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## RESEARCH ARTICLE

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## Key Points:

- About 60% of urban and 20% of desert dust particles presented residuals of coating
- The thickness of shell was found to depend on the size of particle core
- The degree of linear polarization and the scattering in backward directions is sensitive to the aerosol core-shell structure and dimensions

## Supporting Information:

- Supporting Information S1

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 (continued)

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## Microscopic Observations of Core-Shell Particle Structure and Implications for Atmospheric Aerosol Remote Sensing

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**Abstract** Although atmospheric aerosol particles can have complex heterogeneous microstructure, simplified homogeneous particle models are often used in remote sensing applications. In this study, the internal structure of individual atmospheric particles was imaged with the aim of parameterizing particle structural heterogeneity. To this end, ambient urban pollution, desert dust, and biomass burning particles were sampled in northern Europe and western Africa and analyzed by transmission electron microscopy coupled with energy dispersive X-ray spectroscopy. Among 8,441 observed particles, about 60% of urban and 20% of desert dust particles presented residuals of coating compounds in the form of a halo surrounding a solid core. Graphic outlining of core and halo areas by image analysis revealed a dependence between halo and core dimensions as well as a greater ratio of halos thickness to total particle diameter (core plus halo) for smaller cores than for larger ones. In the case of urban pollution, the mean ratio for submicrometer and supermicrometer size fractions was 0.25 and 0.19, respectively. The corresponding mean values in the desert dust case were somewhat lower (0.22 and 0.14, respectively), but show a similar decreasing trend. Under the assumption that the halo dimension is proportional to the thickness of the particle shell, the obtained core versus shell dependencies were implemented in numerical calculations of aerosol optical characteristics. Different scenarios of the core-shell dependencies were analyzed with respect to the influence on aerosol optical characteristics, bringing insights into sensitivity to parameterization of the core-shell particle model in remote sensing algorithms.

### 1. Introduction

Atmospheric aerosols are typically a heterogeneous mixture of particles with different size, shape, and internal structure with various chemical compositions. Electron microscopic observations of thousands of particles can unravel the physical mixing state of atmospheric particles. External as well as internal mixtures of particles were evidenced by numerous studies in different atmospheric conditions (Deboudt et al., 2010; Fan et al., 2016; Hamacher-Barth et al., 2016; Hand et al., 2010; Healy et al., 2013; Marris et al., 2013; Moffet et al., 2010; Pósfai et al., 2013; Pósfai & Buseck, 2010; Sobanska et al., 2014; Young et al., 2016). In particular, the internal structure at the particle scale can take the form of inclusions and coatings (Laskina et al., 2013; Mikhailov et al., 2015) and can represent a significant fraction of investigated atmospheric particles, even outnumbering the homogeneous ones (Li & Shao, 2009a, 2009ab).

The amount of light extinction can be accurately calculated knowing the complex refractive index, the size, the shape, and the mixing state of an ensemble of particles. The assumptions of particle homogeneity and spherical shape are the common simplifications enabling fast computations with a minimal number of variables. However, the physical mixing state and the shape of particles can strongly affect their optical properties. For instance, the influence of particle shape on atmospheric aerosol optical characteristics is modeled by an ensemble of randomly oriented spheroids (Dubovik et al., 2006; Mishchenko & Travis, 1994) and is presented in remote sensing algorithms as distribution of aspect ratios and fractions of spherical and nonspherical particles (Dubovik et al., 2006). The internal structure at the particle scale can also produce important features of optical characteristics (Fuller, 1995; Fuller & Kreidenweis, 1999). The absorption and scattering properties of an ensemble of aerosol particles are strongly dependent on the mixing scenario used, either external or internal (Bond et al., 2006; Lesins et al., 2002; Liu et al., 2014; Ramachandran & Srivastava, 2013).

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Some models treat the internally mixed components assuming a particle is composed of a homogeneous mixture of different species; thus, the complex refractive index of two or more components are mixed based on one of the effective medium approximation rules, for example, Maxwell-Garnett theory, Bruggeman theory, and volume weighted (Easter et al., 2004; K. Zhang et al., 2012). Another commonly used model of the internal structure is the concentric multilayered particles (Stamnes et al., 1988; Yang et al., 2002). For instance, previous calculations have shown that the absorption is enhanced when a nonabsorbing material coats a soot particle (Bond et al., 2006; Cappa et al., 2012; Kahnert, 2015; Mishchenko et al., 2014; Schwarz et al., 2008). Furthermore, changes in optical properties have been discussed by Bauer et al. (2007) for the case of mineral dust coated with sulfate and nitrate secondary products. The influence of structural inhomogeneity has also been the subject of studies in laboratory (Lang-Yona et al., 2010) and in remote sensing observations (Derimian et al., 2017; Li et al., 2013; Schuster et al., 2009). However, in contrast to the particle shape effect, the internal structure of particles is not considered in aerosol remote sensing applications.

In this study, we report microscopic observations of core-shell particles sampled in different regions and environmental conditions. These core-shell structures are typically formed when aerosol particles interact with water vapor and/or various reactive gaseous species during their transport in the atmosphere. This involves gas condensation and/or heterogeneous reactions at the particle surface. We specifically investigate core-shell particles collected in an urban environment during a particulate pollution event and in a desert environment during biomass burning intrusion. Such events favor the formation of core-shell structures (Laskin et al., 2016; Niu et al., 2015; Tang et al., 2016). This study therefore relies on two field campaigns conducted in northern France and western Africa, Senegal, in order to investigate whether a parameterization of the core-shell structure is possible. We then illustrate how aerosol optical characteristics change for representative particle size distributions, as a function of core-shell dimensions and chemical composition.

## 2. Materials and Methods

### 2.1. Sampling Sites

Intensive field observations were carried out in the metropolitan area of Lille, northern France (50°36′29″N, 3°8′25″E), during a particulate pollution event occurred in March 2014 affecting northwestern Europe with markedly elevated particulate matter (PM) concentrations (Elliot et al., 2016; Smith et al., 2015; Vieno et al., 2016). The Lille site, hereafter referred to as *urban environment*, is a long-term AERONET site (Holben et al., 1998) equipped with a micro-Lidar (CIMEL Electronique S.A.S). Additional description of the site can be found in Bovchaliuk et al. (2016) and Mortier et al. (2013).

SHADOW (SaHaran Dust Over West Africa) campaign was carried out from March to April 2015 and from December 2015 to January 2016 in the coastal city of Mbour, Senegal, western Africa (14°23′38″N, 16°57′32″W), located 80 km south of Dakar. This campaign aimed at investigating the microphysical and microchemical properties of desert dust outbreaks and biomass burning intrusions. More details on this campaign can be found elsewhere (Bovchaliuk et al., 2016; Péré et al., 2018; Rivellini et al., 2017; Veselovskii et al., 2016). The Mbour site, hereafter referred to as *desert environment*, is a long-term AERONET site (named Dakar in AERONET), which is equipped with a CIMEL micro-Lidar (Mortier et al., 2016).

Airborne particles were collected within the transported dust and biomass aerosol layers. The same impactor and collection substrate were used in both sampling campaigns. Atmospheric particles were collected using a 4-stage personal cascade impactor (Sioutas, SKC Inc.) at a flow rate of 9 L/min (Singh et al., 2003). The size segregation of particles was according to the following aerodynamic diameter ( $d_{aer}$ ) ranges:  $d_{aer} > 2.5 \mu\text{m}$ ;  $1.0 < d_{aer} < 2.5 \mu\text{m}$ ;  $0.50 < d_{aer} < 1.0 \mu\text{m}$ ; and  $0.25 < d_{aer} < 0.50 \mu\text{m}$ . Particles were impacted onto Formvar/Carbon coated 200 mesh copper transmission electron microscope (TEM) grids (Ted Pella Inc.). More details about particle samplings are provided in the supporting information.

### 2.2. Transmission Electron Microscopy

TEM has been proven to be a suitable technique for providing information on structure, morphology, and chemical composition of individual particles (Adachi et al., 2010; Adachi & Buseck, 2013; Laskin et al., 2006; Li et al., 2011; Pósfai et al., 2013; Verleysen et al., 2014). However, some compounds, especially volatile species, are prone to degradation in the high vacuum conditions of the TEM (Pósfai et al., 1998; Reid, Eck, et al., 2005). This effect strongly depends on the composition of aerosol particles. Refractory

compounds, such as fresh soot, mineral dust, or metallic particles remain unchanged, while semivolatile and water soluble compounds are evaporated within the high vacuum chamber of TEM. Moreover, some particles are vulnerable to radiation damage caused by the incident electrons. To avoid this effect, we initially acquired electron micrographs of particles from the entire grid, prior to energy dispersive X-ray (EDX) analysis of particles. In the case of core-shell particles, the coating compounds form a halo. During EDX analysis, the beam rasters the core only, because the spectra of the halo cannot be acquired due to the low material remaining after evaporation in the vacuum of the microscope chamber. This fact, together with the circular appearance of the halo, indicates that most of the particle coating was composed of volatile liquids. Our observations are in line with an experiment conducted by Pósfai et al. (1998) on liquid particles impacted on the same type of substrate as in our work. In this experiment, the cross-sectional atomic force microscopy profiling evidenced particles with a hemispherical shape after impaction. Subsequent observation of the same particles by TEM revealed that volume loss (mostly water or semivolatile compounds) occurred along with vacuum in the TEM chamber and a residue is left, forming circular halos on the substrate around the dried particles. The particle drying in TEM is taken here as an advantage for revealing the refractory core inside a halo composed of liquid shell residuals. Individual particles were examined using a TEM (Tecnai G2-20, FEI) operating at 200 kV accelerating voltage (LaB6 filament) fitted with a Gatan ORIUS SC1000 CCD camera. The elemental composition of particles was determined using an EDX spectrometer (EDAX Inc.) with a Si (Li) thin window detector having an active surface of 30 mm<sup>2</sup> and an energy resolution of 136 eV (for MnK<sub>α</sub>).

### 2.3. Image Analysis

TEM images were processed using FIJI (Schindelin et al., 2012) based on ImageJ (Schneider et al., 2012). This software package is commonly used for counting and measuring the surface area of atmospheric particles imaged by electron microscopes (Bescond et al., 2014; Huffman et al., 2012; Rocha-Lima et al., 2014). Using this tool, the projected surface area of halo residual and core of particles was measured, assuming that they are proportional to the cross section of real atmospheric particles. Such methodology was applied also by Chou et al. (2008), Hamacher-Barth et al. (2013), Li and Shao (2009a, 2009ab), and Pósfai et al. (2003). For quantifying the particle internal structure, the particle projected surface area was measured by counting the number of pixels comprised in 2-D-projected particle. To ensure accurate measurements, a series of image treatments were necessary, by manually adjusting the contrast and brightness of each electron micrograph according to the gray level threshold. To evaluate the accuracy of surface area measurements, particles of different sizes were digitalized at different magnifications up to 70,000X. A maximum of 2% difference in measured surface area at different magnifications was estimated. A typical electron micrograph and the corresponding treated image are presented in Figure 1. Some particles were excluded from the analysis due to the lack of clear contrast between the gray level of core and halo, for example, the particle marked with a green arrow in Figure 1a.

Considering that the projected area of a particle ( $A_{\text{proj. core, total}}$ ) is equal to the area of a circle that covers the same surface, one can calculate an equivalent diameter of the core ( $d_{\text{core}}$ ) or of the total diameter of core plus halo ( $d_{\text{total}}$ ). The thickness of halo ( $\Delta_{\text{halo}}$ ) can be defined as follows:

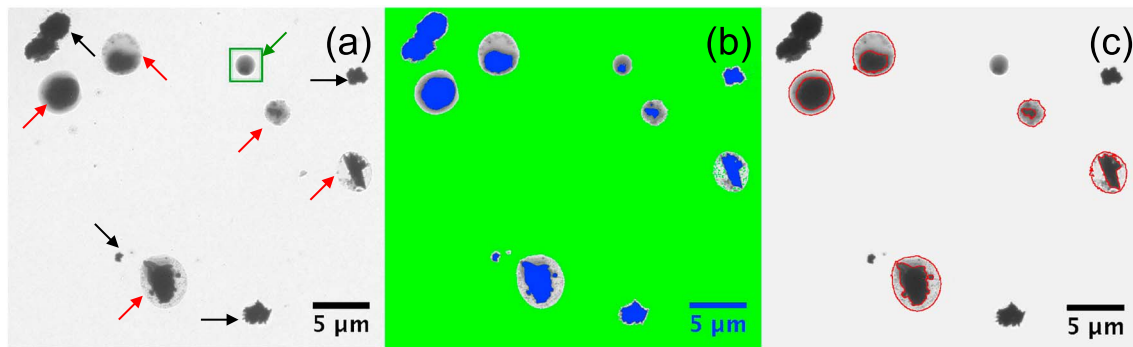
$$\Delta_{\text{halo}} = \frac{d_{\text{total}} - d_{\text{core}}}{2}. \quad (1)$$

The particle image analysis provides also Feret's diameters (denoted as  $F_{\text{max}}$  and  $F_{\text{min}}$ ), which are defined as the maximum and minimum caliper, respectively. We can therefore calculate the ratio between  $F_{\text{max}}$  and  $F_{\text{min}}$  to obtain the particle axis ratio describing the shape of particles.

## 3. Results and Discussions

### 3.1. Description of the Case Study Events

The urban pollution sampling was conducted during a widespread pollution episode occurred in northwestern Europe in March 2014 (Elliot et al., 2016; Smith et al., 2015; Vieno et al., 2016). This pollution event was reported to cause ~600 deaths and ~1,500 emergency hospitalizations in the United Kingdom (Macintyre et al., 2016). Atmospheric particulate matter was collected on 13 March in a near-ground pollution layer

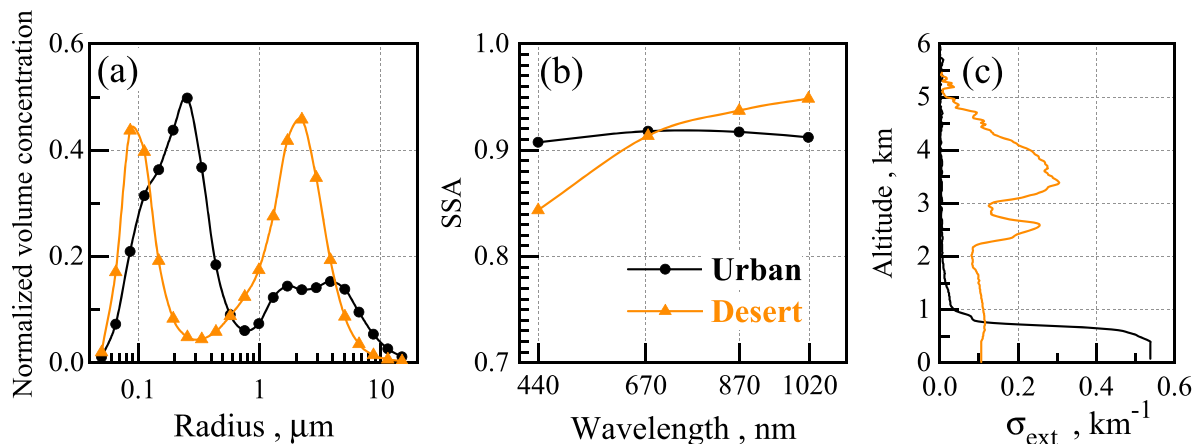


**Figure 1.** Illustration of the methodology for graphic outlining of the particle surface area: (a) electron micrograph of particles, where black arrows show uncoated particles, red arrows show coated particles, green arrow shows an example of a particle excluded from the analysis due to the lack of clear contrast; (b) threshold micrograph, where blue, gray, and green colors represent the core, the residual halo, and the background, respectively; (c) the selected cores and residual halos contoured by red line.

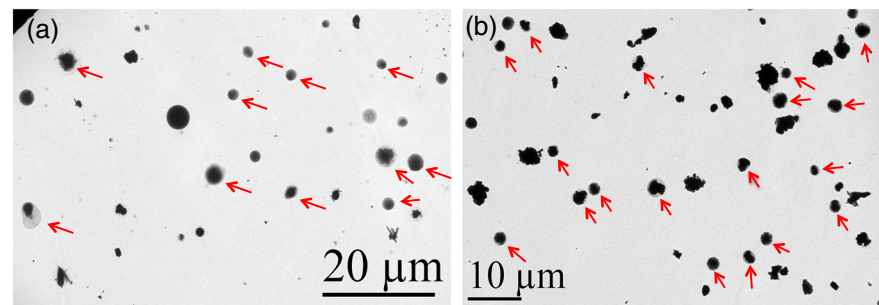
where PM mass was dominated by  $PM_{2.5}$  representing 86% of  $PM_{10}$ . The detailed optical and in situ measurements conducted during this episode are presented in Figure S1 accompanied by the references thereby (Dubovik, Holben, Eck, et al., 2002; Eck et al., 1999; Mortier et al., 2013).

The desert dust event with biomass burning intrusion occurred during the dry season, when the biomass burning aerosol from anthropogenic activities in Sahelian and sub-Saharan regions frequently reach the site (Hand et al., 2010; Haywood et al., 2008; Osborne et al., 2008) and are transported over a dust layer (Léon et al., 2009; Mortier et al., 2016). Aerosols were sampled on 20 January 2016 at 3.7 km altitude in an atmospheric layer where biomass burning particles were mixed with desert dust. This event is described in details in Figures S2 and S3 complemented by the references thereby (Deboudt et al., 2010; Engelhart et al., 2011; Fard et al., 2017; Flament et al., 2011; Kreidenweis et al., 2008; Mortier et al., 2016; Nguyen et al., 2016; Tan et al., 2017).

The differences in the aerosol microphysical and optical properties during the two case studies are illustrated by the AERONET derived column integrated size distributions (Figure 2a), the spectral single scattering albedo (SSA; Figure 2b) and the lidar derived vertical profiles of extinction coefficient (Figure 2c). In the case of urban pollution, the fine mode dominates the size distribution. In the case of desert dust event with biomass burning intrusions, the volume size distribution is characterized by practically equal fine and coarse modes representing a mixed aerosol type. The fine mode urban particles ( $r_{mode\ fine} = 0.25\ \mu m$ ) are larger than the fine mode particles from the case of the desert dust and biomass burning mixture ( $r_{mode\ fine} = 0.08\ \mu m$ ). The SSA of about 0.9 in the case of urban environment shows that the



**Figure 2.** Comparisons of AERONET derived (a) size distribution normalized to the total volume concentrations, (b) spectral SSA, and (c) lidar derived extinction profiles for sampling in urban and desert environments represented with black and orange lines, respectively. SSA = single scattering albedo.



**Figure 3.** Overview of particles collected in  $1.0 < d_{aer} < 2.5 \mu\text{m}$  size fraction (a) in urban environment and (b) in desert environment during biomass burning intrusion. Red arrows point to particles that present a halo.

aerosols are low light-absorbing. In the case of desert environment, a stronger absorption appears at shorter wavelengths, which is typical for desert dust due to the presence of iron oxides. At the same time, the values are quite low ( $\sim 0.85$ ), which can be explained by the presence of biomass burning, known to be more light-absorbing (Reid, Eck, et al., 2005; Reid, Koppmann, et al., 2005). The extinction profile in the case of urban environment shows that the aerosols are concentrated in the lower part of the troposphere (Figure 2c), while in desert environment, the extinction profile indicates transport of two aerosol layers at altitudes of about 2 to 3 and 3 to 5 km.

### 3.2. Physicochemical Characteristics of Core-Shell Particles

Figure 3 presents electron micrographs of typical particles collected in urban and desert environments. Observed particles were categorized in two groups, those that present a halo (identified by red arrows) and those without halo, representing coated and not coated particles, respectively. Hereafter, particles that present a halo are termed *coated urban particles* and *coated desert particles*.

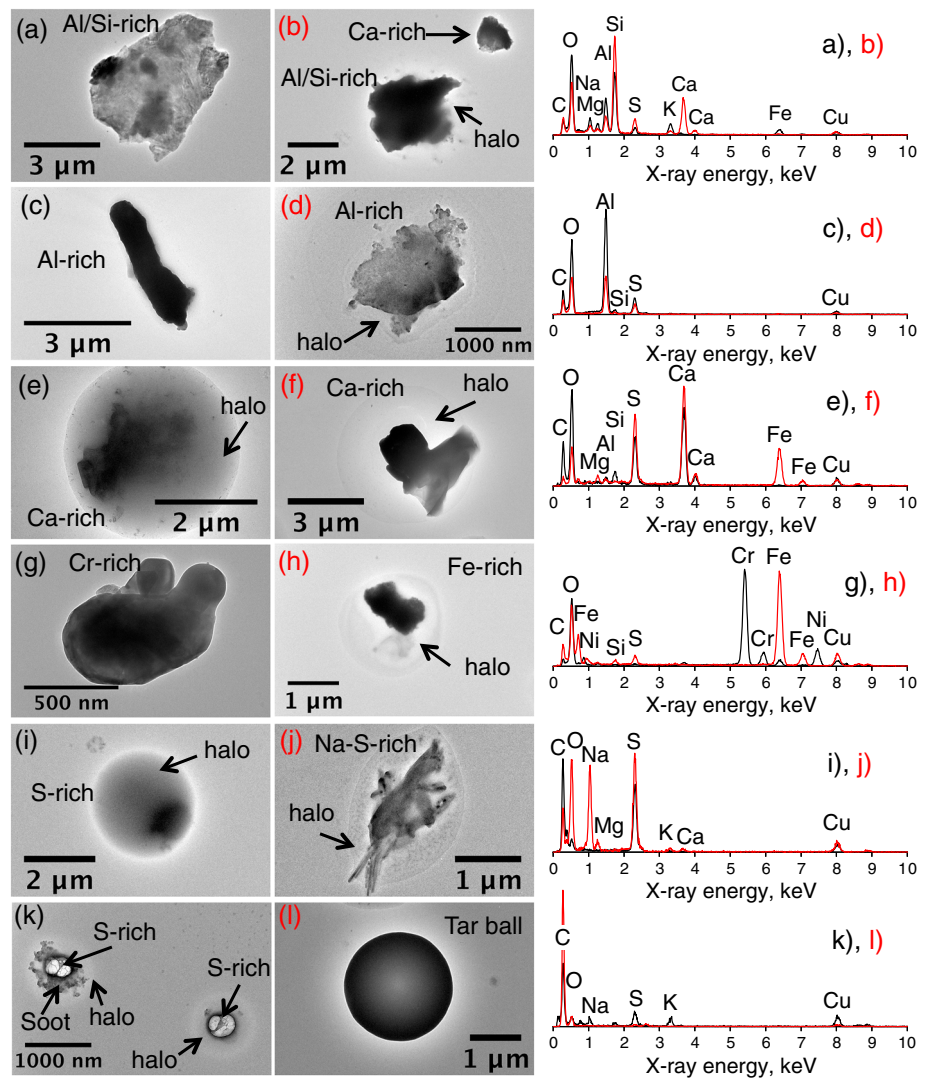
An overview of particles collected in the urban and desert environments is presented in Figures S4 and S5. Coating of atmospheric particles is often resulting from enhanced hygroscopicity due to aging mechanisms such as coagulation, condensation, and heterogeneous chemical reactions (Khalizov et al., 2009; Moffet et al., 2010; Müller et al., 2017). Presence of coating was reported in numerous studies in urban agglomerations (Li & Shao, 2009a, 2009ab; Niemi et al., 2006; Niu et al., 2015; Pirjola et al., 2017) and desert environments (Derimian et al., 2017; Kandler et al., 2007; Laskin et al., 2005). A previous study by Deboudt et al. (2010) of the particle mixing state at the Mbour site showed that marine and carbonaceous compounds can form coatings on mineral dust particles.

Figures 4 and 5 present electron micrographs of individual particles collected in urban and desert environments, respectively. Sixty-one urban particles and 73 desert particles, randomly chosen from all four aerodynamic diameter ranges, were chemically analyzed. Among them, 36 urban and 29 desert particles presented a halo. The major elements common to studied particles were C, O, S, Na, K, Ca, Al, Si, Fe, Cr, and Ni. The sample from the urban pollution event additionally contained Mn and Zn. The sample from the dust event with biomass burning intrusion additionally contained P and Ti. Based on their main elemental composition, all the analyzed particles were sorted into eight groups: (1) Al/Si-rich; (2) Al-rich (particles exclusively found in the urban pollution sample) or Si-rich (particles exclusively found in the desert dust sample); (3) Ca-rich; (4) transition metal-rich (Fe, Cr, Ni, also containing Ti-rich particles in the desert dust sample, and Mn-Zn-rich particles in the urban pollution sample); (5) C/S/K-rich (also containing P for particles from the desert dust sample); (6) Na-rich; (7) soot; and (8) tar balls.

#### 3.2.1. Urban Particles

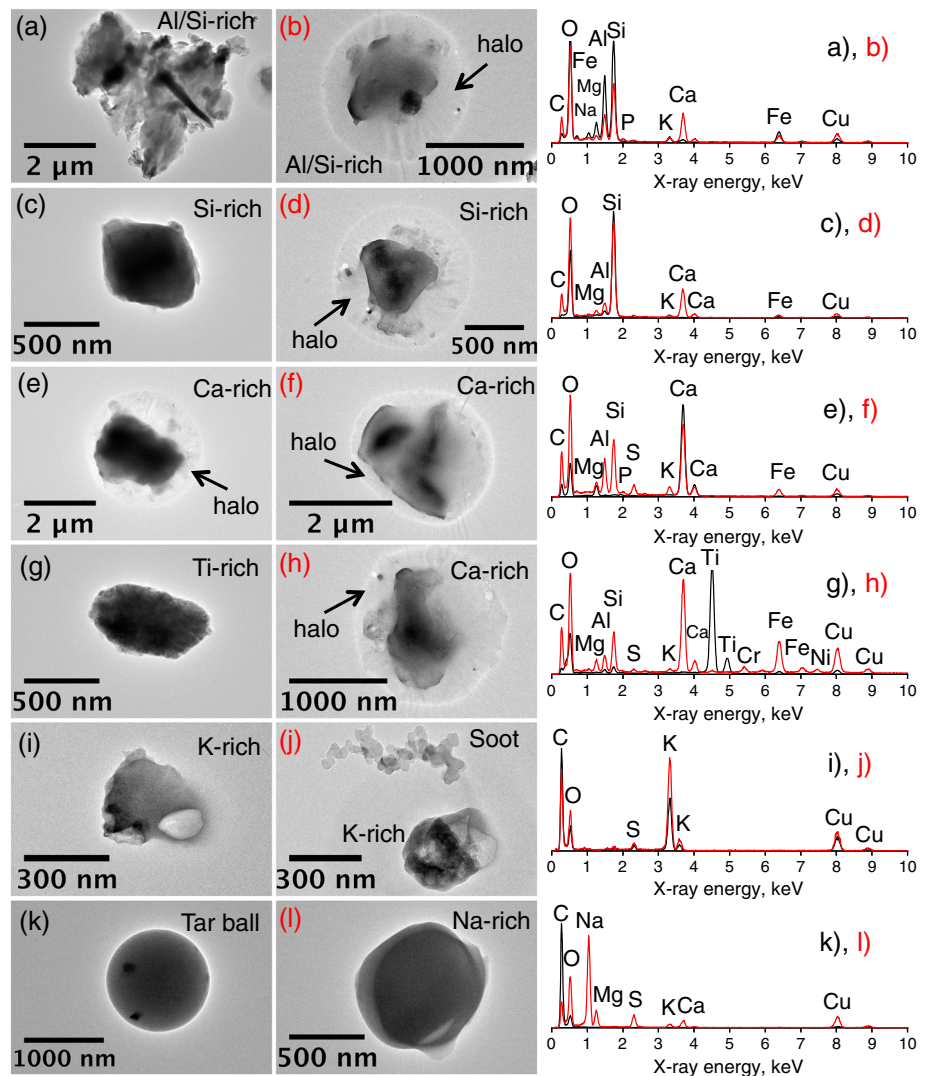
Particles with coating residuals were found in all particle types except tar balls.

(1) **Al/Si-rich** particles can also contain Ca, Mg, and Fe. Their shape was mostly angular (Figures 4a and 4b), which indicates soil erosion origin (Choël et al., 2007). Coated Al/Si-rich particles were also found (Figure 4b) with variable traces of S, which suggests aging processes with S-containing species, most probably as a result of surface coagulation and condensation (Fan et al., 2016; Li & Shao, 2009a, 2009ab; Sullivan et al., 2007). In addition, some Al/Si-rich particles also contained traces of K (not shown),



**Figure 4.** Electron micrographs of urban particles and their corresponding energy dispersive X-ray spectra of (a) AlSi-rich, (b) AlSi-rich with halo and Ca-rich, (c) Al-rich, (d) Al-rich with halo, (e, f) Ca-rich with halo, (g) Cr-rich, (h) Fe-rich with halo, (i) S-rich with halo, (j) Na-S-rich with halo, (k) soot attached to S-rich with halo, and (l) tar ball particles.

which are markers of biomass burning most probably from residential wood heating. (2) **Al-rich** particles contained S or Si as minor elements. They have an elongated shape (Figure 4c) and some of them were encapsulated into a host (Figure 4d). They most probably originate from soil dust (Shi et al., 2009) or anthropogenic emissions (Hoflich et al., 2005). (3) **Ca-rich** particles were found with high O and S contents and were sometimes mixed with Al/Si. Some of them presented minor traces of Fe, Mg, P, Na, K, and occasionally Zn. A Ca-rich particle with no halo is illustrated in Figure 4b (upper right particle). The coated Ca-rich particles have angular shapes and circular halo (Figures 4e and 4f). (4) **Transition metal-rich** particles were subcategorized into Zn-Mn-Cr-Ni-rich (Figure 4g) and Fe-rich particles. The Zn-Mn-Cr-Ni-rich with abundant O presented also traces of Fe, Mg, Al, Si, P, and K. These particles may result from tailpipe exhaust, roadway dust, residual of heating fuels but also from brakes and tire abrasions. Another potential source may be from the subway wheels and trails, which are located at a distance of few hundred meters near the urban sampling site. Fe-rich particles had high O content and some of them presented traces of S, P, Na, Mg, Al, Si, K, Ca, Mn, Zn, and Cl. Some Fe-rich particles presented angular shapes and a circular residual halo (Figure 4h). Pure Fe-rich particles have been found to have circular shape. (5) **C/S/P/K-rich** particles include particles rich in C (but not having the shape



**Figure 5.** Electron micrographs and corresponding energy dispersive X-ray spectra of particles collected at 3.7 km altitude in desert environment during biomass burning event: (a) Al/Si-rich, (b) Al/Si-rich with halo, (c) Si-rich, (d) Si-rich with halo, (e, f, and h) Ca-rich with halo, (g) Ti-rich, (i) K-rich, (j) soot and K-rich, (k) tar ball, and (l) Na-rich particles.

of nanospheres aggregates as soot) or S or P or K or combinations of two or three elements and some of them presented minor Mg (Figure 4i). This category of particles is considered as markers of wood combustion processes. Some particles from this category were strongly beam-sensitive. (6) **Na-rich** particles such as aged sea spray aerosol originating most probably from the northwestern coast of France were also found (Figure 4j). The corresponding X-ray spectrum displays minor K and Ca peaks as well as an intensity ratio of Na to Mg (10:1) matching the elemental ratios reported for aged sea spray particles in the southeast United States by Bondy, Wang, et al. (2017). The halo in this case could be of marine origin. (7) **Soot** particles are mostly distinguishable by their form of chain-like aggregates of nanospheres. In addition to C, some of them contained minor traces of S and/or Si. They are emitted by various pollution sources such as diesel exhaust, industrial emissions, and domestic fires (Fan et al., 2016). These particles can evolve by condensation and coagulation with sulfates and water-like compounds (Johnson et al., 2005; Niemi et al., 2006; Pirjola et al., 2017). Some soot particles have been found internally mixed with sulfate and presented a circular halo (Figure 4k). (8) **Tar balls** are round carbonaceous particles stable under the electron beam (Figure 4l). They usually originate from smoldering burning combustion (Chakrabarty et al., 2010).



### 3.2.2. Particles in Desert Environment Under Biomass Burning Intrusion

Contrary to urban particles, only particles from aluminosilicate-rich, silicate-rich, and Ca-rich types were observed with residuals of coating compounds.

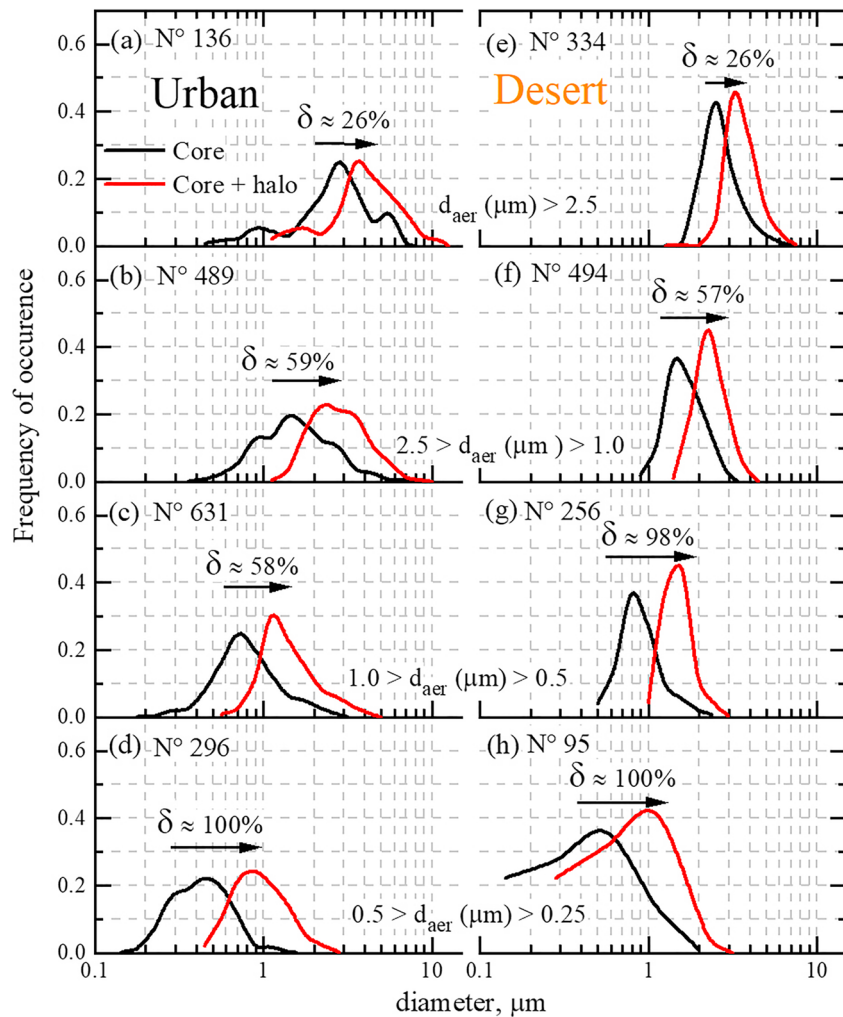
(1) **Al/Si-rich** particles presented irregular shapes (Figure 5a) and some of them presented residuals of liquid coating compounds (Figure 5b). These Al/Si-rich particles presented traces of Ca, Mg, Fe, Na, P, K, S, and Ti. Based on the classification from Chou et al. (2008), aluminosilicate particles were mostly feldspar (intensity ratio Si/Al  $\sim$ 3), illite (Si/Al  $>$  2) and kaolinite (Si/Al  $\sim$ 1). (2) **Si-rich** particles contained traces of Fe, Mg, Ca, Na, Mg, S, and K. They presented angular shapes. Quartz particles were observed without halo (Figure 5c) and with halo (Figure 5d). (3) **Ca-rich** particles were mostly found with halo (Figures 5e, 5f, and 5h). These particles contained traces of S, K, P, Na, Fe, Mg, Ti, Mn, and Ni. Calcium-rich particles can be in the form of calcium carbonate (CaCO<sub>3</sub>) and dolomite (CaMg (CO<sub>3</sub>)<sub>2</sub>). During transport, they could be partially converted into calcium nitrate followed by the deliquescence of the calcium nitrate product (Krueger, 2003). The deliquescent calcium nitrate shell could have formed a halo upon dehydration in the TEM chamber. (4) **Transition metal-rich** particles (Ti-rich, Zn-rich, and Fe-rich) were found without halo (Figure 5g). (5) **C/S/K-rich** particles (Figures 5i and 5j) are carbonaceous particles with inorganic K-sulfate inclusions typically found in biomass smoke. They have a rounded morphology, did not present a halo, and were beam-sensitive. (6) **Soot** particles easily identified in the form of nanospheres aggregated together in a chain-like structure were observed (Figure 5j). (7) **Tar balls** are other carbonaceous particles that are resistant to electron beam damage with a characteristic spherical shape typical of wildfire emissions (China et al., 2013; Figure 5k). (8) **Na-rich** particles contained low amount of Cl, indicating aged sea-salt particles converted to sodium nitrate and sodium sulfate (Figure 5l). They were highly sensitive to beam damage.

Biomass burning particles sampled in desert environment were found predominant in the submicrometer size fractions. Desert dust was found more abundant in the supermicrometer size fractions. Indeed, desert dust particles may be transformed during transport through multiphase chemistry, resulting in internal mixing with condensed-phase organic constituents (Laskin et al., 2016). Nitrates and sulfates can uptake onto mineral dust by forming a layer around the particle and transforming the shape of the nonspherical mineral dust into a spherical one (Hwang & Ro, 2006; Kojima et al., 2006; Laskin et al., 2005; Li & Shao, 2009a, 2009ab; Matsuki et al., 2005; Sullivan et al., 2007; Tang et al., 2016; D. Zhang et al., 2000). The presence of K and S in dust particles could indicate coatings of mineral desert dust with K-sulfate, which is a marker of biomass burning.

### 3.3. Dependence Between Dimensions of Core and Size of Halo

TEM observations of 8,531 particles were used to describe their internal structure at individual particle scale. Among the 2,569 observed particles in urban environment, 60% presented a halo. In desert environment, among the 5,872 observed particles, 20% presented a halo. The data can be accessed from Unga (2018). The number size distribution of the particles presenting a halo is presented in Figure 6: as the size fraction becomes smaller, the relative shift in the particle size due to the presence of halo becomes systematically larger, that is, the relative shift of the mode diameter ( $\delta$ ). It indicates that the smaller particles tend to have larger halos for both urban and desert dust cases. However, the width of the size distribution in the case of urban particles is notably larger than that of desert dust particles due to differing particle types, as described in section 3.2.

The study of the halo thickness ( $\Delta_{\text{halo}}$ ) according to the core size ( $d_{\text{core}}$ ) confirms a clear dependency between the dimensions of cores and halos (Figure 7). In general, for both urban and desert dust particles,  $\Delta_{\text{halo}}$  increases with  $d_{\text{core}}$  but the slope of the increase is steeper for smaller  $d_{\text{core}}$  (see also insert table in Figure 7). It is notable that the mean  $\Delta_{\text{halo}}$  for urban particles is higher than the one for desert particles. At the same time, the dispersion of  $\Delta_{\text{halo}}$  is higher in the case of urban particles than in the case of desert particles ( $\sim$ 0.4 vs  $\sim$ 0.3, respectively). This larger dispersion can be due to a more variable aerosol composition that affects the particle shell, for example, Laskina et al. (2015). Indeed, if we assume that the halo size is proportional to the thickness of particle shell (material surrounding a particle before it was sampled on the substrate), then a larger relative dispersion of  $\Delta_{\text{halo}}$  is in line with the stronger diversity of chemical composition of urban particles. The thickness of halo is also expected to vary according to the chemical composition of shells themselves. Thus, the chemical composition of shells, along with the chemical composition of cores, is expected to contribute to the dispersion of  $\Delta_{\text{halo}}$  as a function of  $d_{\text{core}}$ . Other factors such as relative

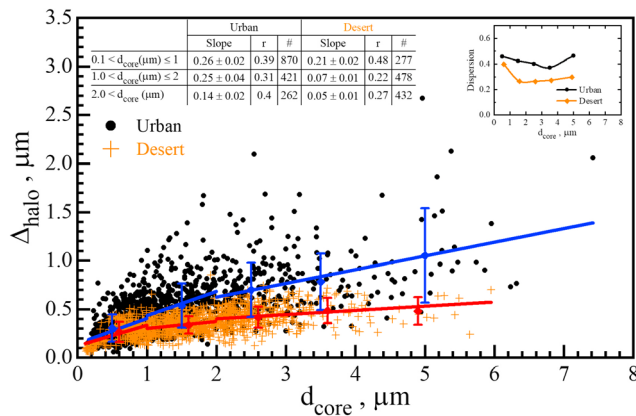


**Figure 6.** Number size distributions normalized to the total number of particles in (a), (e)  $d_{aer} > 2.5 \mu\text{m}$ , (b), (f)  $1.0 < d_{aer} < 2.5 \mu\text{m}$ , (c), (g)  $0.50 < d_{aer} < 1.0 \mu\text{m}$ , and (d), (h)  $0.25 < d_{aer} < 0.50 \mu\text{m}$  size fractions. Left and right columns correspond to sampling in urban and desert environment, respectively. Black and red lines represent the distributions for core and core plus halo diameters, respectively.  $\delta$  represents the percentage of the mode diameter shift.  $N^\circ$  is the number of analyzed particles.

humidity or availability of reactive gaseous species can also influence the thickness of shell. So, although the present study is limited to specific cases, the data reveal that dependence between the dimensions of  $\Delta_{halo}$  and  $d_{core}$  exists and enable to evaluate a possible range of variability in case of urban and desert aerosol type. The main objective of the study is to parameterize aerosol core-shell structure in remote sensing algorithms. Thus, we should also consider a possible limited sensitivity of optical characteristics to core and shell size dependences. To clarify this question, microscopic observations of core-shell structures from the two described case studies are summarized in a set of parameters and several numerical calculations of aerosol optical characteristics are conducted (see section 3.5).

### 3.4. Parameterizing Core-Shell Dependencies

The relative contribution of  $\Delta_{halo}$  to the total particle size ( $\Delta_{halo}/d_{total}$ ), the mean  $\Delta_{halo}$ , and the corresponding  $d_{core}$  can be useful parameters to characterize the core-shell structure. For instance, the ratio  $\Delta_{halo}/d_{total}$  indicates the fraction of the coating material from the total particle volume. The mean values and the corresponding standard deviations of  $d_{core}$ ,  $\Delta_{halo}$ , and  $\Delta_{halo}/d_{total}$  for all particles and for submicrometer and supermicrometer size fractions, for urban and desert environment cases, are presented in Table 1.



**Figure 7.** Thickness of halo ( $\Delta_{halo}$ ) versus diameter of particle core ( $d_{core}$ ) for core-shell particles collected in all size fractions. Black dots and orange crosses correspond to particles collected in urban and desert environment, respectively. The blue and red diamonds with corresponding vertical lines represent the means with standard deviations for three subintervals of  $d_{core}$ . Dispersions, calculated as the ratio of Std. Dev. to the mean, are also presented in the insert graph.

In addition, the ratio of  $\Delta_{halo}/d_{total}$  can be evaluated as a continuous function of the particle size ( $d_{core}$ ), that is, fitted by an equation, for example, as equation (2):

$$\frac{\Delta_{halo}}{d_{total}} = b + c \cdot \exp(a \cdot d_{core}), \quad (2)$$

whose parameters and coefficient of determination ( $R^2$ ) for urban and desert particles are reported in Table 2.

The obtained coefficients show that the ratio is higher for small particles in both urban and desert cases. As the diameter of core increases,  $\Delta_{halo}/d_{total}$  decreases and becomes constant. In the study by Moffet et al. (2016) on black carbon coatings it was also found that smaller particles have thicker shell, which supports the findings in our case studies. In addition, Ibrahim et al. (2018) also showed that smaller mineral dust particles adsorb water more efficiently. It is interesting to note that our finding is also in line with the diffusion growth theory of cloud droplets that states the faster growth for the smaller droplets. That is, although our data present only a snapshot in time, it indicates that the smaller particles grew larger.

### 3.5. Axis Ratio

Besides the core-shell structure, the particle shape is also known as being important for optical properties of atmospheric aerosols. In addition, since optical properties of core-shell particles are usually modeled by Mie calculations for concentric spheres, a question about the extent of nonsphericity of the observed particles can arise. The particle axis ratio is a parameter that characterizes nonsphericity and it is obtained in this study from the analysis of electron micrographs. Histograms of axis ratio of particles surrounded by halo (core part only, denoted as *particle cores*) and particles without halo (denoted as *not coated particles*) for urban and desert cases are presented in Figure 8. Overall, the range of the axis ratio of particle cores was found to vary from about 1 (spherical particles) to 3. The mean axis ratio of coated cores is  $1.37 \pm 0.30$  ( $\pm$ Standard Deviation) in the case of urban particles and  $1.31 \pm 0.23$  for desert dust particles. Figure 8 shows that coated particles appear more spherical, for both urban and desert cases. These results are in favor of the use of the concentric spheres model for calculations of aerosol optical characteristics.

It should be noted here that, in the case of desert environments, the particles collected in the smallest size fraction were mainly not coated spherical biomass burning particles, which makes the axis ratio of not coated particles to be closer to 1 in desert case. Nevertheless, Figure 8 clearly shows that the presence of coatings shifts the whole histogram of particle cores toward smaller axis ratios, which is true for both urban and desert cases; that is, the coated particles have tendency to be more spherical.

### 3.6. Optical Properties

The effect of core-shell particle structure on optical properties was evidenced in various studies, either by Mie codes (Lesins et al., 2002; Ramachandran & Srivastava, 2013), or by discrete dipole

**Table 1**

Mean and Corresponding Standard Deviation of  $d_{core}$ ,  $\Delta_{halo}$  and  $\Delta_{halo}/d_{total}$  for all Sizes and for Submicrometer and Supermicrometer Size Fractions of  $d_{core}$

	Urban			Desert		
	All sizes (N° = 1,553)	$d_{core} < 1 \mu m$ (N° = 866)	$d_{core} > 1 \mu m$ (N° = 687)	All sizes (N° = 1187)	$d_{core} < 1 \mu m$ (N° = 276)	$d_{core} > 1 \mu m$ (N° = 911)
$d_{core}$ (μm)	1.24 ± 1.00	0.61 ± 0.21	2.03 ± 1.02	1.74 ± 0.92	0.67 ± 0.24	2.06 ± 0.80
$\Delta_{halo}$ (μm)	0.45 ± 0.28	0.31 ± 0.14	0.63 ± 0.30	0.35 ± 0.12	0.26 ± 0.11	0.38 ± 0.11
$\Delta_{halo}/d_{total}$	0.22 ± 0.06	0.25 ± 0.05	0.19 ± 0.05	0.16 ± 0.05	0.22 ± 0.05	0.14 ± 0.03

Note. N° denotes the number of particles within each size range.

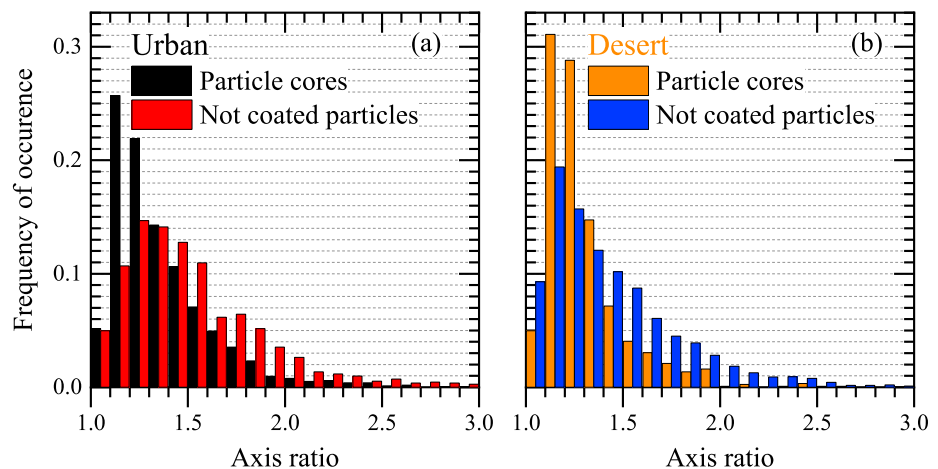
**Table 2**  
Parameters of Equation (4) and Coefficient of Determination ( $R^2$ ) for Urban and Desert Particles

	Urban	Desert
b	$0.16 \pm 0.005$	$0.09 \pm 0.04$
c	$0.16 \pm 0.006$	$0.21 \pm 0.005$
a	$-1.03 \pm 0.01$	$-0.82 \pm 0.05$
$R^2$	0.37	0.65

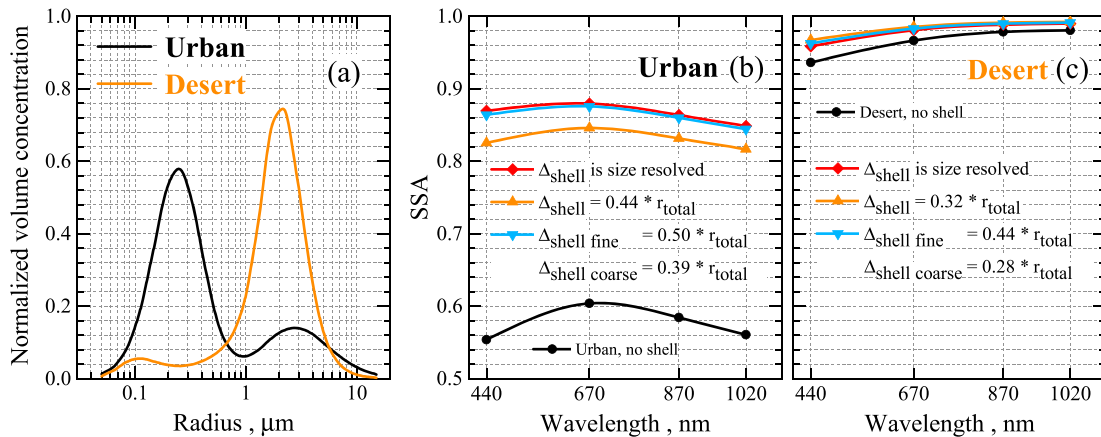
approximations models (Scarnato et al., 2013; Wu et al., 2016), or by superposition T-Matrix method (Cheng et al., 2014). For sensitivity tests and quantification of coated particle effect on optical properties, some studies assume a shell to core diameter ratio of 2.0 in Cheng et al. (2015), or the shell thickness to core radius ranges from 0.02 to 0.2 in Yin and Liu (2010), or it is calculated from the mass and density of the core and the shell (Ramachandran & Srivastava, 2013). Here we employ the microscopic observations of real airborne particles sampled in urban and desert environments and examine three scenarios

of different ways to distribute the thickness of shell on the ensemble of cores. These scenarios are chosen as possible parameterization of the core-shell particles that can be proposed for remote sensing algorithms. We assume that the thickness of halo observed on the substrates is proportional to the real thickness of shell of a coated atmospheric particle. Indeed, the observed halo should be at least in the dimension of cross section of coated particle, however the halo can also be larger due to the impaction during the sampling and to the wettability of the substrate. Therefore, some overestimation of the shell dimension can be possible. At the same time, experience of microscopic observations show that the wetted particles often stay in a liquid form also after the sampling on a substrate; the particles are dried later during the electron micrographs image acquisition, thus we can consider that all particles suffer the same effect in TEM vacuum and during the image acquisition. Given this, and that the wettability of the substrates is the same, it can be expected that the halo dimension is a suitable representation of the shell dimension. Such strategy was used by Moffet et al. (2016) to determine the concentricity between black carbon inclusions particles and their host, where they showed that the majority of black carbon cores are close to the center of their host. In addition, in this work we test the relative dependencies between the shell and core dimensions, rather than using the absolute values of particle dimensions. The coating thickness is represented by the ratio  $\Delta_{shell}/r_{total}$ , where  $\Delta_{shell}$  is defined as the difference between the total particle radius and the core radius, that is, the contribution of particle shell thickness to the total particle radius. Thus, the presented above  $\Delta_{halo}/d_{total}$  is proportional to  $\Delta_{shell}/r_{total}$  by a factor of two. In this section, we switch from diameters to radii because the aerosol size in remote sensing is commonly described by the radius.

The following computational scenarios are presented: Scenario 1,  $\Delta_{shell}/r_{total}$  is a continuous function of the total radius ( $\Delta_{shell}$  is size resolved), as defined by equation (2); Scenario 2,  $\Delta_{shell}/r_{total}$  is a fixed mean value for all sizes of particles (i.e., 0.44 for urban case and 0.32 for desert case); and Scenario 3,  $\Delta_{shell}/r_{total}$  is discretized in two mean values, one for fine and one for coarse mode particles, as presented in section 3.4. It should be mentioned that some studies (Bondy, Kirpes, et al., 2017; Grassian & Tivanski, 2018) showed that particles can be also coated by much thin thickness of shell than the ones assumed



**Figure 8.** Histograms of axis ratio of particles with halo (core part only, denoted as *particle cores*) and particles without halo (denoted as *not coated particles*) for (a) urban and (b) desert cases.



**Figure 9.** (a) Normalized volume size distributions representative for urban and desert aerosol cases (black and orange curves, respectively). SSA for (b) urban and (c) desert aerosol cases. Black lines represent the SSA of urban and desert aerosols without coating, red lines represent the case with coating where the fraction of  $\Delta_{shell}$  is a continuous function of particle radius defined by the equation (2), orange lines represent the case where the fraction of  $\Delta_{shell}$  has same mean value for all particles sizes, blue lines correspond to the case where the fraction of  $\Delta_{shell}$  is different for the fine and coarse modes and corresponds to the values reported in section 3.4. SSA = single scattering albedo.

in our scenarios. In our work we do not present scenarios with very thin shells because calculations conducted using  $\Delta_{shell}/r_{total}$  of 0.1 (not shown here) indicated no significant changes in optical properties compared to a homogeneous particle case (i.e., no shell).

To examine the influence of coatings on optical properties of atmospheric particles, we analyzed the changes induced in spectral SSA ( $\omega_0$ ), directional scattering ( $P11(\theta, \lambda) \times AOT_{scat}(\lambda)$ ), and degree of linear polarization ( $-P12(\theta, \lambda)/P11(\theta, \lambda)$ ). We performed tests using the assumption of concentric core-shell particles with volume size distribution typical for urban and desert dust aerosol (Dubovik, Holben, Lapyonok, et al., 2002), as presented in Figure 9a. For the urban environment case, the assumed spectral complex refractive indices ( $m$ ) is  $m = 1.59 + 0.172i/1.59 + 0.123i/1.59 + 0.119i/1.59 + 0.119i/at$  wavelengths 440/670/870/1020 nm, respectively; that represents a volume weighted mixture between 15% of black carbon ( $m = 1.97 + 0.79i$  spectrally independent; Bond & Bergstrom, 2006) and 85% of brown carbon ( $m = 1.54 + 0.0043i/1.54 + 0.0008i/1.54 + 0.0005i/1.54 + 0.0002i$  at 440/670/870/1020 nm; Dey et al., 2006). In the case of desert particles we used a complex refractive index from Dubovik, Holben, Eck, et al. (2002), Bahrain/Persian Gulf site, which is  $1.55 + 0.0025i/0.0014i/0.0010i/0.0010i$  at 440/670/870/1020 nm, respectively. The coating material is assumed to be nonabsorbing and to be composed of a mixture of ammonium sulfate and water at 90% RH (Table 1 from Erlick et al., 2011) with spectrally independent complex refractive index of  $1.37 + 2.084 \times 10^8i$ , since presence of ultrapure water (real part equal 1.33) is unlikely in the atmosphere. It has to be mentioned that an effect of changing the particle size can be more important than the effect of change in the particle structure (thickness of the coating). Therefore, in the calculations presented here, the volume size distributions are fixed, thus the increase in the thickness of the coating layer is compensated by the proportional decrease of core radius. The comparison of the optical properties is made between coated particles, with the refractive indices for core and shell as previously described, and homogeneous particles with the refractive index of core (denoted as *urban, no shell* and *desert, no shell*).

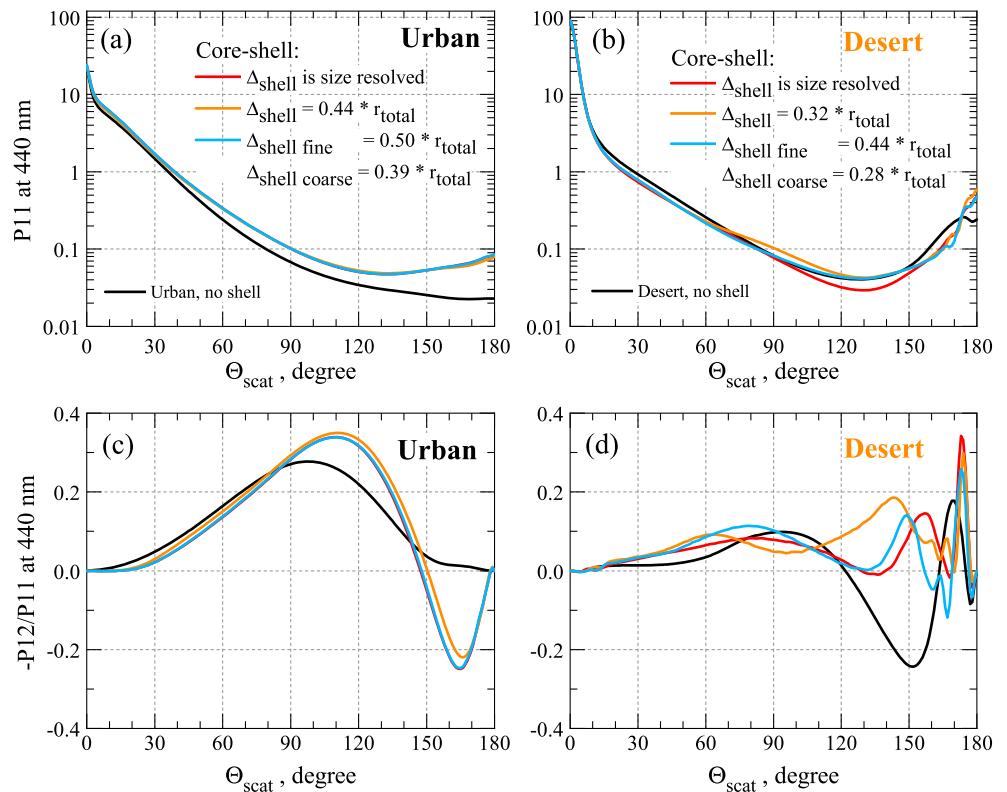
The SSA ( $\omega_0$ ) is the scattering effectiveness relative to total extinction and is defined as

$$\omega_0 = \frac{\sigma_{sca}}{\sigma_{sca} + \sigma_{abs}}, \quad (3)$$

where  $\sigma_{sca}$  and  $\sigma_{abs}$  are the scattering and absorption coefficients. The spectral directional scattering is described by  $P11(\theta, \lambda)$  element of the phase matrix that satisfies the following normalization condition:

$$\frac{1}{2} \int_0^\pi P11(\lambda, \theta) \cdot \sin\theta d\theta = 1. \quad (4)$$

The spectral degree of linear polarization is defined as the ratio of  $-P12(\theta)$  to  $P11(\theta)$  elements of the phase matrix, for single scattering of not polarized incident electromagnetic radiation.

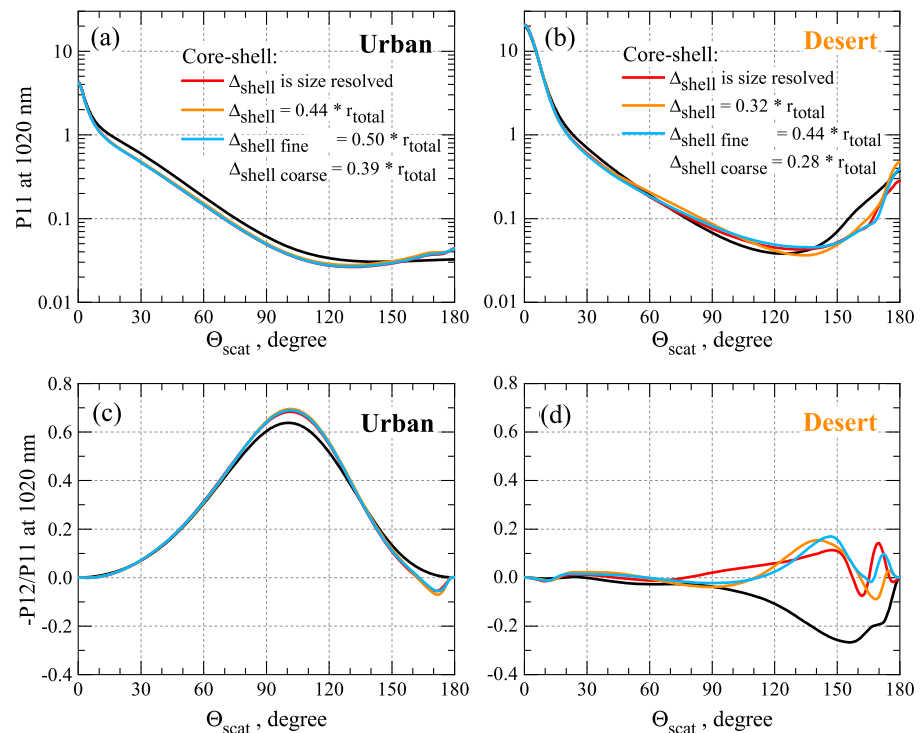


**Figure 10.** (a), (c) Phase function ( $P_{11}(\theta)$ ) and degree of linear polarization ( $-P_{12}(\theta)/P_{11}(\theta)$ ) at 440 nm for the case of urban and (b), (d) of desert environments. The color code description is the same as in Figures 9b and 9c.

In order to conduct the calculations we created a numerical tool that involves the Mie code solving Maxwell's equations for concentric core-shell spheres (Yang et al., 2002), which represents an adaptation of W. Wiscombe's code (Stamnes et al., 1988), and a subroutine for calculating optical characteristics of a polydispersed particle ensemble (Dubovik et al., 2006). The advantage of the Mie modeling is first of all in the computation speed. In general, the randomly oriented spheroids with coating can be used to model aerosol nonsphericity. However, similar to T-Matix for homogeneous spheroids, we expect that the computations will be highly time consuming and there can also be a problem with convergence for the full range of considered sizes and aspect ratios, which is a known problem of the T-Matix code. Computations using other options, for example, the discrete dipole approximation, are even more time consuming and difficult to apply for a realistic range of aerosol sizes. On the other side, the expectation is that the coated particles should be more spherical, as follows from the above analysis in Figure 8. Figure 8 also shows that in the case of urban and desert particles, 53% and 65%, respectively, of the coated particles have the axis ratio between 1 and 1.3. Thus, more than half of the particle cores have nearly spherical shape. Nevertheless, we acknowledge the importance of nonsphericity for optical properties of coated particles, especially because nonsphericity smooths the backward scattering features.

The results of calculations presented in Figure 9b show that when an ensemble of absorbing particle cores is coated by a nonabsorbing shell,  $\omega_0$  significantly increases, meaning increasing of scattering effectiveness. The same effect is observed in the case of desert particles, but less pronounced, as illustrated in Figure 9c. Note that the increase in SSA is not contradictory with the absorption enhancement due to the lensing effect, which is defined as the ratio of the  $\sigma_{abs}$  of coated particles to the  $\sigma_{abs}$  of the core only, for example, Fierce et al. (2016). The lensing effect holds for the presented core-shell calculations as well, however, the SSA increases because the increase in  $\sigma_{sca}$  is stronger than the increase in  $\sigma_{abs}$ , for example, in agreement with the results reported by Cheng et al. (2014).

Figure 10a shows that  $P_{11}(\theta)$  at 440 nm for coated urban particles differs from the homogeneous case, especially in the backscatter direction, however, the way how the thickness of shell is distributed does not



**Figure 11.** Same as Figure 10, but for 1,020 nm wavelength.

produce an important variability.  $P_{11}(130^\circ \leq \theta \leq 180^\circ)$  at 440 nm for the three scenarios was found higher than for the homogeneous case, for example, by  $\sim 50\%$  at  $\theta = 130^\circ$  and by  $\sim 250\%$  at  $\theta = 180^\circ$ . The differences in  $P_{11}(\theta)$  due to how the thickness of shell is distributed become pronounced in the case of coarse mode dominating particles (Figure 10b). In this case,  $P_{11}(160^\circ \leq \theta \leq 170^\circ)$  at 440 nm was found lower than the homogeneous case by  $\sim 50\%$ , however,  $P_{11}(\theta = 180^\circ)$  at 440 nm was found higher by  $\sim 100\%$  for Scenarios 1 and 3 and by 140% for Scenario 2. Noteworthy, in both cases of fine and coarse mode dominating particles, the differences occur in the backward scattering directions, that can have implications for instruments that mainly measure the backscatter signal, for example, satellite observation of reflected radiation or lidar system. The variability in degree of linear polarization ( $-P_{12}(\theta)/P_{11}(\theta)$  at 440 nm) responds much stronger to the shell thickness distribution, for both fine and coarse dominating volume size distributions (Figures 10c and 10d).  $-P_{12}(\theta)/P_{11}(\theta)$  at 440 nm also presents a much stronger difference versus the homogeneous scenario, both for desert and urban cases. The differences are distinguishable in side and backward scattering directions. In the case of fine mode dominating particles, the scenario when  $\Delta_{shell}/r_{total}$  is fixed for all sizes (Scenario 2) is only slightly distinguishable from the rest of the scenarios. However, the differences in  $-P_{12}(\theta)/P_{11}(\theta)$  becomes much more important in the case of coarse mode dominating particles; all three scenarios give noticeable differences in this case.

It can be expected that the effect of the coating and the way how the shell thickness is distributed on the ensemble of cores will be manifested differently at different wavelengths. In order to examine the spectral dependence of optical characteristics, the phase function and degree of linear polarization at 1,020 nm are presented in Figure 11. In the case of fine and coarse mode dominating particles,  $P_{11}(\theta)$  and  $-P_{12}(\theta)/P_{11}(\theta)$  at 1,020 nm exert sensitivity to the appearance of coatings versus homogeneous particles, that is, the differences appear in side and backward scattering directions, similar to 440 nm. However, the influence of  $\Delta_{shell}/r_{total}$  distribution is diminished with increase of the wavelength. In fact, an increase of the wavelength in this case can be equivalent to a decrease of the coating dimension.

Significance of the differences in the phase function and the degree of linear polarization due to the coating merits a separate study, dedicated to evaluating the effect on the aerosol microphysical characteristics retrievals. It should be tested for different levels of noise and involving multiple scattering. Meanwhile, a

preliminary assessment of the difference, obtained under single scattering approximation, shows that the effects can be comparable with those of particle nonsphericity or varying complex refractive index, for example, Figures 27 to 30 in Dubovik et al. (2006).

#### 4. Summary and Conclusions

The individual particle analysis presented in this work shows that, during an urban pollution event in northern France, the majority of particles sampled had a coating. The coating was also found on airborne particles sampled at altitude of 3.7 km in desert environment of western Africa. Possibility of coating of anthropogenic and dust particles is in agreement with a number of previous laboratory and field works (Dentener et al., 1996; Falkovich et al., 2004; Krueger, 2003; Krueger et al., 2004; Laskin et al., 2005; Zuberi et al., 2005). The main goals of the presented study consisted in a statistical analysis of collected particle core and shell dimensions derived from microscopic observations and in finding relationships between them for a possible parameterization in remote sensing applications. It was found that in urban environment during an elevated pollution event, the coated particles outnumbered (60% of 2,569 analyzed particles) the not coated ones. In the desert environment, the coated particles represented 20% of 5,872 analyzed particles. It was found that the size of the halo generally increases with the size of the core, however, the increase is steeper for smaller particles. The ratio of halo thickness to total particle diameter was evaluated for different size fractions. The relative contribution of the halo thickness to the total particle diameter was found to be more important for the smaller particles. Assuming that the dimensions of halo are representative for the dimensions of the particle shell, the obtained results served for parameterizing different scenarios of the shell thickness distribution. The changes in calculated aerosol optical properties due to different ways of parameterization were examined. A series of calculations for the urban and desert aerosol types revealed that despite a pronounced difference between presence and absence of shell, the variability in aerosol optical characteristics due to different ways to parameterize the dimensions of shell is quite weak in the case of fine mode dominating particles. However, in the case of coarse mode dominating particles, the way to represent the thickness of shell becomes important. Generally, the scattering in side and backward directions is most sensitive to the presence of coating and to the different representations of shell dimensions. The degree of linear polarization appears as the most sensitive to the presence of the core-shell structure, the variability in its dimensions, and the way to parameterize it. In support of the use of a spherical particle model for calculations of core-shell aerosol optical characteristics, it was found that the axis ratios of coated cores are shifted toward smaller values as compared to not coated particles; this fact indicates that the particles that experienced coating tend to be more spherical.

Because one of the difficulties is to quantify the complex aerosol morphology by a reasonable number of parameters, the obtained information can be particularly valuable for parameterization of atmospheric aerosol core-shell structure and implementation in advanced remote sensing algorithms.

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