

**Response to the reviewer 1 comments for “Mixing states of Amazon-basin aerosol particles transported over long distances using transmission electron microscopy” by Adachi et al.**

Referee comments are shown in black, normal font.

5 **Authors replies are shown in red bold font.**

***Revised texts are shown in red, bold and italic font.***

Anonymous Referee #1

In this study, composition of Amazon-basin aerosol particles has been studied using transmission electron microscopy (TEM).  
10 Aerosol particles were collected during the Green Ocean Amazon campaign in 2014 and over 10000 particles were analyzed. TEM has a very high spatial resolution, which allows the analysis of the composition of individual particles in very detail. However, it has some disadvantages such as particle evaporation during analysis. The results showed that particles have different composition, size distribution and number fractions based on they origin and the particles were mixed to more complex structures during their transport in the atmosphere. In general, aerosol particles play an important role in atmospheric  
15 processes and the composition of particles is necessary to know when they influence on the climate is studied. Thus, the study is important and topical. To my knowledge, this kind of detailed study on individual particles by TEM has not been done before from Amazon-basin particles. Furthermore, it reveals novel information of particle composition, origin and transport. The used methods are very suitable for analysis of composition of individual particles. The manuscript (MS) is quite well organized and written. The content on the MS is in the scope of journal. Thus, the MS is suitable for publication in this journal.  
20 However, I have some comments, suggestions and technical corrections that should be considered and discussed before publication.

**Authors reply: We appreciate the reviewer’s comments to improve our manuscript. We considered all reviewer’s comments and revised our manuscript based on the suggestions.**

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1-1. Main comment:

The main conclusion is that many aerosol particles change their composition by mixing during transport. TEM results showed that analyzed particles are often mixtures of particles from different origins (and composition) indicating that particles have been coagulated in the atmosphere during the transport. How have you ensured that the particles have not just agglomerated  
30 on the TEM grid during collection? Have you estimated how many particles per unit area you can collected onto TEM grid in order to avoid particles agglomeration during sampling (i.e. the particles are separately on TEM grid)? Please estimate particle agglomeration on TEM grid and clarify this in the revised version of MS.

**The particle concentrations on the substrates in the Amazon samples were generally much lower than those in urban  
35 plume samples (e.g., Tokyo, Japan; Adachi et al. 2016) because of the clean environment in the Amazon basin. We chose 30 min sampling time with 1 L/min flow rate, and the sampling condition worked well for collecting particles with not too sparse but not having many agglomerations. The medium number concentration is 0.16 particle per  $\mu\text{m}^2$ , and the total particle area over the analyzed area is 7%. The results indicate that most particles are dispersed on the substrates. We also avoided areas that having overloaded particles, i.e., the area just below the impactor nozzle tends  
40 to have too many particles. Comparing to uniform substrates (e.g., formvar substrates), lacey carbon substrates prevent liquid particles from spreading over the substrate and forming mixed particles on the substrate.**

**Nevertheless, although we minimized the possibility to having agglomerated particles on the substrates, it is still possible that some particles were overlapped on the substrate when collected. If such particles occurred, we would overestimate**

the number fractions of internally mixed particles. Based on the particle area over the analyzed area (7%), we estimated the uncertainty is at most 10% and mentioned the value in the revised text.

*The lacey carbon substrates minimize interference from the substrate during the particle composition measurements and a spread of liquid particles over the substrate. We used 30-min collection times at a 1.0 L/min flow rate to have appropriate particle number concentration on the substrates.*

We randomly chose two to seven areas that do not have too many particles with a magnification of 6,000 (23×23 μm) to avoid particles that overlap on the substrate. Each field of view includes ~74 particles on average, resulting in ~7% of particle area among the field of views. As a result, we reduced the chance to analyze particles that agglomerate on the substrate. Nevertheless, it is still possible that some particles overlapped on the substrates. We evaluate that the overestimation for the number fraction measurements of internally mixed particles is less than 10% based on the particle area fractions.

Specific comments/technical corrections:

1-2. Structure of the MS is now: 1 Introduction, 2 Methods, 3. Results, 4 Discussion, and 5 Conclusions. The structure where Results and Discussion are combined into one chapter could be clearer. Now Results chapter also contains some discussion.

**The sections “3 Results” and “4 Discussion” are combined to “3 Results and discussion”. The discussion section is revised to “3.3 Possible mixing processes and implications to the climate”**

1-3. Line 186: . . . shows a positive correlation => Please indicate correlation coefficient/R<sup>2</sup>.

1-4. Line 197-198: . . . show a positive correlation => Please indicate correlation coefficient/R<sup>2</sup>.

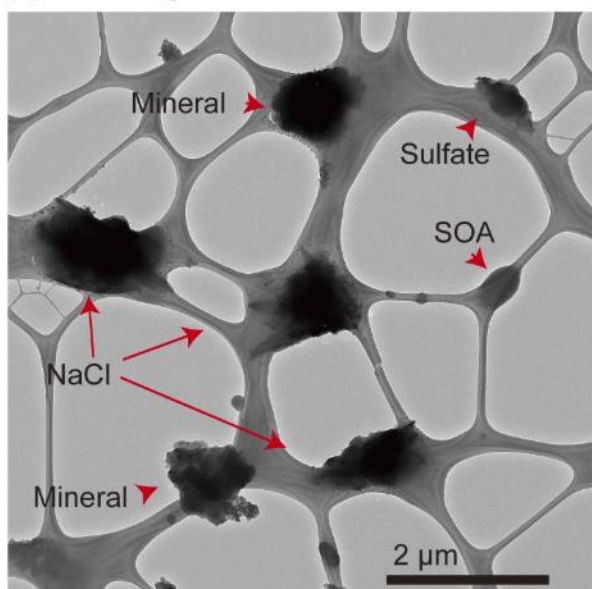
**R<sup>2</sup> values were added to the caption.**

*Coefficients R<sup>2</sup> of determination for (a), (b), and (c) were 0.60, 0.47, and 0.24 for the LRT period samples and 0.18, 0.66, and 0.40 for other samples, respectively. Trend lines are shown in red and blue broken lines for LRT period and other samples, respectively. The correlation between Si and Al for other samples (a) is relatively low because of possible contributions from two sources (LRT and local dusts).*

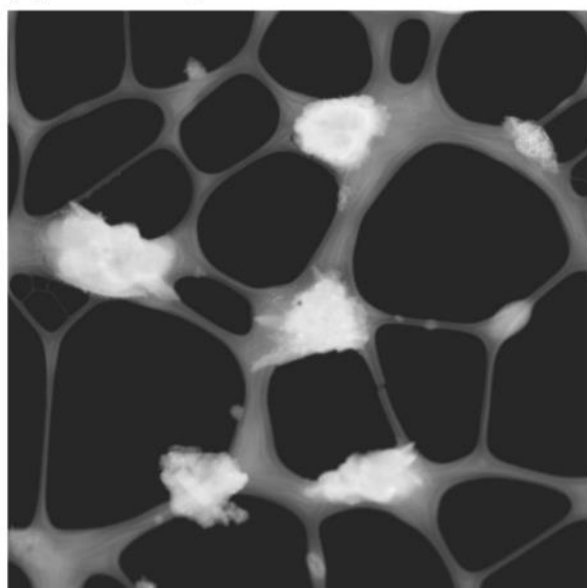
1-5. Line 238-239: Na, Mg, and Cl are commonly used tracers of sea-salt particles. . . => Why element map for Mg is not shown in the figures?

**Mg-mapping images were added in the revised Figure 11. A lack of figure space was the reason for not having the Mg mapping image in the original figures, and thus we divided the figure into two.**

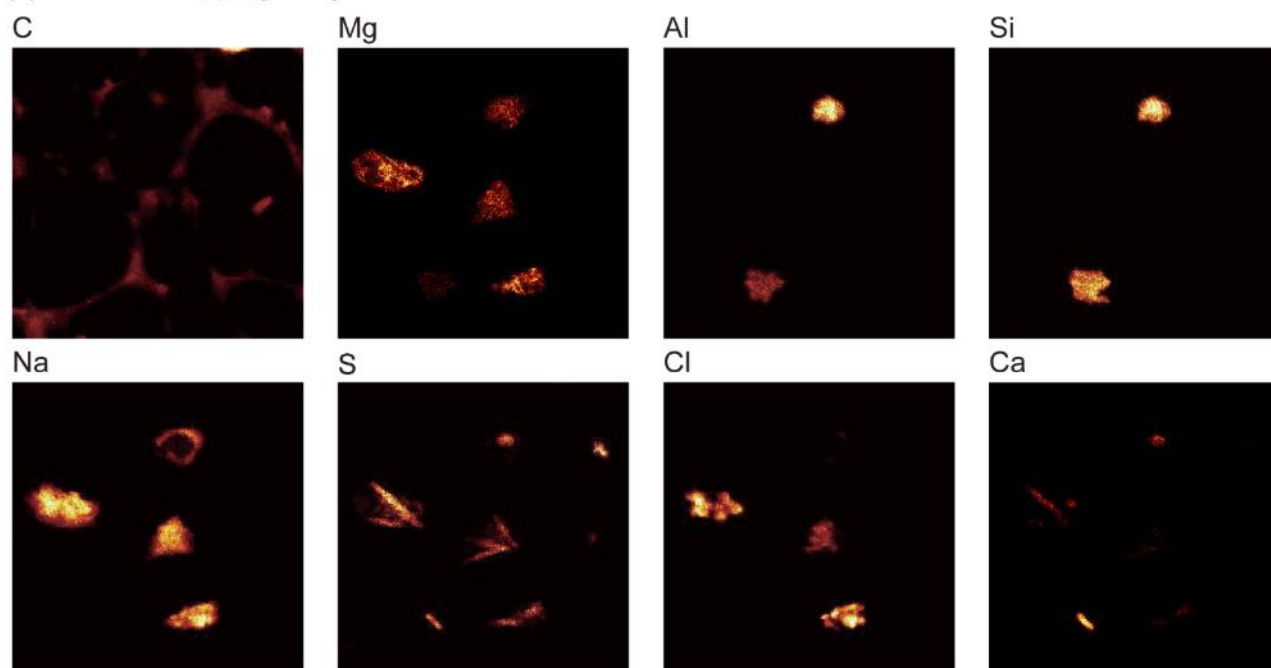
(a) TEM image



(b) STEM image



(c) Element mapping images



*Figure 11. Shapes and compositions of sea-salt particles. (a) TEM, (b) STEM, and (c) element mapping images of sea-salt and mineral particles. These sea-salt particles also contain S as sulfate. The sample was collected from 12:00-12:30, 2 February, 2014.*

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85 1-6. Line 245-246: The deformed shapes of Na-bearing particles on the substrate suggest that they were hydrated when collected (Fig. 7). => Is it possible that particles are already hydrated before collection in the atmosphere? Please clarify.

**Yes. The text was revised.**

90 *The deformed shapes of Na-bearing particles on the substrate suggest that they were hydrated in the atmosphere and on the substrates when collected (Fig. 11).*

1-7. Line 322: . . . form internally mixed particles => Is the impact of internally mixed particle of climate different than that of externally mixed particle?

95 **Yes. We mentioned the effect in this section and the conclusion.**

*Although such complex mixing states are common for anthropogenic aerosol particles (e.g., Ching et al., 2019), we found that particles from natural sources can also be mixed during LRT and form internally mixed particles, resulting in different hygroscopicity and optical properties.*

*Conclusion:*

100 *When mineral particles or other hydrophilic-primary particles are mixed with sea salt or sulfate, they can absorb water efficiently, resulting in increasing CCN activity, changing the optical properties, and accelerating their removal from the atmosphere, all of which should be taken into account when considering their actual occurrence in the atmosphere to evaluate their climate influences.*

105 1-8. Line 330-331: Sea-salt and sulfate particles commonly occur on the surfaces of mineral and PBA particles. => Is the simple reason that they are just wetted in the atmosphere (or during sampling)? Please clarify in the MS.

**We think that there are two possible processes to form the mixtures. First process is coagulation, which is a process that, for example, sulfate particles collide with mineral dust particles in the atmosphere. Both hydrated and non-hydrated sulfate (and sea salt) can coagulate with mineral-dust particles. Second possible mixing process is condensation. Gases  $\text{H}_2\text{SO}_4$ , for example, condenses on the mineral-dust surface. Hydrated particles can spread over a substrate and form an internal mixture when they directly deposit on the post-deposit particles on the substrate. However, the process is not the main process to form the mixed particles, as mentioned in our reply in 1-1. As the LRT particles have more processed mixed particles than other background particles, we interpret that the mixings mainly occurred during the LRT.**

*As the LRT particles have more processed mixed particles than other background particles, we interpret that the mixings mainly occurred during the LRT through coagulation, condensation, or both.*

References:

120 1-9. Authors of the MS have many own references in the reference list (e.g. Adachi 7 the first author references, Artaxo 5). Please check that all references are needed and remove unnecessary references.

**We removed Adachi and Buseck (2011) and Artaxo et al. (1988) from the reference list as the references overlap with others.**

125  
Figures:

**The authors' general comments for figures: The original figures were partially unclear because of low resolutions in the pdf file (due to the size limit of the pdf file). We hope the problem will be clarified when published on ACP. We also divided some figures into two so that we can have more space for each panel.**

130 1-10. Figure 1. The smallest fonts are too small, practically texts are not readable (legend texts, x-axis labels, periods text). Please increase font size (double it in the smallest ones).

The figure 1 was revised and divided into two figures (Figs. 1 and 2) to have a space for large texts and additional TEM images.

1-11. Figure 2. Too small fonts. Color bars too small (especially (c)). Yellow shaded area is too light to see, especially in print (a).

Revised. The figure was divided into two figures (Figs. 3 and 4) to have a space for large texts and color bars.

1-12. Figure 3. Data points and error bars not clear in (d)–(f). Fonts of numbers too small. Please plot 1:1, 1:2 or 1:n lines show assumed relations (or trendlines with  $R^2$  values).

The figure was revised and divided into two figures (Figs. 6 and 7) to have a space for large texts and an additional TEM image (Mg). Trend and 1:n lines are added.  $R^2$  values were also added to the caption.

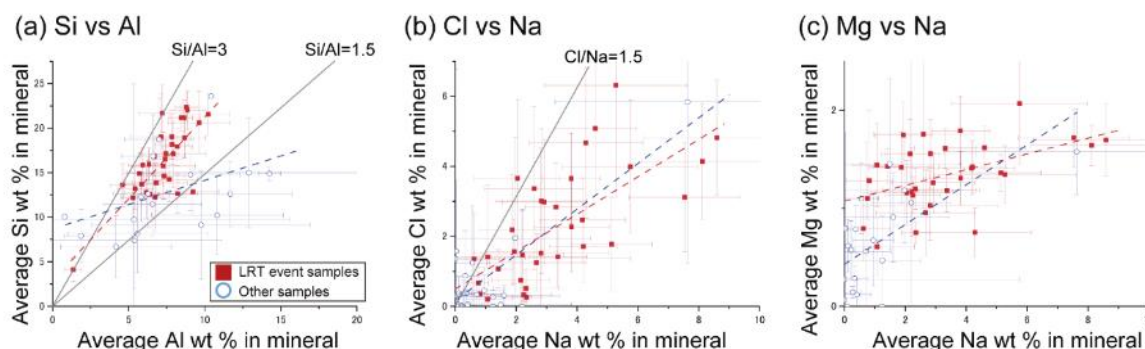


Figure 7. Relations (a) between average Si and Al weight % in mineral particles, (b) between average Cl and Na weight % in mineral particles, and (c) between average Mg and Na weight % in mineral particles. Red squares indicate sample averaged values for LRT period samples. Blue open circles indicate sample average values for other (non-LRT period) samples. The sample from 9:00 on 6 February had only one mineral particle and is not shown in the plots because it has a large Al fraction and no Na (0, 30, and 1 weight % for Na, Al, and Si, respectively). Coefficients  $R^2$  of determination for (a), (b), and (c) were 0.60, 0.47, and 0.24 for the LRT period samples and 0.18, 0.66, and 0.40 for other samples, respectively. Trend lines are shown in red and blue broken lines for LRT period and other samples, respectively. The correlation between Si and Al for other samples (a) is relatively low because of possible contributions from two sources (LRT and local dusts). Error bars indicate the 95% confidence intervals.

1-13. Figure 4. Too small fonts (especially legend texts) and unclear plots. Please make clearer plots. Sulfates, carbonaceous and K-bearing have the highest values at smaller particles. Are they formed via new particle formation? What is reason?

The figure was revised. Carbonaceous and sulfate particles have the highest number fraction at the smallest size bin, although K-bearing particles have the highest number fraction at ~400 nm (the third bin). The size distributions in our study generally agree with that in Pöschl et al. (2010). New particle formation hardly occurs near the ground in the Amazon basin (e.g., Pöhlker et al., 2012) but can happen in the lower free troposphere (Wang et al., 2016). Particles

from new particle formation are transported to the boundary layer, and condensation on such preexisting particles can be a pass to form these particles.

170 *Wang et al. (2016a) showed that small particles are transported from the free troposphere into the boundary layer by vertical transports during precipitation events, and such particles can be nuclei of the SOA particles in the background condition. The size-dependent number fractions of samples from other period are roughly consistent with the results during the AMAZE-08 campaign (Pöschl et al., 2010).*

**References:**

175 Pöhlker, C. et al.: Biogenic Potassium Salt Particles as Seeds for Secondary Organic Aerosol in the Amazon, Science, 337, 1075-1078, 10.1126/science.1223264, 2012.

Pöschl, U. et al.: Rainforest Aerosols as Biogenic Nuclei of Clouds and Precipitation in the Amazon, Science, 329, 1513-1516, 10.1126/science.1191056, 2010.

180 Wang, J., et al.: Amazon boundary layer aerosol concentration sustained by vertical transport during rainfall, Nature, 539, 416-419, 10.1038/nature19819, 2016a.

1-14. Figure 5. Plot d) is unclear.

**The figure was revised.**

185 1-15. Figure 6. Does water vapor change the shape of PBA particles (see e.g. 2nd image form bottom/left)? Please clarify.

**It is possible. PBA particles can absorb water and change their shapes. We added the following sentence in the caption. As these PBA particles were observed under vacuum, they can have inflated shapes when observed in an ambient condition.**

190 1-16. Figure 7. Plots d)-f) are unclear (too small fonts).

**The figure was revised and divided into two figures (Figs. 10 and 11) to have a space for large texts**

1-17. Supporting Figure 3a, 4a and 5a. Please indicate acronym PBOA (PBA?).

195 **PBOA should be PBA. The figures were corrected.**

200 **Response to the reviewer 2 comments for “Mixing states of Amazon-basin aerosol particles transported over long distances using transmission electron microscopy” by Adachi et al.**

Referee comments are shown in black, normal font.

**Authors replies are shown in red bold font.**

205 ***Revised texts are shown in red, bold and italic font.***

Anonymous Referee #2

Received and published: 4 July 2020

The study works on individual aerosol particles collected in Amazon basin where is important for carbon cycle as the green  
210 ocean in the world. The authors collected the aerosol particles during the Green Ocean Amazon campaign at T3 site. They  
used TEM to analyzed different kinds of particles during the LRT particles. They carefully divided particle types based on  
their compositions and mixing states. Also, they accounted for their number fractions and compared them during LRT and  
non-LRT periods in the Amazons. Certainly, the study is critical important to understand properties of background aerosols  
and LRT particles in the Amazons. Finally, they found these particles are internally mixed particles, in particular, sulfate and  
215 sea salts as important coatings. Therefore, I think that the knowledge is filled into the gaps in the Amazon.

Before the paper accepted, I would like have some minor comments here.

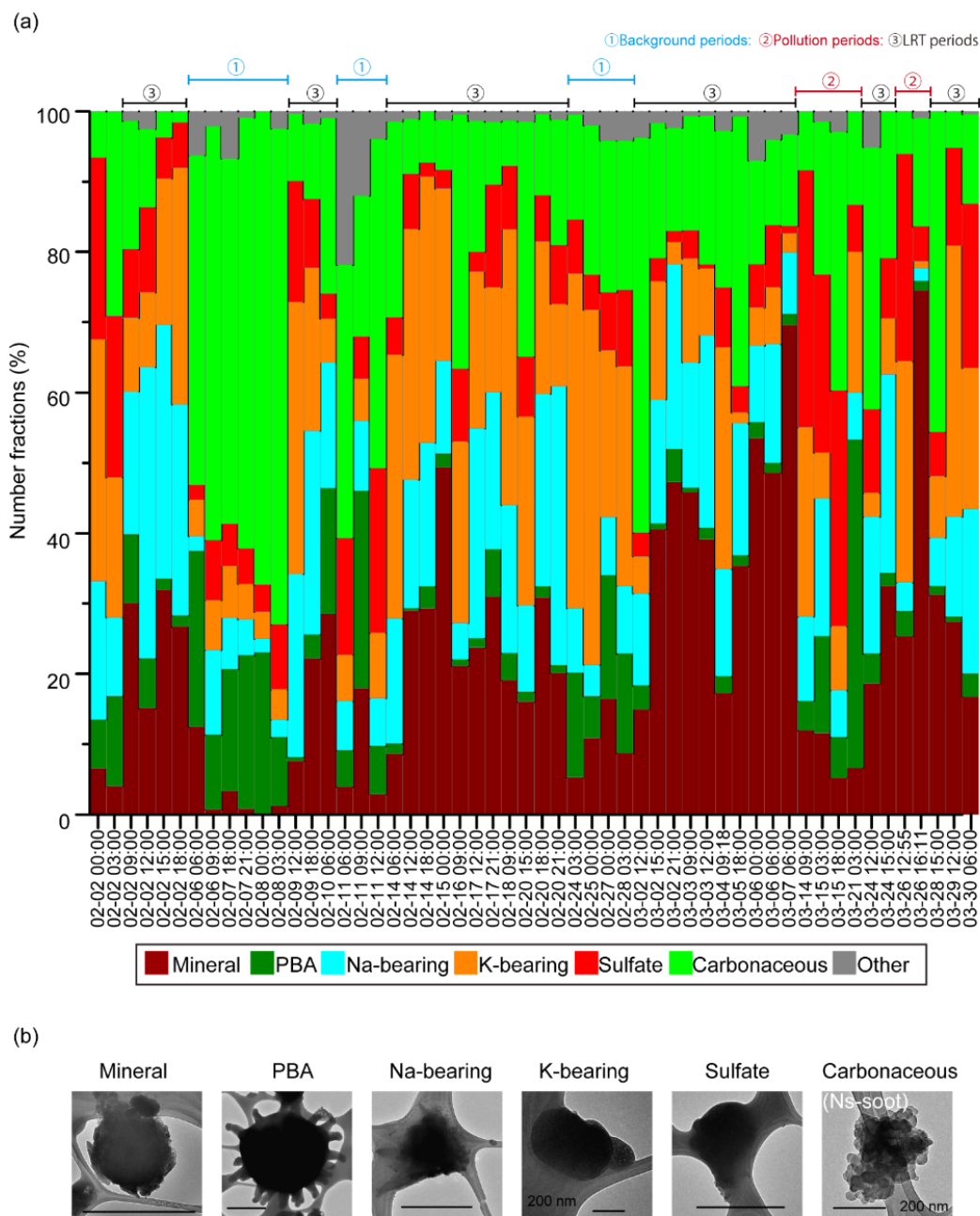
**Authors reply: We appreciate the reviewer’s comments to improve our manuscript. We considered all reviewer’s  
comments and revised our manuscript based on the suggestions.**

220

2-1. (1) I might suggest that the authors need to add clear TEM images as the Figure 1 including different types of particles,  
such as K-bearing, Sulfate, soot, and mineral particles. Then you can give the Figure showing their number fractions. The  
potential readers might be know better clear the particle types.

225 **We added representative TEM images of each particle type in the revised Fig. 1.**





**Figure 1.** Number fractions of each aerosol particle type for all analysed samples (a) and the representative TEM images of each particle type (b). Scale bars for Mineral, PBA, Na-bearing, and sulfate are 1  $\mu\text{m}$ , and those for K-bearing and carbonaceous are 200 nm. Compositions and low-magnification images of these particles are shown in Fig. S2 (mineral), Fig. S5 (PBA), Fig. 11 (Na-bearing), Fig. S7 (K-bearing), Fig S8 (sulfate), and Fig. S7 (carbonaceous). Samples were divided into LRT and other periods (bars in the panel (a)). Other periods were further divided into pollution periods (14, 15, and 26 March, 2014) and background periods (all other periods except the pollution periods and 2 February, 2014) based on the classification by de Sá et al. (2018). Samples collected on 2 February were outside of the measurement period by de Sá et al.

2-2. (2) It is better to add more discussion. I noticed that they didn't deploy more discussion in discussion part. I might suggest that you need to consider the result from LRT and non-LRT. What are they different? And how could they have large impacts on ecology or climate? Also, the authors can add discussions on mixing structure of different aerosol components. These could be have more literature and scientific discussion should be enhanced.



We combined the results and discussion sections in the revised manuscript (please also see our reply to 1-2). Now we have only “results and discussion” section and have more discussion than the original based on the reviewers’ suggestions.

#### 245 Examples of additional discussions.

*The size-dependent number fractions of samples from other period are roughly consistent with the results during the AMAZE-08 campaign (Pöschl et al., 2010).*

*Nitrate can also react with NaCl and form sodium nitrate. However, we did not observe it in this study because of lower concentrations of nitrate than sulfate during the campaign (de Sá et al., 2018) and insensitivity of nitrate detection in the*

250 *current TEM analysis.*

*Wang et al. (2016a) showed that small particles are transported from the free troposphere into the boundary layer by vertical transports during precipitation events, and such particles can be nuclei of the SOA particles in the background condition. As the LRT particles have more processed mixed particles than other background particles, we interpret that the mixings mainly occurred during the LRT through coagulation, condensation, or both.*

255

Some minor comments:

2-3. L58: coated by acidic gas condensation

**Revised as follows.**

260 *Aerosol particles coagulate and can become coated by volatile organic compounds or acid gas condensation.*

2-4. L165 during the IOP1 (Figure 2)

**It was revised as follows.**

265 *The model simulation shows that the horizontal distributions of mineral dust concentration at the surface level during the six LRT periods and the vertical distributions on 7 March, when the largest LRT periods occurred during IOP1 (Fig. 4).*

2-5. L200, Did you observe the NaNO<sub>3</sub>? NaCl can easily react with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> forming NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>.

270 We do not have evidence of NaNO<sub>3</sub> in our measurements, although we observed sodium sulfate (original Fig. 7, now Fig 11) and ammonium sulfate (Fig. S8). The possible reasons are as follows. First, nitrate concentration was low, i.e., ~20% of that of sulfate; 0.03-0.12 (nitrate) and 0.15-0.57 (sulfate) μgm<sup>-3</sup> (de Sa et al., 2018). Second, nitrate can be volatile and be lost during sampling, storage, and analysis. Third, TEM analysis is insensitive to detect nitrate when it occurs with ammonium sulfate because both include N. Fourth, we measured relatively small sea-salt particles, whereas

275 nitrate prefers to stay with large particles. We added the following explanation in the revised text.

*Nitrate can also react with NaCl and form sodium nitrate. However, we did not observe it in this study because of lower concentrations of nitrate than sulfate during the campaign (de Sá et al., 2018) and insensitivity of nitrate detection in the current TEM analysis.*

de Sá, S. S., et al.: Urban influence on the concentration and composition of submicron particulate matter in central Amazonia, *Atmospheric Chemistry and Physics*, 18, 12185-12206, 10.5194/acp-18-12185-2018, 2018.

280

2-6. L223, you observed the 600 nm and >2  $\mu$ m. Recently, Li et al., (2020) found two modes, suggesting different types of biological particles. I am wondering whether the authors observe observed more types with different morphologies. Here the PBA name can be changed to PBAP. PBAP can be more acceptable in many studies such(Després et al., 2012); (Pöhlker et al., 2012); (Li et al., 2020).

**We did not find specific bioaerosol particles in the small size. We think fragmented fungal spores (China et al., 2016) contributed to these particles. Although both PBA and PBAP are used for the acronym, we prefer keeping PBA in our manuscript because we termed aerosol species as xx + particle (e.g., sea-salt + particle and mineral + particle). Please find that Pöhlker et al. (2012) uses “primary biological aerosols (PBA)” in their Fig. 4.**

*These particles include fungal spores, pollen, bacteria, algae, protozoa, and fragments of plants and organisms (Després et al., 2012; Li et al., 2020) and are known sources of K, Na, P, Cl, and Fe in the Amazon basin (Artaxo et al., 1993; Krejci et al., 2005; Wu et al., 2019).*

**PBA particles >2  $\mu$ m show unique shapes (Fig. 9), whereas small PBA particles can include fragmented fungal spores (China et al., 2016).**

2-7. L227-229, The diurnal variations can commonly occur in the forests in the worlds. The emission mechanisms could be very complicated depending on winds, RH, and Temperature on plants and soil (Li et al., 2020)(Elbert et al., 2007).

**Agree. We revised the sentence as followed.**

*The number fractions of PBA particles during the night can be enhanced by high relative humidity (RH), which increases active PBA particle emissions from plants, wind speed, and temperatures (Li et al., 2020; Elbert et al., 2007; Graham et al., 2003; Huffman et al., 2012; Whitehead et al., 2016).*

2-8. L251, Again, what about nitrate.

**We added the following sentence here.**

*Nitrate can also react with NaCl and form sodium nitrate. However, we did not observe it in this study because of lower concentrations of nitrate than sulfate during the campaign (de Sá et al., 2018) and insensitivity of nitrate detection in the current TEM analysis.*

2-9. L270, Here the authors found 10% sulfate. Maybe need to add one TEM image to show their morphology in Figure 1?

**We added a sulfate image in Fig. 1 as well as in Fig. S8.**

2-10. L289, Maybe add one TEM image showing the SOA and POA? As the authors found many sulfate particles. The SOA is internally mixed with sulfate as its coating? For example, Li et al. (2016) shows most of SOA coat on secondary inorganic particles in the forest and remote air.

**SOA can be a coating over sulfate or others. We added a sentence in Fig. S8 caption. The representative images are shown in Fig. S3, S8, and S9. SOA was also marked in revised Fig. 11.**

*Carbon occurs around the sulfate, showing that the sulfates are coated by secondary organic matters and have ns-soot inclusions.*

325

2-11. L294, why did the authors used biofuel not biomass here?

**During the wet season, there is almost no biomass burning. Instead, local residents burn biofuel for cooking or brick kilns, which contributes to the source of ns-soot.**

330 *Ns-soot particles that are internally mixed with K-bearing particles can originate from LRT (Saturno et al., 2018) or local biofuel burning for cooking or brick kilns (Martin et al., 2016).*

2-12. L308 other aerosol components

335 2-13. L309 form various internal mixtures. As Li et al., raise the concept models of mixing structure. The sulfate can be core with SOA coating. They also can be coating on mineral, POA or others.

**The sentence was revised as follows. Please also see our replies to 2-10.**

*Sulfate particles are commonly coagulated or condensed with other aerosol components to form various internal mixtures.*

340

# Mixing states of Amazon-basin aerosol particles transported over long distances using transmission electron microscopy

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350 Joel F. de Brito<sup>3,b</sup>, Paulo Artaxo<sup>3</sup>, Glauber G. Cirino<sup>4,c</sup>, Arthur J. Sedlacek III<sup>5</sup>, Peter R. Buseck<sup>6</sup>

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**Abstract.** The Amazon basin is important for understanding the global climate both because of its carbon  
360 cycle and as a laboratory for obtaining basic knowledge of the continental background atmosphere. Aerosol particles play an important role in the climate and weather, and knowledge of their compositions and mixing states is necessary to understand their influence on the climate. For this study, we collected aerosol particles from the Amazon basin during the Green Ocean Amazon (GoAmazon2014/5) campaign (February to March 2014) at the T3 site, which locates about 70 km from Manaus, and analyzed using  
365 transmission electron microscopy (TEM). TEM has better spatial resolution than other instruments, which enables us to analyse the occurrences of components that attach to or are embedded within other particles. Based on the TEM results of more than 10,000 particles from several transport events, this study shows the occurrences of individual particles including compositions, size distributions, number fractions, and possible sources of materials that mix with other particles. Aerosol particles during the wet season were  
370 from both natural sources such as the Amazon forest, Saharan desert, Atlantic Ocean, and African biomass burning and anthropogenic sources such as Manaus and local emissions. These particles mix together at an individual particle scale. The number fractions of mineral dust and sea-salt particles increased almost three-fold when long-range transport (LRT) from the African continent occurred. Nearly 20% of mineral dust and primary biological aerosol particles attached sea salts on their surfaces. Sulfates were also  
375 internally mixed with sea-salt and mineral dust particles. The TEM element mapping images showed that several components with sizes of hundreds of nanometres from different sources commonly occur within individual LRT aerosol particles. We conclude that many aerosol particles from natural sources change their compositions by mixing during transport. The compositions and mixing states of these particles after emission result in changes in their hygroscopic and optical properties and should be considered when  
380 assessing their effects on climate.

## 1 Introduction

The Amazon basin can exhibit clean atmospheric conditions at times during the wet season and thus is uniquely useful for understanding aerosol particles from natural background sources (Martin et al., 2010a, 2016). Natural aerosol particles are important for meteorological and climatological influences on this region. Knowledge of background atmospheric conditions is critical for understanding pre-industrial conditions and, in turn, the climate changes caused by human activity (Andreae 2007; Carslaw et al., 2013; Wang et al., 2016a). To understand the sources, abundances, sizes, and compositions of Amazon aerosol particles, various atmospheric measurements have been conducted such as the Amazonian Aerosol Characterization Experiment 2008 (AMAZE-2008), South American Biomass Burning Analysis (SAMBBA), and the Green Ocean Amazon (GoAmazon2014/5) campaigns (Andreae et al., 2015; Bateman et al., 2015; Brito et al., 2014; Cirino et al., 2018; Martin et al., 2010a, 2016, 2017). As a result, long-range transport (LRT) from Africa and the Atlantic Ocean was established as an important pathway for mineral dust (hereafter mineral) and sea salt to the Amazon during the wet season (Artaxo et al., 1988, 1990, 1995; Formenti et al., 2001; Krejci et al., 2005; Moran-Zuloaga et al., 2018; Wang et al., 2016b; Worobiec et al., 2007). Biological emissions are also being recognized as possible sources of inorganic-salt particles containing elements such as K and Na (Pöhlker et al., 2012; China et al., 2018). These particles are mixed within individual particles, and thus, observations of their occurrence at sizes of hundreds of nanometres or smaller are needed to understand their mixing processes in the atmosphere.

Aerosol particles coagulate and can become coated by volatile organic compounds or acid gas condensation. Such changes affect particle mixing states and compositions (Adachi et al., 2008). The mixing states can significantly affect particle hygroscopicity, optical properties, and compositions (Adachi et al., 2010, 2011; ~~Adachi and Buseck, 2011~~; Cappa, et al., 2012; Fraund et al., 2017). It is important to understand and evaluate particle mixing states to accurately simulate the influences of aerosol particles on the climate (Oshima et al., 2009).

Transmission electron microscopy (TEM) is well suited for determining the shapes, mixing states, and compositions of individual particles smaller than 2  $\mu\text{m}$  (Li et al., 2016). TEM measurements have both advantages and limitations relative to other analytical methods. The advantages of TEM analyses are that they can measure particles smaller than several hundred nanometres, which is the dominant size in terms of particle number concentration. To date, studies have analysed individual particle compositions from samples collected from the Amazon basin using scanning electron microscopy (SEM), scanning transmission X-ray microscopy (STXM), and electron probe X-ray microanalysis (EPMA) (e.g., Worobiec et al., 2007; Fraund et al., 2017; Krejci et al., 2005; China et al., 2018; Huffman et al. 2012; Wu et al., 2019). Although each instrument has its advantages and limitations, TEM has better spatial resolution ( $\sim 0.1$  nm; Li et al. (2016)) than other instruments, which enables us to analyse the shapes and compositions of components with sizes of tens to hundreds of nanometres that attach to other particles.

Furthermore, TEM analyses can image the internal structures of individual particles. TEM can also measure refractory materials that are difficult or impossible to detect using other methods, for example, certain types of on-line aerosol mass spectrometry. Limitations of TEM measurement include that it can only be used for particles on substrates, resulting in a loss of volatile material during sampling and analysis, interference from the substrate, and a lower time resolution than that of on-line instruments.

The GoAmazon2014/5 campaign was conducted in 2014 and 2015 and aimed to address questions related to climate processes, perturbations from human activities, and the terrestrial ecosystem in the Amazon basin (Martin et al., 2016). Our study focused on TEM samples collected during intensive observation period (IOP) 1 from 1 February to 31 March, 2014. The goals of this study are to characterize individual aerosol particles collected from the central Amazon basin during the wet season and to measure these particle occurrences and detailed mixing states at an individual-particle level for implications regarding their regional emissions, regional-to-hemispheric scale transport, particle mixing processes, and climate effects.

## 2 Methods

### 2.1 Campaign and sampling

During the GoAmazon2014/5 campaign, atmospheric measurements were conducted at nine research sites and using two aircraft (Martin et al., 2016). We mainly collected TEM samples at the T3 site (3.2133S, 60.5987W), which is 70 km from Manaus and was the most comprehensively instrumented site including the Atmospheric Radiation Measurement (ARM) Mobile Facility One (AMF-1) and the ARM Mobile Aerosol Observing System (MAOS) (Mather and Voyles, 2013). The details of the campaign are described in Martin et al. (2016).

TEM sampling during IOP1 was conducted at the MAOS container using a shared inlet. We used a TEM aerosol sampler (AS-16W, Arios, Tokyo, Japan) with two impactor stages that collect particles with ~0.1-0.7- $\mu\text{m}$  aerodynamic diameter (50% cutoff diameter) on the fine-mode stage and >0.7  $\mu\text{m}$  on the coarse-mode stage. In this study, we used fine-stage samples to focus on fine-mode particles that are abundant in number but have not been analyzed in detail in this area using TEM. The sampler can mount 16 TEM grids (200 mesh Cu grids with lacey carbon substrates (Ted Pella, CA, USA, Type 01881)) attached to an aluminum plate that rotates with a pre-set timer. The lacey carbon substrates minimize interference from the substrate during the particle composition measurements and a spread of liquid particles over the substrate. We used 30-min collection times at a 1.0 L/min flow rate to have appropriate particle number concentration on the substrates. ~~and We collected samples with~~ 2.5 h interval, i.e., eight samples per day from 1 February to 31 March, 2014 (~500 TEM samples total).

## 2.2 TEM analysis

We used a 120 kV transmission electron microscope (JEM-1400, JEOL, Tokyo, Japan) with a scanning mode (scanning transmission electron microscopy; STEM) equipped with an energy-dispersive X-ray spectrometer (EDS; X-max 80, Oxford Instruments, Tokyo, Japan). We obtained representative TEM images of all grid samples (~30 TEM images per sample). Then, 54 samples were selected for individual particle analyses based on the TEM images to cover the sampling periods with high mineral particle fractions and other periods of interest (e.g., pollution period and primary biological aerosol (PBA)-dominant periods). These periods were compared with the model experiments and the observations using a high-resolution time-of-flight aerosol mass spectrometer (de Sá et al., 2018) and were classified into LRT, pollution, and background periods (Fig. 1).

Semi-automated particle analysis with 20 seconds of EDS measurement was used for individual particle analyses. The same measurements yielded particle sizes (area-equivalent diameters) from segmented binary images. As some particles (e.g., sulfate) can be damaged by an electron beam exposure during the EDS analysis, we used the STEM images taken before the EDS measurements for the size measurements. Here, the geometric diameters (area equivalent diameter) can be larger than the aerodynamic diameters when particles are flat or have low densities, and bouncing from the coarse stage to the fine stage is possible (Bateman et al., 2017). As a result, although the sampler collects particles with an aerodynamic diameter of ~0.1-0.7  $\mu\text{m}$ , we have particles up to 3  $\mu\text{m}$  in area-equivalent diameter. During the STEM-EDS analyses, we analysed all particles larger than 180 nm ~~in two or more fields of view with magnifications from 5,000 to 12,000~~ to measure >200 particles per sample. We randomly chose two to seven areas that do not have too many particles with a magnification of 6,000 (23×23  $\mu\text{m}$ ) to avoid particles that overlap on the substrate. Each field of view includes ~74 particles on average, resulting in ~7% of particle area among the field of views. As a result, we reduced the chance to analyze particles that agglomerate on the substrate. Nevertheless, it is still possible that some particles overlapped on the substrates. We evaluate that the overestimation for the number fraction measurements of internally mixed particles is less than 10% based on the particle area fractions. Detailed information of the analysis is also described in Adachi et al. (2018; 2019) and Ching et al. (2019).

Measured particles were classified into seven categories based on their compositions, i.e., particles containing both Al and Fe as a proxy of mineral particles, P-bearing particles as a proxy of PBA particles, Na-bearing particles as a proxy of sea salt and biological salt, S-bearing particles as a proxy of sulfate, K-bearing particles as a proxy of potassium salt, C-rich particles as a proxy of carbonaceous particles, and others (Fig. S1). As Na-bearing particles can include both marine and biological sources, as proposed by China et al. (2018), we use “sea salt” for those having specific Mg and Na ratios ( $0.05 < \text{Mg}/\text{Na} < 0.3$ ) (Fig. S1). Particles that fall into more than two types (e.g., mineral + sulfate) were



classified into the upper categories in the flow chart presented in Fig. S1. We checked their shapes individually and confirmed that most particles were classified appropriately. Exceptions that were categorized as “other” totalled ~3% of all particles and included metal, fly ash, and mineral particles without Al and Fe (Fig. 42). Nanosphere soot (ns-soot) particles are defined by their aggregated nanosphere structure and the graphitic-like microstructures observed using TEM (Buseck et al., 2014). They are grouped into the carbonaceous category because they do not have characteristic elements other than C.

## 2.3 Model description

We used the Meteorological Research Institute Earth System Model version 2 (MRI-ESM2; Yukimoto et al., 2019; Oshima et al., 2020) to evaluate the LRT periods and the sources and transport of LRT mineral particles to the Amazon basin (Figs. 23 and 4). For this study, we modified the original model configuration and used only atmospheric (the atmospheric general circulation model (AGCM) with land processes (MRI-AGCM3.5)) and aerosol (the Model of Aerosol Species in the Global Atmosphere mark-2 (MASINGAR mk-2)) component models. The model employs horizontal resolutions with an approximately 120-km grid (TL159) and 80 vertical layers from the surface to a model top of 0.01 hPa in a hybrid sigma-pressure coordinate system. The model simulation was performed from January 2008 to December 2015 after a 1-year spin-up run using the prescribed sea surface temperature data (Ishii et al., 2005). In the model simulation, the horizontal wind fields in the AGCM were nudged towards the 6-hourly Japanese 55-year Reanalysis data (Kobayashi et al. 2015). We used the monthly anthropogenic emissions dataset by Lamarque et al. (2010) and the daily biomass-burning emissions from the global fire assimilation system dataset by Kaiser et al. (2012). Mineral (dust) and sea-salt emissions were calculated depending on the meteorological conditions in the model (Tanaka and Chiba, 2005; Yumimoto et al., 2017).

## 3 Results and discussion

### 3.1 Model simulation

The model simulation characterized six LRT periods that have mineral dust concentration peaks greater than  $10 \mu\text{g}/\text{m}^3$  during IOP1 (Fig. 2a3). The LRT periods cover the high-mineral particle samples of the TEM analysis, and we identify these TEM samples as LRT samples. These periods also generally overlap those of Moran-Zuloaga et al. (2018), who measured aerosol mass concentrations from 1 to  $10 \mu\text{m}$  (coarse mode) at the Amazon Tall Tower Observatory (ATTO) during the campaign, and are consistent with the dust events from the MODIS satellite observations (<https://worldview.earthdata.nasa.gov/>). The model simulation shows that the modelled horizontal distributions of mineral dust concentration at the surface level during the six LRT periods and the vertical distributions on 7 March, when the largest LRT periods occurred during IOP1, are shown in

(Fig. 24). The model results indicate that these mineral dust particles originated from the Saharan desert, followed by easterly transport in the lower troposphere over the Atlantic Ocean to the Amazon basin (Fig. 2b, c).

## 3.2 Shapes, compositions, and sizes of aerosol particles

Representative particle images with elemental maps (e.g., Figs. 3 and S2-10), size distributions, and size-dependent number fractions for each particle category (Fig. 45) were analysed with TEM. Here, we show the sizes, shapes, and mixing states of individual particles for each particle type.

### 3.2.1 Mineral particles

Tens of Tg per year of mineral particles from the Saharan desert are transported to the Amazon basin (Graham et al., 2003; Swap et al., 1992; Wang et al., 2016b; Yu et al., 2015) and provide Fe and P nutrients for forests (Bristow et al., 2010). Such mineral particles also contribute to ice-nucleating particles (INPs) to form ice clouds (Prennei et al., 2009).

Mineral particles were defined as those containing both Al and Fe, although Na, Si, Ca, S, or K were also detected in most mineral particles (Figs. 3-6 and S2). These particles are typically crystalline, appear darker than other particles, and have irregular edges in TEM images (Fig. 3a). They have a broad size distribution with a relatively large modal peak (~1.3-1.6  $\mu\text{m}$  in area-equivalent diameter) (Fig. 45a). The number fractions sporadically increase (Fig. 1a), coordinating with LRT from Africa in the model (Figs. 3 and 24).

Most mineral particles consist of Al- and Si-bearing clay minerals (e.g., illite and kaolinite). These minerals are aggregated with other minerals such as quartz (Si-O), K-feldspar (K-Al-Si), and small (~100 nm) grains that contain Fe and O or Ca and S (Figs. 3-6 and S2). The average weight % of Al and Si in mineral particles in each sample shows a positive correlation for samples from both LRT and other periods (Fig. 3d). The values for Si/Al between 1.5 and 3 for LRT period samples are roughly consistent with bulk measurements of Amazon aerosol in other studies (Artaxo et al., 2002; Caquineau et al., 1998; Martin et al., 2010b; Moran-Zuloaga et al., 2018; Rizzolo et al., 2017). More than half of the mineral particles are within this Si/Al range, and their possible source is the Saharan desert judging from our and other model studies (e.g., Moran-Zuloaga et al., 2018). On the other hand, the average ratios of Si/Al in several non-LRT samples (e.g., the sample from 26 March, 16:11) are lower than those in the LRT samples (Fig. 3d). This result suggests that the mineralogy and compositions of mineral particles are different between LRT and other periods and that the latter can have local sources around the sampling site (e.g., farm and road).

Over half of the mineral particles have Na-bearing particles such as NaCl, Na<sub>2</sub>SO<sub>4</sub>, or their mixtures on their surfaces. The weight % values of Na-Cl and Na-Mg in the mineral particles show a positive correlation (Fig. 3e, f), and ~26% of mineral particles from all samples are internally mixed with sea-

salt components. The values of Cl/Na are lower than those in NaCl (Cl/Na ~1.5) because some Cl was replaced by sulfate, forming Na<sub>2</sub>SO<sub>4</sub>. LRT samples have higher Na, Cl, and Mg fractions than other samples (Fig. ~~3e~~ and ~~3f~~7), suggesting that the LRT particles were mixed with sea salt during transport, possibly when travelling near the surface of the Atlantic Ocean (Fig. ~~2e~~4). Lidar measurements observed similar LRT of dust and biomass burning from Africa in the lowermost 2 km of the atmosphere during the AMAZE-2008 campaign (Baars et al., 2012). Such mixing of mineral and sea salt in the Amazon basin is consistent with studies using particle-induced X-ray emission (PIXE) for filter bulk measurements (Artaxo et al., 1990) or an electron-probe microanalyser and a scanning electron microscope for individual-particle measurements (e.g., Worobiec et al., 2007; Wu et al., 2019), and we show here that sea salt occurs on the mineral particles as grains several hundred nanometres in size (Figs. ~~3-6~~ and S6).

### 3.2.2 Primary biological aerosol (PBA) particles

PBA particles are important in the Amazon basin because of their abundance and contributions to the regional climate and weather (Martin et al., 2010b; Pöschl et al., 2010). These particles include fungal spores, pollen, bacteria, algae, protozoa, and fragments of plants and organisms (~~Després~~Despres et al., 2012; [Li et al., 2020](#)) and are known sources of K, Na, P, Cl, and Fe in the Amazon basin (Artaxo et al., 1993; Krejci et al., 2005; Wu et al., 2019). Biological sources in the Amazon can also emit K and Na salts as fine aerosol particles and influence new particle formation and cloud formation, respectively (China et al., 2016, 2018; Pöhlker et al., 2012), and act as INPs (Prenni et al., 2009).

PBA particles mainly consist of C and O and contain P, S, N, K, Cl, and Na as minor components (Fig. ~~58~~58). We used P as a tracer for PBA particles to distinguish them from other primary or secondary organic aerosol particles. Elemental distributions of PBA particles show that P occurs either uniformly within particles (Fig. ~~58~~58; Fig. S3) or as phosphate (Fig. S4). PBA particle shapes depend on the types of biological sources (Fig. ~~69~~69), although exact source identification requires measurements such as DNA analysis. The size distribution in the PBA particles has two peaks: ~600 nm and >2 µm (Fig. ~~45~~45). PBA particles >2 µm show unique shapes (Fig. ~~69~~69), whereas small PBA particles can include fragmented fungal spores (China et al., 2016). The size distributions and shapes of large PBA particles are consistent with those described by Huffman et al. (2012), who measured PBA particles during the AMAZE-08 campaign. Relative number fractions of PBA particles are higher during non-LRT periods than LRT periods (Figs. ~~4b~~ and ~~4e~~2), given that they are emitted within the Basin. PBA number fractions also show diurnal changes; i.e., they are high during the night (3 am in local time) and low during the day (3 pm) (Fig. ~~58d~~58d). The ~~increases in the~~ number fractions of PBA particles during the night ~~can be enhanced~~ caused by high relative humidity (RH), which ~~increases~~enhances active PBA particle emissions from plants, wind speed, and temperatures (Li et al., 2020; Elbert et al., 2007; Graham et al., 2003; Huffman et al., 2012; Whitehead et al., 2016). Various PBA particles are mixed

with other materials such as minerals, sulfate, Na-bearing particles, or ns-soot (Fig. [5-8](#) and S5). For example, PBA particles in Figs. [5-8](#) and S5 attach ns-soot, and that in Fig. S3 attaches a mineral particle. The number fractions of internally mixed PBA particles with sea salt are approximately 20% (Fig. [7e10](#)). Na occurs on the PBA particle surface as coatings (Fig. S10) or as particle constituents (Fig. [58](#)).

### 3.2.3 Sea-salt particles

Sea-salt particles are emitted from the ocean and act as efficient cloud-condensation nuclei (CCN). Na, Mg, and Cl are commonly used tracers of sea-salt particles, although Cl can be replaced by sulfate and nitrate in the atmosphere (Adachi and Buseck, 2015; Gard et al., 1998; Yoshizue et al., 2019). In this study, although the sampling site is far from the ocean (>1,000 km), we commonly observed sea-salt particles and their mixtures with mineral particles (Fig. [3-6](#) and S6), sulfate (Fig. [711](#)), and PBA particles (Fig. S10). Na-bearing particles, which include both marine and biological sources, have a broad size distribution, with a mode size of ~600 nm (Fig. [45](#)). Number fractions of Na-bearing particles are more abundant during LRT periods than in other periods (Figs. [12-and-4](#)). The deformed shapes of Na-bearing particles on the substrate suggest that they were hydrated in the atmosphere and on the substrates when collected (Fig. [711](#)).

The weight % ratios among Na and Mg within Na-bearing particles show that more than 70% is sea salt that has a Mg/Na weight % between 0.05 and 0.3 (Fig. [710](#)). Some remaining particles can be sea salt because the Mg weight % is lower than the detection limit (~0.1 weight %) within the Na-bearing particles having relatively low Na weight %. A stoichiometry calculation using S and Cl weight % indicates that ~74 % in mol fractions of Cl was replaced with sulfate. Nitrate can also react with NaCl and form sodium nitrate. However, we did not observe it in this study because of lower concentrations of nitrate than sulfate during the campaign (de Sá et al., 2018) and insensitivity of nitrate detection in the current TEM analysis. Such-Internally mixed sea-salt fractions are higher in samples from LRT periods than those in other periods (Fig. [7-d-f10c](#)).

### 3.2.4 K-bearing particles

Potassium is one of the key elements in the Amazon basin that acts as a seed to form secondary organic aerosol particles (Pöhlker et al., 2012). Potassium-bearing particles have a modal peak at 400 nm, and their number fractions are similar between LRT periods and other periods (Fig. [45](#)). Many K-bearing particles consist of inorganic salts and include S as sulfate (Fig. S7), C as ns-soot or organic matter (Fig. S7), Cl as chloride (Fig. S5), or their mixtures. In addition, K occurs in mineral dust particles (Figs. [3-6](#) and S2) and PBA (Figs. S3 and S4) as a minor component. Potassium is a common constituent of mineral dust such as K-feldspar and an essential component of biological species and was detected in ~80% of all our analysed particles, mostly as minor fractions.

620 Pöhlker et al. (2012) found K in nearly all particles and observed that the K mass fraction increased for smaller particles in samples collected at the ATTO site, which has a negligible influence from Manaus. The authors suggested that the K was from biogenic sources but not biomass burning because of a lack of ns-soot particles. In contrast, our samples include K-bearing particles with ns-soot particles (Fig. S7), and the mixing state is similar to that in biomass burning (Li et al., 2003; Wu et al., 2019; Yokelson et al., 2007). Thus, although there were few wildfires during the wet season, biomass burning from LRT, local biofuel burning, and other anthropogenic sources can contribute to our K-bearing particles collected at the T3 site.

### 3.2.5 Sulfate

Nearly 10% of all particles are classified as sulfate (Fig. 42), although S was detected from ~90% of all analysed particles as a minor component of mineral, PBA, and Na- and K-bearing particles. The size distribution of sulfate has a modal peak at ~400 nm (Fig. 45). Nearly 80% of sulfate particles include N, K (<2 weight %), or both, suggesting that they are mostly ammonium or potassium sulfate (Fig. S8). Anthropogenic pollutants including sulfate from Manaus were sporadically transported to the T3 site (de Sá et al., 2017). For example, during the period that was classified as polluted conditions from Manaus (de Sá et al., 2018), the TEM samples have approximately three times higher sulfate number fractions than those from background periods (Figs. 42 and S8). Sulfate in the Amazon can be formed by the reactions of SO<sub>2</sub>, dimethyl sulfide (DMS), H<sub>2</sub>S, or CS<sub>2</sub> emitted from local sources (e.g., plants, microorganisms, and anthropogenic emissions) and LRT sources (e.g., biomass burning and anthropogenic emissions from Africa and the Atlantic Ocean) (Martin et al., 2010b).

### 640 3.2.6 Carbonaceous particles

Carbonaceous particles include secondary or primary organic aerosol (SOA and POA, respectively), tarball, and ns-soot particles (Fig. S9). The vapor pressure of volatile and semi-volatile organic compounds was too high to retain them in the particles after sampling and during the TEM analysis, resulting in the loss of the volatile fraction from the particles collected on the TEM grids. Thus, the carbonaceous particle fractions can be underestimated, and we focus only on the non-volatile fractions.

Carbonaceous particles have higher fractions at smaller sizes for both the LRT period and other samples (Fig. 45). SOA particles are organic particles having round shapes with deformation on the substrate when collected (e.g., Fig 11). These particles form through oxidation of low-volatile organic matter emitted from both natural and anthropogenic sources (de Sá et al., 2018). Wang et al. (2016a) showed that small particles are transported from the free troposphere into the boundary layer by vertical transports during precipitation events, and such particles can be nuclei of the SOA particles in the background condition. Tarballs originate from biomass burning and have an amorphous structure and spherical shapes on the substrate (Adachi et al., 2019), and their number fractions are <1% in our samples. Ns-soot particles that

are internally mixed with K-bearing particles can originate from LRT (Saturno et al., 2018) or local  
655 biofuel burning for cooking or brick kilns (Martin et al., 2016). Other ns-soot particles can be from  
anthropogenic sources such as Manaus and neighbouring cities (Glicker et al., 2019). Ns-soot particles  
are attached to or embedded within the mineral, sulfate, organic, Na- and K-bearing, or PBA particles  
(Figs. 36, 58, S2, S5, and S7). As ns-soot particles absorb light, they can change the optical properties of  
these mixed particles into more light-absorbing particles.

#### 660 **4-Discussion3.3 Possible mixing processes and implications to the climate**

Number fractions of aerosol particle types as a function of sizes largely differ between the LRT period  
and other samples (Fig. 45). The size-dependent number fractions of samples from other period are  
roughly consistent with the results during the AMAZE-08 campaign (Pöschl et al., 2010). At large particle  
sizes ( $>2\ \mu\text{m}$ ), mineral and PBA particles are dominant during LRT and other periods, respectively,  
665 whereas carbonaceous particles dominate in fine particles for both periods. During the LRT periods, most  
mineral and biomass burning particles such as K-bearing and ns-soot particles could originate from the  
African continent, and the sea-salt particles came from the Atlantic Ocean. We assume that these particles  
were coagulated or condensed during transport (Fig. 812).

Many Na-bearing particles are internally mixed with mineral and PBA particles (Fig. S6) or on the  
670 surfaces of biological particles (Fig. S10). In the LRT samples, more than 20% of the mineral and PBA  
particles contain sea salt. Sulfate particles are commonly coagulated or condensed with other aerosol  
components to form various internal mixtures. We found correlations of sample average  
weight % of S between Na-bearing and mineral particles (Fig. 913). The results suggest that mixing  
with sulfate occurred during LRT over the Atlantic Ocean and above the Amazon basin rather than at  
675 their source regions (Fig. 812).

In the Amazon forest, the RH commonly exceeds  $>80\%$  during the night. The mixing states of mineral  
and PBA particles suggest that hygroscopic particles such as NaCl and  $(\text{NH}_4)_2\text{SO}_4$  deliquesce on the  
surface of these host particles under high RH conditions and thus they increase their sizes by absorbing  
water.

680 The detailed mixing states of individual particles are important to understand their contributions to the  
climate. In our samples, most particles consist of several components from sources such as the Amazon  
forest, Saharan desert, Atlantic Ocean, and African biomass burning, some of which are separated by  
thousands of kilometres (Fig. 812). Although such complex mixing states are common for  
anthropogenic aerosol particles (e.g., Ching et al., 2019), we found that particles from natural sources  
685 can also be mixed during LRT and form internally mixed particles, resulting in different hygroscopicity  
and optical properties.



## 5.4 Conclusions

The compositions and mixing states of individual particles from natural sources in the Amazon basin are important for understanding their roles in cloud formation and radiative forcing as well as for transport and removal processes. It is difficult to evaluate the compositions and mixing states of refractory particles using on-line instruments. In contrast, the TEM results show that primary particles, including minerals, sea salt, and PBA, dominate in the fine mode particles during the wet season, and their number fractions vary depending on whether they originate from LRT or local sources. This study shows the mixing states of these particles, focusing on the occurrences of individual components on particles, with sizes ranging from hundreds of nanometres to several micrometres. Sea-salt and sulfate particles commonly occur on the surfaces of mineral and PBA particles. As the LRT particles have more processed mixed particles than other background particles, we interpret that the mixings mainly occurred during the LRT through coagulation, condensation, or both. The element mapping images also showed that K and Na occurred either as attached inorganic salts or as constituents of PBA and mineral particles. Our model simulation suggests that mineral particles during LRT periods originated from the Saharan desert. Although mineral particles are originally hydrophobic, the LRT mineral particles can become hygroscopic by mixing with sea-salt and sulfate particles.

This study focuses on individual particles from samples collected during the wet season in the Amazon basin. Many particles are internally mixed with other components and can have different hygroscopicity and optical properties from their original sources/states. Although previous studies suggested possible local biological sources for K and Na, our observations show that they could originate from sources of both LRT and local sources. We conclude that many primary particles from natural sources become internally mixed and change compositions while travelling across long distances and various environments. When mineral particles or other hydrophilic-primary particles are mixed with sea salt or sulfate, they can absorb water efficiently, resulting in increasing CCN activity, changing the optical properties, and accelerating their removal from the atmosphere, all of which should be taken into account when considering their actual occurrence in the atmosphere to evaluate their climate influences.

## Data and code availability

The data sets used in this publication are available at the ARM Climate Research Facility database for the GoAmazon2014/5 experiment (<https://www.arm.gov/research/campaigns/amf2014goamazon>). The TEM data and the simulation data used in this publication are available upon request (adachik@mri-jma.go.jp). Access to the MRI-ESM2 code is available under a collaboration framework with MRI.



## Author contributions

KA and PB planned the TEM experiments. KA carried out the TEM analyses and data processing. KA, ZG, SSdS, APB, JB, GGC, and AJS carried out the TEM sampling and field observations. STM and PA supervised the GoAmazon2014/5 campaign and TEM sampling. NO performed the simulations. KA prepared the manuscript with contributions from all co-authors.

## Competing interests

The authors declare that they have no conflict of interest.

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## References

- Adachi, K. and Buseck, P. R.: Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City, Atmos. Chem. Phys., 8, 6469–6481, <https://doi.org/10.5194/acp-8-6469-2008>, 2008.
- Adachi, K., Chung, S. H., and Buseck, P. R.: Shapes of soot aerosol particles and implications for their effects on climate, Journal of Geophysical Research, 115, 10.1029/2009jd012868, 2010.

750

~~Adachi, K., and Buseck, P. R.: Atmospheric tar balls from biomass burning in Mexico, Journal of Geophysical Research, 116, 10.1029/2010jd015102, 2011.~~

Adachi, K., Freney, E. J., and Buseck, P. R.: Shapes of internally mixed hygroscopic aerosol particles after deliquescence, and their effect on light scattering, *Geophysical Research Letters*, 38, 10.1029/2011gl047540, 2011.

755

Adachi, K., and Buseck, P. R.: Changes in shape and composition of sea-salt particles upon aging in an urban atmosphere, *Atmospheric Environment*, 100, 1-9, 10.1016/j.atmosenv.2014.10.036, 2015.

Adachi, K., Sedlacek, A. J., Kleinman, L., Chand, D., Hubbe, J. M., and Buseck, P. R.: Volume changes upon heating of aerosol particles from biomass burning using transmission electron microscopy, *Aerosol Science and Technology*, 52, 46-56, 10.1080/02786826.2017.1373181, 2018.

760

Adachi, K., Sedlacek, A. J., III, Kleinman, L., Springston, S. R., Wang, J., Chand, D., Hubbe, J. M., Shilling, J. E., Onasch, T. B., Kinase, T., Sakata, K., Takahashi, Y., and Buseck, P. R.: Spherical tarball particles form through rapid chemical and physical changes of organic matter in biomass-burning smoke, *Proc Natl Acad Sci U S A*, 116, 19336-19341, 10.1073/pnas.1900129116, 2019.

765

Andreae, M. O.: Aerosols before pollution, *Science*, 315, 50-51, 10.1126/science.1136529, 2007.

Andreae, M. O., Acevedo, O. C., Araùjo, A., Artaxo, P., Barbosa, C. G. G., Barbosa, H. M. J., Brito, J., Carbone, S., Chi, X., Cintra, B. B. L., da Silva, N. F., Dias, N. L., Dias-Júnior, C. Q., Ditas, F., Ditz, R., Godoi, A. F. L., Godoi, R. H. M., Heimann, M., Hoffmann, T., Kesselmeier, J., Könemann, T., Krüger, M. L., Lavric, J. V., Manzi, A. O., Lopes, A. P., Martins, D. L., Mikhailov, E. F., Moran-Zuloaga, D., Nelson, B. W., Nölscher, A. C., Santos Nogueira, D., Piedade, M. T. F., Pöhlker, C., Pöschl, U., Quesada, C. A., Rizzo, L. V., Ro, C. U., Ruckteschler, N., Sá, L. D. A., de Oliveira Sá, M., Sales, C. B., dos Santos, R. M. N., Saturno, J., Schöngart, J., Sörgel, M., de Souza, C. M., de Souza, R. A. F., Su, H., Targhetta, N., Tóta, J., Trebs, I., Trumbore, S., van Eijck, A., Walter, D., Wang, Z., Weber, B., Williams, J., Winderlich, J., Wittmann, F., Wolff, S., and Yáñez-Serrano, A. M.: The Amazon Tall Tower Observatory (ATTO): overview of pilot measurements on ecosystem ecology, meteorology, trace gases, and aerosols, *Atmospheric Chemistry and Physics*, 15, 10723-10776, 10.5194/acp-15-10723-2015, 2015.

770

775

780

~~Artaxo, P., Storms, H., Bruynseels, F., Van Grieken, R., and Maenhaut, W.: Composition and sources of aerosols from the Amazon Basin, J. Geophys. Res., 93, 1605–1615, doi:10.1029/JD093iD02p01605, 1988.~~

Artaxo, P., Maenhaut, W., Storms, H., and Van Grieken, R.: Aerosol characteristics and sources for the Amazon Basin during the wet season, *J. Geophys. Res.*, 95, 16971–16985, doi:10.1029/JD095iD10p16971, 1990.

- 785 Artaxo, P., Gerab, F., Rabello, M. L. C.: Elemental composition of aerosol particles from two atmospheric monitoring stations in the Amazon Basin, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 75, 277-281, 1993.
- Artaxo, P., Hansson, H. C.: Size distribution of biogenic aerosol particles from the amazon basin, *Atmospheric Environment*, 29, 393-402, 1995.
- 790 Artaxo, P.: Physical and chemical properties of aerosols in the wet and dry seasons in Rondônia, Amazonia, *Journal of Geophysical Research*, 107, 10.1029/2001jd000666, 2002.
- Baars, H., Ansmann, A., Althausen, D., Engelmann, R., Heese, B., Müller, D., Artaxo, P., Paixao, M., Pauliquevis, T., and Souza R.: Aerosol profiling with lidar in the Amazon Basin during the wet and dry season, *J. Geophys. Res.*, 117, D21201, doi:10.1029/2012JD018338, 2012.
- 795 Bateman, A. P., Gong, Z., Liu, P., Sato, B., Cirino, G., Zhang, Y., Artaxo, P., Bertram, A. K., Manzi, A. O., Rizzo, L. V., Souza, R. A. F., Zaveri, R. A., and Martin, S. T.: Sub-micrometre particulate matter is primarily in liquid form over Amazon rainforest, *Nature Geoscience*, 9, 34-37, 10.1038/ngeo2599, 2015.
- Bateman, A. P., Gong, Z., Harder, T. H., de Sá, S. S., Wang, B., Castillo, P., China, S., Liu, Y., amp, apos, 800 Brien, R. E., Palm, B. B., Shiu, H.-W., Cirino, G. G., Thalman, R., Adachi, K., Alexander, M. L., Artaxo, P., Bertram, A. K., Buseck, P. R., Gilles, M. K., Jimenez, J. L., Laskin, A., Manzi, A. O., Sedlacek, A., Souza, R. A. F., Wang, J., Zaveri, R., and Martin, S. T.: Anthropogenic influences on the physical state of submicron particulate matter over a tropical forest, *Atmospheric Chemistry and Physics*, 17, 1759-1773, 10.5194/acp-17-1759-2017, 2017.
- 805 Brito, J., Rizzo, L. V., Morgan, W. T., Coe, H., Johnson, B., Haywood, J., Longo, K., Freitas, S., Andreae, M. O., and Artaxo, P.: Ground-based aerosol characterization during the South American Biomass Burning Analysis (SAMBBA) field experiment, *Atmos. Chem. Phys.*, 14, 12069–12083, <https://doi.org/10.5194/acp-14-12069-2014>, 2014.
- Bristow, C. S., Hudson-Edwards, K. A., and Chappell, A.: Fertilizing the Amazon and equatorial Atlantic 810 with West African dust, *Geophysical Research Letters*, 37, L14807, 10.1029/2010gl043486, 2010.
- Buseck, P. R., Adachi, K., Gelencsér, A., Tompa, É., and Pósfai, M.: Ns-Soot: A Material-Based Term for Strongly Light-Absorbing Carbonaceous Particles, *Aerosol Science and Technology*, 48, 777-788, 10.1080/02786826.2014.919374, 2014.
- 815 Cappa, C. D., Onasch, T. B., Massoli, P., Worsnop, D. R., Bates, T. S., Cross, E. S., Davidovits, P., Hakala, J., Hayden, K. L., Jobson, B. T., Kolesar, K. R., Lack, D. A., Lerner, B. M., Li, S.-M., Mellon, D., Nuaaman, I., Olfert, J. S., Petäjä, T., Quinn, P. K., Song, C., Subramanian, R., Williams, E. J., and Zaveri, R. A.: Radiative Absorption Enhancements Due to the Mixing State of Atmospheric Black Carbon, *Science*, 337, 1078-1081, 10.1126/science.1223447, 2012.

- 820 Caquineau, S., Gaudichet, A., Gomes, L., Magonthier, M.-C., and Chatenet, B.: Saharan dust: Clay ratio as a relevant tracer to assess the origin of soil-derived aerosols, *Geophysical Research Letters*, 25, 983-986, 10.1029/98gl00569, 1998.
- Carslaw, K. S., Lee, L. A., Reddington, C. L., Pringle, K. J., Rap, A., Forster, P. M., Mann, G. W., Spracklen, D. V., Woodhouse, M., Regayre, L. A., and Pierce, J. R.: Large contribution of  
825 natural aerosols to uncertainty in indirect forcing, *Nature*, 503, 67–71, <https://doi.org/10.1038/nature12674>, 2013.
- China, S., Wang, B., Weis, J., Rizzo, L., Brito, J., Cirino, G. G., Kovarik, L., Artaxo, P., Gilles, M. K., and Laskin, A.: Rupturing of Biological Spores As a Source of Secondary Particles in Amazonia, *Environ Sci Technol*, 50, 12179-12186, 10.1021/acs.est.6b02896, 2016.
- 830 China, S., Burrows, S. M., Wang, B., Harder, T. H., Weis, J., Tanarhte, M., Rizzo, L. V., Brito, J., Cirino, G. G., Ma, P. L., Cliff, J., Artaxo, P., Gilles, M. K., and Laskin, A.: Fungal spores as a source of sodium salt particles in the Amazon basin, *Nat Commun*, 9, 4793, 10.1038/s41467-018-07066-4, 2018.
- Ching, J., Adachi, K., Zaizen, Y., Igarashi, Y., and Kajino, M.: Aerosol mixing state revealed by  
835 transmission electron microscopy pertaining to cloud formation and human airway deposition, *npj Climate and Atmospheric Science*, 2, 10.1038/s41612-019-0081-9, 2019.
- Cirino, G., Brito, J., Barbosa, H. M. J., Rizzo, L. V., Tunved, P., de Sá, S. S., Jimenez, J. L., Palm, B. B., Carbone, S., Lavric, J. V., Souza, R. A. F., Wolff, S., Walter, D., Tota, J., Oliveira, M. B. L., Martin, S. T., and Artaxo, P.: Observations of Manaus urban plume evolution and interaction  
840 with biogenic emissions in GoAmazon 2014/5, *Atmospheric Environment*, 191, 513-524, 10.1016/j.atmosenv.2018.08.031, 2018.
- de Sá, S. S., Palm, B. B., Campuzano-Jost, P., Day, D. A., Hu, W., Isaacman-VanWertz, G., Yee, L. D., Brito, J., Carbone, S., Ribeiro, I. O., Cirino, G. G., Liu, Y., Thalman, R., Sedlacek, A., Funk, A., Schumacher, C., Shilling, J. E., Schneider, J., Artaxo, P., Goldstein, A. H., Souza, R. A. F.,  
845 Wang, J., McKinney, K. A., Barbosa, H., Alexander, M. L., Jimenez, J. L., and Martin, S. T.: Urban influence on the concentration and composition of submicron particulate matter in central Amazonia, *Atmospheric Chemistry and Physics*, 18, 12185-12206, 10.5194/acp-18-12185-2018, 2018.
- de Sá, S. S., Palm, B. B., Campuzano-Jost, P., Day, D. A., Newburn, M. K., Hu, W., Isaacman-VanWertz, G., Yee, L. D., Thalman, R., Brito, J., Carbone, S., Artaxo, P., Goldstein, A. H., Manzi, A. O.,  
850 Souza, R. A. F., Mei, F., Shilling, J. E., Springston, S. R., Wang, J., Surratt, J. D., Alexander, M. L., Jimenez, J. L., and Martin, S. T.: Influence of urban pollution on the production of organic particulate matter from isoprene epoxydiols in central Amazonia, *Atmos. Chem. Phys.*, 17, 6611–6629, <https://doi.org/10.5194/acp-17-6611-2017>, 2017.

- 855 Després, V., Huffman, J. A., Burrows, S. M., Hoose, C., Safatov, A., Buryak, G., Fröhlich-Nowoisky, J.,  
Elbert, W., Andreae, M., Pöschl, U., and Jaenicke, R.: Primary biological aerosol particles in  
the atmosphere: a review, *Tellus B: Chemical and Physical Meteorology*, 64, 15598,  
10.3402/tellusb.v64i0.15598, 2012.
- Elbert, W., Taylor, P. E., Andreae, M. O., and Pöschl, U.: Contribution of fungi to primary biogenic  
860 aerosols in the atmosphere: wet and dry discharged spores, carbohydrates, and inorganic ions,  
*Atmos. Chem. Phys.*, 7, 4569–4588, <https://doi.org/10.5194/acp-7-4569-2007>, 2007.
- Formenti, P., Andreae, M. O., Lange, L., Roberts, G., Cafmeyer, J., Rajta, I., Maenhaut, W., Holben, B.  
N., Artaxo, P., and Lelieveld, J.: Saharan dust in Brazil and Suriname during the Large-Scale  
Biosphere-Atmosphere Experiment in Amazonia (LBA) - Cooperative LBA Regional  
865 Experiment (CLAIRE) in March 1998, *Journal of Geophysical Research: Atmospheres*, 106,  
14919-14934, 10.1029/2000jd900827, 2001.
- Fraund, M., Pham, D., Bonanno, D., Harder, T., Wang, B., Brito, J., de Sá, S., Carbone, S., China, S.,  
Artaxo, P., Martin, S., Pöhlker, C., Andreae, M., Laskin, A., Gilles, M., and Moffet, R.:  
Elemental Mixing State of Aerosol Particles Collected in Central Amazonia during  
870 GoAmazon2014/15, *Atmosphere*, 8, 173, 10.3390/atmos8090173, 2017.
- Gard, E. E., Kleeman, M. J., Gross, D. S., Hughes, L. S., Allen, J. O., Morrical, B. D., Fergenson, D. P.,  
Dienes, T., E. Gälli, M., Johnson, R. J., Cass, G. R., and Prather, K. A.: Direct Observation of  
Heterogeneous Chemistry in the Atmosphere, *Science*, 279, 1184-1187,  
10.1126/science.279.5354.1184, 1998.
- 875 Glicker, H. S., Lawler, M. J., Ortega, J., de Sá, S. S., Martin, S. T., Artaxo, P., Vega Bustillos, O., de  
Souza, R., Tota, J., Carlton, A., and Smith, J. N.: Chemical composition of ultrafine aerosol  
particles in central Amazonia during the wet season, *Atmospheric Chemistry and Physics*, 19,  
13053-13066, 10.5194/acp-19-13053-2019, 2019.
- Graham, B., Guyon, P., Maenhaut, W., Taylor, P. E., Ebert, M., Matthias-Maser, S., Mayol-Bracero, O.  
880 L., Godoi, R. H. M., Artaxo, P., Meixner, F. X., Moura, M. A. L., Rocha, C. H. E. D. A.,  
Grieken, R. V., Glovsky, M. M., Flagan, R. C., and Andreae, M. O.: Composition and diurnal  
variability of the natural Amazonian aerosol, *Journal of Geophysical Research: Atmospheres*,  
108, n/a-n/a, 10.1029/2003jd004049, 2003.
- Huffman, J. A., Sinha, B., Garland, R. M., Snee-Pollmann, A., Gunthe, S. S., Artaxo, P., Martin, S. T.,  
885 Andreae, M. O., and Pöschl, U.: Size distributions and temporal variations of biological aerosol  
particles in the Amazon rainforest characterized by microscopy and real-time UV-APS  
fluorescence techniques during AMAZE-08, *Atmospheric Chemistry and Physics*, 12, 11997-  
12019, 10.5194/acp-12-11997-2012, 2012.

- Ishii, M., Shouji, A., Sugimoto, S., and Matsumoto, T.: Objective analyses of sea-surface temperature and marine meteorological variables for the 20th century using ICOADS and the Kobe Collection, *Int. J. Climatol.*, 25, 865–879, doi:10.1002/joc.1169, 2005.
- Kaiser, J. W., Heil, A., Andreae, M. O., Benedetti, A., Chubarova, N., Jones, L., Morcrette, J.-J., Razinger, M., Schultz, M. G., Suttie, M., and van der Werf, G. R.: Biomass burning emissions estimated with a global fire assimilation system based on observed fire radiative power, *Biogeosciences*, 9, 527–554, <https://doi.org/10.5194/bg-9-527-2012>, 2012.
- Kobayashi, S., Ota, Y., Harada, Y., Ebata, A., Moriya, M., Onoda, H., Onogi, K., Kamahori, H., Kobayashi, C., Endo, H., Miyaoka, K., and Takahashi, K.: The JRA-55 Reanalysis: General Specifications and Basic Characteristics, *J. Meteorol. Soc. Jpn.* 93, 5–48, <https://doi.org/10.2151/jmsj.2015-001>, 2015.
- Krejci, R., Ström, J., de Reus, M., and Sahle, W.: Single particle analysis of the accumulation mode aerosol over the northeast Amazonian tropical rain forest, Surinam, South America, *Atmos. Chem. Phys.*, 5, 3331–3344, <https://doi.org/10.5194/acp-5-3331-2005>, 2005.
- Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., Owen, B., Schultz, M. G., Shindell, D., Smith, S. J., Stehfest, E., Van Aardenne, J., Cooper, O. R., Kainuma, M., Mahowald, N., McConnell, J. R., Naik, V., Riahi, K., and van Vuuren, D. P.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, *Atmos. Chem. Phys.*, 10, 7017–7039, <https://doi.org/10.5194/acp-10-7017-2010>, 2010.
- Li, W., Shao, L., Zhang, D., Ro, C.-U., Hu, M., Bi, X., Geng, H., Matsuki, A., Niu, H., and Chen, J.: A review of single aerosol particle studies in the atmosphere of East Asia: morphology, mixing state, source, and heterogeneous reactions, *Journal of Cleaner Production*, 112, 1330–1349, 10.1016/j.jclepro.2015.04.050, 2016.
- Li, W., Liu, L., Xu, L., Zhang, J., Yuan, Q., Ding, X., Hu, W., Fu, P., and Zhang, D.: Overview of primary biological aerosol particles from a Chinese boreal forest: Insight into morphology, size, and mixing state at microscopic scale, *Science of The Total Environment*, 719, 137520, <https://doi.org/10.1016/j.scitotenv.2020.137520>, 2020.
- Li, J., Pósfai, M., Hobbs, P. V., and Buseck, P. R.: Individual aerosol particles from biomass burning in southern Africa: 2, Compositions and aging of inorganic particles, *Journal of Geophysical Research: Atmospheres*, 108, n/a–n/a, 10.1029/2002jd002310, 2003.
- Martin, S. T., Andreae, M. O., Althausen, D., Artaxo, P., Baars, H., Borrmann, S., Chen, Q., Farmer, D. K., Guenther, A., Gunthe, S. S., Jimenez, J. L., Karl, T., Longo, K., Manzi, A., Müller, T., Pauliquevis, T., Petters, M. D., Prenni, A. J., Pöschl, U., Rizzo, L. V., Schneider, J., Smith, J. N., Swietlicki, E., Tota, J., Wang, J., Wiedensohler, A., and Zorn, S. R.: An overview of the

- Amazonian Aerosol Characterization Experiment 2008 (AMAZE-08), *Atmospheric Chemistry and Physics*, 10, 11415-11438, 10.5194/acp-10-11415-2010, 2010a.
- 925 Martin, S. T., Artaxo, P., Machado, L., Manzi, A. O., Souza, R. A. F., Schumacher, C., Wang, J., Biscaro, T., Brito, J., Calheiros, A., Jardine, K., Medeiros, A., Portela, B., Sá, S. S. d., Adachi, K., Aiken, A. C., Albrecht, R., Alexander, L., Andreae, M. O., Barbosa, H. M. J., Buseck, P., Chand, D., Comstock, J. M., Day, D. A., Dubey, M., Fan, J., Fast, J., Fisch, G., Fortner, E., Giangrande, S., Gilles, M., Goldstein, A. H., Guenther, A., Hubbe, J., Jensen, M., Jimenez, J. L., Keutsch, F. N., Kim, S., Kuang, C., Laskin, A., McKinney, K., Mei, F., Miller, M., Nascimento, R., Pauliquevis, T., Pekour, M., Peres, J., Petäjä, T., Pöhlker, C., Pöschl, U., Rizzo, L., Schmid, B., Shilling, J. E., Dias, M. A. S., Smith, J. N., Tomlinson, J. M., Tóta, J., and Wendisch, M.: The Green Ocean Amazon Experiment (GoAmazon2014/5) Observes Pollution Affecting
- 930 Gases, Aerosols, Clouds, and Rainfall over the Rain Forest, *Bulletin of the American Meteorological Society*, 98, 981-997, 10.1175/bams-d-15-00221.1, 2017.
- Martin, S. T., Andreae, M. O., Artaxo, P., Baumgardner, D., Chen, Q., Goldstein, A. H., Guenther, A., Heald, C. L., Mayol-Bracero, O. L., McMurry, P. H., Pauliquevis, T., Pöschl, U., Prather, K. A., Roberts, G. C., Saleska, S. R., Silva Dias, M. A., Spracklen, D. V., Swietlicki, E., and Trebs, I.: Sources and properties of Amazonian aerosol particles, *Reviews of Geophysics*, 48,
- 940 10.1029/2008rg000280, 2010b.
- Martin, S. T., Artaxo, P., Machado, L. A. T., Manzi, A. O., Souza, R. A. F., Schumacher, C., Wang, J., Andreae, M. O., Barbosa, H. M. J., Fan, J., Fisch, G., Goldstein, A. H., Guenther, A., Jimenez, J. L., Pöschl, U., Silva Dias, M. A., Smith, J. N., and Wendisch, M.: Introduction: Observations and Modeling of the Green Ocean Amazon (GoAmazon2014/5), *Atmospheric Chemistry and Physics*, 16, 4785-4797, 10.5194/acp-16-4785-2016, 2016.
- 945 Mather, J. H., and Voyles, J. W.: The Arm Climate Research Facility: A Review of Structure and Capabilities, *Bulletin of the American Meteorological Society*, 94, 377-392, 10.1175/bams-d-11-00218.1, 2013.
- 950 Moran-Zuloaga, D., Ditas, F., Walter, D., Saturno, J., Brito, J., Carbone, S., Chi, X., Hrabě de Angelis, I., Baars, H., Godoi, R. H. M., Heese, B., Holanda, B. A., Lavrič, J. V., Martin, S. T., Ming, J., Pöhlker, M. L., Ruckteschler, N., Su, H., Wang, Y., Wang, Q., Wang, Z., Weber, B., Wolff, S., Artaxo, P., Pöschl, U., Andreae, M. O., and Pöhlker, C.: Long-term study on coarse mode aerosols in the Amazon rain forest with the frequent intrusion of Saharan dust plumes, *Atmospheric Chemistry and Physics*, 18, 10055-10088, 10.5194/acp-18-10055-2018, 2018.
- 955 Oshima, N., Koike, M., Zhang, Y., Kondo, Y., Moteki, N., Takegawa, N., and Miyazaki, Y.: Aging of black carbon in outflow from anthropogenic sources using a mixing state resolved model: Model development and evaluation, *Journal of Geophysical Research: Atmospheres*, 114, 10.1029/2008jd010680, 2009.



- 960 Oshima, N., Yukimoto, S., Deushi, M., Koshiro, T., Kawai, H., Tanaka, T. Y., and Yoshida, K.: Global and Arctic effective radiative forcing of anthropogenic gases and aerosols in MRI-ESM2.0, *Progress in Earth and Planetary Science*, 7, 38, <https://doi.org/10.1186/s40645-020-00348-w>, 2020.
- Pöhlker, C., Wiedemann, K. T., Sinha, B., Shiraiwa, M., Gunthe, S. S., Smith, M., Su, H., Artaxo, P.,  
965 Chen, Q., Cheng, Y., Elbert, W., Gilles, M. K., Kilcoyne, A. L. D., Moffet, R. C., Weigand, M., Martin, S. T., Pöschl, U., and Andreae, M. O.: Biogenic Potassium Salt Particles as Seeds for Secondary Organic Aerosol in the Amazon, *Science*, 337, 1075-1078, 10.1126/science.1223264, 2012.
- Pöschl, U., Martin, S. T., Sinha, B., Chen, Q., Gunthe, S. S., Huffman, J. A., Borrmann, S., Farmer, D.  
970 K., Garland, R. M., Helas, G., Jimenez, J. L., King, S. M., Manzi, A., Mikhailov, E., Pauliquevis, T., Petters, M. D., Prenni, A. J., Roldin, P., Rose, D., Schneider, J., Su, H., Zorn, S. R., Artaxo, P., and Andreae, M. O.: Rainforest Aerosols as Biogenic Nuclei of Clouds and Precipitation in the Amazon, *Science*, 329, 1513-1516, 10.1126/science.1191056, 2010.
- Prenni, A. J., Petters, M. D., Kreidenweis, S. M., Heald, C. L., Martin, S. T., Artaxo, P., Garland, R. M.,  
975 Wollny, A. G., and Pöschl, U.: Relative roles of biogenic emissions and Saharan dust as ice nuclei in the Amazon basin, *Nature Geoscience*, 2, 402-405, 10.1038/ngeo517, 2009.
- Rizzolo, J. A., Barbosa, C. G. G., Borillo, G. C., Godoi, A. F. L., Souza, R. A. F., Andreoli, R. V., Manzi, A. O., Sá, M. O., Alves, E. G., Pöhlker, C., Angelis, I. H., Ditas, F., Saturno, J., Moran-Zuloaga, D., Rizzo, L. V., Rosário, N. E., Pauliquevis, T., Santos, R. M. N., Yamamoto, C. I., Andreae, M. O., Artaxo, P., Taylor, P. E., and Godoi, R. H. M.: Soluble iron nutrients in Saharan dust over the central Amazon rainforest, *Atmospheric Chemistry and Physics*, 17, 2673-2687, 10.5194/acp-17-2673-2017, 2017.
- 980 Saturno, J., Holanda, B. A., Pöhlker, C., Ditas, F., Wang, Q., Moran-Zuloaga, D., Brito, J., Carbone, S., Cheng, Y., Chi, X., Ditas, J., Hoffmann, T., Hrabě de Angelis, I., Könemann, T., Lavrič, J. V., Ma, N., Ming, J., Paulsen, H., Pöhlker, M. L., Rizzo, L. V., Schlag, P., Su, H., Walter, D., Wolff, S., Zhang, Y., Artaxo, P., Pöschl, U., and Andreae, M. O.: Black and brown carbon over central Amazonia: long-term aerosol measurements at the ATTO site, *Atmos. Chem. Phys.*, 18, 12817–12843, <https://doi.org/10.5194/acp-18-12817-2018>, 2018.
- 985 Swap, R., Garstang, M., Greco, S., Talbot, R., and Kållberg, P.: Saharan dust in the Amazon Basin, *Tellus B: Chemical and Physical Meteorology*, 44, 133-149, 10.3402/tellusb.v44i2.15434, 2017.
- Tanaka, T. Y. and Chiba, M.: Global simulation of dust aerosol with a chemical transport model, *MASINGAR. J. Meteor. Soc. Japan*, 83A, 255–278, 2005.
- 990 Wang, J., Krejci, R., Giangrande, S., Kuang, C., Barbosa, H. M., Brito, J., Carbone, S., Chi, X., Comstock, J., Ditas, F., Lavric, J., Manninen, H. E., Mei, F., Moran-Zuloaga, D., Pöhlker, C., Pöhlker, M. L., Saturno, J., Schmid, B., Souza, R. A., Springston, S. R., Tomlinson, J. M., Toto, T., Walter,
- 995

D., Wimmer, D., Smith, J. N., Kulmala, M., Machado, L. A., Artaxo, P., Andreae, M. O., Petaja, T., and Martin, S. T.: Amazon boundary layer aerosol concentration sustained by vertical transport during rainfall, *Nature*, 539, 416-419, 10.1038/nature19819, 2016a.

1000 Wang, Q., Saturno, J., Chi, X., Walter, D., Lavric, J. V., Moran-Zuloaga, D., Ditas, F., Pöhlker, C., Brito, J., Carbone, S., Artaxo, P., and Andreae, M. O.: Modeling investigation of light-absorbing aerosols in the Amazon Basin during the wet season, *Atmospheric Chemistry and Physics*, 16, 14775-14794, 10.5194/acp-16-14775-2016, 2016b.

Whitehead, J. D., Darbyshire, E., Brito, J., Barbosa, H. M. J., Crawford, I., Stern, R., Gallagher, M. W., Kaye, P. H., Allan, J. D., Coe, H., Artaxo, P., and McFiggans, G.: Biogenic cloud nuclei in the  
1005 central Amazon during the transition from wet to dry season, *Atmospheric Chemistry and Physics*, 16, 9727-9743, 10.5194/acp-16-9727-2016, 2016.

Wittmaack, K.: Brochosomes produced by leafhoppers-a widely unknown, yet highly abundant species of bioaerosols in ambient air, *Atmospheric Environment*, 39, 1173-1180, 10.1016/j.atmosenv.2004.11.003, 2005.

1010 Worobiec, A., Szalóki, I., Osán, J., Maenhaut, W., Anna Stefaniak, E., and Van Grieken, R.: Characterisation of Amazon Basin aerosols at the individual particle level by X-ray microanalytical techniques, *Atmospheric Environment*, 41, 9217-9230, 10.1016/j.atmosenv.2007.07.056, 2007.

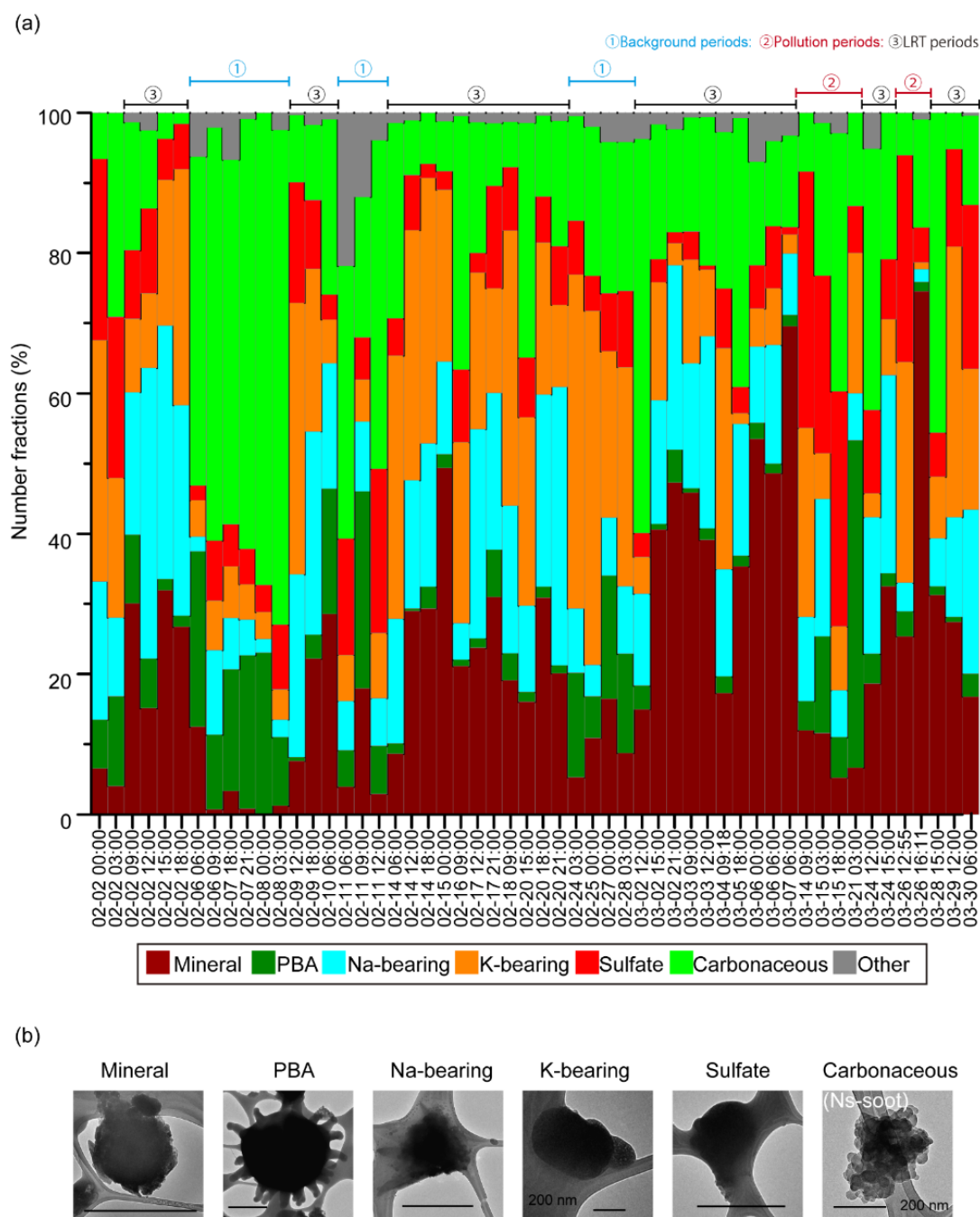
1015 Wu, L., Li, X., Kim, H., Geng, H., Godoi, R. H. M., Barbosa, C. G. G., Godoi, A. F. L., Yamamoto, C. I., de Souza, R. A. F., Pöhlker, C., Andreae, M. O., and Ro, C.-U.: Single-particle characterization of aerosols collected at a remote site in the Amazonian rainforest and an urban site in Manaus, Brazil, *Atmospheric Chemistry and Physics*, 19, 1221-1240, 10.5194/acp-19-1221-2019, 2019.

1020 Yokelson, R. J., Urbanski, S. P., Atlas, E. L., Toohey, D. W., Alvarado, E. C., Crounse, J. D., Wennberg, P. O., Fisher, M. E., Wold, C. E., Campos, T. L., Adachi, K., Buseck, P. R., and Hao, W. M.: Emissions from forest fires near Mexico City, *Atmos. Chem. Phys.*, 7, 5569–5584, <https://doi.org/10.5194/acp-7-5569-2007>, 2007.

Yoshizue, M., Iwamoto, Y., Adachi, K., Kato, S., Sun, S., Miura, K., and Uematsu, M.: Individual particle analysis of marine aerosols collected during the North–South transect cruise in the Pacific  
1025 Ocean and its marginal seas, *Journal of Oceanography*, 75, 513-524, 10.1007/s10872-019-00519-4, 2019.

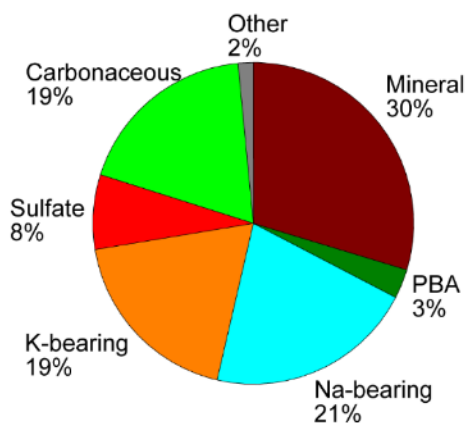
1030 Yu, H., Chin, M., Yuan, T., Bian, H., Remer, L. A., Prospero, J. M., Omar, A., Winker, D., Yang, Y., Zhang, Y., Zhang, Z., and Zhao, C.: The fertilizing role of African dust in the Amazon rainforest: A first multiyear assessment based on data from Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations, *Geophysical Research Letters*, 42, 1984-1991, 10.1002/2015gl063040, 2015.

- 1035 Yukimoto, S., Kawai, H., Koshiro, T., Oshima, N., Yoshida, K., Urakawa, S., Tsujino, H., Deushi, M.,  
Tanaka, T., Hosaka, M., Yabu, S., Yoshimura, H., Shindo, E., Mizuta, R., Obata, A., Adachi,  
Y., and Ishii, M.: The Meteorological Research Institute Earth System Model version 2.0, MRI-  
ESM2.0: Description and basic evaluation of the physical component, *J. Meteor. Soc. Jpn.*, 97,  
931–965, <https://doi.org/10.2151/jmsj.2019-051>, 2019.
- Yumimoto, K., Tanaka, T. Y., Oshima, N., and Maki, T.: JRAero: the Japanese Reanalysis for Aerosol  
v1.0, *Geosci. Model Dev.*, 10, 3225–3253, <https://doi.org/10.5194/gmd-10-3225-2017>, 2017.

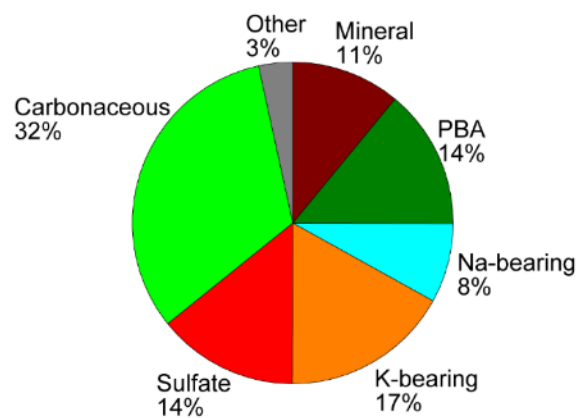


**Figure 1a.** Number fractions of each aerosol particle type for all analysed samples (a) and the representative TEM images of each particle type (b). Scale bars for Mineral, PBA, Na-bearing, and sulfate are 1  $\mu\text{m}$ , and those for K-bearing and carbonaceous are 200 nm. Compositions and low-magnification images of these particles are shown in Fig. S2 (mineral), Fig. S5 (PBA), Fig. 11 (Na-bearing), Fig. S7 (K-bearing), Fig S8 (sulfate), and Fig. S7 (carbonaceous). Samples were divided into LRT and other periods (bars in the panel (a)-top). Other periods were further divided into pollution periods (14, 15, and 26 March, 2014) and background periods (all other periods except the pollution periods and 2 February, 2014) based on the classification by de Sá et al. (2018). Samples collected on 2 February were outside of the measurement period by de Sá et al.

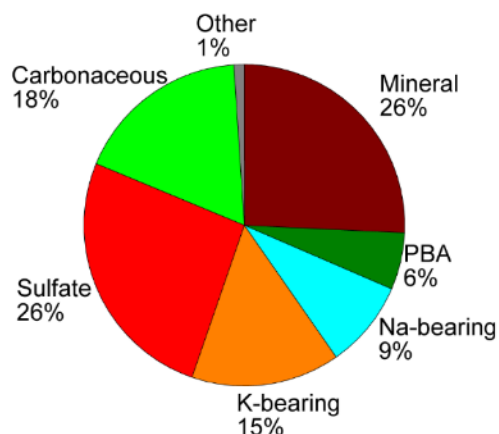
a) Long-range transport period samples



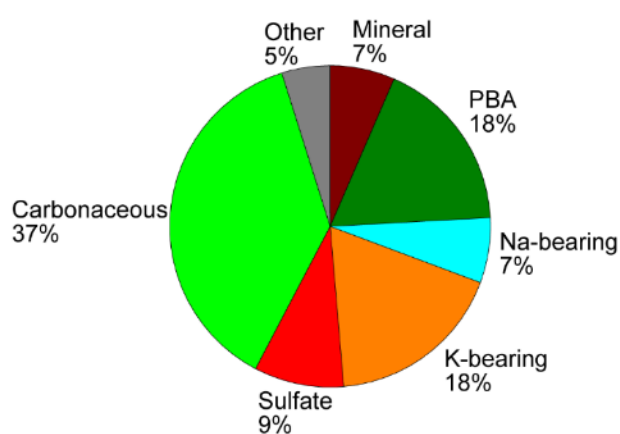
b) Other period samples



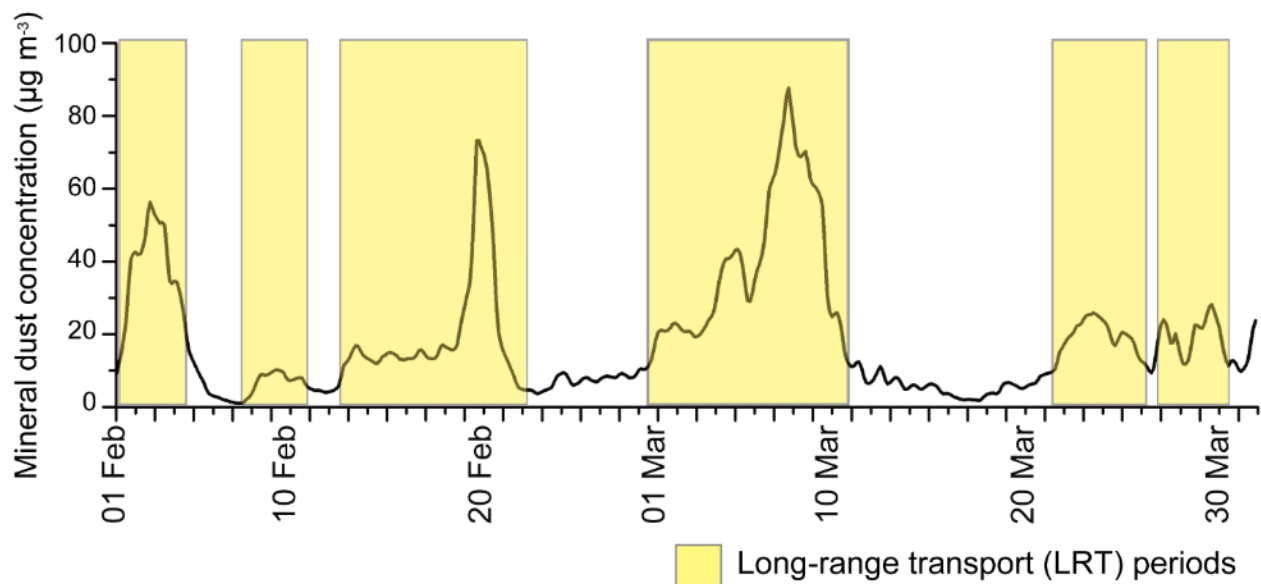
c) Pollution period samples



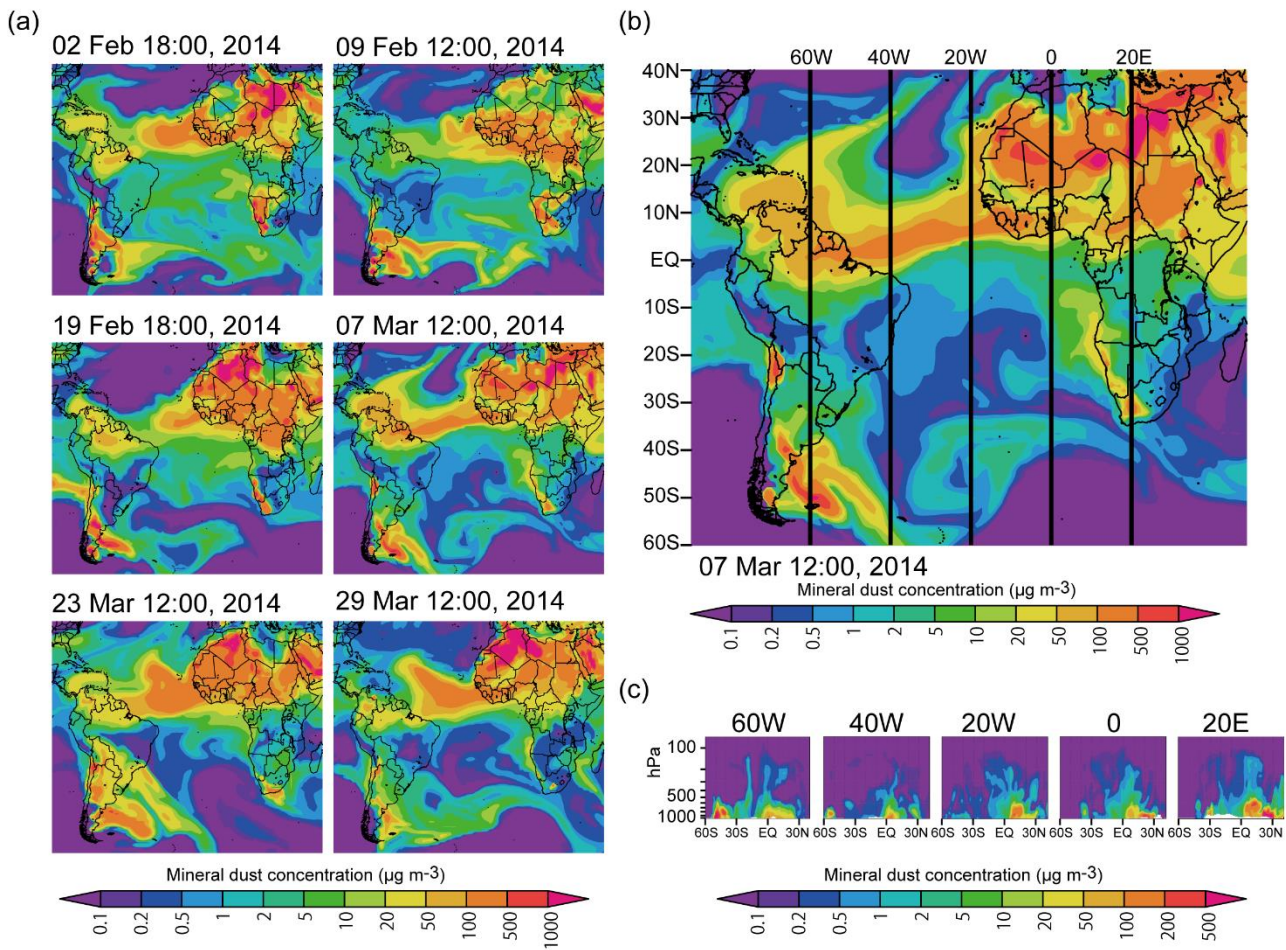
d) Background period samples



**Figure 1b2.** Number fractions of each aerosol particle type for ~~(a) all analysed samples and~~ average values during the ~~(ab)~~ LRT period and ~~(eb)~~ other period samples. Other periods were further divided into ~~(dc)~~ pollution periods (14, 15, and 26 March, 2014) and ~~(ed)~~ background periods. See Figure 1 for the sample classifications. ~~(all other periods except the pollution periods and 2 February, 2014) based on the classification by de Sá et al. (2018). Samples collected on 2 February were outside of the measurement period by de Sá et al.~~



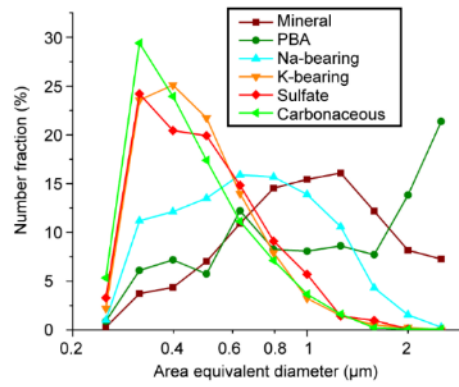
1060 **Figure 2a3.** Model simulations of temporal variation of mineral dust mass concentrations at the T3 site. Yellow screens show LRT periods.



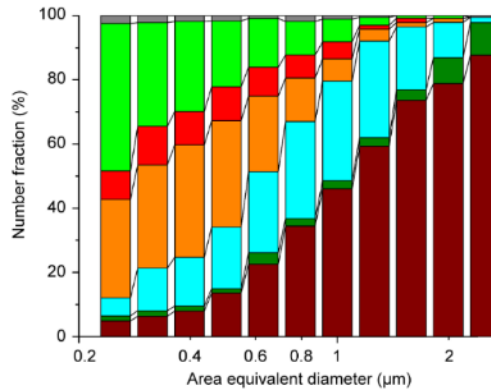
1065 **Figure 2b4.** Model simulations of snapshots of (a) horizontal distributions of mineral dust concentrations at the surface level for each LRT period and (b) horizontal and (c) vertical distributions in a specific LRT event (7 March, 2014). The panels (c) show the vertical distributions of mineral dust concentrations along the longitudes (black lines) in the panel (b).



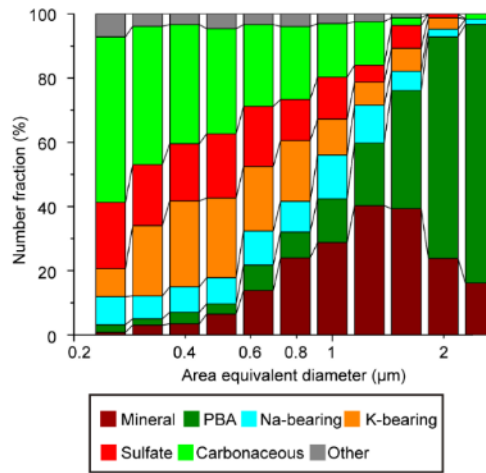
(a) Size distributions



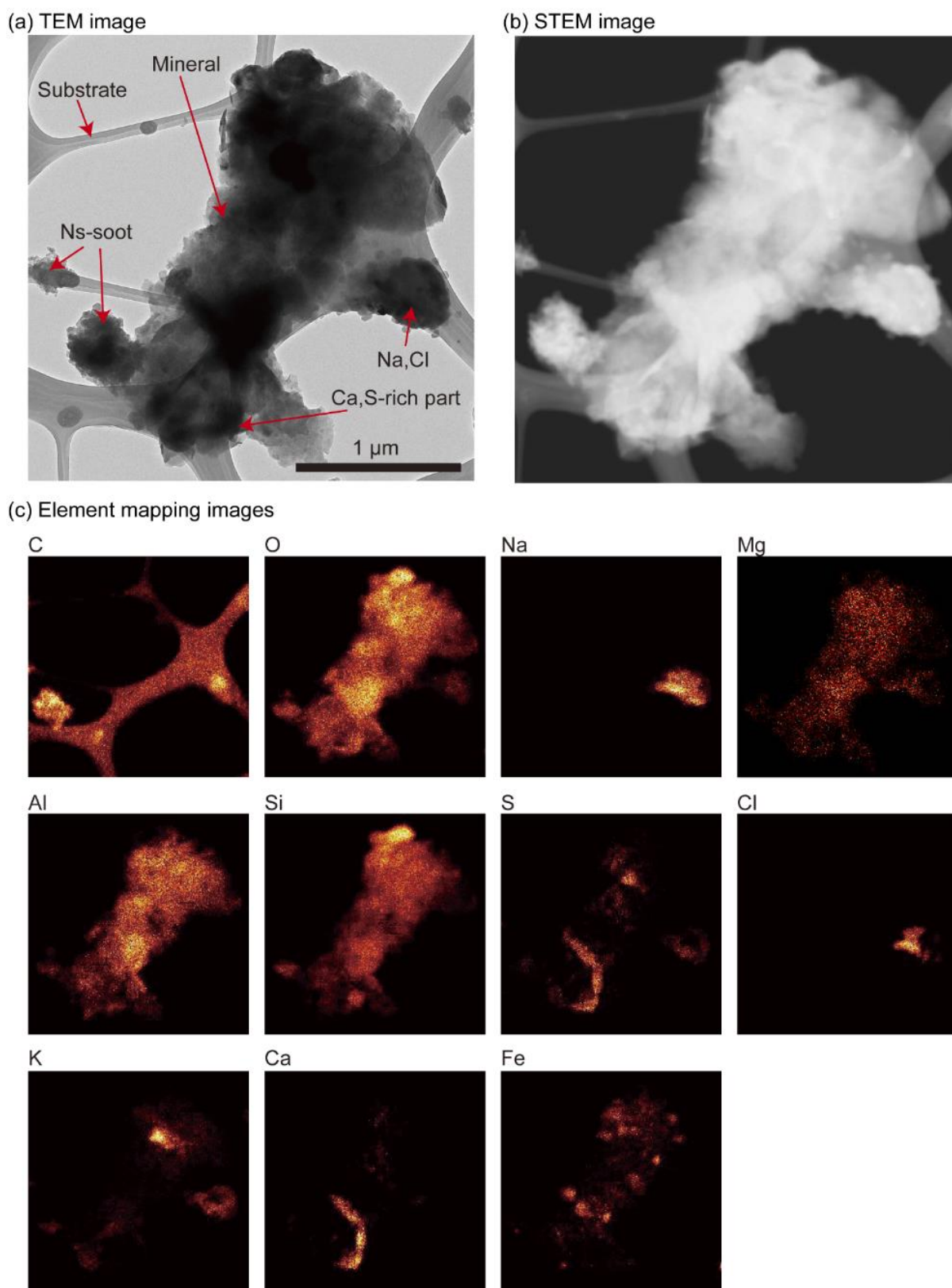
(b) Number fractions for LRT periods



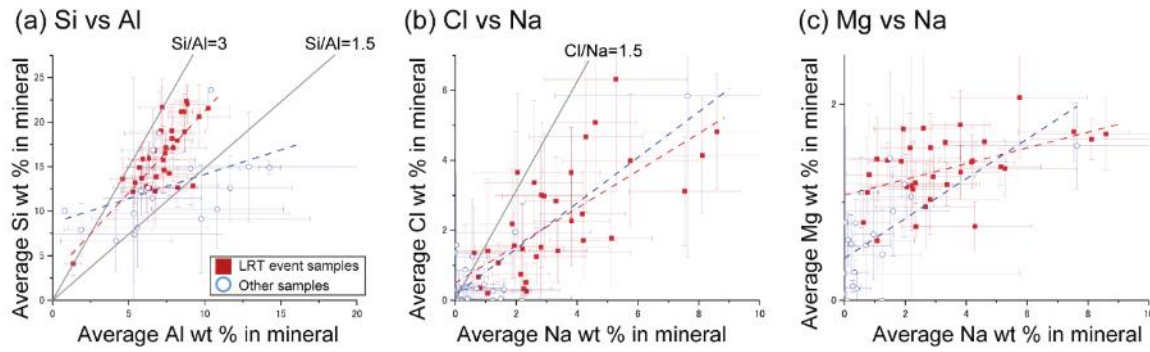
(c) Number fractions for other periods



**Figure 45.** Size distributions and number fractions of each aerosol type. (a) Size distributions of each aerosol particle type among all samples. The Y-axis shows the number fractions for each bin. N=2519 (mineral), 557 (PBA particle), 1806 (Na-bearing particle), 2223 (K-bearing particle), 1120 (sulfate), 2289 (carbonaceous particle), and 221 (other; not shown). Size-dependent number fractions of each aerosol particle type for (b) LRT periods and (c) other samples. ~~The size measurements and particle classifications are the same as in Fig. 1.~~ N=7769 (LRT periods) and 2966 (other periods). Size bins are shown on a log scale, and the size ranges are <0.25, 0.25-0.32, 0.32-0.40, 0.40-0.50, 0.50-0.63, 0.63-0.79, 0.79-1.00, 1.00-1.26, 1.26-1.58, 1.58-2.00, and >2.00  $\mu\text{m}$ .

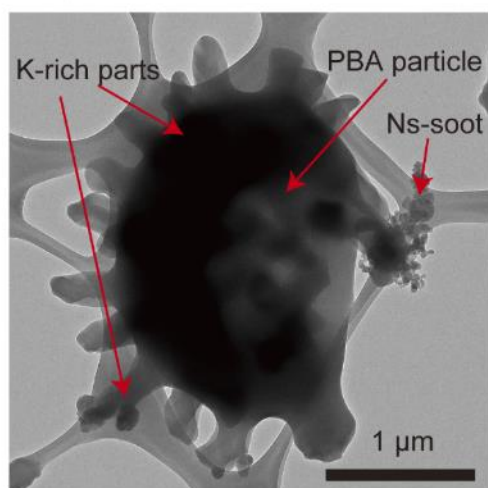


**Figure 3a6.** Shape and compositions of mineral particles. (a) TEM, (b) STEM, and (c) element mapping images of a mineral particle. This particle was obtained from the sample collected during 15:00-15:30, 2 March, 2014 on a lacey carbon substrate.

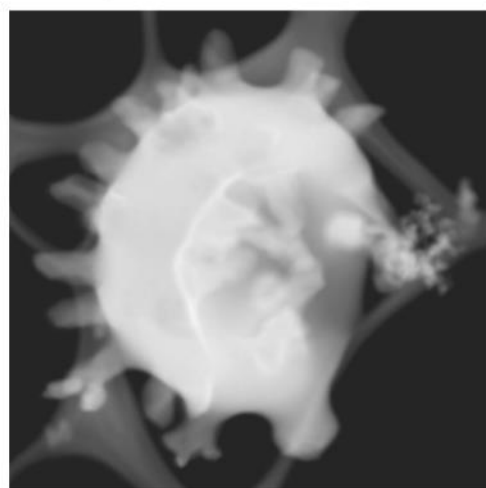


**Figure 7.** (a) Relations (a) between average Si and Al weight % in mineral particles, (eb) between average Cl and Na weight % in mineral particles, and (fc) between average Mg and Na weight % in mineral particles. Red squares indicate sample averaged values for LRT period samples. Blue open circles indicate sample average values for other (non-LRT period) samples. The sample from 9:00 on 6 February had only one mineral particle and is not shown in the plots because it has a large Al fraction and no Na (0, 30, and 1 weight % for Na, Al, and Si, respectively). Coefficients  $R^2$  of determination for (a), (b), and (c) were 0.60, 0.47, and 0.24 for the LRT period samples and 0.18, 0.66, and 0.40 for other samples, respectively. Trend lines are shown in red and blue broken lines for LRT period and other samples, respectively. The correlation between Si and Al for other samples (a) is relatively low because of possible contributions from two sources (LRT and local dusts). Error bars indicate the 95% confidence intervals.

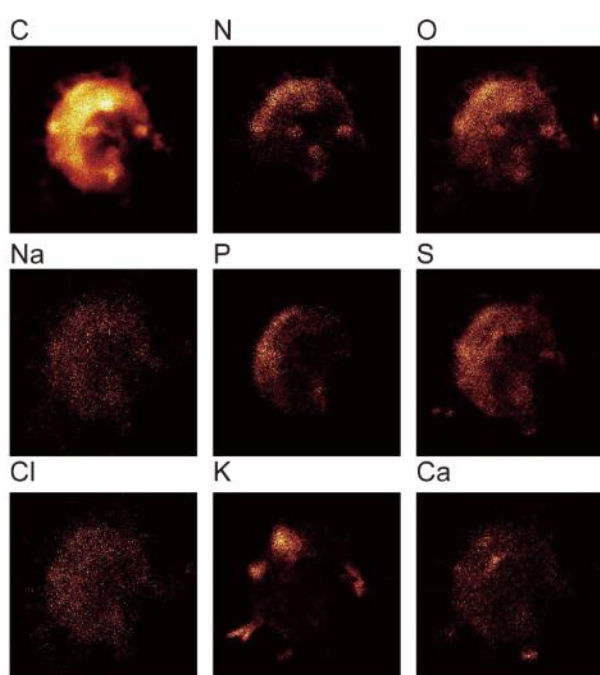
(a) TEM image



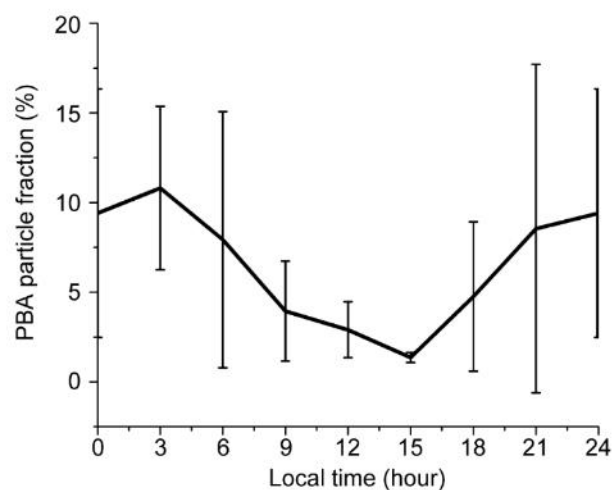
(b) STEM image



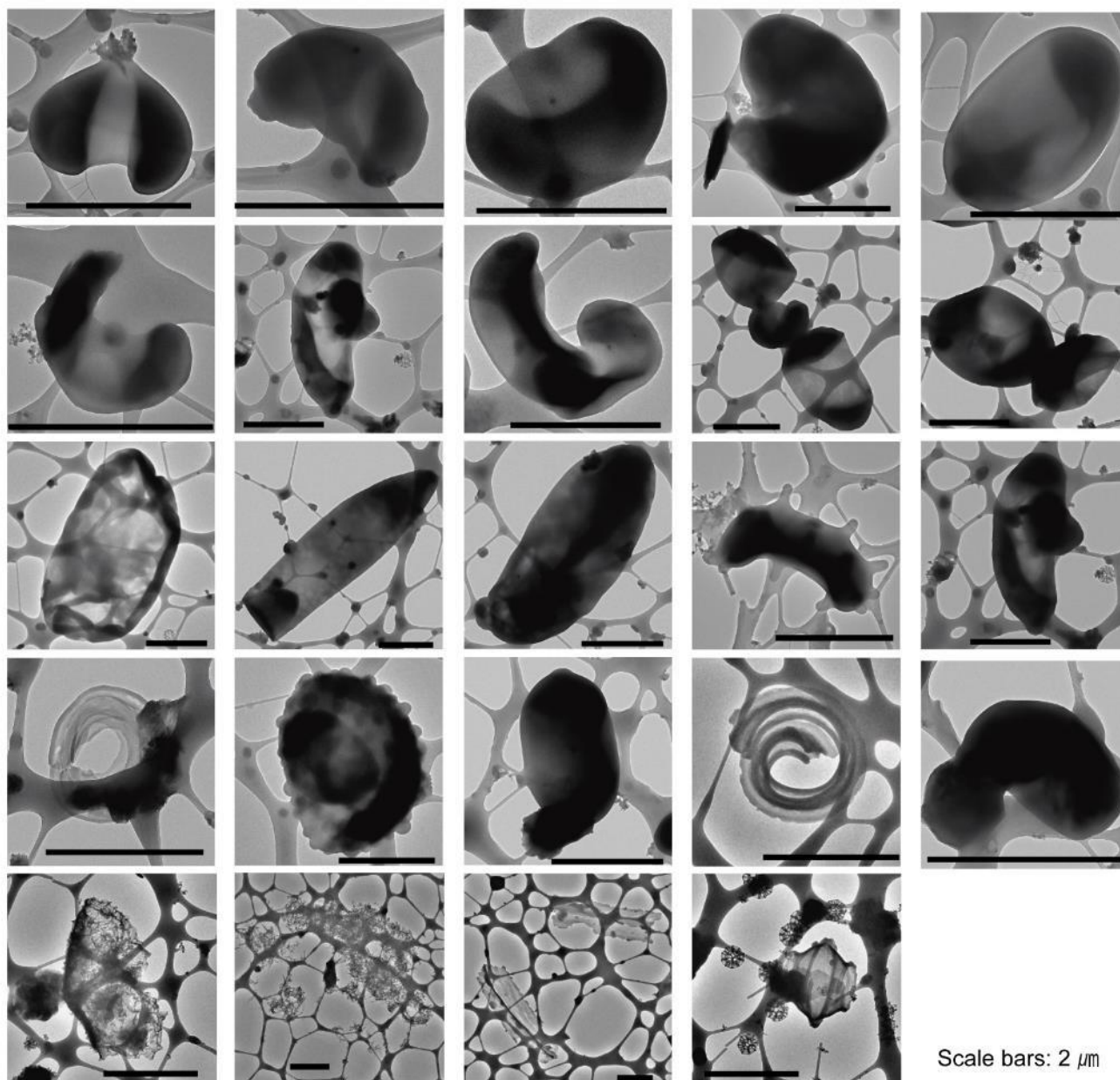
(c) Element mapping images



(d) Diurnal number fraction

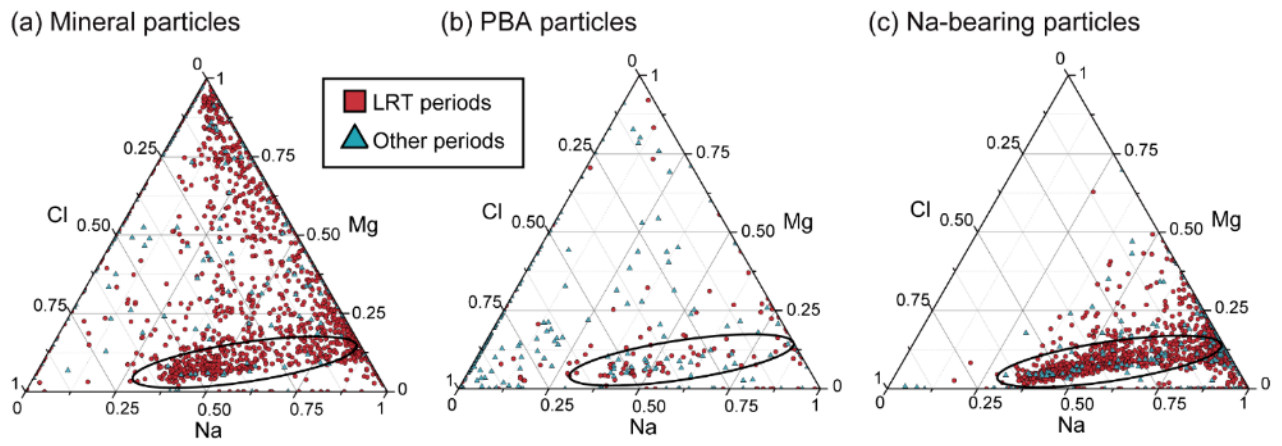


**Figure 58.** Shape, compositions, and diurnal abundance of PBA particles. (a) TEM, (b) STEM, and (c) element mapping images of a PBA particle. This particle contains K-rich and C-N-O-rich grains and attaches an ns-soot particle. The sample was collected from 0:00-0:30, 27 February, 2014. (d) Diurnal number fractions of PBA particles. The fractions were averaged values for all samples. Error bars indicate the 95% confidence intervals.



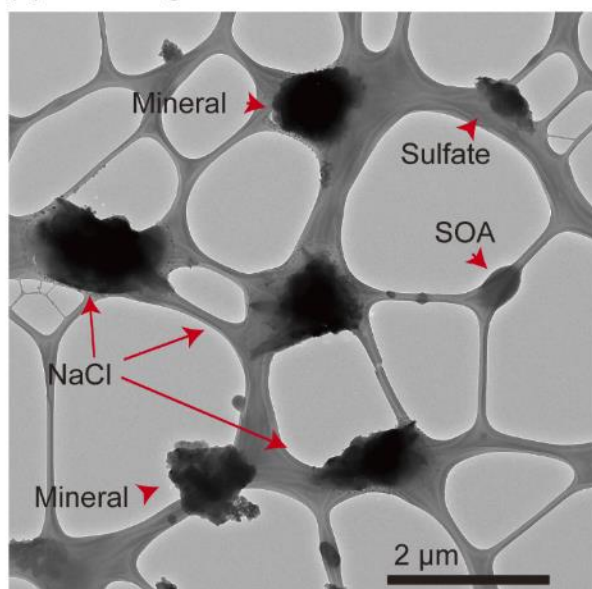
105 **Figure 69.** Examples of TEM images of PBA and the relevant particles. The TEM images were obtained  
 from samples collected during other (background) periods (09:00, 7 February; 15:00, 10 February; 0:00,  
 27 February; 3:00, 15 March, 2014; and 09:00, 18 March, 2014). Brochosome particles, which originate  
 from leafhoppers (Wittmaack, 2005), were abundant in some samples (e.g., bottom right image) and were  
 included in the “other” category because they do not contain P. Some particles were too fragile to analyse  
 1110 the compositions (e.g., three images from the bottom left image), although their shapes imply that they  
 have biological sources. As these PBA particles were observed under vacuum, they can have inflated  
 shapes when observed in an ambient condition.



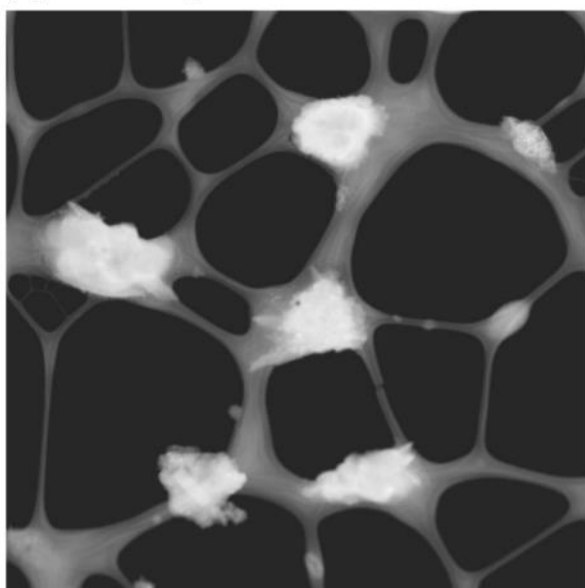


**Figure 10.** Weight % ratios among Na, Mg, and Cl within (a) mineral particles, (b) PBA particles, and (c) Na-bearing sea-salt particles. The black ellipse areas indicate typical sea-salt compositions from a marine source.

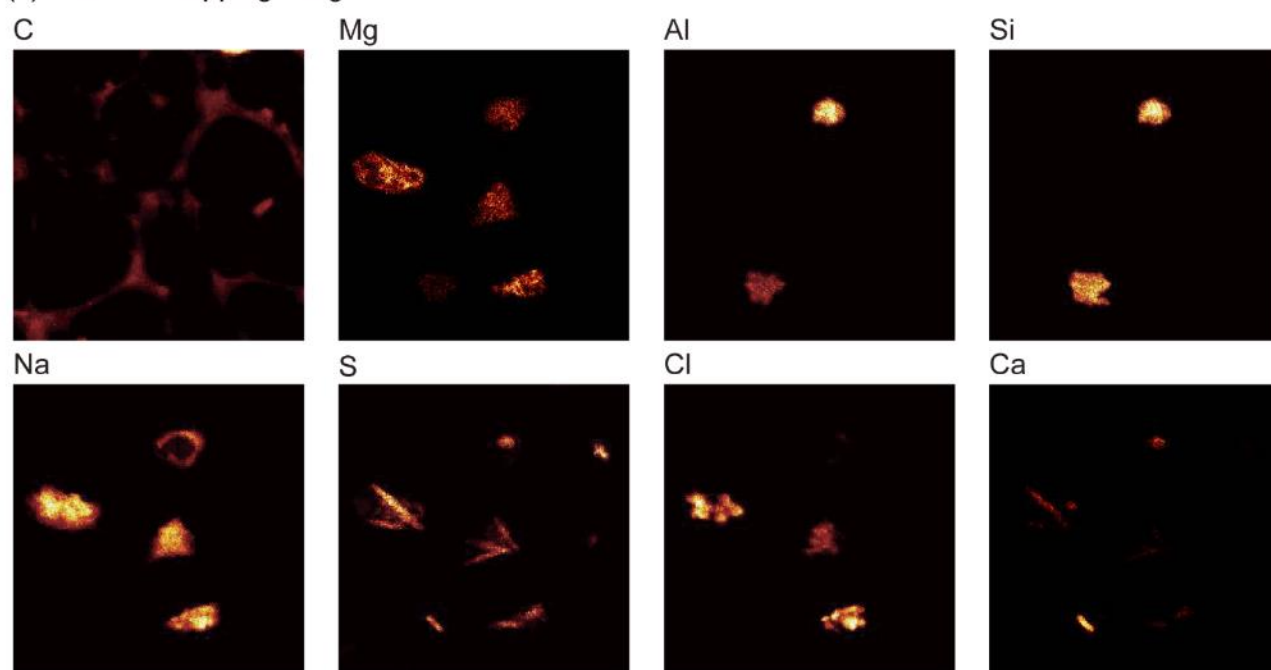
(a) TEM image



(b) STEM image



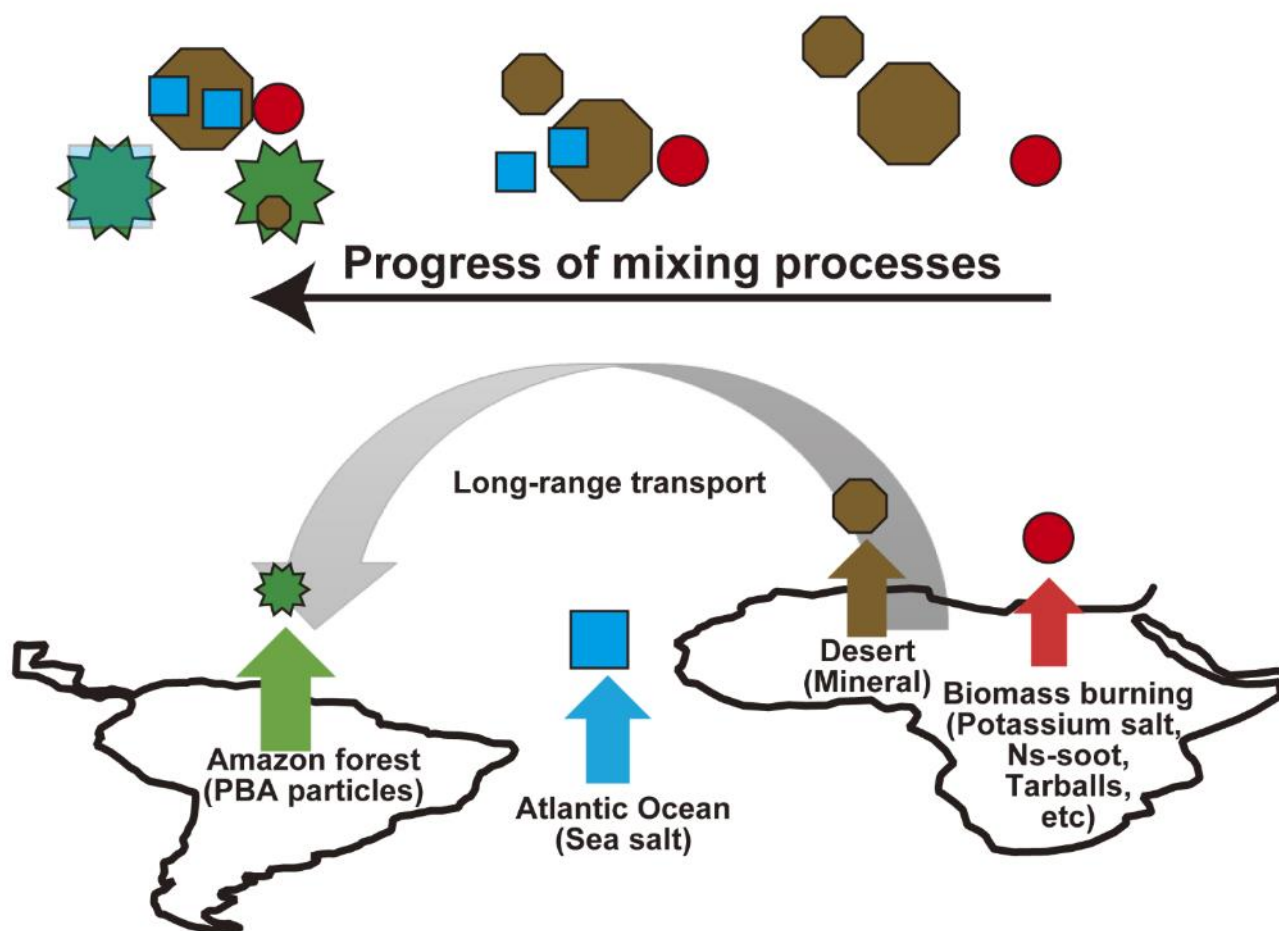
(c) Element mapping images



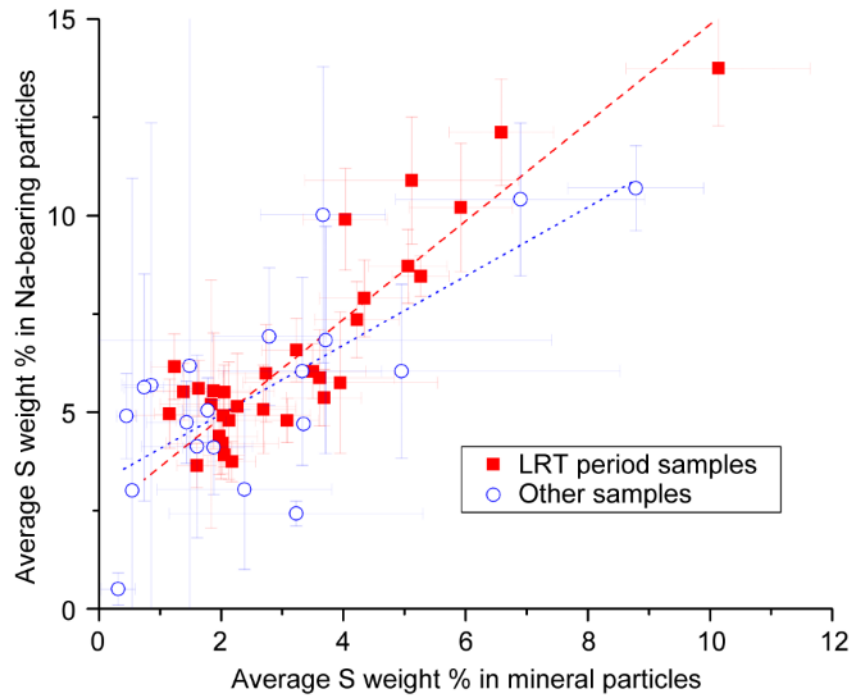
120 **Figure 711.** Shapes and compositions of sea-salt particles. (a) TEM, (b) STEM, and (c) element mapping  
images of sea-salt and mineral particles. These sea-salt particles also contain S as sulfate. The sample was  
collected from 12:00-12:30, 2 February, 2014. ~~Weight % ratios among Na, Mg, and Cl within (d) mineral  
particles, (e) PBA particles, and (f) sea salt particles. The black ellipse areas indicate typical sea salt  
compositions from a marine source.~~

125





130 **Figure 812.** Schematic image of possible particle sources and transport pathways. Top images show the progress of individual-particle mixings during LRT. The bottom image shows possible major sources for each particle (Martin et al., 2010b).



135 **Figure 913.** The relation between average S weight % in sea-salt and mineral particles within LRT periods (open red squares) and other (blue circles) samples. Coefficients  $R^2$  of determination were 0.80 and 0.51 for the LRT period (red dashed line) and other samples (blue dotted line), respectively.