

# Energetically Stringent Quantification Derivation of Water Vapor Supersaturation at Cloud Base

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**Abstract.** Current in situ measurements of water vapor supersaturation ( $S_v$ ) at cloud bases are highly uncertain due to instrumental limitations. Consequently,  $S_v$  is commonly estimated using cloud microphysical models and parametrizations. Here, we derive  $S_v$  at cloud base from in situ measurements of liquid clouds through calculations of the energy and water vapor budgets during cloud formation. To this end, we formulate the energy budget of an adiabatically ascending saturated air parcel at cloud base, where changes in the thermodynamic state variables are approximated as quasi-isobaric. Under these conditions, the latent heat released during condensational droplet growth ( $Q$ ) is determined by the corresponding enthalpy change associated with the phase transition from water vapor to liquid water. According to the first law of thermodynamics,  $Q$  is redistributed between changes in internal energy ( $\Delta U$ ) and water vapor expansion work ( $W_s$ ). Within this diagnostic framework, part of the latent energy is therefore associated with  $W_s$ , reducing the amount of liquid water formed relative to the limiting case in which the entire latent energy contributes to droplet growth. The supersaturations relative to liquid water ( $S_l$ ) and water vapor ( $S_v$ ) are estimated from the fractions of  $Q$  associated with  $\Delta U$  and  $W_s$ , respectively. This framework enables the derivation of  $S_v$  from airborne cloud-base measurements through thermodynamic constraints on latent-energy partitioning during condensational growth. We derive and quantify water-vapor supersaturation ( $S_v$ ) in cloud warm (only liquid water containing) at warm cloud base by describing the ascent of a saturated (cloudy) air parcel as a reversible cloud-adiabatic process, that adiabatically changes its state variables. Changes of the thermodynamic state parameters of the air can be heat air water and In this framework, the parcel's isobaric enthalpy is conserved along the ascent. The latent heat release ( $Q$ ) during condensational growth of cloud condensation nuclei (CCN) and droplets is internally redistributed according to the first law of thermodynamics, such that the energy balance is partitioned between the air parcel's internal energy ( $U$ ) and the saturation work of water vapor ( $W_s$ ). We find that within this diagnostic framework, the vapor-phase supersaturations are estimated from fractions of the energy budget  $Q$  associated with internal change  $\Delta U$  and water vapor expansion work  $W_s$ , corresponds to liquid-phase supersaturation ( $S_l$ ) and  $S_v$ , respectively. Closure analyses of using airborne measurements at cloud bases of growing cumuli over the Amazon Basin, we demonstrate that the droplet number concentration  $N_d$  scales with  $S_v$  and agrees

within the uncertainty range with the  $CCN(S_v)$  activation spectra measured below cloud base. This new methodology approach allows the calculation of  $N_d(S_v)$  spectra from airborne measurements at cloud bases. Our results suggest that adiabatic models assuming full conversion of phase change energy into condensational growth tend to overestimate the liquid water content. During the cloud parcel ascent, a finite fraction of this energy is expended as vapor expansion work, reducing the amount available for vapor-to-liquid conversion. Neglecting this energetic partition leads to an overestimation of the latent heat released during condensational growth of particles, cloud parcel buoyancy and vertical acceleration. Airborne measurements at the cloud bases of growing cumuli over the Amazon Basin demonstrate that the derived droplet number concentration as a function of  $S_v$  agree, within measurement uncertainties, with sub-cloud measurements of  $S_v$  activation spectra of cloud condensation nuclei.

## 1 Introduction

Understanding a realistic representation of cloud formation processes and their impact on the atmospheric energy budget and water cycle is crucial for accurate numerical weather prediction and reliable climate projection models (IPCC, 2021). Liquid water cloud droplets form in a rising humid (i.e. water vapor containing) air parcel, which expands during ascent due to decreasing air pressure. The expansion causes and as a result a cooling of the air parcels during ascent until the relative humidity (RH) exceeds 100 % (water vapor supersaturation,  $S_v$ ) with respect to liquid water. Liquid water cloud droplets form in a rising humid air parcel, which expands due to decreasing air pressure and as a result cools during ascent until supersaturation with respect to liquid water is reached. Subsequently, the water vapor condenses onto surfaces provided by a subset of the preexisting aerosol particles that act as cloud condensation nuclei (CCN). The condensation of water vapor on aerosol particles and the subsequent activation and growth of cloud droplets are described by the Köhler theory (Köhler, 1936). This theory describes quantifies the equilibrium saturation ratio (or equilibrium RH) over an aqueous solution droplet as a function of droplet size, accounting for curvature (Kelvin-effect) and solute (Raoult-effect) effects. It, and defines the critical  $S_v$  at which CCN particles are activated to form into cloud droplets. Due to the particle size dependence inherent in Köhler theory, the growth of once a salty droplets and  $S_v$  beyond diameters of about 1-2  $\mu\text{m}$ . Their is are controlled determined by the thermodynamic state of the cloudy air parcel rather than by the physicochemical properties of the original aerosol-CCN particles (Khain and Pinsky, 2018; Petters and Kreidenweis, 2007; Pinsky et al., 2012). Despite extensive efforts during numerous field observations, airborne in situ measurements of  $S_v$  in clouds are highly uncertain due to instrumental limitations. Since RH is commonly derived from measurements of air temperature and water vapor mass mixing ratio. The, the combined uncertainties of these parameters resulting in errors of about 5-10 % for the calculated RH (Kaufmann et al., 2018; Namdari et al., 2025), which is much larger than the actual those values of  $S_v$  typically observed in cumulus clouds ( $\sim 0.1 - 1 \%$ ) and set in CCN counters under controlled conditions (Roberts and Nenes, 2005; Rose et al., 2008). Thus,  $S_v$  at warm cloud bases of warm (i.e., only liquid water containing) cumulus clouds often is a parameter currently needs to be estimated using numerical modeling and parametrizations based on Köhler theory. It, and

remains an inferred indirectly retrieved quantity -and its accuracy is limited restricted-by certain assumptions. In general, current methods to quantify  $S_v$  are and lacking a thermodynamically constrained foundation that could be validated with independent airborne in situ measurements (Campos Braga et al., 2017a; Pinsky et al., 2012; Rosenfeld et al., 2016;

70 Twomey, 1959; Varghese and Prabhakaran, 2025).

In this study we introduce a new method to derive  $S_v$  during the early stage of warm cloud formation using thermodynamic and cloud microphysical observations in combination with heat budget considerations. Microphysical cloud models [e.g., (Khain and Pinsky, 2018; Korolev and Mazin, 2003)] explicitly calculate the water vapor budget for -and-adiabatic conditions changes of thermodynamic state during this process by assuming of a saturated air parcel adiabatic-where the

75 condensational growth of cloud droplets is controlled by the saturation ratio. Based on the thermodynamic equations governing temperature, water vapor mixing ratio and the Clayperon-Clausius relation, the water vapor budget during cloud formation can be calculated water is given as a function of the change in  $S_v$  per unit time as follows:

$$\frac{dS_v}{dt} = P - C_d. \quad (1)$$

Where, Physically, the  $P$  (production term) term represents the increasing of  $S_v$  by cooling induring the adiabatic ascent

80 ( $P = A_1 \cdot w$ ), and the  $C_d$  (condensation term) term describes-is the decreasing of  $S_v$  due to the condensation of water vapor on CCN particles and droplets ( $C_d = A_2 \cdot d(LWC)/dt$ ) (see Appendix A for complete description of these terms).  $A_1$  and  $A_2$  are thermodynamic coefficients associated with the Clausius–Clapeyron equation describing the dependence of saturation water vapor pressure on temperature. water- $w$  is the updraft speedvelocity ( $dz/dt$ ) of the rising air parcel and LWC represents the liquid water content.

85 For warm cloud bases Despite extensive field observations and numerical modeling based on Köhler theory, the water-vapor supersaturation ( $S_v$ ) at cloud base remains an inferred quantity restricted by certain assumptions and lacking a thermodynamically constrained foundation that could be validated by in situ measurements.

,  $S_v$  is typically inferred through parameterizations that associate parcel dynamics (i.e.,  $w$ ) and CCN properties to droplet activation (Ghan et al., 2011; Reutter et al., 2009; Twomey, 1959). A foundational contribution was made by Twomey

90 (1959), who was the first who formulated a parameterization relating the CCN spectrum to the  $S_v$  in a rising cloud parcel. The parametrization established a practical basis for predicting the number concentration of droplets ( $N_d$ ) at cloud bases from CCN properties just below cloud bases and in cloud  $w$ -conditions. From this information, the  $S_v$  activation spectra of number concentration of CCN [ $N_{CCN}(S_v)$ ] were are estimated for different atmospheric conditions. Several studies based on Twomey’s parametrizations remain widely implemented in cloud microphysical schemes (Ervens et al., 2010; Feingold and

95 Heymsfield, 1992; Ghan et al., 2011; Khain et al., 2015; Reutter et al., 2009; Varghese and Prabhakaran, 2025), either in their original form or through modifications that account for additional processes such as entrainment of dry air and, CCN composition-ete. These parametrizations are typically validated through so-called  $N_d$  closure analysis, where simulated and

measured  $N_d$  are compared adjusted. The, and typically agreement achieved from this analysis closure are about ranges between 20-30 % for average concentrations. Furthermore,  $N_{CCN}(S_v)$  spectra are also estimated based on satellite retrievals (Rosenfeld et al., 2016), in which clouds are treated as CCN chambers and thermodynamic and as well as microphysical properties estimated for cloud bases are implemented to calculate  $N_d(S_v)$  (Konwar et al., 2012; Pinsky et al., 2012; Rosenfeld et al., 2014; Zheng and Rosenfeld, 2015). The accuracy of satellite retrievals accuracy of  $N_d(S_v)$  individual satellite overpasses is about 25-30 % when compared with ground-based  $N_{CCN}(S_v)$  CCN( $S_v$ )-measurements.

Modeling and observational studies have been performed in various parts of the world to improve our understanding of the relationship between aerosol particle properties and their ability to form cloud droplets as a function of  $S_v$  (Ervens et al., 2010; Kleinheins et al., 2025; Kulkarni et al., 2023; Pöhlker et al., 2016; Rissler et al., 2004; Wang et al., 2008). Similar analyses were performed from measurements of CCN( $S_v$ )-spectra below cloud bases and parametrizations of the number concentration of droplets ( $N_d$ ) as a function  $S_v$  in clouds. These studies compare the predicted number concentration of CCN according to Köhler theory based on particle size and composition to CCN number concentrations based on derived from Köhler theory, as a function of particle size and chemical composition, with results from CCN counting instruments at different  $S_v$ . Furthermore,  $N_d$  at cloud bases is commonly calculated in adiabatic cloud models based on the hygroscopic growth of CCN particles within a rising humid air parcel with a prescribed hygroscopicity ( $\kappa$ ) of the CCN particles and an updraft velocity  $w$  (Braga et al., 2021a; Pöhlker et al., 2021; Reutter et al., 2009; Varghese and Prabhakaran, 2025). These models simulate the expansion and the corresponding cooling of the air parcel, the resulting changes in relative humidity ( $RH_v$ ), or saturation ratio, and the activation followed by condensational growth of cloud droplets. Even though parametrizations based on CCN( $S_v$ ) successfully explain the  $N_d$  measured at cloud bases, the estimated  $S_v$  that results from uncertainty of the prescribed updraft velocity of the air parcel and the CCN number concentrations, size, and chemical composition. From closure analysis using adiabatic parcel model predictions results, Braga et al., (2021a) observed that  $w$  and  $\kappa$  are critical factors in determining  $N_d$  at cloud bases number, particularly in the unique environments of the Amazon Basin during the dry (polluted) season and the clean conditions at of the Atlantic Ocean. The results indicated that while larger accumulation mode CCN particles dominate cloud formation over land, smaller Aitken mode CCN particles play a significantly role in cleaner marine air masses. A dedicated analysis confirming these findings is described by Pöhlker et al. (2021). The authors establishes conclude that while  $w$  and  $\kappa$  are critical for CCN activation into cloud droplets, the contribution of Aitken mode particles is most significant in clean environments or deep convective clouds. Conversely, in polluted air masses, number high concentrations of larger particles suppress the  $S_v$  required to activate smaller ones. Through this sensitivity analysis, the authors clarify the thresholds where aerosol properties and  $w$  intersect to dictated determine cloud microphysics responses.

In this study, we propose a method to quantify derive  $S_v$  at cloud bases for an ascending saturated parcel considering the energy and water vapor budgets during the condensational growth process. To this end, the energy balance of a cloud-adiabatic parcel is calculated under the assumption of conserved-isobaric enthalpy conserved during adiabatic processes. The

total energy of a saturated air parcel is constrained by the enthalpy difference ( $dH$ ) of the phase change from water vapor to liquid water and the latent heat released ( $Q$ ), where  $\delta Q = dH$ . From the first law of thermodynamics, this energy is internally partitioned between changes in internal energy ( $\Delta U$ ) and the expansion work of water vapor ( $W_s$ ). Accordingly, the liquid-phase supersaturation ( $S_l$ ) and vapor supersaturation ( $S_v$ ) are defined as the respective fractions of  $Q$  associated with  $\Delta U$  and  $W_s$ .

The proposed method is evaluated using in situ measurements of cloud properties and compared with  $N_{CCN}(S_v)$  CCN( $S_v$ ) observations below cloud bases. In this framework, we rely on the reversibility of the cloud-adiabatic parcel under conserved isobaric enthalpy, in which  $Q$  is directly calculated based on derived from measured liquid water content—LWC, air temperature ( $T$ ) and pressure ( $p$ ),  $T$  and  $p$  at cloud bases, while  $\Delta U$ , and  $W_s$ ,  $S_l$  and  $S_v$  are diagnostically estimated based on the adiabatic assumptions described. Unlike conventional parcel-model or CCN-closure approaches, which estimate  $S_v$  from prescribed updraft velocity  $w$  and aerosol CCN properties, the present method diagnoses cloud-base supersaturation from measured liquid water content, temperature, and pressure through a thermodynamic energy-budget closure. The airborne cloud base airborne measurements data were collected within growing convective cumuli over the Amazon Basin in September 2014 during the ACRIDICON-CHUVA campaign (Wendisch et al., 2016) were conducted over the Amazon Basin at the cloud bases of growing convective cumuli. The data were collected in September 2014 during the ACRIDICON-CHUVA campaign. Clouds were probed under, encompassing polluted conditions over forested and deforested regions, and under clean marine conditions over the adjacent Atlantic Ocean near the Brazilian coast. The resulting  $N_d(S_v)$  spectra at cloud base, obtained measured at cloud bases were compared for eight flight segments, are compared with the  $N_{CCN}(S_v)$  CCN( $S_v$ ) spectra measured below cloud bases. This analysis tests the robustness of the underlying physical assumptions, as to evaluate the validity of the physical basis for cloud supersaturation estimates.  $N_d(S_v)$  at cloud base is expected to represent the  $N_{CCN}(S_v)$  CCN( $S_v$ ) population below cloud bases. The following section 2 presents the proposed method and its underlying physical formulation laws, while the results and discussion are provided in the subsequent sections. Table A1 in the Appendix lists and defines the symbols used in this manuscript. Table 1 explains the variables described in this manuscript.

In this framework,  $S_v$  increases with height above the lifting condensation level due to adiabatic cooling of the rising air parcel and further on decreases as the condensational growth of activated CCN depletes water vapor in the saturated parcel. In this study, we derive  $S_v$  at cloud base by describing the ascent of a saturated air parcel as a reversible cloud-adiabatic process.  $S_v$  is quantified from the energetic budget of the saturated parcel calculated under the assumption of conserved isobaric enthalpy. We consider that the atmospheric pressure variability at cloud-base layer is negligible, typically in the order of  $10^{-3}$  ( $\approx 0.1 - 0.3\%$ ) relative to ambient pressure. The maximum energy available for the conversion of water vapor into liquid water is given by the magnitude of the sensible enthalpy change associated with adiabatic cooling during

saturated parcel ascent. This energy is released as latent heat ( $Q$ ) during condensation of water vapor on CCN and cloud droplets. The resulting energetic balance follows the first law of thermodynamics, such that the latent heat release is partitioned between the change in internal energy of the parcel ( $\Delta U$ ) and the saturation work of water vapor ( $W_s$ ), i.e.,  $Q = \Delta U + W_s$ . This partition provides an energetic basis to decompose cloud supersaturation into a liquid ( $S_l$ ) contribution associated with  $\Delta U$ , and a vapor ( $S_v$ ) contribution associated with  $W_s$  (i.e.,  $S_l \propto \Delta U/Q$  and  $S_v \propto W_s/Q$ ).

Figure 1 schematizes the energetic closure at cloud base. A saturated parcel at cloud base ( $T_0, p_0$ ) undergoes a small upward displacement to slightly lower pressure ( $p < p_0$ ), cooling adiabatically to temperature  $T$ . Under the assumption of conserved isobaric enthalpy, the parcel is characterized by a constant equivalent temperature ( $T_e$ ) during the cloud-base ascent. In the absence of condensation and for a small pressure change, the sensible enthalpy change associated with adiabatic cooling is limited by  $c_{p,cloud}(T_0 - T)$ , which represents the upper bound on the parcel's decrease in sensible enthalpy between the two thermodynamic states. Under conserved enthalpy, this change in sensible enthalpy defines the maximum latent heat that would be required for the conversion of water vapor into liquid water, i.e.,  $Q \approx c_{p,cloud}(T_0 - T)$ . However, the pressure decrease necessarily implies expansion of the water vapor component, and a fraction of the latent heat released is expended as saturation work. The term  $W_s$  accounts for the energy associated with this vapor expansion as the parcel adjusts to the lower pressure, thereby reducing the energy available to offset the sensible cooling and consequently limiting the conversion of water vapor into liquid water relative to the case in which  $W_s$  is neglected.

To apply our method for in-situ measurements of cloud properties, we rely on the reversibility of the cloud adiabatic parcel under conserved isobaric enthalpy, in which  $Q$  is directly calculated based on measured liquid water content ( $LWC$ ),  $T$  and  $p$  at cloud bases, while  $\Delta U$  and  $W_s$  are estimated based on the adiabatic assumptions described. The airborne measurements were conducted over the Amazon Basin at the cloud bases of growing convective cumuli. The data were collected in September 2014 during the ACRIDICON-CHUVA campaign. Clouds were probed under polluted conditions over forested and deforested regions, and under clean marine conditions over the Atlantic Ocean near the Brazilian coast. The  $N_d(S_v)$  spectra measured at cloud bases were compared with the CCN( $S_v$ ) spectra measured below cloud bases to evaluate the validity of the physical basis for cloud supersaturation estimates.

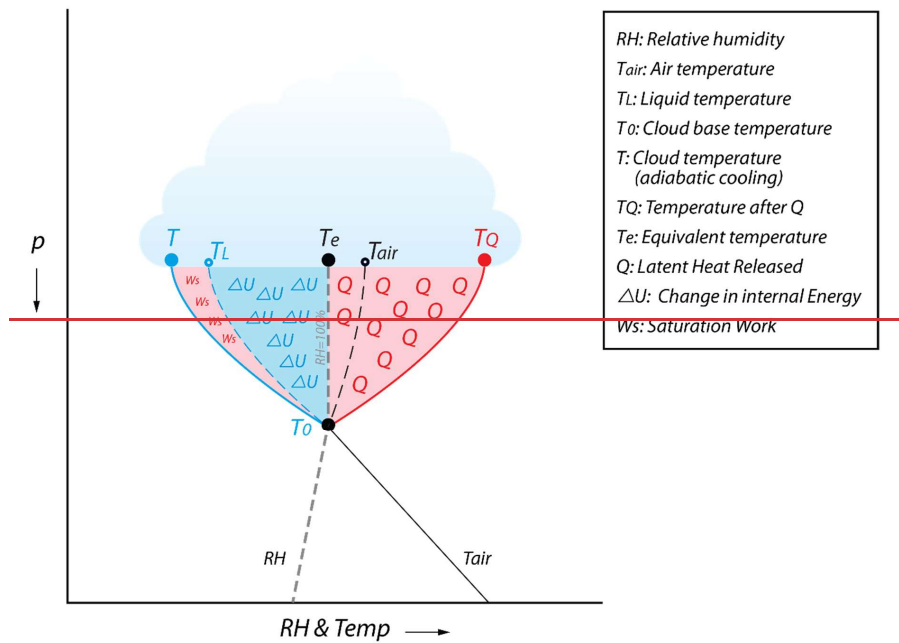


Figure 1. Energy balance of a cloud-adiabatic parcel at cloud-base under the assumption of conserved isobaric enthalpy ( $T_e$  is constant). Below cloud base, the moist air parcel ascends due to buoyant force,  $T_{air}$  decreases with altitude while  $RH$  increases up to saturation level of water vapor ( $RH = 100\%$ ) at cloud base ( $T_0$ ). Above this level, the ascending saturated parcel cools adiabatically as pressure ( $p$ ) slightly decreases to a given level ( $T$ ). This process leads to water vapor supersaturation when condensational particle growth is neglected, due to the lower internal energy of the saturated parcel. Under the assumption of conserved isobaric enthalpy, the latent heat released by condensation ( $Q$ ) is proportional to the cooling rate from  $T_0$  to  $T$ . During the condensational growth of CCN particles and droplets,  $Q$  is balanced with the decrease in internal energy ( $\Delta U$ ) and saturation work of water vapor ( $Ws$ ), resulting in a temperature of the liquid parcel ( $T_L$ ) that is warmer than  $T$ . The associated energy balance produces an inversion in the vertical profile of  $T_{air}$  where the cloud is formed.

## 2 Methods

We present a new, physically based formulation to quantify  $S_v$  in aadiabatically-adiabatic, saturated (with respect to water vapor over a plane liquid water surface) air parcel near cloud base, grounded in the coupled energy and water vapor budgets during the condensational growth. Near cloud base, the parcel ascends through it appears justified to assume that the parcel changes its thermodynamic state variables is assumed isobaric due to the small pressure variations-, typically ( $\sim$ about 0.1 - 0.3 %) relative to ambient conditions. We, therefore, treat the thermodynamic transformation locally as quasi-isobaric, while retaining the physical effect of water vapor expansion in the work term. This approximation allows the energy budget to be expressed per unit mass of dry air as a partition between the internal energy change associated with condensational growth and the work associated with water-vapor expansion. Under saturated quasi-isobaric conditions, the energy budget is governed by pressure and temperature, and the partitioning between  $\Delta U$  and  $W_s$  remains process-dependent. And under the local quasi-isobaric approximation with conserved specific enthalpy, the system is thermodynamically reversible, allowing the energy budget to be determined from the temperature change ( $\Delta T$ ) during cooling or, equivalently, from  $Q$  for a given liquid water content. In this study, the variables are expressed as specific quantities (denoted by uppercase symbols). To recover the corresponding extensive quantities, these terms must be multiplied by the mass of dry air.

It is well known that Under quasi-isobaric adiabatic conditions, the specific enthalpy stay constant during adiabatic changes of state in general of the parcel is conserved, also in both for dry-adiabatic and case of cloud-adiabatic processes, not only dry-adiabatic ones.  $\delta q_p h_p$  quasi-didw  $\delta q d u d w$

finite the released energy is associated with water expansion work, not all of the available energy is assigned to the internal energy change associated with vapor to water conversion Within this diagnostic framework waterwater saturated quasi- And under the local quasi- approximation with conserved specific Figure 1 schematizes the energy budget at cloud base. A saturated air parcel at cloud base ( $T_0, p_0$ ) undergoes a small upward displacement to slightly lower pressure ( $p < p_0$ ), cooling adiabatically to temperature  $T$ . Because the pressure change across the analysed cloud-base layer is small, the thermodynamic transformation can be treated locally as quasi-isobaric for the energy-budget calculation. Under the assumption of conserved isobaric approximation, the specific enthalpy ( $p = p_0$ ) of the parcel is conserved and, the resulting air temperature is constant, i.e., the latent-heat-equivalent temperature ( $T_0$ ) remains nearly constant, during the cloud-base ascent. The sensible enthalpy change ( $dH$ ) associated with adiabatic cooling is limited by  $c_{p,cloud} (T_0 - T)$ , where  $c_{p,cloud}$  is the specific heat capacity of cloudy air.  $dH$  represents the upper bound on the parcel's decrease in sensible enthalpy between the two thermodynamic states. Under conserved enthalpy,  $dH$  constrains the latent heat released during the conversion of water vapor into liquid water, i.e.,  $Q = -c_{p,cloud} (T_0 - T)$ . From the energy partition according to the first law of thermodynamics,  $Q$

235  $= \Delta U + W_s$ , and the resulting air temperature ( $T_{air}$ ) is cooler than  $T_Q$ . Similarly, the temperature of the saturated parcel is slightly warmer when considering the  $W_s$  term (i.e.,  $T_{ws} > T$ ). The energy expended on water vapor expansion during this process results in an excess of water vapor ( $S_v$ ) relative to the case in which the water vapor is fully condensed.

240 In situ measurements at the cloud bases of growing cumulus clouds are used to evaluate the theoretical assumptions.  $N_{CCN}(S_v)$  spectra measured just below cloud base, prior to cloud measurements, are compared with the  $N_d(S_v)$  spectra derived at cloud base during flights in the Central Amazon. The  $N_d(S_v)$  spectrum is considered representative of the  $N_{CCN}(S_v)$  population below cloud base that, after buoyant ascent, is activated into cloud droplets. The following subsections describe the steps of the proposed method, its underlying physical formulation, and the cloud, meteorological, and CCN measurements used in this study.

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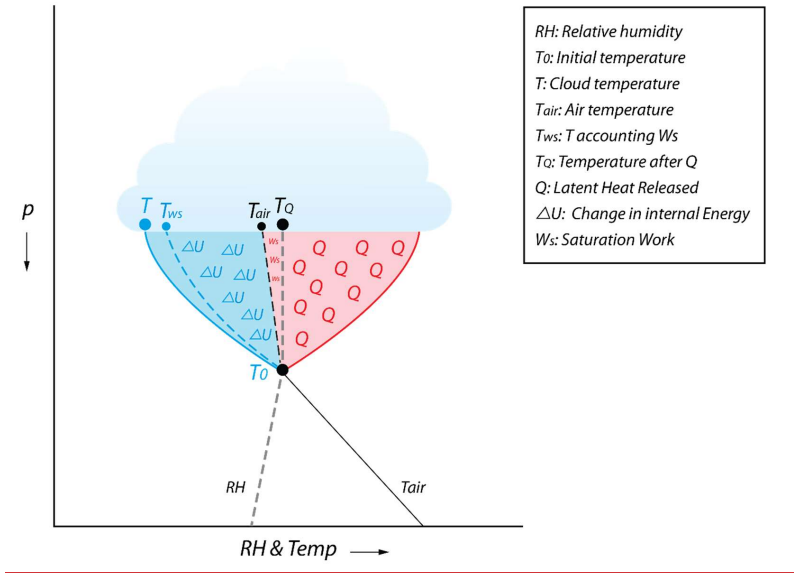


Figure 1. Energy balance of a cloud-adiabatic air parcel at cloud base assuming under a local quasi-isobaric conditions approximation. Below cloud base, the moist air parcel ascends due to buoyancy.  $T_{\text{air}}$  decreases with altitude while RH increases up to the saturation level of water vapor ( $\text{RH} = 100\%$ ), where the temperature and pressure are  $T_0$  and  $p_0$ , respectively. Above this level, the ascending saturated parcel cools adiabatically as pressure ( $p$ ) decreases slightly to a given and the parcel reaches temperature ( $T$ ). Note that for the local quasi-isobaric assumption  $p = p_0$  approximation used in the energy-budget calculation, the pressure variation across the analyzed cloud-base layer is assumed small/negligible relative to the ambient pressure. The total energy of the parcel is given by the latent heat released during condensation ( $Q$ ), which is proportional to the changing of enthalpy change resulting from the water vapor to liquid water conversion. In the schematic representation, the conserved equivalent temperature is expressed as  $T_e$ . From the first law of thermodynamics for isobaric conditions, the energy of the closed thermodynamic system  $Q$  is partitioned into the internal energy change ( $\Delta U$ ) and saturation work of water vapor ( $W_s$ ). As a result,  $T_{\text{air}}$  is warmer than  $T$  and cooler than the temperature corresponding to the case in which water vapor is fully condensed ( $T_0$ ). Similarly,  $T$  is slightly warmer due to the  $W_s$  term is included, the effective saturated parcel temperature (i.e.,  $T_{\text{ws}}$ ) is becomes slightly warmer than the purely expanded state, i.e.,  $T_{\text{ws}} > T$ . The energy expended on water vapor expansion ( $W_s$ ) during this process results in an excess of water vapor ( $S_e$ ) relative to the case of complete condensation. The  $Q$  region schematically mirrors the total energetic partition shown on the left-hand side of the figure.

To incorporate the thermodynamic constraints of the proposed energy balance at cloud base and calculate the supersaturations at cloud bases, we expanded the classical RH formulation for saturated conditions and derived a new expression for the relative humidity ( $\text{RH}_e$ ).  $\text{RH}_e$  is calculated from the Clausius-Clapeyron equation for a water-vapor-saturated, rising air parcel undergoing expansion (cooling) at temperatures  $\geq 0^\circ\text{C}$ . The degree of cooling (e.g., from  $T_0$  to  $T$  shown in Figure 1) determine  $\text{RH}_e$  and the cloud supersaturation ( $S_e$ ) at cloud bases. In these conditions, the parcel saturated with water vapor has  $\text{RH}_e \leq 100\%$ ;  $S_e$  results from vapor excess relative to the initial (warmer) saturation condition ( $\text{RH}_e = 100\%$ ), and it is assumed that initially  $S_e$  is not diminished by condensation of water vapor on the CCNs or droplets. Under the assumption of conserved isobaric enthalpy, we associate  $S_e$  from adiabatic cooling to the latent heat of condensation  $Q$ , which is further partitioned into contributions from the liquid phase ( $S_l$ ) and the vapor phase ( $S_v$ ). Since  $S_e$  is derived from a single temperature gradient, it corresponds to those values of a CCN counter, in which the vapor density results solely from a thermal gradient under saturated conditions.

In situ measurements at the cloud bases of growing cumulus clouds were used to validate our theoretical assumptions. The measurements over the Amazon during the ACRIDICON-CHUVA campaign were conducted in clean and polluted conditions across different land cover types (forested, deforested, and urban) and over the Atlantic Ocean. The  $N_{\text{CCN}}(S_e)$  spectra measured just below cloud base prior to cloud base penetrations were used for comparison with the  $N_d(S_e)$  spectra calculated at cloud bases during flights in the Central Amazon.  $N_{\text{CCN}}(S_e)$  The following sections describe the calculations of the thermodynamic, energetic and microphysical properties of clouds, and the data from cloud and meteorological probes and CCN counters used in this study. Table 1 explains the variables described in this section.

## 2.1 Calculation of the latent heat of condensation *Description of RH<sub>c</sub> and S<sub>c</sub> derivation*

The total energy of the saturated parcel is limited by the enthalpy difference of the phase change from vapor to liquid,  $\delta Q = dH$ , and can be written in finite forms as follows:

$$\delta Q = dH \quad \therefore \quad L_v \cdot q_l = -c_{p,cloud} \cdot \Delta T = -c_{p,cloud} \cdot (T_0 - T). \quad (2)$$

Where  $q_l$  is the liquid water mixing ratio ( $\text{kg}^{-1} \text{kg}^{-1}$ ),  $c_{p,cloud}$  is the specific heat capacity of cloudy air ( $\text{J kg}^{-1} \text{K}^{-1}$ ), and  $L_v$  is the latent heating of vaporization ( $\text{J kg}^{-1}$ ). The  $q_l$  and  $c_{p,cloud}$  are defined as the following:

$$q_l = LWC / \rho_{air}, \quad (3)$$

and,

$$c_{p,cloud} = c_{pd} + c_{pv} \cdot r_s + c_{pl} \cdot q_l. \quad (4)$$

Where,  $\rho_{air}$  is the dry air density ( $\text{kg m}^{-3}$ ), LWC is the liquid water content ( $\text{kg m}^{-3}$ ),  $r_s$  is the saturation water vapor mixing ratio ( $\text{kg}^{-1} \text{kg}^{-1}$ ),  $c_{pd}$  is the specific heat of dry air at constant pressure ( $1005 \text{ J kg}^{-1} \text{K}^{-1}$ ),  $c_{pv}$  is the specific heat of water vapor at constant pressure ( $1850 \text{ J kg}^{-1} \text{K}^{-1}$ ),  $c_{pl}$  is the specific heat of liquid water at constant pressure ( $4218 \text{ J kg}^{-1} \text{K}^{-1}$ ). (Rogers and YAU, 1989) (Rogers and YAU, 1989) We assume the warmer temperature ( $T_0$ ) in the  $c_{p,cloud}$  and  $L_v$  calculations, as it represents the initial condition of the saturated parcel. For small temperature differences at cloud base ( $< \sim 1 \text{ K}$ ),  $c_{p,cloud}$  varies only weakly with  $r_s$  and  $q_l$ . Since  $T$  and  $T_0$  represent the temperatures of a saturated parcel under isobaric conditions, they are equivalent to the dew-point temperature at the corresponding pressure. Furthermore,  $r_s$  is calculated as follows:

$$r_s = (R_d / R_v) \cdot \frac{e_s(T)}{p - e_s(T)}, \quad (5)$$

Where  $R_v$  is the gas constant for water vapor ( $461.5 \text{ J kg}^{-1} \text{K}^{-1}$ ),  $R_d$  is the gas constant for dry air ( $287.05 \text{ J kg}^{-1} \text{K}^{-1}$ ), and  $e_s(T)$  is the saturation water vapor pressure (Pa) (Bolton, 1980; Rogers and YAU, 1989). The values of  $e_s$  can be calculated for a wide range of temperatures in Celsius ( $-30 \text{ }^\circ\text{C} \leq T_c \leq 35 \text{ }^\circ\text{C}$ ) with minor uncertainties ( $\sim 0.1\%$ ) as follows:

$$e_s = 611.2 \cdot \exp\left(\frac{17.67 \cdot T_c}{T_c + 243.5}\right) \quad (6)$$

During the phase change, the internal energy decreases ( $T_0 > T$ ) as  $q_l$  and  $Q$  increase. The phase change process leads to an increase in the air temperature, represented here by the latent-heat-equivalent temperature ( $T_0$ ), which is approximately conserved during the ascent, i.e.:

$$T_Q = T + \Delta T_Q \approx T_0 \quad (7)$$

Where,  $\Delta T_Q = \frac{L_v q_l}{c_{p,cloud}}$  (8)

## 2.2 Cloud Supersaturation

The formulation of RH describes the amount of water vapor in the air relative to the maximum amount of water vapor the air can hold for a given temperature, i.e., the saturation ratio, and is defined as follows:

$$RH = 100 \cdot \frac{e(T)}{e_s(T)} \quad [\%] \quad (9)$$

Where  $e(T)$  is the ambient water vapor pressure (Pa). For a saturated parcel or cloud undergoing cooling (from  $T_0$  to  $T$ ) the reference-state saturation ratio ( $RH_c$ ) is calculated as follows:

$$RH_c = 100 \cdot \frac{e_s(T)}{e_s(T_0)} \quad [\%] \quad (10)$$

and the cloud supersaturation ( $S_c$ ) is formulated as follows:

$$S_c = RH_s - RH_c = 100 - RH_c \quad [\%] \quad (11)$$

where  $RH_s = 100\%$  is the saturation ratio at the reference state ( $T_0$ ), and  $S_c$  expresses the thermodynamic excess of water vapor relative to equilibrium with respect to liquid water at the reference state. Since the cooling process is related to the increase of  $q_l$  (shown in Eq. 2), the increase in  $S_c$  is associated with vapor-liquid conversion and  $Q$ .

$$RH_e S_e = RH_s - RH_e = 100 - RH_e \quad [\%] \quad (11)$$

### 2.3.3 Calculation of energy budget from the first law of thermodynamics

According to the first law of thermodynamics, the change in internal energy of a closed system is determined by the balance between heat exchange and pressure-volume work. For an isobaric process involving only pressure-volume work, the change in enthalpy ( $dH$ ) can be interpreted as the sum of the change in internal energy and the expansion work performed by the system. Under adiabatic conditions, the  $dH$  equals the heat exchanged at constant pressure by a saturated parcel. Thus, for a saturated parcel undergoing condensational growth from the reference state, the latent heat released ( $\delta Q = dH$ ) is the source of heat in the thermodynamic system, and the energy budget can be calculated following the first law as follows:

$$Q = \Delta U + W_s \quad (12)$$

where  $Q$  represents the latent heat released by condensation,  $\Delta U$  is the change in internal energy of the parcel associated with vapor-liquid conversion, and  $W_s$  is the specific work done by water vapor during expansion. The terms of  $\Delta U$  and  $W_s$  are calculated for an ascending saturated parcel as follows:

$$\Delta U = -c_{p,cloud} \cdot (T_0 - T_{ws}) \quad (13)$$

Commented [MW1]: Here T is th the dew point temperature!

and,

$$W_s = r_s \cdot \int_{\alpha_{vs0}}^{\alpha_{vs}} e_s d\alpha_v = r_s \cdot \int_{\alpha_{vs0}}^{\alpha_{vs}} \frac{R_v \cdot T}{\alpha_v} d\alpha_v \approx r_{s0} \cdot R_v \cdot T_0 \cdot \ln\left(\frac{\alpha_{vs}}{\alpha_{vs0}}\right) = r_{s0} \cdot R_v \cdot T_0 \cdot \ln\left(\frac{T}{T_0} \cdot \frac{e_s(T_0)}{e_s(T)}\right) \quad (14)$$

Where  $\alpha_v$  is the specific volume of water vapor for saturated conditions ( $\text{m}^3 \text{kg}^{-1}$ ). The  $W_s$  term represents the effective thermodynamic work associated with changes in the specific volume of saturated water vapor during cloud-adiabatic cooling. Under quasi-isobaric conditions and small cloud base cooling intervals, the integration is referenced to the initial thermodynamic state of the ascending saturated parcel ( $T_0$ ), and  $W_s$  depends primarily on  $T_0$  and  $T$ .

Analogous to Equation 2, the energy budget from Equation 12 can be calculated as follows:

$$L_v \cdot q_l = -c_{p,cloud} \cdot \Delta T_{ws} + r_{s0} \cdot R_v \cdot T_0 \cdot \ln\left(\frac{\alpha_{vs}}{\alpha_{vs0}}\right) \quad (15)$$

or,

$$L_v \cdot q_l - r_{s0} \cdot R_v \cdot T_0 \cdot \ln\left(\frac{\alpha_{vs}}{\alpha_{vs0}}\right) = -c_{p,cloud} \cdot (T_0 - T_{ws}) \quad (16)$$

From this budget,  $T_{ws}$ , the saturated temperature, is slightly warmer than  $T$  calculated in Equation 2 due to the  $W_s$  term. Similarly, the resulting air temperature ( $T_{air}$ , shown in Figure 1) will be slightly cooler than  $T_0$  due to the  $W_s$  term. Thus,  $T_{air}$  is calculated as follows:

$$T_{air} = T + \Delta T_Q - \left(\frac{W_s}{c_{p,cloud}}\right) \quad (17)$$

The differences of the saturated temperatures ( $T_{ws} - T$ ) and air temperature ( $T_0 - T_{air}$ ) are the same.

#### 2.4.3.4 Reversibility of the energy budget of the saturated parcel

The reversibility of the energy budget for isobaric conditions relies on the fact that the magnitude of the total latent energy ( $\delta Q = dH$ ) can be expressed equivalently in terms of either LWC or the temperature difference ( $\Delta T$ ) between two saturated states.

In Section 2.1, we show that the relationship between LWC and  $\Delta T$  is one-to-one since the parameters are calculated as a function of the initial thermodynamic properties of the saturated parcel. In this framework, this dependence is treated explicitly through an iterative solution, ensuring consistency between condensate and heat capacity.

When the total energy is partitioned as  $Q = \Delta U + W_s$ , the internal-energy component represents a reduced cooling of the saturated parcel compared to the case without accounting for the work term  $W_s$ . Despite this partitioning, the functional dependence between  $q_l$  and  $\Delta T_{ws}$  remains unchanged, so the relationship between thermodynamic variables remains one-to-one. Since the parameters at  $W_s$ ,  $c_{p,cloud}$  and  $L_v$  are calculated for the initial conditions of the parcel ( $T_0$ ), the reversibility of

the heat budget is preserved, ensuring a consistent and reversible relationship between condensate and temperature within the proposed framework. The numerical differences while applying equations 2 and 12 to calculate  $Q$  are negligible ( $< \sim 0.01\%$ ). The differences between the thermodynamic and energetic components of the cloud parcel for simulations with a range of initial temperatures  $T_0$  (2°C to 30°C) and adiabatic cooling magnitudes ( $\Delta T$ ) are presented in Section S1 of the Supplementary Material. The calculations are performed for the energy and vapor budgets at an atmospheric pressure of 950 hPa, similar as shown in the section 3.1.

#### 2.5.4.5 Calculation of liquid and water vapor supersaturation

The calculation of liquid supersaturation ( $S_l$ ) and water vapor supersaturation ( $S_v$ ) from the cloud supersaturation ( $S_c$ ) is performed as a function of the energy budget formulation described in section 2.3, where  $S_l$  and  $S_v$  are the energy contributions of  $\Delta U$  and  $W_s$  in the total energy of the saturated parcel ( $Q$ ), respectively.

The signs in the energy balance equations shown above describe the direction of energy transfer. However,  $S_l$  and  $S_v$  are not directional variables. They represent the partition of  $S_c$  considering the energy budget, which is defined from the absolute magnitudes of the energetic contributions, and thus, for a given latent heat released, due to condensation  $S_l$  and  $S_v$  are calculated as follows:

$$S_l = S_c \cdot \frac{|\Delta U|}{Q} \quad [\%] \quad (18)_1$$

$$S_v = S_c \cdot \frac{W_s}{Q} \quad [\%] \quad (19)_2$$

Where,

$$S_c = S_l + S_v \quad [\%] \quad (20)$$

The formulation of RH describes the amount of water vapor in the air relative to the amount of water vapor in the air when it is saturated for a given temperature, i.e., the saturation ratio, and is defined as follows:

$$RH = \frac{e(T)}{e_s(T)} \quad (1)$$

Where  $e(T)$  is the water vapor pressure (Pa),  $e_s(T)$  is the saturation water vapor pressure (Pa), and  $T$  is the air temperature (K or °C). The values of  $e_s$  can be calculated for a wide range of temperatures ( $-30^\circ\text{C} \leq T_e \leq 35^\circ\text{C}$ ) with minor uncertainties ( $\sim 0.1\%$ ) as follows:

$$e_s = 611.2 \cdot \exp\left(\frac{17.67 + T_e}{T_e + 243.5}\right) [Pa] \quad (2)$$

The classical definition of water vapor supersaturation ( $S_v$ ) as a function of RH is the following:

$$S_p = \frac{e(T) - e_s(T)}{e_s(T)} = RH - 1 \quad (3)$$

390 Where  $RH = 1$  (or 100%) is the relative humidity of a saturated parcel. The assumption behind taking  $RH = 100\%$  as the saturation threshold is that  $e_s(T)$  is defined as the equilibrium vapor pressure over a flat surface of pure liquid water. In this condition, evaporation and condensation are balanced. This is based on the Clausius–Clapeyron relation, which describes  $e_s(T)$  as the vapor pressure at which liquid water and vapor coexist in thermodynamic equilibrium at temperature  $T$ . Thus,  $S_p$  is positive when  $RH > 1$  (condensation > evaporation), null at equilibrium state (condensation = evaporation), and negative under subsaturated conditions (condensation < evaporation).

An ascending air parcel in the lower troposphere reaches saturation through a transient non-equilibrium state, where cooling initially exceeds the rate of condensation. This process occurs because decreasing pressure with altitude promotes the expansion of water vapor, which does work and cools adiabatically in the absence of any heat added to the air parcel. When the air parcel reaches saturation of water vapor, latent heat is released as CCN particles activate into cloud droplets and grow by condensation. The relative humidity of a saturated parcel or cloud ( $RH_c$ ) under expansion is as follows:

$$RH_c = \frac{e_s(T)}{e_s(T_0)} \quad (4)$$

Where  $e_s(T_0)$  is the vapor pressure at the reference level, and  $e_s(T)$  is the vapor pressure given at a higher level. In this study, the reference level is the cloud base (or the lifting condensation level); thus, at higher levels, the cloud parcel is cooler, leading to  $RH_c < 1$ .

405 At the earliest stages of condensational growth, a rising saturated parcel cools by expansion and decreases the internal energy while warming due to latent heat release. When the enthalpy is conserved with height, the equivalent temperature ( $T_e$ ) is constant, even though the actual temperature varies along the cloud-adiabatic lapse rate.  $T_e$  can be written as:

$$T_e = T + \Delta T_Q \quad [K] \quad (5)$$

410 Where  $T$  is the air temperature after adiabatic cooling, and  $\Delta T_Q$  is the temperature increase that would occur if all water vapor condensed and its latent heat were used to warm the air.

Another important physical property of a saturated parcel is the relationship between  $e_s(T)$  and the specific volume of water vapor ( $\alpha_v$ ), described as follows:

$$e_s(T) = \frac{R_v \cdot T}{\alpha_v} \quad [Pa] \quad (6)$$

Where  $R_v$  is the gas constant for water vapor ( $461.5 \text{ J kg}^{-1} \text{ K}^{-1}$ ). The  $\alpha_v$  and the water vapor density ( $\rho_v = \alpha_v^{-1}$ ) are inherently governed by the Clausius–Clapeyron relation through the temperature dependence of  $e_s(T)$ , where  $\rho_v$  defines the mass of water vapor per cubic meter of saturated air.

Equation 6 shows that  $e_s(T)$  depends inversely on the  $\alpha_v$ . For a saturated parcel expanding and cooling,  $\alpha_v$  increases (due to decreasing pressure  $p$ ) and hence  $e_s(T)$  decreases. The relationship between  $\alpha_v$  and  $p$  for a saturated parcel can be given by the following equation:

$$\alpha_v = \frac{R_v \cdot T \cdot (r_s + R_d/R_v)}{r_s \cdot p} \quad [\text{m}^3 \text{kg}^{-1}] \quad (7)$$

Where  $R_d$  is the gas constant for dry air ( $287.05 \text{ J kg}^{-1} \text{ K}^{-1}$ ), and  $r_s$  is the saturation water vapor mixing ratio ( $\text{kg}^{-1} \text{kg}^{-1}$ ), which can be calculated as follows:

$$r_s = (R_d/R_v) \cdot \frac{e_s(T)}{p - e_s(T)} \quad [\text{kg}^{-1} \text{kg}^{-1}] \quad (8)$$

From equations 1, 4, 5, and 6, the  $\text{RH}_e$  can be described as an isothermal condition in terms of  $T_e$  as a function of  $\alpha_v$  in different levels near cloud bases as follows:

$$\text{RH}_e = \frac{\frac{R_v \cdot T_e}{\alpha_v}}{\frac{R_v \cdot T_e}{\alpha_{v0}}} \quad (9)$$

Where  $\alpha_{v0}$  is the specific volume of water vapor at a reference level, and  $\alpha_v$  is the specific volume of water vapor after expansion. Expanding Equation 9 from Equation 6,  $\text{RH}_e$  can be expressed as the following:

$$\text{RH}_e = \frac{\alpha_{v0}}{\alpha_v} = \frac{\rho_v}{\rho_{v0}} = \frac{T_v}{T} \cdot \frac{e_s(T)}{e_s(T_0)} \quad (10)$$

Where  $T_0$  and  $\rho_{v0}$  denote the temperature and vapor density of the saturated parcel at the reference (cloud base) state, and  $T$  and  $\rho_v$  represent the corresponding temperature and vapor density of the parcel after adiabatic expansion. For cloud bases,  $T = T_0$  and  $\text{RH}_e = \text{RH} = 1$ , and above cloud bases,  $\text{RH}_e < 1$  since the vapor density is not lost by condensation.

Note that for a saturated parcel, the expansion is governed by temperature through the Clausius–Clapeyron relation, as  $e_s(T)$  decreases exponentially with cooling. Therefore, Equation 10 can be expanded based on a first approximation of the

Clausius–Clapeyron equation for a constant Latent Heating of Vaporization ( $L_v$ ), in which the following formulation is valid:

$$\frac{e_s(T)}{e_s(T_0)} = \exp \left[ \frac{L_v}{R_v} \cdot \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (11)$$

$L_v$  depends weakly on temperature change, about 6% for temperatures between  $-30^\circ\text{C}$  and  $30^\circ\text{C}$ . In this study, we calculate  $L_v$  as a function of temperature (in  $^\circ\text{C}$ ) using the equation below:

$$L_v = (2.501 - 0.00237 \cdot T) \cdot 10^6 \text{ [J kg}^{-1}\text{]} \quad (12)$$

440 From Equations 10 and 11,  $RH_e$  can be written (in percentage) as follows:

$$RH_e = 100 \cdot \left( \frac{T_0}{T} \right) \cdot \exp \left[ \frac{L_v}{R_v} \cdot \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \text{ [%]} \quad (13)$$

And from Equation 13, the supersaturation of the cloud ( $S_e$ ) can be calculated as follows:

$$S_e = 100 - RH_e \text{ [%]} \quad (14)$$

445 Equation 14 describes  $S_e$  above cloud base, where  $RH = 100\%$  is the physical basis condition for saturation. During the cloud parcel ascent, when condensation of CCN and droplets is neglected,  $RH_e < 100\%$  and  $S_e$  is the excess of vapor density resulting from the warmer parcel ascent with a saturation threshold of 100%. Thus,  $S_e$  accounts for the vapor-phase ( $S_v$ ) and liquid-phase ( $S_l$ ) supersaturation. Note that in Equation 3,  $S_v$  is a local relative condition for vapor excess for a cloud parcel saturated at  $RH = 100\%$ , while  $S_e$  is a relative condition for liquid and vapor excess in a cloud parcel saturated in  $RH_e < 100\%$ .

450 In this study,  $RH_e$  and cloud supersaturations (see Section 2.3) are calculated for cloud bases where temperature gradients have typically do not exceed  $\sim 1 \text{ K}$ . For modelling purposes, the calculation of  $RH_e$  and cloud supersaturation may be performed using smaller temperature gradients to reduce thermodynamic uncertainty. Furthermore, the calculation of  $RH_e$  must account for the  $S_v$  remaining after the first and subsequent time steps of the saturated parcel ascent, as this residual represents excess vapor density that was not converted into liquid water.

## 455 2.2 The Energy Balance in the Cloud Adiabatic Ascent

Figure 1 described the energy balance of a cloud-adiabatic parcel near cloud base under the assumption of conserved isobaric enthalpy. The energy balance assumptions are detailed in the following steps:

1. Buoyancy-driven ascent and pre-condensation cooling: the saturated parcel rises from cloud base ( $T_0, p_0$ ) due to a positive buoyancy force generated by its lower density relative to the surrounding air. During this initial upward displacement, no condensation has yet occurred, and the parcel cools adiabatically and retains its initial vapor density ( $\rho_{v,0}$ ) and mixing ratio ( $r_{v,0}$ ). This brief ascent produces a thermodynamic vapor excess, since the  $\rho_{v,0}$  exceeds the saturation vapor density ( $\rho_v$ ) at the cooler temperature  $T$ .
2. Energetic requirement imposed by conserved isobaric cloud enthalpy: for a reversible cloud-adiabatic parcel the sensible enthalpy resulting from adiabatic cooling from  $T_0$  to  $T$  defines the latent heating requirement that condensation must subsequently supply for the parcel to return to the saturated cloud-adiabatic state. The cloud-enthalpy constraint in terms of the magnitude of energy is calculated as follows:

$$Q = L_v \cdot q_t = (c_{p,cloud} \cdot (T_0 - T)) = |\Delta U| \text{ [J kg}^{-1}\text{]} \quad (15)$$

Where  $q_l$  is the liquid-water mixing ratio ( $\text{kg}^{-1}\text{kg}^{-1}$ ),  $c_{p,cloud}$  is the specific heat capacity of cloudy air ( $\text{J kg}^{-1}\text{K}^{-1}$ ). The  $q_l$  and  $c_{p,cloud}$  are defined as the following:

$$q_l = LWC / \rho_{air} \quad (16)$$

and;

$$c_{p,cloud} = c_{pa} + c_{pv} \cdot r_s + c_{pl} \cdot q_l \quad (17)$$

Where,  $\rho_{air}$  is the dry air density ( $\text{kg m}^{-3}$ ),  $LWC$  is the liquid-water content ( $\text{kg m}^{-3}$ ),  $r_s$  is the saturation-water-vapor mixing ratio ( $\text{kg}^{-1}\text{kg}^{-1}$ ),  $c_{pa}$  is the specific heat of dry air at constant pressure ( $1005 \text{ J kg}^{-1}\text{K}^{-1}$ ),  $c_{pv}$  is the specific heat of water vapor at constant pressure ( $1850 \text{ J kg}^{-1}\text{K}^{-1}$ ),  $c_{pl}$  is the specific heat of liquid-water at constant pressure ( $4218 \text{ J kg}^{-1}\text{K}^{-1}$ ). Note that the specific heat of moist air is assumed to be at constant pressure since it varies very weakly (about 2%) between  $-30^\circ\text{C}$  and  $30^\circ\text{C}$ .

3. ——— Condensational growth and the first law of thermodynamic partitioning: as the parcel reaches supersaturation at the cooler level, condensation starts. The latent heat release ( $Q$ ) is balanced by the decrease in internal energy due to condensation and the mechanical expansion of water vapor, as expressed by the saturation-work term  $W_s$ . The first law of thermodynamics, expressed in terms of the magnitudes of the energy components for a reversible saturated parcel, is:

$$Q = |\Delta U_{ws}| + W_s \quad (18)$$

Where,  $\Delta U_{ws}$  is the change in internal energy, including  $W_s$  in the energy balance. The heat added to the system ( $Q$ ) must satisfy the following balance:

$$|\Delta U_{ws}| = Q - W_s = \left( c_{p,cloud} \cdot (T_u - T_{ws}) \right) \quad [\text{J kg}^{-1}] \quad (19)$$

Where  $T_{ws}$  is the effective temperature of the cloud parcel (or  $T_L$  shown in Figure 1). For modelling purposes, when  $LWC$  is estimated,  $Q$  results from the temperature gradient during adiabatic cooling ( $\Delta U$ ) for a given thermodynamic condition; while for airborne measurements,  $Q$  is calculated from  $LWC$ ,  $p$ ,  $T$  and  $T_\theta$  (estimated). The term  $W_s$  can be calculated as a function of  $r_s$  and  $\alpha_v$  as follows:

$$W_s = \int_{\alpha_{v0}}^{\alpha_v} \frac{R_v \cdot T_{ws} \cdot r_s}{\alpha} d\alpha \propto [\text{J kg}^{-1}] \quad (20)$$

And expanding this equation can be written as follows:

$$W_s = r_s \cdot R_v \cdot T_{ws} \cdot \ln \left( \frac{\alpha_v}{\alpha_{v0}} \right) = r_s \cdot R_v \cdot T_{ws} \cdot \ln \left( \frac{T_{ws} \cdot e_s(T_\theta)}{T_\theta \cdot e_s(T_{ws})} \right) \quad [\text{J kg}^{-1}] \quad (21)$$

Equation 21 emphasizes that any measurable work done by water vapor during expansion can be interpreted as a quantifiable entropy loss by the saturated parcel. Furthermore,  $W_s$  is linearly dependent on  $T_{ws}$  and  $r_{s^*}$  and is closely associated with RH<sub>0</sub> (see Eq. 10).

In the lower troposphere, these microphysical processes occur within a turbulent environment, where expansion, condensation, and latent heat release can occur almost simultaneously and continuously interact. However, for modeling purposes, this sequence is treated as a stepwise process to isolate the thermodynamic contributions of each term in the energy balance, in which the time scale for buoyant expansion to increase vapor density is faster than the microphysical time scale for condensational growth to remove vapor excess.

### 2.3 Cloud Supersaturation Partition (Liquid and Vapor phases)

The energy balance calculated from Eqs. 15 and 19 show that the temperature gradient during the cooling process is different when considering or not  $W_s$ . Nevertheless, the total energy  $Q$  is conserved. Here, we associate the supersaturation of liquid ( $S_l$ ) and vapor ( $S_v$ ) phases with these differences in the temperature gradients. The temperature gradient ( $T_0 - T$ ) is associated with the parcel  $LWC$  and  $Q$  to  $S_0$  (calculated in Section 2.1).  $S_l$  and  $S_v$  are calculated as a function of the total energy released during the condensational growth given by  $Q$ , where  $\Delta U_{ws}$  and  $W_s$  are the energies associated with the liquid and gas phases of  $S_0$  as follows:

$$S_l = S_0 \cdot \frac{|\Delta U_{ws}|}{Q} [\%] \quad (22)$$

and,

$$S_v = S_0 \cdot \frac{|W_s|}{Q} [\%] \quad (23)$$

and,

$$S_0 = S_l + S_v [\%] \quad (24)$$

Equations 22-24 describe the relationships between  $S_0$ ,  $S_l$  and  $S_v$  to the energy balance in a saturated parcel in which the isobaric enthalpy is conserved. The fraction of  $S_l$  ( $FS_l$ ) in  $S_0$  is associated with the decrease of the internal energy of the saturated parcel (given by equation 22), and the fraction of  $S_v$  ( $FS_v$ ) in  $S_0$  is associated with  $W_s$  (given by equation 23).

### 2.654 Closure analysis from airborne measurements at cloud bases

The calculations of RH<sub>c</sub> and cloud supersaturations ( $S_c$ ,  $S_l$  and  $S_v$ ) at cloud bases are performed as a function of using the measurements from cloud probes and meteorological sensors on board the HALO aircraft. Table 12 summarizes the

general thermodynamic conditions and time intervals of cloud properties measured at cloud bases. The cloud measurements were conducted with the Cloud Combination Probe - Cloud Droplet Probe (CCP-CDP) (Lance, 2012). In this study, we focus on the initial stage of cloud formation. Therefore, only 1 Hz cloud passes (individual in-cloud sampling intervals) with and thus, cloud passes with a number concentration of droplets ( $N_d$ ) greater than  $20 \text{ cm}^{-3}$ , developing in under updraft conditions, are considered. This threshold of  $N_d = 20 \text{ cm}^{-3}$  is used to avoid haze and well-mixed cloud elements in the analysis. Furthermore, cloud passes with measured raindrops are removed from our analysis. (Campos Braga et al., 2017) In the supplementary material (Section S2), we present the sensitivity analysis assuming the proposed threshold for cloud identification and varying the values of  $N_d$  and LWC for the derived supersaturations and their relationships. These analysis shows that the derived supersaturations and their relationships assuming the proposed threshold ( $N_d > 20 \text{ cm}^{-3}$ ) are robust with respect to variations in cloud identification criteria. The remaining variability is primarily driven by environmental heterogeneity and turbulence rather than by the threshold definition itself.

The closure analysis relies on the reversibility of the cloud adiabatic parcel as described in the previous section 2.4. The calculations of  $RH_c$ ,  $S_c$ ,  $S_l$  and  $S_v$  require the information of  $p$ , LWC,  $T$ , and  $T_0$  near cloud bases. From the airborne data at cloud bases,  $p$ ,  $T$  and LWC are measured. Therefore, we estimate  $T_0$  and  $T_{\text{air}0\text{ws}}$  for each cloud pass. Below are the sequential steps used in our analysis:

1. First,  $T_0$  (or  $T_0$ ) is iteratively estimated for each cloud pass from is estimated based on the measured  $Q$  (calculated from LWC,  $T$  and  $p$ ) using Eq. for each cloud pass iteratively using equation 152.  $RH_c$  and  $S_c$  are subsequently calculated from  $T$  and estimated  $T_0$  and estimated  $T_0$  ( $T_0 > T$ ) using equations 13 and 14.
2. The process is repeated by, considering both  $Q$ , calculated in the first step, and  $W_s$  in the energy budget (see Eq. 1816), which results in an estimated air temperature which leads to a cooler estimated  $T_0$  ( $T_{0\text{ws}}$ ,  $T_{\text{air}}$ ) lower than  $T_0$  obtained in step 1, such that  $T_0 > T_{\text{air}0\text{ws}} > T$ . From this closure analysis, the values of  $\Delta U_{\text{ws}}$  and  $W_s$  are estimated, and  $S_l$  and  $S_v$  are subsequently calculated with equations Eqs. 22-18 and 2319, respectively.

During flights AC11, AC14 and AC17, the  $N_{\text{CCN}}(S_v)$  spectra from two CCN counters (CCNa and CCNb) were measured below cloud base prior to cloud base measurements with the CCP-CDP probe. This comparison provides an important evaluation of the derived water vapor component of cloud supersaturation ( $S_v$ ), since CCN chamber measurements are independent of in-cloud condensational growth processes. The  $N_d(S_v)$  spectra were converted to standard temperature and pressure (STP) conditions before comparison. The comparison between  $N_d(S_v)$  and  $N_{\text{CCN}}(S_v)$  aimed to evaluate the physical consistency of the proposed thermodynamical framework. In the CCN counters,  $S_v$  is determined from the Köhler theory using particles with a known physicochemical composition, typically ammonium sulfate, and is therefore independent of cloud processes.

## 2.5.75 Aircraft Data

### 2.575.1 Meteorological measurements

HALO was equipped with a meteorological sensor system (Basic HALO Measurement And Sensor System– BAHAMAS) located at the nose of the aircraft (Wendisch et al., 2016). The water vapor mixing ratio and derived humidity quantities were measured by the Sophisticated Hygrometer for Atmospheric Research (SHARC). The uncertainties for measurements at a frequency resolution of 1 Hz of air pressure, temperature, relative humidity, mixing ratio, and wind speed are about 3 Pa, 0.5 K, 5 %, 4% and  $0.3 \text{ m s}^{-1}$ , respectively (Mallaun et al., 2015).

### 2.575.2 Cloud probe and CCN measurements

The measurements of cloud properties over the Amazon Basin were performed at a frequency resolution of 1 Hz by the CCP mounted below the wings of the aircraft (Lance, 2012). CCP combines two detectors, the Cloud Droplet Probe (CDP) and the grayscale Cloud Imaging Probe (CIPgs), which allow the measurement of droplets with a size range of 3-960  $\mu\text{m}$ . In this study, the integrated water content of CDP for bin diameters ranging from 3-50  $\mu\text{m}$  was used to calculate the LWC at warm cloud bases. The measurements were validated by another cloud probe (Cloud and Aerosol Spectrometer with depolarization, CAS-DPOL) and a hot wire King probe (Campos Braga et al., 2017). The integrated water content of CIPgs for bin diameters greater than 50  $\mu\text{m}$  was used to calculate the Rainwater Content (RWC). Only cloud passes without rain droplets (i.e.,  $\text{RWC} = 0 \text{ g m}^{-3}$ ) are used in our analysis.

### 2.5.3 CCN measurements

During the ACRIDICON-CHUVA campaign, CCN number concentrations were measured at a frequency resolution of 1 Hz onboard HALO using a two-column CCNC [CCN-200; columns A (CCNa) and B (CCNb)], which is a continuous-flow longitudinal thermal-gradient instrument manufactured by Droplet Measurement Technologies (DMT) (Roberts and Nenes, 2005). In the instrument, the sampled aerosol particles are exposed to a set supersaturation and absorb water depending on their size and chemical composition. Particles that grow to droplets larger than 1  $\mu\text{m}$  in diameter are counted as CCN at that  $S_v$ . two CCN chambers were operating on board the HALO aircraft. CCNa measured CCN concentrations with cycled  $S_v$  between 0.2 and 0.55 % at 100 s intervals, and CCNb measured CCN concentrations with a fixed  $S_v \sim 0.55$  %. Table 23 summarizes the general thermodynamic conditions and the time intervals during which CCN measurements were conducted below cloud base. The  $N_{\text{CCN}}(S_v)$  CCN( $S_v$ ) spectrum measurements of the chambers was compared to the measured  $N_d$  and calculated  $S_v$  for three flights where  $N_d(S_v)$  and  $N_{\text{CCN}}(S_v)$  CCN( $S_v$ ) had the same range of  $S_v$  values. The CCN( $S_v$ ) spectra were measured below cloud bases prior to cloud base measurements. CCN number concentrations were measured onboard HALO using a two-column CCNC (CCN-200; columns A and B), which is a continuous-flow longitudinal thermal-gradient instrument manufactured by Droplet Measurement Technologies (DMT) (Roberts and Nenes, 2005). The instrument measures CCN number concentration as a function of water vapor supersaturation ( $S_v$ ) at a frequency

resolution of 1 Hz. In the instrument, the sampled aerosol particles are exposed to a set supersaturation and absorb water depending on their size and chemical composition. Particles that grow to droplets larger than 1  $\mu\text{m}$  in diameter are counted as CCN at that  $S_v$ .

The estimated uncertainty in measurements of CCN number concentration during the ACRIDICON-CHUVA campaign is about 20% (10%) on average for large (small) concentrations (Campos Braga et al., 2017). For measurements on polluted conditions during flights AC11, AC14 and AC17, the estimated uncertainties in CCN concentrations are about 10%. In addition, the estimated uncertainty in  $S_v$  values is about 14% on average, resulting from the uncertainties of 10% from counting efficiencies and 10% due to calibration accuracy. Sample air for the aerosol measurements was obtained from two different inlets: (i) the HALO aerosol submicron inlet (HASI) and (ii) the HALO counterflow virtual impactor (HALO-CVI). The CCN-200 provides the possibility to measure from both inlets in parallel or at two different values of  $S_v$ .

### 2.5.4.3 Airborne meteorological and cloud properties uncertainties

During the ACRIDICON-CHUVA campaign, the resulting uncertainty in the measured  $N_d$  and LWC by CCP-CDP with 1 Hz resolution was about 10% (Campos Braga et al., 2017). The uncertainty of rain-water content (RWC) measurements was about 30% (Braga et al., 2017b, 2021b). RWC uncertainties are less relevant to this study since we are focused on shallow cumulus clouds in the initiation stage of development, which typically have no rain droplets.

(Campos Braga et al., 2017) The measurement uncertainties of the energy budget parameters were calculated using a Monte Carlo method (JCGM, 2008) and are described in section S2.2 in the Supplementary Material. The uncertainties in the meteorological measurements from the BAHAMAS system translate into an estimated average uncertainty of about 0.24% (typically < 1% for 1 Hz data) in the derived  $RH_c$ . The relative uncertainties of the energy terms are about 10% for  $Q$  and  $\Delta U$ , and 13% for  $W_s$ . Propagating these errors yields overall uncertainties of ~10% for  $S_c$  and  $S_i$ , and ~12% for  $S_v$ . The uncertainties of energy terms and supersaturations are mostly sensitive to the LWC uncertainties. Baumgardner et al. (2017) reports that expected range of uncertainties in LWC and  $N_d$  is between 10% and 30%. For LWC uncertainty of 30%, the relative uncertainties of the energy terms are about 29% for  $Q$  and  $\Delta U$ , and 38% for  $W_s$ . Propagating these errors yields overall uncertainties of ~28% for  $S_c$  and  $S_i$ , and ~36% for  $S_v$ .

The uncertainties of the power-law relationship  $N_d = C \cdot S_v^k$  fitted for each flight segment shown in this manuscript were also calculated using Monte Carlo uncertainty propagation (using 10% for  $N_d$  and 12.6% for  $S_v$ ). These calculations are presented in Section S2.3 of the Supplementary Material. Across all flights, the exponent is well constrained with uncertainties of  $\sigma k \approx 0.01$ –0.03, while the  $C$  shows relative uncertainties of approximately 2–6%. Higher measurement uncertainties increase the scatter in the power-law relationships  $N_d$ - $S$  (shown in Tables S4-S6). Our analysis show a systematic decrease in both  $C$  and  $k$  when uncertainties increase, indicating that uncertainty propagation affects not only the precision but also the magnitude of the fitted parameters. Despite these shifts, the power-law relationship remains consistent across thresholds and flights, and

the variations in  $C$  and  $k$  are within the broader uncertainty range of the estimates. This indicates that while increased uncertainties reduce the strength of the statistical fit and slightly bias the parameter values, they do not alter the underlying physical dependence of  $N_0$  on  $S_c$ ,  $S_l$ , and  $S_v$ .

Temperature measurements of the considered air parcel at cloud base during individual cloud passes exhibited both cooler and warmer values relative to the surrounding air. This variability arises from the measurement process itself: liquid water impinging on the sensor can induce evaporative cooling, whereas latent heat release from condensational growth and buoyant cloud elements may locally warm the sensor. Nevertheless, these effects are estimated to remain within the nominal uncertainty of the temperature probe ( $\pm 0.5$  K). Uncertainties in the meteorological measurements from the BAHAMAS system translate into an estimated 4–5% uncertainty in the derived  $RH_0$  and  $S_c$ . The uncertainties of the energy terms were approximately 10% for  $Q$ , 11–15% for  $\Delta U$ , and 10–11% for  $W_s$ . Propagating these errors yields overall uncertainties of —15–17% for  $S_l$  and —12% for  $S_v$ . The numerical differences between the energy budget calculations performed in the first and second steps described in section 2.4 were negligible ( $< -0.01\%$  on average).

Table 1. List of symbols, variables and physical constants. → [Move to Appendix](#)

| Symbol          | Description                                                                 | Units                              |
|-----------------|-----------------------------------------------------------------------------|------------------------------------|
| RH              | Relative Humidity                                                           | —or %                              |
| RH <sub>c</sub> | Cloud Relative Humidity                                                     | —or %                              |
| $S$             | Supersaturation (general, dimensionless)                                    | —or %                              |
| $S_c$           | Cloud Supersaturation                                                       | %                                  |
| $S_l$           | Liquid-phase Supersaturation                                                | %                                  |
| $FS_l$          | Fraction of $S_l$ from $S_c$                                                | —                                  |
| $S_v$           | Vapor-phase Supersaturation                                                 | %                                  |
| $FS_v$          | Fraction of $S_v$ from $S_c$                                                | —                                  |
| $E$             | Water-vapor pressure                                                        | Pa                                 |
| $e_s$           | Saturation vapor pressure                                                   | Pa                                 |
| $T$             | Air temperature                                                             | K                                  |
| $T_{ws}$        | Effective (or Liquid) temperature of the saturated parcel considering $W_s$ | K                                  |
| $T_0$           | Reference temperature (cloud base)                                          | K                                  |
| $T_{0ws}$       | Cloud base temperature from closure analysis considering $W_s$              | K                                  |
| $T_e$           | Equivalent temperature                                                      | K                                  |
| $\Delta T_Q$    | Temperature change of saturated parcel due to $Q$                           | K                                  |
| $L_v$           | Latent heat of vaporization                                                 | J kg <sup>-1</sup>                 |
| $Q$             | Latent heating released                                                     | J kg <sup>-1</sup>                 |
| $\Delta U$      | Change in internal energy                                                   | J kg <sup>-1</sup>                 |
| $\Delta U_{ws}$ | Change in internal energy including $W_s$                                   | J kg <sup>-1</sup>                 |
| $W_s$           | Saturation work                                                             | J kg <sup>-1</sup>                 |
| $P$             | Pressure of the air parcel                                                  | Pa                                 |
| $q_l$           | Liquid water mixing ratio                                                   | kg kg <sup>-1</sup>                |
| $r_s$           | Saturation mixing ratio                                                     | kg kg <sup>-1</sup>                |
| $\rho_{air}$    | Air density                                                                 | kg m <sup>-3</sup>                 |
| $\rho_v$        | Water vapor density                                                         | kg m <sup>-3</sup>                 |
| $\alpha_v$      | Specific volume of water vapor                                              | m <sup>3</sup> kg <sup>-1</sup>    |
| $c_{pd}$        | Specific heat of dry air (at constant pressure)                             | J kg <sup>-1</sup> K <sup>-1</sup> |
| $c_{pv}$        | Specific heat of water vapor (at constant pressure)                         | J kg <sup>-1</sup> K <sup>-1</sup> |
| $c_{pl}$        | Specific heat of liquid water (at constant pressure)                        | J kg <sup>-1</sup> K <sup>-1</sup> |

|               |                                                               |                                |
|---------------|---------------------------------------------------------------|--------------------------------|
| $c_{p,cloud}$ | Specific heat capacity of cloud air<br>(at constant pressure) | $J\,kg^{-1}\,K^{-1}$           |
| $R_d$         | Gas constant for dry air                                      | $J\,kg^{-1}\,K^{-1}$           |
| $R_v$         | Gas constant for water vapor                                  | $J\,kg^{-1}\,K^{-1}$           |
| $N_d$         | Cloud droplet number<br>concentration                         | $cm^{-3}$                      |
| $r_e$         | Cloud droplet effective radius                                | $\mu m$                        |
| $LWC$         | Liquid Water Content                                          | $kg\,m^{-3}$ (or $g\,m^{-3}$ ) |
| $RWC$         | Rainwater Content                                             | $g\,m^{-3}$                    |

635 **Table 12.** Summary of cloud base 1 Hz CCP-CDP measurements conditions, including sampling duration and mean  
thermodynamic conditions for each analysed flight segment.Summary of measurement parameters at cloud bases for  
flights during the ACRIDICON-CHUVA campaign.

| Flight | Date in<br>2014 | Initial<br>Time<br>(UTC) | End<br>Time<br>(UTC) | Period of<br>CloudDuration<br>Measurementsof<br>Measurements<br>(s) | Average<br>Altitude<br>(m) | Average<br>Pressure<br>(hPa) | Average<br>Temperature<br>(°C) |
|--------|-----------------|--------------------------|----------------------|---------------------------------------------------------------------|----------------------------|------------------------------|--------------------------------|
| AC07   | 6-Sep           | 17:58:00                 | 18:12:50             | 77                                                                  | 1910                       | 812.3                        | 16.2                           |
| AC09   | 11-Sep          | 15:41:10                 | 15:53:20             | 41                                                                  | 1220                       | 878.85                       | 19.5                           |
| AC11   | 16-Sep          | 17:53:00                 | 18:05:50             | 33                                                                  | 1896                       | 812.28                       | 16.2                           |
| AC14   | 21-Sep          | 15:36:40                 | 15:57:30             | 73                                                                  | 1602                       | 843.4                        | 17.67                          |
| AC17a  | 27-Sep          | 15:11:40                 | 15:28:40             | 121                                                                 | 1589                       | 843.28                       | 17.6                           |
| AC17b  | 27-Sep          | 17:07:00                 | 17:17:00             | 64                                                                  | 1902                       | 812.3                        | 16.15                          |
| AC18   | 28-Sep          | 16:46:05                 | 16:55:40             | 99                                                                  | 1711                       | 834.07                       | 17.18                          |
| AC19   | 20-Sep          | 17:27:50                 | 17:37:40             | 163                                                                 | 606.5                      | 942.59                       | 22.26                          |

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**Table 32.** Summary of below cloud base 1 Hz CCN measurement conditions, including sampling duration and mean thermodynamic conditions for each analysed flight segment.  
Summary of CCN measurements parameters below cloud bases for flights during the ACRIDICON-CHUVA campaign.

| Flight | Date in 2014 | Initial Time (UTC) | End Time (UTC) | Period of CCN Duration of Measurements (s) | Average Altitude (m) | Average Pressure (hPa) | Average Temperature (°C) |
|--------|--------------|--------------------|----------------|--------------------------------------------|----------------------|------------------------|--------------------------|
| AC11   | 16-Sep       | 17:39:10           | 17:50:00       | 650                                        | 450.93               | 958.91                 | 28.06                    |
| AC14   | 21-Sep       | 15:25:00           | 15:33:20       | 500                                        | 954.9                | 908.77                 | 22.85                    |
| AC17a  | 27-Sep       | 14:55:00           | 15:06:40       | 700                                        | 941.81               | 908.77                 | 22.87                    |
| AC17b  | 27-Sep       | 16:52:30           | 17:01:40       | 550                                        | 1255.4               | 875.67                 | 21.85                    |

### 3 Results

#### 3.1 *Cloud Supersaturations at cloud bases of Amazonian Clouds* Energetic Budget and Supersaturations at Cloud bases

To illustrate the thermodynamic basis of the energetic budget analysis at cloud base, we first describe the fundamental relationships between the initial temperature of the saturated parcel ( $T_0$ ) and adiabatic cooling  $\Delta T$  resulting from the ascent for  $T_0$  ranging from 2°C to 30°C. Figure 2 shows the simulated values of LWC,  $Q$ ,  $\Delta U$ , and  $W_s$  resulting from the energy balance at a pressure level of 950 hPa. All quantities from the energy balance are expressed as positive values to represent the partition of the total energy ( $Q$ ) during the condensational growth. In the case in which water vapor is fully condensed ( $Q = dH$ ) the LWC (solid lines) increase almost linearly with cooling rate for different  $T_0$ . For the same cooling rate, a slightly larger LWC is calculated for lower temperatures owing to the higher dry air density of the saturated parcel. When accounting for  $W_s$  in the energy budget, the resulting values of LWC (dotted lines) are relatively smaller. At 950 hPa, the fractional reduction in LWC due to  $W_s$  increases approximately linearly with temperature, ranging from about 4-6% at low temperatures (~ 2-6 °C) to 15-20% at higher temperatures (~ 25-30 °C) (see Figure S1). The values of  $\Delta U$  are slightly smaller than  $Q$  since the total energy is partitioned with  $W_s$ , which increases approximately linearly with temperature and logarithmically with the cooling rate.

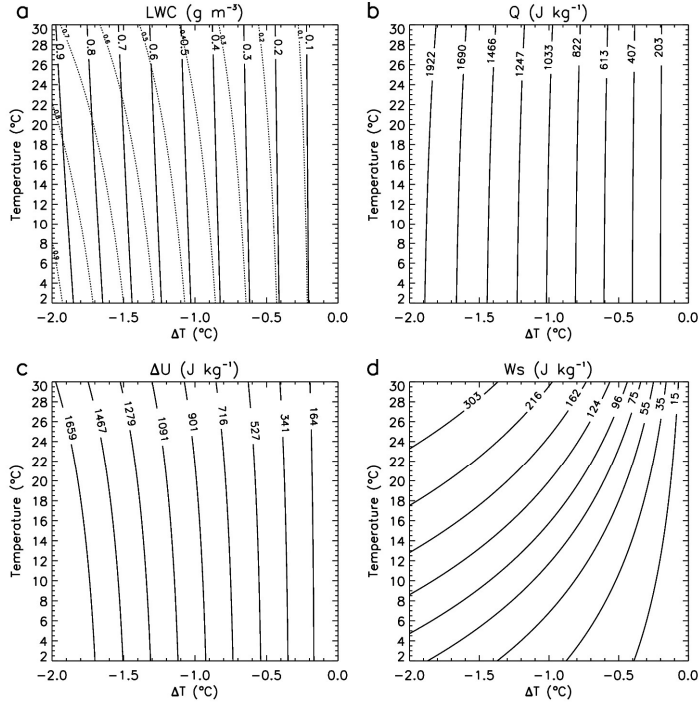
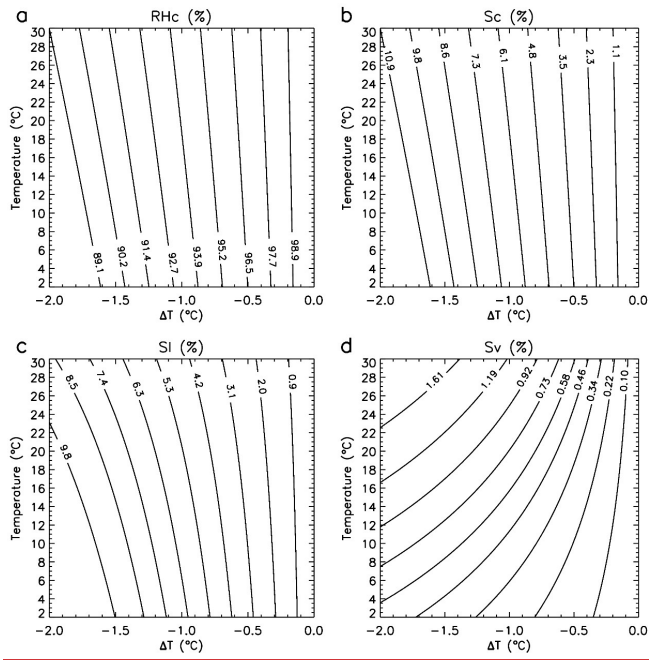


Figure 2. (a) Contours of Liquid Water Content (LWC) values of cloud adiabatic parcels as a function of initial temperature  $T_0$  (y-axis) and adiabatic cooling rate ( $\Delta T$ ) (x-axis) at 950 hPa. Dotted lines indicate the LWC resulting from the energy budget ( $W_s$  term leads to LWC decrease for the same  $\Delta T$ ). Similar for (b) Latent heat of condensation ( $Q$ ), (c) Magnitude of internal-energy change ( $|\Delta U|$ ), and (d) saturation work ( $W_s$ ).

Figure 3 shows the corresponding values of  $RH_c$ ,  $S_c$ ,  $S_l$ , and  $S_v$  derived from the energy budget framework. Figures 3a-b show  $RH_c$  decreasing below 100%, with a corresponding increase of  $S_c$  above 0% as a function of the prescribed adiabatic cooling. For a given cooling magnitude, the increase in  $S_c$  becomes slightly smaller at warmer temperatures because the fractional reduction in  $RH_c$ ,  $[e_s(T)/e_s(T_0)]$  for a fixed  $\Delta T$  decreases slightly with increasing  $T_0$ , consistent with the temperature dependence of the Clausius-Clapeyron relation. Figures 3c-d show the partitioning of  $S_c$  into  $S_l$  and  $S_v$  resulting from the energy budget analysis. The values of  $S_l$  are about one order of magnitude larger than  $S_v$ , indicating that most of the enthalpy change associated with adiabatic cooling and condensation contributes to vapor-to-liquid conversion and

680 condensational growth, while  $W_s$  represents a smaller fraction of the total energy budget. Since  $W_s$  increases with  $T_0$ ,  $S_v$  becomes relatively larger under warmer cloud-base conditions for the same cooling magnitude, whereas the opposite behaviour is observed for  $S_l$ . This emphasizes the increasing contribution of saturation work to the total energy budget at warmer temperatures, which enhances  $S_v$  while reducing the condensational growth of cloud particles.



685 Figure 3. (a) Contours of reference-state saturation ratio ( $RH_c$ ) as a function of initial temperature  $T_0$  (y-axis) and adiabatic cooling rate ( $\Delta T$ ) (x-axis) for saturated parcels at 950 hPa. (b), (c) and (d) Similar to cloud supersaturation ( $S_c$ ), liquid-phase supersaturation ( $S_l$ ), and for water vapor supersaturation ( $S_v$ ), respectively.

690 These relationships between energetic partitioning and the vapor budget remain qualitatively similar under lower-pressure conditions. However, as pressure decreases, the LWC is reduced because the density of dry air decreases. Furthermore, for a given  $T_0$  and  $\Delta T$ , the magnitude of  $W_s$  is slightly enhanced at lower pressures due to the larger saturation mixing ratio (see Eq. 5), thereby increasing the contribution of water vapor expansion to the total energy budget. Consequently, a smaller fraction of the enthalpy change associated with cooling and condensation contributes to vapor-to-liquid conversion and

condensational growth. At 850 hPa, for example, the reduction in LWC associated with  $W_s$  ranges from approximately 5-7% at low temperatures ( $\sim 2-6^\circ\text{C}$ ) to about 18-22% at higher temperatures ( $\sim 25-30^\circ\text{C}$ ) (Figure S2). The larger contribution of  $W_s$  to the energy budget leads to slightly larger  $S_v$  and smaller  $S_l$  relatively to those at 950 hPa.

### 3.2 Cloud Supersaturations at cloud bases of Amazonian Clouds

Cloud supersaturations were calculated from cloud-base measurements over the Amazon Basin across eight flight segments (see Table 2). These observations encompassed diverse environments, including the Central Amazon under the influence of urban pollution, forested regions in the north-northwest, the southern deforestation arc, and the Atlantic Ocean sector (Figure S1 shows the locations of measurements at the cloud bases). The Amazon Basin provides a particularly useful testbed for this the cloud base closure analysis because the same aircraft and instrumentation sampled a wide aerosol gradient range of cloud base environments, from relatively clean marine and forested conditions to polluted air masses influenced by biomass burning and the Manaus urban plume (see the locations of the cloud base measurements at Fig. S3). (Wendisch et al. 2016; Braga et al., Cecchini et al....).

Figure 42 illustrates a case study of the dependence of droplet number concentrations  $N_d$  at cloud base on RH,  $RH_c$ , cloud supersaturations ( $S_c$ ,  $S_l$ ,  $S_v$ ), and the associated magnitude of energy/energetic terms ( $Q$ ,  $\Delta U$ ,  $W_s$ ) derived from measurements collected during Flight AC14. During this flight leg, cloud bases of developing cumuli were sampled under RH conditions were measured ranging from  $\sim 60\%$  to  $\sim 102\%$ , at an altitude of about at about 1600 m and temperatures near altitude and at  $17.6^\circ\text{C}$ . Figure 42a shows that RH (in black) generally increases as a function of  $N_d$  even though in most cloud passes RH is smaller than 100%. This variability in RH measurements arises from the characteristics of in situ temperature measurements: liquid water impinging on the sensor can induce evaporative cooling, whereas the latent heat released during particle condensational growth and buoyant air volumes may locally warm the sensor.  $RH_c$  (in red) decreases consistently with  $N_d$  associated with higher liquid water content LWC. The cloud passes where  $RH < RH_c$ , may the local vapor pressure  $e(T)$  is typically smaller than expected from the cooling trajectory of the initially saturated parcel, suggesting enhanced entrainment of unsaturated environmental air and reduced condensational growth (see Figure S4) indicate that the cloud parcels are likely more affected by entrainment of unsaturated air. Under such conditions, smaller droplets evaporate preferentially due to the inhomogeneous nature of mixing in convective clouds. This selective evaporation reduces the local LWC, and the remaining droplet population is biased toward droplets formed on CCN with higher hygroscopicity, which are more resistant to evaporation. Conversely, for cases in which  $RH > RH_c$ , indicate that the parcel retains a larger vapor content relative to theoretical calculations, favouring continued condensational growth, enhanced  $S_v$ , may reflect cloud elements exhibit stronger locally enhanced buoyancy and more vigorous condensational growth, yielding higher  $N_d$  for a given CCN population. These conditions correspond to elevated cloud supersaturation and enhanced LWC.

Figure 4b shows the dependence of  $N_d$  on  $S_v$  and  $S_l$  at cloud base. Both  $S_l$  and  $S_v$  increase with  $N_d$ , although  $S_v$  remains nearly one order of magnitude smaller than  $S_l$ . The calculated  $S_v$  values exhibit the expected positive relationship between

supersaturation and droplet concentration commonly observed in CCN activation spectra. The  $N_d(S_v)$  relationship exhibits substantial variability at cloud base owing to the inhomogeneous and turbulent nature of the in situ measurements. The dispersion is particularly enhanced for cases in which relatively large  $N_d$  values are associated with small  $S_v$ , corresponding to conditions where the local vapor pressure remains below the theoretical simulations ( $RH < RH_c$ ). Nevertheless, most of the measured water vapor pressures remain within the estimated uncertainty range of the theoretical estimates (see Fig. S4), indicating that the overall  $N_d$ - $S_v$  relationship remains representative of the cloud base thermodynamic conditions. Figure 4c presents the energy budget components as a function of  $S_v$ , while Figure 4d depicts the cloud supersaturations derived from the measured LWC. These figures show that the total energy ( $Q$ ) increases strongly with LWC and is dominated by changes in internal energy ( $\Delta U/Q$ ;  $\sim 90\%$  on average), while the contribution from saturation work ( $W_s$ ) is comparatively minor.

Similar characteristics of the energy budget were observed for the different flight legs measured in the Amazon Basin and Atlantic Ocean (Figures S5-S18). In these flight segments, most of the measured water vapor pressures were within the estimated uncertainty range of the theoretical cloud-adiabatic estimates. The estimated fraction of  $\Delta U/Q$  accounted for  $\sim 88$ - $91\%$  in the energy budget, lower values were measured for warmer (marine) clouds during flight AC19. As shown in Section 3.1,  $S_v$  has a strong linear dependence on temperature, since this supersaturation component is associated with the  $W_s$  term.

These results show that in warmer environments, a larger amount of energy relative to  $Q$  is expended for the air parcel's expansion, leading to a smaller decrease in the cloud parcel's internal energy and a lower cooling rate.

Flight AC14: Central Amazon

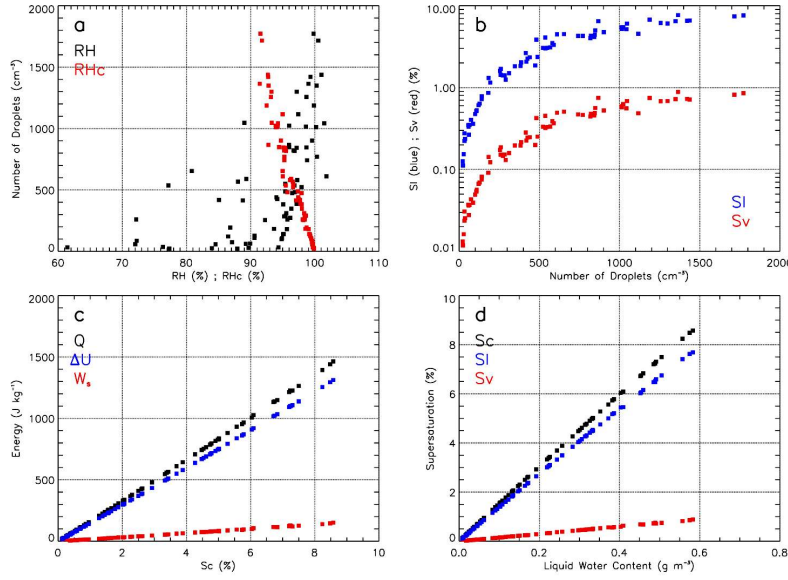


**Figure 4. Cloud microphysical and thermodynamic properties measured at cloud bases of growing convective cumuli during Flight AC14. (a) RH versus  $N_d$  (black) and  $RH_c$  versus  $N_d$  (red). (b)  $N_d$  versus  $S_i$  (blue) and  $N_d$  versus  $S_v$  (red). (c)  $S_c$  versus  $Q$ ,  $|\Delta U|$ , and  $W_s$ . (d) LWC versus  $S_c$ ,  $S_i$ , and  $S_v$ .**

Figure 2b shows the dependence of  $N_d$  on  $S_v$  and  $S_i$  at cloud base. Both  $S_i$  and  $S_v$  increase with  $N_d$ , although  $S_v$  remains nearly one order of magnitude smaller than  $S_i$ . Figure 2c presents the energy budget components as a function of  $S_c$ , while Figure 2d depicts the cloud supersaturations derived from the measured LWC. These figures show that the total energy ( $Q$ ) increases strongly with LWC and is dominated by changes in internal energy ( $\Delta U$ ;  $\sim 89\%$  on average), while the contribution from saturation work ( $W_s$ ) is comparatively minor.

The fractions of liquid water and water vapor supersaturations ( $F_{S_i}$  and  $F_{S_v}$ , respectively) as a function of  $S_c$  at cloud bases are shown in Figure 3 for the different flight legs measured in the Amazon Basin (see also the closure analysis for all flight segments in Figs. S2–S8). During these flights,  $F_{S_i}$  accounted for  $\sim 88$ – $90\%$  of the  $S_c$ , and lower  $F_{S_i}$  values were measured for

warmer (marine) clouds during flight AC19.  $F_{S_v}$  has a strong linear dependence on temperature, since this supersaturation component is associated with the  $W_s$  term, which is proportional to the air parcel temperature and saturated mixing ratio (higher at warmer temperatures). These results show that in warmer environments, a larger amount of energy relative to  $Q$  is used for the air parcel's expansion, leading to a smaller decrease in the cloud parcel's internal energy and a lower cooling rate. We performed simulations that confirm these findings across a range of thermodynamic conditions (temperature, pressure, and cooling rate) and describe their effects on the energy budget and cloud supersaturation of saturated air parcels in Section S4. Figure 5 shows the droplet number spectra as a function of cloud supersaturations ( $S_c$ ,  $S_l$ ,  $S_v$ ),  $N_d(S)$ , derived from cloud base measurements for all flight segments (see Tables 3-5 for the statistics of the fit parameters).

Figure 4 summarizes the  $N_d(S_v)$  spectra at cloud bases for all analyzed flight segments under different atmospheric conditions across the Amazon region. The droplet number spectra  $N_d(S_v)$  were derived using power-law fits of the form  $N_d = C \cdot S_v^k$ , where  $C$  is a scaling factor and  $k$  is the spectral exponent. Across all three supersaturations derived larger values of  $C$  and  $k$  parameters are estimated for aerosol-rich conditions (e.g., AC07). Larger  $k$  values indicate stronger sensitivity of droplet activation to  $S_v$ , consistent with aerosol-rich conditions (e.g., AC07), whereas smaller  $C$  and  $k$  values (e.g., AC19) reflect more CCN-limited regimes. The values of  $C$  and  $k$  have closer values for the power-law fits of  $N_d-S_c$  and  $N_d-S_l$  due to the similar values of  $Q$  and  $\Delta U$  in the energetic budget partition ( $\Delta U \sim 0.9 \cdot Q$ ). The high correlation coefficients of determination ( $R^2 \geq 0.9387$ ) and low root-mean-square errors (RMSE  $< 0.3$ ) indicate robust agreement between the fitted relationships and the observations show robust agreement between observations under different atmospheric conditions. The tables show that the values of  $R^2$  are sensitive to sample size, and larger cloud base datasets typically result in lower  $R^2$  values due to the inclusion of a broader range of atmospheric variability. In our observations, larger samples encompass more heterogeneous conditions in updraft velocity, turbulence intensity, and CCN concentrations, which increase scatter in the  $N_d-S$  relationships. Nevertheless, the fitted parameters  $C$  and  $k$  remain relatively stable across the different environmental conditions owing to the underlying physical dependence between  $N_d$  and  $S$ . A more detailed description of this analysis accounting for different cloud detection thresholds and measurements uncertainties is provided in Section S2.3 of the Supplementary Material.

The  $N_d(S_v)$  spectra calculated from the energetic budget analysis at cloud base are comparable to the  $N_{CCN}(S_v)$  spectra observed near the surface level over marine regions and the Amazon Basin during the dry season (Campos Braga et al., 2017; Khain and Pinsky, 2018; Pöhlker et al., 2016). The  $N_d(S_v)$  spectra indicate that under clean marine conditions (flight AC19), the estimated number of droplets  $N_d$  expected to activate at cloud base is about  $72540 \text{ cm}^{-3}$  at  $S_v = 1\%$ . The maximum estimated  $S_v$  derived from the measurements is 0.27%, corresponding to an adiabatic cooling ( $\Delta T_c$ ) of 0.4 °C resulting from the closure analysis. In contrast, for measurements obtained under more polluted conditions over forested regions, during flights AC09 and AC18 show  $N_d$  values is roughly twice as large for the same  $S_v$ . The maximum estimated  $S_v$  values derived from measurements were 0.34% ( $\Delta T_c = 0.53 \text{ °C}$ ) and 0.44% ( $\Delta T_c = 0.71 \text{ °C}$ ) for flights AC09 and AC18, respectively. Even higher larger  $N_d$  ( $S_v = 1\%$ ) values are estimated for are observed the data over the Central Amazon and the

790 deforestation arc, where ~~the droplet concentrations the measured CCN concentrations were~~ more strongly influenced  
 by emissions from urban activities and biomass burning. The largest estimated  $S_v$  value derived from the measurements  
 (1.15%) was calculated for flight leg AC17a corresponding to a  $\Delta T_c$  of 1.81 °C.

The ~~C~~clouds ~~properties forming~~observed under CCN-limited regimes were generally associated with regions of ~~lower~~weaker  
 buoyant forcing, where ~~lower~~resulting in lower LWC ~~LWC~~ and weaker updraft speeds ~~w~~ were measured. (with maximum  
 795 values  $\sim 2 \text{ m s}^{-1}$  (see Figure S19). In contrast, aerosol-rich environments were associated with stronger buoyant forcing and  
 enhanced adiabatic cooling at cloud base, leading to larger LWC, higher  $S_v$ , and stronger  $w$  (up to  $\sim 4 \text{ m s}^{-1}$ ) ~~in more polluted~~  
~~environments, buoyant forcing at cloud bases contributes more strongly to droplet formation, as evidenced by higher updraft~~  
~~speeds~~. Enhanced buoyant forcing also increased the variability of cloud-base measurements by strengthening fluctuations in  
 the thermodynamic state of the cloud parcel (LWC,  $T$ , and  $p$ ), which are the primary variables used in the energy budget and  
 800 supersaturation calculations. However, the uncertainties in  $S_v$  do not scale directly with buoyant forcing itself, but rather with  
 the uncertainty in these thermodynamic and microphysical measurements (see Section S2.2). Consequently, the largest  
 observed  $S_v$  and  $w$  values were generally associated with larger cloud base LWC values, consistent with stronger adiabatic  
 cooling and enhanced condensational growth.

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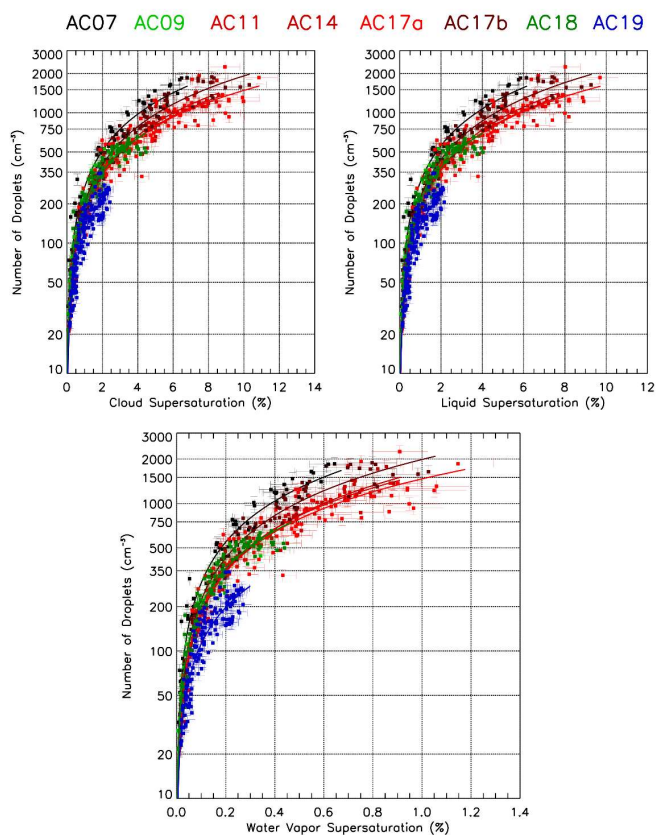
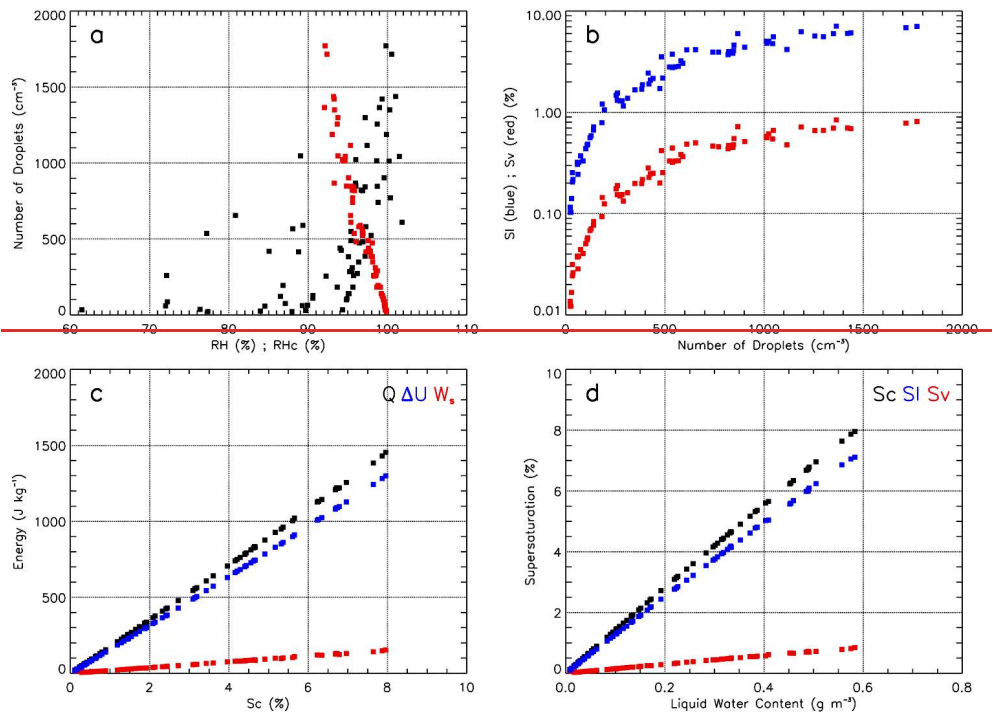


**Figure 5.** a)  $S_c$  vs.  $N_d$  for multiple flight segments (AC07, AC09, AC11, AC14, AC17a, AC17b, AC18, and AC19). Colored markers represent in-situ measurements, while solid curves correspond to power-law fits of the form  $N_d = C \cdot S_c^k$ . The colored markers correspond to different aerosol backgrounds in the Amazon region (red: Central Amazon, green: Northwestern Amazon, blue: Atlantic Ocean). b) and c) Similar for  $S_l$  vs.  $N_d$  and  $S_v$  vs.  $N_d$ , respectively. Error bars indicate the uncertainties of  $N_d$  (10%),  $S_c$  (~9.5%),  $S_l$  (~9.2%) and  $S_v$  (~12.6%). The statistics of the power-law fits are presented in Tables 3, 4 and 5.

**Table 3.**

815 Power-law fit parameters for the relationship  $N_d = C \cdot S_v^k$  derived from log-log regression for each flight leg. The coefficients  $C$  and  $k$  are reported as Monte Carlo means  $\pm 1\sigma$  ( $N_r = 5000$  realizations). The coefficient of determination ( $R^2$ ) and root-mean-square error (RMSE) are calculated from the nominal fit in logarithmic space. The uncertainties of  $N_d$  and  $S_v$  assumed in the calculations are 10% and 12.6%, respectively. Columns list: Flight leg,  $C$ ,  $\sigma C$ ,  $k$ ,  $\sigma k$ ,  $R^2$ , RMSE, and sample size (N).

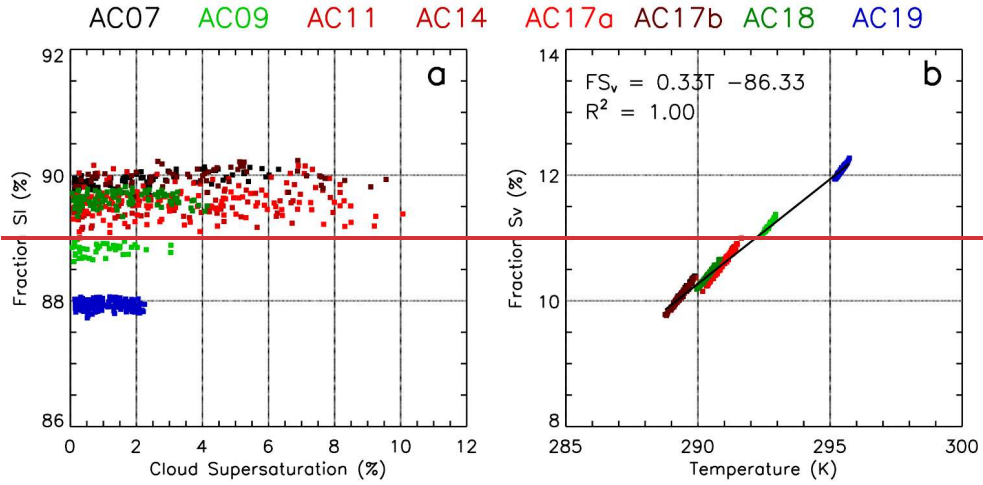
Flight AC14: Central Amazon



820 **Figure 2.** Cloud microphysical and thermodynamic properties measured at cloud bases of growing convective cumuli during Flight AC14. (a) RH versus  $N_d$  (black) and RHc versus  $N_d$  (red). Values shown for RHc do not account for the additional  $S_v$ . (b)  $N_d$  versus  $S_i$  (blue) and  $N_d$  versus  $S_v$  (red). (c)  $S_c$  versus  $Q_r$ ,  $|\Delta U_{ws}|$  (indicated as  $\Delta U$  for simplicity), and  $W_s$ . (d) LWC versus  $S_c$ ,  $S_i$ , and  $S_v$ .

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| Flight | $C$     | $\alpha C$ | $k$   | $\alpha k$ | $R^2$ | RMSE  | N   |
|--------|---------|------------|-------|------------|-------|-------|-----|
| AC07   | 2417.38 | 80.01      | 0.923 | 0.014      | 0.958 | 0.249 | 77  |
| AC09   | 1352.97 | 83.48      | 0.828 | 0.022      | 0.952 | 0.19  | 41  |
| AC11   | 1567.29 | 66.16      | 0.925 | 0.027      | 0.982 | 0.125 | 33  |
| AC14   | 1644.66 | 51.57      | 0.974 | 0.015      | 0.981 | 0.164 | 73  |
| AC17a  | 1467.06 | 33.21      | 0.904 | 0.012      | 0.947 | 0.26  | 121 |
| AC17b  | 1985.79 | 63.35      | 0.955 | 0.018      | 0.975 | 0.161 | 64  |
| AC18   | 1420.38 | 50.03      | 0.847 | 0.015      | 0.94  | 0.213 | 99  |
| AC19   | 743.72  | 27.24      | 0.824 | 0.015      | 0.874 | 0.24  | 163 |



830 **Figure 3.** (a) Fraction of liquid-phase supersaturation ( $S_i$ ) as a function of cloud supersaturation ( $S_c$ ) for eight cloud  
835 segments (AC07, AC09, AC11, AC14, AC17a, AC17b, AC18, AC19). (b) Fraction of water vapor supersaturation ( $S_v$ )  
as a function of cloud temperature.

**Table 4.** Similar to Table 3 for power-law fit parameters for the relationship  $N_d = C \cdot S_i^k$  derived from log-log  
835 regression. The uncertainties of  $N_d$  and  $S_i$  assumed in the calculations are 10% and 9.2%, respectively.

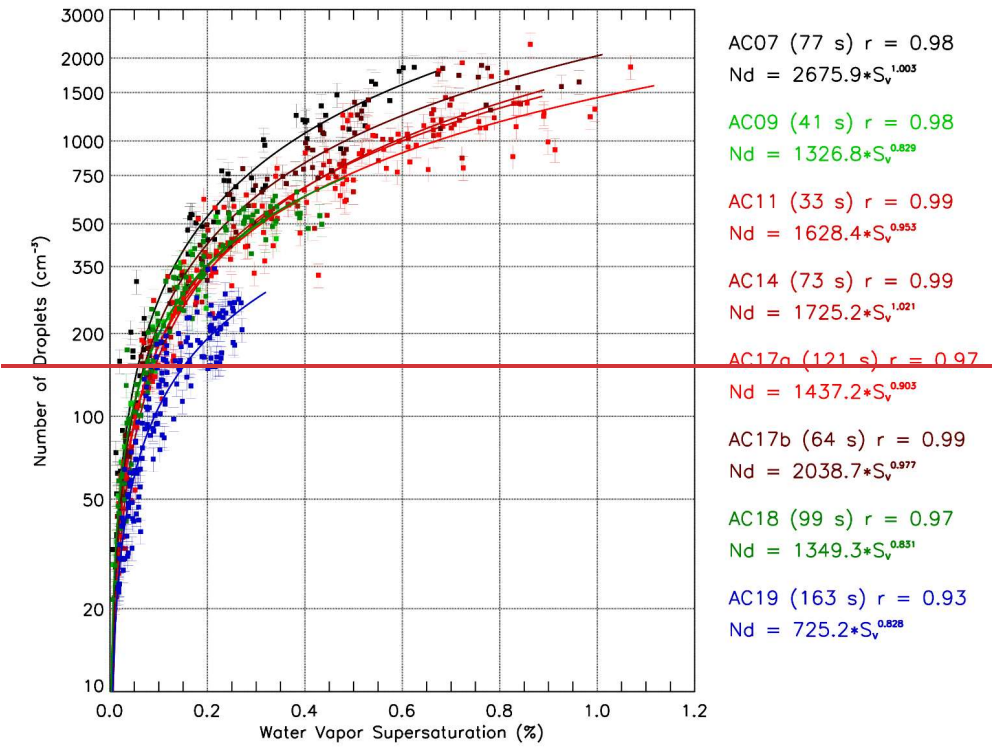
| Flight | C      | $\sigma C$ | k     | $\sigma k$ | R <sup>2</sup> | RMSE  | N   |
|--------|--------|------------|-------|------------|----------------|-------|-----|
| AC07   | 294.68 | 5.18       | 0.929 | 0.014      | 0.958          | 0.249 | 77  |
| AC09   | 224.36 | 5.47       | 0.832 | 0.022      | 0.953          | 0.188 | 41  |
| AC11   | 188.26 | 7.58       | 0.953 | 0.028      | 0.983          | 0.12  | 33  |
| AC14   | 187.47 | 3.87       | 0.989 | 0.016      | 0.983          | 0.157 | 73  |
| AC17a  | 194.28 | 3.13       | 0.924 | 0.012      | 0.951          | 0.251 | 121 |
| AC17b  | 224.05 | 5.82       | 0.973 | 0.019      | 0.977          | 0.153 | 64  |
| AC18   | 210.78 | 3.17       | 0.856 | 0.015      | 0.942          | 0.209 | 99  |
| AC19   | 133.77 | 1.57       | 0.832 | 0.015      | 0.876          | 0.238 | 163 |

Figure 4 summarizes the  $N_d(S_c)$  spectra at cloud bases for all analyzed flight segments under different atmospheric conditions across the Amazon region. The droplet number spectra  $N_d(S_c)$  were derived using power-law fits of the form  $N_d = C \cdot S_c^k$ , where C is a scaling factor and k is the spectral exponent. Larger k values indicate stronger sensitivity of droplet activation to  $S_c$ , consistent with aerosol-rich conditions (e.g., AC07), whereas smaller k values (e.g., AC19) reflect more CCN-limited regimes. The high correlation coefficients ( $r \geq 0.93$ ) show robust agreement between observations under different atmospheric conditions. The  $N_d(S_c)$  spectra indicate that under marine conditions (flight AC19), the number of droplets expected to activate at cloud base is about  $725 \text{ cm}^{-3}$  at  $S_c = 1\%$ . For measurements over forested regions, during flights AC09 and AC18,  $N_d$  is roughly twice as large for the same  $S_c$ . Even higher values are observed over the Central Amazon and the deforestation are, where the measured CCN concentrations were more influenced by emissions from urban activities and biomass burning. Clouds forming under CCN-limited regimes were associated with regions of lower buoyant forcing, where lower LWC and updraft speeds were measured (see Figure S9). In contrast, in more polluted environments, buoyant forcing at cloud bases contributes more strongly to droplet formation, as evidenced by higher updraft speeds.

**Table 5. Similar to Table 3 for power-law fit parameters for the relationship  $N_d = C \cdot S_c^k$  derived from log-log regression. The uncertainties of  $N_d$  and  $S_c$  assumed in the calculations are 10% and 9.5%, respectively.**

| Flight | C      | $\sigma C$ | k     | $\sigma k$ | R <sup>2</sup> | RMSE  | N  |
|--------|--------|------------|-------|------------|----------------|-------|----|
| AC07   | 269.19 | 4.81       | 0.928 | 0.014      | 0.958          | 0.249 | 77 |
| AC09   | 205.06 | 4.82       | 0.831 | 0.022      | 0.953          | 0.188 | 41 |
| AC11   | 171.78 | 7.26       | 0.95  | 0.028      | 0.983          | 0.12  | 33 |

|       |        |      |       |       |       |       |     |
|-------|--------|------|-------|-------|-------|-------|-----|
| AC14  | 169.44 | 3.62 | 0.987 | 0.016 | 0.983 | 0.157 | 73  |
| AC17a | 176.91 | 2.96 | 0.922 | 0.012 | 0.95  | 0.252 | 121 |
| AC17b | 203.88 | 5.54 | 0.971 | 0.019 | 0.977 | 0.153 | 64  |
| AC18  | 193.53 | 2.97 | 0.855 | 0.015 | 0.942 | 0.209 | 99  |
| AC19  | 121.32 | 1.37 | 0.831 | 0.015 | 0.876 | 0.238 | 163 |



860 **Figure 4.**  $S_v$  vs.  $N_d$  for multiple flight segments (AC07, AC09, AC11, AC14, AC17a, AC17b, AC18, and AC19). Colored markers represent in-situ measurements, while solid curves correspond to power-law fits of the form  $N_d = C \cdot S_v^k$ . The correlation coefficient ( $r$ ) of the fit for each flight segment is also indicated. The duration of each analyzed period is given in parentheses. Error bars indicate the uncertainties of  $N_d$  (10%).

Similar results were observed for the  $N_d(S_l)$  and  $N_d(S_v)$  spectra, as shown in Figures S10 and S11, owing to the nearly-linear relationship between cloud supersaturations. The  $N_d(S_l)$  and  $N_d(S_v)$  spectra were derived using similar power-law fits as the water-vapor component. Since  $S_l$  is associated with the cooling of the cloud parcel, it reflects the relationship between  $LWC$  and  $N_d$ , where  $N_d$  increases steeply for  $S_l < 2\%$  before gradually leveling off toward higher values. By incorporating both the liquid ( $S_l$ ) and vapor ( $S_v$ ) components of supersaturation, the  $N_d(S_v)$  spectra yield correlation coefficients similar to  $N_d(S_l)$  and  $N_d(S_v)$  spectra. The consistently high correlations across clean and polluted regimes in the Amazon Basin and Atlantic Ocean indicate that  $N_d$  is well constrained by  $S_{cs}$ ,  $S_l$ , or  $S_v$ .

### 3.3.2 Comparison of $N_d(S_v)$ spectra vs. $N_{CCN}(S_v)$ spectra in the Central Amazon

The comparison of  $N_d(S_v)$  spectra vs.  $N_{CCN}(S_v)$  spectra is performed for four flight segments in Central Amazon, AC11, AC14, AC17a, and AC17b. The  $N_d(S_v)$  spectra are interpreted as representative of the sub-cloud  $N_{CCN}(S_v)$  population that was activated into cloud droplets after buoyant ascent to cloud base. During flights AC14 and AC17, the  $N_{CCN}(S_v)$  measurements were performed about 700 m below cloud base altitude, while during flight AC11, they were performed about 1400 m below cloud base (Tables 1 and 2). Therefore, the comparison should be interpreted as a closure between nearby sub-cloud CCN populations and cloud base droplet activation rather than as a strict Lagrangian comparison of identical air parcels.

The  $N_d(S_v)$  spectra calculated from the energetic budget analysis at cloud bases show a similar magnitude of  $CCN(S_v)$  spectra observed below cloud bases in our previous study (Campos Braga et al., 2017). For four flight segments in the Central Amazon, AC11, AC14, AC17a, and AC17b, the  $CCN(S_v)$  spectra were measured just below cloud base prior to cloud base measurements with the CCP-CDP probe (see Section 2.5 for airborne measurements description). These measurements allowed comparison of the calculated values of  $N_d(S_v)$  measured at cloud bases with  $CCN(S_v)$  spectra measured below cloud bases. This analysis is essential to validate the water vapor component of cloud supersaturation, since CCN chamber measurements are not affected by condensational growth processes. For this comparison, the  $N_d(S_v)$  spectra were converted to standard temperature and pressure (STP) conditions. During flights AC14 and AC17, the  $CCN(S_v)$  measurements were performed about 700 m below cloud base altitude, while during flight AC11, they were performed about 1400 m below cloud base (see Table 3 for additional details). Therefore, the comparison should be interpreted as a closure between nearby sub-cloud CCN populations and cloud-base droplet activation, rather than as a strict Lagrangian match between identical air parcels.

Figure 65 shows  $N_{CCN}(S_v)$  spectra measured with CCNa for supersaturations  $S_v$  ranging from  $\sim$  about 0.2% to  $\sim$  almost 0.55% (red marks) during flight AC17, and over a narrower  $S_v$  range for flights AC11 and AC14, while  $N_{CCN}(S_v)$  from CCNb was measured with a fixed  $S_v$  at  $\sim$  0.55% (blue marks). The corresponding  $N_d(S_v)$  spectra and the power-law fit parameters for each flight segment are shown in black. The fixed- $S_v$  measurements from CCNb illustrate the variability of sub-cloud CCN concentrations for each flight segment. For segments AC11, AC14 and AC17a, the differences between minimum and maximum  $N_{CCN}(S_v)$  exceeded  $1300 \text{ cm}^{-3}$ , whereas during AC17b this range remained below  $700 \text{ cm}^{-3}$ . The large variability in  $N_{CCN}(S_v)$  is associated with heterogeneous air masses influenced by pollution plumes from biomass-burning and urban emissions. Under these conditions, the typical monotonic increase of  $N_{CCN}(S_v)$  with increasing  $S_v$  is not consistently observed in the CCNa measurements. This effect of pollution plumes in CCNa measurements is clearly shown in the figure where larger concentrations were measured for smaller  $S_v$ . In the flight segment AC17b, where a smaller variability of  $N_{CCN}(S_v)$  is observed in the CCNb sampling,  $N_{CCN}(S_v)$  measurements from CCNa are more consistent with those observed in homogenous air masses.

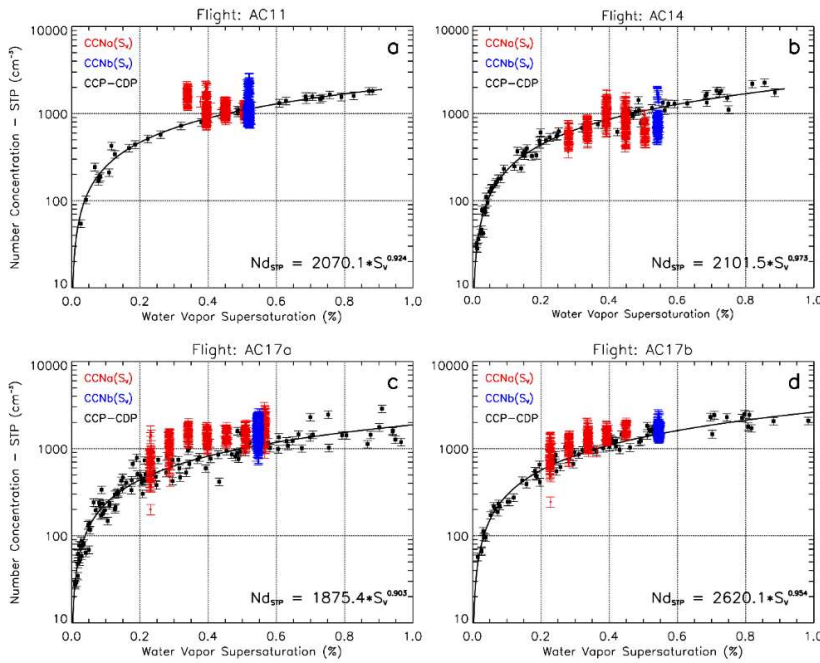


Figure 6. (a)  $S_v$  vs.  $N_d$  measured at cloud bases (black dots), and  $S_v$  vs. CCN concentrations measured below cloud bases (CCNa( $S_v$ ) in red and CCNb( $S_v$ ) in blue) during Flight AC11.  $N_d$  and CCN concentrations are calculated at standard

temperature (0°C) and pressure (1013.25 hPa) (STP). Solid curves correspond to power-law fits of the form  $N_d = C \cdot S_v^k$ . (b), (c), and (d), similar data from flight legs AC14, AC17a, and AC17b, respectively. Error bars indicate the estimated uncertainties of  $N_d$  and CCN concentrations (10%). Uncertainties of  $S_v$  from CCN counters (14%) and theoretically derived (~12.6%) are not shown for clarity.

Figure 7 shows the  $N_d(S_v)$  spectra and the  $N_{CCN}(S_v)$  measurements for time intervals during which both CCNa and CCNb were operating and the sampling duration exceeded 20 s (~1 km horizontal distance). The  $N_{CCN}(S_v)$  measurements are displayed using the same color for each fixed- $S_v$  cycle of the CCNa measurements. The measurements during Flight AC11 exhibit a clear influence of pollution plumes, with CCN concentrations reaching up to ~2000 cm<sup>-3</sup> in both counters measuring in different  $S_v$ . Large concentration peaks are frequently observed in flight segment AC17a for a wide range of  $S_v$  measurements. Overall, most  $N_d(S_v)$  and  $N_{CCN}(S_v)$  values remain within the combined uncertainty bounds, whereas the largest deviations are associated with variability in polluted air masses and with derived  $N_d(S_v)$  values from cloud passes more strongly affected by the entrainment and mixing of dry air. The spatial and temporal heterogeneity of the sampled air masses during AC11, AC14, and AC17a also contributes to deviations in the fitted relationships over specific supersaturation ranges (e.g., near  $S_v \approx 0.55\%$  during AC14). Additional discrepancies between  $N_d(S_v)$  and  $N_{CCN}(S_v)$  concentrations may arise from differences in the particle diameter ( $d$ ) detection ranges of the CCP-CDP probe (approximately 3-50 μm) and the CCN counters (activated droplets with  $d \gtrsim 1$  μm), since the CCN counters may detect activated particles that have not yet grown to the minimum detectable size of the CCP-CDP probe at cloud base.

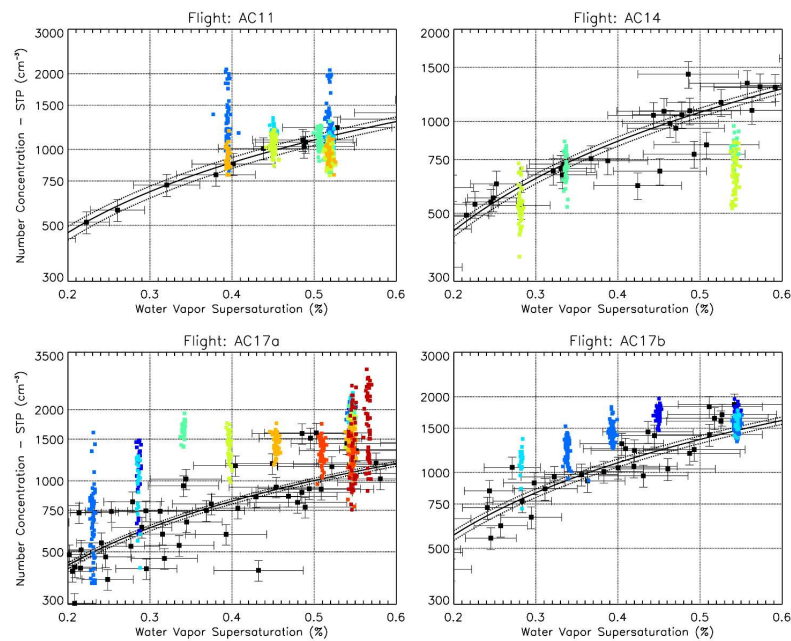


**Figure 7. Relationship between cloud-base  $N_d(S_v)$  spectra and sub-cloud  $N_{ccn}(S_v)$  measurements for flight segments AC11, AC14, AC17a, and AC17b over Central Amazon. Black symbols show the  $N_d(S_v)$  observations at cloud base with the corresponding power-law fits, while colored symbols represent  $N_{ccn}(S_v)$  measurements from CCNa and CCNb. The colored measurements are grouped according to individual CCNa supersaturation cycles with fixed  $S_v$ . Only periods with simultaneous operation of both CCN counters and sampling durations longer than 20 s ( $\sim 1$  km horizontal distance) are included. Error bars indicate the estimated uncertainties of  $N_d$  (10%) and  $S_v$  ( $\sim 12.6\%$ ). Uncertainties of  $S_v$  from CCN counters (14%) and in CCN concentrations (10%) are not shown for clarity.**

The figure shows that the  $N_d(S_v)$  spectra generally agree within the uncertainty range with the CCN( $S_v$ ) activation spectra for all flights. During flight AC11, a relatively higher concentration of particles was measured at  $S_v \sim 0.35\%$  by the CCN chamber, while for  $S_v > 0.35\%$  CCN( $S_v$ ) measurements from both chambers were within the uncertainty range of the  $N_d(S_v)$  spectra ( $\sim 10\%$ ). Discrepancies between  $N_d$  and CCN concentrations at each  $S_v$  primarily reflect differences between the aerosol population sampled several hundred meters below cloud base (about 1400 m) and the fraction of particles subsequently activated at cloud base. Furthermore, CCN counters measure particles that grow to droplets larger than  $1 \mu\text{m}$  in

diameter ( $d$ ), while  $N_d$  concentrations are measured for  $d > 1.5 \mu\text{m}$  with CCP-CDP (below this size, the probe has negligible accuracy). Additional deviations may arise from spatial and temporal variations in CCN hygroscopicity between sub-cloud and near-cloud airmasses, which modulate the effective critical  $S_v$  measured by CCN counters. In situ temperature measurements during cloud penetrations are also subject to turbulent fluctuations, leading to higher uncertainties in the  $S_v$  inferred from cloud measurements.

An improved agreement between  $\text{CCN}(S_v)$  and  $N_d(S_v)$  spectra is shown during the flight legs AC14, AC17a, and AC17b. During these flights, sub-cloud measurements were performed closer to the cloud base ( $\sim 700$  m vertical distance below cloud base), which enhances the probability that the measured population of CCN particles was representative of those activated to cloud droplets at cloud bases. During flight AC14, the  $\text{CCN}(S_v)$  measurements show higher variability, probably affected by the aerosol perturbation from the Manaus urban plume (Campos Braga et al., 2017). The  $\text{CCN}(S_v)$  spectra from the two flight legs during flight AC17 show the expected trend where the CCN concentrations increase with  $S_v$ . In these cases, the overestimation of CCN concentrations appears reliable in comparison to  $N_d$  for the same  $S_v$ , which seems caused mainly due to differences in the droplet size ranges measured by the CCN counter and cloud probe. Furthermore, values outside the uncertainty range of  $N_d(S_v)$  spectra might be influenced by pollution plumes.

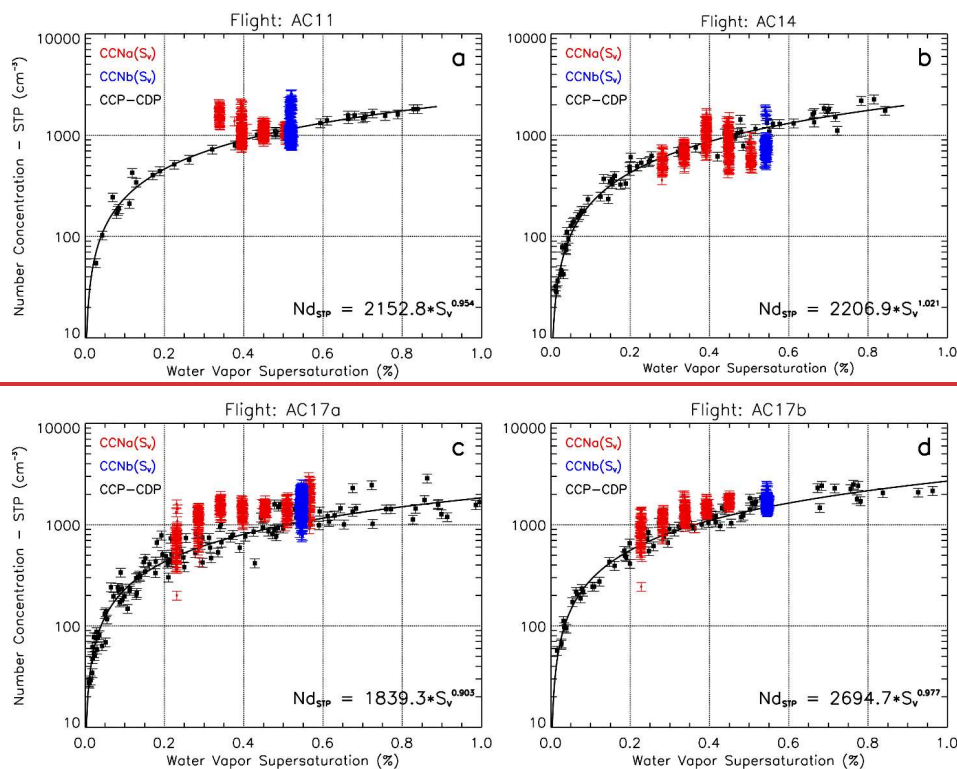


**Figure 5.** (a)  $S_v$  vs.  $N_d$  measured at cloud bases (black dots); and  $S_v$  vs. CCN concentrations measured below cloud bases (CCNa( $S_v$ ) in red and CCNb( $S_v$ ) in blue) during Flight AC11.  $N_d$  and CCN concentrations are calculated at standard temperature and pressure (STP). Solid curves correspond to power-law fits of the form  $N_d = C \cdot S_v^k$ . (b), (c), and (d), similar for data from flight legs AC14, AC17a, and AC17b, respectively. Error bars indicate the estimated uncertainties of  $N_d$  and CCN( $S_v$ ) concentrations (10%).

#### 4 Conclusions

The thermodynamic energy budget analysis introduced in this study shows that water vapor supersaturation ( $S_v$ ) at the bases of warm cumulus clouds can reliably be quantified diagnostically estimated by treating the ascent of a saturated parcel as a cloud-adiabatic process with conserved isobaric enthalpy. Airborne observations over the Central Amazon reveal

that  $N_d(S_v)$  spectra at cloud base agree within the uncertainty range of  $N_{CCN}(S_v)$  spectra measured below cloud base, indicating that the water vapor pressure derived from the thermodynamic equations is physically consistent with that generated in CCN counters. In both cases, the water vapor ~~density-pressure~~ results from a thermal gradient under saturated conditions. In CCN counters,  $S_v$  is produced within a continuous-flow chamber by imposing controlled temperature gradients (warmer downstream) along wet walls. These gradients promote differential diffusion of water vapor and heat, leading to an enhanced water vapor pressure along the flow axis that exceeds saturation at the local air temperature. In the proposed diagnostic framework, the  $S_v$  calculated-inferred from cloud base measurements represents the vapor-phase contribution to cloud supersaturation resulting from adiabatic cooling and is associated with the fraction of the latent energy partitioned into the adiabatic cooling energy assigned to water-vapor expansion work is the fraction of the adiabatic cooling energy during the buoyant ascent of the saturated parcel associated with the expansion work of the water vapor in the air parcel ( $W_s$ ) during the condensational growth.

The calculated  $N_d(S_v)$  spectra at cloud bases in different thermodynamic and aerosol conditions over the Amazon Basin and Atlantic Ocean have shown a typical variability expected ~~by at ground-based  $N_{CCN}(S_v)$  spectra measured in clean and polluted conditions (Khain and Pinsky, 2018; Pöhlker et al., 2016).~~ However, the methodology relies on several idealized assumptions - thermodynamic reversibility, negligible entrainment (adiabaticity), and accurate in situ microphysical and thermodynamic measurements - that may not fully capture the complexity of heterogeneous and highly turbulent cloud bases. Despite these ~~limitationsassumptions~~, the suggested methodology adds new insights for the modelling of cloud base supersaturation and energetics, offering a physically consistent constraint on droplet activation and condensational growth. (Khain et al., 2015; Khain and Pinsky, 2018; Korolev and Mazin, 2003; Pinsky et al., 2012; Prabhakaran et al., 2020). It allows estimating  $N_d$  as a function of cloud supersaturation ( $S_c$ ,  $S_l$ , and  $S_v$ ) using in situ measurements of cloud microphysical properties. Under the assumption of conserved isobaric enthalpy at cloud base, the energy budget and cloud supersaturation components ( $S_c$ ,  $S_l$ , and  $S_v$ ) of the saturated parcel production of supersaturation and the resulting microphysical properties can be inferred-estimated from the temperature change during adiabatic cooling or, equivalently, from in situ measurements of liquid water content, which constrain the enthalpy change associated with the conversion of water vapor into liquid water, from the vertical evolution of a saturated parcel following the cloud-adiabatic lapse rate ( $\sim 3-8 \text{ K km}^{-1}$ ) relative to the dry adiabatic ascent ( $\sim 9.8 \text{ K km}^{-1}$ ). Our results suggest that the adiabatic LWC calculated by parcel models overestimates the amount of water vapor that can condense into liquid water since they Within the proposed framework, neglecting the energetic cost of water vapor expansion ( $W_s$ ) assigns a larger fraction of the available energy to vapor-to-liquid conversion, during the ascent of the saturated parcel. The practical consequence for the energy budget is an This suggests a possible tendency to overestimation-overestimate of the condensate production, latent heating, +released during condensational growth of CCN and cloud droplets, which in turn leads to an overestimation of the cloud parcel-buoyancy and associated updraft speeds-velocities in simplified parcel calculations that do not explicitly account for this energetic partition.

Future studies applying energetic budget analyses to in situ measurements ~~can be extended~~ may extend this framework to calculate ~~estimate~~ cloud supersaturation  $S_v$  at cloud bases in other regions of the globe with ~~characterized by~~ different aerosol and thermodynamic conditions. The method described in this manuscript is especially relevant when  $N_{CCN}(S_v)$  measurements are unavailable. ~~The method described in this manuscript is especially relevant when  $N_{CCN}(S_v)$  measurements are unavailable.~~ Furthermore, the thermodynamic evolution of cloudy parcels can be investigated within the context of the energetic budget to infer  $S_v$  from the vertical profiles of air temperature and dew-point temperature, with the parcel evolution physically interpreted in terms of dry- and cloud-adiabatic cooling. ~~Furthermore, the vertical profiles of microphysical properties within adiabatic cloud parcels should be examined in the context of the energetic budget to infer supersaturation at cloud bases and above, including the ice and mixed-phase regimes.~~ Such extensions would enable a more comprehensive quantification of the coupled microphysical ~~and~~ energetic responses of clouds under diverse atmospheric conditions, ~~encompassing including~~ aerosol-cloud interactions, droplet-condensational droplet growth and evaporation, ~~and ice-phase processes.~~

#### Appendix A

The derivation of Eq. (1) can be found in cloud physics textbooks such as Rogers and Yau (1989) and Pinsky and Khain (2018), which describe the supersaturation tendency equation over water for an adiabatically ascending air parcel under the assumption of small supersaturation ( $|S_v| \ll 1$ ):

$$\frac{dS_v}{dt} = A_1 \cdot w + A_2 \frac{dLWC}{dt} \quad [s^{-1}] \quad (A.1)$$

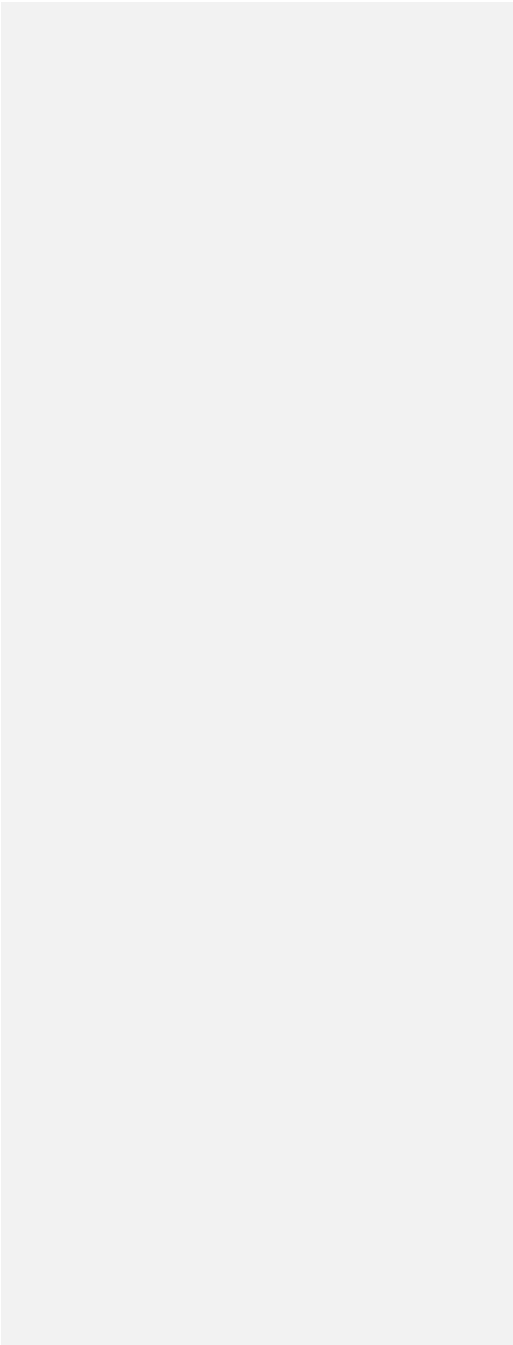
Where,  $A_1$  and  $A_2$  are given by:

$$A_1 = \frac{g}{T} \left( \frac{L_v}{c_{pd} R_v T} - \frac{1}{R_d} \right) \quad (A.2)$$

$$A_2 = \frac{1}{\rho_v} + \frac{L_v^2}{c_{pd} R_v T^2 \rho_{air}} \quad (A.3)$$

The equations are derived from the thermodynamic equations governing temperature, water vapor mixing ratio, and the Clausius–Clapeyron relation. The coefficient  $A_1$  represents the production of supersaturation by adiabatic cooling during parcel ascent, whereas  $A_2$  represents the depletion of supersaturation associated with condensational growth, vapor depletion, and latent heat release.

|



035 **Table A1. List of symbols, variables, and physical constants used in this study. Thermodynamic variables are expressed as specific quantities per unit mass of dry air. Uppercase notation is retained for consistency with the energetic framework. The corresponding extensive quantities are obtained by multiplying by the mass of dry air.**

| Symbol       | Description                                           | Units                              |
|--------------|-------------------------------------------------------|------------------------------------|
| $RH$         | Relative Humidity                                     | - or %                             |
| $RH_c$       | Reference-state saturation ratio                      | - or %                             |
| $RH_s$       | Saturation ratio at the reference state $T_0$         | - or %                             |
| $S$          | Supersaturation (general)                             | - or %                             |
| $S_c$        | Cloud Supersaturation                                 | %                                  |
| $S_l$        | Liquid-phase Supersaturation                          | %                                  |
| $S_v$        | Vapor-phase Supersaturation                           | %                                  |
| $e$          | Water vapor pressure                                  | Pa                                 |
| $e_s$        | Saturation water vapor pressure                       | Pa                                 |
| $T$          | Temperature of the saturated parcel                   | K                                  |
| $T_c$        | Air Temperature in Celsius                            | °C                                 |
| $T_{ws}$     | Temperature of the saturated parcel considering $W_s$ | K                                  |
| $T_0$        | Initial saturated temperature at cloud base           | K                                  |
| $T_{air}$    | Air temperature after energetic partition             | K                                  |
| $T_Q$        | Latent-heat-equivalent temperature                    | K                                  |
| $\Delta T$   | Adiabatic cooling magnitude                           | K or °C                            |
| $\Delta T_c$ | Adiabatic cooling magnitude from closure analysis     | K or °C                            |
| $\Delta T_Q$ | Temperature change associated with latent heating     | K                                  |
| $L_v$        | Latent heat of vaporization                           | J kg <sup>-1</sup>                 |
| $Q$          | Latent heat released by condensation                  | J kg <sup>-1</sup>                 |
| $\delta Q$   | Differential latent heat release                      | J kg <sup>-1</sup>                 |
| $dH$         | Enthalpy change                                       | J kg <sup>-1</sup>                 |
| $\Delta U$   | Change in internal energy                             | J kg <sup>-1</sup>                 |
| $W_s$        | Saturation work                                       | J kg <sup>-1</sup>                 |
| $p$          | Pressure of the cloudy parcel                         | Pa                                 |
| $p_0$        | Reference pressure of the cloudy parcel               | Pa                                 |
| $q_l$        | Liquid water mixing ratio                             | kg kg <sup>-1</sup>                |
| $r_s$        | Saturation mixing ratio                               | kg kg <sup>-1</sup>                |
| $\rho_{air}$ | Dry air density                                       | kg m <sup>-3</sup>                 |
| $\alpha_v$   | Specific volume of water vapor                        | m <sup>3</sup> kg <sup>-1</sup>    |
| $c_{pd}$     | Specific heat of dry air at constant pressure         | J kg <sup>-1</sup> K <sup>-1</sup> |

|               |                                                                 |                                |
|---------------|-----------------------------------------------------------------|--------------------------------|
| $C_{pv}$      | <u>Specific heat of water vapor at constant pressure</u>        | $J\ kg^{-1}\ K^{-1}$           |
| $C_{pl}$      | <u>Specific heat of liquid water at constant pressure</u>       | $J\ kg^{-1}\ K^{-1}$           |
| $C_{p,cloud}$ | <u>Specific heat capacity of cloud air at constant pressure</u> | $J\ kg^{-1}\ K^{-1}$           |
| $R_d$         | <u>Gas constant for dry air</u>                                 | $J\ kg^{-1}\ K^{-1}$           |
| $R_v$         | <u>Gas constant for water vapor</u>                             | $J\ kg^{-1}\ K^{-1}$           |
| $A_1$         | <u>Thermodynamic coefficient for supersaturation production</u> | $m^{-1}$                       |
| $A_2$         | <u>Thermodynamic coefficient for condensational depletion</u>   | $m^3\ kg^{-1}$                 |
| $P$           | <u>Supersaturation production term</u>                          | $s^{-1}$                       |
| $C_d$         | <u>Condensation depletion term</u>                              | $s^{-1}$                       |
| $N_d$         | <u>Cloud droplet number concentration</u>                       | $cm^{-3}$                      |
| $LWC$         | <u>Liquid Water Content</u>                                     | $kg\ m^{-3}$ (or $g\ m^{-3}$ ) |
| $RWC$         | <u>Rainwater Content</u>                                        | $g\ m^{-3}$                    |
| $w$           | <u>Vertical velocity / updraft velocity</u>                     | $m\ s^{-1}$                    |
| $CCN$         | <u>Cloud Condensation Nuclei</u>                                | $z$                            |
| $N_{CCN}$     | <u>Number concentration of CCN</u>                              | $cm^{-3}$                      |
| $CCNa$        | <u>CCN counter column A</u>                                     | $z$                            |
| $CCNb$        | <u>CCN counter column B</u>                                     | $z$                            |
| $C$           | <u>Scaling coefficient of power-law fit</u>                     | $cm^{-3}$                      |
| $k$           | <u>Exponent of power-law fit</u>                                | $z$                            |
| $\kappa$      | <u>Particle hygroscopicity</u>                                  | $z$                            |
| $RMSE$        | <u>Root mean square error</u>                                   | $z$                            |
| $\sigma_C$    | <u>Uncertainty of coefficient <math>C</math></u>                | $z$                            |
| $\sigma_k$    | <u>Uncertainty of exponent <math>k</math></u>                   | $z$                            |
| $N_r$         | <u>Number of Monte Carlo realizations</u>                       | $z$                            |
| $N$           | <u>Sample size</u>                                              | $z$                            |
| $R^2$         | <u>Coefficient of determination</u>                             | $z$                            |
| $CCP$         | <u>Cloud Combination Probe</u>                                  | $z$                            |
| $CDP$         | <u>Cloud Droplet Probe</u>                                      | $z$                            |
| $CIP_{gs}$    | <u>Cloud Imaging Probe grayscale</u>                            | $z$                            |
| $CAS-DPOL$    | <u>Cloud and Aerosol Spectrometer with depolarization</u>       | $z$                            |
| $SHARC$       | <u>Sophisticated Hygrometer for Atmospheric Research</u>        | $z$                            |
| $HASI$        | <u>HALO aerosol submicron inlet</u>                             | $z$                            |
| $HALO-CVI$    | <u>HALO counterflow virtual impactor</u>                        | $z$                            |
| $STP$         | <u>Standard temperature and pressure</u>                        | $z$                            |

**Data availability**

The ACRIDICON-CHUVA HALO aircraft data are available from the HALO database: [The data used in this study can be found at https://halo-db.pa.op.dlr.de/mission/5](https://halo-db.pa.op.dlr.de/mission/5). [Derived quantities used in this analysis are available from the corresponding author upon reasonable request.](#)

**Author contributions**

Conceptualization: RCB.  
Methodology: RCB.  
Investigation: RCB.  
Visualization: RCB.  
Supervision: DH.  
Writing—original draft: RCB, DH.  
Writing—review & editing: RCB, DH, MW and RA.

**Competing interests**

The authors declare they have no competing interests.

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