Composition and mixing state of atmospheric aerosols determined by electron microscopy: method development and application to aged Saharan dust deposition in the Caribbean boundary layer

Konrad Kandler¹, Kilian Schneiders¹, Martin Ebert¹, Markus Hartmann¹, Stephan Weinbruch¹, Maria Prass², Christopher Pöhlker²

¹Institute for Applied Geosciences, Technical University Darmstadt, 64287 Darmstadt, Germany
²Max Planck Institute for Chemistry, Multiphase Chemistry Department, 55128 Mainz, Germany

Correspondence to: K. Kandler (kandler@geo.tu-darmstadt.de)

Abstract. The microphysical properties, composition and mixing state of mineral dust, sea-salt and secondary compounds were measured by active and passive aerosol sampling followed by electron microscopy and X-ray fluorescence in the Caribbean marine boundary layer. Measurements were carried out at Ragged Point, Barbados during June/July 2013 and August 2016. Techniques were developed to conclude from collected aerosol on atmospheric concentrations and aerosol mixing-state, and different models were compared. It became obvious that in the diameter range with the highest dust deposition the models disagree by more than two orders of magnitude. Aerosol at Ragged Point was dominated by dust, sea-salt and soluble sulfates in varying proportions. Contribution of sea-salt was dependent on local wind speed. Sulfate concentrations were linked to long-range transport from Africa / Europe and South America / Southern Atlantic Ocean. Dust sources were in Western Africa. The total dust deposition observed was 10 mg m⁻² d⁻¹ (range 0.5–47 mg m⁻² d⁻¹), of which 0.67 mg m⁻² d⁻¹ was iron and 0.001 mg m⁻² d⁻¹ phosphorus. Iron deposition had two sources, mainly silicate particles from Africa, and particularly in 2016 a lower contribution of small iron-rich particles from South America or Barbados of probably anthropogenic origin. Dust particles were mixed internally to a minor fraction (10 %), mostly with sea-salt and less frequently with sulfate. It was estimated that average dust deposition velocity under ambient conditions is increased by the internal mixture by 30–140 % for particles between 1 and 10 µm dust aerodynamic diameter, with approximately 35 % at the mass median diameter of deposition (7.0 µm). For this size, an effective deposition velocity of 6.4 mm/s (geometric standard deviation of 3.1 over all individual particles) was observed.

1 Introduction

Mineral dust and sea-salt are globally the most abundant aerosol types in the atmosphere (Andreae 1995; Grini et al. 2005). They are considerably affecting the earth’s radiation budget (Liao et al. 1998; Choobari et al. 2014) and have impact on cloud processes (Koehler et al. 2009; Tang et al. 2016; Karydis et al. 2017). Over the North Atlantic Ocean, large amounts of dust are transported westwards in the Saharan Air Layer, until they reach the Caribbean (Karyampudi et al. 1999; Prospero et al. 2009). Here, dust usually does not cross the Central American Dust Barrier (Nowottnick et al. 2011). Instead, it is down-mixed into the marine boundary layer by turbulent and convective processes and removed from the atmosphere by wet and dry deposition processes. These processes are not yet fully understood (Prospero et al. 2009; Nowottnick et al. 2011).
During its transport, mineral dust may undergo modifications by chemical processing, cloud processing or microphysical effects (Andreae et al. 1986; Falkovich et al. 2001; Matsuki et al. 2005; Sullivan et al. 2007a; Sullivan et al. 2007b). Different processes are expected to lead to different modifications (e.g., Fitzgerald et al. 2015). These processes will change the composition and particle size of dust, and thus modify its radiative properties and cloud impacts. To assess the mixing state of mineral dust, techniques considering single particles are required. While there have been investigations on dust mixing state in the past (Zhang et al. 1999; Zhang et al. 2004; Dall’Osto et al. 2010; Deboudt et al. 2010; Kandler et al. 2011a; Fitzgerald et al. 2015), the data basis is still limited. In the present work, we present results from two field campaigns in summers 2013 and 2016, where the aerosol in the marine boundary layer at Ragged Point in Barbados was collected by active and passive sampling techniques.

A particular challenge for these campaigns was the high wind speed and the high humidities at the sampling site. Therefore, the present publication consists of an extended methodical section with three major topics and a methodical as well as atmosphere-related results section. One methodical section deals with the determination of composition and mixing state of individual particles, taking into account quantification artifacts and modeling the dust- and non-dust components as well as their hygroscopic behavior. A second section is on particle collection representativeness and models relating atmospheric concentration and deposition, taking into account the single particle properties at ambient conditions. Finally, when aerosol mixing state is assessed based on offline aerosol analysis, considerations on coincidental mixing have to be made to ensure the representativeness of the results for the atmosphere. Therefore, in a third section these fundamental considerations based on model as well as experimental data are presented. In the result section, we report first on these theoretical and experimental methodical aspects, before we then discuss the atmospheric implications of the measurements.

2 Methods

2.1 Particle sampling and location

Aerosol was sampled at Ragged Point, Barbados (13° 9’ 54” N, 59° 25’ 56” W) from June 14 until July 15, 2013, and from August 6 until August 28, 2016. Sampling was performed on top of the measurement tower, approximately 17 m above the bluff (Zamora et al. 2011), which descends 30 m to the sea surface. Particles were collected on pure carbon adhesive (Spectro Tabs, Plano GmbH, Wetzlar, Germany) mounted on standard SEM aluminum stubs (Free-wing impactor, Dry particulate deposition sampler) or pure nickel plates (cascade impactor).

2.1.1 Free-wing impactor (FWI)

A FWI was constructed for inlet-free collection of particles larger than 5 µm in diameter. A FWI consists in general of a rotating arm with a sampling substrate attached, which acts as body impactor (see Fig. S1 in electronic supplement). Rotation speed, wind speed and sample substrate geometry determine the particle size cut-off for collection. FWI applied in previous investigations were constructed with a rigid setup, so adaptation to actual meteorological conditions (i.e. perpendicular adjustment of the impaction vector) needed to be performed by hand or was neglected (Jaenicke et al. 1967; Noll 1970; Noll et al. 1985; Kandler et al. 2009). The present setup achieves perpendicularity by self-adjustment of the flexibly mounted sampling substrate to the sum vector of wind and rotary movement. This is performed by addition of a small wind vane at the rotating arm adjusting the angle.
of the substrate. The rotating arm is driven by a stepper motor, which is mounted on a larger wind
vane, aligning the construction with the horizontal wind vector. To ensure that the wind vanes
respond only to the dynamic pressure, any imbalance in the setup must be avoided. The arm length
of the FWI is 0.25 m. With a constant rotation frequency of 10 Hz and the wind speeds at the
sampling location, particle impaction speeds between 16.4 and 20.2 m/s were achieved. This
corresponded to sampling volumes of air between 2.7 and 14.7 m³ for the present campaign. While
in principle the FWI could disturb its own flow field in low wind situations – the sample collector may
be influenced by its own wake from the previous rotation – this was not an issue for the present
work, as the distance of the sampling volume shifted by the wind between the same angular
positions of two consecutive rotations was always larger than 0.45 m. This is a large and therefore
safe distance in comparison to the small diameter of the sampling substrate and the counterweight
(12.5 mm and 25 mm, respectively). In total, 30 samples were collected during the campaign in 2013.

2.1.2 Dry particulate deposition sampler (DPDS)
The DPDS used in the present work is derived from the flat plate sampler of Ott et al. (2008b), which
performed best with respect to wind speed dependence in their tests. It consists of two round brass
plates (top plate diameter 203 mm, bottom plate 127 mm, thickness 1 mm each) mounted in a
distance of 16 mm. In contrast to the referred design, the one used here has a cylindrical dip in the
lower plate, which removes the sampling substrate – a SEM stub with a height of 3.2 mm – from the
airflow, reducing the flow disturbance. The dip is larger than the SEM stub and has small holes in the
bottom to catch and dispose droplets creeping across the lower plate due to the wind dynamical
pressure. The top surface of the SEM stub is located 5 mm below the lower plate’s top surface.
Larger droplets (> 1 mm) are prevented by this setup from reaching the SEM stub surface at the local
wind speeds (Ott et al. 2008b). A total of 29 samples were collected in 2013 and 22 in 2016.

2.1.3 Cascade impactor (CI)
While the principle design of the used CI is described by Kandler et al. (2007), a new version with a
larger housing, but with the same collection characteristics, was deployed in the present work. An
omnidirectional inlet with a central flow deflector cone was used, whose transmission is discussed in
section 2.4.3. The impactor was operated at a flow rate of 0.48 l/min, which is set by a critical nozzle.
Nozzle diameters of 2.04, 1.31, 0.71, 0.49, 0.38, and 0.25 mm were used, corresponding to nominal
cut-off aerodynamic diameters of 5.2, 2.7, 1.0, 0.54, 0.33, and 0.1 µm, respectively. Sampling times
were adjusted to the estimated aerosol concentration and ranged between 10 and 60 min for the
supermicron and between 12 and 45 s for the submicron fraction. A total of 30 CI samples were
collected in 2013.

2.2 Meteorological data, backward trajectory analyses and high-volume
sampling / mass concentrations
In 2013, meteorological data was obtained at Ragged Point directly next to the particle sampling
devices. In 2016 wind, temperature and relative humidity were measured in parallel at The Barbados
Cloud Observatory at Deebles Point, which is located 400 m across a small cove to the southeast
(Stevens et al. 2016).
The measurements in 2013 are grouped into two time periods divided by the passage of the tropical
storm Chantal, which changed the atmospheric structure and air mass origin (Weinzierl et al. 2017).
The period from June 14 to July 8 will be referred to as pre-storm, the one from July 10 to 15 as post-
storm.
Backward trajectories were calculated with Hysplit 4 rev. 761 (Stein et al. 2015) based on Global Data Assimilation System (GDAS) with 0.5° grid resolution (NOAA-ARL 2017). A backward-trajectory ensemble consisting of a grid of 3x3 trajectories ending at 13.16483 (±0.5°) N and 59.43203 (±0.5°) W at each altitude above sea level (300, 500, 700, 1000, 1500, and 2500 m) was calculated. Backward trajectory length was 10 days in 1-hour steps, and an ensemble calculation was started for every hour during the sample collection periods. Taking into account particle concentrations and deposition rates as well as chemical properties, potential source contribution functions (PSCF) were calculated (Ashbaugh et al. 1985) with a boundary layer approach. For each trajectory point it was checked, whether the trajectory altitude was below the lowest boundary layer height provided by the GDAS data set. If this condition was met, this particular point was regarded as a potential aerosol injection spot and counted into the according source grid cell of 1° x 1° size. For determining possible sources, all trajectories originating during collection of a particular sample were attributed with sample properties of interest. Finally, the average for each source grid cell was calculated and then weighted with a function based on the number of points in the cell to avoid an overrepresentation of cells with high statistical uncertainty. The weighting function is generalized from the step function of Xu et al. (2010) as

\[ w_{\text{PSCF}} = \exp \left[ -2.93 \left( \frac{W_j}{\bar{W}} + 0.89 \right)^{-2.94} \right] \]

with \( W_j \) the number of trajectory points counted in cell number \( j \), \( \bar{W} \) the average number of trajectory points per cell.

As result, a map based on PSCF shows regions with typically high or low values for airmasses passing through the boundary layer in according grid cells. Note that by this approach, sources contributing to advected aerosol can be identified, but local sources of course will not provide a usable signal. Also, aerosol from remote sources might be transported inside the boundary layer and, thus, would be attributed to also the transport path in addition to its source.

### 2.3 Scanning electron microscopy: individual particle composition, analytical and statistical uncertainties

About 22,000 individual particles (FWI), 65,700 (DPDS) and 26,500 (CI) were analyzed with a scanning electron microscope (SEM; FEI ESEM Quanta 200 FEG and 400 FEG, FEI, Eindhoven, The Netherlands) combined with an energy-dispersive X-ray analysis (EDX; EDAX Phoenix, EDAX, Tilburg, The Netherlands and Oxford X-Max 120, Oxford Instruments, Abingdon, United Kingdom). The samples were analyzed under vacuum conditions (approximately 10^-2 Pa) without any pretreatment. Before automated analysis, samples were screened for surface defects, distinctive unusual particles shapes or deposition patterns indicating possible artifacts or contamination, and traces of liquids. Areas with surface defects (holes and bubbles in the substrate) were excluded from further data processing. The remaining areas were free from artifacts. However, FWI samples suffered in general from the presence of dried sea-spray droplets. Sample analysis was performed automatically by the software-controlled electron microscope (software EDAX/AMETEK GENESIS 5.231 and Oxford Aztec 3.3).

Automated particle segmentation from the background was performed with the backscatter electron signal. An acceleration voltage of 12.5 kV, a ‘spot size S’ (beam diameter about 3 nm) and a working distance of approximately 10 mm were used. Scanning resolution was adjusted to the particles size. For the FWI and DPDS samples 140 to 300 nm/pixel were used, for the CI samples 180 or 360 nm/pixel for the stage containing the largest particles (mainly particles larger than 2.5 µm diameter)
5 and 73 nm/pixel for the stages containing smaller particles. An X-ray signal collection time between 15 s and 20 s (EDAX) and 2 s (Oxford) for each particle was used (yielding 40,000–100,000 total counts), during which the beam was scanned over the particle cross section area.

The image analysis integrated into the SEM-EDX software determines the particles size as projected area diameter:

\[ d_g = \sqrt{4B/\pi} \]  

(2)

with \( B \) the area covered by the particle on the sample substrate.

Following Ott et al. (2008a), the volume-equivalent diameter is estimated from the projected area diameter via the volumetric shape factor expressed by particle projected area and perimeter as

\[ d_v = \frac{4\pi B}{P} d_g = \frac{1}{P} \sqrt{64\pi B^3} \]  

(3)

with \( P \) the perimeter of the particle.

In addition, for the assessment of particle coverage homogeneity and size distribution determination series of 1,000 to 2,700 images were acquired for each sample. They were analyzed by the Software Fiji/ImageJ 1.51d (Rasband 2015), using also Eq. (2) for particle size determination after application of a “triangle” type auto threshold for particles segmentation (refer to Fiji/ImageJ documentation for further details).

2.3.1 Quantification of elemental composition

Fully quantitative results in EDX analysis can only be reached under specific sample conditions. When the composition of an analyzed spot is derived from an X-ray spectrum, the sample geometry has to be considered. Besides assuming perfect smoothness and homogeneity, commonly either infinite sample depth (i.e. significantly larger than the interaction volume of a few µm) or presence of an infinitely thin film is assumed. In the former case, a ‘ZAF’ correction can be applied (Trincavelli et al. 2014), in the latter for example the Cliff-Lorimer method (Cliff et al. 1975). However, for particles these assumptions and the resulting quantifications are not valid, as shown by Laskin et al. (2006) in their Fig. 3. To overcome this problem, several standard-less techniques can be applied (Trincavelli et al. 2014), for example a Monte Carlo simulation of the interaction volume can be used (Ro et al. 2003). Alternatively, particle ZAF algorithms can be applied at least for larger particles with diameters above 1 µm (Armstrong 1991; Weinbruch et al. 1997). In the present work, however, an approach with less computational cost is applied. First, on the measurement side, a lower acceleration voltage–12.5 kV instead of 20 kV in comparative studies – eases the particle morphology problem.

Second, on the data analysis side by combining the above-mentioned correction methods as function of particle size, a higher accuracy can be achieved. In principle, particle smaller than a limit size are considered as thin films and particles large than a second limit are considered to be of infinite depth. Between the limiting sizes, values are interpolated. To determine the best interpolation method, samples with well-known composition (sodium chloride, albite) were milled to obtain particle standards with sizes between 1 and 30 µm. Particles were dispersed in clean air, re-deposited on the same sampling substrate and analyzed like described above. Several non-linear interpolation schemes were tested; the best results were obtained with:
with \( \langle X \rangle \) the corrected concentration of a particular element in the beam interaction volume, \( X_{\text{CL}} \) the element concentration determined by the Cliff-Lorrimer method, \( X_{\text{ZAF}} \) the element concentration determined by the ZAF method, \( d_l = 1.5 \, \mu m \) the lower interpolation range size limit, \( d_u = 30 \, \mu m \) the upper interpolation range size limit.

Note that the concentrations are always normalized to 100 % of the beam interaction volume, which can include besides the particle also the substrate; i.e. they do only indirectly represent an amount of matter with respect to the particle. The correction is identical for atomic and mass concentrations; in the present manuscript, atomic concentrations are used unless otherwise specified.

The result of the correction as function of particle size is shown in Fig. 1. It becomes clearly visible that the accuracy of the quantification is strongly improved, while the major uncertainty remaining originates from the particle to particle variation. This uncertainty depends on the noise in the analysis system, but is also related to particle surface morphology and its variability. The latter affects the X-ray signal mainly by unknown absorption path lengths, particularly for the lighter elements, as illustrated by Fletcher et al. (2011). The measurements shown here were performed at 20 kV acceleration voltage; at 12.5 kV as used for the sample analyses, the problems are considerably less pronounced.

Application to a sample of atmospheric particles is shown in Fig. 2. Particles dominated by Na and Cl were selected from all DPDS samples, and the positive and negative ion contributions were calculated for each particle from the determined concentration. It becomes obvious, that for a wide size range the applied correction works well and produces therefore unbiased relative concentrations for the considered elements. The outliers may occur due to noise, the negligence of C, N and O compounds or an internal mixture of sea-salt with dust (e.g., NaAlSiO₄, FeS).

Using the measured and corrected atomic concentrations, an element index is defined as:

\[
|X_i| = \frac{\langle X_i \rangle}{\sum \langle X \rangle}
\]

with \( |X_i| \) element index of a particular element with arbitrary index \( i \), \( \sum \langle X \rangle \) sum of all considered elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, if not stated differently).

### 2.3.2 Analytical measurement errors

A typical deposition sample (collected between June 21, 2013, 13:46 and June 22, 15:02, local time) was analyzed 29 times with a signal collection time per particle of 16 s. The same 300 particles were analyzed each time. For illustration of the typical precision, the particles consisting mainly of Na and Cl were selected from. Fig. 3 illustrates the average composition and standard deviation (1 σ) for each particle. The average values show a typical behavior for atmospheric sea-salt with a slightly depleted Cl and enriched S concentration (e.g., McInnes et al. 1994). The precision – shown as relative standard deviation – increases with particle size. This is caused by the increasing amount of...
material contributing to the particle’s signal up to a point at about 3 µm particles, from which the 
beam excitation volume is completely inside the particle. For the major compounds, the precision is 
in the range of 2 % relative standard deviation. For minor compounds, it is between 10 and 20 % for 
particles 3 µm and larger, but can exceed 100 % for the smallest ones. The latter high uncertainties 
could be decreased with suitable working conditions (magnification, measurement time), but are not 
focus of the present paper.

The uncertainty in particle diameter also depends on its size. For particles with 2 µm diameter, the 
relative standard deviation is about 1.5 % decreasing to less than 1 % for particles larger than 3 µm.
This is in the same range as the systematic accuracy of SEM (1–2 %).

2.3.3 Estimation of the dust contribution to each single particle in a dust / sea-salt / 
sulfate mixture and the size of the according dust inclusion

Sampling was performed in a region where locally emitted sea-salt aerosol and other soluble species 
are mixed with long-range transported mineral dust. As in particular the mineral dust contribution is 
of special interest, dis-entangling the particle populations and considering them separately an 
important task.

To calculate the size of a dust inclusion and the according volume fraction for an internally mixed 
particle from the chemical composition, the different elemental contributions have to be attributed 
to the dust or non-dust component. This analysis is restricted in the present work to the major 
compounds only. For Al, Si, P, Ti and Fe it can be safely assumed that they belong to the dust 
component, and S and Cl can be attributed to the non-dust component. Na, Mg, K and Ca, however, 
are ambiguous and can be present in fractions. Therefore, a model is needed to estimate the 
contribution of the ambiguous elements from the dust and non-dust component based on the single 
particle chemical composition.

A problem arises here from the error in chemical quantification due to matrix composition and 
particle geometry. While the correction outlined in section 2.3.1 adjusts the quantification accuracy 
of the average particle composition, for single particles because of their unknown geometry and 
surface orientation angles, still a considerable error in element quantification can occur. In particular, 
a bias between light and heavier elements can be introduced by unaccounted X-ray absorption, 
which can lead to under- as well as overestimation of the relative contribution of light elements 
(Fletcher et al. 2011). As for the present aerosol the major cations (Na\(^+\), Mg\(^{2+}\)) are light in comparison 
to the major anions (Cl\(^-\), S of SO\(_{4}\)^{2-}), a quantification bias will lead to an error in component 
attrbution. Particularly, an overestimation of the light elements will yield – by attribution of the ion 
balance excess to the dust component – to an overestimation of the dust contribution. Therefore, 
two model pathways are applied: an upper limit estimate, where a possibly overestimated fraction of 
the ambiguous elements is attributed to the dust component, and a lower limit estimate, where all 
ambiguous elements are attributed to the non-dust component.

The following assumptions are made:

1. There is exactly one dust inclusion in each mixed particle
2. Carbonaceous matter does not contribute
3. Ca contributes to dust as carbonate
4. Ca contributes to non-dust as sulfate / chloride
5. Fe contributes to dust as Fe\(^{3+}\)
6. S contributes as sulfate
Na, Mg, Al, Si, P, K, Ti and Fe contribute to the dust according to their oxide weights. N-containing compounds contribute only in case of a non-neutral ion balance as ammonium and nitrate. Dust density is \( \rho_{\text{dust}} = 2650 \text{ kg/m}^3 \), non-dust density is \( \rho_{\text{nondust}} = 2200 \text{ kg/m}^3 \), averaged from typical dust and non-dust constituents: illite, kaolinite, muscovite, quartz, albite, microcline, calcite, gypsum, halite, sodium sulfate minerals in different hydratation states, and mascagnite (Deer et al. 1992; Warneck et al. 2012).

**Estimation of the upper limit**

Following the above-listed assumptions, the apparent cation/anion charge ratio is defined as:

\[
\frac{r_{\text{cat}}}{\sum cations_{\text{charge}}} = \frac{\sum \text{cations}_{\text{charge}}}{\sum \text{anions}_{\text{charge}}} \tag{6}
\]

with \( \sum cations_{\text{charge}} = |Na| + 2|Mg| + |K| + 2|Ca| \), apparent sum of cation charges, and \( \sum anions_{\text{charge}} = |Cl| + 2|S| \), apparent sum of anion charges. Note that \( |X| \) denotes the concentration of element \( X \) given as atomic (i.e. molar) fraction relative to the sum of all quantified element concentrations with the exclusion of O and lighter elements.

If \( r_{\text{cat}} > 1 \), it is assumed in the upper limit estimate that the excess in the apparent sum of cation charges is produced by the dust contribution. Thus, the dust contribution is calculated as the ion balance excess as:

\[
c_{\text{dust}} = \frac{r_{\text{cat}} - 1}{r_{\text{cat}}} = \frac{\sum cations_{\text{charge}} - \sum anions_{\text{charge}}}{\sum cations_{\text{charge}}} \tag{7}
\]

Cation excess

If \( c_{\text{dust}} > 0 \), an equal fraction of each element’s apparent cation contribution excess is attributed to dust, i.e. the ion charge balance is virtually neutralized for the non-dust component. The dust and non-dust masses are calculated as (see also Table S1 in electronic supplement):

\[
m_{\text{dust}} = \sum dust_{\text{oxides}} + c_{\text{dust}} \sum cations_{\text{oxide}} \tag{8}
\]

with \( \sum dust_{\text{oxides}} = Al_{\text{oxide}} + Si_{\text{oxide}} + P_{\text{oxide}} + Ti_{\text{oxide}} + Fe_{\text{oxide}} \), and \( \sum cations_{\text{oxide}} = Na_{\text{oxide}} + Mg_{\text{oxide}} + K_{\text{oxide}} + Ca_{\text{carbonate}} \).

Note that stable sulfates (gypsum / anhydrite, alunite) are assigned to the non-dust component.

\[
m_{\text{nondust}} = (1 - c_{\text{dust}}) \sum cations_{\text{mass}} + \sum anions_{\text{mass}} \tag{9}
\]

with \( \sum cations_{\text{mass}} = Na_{\text{mass}} + Mg_{\text{mass}} + K_{\text{mass}} + Ca_{\text{mass}} \), and \( \sum anions_{\text{mass}} = Cl_{\text{mass}} + SO_{4}^{2-}_{\text{mass}} \).

The mass contributions are calculated as shown in Table S1 in the electronic supplement.
Cation deficit

If \( c_{\text{dust}} < 0 \), i.e. there is a cation deficit, the missing cation is assumed to be ammonium. The dust and non-dust masses are then calculated as

\[
m_{\text{dust}} = \sum \text{oxides} \tag{10}
\]

\[
m_{\text{nondust}} = \sum \text{cations}_{\text{mass}} + \sum \text{anions}_{\text{mass}} + \text{NH}_4^+_{\text{mass}} \tag{11}
\]

For calculation of the ammonium mass \( \text{NH}_4^+_{\text{mass}} \) see Table S1 in the electronic supplement.

**Estimation of the lower limit**

The dust mass for lower limit estimate of the dust contribution is calculated according to Eq. (10). The non-dust mass is calculated for \( c_{\text{dust}} < 0 \) according to Eq. (11). For \( c_{\text{dust}} > 0 \) nitrate is assumed to be the missing anion and the non-dust mass is calculated as

\[
m_{\text{nondust}} = \sum \text{cations}_{\text{mass}} + \sum \text{anions}_{\text{mass}} + \text{NO}_3^-_{\text{mass}} \tag{12}
\]

Refer to Table S1 in the electronic supplement for calculation of the nitrate mass.

**Calculation of the dust fraction**

From the dust and non-dust mass contributions, the dust volume contribution to the particle is calculated as

\[
f_{\text{dust}} = \frac{m_{\text{dust}} \rho_{\text{dust}}}{\rho_{\text{dust}} \cdot m_{\text{nondust}} \rho_{\text{nondust}}} = \frac{m_{\text{dust}}}{m_{\text{dust}} + m_{\text{nondust}}} \tag{13}
\]

and the diameter of the resulting dust inclusion as

\[
\frac{\pi}{6} d_{v,\text{dust}}^3 = f_{\text{dust}} \frac{\pi}{6} d_v^3 \Rightarrow d_{v,\text{dust}} = \left( \frac{f_{\text{dust}}}{1} \right) d_v \tag{14}
\]

The model outlined here by suffer from systematic errors:

1. In the presence of larger amount of nitrate and ammonium or organics, the dust contribution will be overestimated, as the regarded composition is fitted to the apparent particle volume. However, in Barbados the concentration of these compounds is usually small in comparison to the dust (Lepple et al. 1976; Savoie et al. 1992; Eglinton et al. 2002; Prospero et al. 2009; Zamora et al. 2011).
2. The density values are averages for the assumed components, and the real density of a particle may be smaller or larger. However, the density range for the components in question is small (dust: 2300 to 3000 kg/m³, non-dust 1800 to 2600 kg/m³ at maximum), so the error is considered to be less than 10 %.
3. The mass contribution is estimated by ion charge balances. If for the ambiguous elements an inhomogeneous distribution of univalent and bivalent elements exists (e.g., univalent like Na favoring the non-dust component and bivalent like Ca favoring the dust component), an error of less than 5 % in diameter can occur. With an assumption of 5 % iron content in dust, the maximum error due to the Fe\(^{3+}\) assumption is less than 0.2 % in diameter.
The upper and lower estimates yield diameters, which differ for the dust core diameter in average by 25 %; for 75 % of the particles the difference is less than a factor of two. From the analytical errors in ratios for major compounds (less than 10 % systematically and 6 % repetition uncertainty), an dust core size uncertainty of about 6 % is estimated, as long as the core is larger than 10 % of the particle. An overall analytical uncertainty of 15 % relative core size is estimated. In conjunction with the upper/lower limit estimates, an overall core size error of 25 % is considered appropriate.

**Estimation of a geometrical iron-availability index**

Iron bioavailability in general is depending on different chemical and microphysical parameters as well as residence time in chemically aggressive environments (Shi et al. 2011a; Shi et al. 2012). If considering a homogeneous iron distribution in larger and smaller particles, it seems plausible that the distance to the surface – therefore the surface to volume ratio – should have an impact on the short-term iron accessibility (e.g., Baker et al. 2006; Shi et al. 2011b). Therefore, as first order estimate we define a geometrical surface iron availability index SIAI (after virtual dissolution of the soluble compounds) as

\[
SIAI = \frac{Fe_{oxide}}{m_{dust}} 4\pi d_{p,dust}^2
\]

(15)

### 2.3.4 Particle classification and relative ion balance

For assessing the abundances and counting statistics of certain particle types, the particles were classified into different groups and classes. Based on the element index and additional elemental ratios, a set of rules used in former mineral dust investigations in a marine environment was applied therefore. For details refer to Kandler et al. (2011a).

In addition, a relative ion balance is defined for single particles as:

\[
IB_{rel} = \frac{(Na) + 2(Mg) + (K) + 2(Ca) - (Cl) - 2(S)}{(Na) + (Mg) + 2(Ca) + (Cl) + 2(S)}
\]

(16)

A positive relative ion balance – i.e. an excess of positive ions – would indicate an undetected presence of negative ions like NO$_3^-$ or CO$_3^{2-}$, a negative one such of H$^+$ or NH$_3^+$, which all can’t be (reliably) quantified by EDX. The relative ion balance is calculated only for particles classified into the soluble sulfate or sea-salt classes (see below for classification scheme).

### 2.3.5 Statistical uncertainty of total volumes / masses and relative number abundances from single particle measurements

When assessing the uncertainty of values based on counted occurrences, frequently the counting statistics are assumed to follow a Poisson distribution. However, when calculating total aerosol masses or volumes, besides the measurement errors in particular the – usually few – large particles can introduce a considerable statistical uncertainty, which is not necessarily accounted for by the distribution assumption. Therefore, estimates of the statistical uncertainty based on single particle counts for an a priori unknown frequency distribution (i.e. the counting frequency distribution modified by the also unknown particle size distribution) either require reasonable assumptions or distribution-independent estimators. In the present work, the uncertainty is estimated by a bootstrap approach with Monte Carlo approximation (Efron 1979). Furthermore, the results of the generally robust bootstrap approach (Efron 2003) are compared to a more simple approach, where the counting statistics is assumed to follow a Poisson distribution. The Gaussian error propagation is then calculated for the latter case.
For the bootstrap approach, a considerable number of data replications are necessary (Carpenter et al. 2000; Pattengale et al. 2010). On the actual number, different recommendations exist with more than 1000 being among the most common (Carpenter et al. 2000). As higher numbers lead to smaller errors in the uncertainty estimate, 10,000 replications for each sample were performed in the present work.

For the Poisson approach, with a counting error of $\Delta n = 1$ for a single particle count ($n = 1$), the Gaussian error propagation of the standard deviation for a sum of particle volumes $V_k$ resolves to

$$\Delta V = \sqrt{\sum_k \left( \frac{\partial}{\partial n_k} n V_k \right)^2 + \sum_k \left( \frac{\partial}{\partial V_k} n V_k \right)^2} = \sqrt{\sum_k V_k^2 + \sum_k \Delta V_k^2}$$  \hspace{1cm} (17)

with $n_k$ the number of particles with Volume $V_k$, in this case always 1, $\Delta V_k$ the volume measurement error, $k$ the index for the single particles.

Similar considerations apply for the mass calculations.

The two-sided 95 % confidence interval is estimated for the Poisson distribution case as 1.96 times the standard deviation, and for the bootstrap case as the 0.025 to 0.975 quantile range of the bootstrap replications (bias corrected and accelerated method; DiCiccio et al. 1996; Carpenter et al. 2000).

Considering only the statistical uncertainty from Eq. (17), the distribution-based approach can be compared to the bootstrap approach in terms of relative statistical uncertainty for the volume estimated from two methods (Fig. 4). Clearly, the Poisson assumption underestimates the lower limit of the two-sided 95 % confidence interval (i.e. overestimates the uncertainty), providing even physically meaningless negative numbers. In contrast, the bootstrap approach yields more precise estimates (see also Efron 2003). For the upper limit of the interval, the Poisson approach seems to underestimate the uncertainty, in particular with respect to the high volumes which can be present in single particles (Fig. 4, left). When restricting the size range to particles of 1 $\mu$m to 20 $\mu$m in diameter (Fig. 4, right), as expected the differences in confidence interval limits become much smaller and stay mostly below 20 % difference between the two approaches. Note in particular the impact of the volume in the single largest particle. For the present work, the bootstrap approach is preferred.

For the assessment of the confidence interval of relative counting abundances, frequently a confidence interval based on a binomial distribution is used as estimate (Agresti et al. 1998), i.e. for a relative number abundance of a certain particle type class $r$ the two-sided 95 % confidence interval is approximated as (Hartung et al. 2005)

$$CL_{0.025,0.975} = \frac{3.84 + 2r + \sqrt{3.84 (3.84 + 4r^2 - r)}}{2(n + 3.84)}$$  \hspace{1cm} (18)

with $r$ the count of particles in that class, $n$ the total number of particles.

The two approaches show much closer agreement here than in the previous case (see Fig. S2 in electronic supplement). Note that if the common Wald confidence interval is used (Agresti et al.
Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-417
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 2 May 2018
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1998), with lower absolute particle numbers in a class, an increasing tendency of over/underestimation similar to the previous case occurs up to meaningless negative values in the binomial case. For sake of consistence, in the present work also for the relative abundances the robust bootstrap approach for estimation of the confidence intervals was chosen.

2.4 Collection efficiency and deposition velocity relating atmospheric concentrations to deposition rates

2.4.1 Determining the size distributions from the free-wing impactor measurements

Obtaining the atmospheric size distribution and representative contributions of particle populations with different hygroscopicity from the FWI requires a set of corrections. These corrections are applied to each single particle as a function of its size and composition and the thermodynamic conditions during sampling by weighting its count with the product of all correction functions. First, a window correction accounting for the exclusion of particles at the analysis image border is applied (Kandler et al. 2009):

\[
c_w = \frac{w_x w_y}{(w_x - d_p)(w_y - d_p)}
\]

Second, the collection efficiency of the FWI has to be regarded. Therefore, the ambient particle diameter at the time of collection has to be estimated by accounting for the hygroscopic particle growth:

\[
d_{\text{amb}} = d_v g_{\text{hyg}}
\]

with \(g_{\text{hyg}}\) the hygroscopic growth factor.

Hygroscopic growth can be estimated from the hygroscopicity parameter \(\kappa\) (Petters et al. 2007) as

\[
g_{\text{hyg}} = \left(1 + \frac{a_w}{1 - a_w} \kappa \right)^{\frac{1}{3}}
\]

with \(a_w\) the water activity.

As only super-micron particles are considered in this part of the study, the water activity can be equated with the relative humidity given as fraction. The hygroscopicity parameter can be determined as volume-weighted average of the hygroscopicity parameters of the major contributing components (Petters et al. 2007). Assuming a mixture of sodium sulfate and sodium chloride as the components dominating the hygroscopic growth and assigning the dust component zero hygroscopicity, the hygroscopicity parameter is approximated from the volume contributions as

\[
\kappa = (1 - f_{\text{dust}}) \frac{0.68 \times Na_2SO_4_{\text{volume}} + 1.12 \times NaCl_{\text{volume}}}{Na_2SO_4_{\text{volume}} + NaCl_{\text{volume}}}
\]

For the calculation of the volume contributions, refer to Table S1 in the electronic supplement.

The collection efficiency \(E(P)\) is parameterized (see below) from the experimentally determined values for discs given by May et al. (1967) as a function of impaction parameter \(P\):

\[
P = \frac{S}{D}
\]
with \( S \) stopping distance, \( D \) characteristic dimension, here 12.5 mm. While \( P \) equals to the Stokes number within the Stokes regime, in the current work the particle Reynolds numbers are considerably higher. In this regime, in analogy to Hinds (1999) the stopping distance can be approximated with better than 3\% accuracy as

\[
S = \frac{\rho_{amb} d_{amb}}{\rho_a \sqrt{\chi}} \left[ \frac{1}{Re^3_p} - \sqrt{6} \tan^{-1} \left( \frac{Re^2_p}{\sqrt{6}} \right) \right]
\]  

(24)

with \( \rho_{amb} \) ambient particle density, estimated from chemical composition and growth factor, \( \rho_a \) air density, \( \chi \) aerodynamic shape factor.

Results of the trigonometric function must be given as radian. The dry aerodynamic shape factor is assumed as constant similar to Ott et al. (2008a), but is interpolated for particles mixed with water as a function of the hygroscopic growth factor:

\[
\chi = \begin{cases} 
1 + (\chi_0 - 1) \left( 1 - \frac{g_{hyg} - 1}{g_{hyg,lim}} \right) & \text{if } g_{hyg} < g_{hyg,lim} \\
1 & \text{if } g_{hyg} > g_{hyg,lim}
\end{cases}
\]  

(25)

with \( \chi_0 = 1.4 \) an estimated dry shape factor (Ott et al. 2008a) \( g_{hyg,lim} = 1.3 \) a hygroscopic growth factor at which the particles are assumed to be spherical.

The particle Reynolds number is

\[
Re_p = \frac{\rho_a v_i d_{amb}}{\eta \sqrt{\chi}}
\]  

(26)

with \( v_i = \sqrt{v_r^2 + v^2} \) the impaction velocity, \( v_r = 2\pi l f_r \) the speed of the collector in the plane of rotation, \( l \) the collector arm length, \( f_r \) the rotation frequency, \( v \) the wind speed, \( \eta \) the viscosity of the air.

The stopping distances calculated by Eq. (24) are well in accordance with the parameterization curves shown by May et al. (1967).

The collection \( E(P) \) efficiency for \( P > 0.125 \) is then parameterized (see Fig. S3 in the electronic supplement) and the according correction is

\[
c_e = \frac{1}{E(P)} = \exp \left( \frac{0.28}{P} \right)
\]  

(27)

The total investigated volume for the concentration calculations is determined by

\[
V_i = A v_i t_i
\]  

(28)
with \( A \) the analyzed area, \( t_i \) the sample collection time.

The atmospheric concentration is finally

\[
C(d_{amb}) = \frac{1}{V_i} \sum_k c_w(d_{p,k}) c_e(d_{amb,k})
\]

(29)

with \( k \) index of the particle.

Potential systematic error sources for this calculation are mainly the uncertainty in collection efficiency, given the considerable spread in data points in the according literature (Golovin et al. 1962; May et al. 1967), and any bias in particle size.

2.4.2 Determining the airborne size distributions from the sedimentation sampler measurements

Similar to the previous section, sampling efficiency considerations are necessary for the sedimentation sampler. For the supermicron particle size range sedimentation and turbulent impaction dominate the particle deposition velocity (as for example illustrated by Piskunov 2009). To calculate the turbulent impaction velocity, which depends on the wind speed, the friction velocity is needed. As the opposing inner boundary layers of the sampler plates are always separated for the considered range of wind speeds (boundary layer thickness between 4.5 mm and 2 mm for wind speeds between 3.5 m/s and 13.5 m/s; Munson et al. 2013), the flow inside the sampler is approximated as flow over a smooth flat plate (the lower plate). The friction velocity is calculated as recommended by Wood (1981):

\[
u^* = \frac{v}{\sqrt{2}} (2 \log_{10} Re_x - 0.65)^{-1.15}
\]

(30)

with \( Re_x = \frac{\rho_a u x}{\eta} \) the flow Reynolds number at the sampling stub location, \( x \) the distance from the lower plate edge to the center of the sampling stub (6.3 cm).

Considering the flow inside the sampler as tube flow (Liu et al. 1974) would lead to friction velocities differing by less than 5 %.

A variety of models estimating the particles deposition speed were published (Sehmel 1973; Slinn et al. 1980; Noll et al. 2001; Wagner et al. 2001; Aluko et al. 2006; Piskunov 2009; Petroff et al. 2010). They yield considerable different results, possibly due to negligence of unaccounted forces (e.g., Lai et al. 2005), the way of determining the relevant friction velocity, or other model assumptions. For the present work, the formalism of Piskunov (2009) was selected, as it derives the deposition velocity rather from physical principles instead of parameterizing a specific measurement setup. The deposition velocity is estimated by the following formalism:

\[
u_d = \frac{u^*}{f_1 + f_2}
\]

(31)

\[
f_1 = \frac{u^* \exp(-1.2r^*)}{v_{Stk}^2} \left[ 1 - \exp \left( -13.204 Sc \frac{v_{Stk}^2}{u^*} \right) \right]
\]

(32)
with \( \text{Sc} = \frac{\eta}{\rho_a c_D} = \frac{3 \pi \eta^2}{\rho_a k_B \frac{\lambda}{c_c \sqrt{T}} d_{amb}} \)

the Schmidt number,

\( C_D \)

the particle diffusion coefficient,

\( k_B \)

the Boltzmann constant,

\( T \)

the ambient temperature,

\( \lambda = \frac{k_B T}{\sqrt{2 \pi d_m^2 \rho}} \)

the mean free path,

\( d_m = 3.68 \times 10^{-10} \text{ m} \)

the average diameter of an air molecule,

\( P \)

the ambient pressure,

\( v_{Stk} = \frac{12 \eta \sqrt{T}}{0.42 C_c \rho_a \frac{d_m}{d_{amb}}} \left[ 1 + \frac{0.42 C_c^2 \rho_a \rho_{amb}}{108 \eta^2} \left( \frac{d_m}{d_{amb}} \right)^{3} \left( 1 - \frac{\rho_a}{\rho_{amb}} \right) \right] \frac{g}{g - 1} \)

the gravitational settling velocity,

\( g \)

the gravitational acceleration;

\( f_2 = \frac{1 - \exp \left[ -\gamma \left( 1 + \frac{v_{Stk}}{u'} \right) \right] \left( \frac{P_T}{p_T + v_{Stk} / u'} \right)}{f_0} \) (33)

with \( \gamma = \frac{0.46115 \pi^4}{(1+0.3859 \pi^4)(1+0.1193 \pi^4+6.613 \pi^2)} \)

the dimensionless relaxation time,

\( \tau^+ = \frac{u'^2 \rho_a v_{Stk}}{\eta g} \)

the dimensionless relaxation time,

\( p_T = \frac{\tau^+(1+0.3859 \pi^4)}{65.06 (1+0.1193 \pi^4)^2} \)

The atmospheric concentrations are then

\( C(d_{amb}) = \frac{1}{A t_i} \sum_k C_p(d_{p,k}) \) (34)

A major bias for this calculation originates from the uncertainty in (turbulent) deposition velocity.

The deposition velocity calculated by different formalisms for a series of deposition samples is shown in Fig. 5. The aerodynamic diameter used here is calculated as:

\( d_a = \sqrt{\frac{\rho_{amb}}{\rho_a \chi}} d_{amb} \) (35)

with \( \rho_a = 1000 \text{ kg m}^{-3} \) unity density.

The spread in deposition velocity for each model is caused mainly by the different wind speeds during exposure, but also by the variation in relative humidity and, to a lesser extent, by other thermodynamic conditions. However, it becomes strikingly obvious that in the size range where most of the atmospheric dust deposition occurs – i.e. between 2 and 50 µm in diameter at Barbados (Mahowald et al. 2014; van der Does et al. 2016) –, the models disagree by more than two orders of magnitude. Besides the uncertainty derived from selection of a particular model, the sphericity assumption and the related drag effects may lead to a bias in deposition flux, most probably mainly influencing the turbulent deposition regime around 10 µm particle diameter. An additional measurement bias might be introduced by the parallelism assumption underlying all the stable boundary layer calculations, i.e. that the air flow must be parallel to the plate. While the vertical
component of the wind speed under atmospheric conditions is usually small in comparison to the horizontal ones, still ‘inlet’ losses might occur even due to small non-parallel components. These inlet losses are expected to affect mainly the largest particles sizes.

2.4.3 Impactor inlets

The impactor sampler was used with two types of inlets. For particles larger than approximately 2.5 \( \mu \text{m} \) aerodynamic diameter, a pseudo-isoaxial inlet orientation with sub-isokinetic sampling was used. Smaller particles were collected with an omnidirectional inlet. As particles were analyzed separately for each size class, the inlet efficiency does not play a primary role for the results, still it must be considered. Literature on an accurate estimation of inlet transmission for a ratio between ambient wind speed and impactor inlet flow velocity in the range of 100:1 is not existing. However, from Paik et al. (2002) and Hangal et al. (1990) in conjunction with the observation of Li et al. (2002) regarding the applicability of thin walled nozzle formulas to blunt samplers, it may be conclude that:

a) particles larger than 2.5 \( \mu \text{m} \) aerodynamic diameter would be increasingly enriched with increasing particle sizes. Enrichment factors for thin-walled nozzles would be in the range of 2–4 for 10 \( \mu \text{m} \) particles and 20–50 for 100 \( \mu \text{m} \) particles. As the sampler had a blunt inlet, the actual enrichment factors are probably considerably lower.

b) particles smaller than 2.5 \( \mu \text{m} \) would be comparatively unbiased at low Stokes numbers; see also Wen et al. (2000).

For a dry aerosol, these size-selective inlet losses would not considerably bias the relative chemical composition. In the present humid environment with partly soluble species, though, it can lead to an overestimation of non-hygroscopic species for particle sizes in the vicinity of the inlet cut-off, if the hygroscopic growth is not explicitly considered. The problem is somewhat diminished by the fact that by water-absorption the density of the particles decreases and, consequently, the Stokes number increases only sub-proportionally to the square of the particle diameter. Nevertheless, the hygroscopic growth should be explicitly accounted for. Therefore, the model from Eq. (20) is applied based on the measured geometric diameter and chemical composition, and ambient chemical compositions are computed.

2.5 Modelling deposition statistics and artifacts of mixing state

When particles are deposited to a substrate, they might touch each other and form an internal mixture, which is not representative for the atmosphere. While the lower limit of coincidental internal particle mixture on a substrate is easily defined – it equals the ratio of the area covered by particles to the total analysed area for an infinitesimally small depositing particle – the assessment is much more complex for larger particles following a wide size distribution function.

Therefore, in the first step the deposition process was simulated by a series of Monte Carlo models. For input, the average size distribution measured at Cape Verde (Kandler et al. 2011b) – hereafter CV-ground – and the median one measured airborne for aged dust (Weinzierl et al. 2011) – hereafter CV-air – were used. These size distributions mainly differ in the concentration of supermicron particles. The deposition velocity formulation after Piskunov (2009) was used. The modeled deposition area is 5 mm x 5 mm, meteorological conditions were assumed as totally dry, 20 °C, sea level pressure and a friction velocity of 0.2 m/s. Particles were virtually dropped onto the deposition surface until either a certain fractional area coverage by particles or a simulated deposition time limit was reached. Eighteen different area coverages were simulated for a two-component external
mixture (particle density 2200 kg/m³) with components number ratios of 50% / 50%, 75% / 25%, 90%
% / 10%, 95% / 5%, 97% / 3%, and 99% / 1% for CV-ground, and nine area coverages with number
ratios of 50% / 50%, 90% / 10%, and 99% / 1% for CV-air. Each model was run 1000 times (200
times in case of 0.1 and larger fraction area coverages) to assess the statistical uncertainty. In a
second series, for CV-ground a tri-component external mixture of sodium sulfate (particle density
1770 kg/m³), dust (2700 kg/m³) and sea-salt (2170 kg/m³) was used as input. The size-dependent
component number contributions were taken from measurements at Cape Verde (Schladitz et al.
2011). After the simulated deposition, particle agglomerates on the substrate with touching contours
were merged into a new particle with the sum of the volumes and proportionate chemical
composition.

To investigate the relevance of mixing artifacts caused by particle sampling, the sensitivity of
SEM/EDX analysis has to be considered. Internal mixtures can be only detected by SEM/EDX, if the
minor component exceeds the limit of detection. At an acceleration voltage of 12.5 kV the primary X-
ray excitation volume is in the range of 0.5 µm to 1.5 µm diameter, depending on the matrix
elements (Goldstein et al. 2003). As we consider mainly supermicron particles, the excitation volume
is expected to be mainly inside the particles. According to our experience an X-ray peak becomes
detectable at about 0.3% concentration. Therefore, a 1% contribution of an element to the particle
volume will be definitely detectable. Thus, a particle containing more than 1% material from another
particle type is considered as detectable mixture in the model. A particle containing more than 20% is
denominated as strong internal mixture. Note that for smaller particles, when the excitation
volume would extend into the substrate, larger contributions to the particle volume would be
required.

Besides these fundamental considerations, in the second step a mixing model was applied to each
sample, based on its measured composition. Random particles were virtually selected from the pure
components of the measured set of particles and placed at random positions inside a virtual area
with the same size as the one analyzed in SEM/EDX, until the same area coverage as of the real
sample was reached. Internal mixtures artificially produced on the substrate were counted, if their
mixing would have been detected by SEM/EDX applying the rules for mixed particle classification.
This process was repeated 10,000 times. The upper 95% confidence interval limit of mixtures
modeled by the Monte Carlo simulation was considered as limit of detection for internal mixtures,
and the median of the produced mixtures was regarded as systematic error and was subtracted from
the mixtures detected in the real samples.

In the third step, the single mixing probability (SMP) for each binary pure compound combination
was calculated by selecting 100,000 random pure-composition particles from the measured data set
for each sample, mixing them virtually and determining, whether they would be detected as mixed.
This was carried out one time without any size restrictions and a second time with only selecting
particles not more than a factor of 3 different in size. The latter was done to account for the fact that
in a turbulent environment and in the regarded size range, the collision efficiency is highest for
particles of similar size (Pinsky et al. 1999; Wang et al. 2005).

2.5.1 Simulating particle mixtures due to longer exposure times
While in the modeling section particles are assumed to be spherical, this is typically not the case for
natural aerosol like mineral dust particles. Therefore, a second approach based on particles images
was used to estimate the effect of internal particle mixture on the substrate, i.e. taking into account
Due to the large number of images required, this approach could only be used for assessing the size statistics, but not for the chemical composition. All segmented images of each deposition sample were subject to particle size analysis. In following steps, a number of 2, 3, 5, 10, 15, or 20 segmented images of the same sample were combined into a single image, simulating an extension of exposure time by the according factor. This approach inherently assumes a constant size distribution during exposure and a random particle deposition. The resulting images were then subject to the same particle analysis, yielding apparent size distributions after a coincidental mixing. In contrast to the pure modeling approach, here the true size distribution is not known because even the lowest coverage samples might contain internal mixtures. Certainly though, the lowest coverage sample is closest to the true size distribution and therefore will be used as reference.

3 Results and Discussion

3.1 Uncertainty of measurements for the new collection techniques and determination of mixing state

3.1.1 Area homogeneity of collected particles

**Free-wing impactor (FWI)**

To assess the homogeneity of particle distribution, for each sample the center 80 mm² (about 65 % of the total sample area) were scanned with approximately one thousand SEM images (approximately one third coverage), and the average particle density was determined for each mm² as function of \( d_p \). For particles between 4 µm and 8 µm in diameter (see Fig. S4 in electronic supplement) no systematic bias in particle density is visible, except for a slight enhancement toward the borders in a few cases. The remaining variability remains probably linked to statistical uncertainty and surface defects interpreted as particles by the automatic segmentation algorithm. However, the density variations between each mm² remain below a factor of 2. As commonly 20 to 100 mm² are analyzed, the inhomogeneity can be regarded as minor error. For larger particles, the uncertainty due to counting statistics becomes dominant.

**Dry particle deposition sampler (DPDS)**

Similar to above, for the DPDS deposition density homogeneity was assessed, but in this case nearly all of the central 80 mm² were scanned. In about half of the samples, a crescent-shaped density gradient can be observed (see Fig. S5 in electronic supplement). This gradient most probably originates from a stationary wave introduced by the recession of the sample substrate slightly below the primary plane of the DPDS. Depending on the analysis location, a bias in the range of factor 2 to 3 in deposited particle number can occur. Therefore, the fields of analysis for the chemical composition and size distribution discussion below were homogeneously distributed over the sample surface at a regular distance. Also with the DPDS, for larger particles the uncertainty due to counting statistics becomes dominant.

3.1.2 Impact of area coverage and counting statistics on size distribution and total volume

Fig. 6 shows the apparent number and volume size distributions of particles deposited from aerosols with CV-ground or CV-air size distribution for different area coverages, equaling different exposure times. As it is to be expected, for short exposure times there is a considerable counting error, which...
decreases to less than 10 % for the smaller particles at area coverages of 0.01 and higher. In median,
no particle larger than 50 µm would be detected in deposition area for area coverages smaller than
0.0025, and more than 0.005 are necessary to collect more than 5 particles (not shown in graphs). As
opposing trend there is a bias in size distribution towards lower concentrations and larger particles,
which starts getting relevant at coverages of 0.1. This bias is introduced by the coincidental clumping,
a second particle depositing on an already deposited one. As result, for the given aerosol size
distributions, an area coverage of 0.03 to 0.05 seems most appropriate to get a size distribution
influenced least by counting errors and sampling/mixing bias.

Generally similar, but more pronounced effects can be observed, if the second approach – simulating
longer exposure times by combining real microscope images – is used. Fig. 7 shows for three samples
– low, medium and high area coverages – the evolution of the size distribution due to simulated
longer exposure times. In case of high dust deposition rates and long exposure times, particles
smaller than 10 µm in diameter would be underestimated by a factor of more than 2, while larger
particles would be considerable overrepresented. A shift in the modal diameter of 50 % towards
larger size could be the result. However, at the large end of the volume size distribution, counting
statistics might considerably influence the total particle mass uncertainty, even at these long
simulated exposition times.

If total mass deposition is estimated from the microscope images, one can set up a relation of total
volume and apparent area coverage, which might serve as a quick estimate of total deposited
particle mass (Fig. 8). If the result of the fit function is multiplied with an approximate particle
density, the result gives the deposition as mg/m² with an uncertainty of factor 2. As expected, the fit
function starts to underestimate the volume / mass for high area coverage.

When calculating total mass / volume from small amounts of material, special attention has to be
paid to the errors introduced by counting statistics. Table 1 gives an overview for deposition
simulation results based on a typical area, which would be used for automated single particle
analysis. Two size distributions were considered with different abundance of large particles. Using
the CV-ground size distribution, we observe an uncertainty of a factor of 2 for the total mass (95 %
two-sided confidence interval), when 3,000 particles are counted, which are equivalent to 8 µg of
mass. If only particles between 1 and 32 µm in diameter are regarded, a relative uncertainty of 20 %
is achieved with 1,500 particles. When analyzing about 100 µg of particle mass, the statistical error is
in the range of 30 % mass in case of CV-ground size distribution and 15 % for CV-air. It can be
concluded here that a minimum number of 5,000 to 10,000 single particle measurements would be
desirable to stabilize the total mass concentration in the range of 10 % uncertainty. As this number is
usually not reached in SEM studies (e.g., Reid et al. 2003; Coz et al. 2009; Kandler et al. 2011a),
additional attention should be paid to larger particles, e.g. by analyzing larger sample areas, to
deceive the uncertainty in mass (see also Fig. 4). Note that the same considerations in principle
apply to bulk investigations, when only small amounts of mass are analyzed, but are not commonly
stated.

3.1.3 Amount of coincidental internal particle mixtures

When assessing the mixing state of particles from an offline single particle technique, coincidental
internal particle mixture has to be taken into account. Fig. 9 shows the upper 95 % confidence limit
of apparent fractions of internally mixed particles for a two-component system as function of source
component ratio and area coverage for detectable strong internal mixtures (refer to section 2.5; data
are given in the electronic supplement, Table S2 and Table S3). These numbers can be considered as detection limit for fractions of internal mixed particles. As to be expected, higher area coverage yields higher mixture probability. No significant mixture for submicron particles occurs in these cases. In particular, if both components are present in equal amounts, mixing probabilities become high already for covered area fraction of a few percent. Note also the different size maximum for strong versus detectable mixture.

Applying the same model type based on the CV-ground size distribution to a ternary modal composition distribution of sulfate, sea-salt and dust as described in section 2.5, mixing probabilities for a specific atmospheric composition can be estimated (Fig. 10). Note the different color bar scale. It becomes instantly obvious that the mixing probabilities are much lower than in the homogeneous case. Mixtures between sulfate and sea-salt as well as ternary mixture are absent. The relative fraction of internally mixed particles is lower by an order of magnitude. This can be explained by the fact that the defined relative detection limits of 20 % and 1 % restrict the detection of mixing to mixing partners not differing in size by more than a factor of 1.59 (strong mixing) and 4.6 (detectable mixing). But because different aerosol type are mainly present in different size regimes here (Schladitz et al. 2011), the mixture can only be efficient for size ranges, where these component have an overlap. In general, however, also here mixture increases with particle size.

It can be concluded here that mixing studies for large particles are generally very difficult. Many particles need to be collected in total to ensure reliable counting statistics, which leads in consequence to high mixing probabilities. This issue is of less concern for particles smaller than 10 µm for the given size distributions and in cases, where the aerosol has a strong dependence of composition on particle size. It also emphasizes that mixing studies should be accompanied by mixture modeling as performed below.

## 3.2 Field Measurements – methodical aspect

### 3.2.1 Comparison of atmospheric size and volume concentrations

Using the FWI sampling efficiencies outlined in section 2.3.3 and the DPDS deposition velocities from 2.4.1, one can calculate the atmospheric size distribution derived by the two techniques. Fig. 11 shows the average size distributions for the post- and pre-storm periods based on different deposition velocity models for total and upper estimate dust mass concentrations. The lower dust estimate (not shown) exhibits qualitatively the same behavior. It is evident that there is a large discrepancy between the different models as well as between the DPDS and FWI measurements. The discrepancy is clearly larger than the statistical uncertainties. While the total mass median diameter derived from DPDS (Piskunov model) is around 5 µm particle diameter, for the FWI it is approximately 25 µm. A dust size distribution measured in the Saharan Air Layer in 2.3 km altitude (computed from data shown by Weinzierl et al. 2017) contains the same mode around 4 µm diameter, but shows a secondary maximum at 10 µm, which is not found by the ground-based measurements. It is interesting to note that these values get closer, when only the dust fraction is considered, indicating a connection of the discrepancy with the hygroscopic growth (e.g., growth or density misestimate). Two other reasons for the discrepancy might be for the FWI an uncertain collection efficiency and particle losses due to non-parallel flow for the DPDS. The FWI has 50 % collection efficiency around 11 µm particle aerodynamic diameter, so for smaller particles – the majority by far – the efficiency correction function may yield unrealistic values. The DPDS model assumptions require a well oriented flow. At the high wind speeds, a non-zero angle-of-attack flow
might lead to considerable particle losses for the larger particles. This might for example be caused by an increased boundary layer thickness over the lower plate. Such an angular flow was observed at the measurement site due to the cape orography. When total mass is calculated from deposition, it can be compared to dust concentration measurements with a high volume filter sampler. Fig. 12 shows time series of mass concentrations measured by the high-volume sampler, estimated from dry deposition measurements as well as the raw dry deposition flux densities. For dry deposition uncertainties derived from the low / upper estimates as well as from counting statistics are shown. A few things can be learned from this data. With respect to the deposition model, the Piskunov model performs rather well. The average of the high-volume sampler mass concentration time series (see Table 2) is close to the lower estimate of the Piskunov model, while the higher estimate overestimates the mass concentration. The other models deviate considerably more, as to be expected from the deposition velocity differences (Fig. 5). The ratio of the mass concentration estimate to the mass flux density varies over slightly more than one order of magnitude, depending mainly on the size distribution and wind conditions. High volume and deposition-estimated mass concentrations as well as the mass flux densities follow qualitatively the same pattern in showing low concentration and high concentration periods. The absolute numbers, however, deviate significantly. For sub-periods, the correlation quality seems to be different. E.g., starting from June 21, the correlation of mass flux with high volume mass concentrations seems to be better than the one with deposition estimated concentrations; for the period before June 21 situation is converse. No direct link of the correlations with any meteorological variable was found, indicating that the deviations depend in part on erroneous assumptions in the model. For example, tuning other deposition velocity models by arbitrary factors can lead to a better agreement of actively and passively determined mass concentrations for this particular data set (Fig. S9 in electronic supplement), but the data basis is too small for a robust tuning without physical backing. Moreover, disagreement might also be caused by physical measurement biases like unknown size-dependent inlet efficiency for the high-volume sampler or angular inflow for the DPDS.

3.3 Field Measurements – atmospheric and aerosol aspects

3.3.1 Aerosol composition

Overall aerosol composition (i.e. the relative number abundance of the different particle groups) was measured by electron microscopy single particle analysis (Fig. 13). The relative abundance of soluble sulfate is highest for the smallest particle sizes, which is in good accordance with previous measurements in the eastern Atlantic Ocean (Kandler et al. 2011a). After the storm passage, higher sulfate abundances – soluble as well as stable – are observed in 2013, which are similar to those observed in 2016. The sea-salt abundance is higher for the pre-storm period in 2013, which is in agreement with the wind speeds observed (see below). In 2016, a much higher abundance of small Fe-rich particles (contained in the oxides/hydroxides class) is observed compared to the pre-storm period in 2013. For the post-storm period in 2013, minor amounts of these particles are visible. Overall, an average dust deposition of 10 mg m$^{-2}$ d$^{-1}$ (range 0.5–47 mg m$^{-2}$ d$^{-1}$) is observed (Fig. 14). While a strict disambiguation can’t be done elements also found in sea-salt, Al, Si, P, Ti, and Fe are most likely derived from dust only and are therefore also shown in the graph. At Barbados, Fe contributes 0.67 (0.01–3.3) mg m$^{-2}$ d$^{-1}$ to deposition, while phosphorous adds only 0.001 mg m$^{-2}$ d$^{-1}$; however, P is below the detection limit on two thirds of the days. The cumulative size distribution shows that in particular P and Ti are located preferentially within smaller particles. Al, Si and Fe show
generally a similar size distribution. As corroborated by the results above, Fe is slightly more present in particles smaller than 5 µm, but the impact of these periods with small Fe-rich particles on total Fe deposition is obviously small, owing to the lower overall deposition rate during these periods.

### 3.3.2 Airmass history and potential aerosol sources

The airmass provenance of the sampling periods in 2013 and 2016 is generally similar. The trajectories mostly followed the trade-wind path from North-West Africa and East Atlantic Ocean to Barbados (Fig. S6 in electronic supplement). In 2013, the air was coming more frequently from Western African than in 2016. After the tropical storm Chantal in 2013, the airmass origin shifted slightly to more southern regions. In a few cases in 2013, air from the North-West Atlantic Ocean was recirculated into the trade-wind path. In 2016, airmasses from North-East Southern America were more frequent than in 2016.

The sea-salt deposition rates are not linked to air mass provenance (not shown). The dust provenance for both years (Fig. 15) is – as expected – pointing to West Africa. This source region is also identified by isotope measurements in July/August 2013 (Bozlaker et al. 2018). The soluble sulfate deposition is generally linked to three regions, the Atlantic Ocean, West Africa and south west Europe. In particular in 2016, the sulfate sources appear to be located more in Europe and less in Africa. The relative ion balance shows mostly slightly negative values indicating presence of NH$_4^+$ or H$. Interestingly, a positive ion excess is observed for European sulfate in 2016, indicating possible presence of NO$_3^-$. These observations support the hypothesis that sulfate associated with dust events at Barbados partly might originate from secondary processing of European precursors (Li-Jones et al. 1998).

Iron contribution from dust is of particular interest for marine ecosystems. Therefore, Fig. 16 shows in the upper panel the silicate SIAI as proxy for quick iron availability. It is obvious, that the iron-containing silicate particle source is located in West Africa. Northern and southern West Africa as source regions can’t be distinguished after trans-Atlantic transport, in contrast to investigations close to the source (Kandler et al. 2007). This is consistent with observations based on isotope analysis, where also a homogeneous composition has been observed at Barbados (Bozlaker et al. 2018). In comparison with Fig. 15, a slightly higher SIAI can be observed in 2016 than in 2013, while the dust deposition rates in contrast are lower. While the total iron deposition correlates well with dust deposition (not shown), similar to observations by Trapp et al. (2010), for the SIAI an inverse relationship is found at Barbados with higher dust deposition rates leading to lower ratios of SIAI to total dust. This correlates to previous findings, where iron solubility decreased with increasing dust concentration (Shi et al. 2011b; Sholkovitz et al. 2012), though no direct causal relationship can be derived (Shi et al. 2011a). As the finding indicates a higher iron contribution from smaller particles, the lower row of Fig. 16 shows the Fe contribution by small iron-rich grains. While in 2013 the contribution of this particle type is generally low, in 2016, when trajectories cross the North-Eastern tip of South America, there is a low input during low-dust situations. However, trajectories arriving straight from south east would also cross Barbados before arrival, so there might also local contribution from the island. Taking a closer look at these particles (Fig. S7 in the electronic supplement) it reveals that they differ in structure from usual mineral dust particles (Moreno et al. 2006; Scheuven et al. 2011; Deboudt et al. 2012), but resemble more closely material from industrial or combustion processes (Fu et al. 2014; Hu et al. 2015; Li et al. 2016). This observation is interpreted as evidence for an anthropogenic iron input into a marine environment. This is of
particular interest, as according to previous work, the bioavailability of anthropogenic iron is usually
higher than provided by natural sources (Desboeufs et al. 2005; Sedwick et al. 2007; Fu et al. 2014).

3.3.3 Sea-salt composition

When considering sea-salt composition, it is assumed generally that except from the sulfate content,
aerosol produced from sea-water has a major composition resembling the bulk sea-water (Lewis et
al. 2004). However, it was recently shown in the Arctic that a fractionation can occur also with
respect to the major composition (Salter et al. 2016). At Barbados, an increasing positive deviation
from the nominal value of 0.022 with decreasing particle size is observed for the Ca/Na atomic ratio
of sea-salt particles (Fig. 17). This indicates that the same effects found by Salter et al. (2016) are
present in Caribbean sea-salt production. According to the authors, these might be linked to an
enrichment of Ca in sea surface micro-layers, but details are not yet known.

3.3.4 Abundance of mixed particles

If we consider the abundance of mixed particles at Barbados, a complex picture emerges as function
of particle size, time period and available mixing partners (Fig. 18). It can be observed that the total
deposition rate for all particle types is linked to the wind speed, what is to be expected from the
physical process (see for example Fig. S8 in electronic supplement). The higher sea-salt deposition
rates and also higher concentrations in 2013 in comparison to 2016 are also linked to the wind
speed, showing the local sea-salt production. In contrast, the dust concentration is slightly lower for
higher wind speeds (Fig. S8) for both years. With increasing particle size, the relative abundance of
internal dust/sea-salt mixtures increases (Fig. 18), but these mixtures only occur when considerable
amounts of sea-salt are present. This is different for the internal mixture with sulfate. While there
are similar ratios of dust and sulfate particles observed in the second half of the 2013 data as in
2016, in 2013, dust/sulfate mixtures are practically absent. Assuming that higher wind speeds in 2013
should lead to more internal mixing due to increased turbulence, this is clearly indicating that in
contrast to the sea-salt/dust mixture, the sulfate/dust mixture has a non-local origin (e.g., Usher et
al. 2002).

This is corroborated by the dependence of internal mixtures relative abundance on the single mixing
probability (Fig. S10 in the electronic supplement). If one considers here the binary number fraction
of mixed particles – i.e. ratio of binary mixed particles to pure compounds – as function of the size-
restricted single mixing probability, there is a weak positive correlation for dust/sea-salt mixtures for
particles larger than 2 µm diameter, but no correlation for dust/sulfate mixtures. Moreover, for
similar single mixing probabilities, the binary number fraction of mixed particles appears slightly
higher for higher deposition rates. As the collision efficiency depends on the square of the number
concentration (Sundaram et al. 1997), this supports the hypothesis of a locally produced internal
mixture of sea-salt and dust and a non-local production of sulfate and dust, the latter having most
probably cloud processing involved (Andreae et al. 1986; Niimura et al. 1998).

The overall ratio of dust/sea-salt internal mixture abundance to all dust- and sea-salt-particles
increases from 0.01–0.03 for 1 µm particles to 0.1–0.7 for particles of 8–16 µm in diameter, whereas
for dust/sulfate mixtures the ratio of 0.01–0.02 is not dependent on particle size. Denjean et al.
(2015) report mixed particle abundances of 0.16–0.3, but do not state a size range, so the data can’t
be compared directly.
If the findings on Barbados are compared to measurements in the eastern Atlantic Ocean (Kandler et al. 2011a), a generally lower abundance of internally mixed particles with respect to dust/sulfate is observed, while comparable abundances of sea-salt/dust mixtures are found. While the latter can be explained by similar wind conditions and comparable single mixing probabilities, the former seems to be caused by different aging conditions. Dust arriving over Barbados is transported mostly in the dry Saharan Air Layer (e.g., Schütz 1980), while dust arriving during winter-time at Cape Verde is transported inside the humid marine boundary layer (Chiapello et al. 1995; Kandler et al. 2011b). Therefore, considerably higher chemical processing rates at Cape Verde due to the higher humidity can be expected (Dlugi et al. 1981; Ullerstam et al. 2002), even though the transport time is most likely shorter. In addition, the boundary layer most probably provides higher concentrations of sulfur compounds for reaction (Davison et al. 1996; Andreae et al. 2000).

Change in dust behavior due to internal particle mixing

If dust particles become internally mixed, their mass, size and hygroscopic behavior change. Therefore, they will have modified deposition velocities as well as hygroscopic properties. Fig. 19 shows the increases in deposition velocities for mixed particles observed at Ragged Point in 2013 and 2016. For the both mixtures (dust/sea-salt and dust/sulfate), an increase at ambient conditions of a factor of 2–3 is observed for submicron dust particles, which rises to a factor of 5–10 for particles of 3 µm dust core diameter. As a result, the dust average deposition velocity for particles between 1 and 10 µm aerodynamic diameter is increased by 30–140 % at ambient conditions (Fig. 20). Considering a mass mean aerodynamic diameter in deposition of 7.0 µm, at ambient conditions dust deposition velocity is 6.4 mm/s, which is an enhancement by approximately 35 % over the unmixed state. This overall value is in the range estimated by Prospero et al. (2009). The enhancement will become more pronounced at higher humidities. It has to be emphasized that this estimate is a lower limit, as there most likely exist mixed particles with a smaller contribution of hygroscopic material, which remaining undetected by our analytical approach. At higher humidities, this smaller contribution nevertheless will increase the deposition velocity of the mixtures. While we observe similar relative abundances of mixed particles to previous work in Asian dust outflow Zhang (2008), our estimate of impact on deposition is considerably higher, which is mainly related to the use of the Piskunov model taking into account turbulent deposition over a Stokes settling approach.

An internal mixture of dust with a soluble compound will also modify the in-cloud behavior of the dust particles. As Denjean et al. (2015) have shown, in the Caribbean only dust particles internally mixed with soluble compounds exhibit considerable hygroscopic growth. Therefore, if the mixed dust particles are entrained into a cloud, they would preferentially be activated into a cloud droplet in comparison to unmixed. This according cloud droplets would then contain a potential effective ice-nucleating particle (DeMott et al. 2003). Because the ice-nucleating efficiency of a mixed droplet would follow the most efficient compound (Augustin-Bauditz et al. 2016), these droplets would at according temperatures become ice particles by immersion freezing (Marcolli et al. 2007; Niemand et al. 2012). We may hypothesize that along this path – by internal mixture with soluble compounds – the atmospheric ice-nucleating efficiency of dust particles could be enhanced. For example, within mixed-phase clouds at a free-troposphere station, high abundances of internally mixed particles were found as ice-nucleating particles or ice particle residues (Ebert et al. 2011; Worringen et al. 2015). Note that this mixing path is probably restricted to immersion freezing (Eastwood et al. 2009).
4 Summary and Conclusions

Aerosol deposition measurements by means of passive samplers were carried out on a daily basis at Ragged Point, Barbados in June/July 2013 and August 2016. In addition, active aerosol collection was performed with a cascade and a novel free-wing impactor. Size, shape and composition of about 110,000 particles were determined by electron microscopy. Focus was placed in this work on measurement accuracy of chemical composition and mixing state determination for individual particles.

Ragged Point, in particular in 2013, is a high-wind and high-humidity environment, which considerably influences representativeness and accuracy of the different sampling techniques. A deposition model including chemistry-dependent hygroscopic growth was adapted to the sampling situation to assess atmospheric concentration of large particles. Fair agreement was reached between passive and active techniques regarding mass concentration, but clear discrepancies were observed for particle size distribution.

Special attention was paid to the mixing state of dust particles. A model was developed to assess the mixing state of airborne particles by correcting for sampling artifacts due to particle overload leading to coincidental internal mixing of particles on the substrate (i.e., not representative for the airborne state). Different approaches were tested based on model size distributions and observed particle deposition images. It was found that the size distribution is only weakly affected for substrate area coverages with particles below 10%. The chemical composition of mixtures, however, is already affected at much lower area coverages of < 1%.

During our measurement campaigns, the aerosol was dominated by dust, sea-salt and sulfate in changing proportions. The sea-salt concentration at Ragged Point is mainly depending on wind speed. Back trajectory analysis showed that dust is originating from the usual sources in West Africa. Sulfate showed three major potential source areas, Africa, Europe and Atlantic Ocean. Particularly in 2013, sulfate was more linked to the African source, while in 2016 southwest Europe occurred as potential source, with a possible contribution of nitrate. In 2016 for short time periods, contributions to iron deposition from probably anthropogenic sources (potentially as magnetite) from South America or the island of Barbados were observed.

It was further found that internal mixing of dust and sea-salt is depending on local wind speed, and we, thus, hypothesize that it is produced locally, most likely by turbulent processes. In contrast, mixtures of dust and soluble sulfates are presumably not produced locally, but may have formed during the inter-continental transport. Even though the overall amount of internally mixed particles is comparatively low, a considerable impact on total dust deposition velocity is estimated. In addition, a pathway is hypothesized by which the ice-nucleation efficiency of dust can be increased by mixing with soluble compounds during or after the long-range transport.

For future work, some conclusions can be drawn from our observations:

- If different techniques for deposition and/or atmospheric concentration measurements are compared, it is crucial to measure particles size distributions. We observed in some cases that total mass concentration can compare rather well, even though size distributions – and therefore collection efficiencies – are considerably different.
A better understanding – in theory as well as in experimental use – of particle deposition and collection efficiencies is required in particular under high wind-situations, where turbulent transport has a considerable impact. This most probably applies to a wide range of deposition samplers, not only these used in this work. When mixing state investigations are done based on collected aerosol particles, the impact of coincidental mixtures on the substrate must be assessed, unless the area coverage with particles is very low (<< 1%). This is particularly the case for larger particles (> 5 µm diameter) and for aerosols in the same size range, where similar abundances of different mixing partners exist. Internal particle mixing most likely has a considerable influence on dust deposition speed and on the impact of dust on clouds. Future models regarding dust deposition should take a deposition speed enhancement by internal mixing into account. However, more systematic investigations are needed to better understand the mixing processes. With respect to the cloud impact if mixing via a more efficient incorporation of immersion freezing ice nuclei into cloud droplets by preferential activation, future ice nucleation chamber experiments are needed to assess the importance of this effect. Finally, a larger data basis beyond the observation of single events is required to assess the anthropogenic influence on the iron deposition into the Oceans, besides the input by mineral dust. This data base needs to be acquired with a high time resolution (maximum days) to match the duration of the observed deposition events. Also, these time series would need to cover months to years at Barbados, given the probably infrequent occurrence of these events.

5 Data availability
The data sets of all particles used for this investigation including particle size, shape, and composition are given as text tables in the electronic supplement along with a data overview.

6 Author contribution
KK designed the experiment. KK and MH carried out field work in 2013. MP and CP carried out the field work in 2016. KK and KS analyzed the samples. KK programmed the models and data processing code. KK, SW and ME analyzed data and prepared the manuscript. All authors contributed in data discussion and manuscript finalization.

7 Competing interests
The authors declare that they have no conflict of interest.

8 Acknowledgements
We acknowledge financial support from the German Research foundation (DFG grant KA 2280/2-1 and KA 2280/3-1). We thank Joseph Prospero for his valuable comments on the manuscript and discussion; his wind and mass concentration data were obtained under National Science Foundation (NSF) grant AGS-0962256. The authors gratefully acknowledge the NOAA Air Resources Laboratory
(ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication.

### Literature


Table 1: Relationships between area coverage of the simulated 5 mm x 5 mm analysis field, particle numbers, particle masses and uncertainties. Upper part: CV-ground size distribution, lower part: CV-air size distribution. A bulk density of 2500 kg/m³ was assumed for the mass estimation from particle volume. Abbreviations: SP coverage = ratio of the sum of single particle cross sections to the analysis field; apparent coverage = fraction of area covered by the particles after deposition; \( N_{>1} \) = Number of particles larger than 1 µm diameter; \( PM_{>1} \) = Total mass of particles larger than 1 µm diameter (approx. 99.99 % of total mass); \( PM_{1-32} \) = total mass of particles between 1 µm and 32 µm diameter (approx. 50 % of total mass for source-near size distribution, 67 % for aged one). Relative uncertainty is given as the ratio of the upper and lower bounds of the central 95 % quantile to the median of 1000 (200 for SP coverage >= 0.1) repetitions of deposition simulation.

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<th>( PM_{&gt;1} ), µg</th>
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Table 2: Average dust mass concentrations estimated from deposited particle mass applying various deposition models. Lower and upper refer to different dust fraction estimates (see Eq. (6) and (12)).

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<td>Aluko et al. (2006)</td>
<td>58</td>
<td>85</td>
</tr>
<tr>
<td>Piskunov (2009)</td>
<td>32</td>
<td>47</td>
</tr>
<tr>
<td>Wagner et al. (2001)</td>
<td>81</td>
<td>115</td>
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<tr>
<td>High-volume sampler</td>
<td>26</td>
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</table>
Fig. 1: Comparison of the Na/Cl ratio of sodium chloride powder as function of particle size, corrected by the methods Cliff-Lorrimer, ZAF and interpolated. Measurements were performed at 20 kV acceleration voltage. The sodium chloride nominal ratio is shown as orange line. The linear regression of the interpolated correction is shown as black striped line.

Fig. 2: Calculated ion balance for all beam interaction volumes containing particles dominated by Na and Cl. Particles were collected by the DPDS. The axes are scaled in arbitrary units of percent × unit charges. Smaller particles yield smaller values as they only fill a fraction of the beam interaction volume. Particle size is color-coded; note that all particles between 0.6 µm and 1 µm in size are shown as blue, and between 10 µm and 25 µm as red. The black diagonal lines show the 10 % deviation cone.

Fig. 3: Mean element index only using Na, Mg, S, Cl, and Ca for normalization, and according standard deviation (1 σ) for NaCl-dominated particles from a typical atmospheric sample as function of particle size. Note that relative standard deviation for Ca is not shown due to frequent values below the detection limit.

Fig. 4: Comparison of the relative two-sided 95 % confidence interval limits for bootstrap and Poisson approaches. Values shown are the confidence interval limits for the total deposited particle volume divided by this volume. Data basis are the deposition samples at Ragged Point of 2013. Left: for all particles; right: for particles between 1 µm and 20 µm diameter. The color shows the fraction of the total volume present in the single largest particle. Note the different scales between the graphs.

Fig. 5: Deposition velocity to a smooth surface calculated by different deposition models for the samples of 2013, taking into account the ambient thermodynamic conditions and the particle composition. a: Stokes settling; b: Noll et al. (2001); c: Noll et al. (1989); d: Aluko et al. (2006); e: Piskunov (2009); f: Wagner et al. (2001)

Fig. 6: Number (left column) and volume size distributions (right column) of deposition rates as function of projected area diameter modeled for Cape Verde aerosol as derived from a 5 mm x 5 mm analysis field. The upper row is based on CV-ground, the lower on CV-air size distributions. The grey curve shows the original size distribution of deposited particles, the colored points with whiskers give median and central 95 % quantile of 1000 repetitions (200 for 0.093 and 0.172/0.173) for distributions calculated from samples with different area fractions covered by particles.

Fig. 7: Number (left column) and volume size distributions (right column) of deposited particles measured at Ragged Point and extrapolated change as function of particle projected area diameter and area coverage fraction, simulating a longer exposure time. Different colors show different factors of exposure increase (5x, 10x, 15x, 20x). Resulting coverage fractions are given in the figure keys.

Fig. 8: Particle volume per area calculated from single particle measurements as function of the fractional area coverage. Blue symbols denote the unmodified samples, red symbols the simulation of higher coverage by factors of 2, 3, 5, 10, 15, and 20. Error bars denote the two-sided 95 % confidence interval. The fit function shown as black dashed line is calculated as $y = e^{x \ln(a) + b}$; $[y] = m^3/m^2$; $a = 0.957 \pm 0.041$; $b = 3.57 \pm 0.06$; $x$ is the fractional area coverage.
Fig. 9: Upper 95% quantile of the fractions of internally mixed particles due to coincidental mixture on the substrate (color scale) as function of the projected area diameter and substrate area coverage, for a two-component system. Strong mixture refers to a minimum particle volume fraction of the other component of 20%, detectable mixture refers to 1%. Ratios of the two components in the base aerosol are given as percentages above each plot.

Fig. 10: Upper 95% quantile of the fractions of internally mixed particles due to coincidental mixing on the substrate (color scale), for a dust/sea-salt/sulfate system with measured composition and CV-ground size distribution. Strong mixture refers to a minimum particle volume fraction of the other component of 20%, detectable mixture refers to 1%. Mixing compounds are given on top of each graph. Sulfate/sea-salt and ternary mixtures practically do not form coincidentally.

Fig. 11: Average atmospheric mass size distribution densities derived from DPDS and FWI measurements. Left: period from July 10 to 15, 2013; right: from June 14 to July 8, 2013. Different colors refer to different deposition velocity estimates as shown in Fig. 5. Solid lines refer to total mass concentrations, dashed ones to the dust mass estimated from the chemical composition (upper limit estimate). Error bars show the central 95% confidence interval. Pink crosses show a size distribution measured in the Saharan air layer on June 22, 2013 (Weinzierl et al. 2017). Note that for particles smaller than 10 µm the FWI data may contain a considerable bias in calculation.

Fig. 12: Dust mass concentration and flux density time series derived from DPDS compared to such obtained from high-volume sampler (Kristensen et al. 2016). The darker brown bar shows the range from lower to upper estimate, the blue triangles the lower and upper estimate of dust deposition flux density. The date refers to the year 2013.

Fig. 13: Size dependence of the relative number abundance of major particle types as derived from single particle analysis of deposited aerosol.

Fig. 14: Left: box plot of daily mass deposition rate for total dust and dust-derived elements at Barbados for 2013 and 2016. Right: cumulative mass deposition flux as function of aerodynamic particle diameter for dust and dust-derived elements. Note that for P and Ti in the latter plot two particles containing each more than 10% of the total deposited mass have been removed from the data set.

Fig. 15: Potential source contribution functions (PSCF) of deposited material: dust (upper row), total soluble sulfate (central row) and relative ion balance for sulfate particles (lower row) for 2013 and 2016 at Ragged Point. Note that for dust, potential provenance is calculated for Saharan Air Layer transport only (i.e. trajectory arrival altitudes > 1500 m).

Fig. 16: Iron availability (SIAI) and deposition potential source contribution functions (PSCF) for 2013 and 2016. Upper row: geometric iron availability index, only silicate particles counted; trajectories arriving 1500–3000 m over Ragged Point. Lower row: mass deposition rate of Fe-rich particles smaller than 4 µm in diameter; trajectories arriving lower than 1500 m over Ragged Point.

Fig. 17: Ca/Na atomic ratio as function of particle dry diameter for all sea-salt particles collected at Ragged Point in 2013. Different samplers are shown by color: CI blue, DPDS red, and FWI brown.
Fig. 18: Time-series of wind and particle number deposition rates for pure compounds and internally mixed particles for June/July 2013 and August 2016. Particle size ranges are given in the top left of each graph. The limit of detection for the number of internally mixed particles is shown as line in the according color. Where only the detection limit for silicate/sulfate mixtures is visible, both limits are identical.

Fig. 19: Deposition velocities calculated with the Piskunov model for internal admixture of sea-salt (left) or sulfate (right) for the mixed particles observed at Ragged Point. Velocities are given for the unmixed dust core and internal mixtures at dry conditions, at ambient relative humidity, and at 90 % relative humidity. The lines show the according means. Note that variation in deposition velocity for the same dust core size arises from variation in wind speed and admixed fraction.

Fig. 20: Effective deposition velocity for all dust-containing particles observed at Ragged Point. The blue curves take into account internal mixing and hygroscopic growth at ambient conditions, whereas the orange only regards the dry dust fraction of the particles. In addition, cumulative mass distribution is shown on the inverted right axis. Particle size is given as aerodynamic diameter for the dust fraction of a particle. For the ambient deposition velocity, the geometric mean for each size class is shown in conjunction with the 1 geometric standard deviation range.
Fig. 02
Fig. 03

[Graph showing the relationship between particle diameter (μm) and the reduced element index, with different markers for Na, Mg, Ca, Cl, and S, along with the relative standard deviation.]
Fig. 04
Fig. 07
Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-417
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 2 May 2018
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Fig. 09

**Detectable mixture: CV-ground**

**Strong mixture: CV-ground**

**Detectable mixture: CV-air**

**Strong mixture: CV-air**
Fig. 10

**Strong mixture**

**Detectable mixture**
Fig. 11
Fig. 13

The figure shows the relative abundance of aerosol particles as a function of aerodynamic diameter in μm for different years and conditions.

- **2013 pre-storm**
- **2013 post-storm**
- **2016**

The categories include:
- Other
- Complex mixtures
- Stable sulfates
- Sulfate/silicate mixtures
- Soluble sulfates
- Sea-salt
- Sea-salt/silicate mixtures
- Silicates
- Ca-rich
- Oxides/hydroxides
Fig. 14
**Fig. 15**

*Figures showing deposition rate of sulfate and the relative ion balance for sulfate in 2013 and 2016.*
Fig. 17
Fig. 18
Fig. 19
Fig. 20

![Graph showing deposition velocity and cumulative mass fraction as functions of dust particle/core aerodynamic diameter, μm.](image)