of both pseudo-adiabatic and adiabatic ascents of air parcels (Partridge et al., 2011, 2012). ICPM simulates the condensation and evaporation of water vapor on aerosol particles, particle activation to cloud droplet, unstable growth, collision and coalescence between droplets, and aqueous phase sulphur chemistry.
The model can be initialized with aerosol populations consisting of one or more internal or external mixtures of sulfuric acid, ammonium bisulfate, ammonium sulfate, OA, black carbon, mineral dust and sea salt. The PNSD are presented in a moving-center binned microphysics scheme comprising 400 size bins between 5 nm and 5 μm in dry radii, which are constructed at model initialization from the three parameters describing log-normal size distributions for the $i$ number of modes – the geometric mean diameter ($D_i$), the total mode number concentration ($N_i$), and the geometric standard deviation ($σ_i$). The model can be initialized with up to four log-normal aerosol modes. The ICPM further provides time evolutions of key thermodynamic and microphysical parameters e.g., the air parcel temperature ($T$), pressure ($p$), supersaturation ($s$), altitude ($z$) and the aerosol particle and hydrometeor size distributions.

The dynamical equations used in the ICPM to simulate the adiabatic ascending air parcel equations are same to those presented by Lee and Pruppacher (1977), where the vertical parcel displacements are determined by the updraft velocity ($w$, set to a fixed positive constant value in the ICPM simulations):

$$\frac{dz}{dt} = w.$$  \hspace{1cm} (1)

The changes in pressure are calculated assuming hydrostatic balance and the temperature decrease along the ascent follows the dry adiabatic lapse rate while also accounting for the latent heat release due to condensation:

$$-\frac{dT}{dt} = g\frac{w}{c_{p,a}} + \frac{L_v}{c_{p,a}} \frac{dx_v}{dt} + \mu_j \left[ \frac{L_v}{c_{p,a}} (x_v - x'_v) + (T - T') \right] W$$  \hspace{1cm} (2)

where $g$ is the acceleration of gravity, $L_v$ the latent heat of evaporation, $c_{p,a}$ the specific heat capacity of air and $x_v$ the water vapor mixing ratio of the air parcel, $μ_j$ is the entrainment rate describing mixing of parcel air with environmental air characterized with $x'_v$ and $T'$. In this study, in which adiabatic simulations are performed, entrainment is not considered ($μ_j = 0$). The water vapor mixing ratio in the air parcel changes with the evolving ambient supersaturation:

$$\frac{dx_v}{dt} = \frac{ρ_v}{c_{v,a}} \frac{dx_v}{dt} - (1 + s) \left[ \frac{ε L_v}{R_a T^2} \frac{dT}{dt} + \frac{g}{R_a T} W \right],$$  \hspace{1cm} (3)

where $ε = R_v / R_a = M_v / M_a = 0.622$ i.e., the ratio between the specific gas constants for air and water vapor or alternatively the molecular weight of water and air. $c_{v,a}$ is the saturation vapor pressure of water. To solve the ordinary differential equations (Eqs. 2–3), the time derivate of the water vapor mixing is approximated as

$$\frac{dx_v}{dt} \approx -\frac{Δx_v}{Δt} = μ_j (x_v - x'_v + x_l) w$$  \hspace{1cm} (4)

where $Δt$ is the model time step ($10^{-3}$ seconds) and the liquid water mixing ratio ($x_l$) is calculated as a sum of the liquid water mixing ratio across all the 400 size bins (index $i$) for each assigned mode composition (index $j$):

$$Γ_w = K_w \sum_{i=1}^{400} \sum_{j=1}^{40} \sum_{l=1}^{3} \frac{n_l(r_l)}{3ρ_a} (r_l^i - r_{l,0,j_l}),$$  \hspace{1cm} (5)

where $ρ_a$ is density of water, $ρ_p$ is the density of the particle dry mass, $n_l$ is the number of particles within size bin $i$ and composition $j$, and finally $r_l$ and $r_{l,0,j_l}$ are the wet and dry radii of the particles, respectively. The wet radii and hence also the particle masses ($m$) change as water condenses onto the particle (indices dropped for simplicity):
\[ \frac{dm}{dt} = 4 \pi \rho_w r^2 \frac{dr}{dt} = \frac{4 \pi \rho_w r (S - S_{eq})}{DIFF \cdot \gamma_s + \frac{L_p}{RT} - \gamma_s} \]  

where \( k \) is the thermal conductivity, and \( DIFF \cdot \gamma_s \) is size-dependent water vapor diffusivity (from Pruppacher and Klett, 1997). Eq. (6) is approximated within the ICPM using a linearized form of the condensation equation (Hänel, 1987). Finally, \( S \) is the ambient saturation ratio \((S = s + 1)\) and \( S_{eq} \) \((S_{eq} = RH / 100\%)\) the equilibrium saturation ratio over the (spherical) wet particle surface, the difference of which determines the quantity of excess vapor for the diffusional growth of the particle. While \( S \) depends on the updraft source and condensation sink (Eq. 3), \( S_{eq} \) depends on the particle wet radius and composition and it can be calculated using the Köhler equation (Köhler, 1936), traditionally expressed as:

\[ S_{eq} = \frac{e}{e_s} = a_e \exp \left( \frac{2 M_w \gamma}{RT \rho_w} \right) \]  

where \( e \) is the vapor pressure of water, \( a_e \) the water activity, \( \gamma \) the droplet surface tension (assumed to be that of water; see Table 1), \( R \) the universal gas constant, \( T \) the droplet temperature and \( r \) the droplet radius. Assuming dilute droplets, Eq. 7 is approximated in ICPM as follows for the equilibrium supersaturation ratio (Hänel, 1987):

\[ S_{eq} \approx \exp \left( \frac{A}{r} - \frac{B}{\gamma_s} \right) \]  

where

\[ A = \frac{2 M_w \gamma}{RT \rho_w} \]  

and

\[ B = \frac{3 n_e M_w}{4 \pi \rho_w} \]  

\( A \) and \( B \) in Eqs. (9) and (10) are the Köhler coefficients, where \( n_e \) is the total number of solutes (mol). The Raoult term (Eq. 10) is reformulated within the ICPM in terms of solute concentrations enabling its adjustments by dissolving or partially dissolving chemical constituents. For detailed descriptions of the \( B \) term, the reader is directed to Roelofs (1992).

\[ \theta_{q} = \frac{C_{p,q}}{C_{p,q} + C_{g,q}} \]  

2.1.1 Gas–particle partitioning of organics

ICPM has been extended to incorporate Köhler and condensation/evaporation equations for organic species of varying volatilities (Lowe, 2020). The volatility distributions are given using the VBS framework (Donahue et al., 2006). Initially, each volatility bin \( q \) contains the sum of gas \((C_{g,q})\) and particle phase concentrations \((C_{p,q})\) of the compounds with a given \( \theta \). The partitioning coefficients for each bin, \( \theta_q \), are defined as

\[ C_p = \sum_q C_{p,q} = \sum_q C_{g+p,q} \theta_q \]
and the partitioning coefficients depend on $C^*$ as follows
\[ \xi_q = \frac{C_p}{C_p + C_q^*}. \] (13)

$\xi_q$ are solved iteratively from Equations (12–13) at model initialization. Similarly, as in the work of Topping et al. (2013), $C_p$ is constrained using the initial PNSD and the organic mass fraction in addition to the relative proportions of the various volatility bins (volatility distribution shape).

The condensation/evaporation equation for organic species is described in the same manner as in Topping et al. (2013) and as shown for water vapor in Eq (6):
\[
\frac{dn_{q}}{dt} = \frac{4\pi \rho \rho_{D} \text{DIFF}_{q}^{*} (S_{q} - S_{eq,q}) e_{q,q}}{\text{DIFF}_{q}^{*} H_{e,q} S_{eq,q} e_{q,q} \left( \frac{H_{eq,q}^0}{RT} \right) + \rho \frac{RT}{M_{q}}} \] (14)

where DIFF$_q^*$ is the gas phase diffusivity (see details in Topping et al., 2013 supplementary information), $H_e$ the enthalpy of vaporization, $e_{q,q}$ the saturation vapor pressure, and $S_{eq,q}$ the equilibrium saturation ratio of organic species in the $q$th volatility bin. $S_{eq,q}$ is calculated following the Köhler equation (Eq. 8) analogy:
\[ S_{eq,q} = a_q \exp \left( \frac{-2\nu_{eq}}{RT} \right) \] (15)

where $a_q$ is the activity of $C_{p,q}$ in the bulk condensed phase, which equals the molar fraction of $C_{p,q}$ due to the ideal solution approach of the study. In the model simulations enabling organic phase transitions, the concentrations of the gas and particle phases integrated over all the volatility bins are saved as model output.

### 2.2 Measurement data from SMEAR II used for ICPM initialization

The observational data used for the ICPM initialization were collected during the Biogenic Aerosols – Effects on Clouds and Climate (BAECC) campaign which took place in 2014 at the Station Measuring Ecosystem–Atmosphere Relationships (SMEAR) II in Hyytiälä, Finland (Petäjä et al., 2016). SMEAR II is a well-characterized atmospheric measurement supersite located within a boreal forest in Southern Finland (61°51’N, 24°17’E; Hari and Kulmala, 2005). The surroundings of the measurement site are mostly forested (80% within a 5 km radius and 65% within a 50 km radius; Williams et al., 2011). The atmospheric composition measured at the site suggests strong influence of biogenic emissions on aerosol and aerosol precursor (i.e., biogenic VOCs, BVOCs) concentrations (e.g., Hakola et al., 2012; Yan et al., 2016; Allan et al., 2006; Heikkinen et al., 2021).

Anthropogenic influence is pronounced when air masses arrive from heavily industrialized areas such as St Petersburg, Russia (Kulmala et al., 2000).

The PNSD for the ICPM initialization are obtained from the Differential Mobility Particle Sizer (DMPS) measurements from SMEAR II performed within the forest canopy (Aalto et al., 2001; Petäjä et al., 2016). Since ICPM takes in the log-normal parameters that the size distribution comprises ($N$, $D$, $\sigma$), also the fitting of the PNSD is performed. This is done using the Hussein et al. (2005) algorithm that allows fitting 1–4 modes into the measured distributions and decides the optimal number of modes. For the BAECC data set, the optimal number would always be between three and four modes, with a higher number of modes generally yielding a better fit to the observational data as expected. Despite the optimal number of 3–4 modes, the maximum number of modes is restricted to two as the agreement between the fitted and measured distributions remained good considering the experimental uncertainties, and including two modes only instead of four considerably sped up the simulations.
Moreover, the DMPS is suitable for sampling aerosol particles of ca. 3–1000 nm in size (electrical mobility equivalent diameter) and hence does not capture the coarse mode. In addition, the Aitken mode at SMEAR II typically originates from a growing nucleation mode. In more polluted environments, where small particles have sources other than new particle formation, simplifications like this might not be appropriate. The PNSD time series measured during BAECC is shown in Fig. 1a. It shows clearly the growth of nucleation mode to Aitken mode on several occasions. Statistics regarding the log-normal parameters of the fitted data during BAECC are provided in Table 1. The bimodal fits are also calculated for the years 2012–2017. These data are used later to evaluate the frequency of times size distributions yielding high ΔCDNC appear in long-term data.

The aerosol chemical composition for ICPM initialization are obtained from Aerosol Chemical Speciation Monitor (ACSM; Ng et al., 2011) measurements performed within the forest canopy (Heikkinen et al., 2020). The ACSM measures the non-refractory (NR) sub-micrometer particulate matter (PM1) chemical composition, which means that the reported composition is restricted to organics, sulfate, nitrate, chloride and ammonium. The salts measured by the instrument do not include sea salt, because it typically exists in the coarse mode and does not fully evaporate at the ACSM vaporizer temperature of 600°C. The latter reason restricts the instrument also from detecting black carbon (BC). The composition from the ACSM measurements is shown in Fig. 1b. Statistics regarding the organic mass fractions ($f_{org}$) are shown in Table 2. The ACSM data are further used to derive volatility distributions similar to those utilized by Topping et al. (2013; see Sect. 2.3.1 for details).

An iodide FIGAERO-I-CIMS, sampling above the forest canopy in a ca. 30 m tower, is used to retrieve molecular composition and volatility distributions of gas- and particle-phase species during BAECC (Mohr et al., 2017, 2019; Schobesberger et al., 2016; Lee et al., 2018, 2020; see Sect. 2.3.2 for details). The Filter Inlet for Gases and AEROsols (FIGAERO; Lopez-Hilfiker et al., 2014) coupled with a CIMS (the coupling of these instruments hereafter referred to as FIGAERO-I-CIMS) stands as one of the very few instruments capable of performing near-simultaneous measurements of both gas and particle phases. The FIGAERO inlet allows the gas phase to be sampled while aerosol particles are collected on a Teflon filter, and after sufficient particle deposition time the sample is heated and the evaporated molecules are measured similarly to the gas phase. The heating procedure, which typically reaches a maximum temperature of around 200°C can, however, cause thermal fragmentation of molecules (Lopez-Hilfiker et al., 2015). This leads to the detection of small molecular fragments, which get assigned a higher $C^*$ than that of the parent molecule, which can be seen in the FIGAERO-I-CIMS thermograms when compounds with high $C^*$ vaporize at exceptionally high temperatures. In addition to the indistinguishable isomers from any of the phases from online FIGAERO-I-CIMS measurements (or any other mass spectrometer for that matter), thermal fragmentations add to the uncertainty of volatility distributions retrieved from these data.

The parcel model simulations are initialized at 90% RH, which is most of the time higher than that measured at ground level. An interpolated radiosonde data product from the BAECC campaign (ARM Data Center, 2014) is used to find temperatures matching 90% RH. Both the temperature measured near ground level (8.4 m above ground level) and the temperature corresponding to 90% RH are shown in Fig. 1c. While these temperatures show similar temporal behavior at times, major differences exist, which can arise from instable temperature profiles as well as sudden changes in air masses that the interpolated data product built from sondes sent three times a day fails to capture. The PNSD and aerosol chemical composition measured near ground level are assumed to be identical to those at 90% humidity, because measurement data at higher altitudes is not...
available. The volatility distributions retrieved from the FIGAERO-I-CIMS and ACSM data are adjusted to the
temperatures obtained from the interpolated radiosonde data product (see Sects. 2.3.1 and 2.3.2 for details).

2.3 Volatility distributions

The total organic (gas + particle phase) volatility distributions are provided as inputs for the ICPM (see Sect.
2.1.1). To compare the results from this work to those of Topping et al. (2013), and to assess the changes in co-
ondensation driven ΔCDNC due to volatility distribution updates from the old particle-phase derived
distributions (denoted with CJ; see Sect. 2.3.1) to FIGAERO-I-CIMS-derived distributions (here denoted with F;
see Sect. 2.3.2), both approaches are used. The term “volatility distribution shape” refers to the relative proportions
of organic mass in each volatility bin, which remain fixed when the partitioning coefficients are iterated (see Eqs.
11–13 in Sect. 2.1.1).

2.3.1 Volatility distributions based on ACSM measurements (CJ distributions)

Previous to the development of the FIGAERO-I-CIMS, organic volatility distributions were probed only through
particle phase measurements (e.g., Huffman et al., 2009b), which enabled volatility constraints of relatively low
volatility species (Cappa and Jimenez, 2010). More precisely, these early generation OA volatility distributions
were obtained from e.g. Aerosol Mass Spectrometer (AMS; Canagaratna et al., 2007) measurements coupled with
a thermal denuder (TD; e.g., Huffman et al., 2009a, b). The TD-AMS measurements provide thermograms (mass
fractions remaining in the particle phase as a function of TD temperature of ca. 25–250 °C that could be assigned
to individual OA components i.e., low-volatility oxygenated organic aerosol (LV-OOA), semi-volatile
oxygenated organic aerosol (SV-OOA), hydrocarbon-like OA (HOA) and biomass burning OA (BBOA). Cappa
and Jimenez (2010) then reproduced such thermograms using a kinetic evaporation model (Cappa, 2010) through
fitted OA volatility distributions. In this paper, volatility distributions of this kind are referred to as CJ
distributions. It is important to keep in mind that the general CJ volatility distribution shape (i.e., the relative
proportions of the volatility bins) is assumed to be of the form $C_i^{\text{vol}} = a_1 + a_2 \exp(a_3 (\log \text{C}_i - 3))$, which was
motivated by previous studies on organic aerosol volatility distribution shapes retrieved from chamber
experiments (Presto and Donahue, 2006; Robinson et al., 2007), with $a_1, a_2$ and $a_3$ as fitting parameters. Later
theoretical work on OA volatility distribution retrievals from TD data states, however, that due to uncertainties
associated with the enthalpy of vaporization (ΔH_vap), mass accommodation coefficients, and volatility distribution
shapes, the attained distributions can be reproduced with several combinations of the three (Karnezi et al., 2014).

To calculate the CJ distributions for the BAECC OA types, the LV-OOA, SV-OOA and primary organic
aerosol (POA; taken as a mix of HOA and BBOA) from the SMEAR II ACSM long-term data set are utilized
(Heikkinen et al., 2021). During BAECC, the organic aerosol comprised 63% LV-OOA, 32% SV-OOA and only
5% POA on average. Using the time-dependent mass fractions of each OA type, mass-weighted average CJ
volatility distributions for each of the model initialization scenarios (97 of them) are calculated. The HOA
volatility distribution is used for POA (due to the low abundance of levoglucosan in the ACSM mass spectrum;
Heikkinen et al., 2021). Topping et al. (2013) utilized the $\log_{10} C^e$ range of [-6, 3] in their simulations and their
example is followed in this work. The CJ volatility distributions have been reported for 298.15 K (Cappa and
Jimenez, 2010). As the ICPM simulations are initialized at different temperatures, accounting for the impact these
temperature changes had on the volatility distributions is necessary. The relationship between temperature, $\Delta H_{\text{vap}}$, and $C^*$ is accounted for through an Arrhenius-type Clausius-Clapeyron relation:

$$C^* = C^*(T_{\text{ref}}) \exp \left(\frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right),$$

where $R$ is the universal gas constant and $T$ is the ambient temperature in Kelvin (the ICPM initialization temperature), and $T_{\text{ref}}$ is 298.15 K. For the relationship between $\Delta H_{\text{vap}}$ (in J mol$^{-1}$) and $C^*$ the semi-empirical parameterization under 300 K provided in Epstein et al. (2010) is used:

$$\Delta H_{\text{vap}} = -11\log_{10}C^*(T_{\text{ref}}) + 129,$$

where $\Delta H_{\text{vap}}$ is the change in heat (enthalpy) of vaporization in kJ mol$^{-1}$. A lower limit of 20 kJ mol$^{-1}$ is set to the $\Delta H_{\text{vap}}$, which is close to the $\Delta H_{\text{vap}}$ determined for formic acid (NIST Chemistry WebBook, 2022). Eq. (17) would otherwise provide too low, unphysical and even negative values. After the temperature adjustments, the volatility distributions are binned to ranges between $\log_{10}C^* = [-8, 3]$ spaced by one decade in $C^*$ as after adjustments with Eqs. (16–17). The lower limit is reduced by two orders of magnitude, but the upper limit remains as the initialization temperatures did not exceed 300 K. The campaign average CJ volatility distribution is shown with black bars in Fig. 2a. However, each simulation utilizes a unique distribution constructed using the LV-OOA, SV-OOA, and POA time series.

2.3.2 Volatility distributions based on FIGAERO-I-CIMS measurements (F distributions)

Organic aerosol volatility distributions from FIGAERO-I-CIMS measurements conducted during BAECC (Mohr et al., 2017, 2019; Schobesberger et al., 2016; Lee et al., 2018, 2020) are also derived. It can be assumed that the FIGAERO-I-CIMS detected most of the OA measured with the ACSM. This is because with the iodide adduct ionization, FIGAERO-I-CIMS is most sensitive to oxidized organic species, such as organic acids (Lutz et al., 2019), but not sensitive to non-oxidized hydrocarbons (dominating AMS-derived HOA) and as mentioned in Sect. 2.3.1. The OA measured with the ACSM comprised on average 95% oxygenated organic aerosol (LV-OOA + SV-OOA), which is generally thought to represent organic acids (Yatavelli et al., 2015). The agreement between the two measurements is supported by the comparison between the daytime FIGAERO-I-CIMS particle phase signal (of identified ions) and the OA mass concentration retrieved from ACSM measurements provided in Fig. S1. While the quantification of the FIGAERO-I-CIMS measurements remains challenging and therefore a quantitative comparison between the concentrations is uncertain, the high correlation between measurement data (Pearson $R = 0.79$) proves that the instruments generally sample the same aerosol population. Notably, the ICPM simulations obtain OA mass fraction ($f_{\text{OA}}$) only from the ACSM measurements. The volatility distributions are derived from FIGAERO-I-CIMS data using molecular formula parameterizations derived under 300 K in Li et al. (2016):

$$\log_{10}C^*(T_{\text{ref}}) = (b_C - n_C)h_C - n_Oh_O - 2\frac{n_Cn_O}{(n_C+n_O)}b_{\text{CO}} - n_Nh_N,$$

where $n_C^*$ is a reference carbon number; $b_C$, $b_O$, and $b_N$ are the contributions of each carbon, oxygen, and nitrogen atom to the $\log_{10} C^*$, respectively; $b_{\text{CO}}$ is a so-called carbon-oxygen non-ideality parameter (Donahue et al., 2011); $n_C$, $n_O$, and $n_N$ are the numbers of carbon, oxygen, and nitrogen atoms in the molecular formulae assigned for the FIGAERO-I-CIMS data during high resolution peak fitting of the measured mass spectra. The $b$-values utilized are listed in Li et al. (2016). In their recent work, Huang et al. (2021) derived volatility distributions from various...
organic vapor measurements from SMEAR II. They adjusted the Li et al. parameterization for organic nitrates. As shown in Isaacman–VanWertx and Aumont (2021), the utilization of the Li et al. parameterization for OA-rich inorganic nitrates leads to biased vapor pressure estimates. Organic nitrates are known to form in the boreal air as a result of nitrate radical chemistry, which is pronounced during night, along with daytime oxidation of monoterpenes in the presence of nitric oxide (e.g., Yan et al., 2016; Zhang et al., 2020). To account for these nitrates, Huang et al. (2021) followed the suggestions presented in Daumit et al. (2013) and treated all the nitrate functional groups as hydroxyl (—OH) groups. Given that the focus of this study is on the same measurement site as Huang et al. (2021), their methodology for deriving a volatility distribution from the FIGAERO-I-CIMS is followed here. Once the volatility distributions are constructed using Eq. (18) for 300 K (reference temperature), their adjustments to the parcel model simulation initial temperatures using Eqs. (16–17) are performed.

The volatilities are calculated for the 1596 ions identified by the FIGAERO-I-CIMS measurements and afterwards binned with one decade spacing so that all the extremely low volatility organic compounds (ELVOC) are summed into one bin at $C^* = 10^{-4}$ $\mu$g m$^{-3}$. This is assumed to be appropriate as ELVOCs contain little or no gas phase signals post-initialization (See Sect. 2.1.1). The highest volatilities reached $C^* = 10^{7}$ $\mu$g m$^{-3}$, which is therefore set as the upper limit of the volatility distribution. Following from this, the volatility span is $\log_{10}C^* = [-4, 7]$. The campaign average volatility distribution is shown in red bars in Fig. 2a. The average CJ distribution exhibits generally higher fractions in the ELVOC region as compared to the F distribution (Fig. 2a). This mostly results from the low or non-existent SVOC and IVOC concentrations in the CJ distribution. The F distributions show a remarkable agreement with the organic volatility distributions from the BEACHON-RoMBAS field campaign conducted at the Manitou Experimental Forest Observatory in the Colorado Rocky Mountains in summer 2011 (Hunter et al., 2017, see Fig. 2a). Hunter et al. (2017) derived a volatility distribution for the total atmospheric reactive carbon (other than CH$_4$, CO$_2$ and CO) using six different types of measurements and assuming minimal overlap among the measured species. This volatility distribution is displayed in Fig. 2a after shifting it to the mean ICPM initialization temperature (280 K) using Eqs. (16–17) and subtracting VOC signals from it for comparison.

In Figs. 2b and c the partitioning coefficients $\xi_{s}$ (see Eq. 11) from the ICPM initialization (see Sect. 2.1.1) against the partitioning suggested by the measurements is compared, after accounting for the temperature differences between ground level and ICPM initialization temperatures using Eqs. (16–17). The concentrations in volatility bins with $\log_{10}C^* \leq 1$ agree, suggesting that the majority of the organics in these bins are in the particle phase. Similarly, the agreement in the highest volatility bin ($\log_{10}C^* = 7$) suggests the presence of gas-phase compounds only in both distributions. The estimations of the gas phase vary between $\log_{10}C^* = 1$ and 7, showing a higher gas-phase fraction for the modelled partitioning coefficients. This variability can result from numerous reasons, which apart from uncertainties related to measurements and parameterizations include viscous particle coatings inhibiting equilibration between gas and particle phases, and therefore showing high particle-phase concentrations of high-volatility compounds in the observations. Alternatively, these concentrations can also result from thermal decomposition of lower volatility products during the FIGAERO-I-CIMS heating process (Lopez-Hilfiker et al., 2015) or from the tendency of the Eq. (18) parameterization to underestimate (despite treating the −NO$_2$ groups at −OH groups) the volatility of organic nitrates (Graham et al., 2022), shown to be abundant in the BAECC FIGAERO-I-CIMS data set (Fig. 2e). Understanding these differences is important and requires further analysis.
The molecular composition of the gas-phase compounds detected by the I-CIMS during BAECC are analyzed and presented in detail in Lee et al. (2018). In the following, the average composition of each volatility bin during daytime is briefly described. Except for the highest volatility bin, nitrogen-containing species (CHON), which are prominently organic nitrates at SMEAR II (Huang et al., 2021), make up significant mass fractions of each bin in the gas phase (Fig. 2e). Fig. 2f shows the concentration of the gas-phase compounds as a function of the compound carbon and oxygen atom numbers. The figure shows how ELVOCs and LVOCs have the highest numbers of both carbon and oxygen atoms. IVOCs and SVOCs comprise compounds with highly variable carbon skeleton lengths, but the number of oxygen atoms per compound remains low, notably always lowest for IVOCs and VOCs. Formic acid (HCOOH) makes up most of the gas phase signal. It is distributed in the most volatile volatility bin \( (C^* = 10^7 \mu g \text{ m}^3) \). HCOOH is one of the most abundant carboxylic acids in the atmosphere and rain water (e.g., Galloway et al., 1982; Millet et al., 2015 and references therein) and is known to have various sources and precursors (Millet et al., 2015). The I-CIMS measurements discussed here were also performed as part of an eddy covariance flux measurement setup during BAECC (Schobesberger et al., 2016). These flux measurements provided insight into the high HCOOH concentrations possibly due to high emissions from the boreal forest ecosystem. More details from these results can be found in Schobesberger et al. (2016).

### 2.4 ICPM simulation setup

97 daytime scenarios are simulated with ICPM initialization data from BAECC (see Fig. 1a, red crosses). The configuration of ICPM used in this study only considers the adiabatic ascent of an air parcel, without treatment of droplet collision and coalescence, aqueous phase sulfur chemistry or entrainment. Each modelled scenario has log-normal parameters describing a bimodal aerosol size distribution form DMPS measurements followed by Hussein et al. (2005) fitting algorithm. Also, the organic mass fraction from ACSM measurements is given as an input. Organics are present in the simulations as an internal mixture with ammonium sulfate as nitrate is assumed to be organic nitrate (Lee et al., 2018) and the measured sulfate is assumed to be ammonium sulfate, which is generally a good approximation at SMEAR II (Heikkinen et al., 2020). For the simulations performed here, BC is not included given its small (about <5%) contribution to PM1 mass from late spring to summer (Luoma, 2021).

The ICPM initialization temperature is taken from interpolated radiosonde data that represents the 90% initialization RH. The atmospheric pressure was set to 980 hPa in all simulation scenarios. The simulations are performed for updraft velocities of 0.1 m s\(^{-1}\), 0.3 m s\(^{-1}\), and 1.0 m s\(^{-1}\), with and without co-condensation for the F distribution. Additional 97 simulations are performed using the 0.3 m s\(^{-1}\) updraft with the CJ volatility distribution.

Only daytime data (local time between 10:00 and 19:00) are used for the model initializations. Table 1 contains a summary of the simulation input data, which also contains the values used for accommodation coefficient, surface tension, the effective soluble fraction of organics as well as the model time step and number of PNSD size bins. The simulation output, discussed later in the results section of the paper (Sect. 3), is summarized in Table 2. The output data are averaged to a fixed height output grid spaced with a two-meter resolution.

### 2.5 UK Earth System Model (UKESM1) simulations

To evaluate the frequency of times size distributions yielding high ACDCN (which is the percent-change in CDNC due to co-condensation) during BAECC would become evident over the boreal biome in an ESM if a parameterization of co-condensation was implemented, the United Kingdom Earth System Model (UKESM1,
Sellar et al., 2019; Mulcahy et al., 2020) is utilized. The simulations performed with UKESM1 are configured for Atmospheric Model Intercomparison Project (AMIP) style simulations, where UKESM1 is run in its atmosphere-only configuration with time-evolving sea surface temperature and sea ice as well as prescribed marine biogenic emissions from fully coupled model simulations. In addition to the HadGEM3-GC3.1 core physical dynamical model of the atmosphere, land, ocean and sea ice systems (Ridley et al., 2018; Storkey et al., 2018; Walters et al., 2017), UKESM1 also contains additional component models for atmospheric chemistry and ocean and terrestrial biogeochemistry for carbon and nitrogen cycle representation. A N96L85 horizontal resolution structure (1.875° × 1.25° longitude–latitude, which corresponds roughly a horizontal resolution of 135 km) is chosen for the simulations and the vertical space is split to 85 levels (50 levels between 0 and 18 km and 35 levels between 18 and 85 km). In this study the model is run in a nudged configuration (horizontal wind nudging (but not temperature) between model levels 12 and 80 with a constant 6-hour relaxation time), for the years 2009–2013 inclusively. External forcing and emission datasets are consistent with the Coupled Model Intercomparison Project Phase 6 (CMIP6) implementation as described in Sellar et al. (2020). The simulation setup is same as in the Aerosol Comparisons between Observations and Models (AeroCom) Phase III GCM Trajectory experiment (AeroCom, 2022; Kim et al., 2023, in prep.).

The UKESM1 aerosol scheme represents the particle size distributions with five log-normal modes: the nucleation soluble mode, Aitken soluble and insoluble modes, accumulation soluble mode, and coarse soluble mode (Mulcahy et al., 2020). The aerosol microphysical processes of new particle formation (NPF), condensation, coagulation, wet scavenging, dry deposition and cloud processing are handled with GLOMAP (Global Model of Aerosol Processes; Mann et al., 2010; Mulcahy et al., 2020). The UKESM1 NPF mechanism follows the parameterization derived in Vehkamäki et al. (2002) for binary homogeneous nucleation of H2SO4 and water. Separate boundary layer NPF is not included in the simulations (Mulcahy et al., 2020). The soluble aerosol size distribution lognormal aerosol modal parameters (nucleation mode, soluble Aitken mode and soluble accumulation mode) and updraft velocities with a 3-hour time resolution at cloud base of stratiform clouds are used. These diagnostics are subsequently masked to include only data in which activated aerosol particles exceeds zero and the temperature exceeds 237.15 K in keeping with criteria used by the droplet activation scheme. The PNSD modal parameters are used to construct aerosol size distributions. In UKESM1 the geometric standard deviations are fixed parameters. The same values are used for consistency for the modes that are accounted for in this work. The geometric standard deviation for UKESM1 Nucleation soluble mode and the Aitken soluble mode is 1.59, and for the accumulation soluble mode it is 1.40. UKESM1 outputs for the Aitken insoluble mode and coarse mode are not used in analysis performed in this study because they do not contribute to CCN in the model representation of cloud droplet activation.

3 Results and discussion

3.1 Organic condensation: time and volatility dependencies

The first cloud parcel model simulation results (Fig. 3) correspond to initializing the model with data collected on May 11, 2014 at 11:30 EET (East European winter time). This simulation is identified from the full dataset as one that represents a strong cloud response to co-condensation of organics and water. Fig. 3a shows the vertical evolution of total SVOC and IVOC concentrations in the gas phase for the three different updraft scenarios ($u_e =$ 0.1, 0.3, or 1 m s$^{-1}$, respectively). Both SVOC and IVOC concentrations decrease significantly along the adiabatic
ascent in subsaturated conditions below cloud base (CB, RH<sub>CB</sub> = 100%). “Below CB” is defined as the ascent from RH = 90% upwards as long as RH < 100%. SVOCs and IVOCs are further scavenged inside the cloud in saturated conditions. This result is in line with Bardakov et al. (2020), who modelled complete gas removal of volatility bins up to roughly log<sub>10</sub>C* = 9 within convective clouds.

When considering all 97 simulations, the net mass fractions of organics condensed below CB are on average 91, 72 and 35% for the 0.1, 0.3 and 1.0 m s<sup>-1</sup> updraft, respectively, which in absolute concentrations means additions of 1.8, 1.4, and 0.7 μg m<sup>-3</sup> to the aerosol particle soluble mass (Table 2). The yielded mass concentrations are in the same order of magnitude of the PM<sub>1</sub> mass concentrations measured during BAECC (interquartile range, IQR: 0.95, 1.95, and 3.22 μg m<sup>-3</sup> from ACSM data), which means that such organic condensation along the adiabatic ascents simulated here would yield roughly a doubling of the soluble mass due to SVOC and IVOC condensation below CB. These numbers should, however, be assessed with caution as an ideal liquid phase, as well as partitioning being determined by mole fractions of water-soluble organics are assumed in this work (Sect. 2.1.1).

Topping et al. (2013) looked into the assumption of ideality in their supplementary material. They found it to enhance the amount of modelled organic condensate as compared to a non-ideal case. However, their simulations exploring non-ideality with organic activity coefficients predicted with the UNIFAC method (UNIQUAC Functional-group Activity Coefficients; Fredenslund et al., 1975) or solubilities still led to significant amounts of condensed organic mass. The impact of the ideality assumption was shown to be most significant in their highest volatility bin (C* = 1000 μg m<sup>-3</sup>). Activity coefficients and solubilities of organics should in the future be better constrained to assess the impact on volatility bins of log<sub>10</sub>C* > 3, which was not explored in Topping et al. (2013). As discussed in the Topping et al. (2013) supplementary information, it is likely that solubility decreases towards the higher volatility bins.

Further investigation on how efficiently different volatility bins condensed along the adiabatic ascents across all the 97 simulation scenarios repeated with the three fixed updraft velocities is also performed (Fig. 4). In the 0.1 m s<sup>-1</sup> updraft scenario, almost all organic vapor condenses up to log<sub>10</sub>C* = 5 and the condensation capability of the highest volatility bin (log<sub>10</sub>C* = 7) shows the highest variability (30–100% condensed below CB; Fig. 4a). The same features can be observed with the 0.3 m s<sup>-1</sup> and 1.0 m s<sup>-1</sup> updraft simulations, although the fraction of organic vapor condensed per volatility bin is reduced (in the w = 1 m s<sup>-1</sup> scenarios only ca. 40% of the vapor condenses below CB (Figs. 4b–c). The results from these simulations reveal that there is enough time under slow adiabatic ascents for most of the organic vapor to condense.

Figures 4d–f show the simulated organic condensate concentrations for each volatility bin. While the fraction condensed for the highest volatility bin is lowest (Figs. 4a–c), the absolute concentrations are amongst the highest due to the high availability of organic vapor in the highest volatility bin (mostly HCOOH; Sect. 2.3.2). The condensation efficiency of the highest volatility bin shows a high ICPM initialization temperature dependence. If the model initialization takes place at 270 K, up to 100% of the organic vapor in the bin condenses, while if the ascent starts at 290 K, only 40% of the mass concentration is transferred to the condensed phase below CB (Figs. 4g–i). A closer look into Figs. 4g–i reveals that under similar temperature, the condensation of the log<sub>10</sub>C* = 7 bin is most efficient in the presence of a high concentration of accumulation mode particles. This suggests that these organic vapors are likely to condense onto larger particles, which are susceptible to be activated into cloud droplets regardless of co-condensation. Similar correlations are observed to a lesser extent with the
log_{10}C^* = 6 volatility bin (not shown). In this work, the information of the size ranges of particles which the high-volatility IVOCs condense onto is lacking. Therefore, more systematic studies should be conducted to better understand whether the condensation of the high-volatility IVOCs onto ultrafine particles is sufficient enough to lead to droplet activation.

As the results from Figure 4 underline the time-dependence of co-condensation, it is worth remembering that the ICPM initialization RH is set to 90% (see Sect. 2.4). If the initial RH was set to a lower value, more time would be available for co-condensation before reaching CB, and if the initial RH was set to a higher value, less time would be available. While the decision of maintaining a fixed initial RH for the different simulations is proven useful for this study as it eases the data interpretation process, it should be acknowledged that the initial RH could be better constrained in future simulations.

### 3.2 Impact of updraft velocity on the sensitivity of cloud microphysics to organic vapor condensation

As explained previously in Topping et al. (2013), the CDNC enhancements associated with co-condensation arise from the enhancement in organic solution concentration, which decreases the critical supersaturation (s*) needed for a given particle to activate. The s* reductions from 0.15% to 0.10% for the May 11, 2014 at 11:30 EET case are shown in Fig. 3b, and correspond to a dry radius of 71.9 nm (i.e., the smallest activated dry radius when co-condensation is disabled, r_{aCC}^*, and w = 0.1 m s^{-1}; Table 2). Fig. S.2 shows the development of the wet particle size as a function of altitude in the ICPM simulation summarized in Fig. 3. It clearly demonstrates the differences introduced by co-condensation through the activation of new size bins (4 size bins in total when w = 0.1 m s^{-1}) that remain as interstitial aerosol particles in the simulations, where co-condensation is turned off. The enhanced growth of more particles due to co-condensation enhances the water vapor condensation sink, which leads to a reduction in the achieved maximum ambient supersaturations (s_{max}; see Fig. 3c for the May 11 case and Table 2 summarizing all the 97 simulations). As the updraft is the same in simulations performed with and without co-condensation, the condensation sink dictates the changes in s_{max} (Eq. 3). A reduced s_{max} would typically lower the number of aerosol particles activating into cloud droplets, but here the suppressions in s* are greater than the reductions in s_{max}, which therefore leads to an enhanced CDNC (see Fig. 3b–c for the May 11 case). This can be interpreted as a competition effect between the s_{max} and s* reductions, respectively, which the s* reduction wins.

When examining the 0.1 m s^{-1} updraft case in the May 11th simulation shown in Fig. 3, the s_{max} is reduced 12.5% (from 0.16% to 0.14%), which is less significant than the s* reduction of about 33% (from 0.15% to 0.10%; Fig. 3b). This leads to a 22% enhancement in CDNC (Fig. 3d) as r^* reduces from 72 nm to 66 nm (Δr^* ≈ 6 nm). Fig. 3e finally shows the droplet spectrum for the May 11 case, which highlights the consistent shift of droplet sizes to smaller diameters due to organic co-condensation (see also Fig. S.2, which displays the same May 11th simulation with w = 0.1 m s^{-1}).

The modelled BAECC campaign median CDNC values (over the 97 simulations) without co-condensation are on average 161, 300 and 530 cm^{-3} in modeling scenarios utilizing 0.1 m s^{-1}, 0.3 m s^{-1}, and 1.0 m s^{-1} updrafts, respectively (Table 2). CDNC is shown to correlate well with the accumulation mode number concentration (N_a), and at times with the Aitken mode number concentration (N_i) if the Aitken mode particles are large enough in size and accompanied with strong enough updrafts and a low N_i (Fig. S.3). The reductions in the smallest activated critical radii due to co-condensation are on average 8.2, 6.6, and 5.9 nm for the modeling scenarios utilizing 0.1 m s^{-1}, 0.3 m s^{-1}, and 1.0 m s^{-1} updrafts, respectively, and the corresponding median ΔCDNC...
are 16.8, 23.3 and 20.6%, respectively (Table 2 and Fig. 5a). The swarm plot on Fig. 5a shows that ΔCDNC and
CDNC do not correlate i.e., high susceptibility is in this case not predicted specifically for low CDNC.

On average during the BAECC simulation period (97 simulations), the highest ΔCDNC are found when
initializing the model with a 0.3 m s⁻¹ updraft velocity (also visible in Fig. 3d for the May 11 case) followed by
ΔCDNC predictions for the 1 m s⁻¹ case. In the latter, high supersaturations are achieved leading to the formation
of many cloud droplets, yet the effects of co-condensation remained less pronounced as the high ascent speed
poses kinetic limitations for organic condensation (see Sect. 3.1 and Fig. 4). Despite the highest organic uptake in
the 0.1 m s⁻¹ updraft simulations (Fig. 4a, d), the ΔCDNC remains the lowest. This can be explained by the low
smax, which remains insufficient for the activation of small particles and kept the smallest activated dry diameter
on average at 63.7 nm (Table 2). As the Aitken mode possesses most particles in terms of number (Table 1), the
few nm reductions in r⁺ affect ΔCDNC the most when taking place at the steep slopes between the Aitken and
accumulation mode, which does not happen in the simulations performed with 0.1 m s⁻¹ updraft.

An additional set of simulations using the CJ volatility distribution with the 0.3 m s⁻¹ updraft velocity are
performed to assess the comparability of our simulations to Topping et al. (2013) and to evaluate the impact of
the volatility distribution upgrade from CJ to F. Results from these simulations are summarized in Table 2, but
also visualized in black in Figs. 3 and 5a. The ΔCDNC predicted in the simulations using CJ volatility distributions
are lower (ΔCDNC = 12.4%) than those predicted using the F distribution, but fall within the variability reported
in Topping et al. (2013; ΔCDNC of ~5–55%). The difference between the simulations performed with CJ and F
volatility distributions, respectively, can be explained by the lower organic vapor concentration in the CJ
distribution at model initialization, leading to a lower amount of soluble mass at CB (Table 2; Fig. S.4). This result
highlights that significant quantities of co-condensable organic vapors are distributed in the higher volatility bins
and these concentrations should not be neglected in further co-condensation studies.

3.3 Impact of initial aerosol size distribution and organic vapor concentration on the sensitivity of CDNC
to organic vapor condensation

The importance of Aitken mode in ΔCDNC associated with turning co-condensation on in ICPM is exemplified
in Fig. 5b for the 0.3 m s⁻¹ updraft simulations. In this figure, the initial dry PNSD are averaged from the
simulations with the highest 50% and lowest 50% modelled ΔCDNC, respectively. The PNSD corresponding to
the highest 50% of the modelled ΔCDNC has a very minor accumulation mode and a large Aitken mode (with
respect to the mode total number concentrations i.e., N₂ and N₁, respectively). It is therefore named as PNSD₁M₂,
where NUM refers to a strong nascent ultrafine mode characteristic of the shown size distribution. The PNSD
corresponding to the lowest 50% of the modelled ΔCDNC is strongly bimodal, where the Aitken and accumulation
modes are almost equal in terms of N. Moreover, the two modes are separated by a clear Hoppel minimum (Hoppel
and Frick, 1990). Hoppel minimum is characteristic for particulate matter, which has undergone cloud processing.
This result underlines that environments rich in particles from a local source would be more susceptible to high
ΔCDNC due to co-condensation while regions with aged and cloud processed size distributions are affected less
(ΔCDNC<20% in our simulations; Fig. 5a).

Interestingly, a nascent ultrafine aerosol particle mode (NUM) was found to be important when looking
into suitable conditions for large increase in CDNC caused by surface active organics (Lowe et al., 2019;
Ovdanevaite et al., 2017). Lowe et al. (2019) utilized the same CPM as used in this study (notably without co-
condensation), but enabled a fraction of the particulate organics to form a thin, max. 0.2 nm thick film around the particle. The film was characterized by a surface tension of 40 mN m\(^{-1}\) as opposed to the surface tension of pure water (72.8 mN m\(^{-1}\)). The idea of this compressed film (CF) approach was to simulate the surface tension reductions caused by organic species leading to the activation of smaller particles to cloud droplets at the coastal Mace Head site (Ovadnevaite et al., 2017). Through sensitivity studies, Lowe et al. (2019) found that the largest percent change in CDNC due to surface active organics (>10%) took place in Mace Head when \(N_c < aN_{\text{CF}} + c\) (\(a = 602, b = 0.0884, c = -766\)). The increase in CDNC in the Lowe et al. (2019) study was also attributed to the reduction in \(\kappa\) when comparing against simulations where the surface tension was that of water. Moreover, the same competition effect between \(S_{\text{max}}\) and \(\kappa\) reductions – as described here in Sect. 3.2 – was demonstrated in their study, but just triggered by different chemical parameters. The sensitivity of the CDNC enhancements to \(\Delta\text{CDNC}\) in this study as well as in Lowe et al. (2019) demonstrates that the activation of fresh and non-cloud-processed aerosol particles is susceptible to small reductions in \(\kappa\); that can be triggered e.g., by organic surfactants or co-condensation. Importantly, potential surface activity also affects the CCN activation behavior of atmospheric organics (Ruehl et al., 2012, 2016; Lowe et al., 2019), correlating with volatility and solubility. The combined effect of all these three properties needs to be thoroughly investigated, because of the potential of the organic film to suppress the solute effect (Sorjamaa et al., 2004) and thereby co-condensation and its effects on \(\Delta\text{CDNC}\).

In conjunction with the \(\Delta\text{CDNC}\) susceptibility to PNSD\(_{\text{NUM}}\), this study most critically highlights the importance of incorporating multimodal, and representative size distributions in process modeling studies examining the cloud response to surface active organics, or co-condensation. Topping et al. (2013), for example, used monomodal distributions (with varying log-normal parameters) in their study, which could lead to overestimation of \(\Delta\text{CDNC}\) as size distributions with Hoppel minima are not explored. Multimodal distributions were used later by Crooks et al. (2018), but further explanation of the cloud response of the update remained lacking. In summary, our results suggest that in clean environments with a local source of ultrafine particles, such as the boreal forest or marine environments, organic species in the presence of a NUM-featured PNSD can have a significant impact on cloud properties either via co-condensation or through surface tension reductions.

Subsequently, a dry PNSD-based criteria for identifying regimes (conditions) in which co-condensation has the highest impact on CDNC are defined. It is found that restricting the ratio between the accumulation and Aitken mode geometric mean diameters in the initial dry PNSD to below six (i.e., \(D_2/D_1<6\)) and the Aitken mode number concentration to exceed 1000 cm\(^{-3}\) (i.e., \(N_1>1000\) cm\(^{-3}\)) would yield \(\Delta\text{CDNC} >20\%\) in our simulations. By using the diameter ratio criterion, size distributions without a distinguishable Hoppel minimum are selected, which is characteristic in the simulations yielding the highest \(\Delta\text{CDNC}\) (Fig. 5b) and the high \(N_1\) ensures a high concentration of aerosol particles potentially activating into cloud droplets. Fig. 5d shows the \(\Delta\text{CDNC}\) as a function of \(D_2/D_1, N_1\) and the Pearson correlation coefficient with PNSD\(_{\text{NUM}}\) (0.3 m s\(^{-1}\) updraft case). The simulations with the initial dry PNSD fulfilling the criteria are highlighted with white crosses. Most of the high \(\Delta\text{CDNC}\) are well captured, and at those times the correlation with the PNSD\(_{\text{NUM}}\) is high (Pearson \(R>0.7\)). The simulations fulfilling the dry PNSD-based criteria are marked also in Fig. 5c showing that most of the high \(\Delta\text{CDNC}\) are captured, which again highlights the critical role of the aerosol size distribution representation in capturing the co-condensation driven \(\Delta\text{CDNC}\).
In addition to the PNSD_{NUM} features, also the initial organic vapor concentration (\(C_{g}^{\text{INIT}}\)) influences the modeled AD DNC. This relationship is depicted in Fig. 5c using the ICPM simulations corresponding to 0.3 m s\(^{-1}\) updrafts. The \(y\)-axis represents the modeled AD DNC and the \(x\)-axis the organic vapor concentration distributed in \(\log_{10}C^*\) bins within [-4, 4] (denoted as \(C_{g}^{\text{INIT}}\)) i.e., in bins that do not show high dependency on \(N\); or initial temperature (see Sect. 3.2 for details). The relationship is not straightforward, but linear increases in AD DNC as a function of \(C_{g}^{\text{INIT}}\) can be seen under constant, yet sufficiently high \(s_{\text{max}}\) (here >0.2\%). Under the modelled scenarios where \(s_{\text{max}}>0.2\%\), the \(C_{g}^{\text{INIT}}\) remains low, mostly below 2 μg m\(^{-3}\), and the highest enhancements are achieved when \(C_{g}^{\text{INIT}}\) is ≤1 μg m\(^{-3}\) because the soluble organic mass is distributed to more particles. The markers in Fig. 5c are color-coded by the initial PNSD surface area, which under a constant updraft anticorrelates with \(s_{\text{max}}\) (see Eq. 3). AD DNC shows high sensitivity to \(C_{g}^{\text{INIT}}\) when the dry PNSD surface area stays below a 100 μm\(^{2}\) cm\(^{-3}\) threshold. Based on this analysis, it can be concluded that in the presence of a NUM-featured PNSD enabling the formation of high supersaturations (the dry PNSD surface area stays below 100 μm\(^{2}\) cm\(^{-3}\)), an adiabatic ascent with an updraft of 0.1 or 0.3 m s\(^{-1}\) can yield ΔCDNC of >40% if 1 μg m\(^{-3}\) of co-condensable organic vapor is present in the rising air. This is a likely occurrence in the spring and summertime boreal forest (Huang et al., 2021). The simulations performed with the highest updraft velocity (\(w = 1.0\) m s\(^{-1}\)) yield lower ΔCDNC under these clean conditions (ΔCDNC does not exceed 40%) even though the simulated \(s_{\text{max}}\) increase as opposed to the results obtained with lower updrafts (e.g. Table 2), because of the kinetic limitations hindering co-condensation (see Sect. 3.1).

### 3.4 Expected seasonality in the impact of co-condensation on CDNC at SMEAR II

In the following, the seasonality of the dry PNSD surface area at SMEAR II (6-year-long time series, 2012–2017) is investigated to estimate how often it stays below the previously mentioned threshold of 100 μm\(^{2}\) cm\(^{-3}\) i.e., times when only 1 μg m\(^{-3}\) of co-condensable organic vapor present in the rising air could yield significant AD DNC. This is followed by an investigation of the frequency of the PNSD criteria (\(Dz/Dt<6\) and \(N>1000\) cm\(^{-3}\)) fulfillments in the long-term size distribution measurements at SMEAR II.

Fig. 6a shows the seasonality of the dry surface area at SMEAR II. During daytime (9–19 EET) the surface area stays below the previously mentioned threshold 86% of the time during the 2012–2017 measurement period (Fig. S.5), which suggests that under 0.3 m s\(^{-1}\) updraft velocities, generation of \(s_{\text{max}}>0.2\%\) at this site is likely. During summer months, the likelihood of surpassing the dry PNSD surface area threshold of 100 μm\(^{2}\) cm\(^{-3}\) increases to 22% from 10% (Fig. S.5) due to biogenic SOA formation (Tunved et al., 2006), which grows the accumulation mode in the PNSD. Biogenic SOA formation depends on the SOA precursor i.e., BVOC emissions and concentrations. Monoterpene concentrations are highest at SMEAR II in summer (Kontkanen et al., 2016; Hakola et al., 2012) as their emissions are strongly temperature-driven (Guenther et al., 1993). The organic vapor concentration available for co-condensation is therefore also highest in summer, but due to the enhanced surface area, the soluble organic mass is distributed to more particles dampening the cloud response to co-condensation. However, the monoterpene emission period is longer than just summer, and elevated monoterpene concentrations can be observed throughout the thermal growing season (when the daily average temperature is above 5°C; Kontkanen et al., 2016; Hakola et al., 2012). Therefore, monoterpene emissions take place also at times when the dry PNSD surface area stays below the 100 μm\(^{2}\) cm\(^{-3}\) threshold.
Fig. 6b shows the dry PNSD surface area derived from the long-term PNSD measurements at SMEAR II as a function of temperature. When the ambient temperature exceeds 5°C, the dry PNSD surface area starts to increase with increasing temperature. The dry PNSD surface areas and ambient temperatures (from 8.4 m height; Fig. 1c) from the BAECC simulation period are also shown to highlight the fact that the BAECC sample represents well the long-term statistics of the thermal growing season, providing confidence in the representativity of the BAEC sampling period for this boreal environment. The BAECC samples are color-coded by the modelled ΔCDNC. The highest ΔCDNC (i.e., ΔCDNC > 40%) are modeled when the dry PNSD surface areas are below the 100 μm² cm⁻³ threshold. Importantly, most of these model scenarios yielding ΔCDNC > 40% coincide with ambient temperatures between 5 and 8°C i.e., at times when the monoterpene concentrations are not at their highest yet sufficient concentrations of organic vapor are still present to cause a large cloud response. It can thereby be concluded that the highest ΔCDNC due to co-condensation can be expected in thermal Spring and Fall. However, due to the seasonality in hygroscopicity and the slightly higher κ in spring and autumn (as opposed to summer; Fig. 6a) the likelihoods of obtaining s max exceeding 0.2% to yield significant ΔCDNC can be somewhat buffered due to hygroscopic growth.

Next, the frequency to which the PNSD criteria (D2/D1<6 and N1>1000 cm⁻³) are fulfilled in the long-term size distribution measurements is examined. For this purpose, the same 6-year PNSD data set collected at SMEAR II fitted with two log-normal size distributions (Hussein et al., 2005) is utilized. The percentage of times the criteria are met is shown in Fig. 7a. The highest frequencies (30–40% of the time) are observed in April, May and September, which correlates with the new particle formation (NPF) frequency at the site (Nieminen et al., 2014; Dada et al., 2017). The monthly median size distributions fulfilling the criteria are shown in Fig. 7c. They all clearly exhibit the lack of a Hoppel minimum, similarly to PNSDNUM, and suggest a potentially high impact of newly formed particles on cloud properties through co-condensation. The results again clearly emphasize the need of accurate representation of aerosol size distributions and lifecycle in models (such as other CPMs or global circulation models, GCMs) to account for the impacts of co-condensation and the strong seasonality to be expected in the magnitudes in ΔCDNC.

3.5 Expected spatiotemporal variability in the impact of co-condensation on CDNC over the boreal biome

In this section the SMEAR II results are compared against a 5-year UKESM1 simulation (see Sect. 2.5; analysis restricted to the boreal biome). While the SMEAR II PNSD data are retrieved at ground level, utilization of the UKESM1 modal parameters (only soluble modes considered) from CB is chosen, because these PNSD log-normal parameters would actually meet the cloud droplet activation scheme in the model. The monthly averages of the percentage of times the criteria (D2/D1<6 and N1>1000 cm⁻³) are fulfilled in the boreal grids are shown in Fig. 7b. Here, the Aitken mode geometric mean diameter and total number concentration (D1, N1) and accumulation mode geometric mean diameter (D2) are obtained from the soluble Aitken and accumulation modal parameters (see Sect. 2.5 for more details regarding the UKESM1 modes). The frequencies, which remain roughly well below 6%, are in general much lower than observed at SMEAR II. This can be explained by the lack of the boundary layer NPF process in the UKESM1 simulations (Sect 2.5). Therefore, the UKESM1 results can be taken as the lower estimate.

Fig. 7d displays the monthly median PNSD in the boreal grid cells fulfilling the criteria (D2/D1<6 and N1>1000 cm⁻³), which are constructed from the soluble Nucleation, soluble Aitken and soluble accumulation mode modal parameters from the UKESM1 simulations when the criteria are fulfilled (criteria only uses soluble Aitken and
soluble accumulation modes). The size distributions calculated using these UKESM1 modal parameters are in general less similar to the PNSD$_{	ext{SUM}}$ than the monthly median SMEAR II size distributions are (Fig. 7c), because they have more distinguished multimodal shapes. However, they still feature a minor accumulation mode in the presence of a large Aitken mode (with respect to $N$).

The UKESM1 results suggest strong spatiotemporal variability in the co-condensation driven $\Delta$CDNC should be expected if this process were to be represented in GCMs. Consistently with the SMEAR II observations (Fig. 7a), spring months stand out as the times when the criteria are most likely to be met, but the other peak in the frequency, expected in September at SMEAR II, cannot be seen. Another interesting feature is the large spatial variability in the frequency. In March and April, a very evident hotspot can be seen in the southern parts of the boreal forest, more precisely in the north of Kazakhstan. When the whole northern hemisphere is displayed, it is clear that the hot spot region extends over Europe during Spring (Fig. S.6) when the conditions favor the formation, growth and survival of small particles (Kerminen et al., 2018) as shown in Fig. S7 in terms of nucleation mode number concentration. The result therefore suggests high co-condensation potential in areas rich in ultrafine particles. The cloud response of co-condensation in an extended domain covering most of Eurasia could be an interesting follow-up study. However, such a study should incorporate also the condensation of nitric acid and ammonia, the concentrations of which are presumably abundant in the regions, where the co-condensation PNSD criteria are met (Kakavas et al., 2022). As this “Kazakhstan hotspot” is connected to aerosol phenomenology outside the boreal biome, the analysis is not continued further. Another evident springtime hot spot is located in North America, near the Rocky Mountains, but the updraft velocities at the area are not within the desired range ([0.2, 0.5] m s$^{-1}$) to yield significant cloud response from co-condensation (Fig. 7b).

Aside from these hotspots, it is notable that the overall background of the frequency of the times the criteria are met in the latitude range of [0, 75] °E increases from <2% to 2–6% when moving from March to April. This background stays elevated until June. Smaller hotspots within this area are visible and they correspond to regions known with high sulfur dioxide (SO$_2$) emissions, such as the Kola peninsula. The Kola peninsula SO$_2$ emissions have shown to trigger NPF events measured at SMEAR I in Finnish Eastern Lapland (e.g., Kyrö et al., 2014). An interesting next step would be to see how Fig. 7b changes with UKESM1 simulations incorporating boundary layer NPF and whether the percentage of times the criteria are met increases to values comparable with the SMEAR II observations and whether the frequency becomes larger also in Fall. Another interesting observation to be made from Fig. 7b is that no significant impact of co-condensation would be expected in UKESM1 in most of Siberia (East and Northeastern Siberia), which can be explained by the lack of nucleation mode particles in the UKESM1 simulations over the region (Fig. S.7).

4 Conclusions

This study focuses on the role of the co-condensation of organic vapor and water on warm cloud microphysics in a boreal forest environment. Co-condensation has been proposed as a potentially significant process contributing to the feedbacks between VOC emissions, SOA loadings, cloud formation and climate. Boreal forests account for about a third of the Earth’s forested area and are potentially significant sources of such co-condensing species.

First, ICPM model is used to perform simulations for the BAECC measurement campaign which took place at the SMEAR II station in Southern Finland during 2014 (Petäjä et al., 2016). The measurement setup during BAECC was very advanced, enabling the initialization of ICPM with state-of-the art data describing the
ambient aerosol physical and chemical properties. The measurements conducted with the FIGAERO-I-CIMS (e.g., Mohr et al., 2017) are of high importance for this study due to the simultaneous measurements of organic particle and vapor species. These data enable the incorporation of organic vapors from a broad volatility range into the ICPM simulations. The previous modeling work on this topic used volatility distributions based on particle-phase measurements only, resulting in overall lower volatility and contributions of semi- and intermediate volatility organic vapor.

The results from the ICPM simulations reveal that a competition effect exists between the reductions in maximum supersaturations and critical supersaturations needed for aerosol particle activation into cloud droplets. The reductions in critical supersaturations are greater than the reductions in maximum supersaturation, which results in the simulated CDNC enhancements (simulations with co-condensation are compared against simulations without it under same meteorological conditions). The CDNC enhancements are of the order of 20% under realistic updraft velocities (0.1, 0.3, and 1 m s\(^{-1}\)) and correspond to reductions of 12–16 nm in the smallest activated dry diameters (144 to 126 nm, 102 to 88.6 nm, 72 to 61 nm for the 0.1, 0.3, and 1 m s\(^{-1}\) updraft scenarios, respectively). The activation of smaller particles into cloud droplets results, as expected, in the formation of more numerous smaller cloud droplets. The critical supersaturation suppressions result from the additions of soluble organic mass below cloud base along the simulated air parcels’ adiabatic ascents while the reductions in maximum supersaturation are caused by the increasing condensation sink provided by more cloud droplets (the source of supersaturation is fixed as the meteorological conditions between simulations with and without co-condensation are kept constant).

The predicted CDNC enhancements are highest for the 0.3 m s\(^{-1}\) updraft velocities and depend on several, at least partly, interlinked parameters (see also Lowe et al., 2019). One parameter affecting the modelled CDNC is the availability of the co-condensable organic vapors, which in turn depend on the updraft velocities and the features of the organic volatility distribution. Most organic vapor condenses under the slowest adiabatic ascents and least in the highest degree prior reaching the cloud base. Organic vapors of higher volatility involving species such as formic acid condense less efficiently and their condensation is sensitive to the model initialization temperature and the presence of large particles, which are likely to activate regardless of co-condensation. Therefore, small enhancements in particularly SVOC and lower-volatility IVOC concentrations lead to significant enhancements in CDNC, while increases in the most volatile IVOCs and formic acid do not affect CDNC much.

The simulations performed with 0.3 m s\(^{-1}\) updrafts are repeated using volatility distributions from previous co-condensation studies (Cappa and Jimenez, 2010; Topping et al., 2013; Crooks et al., 2018). By doing so, the BAECC campaign median CDNC enhancement decreased from 23.3 to 12.4%. This result is explained by the lower SVOC and IVOC concentrations in previous studies, highlighting the added value of capturing these higher volatility bins within the VBS representations of atmospheric organic species. On the other hand, adding information on the LVOC and ELVOC range do not significantly influence the CDNC enhancements due to co-condensation.

The sensitivity of the modelled ΔCDNC to organic vapor concentrations is strongest when high maximum supersaturations (\(s_{\text{max}}>0.2\%\) for the 0.3 m s\(^{-1}\) updraft scenarios) are reached. Such conditions are achieved when the dry PNSD surface area (a proxy for the condensation sink) remains below 100 μm\(^2\) cm\(^{-3}\). Under
those conditions, CDNC enhancements exceeding 40% are predicted for conditions in which roughly 1 μg m^{-3} of co-condensable organic vapor is present.

Besides the updraft velocities and the availability of co-condensable vapors, the CDNC enhancements depend critically on the size distribution of the initial aerosol population. Highest CDNC enhancements are generally achieved when the model is initialized with a relatively weak accumulation mode combined with a large nascent ultrafine particle mode with a geometric mean diameter of ca. 40 nm, with no visible Hoppel minimum present in the distribution. Such conditions are observed most frequently in Spring and September (about 30–40% of the time in years 2012–2017), when new particle formation events take place at SMEAR II.

Further on, UKESM simulations (years 2009–2013) are utilized to investigate the potential impact of including the process of co-condensation on droplet formation in this model over the whole boreal biome using the criteria developed from the SMEAR II case to identify most susceptible PNSD conditions. Aside from two hotspots (one near the Rocky Mountains in North America, one over northern Kazakhstan, which are not analyzed further), the presence of suitable PNSD is most frequent over Fennoscandia and western parts of Siberia in spring, yet the frequencies at which those PNSD are modelled remained much lower than those obtained from the long-term SMEAR II PNSD measurements (2–6% in UKESM1). It is likely that the incorporation of boundary layer NPF in UKESM will increase this frequency. Perhaps surprisingly, suitable PNSD are never modeled over most of Siberia, suggesting that for the model configuration of UKESM1 used in this study, the process of co-condensation would not be expected to have an influence on droplet formation in this area. This is due to the low concentration of ultrafine particle particles modeled in the area.

In summary, these results highlight the potential significance of co-condensation in pristine boreal environments with a nascent ultrafine particle mode present. Such conditions are met over Fennoscandia and Western parts of Siberia in Spring and to a lesser extent in the Fall, when NPF takes place. For future modelling purposes, it is vital to stress the importance of the accurate representation of PNSD for capturing the role of co-condensation of organics on CDNC enhancements. Because the modelled CDNC enhancements are so significant, further research focus especially regarding observations of the co-condensation should be targeted in the future to motivate future assessments of co-condensation-driven radiative forcing. Perhaps this work inspires aircraft measurements (of the relevant parameters discussed in this paper) to take place over the Fennoscandia in the future to finally narrow down the importance of co-condensation.
Data availability

The ICPM input and outputs for reproducing the figures will be available on the Bolin Centre database.

Competing interests

The authors have the following competing interests: Some authors are members of the editorial board of Atmospheric Chemistry and Physics. The peer-review process will be guided by an independent editor. On or more authors have received funding from European Union’s Horizon 2020 research and innovation programme, European Research Council, Knut and Alice Wallenberg foundation, Academy of Finland and US Department of Energy, and/or support from ACTRIS Translational Access and ACTRIS-HY. The authors have no other competing interests to declare.

Author contributions

LH, IR, DGP and CM conceptualized the idea of the study. LH prepared the model input data performed the simulations, analyzed the simulation output, made the figures and wrote the manuscript with contributions from the coauthors. TP designed and led the BAECC campaign. CM performed the FIGAERO-I-CIMS measurements, WH processed and delivered the FIGAERO-I-CIMS data and gave input on the volatility distribution calculation. RR assisted with the radiosonde data and provided the hygroscopicity seasonal cycle data. ET and DGP performed the UKESM1 simulations and DGP designed and processed the data for analysis input parameters to droplet activation parameterization. SB visualized the UKESM1 data and gave input on the data interpretation. LH wrote the paper with input from all co-authors.

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Tables

Table 1: Overview of the simulation input parameters that remain unchanged in all of the simulation sets conducted with or without co-condensation. The updraft velocities, organic volatility distributions and vapor concentrations that change between simulation sets are reported in Table 2 together with the median model outputs. The time series of these model input data are shown in Fig. 1. All the modelling scenarios are initiated at 90% relative humidity.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aitken mode number conc. (N_1 [\text{cm}^{-3}])</td>
<td>160</td>
<td>12,316</td>
<td>1,491</td>
</tr>
<tr>
<td>Accumulation mode number conc. (N_2 [\text{cm}^{-3}])</td>
<td>44</td>
<td>2,433</td>
<td>560</td>
</tr>
<tr>
<td>Aitken mode geometric mean dry diameter (D_1 [\text{nm}])</td>
<td>7.1</td>
<td>71.0</td>
<td>23.8</td>
</tr>
<tr>
<td>Accumulation mode geometric mean dry diameter (D_2 [\text{nm}])</td>
<td>62.6</td>
<td>201.9</td>
<td>115.3</td>
</tr>
<tr>
<td>Geom. standard deviation of Aitken mode (\sigma_1 )</td>
<td>1.50</td>
<td>2.08</td>
<td>1.75</td>
</tr>
<tr>
<td>Geom. standard deviation of accumulation mode (\sigma_2 )</td>
<td>1.33</td>
<td>2.06</td>
<td>1.75</td>
</tr>
<tr>
<td>Number of PNSD size bins</td>
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<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Organic mass fraction (f_{\text{org}} %) )</td>
<td>25</td>
<td>84</td>
<td>68</td>
</tr>
<tr>
<td>Initial (T [\text{K}] )</td>
<td>271</td>
<td>295</td>
<td>279</td>
</tr>
<tr>
<td>Initial (p [\text{hPa}] )</td>
<td>980</td>
<td>980</td>
<td>980</td>
</tr>
<tr>
<td>Mass accommodation coefficient (\alpha )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Effective soluble fraction of organics</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Surface tension (\gamma [\text{mN} \cdot \text{m}^{-1}] )</td>
<td>72.8</td>
<td>72.8</td>
<td>72.8</td>
</tr>
<tr>
<td>ICPM time step ([\text{s}] )</td>
<td>(10^{-3})</td>
<td>(10^{-3})</td>
<td>(10^{-3})</td>
</tr>
</tbody>
</table>

\(^a\) Retrieved from fits assigned onto the measured aerosol size distributions (Aalto et al., 2001) using a fitting algorithm by Hussein et al. (2005).

\(^b\) Retrieved from aerosol chemical composition measurements (Heikkinen et al., 2020).

\(^c\) Retrieved from radiosonde data (ARM Data Center, 2014). The temperatures shown were recorded when the relative humidity measured by the radiosonde reached 90%, i.e., the initial relative humidity used for the adiabatic ascents.
### Table 2
Overview of the simulation output for the no co-condensation (noCC) and co-condensation (CC) simulations performed using varying updraft velocities.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Median values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatility distribution (^a)</td>
<td>F CJ F F</td>
</tr>
<tr>
<td>Updraft velocity (w) [m s(^{-1})] (^a)</td>
<td>0.1 0.3 0.3 1.0</td>
</tr>
<tr>
<td>Parcel displacement before CB [m]</td>
<td>190 190 190 190</td>
</tr>
<tr>
<td>Cloud droplet number conc. CDNC(_{noCC}) [cm(^{-3})] (^b)</td>
<td>161 300 300 530</td>
</tr>
<tr>
<td>Cloud droplet number conc. CDNC(_{CC}) [cm(^{-3})] (^b)</td>
<td>190 358 411 645</td>
</tr>
<tr>
<td>CDNC enhancement (\Delta) CDNC [%] (^b)</td>
<td>16.8 12.4 23.3 20.6</td>
</tr>
<tr>
<td>Maximum supersaturation (s_{max}^{noCC}) [%]</td>
<td>0.15 0.24 0.24 0.41</td>
</tr>
<tr>
<td>Maximum supersaturation (s_{max}^{CC}) [%]</td>
<td>0.14 0.23 0.22 0.38</td>
</tr>
<tr>
<td>Smallest activated dry radius (r_{noCC}^{*}) [nm]</td>
<td>71.9 50.9 50.9 36.0</td>
</tr>
<tr>
<td>Smallest activated dry radius (r_{CC}^{*}) [nm]</td>
<td>63.7 46.7 44.3 30.3</td>
</tr>
<tr>
<td>Initial organic vapor conc. (\Sigma c_g^{init}) [µg m(^{-3})]</td>
<td>1.99 1.07 1.99 1.99</td>
</tr>
<tr>
<td>Organic vapor condensed below cloud base (\Sigma c_g^{init} - \Sigma c_g^{cb}) [µg m(^{-3})]</td>
<td>1.81 0.66 1.43 0.69</td>
</tr>
<tr>
<td>Fraction of organic vapor condensed below cloud base (\Delta C_g^{init-cb}) [%]</td>
<td>91.0 61.7 71.9 34.7</td>
</tr>
</tbody>
</table>

\(^a\) Model input parameters crucial for understanding the differences between the co-condensation simulation model outputs.

\(^b\) The CDNC represent the integrated number concentration in size bins exceeding the critical radius in size at 50 meters above cloud base (CB).
Figures

(a) Time-series of the particle number size distribution in the time period of interest during BAECC. The time points used for the ICPM initialization are shown as orange crosses. (b) The non-refractory (NR) chemical composition of sub-micrometer aerosol particles for the same time period. (c) The time series of ambient temperature near ground level (8.4 m a.g.l.) is shown in blue and the ICPM initialization temperature corresponding to RH = 90% from the interpolated radiosonde data product is shown in orange. The subpanels have a common x-axis representing the East European winter time (UTC+2).
Figure 2 (a) The normalized volatility distributions \((C_g + C_p)\) from Cappa and Jimenez (2010; CJ) and the BAECC FIGAERO-I-CIMS measurements (F) using the modified Li et al. (2016) molecular formulae-based parameterizations. A volatility distribution from Hunter et al. (2017) constructed from the BEACHON-RoMBAS measurement campaign is shown in the dashed bars. The volatility ranges for ELVOC, LVOC, SVOC and IVOC/VOC are shown in color scales. These \(C^*\) limits apply throughout the paper. (b–e) The partitioning predicted based on the FIGAERO-I-CIMS gas- and particle-phase measurements and the ICPM, respectively. (d) A scatterplot drawn between the FIGAERO-I-CIMS derived partitioning coefficients \((\xi_{\text{meas}})\) and ICPM derived coefficients \((\xi_{\text{mod}})\) for the 12 different volatility bins. Panels (e–f) represent the gas phase molecular composition from the FIGAERO-I-CIMS: panel (e) the distribution between organic nitrates and non-nitrates and panel (f) the degree of oxygenation in the form of oxygen and carbon numbers. The marker size in panel f corresponds to the concentration of signal for the given \(n_C\) and \(n_O\) combination.
Figure 3 A summary of simulated cloud microphysics on May 11, 11:30 EET during the BAECC campaign. Simulations are performed both with and without organic condensation (red and blue lines, respectively) for three different updraft velocities (see line styles from panel a). The initial temperature is 279 K, pressure 980 hPa and supersaturation −0.1% (RH = 90%). (a) The concentration of SVOCs and IVOCs in the gas phase as a function of distance from cloud base (CB). (b) The absolute change in critical supersaturation as a function of soluble mass added along the ascent by condensing organics. The markers represent the reductions at the maximum supersaturation ($s_{\text{max}}$). (c-d) The evolution of the $s_{\text{max}}$ and CDNC with altitude, respectively. (e) The droplet spectra 50 meters above CB. Size bins exceeding the critical diameter as predicted by Köhler theory are calculated as cloud droplets. The red lines are obtained with F volatility distributions and the black with CI (Fig. 2a). The line type specifications in panels d–e follow those shown in panel a and the colors used in panels d–e are documented in the panel c legend.
Figure 4: Box plots showing the fractions (a–c) and absolute concentrations (d–f) of vapor condensed below cloud base per volatility bin for the 0.1, 0.3 and 1.0 m s$^{-1}$ updraft scenarios, respectively. The volatility ranges in panels a–f start from log$_{10}$C$^*$ = 0 because of the negligible gas-phase concentrations in the lower volatility bins. The final row (g–i) shows how the fraction of vapor condensed from the highest volatility bin (y-axis) behaves as a function of ICPM initialization temperature (x-axis), accumulation mode number concentration (marker size) and total initial organic vapor concentration (marker color).
Figure 5 (a) Box plots showing the predicted $\Delta$CDNC (using F volatility distributions) due to co-condensation in the three different modelling scenarios (0.1, 0.3 and 1.0 m s$^{-1}$ updrafts). The median ($Q_{50}$) $\Delta$CDNC yielded using the CJ distribution is shown with a black cross. The colorful markers represent CDNC (without accounting for co-condensation) in form of a swarmplot. (b) The median initial dry size distributions calculated from the simulations exceeding the 75th percentile in $\Delta$CDNC ($\rightarrow Q_{75}$; thick lines) and remaining below the 25th percentile ($\rightarrow Q_{25}$; thin lines), respectively. The median is calculated by taking a median of the log-normal parameters from both sets of simulations (in black) and from the measurement data (in grey). The data are shown for the simulation performed with a 0.3 m s$^{-1}$ updraft. (c) The relationship between the modeled $\Delta$CDNC and the initial organic vapor concentration within the log$_{10} C$ range from $-4$ to $4$ ($C_{g,x}^{\text{INIT}}$). The marker color-coding represents the initial dry size distribution surface area ($A$). The plot background is colored with the modeled maximum supersaturations ($s_{\text{max}}$). These are calculated from $s_{\text{max}}$ binned $\Delta$CDNC vs $C_{g,x}^{\text{INIT}}$ linear fit 90% confidence intervals (CI; area between CI is colored). The figure shows that $A$ anticorrelates with $s_{\text{max}}$ (see Eq. 3). The data are shown for the simulations performed with a 0.3 m s$^{-1}$ updraft only.
Figure 6 (a) The seasonal cycle of the dry aerosol size distribution surface area (S) calculated from the long-term aerosol size distribution observations (2012–2017; left y-axis), where the markers represent the median values, the darkest shading the interquartile range and the lighter shading the area between the 5th and 95th percentiles. The panel also contains the median seasonal cycles of organic mass fraction and the κ hygroscopicity parameter compiled from the same long-term period (right y-axis). The green horizontal line refers to the dry surface area threshold of 100 μm$^2$ cm$^{-3}$ from Fig. 5, under which the greatest ΔCDNC are modeled using the BAECC data. (b) A density plot showing the observations of S under different ambient temperatures during the 2012–2017 long-term period. The A threshold of 100 μm$^2$ cm$^{-3}$ is again shown with the horizontal green line. The vertical dashed green line is a rough estimate for the start of the thermal growing season, which also refers to the starting point of the majority of the BVOC emissions. The markers show the ICPM simulation data color-coded with the associated ΔCDNC (simulations yielding the ΔCDNC below the 25th percentile are shown in blue, simulations yielding ΔCDNC above the 75th percentile in red and the simulations between those limits are shown in white).
Figure 7 (a) Percentage of times the criteria ($D_2/D_1<6$ and $N_1>1000$ cm$^{-3}$) are met at SMEAR II between the 2012–2017 measurement period. $D_2$, $D_1$, and $N_1$ are attained from bimodal fits calculated for the measured PNSD using the Hussein et al. (2005) algorithm. (b) The percentage of times the criteria are met in a 2009–2013 UKESM1 simulation. $D_2$, $D_1$, and $N_1$ are the modal parameters representing the soluble accumulation mode and soluble Aitken mode parameters. The gray markers refer to boreal grid cells, where the median updraft velocity at cloud base is between 0.2 and 0.5 m s$^{-1}$. (c–d) Monthly median size distributions from the long-term PNSD measurements at SMEAR II and UKESM1 simulation, respectively. The UKESM1 size distributions are calculated from the log-normal PNSD parameters for nucleation, soluble Aitken and soluble accumulation modes assuming geometric standard deviations of $\sigma = 1.59$ for nucleation and soluble Aitken modes and $\sigma = 1.4$ for the soluble accumulation mode. The soluble coarse mode is not included in the analysis.
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