LETTERS
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Relative roles of biogenic emissions and Saharan dust as ice nuclei in the Amazon basin

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Some aerosol particles, known as ice nuclei, can initiate ice formation in clouds, thereby influencing precipitation, cloud dynamics and the amount of incoming and outgoing solar radiation. In the absence of biomass burning, aerosol mass concentrations in the Amazon basin are low[1]. Tropical forests emit primary biological particles directly into the atmosphere; secondary organic aerosols form from the emission and oxidation of biogenic gases[2]. In addition, particles derived from biomass burning in central Africa, marine aerosols, and wind-blown dust from North Africa[3–5] often reach the central part of the Amazon basin during the wet season. The contribution of these aerosol sources to ice nucleation in the region is uncertain. Here we present observations of the concentration and elemental composition of ice nuclei in the Amazon basin during the wet season. Using transmission electron microscopy combined with energy-dispersive X-ray spectroscopy, we show that ice nuclei are primarily composed of carbonaceous material and dust. We show that biological particles dominate the carbonaceous fraction, whereas import of Saharan dust explains the intermittent appearance of dust-containing nuclei. We conclude that ice-nucleus concentration and abundance can be explained almost entirely by local emissions of biological particles supplemented by import of Saharan dust. Using a simple model, we tentatively suggest that the contribution of local biological particles to ice nucleation is increased at higher atmospheric temperatures, whereas the contribution of dust particles is increased at lower temperatures.

Approximately two-thirds of global precipitation occurs between latitudes 30° S and 30° N (ref. 6), with an average annual precipitation of ~2.6 m in the Amazon basin[7]. Vigorous convective cells form during easterly flow, with a mixed-phase (liquid and ice) cloud layer and frequent lightning[8]. These systems can be local in origin or can be synoptic scale systems that form along the northeastern coast of Brazil and move southwest to the vicinity of central Amazonia[9].

Although some studies have investigated cloud-condensation nuclei in this region[10,11], including their role in cold-cloud processes[12,13], until now no studies have directly sampled ice nuclei. At temperatures warmer than about −36 °C, ice nuclei are those particles responsible for initiating ice nucleation. Ice-phase processes influence precipitation initiation, cloud lifetime, cloud scale dynamics and radiative forcing[14–16], and both lightning frequency and instantaneous rain rate have been shown to be highly correlated with ice water content in this region[14]. This letter presents data on ice-nucleus number concentration and elemental composition in the Amazon basin. Using these data and complementary measurements of aerosol composition, we constrain contributions of biogeochemical sources of ice nuclei to better understand the role of transcontinental transport and local biogenic emissions in influencing ice formation in mixed-phase clouds in this region.

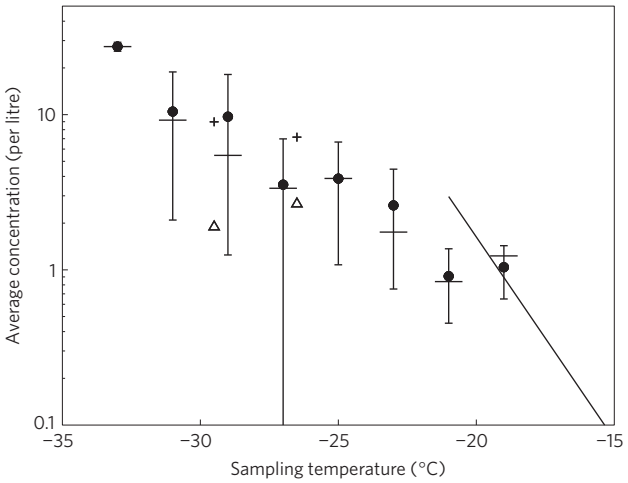

Figure 1 | Ice-nucleus number concentrations. Summary from all measurements collected during AMAZE-08. Data are binned in 2 °C increments and are presented as the mean (filled circle) and median (horizontal lines) ice-nucleus concentration as a function of temperature, corrected to standard temperature and pressure (0 °C and 1 atm). The variability in concentration (one standard deviation) at each temperature is also shown. For comparison, a global composite of ice-nucleus concentrations is shown (Fletcher[19], solid line), as well as data for the mid-latitudes: Richardson *et al.*[20] (triangles) and DeMott *et al.*[18] (plus symbols).

Measurements were conducted as part of the Amazonian Aerosol Characterization Experiment 2008 (AMAZE-08) from 9 February to 9 March 2008 at Tower TT34 (02°35.675′ S, 060°12.557′ W) in the Reserva Biologica do Cuieiras in central Amazonia, Brazil. The site, 60 km north northwest of Manaus, is located within a pristine rainforest. This time period falls near the peak of the wet season, when winds come predominantly from the east northeast across 1,600 km of forest undisturbed by anthropogenic activities. Ice nuclei were measured using a continuous flow diffusion chamber (CFDC). This instrument enables observation of freezing

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Table 1 | Ice-nuclei composition.

Date	Ice nuclei (per litre)	Dust	Carbonaceous	Dust + carbonaceous	Dust + sulphate
26 Feb.	33.7	0.19	0.76	0.03	0.02
28 Feb.	24.2	0.80	0.20	0	0
1 Mar.	12.1	0.84	0.16	0	0
4 Mar. Sample 1	10.5	0.70	0.19	0.04	0.07
4 Mar. Sample 2	13.5	0.19	0.69	0.05	0.07
6 Mar.	4.4	0.15	0.73	0.12	0
7 Mar.	0.9	0.34	0.58	0.03	0.05

Number fraction of analysed ice nuclei that contain metal oxides/dust, carbonaceous material, mixtures of these components, and dust with sulphate. Also shown are ice-nucleus concentrations during the sampling periods.

at controlled temperatures and humidities[17]. An inertial impactor immediately downstream of the CFDC captures the ice nuclei that have activated as ice particles in the chamber on transmission electron microscopy (TEM) grids.

Measured ice-nucleus concentrations were approximately 1–10 per litre over the temperature range −20 to −30 °C and show an order of magnitude increase over ∼10 °C (Fig. 1). For comparison, particle number concentrations in this region are typically 200–400 cm^{-3} during the wet season, so that ∼1 in 10^5 particles serve as ice nuclei over this temperature range. The variability in concentration (one standard deviation) at each temperature is also shown in Fig. 1, with each temperature representing from 2 to 22 h of data. Data from other locations are also shown in Fig. 1 (refs 18–20), indicating ice-nucleus concentrations comparable to those observed during AMAZE-08.

Elemental compositions of the residual nuclei were characterized using TEM with energy-dispersive X-ray spectroscopy[20] (TEM-EDX). Data were collected during seven sampling periods, with all samples collected at −30 °C. Results are summarized in Table 1. Dust and carbonaceous particles comprise most of the ice nuclei, with contributions varying by date. Intermittent transcontinental transport of Saharan dust during the project (Fig. 2) was predicted by simulations using a global chemical transport model (GEOS-Chem) and was reflected in particle composition measurements from particle-induced X-ray emission (PIXE) analysis. Transport of dust to the Amazon basin is due to the seasonal latitudinal oscillation of the Intertropical Convergence Zone[5]. The fraction of ice nuclei that is dust, determined from TEM analysis of ice-nucleus residuals, is clearly tied to dust mass concentrations from PIXE measurements and GEOS-Chem simulations. Ice-nucleus number concentrations at -30 ± 3 °C also seem associated with PIXE dust mass concentrations, although to a lesser extent. The GEOS-Chem simulations suggest rapid changes in dust concentrations that are not captured by the PIXE data, but which probably influenced the ice-nucleus measurements. Taken together, these data demonstrate an important role for the long-range transport of dust as a source of ice nuclei to the Amazon basin during the wet season.

Ice-nucleus composition measurements also suggest an important role for carbonaceous particles. No soot particles were observed in the TEM images, suggesting that biomass-burning particles are not a likely source of the carbonaceous ice nuclei. The carbonaceous ice nuclei also may be secondary organic aerosol (SOA). However, ice-nucleus concentrations are weakly correlated with organic mass ($R = 0.26$), which is expected to have a strong SOA influence under conditions prevailing in the Amazon basin, and negatively correlated ($R = -0.54$) with organic mass fraction of the ambient aerosol, as determined from the aerosol mass spectrometer (AMS). Data are limited to measurements at -30 ± 3 °C for the correlation to avoid complications stemming from the observed temperature dependence of ice-nucleus concentrations; this temperature range includes approximately half of the ice-nucleus data. The relative scarcity of mixed dust and carbonaceous particles observed as ice nuclei, shown in Table 1, also suggests that dust mixed with carbonaceous material, presumably SOA, does not contribute significantly to the ice-nucleus population. This is generally consistent with the observation that condensation of SOA onto dust degrades the ice nucleation efficiency of dust at cirrus cloud temperatures[21]. Similarly, the near absence of ice nuclei composed of mixed dust and sulphate suggests that such coatings may affect the ability of these particles to act as ice nuclei.

The remaining potential source for carbonaceous ice nuclei in this region is primary biological particles[22,23]. These particles are comprised of bacteria, pollen, spores, algae, protozoa, fungi, leaf fragments and fragments of insects. Bacteria and fungal spores have both been shown to be associated with precipitation at other locations[24,25]. Although we did not have a direct measure of the biological content of ice nuclei, total number concentrations of biological particles were estimated using an ultraviolet aerodynamic particle sizer (APS), which detects biological matter through laser-induced fluorescence at 349 nm. The measured fluorescence is thought to be mainly produced by nicotinamide adenine dinucleotide phosphate, which is found in all living cells[26]. The ultraviolet APS did not run continuously throughout the project, and so comparisons with this instrument are derived from ∼34 h of data. Nonetheless, ice-nucleus number concentrations at -30 ± 3 °C show a modest correlation to biological-particle concentrations for particles in the size range 0.54–1.38 μm ($R = 0.54$, $N = 111$ for ∼15 min averaged data), comparable to the sizes measured using the CFDC. When data are limited to include only aerosol weakly influenced by sources outside the basin, determined from analysis of sulphate mass loadings from an AMS and aimed at eliminating contributions from dust concentration variability, ice nuclei and biological particles show a stronger correlation ($R = 0.72$, $N = 35$ for ∼15 min averaged data). We infer that the carbonaceous fraction observed using TEM is probably dominated by primary biological aerosol particles.

Conceptually, then, ice-nucleus concentrations are explained by local emissions of primary biological particles augmented by transcontinental import of dust. We can thus use a simple model to describe ice-nucleus concentrations in the Amazon basin based on aerosol measurements from the ultraviolet APS. For temperatures explored in this study, the activity of an ice-nucleus-active bacterium such as *Pseudomonas syringae* is not expected to show much of a temperature dependence[27]. Using these bacteria as surrogates for all biological ice nuclei, no prescribed temperature dependence of ice-nucleus concentration is used for biological particles. In contrast, recent studies have shown a strong temperature dependence for the ice-nucleus activity of dust[28]. We expect that this temperature dependence partially drives the temperature-dependent ice-nucleus concentrations shown in

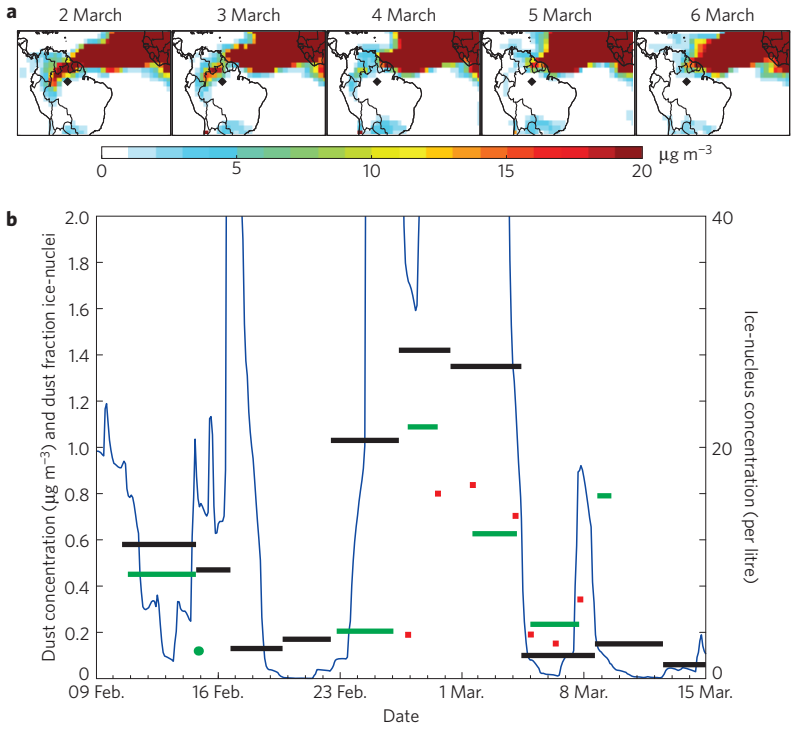

Figure 2 | Dust relation to ice-nucleus measurements. Dust concentrations during AMAZE-08. **a**, GEOS-Chem simulated dust from 2–6 March at 18 UTC. The field site, shown as a black diamond, typically fell near the edge of the plumes. Colour scale is saturated. **b**, Fine-dust concentrations from PIXE measurements (black rectangles; $\mu g\,m^{-3}$; <2 μm, linewidths correspond to collection times) and GEOS-Chem simulations (blue line; $\mu g\,m^{-3}$; <1.8 μm). Also shown are the ice-nuclei fraction composed of dust (red squares) as determined from TEM-EDX and average ice-nucleus concentrations at −30 °C (green rectangles); linewidths designate sampling periods, although data were not necessarily collected continuously throughout these periods.

Fig. 1. On the basis of these considerations, we propose the following model to fit our data:

$$N_{IN} = N_T \cdot X_{Dust} \cdot f(T)_{Dust} + N_{Bio} \cdot \phi_{BioIN} \quad (1)$$

where N_{IN} is the number concentration of ice nuclei determined from CFDC measurements, N_T is the total particle number concentration in the size range of 0.54–1.38 μm determined from ultraviolet-APS measurements (0.05–7.9 cm^{-3} during ice-nucleus measurement periods), X_{Dust} is the fraction of particles that are dust, $f(T)_{Dust}$ is the temperature dependence of ice-nucleus activity for dust, expressed as the fraction of particles that nucleate ice at a given temperature, N_{Bio} is the biological-particle number concentration in the size range of 0.54–1.38 μm determined from ultraviolet-APS measurements (0.7–47 per litre during ice-nucleus measurement periods) and ϕ_{BioIN} is the fraction of biological particles that serve as ice nuclei. We note that the ice nucleation efficiency of dust as a function of processing conditions may vary considerably with mineralogy[28]. Here, we use a temperature dependence determined from laboratory measurements by our group (unpublished) for Saharan dust transported from North Africa and deposited in the Canary Islands, $f(T)_{Dust} = 7.12 \times 10^{-10} \cdot \exp(-0.572 \times \text{Temp (°C)})$. We expect that this provides a reasonably good proxy for the dust that is transported to the Amazon basin. Using equation (1), we solve for X_{Dust} and ϕ_{BioIN}. The best fit to the data gives $X_{Dust} = 0.10 \pm 0.04$ (95% confidence). This is consistent with PIXE measurements, which show that dust comprised 4–37% of the fine-particle mass during AMAZE-08. This analysis also yields $\phi_{BioIN} = 0.21 \pm 0.18$ (95% confidence).

Using these fitted values for X_{Dust} and ϕ_{BioIN}, we calculate ice-nucleus concentrations for each of the measurement periods using ultraviolet-APS data. This fit is shown in Fig. 3 for 6 days during the study, the time period with the greatest overlap between the CDFC and ultraviolet-APS measurements. During this time period, a range of processing temperatures was explored (−18 to −31 °C). The fit does an excellent job of reproducing the trends in the ice-nucleus concentration, but does not fully capture some of the extreme values. Other time periods (~18 h of data spread over 13 days) show similar agreement ($R = 0.59$ for the entire data set) in response to changes in the number and type of aerosol measured.

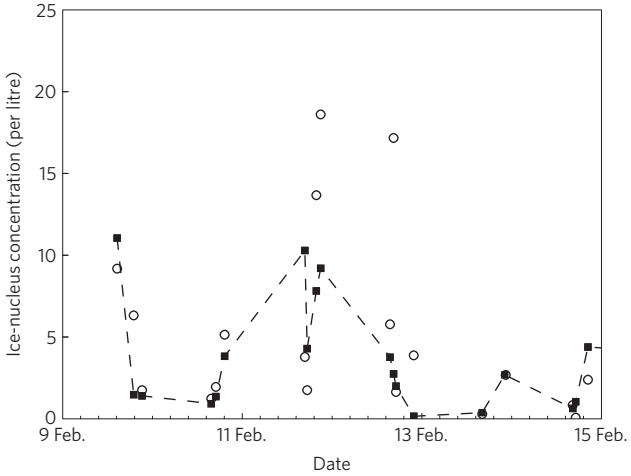

Figure 3 | Predicted ice-nucleus number concentrations. Measured (circles) and predicted (filled squares) ice-nucleus concentrations for a 6 day measurement period for CFDC processing temperatures of −18 to −31 °C. The filled squares represent the points of the calculations; the dashed lines are to guide the eye.

Given the good agreement between the simple model and the ice-nucleus measurements, we can speculate on the role of each

of these particle types during the wet season in the Amazon basin. At temperatures warmer than about −25 °C, biological particles seem to dominate the ice-nucleus population, although ice-nucleus number concentrations are only of the order of 1–2 per litre at these temperatures. These ice nuclei will be the first to initiate ice formation in clouds, and thus despite their low number concentrations, primary biological aerosol particles will have an important role in precipitation and cloud dynamics. At temperatures colder than −27 °C, dust becomes increasingly more important, with ice-nucleus number directly tied to dust number concentrations. We note that the inferred temperature dependence is driven by the form of equation (1), and the ice-nucleus composition data, collected at only one temperature, cannot fully corroborate this result. Future experiments will be designed to determine ice-nucleus composition as a function of temperature to better explore such a temperature dependence in ambient particles.

Methods

Aerosol particles were sampled through an inlet from the top of TT34 to a container at the base through a 3/4 inch stainless-steel laminar aerosol sampling line. A self-regenerating dryer maintained the relative humidity in the sampling line between 14–41% for the CFDC sampling periods. The inlet was at 38.75 m, and the canopy near the tower varied between 30 and 35 m. The CFDC was run at conditions supersaturated with respect to liquid water, so that condensation and immersion freezing are expected to dominate measured ice-nucleus concentrations, although there may also be contributions from deposition nucleation. Approximately 73 h of 1 Hz data were collected over the entire study. To improve signal-to-noise, data were averaged over 15–60 min for comparison with other measurements. An inlet impactor upstream of the CFDC removes particles larger than ~1.3 μm. This may remove particles that serve as ice nuclei, but it is necessary for differentiating ice nuclei from large aerosol particles. For TEM analysis, approximately 40 particles were analysed during each sampling period.

The non-refractory aerosol composition was determined using an Aerodyne high-resolution time-of-flight AMS. These data were used to determine whether the site was strongly or weakly influenced by airmasses outside the basin, on the basis of sulphate mass loadings. Mass concentrations of dust were determined from chemical analysis of filters using PIXE. Size-resolved number concentrations of total and biological aerosol were determined using an ultraviolet APS (TSI 3314; 0.5–20 μm). The detection efficiency of the ultraviolet APS is below 100% for particles with diameters <1.0 μm, and so the data presented here represent a lower limit for particle concentrations in this size range. Biological particles are detected by fluorescence in the ultraviolet APS. Although certain organic and inorganic species also may fluoresce and thus interfere with the ultraviolet-APS signal, previous measurements have shown that the dominant fluorescence signal from ambient measurements comes from biological particles[29], and biological number concentrations measured in this study were not correlated with either organic mass determined from the AMS ($R = 0.05$) or total particle number concentrations measured using the ultraviolet APS ($R = 0.08$). For the case of dust, measurements are also compared with global chemical transport model simulations (GEOS-Chem; v.8.01.01; http://www-as.harvard.edu/chemistry/trop/geos/index.html). The mineral dust module in GEOS-Chem includes the mobilization of dust from the surface, gravitational settling and wet and dry deposition[30].

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Author contributions

A.J.P. and M.D.P. carried out ice-nucleus measurements, processed ice-nucleus data and analysed ice-nucleus data in the context of the aerosol measurements. S.M.K. aided in the ice-nucleus analysis and in writing the manuscript. C.L.H. did simulations with GEOS-Chem. S.T.M. served as one of the project organizers of AMAZE-08 and helped with interpretation of AMS data. P.A. served as one of the project organizers of AMAZE-08, made the PIXE measurements and helped with interpretation of PIXE data. R.M.G. carried out the ultraviolet-APS measurements and helped process ultraviolet-APS data. A.G.W. helped process ultraviolet-APS data and helped with interpretation of ultraviolet-APS data. U.P. served as PI for ultraviolet-APS measurements and helped with interpretation of ultraviolet-APS data.

Additional information

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