Marine submicron aerosol gradients, sources and sinks

D. Ceburnis[1], M. Rinaldi[2], J. Ovadnevaite[1], G. Martucci[1], L. Giulianelli[2], C.D. O'Dowd[1]

[1]School of Physics and Centre for Climate & Air Pollution Studies, Ryan Institute, National University of Ireland, Galway, University Road, Galway, Ireland

[2]Institute of Atmospheric Sciences and Climate, National Research Council, Bologna, Italy

Correspondence to: D. Ceburnis (darius.ceburnis@nuigalway.ie)

Abstract

Aerosol principal sources and sinks over NE Atlantic waters were studied through the deployment of an aerosol chemistry gradient sampling system. The chemical gradients of primary and secondary aerosol components, specifically, sea salt, water insoluble organic matter (WIOM), water soluble organic matter (WSOM), nitrate, ammonium, oxalate, amines, methanesulfonic acid (MSA) and water soluble organic nitrogen (WSON) were examined in great detail. Sea salt fluxes were estimated by the boundary layer box model and ranged from 0.3 to 3.5 ng m^{-2} s^{-1} over the wind speed range of 5-12 m s^{-1} and compared well with the derived fluxes from existing sea salt source parameterisations. The observed seasonal pattern of sea salt gradients was mainly driven by wind stress in addition to yet unquantified effect of marine OM modifying fractional contributions of SS and OM in sea spray. WIOM gradients were a complex combination of rising and waning biological activity, especially in the flux footprint area, and wind-driven primary sea spray production supporting the coupling of recently developed sea spray and marine OM parameterisations.

1.   Introduction

Marine aerosols contribute significantly to the global radiative budget and consequently, changes in marine aerosol abundance and/or chemical composition have an impact on climate change through both direct and indirect effects. The Northeast Atlantic region is of particular interest due to a combination of storminess, prevailing westerlies bringing marine air masses into continental Europe, and biological activity in surface waters significantly affecting chemical composition of atmospheric particulate matter (O'Dowd et al., 2004). Organic matter (OM) has been observed in marine aerosol particles for many decades and has been linked to fractional contribution of OM transferred from the sea-surface into the tropospheric boundary layer through bubble-mediated production processes (Blanchard, 1964; Hoffman and Duce, 1977; Middlebrook et al., 1998; Oppo et al., 1999; Russell et al., 2010).

There has been a significant progress in understanding marine aerosol composition, which has been identified to consist of significant amounts of organic matter (Cavalli et al., 2004; Sciare et al., 2009) both water-soluble and water-insoluble. It has historically progressed from mainly consisting of sea salt and non-sea salt sulphate (Charlson et al., 1987; O'Dowd et al., 1997) to complex primary biogenic organic mixtures and states (dissolved, particulate, colloidal or nanogel) (Cavalli et al., 2004; Leck and Bigg, 2005; Russell et al., 2010; Decesari et al., 2011) as well as secondary organic compounds like organic acids (Kawamura and Sakaguchi, 1999; Mochida et al., 2002; Turekian et al., 2003; Rinaldi et al., 2011) and recently discovered biogenic amines (Facchini et al., 2008a; Muller et al., 2009). The findings of Ceburnis et al. (2008) and Facchini et al. (2008b) independently confirmed that water insoluble organic carbon (WIOC) in marine atmosphere has primary origin while water soluble organic carbon (WSOC) is mainly secondary or processed primary (Decesari et al., 2011). However, studies of Keene et al. (2007) and Russell et al. (2010) evidenced that even WSOC can largely be of primary origin.

After significant fraction of marine sea spray particles was found to contain biogenic organic matter compounds (O'Dowd et al., 2004) it became even more important to determine principal sources and sinks of marine organic matter. Tentatively, the source of biogenic marine organic matter has been linked to the ocean surface and driven by a biological activity in surface waters based on a

68   seasonality pattern of organic matter and chlorophyll-a (Yoon et al., 2007; Sciare

69   et al., 2009) or regression analysis (O'Dowd et al., 2008; Russell et al., 2010).

70   Furthermore, the first quantitative estimate of submicron aerosol organic matter

71   in oceanic environment has been performed by Ceburnis et al. (2011) using dual

72   carbon isotope analysis that showed over 80% of organic matter in clean marine

73   air masses is of marine biogenic origin. A pilot study based on concentration

74   gradient method performed in marine environment by Ceburnis et al. (2008)

75   revealed that water soluble organic matter is largely produced by secondary

76   processes while water insoluble organic matter is of primary origin.

77   This study is the extension of the study by Ceburnis et al. (2008) through the

78   combination of off-line chemical analysis of samples and the measurements of

79   boundary layer height, expansion of the range of chemical species and extension

80   of the timescale to consider seasonal pattern of primary production. Contrary to

81   the above study the flux-gradient method was not attempted due to the

82   uncertainty of the averaged coefficient of turbulent transfer derived from eddy-

83   covariance method, but instead sea salt fluxes were estimated by the boundary

84   layer box model.

85

86   **2.   Experimental methods**

87   The flux of sea-spray aerosols has been studied previously as sea salt mass fluxes

88   or aerosol size and number flux (O'Dowd and De Leeuw, 2007; de Leeuw et al.,

89   2011). Apart from few studies, the flux experiments have typically focused on

90   super-micron sized particles. Eddy covariance method for studying submicron

91   particle fluxes was first used by Buzorius et al. (1998) estimating submicron

92   particle fluxes and sinks and has been since applied in a variety of environments:

93   boreal and tropical forest (Buzorius et al., 1998; Ahlm et al., 2009), ocean

94   (Nilsson et al., 2001; Geever et al., 2005; Norris et al., 2008; Brooks et al., 2009),

95   desert (Fratini et al., 2007) and urban (Martensson et al., 2006; Martin et al.,

96   2009). Eddy-covariance method is typically used to study total particles fluxes.

97   The technique has been modified into relaxed eddy-covariance method to allow

98   studying size-segregated particle fluxes (Gaman et al., 2004) or disjunct eddy

99   covariance method (Held et al., 2007) employing slower response instruments. It

100   should be noted, however, that while number of sea spray particles is dominated

101   by submicron particles, mass is dominated by super-micron sizes and not a single

102 method is capable of measuring particles around the important boundary of 1
103 micrometer. None of the above techniques were suitable for studying chemically
104 resolved fluxes, because chemical analysis typically requires long sampling time
105 (many hours for off-line chemical analysis). Most recently, however, eddy-
106 covariance system coupled with high resolution aerosol mass spectrometer has
107 been used to study chemically resolved fluxes (Nemitz et al., 2008; Farmer et al.,
108 2011), but those were largely limited to areas with relatively high concentration
109 of species.

110 The study of chemical gradients in a relatively clean marine atmosphere
111 represents a great challenge due to generally low absolute species concentrations
112 and the lack of appropriate experimental methods. The rationale of choosing the
113 gradient method was based on the fact that persistent fluxes must produce
114 concentration gradients with their sign depending on the source and assuming
115 that recurrent eddies allow sampling for certain number of hours to meet
116 analytical requirements of chemical species. Additional challenges exist when it
117 comes to reactive species (organic matter) due to chemical transformation during
118 transport to the sampling location or extended sampling durations. A
119 combination of continuous production (or removal) of particles and turbulent
120 eddies of varying magnitude within the boundary layer should establish
121 concentration profiles. The profiles, therefore, are a net result of the competition
122 between upward and downward eddies averaged over time. The persistent
123 surface source will manifest itself in a decreasing concentration away from the
124 source. The absence of the surface source should result in an increasing
125 concentration profile as particles are removed to the surface through deposition
126 processes.

127

128 **2.1   Sampling set-up and auxiliary measurements**

129 A new set-up to study gradients and corresponding flux estimate was installed at
130 Mace Head Atmospheric Research Station on the west coast of Ireland (Jennings
131 et al., 2003; O'Connor et al., 2008) comprising PM1 samplers installed at three
132 different heights (3 m ,10 m, and 30 m).

133 Chemical fluxes were estimated by a simplified box model according to the
134 method outlined by Ovadnevaite et al. (2012):

$$F = \frac{C \times H_{BL}}{\tau} \qquad (1)$$

135

136 where C was the concentration measured at 30 m height, H_{BL} was the measured

137 boundary layer height averaged over the sample duration and τ was boundary

138 layer filling time (fixed at 2 days with the uncertainty of ±1day).

139 The above method was critically assessed by Lewis & Schwartz (2013) who

140 argued that the method can hardly provide information on wind speed

141 dependence. Indeed, estimated fluxes cannot be strictly related to particular wind

142 speed because the corresponding boundary layer filling time was not constant

143 and the local wind speed may not have been accurate with regard to any

144 particular wind speed where primary production occurred. However, the method

145 was only used in this study to roughly estimate the fluxes without attempting to

146 derive a parameterisation but rather to provide an estimate.

147 LIDAR measurements (Jenoptik/Lufft and Vaisala ceilometers) are continuously

148 conducted at Mace Head and a dedicated algorithm for temporal height tracking

149 (THT) (Haeffelin et al., 2012; Milroy et al., 2012) using the backscatter profiles

150 measured by the LIDAR was used to identify the surface mixed layers (SML)

151 and the decoupled residual layers (DRL), both important parameters when

152 considering boundary layer filled by primary fluxes.

153 The chlorophyll satellite data (daily, 1° spatial resolution) were obtained from

154 GlobColour (http://www.globcolour.info). They result from the merging of

155 Medium-Resolution Imaging Spectrometer (MERIS), Moderate Resolution

156 Imaging Spectroradiometer (MODIS), and Sea-viewing Wide Field-of-view

157 Sensor (SeaWiFS) data, using advanced retrieval based on fitting an in-water

158 biooptical model to the merged set of observed normalized water-leaving

159 radiances. A thorough description of the data treatment can be found in Rinaldi et

160 al.(2013).

161

162 **2.2   Sampling strategy**

163 Meteorological records demonstrate that on average marine westerly air masses

164 account for over 50% of time at the station (Cooke et al., 1997; Jennings et al.,

165 2003). The gradient measurement system PM1 samplers (Sven Leckel

166 Ingenieurbüro GmbH) ran in parallel at a flow rate of 38 lpm. Samples were

167 collected in clean marine conditions (wind direction 190 < WD < 300 and

168   Condensation Particle Counter (CPC) concentrations < 700 particles cm^{-3}) using

169   an automated sampling system on quartz filters for the analysis of both organic

170   and inorganic components of marine aerosol. The system operated day and night

171   whenever the above clean marine conditions were met. Active control of the

172   sampling conditions excluded sampling during occasional short-term spikes of

173   CPC concentrations either due to coastal nucleation events or occasional local

174   ship traffic. Post-sampling analysis revealed that such air masses did not have

175   contact with land for 4-5 days (as confirmed by air mass back-trajectories) and

176   black carbon (BC) concentration measured by an Aaethalometer (AE-16, Magee

177   Scientific, single wavelength at 880 nm) did not exceed 50 ng m^{-3}. Such air

178   masses have been typically spending the last 48 hours (at least) in the marine

179   boundary layer as documented by Cavalli et al. (2004) and Ceburnis et al. (2011).

180   The latter study quantitatively demonstrated that in clean marine air masses

181   anthropogenic carbon species typically contributed to 8-20% of the total carbon

182   mass which should be applicable to other anthropogenic species due to internally

183   mixed anthropogenic aerosol far from the source. It is important to note that

184   clean marine samples collected at Mace Head are representative of the open

185   ocean environment considering chemical and physical similarities between open

186   ocean and coastal (Mace Head) samples (Rinaldi et al., 2009). The marine air

187   criteria used at Mace Head were demonstrated to be sufficient for ensuring that

188   anthropogenic and coastal effects are minimised to guarantee a dominant, if not

189   at times overwhelming natural marine aerosol signal as detailed in the study of

190   O'Dowd et al.(2014).

191

192   2.3   Off-line chemical analysis and concentration gradients

193   Fifteen PM1 gradient samples were collected during 13 month period in clean

194   marine conditions as listed in Table 1. The sampling strategy aimed at capturing

195   two samples per month providing that clean marine conditions were prevailing

196   and each sample duration lasted on average 50% of time during the calendar

197   week.

198   The samples were analysed for a wide range of chemical species present in

199   aerosol particles: sodium (a marker for sea salt (SS)), non-sea-salt sulphate

200   (nssSO$_4$), nitrate (NO$_3$), ammonium (NH$_4$), methanesulphonic acid (MSA), total

201   carbon (TC), oxalate (Oxa), (analytical details can be found in Cavalli et al.

202 (2004)), water soluble organic carbon (WSOC), water insoluble organic carbon
203 (WIOC) (Rinaldi et al., 2009), water soluble organic nitrogen (WSON), total
204 nitrogen (TN), dimethylamine (DMA) and diethylamine (DEA) (Facchini et al.,
205 2008a). WIOC was calculated as WIOC=TC-WSOC while WSON was
206 calculated as WSON=TN-WSIN (water soluble inorganic nitrogen). WSOM
207 (water soluble organic matter) was calculated as WSOC*1.8 and WIOM (water
208 insoluble organic matter) was calculated as WIOC*1.4 (Decesari et al., 2007;
209 Facchini et al., 2008b). Sea salt concentration was calculated as SS=Na*3.1
210 (Seinfeld and Pandis, 2006). The absolute concentration ranges of all measured
211 components are summarised in Table 2.

212 Normalised averaged concentration profiles of all measured chemical species
213 were obtained as follows: for each aerosol component, only samples for which
214 concentrations above the detection limit were observed at all three sampling
215 altitudes were used in data analysis. Normalisation was done by dividing the
216 concentration at every height by the sum concentration of three levels thus giving
217 the same weight to every profile for averaging purposes. After normalisation, the
218 profiles of each mass category were averaged, resulting in statistically
219 meaningful variances around the mean value and presented as an average and its
220 standard deviation. The normalised averaged concentration profiles allowed
221 classification and categorisation of the profiles, but the normalised data were not
222 used for calculating gradients and fluxes. The main features were similar to the
223 ones documented by (Ceburnis et al., 2008): decreasing concentration with
224 height, or negative gradient, was common of species produced at the surface by
225 primary processes while increasing concentration with height, or positive
226 gradient, was common of species produced by secondary processes in the
227 atmosphere aloft or within the marine boundary layer.

228 Concentration gradients of various chemical species were obtained by linear fit
229 of the concentration profile (except WSOM). A detailed discussion of potential
230 influence of local sources (surf-zone) to the gradient can be found in (Ceburnis et
231 al., 2008) and reconsidered in the Results section.

232

233 **2.4 Errors and uncertainties**

234   The uncertainty of estimated boundary layer fluxes was dependent on the

235   cumulative uncertainty of the measured species concentration, boundary layer

236   height and boundary layer filling time:

237                           $$\frac{\partial F}{F} = \sqrt{\left(\frac{\partial C}{C}\right)^2 + \left(\frac{\partial H_{BL}}{H_{BL}}\right)^2 + \left(\frac{\partial \tau}{\tau}\right)^2}$$ (2)

238   where the assigned boundary layer filling time uncertainty (50%) was

239   dominating the combined uncertainty due to relatively small concentration

240   uncertainty (5%) and boundary layer height uncertainty (10%).

241   The relative uncertainty of the organic matter fractional contribution to sea spray

242   (OM_{ss}=WIOM/(WIOM+SS)), where the variable WIOM appeared in both

243   nominator and denominator and WIOM represented total sea spray OM, resulted

244   in a more complicated equation of the combined propagated uncertainty of the

245   OM fractional contribution:

246                           $$\frac{\delta OM_{ss}}{OM_{ss}} = \frac{SS}{(SS+WIOM)} \sqrt{\left(\frac{\partial WIOM}{WIOM}\right)^2 + \left(\frac{\partial SS}{SS}\right)^2}$$ (3)

247   where the ratio in front of the square root is the fractional contribution of sea salt

248   in sea spray resulting in the fractional uncertainty of the OM fractional

249   contribution dependent on the sea salt fractional contribution and, therefore,

250   always smaller than the additively combined fractional uncertainty of sea salt and

251   WIOM measurement.

252   The uncertainty of the fitted functional relationships obtained from the discretely

253   measured values was presented with the 95% confidence bands which was

254   conceptually different from the fractional uncertainties of individual values. The

255   confidence bands also helped to define the best fitted function (e.g. linear or

256   power law) as unrealistic fits had very low or no confidence at all. Typically, the

257   confidence bands become narrower as the number of points increases and/or their

258   scatter decreases. The presentation of the confidence bands provided the physical

259   meaning of the points residing outside the confidence bands. An individual point

260   which is outside the confidence bands suggests a higher order of the relationship

261   or an unaccounted freak error. Several of such cases will be discussed

262   accordingly.

263

264   **3   Results and Discussions**

265   The measurements at three different heights allow resolving the vertical
266   concentration profiles of different chemical species and the magnitude of the
267   sources and sinks shaping the profiles. Most of them were non-linear, but well
268   interpretable having studied concentration and flux footprints in detail in the
269   previous pilot study of (Ceburnis et al., 2008). It is important to note that the
270   footprint of the measured absolute concentration was of many tens to hundreds of
271   kilometres offshore while the footprint of the concentration gradient was within
272   about 10 km from the measurement location, i.e. coastal waters (Ceburnis et al.,
273   2008). The surf zone emissions may have had certain influence on the
274   concentrations of sea salt or sea-spray at the lowest level of 3 m, particularly for
275   low wind speeds, practically disappearing at higher winds (O'Dowd et al., 2014),
276   but had little or no impact on secondary organic aerosol. The different distances
277   of the flux footprint arise from emissions contributing to the concentration at
278   different heights. The flux footprint of the 90% concentration difference between
279   3 and 10 meters is 0.2-1.2 km while the footprint of the 90% of the difference
280   between 10 and 30 meters extends to 5 km (Figure 1, Ceburnis et al. 2008). The
281   remaining 10% of the contribution extends well beyond 5 km, perhaps 10 km
282   distance being a safe approximation. A condensation potential could have also
283   contributed to the concentration differences of certain species as the time
284   required for the air parcel to cover 10 km distance is about 15 min which is more
285   than sufficient to achieve gas-aerosol equilibrium, e.g. (Meng and Seinfeld,
286   1996; O'Dowd et al., 2000).
287
288   ## 3.1   Concentration gradient profiles
289
290   ### 3.1.1 Primary components
291   The concentration profile of sea salt (top left in Figure 1) was unambiguously
292   surface sourced or primary, i.e. concentration was decreasing vertically. Some of
293   the individual profiles were sharper than others, but all were primary with only
294   three exceptions where the profiles were distorted at lower heights possibly
295   partly due to measurement errors and partly due to boundary layer dynamics and
296   changes in sea state during the sampling period (ascending and descending wind
297   regimes). However, as it was stated earlier, surf-zone emissions could have had
298   influenced the concentration value at the lowest level of 3 meters.

299 Interestingly, similar "negative gradient" concentration profiles were obtained
300 for nitrate and oxalate. However, those profiles were slightly, but repeatedly
301 (systematically) distorted, i.e. the concentrations of oxalate and nitrate
302 significantly diverged from the sea salt one at the lowest sampling height of 3
303 meters while following the sea salt profile above 10 meters. It is well established
304 that nitrate is produced by secondary processes and mainly manifesting itself
305 through condensed nitric acid on pre-existing sea salt particles in the absence of
306 anthropogenic ammonium nitrate. Sea salt particles at the lowest level were the
307 freshest having the closest flux footprint and, consequently, adsorbed the least
308 amount of condensable nitric or oxalic acid compared to higher levels. Similarly
309 to nitrate, oxalic acid could have been condensing on pre-existing sea salt
310 particles as well despite more diverse chemical pathways of oxalic acid (some of
311 the oxalate could also be produced by oxidation of organic matter inside sea-
312 spray particles (Rinaldi et al., 2011) and, therefore, manifesting itself as
313 "primary" species. The concentration profile of oxalate was similar to that of
314 nitrate and could indicate that a significant amount of oxalate is produced in the
315 atmosphere aloft subsequently condensing onto primary sea spray particles due
316 to its acidic nature.
317 The water insoluble organic matter (WIOM) concentration profiles were split
318 between three main categories: production (5 profiles), removal (6 profiles) and
319 mixed profiles (4 profiles) (bottom right of Figure 1). Given that fractional
320 contribution of OM in primary sea spray is related to the enrichment of organic
321 matter at the ocean surface, this range of behaviour can be interpreted in terms of
322 the location of biologically active region relative to the flux footprint. The wind
323 speed has been reported to have an effect on fractional contribution of OM, but
324 quantitative effect is unclear and will be discussed in more detail in section 3.4.
325 The biologically active water patches within the flux footprint (~10 km form the
326 measurement location) were responsible whether WIOM was produced or
327 removed from the surface layer, or a combination of both processes. Therefore, a
328 mixed profile was pointing at the production at a longer distance from the coast
329 and the removal close to the measurement location. Thus the removal profile was
330 pointing both at the deposition within the flux footprint area and/or the absence
331 of biological activity in surface waters within the flux footprint area. The WIOM
332 production by the secondary processes cannot be completely excluded either, but

333   we have no evidence of that. It is worth noting that the production profiles were

334   observed in early spring (March until early May) when biological activity is high

335   at the coast and during late summer (late July-August) when biological activity

336   has a second maximum identified by the chlorophyll proxy (Yoon et al., 2007).

337   In contrast, the removal profile was observed during late spring and early

338   summer when biological activity is retreating away from the coast into the open

339   ocean. Despite a general pattern of the evolution of biological activity presented

340   by Yoon et al. (2007), it should be stressed that biological activity is very patchy

341   all over the ocean including coastal areas and the phytoplankton blooms are

342   generally governed by the availability of nutrients which themselves are supplied

343   by ocean currents and upwelling and become unpredictable on a day-to-week

344   time scale.

345

346   **3.1.2 Secondary components**

347   The inorganic secondary species ($nssSO_4$ and NH_4) are presented in top right of

348   Figure 1 along with an aerosol neutralisation profile considering only ammonium

349   and sulphate which will be discussed later. Ammonium profile was clearly

350   secondary, as expected, due to ammonia being the principal gaseous neutralizing

351   agent in the marine boundary layer. It should be noted that the concentration

352   profile of $nssSO_4$ was pretty constant and did not follow that of the ammonium

353   profile as it could be expected considering that sulphuric acid is the main acidic

354   species in the marine boundary layer, typically neutralized by ammonium.

355    $NssSO_4$ was calculated as the difference between two relatively large numbers

356   (total measured SO_4 minus sea-salt SO_4 as inferred from a conservative tracer

357   such as Na ion). As sea salt concentration was changing quite dramatically with

358   height especially in moderate to high wind speed during winter, some ambiguity

359   must be acknowledged before interpreting $nssSO_4$ profile. In fact, if the winter

360   sulphate profiles were excluded from the average that would have improved the

361   average profile. In any event $nssSO_4$ concentrations at three different heights

362   were not significantly different (overlapping error bars), preventing any

363   conclusions with respect to apparently secondary $nssSO_4$. The uncertainty in nss-

364   sulphate determination can be the reason of the difference with respect to the

365   profile of ammonium. Looking at the profiles, it can be observed that marine

366   aerosol sampled at Mace Head is more neutralized at 30 m than closer to the sea

367   level (Figure 1 (top right) and Figure 2), even though neutralization of sulphuric

368   acid is never complete, due to scarcity of ammonia in the marine boundary layer.

369   Figure 2 shows calculated ammonium (considering neutralisation of sulphate

370   only as nitrate was more likely to be neutralised by sodium (causing chloride

371   depletion) due to scarcity of ammonia in the marine boundary layer) versus

372   measured ammonium revealing significant but consistent differences in

373   neutralisation pattern at three different heights. The neutralization profile can be

374   driven by the gaseous ammonia vertical profile, which we have no hint about, or

375   can be an indication of the importance of in-cloud processes of sulphate

376   neutralization considering also that measurements at the lowest level were

377   somewhat perturbed due to surf-zone fluxes. In fact, if the neutralization of

378   acidic sulphates occurred prevalently in clouds, after scavenging of gaseous

379   ammonia into acidic droplets, this process would occur more likely at the top of

380   the marine boundary layer, were cloud layers form, justifying the observed

381   neutralization profile.

382   The secondary organic species (MSA, WSOM and WSON) are presented in the

383   bottom left of Figure 1. The MSA exhibited a "mixed profile" with steep increase

384   of concentration between 3 and 10 m, typical of secondary products and

385   decreasing profile between 10 and 30 m, likely due to condensation of MSA on

386   sea salt particles (Hopkins et al., 2008) that causes an apparently primary profile.

387   A clear secondary profile was observed for WSOM also, reaffirming the

388   conclusion of Ceburnis et al. (2008) on the secondary origin of WSOM. The

389   water soluble organic nitrogen concentration pattern is presented in the bottom

390   left of Figure 1. WSON presents a mixed profile, therefore, it is not possible to

391   attribute it to primary or secondary formation processes unambiguously. WSON

392   concentration in aerosol samples is generally difficult to quantify as it is

393   calculated as the difference between the total nitrogen (TN) and the water soluble

394   inorganic nitrogen (WSIN) – both numbers of similar magnitude. As a result,

395   only 7 complete profiles could be derived out of 15 samples and should,

396   therefore, be considered cautiously (8 profiles were discarded as incomplete, i.e.

397   missing determined concentration at one or two levels). Along with WSON,

398   aliphatic amines were analysed following Facchini et al. (2008a). WSON, DMA

399   and DEA are minor constituents of marine aerosol, together typically accounting

400   for 10% of secondary organic aerosol (Facchini et al., 2008a). While the

401   magnitude of their absolute concentrations maybe misleading – amines can be

402   important species facilitating new particle production in the marine atmosphere

403   (Dall'Osto et al., 2012) – quantification of their concentration by offline chemical

404   analysis is always challenging. Concentrations of DMA and DEA at the lowest

405   height were mostly below detection limit and, therefore, no profile can be

406   provided for these species with confidence. However, the fact that detectable

407   concentrations were always observed at 30 m, strongly suggests a secondary

408   origin for DMA and DEA.

409   The well-established aerosol chemical compounds such as nitrate, oxalate, MSA

410   and less well established WSON were all studied for the first time using flux-

411   gradient method. The concentration profiles of the above compounds have not

412   demonstrated that the species were secondary, despite well-established

413   knowledge of their secondary formation in the atmosphere aloft (boundary layer,

414   clouds or free troposphere) (Seinfeld and Pandis, 2006; Facchini et al., 2008a;

415   Rinaldi et al., 2011). Figure 3 is presented for elucidating an apparent "primary"

416   profile of nitrate and oxalate which is due to aforementioned species condensing

417   or reacting with sea spray particles. MSA by contrast has the weakest if any

418   relationship with sea salt. Figure 3 (top left) presents the relationship between

419   nitrate and sea salt mass which appears as linear with the exception of 2-3

420   outliers. The outliers likely appeared due to the presence of trace amounts of

421   ammonium nitrate. Ammonium nitrate is generally considered as anthropogenic

422   species and can be present in trace amounts due to pollution background. The

423   trace amount was really small, 20-30 ng m^{-3} of nitrate only re-affirming

424   cleanness of the marine atmosphere studied at Mace Head. Despite a strong

425   similarity in concentration pattern of nitrate and primary sea salt it is

426   inconceivable that a significant amount of primary nitrate can be produced

427   (nitrate is a tracer nutrient in sea water) and, therefore, must be derived by

428   condensation of nitric acid on pre-existing sea salt.

429   The relationship of sea salt and oxalate (top right plot of Figure 3) was slightly

430   different from nitrate and somewhat similar to MSA. While oxalate (and MSA)

431   can indeed condense on pre-existing sea salt particles, its chemical pathways of

432   secondary production are different and more diverse than that of nitrate as were

433   detailed by Rinaldi et al. (2011). Oxalate can also be present in sea-spray

434   particles via oxidation of organic matter in sea-spray and, therefore, dependent

435 on biological activity of the ocean. As opposed to nitrate, the oxalate was not

436 enhanced in the presence of copious amounts of sea salt particles suggesting that

437 oxalic acid is not an ever present species in the boundary layer which would

438 readily condense on sea salt. The same was true for MSA which showed even

439 less of a relationship with the sea salt mass (bottom left of Figure 3). MSA

440 production is photochemically driven and time limited considering the gradient

441 footprint of 0.2-10 km in the coastal zone. The water soluble organic nitrogen

442 (WSON) is a relatively less studied class of chemical compounds of which

443 amines are the best known compounds (Facchini et al., 2008a). The observed

444 concentrations of DEA, DMA and WSON were very similar to the ones

445 documented by Facchini et al. (2008a) in clean marine air masses. Both WSON

446 and the sum of dimethylamine (DMA) and diethylamine (DEA) exhibited a

447 relationship with water soluble organic carbon (WSOC) (bottom right of Figure

448 3) with positive correlations ($r = 0.58$ and $r = 0.37$, $P<<0.01$). Note, that the sum

449 of amines is presented in absolute concentration while that of WSON as a mass

450 of nitrogen. The comparison between the WSON and the sum of amines

451 suggested that the amines were likely the dominant species of WSON, but

452 difficult to determine due to detection limit as noted above.

453 WSOC/WSON/DEA/DMA relationship is presented in Figure 3 (bottom right)

454 for exploratory purposes as these interrelationships have not been examined or

455 discussed in the context of marine aerosol.

456

457 **3.2   WIOM and chlorophyll-a relationship**

458 Gantt et al. (2011) suggested that fractional contribution of organic matter in sea

459 spray particles depends not only on the biological activity in oceanic surface

460 waters, but also the wind speed at the point of emission. The data of this study

461 were examined according to the approach of Gantt et al. (2011). Figure 4

462 presents inter-relationship between fractional organic matter contribution to sea

463 spray (OM_{ss}=WIOM/(WIOM+SS)), wind speed using the data set of this study

464 which were not part of the dataset used by Gantt et al. (2011) and chlorophyll-a

465 concentration in the open ocean area area upwind from Mace Head as examined

466 in Rinaldi et al. (2013). Open ocean region was 10x10deg or roughly 1000x1000

467 km upwind from Mace Head. Only WIOM was taken into account in calculating

468 fractional contribution of OM in sea spray. Notwithstanding the fact that a

469 fraction of measured WSOM was associated with sea spray and formed by
470 processing primary WIOM, quantitative assessment is beyond current
471 knowledge. Both relationships were statistically significant (P<<0.01) and
472 explained 58% of the variance (top plots) suggesting an overlap. The obtained
473 relationships agree well with the relationship reported by Rinaldi et al. (2013)
474 based on an extended dataset (reaching 70% OM fractional contribution at 1.0 μg
475 m^{-3}). Further, when the former relationship is coloured by the chlorophyll-a
476 concentration in the oceanic region upfront of the measurement location at Mace
477 Head, no apparent pattern can be discerned (bottom plot) apart from general
478 mutual relationship. It can be concluded, that while the OM_{ss} dependence on
479 wind speed is significant it may actually be weaker than the OM_{ss} and
480 chlorophyll-a relationship due to inter-dependence of wind speed and
481 chlorophyll-a. Typically, wind speed is higher in winter when chlorophyll-a
482 concentration is at its lowest and vice versa – thereby contributing to the
483 excessive covariance of OM_{ss} and wind speed. Note that seasonal inverse
484 relationship between wind speed and chlorophyll-a is simply a coincidence. The
485 direct effect of wind speed could be elucidated if very low OM fractional
486 contributions were often observed during summer or high fractional
487 contributions during winter which was never the case with very few exceptions
488 (only two). However, it is hardly a coincidence that the two points (top right plot
489 in Figure 4) with rather similar chlorophyll-a concentration (~0.4 μg m^{-3})
490 residing outside the 95% confidence bands are the ones characterised with the
491 lowest and the highest wind speed re-affirming that the effect of wind speed is
492 real, but difficult to separate from the OM_{ss} and chlorophyll-a relationship. In
493 conclusion, wind stress is the driver of primary sea spray production, but
494 biological productivity is modifying sea spray chemical composition. Last but
495 not least, it is important to note that the chlorophyll-a concentration is only useful
496 as a proxy of biological activity which can affect a fraction of primary organic
497 matter in sea spray in different ways depending on the trophic level interactions
498 (O'Dowd et al., 2015).
499
500 **3.3 Flux estimates and implications for existing sea spray source**
501 **functions**
502

503 The surface mixed layer (SML) height obtained from LIDAR measurements
504 varied in the range of 846-1102 meters among the eight periods for which
505 overlapping LIDAR measurements were available. An occasional formation of
506 nocturnal boundary layer was ignored here due to the nature and resolution of the
507 gradient samples. It is important to note that the boundary layer filling time
508 constant τ is a feature of a particular low pressure system(s) arriving at the point
509 of observation in a connecting flow. However, the sample deployment time (7
510 days) and the actual number of sampled hours within particular sector prevented
511 estimating sample dependent constant τ which was set at 2 days with the
512 uncertainty of ±1day. SML measurements were available for 10 out of 15
513 gradient samples. The sea salt fluxes estimated using Equation 1 (and using sea
514 salt concentration at 30m height) ranged from 0.3 to 3.5 ng m^{-2} s^{-1} over the wind
515 speed range of 5-12 m s^{-1}. Concurrently, estimated WIOM fluxes ranged from
516 0.3 to 2.2 ng m^{-2} s^{-1} over the same wind speed range and were inversely related to
517 SS fluxes, i.e. highest SS flux estimates were accompanied by the lowest WIOM
518 fluxes conforming to fractional OM considerations in section 3.2.
519 Given the uncertainty of the estimated sea salt fluxes over the wind speed range,
520 it was necessary to compare it with the available sea spray source functions.
521 Equally important was to cover a wide range of methods used to derive fluxes.
522 Figure 5 presents the source functions for which submicron sea salt mass could
523 have been calculated and include the following: Callaghan (2013), Clarke et al.
524 (2006), Fuentes et al. (2010), Gong-Monahan (Gong, 2003), Martensson et al.
525 (2003), Ovadnevaite et al. (2012; 2013) and the boundary layer box model
526 estimates of this study. Clarke et al. (2006), Fuentes et al. (2010) and Martensson
527 et al. (2003) parameterisations were derived in either laboratory conditions or in-
528 situ surf breaking waves and coupled with Monahan and Muircheartaigh (1980)
529 whitecap parameterisation to yield flux wind speed relationship. All of the above
530 parameterisations were based on exploring SMPS measurement data. Gong et al.
531 (2003) used an original Monahan (Monahan et al., 1982) parameterisation
532 obtained in the laboratory experiment and adjusted for the size range <0.2 μm.
533 Callaghan (2013) used in-situ whitecap measurements developing a discrete
534 whitecap method and Gong (2003) parameterisation to obtain submicrometer sea
535 salt mass flux and wind speed parameterisation. While the Callaghan (2013)
536 paper proposes a new SSA source function, it pulls the whitecap parameterisation

537   from the Callaghan et al. (2008) paper. One of the primary findings of the
538   Callaghan (2013) work was the importance of choosing the correct whitecap
539   timescale for the discrete whitecap method in particular. Finally, Ovadnevaite et
540   al. (2012; 2013) and gradient method of this study used ambient measurement
541   data (real-time AMS sea salt measurements, SMPS measurements and PM1
542   gradient measurements, respectively), but were completely independent of each
543   other and different in terms of the utilised methods. It should be noted that,
544   despite the fact that the latter methods estimated net fluxes as opposed to
545   production fluxes measured in the laboratory experiments, deposition fluxes are
546   typically small, in the order of 2-4% in the submicron particle range (Hoppel et
547   al., 2002). The presented parameterisations fall into two regimes as seen in
548   Figure 4: Clarke et al. (2006), Fuentes et al. (2010), Gong (2003) and Martensson
549   et al. (2003) parameterisations exhibit a significantly higher wind-speed
550   dependency compared to the more recent parameterisations by Callaghan (2013)
551   or Ovadnevaite et al. (2012; 2013). The split into regimes is even more apparent
552   on a linear flux scale. It must be noted that up until now majority of global or
553   regional scale models used one of the former four parameterisations (Gong,
554   2003; Martensson et al., 2003; Clarke et al., 2006; Fuentes et al., 2010) typically
555   resulting in the overestimated mass concentrations (e.g. (Textor et al., 2006; de
556   Leeuw et al., 2011). It should be also noted that the applicability of the Clarke et
557   al.(2006), Fuentes et al. (2010) and Martensson et al. (2003) parameterisations
558   come more questionably for higher wind speeds as the divergence between the
559   more recent parameterisations becomes progressively greater and the slope of the
560   dependency curve becomes unrealistically steep.
561   Figure 5 reiterates the conclusion made by Ovadnevaite et al. (2012) that the sea
562   spray parameterisations needed further improvements in both whitecap
563   parameterisation, now addressed by Callaghan (2013); and the more realistic
564   differential aerosol productivity term recently advanced by Ovadnevaite et
565   al.(2013). It is reasonable to suggest that the laboratory experiments or the *in-situ*
566   surf breaking waves were most likely unable to realistically replicate air
567   entrainment by the open ocean breaking waves and consequently formed bubble
568   plumes, resulting in unrealistic whitecap coverage and/or size distributions. The
569   most recently developed parameterisation by Ovadnevaite et al. (2013) advanced
570   even further by introducing Reynolds number instead of a commonly used wind

571   speed, thereby removing the uncertainty related to the sea wave state (during

572   rising or waning winds) and implicitly containing sea surface water temperature

573   and salinity which have been both implicated to altering aerosol production

574   (Martensson et al., 2003; Jaegle et al., 2011; Zabori et al., 2012).

575   It can be argued that the new whitecap parameterisation of Callaghan et al.

576   (2013) coupled with Clarke et al. (2006), Fuentes et al. (2010) and Martensson et

577   al. (2003) parameterisations would bring all of them closer to the more recent

578   parameterisations, however, it is important to make few distinctive comments.

579   While the Gong-Monahan parameterisation has decreased the sea salt mass flux

580   when coupled with Callaghan (2013) whitecap parameterisation instead of the

581   original Monahan (Monahan et al., 1982) whitecap parameterisation, the size

582   resolved flux remains unrealistic due to the arbitrary adjusted submicron size

583   distribution below 0.2 µm (Gong, 2003). A single mode centred at around 100

584   nm fails to reproducing submicron size distributions observed in ambient air in

585   stormy maritime boundary layer (Ovadnevaite et al., 2013). Similarly, Clarke et

586   al. (2006), Fuentes et al. (2010) and Martensson et al. (2003) parameterisations,

587   even when coupled with Callaghan (2013) whitecap parameterisation, would still

588   predict concentrations far in excess of observed concentrations. The size resolved

589   fluxes are crucial in predicting direct and indirect climate effects and have to be

590   benchmarked against the ambient rather than the laboratory measurements unless

591   both reasonably agree.

592

593   **3.4   Seasonality of observed concentrations, gradients and**
594   **estimated fluxes**

595   The sampling strategy aimed at capturing two samples per month providing that

596   clean marine conditions were prevailing and each sample lasted on average 50%

597   of time during the calendar week. In reality, fifteen samples were collected

598   covering full year (April 2008 – May 2009) as listed in Table 1. The observed

599   seasonal cycle may not have been typical, but allowed to examine gradients and

600   corresponding flux estimates associated with varying oceanic conditions

601   throughout the calendar year.

602   The observed chemical species concentrations have been typical of those

603   documented at Mace Head by Yoon et al. (2007) and Ovadnevaite et al. (2014).

604   Sea salt concentrations and respective estimated fluxes by the box model were

605   generally largest in winter (0.2-0.85 µg m^{-3} and 1.2-3.5 ng m^{-2} s^{-1}, respectively)

606   and smallest in summer (0.08-0.55 µg m^{-3} and 0.3-1.1 ng m^{-2} s^{-1}, respectively)

607   which was mainly due to the wind pattern over the North East Atlantic (Jennings

608   et al., 2003; O'Dowd et al., 2014). However, the occurrence of deep low pressure

609   system in e.g. September 2008 with corresponding high winds resulted in high

610   sea salt concentrations and large fluxes despite seasonal pattern suggesting

611   otherwise. On the other hand, it has been suggested that sea salt can be replaced

612   in primary sea spray by primary marine OM (Oppo et al., 1999; Facchini et al.,

613   2008b) in which case sea salt fluxes estimated from observed concentrations

614   would become smaller. Vaishya et al. (2012) showed that aerosol scattering

615   dependence on the wind is different between contrasting seasons suggesting the

616   effect of primary marine OM on sea spray production. However, considering the

617   uncertainties of the estimated flux by the box model, a quantitative proof of the

618   aforementioned effect was not possible.

619   The WIOM concentrations and gradients revealed a much more complex pattern.

620   The absolute concentrations were lower in winter (0.06 - 0.19 µg m^{-3}) and higher

621   in summer (0.1 - 0.44 µg m^{-3}), following the pattern of oceanic biological

622   activity lately reaffirmed by Ovadnevaite et al. (2014). The seasonal variation of

623   WIOM gradients and estimated fluxes, however, was different as the gradients

624   depended on biological activity in the flux footprint region (0.2-10 km from the

625   coast) while the fluxes depended both on the biological activity and wind speed

626   dependent sea spray production in the flux footprint area. The three distinct

627   profiles of WIOM gradients presented in Figure 3 clustered in characteristic

628   periods. The removal gradient prevailed in late spring and early summer when

629   biological activity was waning close to the coast. Yoon et al. (2007)

630   demonstrated that biological activity revealed by chlorophyll proxy has been

631   typically starting at the coast early in the season and then gradually moving off-

632   shore and northward, thereby affecting the WIOM gradients and corresponding

633   fluxes. The production gradient manifested itself during late summer and early

634   spring, reaffirming conclusions made by Yoon et al. (2007) about the presence of

635   two or more phytoplankton bloom peaks during the biologically active season.

636   The mixed WIOM profile prevailed during autumn when biological activity was

637   waning over the North East Atlantic, but at the same time shifting closer to the

638   coast. The spatial resolution of satellite chlorophyll data and the large errors

639 associated with coastal interfaces in particular (Darecki and Stramski, 2004;
640 Gregg and Casey, 2007) prevented exploring the relationship between coastal
641 biological activity and WIOM gradients and its fractional contribution to sea
642 spray. Previous chapter demonstrated that open ocean biological activity revealed
643 by the chlorophyll proxy upwind from Mace Head correlated well with the
644 WIOM fractional contribution to sea spray validating the seasonal pattern of
645 WIOM gradients and fluxes. Therefore, despite WIOM gradient profiles were
646 found dependent on biological activity in the flux footprint area (0.2-10 km) that
647 did not invalidate a relationship between WIOM and chlorophyll in the open
648 ocean over the North East Atlantic. Recently, Long et al. (2014) demonstrated a
649 diurnal signal in primary marine OM production suggesting that sunlight-
650 mediated biogenic surfactants may have a previously overlooked role. Time
651 resolution of the gradient samples (weekly) and randomness of clean sector
652 sampling during day and night, prevented exploring the effect in this study.
653 However, the results of this study do not contradict the above study either as the
654 primary marine OM production would be enhanced in summer compared to other
655 seasons following radiation pattern.

656

657

658 **4   Conclusions**

659 Marine aerosol sources, sinks and estimated sea salt fluxes were studied over the
660 entire year by the gradient method. The chemical gradients of primary species,
661 such as sea salt, and more generally sea-spray were found to show strong
662 production flux. The fractional contribution of organic matter in submicron
663 aerosol depended linearly on chlorophyll-a concentration conforming to
664 previously published relationships. The study of certain secondary species
665 (nitrate, oxalate, MSA, WSON) was performed for the first time revealing their
666 mainly secondary origin, but also interactions with primary sea spray. The
667 seasonal pattern of concentrations, gradients and estimated fluxes by the box
668 model highlighted complex interactions between biological activity, especially in
669 the flux footprint area, and wind driven sea spray production. The estimated sea
670 salt mass fluxes by the box model compared well with sea salt source functions
671 which used carefully selected ambient measurement data. The critical evaluation
672 of the range of available flux-wind-speed parameterisations highlighted

673   significant advances in the development of the sea spray source function for the

674   benefit of global climate models.

675

688

689   **References**

690   Ahlm, L., Nilsson, E. D., Krejci, R., Martensson, E. M., Vogt, M., and Artaxo,
691   P.: Aerosol number fluxes over the Amazon rain forest during the wet season,
692   Atmos. Chem. Phys., 9, 9381-9400, 2009.

693   Blanchard, D. C.: Sea-to-air transport of surface active material, Science, 146,
694   396-397, 1964.

695   Brooks, I. M., Yelland, M. J., Upstill-Goddard, R. C., Nightingale, P. D., Archer,
696   S., d'Asaro, E., Beale, R., Beatty, C., Blomquist, B., Bloom, A. A., Brooks, B. J.,
697   Cluderay, J., Coles, D., Dacey, J., DeGrandpre, M., Dixon, J., Drennan, W. M.,
698   Gabriele, J., Goldson, L., Hardman-Mountford, N., Hill, M. K., Horn, M., Hsueh,
699   P. C., Huebert, B., de Leeuw, G., Leighton, T. G., Liddicoat, M., Lingard, J. J.
700   N., McNeil, C., McQuaid, J. B., Moat, B. I., Moore, G., Neill, C., Norris, S. J.,
701   O'Doherty, S., Pascal, R. W., Prytherch, J., Rebozo, M., Sahlee, E., Salter, M.,
702   Schuster, U., Skjelvan, I., Slagter, H., Smith, M. H., Smith, P. D., Srokosz, M.,
703   Stephens, J. A., Taylor, P. K., Telszewski, M., Walsh, R., Ward, B., Woolf, D.
704   K., Young, D., and Zemmelink, H.: Physical Exchanges at the Air-Ses Interface
705   Uk-Solas Field Measurements, Bulletin of the American Meteorological Society,
706   90, 629-644, 10.1175/2008bams2578.1, 2009.

707   Buzorius, G., Rannik, U., Makela, J. M., Vesala, T., and Kulmala, M.: Vertical
708   aerosol particle fluxes measured by eddy covariance technique using
709   condensational particle counter, Journal of Aerosol Science, 29, 157-171,
710   10.1016/s0021-8502(97)00458-8, 1998.

711   Callaghan, A., de Leeuw, G., Cohen, L., and O'Dowd, C. D.: Relationship of
712   oceanic whitecap coverage to wind speed and wind history, Geophys. Res. Lett.,
713   35, L23609,
714   10.1029/2008gl036165, 2008.

715   Callaghan, A. H.: An improved whitecap timescale for sea spray aerosol
716   production flux modeling using the discrete whitecap method, J. Geophys. Res.-
717   Atmos., 118, 9997-10010, 10.1002/jgrd.50768, 2013.

718   Cavalli, F., Facchini, M. C., Decesari, S., Mircea, M., Emblico, L., Fuzzi, S.,
719   Ceburnis, D., Yoon, Y. J., O'Dowd, C. D., Putaud, J. P., and Dell'Acqua, A.:
720   Advances in characterization of size-resolved organic matter in marine aerosol
721   over the North Atlantic, J. Geophys. Res.-Atmos., 109, D24215,
722   10.1029/2004jd005137, 2004.

723   Ceburnis, D., Garbaras, A., Szidat, S., Rinaldi, M., Fahrni, S., Perron, N.,
724   Wacker, L., Leinert, S., Remeikis, V., Facchini, M. C., Prevot, A. S. H.,
725   Jennings, S. G., Ramonet, M., and O'Dowd, C. D.: Quantification of the
726   carbonaceous matter origin in submicron marine aerosol by C-13 and C-14
727   isotope analysis, Atmos. Chem. Phys., 11, 8593-8606, 10.5194/acp-11-8593-
728   2011, 2011.

729   Ceburnis, D., O'Dowd, C. D., Jennings, G. S., Facchini, M. C., Emblico, L.,
730   Decesari, S., Fuzzi, S., and Sakalys, J.: Marine aerosol chemistry gradients:

731   Elucidating primary and secondary processes and fluxes, Geophys. Res. Lett., 35,
732   L07804, 10.1029/2008gl033462, 2008.

733   Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic
734   phytoplankton, atmospheric sulfur, cloud albedo and climate, Nature, 326, 655-
735   661, 1987.

736   Clarke, A. D., Owens, S. R., and Zhou, J. C.: An ultrafine sea-salt flux from
737   breaking waves: Implications for cloud condensation nuclei in the remote marine
738   atmosphere, J. Geophys. Res.-Atmos., 111, 10.1029/2005jd006565, 2006.

739   Cooke, W. F., Jennings, S. G., and Spain, T. G.: Black carbon measurements at
740   Mace Head, 1989-1996, J. Geophys. Res.-Atmos., 102, 25339-25346,
741   10.1029/97jd01430, 1997.

742   Dall'Osto, M., Ceburnis, D., Monahan, C., Worsnop, D. R., Bialek, J., Kulmala,
743   M., Kurten, T., Ehn, M., Wenger, J., Sodeau, J., Healy, R., and O'Dowd, C.:
744   Nitrogenated and aliphatic organic vapors as possible drivers for marine
745   secondary organic aerosol growth, J. Geophys. Res.-Atmos., 117,
746   10.1029/2012jd017522, 2012.

747   Darecki, M., and Stramski, D.: An evaluation of MODIS and SeaWiFS bio-
748   optical algorithms in the Baltic Sea, Remote Sensing of Environment, 89, 326-
749   350, 10.1016/j.rse.2003.10.012, 2004.

750   de Leeuw, G., Andreas, E. L., Anguelova, M. D., Fairall, C. W., Lewis, E. R.,
751   O'Dowd, C., Schulz, M., and Schwartz, S. E.: Production flux of sea spray
752   aerosol, Reviews of Geophysics, 49, Rg2001, 10.1029/2010rg000349, 2011.

753   Decesari, S., Finessi, E., Rinaldi, M., Paglione, M., Fuzzi, S., Stephanou, E. G.,
754   Tziaras, T., Spyros, A., Ceburnis, D., O'Dowd, C., Dall'Osto, M., Harrison, R.
755   M., Allan, J., Coe, H., and Facchini, M. C.: Primary and secondary marine
756   organic aerosols over the North Atlantic Ocean during the MAP experiment, J.
757   Geophys. Res.-Atmos., 116, D22210, 10.1029/2011jd016204, 2011.

758   Decesari, S., Mircea, M., Cavalli, F., Fuzzi, S., Moretti, F., Tagliavini, E., and
759   Facchini, M. C.: Source attribution of water-soluble organic aerosol by nuclear
760   magnetic resonance spectroscopy, Environ. Sci. Technol., 41, 2479-2484, Doi
761   10.1021/Es0617111, 2007.

762   Facchini, M. C., Decesari, S., Rinaldi, M., Carbone, C., Finessi, E., Mircea, M.,
763   Fuzzi, S., Moretti, F., Tagliavini, E., Ceburnis, D., and O'Dowd, C. D.: Important
764   Source of Marine Secondary Organic Aerosol from Biogenic Amines, Environ.
765   Sci. Technol., 42, 9116-9121, 10.1021/Es8018385, 2008a.

766   Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M.,
767   Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M.,
768   Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated
769   by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35, L17814,
770   10.1029/2008gl034210, 2008b.

771   Farmer, D. K., Kimmel, J. R., Phillips, G., Docherty, K. S., Worsnop, D. R.,
772   Sueper, D., Nemitz, E., and Jimenez, J. L.: Eddy covariance measurements with
773   high-resolution time-of-flight aerosol mass spectrometry: a new approach to
774   chemically resolved aerosol fluxes, Atmospheric Measurement Techniques, 4,
775   1275-1289, 10.5194/amt-4-1275-2011, 2011.

776   Fratini, G., Ciccioli, P., Febo, A., Forgione, A., and Valentini, R.: Size-
777   segregated fluxes of mineral dust from a desert area of northern China by eddy
778   covariance, Atmos. Chem. Phys., 7, 2839-2854, 2007.

779   Fuentes, E., Coe, H., Green, D., de Leeuw, G., and McFiggans, G.: On the
780   impacts of phytoplankton-derived organic matter on the properties of the primary
781   marine aerosol - Part 1: Source fluxes, Atmos. Chem. Phys., 10, 9295-9317, DOI
782   10.5194/acp-10-9295-2010, 2010.

783   Gaman, A., Rannik, U., Aalto, P., Pohja, T., Siivola, E., Kulmala, M., and
784   Vesala, T.: Relaxed eddy accumulation system for size-resolved aerosol particle
785   flux measurements, Journal of Atmospheric and Oceanic Technology, 21, 933-
786   943, 10.1175/1520-0426, 2004.

787   Gantt, B., Meskhidze, N., Facchini, M. C., Rinaldi, M., Ceburnis, D., and
788   O'Dowd, C.: Wind speed dependent size-resolved parameterization for the
789   organic mass fraction of sea spray aerosol, Atmos. Chem. Phys., 11, 8777-8790,
790   10.5194/acp-11-8777-2011, 2011.

791   Geever, M., O'Dowd, C. D., van Ekeren, S., Flanagan, R., Nilsson, E. D., de
792   Leeuw, G., and Rannik, U.: Submicron sea spray fluxes, Geophys. Res. Lett., 32,
793   Artn L15810, 10.1029/2005gl023081, 2005.

794   Gong, S. L.: A parameterization of sea-salt aerosol source function for sub- and
795   super-micron particles, Glob. Biogeochem. Cycle, 17, 10.1029/2003gb002079,
796   2003.

797   Gregg, W. W., and Casey, N. W.: Sampling biases in MODIS and SeaWiFS
798   ocean chlorophyll data, Remote Sensing of Environment, 111, 25-35,
799   10.1016/j.rse.2007.03.008, 2007.

800   Haeffelin, M., Angelini, F., Morille, Y., Martucci, G., Frey, S., Gobbi, G. P.,
801   Lolli, S., O'Dowd, C. D., Sauvage, L., Xueref-Remy, I., Wastine, B., and Feist,
802   D. G.: Evaluation of Mixing-Height Retrievals from Automatic Profiling Lidars
803   and Ceilometers in View of Future Integrated Networks in Europe, Bound.-Layer
804   Meteor., 143, 49-75, 10.1007/s10546-011-9643-z, 2012.

805   Held, A., Niessner, R., Bosveld, F., Wrzesinsky, T., and Klemm, O.: Evaluation
806   and application of an electrical low pressure impactor in disjunct eddy
807   covariance aerosol flux measurements, Aerosol Science and Technology, 41,
808   510-519, 10.1080/02786820701227719, 2007.

809   Hoffman, E. J., and Duce, R. A.: Organic-carbon in marine atmospheric
810   particulate matter - concentration and particle-size distribution, Geophys. Res.
811   Lett., 4, 449-452, 1977.

812 Hopkins, R. J., Desyaterik, Y., Tivanski, A. V., Zaveri, R. A., Berkowitz, C. M.,
813 Tyliszczak, T., Gilles, M. K., and Laskin, A.: Chemical speciation of sulfur in
814 marine cloud droplets and particles: Analysis of individual particles from the
815 marine boundary layer over the California current, J. Geophys. Res.-Atmos., 113,
816 10.1029/2007jd008954, 2008.

817 Hoppel, W. A., Frick, G. M., and Fitzgerald, J. W.: Surface source function for
818 sea-salt aerosol and aerosol dry deposition to the ocean surface, J. Geophys.
819 Res.-Atmos., 107, 4382, 10.1029/2001jd002014, 2002.

820 Jaegle, L., Quinn, P. K., Bates, T. S., Alexander, B., and Lin, J. T.: Global
821 distribution of sea salt aerosols: new constraints from in situ and remote sensing
822 observations, Atmos. Chem. Phys., 11, 3137-3157, 10.5194/acp-11-3137-2011,
823 2011.

824 Jennings, S. G., Kleefeld, C., O'Dowd, C. D., Junker, C., Spain, T. G., O'Brien,
825 P., Roddy, A. F., and O'Connor, T. C.: Mace head atmospheric research station
826 characterization of aerosol radiative parameters, Boreal Environment Research,
827 8, 303-314, 2003.

828 Kawamura, K., and Sakaguchi, F.: Molecular distributions of water soluble
829 dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, J.
830 Geophys. Res.-Atmos., 104, 3501-3509, 1999.

831 Keene, W. C., Maring, H., Maben, J. R., Kieber, D. J., Pszenny, A. A. P., Dahl,
832 E. E., Izaguirre, M. A., Davis, A. J., Long, M. S., Zhou, X. L., Smoydzin, L., and
833 Sander, R.: Chemical and physical characteristics of nascent aerosols produced
834 by bursting bubbles at a model air-sea interface, J. Geophys. Res.-Atmos., 112,
835 D21202
836 10.1029/2007jd008464, 2007.

837 Leck, C., and Bigg, E. K.: Source and evolution of the marine aerosol - A new
838 perspective, Geophys. Res. Lett., 32, L19803, 10.1029/2005gl023651, 2005.

839 Lewis, E. R., Schwartz, S. E., Lewis, E. R., and Schwartz, S. E.: Sea Salt Aerosol
840 Production Fluxes: Estimates and Critical Analysis, in: Sea Salt Aerosol
841 Production: Mechanisms, Methods, Measurements and Models—A Critical
842 Review, American Geophysical Union, 299-344, 2013.

843 Long, M. S., Keene, W. C., Kieber, D. J., Frossard, A. A., Russell, L. M.,
844 Maben, J. R., Kinsey, J. D., Quinn, P. K., and Bates, T. S.: Light-enhanced
845 primary marine aerosol production from biologically productive seawater,
846 Geophys. Res. Lett., 41, 2014GL059436, 10.1002/2014GL059436, 2014.

847 Martensson, E. M., Nilsson, E. D., Buzorius, G., and Johansson, C.: Eddy
848 covariance measurements and parameterisation of traffic related particle
849 emissions in an urban environment, Atmos. Chem. Phys., 6, 769-785, 2006.

850 Martensson, E. M., Nilsson, E. D., de Leeuw, G., Cohen, L. H., and Hansson, H.
851 C.: Laboratory simulations and parameterization of the primary marine aerosol
852 production, J. Geophys. Res.-Atmos., 108, 4297,

853   10.1029/2002jd002263, 2003.

854   Martin, C. L., Longley, I. D., Dorsey, J. R., Thomas, R. M., Gallagher, M. W.,
855   and Nemitz, E.: Ultrafine particle fluxes above four major European cities,
856   Atmos. Environ., 43, 4714-4721, 10.1016/j.atmosenv.2008.10.009, 2009.

857   Meng, Z., and Seinfeld, J. H.: Time scales to achieve atmospheric gas-aerosol
858   equilibrium for volatile species, Atmos. Environ., 30, 2889-2900,
859   http://dx.doi.org/10.1016/1352-2310(95)00493-9, 1996.

860   Middlebrook, A. M., Murphy, D. M., and Thomson, D. S.: Observations of
861   organic material in individual marine particles at Cape Grim during the First
862   Aerosol Characterization Experiment (ACE 1), J. Geophys. Res.-Atmos., 103,
863   16475-16483, 1998.

864   Milroy, C., Martucci, G., Lolli, S., Loaec, S., Sauvage, L., Xueref-Remy, I.,
865   Lavric, J. V., Ciais, P., Feist, D. G., Biavati, G., and O'Dowd, C. D.: An
866   Assessment of Pseudo-Operational Ground-Based Light Detection and Ranging
867   Sensors to Determine the Boundary-Layer Structure in the Coastal Atmosphere,
868   Adv. Meteorol., 10.1155/2012/929080, 2012.

869   Mochida, M., Kitamori, Y., Kawamura, K., Nojiri, Y., and Suzuki, K.: Fatty
870   acids in the marine atmosphere: Factors governing their concentrations and
871   evaluation of organic films on sea-salt particles, J. Geophys. Res.-Atmos., 107,
872   4325, 10.1029/2001jd001278, 2002.

873   Monahan, E. C., Davidson, K. L., and Spiel, D. E.: Whitecap Aerosol
874   Productivity Deduced from Simulation Tank Measurements, Journal of
875   Geophysical Research-Oceans and Atmospheres, 87, 8898-8904, 1982.

876   Monahan, E. C., and Muircheartaigh, I. O.: Optimal Power-Law Description of
877   Oceanic Whitecap Coverage Dependence on Wind-Speed, J Phys Oceanogr, 10,
878   2094-2099, 1980.

879   Muller, C., Iinuma, Y., Karstensen, J., van Pinxteren, D., Lehmann, S., Gnauk,
880   T., and Herrmann, H.: Seasonal variation of aliphatic amines in marine sub-
881   micrometer particles at the Cape Verde islands, Atmos. Chem. Phys., 9, 9587-
882   9597, 2009.

883   Nemitz, E., Jimenez, J. L., Huffman, J. A., Ulbrich, I. M., Canagaratna, M. R.,
884   Worsnop, D. R., and Guenther, A. B.: An eddy-covariance system for the
885   measurement of surface/atmosphere exchange fluxes of submicron aerosol
886   chemical species - First application above an urban area, Aerosol Science and
887   Technology, 42, 636-657, 10.1080/02786820802227352, 2008.

888   Nilsson, E. D., Rannik, U., Kulmala, M., Buzorius, G., and O'Dowd, C. D.:
889   Effects of continental boundary layer evolution, convection, turbulence and
890   entrainment, on aerosol formation, Tellus Ser. B-Chem. Phys. Meteorol., 53,
891   441-461, 2001.

892 Norris, S. J., Brooks, I. M., de Leeuw, G., Smith, M. H., Moerman, M., and
893 Lingard, J. J. N.: Eddy covariance measurements of sea spray particles over the
894 Atlantic Ocean, Atmos. Chem. Phys., 8, 555-563, 2008.

895 O'Connor, T. C., Jennings, S. G., and O'Dowd, C. D.: Highlights of fifty years of
896 atmospheric aerosol research at Mace Head, Atmospheric Research, 90, 338-355,
897 10.1016/j.atmosres.2008.08.014, 2008.

898 O'Dowd, C., Ceburnis, D., Ovadnevaite, J., Vaishya, A., Rinaldi, M., and
899 Facchini, M. C.: Do anthropogenic, continental or coastal aerosol sources impact
900 on a marine aerosol signature at Mace Head?, Atmos. Chem. Phys., 14, 10687-
901 10704, 10.5194/acp-14-10687-2014, 2014.

902 O'Dowd, C. D., and De Leeuw, G.: Marine aerosol production: a review of the
903 current knowledge, Philosophical Transactions of the Royal Society a-
904 Mathematical Physical and Engineering Sciences, 365, 1753-1774,
905 10.1098/rsta.2007.2043, 2007.

906 O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari,
907 S., Fuzzi, S., Yoon, Y. J., and Putaud, J. P.: Biogenically driven organic
908 contribution to marine aerosol, Nature, 431, 676-680, 10.1038/Nature02959,
909 2004.

910 O'Dowd, C. D., Langmann, B., Varghese, S., Scannell, C., Ceburnis, D., and
911 Facchini, M. C.: A combined organic-inorganic sea-spray source function,
912 Geophys. Res. Lett., 35, L01801, 10.1029/2007gl030331, 2008.

913 O'Dowd, C. D., Lowe, J. A., and Smith, M. H.: The effect of clouds on aerosol
914 growth in the rural atmosphere, Atmospheric Research, 54, 201-221, 2000.

915 O'Dowd, C. D., Smith, M. H., Consterdine, I. E., and Lowe, J. A.: Marine
916 aerosol, sea-salt, and the marine sulphur cycle: A short review, Atmos. Environ.,
917 31, 73-80, 1997.

918 O'Dowd, C., Ceburnis, D., Ovadnevaite, J., Bialek, J., Stengel, D. B., Zacharias,
919 M., Nitschke, U., Connan, S., Rinaldi, M., Fuzzi, S., Decesari, S., Cristina
920 Facchini, M., Marullo, S., Santoleri, R., Dell'Anno, A., Corinaldesi, C.,
921 Tangherlini, M., and Danovaro, R.: Connecting marine productivity to sea-spray
922 via nanoscale biological processes: Phytoplankton Dance or Death Disco?,
923 Scientific Reports, 5, 14883, 10.1038/srep14883, 2015.

924 Oppo, C., Bellandi, S., Innocenti, N. D., Stortini, A. M., Loglio, G., Schiavuta,
925 E., and Cini, R.: Surfactant components of marine organic matter as agents for
926 biogeochemical fractionation and pollutant transport via marine aerosols, Marine
927 Chemistry, 63, 235-253, 1999.

928 Ovadnevaite, J., Ceburnis, D., Canagaratna, M., Berresheim, H., Bialek, J.,
929 Martucci, G., Worsnop, D. R., and O'Dowd, C.: On the effect of wind speed on
930 submicron sea salt mass concentrations and source fluxes, J. Geophys. Res.-
931 Atmos., 117, 10.1029/2011jd017379, 2012.

932   Ovadnevaite, J., Ceburnis, D., Leinert, S., Dall'Osto, M., Canagaratna, M.,
933   O'Doherty, S., Berresheim, H., and O'Dowd, C.: Submicron NE Atlantic marine
934   aerosol chemical composition and abundance: Seasonal trends and air mass
935   categorization, J. Geophys. Res.-Atmos., 119, 11850-11863,
936   10.1002/2013jd021330, 2014.

937   Ovadnevaite, J., Manders, A., de Leeuw, G., Monahan, C., Ceburnis, D., and
938   O'Dowd, C. D.: A sea spray aerosol flux parameterization encapsulating wave
939   state, Atmos. Chem. Phys. Discuss., 13, 23139-23171, 10.5194/acpd-13-23139-
940   2013, 2013.

941   Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Fuzzi, S., Ceburnis, D.,
942   O'Dowd, C. D., Sciare, J., Burrows, J. P., Vrekoussis, M., Ervens, B., Tsigaridis,
943   K., and Facchini, M. C.: Evidence of a natural marine source of oxalic acid and a
944   possible link to glyoxal, J. Geophys. Res.-Atmos., 116, D16204,
945   10.1029/2011jd015659, 2011.

946   Rinaldi, M., Facchini, M. C., Decesari, S., Carbone, C., Finessi, E., Mircea, M.,
947   Fuzzi, S., Ceburnis, D., Ehn, M., Kulmala, M., de Leeuw, G., and O'Dowd, C.
948   D.: On the representativeness of coastal aerosol studies to open ocean studies:
949   Mace Head - a case study, Atmos. Chem. Phys., 9, 9635-9646, 2009.

950   Rinaldi, M., Fuzzi, S., Decesari, S., Marullo, S., Santoleri, R., Provenzale, A.,
951   von Hardenberg, J., Ceburnis, D., Vaishya, A., O'Dowd, C. D., and Facchini, M.
952   C.: Is chlorophyll-a the best surrogate for organic matter enrichment in
953   submicron primary marine aerosol?, J. Geophys. Res.-Atmos., 118, 4964-4973,
954   10.1002/jgrd.50417, 2013.

955   Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.:
956   Carbohydrate-like composition of submicron atmospheric particles and their
957   production from ocean bubble bursting, Proceedings of the National Academy of
958   Sciences of the United States of America, 107, 6652-6657,
959   10.1073/pnas.0908905107, 2010.

960   Sciare, J., Favez, O., Sarda-Esteve, R., Oikonomou, K., Cachier, H., and Kazan,
961   V.: Long-term observations of carbonaceous aerosols in the Austral Ocean
962   atmosphere: Evidence of a biogenic marine organic source, J. Geophys. Res.-
963   Atmos., 114, D15302, 10.1029/2009jd011998, 2009.

964   Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics – from air
965   pollution to climate change Wiley Interscience, New York, 1232 pp., 2006.

966   Textor, C., Schulz, M., Guibert, S., Kinne, S., Balkanski, Y., Bauer, S., Berntsen,
967   T., Berglen, T., Boucher, O., Chin, M., Dentener, F., Diehl, T., Easter, R.,
968   Feichter, H., Fillmore, D., Ghan, S., Ginoux, P., Gong, S., Kristjansson, J. E.,
969   Krol, M., Lauer, A., Lamarque, J. F., Liu, X., Montanaro, V., Myhre, G., Penner,
970   J., Pitari, G., Reddy, S., Seland, O., Stier, P., Takemura, T., and Tie, X.: Analysis
971   and quantification of the diversities of aerosol life cycles within AeroCom,
972   Atmos. Chem. Phys., 6, 1777-1813, 2006.

973 Turekian, V. C., Macko, S. A., and Keene, W. C.: Concentrations, isotopic
974 compositions, and sources of size-resolved, particulate organic carbon and
975 oxalate in near-surface marine air at Bermuda during spring, J. Geophys. Res.-
976 Atmos., 108, 4157, 10.1029/2002jd002053, 2003.

977 Vaishya, A., Jennings, S. G., and O'Dowd, C.: Wind-driven influences on aerosol
978 light scattering in north-east Atlantic air, Geophys. Res. Lett., 39,
979 10.1029/2011gl050556, 2012.

980 Yoon, Y. J., Ceburnis, D., Cavalli, F., Jourdan, O., Putaud, J. P., Facchini, M. C.,
981 Decesari, S., Fuzzi, S., Sellegri, K., Jennings, S. G., and O'Dowd, C. D.:
982 Seasonal characteristics of the physicochemical properties of North Atlantic
983 marine atmospheric aerosols, J. Geophys. Res.-Atmos., 112, D04206,
984 10.1029/2005jd007044, 2007.

985 Zabori, J., Matisans, M., Krejci, R., Nilsson, E. D., and Strom, J.: Artificial
986 primary marine aerosol production: a laboratory study with varying water
987 temperature, salinity, and succinic acid concentration, Atmos. Chem. Phys., 12,
988 10709-10724, 10.5194/acp-12-10709-2012, 2012.
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991   Table 1. Gradient sample weekly collection time scale and the number of hours

992   each sample was sampled during 13 month period in 2008-2009.

Sampling period	Dura tion, h	Sampling period	Dura tion, h	Sampling period	Dura tion, h
10-15/04/2008	36.8	30/06-07/07/2008	24.4	11-18/12/2008	72.8
24-29/04/2008	72.6	14-22/07/2008	147.5	14-21/01/2009	74.8
29/04-07/05/2008	10.3	22-29/08/2008	146.5	25/02-04/03/2009	131.5
27/05-06/06/2008	53.0	08-18/09/2008	84.0	04-11/03/2009	121.5
25/06-30/06/2008	69.3	30/09-10/10/2008	106.7	05-12/05/2009	87.7

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995   Table 2. Absolute concentration ranges of measured chemical species.

Chemical species	Concentration range, $\mu g\ m^{-3}$
Sea salt (SS)	0.066-2.571
Nss SO_4	0.042-0.829
NO_3	0.001-0.037
NH_4	0.001-0.127
MSA	0.002-0.428
WSOM	0.047-1.568
WIOM	0.061-0.990
WSON	0.001-0.071
DMA	0.001-0.052
DEA	0.001-0.082
Oxalate	0.002-0.059

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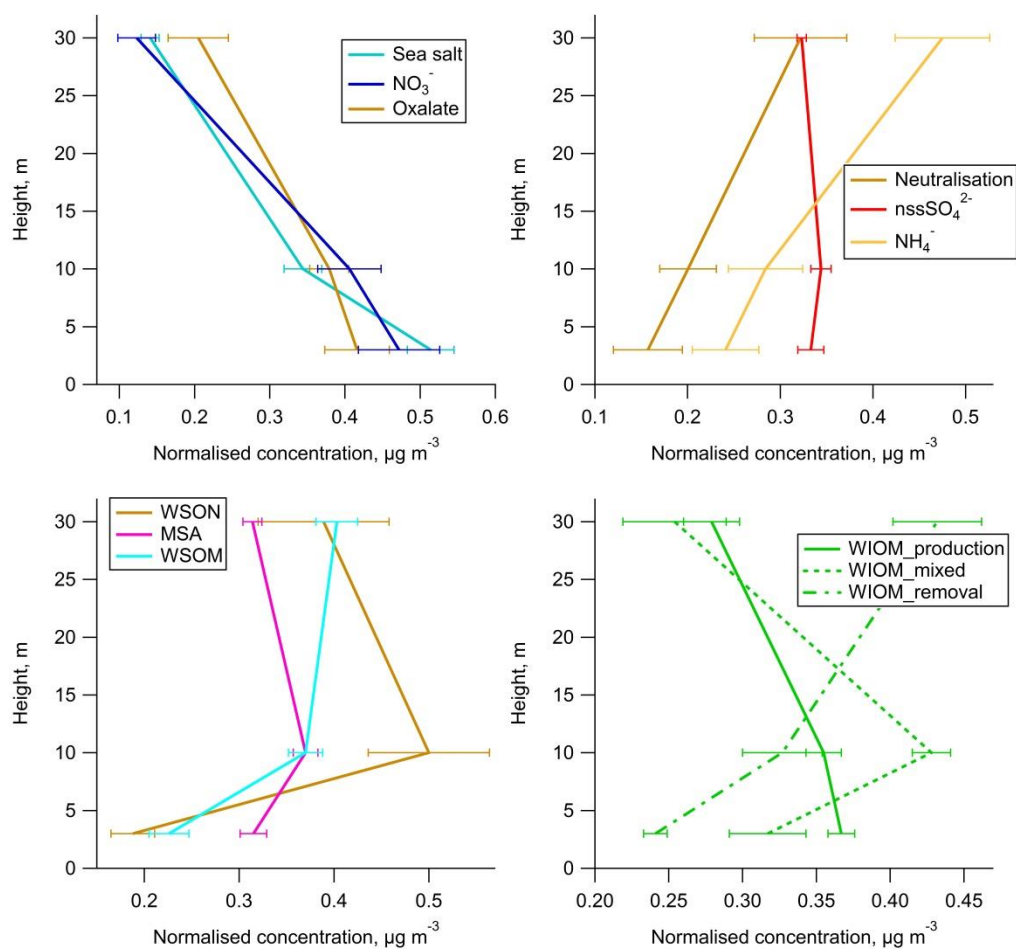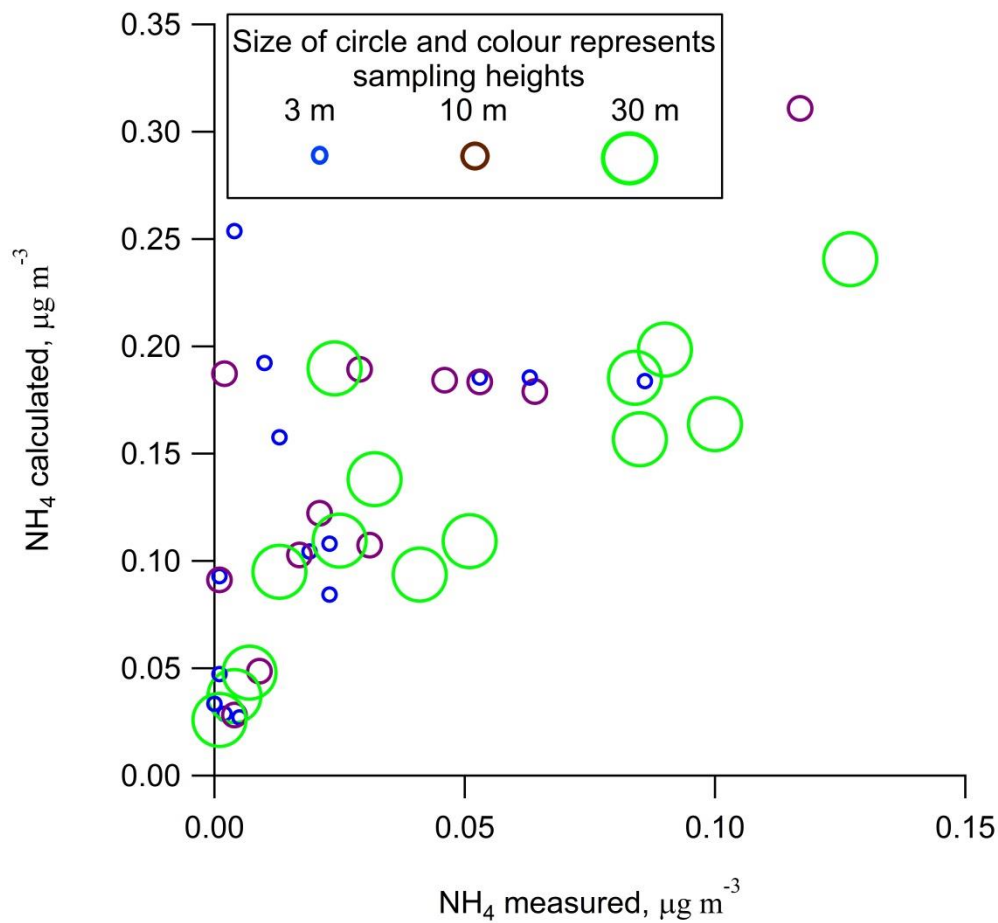
Figure 1. The gradient profiles of chemical species studied: species resembling
primary production (top left); inorganic species resembling secondary production
(top right); organic secondary species (bottom left) and water insoluble organic
matter split into production, removal and mixed profiles (bottom right).

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1010 Figure 2. A scatter plot of sulphate neutralisation by ammonium with respect to
1011 sampling height. Marine aerosol sampled at Mace Head is more neutralized at 30
1012 m than closer to the sea level, but is never complete, due to scarcity of ammonia
1013 in the marine boundary layer. The calculated ammonium on Y axis takes into
1014 account neutralisation of sulphate only as nitrate was more likely to be
1015 neutralised by sodium (causing chloride depletion).
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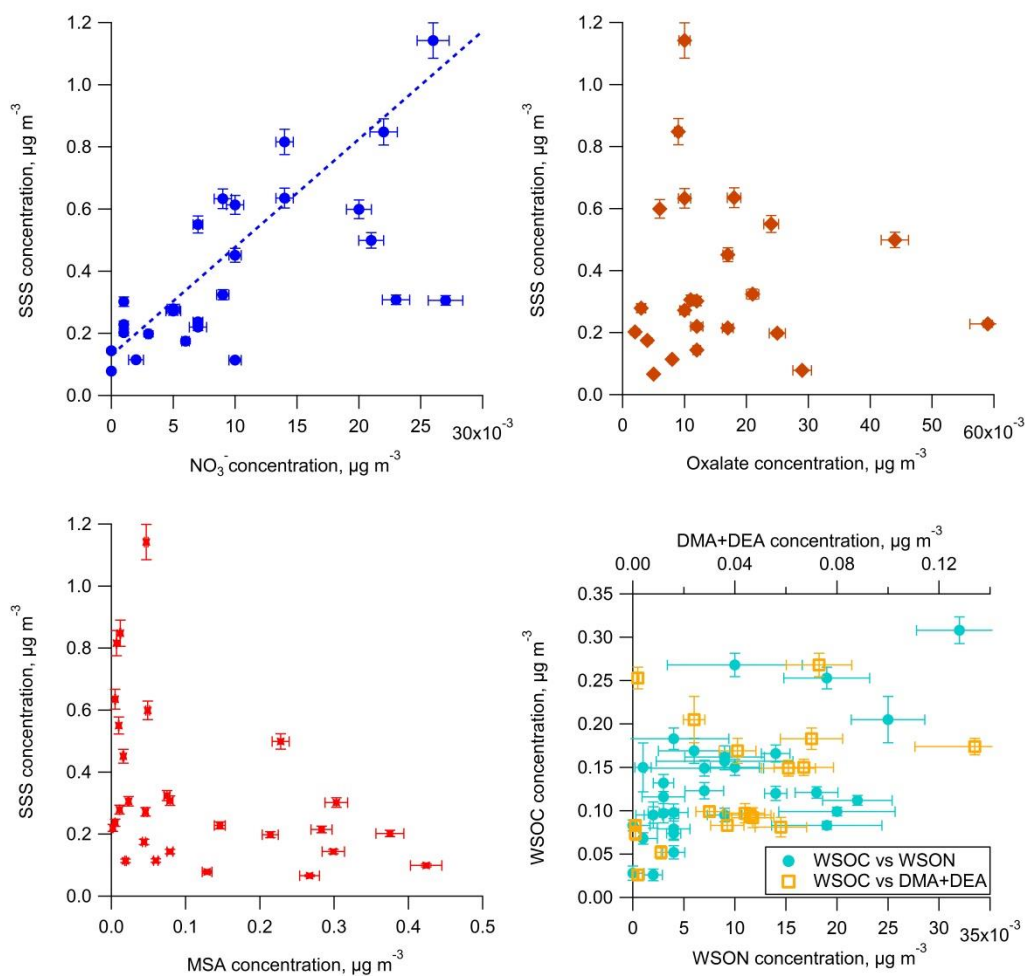
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1019 Figure 3. Plots of sea salt and secondary species which resembled primary
1020 production concentration pattern: SS vs NO$_3$ (top left); SS vs Oxalate (top right);
1021 SS vs MSA (bottom left) and WSOC vs WSON (also plotted as the sum of
1022 dimethylamine and diethylamine)(bottom right). Note, that WSOC and WSON
1023 concentration are presented as µg of carbon or nitrogen mass, respectively, while
1024 all other species reported in absolute species concentrations.
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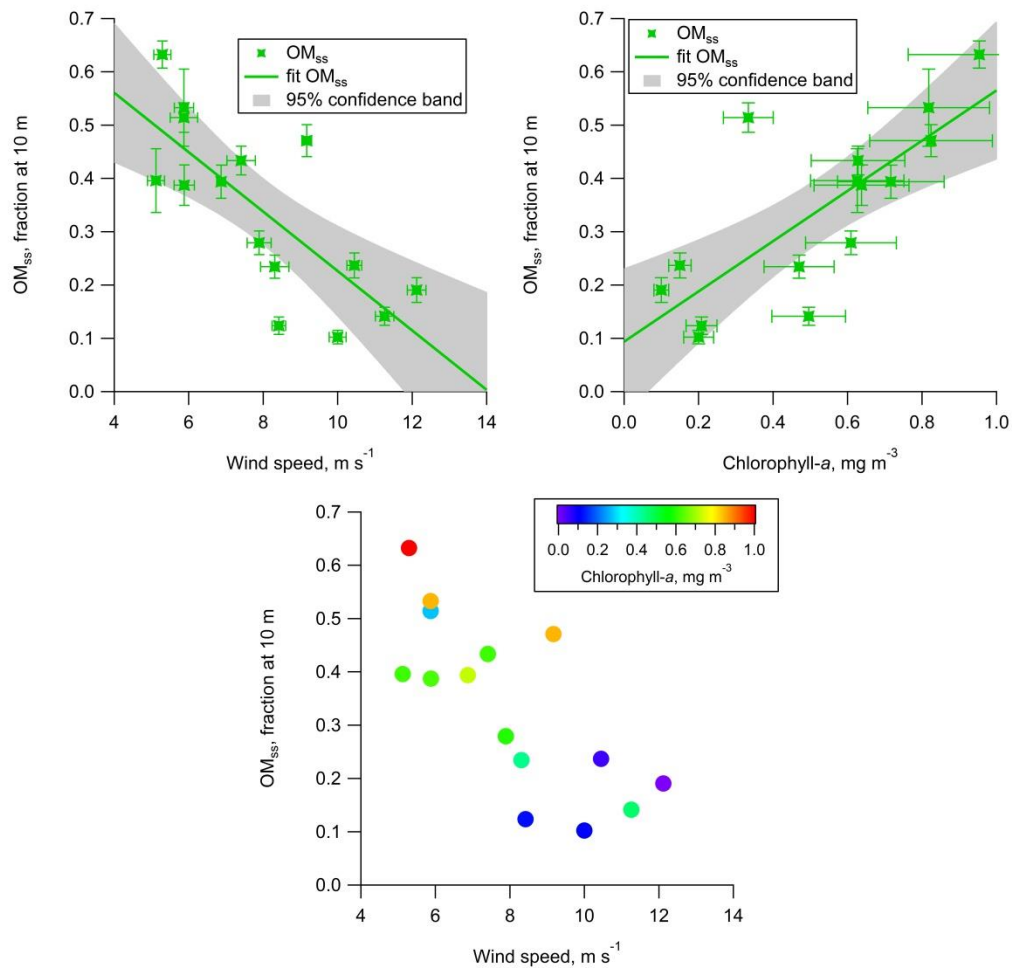
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1028   Figure 4. Effect of wind speed and chlorophyll-a concentration on the fractional

1029   contribution of organic matter in sea spray particles (OM_{ss}): OM_{ss} vs WS (top

1030   left); OM_{ss} vs chlorophyll-a (top right) and OM_{ss} vs WS coloured by chlorophyll-

1031   a (bottom). Individual uncertainties of the flux and wind speed marked with caps

1032   while the grey area denotes 95% confidence bands of the fitted parameterisation.

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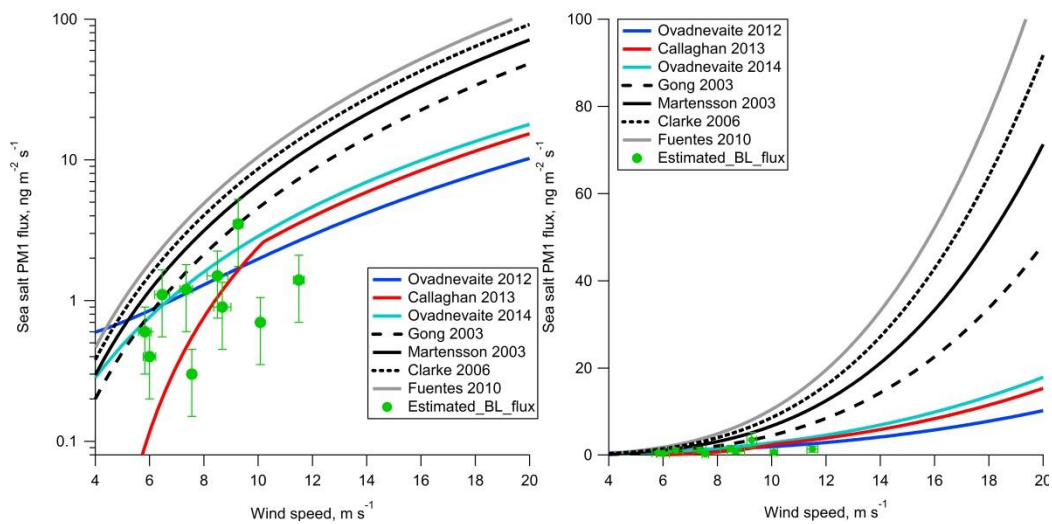
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Figure 5. A comparison of the most often used and recently developed sea spray and wind speed parameterisations in log scale (left) and linear scale (right). The estimated boundary layer fluxes by the box model (green circles) were not fitted against the wind speed due to the uncertainty related to the boundary layer filling time constant constituting the bulk of the total uncertainty.

1041

1042 Table S1. Measurement uncertainties of concentration profiles for individual
1043 chemical species.

ID sample	Height	NH4	NO3	WSON	WSOC	WIOC	Na	SO4	dma	dea	Oxa	MSA	Nss SO4
MH100408	3	6%	5%	92%	16%	11%	5%	5%	<DL	<DL	5%	5%	6%
MH100408	10	5%	5%	61%	13%	10%	5%	5%	<DL	<DL	5%	5%	6%
MH100408	30	5%	5%	55%	9%	9%	5%	5%	9%	15%	5%	5%	5%
MH240408	3	8%	5%	49%	10%	12%	5%	5%	<DL	<DL	5%	5%	6%
MH240408	10	5%	5%	27%	8%	10%	5%	5%	<DL	<DL	5%	5%	6%
MH240408	30	5%	29%	77%	6%	9%	5%	5%	9%	15%	5%	5%	5%
MH290408	3	29%	5%	<DL	49%	26%	5%	5%	<DL	<DL	<DL	5%	6%
MH290408	10	32%	5%	<DL	22%	29%	5%	5%	<DL	<DL	<DL	5%	6%
MH290408	30	13%	24%	10%	7%	15%	5%	5%	9%	15%	<DL	5%	5%
MH270508	3	5%	5%	<DL	8%	12%	5%	5%	<DL	<DL	5%	5%	6%
MH270508	10	5%	8%	41%	8%	10%	5%	5%	<DL	<DL	10%	5%	5%
MH270508	30	5%	<DL	125%	7%	10%	5%	5%	9%	15%	<DL	5%	5%
MH250608	3	20%	5%	34%	7%	15%	5%	5%	9%	<DL	5%	5%	7%
MH250608	10	5%	11%	77%	6%	11%	5%	5%	<DL	<DL	5%	5%	5%
MH250608	30	5%	<DL	<DL	5%	11%	5%	5%	9%	15%	<DL	5%	5%
MH300608	3	<DL	5%	<DL	22%	22%	5%	5%	<DL	<DL	5%	5%	6%
MH300608	10	<DL	5%	105%	19%	15%	5%	5%	<DL	<DL	5%	5%	6%
MH300608	30	7%	7%	15%	13%	13%	5%	5%	9%	15%	5%	5%	5%
MH140708	3	5%	32%	28%	6%	10%	5%	5%	9%	15%	5%	5%	5%
MH140708	10	5%	<DL	15%	5%	12%	5%	5%	<DL	<DL	5%	5%	5%
MH140708	30	5%	<DL	28%	5%	13%	5%	5%	9%	15%	5%	5%	5%
MH220808	3	5%	5%	23%	5%	19%	5%	5%	9%	15%	5%	5%	5%
MH220808	10	5%	5%	13%	5%	24%	5%	5%	<DL	<DL	5%	5%	5%
MH220808	30	5%	41%	63%	5%	21%	5%	5%	9%	15%	5%	5%	5%
MH080908	3	54%	5%	19%	11%	12%	5%	5%	<DL	15%	5%	5%	7%
MH080908	10	85%	5%	8%	7%	10%	5%	5%	<DL	<DL	5%	5%	6%
MH080908	30	5%	5%	18%	8%	12%	5%	5%	9%	15%	5%	5%	6%
MH011008	3	5%	8%	9780%	29%	14%	5%	5%	<DL	15%	<DL	5%	9%
MH011008	10	5%	5%	<DL	18%	11%	5%	5%	<DL	<DL	5%	5%	7%
MH011008	30	5%	10%	28%	15%	12%	5%	5%	9%	15%	22%	5%	7%
MH111208	3	17%	8%	<DL	38%	13%	5%	5%	<DL	<DL	7%	27%	9%
MH111208	10	<DL	5%	45%	15%	11%	5%	5%	<DL	<DL	6%	12%	7%
MH111208	30	5%	10%	<DL	14%	23%	5%	5%	9%	15%	8%	22%	6%
MH140109	3	23%	5%	<DL	23%	15%	5%	5%	<DL	<DL	10%	<DL	21%
MH140109	10	<DL	8%	<DL	13%	14%	5%	5%	9%	15%	11%	<DL	16%
MH140109	30	<DL	7%	52%	11%	25%	5%	5%	9%	15%	<DL	<DL	13%
MH250209	3	5%	5%	100%	10%	12%	5%	5%	<DL	<DL	5%	5%	7%
MH250209	10	5%	5%	12%	5%	14%	5%	5%	<DL	<DL	6%	5%	6%
MH250209	30	5%	5%	678%	8%	13%	5%	5%	9%	15%	5%	5%	6%
MH040309	3	5%	5%	<DL	<DL	5%	5%	5%	<DL	<DL	7%	5%	14%
MH040309	10	5%	5%	<DL	24%	13%	5%	5%	<DL	<DL	<DL	5%	12%
MH040309	30	6%	6%	40%	26%	17%	5%	5%	9%	15%	<DL	6%	7%
MH050509	3	5%	5%	33%	10%	11%	5%	5%	<DL	<DL	16%	5%	6%
MH050509	10	5%	5%	10%	6%	13%	5%	5%	<DL	<DL	9%	5%	6%
MH050509	30	5%	12%	23%	6%	19%	5%	5%	9%	15%	8%	5%	5%

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