

Enrichment of organic nitrogen in primary biological particles during advection over the North Atlantic

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3 **Enrichment of Organic Nitrogen in**
4 **Primary Biological Particles during**
5 **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 (PBAP).
- Minor presence of organic nitrogen and alkylamines in SD-PBAP 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, ATOFMS, single particle, aerosol aging.

74 **Abstract**

75

76 Using a number of datasets from single particle Aerosol Time-Of-Flight Mass Spectrometry
77 (ATOFMS) measurements, we show only a minor presence of Organic Nitrogen (ON)
78 species in Saharan dust particles (aerosol size range 0.2-3 μ m) collected at their origin. ON
79 enhancement is not observed on Saharan dust particles after atmospheric transport (48-
80 96 hours) either over the Tropical Ocean in the vicinity of Cape Verde, over the North
81 Atlantic Ocean. In the negative ATOFMS mass spectra, signals due to ON species were
82 found weak in biological particles (rich in potassium and phosphate) in their source area,
83 and signals due to alkylamines in the positive ATOFMS mass spectra were not found. In
84 striking contrast, biological particles travelling within aerosol dust plumes are found to be
85 enriched in ON species - including alkylamines - in North Atlantic Ocean air (Mace Head,
86 Ireland), as seen in both positive and negative ATOFMS mass spectra. Contrary to filter
87 based aerosol techniques which report ON enrichment within Saharan dust, our single
88 particle mass spectrometry data - allowing study of the aerosol mixing state - suggests
89 that the aging biological particles and not the associated transported aging Saharan dust
90 may be a source of ON species. We suggest biogeochemical processes occurring in the
91 atmosphere in which biological particles are responsible for ON production. This may be
92 an important source of nutrients to the ocean via atmospheric deposition.

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106 **1. Introduction**

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

131

132 The correct apportionment of ON sources is particularly important in the marine
133 atmosphere because of the role that depositing ON plays in enhancing ocean productivity
134 (Duce et al., 2008). Anthropogenic, agricultural and biomass burning sources of ON are
135 mainly important in cases when terrestrial air masses travel over marine areas (Jickells et
136 al., 2013). Less is known of the importance of ON marine emissions. Primary marine
137 emissions of ON in the form of amino acids and their derivatives have been reported

138 (Graber and Rudich, 2006; Altieri et al. 2009; Geddes et al. 2009). Gas-to-particle
139 secondary organic aerosol reactions of gaseous amines with sulphuric acid have also
140 been found in marine aerosol over the North Atlantic (Facchini et al., 2008) and Pacific
141 Ocean (Sorooshian et al. 2008; Miyazaki et al. 2010; 2011). The Tropical NE Atlantic
142 marine atmosphere presents a peculiarly intricate scenario with a diverse, variable and
143 complex mixture of ON aerosol sources (Baker et al., 2010). Lesworth et al. (2010)
144 reported a wide range of ON concentrations associated with both coarse ($>1\mu\text{m}$) and fine
145 ($<1\mu\text{m}$) particles, apportioning them to African dust sources and to anthropogenic
146 emissions from Europe. Other studies carried out in the Eastern Mediterranean (Violaky et
147 al. 2010; Violaki and Mihalopoulos 2010) also stress that combustion processes and
148 African dust are an important source of ON. By contrast, ON of marine origin seems to
149 play a small role in these sub-tropical marine regions (Muller et al., 2009). Although these
150 studies stress the importance of dust for the marine ON budgets in air, the low sampling
151 time resolution (1-4 days) and off-line analysis that the authors used, do not allow them to
152 conclude whether the ON is associated directly with dust particles or with the large
153 quantities of PBAP that are ejected into the atmosphere with the dust events (Kellogg and
154 Griffin 2006).

155
156 Aside from the complexity and diverse sources of ON, there are also two main issues
157 associated with sampling and analysing ambient ON aerosols. First, the concentration of
158 ON is often estimated by measuring concentrations of total nitrogen and subtracting the
159 concentrations of NO_3^- and NH_4^+ , which propagates errors from the three individual
160 species and leads to uncertainties in the ON analytical concentrations. Second, most of
161 the current measurements are carried out with off-line filter measurements (Sullivan and
162 Prather, 2005), which do not allow information on the ON mixing state and hence
163 challenge the aerosol source apportionment. An aerosol population is broadly "internally
164 mixed" when all single particles have the same chemical composition (equal to the bulk
165 composition). By contrast, an aerosol population is "externally mixed" when single particles
166 have a different chemical composition. In order to reduce uncertainty on ON-containing
167 aerosols, Jickells et al. (2013) stressed the importance of deploying new technologies.
168 Detection of PBAPs by real-time (RT) techniques for autonomous, online detection and
169 characterization of PBAP properties has become increasingly important for research

170 purposes (Hoffman et al., 2019). Single particle mass spectrometry (SPMS) - techniques
171 that ablate and ionize single aerosol particles - is capable of PBAP detection, although the
172 interpretation of SPMS mass spectra is challenging and requires extensive human
173 interaction. For example, amino acids are ubiquitous compounds with an integral role in
174 atmospheric bioaerosol compositions (Ge et al., 2011). Previous SPMS identified amino
175 acids in PBAP particles (Ferguson et al., 2004; Russell et al., 2004; Czerwieniec et al,
176 2005, Schneider et al., 2011). However, difference in ionization laser wavelengths may
177 produce different single-particle mass spectra, and therefore, specific markers for amino
178 acids do not exist.

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

187
188 The large ATOFMS datasets used in this work were previously used to study the variation
189 of the mixing state of Saharan dust particles with atmospheric transport (Dall’Osto et al.,
190 2010a) during the DODO project; and to study the aerosol properties associated with air
191 masses arriving into the North East Atlantic during the 2008 Mace Head EUCAARI
192 intensive observing period (Dall’Osto et al., 2010b). The current study aims - for the first
193 time - to specifically presents an ATOFMS analysis looking at the properties of specific
194 clusters - including biological particles - and comparing the temporal trends with black
195 carbon and dimethyl sulphide concentrations across different locations. We focus our
196 attention on Saharan dust and biological particles found at their origins, as well as on
197 those sampled during ambient field measurements over both Tropical and North Atlantic
198 Oceans. The aims of this study include: (1) to elucidate if Saharan dust or the associated
199 terrestrial PBAP contains ON, (2) to understand if ON in natural aerosols has mainly a
200 primary or a secondary origin and (3) to discuss whether aerosol aging results in a
201 degradation or production of ON.

202 **2. Methodology**

203

204 **2.1 Atmospheric measurements**

205

206 **2.1.1 ATOFMS**

207

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

223

224 **2.1.2 Dimethyl sulphide (DMS) measurements**

225

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

229

230 **2.1.3 Black Carbon (BC) measurements**

231

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

235

236 **2.2 Laboratory and field studies**

237

238 In this study, we utilized previously published Saharan dust ATOFMS data from our
239 laboratories (Dall’Osto et al., 2010a) for the presence of ON. The Sahara Sahel Dust
240 Corridor (SSDC) is a huge zone lying between latitudes 12° N and 28° N and running
241 4000 km east-west from Chad to Mauritania (Moreno et al., 2006). During low wind
242 conditions, four different samples of SSDC desert soil, road, and aeolian dusts were
243 collected. A summary of the SSDC locations is discussed elsewhere (Moreno et al., 2006;
244 Dall’Osto et al., 2010a). Briefly, three dust samples were taken from the Saharan region,
245 and one from Algeria. Each dust sample was put into a flask in a sonicator, a suspension
246 of dust particles under filtered lab air flow was created, and single particles mass spectra
247 were obtained with the ATOFMS. About 1,000 single particle mass spectra were collected
248 for each of the four dust samples.

249

250 For this study, we also utilized ATOFMS datasets collected in two previous field studies.
251 This gives the possibility to compare single particle mass spectra from airborne particles
252 with those obtained from the Saharan dust particles analyzed in the laboratory. During
253 August and September 2002 The North Atlantic Marine Boundary Layer Experiment
254 (NAMBLEX) took place at Mace Head, Ireland (Heard et al., 2006). The Atmospheric
255 Research Station at Mace Head allows westerly exposure to the North Atlantic ocean
256 (clean sector, 180 degrees through west to 300 degrees) and the opportunity to study
257 atmospheric composition under Northern Hemispheric background conditions. Also, within
258 the Dust Outflow and Deposition to the Ocean (SOLAS-DODO) project (McConnell et al.
259 2008), an ATOFMS was deployed during a research cruise (P332) in the vicinity of the
260 Cape Verde Islands (January-February 2006) on board the research vessel FS Poseidon
261 as part of the UK-SOLAS programme. The study areas are summarized in Fig. 1:

262

- 263
- 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).
- 264
- 265
- 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).
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- 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).
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275 **2.3 Data analysis**

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

286 Finally, air mass back trajectories of the air masses arriving at the different study areas
287 were calculated at four arrival times for each day of the campaign (00:00, 06:00, 12:00 and
288 18:00 UTC), depicting the path taken by the air mass reaching the sampling site over the
289 previous five days. The back trajectories were run using the on-line HYSPLIT model
290 developed by the National Oceanic and Atmospheric Administration (NOAA) (Draxler and
291 Rolph, 2003).

292

293 **3. Results**

294

295 The ART-2a algorithm generated a number of clusters used to describe the ATOFMS
296 mass spectra. Most of the obtained particle types were associated with anthropogenic
297 sources (fresh and aged combustion related aerosols), sea salt, ship emissions,
298 secondary aerosol of inorganic nature, some of which were already discussed elsewhere
299 (Dall'Osto et al., 2004; 2006, 2010a,b). Table 1 shows a summary of the previous results,
300 and put it in context with the current specific ON analysis. Table 1 shows that Saharan
301 dust particles and biological particles were detected in all the ATOFMS datasets
302 presented. ATOFMS has already proved to be a good tool able to separate dust (mainly
303 Ca-rich or Al-Si rich) and biological particles (Fergenson et al., 2004; Pratt et al., 2009).
304 Briefly, biological mass spectral signatures can be differentiated from dust on the basis of
305 abundant organic and phosphorus ions, as well as a lack of key dust markers, such as
306 aluminium and silicates. Within the main objective of this work, the ATOFMS is a very
307 sensitive instrument towards ON (m/z - 26 and m/z -42, due to $[\text{CN}]^-$ and $[\text{CNO}]^-$,
308 respectively), and many alkylamines (Angelino et al. 2001; Moffet et al. 2008; Pratt et al.
309 2009; Healy et al., 2015; Dall'Osto et al., 2016).

310 Figure 2 shows the positive and negative ART-2a ATOFMS mass spectra of dust particles
311 and PBAP detected at their source (Saharan dust particles collected in Africa; Fig. 2 a, b,
312 respectively); during the SOLAS-DODO cruise around Cape Verde (Fig. 2 c, d,
313 respectively) and during the NAMBLEX field study at Mace Head, Ireland (Fig. 2e, f,
314 respectively). It is clear that ATOFMS mass spectra of Saharan dust particles (Fig. 2 a, c,
315 e) shows peaks due to most common ion species characteristic of crustal materials
316 including aluminum (m/z 27 $[\text{Al}]^+$), calcium (m/z 40 $[\text{Ca}]^+$ and 56 $[\text{CaO}]^+$), titanium (m/z 48
317 $[\text{Ti}]^+$ and 64 $[\text{TiO}]^+$), lithium (m/z 7 $[\text{Li}]^+$) and iron (54 $^{54}[\text{Fe}]^+$ and 56 $^{54}[\text{Fe}]^+$). Peaks for other
318 metals such as sodium (m/z 23 $[\text{Na}]^+$), magnesium (m/z 24 $^{24}[\text{Mg}]^+$, 25 $^{25}[\text{Mg}]^+$) and
319 potassium (m/z 39 $[\text{K}]^+$) can also be seen. In addition, other peaks for calcium (57
320 $[\text{CaOH}]^+$, 96 $[\text{Ca}_2\text{O}]^+$ and 113 $[(\text{CaO})_2\text{H}]^+$) were detected but at low intensity. The negative
321 particle mass spectra in Figure 2 (a, c, e) show ions from oxygen (m/z -16 $^{16}[\text{O}]^-$, -17 $[\text{OH}]^-$),
322 chloride (m/z -35 $^{35}[\text{Cl}]^-$, -37 $^{37}[\text{Cl}]^-$), phosphate (m/z -63 $[\text{PO}_2]^-$ and m/z -79 $[\text{PO}_3]^-$), a
323 small abundance of -46 $[\text{NO}_2]^-$ and -62 $[\text{NO}_3]^-$. It is important to note that in these Al/Si-
324 rich Saharan dust particles, peaks of silicate at m/z -60 $[\text{SiO}_2]^-$ and -76 $[\text{SiO}_3]^-$ dominate
325 the negative spectra. This is further discussed in Dall'Osto et al. (2004, 2010a), where

326 Al/Si-rich dust particles consistent with Saharan dusts which are dominated by SiO₂ and
327 Al₂O₃ (Goudie and Middleton, 2001) were observed.

328 Few particles found in Saharan soil dust samples (<4%) were internally mixed with ON
329 species. We have previously reported that both organic and organic nitrogen species were
330 more commonly associated with Saharan dust particles collected in the source region
331 relative to the atmospheric Saharan dust particles sampled during the two field studies
332 (SOLAS-DODO and NAMBLEX, Dall'Osto et al. 2010a). It is possible that some of these
333 ON components may be mineralized (a process by which organic N is converted to plant-
334 available inorganic forms) during atmospheric transport. This is supported by the
335 observation that Saharan dust particles with shorter atmospheric residence, i.e. collected
336 near the Cape Verde Islands (Fig 1, 2c, DODO experiment), showing increased internally
337 mixed nitrate (possibly mineralized ON). In addition, this can be seen also in the Saharan
338 dust particles with longer atmospheric residence times, i.e. collected on the coast of
339 Ireland (Fig. 1, 2e, NAMBLEX experiment) showing also a very high degree of internally
340 mixed secondary species including nitrate (m/z -46, see also Dall'Osto et al., 2010a).
341 Overall, our studies suggest that fresh Saharan dust is not a major source of ON. It is
342 important to stress that no clear peaks associated to alkylamines (Healy et al., 2015;
343 Dall'Osto et al., 2016) were detected in any of the Saharan dust particle types (Fig. 2 a, c,
344 e).

345 With regard to biological particles, those were detected in all the datasets: the Saharan
346 soil dust samples and the two ATOFMS ambient field studies (Table 1, Fig. 2). A strong
347 peak at m/z 39 is usually seen in the positive mass spectra, whereas the negative
348 spectrum is usually dominated by phosphate [PO₂]⁻ m/z -63 and [PO₃]⁻ m/z -79) and often
349 also internally mixed with ON species (Pratt et al. 2009). Biological particles detected in
350 Saharan dust samples and over the Tropical Ocean had a weak signal associated with ON
351 and amines. Our results - showed in Fig. 2 - suggest that fresh PBAP are lacking in ON
352 signal, both at their origin (dust samples collected in Africa) and after a few days of
353 transport (Cape Verde region). By striking contrast, 19% of PBAP detected at Mace Head
354 were internally mixed with ON compounds. By querying the ATOFMS NAMBLEX dataset,
355 it was found that the majority (>99%) of the signal due to ON and amines species was
356 associated with a specific PBAP type (Fig. 2 f), indicating that this is a major source of ON
357 sampled over the North Atlantic. Additionally, strong peaks of alkylamines are seen in the

358 positive mass spectra, including m/z 58 [$C_2H_5NH=CH_2$]⁺, m/z 59 ([$N(CH_3)_3$]⁺ and m/z 86
359 [(C_2H_5)₂ $N=CH_2$]⁺ (Dall'Osto et al., 2016). The peak of m/z 74 and m/z 104 (potentially
360 [$C_2H_4NO_2$]⁺ and [$C_3H_6NO_3$]⁺, respectively) were previously attributed to organic nitrogen
361 peaks including alkylamines (Angelino et al., 2001). A previous study in the city of
362 Barcelona (Spain) found that m/z 104 was found to be to be linked alkylamines of primary
363 aerosol origin, whereas m/z 74 alkylamines of secondary aerosol origin (Dall'Osto et al.,
364 2016). This particle type (Fig. 2 f) presented an aerosol size distribution centred at about
365 2 μ m, shifted towards an even larger modes than Al-Si Saharan particles (Dall'Osto et al.
366 2004). An overview the differences in spectra for the PBAP NAMBLEX (aged transported
367 PBAP) and its origin (PBAP Saharan region) or in the Tropical Ocean (PBAP DODO) can
368 be seen in Figure 3, which show the subtraction spectrum for PBAP NAMBLEX minus
369 PBAP DODO (Fig. 4a) and for PBAP NAMBLEX minus PBAP Saharan dust origin (Fig.
370 4b). The positive ion spectrum for PBAP NAMBLEX is enhanced in organic nitrogen and
371 alkylamines (m/z 59, 74, 86, 104), whilst the negative is enriched in nitrate peaks (m/z -46,
372 -62) and organic nitrogen (m/z - 42). A representative ATOFMS single particle mass
373 spectrum of the PBAP particle carrying ON (Fig. 2 f) is presented in Figure 4, showing a
374 strong peak at m/z 39 likely to be due to potassium [K], and minor peaks at m/z 23 [Na]
375 and m/z 56 [Fe] in the positive mass spectra. In the negative mass spectra, ON peaks are
376 found at m/z -26 [CN] and m/z -42 [CNO], along with phosphate (m/z -63 and m/z -79) and
377 methanesulfonic acid MSA (m/z -95). The mass spectrum has features that are generally
378 attributed to vegetative debris (potassium-phosphate) except that it is internally mixed with
379 ON species. Major ion peaks in the positive mass spectra at m/z 58, 59, 74, 86, and 104,
380 118 and 154 are all consistent with ON ATOFMS mass spectra peaks detected in previous
381 field and laboratory studies (Angelino et al. 2001, Moffet et al. 2008, Healy et al., 2015:
382 Dall'Osto et al., 2016).

383 In order to investigate the origin of the dominant PBAP associated with ON during
384 NAMBLEX, we separated the field study sampling period accordingly to three main air
385 mass categories (marine Tropical, marine Polar-Arctic and European continental Polar –
386 mT, mP-mA and cP respectively, Dall'Osto et al. 2010b). We found - as expected - higher
387 values of BC for cP air masses (209 ± 197 ng m^{-3}) relative to mT (51 ± 23 ng m^{-3}) and the
388 very clean mP-mA ones (33 ± 21 ng m^{-3}) (Figure 4a). DMS concentrations - by contrast -
389 were much higher for mT air masses (507 ± 120 pptV) than for cP (105 ± 110 pptV) and mP-

390 mA (140 ± 120 pptV) (Figure 4b). Other studies (Dall'Osto et al. 2010b, Bassford et al.
391 1999) have also indicated that during mT air masses the vast majority of DMS and MSA
392 observed at the Mace Head site had been transported significant distances from the mid
393 tropical Atlantic. Figure 4c shows that biological particles were detected at about double
394 the concentration (t-test, 95%, 1.31 ± 1 and 2.67 ± 2 respectively) for mT relative to cP air
395 masses. This PBAP type was found in association with Al-Si particles detected in the
396 same study and attributed to dust particles, mainly detected during mT air masses and to a
397 lesser extent during cP air masses (Dall'Osto et al 2004, 2010a, Figure 3d). An increase in
398 microbial concentrations during dust storms has previously been reported and can be two
399 orders of magnitude higher than under non-dusty conditions (Hara and Zhang 2012,
400 Yamaguchi et al 2014, Mazar et al. 2016). In conclusion, the PBAP associated with ON
401 were likely transported to the North Atlantic together with dust events, which may have
402 originated in the Sahara-Sahel region and travelled over the Tropical Ocean. During their
403 atmospheric travel time, the PBAP injected with dust events, seem to first be low in ON as
404 we observed during the SOLAS-DODO measurements and then get enriched with ON with
405 atmospheric transport as we observed during the NAMBLEX measurements.

406

407 **4. Discussion and Conclusion**

408

409 The first conclusion of this study is that (within the $0.2-3\mu\text{m}$ size) the ON aerosol
410 concentrations reported over the Tropical Ocean - at least during the study period - are
411 likely to be contained within the terrestrial PBAP travelling in association with Saharan dust
412 and not with the dust particle themselves. Saharan dust is also not found to be enhanced
413 in ON species when detected over the North Atlantic. Overall, our single particle mass
414 spectrometry measurements collected at high time resolution over a large geographical
415 area, suggest that Saharan dust particles are not rich in ON, either at their origin, or in the
416 Cape Verde region. The second conclusion of this study is that the PBAP that are injected
417 into the atmosphere together with dust events are the aerosol particles that contain ON
418 compounds. Furthermore, it appears that these biological particles get enriched in ON
419 species during their atmospheric residence. The low associated BC concentrations make
420 an anthropogenic influence unlikely.

421 Previous ATOFMS studies discovered existence of different ON groups (alkylamines,
422 proteins, amino acids etc.) in aerosols and reported their involvement in atmospheric
423 processes, including indoor tobacco smoke (Dall'Osto et al., 2007), cloud/fog processing
424 (Rehbein et al., 2011), primary traffic pollution (Angelino et al., 2001; Dall'Osto et al.,
425 2016), non-salt organic aerosol products through reaction with oxidizing agents (Murphy et
426 al., 2007, Pratt et al., 2009) and marine aerosol reactions (Dall'Osto et al., 2012; Healy et
427 al., 2015). However, it is important to note that - in this study - ON was found internally
428 mixed with biological particles and externally mixed with other aerosols, therefore we can
429 conclude that ON is not formed by condensation of secondary semi-volatile organic
430 nitrogen species as these compounds would condense on the whole aerosol population.

431
432 An explanation for the ON enrichment of the aging PBAP can only be speculative at this
433 stage. Previous studies have demonstrated that viable airborne micro-organisms present
434 in the atmosphere can contribute to atmospheric chemistry through degradation
435 processes, as well as chemical change due to the release or desorption of molecules from
436 microbiological entities (Deguillaume et al. 2008; Cote et al., 2008). Airborne metabolically
437 active microorganisms, for example fungal and bacterial cells, can transform chemical
438 constituents of the atmosphere by metabolic activity and have been implicated in the
439 nitrogen and carbon cycling in clouds (Hill et al. 2007, Cote et al 2008, Vaithilingom et al
440 2013, Krumnis et al. 2014, Amato et al 2017, Šantl-Temkiv et al 2018). Nitrogen can be
441 microbially incorporated into organic compounds through the processes of fixation and
442 assimilation. Different prokaryotes - including Cyanobacteria - which are commonly found
443 in the atmosphere (reviewed in Genitsaris et al. 2011), are capable of nitrogen fixation and
444 can convert atmospheric nitrogen into biologically accessible ammonia. Assimilation of
445 inorganic nitrogen is performed by diverse bacteria and fungi, who can convert nitrate and
446 ammonia into different forms of ON. It is not known at this stage if the association of ON
447 with aging biological particles is due to the metabolic activity of microorganisms externally
448 mixed with Saharan dust plumes, which have travelled to the North Atlantic region. The
449 long distance transport of microorganisms with dust particles has been shown to
450 negatively affect the viability of microbial cells as <40% of all bacterial cells were found
451 viable compared to >70% of non-dust-associated cells (Hara and Zhang 2012). Despite
452 this, the absolute number of viable microorganisms travelling with dust storms remained

453 high. It may be that these viable microbial cells may maintain their metabolic activity and
454 affect the atmospheric nitrogen cycle. Further multidisciplinary studies on the impact of
455 airborne micro-organisms and possible chemical mechanisms are recommended to
456 underpin these findings.

457

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

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470 In conclusion, using on-line single particle aerosol mass spectrometry, we show that fresh
471 and aged Saharan dust aerosols are not a major source of ON. Furthermore, we find that
472 biological particles – likely of terrestrial origin – are enriched in ON during atmospheric
473 transport. We hypothesize that microbial processes may generate ON through nitrogen
474 fixation and assimilation during the atmospheric residence of microbial cells, which results
475 in an enrichment of ON compounds within the cell. Coarser particles possess higher dry
476 deposition rates and such microorganisms internally mixed with ON may be an important
477 source of nitrogen, which is an essential nutrient in North Atlantic Ocean marine
478 ecosystems. González Benítez et al. (2009) found that dry deposition of particles was the
479 main contributor of N-containing species in bulk rain samples, which were not strongly
480 associated with either combustion or agricultural sources alone (González Benítez et al.
481 2010). Our data do not rule out a suggestion that SOA production of amines is important
482 for the marine atmosphere when considering the fine particle mode (Facchini et al. 2008,
483 Muller et al. 2009), but we propose an additional source for the total ON concentrations in

484 the coarse aerosols mode that has a natural origin. Further studies are needed in order to
485 validate the event reported in this study.

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490

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LIST OF TABLES AND FIGURES

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).

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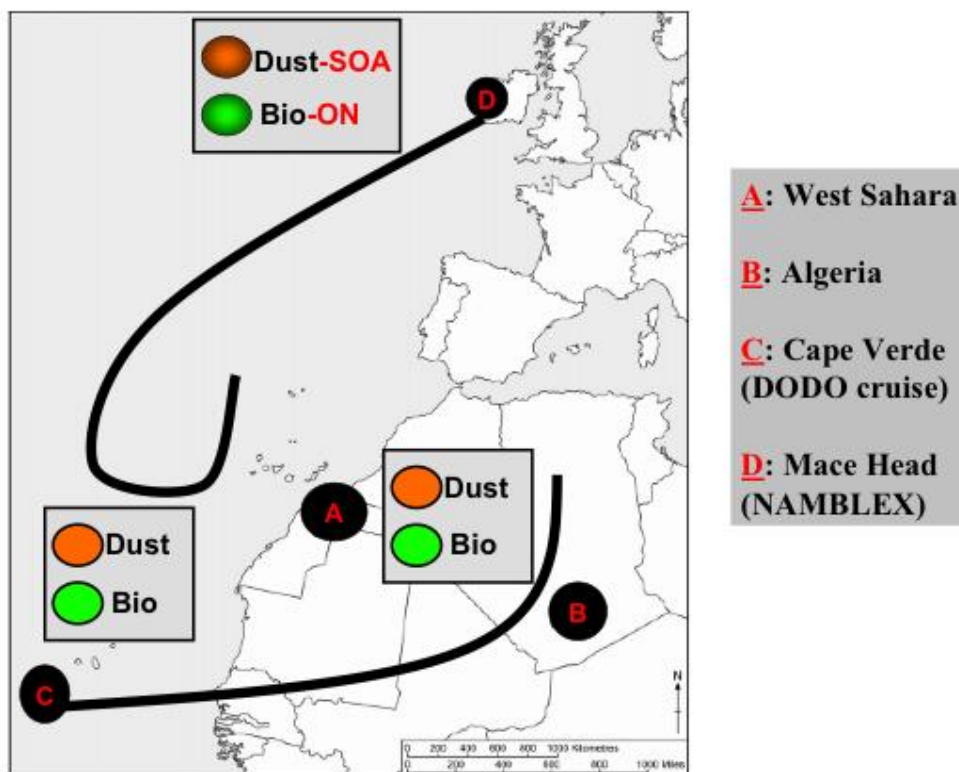
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	Number of ATOFMS mass spectra	Saharan dust particles (% by number)	Biological particles (% by number)	Others (% by number)
Saharan soil samples	4,205	55	10	>35
DODO (Tropical Ocean)	187,205	1.1	0.01	>98
NAMBLEX (North Atlantic Ocean)	191,504	1.0	0.01	>98

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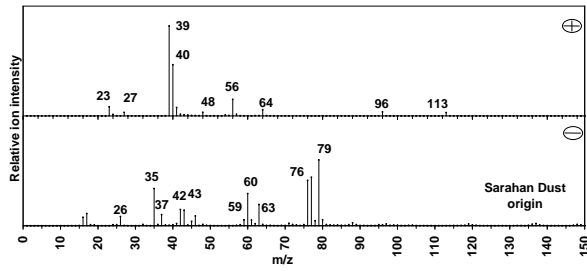
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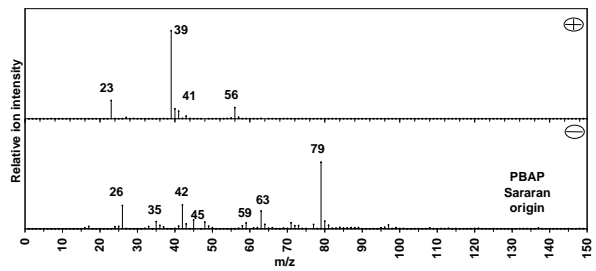
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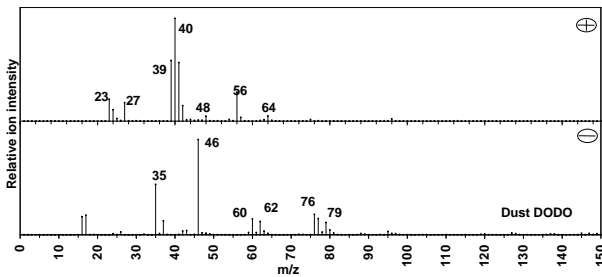


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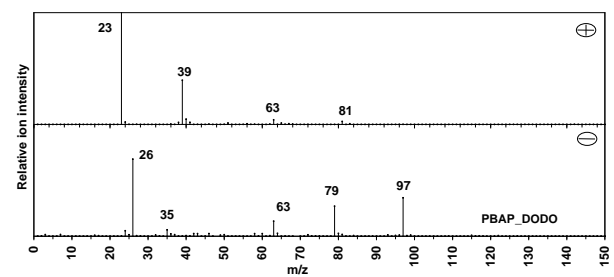


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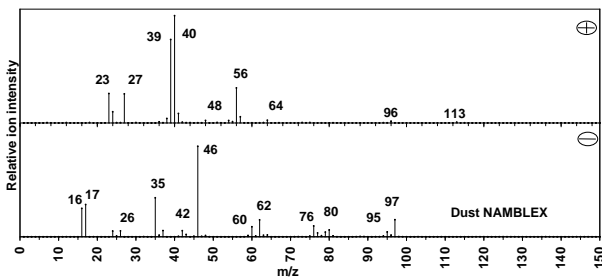


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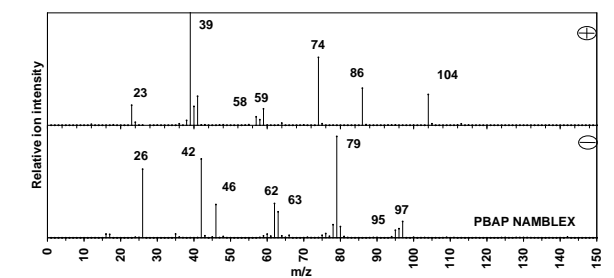


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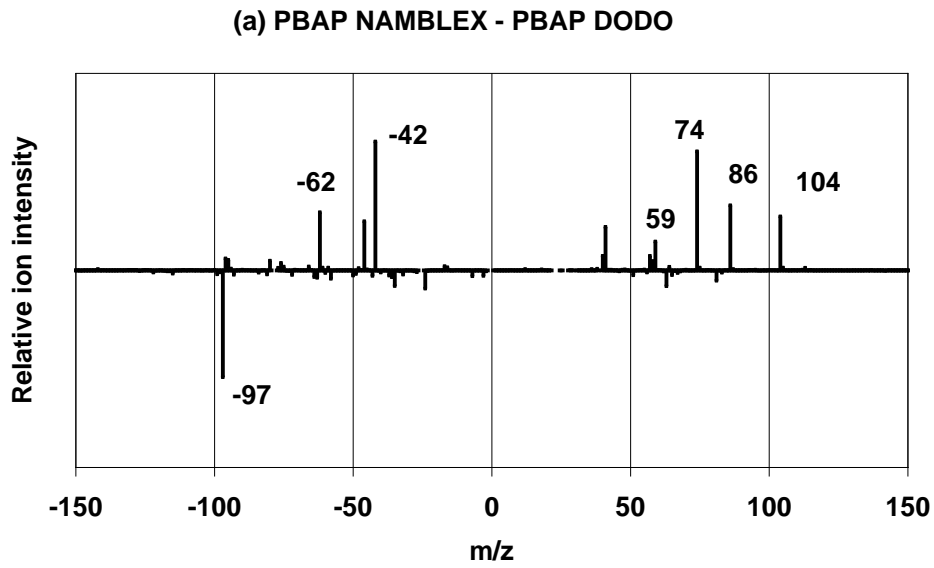
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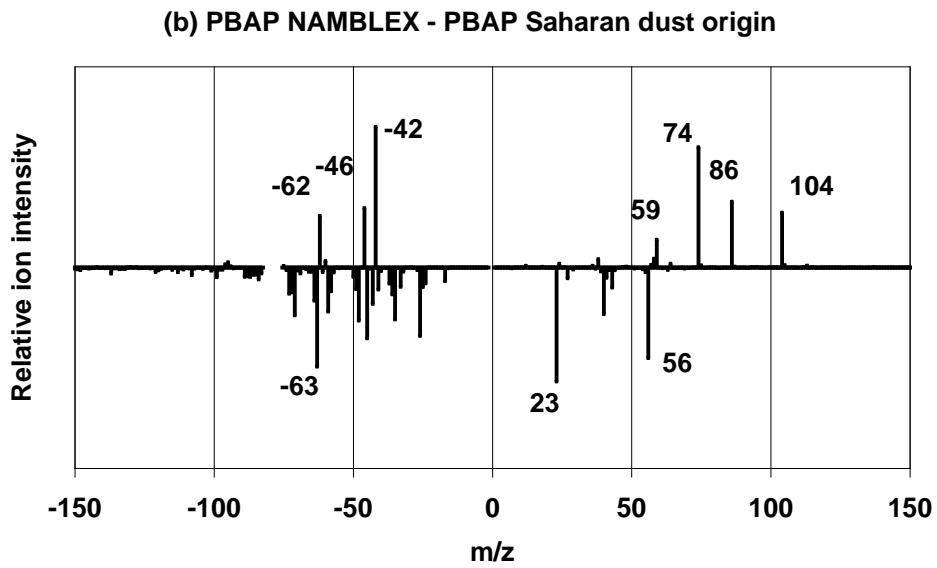
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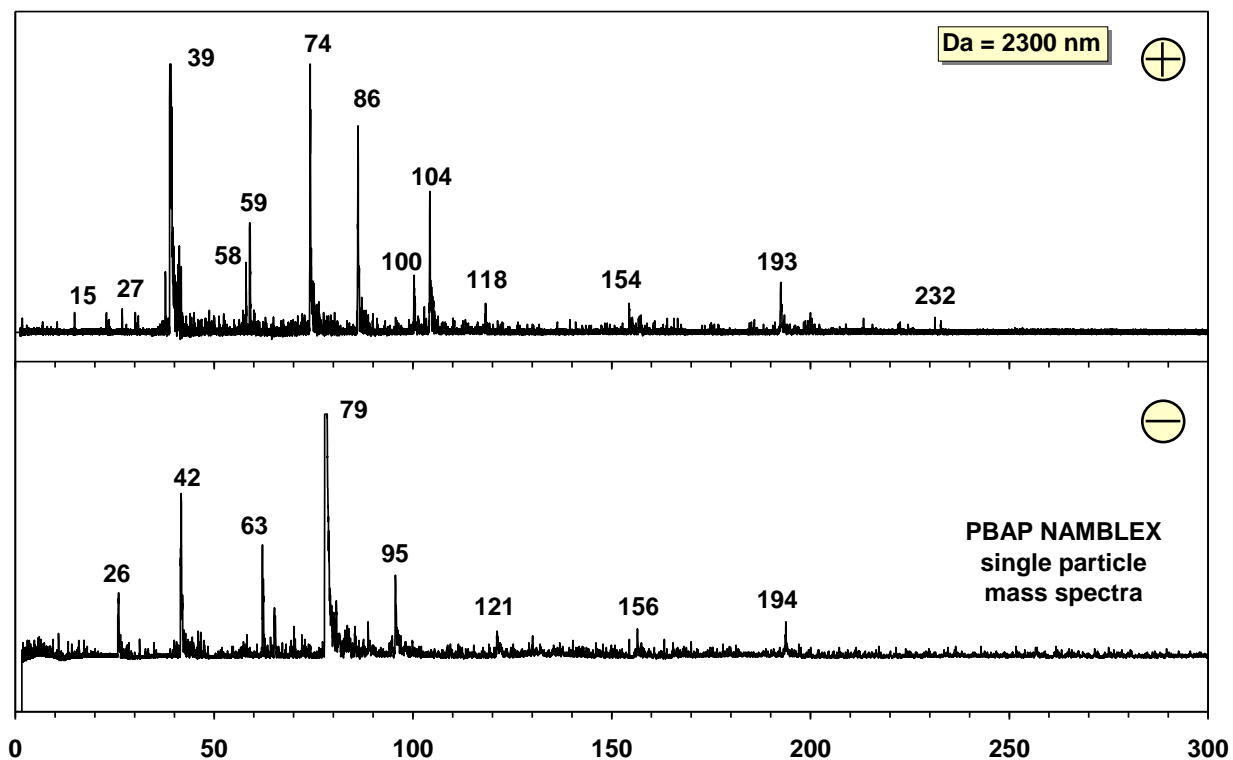
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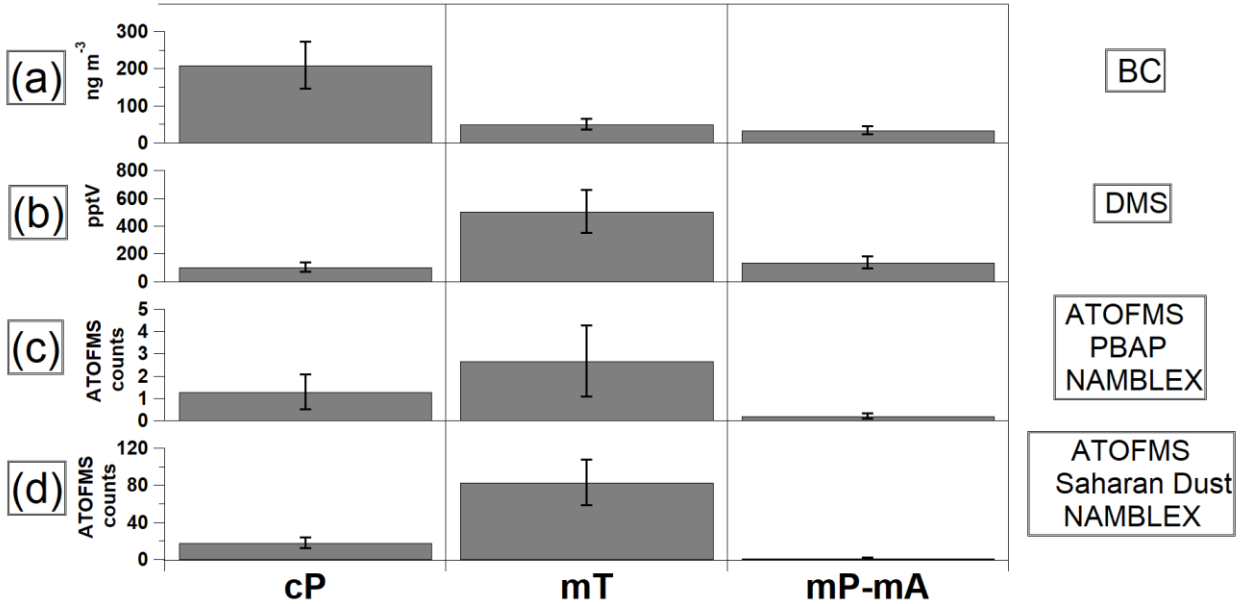
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