Enrichment of Organic Nitrogen in Primary Biological Particles during advection over the North Atlantic

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Key points:

- Single particle data collected over Saharan desert-Tropical-North Atlantic Ocean.
- Data used to study Saharan dust (SD) and Primary Biogenic Aerosol Particles (PABP).
- Minor presence of organic nitrogen and alkylamines in SD-PBAB at their origin.
- PBAP are found to be enriched in alkylamines in North Atlantic Ocean air.
- Atmospheric biogeochemical processes may be responsible for detected alkylamines.

Keywords: Organic nitrogen, biological particles, ATOFMF, single particle, aerosol aging.
Abstract

Using a number of datasets from single particle Aerosol Time-Of-Flight Mass Spectrometry (ATOFMS) measurements, we show only a minor presence of Organic Nitrogen (ON) species in Saharan dust particles (aerosol size range 0.2-3μm) collected at their origin. ON enhancement is not observed on Saharan dust particles after atmospheric transport (48-96 hours) either over the Tropical Ocean in the vicinity of Cape Verde, over the North Atlantic Ocean. In the negative ATOFMS mass spectra, signals due to ON species were found weaks in biological particles (rich in potassium and phosphate) in their source area, and signals due to alkylamines in the positive ATOFMS mass spectra were not found. In striking contrast, biological particles travelling within aerosol dust plumes are found to be enriched in ON species - including alkylamines - in North Atlantic Ocean air (Mace Head, Ireland), as seen in both positive and negative ATOFMS mass spectra. Contrary to filter based aerosol techniques which report ON enrichment within Saharan dust, our single particle mass spectrometry data - allowing study of the aerosol mixing state - suggests that the aging biological particles and not the associated transported aging Saharan dust may be a source of ON species. We suggest biogeochemical processes occurring in the atmosphere in which biological particles are responsible for ON production. This may be an important source of nutrients to the ocean via atmospheric deposition.
1. Introduction

Organic nitrogen (ON) represents a consistent fraction of the total atmospheric nitrogen and is an ubiquitous component of the atmospheric aerosols (Galloway et al., 2008; DeLong, E., 2009). Aerosol deposition and in particular the deposition of ON, to marine environments, where auto- and heterotrophic microbial communities are often nutrient-limited, may affect community composition, productivity and consequently the marine carbon cycle, including carbon sequestration (Cornell et al., 2003; Cape et al., 2011). Organic nitrogen is found as a complex mixture of materials from multiple natural and anthropogenic sources. Kanakidou et al. (2012) estimated that 45% of the total ON atmospheric flux to the ocean comes from combustion sources, 32% from primary biological aerosol particles (PBAP), 1% from soil dust, 20% from ocean primary emissions and 3% from ocean secondary emissions. However, large uncertainties are associated with N emissions and the magnitude and impacts of anthropogenic atmospheric nitrogen inputs on the ocean (Kanakidou et al., 2016; Jickells et al., 2017, Kanakidou et al., 2018). Altieri et al. (2016) suggested that anthropogenic activity is not a significant source of organic N to the marine atmosphere over the North Atlantic, despite large pollution sources present in North America. Other bio-aerosol studies also suggest that PBAP may account for almost a third of ON in the marine atmosphere (Cote et al. 2008, Tittensor et al., 2010; Vaïtilingom et al. 2013, Krumnis et al. 2014, Miriokefalitakis et al., 2017; Amato et al. 2017, Šantl-Temkiv et al. 2018). A fraction of PBAP may be able to sustain microbial activity in the atmosphere and could also therefore be involved in atmospheric ON processing (Hill et al., 2007). For example, Šantl-Temkiv et al (2013) suggested that bacterial cells present in cloud droplets may have been responsible for the process of ON mineralization to inorganic nitrogen that the studies observed in the clouds.

The correct apportionment of ON sources is particularly important in the marine atmosphere because of the role that depositing ON plays in enhancing ocean productivity (Duce et al., 2008). Anthropogenic, agricultural and biomass burning sources of ON are mainly important in cases when terrestrial air masses travel over marine areas (Jickells et al., 2013). Less is known of the importance of ON marine emissions. Primary marine emissions of ON in the form of amino acids and their derivatives have been reported
(Graber and Rudich, 2006; Altieri et al. 2009; Geddes et al. 2009). Gas-to-particle secondary organic aerosol reactions of gaseous amines with sulphuric acid have also been found in marine aerosol over the North Atlantic (Facchini et al., 2008) and Pacific Ocean (Sorooshian et al. 2008; Miyazaki et al. 2010; 2011). The Tropical NE Atlantic marine atmosphere presents a peculiarly intricate scenario with a diverse, variable and complex mixture of ON aerosol sources (Baker et al., 2010). Lesworth et al. (2010) reported a wide range of ON concentrations associated with both coarse (>1µm) and fine (<1µm) particles, apportioning them to African dust sources and to anthropogenic emissions from Europe. Other studies carried out in the Eastern Mediterranean (Violaky et al. 2010; Violaki and Mihalopoulos 2010) also stress that combustion processes and African dust are an important source of ON. By contrast, ON of marine origin seems to play a small role in these sub-tropical marine regions (Muller et al., 2009). Although these studies stress the importance of dust for the marine ON budgets in air, the low sampling time resolution (1-4 days) and off-line analysis that the authors used, do not allow them to conclude whether the ON is associated directly with dust particles or with the large quantities of PBAP that are ejected into the atmosphere with the dust events (Kellogg and Griffin 2006).

Aside from the complexity and diverse sources of ON, there are also two main issues associated with sampling and analysing ambient ON aerosols. First, the concentration of ON is often estimated by measuring concentrations of total nitrogen and subtracting the concentrations of NO$_3^-$ and NH$_4^+$, which propagates errors from the three individual species and leads to uncertainties in the ON analytical concentrations. Second, most of the current measurements are carried out with off-line filter measurements (Sullivan and Prather, 2005), which do not allow information on the ON mixing state and hence challenge the aerosol source apportionment. An aerosol population is broadly "internally mixed" when all single particles have the same chemical composition (equal to the bulk composition). By contrast, an aerosol population is "externally mixed" when single particles have a different chemical composition. In order to reduce uncertainty on ON-containing aerosols, Jickells et al. (2013) stressed the importance of deploying new technologies. Detection of PBAPs by real-time (RT) techniques for autonomous, online detection and characterization of PBAP properties has become increasingly important for research.
purposes (Hoffman et al., 2019). Single particle mass spectrometry (SPMS) - techniques that ablate and ionize single aerosol particles - is capable of PBAP detection, although the interpretation of SPMS mass spectra is challenging and requires extensive human interaction. For example, amino acids are ubiquitous compounds with an integral role in atmospheric bioaerosol compositions (Ge et al., 2011). Previous SPMS identified amino acids in PBAP particles (Fergenson et al., 2004; Russell et al., 2004; Czerwieniec et al., 2005, Schneider et al., 2011). However, difference in ionization laser wavelengths may produce different single-particle mass spectra, and therefore, specific markers for amino acids do not exist.

This study uses state-of-the-art Single Particle Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS; Su et al., 2004) to shed some light on natural aerosols containing ON species. The ATOFMS data herein presented allows us to determine if the aerosol population is internally or externally mixed, a peculiar feature absent in most filtration-based aerosol sampling techniques (Sullivan and Prather, 2005). It is also worth reminding that the ATOFMS is a particularly good aerosol instrument for studying amines and organic nitrogen in general because the LDI laser wavelength (266 nm) ionizes them very efficiently (Angelino et al., 2001; Dall´Osto et al., 2016; Healy et al., 2015).

The large ATOFMS datasets used in this work were previously used to study the variation of the mixing state of Saharan dust particles with atmospheric transport (Dall´Osto et al., 2010a) during the DODO project; and to study the aerosol properties associated with air masses arriving into the North East Atlantic during the 2008 Mace Head EUCAARI intensive observing period (Dall´Osto et al., 2010b). The current study aims - for the first time - to specifically presents an ATOFMS analysis looking at the properties of specific clusters - including biological particles - and comparing the temporal trends with black carbon and dimethyl sulphide concentrations across different locations. We focus our attention on Saharan dust and biological particles found at their origins, as well as on those sampled during ambient field measurements over both Tropical and North Atlantic Oceans. The aims of this study include: (1) to elucidate if Saharan dust or the associated terrestrial PBAP contains ON, (2) to understand if ON in natural aerosols has mainly a primary or a secondary origin and (3) to discuss whether aerosol aging results in a degradation or production of ON.
2. Methodology

2.1 Atmospheric measurements

2.1.1 ATOFMS

We deployed an ATOFMS (Model 3800-100, TSI, Inc.), which collects bipolar mass spectra of individual aerosol particles. Briefly, ambient aerosol is focused into a narrow particle beam for sizes between 100 nm and 3 µm (vacuum aerodynamic diameter), following which laser desorption/ionization take place and a positive and a negative single particle mass spectra are obtained. The mass spectrum is only qualitative because the peaks intensities depend strongly on the particle matrix, the coupling between the laser and the particle and the shot to shot variability of the laser (Dall’Osto and Harrison, 2006). However, recent studies (Jeong et al., 2011) report excellent correlations for inorganic species (sulfate, nitrate, and ammonium) but weaker ones between total organic and elemental carbon (EC) detected with ATOFMS and other instruments (Jeong et al., 2011). Furthermore, using a different approach, Healy et al. (2012, 2013) demonstrated that the ATOFMS can deliver good quantitative results for Elemental Carbon (EC) and Organic Carbon (OC) containing particles, when compared with other measurement techniques. Overall, the ATOFMS gives a measure of particle number as function of size and chemical composition, allowing the determination of the mixing state.

2.1.2 Dimethyl sulphide (DMS) measurements

DMS measurements were carried during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) took place at Mace Head, Ireland during summer 2002 (Lewis et al.; 2005), further information can be found elsewhere (Heard et al., 2006).

2.1.3 Black Carbon (BC) measurements
Aerosol absorption (and Black Carbon mass) was measured using both a McGee Scientific Aethalometer AE-16 and a Multi-Angle Absorption Photometer (MAAP) (Dall’Osto et al., 2010b).

2.2 Laboratory and field studies

In this study, we utilized previously published Saharan dust ATOFMS data from our laboratories (Dall’Osto et al., 2010a) for the presence of ON. The Sahara Sahel Dust Corridor (SSDC) is a huge zone lying between latitudes 12° N and 28° N and running 4000 km east-west from Chad to Mauritania (Moreno et al., 2006). During low wind conditions, four different samples of SSDC desert soil, road, and aeolian dusts were collected. A summary of the SSDC locations is discussed elsewhere (Moreno et al., 2006; Dall’Osto et al., 2010a). Briefly, three dust samples were taken from the Saharan region, and one from Algeria. Each dust sample was put into a flask in a sonicator, a suspension of dust particles under filtered lab air flow was created, and single particles mass spectra were obtained with the ATOFMS. About 1,000 single particle mass spectra were collected for each of the four dust samples.

For this study, we also utilized ATOFMS datasets collected in two previous field studies. This gives the possibility to compare single particle mass spectra from airborne particles with those obtained from the Saharan dust particles analyzed in the laboratory. During August and September 2002 The North Atlantic Marine Boundary Layer Experiment (NAMBLEX) took place at Mace Head, Ireland (Heard et al., 2006). The Atmospheric Research Station at Mace Head allows westerly exposure to the North Atlantic ocean (clean sector, 180 degrees through west to 300 degrees) and the opportunity to study atmospheric composition under Northern Hemispheric background conditions. Also, within the Dust Outflow and Deposition to the Ocean (SOLAS-DODO) project (McConnell et al. 2008), an ATOFMS was deployed during a research cruise (P332) in the vicinity of the Cape Verde Islands (January-February 2006) on board the research vessel FS Poseidon as part of the UK-SOLAS programme. The study areas are summarized in Fig. 1:
• Fig 1, Sites A, B: Four samples of desert soil were collected from several regions of the Sahara-Sahel Dust Corridor during low wind conditions and analysed in a laboratory study (4,205 ATOFMS mass spectra, Dall’Osto et al. 2010a).

• Fig 1, Site C: A cruise (research vessel FS Poseidon; P332, Winter 2006) within the Dust Outflow and Deposition to the Ocean (SOLAS-DODO), where an ATOFMS collected 187,205 ATOFMS single particle mass spectra (Rijkenberg et al. 2008).

• Fig. 1, Site D: An ATOFMS operated at the Mace Head Atmospheric Research Station during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX, Summer 2002) collecting 191,504 ATOFMS single particle mass spectra (Dall’Osto et al., 2004).

2.3 Data analysis

The ATOFMS data presented cover a large aerosol size range (100-3000 nm) at a high time resolution (1 hour) which were collected over a large area (Figure 1). ATOFMS single particle positive and negative mass spectra were imported into YAADA (Yet Another ATOFMS Data Analyzer, Song et al., 1999) and single-particle mass spectra were grouped with adaptive resonance theory neural network, ART-2a (learning rate 0.05, vigilance factor 0.85, and 20 iterations). Further details of the parameters can be found elsewhere (Dall’Osto and Harrison, 2006). Briefly, the ART-2a area matrix (AM) of a single particle mass spectra represents the average intensity for each m/z for all particles within a group, reflecting the typical mass spectra of specific aerosol groups.

Finally, air mass back trajectories of the air masses arriving at the different study areas were calculated at four arrival times for each day of the campaign (00:00, 06:00, 12:00 and 18:00 UTC), depicting the path taken by the air mass reaching the sampling site over the previous five days. The back trajectories were run using the on-line HYSPLIT model developed by the National Oceanic and Atmospheric Administration (NOAA) (Draxler and Rolph, 2003).

3. Results
The ART-2a algorithm generated a number of clusters used to describe the ATOFMS mass spectra. Most of the obtained particle types were associated with anthropogenic sources (fresh and aged combustion related aerosols), sea salt, ship emissions, secondary aerosol of inorganic nature, some of which were already discussed elsewhere (Dall’Osto et al., 2004; 2006, 2010a,b). Table 1 shows a summary of the previous results, and put it in context with the current specific ON analysis. Table 1 shows that Saharan dust particles and biological particles were detected in all the ATOFMS datasets presented. ATOFMS has already proved to be a good tool able to separate dust (mainly Ca-rich or Al-Si rich) and biological particles (Fergenson et al., 2004; Pratt et al., 2009).

Briefly, biological mass spectral signatures can be differentiated from dust on the basis of abundant organic and phosphorus ions, as well as a lack of key dust markers, such as aluminium and silicates. Within the main objective of this work, the ATOFMS is a very sensitive instrument towards ON (m/z - 26 and m/z -42, due to [CN]⁻ and [CNO]⁻, respectively), and many alkylamines (Angelino et al. 2001; Moffet et al. 2008; Pratt et al. 2009; Healy et al., 2015; Dall’Osto et al., 2016).

Figure 2 shows the positive and negative ART-2a ATOFMS mass spectra of dust particles and PBAP detected at their source (Saharan dust particles collected in Africa; Fig. 2 a, b, respectively); during the SOLAS-DODO cruise around Cape Verde (Fig. 2 c, d, respectively) and during the NAMBLEX field study at Mace Head, Ireland (Fig. 2e, f, respectively). It is clear that ATOFMS mass spectra of Saharan dust particles (Fig. 2 a, c, e) shows peaks due to most common ion species characteristic of crustal materials including aluminum (m/z 27 [Al]⁺), calcium (m/z 40 [Ca]⁺ and 56 [CaO]⁺), titanium (m/z 48 [Ti]⁺ and 64 [TiO]⁺), lithium (m/z 7 [Li]⁺) and iron (54 ⁵⁴[Fe]⁺ and 56 ⁵⁴[Fe]⁺). Peaks for other metals such as sodium (m/z 23 [Na]⁺), magnesium (m/z 24 ⁴⁰[Mg]⁺, 25 ⁴⁰[Mg]⁺) and potassium (m/z 39 [K]⁺) can also be seen. In addition, other peaks for calcium (57 [CaOH]⁺, 96 [Ca₂O]⁺ and 113 [(CaO)₂H]⁺) were detected but at low intensity. The negative particle mass spectra in Figure 2 (a, c, e) show ions from oxygen (m/z -16 ¹⁶[O]⁻, -17 [OH⁻]), chloride (m/z -35 ³⁵[Cl]⁻, -37 ³⁷[Cl]⁻), phosphate (m/z -63 [PO₂⁻] and m/z -79 [PO₃⁻]), a small abundance of -46 [NO₂⁻]⁻ and -62 [NO₃⁻]. It is important to note that in these Al/Si-rich Saharan dust particles, peaks of of silicate at m/z -60 [SiO₂⁻] and -76 [SiO₃⁻] dominate the negative spectra. This is further discussed in Dall’Osto et al. (2004, 2010a), where...
Al/Si-rich dust particles consistent with Saharan dusts which are dominated by SiO$_2$ and Al$_2$O$_3$ (Goudie and Middleton, 2001) were observed. Few particles found in Saharan soil dust samples (<4%) were internally mixed with ON species. We have previously reported that both organic and organic nitrogen species were more commonly associated with Saharan dust particles collected in the source region relative to the atmospheric Saharan dust particles sampled during the two field studies (SOLAS-DODO and NAMBLEX, Dall’Osto et al. 2010a). It is possible that some of these ON components may be mineralized (a process by which organic N is converted to plant-available inorganic forms) during atmospheric transport. This is supported by the observation that Saharan dust particles with shorter atmospheric residence, i.e. collected near the Cape Verde Islands (Fig 1, 2c, DODO experiment), showing increased internally mixed nitrate (possibly mineralized ON). In addition, this can be seen also in the Saharan dust particles with longer atmospheric residence times, i.e. collected on the coast of Ireland (Fig. 1, 2e, NAMBLEX experiment) showing also a very high degree of internally mixed secondary species including nitrate (m/z -46, see also Dall’Osto et al., 2010a). Overall, our studies suggest that fresh Saharan dust is not a major source of ON. It is important to stress that no clear peaks associated to alkylamines (Healy et al., 2015; Dall’Osto et al., 2016) were detected in any of the Saharan dust particle types (Fig. 2 a, c, e).

With regard to biological particles, those were detected in all the datasets: the Saharan soil dust samples and the two ATOFMS ambient field studies (Table 1, Fig. 2). A strong peak at m/z 39 is usually seen in the positive mass spectra, whereas the negative spectrum is usually dominated by phosphate [PO$_2^-$ m/z -63 and [PO$_3^-$ m/z -79] and often also internally mixed with ON species (Pratt et al. 2009). Biological particles detected in Saharan dust samples and over the Tropical Ocean had a weak signal associated with ON and amines. Our results - showed in Fig. 2 - suggest that fresh PBAP are lacking in ON signal, both at their origin (dust samples collected in Africa) and after a few days of transport (Cape Verde region). By striking contrast, 19% of PBAP detected at Mace Head were internally mixed with ON compounds. By querying the ATOFMS NAMBLEX dataset, it was found that the majority (>99%) of the signal due to ON and amines species was associated with a specific PBAP type (Fig. 2 f), indicating that this is a major source of ON sampled over the North Atlantic. Additionally, strong peaks of alkylamines are seen in the
positive mass spectra, including m/z 58 \([C_2H_5NH=CH_2]^+\), m/z 59 \([\text{[N(CH}_3)_3]^+\) and m/z 86 \([(C_2H_5)_2N=CH_2]^+\) (Dall’Osto et al., 2016). The peak of m/z 74 and m/z 104 (potentially \([C_2H_4NO_2]^+\) and \([C_3H_5NO_3]^+\), respectively) were previously attributed to organic nitrogen peaks including alkylamines (Angelino et al., 2001). A previous study in the city of Barcelona (Spain) found that m/z 104 was found to be linked alkylamines of primary aerosol origin, whereas m/z 74 alkylamines of secondary aerosol origin (Dall’Osto et al., 2016). This particle type (Fig. 2 f) presented an aerosol size distribution centered at about 2μm, shifted towards an even larger modes than Al-Si Saharan particles (Dall’Osto et al., 2004). An overview the differences in spectra for the PBAP NAMBLEX (aged transported PBAP) and its origin (PBAP Saharan region) or in the Tropical Ocean (PBAP DODO) can be seen in Figure 3, which show the subtraction spectrum for PBAP NAMBLEX minus PBAP DODO (Fig. 4a) and for PBAP NAMBLEX minus PBAP Saharan dust origin (Fig. 4b). The positive ion spectrum for PBAP NAMBLEX is enhanced in organic nitrogen and alkylamines (m/z 59, 74, 86, 104), whilst the negative is enriched in nitrate peaks (m/z -46, -62) and organic nitrogen (m/z - 42). A representative ATOFMS single particle mass spectrum of the PBAP particle carrying ON (Fig. 2 f) is presented in Figure 4, showing a strong peak at m/z 39 likely to be due to potassium [K], and minor peaks at m/z 23 [Na] and m/z 56 [Fe] in the positive mass spectra. In the negative mass spectra, ON peaks are found at m/z -26 [CN] and m/z -42 [CNO], along with phosphate (m/z -63 and m/z -79) and methanesulfonic acid MSA (m/z -95). The mass spectrum has features that are generally attributed to vegetative debris (potassium-phosphate) except that it is internally mixed with ON species. Major ion peaks in the positive mass spectra at m/z 58, 59, 74, 86, and 104, 118 and 154 are all consistent with ON ATOFMS mass spectra peaks detected in previous field and laboratory studies (Angelino et al. 2001, Moffet el al. 2008, Healy et al., 2015: Dall’Osto et al., 2016).

In order to investigate the origin of the dominant PBAP associated with ON during NAMBLEX, we separated the field study sampling period accordingly to three main air mass categories (marine Tropical, marine Polar-Arctic and European continental Polar – mT, mP-mA and cP respectively, Dall’Osto et al. 2010b). We found - as expected - higher values of BC for cP air masses (209±197 ng m\(^{-3}\)) relative to mT (51±23 ng m\(^{-3}\)) and the very clean mP-mA ones (33±21 ng m\(^{-3}\)) (Figure 4a). DMS concentrations - by contrast - were much higher for mT air masses (507±120 pptV) than for cP (105±110 pptV) and mP-
mA (140±120 pptV) (Figure 4b). Other studies (Dall’Osto et al. 2010b, Bassford et al. 1999) have also indicated that during mT air masses the vast majority of DMS and MSA observed at the Mace Head site had been transported significant distances from the mid tropical Atlantic. Figure 4c shows that biological particles were detected at about double the concentration (t-test, 95%, 1.31±1 and 2.67±2 respectively) for mT relative to cP air masses. This PBAP type was found in association with Al-Si particles detected in the same study and attributed to dust particles, mainly detected during mT air masses and to a lesser extent during cP air masses (Dall’Osto et al 2004, 2010a, Figure 3d). An increase in microbial concentrations during dust storms has previously been reported and can be two orders of magnitude higher than under non-dusty conditions (Hara and Zhang 2012, Yamaguchi et al 2014, Mazar et al. 2016). In conclusion, the PBAP associated with ON were likely transported to the North Atlantic together with dust events, which may have originated in the Sahara-Sahel region and travelled over the Tropical Ocean. During their atmospheric travel time, the PBAP injected with dust events, seem to first be low in ON as we observed during the SOLAS-DODO measurements and then get enriched with ON with atmospheric transport as we observed during the NAMBLEX measurements.

4. Discussion and Conclusion

The first conclusion of this study is that (within the 0.2-3µm size) the ON aerosol concentrations reported over the Tropical Ocean - at least during the study period - are likely to be contained within the terrestrial PBAP travelling in association with Saharan dust and not with the dust particle themselves. Saharan dust is also not found to be enhanced in ON species when detected over the North Atlantic. Overall, our single particle mass spectrometry measurements collected at high time resolution over a large geographical area, suggest that Saharan dust particles are not rich in ON, either at their origin, or in the Cape Verde region. The second conclusion of this study is that the PBAP that are injected into the atmosphere together with dust events are the aerosol particles that contain ON compounds. Furthermore, it appears that these biological particles get enriched in ON species during their atmospheric residence. The low associated BC concentrations make an anthropogenic influence unlikely.
Previous ATOFMS studies discovered existence of different ON groups (alkylamines, proteins, amino acids etc.) in aerosols and reported their involvement in atmospheric processes, including indoor tobacco smoke (Dall’Osto et al., 2007), cloud/fog processing (Rehbein et al., 2011), primary traffic pollution (Angelino et al., 2001; Dall’Osto et al., 2016), non-salt organic aerosol products through reaction with oxidizing agents (Murphy et al., 2007, Pratt et al., 2009) and marine aerosol reactions (Dall’Osto et al., 2012; Healy et al., 2015). However, it is important to note that - in this study - ON was found internally mixed with biological particles and externally mixed with other aerosols, therefore we can conclude that ON is not formed by condensation of secondary semi-volatile organic nitrogen species as these compounds would condense on the whole aerosol population.

An explanation for the ON enrichment of the aging PBAP can only be speculative at this stage. Previous studies have demonstrated that viable airborne micro-organisms present in the atmosphere can contribute to atmospheric chemistry through degradation processes, as well as chemical change due to the release or desorption of molecules from microbiological entities (Deguillaume et al. 2008; Cote et al., 2008). Airborne metabolically active microorganisms, for example fungal and bacterial cells, can transform chemical constituents of the atmosphere by metabolic activity and have been implicated in the nitrogen and carbon cycling in clouds (Hill et al. 2007, Cote et al 2008, Vaïtilingom et al 2013, Krumnis et al. 2014, Amato et al 2017, Šantl-Temkiv et al 2018). Nitrogen can be microbially incorporated into organic compounds through the processes of fixation and assimilation. Different prokaryotes - including Cyanobacteria - which are commonly found in the atmosphere (reviewed in Genitsaris et al. 2011), are capable of nitrogen fixation and can convert atmospheric nitrogen into biologically accessible ammonia. Assimilation of inorganic nitrogen is performed by diverse bacteria and fungi, who can convert nitrate and ammonia into different forms of ON. It is not known at this stage if the association of ON with aging biological particles is due to the metabolic activity of microorganisms externally mixed with Saharan dust plumes, which have travelled to the North Atlantic region. The long distance transport of microorganisms with dust particles has been shown to negatively affect the viability of microbial cells as <40% of all bacterial cells were found viable compared to >70% of non-dust-associated cells (Hara and Zhang 2012). Despite this, the absolute number of viable microorganisms travelling with dust storms remained
high. It may be that these viable microbial cells may maintain their metabolic activity and affect the atmospheric nitrogen cycle. Further multidisciplinary studies on the impact of airborne micro-organisms and possible chemical mechanisms are recommended to underpin these findings.

Another possible explanation is that the biological particles enriched in ON have a marine origin. However, we detected such biological particles mainly during dust events. Usually, concentration of bacteria over the sea are much lower than over land, and higher concentrations of aerosolized microorganisms during dust events relative to clean background marine conditions are normally observed (Kellog and Griffin 2006, Prospero et al., 2005; Griffin et al., 2006). Furthermore, the ATOFMS mass spectra of ocean-derived particle types are enriched in elements (mainly Na and Mg, Gaston et al., 2011) not found in the biological particles reported in this study.

In conclusion, using on-line single particle aerosol mass spectrometry, we show that fresh and aged Saharan dust aerosols are not a major source of ON. Furthermore, we find that biological particles – likely of terrestrial origin – are enriched in ON during atmospheric transport. We hypothesize that microbial processes may generate ON through nitrogen fixation and assimilation during the atmospheric residence of microbial cells, which results in an enrichment of ON compounds within the cell. Coarser particles possess higher dry deposition rates and such microorganisms internally mixed with ON may be an important source of nitrogen, which is an essential nutrient in North Atlantic Ocean marine ecosystems. González Benítez et al. (2009) found that dry deposition of particles was the main contributor of N-containing species in bulk rain samples, which were not strongly associated with either combustion or agricultural sources alone (González Benítez et al. 2010). Our data do not rule out a suggestion that SOA production of amines is important for the marine atmosphere when considering the fine particle mode (Facchini et al. 2008, Muller et al. 2009), but we propose an additional source for the total ON concentrations in
the coarse aerosols mode that has a natural origin. Further studies are needed in order to validate the event reported in this study.

Acknowledgements

We express our gratitude to the Master and crew of FS Poseidon for support during the cruise. Both the Mace Head sampling and DODO cruise were supported financially by the U.K. Natural Environment Research Council. This work was also funded by the Ireland Higher Education Authority Program for Research in Third Level Institutes – Cycle 5. We thank Dr. A. Lewis for DMS data, as discussed in Heard et al. (2015). The study was also supported by the Spanish Ministry of Economy through project PI-ICE (CTM2017–89117-R) and the Ramon y Cajal fellowship (RYC-2012-11922).

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Table 1. ATOFMS particle clusters identified from the Saharan dust soil samples and from the NAMBLEX and DODO ambient field studies.

Figure 1 Map of sampling locations: (A-B) shows the Saharan dust samples locations; Air mass arriving at Cape Verde (C) are for of a 5-day air mass back trajectory at mid-day at 500 m above the position of the ship during the dust event on 4 Feb 2006, (D) an marine Tropical (mT) air mass arriving at Mace Head (Ireland) at 12:00 LT on 8 December 2002 (Dall’Osto et al. 2004, Rijkenberg et al. 2008, Dall’Osto et al. 2010b). Aerosol transport time between point C and D was estimated to be 3-4 days from air mass trajectories analysis. Green and orange circles shows Saharan dust particles (Dust, orange) and primary biological aerosol particles (Bio, green). In point (D) these are enriched - with transport - in secondary organic aerosols (SOA, Dall’Osto et al., 2010a) and in Organic Nitrogen (ON, this study).

Figure 2 Positive (+) and negative (-) ART-2a ATOFMS mass spectra of Saharan dust particles and PBAP detected during Saharan origin (a, b, respectively); SOLAS-DODO cruise around Cape Verde (c, d, respectively) and NAMBLEX at Mace Head (e, f, respectively).

Figure 3 Positive (+) and negative (-) ART-2a ATOFMS mass spectra for PBAP NAMBLEX minus PBAP DODO (a) and PBAP NAMBLEX minus PBAP Saharan origin (b). Peaks below the horizontal line represents components less abundant in the NAMBLEX than the DODO/Origin; above the line are those with greater abundance.

Figure 4. Single particle positive and negative mass spectra of a single particle (2.3 µm) sampled during the NAMBLEX field study

Figure 5: (a) Black Carbon (Aethalometer AE16) concentrations (ng m⁻³) (b) DMS concentrations (pptV), (c-d) ATOFMS counts for K-P-ON (biological particles) and Dust (Saharan Dust) for cP (European continental Polar), mT (marine Tropical) and mP-mA (marine Polar-Arctic ) air masses (respectively); the three main air mass categories are further described in Dall’Osto et al., (2010b). ATOFMS counts are average counts per hour under mT and cP air masses (47 and 176 hours, respectively; total K-P-ON ATOFMS spectra 130 and 230, respectively).
<table>
<thead>
<tr>
<th></th>
<th>Number of ATOFMS mass spectra</th>
<th>Saharan dust particles (% by number)</th>
<th>Biological particles (% by number)</th>
<th>Others (% by number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saharan soil samples</td>
<td>4,205</td>
<td>55</td>
<td>10</td>
<td>&gt;35</td>
</tr>
<tr>
<td>DODO (Tropical Ocean)</td>
<td>187,205</td>
<td>1.1</td>
<td>0.01</td>
<td>&gt;98</td>
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<td>NAMBLEX (North Atlantic Ocean)</td>
<td>191,504</td>
<td>1.0</td>
<td>0.01</td>
<td>&gt;98</td>
</tr>
</tbody>
</table>

Table 1. ATOFMS particle clusters identified from the Saharan dust soil samples and from the NAMBLEX and DODO ambient field studies.
**Figure 1.** Map of sampling locations: (A-B) shows the Saharan dust samples locations; Air mass arriving at Cape Verde (C) are for of a 5-day air mass back trajectory at mid-day at 500 m above the position of the ship during the dust event on 4 Feb 2006, (D) an marine Tropical (mT) air mass arriving at Mace Head (Ireland) at 12:00 LT on 8 December 2002 (Dall’Osto et al. 2004, Rijkenberg el al. 2008, Dall’Osto et al. 2010b). Aerosol transport time between point C and D was estimated to be 3-4 days from air mass trajectories analysis. Green and orange circles shows Saharan dust particles (Dust, orange) and primary biological aerosol particles (Bio, green). In point (D) these are enriched - with transport - in secondary organic aerosols (SOA, Dall’Osto et al., 2010a) and in Organic Nitrogen (ON, this study).
Figure 2 Positive (+) and negative (-) ART-2a ATOFMS mass spectra of Saharan dust particles and PBAP detected during Saharan origin (a, b, respectively); SOLAS-DODO cruise around Cape Verde (c, d, respectively) and NAMBLEX at Mace Head (e, f, respectively).
Figure 3 Positive (+) and negative (-) ART-2a ATOFMS mass spectra for PBAP NAMBLEX minus PBAP DODO (a) and PBAP NAMBLEX minus PBAP Saharan origin (b). Peaks below the horizontal line represent components less abundant in the NAMBLEX than the DODO/Origin; above the line are those with greater abundance.
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