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Cloud condensation nuclei in the Amazon Basin: "Marine" conditions over a continent?

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Abstract. Cloud condensation nuclei (CCN) are linked to radiative forcing, precipitation, and cloud structure; yet, their role in tropical climates remains largely unknown. CCN concentrations (N_{CCN}) measured during the wet season in the Amazon Basin were surprisingly low (mean N_{CCN} at 1% supersaturation: 267 ± 132 cm^{-3}) and resembled concentrations more typical of marine locations than most continental sites. At low background CCN concentrations, cloud properties are more sensitive to an increase in N_{CCN}. Therefore, enhanced aerosol emissions due to human activity in the Amazon Basin may have a stronger impact on climate than emissions in other continental regions. In spite of the large organic fraction in the Amazonian aerosol, a detailed analysis of number distributions and size-dependent chemical composition indicates that sulfate plays an important role in CCN activity.

Introduction

Cloud condensation nuclei (CCN) are a subset of the atmospheric aerosol population, which undergo rapid growth into cloud droplets at a specified supersaturation. Although the importance of CCN for cloud properties and the subsequent effects on hydrology and climate has long been recognized, measurements of CCN in the tropics, where this vital subset of aerosol may exert its greatest impact, have largely been neglected. Aerosol/CCN/cloud interactions are understudied in the tropics relative to mid-latitudes, especially considering the importance of the tropics to global climate. Anthropogenically-induced changes in tropical regions could potentially lead to a number of climatically important processes in ways that are different from other regions [*Gedney and Valdes,* 2000]. Recent modeling studies suggest that increased CCN concentrations in the tropics change the altitude and mechanism of rain production [*Graf et al.,* 2000]. Because of large-scale atmospheric circulation in the tropics (i.e., International Tropical Convergence Zone and Hadley Circulation), the resulting dynamic effects propagate worldwide, including to higher latitudes, and have a much greater impact on global climate than previously thought [*Oort and Yienger,* 1996; *Graf et al.,* 2000].

Conventionally, a distinction has been made in CCN studies between "marine" and "continental" environments, which are characterized by low and high CCN concentrations (N_{CCN}), respectively [*Squires,* 1956]. Most "continental" measurements have been made in extratropical and usually moderately to heavily polluted regions [*Pruppacher and Klett,* 1997; Tables 9.1-9.4]. In spite of their vast extent, and their key role in climate dynamics, no measurements are available from other humid tropical regions. Because of the large emissions of biogenic hydrocarbons and the intense photochemical activity in the tropics, some authors had predicted a high rate of organic aerosol formation in this region [*Andreae and Crutzen,* 1997]. A strong aerosol source could result in fairly high CCN concentrations in the remote wet tropics, even during the wet season, when frequent rain events provide a strong sink for CCN.

Here, we will discuss results of the first measurements of CCN in the Amazon Basin, and provide insight to their fundamental role in the tropical continental climate, as well as the chemical and physical properties that enable activation and subsequent growth into cloud droplets. We will use these results to examine the validity of the distinction between "marine" and "continental" CCN population types.

The LBA-CLAIRE observations

The measurements were performed during the Cooperative LBA Airborne Regional Experiment (CLAIRE), a part of the Large Scale Biosphere-Atmosphere Experiment in Amazonia (LBA). Sampling occurred from March 28 to April 15, 1998, at a ground site (1°55.5' S, 59°24.8' W; 160 m above sea level) located 125 km northeast of Manaus, in the state of Amazonas, Brazil. Backward airmass trajectories indicate that our site was not adversely affected by anthropogenic sources, as surface air masses originated from the northeast to east; hence had traveled a thousand kilometers over the most remote regions of the Amazon rain forest for almost a week before being sampled.

CCN measurements between 0.15% and 1.5% supersaturation (S) were performed using a static thermal-gradient

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CCN chamber similar to the system described by *Lala and Juisto* [1977]. Instead of the original light-scattering design, the CCN instrument was equipped with a photodiode laser and digital camera to directly determine the CCN concentration from image processing and the calibrated, illuminated volume. An error analysis indicates that for typical aerosol spectra, the overall measurement error is approximately ±10% at 1.5% S and ±30% at 0.15% S. Temperature fluctuations during measurements are usually within 0.1 °C, so the supersaturation is constant within ±0.05% S. Total aerosol concentrations (N_{CN}) were measured using a TSI 3010 Condensation Particle Counter.

Number concentrations of CCN and CN from the LBA-CLAIRE field experiment were low (mean N_{CCN} at 1% S: 267 ± 132 cm^{-3}; mean N_{CN}: 390 ± 250 cm^{-3}; Table 1). The observed variations of N_{CCN} and N_{CN} were primarily related to rainfall and temperature fluctuations (Plate 1). The values of N_{CCN} and N_{CN} are in the range typically considered as "marine". Measurements in North America have also shown instances of low CCN concentrations in the absence of strong anthropogenic sources [*Hobbs et al.,* 1985; *Hudson and Frisbie,* 1991]. Since the transition from "marine" to "continental" is rapid [*Hudson,* 1991], local anthropogenic sources could restore "continental" CCN concentrations soon after precipitation/scavenging events. Such a "restoration" of "continental" CCN, however, is not observed at our site.

Furthermore, we find that the average CCN/CN ratio ($f_{CCN/CN}$) is strikingly high compared to most other "continental" measurements, and resembles much more what is conventionally regarded as "marine" values [*Pruppacher and Klett,* 1997; Tables 9.3-9.4]. The high $f_{CCN/CN}$ ratio observed in Amazonia also implies that there are few particles present in the size range smaller than $CCN_{1.5}$ (at 1.5% S; i.e., diameter < 0.04 μm for Amazonian aerosols of mixed composition). Since these smaller particles are indicative of recent particle formation, our data also suggest a low rate of new particle formation, in contrast to what had been suggested by *Andreae and Crutzen* [1997]. Our measurements of low N_{CCN} are consistent with observations of warm-precipitating clouds in the Amazon Basin [*Mohr et al.,* 1999]. Observations in the field suggest that these cloud systems exhibit the less-developed convective structure that is normally associated with oceanic CCN distributions.

Table 1. Average Measured CCN Spectrum During LBA-CLAIRE.

S [a], %	$N_{CCN\ or\ CN}$, cm^{-3}
0.15	33 ± 24
0.30	101 ± 60
0.60	182 ± 92
1.00	267 ± 132
1.50	320 ± 164
CN[b]	390 ± 250

[a] S is the supersaturation of the CCN measurements.

[b] The average N_{CN} shown in the table is for corresponding CCN measurements. The average N_{CN} from Plate 1 (over the CLAIRE experiment) is 460 ± 320 cm^{-3}.

In spite of the "marine" character of our CCN spectra, the long distance of our site from the ocean (5-7 days of airmass travel) and the high frequency of rainfall under wet season conditions makes it unlikely that marine aerosol made a major contribution to the CCN population at our site. This is supported by our chemical measurements during CLAIRE, which show an average aerosol mass composition for the fine fraction (diameter < 1 μm) of approximately 15% sulfate, 5% other inorganic and 80% organic material. The fine-mode organic material probably originates from a combination of primary biogenic aerosol and the condensation of low and semi-volatile oxidation products of volatile organic carbon species (VOCs; i.e., terpenes) emitted from forest vegetation. Biogenic emissions from the forest vegetation also include a significant sulfur component [*Andreae et al.,* 1990], which could provide a source for the fine-mode sulfate.

A particle's critical supersaturation (S_c) implicitly contains all chemical and dry particle size information pertinent to cloud formation and can be calculated for a multicomponent aerosol by separating the mass distribution into soluble and insoluble components. The critical supersaturation is described by Köhler theory [*Köhler,* 1936; *Pruppacher and Klett,* 1997] and depends primarily on the dissolved solute mass and surface tension. The physical and chemical characteristics of the fine-mode aerosol determine N_{CCN} and the properties responsible for CCN activation. Number and mass distributions were measured using a Differential Mobility Particle Sizer (DMPS) (*J. Zhou et al.*, Sub-micrometer aerosol particle size distribution and hygroscopic growth measurements in the Amazonian rain forest during the wet season, submitted to *J. Geophys. Res.*, 2001) and a multiple-stage cascade impactor (MOUDI, MSP Corp.), respectively. The composition and mass data from the MOUDI impactor samples (e.g., particle-induced X-ray emission and gravimetric analysis) were transformed into a continuous distribution of composition versus size. These measurements allow an independent prediction of CCN activity by using Köhler theory to derive a distribution of S_c versus size. Although no direct measurements of sulfur speciation have been performed on our samples, a stoichiometric balance of anions and cations [*Gerab et al.,* 1998] indicates that fine-particulate sulfate has been partially neutralized by ammonium in nearly a 1:1 molar ratio. Therefore, the model divides the aerosol mass into soluble inorganic (NH_4HSO_4), and insoluble (inorganic and organic) components. The resulting relationship between S_c and particle size is combined with the number distribution to yield an independent prediction of N_{CCN}. Furthermore, $f_{CCN/CN}$ can be determined by the ratio of the calculated N_{CCN} to N_{CN} and compared to measured values. *Novakov and Penner* [1993] performed a similar calculation of CCN activity that was based on an externally mixed aerosol; yet, they also noted that internally mixed estimations of CCN concentrations, as we have done here, were within 10%.

The resulting modeled CCN spectra, from the number and mass distribution closure, are shown in Figure 1. The CCN spectrum based upon a simple model of sulfate and insoluble constituents agrees well with the measured CCN spectrum (Table 1; solid circles in Figure 1). It must be noted, however, that this model does not represent a unique

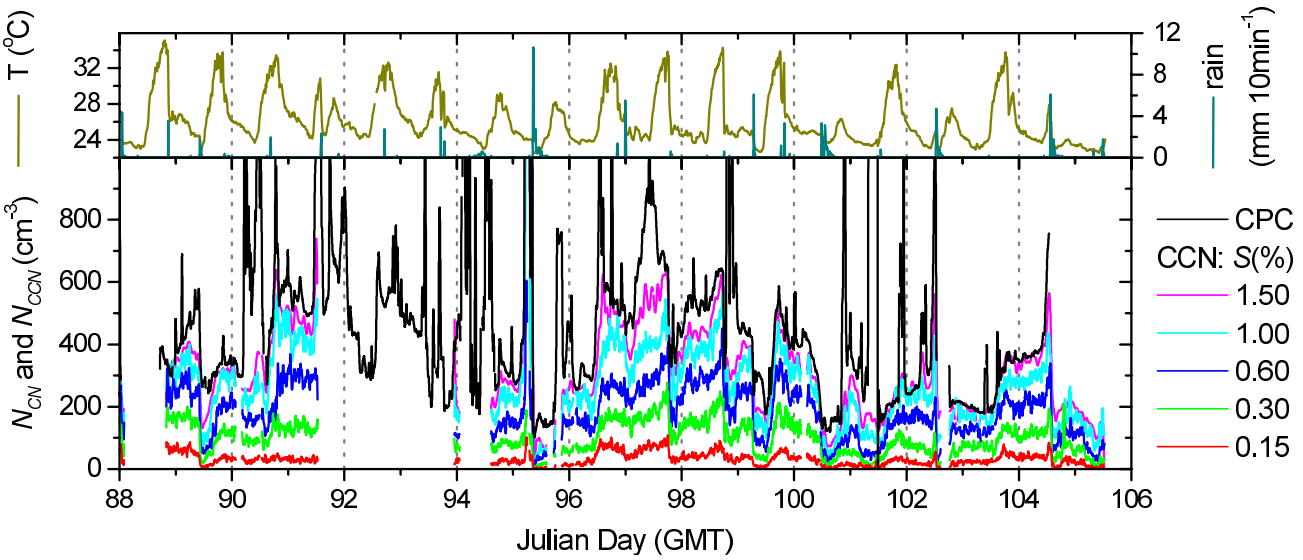

Plate 1. Time series of N_{CCN} and N_{CN}. Ambient temperature and rainfall are shown in the upper graph.

solution; this issue will be explored in detail in a future paper (*G. Roberts et al.*, Sensitivity of CCN spectra on chemical and physical properties of aerosol, submitted to *J. Geophys. Res.*, 2001).

Organic aerosol components affect CCN activity both by providing soluble material and by changing the surface tension of the droplet solution [*Facchini et al.,* 1999]. We applied the relationship between organic carbon concentration and surface tension, used by *Facchini et al.* [1999], to estimate potential influences of surfactants on the CCN spectra in the Amazon Basin. Comparison of our model calculation with the measurements (Figure 1) suggests that a 15% decrease in surface tension at 10^{-2} molarity of dissolved organic carbon is probably the upper limit of the surface tension effects consistent with our results from the Amazon Basin.

Significance of the results

Our results show that low CCN concentrations and high CCN/CN ratios over the unpolluted Amazon Basin resemble conditions previously reported from marine environments, and that they are different from what has been previously thought of as "continental" conditions. This calls into question the conventional distinction between these regimes, and suggests that a more relevant distinction would be between pristine and polluted conditions. Furthermore, it may be necessary to introduce subcategories, such as tropical, temperate, arctic, etc., as climatic conditions and natural aerosol sources of the Amazon Basin do not apply to other regions. It is remarkable that similar CCN and CN concentrations prevail in marine and continental regions, in spite of the different aerosol production mechanisms and particle compositions. A positive feedback cycle has been proposed for the marine atmosphere where drizzle removes CCN from the boundary layer and maintains the low CCN concentrations favorable for precipitation [*Albrecht,* 1989]; a similar feedback cycle may also apply to the rain forest environment. While drizzle removes CCN without significantly effecting smaller particles, atmospheric lifetimes of small particles (i.e., diameter < 0.06 μm) range from hours to a couple of days due to coagulation, scavenging of interstitial aerosol and growth by condensation [*Hoppel et al.,* 1990]. Hence interstitial aerosol grow to become CCN, and cloud processing/scavenging provide a sink to maintain a quasi-steady state number distribution [*Kaufman and Tanré,* 1994].

Studies have shown that modification of cloud properties, such as cloud thickness [*Pincus and Baker,* 1994], albedo,

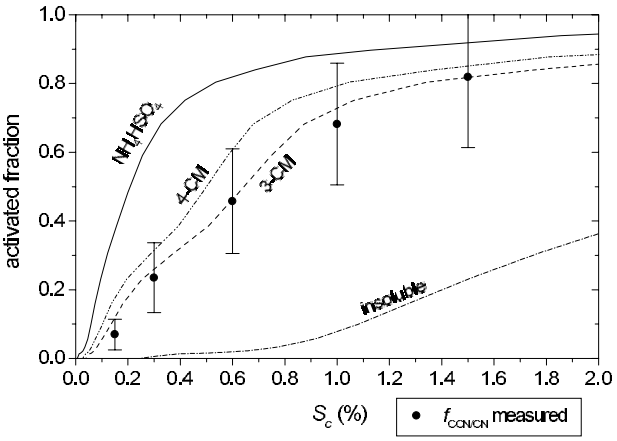

Figure 1. Fraction of aerosol expected to activate as CCN. The three-component (3-CM) example divides the aerosol mass into soluble inorganic (NH_4HSO_4) and insoluble (inorganic and organic) components. The four-component model (4-CM) introduces the effect of 0.01 M dissolved organic carbon and the reduction of surface tension by 15%. Examples of NH_4HSO_4 and insoluble aerosol illustrate the limits of CCN activity based on measured number distributions.

cloud fraction and lifetime [*Albrecht,* 1989], is most sensitive at low initial N_{CCN}. Because of the large thickness typical of convective clouds over the humid tropics, substantial modification of cloud albedo due to increased CCN is not expected. However, because of the low natural CCN abundance in Amazonia, climatic effects related to the impact of CCN on rainfall production could have a greater impact here than in other continental regimes [*Twomey,* 1991; *Graf et al.,* 2000]. CCN measurements have shown that biomass burning smoke aerosol dramatically increases CCN concentrations [*Novakov and Corrigan,* 1996]. This should increase colloidal stability and cloud lifetime, resulting in the well-developed, non-precipitating clouds observed during the burning season, with droplet radii below the threshold required for warm precipitation [*Kaufman and Fraser,* 1997; *Reid et al.,* 1999]. The influence of smoke on rain formation was shown more directly by the analysis of data from the Tropical Rainfall Measuring Mission (TRMM) taken near Kalimantan, where a distinct difference in cloud structure and radar reflectance was seen between clouds influenced by biomass burning and those in cleaner areas. Although Rosenfeld did not perform CCN measurements, it can be inferred from the known CCN-activity of biomass smoke that the smoke-laden air also contained higher CCN concentrations. *Rosenfeld* [1999] showed that the clouds affected by smoke had significantly smaller droplet size and were less likely to precipitate than clouds in adjacent unpolluted areas.

The response of cloud droplet concentration and radius to changes in N_{CCN} is the basis for the modification of precipitation, cloud fraction and indirect forcing. The interaction of these factors controls the heat flux into the rain forest, which is, in return, the primary driver of convective cloud formation. Human activity, such as fossil fuel and biomass burning, modifies physical and chemical properties of the aerosol population - components that dictate CCN activity - and could lead to imbalances in the meteorological cycle within the Amazon Basin and translate to changes in global climate as well.

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