

Biogenic Potassium Salt Particles as Seeds for Secondary Organic Aerosol in the Amazon

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The fine particles serving as cloud condensation nuclei in pristine Amazonian rainforest air consist mostly of secondary organic aerosol. Their origin is enigmatic, however, because new particle formation in the atmosphere is not observed. Here, we show that the growth of organic aerosol particles can be initiated by potassium-salt-rich particles emitted by biota in the rainforest. These particles act as seeds for the condensation of low- or semi-volatile organic compounds from the atmospheric gas phase or multiphase oxidation of isoprene and terpenes. Our findings suggest that the primary emission of biogenic salt particles directly influences the number concentration of cloud condensation nuclei and affects the microphysics of cloud formation and precipitation over the rainforest.

Organic aerosols are ubiquitous in the atmosphere and play important roles in the climate system. They can cool Earth's surface by scattering sunlight or serve as nuclei for water droplets and ice crystals in clouds and precipitation. The properties and origin of organic aerosol particles are, however, still poorly understood, and their effects are among the largest uncertainties in the current understanding of climate (1–3). For reliable assessment and control of the human influence on climate, it is important to understand the natural background sources of atmospheric aerosols (4). One of the few continental regions where aerosols can be studied under near-natural conditions is the Amazon Basin, which has an aerosol burden that is mainly driven by an intensive biosphere-atmosphere interaction (5). Recent investigations indicate that the fine particles serving as cloud condensation nuclei (CCN) in pristine Amazonian rainforest air consist predominantly of secondary organic aerosol (SOA), formed by oxidation of

volatile organic compounds (VOC) and condensation of low- or semi-volatile oxidation products (6, 7). The actual mechanism of initial particle formation, however, remains unclear. In contrast to other vegetated continental regions, ultrafine particles with diameters < 30 nm (nucleation mode particles), which are characteristic for new particle-formation events in which gaseous species condense to form secondary aerosol particles, are almost never observed in pristine boundary layer air over the Amazonian rainforest (5, 8). One possible explanation for the lack of nucleation mode particles in the Amazonian boundary layer could be that the nucleation and the initial growth of new particles take place in the free troposphere, followed by downward transport in the course of convective overturning (9, 10). Alternatively, as we suggest here, the secondary organic material may condense onto preexisting primary particles directly emitted from the rainforest.

We applied scanning transmission x-ray microscopy with near-edge x-ray absorption fine

structure analysis (STXM-NEXAFS), scanning electron microscopy (SEM), and secondary ion mass spectrometry (NanoSIMS) to determine the microstructure and chemical composition of Amazonian organic aerosol particles in the accumulation mode (0.1 to 1 μm diameter). This size range is most relevant to the activation of cloud condensation nuclei (6). The aerosol samples were collected during the wet season (May 2011) at a remote rainforest site [Amazonian Tall Tower Observatory (ATTO) site] 150 km northeast of Manaus, Brazil. The investigated air masses came with the trade wind circulation from the northeast and traveled over some 1000 km of mostly pristine tropical rainforest. For comparison, we also investigated laboratory-generated SOA reference samples from isoprene and terpene oxidation, as well as reference samples generated by spray-drying of pure organic compounds in aqueous solution (11). We used STXM-NEXAFS for the determination of elemental and functional group composition in individual organic aerosol particles (12, 13) and SEM and NanoSIMS for further morphological characterization and independent confirmation of elemental composition.

The Amazonian aerosol samples comprised a mixture of homogeneous droplets and droplets containing internal structures that may be indicative of their atmospheric aging history (Fig. 1, A and B, and fig. S8). The NEXAFS spectra revealed characteristic similarities and differences between the chemical composition of the Amazonian aerosol and laboratory-generated reference samples. The terpene SOA reference particles exhibit a sharp peak representative of carboxylic acid groups (COOH), as well as shoulders indicating carbonyl groups (C=O) and carbon-carbon double bonds (C=C), but no pronounced signal of hydroxy groups (C-OH). Spectra of the isoprene SOA reference particles show a broad peak resulting from COOH and C-OH signals of comparable intensity, a C=O shoulder, and no C=C signal. Spectra of the carbohydrate reference particles exhibit a sharp C-OH peak, no COOH signal, and very weak C=O and C=C shoulders (Fig. 2A).

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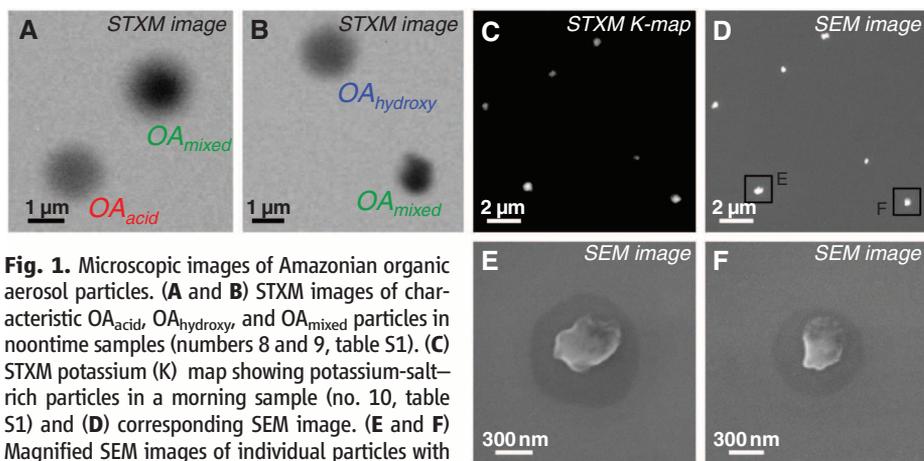


Fig. 1. Microscopic images of Amazonian organic aerosol particles. (A and B) STXM images of characteristic OA_{acid} , $\text{OA}_{\text{hydroxy}}$, and OA_{mixed} particles in noontime samples (numbers 8 and 9, table S1). (C) STXM potassium (K) map showing potassium-salt-rich particles in a morning sample (no. 10, table S1) and (D) corresponding SEM image. (E and F) Magnified SEM images of individual particles with salt core and organic coating [black frames in (D)].

In the Amazonian aerosol samples, three chemically distinct types of organic particles could be assigned to the following categories (Fig. 2A): (i) OA_{acid} particles exhibited spectra with a pronounced COOH peak similar to those of laboratory-generated SOA particles from terpene oxidation; (ii) $OA_{hydroxy}$ particles showed a strong hydroxy group signal similar to pure carbohydrate particles; and (iii) OA_{mixed} particles exhibited spectra resembling a mixture of OA_{acid} and $OA_{hydroxy}$ spectra. All three particle classes contained variable amounts of potassium. The coexistence of chemically distinct types of organic particles indicates the influence of different sources and formation mechanisms in the Amazonian boundary layer. Categories OA_{acid} and $OA_{hydroxy}$ each accounted for about 25% of all particles analyzed in this study, whereas OA_{mixed} was the most abundant particle type and contributed about 50%. Previous studies in Amazonia had shown that terpene- and isoprene-based SOA dominated the mass of organic aerosol (6, 7, 14), which is consistent with our observation of OA_{acid} , $OA_{hydroxy}$, and OA_{mixed} as a mixture of both. In addition to isoprene and terpene oxidation products, carbohydrates associated with primary particle emissions may also contribute to the observed organic matter (15, 16).

The most unexpected finding of our study was the presence of pronounced potassium signals in the NEXAFS spectra of nearly all analyzed organic particles (Fig. 2B). The potassium mass fraction is strongly size-dependent and decreases from ~20% at volume-equivalent particle diameters around 0.15 μm down to ~0.3% for diameters around 1 μm (Fig. 3), with a median value of 2.6% (11) (supplementary text S1.5). This observation suggests that small potassium-salt-rich particles from primary emissions act as seeds for the condensation of organic material and that the primary potassium content is diluted upon particle growth. The occurrence of these potassium-bearing particles has been confirmed by a combination of STXM, SEM, and NanoSIMS. In particular, samples collected during the morning hours show a high abundance of fine particles (~0.2 μm) with strong potassium signals and a low content of organic matter (Fig. 1, C to F, and fig. S7). The STXM and NanoSIMS results indicate that the potassium-rich particles also contain substantial quantities of ammonium cations as well as chloride and sulfate counteranions (11) (supplementary text S1.7).

Potassium-rich particles, in association with soot carbon, are an important component of biomass-burning smoke (17, 18). In our samples, however, we can exclude biomass burning as a source of the potassium-rich particles, because we did not find any particles containing soot carbon. Also, there were no fires detected in the region along the airmass trajectories during our study period (19, 20). Hence, biogenic emissions are the only potential source. Earlier investigations, including online high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS)

(fig. S12), had already reported substantial amounts of potassium associated with biogenic submicrometer aerosol in the Amazon during the wet season (21–23). They were not able to relate the presence of potassium to specific particle types, but the combination of potassium and sulfur has been attributed to local biogenic sources (24–26), which is consistent with the observation of potassium- and sulfate-rich particles in our study. The median atmospheric potassium concentration estimated from our analysis [$\sim 50 \text{ ng m}^{-3}$ for particles in the size range of 0.1 to 1 μm , (11) supplementary text S1.5] is consistent with previous measurement results [18 to 220 ng m^{-3} for particles <2 μm (16)]. Several studies show that active biota, such as plants and fungi, can efficiently release salts into the air (15, 16, 27–30). In particular, the active wet discharge of fungal spores is accompanied by the emission of aqueous droplets that contain potassium, chloride, and carbohydrates as the main osmolytes (11, 16) (supplementary text S2.1). STXM and light micrographs of our samples indicate a high abundance of fungal spores in the coarse particle fraction (>1 μm , fig. S6), which supports the idea of fungal emissions as a plausible source for the observed potassium-rich particles.

SEM images show that the biogenic salt particles in the early morning samples consist of a

strongly electron-scattering salt core embedded in a thin organic coating (Fig. 1, E and F). However, potassium salt cores are not present in particles collected during the daytime. Instead, many particles show an inorganic microgranular material distributed over the entire particle (fig. S8, A and B). The phase separation observed in our samples follows the same pattern and dependence on oxygen-to-carbon ratio as reported in recent studies of liquid-liquid phase separation in organic and mixed organic-inorganic aerosol particles (31–33): $OA_{hydroxy}$ particles with high atomic ratios of oxygen to carbon ($O:C \approx 0.9$ to 1.0) showed no phase separation, whereas OA_{acid} and OA_{mixed} particles with $O:C$ ratios around 0.5 to 0.7 showed internal structures with a COOH-rich core and a C-OH-rich shell (table S4 and fig. S8). These observations indicate a pronounced influence of aqueous processing in deliquesced aerosol particles and cloud or fog droplets on the growth and aging of SOA particles, that is, the formation and evaporation of aqueous droplets in which multiphase chemical reactions can produce secondary organic matter and the inorganic salt seeds can undergo cyclic dissolution and recrystallization. SOA formation by multiphase rather than gas-phase chemistry might also contribute to a suppression of new particle formation (11) (supplementary text S2.3 and S2.4).

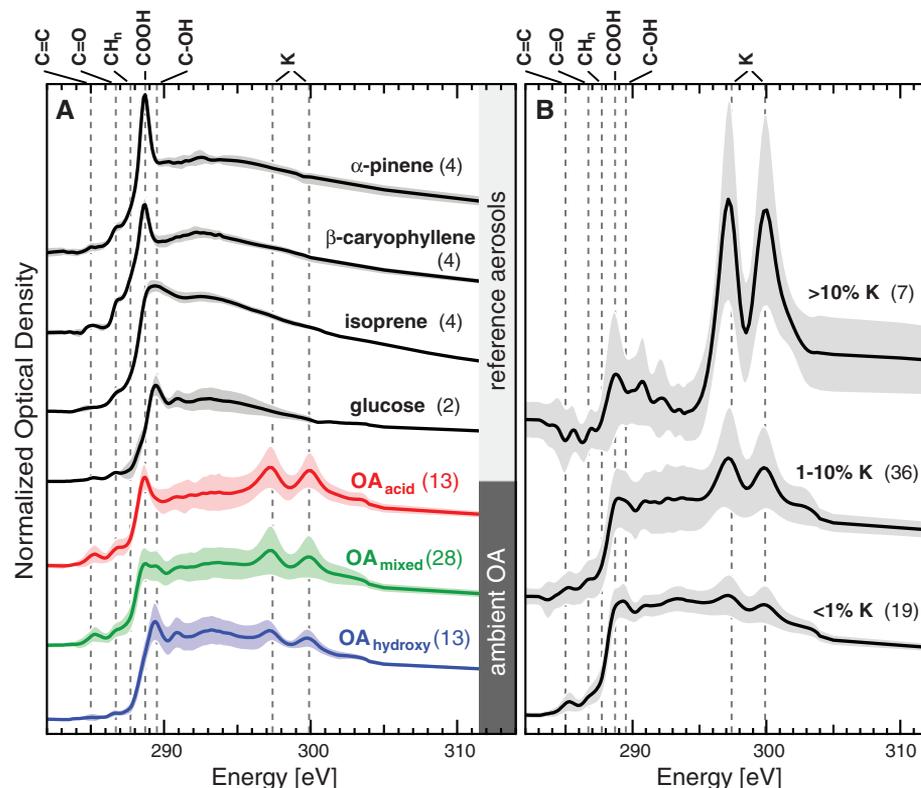


Fig. 2. (A) NEXAFS spectra of (i) laboratory-generated SOA from terpene and isoprene oxidation; (ii) glucose as carbohydrate reference compound from spray-drying of aqueous solution; and (iii) OA_{acid} , OA_{mixed} , and $OA_{hydroxy}$ particles from the Amazon. (B) NEXAFS spectra for Amazonian organic aerosol particles with different potassium (K) mass fractions. Solid lines and shaded areas represent mean spectra and standard deviations. Numbers of analyzed particles are given in parentheses. Vertical lines indicate resonant absorption of organic functional groups and potassium (table S3).

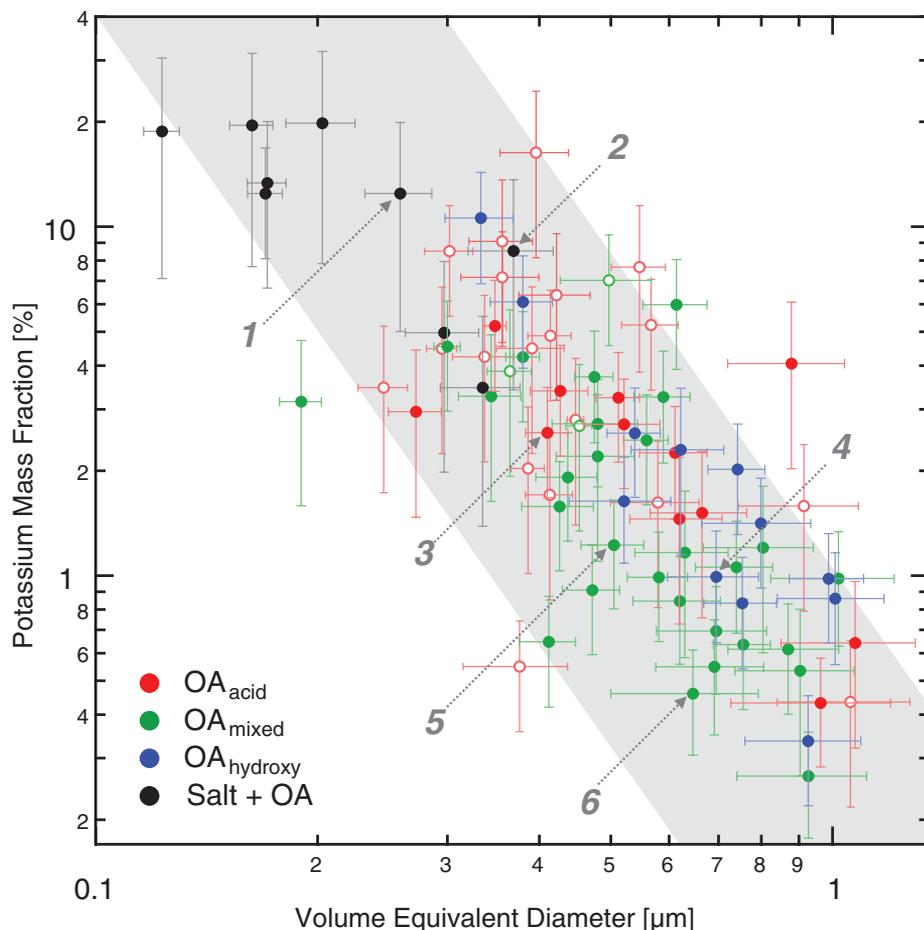
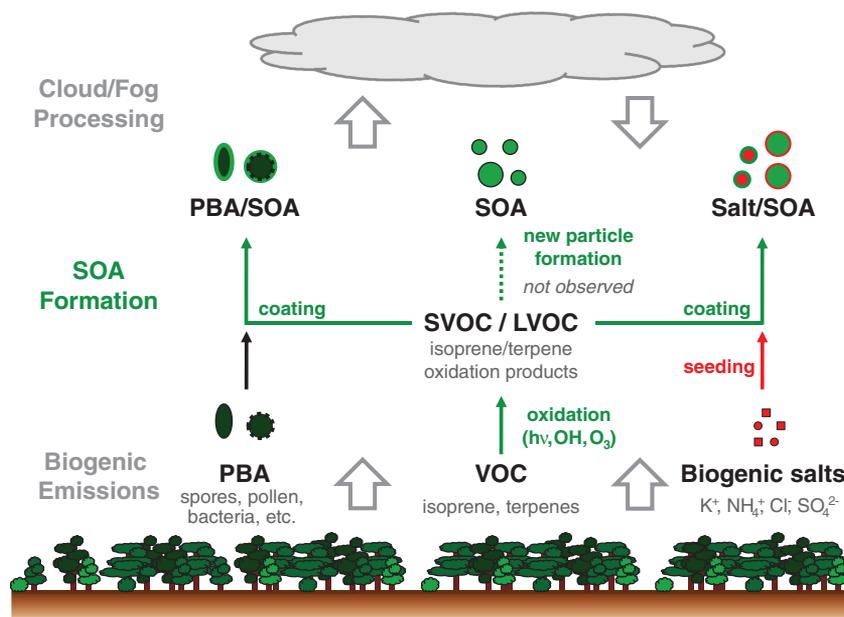


Fig. 3. Size dependence of potassium mass fraction in Amazonian organic aerosol particles. Solid markers represent data from samples collected in this study (ATTO site, 2011), and open markers represent additional data from previously collected samples (ZF2 site, 2010) (11). Numbers and arrows identify individual particles from Fig. 1 (1, F; 2, E; 3 and 5, A; and 4 and 6, B). Shaded area illustrates idealized dilution of primary potassium content upon particle growth by condensation of secondary organic material (inverse third-order dependence on particle diameter) (11). Error bars indicate the estimated uncertainty in calculations of particle size and potassium mass content.

Fig. 4. Sources and processing of organic aerosol in pristine Amazonian boundary layer air. SOA formation by photooxidation of VOC and condensation of semi- and low-volatile organic compounds (SVOC/LVOC) on primary biological aerosols (PBA) that dominate the coarse particle fraction (>1 μm) (5, 6) and on biogenic salt particles that serve as seeds for organic particles dominating the accumulation size range (0.1 to 1 μm).



Of the 77 Amazonian organic aerosol particles analyzed by STXM-NEXAFS, only 3 contained no detectable amount of potassium (<2 fg). The near-ubiquitous presence of potassium suggests that biogenic salt particles emitted from active biota in the rainforest serve as initial seeds for the condensation of VOC oxidation products. This mechanism appears to dominate the formation of SOA particles in the accumulation size range in pristine Amazonian rainforest air (Fig. 4). It can explain why new particle formation events are not observed, even though the aerosol consists largely of secondary organic material formed from gas-phase precursors (11) (supplementary text S2.4). A major implication is that the number concentration of atmospheric aerosol particles in the accumulation size range is partly regulated by the primary emission of potassium-salt-rich particles from biota in the rainforest. Compared with smaller particles in the nucleation and Aitken size range (<0.1 μm), accumulation mode particles are by orders of magnitude more frequently activated as CCN (11) (supplementary text S2.3 and fig. S11B). Thus, the biological sources and emission rates of potassium-salt-rich particles have a direct influence on the initial droplet number and microphysical evolution of clouds over the rainforest, which in turn influence the dynamics of clouds and precipitation as well as their effects on the hydrological cycle and climate.

Our findings support the hypothesis that the Amazonian rainforest ecosystem can be regarded as a biogeochemical reactor in which the formation of clouds and precipitation in the atmosphere are triggered by particles emitted from the biosphere. The connection between biogenic particle emissions and cloud properties in the tropical rainforest ecosystem appears even stronger and more direct than previously assumed (6, 34). In view of the large impact of tropical rainforests on biogeochemistry and climate, the biological

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activity and diversity of particle-emitting organisms seem likely to play important roles in Earth history and future global change.

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Supplementary Materials

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Radiative Absorption Enhancements Due to the Mixing State of Atmospheric Black Carbon

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Atmospheric black carbon (BC) warms Earth's climate, and its reduction has been targeted for near-term climate change mitigation. Models that include forcing by BC assume internal mixing with non-BC aerosol components that enhance BC absorption, often by a factor of ~2; such model estimates have yet to be clearly validated through atmospheric observations. Here, direct in situ measurements of BC absorption enhancements (E_{abs}) and mixing state are reported for two California regions. The observed E_{abs} is small—6% on average at 532 nm—and increases weakly with photochemical aging. The E_{abs} is less than predicted from observationally constrained theoretical calculations, suggesting that many climate models may overestimate warming by BC. These ambient observations stand in contrast to laboratory measurements that show substantial E_{abs} for BC are possible.

Black carbon (BC) in the atmosphere has a strong effect on global and regional climate, with some estimates suggesting that the positive (warming) radiative forcing by BC is second only to CO₂ (1), making it an important near-term climate mitigation target (2, 3). Quantification of the warming caused by BC in global climate models depends explicitly on the mixing state assumed for particles (internal versus external) and, for internal mixtures, the assumed influence of coatings on the magnitude of BC absorption (4–6). Optical properties of internally mixed BC-containing particles can be calculated in various ways, all of which indicate substantially greater absorption than for an equivalent exter-

nal mixture—the absorption by internally mixed BC is “enhanced” because the coatings act as a lens (7). Model estimates of BC radiative forcing are increased by up to a factor of 2 for internally versus externally mixed BC (4, 5), and many models that use external mixtures simply multiply BC absorption by a scaling factor (8) to account for the theoretical absorption enhancement (E_{abs}). However, the magnitude of E_{abs} has not been determined for real atmospheric particles (9, 10), which is crucial as more models describe aerosol distributions as combinations of internal and external mixtures (11).

In this study, direct measurements of E_{abs} and average mixing state for BC in the atmo-

sphere around California are reported from two field campaigns: the 2010 CalNex study and the Carbonaceous Aerosols and Radiative Effects Study (CARES). The CalNex measurements were made onboard the R/V *Atlantis*, whereas the CARES measurements were made at a ground site in the Sacramento urban area (fig. S1) (12). Our observations indicate that the E_{abs} for ambient particles around large urban centers do not vary much with photochemical aging, are significantly less than predicted from traditional core-shell Mie theory, and are in contrast to laboratory experiments, suggesting that the warming by BC may be overestimated in climate models. Further, they indicate a role for absorption by non-BC aerosol components [brown carbon (BrC)] (13) in urban environments at short visible wavelengths.

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Supplementary Materials for

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S1 Materials and Methods

S1.1 Aerosol sampling

Aerosol samples were collected with a single stage impactor (35) on silicon nitride substrates (Si_3N_4 , membrane width 0.5 mm, membrane thickness 100 nm, Silson Ltd, Northampton, UK). The volumetric flow through the impactor was $1\text{-}1.5\text{ l min}^{-1}$, corresponding to a nominal cut-off in the range of $0.5\text{-}0.8\text{ }\mu\text{m}$. On the Si_3N_4 substrate the majority of particles larger than $1\text{ }\mu\text{m}$ was concentrated in a central impaction spot, whereas smaller particles (down to $0.1\text{ }\mu\text{m}$) were collected via diffusive deposition around this spot. Regions of diffusive deposition have been chosen for STXM analysis because of the relatively high abundance of small particles and appropriate particle coverage. The samples were collected 2-2.5 m above ground level. Sampling times between 30 to 60 min ensured appropriate particle coverage on the substrates. The samples were sealed in air-tight containers, and stored at 4°C and 20-30 % relative humidity (RH) in the dark. STXM-NEXAFS analysis was done three weeks, and NanoSIMS and SEM analysis four weeks after collection. Several individual particles were investigated with two STXM instruments (ALS-STXM 5.3.2.2 in Berkeley and four months later at the MAXYMUS-STXM in Berlin, Sect. S1.5). The measurements with the two STXM instruments yielded very similar NEXAFS spectra for the investigated Amazonian SOA samples, and the quantitative analysis gave consistent results.

S1.2 Amazonian aerosols and sampling locations

The samples for this study were collected during the wet season on 13 and 14 May 2011 at a very remote site 150 km NE of the city of Manaus, Brazil, in an untouched forest area (Amazonian Tall Tower Observatory (ATTO) site, 2.14336° S , 59.00056° W , 120 m above sea level) (Table S1). The sampled air masses came mainly from the northeast across $\sim 1000\text{ km}$ of untouched forest areas. Nine-day back trajectories indicated the arrival of air masses from northeastern directions, originating over the Atlantic Ocean in the direction of Cape Verde. Figure S1 shows back trajectories and the cumulative rainfall during this time, which indicates strong wet deposition, and therefore dominance of local and regional aerosol sources. In addition, no soot or other combustion released particles were found in STXM-NEXAFS, SEM, and NanoSIMS analyses. NEXAFS spectra are particularly sensitive to soot and other combustion derived particles that contain a significant amount of aromatic moieties, and therefore, exhibit

strong spectral features at 285 eV (36-38). Hence, the samples are thought to be free of anthropogenic influences such as biomass burning in the Amazon (19-20) and long-range transport of biomass burning emissions from Africa.

An earlier set of samples had been collected on 15 May 2010 at a remote site 60 km NNW of Manaus in Brazil (ZF2 site, 2.59454° S, 60.20929° W, 90 m above sea level) (Table S1). Previously, this site (with K34 and TT34 towers) has been used for field measurement campaigns such as AMAZE-08 (6-7, 34, 39), whereas the ATTO site was established recently (2011). While this study is focused on the samples from the pristine ATTO site, the measurements from the ZF2 samples have been added as independent confirmation for the size dependence of the potassium mass fraction in organic aerosol particles (Fig. 3).

S1.3 Laboratory generated SOA from the Harvard Environmental Chamber

The Harvard Environmental Chamber (40) was operated under continuous flow conditions to generate particles composed of secondary organic material with ammonium sulfate seeds. For all experiments, the chamber relative humidity was 40 %, the temperature was 25°C, and ammonium sulfate seed particles were injected. The secondary organic material samples were produced by photooxidation of isoprene, dark ozonolysis of α -pinene, and dark ozonolysis of β -caryophyllene. The oxygen-to-carbon ratio (O:C) and mass loading of the secondary organic material in the chamber outflow was characterized by an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (41). The recent updates of Chen et al. (42) were applied in the analysis of O:C. A summary of the experimental conditions can be found in Table S2.

The α -pinene and β -caryophyllene ozonolysis experiments largely followed the procedures detailed in Shilling et al. (43) and Chen et al. (44), respectively. Briefly, a solution of α -pinene in 2-butanol or β -caryophyllene in cyclohexane was continually injected into a gently warmed glass bulb using a syringe pump. The solution evaporated in a pure air flow and was swept into the chamber. Ozone was generated outside the chamber by passing a pure air flow around an ultraviolet light and the resulting flow was injected into the chamber. Within the chamber, the reaction of α -pinene or β -caryophyllene with ozone formed secondary products, and those of sufficiently low volatility condensed onto the surfaces of the crystalline seed particles.

The generation of isoprene secondary organic material generally followed the method described in King et al. (45). One alteration was that for these experiments the ammonium sulfate seed particles were deliquesced aqueous droplets. Gas-phase isoprene and hydrogen peroxide (H_2O_2) were injected into the chamber, and isoprene reacted with the OH radicals produced by the photolysis of H_2O_2 by irradiation in the chamber. Some of the products of this reaction were of low volatility and partitioned to the seed particles. The laboratory-generated SOA was collected by impaction sampling on silicon nitride substrates using a single stage impactor (see. Sect. S1.1).

S1.4 Reference aerosols from pure organic compounds

The following chemicals, purchased from Sigma Aldrich, were used as reference standards: serine, aspartic acid, bovine serum albumin (BSA), glucose, and glucosamine-HCl. Chemicals were used without further purification and dissolved in deionized water (Millipore - Milli Q plus 185, 18.2 M Ω cm). Reference aerosol was generated by spray-drying of the pure organic compounds in aqueous solution (1 mmol l⁻¹) using a constant output atomizer operated with filtered particle-free pressurized air (250 kPa, 3 lpm). The polydisperse aerosol flow was dried to a relative humidity of <15 % (silica-gel diffusion dryer). Further, the generated aerosols were passed through a radioactive neutralizer (Kr⁸⁵, 74 MBq or 2 mCi) to generate charge equilibrium, and then to a differential mobility analyzer (DMA; TSI 3080 electrostatic classifier). This facilitated the selection of particles of suitable size for further analysis (0.35-0.6 μm). The output from this DMA was split in two for aerosol sampling (1 lpm) and for a condensation particle counter (TSI 3786, 0.6 lpm) to monitor particle concentration. The reference aerosols were collected by: (i) impaction sampling on Si_3N_4 substrates using a single stage impactor (see. Sect. S1.1) and (ii) electrostatic precipitation on TEM grids (300-mesh copper mesh, 10-15 nm carbon coating, Plano GmbH, Wetzlar, DE) using an electrostatic sampler (46). The STXM analysis of reference samples on both substrates yielded particle diameters in the expected size range, indicating that no particle fragmentation occurred in the course of sampling (i.e. impaction on Si_3N_4 membranes).

SI.5 STXM-NEXAFS measurements and data processing

STXM-NEXAFS analysis was conducted at the Lawrence Berkeley National Laboratory Advanced Light Source (LBNL ALS), Berkeley, CA, USA, at beamline 5.3.2.2 and at the MAXYMUS beamline (UE46_PGM-2) at BESSY II, Helmholtz-Zentrum, Berlin, Germany.

The ALS-STXM instrument is located at the bending magnet beamline 5.3.2.2 at the ALS electron storage ring (1.9 GeV, 500 mA stored current in top-off mode) and provides a photon flux of $\sim 10^7 \text{ s}^{-1}$ in the soft X-ray region (250-800 eV). It is equipped with a spherical grating monochromator (resolving power $E/\Delta E \leq 5000$), a Fresnel zone plate with 25 nm spatial resolution and a phosphor coated Lucite tube coupled with a photomultiplier. Samples are analyzed in a He-filled chamber ($\sim 30 \text{ kPa}$). The accessible energy range (250-800 eV) includes the carbon K-absorption edge (283.8 eV), the potassium $L_{3,2}$ -edge (294.6 eV), the calcium $L_{3,2}$ -edge (349.3 eV), the nitrogen K-edge (400.0 eV) and the oxygen K-edge (531.7 eV) (47). Additional technical specifications are given in Kilcoyne et al. (48).

The MAXYMUS-STXM is located at the tunable undulator beamline UE46_PGM-2 at the BESSY II electron storage ring (1.7 GeV, multibunch mode) and provides a photon flux of $\sim 5 \cdot 10^8 \text{ s}^{-1}$ in the soft X-ray region. The undulator provides X-ray photons with selectable polarization in the range of 120-1900 eV. The STXM is equipped with a plane grating monochromator using a 600 l/mm blazed grating (resolving power $E/\Delta E \leq 8000$ at C-K), a Fresnel zone plate with 31 nm spatial resolution and a phosphor coated Lucite tube coupled with a photomultiplier. The samples were placed in an evacuated chamber ($2\text{-}5 \cdot 10^{-5} \text{ Pa}$). Further information can be found in Follath et al. (49).

Single energy images were recorded by raster-scanning the sample in the focused X-ray beam and measuring the intensity of transmitted monochromatic light as a function of sample position. X-ray absorption spectra were obtained either by recording a sequence of energy image scans or an energy line scan that sampled across the particle. For an energy image scan (“stack”) a series of images of a defined region with closely spaced photon energies is recorded over a certain energy range covering peak features, and with a coarser energy grid outside of the regions with fine structure. For line scans, the X-ray spot is scanned across a particle, then the photon energy is changed and the line rescanned. This yields a plot of transmitted light at each position on the scanned line as a function of energy. We used identical energy protocols (number of

energy points and spacings) for stacks and line scans, ranging from 270 to 600 eV, and spanning the carbon, potassium, calcium, nitrogen and oxygen edges (Fig. S2).

Based on the measured transmitted intensity $I(d)$ the optical density OD was calculated applying Beer-Lambert's law (50):

$$OD = -\ln\left(\frac{I(d)}{I_0}\right) = \mu\rho d$$

where I_0 represents the incident photon flux, μ is the mass absorption coefficient, ρ is the sample density and d the sample thickness. I_0 was obtained as the transmission intensity through a particle free region of the substrate. For $OD < 1.5$, particle sizes were in the linear absorption regime of the Beer-Lambert's law (12) which was assured for all particles reported in this study.

For the analysis of carbon NEXAFS spectra, the pre-edge absorption (mean value between 275 and 284 eV) was subtracted and the spectra were normalized by the carbon K-edge height (mean value between 305 and 320 eV) (51). We used fine structure features from resonant transitions of core electrons into excited states close to the ionization continuum ($1s \rightarrow \pi^*, \sigma^*$) to characterize the functional group composition of OA particles (50, 52). Characteristic transitions are listed in Table S3.

For the analysis of atomic ratios (i.e., O:C, N:C) the heights of the C, N and O absorption edges ΔOD were determined as

$$\Delta OD = OD_{post-edge} - OD_{pre-edge}$$

with carbon post- and pre-edge energies being 320 and 280 eV; nitrogen: 425 and 395 eV; oxygen: 550 and 525 eV (12). The molar ratio of oxygen and carbon n_O/n_C is calculated as

$$\frac{n_O}{n_C} = \frac{\Delta OD_O M_C \mu_{C,post-pre}}{\Delta OD_C M_O \mu_{O,post-pre}}$$

with M as the atomic mass and $\mu_{post-pre}$ as the difference in mass absorption coefficient ($\mu_{C,320-280} = 3.8 \cdot 10^4 \text{ cm}^2 \text{ g}^{-1}$, $\mu_{N,425-395} = 2.8 \cdot 10^4 \text{ cm}^2 \text{ g}^{-1}$, $\mu_{O,550-525} = 2.0 \cdot 10^4 \text{ cm}^2 \text{ g}^{-1}$) (12, 36-37, 47). The ratio n_N/n_C is obtained in an analogous fashion. The calculation of n_O/n_C and n_N/n_C has been verified previously by Moffet et al. (36), and was reconfirmed in this study by means of organic standard compounds and aerosol mass spectrometry data for laboratory-generated SOA. The experimental results show good agreement with the theoretical ratios (see Table S4 and Sect. S2.2).

Based on non-normalized CNO spectra, the potassium mass fraction in organic particles was estimated as described in the following paragraph. In soft X-ray absorption spectra, the potassium L_{3,2}-absorption edge occurs as a characteristic double peak superimposed on the carbon K-edge absorption. Both closely spaced potassium L₃- and L₂-edges consist of pronounced and sharp peaks at the onset of the edge (at 297.4 eV and 299.9 eV) caused by the resonant electron transition from the ground states (2p_{3/2}, 2p_{1/2}) into unoccupied states (3d) in addition to the actual absorption step function due to photo-ionization (50).

In spectra of OA particles with high potassium content, the pronounced potassium doublet and the height of the potassium absorption edge (relative to pre-edge absorption) are resolved. For OA particles with low potassium content only the potassium doublet is strong enough to be detected (Fig. S3). The height of the L_{3,2}-edge, ΔOD_{edge} , is proportional to the number of potassium atoms and can be used to quantify the potassium content. Based on 20 potassium-rich particles the following linear correlation ($R^2 = 0.85$) between ΔOD_{edge} and the height of the L₃-peak ΔOD_{L3} was established:

$$\Delta OD_{edge} = 0.235 \cdot \Delta OD_{L3}$$

This correlation allowed a quantitative estimate of ΔOD_{edge} even for OA particles with low potassium content. The effective potassium detection limit in individual organic particles is given by the minimum ΔOD_{L3} that is resolvable above the spectral noise. It was estimated as ~ 2 fg. Based on Beer-Lambert's law, the following equation was used to calculate the absolute potassium mass, m_K , in individual aerosol particles:

$$m_K = \frac{\Delta OD_{edge} V}{0.7 \mu_{K, post-pre} h}$$

with V as the volume of the impacted OA droplets (= spherical cap), $\mu_{K,310-292} = 7.0 \cdot 10^4 \text{ cm}^2 \text{ g}^{-1}$ as the difference in potassium L-edge mass absorption coefficient for the pre- and post-edge energies 292 and 310 eV (47, 53), h as the height of the impacted droplet, and a geometric factor of 0.7 to account for the average light path through the spherical cap (12). V can be calculated as

$$V = \frac{h\pi}{6} (3a^2 + h^2)$$

with a as the radius of the spherical cap that was measured for all particles based on STXM images (54). The height, h , is not directly accessible but can be estimated based on the measured

OD for C, N, and O. According to Pöschl et al. (6), C, N, and O account for ~80 % of the total mass, m_{total} , of Amazonian aerosol particles in the submicrometer size range. Therefore,

$$m_C + m_N + m_O = 0.8m_{total}$$

with

$$m_x = \frac{OD_x V}{0.7 \mu_{x,post-pre} h}$$

and

$$m_{total} = V \cdot \rho$$

can be converted into

$$h = \frac{1}{0.56\rho} \left(\frac{OD_C}{\mu_C} + \frac{OD_N}{\mu_N} + \frac{OD_O}{\mu_O} \right).$$

Using $\rho = 1.4 \text{ g cm}^{-3}$ as a characteristic density value for OA particles (2), we obtained the radius-to-height ratio a/h with a mean value of ~10. Based on a and a/h , we calculated a volume equivalent diameter D_{ve} for each particle:

$$D_{ve} = \sqrt[3]{3ha^2 + h^3}.$$

According to Martin et al. (5), the fine organic aerosol mass concentration (<2 μm) during the wet season in the Amazon is of the order of ~2 $\mu\text{g m}^{-3}$. Multiplication of this value with an estimated average potassium mass fraction of ~2.6 % (median of all Amazonian OA particles analyzed in this study), yields an average atmospheric potassium concentration level of ~50 ng m^{-3} (estimated uncertainty: factor ~2), which is consistent with previous measurements (18-220 ng m^{-3} , (16)).

SI.6. SEM analysis

Scanning electron microscopy (SEM) images of aerosol particles were acquired using the secondary electron in-lens detector of a high-performance field emission instrument (LEO 1530 FESEM, EHT 10 keV, WD ~9 mm). The in-lens detector enabled detection of thin organic particles and coatings, which are often difficult to detect. The organic nature of SOA droplets and organic components of mixed SOA-inorganic particles were confirmed by NanoSIMS analysis as detailed below. Si_3N_4 windows are mounted on conductive Si wafers; however, the windows

themselves are nonconductive and show strong charging. Therefore, the back of the Si₃N₄ windows was coated with gold prior to SEM and NanoSIMS analysis to prevent charging and enhance the contrast of SOA particles against the substrate.

SI.7. NanoSIMS measurement and data processing

Chemical analysis of aerosol particles was performed using a Cameca NanoSIMS 50 ion microprobe in multi-collection detector mode by sputtering the sample with a ~1 pA Cs⁺ primary ion beam focused into a spot of ~100 nm diameter. The primary ion beam was scanned several times over an area of 4 μm x 4 μm for the chemical analysis of standards, with a dwell time of 1000 μs pixel⁻¹, and images (256 x 256 pixels) were recorded for every scan. The detector dead time was 44 ns and the count rates were corrected accordingly. The energy bandpass slit was set to 20 eV, the entrance slit and aperture slit were decreased to 30 μm x 180 μm and 200 μm x 200 μm, respectively, and the transmission was kept at 50 % to enhance the count rate on small particles. A high transmission is possible because the influence of the quasi simultaneous arrival effect on the quantification of major elements is minor (<1 %) compared to the matrix effects, which introduce a ~20-40 % uncertainty.

On aerosol samples the field of vision was larger (10 μm x 10 μm) to view a representative area of the sample and compare with SEM and STXM images. To remove surface contaminations, all images were pre-sputtered for one cycle. The analysis time varied from 3-20 cycles depending on the number of scans required to collect an appropriate number of counts per pixel on each mass, and on the stability of the compounds investigated.

Secondary ions of ¹²C⁻, ¹⁶O⁻, ¹²C₂⁻, ¹²C¹⁴N⁻, and ³²S⁻ were simultaneously collected in five electron multipliers on standards. For aerosol samples only one proxy for the carbon content of the sample (¹²C⁻ or ¹²C₂⁻) was selected. Instead, ³⁵Cl⁻ was added to the list in order to allow the detection of a larger variety of inorganic salts. For quantification we compared normalized ion counts to the theoretical concentration of the species of interest in a large number of standards. The observed relationship was then used to calculate the concentration of the element of interest in the aerosol samples. This approach is straightforward for all samples that contain sufficient carbon atoms to ionize all of the nitrogen in the sample to CN⁻. The logarithms of the observed calibration factors show a correlation (R² = 0.99) with the electron affinity that is similar to that

typically observed between the logarithm of the relative sensitivity factor (RSF) under Cs^+ bombardment and electron affinity (55).

For 19 salt-rich particles ($<0.3 \mu\text{m}$) from the aerosol samples ATTO_2011_#7 and ATTO_2011_#10 (Table S1) we determined approximate elemental mole fractions of carbon, nitrogen, oxygen, sulfur and chlorine (C:N:O:S:Cl = 0.01:0.09:0.62:0.17:0.02), indicating a relatively high abundance of sulfate ions in the salt core (Fig. S4, particles 1-3).

S1.8. WRF model simulation

In order to obtain the probability density distribution of vertical velocities, P_w , for the Amazonian region during the sampling period, the Weather Research & Forecast model (WRF-ARW-v3.3.1, <http://www.mmm.ucar.edu/wrf/users/>) was applied to simulate the meteorological conditions in the Amazon for the whole of May 2011. The model domain was horizontally configured as 299×249 grid cells with a spatial resolution of $9 \text{ km} \times 9 \text{ km}$. It was centered near Manaus, Brazil, and covers a large part of the Amazon forest region (Fig. S5). There were 34 vertical layers extending to 100 hPa ($\sim 15 \text{ km}$) with 17 layers below 4 km. To allow sufficient time for the model spin-up, we started the simulation on 26 April 2011. Meteorological initial and boundary conditions were interpolated from the NCEP-FNL Operational Global Analysis data (<http://dss.ucar.edu/datasets/ds083.2/>). The sea surface temperature was updated daily during the model simulation with real-time, global sea surface temperature analysis data (RTG_SST, <ftp://polar.ncep.noaa.gov/pub/history/sst>). MODIS land-use data with inland lake information were used to feed into the Noah Land Use scheme. Grid nudging was applied only for the spin-up period (April 26-30, 2011), and afterward the WRF model was set to run freely. An overview of the model configuration is given in Table S5.

S2 Supplementary Text

S2.1 Observations and sources of biogenic salt particles

The elemental composition of aerosol particles in the Amazon Basin during the wet season has been investigated previously, and a variety of different trace elements have been observed (21, 25, 56-60). In supermicrometer particles, two groups of elements have been found: (i) crustal elements such Si, Al, Ca, and Fe mostly from long range transport of Saharan dust, and (ii) “biogenic” elements such as S, K, and P (25). In submicrometer particles, the elements K, P, S, and Zn are frequently observed and mostly attributable to biogenic sources (21-22, 60-61). These elements often exhibit bimodal mass size distributions with relative maxima at $\sim 0.3 \mu\text{m}$ and $\sim 3 \mu\text{m}$ (21, 25-26). The night-time concentrations of K, P, and Zn usually exceed day-time concentrations due to increased microbiological activity (i.e., fungal spore release) during the night (60). Plants, fungi, and other microorganisms are considered to be potential sources of the potassium-salt-rich particles observed in this study (16, 21, 25-26). The following paragraph summarizes current knowledge about biogenic salt emission mechanisms from different organisms.

For the ejection of spores into the air, fungi have developed various active discharge mechanisms that involve hygroscopic water uptake by organic and inorganic solutes to generate osmotic pressure and surface tension effects. The active discharge of spores is accompanied by the emission of a liquid jet which contains inorganic ions and carbohydrates (16). Active wet discharge of *Ascomycota* spores utilizes osmotically pressurized small sacks (asci) which, upon bursting, eject spores and aqueous droplets of the osmotic fluid containing mannitol, potassium and chloride (62). Active wet discharge of *Basidiomycota* spores involves surface tension effects and aqueous droplets containing hexoses, mannitol, phosphate, sodium, and potassium (63-64). Elbert et al. (16) have shown that a major fraction of the potassium concentrations observed in the pristine Amazonian boundary layer can be explained by fungal emissions. X-ray and light microscopic analysis of our samples showed very high abundances of fungal spores in the coarse fraction, supporting the idea that fungal spore ejection is a plausible mechanism for the production of the observed potassium-rich particles (Fig. S6).

In addition to microorganism related emissions, the following plant related salt particle release mechanisms have been described in the literature: (I) transpiration, (II) guttation, (III) leaching of vegetation by rain, and (IV) particle release from leaves due to mechanical abrasion.

Beauford et al. (29-30) suggest that small biogenic salt particles can be released into the air by diffusiophoresis associated with water loss during rapid plant transpiration. Other studies provide experimental evidence that transpiration vapors from different plant species contain salt ions (e.g., Ca^{2+} , Na^+ , K^+ , NH_4^+ ; HCO_3^- , Cl^- , SO_4^{2-}) in considerable concentrations (up to 5 mg l^{-1} in the condensate) (27, 65-67).

Guttation is a common water release mechanism of plants when the water supply from the roots exceeds transpiration losses by the leaves. Since transpiration usually does not occur at night, leaf wetness frequently occurs in the morning hours, distinct from dew, depending on physiological and micrometeorological conditions (68-69). Guttation fluids (xylem sap) contain a mixture of sugars, amino acids, and salt ions, with particularly high K^+ , Ca^{2+} , and Mg^{2+} content (15, 70). Accordingly, guttation has been proposed as one potential origin of airborne trace elements in tropical environments (21, 28).

Leaching of soluble compounds from vegetation surfaces by rain, dew, and mist has been described in various studies (71-73). In addition to organic molecules (i.e., carbohydrates), the ions K^+ , Ca^{2+} , Mg^{2+} , and Mn^{2+} are leached in the largest quantities (73-74). It has been suggested that leaching followed by droplet evaporation can generate airborne particles with high trace metal content (66).

Plant surfaces exposed to the atmosphere are covered with waxes that reduce the loss of water and act as a physical defense barrier against pathogens (69). In particular, epicuticular waxes often form the top layer of plant surfaces and are comprised of submicrometer sized, partly crystalline, particles (75). Such particles as small as 200 nm long and 30 nm wide can be released into the air when the plants are mechanically disturbed (e.g., due to rapid growth, surface abrasion by wind, or microbiological activity) (29-30, 76).

The potassium-rich salt particles observed in this study (Fig. 1C-F) were typically in the size range of 0.1-0.3 μm . Figure S7 shows the size distribution obtained by SEM analysis of a morning sample with relatively high salt particle concentration. The maximum around 0.2 μm is in good agreement with the dilution trend of the potassium content in organic particles (Fig. 3). The grey shaded dilution band in Fig. 3 has been calculated assuming that primary biogenic salt particles in the size range of 0.1-0.3 μm with a density of $2.0\text{-}2.7 \text{ g cm}^{-3}$ (KCl , K_2SO_4) (77) grew by condensation of SOA with a density of $1.0\text{-}1.4 \text{ g cm}^{-3}$ (2). The calculated band covers almost

all data points and suggests that the size distribution shown in Fig. S7 is characteristic for the salt particles serving as seeds for the investigated Amazonian SOA.

S2.2 Validation of STXM elemental ratios

The stoichiometric ratios of organic standard compounds and the STXM elemental ratios for C, N, and O (n_O/n_C and n_N/n_C) generally show good agreement as previously verified by Moffet et al. (36). The results of this study confirm this observation and are summarized in Table S4. The STXM-NEXAFS and AMS derived elemental ratios for laboratory generated SOA show good agreement in n_O/n_C ratios with deviations up to 20 % (Table S4). For laboratory-generated SOA particles, ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ seeds were added to the reaction chamber (Sect. S1.3). For isoprene SOA, ammonium sulfate accounts for a significant mass fraction of the resulting particles (7 % on average), and was observed in the form of a strong ammonium peak at the nitrogen absorption edge (Fig. S2). The mass fraction of ammonium sulfate for terpene SOA (3-4 %; Table S2) is much lower than that for isoprene SOA, corresponding to a weak ammonium peak at the nitrogen absorption edge (Fig. S2). For the STXM analysis, the amount of sulfate was quantified on the basis of the nitrogen content. Accordingly the n_O/n_C ratios were calculated for total oxygen (organics and sulfate) and for organic oxygen only. For the AMS analysis, the amount of sulfate is known and the n_O/n_C ratios were also derived for both cases, including and excluding sulfate.

S2.3 Internal structure, cloud/fog processing and CCN activation of aerosol particles

As discussed in the main text, the investigated Amazonian organic aerosol particles exhibited different types of internal structures that suggest a pronounced influence of cloud and fog processing on SOA formation and aging.

The organic bulk material of many OA_{mixed} particles shows a distinct core-shell structure with COOH-rich material in the core and C-OH-rich material in the shell (Fig. S4 and S8). This internal structure may be caused by cloud/fog processing, because OA_{acid} and $\text{OA}_{\text{hydroxy}}$, which are the main constituents of OA_{mixed} , have different solubilities in water. Upon evaporation of the cloud droplets, the less soluble OA_{acid} material would precipitate first, and the highly soluble hydroxy-rich material (probably sugar- or polyol-like) would form a viscous layer surrounding this core (78). In contrast, $\text{OA}_{\text{hydroxy}}$ occurs as chemically and morphologically homogenous

particles (Fig. S8C). Our findings are consistent with recent studies of liquid-liquid phase separation in organic and mixed organic-inorganic aerosol particles reporting a strong dependence on oxygen-to-carbon ratio of the organic material (31-33): Particles with low atomic ratios of oxygen-to-carbon tend to exhibit phase separation ($O:C \approx 0.5-0.7$ in OA_{acid} and OA_{mixed}), which is not the case for particles with high $O:C$ ratios ($O:C \approx 0.9-1.0$ in $OA_{hydroxy}$; Table S4 and Fig. S8). The hygroscopic salt seeds as well as the variable chemical composition and morphology of the SOA particles suggest that aqueous phase reactions play an important role in particle growth and aging (2, 79).

To estimate the frequency of CCN activation and cloud droplet formation on Amazonian aerosol particles, we performed numerical model simulations using input parameters from this and related earlier studies (Sect. S1.8, (6, 34)). The ability of aerosol particles to act as CCN depends on the particle size, hygroscopicity, and water vapor supersaturation. To form cloud droplets, larger particles require a lower supersaturation, which corresponds to a lower updraft velocity (6, 80-81).

Figure S9 shows the critical updraft velocity for CCN activation of aerosol particles as a function of particle diameter. The curve results from cloud parcel model simulations with detailed spectral microphysics using parameters characteristic for pristine Amazonian aerosols during the wet season as determined in the AMAZE-08 campaign (pristine focus period) (6, 39): hygroscopicity parameter $\kappa = 0.14$; particle number concentration $N = 200 \text{ cm}^{-3}$; number size distribution with two log-normal modes with a relative ratio of $N_2/N_1 = 0.81$ ($N = N_1 + N_2$) and with geometric mean diameter and standard deviation values of $D_{g,1} = 67 \text{ nm}$ and $\sigma_{g,1} = 1.32$ (Aitken mode) and $D_{g,2} = 150 \text{ nm}$ and $\sigma_{g,2} = 1.43$ (accumulation mode, see Fig. S10A).

As indicated by the dashed lines in Fig. S10A, updraft velocities $>0.1 \text{ m s}^{-1}$ are sufficient to activate accumulation mode particles at $\sim 0.15 \mu\text{m}$, whereas the CCN activation of Aitken mode particles at $\sim 0.07 \mu\text{m}$ requires updraft velocities $>1 \text{ m s}^{-1}$. Figure S11A shows the probability density function (P_w) of atmospheric vertical velocities (w) at different altitudes above the Amazonian rainforest during the wet season as calculated with the Weather Research and Forecast model (WRF-ARW-v3.3.1, Sect. S1.8) for the region and period around the aerosol sampling location and time (Fig. S5, May 2011). Combining P_w from Fig. S11A with w_{cri} from

Fig. S9, the probability of CCN activation for aerosol particles of a given size, $P_{\text{act}}(D_p)$, can be estimated as follows:

$$P_{\text{act}}(D_p) = \int_{w_{\text{cri}}}^{\infty} P_w dw \quad \text{with} \quad w_{\text{cri}} = f(D_p)$$

Figure S11B shows P_{act} for different altitudes plotted against the aerosol particle diameter. As expected, P_{act} is highest in the upper boundary layer (1-3 km) where the base of convective clouds usually forms. At altitudes ≥ 1 km, P_{act} is larger than ~ 0.5 % for diameters $> 0.1 \mu\text{m}$, increases exponentially with increasing diameter, and exceeds 5 % for particles $> 0.15 \mu\text{m}$, which account for most of the aerosol particle volume and mass (Fig. S10B) (6). In near-surface air (0.1-0.5 km), P_{act} is less than ~ 0.01 % for particles $< 0.1 \mu\text{m}$, but it increases steeply and exceeds 0.5 % for particles $> 0.15 \mu\text{m}$. The formation of low-lying cloud and fog over the rainforest is a common event in the wet season. The geometric mean value of P_{act} for the entire altitude range of 0.1-3 km can be regarded as an estimate for the effective average probability of CCN activation for aerosol particles in pristine Amazonian boundary layer air. It is multiple orders of magnitude higher for accumulation mode particles ($P_{\text{act}} \approx 2$ % for $D_p \approx 0.15 \mu\text{m}$) than for Aitken mode particles ($P_{\text{act}} < 0.01$ % for $D_p \approx 0.07 \mu\text{m}$). This is consistent with the general assumption that the so-called Hoppel minimum around $\sim 0.1 \mu\text{m}$ separating the Aitken mode and the accumulation mode in the size distribution of aged atmospheric aerosols is due to cloud processing (82). In the size range $> 0.15 \mu\text{m}$, which comprises the particles investigated in this study (Fig. 3) and represents the majority of SOA mass (5-6), the geometric mean value of P_{act} exceeds 2 %. The high probability of CCN activation underlines the importance of large accumulation mode particles for the formation of clouds over the rainforest, and it is consistent with the observation of core-shell structures indicating a pronounced influence of aqueous phase processing in clouds or fog on the formation and aging of SOA in the Amazon.

S2.4 Suppression of new particle formation in the Amazon

Numerous observations in the planetary boundary layer revealed a consistent correlation between sulfuric acid and the concentration of newly formed particles, and consequently sulfuric acid is thought to be the primary vapor responsible for atmospheric nucleation ((83-86) and references therein). Recent modeling studies argue convincingly that the concentration level of gaseous sulfuric acid in the Amazon region is too low to trigger nucleation and new particle

formation (NPF) events, in contrast to what is observed in relatively clean air over most other vegetated continental regions ((8, 85, 87) and references therein). In line with ambient observations, which consistently show that 10^6 - 10^7 molecules cm^{-3} of H_2SO_4 are necessary to produce particle formation events, laboratory studies reported that the threshold concentration of sulfuric acid at which newly formed particles (>3 nm) start to appear is approximately 5 - $7 \cdot 10^6$ molecules cm^{-3} ((85, 88) and references therein). Kanawade et al. (89) calculated a H_2SO_4 concentration of about 1 - $5 \cdot 10^5$ molecules cm^{-3} from the measured SO_2 (0.02-0.03 ppb) (90) and OH ($5.5 \cdot 10^6$ cm^{-3}) (91) over the Amazon basin, which is nearly one order of magnitude lower than the values observed in boreal forest in Finland (92) and in Michigan forest (89). Low- or semi-volatile organic vapors are also found to be involved in the nucleation and subsequent particle growth (85) and some laboratory studies reported that the presence of organics significantly enhances NPF (93-95). On the other hand, an experimental study showed that homomolecular nucleation of organics, such as aromatic acids, in the absence of H_2SO_4 is unlikely to occur under atmospheric conditions (93). In addition, the relatively high isoprene-to-terpene ratio over the Amazon may play a role in suppressing nucleation as discussed by Kiendler-Scharr et al. (96) and Kanawade et al. (89). We assume that these and related issues of atmospheric gas phase chemistry are probably the main reason why NPF is not observed in the Amazon in contrast to boreal forest areas characterized by frequent NPF (97-99).

In addition, the presence of potassium-rich salt particles in a humid environment may indeed enhance the effective condensation sink of organic vapors as outlined below and may thus contribute to suppress new particle formation over the Amazon. The condensation sink (CS) of low-volatile vapors, as determined by the particle size distribution and surface concentration, in pristine Amazonian rainforest air is of the order of $\sim 1 \cdot 10^{-3} \text{ s}^{-1}$ [based on the size distribution data of Zhou et al. (100) and Pöschl et al. (6)], the influence of hygroscopic growth at average RH of 93 % on the particles size distribution has been taken into account by using the measured average κ value during wet season of Amazon as 0.15 (34)]. Physically, the condensation sink in Amazonia is thus of similar magnitude as in pristine boreal forest air (CS = $\sim 4 \cdot 10^{-3} \text{ s}^{-1}$ according to Kulmala et al. (98) and Kanawade et al. (89)). From a chemical perspective, however, aqueous droplets formed by hygroscopic growth of the potassium-rich salt particles in tropical rainforest air are not only a condensation sink for low-volatile vapors, they can also absorb volatile and semi-volatile organic compounds and provide a medium for multi-phase chemical reactions that

may be more efficient in converting VOC into SOA than gas phase chemical reactions followed by “dry condensation” of low-volatile vapors (2, 101-102).

Thus, we suggest and intend to pursue further investigations to unravel and quantify how multi-phase chemistry on potassium-rich salt particles may influence the mechanism and rate of SOA formation and the apparent suppression of new particle formation (nucleation events) over the Amazon and other tropical rainforests compared to mid-latitude and boreal forests, which will require comprehensive field measurements of aerosol particle and precursor gas composition as well as kinetic process studies (laboratory experiments and model calculations).

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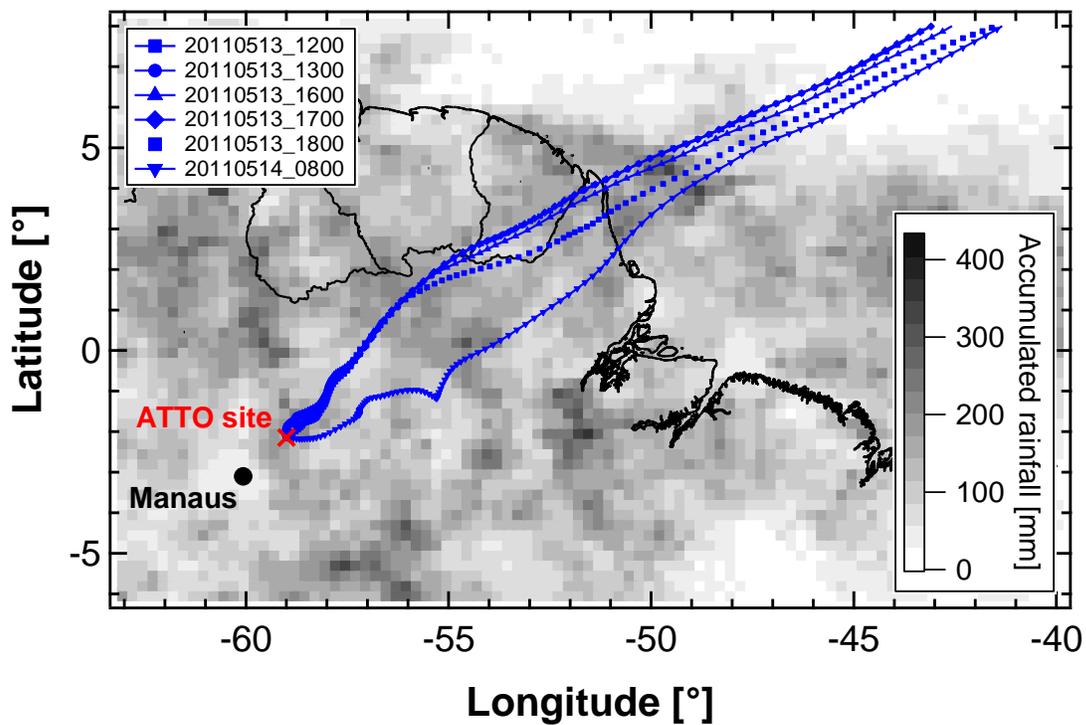


Figure S1. Location of the ATTO site in central Amazonia, Brazil, with back trajectories (HYSPLIT, NOAA-ARL, GDAS1 model, start height 100 m) and cumulative rainfall (tropical rainfall measuring mission TRMM) from 13 to 17 May 2011. Back trajectories are simulated for sampling time of individual impactor samples (Table S1).

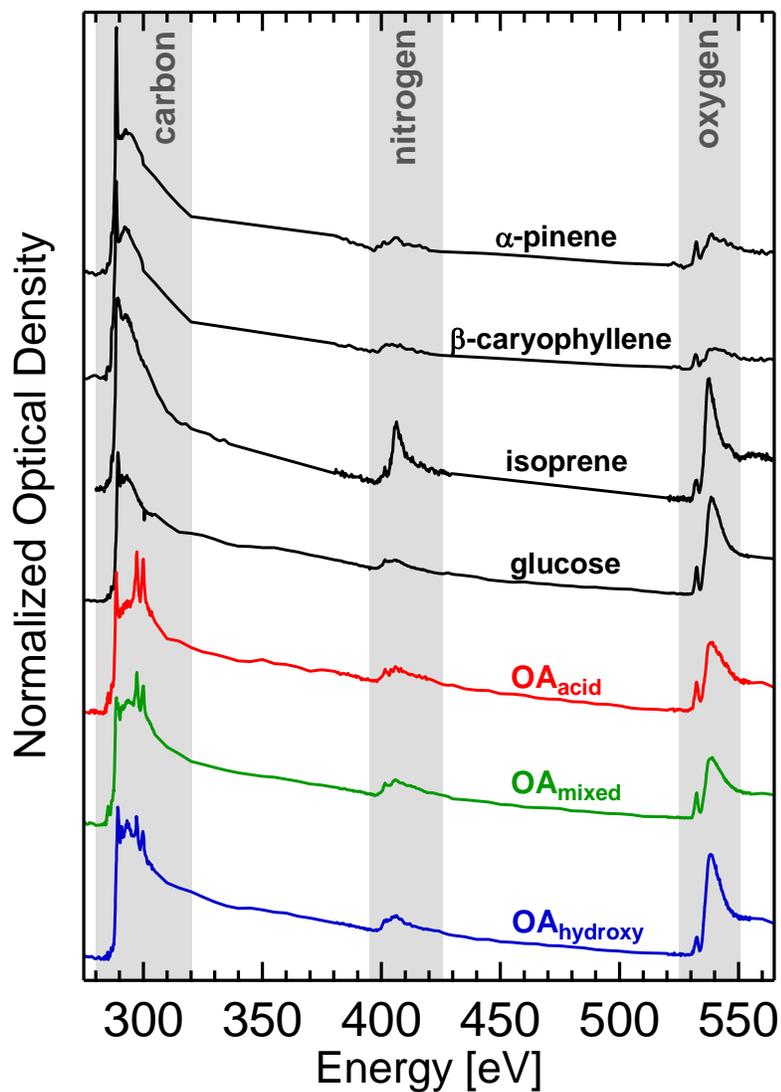


Figure S2. CNO X-ray absorption spectra of (i) laboratory-generated SOA from terpene (α -pinene and β -caryophyllene) and isoprene oxidation, (ii) glucose as reference compound from spray-drying of aqueous solution and (iii) Amazonian OA particles (OA_{acid} , OA_{mixed} , $OA_{hydroxy}$). The spectra cover the K-edges of carbon (283.8 eV), nitrogen (400.0 eV) and oxygen (531.7 eV) as well as the $L_{3,2}$ -edges of potassium (294.6 eV) and calcium (349.3 eV). The carbon edge fine structure for the same spectra is shown in Fig. 2A.

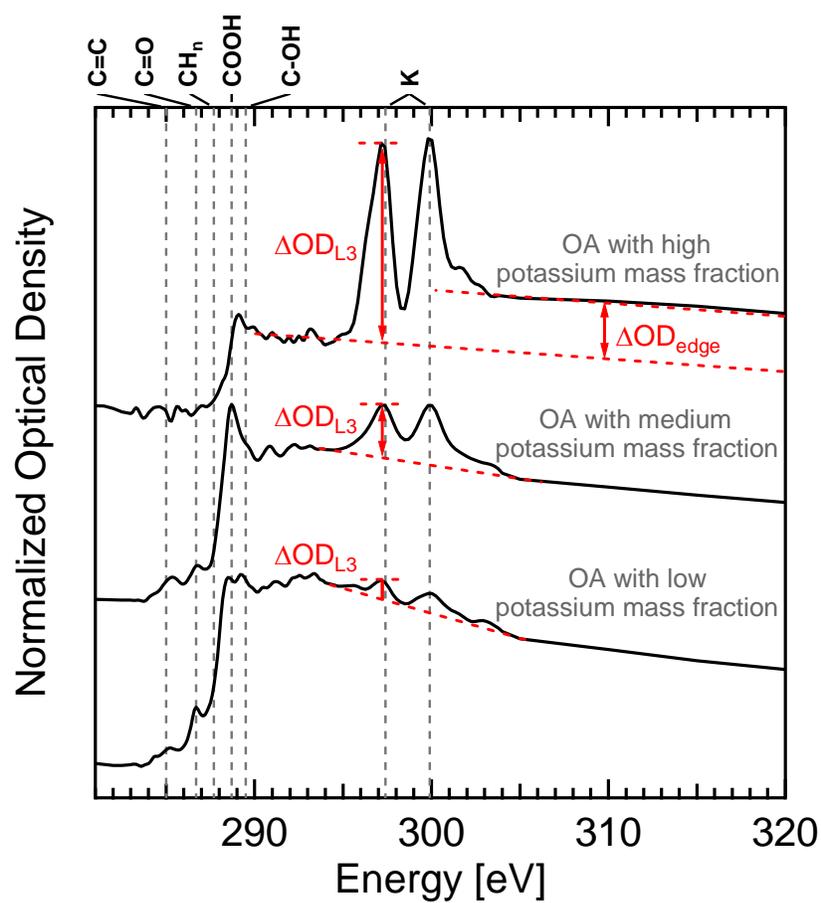


Figure S3. Characteristic spectra of individual Amazonian aerosol particles with different potassium mass fractions. Parameters ΔOD_{edge} and ΔOD_{L3} are used for potassium quantification.

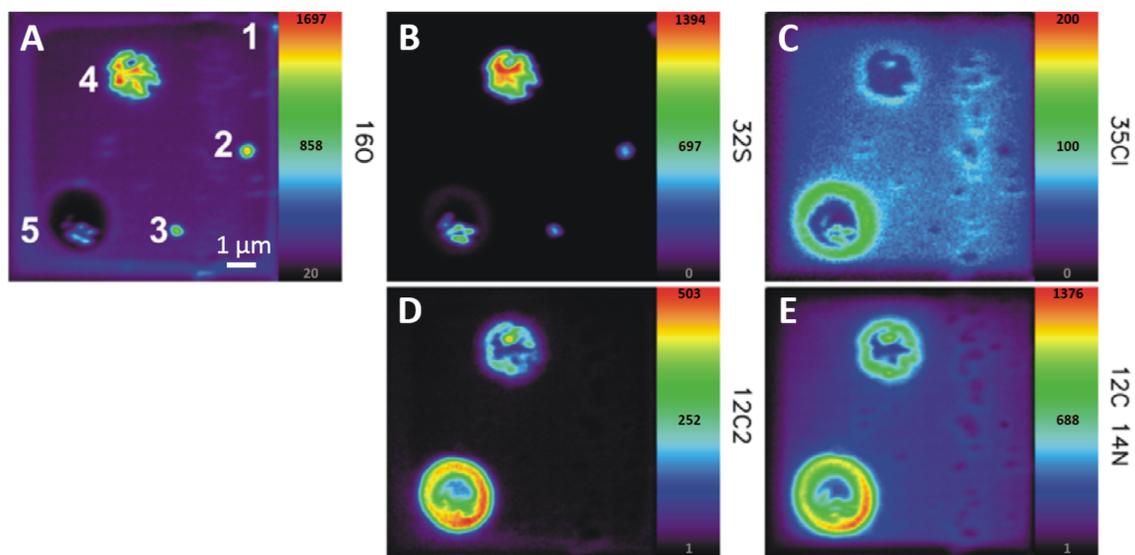


Figure S4. NanoSIMS images exhibiting elemental maps for (A) oxygen, (B) sulfur, (C) chlorine, (D) carbon, and (E) nitrogen of Amazonian aerosol particles. 1, 2, and 3 are small salt-rich particles. 4 and 5 are large OA particles exhibiting pronounced core-shell structures. Color code indicates counts of secondary ions.

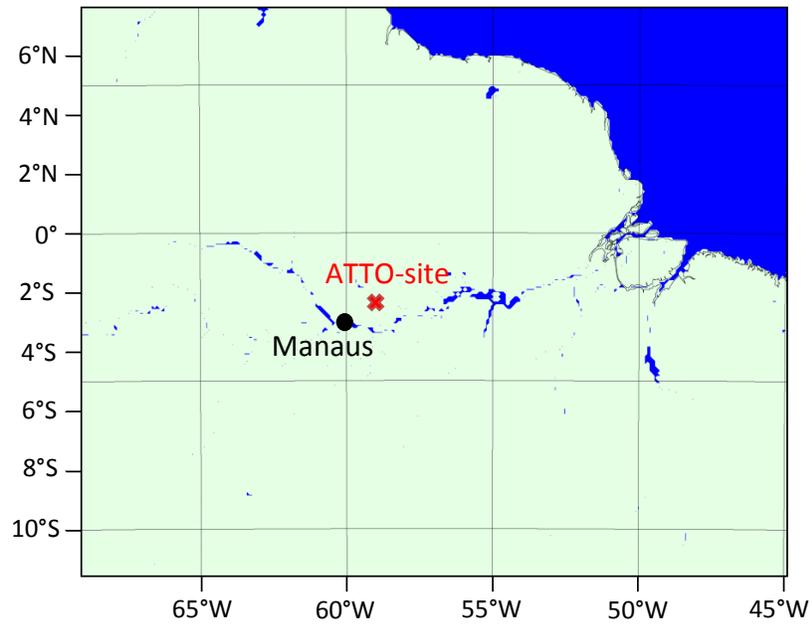


Figure S5. WRF model domain around the sampling location (ATTO site). Updraft velocities were calculated for May 2011 and integrated over the entire rainforest area (green shading).

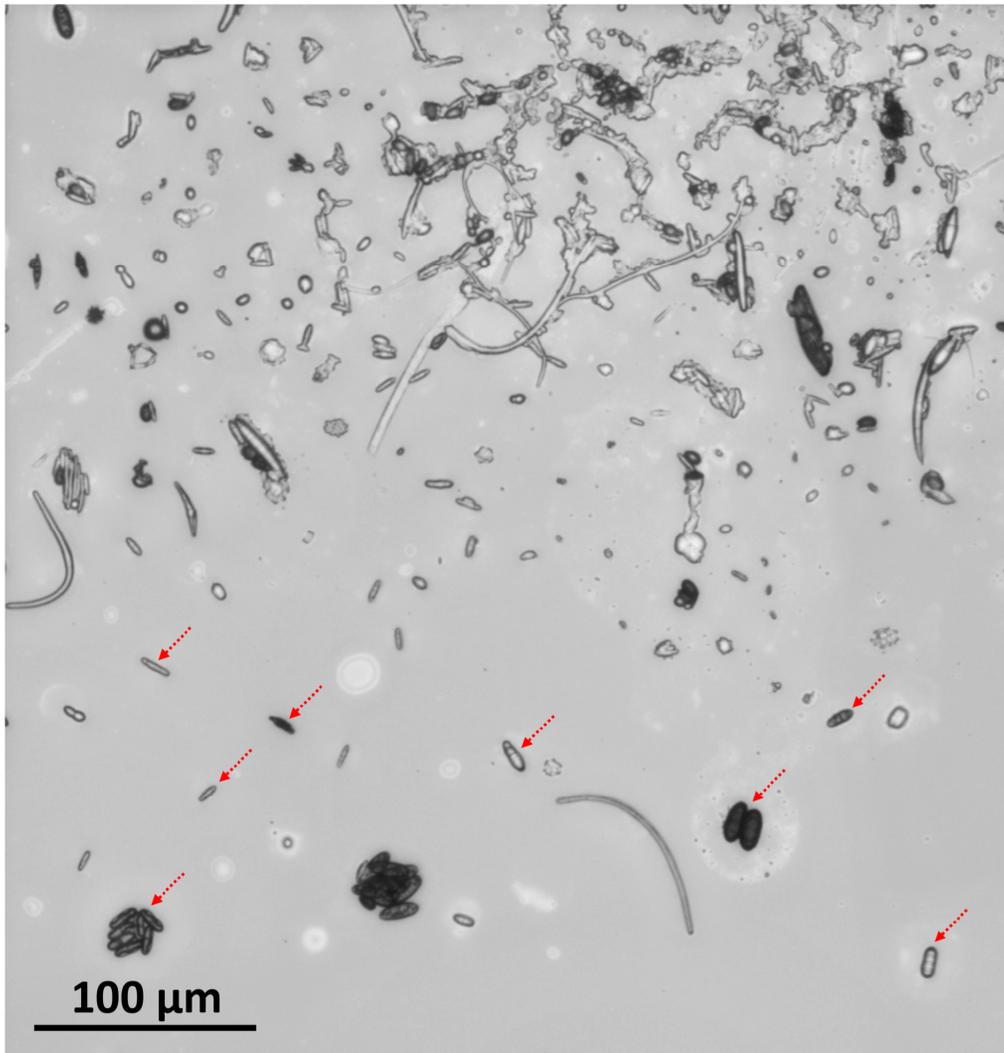


Figure S6. Light microscopy image of coarse mode particles in Amazonian aerosol sample (ATTO_2011_#2; Table S1). A high abundance and diversity of fungal spores was observed (examples are indicated by red arrows).

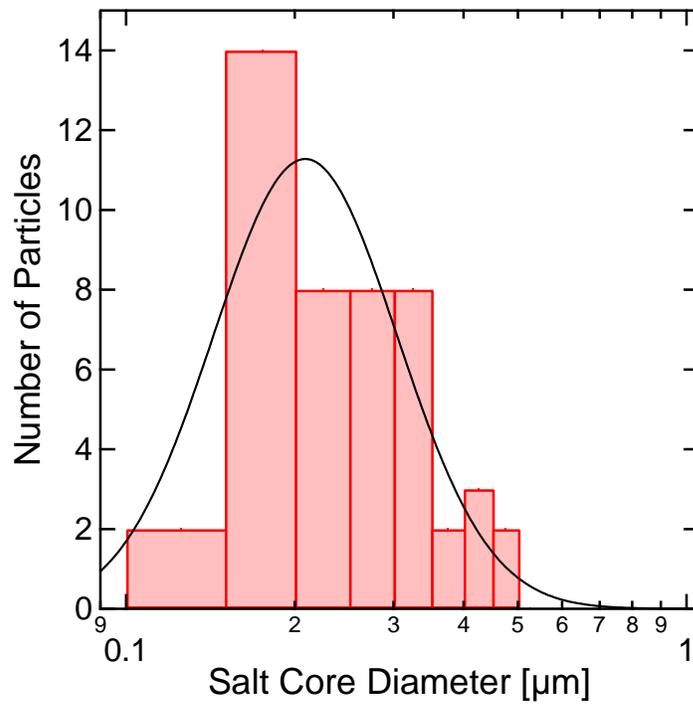


Figure S7. Size distribution of salt cores in the Amazonian aerosol sample ATTO_2011_#10 collected in the morning of 14 May 2011 (Table S1, Sect. 2.1). SEM measurement data (red bars) and lognormal fit (black line) indicate a peak around $\sim 0.2 \mu\text{m}$.

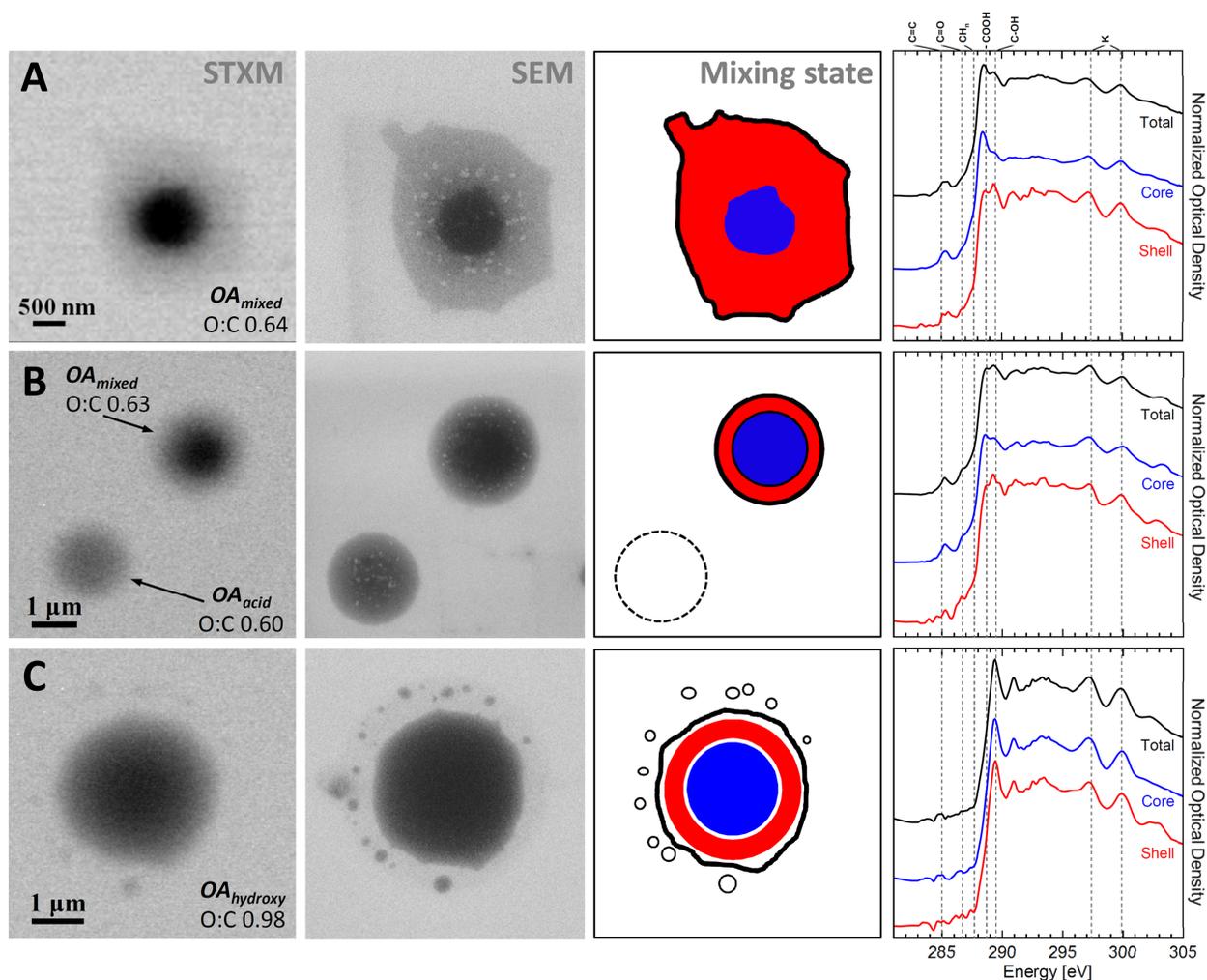


Figure S8. Internal structures of Amazonian organic aerosol particles analyzed by STXM-NEXAFS and SEM. Color code indicates integrated region for corresponding NEXAFS spectra. (A) OA_{mixed} particle with COOH-rich core and thick C-OH-rich coating. (B) OA_{mixed} particle with COOH-rich core and thin C-OH-rich coating. (C) $OA_{hydroxy}$ with homogenous chemical composition. Halos of small satellite droplets were observed for $\sim 50\%$ of $OA_{hydroxy}$ particles ($O:C \approx 0.9-1.0$) but not for OA_{acid} and OA_{mixed} particles ($O:C \approx 0.5-0.7$). The halo satellite droplets were not considered in quantitative analyses of particle size distribution and potassium content.

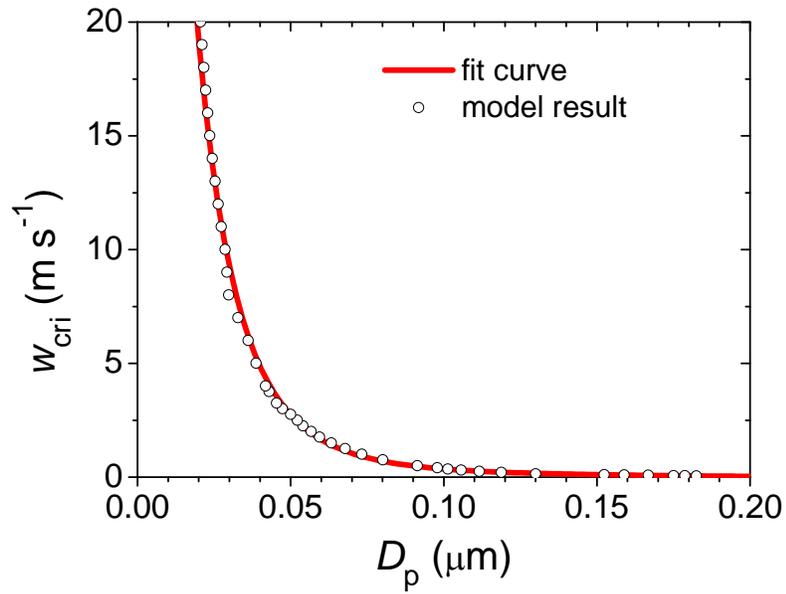


Figure S9. Critical updraft velocity for CCN activation of aerosol particles as a function of particle diameter. The data points are the results of cloud parcel model simulations with detailed spectral microphysics using parameters characteristic for pristine Amazonian aerosols (6, 34). The line is a fit of the form $w_{\text{cri}} = f(D_p) = 10^{(-452 \cdot D_p^3 + 208 \cdot D_p^2 - 40.93 \cdot D_p + 2.021)}$.

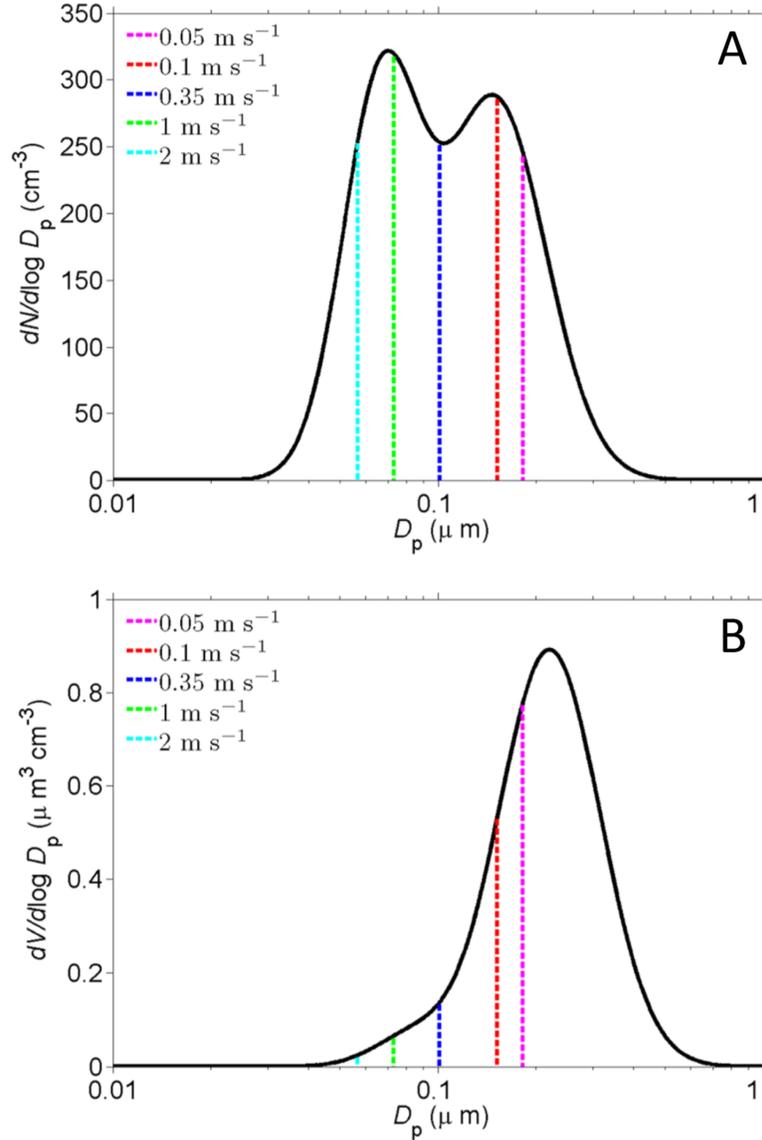


Figure S10. Aerosol size distribution and critical diameters of CCN activation for different updraft velocities ($w = 0.05$ to 2 m s^{-1}) characteristic for pristine Amazonian aerosols. **(A)** Particle number distribution composed of an Aitken mode around $\sim 0.07 \mu\text{m}$ and an accumulation mode around $\sim 0.15 \mu\text{m}$ (6, 34). **(B)** Particle volume distribution corresponding to the bimodal number distribution shown in panel A. Note that the actual volume distribution around $1 \mu\text{m}$ is higher because of coarse particles (primary biological material and mineral dust (6)) that are not included in this analysis, which is focused on the SOA particles dominating the accumulation mode composition.

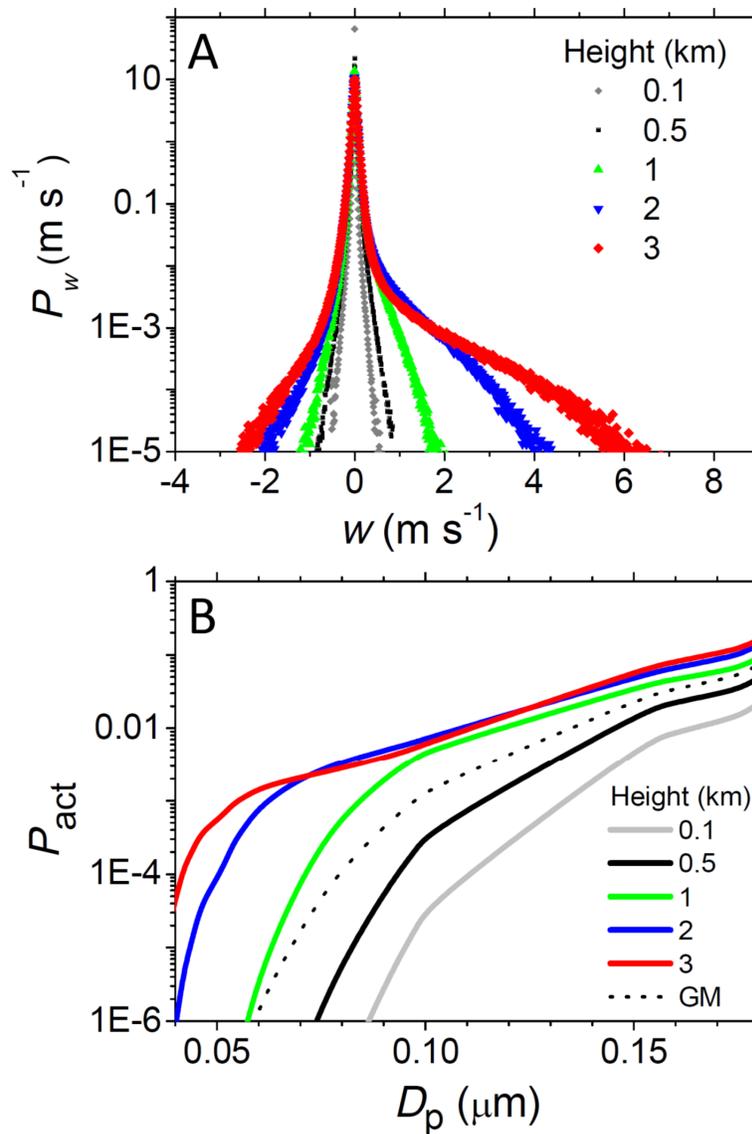


Figure S11. (A) Probability density function, P_w , of atmospheric updraft velocity, w , at different altitudes above the Amazonian rainforest during the wet season as calculated with the Weather Research and Forecast model (WRF-ARW-v3.3.1, Sect. S1.8) for the region and period around the aerosol sampling location and time (Fig. S5, May 2011). (B) CCN activation probability, P_{act} , of particles at diameter D_p . The lines represent results at different heights (GM = geometric mean value).

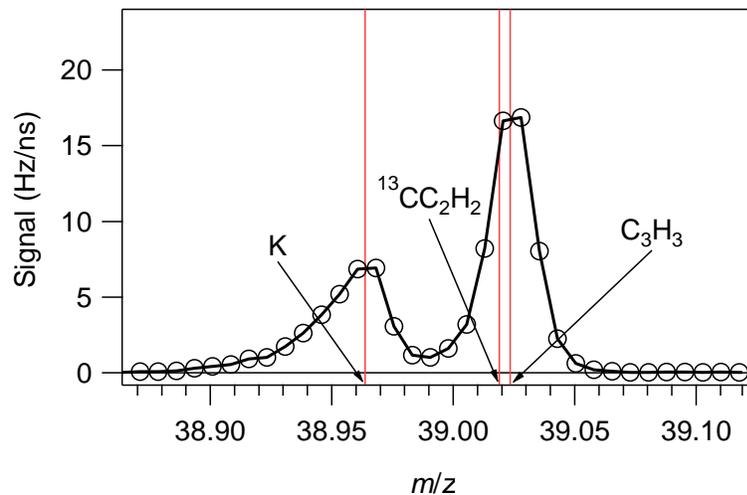


Figure S12. Particle mass spectrum averaged for pristine conditions during AMAZE-08 (“class I”), as detected by high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS, unpublished data) (7, 39).

Table S1. Characteristics of the analyzed aerosol samples.

Sample Name	Sampling Time		Location	STXM setup
ATTO_2011_#1	2011/05/13	11:30-12:20	ATTO site	ALS, BESSY II
ATTO_2011_#2	2011/05/13	12:35-13:15	ATTO site	ALS
ATTO_2011_#7	2011/05/13	15:50-16:23	ATTO site	ALS
ATTO_2011_#8	2011/05/13	16:27-17:07	ATTO site	ALS
ATTO_2011_#9	2011/05/13	17:15-17:55	ATTO site	ALS, BESSY II
ATTO_2011_#10	2011/05/14	07:42-08:42	ATTO site	ALS
ZF2_2010_#3	2010/05/15	06:20-07:20	ZF2/TT34 site	ALS
ZF2_2010_#4	2010/05/15	08:46-09:46	ZF2/TT34 site	ALS
ZF2_2010_#5	2010/05/15	10:25-11:24	ZF2/TT34 site	ALS

Table S2. Experimental parameters for SOA generation in the Harvard Environmental Chamber (GMD = geometric mean diameter, GSD = geometric standard deviation).

VOC	Oxidation	Chamber RH [%]	Ammonium Sulfate Seeds		SOA	
			Dry Diameter [nm]	Concentration [$\mu\text{g m}^{-3}$]	Size Distribution GMD [nm] / GSD	Concentration [$\mu\text{g m}^{-3}$]
Isoprene	photooxidation (H ₂ O ₂ injected, UV lights on)	40	70	2.4	152.4 / 1.44	32.7
α -pinene (+/-)	dark ozonolysis (O ₃ injected, UV lights off)	40	46	1.0	94.2 / 1.58	26.1
β -caryophyllene	dark ozonolysis (O ₃ injected, UV lights off)	40	46	0.5	95.1 / 1.65	18.2

Table S3. Resonance energies of the carbon K-edge NEXAFS features with corresponding functional groups and potassium L-edge transitions. Peak assignments are based on (35, 38, 52, 103-104).

Functionality	Transition	Nominal Energy [eV]
Alkene/aromatic, R(C*=C)R'	1s \rightarrow π^*	285.0 \pm 0.2
Carbonyl groups, R(C*=O)R'	1s \rightarrow π^*	286.7 \pm 0.2
Alkyl, C*H _n (n=1,2,3)	1s \rightarrow $\sigma^*_{\text{C-H}}$	287.7 \pm 0.7
Carboxylic carbonyl, R(C*=O)OH	1s \rightarrow π^*	288.7 \pm 0.3
Hydroxy/ether, OC*H ₂	1s \rightarrow 3p/ σ^*	289.3 \pm 0.2
Potassium, K _{L3}	2p _{3/2} \rightarrow 3d/ σ^*	297.4 \pm 0.2
Potassium, K _{L2}	2p _{1/2} \rightarrow 3d/ σ^*	299.9 \pm 0.2