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## RESEARCH ARTICLE

10.1029/2019JD032246

### Key Points:

- Marine aerosol composition and cloud-relevant properties over the North Atlantic Ocean are driven by phytoplankton activity patterns
- The main source region of marine biogenic aerosol reaching Mace Head was identified between 47°–57°N and 14°–30°W
- The relation is observed on a short time scale (1–2 months) and occurs with a delayed response of about 1–3 weeks

### Supporting Information:

- Supporting Information S1

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## Linking Marine Biological Activity to Aerosol Chemical Composition and Cloud-Relevant Properties Over the North Atlantic Ocean

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**Abstract** The ways in which marine biological activity affects climate, by modifying aerosol properties, are not completely understood, causing high uncertainties in climate predictions. In this work, in situ measurements of aerosol chemical composition, particle number size distribution, cloud condensation nuclei (CCN), and ice-nucleating particle (INP) number concentrations are combined with high-resolution sea surface chlorophyll-a concentration (CHL) and back-trajectory data to elucidate the relationship between oceanic biological activity and marine aerosol. The measurements were performed during an intensive field campaign conducted in late summer (August–September) 2015 at the Mace Head Research Station (MHD). At the short time scale (1–2 months) of the experiment, we observed a clear dependency of the main aerosol physicochemical and cloud-relevant properties on the patterns of biological activity, in specific oceanic regions with a delayed response of about 1–3 weeks. The oceanic region comprised between 47°–57°N and 14°–30°W was identified as the main source of biogenic aerosols during the campaign, with hints of some minor influence of waters up to the Greenland coast. These spatial and temporal relationships demonstrate that the marine biota influences aerosol properties under a variety of features up to the most cloud-relevant properties. Such dependency of aerosol properties with oceanic biological activity was previously reported over the North Atlantic Ocean only for multiyear data sets, where the correlation may be enhanced by coincident seasonalities. A better knowledge of these short time scale interactions may lead to a significant improvement in understanding the ocean-atmosphere-cloud system, with important impacts on climate science.

## 1. Introduction

Ocean-atmosphere interactions play a key role in the climate system, from local to global scale. The ocean, 70% of the Earth surface, is the major source of aerosol particles in the atmosphere, in terms of mass (Vignati et al., 2010). In particular, marine aerosol is considered one of the most significant contributors to the atmospheric particle burden over remote oceanic locations (Cochran et al., 2017; O'Dowd et al., 2008). Marine aerosol particles can be either directly emitted into the atmosphere from the sea surface by wave breaking and bubble bursting (i.e., primary marine aerosols [PMAs] or sea spray aerosols [SSAs]) (Gantt & Meskhidze, 2013; Quinn et al., 2015) or formed through photochemical oxidation and gas-to-particle conversion of ocean-derived gaseous precursors (secondary marine aerosols [SMAs]) (Charlson et al., 1987; O'Dowd et al., 2002; Shaw, 1983). The characteristics of marine aerosol are expected to be dependent on the properties of the nascent seawater and particularly on the ongoing biological activity (Facchini et al., 2008; O'Dowd et al., 2004). The chemical composition, number concentration, and size distribution of marine aerosols determine their ability to influence climate (Brooks & Thornton, 2018; Charlson

et al., 1987; Langmann et al., 2008) by either absorbing and scattering incoming solar radiation (the direct radiative effect) (Murphy et al., 1998; Zhang & Du, 2017) or by modifying cloud formation and its properties (the cloud-albedo or aerosol indirect effect) (DeMott et al., 2016; McCluskey et al., 2018; O'Dowd et al., 2004; Ovadnevaite et al., 2017).

Significant efforts have been made worldwide to explain how marine biological activity affects atmospheric aerosol properties and their seasonality since the 1980s when the (secondary) sulfate-driven phytoplankton-cloud-climate feedback was postulated (Charlson et al., 1987). For instance, Mukai et al. (1995) showed that atmospheric methanesulfonic acid (MSA), a secondary component of marine aerosol formed by dimethylsulfide (DMS) oxidation in the atmosphere, displayed a seasonal variability over Oki Islands, in the Sea of Japan. This seasonality was strongly related to primary production (e.g., phytoplankton) around the islands. Meskhidze and Nenes (2006) reported cloud droplet number concentration over a blooming ocean area twice as high as away from the bloom, with a resulting cloud effective radius reduction by 30%. A clear seasonal pattern was observed for organic aerosols in the southern Indian Ocean by Sciare et al. (2009), which was related to the ocean biological productivity. Miyazaki et al. (2010) observed average concentrations of organic carbon and oxalic acid two to three times higher in marine biologically more influenced aerosols, than in less influenced aerosols. More recently, McCoy et al. (2015) reported that enhanced aerosol number concentration is spatially correlated with regions of high CHL, over the Southern Ocean.

In the North Atlantic (NA), object of the present study, the physical and chemical properties of marine aerosol and their link to oceanic biological activity have been extensively studied (Cavalli et al., 2004; Facchini et al., 2008; O'Dowd et al., 2004; O'Dowd et al., 2008; Rinaldi et al., 2010). During algal/phytoplankton blooming periods, from spring to autumn, the organic fraction was reported to dominate the submicron aerosol mass (up to 63% of the total mass), together with sulfate, while in winter, when biological activity is low, the organic fraction decreases to about 15%, with sea salt (SS) dominating in all the size fractions (O'Dowd et al., 2004). Yoon et al. (2007) reported a clear seasonal trend, resembling that of oceanic biological activity, for several aerosol chemical components, size distribution modal diameters, and optical properties. Using isotopic carbon analysis, Ceburnis et al. (2011) showed unambiguously that over 80% of the marine aerosol organic carbon originated directly from plankton emissions. Contextually, the CCN fraction over the NA Ocean has been associated with the organic enrichment of sea-spray aerosol (Ovadnevaite et al., 2011), potentially introducing new biosphere-climate feedbacks (Quinn & Bates, 2011). Finally, the recent work by Sanchez et al. (2018) pointed out a clear seasonality in the CCN budget over the NA Ocean, related to phytoplankton-induced DMS emissions.

Some specific works suggest a direct coupling between phytoplankton biomass and the production of organic-rich marine primary aerosols over the NA Ocean (Gantt et al., 2011; O'Dowd et al., 2015; Rinaldi et al., 2013), indicating that biological activity has an active role in primary aerosol formation. In details, Rinaldi et al. (2013) reported that an 8-day time-lagged correlation exists between satellite retrieved CHL concentration and organic enrichment in the SSA measured at MHD, analyzing a data set of marine aerosol samples collected from 2002 to 2009. Said paper improved previous works by Langmann et al. (2008) and Vignati et al. (2010) was the first one to introduce the spatio-temporal correlation approach for investigating the relationship between marine aerosol properties and biological activity. O'Dowd et al. (2015) illustrated a clear dependency of the organic fraction of SSA on biological activity with a 24-day time lag by using high-resolution aerosol chemical composition measurements from 2009 to 2011. A big challenge for field measurements is the interpretation of the time lag that exists between the peaks of phytoplankton activity and SSA emission (Lee et al., 2015; McCluskey et al., 2017; Wang et al., 2015).

Indeed, contrasting results have been reported in the last years, regarding the possibility that SSA chemical composition may be affected by organic matter (OM) freshly released by phytoplankton activity. Publications reporting observations taken in the western NA Ocean (Bates et al., 2020; Keene et al., 2017; Kieber et al., 2016; Quinn et al., 2014; Russell et al., 2010) show a constant chemical composition of SSA independently on the season and on the algal blooming stage. These studies concluded that the organic fraction of SSA comes from the large pool of refractory dissolved organic carbon (DOC) in the ocean and that, consequently, chemical transport and climate models could treat the ocean as a uniform organic SSA source, affected only by sea surface temperature (SST).

Other papers, on the contrary, reported evidence of the influence of freshly produced OM by blooming algal species on the chemical composition (and sometimes cloud-relevant properties) of SSA. These works comprise a vast literature of laboratory studies, including the ones performed at the world's largest lab facility of this kind, at NSF-CAICE in San Diego (Cochran et al., 2017; Cochran, Ryder, et al., 2017; Collins et al., 2013; Lee et al., 2015; Prather et al., 2013). Other laboratory studies showing similar results are those by Fuentes et al. (2011) and O'Dowd et al. (2015). Field observations by Ovadnevaite et al. (2011) suggested that hygroscopicity and CCN properties of SSA may change significantly when it originates from highly biologically productive seawaters. More recently, open sea field observations of primary biological particles showed specific spatio-temporal distributions as compared to total aerosols, over the NA Ocean, with a significant relation with seawater CHL (Kasparian et al., 2017). Finally, the model simulations (Burrows et al., 2014) suggested that SSA organics can be contributed by different types of seawater organic compounds, from both fresh and refractory organic carbon, in varying proportions according to the region and season. Overall, we can simply acknowledge the contrasting results reported in the scientific literature on this subject. In conclusion, in our opinion, the actual effect of phytoplankton activity on SSA chemical composition remains controversial.

Primary biogenic aerosols from the sea surface can also act as a source of ice-nucleating particles (INPs) over remote oceans (Bigg, 1973; Bigg & Leck, 2001; Schnell & Vali, 1976) and so modulate the aerosol-cloud-climate interactions by influencing cloud radiative properties, cloud lifetime, and precipitation rates. Recently, the interest of the scientific community on this topic has been fostered by publications confirming the potential climate relevance of the oceanic biogenic source of INPs (Burrows et al., 2013; DeMott et al., 2016; Hartmann et al., 2019; McCluskey et al., 2017; McCluskey et al., 2018; McCluskey et al., 2018; McCluskey, Hill, Sultana, et al., 2018; Vergara-Temprado et al., 2017; Wilson et al., 2015), and, in particular, it has been shown how the ice nucleating properties of SSA evolve during an algal bloom (McCluskey et al., 2017). By contrast, ice nucleating properties have never been associated to SMA in any environment (Kanji et al., 2017; Si et al., 2018; Wilbourn et al., 2020).

The role of oceanic biota in modifying the chemical composition and cloud-relevant properties of the marine aerosol is one of the most intriguing questions in climate studies. In this work, in situ aerosol data measured at MHD, on the west coast of Ireland, are used to investigate the relationship between oceanic biological activity, determined from satellite-derived surface CHL concentration, and physicochemical/cloud-relevant properties of atmospheric aerosol particles over the NA ocean, on a short time scale (~1–2 months). Specific objectives for this study are to (1) characterize the relationship between the main aerosol chemical components and plankton activity during an intensive observation period representative of summer conditions, (2) identify the source regions of biogenic aerosol components of marine origin, active during the campaign, in comparison to those evidenced in previous works using multiyear data sets, and (3) resolve how cloud-relevant properties of marine aerosol are influenced by plankton activity.

## 2. Materials and Methods

### 2.1. In Situ Aerosol Measurements

The aerosol characterization campaign object of this work was carried out between 30 July and 21 September 2015, at the MHD (53.33°N, 09.90°W) Global Atmosphere Watch research station. The station is located on the west coast of Ireland facing westward to the northeast Atlantic Ocean at about 300 m from the waterline and 21 m above the mean sea level. Aerosol measurements were performed through the central aerosol sampling system which inlet is set at 10 m above ground level.

The aerosol chemical composition was measured online by an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) which provides a real-time size-resolved composition of volatile and semivolatile particulate matter (DeCarlo et al., 2006). The HR-ToF-AMS measurements were performed at a time resolution of 10 min, and it was calibrated according to the recommendations by Jimenez et al. (2003) and Allan et al. (2003). It quantifies aerosol chemical composition (PM<sub>1</sub>), covering major inorganic species such as sulfate (SO<sub>4</sub><sup>2-</sup>), ammonia (NH<sub>4</sub><sup>+</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and organic species (OM) in the submicron size range (Canagaratna et al., 2007). The SS concentrations can also be derived following the method described by Ovadnevaite et al. (2012). The MSA concentration was derived from the concentration of mass fragment CH<sub>3</sub>SO<sub>2</sub><sup>+</sup>, following the procedure by Ovadnevaite et al. (2014). A Nafion drier was installed in front of the

HR-ToF-AMS sampling inlet to reduce the relative humidity of the sample to <40%. The OM mass-fraction enrichment ( $OM_{SS}$ ) in marine aerosol was calculated as the contribution of OM mass relative to the total OM plus SS mass. Furthermore, equivalent black carbon (eBC) concentrations measured in situ by a multiangle absorption photometer (MAAP) were used to discriminate anthropogenically impacted air masses.

The submicron aerosol size distributions were measured by a scanning mobility particle sizer (SMPS,  $0.02 < \text{particle diameter } (D_p) < 0.5 \mu\text{m}$ ), where aerosols are neutralized (Kr-85, TSI Model 3077) size discriminated based on their mobility diameter (differential mobility analyzer, TSI Model 3071) and counted by a condensation particle counter (TSI Model 3010). Aerosol sizing instruments were located downstream of Naphion driers ( $RH < 40\%$ ), and thus, size distributions refer to the aerosol dry diameter (Sanchez et al., 2017). According to the particle size distribution, we have selected two dominant modes of particle number concentration: Aitken ( $20 < D_p < 100 \text{ nm}$ ) and accumulation ( $100 < D_p < 500 \text{ nm}$ ) for this study.

CCN measurements were performed with a miniature continuous-flow stream-wise thermal gradient chamber, which measures the concentration of activated CCN over a range of supersaturations (Roberts & Nenes, 2005). The supersaturation range spanned 0.2–0.82%. Further details on SMPS and CCN measurements are reported in Sanchez et al. (2017). For this study, CCN concentrations were selected at three supersaturations ( $0.25, 0.5, 0.75 \pm 10\%$  supersaturation at each level).

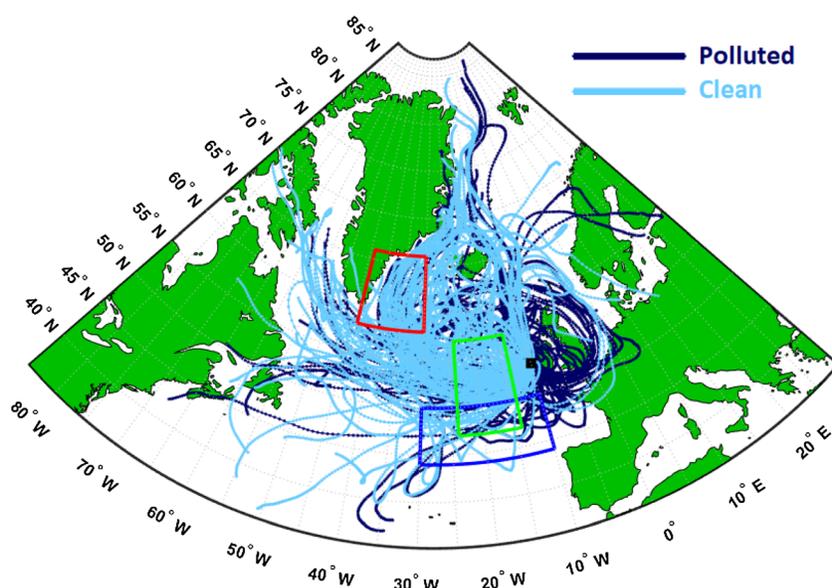
The INP number concentration ( $n_{INP}$ ) was measured by using the off-line dynamic filter processing chamber (DFPC) developed at the CNR-ISAC laboratories in Bologna (Italy), following the procedure described in Santachiara et al. (2010) and Belosi et al. (2017). Briefly, PM1 and PM10 aerosol fractions were simultaneously sampled on nitrocellulose membrane filters (Millipore HABG04700, nominal porosity  $0.45 \mu\text{m}$ ) by mounting different sampling heads (1- and  $10\text{-}\mu\text{m}$  cut point Standard EN 12341, TCR Tecora) in front of the filters. Sampling for INP analyses occurred only in clean marine conditions, to avoid continental influences, as detailed in McCluskey, Hill, Sultana, et al. (2018). The quantification of INPs occurred at an activation temperature ( $T_A$ ) of  $-22^\circ\text{C}$  and in conditions of supersaturation with respect to water ( $S_w$ ) equal to 1.01.

## 2.2. Ocean Color Data

Daily sea surface chlorophyll-a concentration (CHL;  $\text{mg m}^{-3}$ ) data were downloaded from the EU Copernicus Marine Environment Monitoring Service (CMEMS; <http://marine.copernicus.eu/>) based on a multisensor approach (i.e., SeaWiFS, MODIS-Aqua, MERIS, VIIRS, and OLCI-S3A) and on a space-time interpolation to provide the best estimate “Cloud Free” classification (Level-4). The Level-4 product (OCEANCOLOUR\_GLO\_CHL\_L4\_REP\_OBSERVATIONS\_009\_082) is available at  $\sim 4\text{-km}$  spatial resolution. From this global data set, CHL fields were extracted in the study area ( $46^\circ\text{W}\text{--}0^\circ\text{E}$ ;  $40^\circ\text{--}66^\circ\text{N}$ ) from 1 June to 30 September 2015 for applying the time-lag approach. The quality of the CHL extracted from global data was validated by comparing with corresponding local high resolution (i.e., 1 km) data over the same NA domain. The results of the comparison are shown in Figure S1 in the supporting information. In this work, we have chosen to use 4-km data, instead of the higher resolution ones, for computational efficiency.

## 2.3. Spatio-Temporal Correlation Between In Situ Measurements and CHL Data

To explore the relationship between marine aerosol and phytoplankton biomass (in terms of CHL concentration), the data set was analyzed examining only the cleanest air masses with the least continental and/or anthropogenic contamination encountered during the study period. The high-resolution aerosol data have been averaged to hourly mean and filtered against hourly eBC mass concentration as an anthropogenic tracer in order to ensure the cleanliness of the marine air masses. The hourly averages corresponding to eBC not exceeding  $15 \text{ ng m}^{-3}$  was used to reliably exclude anthropogenically impacted air masses (Grigas et al., 2017; O'Dowd et al., 2015; Ovadnevaite et al., 2014; Preissler et al., 2016). The clean marine hourly aerosol data collected at MHD have been averaged daily, in order to be compared with the highest CHL time resolution of 24 hr. Each day with less than 6 continuous hours of clean measurements was removed from the analysis. The Pearson correlation coefficients between atmospheric aerosol concentration and satellite-derived ocean color data, obtained by standard least squares regression, were computed at each grid point covering the NA domain, and for different time lags, to obtain the correlation



**Figure 1.** The 5-day air mass back-trajectories (hourly time step) calculated by the NOAA HYSPLIT model arriving at MHD (represented by black square) sampling station four times per day (00, 06, 12, and 18 hr UTC) at 100 m above the mean sea level during 31 July to 21 September 2015. The blue box area comprises grid coordinates 44°–50°N and 10°–30°W (Region 1; O’Dowd et al., 2015), the green box area comprises grid coordinates 47°–57°N and 14°–24°W (Region 2; Rinaldi et al., 2013), while the red box area comprises grid coordinates 58°–66°N and 30°–44°W (region 3). These boxes delineate high correlation areas, discussed later. Only clean marine BTs (light blue) according to eBC threshold are used for PSCF calculations.

maps presented in the results section, following Rinaldi et al. (2013). The time-lag approach must be applied since surface CHL tracks the growing phase of algal blooms, while the release of phytoplankton exudates, involved in the production of biogenic marine aerosols, occurs mainly at a later stage, during the senescence/demise phase.

#### 2.4. Potential Source Contribution Function

The possible source regions of marine aerosol which have high concentration at a receptor site are identified by the potential source contribution function (PSCF) algorithm using the spatial probability distribution of pathways of air masses that arrived at the sampling site over a time period (Chang et al., 2011; Dall’Osto et al., 2017; Karaca et al., 2009; Polissar et al., 2001). It combines the back-trajectories (BTs) information with the measured data to produce probability fields for potential source regions.

In this study, 5-day BTs (HYSPLIT4 with GDAS data: <https://ready.arl.noaa.gov/HYSPLIT.php>) (Rolph et al., 2017; Stein et al., 2015) arriving 100 m above MHD sampling station were calculated four times (00, 06, 12, and 18 hr UTC) a day for the period from 31 July to 21 September 2015. The aerosol data were averaged over 1 hr (half an hour before and after the arrival time of each BT) to be filtered for hourly eBC (<15 ng m<sup>-3</sup>) to consider only pristine clean marine cases (Figure 1).

The NA domain was divided into 1° × 2° latitude/longitude grid cells (2,250 cells, 762 cells with at least one endpoint) between the limits of clean marine BTs. The conditional probability that the air passing through the *ij*th cell has a high aerosol concentration when arriving at MHD is given by

$$PSCF_{ij} = (m_{ij}/n_{ij}) \times W_{ij},$$

where  $n_{ij}$  is the number of trajectories with segment endpoints in a cell *ij* and  $m_{ij}$  is the subclass ( $m_{ij} < n_{ij}$ ) of trajectories connected to aerosol concentrations above a threshold defined as concentrations above the median. The PSCF values may be affected by grid cells containing a low number of endpoints that may be overestimated so that it is multiplied by a weighting factor,  $W_{ij}$ , (Masiol et al., 2019) as indicated below.  $W_{ij} = 1$  if  $n_{ij} \geq 2\bar{N}$ ,  $W_{ij} = 0.75$  if  $\bar{N} \leq n_{ij} < 2\bar{N}$ ,  $W_{ij} = 0.50$  if  $\bar{N}/2 \leq n_{ij} < \bar{N}$ , and  $W_{ij} = 0.15$  if  $n_{ij} < \bar{N}/2$ , where  $\bar{N}$  is the average number of endpoints over the grid cells with at least one endpoint.

**Table 1**  
Summary of Marine Aerosol Studied Variables and CHL Concentrations for the Study Period

Parameter	Clean marine mean $\pm$ SD (median)	All data mean $\pm$ SD (median)	Sampling period
Aerosol chemical composition			From 31/07/2015 to 21/09/2015
Sea salt: SS ( $\mu\text{g m}^{-3}$ )	$0.16 \pm 0.14$ (0.12)	$0.14 \pm 0.14$ (0.09)	
Organic matter: OM ( $\mu\text{g m}^{-3}$ )	$0.15 \pm 0.14$ (0.11)	$0.54 \pm 0.88$ (0.20)	
Nitrate: $\text{NO}_3^-$ ( $\mu\text{g m}^{-3}$ )	$0.02 \pm 0.01$ (0.01)	$0.08 \pm 0.23$ (0.02)	
Sulfate: $\text{SO}_4^{2-}$ ( $\mu\text{g m}^{-3}$ )	$0.25 \pm 0.18$ (0.22)	$0.44 \pm 0.51$ (0.28)	
Ammonium: $\text{NH}_4^+$ ( $\mu\text{g m}^{-3}$ )	$0.03 \pm 0.02$ (0.02)	$0.11 \pm 0.21$ (0.04)	
Methanesulfonic acid: MSA ( $\mu\text{g m}^{-3}$ )	$0.02 \pm 0.02$ (0.02)	$0.03 \pm 0.02$ (0.02)	
Organic enrichment: $\text{OM}_{\text{SS}}$	$0.51 \pm 0.23$ (0.51)	$0.65 \pm 0.26$ (0.70)	
Equivalent black carbon: eBC ( $\text{ng m}^{-3}$ )	$7.19 \pm 4.42$ (7.19)	$49.97 \pm 104.96$ (13.11)	
Particle number concentration			From 31/07/2015 to 21/09/2015
Aitken: $N_{20-100\text{nm}}$ ( $\text{cm}^{-3}$ )	$401 \pm 323$ (336)	$572 \pm 555$ (401)	
Accumulation: $N_{100-500\text{nm}}$ ( $\text{cm}^{-3}$ )	$96 \pm 43$ (91)	$209 \pm 261$ (122)	
Total: $N_{20-500\text{nm}}$ ( $\text{cm}^{-3}$ )	$497 \pm 334$ (432)	$780 \pm 778$ (531)	
CCN number concentration (supersaturation)			From 31/07/2015 to 31/08/2015
$n\text{CCN}_{0.25}$ ( $\text{cm}^{-3}$ )	$112 \pm 43$ (108)	$150 \pm 99$ (121)	
$n\text{CCN}_{0.50}$ ( $\text{cm}^{-3}$ )	$161 \pm 72$ (144)	$220 \pm 162$ (165)	
$n\text{CCN}_{0.75}$ ( $\text{cm}^{-3}$ )	$252 \pm 119$ (222)	$312 \pm 202$ (253)	
INP number concentration ( $T_A = -22^\circ\text{C}$ , $S_w = 1.01$ )			25 samples From 30/07/2015 to 28/08/2015
$n\text{INP}_{\text{PM1}}$ ( $\text{m}^{-3}$ )	$2.7 \pm 2.8$ (2.3)		
$n\text{INP}_{\text{PM10}}$ ( $\text{m}^{-3}$ )	$10.1 \pm 8.8$ (7.8)		
Chlorophyll-a			From 01/07/2015 to 30/09/2015
CHL- Region 1 ( $\text{mg m}^{-3}$ )	$0.37 \pm 0.07$ (0.36)		
CHL- Region 2 ( $\text{mg m}^{-3}$ )	$0.48 \pm 0.10$ (0.46)		
CHL- Region 3 ( $\text{mg m}^{-3}$ )	$0.36 \pm 0.04$ (0.35)		

Note. Cases with hourly eBC concentrations  $< 15 \text{ ng m}^{-3}$  were classified as clean marine that are likely not influenced by anthropogenic sources. PM1 and PM10 correspond to total particulate matter less than 1 and 10  $\mu\text{m}$  diameter, respectively. The average CHL at different regions of interest as shown in Figure 1.

### 3. Results

#### 3.1. Overview of Aerosol Properties During the Campaign

The aerosol chemical composition, particle number, CCN and INP concentrations in clean marine and all sectors, are summarized in Table 1. Figures S2–S5 display the time-series plots of all the studied aerosol variables in clean conditions during the campaign, paired with CHL data. In general, with the exception of SS, the concentrations of aerosol components were lower in clean marine conditions, consistent with a previous comparison by Dall'Osto et al. (2010). In clean marine air, aerosol size distributions display bimodality (Dall'Osto et al., 2010; Hoppel et al., 1990) with an Aitken and accumulation mode. In the Aitken mode size range, the average particle number concentration was  $401 \pm 323 \text{ cm}^{-3}$ , while it was  $96 \pm 43 \text{ cm}^{-3}$  in the accumulation mode range. The number concentration of CCN ranged from  $112 \pm 43 \text{ cm}^{-3}$ , at 0.25% supersaturation, to  $252 \pm 119 \text{ cm}^{-3}$ , at 0.75% supersaturation. CCN concentrations in the different sectors are in agreement with long-term measurements by Reade et al. (2006). The study average number of INPs ( $T_A = -22^\circ\text{C}$ ,  $S_w = 1.01$ ) was  $2.7 \pm 2.8$  ( $10.1 \pm 8.8$ )  $\text{m}^{-3}$  in PM1 (PM10) fractions, respectively, as already reported by McCluskey, Hill, Sultana, et al. (2018).

In order to investigate the relation between phytoplankton activity and marine aerosol production, we attempted a spatial source attribution for the marine aerosol observed at MHD. This was done by deploying aerosol chemical composition and number concentration data, following a multistep approach (Mansour et al., 2020). The approach is based on spatio-temporal correlation analysis between aerosol parameters and surface CHL concentration, BT analysis and the PSCF algorithm. Only source regions that are plausible according to all the above three methods have been considered as reliably identified source. Consequently, the evidenced correlation between aerosol parameters (including the cloud-relevant properties) and CHL concentration, within the identified source region, has been considered as resulting from a physical mechanism (i.e., the correlation is causal, not casual). It is worth highlighting that the spatio-temporal correlation and the PSCF approaches are totally independent and based on different principles. The fact that the

source region identification is confirmed by two independent methods strongly supports the reliability of the results discussed below.

### 3.2. Spatio-Temporal Correlation With CHL

Following the approach introduced by Rinaldi et al. (2013), further used by O'Dowd et al. (2015), the spatial distributions of the correlation coefficient between aerosol physicochemical properties measured at MHD and surface CHL concentration at each grid point of the NA domain were investigated considering different time lags. The time lag between the CHL time series and aerosol properties has to be considered in order to take into account the time scale of the biochemical processes responsible for the production of transferable OM (in case of PMA) or gaseous precursors (for SMA) in the seawater, after the phytoplankton growing phase. In the latter case, the time lag comprises also the atmospheric processing time necessary to convert gaseous precursors into particulate matter.

The basic assumption for the time-lagged correlation approach is that marine biological aerosol should follow the evolution of marine biological activity (traced by CHL). For this reason, we looked for positively correlating sea regions: in our interpretation, these regions have a higher probability of being related to the observed aerosol properties.

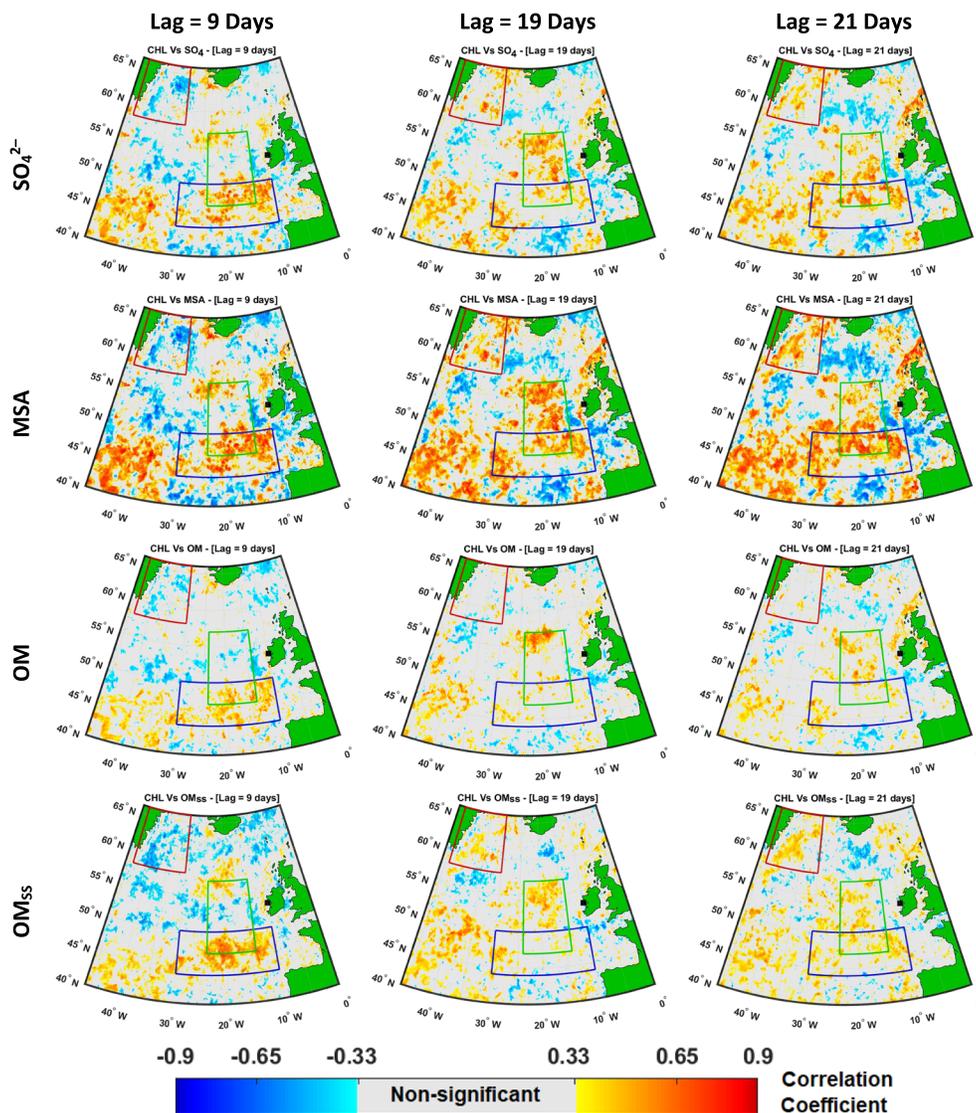
A general analysis of the obtained results evidenced three main positively correlating oceanic regions. Two broadly coincides with those evidenced by O'Dowd et al. (2015), between 44°–50°N and 10°–30°W (hereafter Region 1; blue box), and by Rinaldi et al. (2013), between 47°–57°N and 14°–24°W (Region 2; green box), as shown in Figure 1. These two regions were described as the ocean regions exerting the maximum influence on the chemical composition of SSA sampled at MHD by two distinct multiyear data sets, and they already approximate the regions of maximum correlation observed in the present study. Another area of high correlation is found comprising the grid coordinates 58°–66°N and 30°–44°W (Region 3; red box). These three regions of high correlation are consistently located upwind of MHD as illustrated from 5-day air mass BTs as shown in Figure 1, even though it is clear that Region 1 is less interested than the other two from air masses reaching MHD during the study period.

#### 3.2.1. Aerosol Chemical Composition

The spatial distributions of the correlation coefficient ( $R$ ) obtained with different time lags between CHL and daily averaged  $\text{SO}_4^{2-}$ , MSA, OM, and  $\text{OM}_{\text{SS}}$  data are shown in Figure 2. In all the presented correlation maps, the yellow/red (blue) colors represent positive (negative) significant correlation coefficients at 95% confidence level, while the gray color represents the non-significant ones. The maps (Figure 2) show a significant correlation in the three specific regions in the NA with different time delays. The number of pixels that have significant negative correlation within those regions is negligible, indicating an overall positive correlation for the evidenced areas. The southwestern belt of high correlations in the bottom left corner of the maps is not considered in this study as it is not supported by the BTs pattern (Figure 1) and, therefore, a relationship with aerosol measurements at MHD is not to be expected. In that area, high correlations may be due to the similarity of CHL seasonal cycles (Lacour et al., 2015) with Region 1, which could produce a false-positive result because of noncausal correlations, as clearly supported by the spatial distribution of weakly mean CHL concentration (Figure S6).

Figure 3 illustrates the behavior of the correlations, within the three regions, as a function of the considered time lag between the CHL and the aerosol properties time series. In general, over the three regions, there is an increase in correlation coefficient as a function of the time lag, generally after about 1 week toward 20–25 days. Region 1 shows two maxima (bimodal shape) with the first one after 8–9 days and the second maximum between 20 and 25 days. In the second region (green box), the correlation becomes significant after 8- to 10-day lag for MSA and  $\text{SO}_4^{2-}$ , but the best correlation occurs at 19-day time lag for all other chemical components. In the third region (red box), significant correlations were observed for all components after a time lag of about 18–20 days, except for OM.

Figure 3 also shows that  $\text{NH}_4^+$  follows the profile of  $\text{SO}_4^{2-}$ , although with lower correlation values ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and SS correlation maps are provided in Figure S8). This result is consistent with the fact that  $\text{NH}_4^+$  is the main ion to neutralize sulfuric acid in the marine boundary layer (Huntzicker et al., 1980; Marti et al., 1997). No significant correlation was observed for  $\text{NO}_3^-$ , which is reasonable since  $\text{NO}_3^-$  is almost



**Figure 2.** Examples of correlation coefficient spatial distribution between the main aerosol chemical composition measured at MHD and CHL concentration over the North Atlantic Ocean for 9 days (left), 19 days (middle), and 21 days (right) time lag, considering only clean marine air masses. In all correlation maps, the gray color represents nonsignificant correlation coefficients at 95% confidence level, the black square corresponds to MHD station, and the regions of interests are shown as blue (Region 1), green (Region 2), and red (Region 3) boxes.

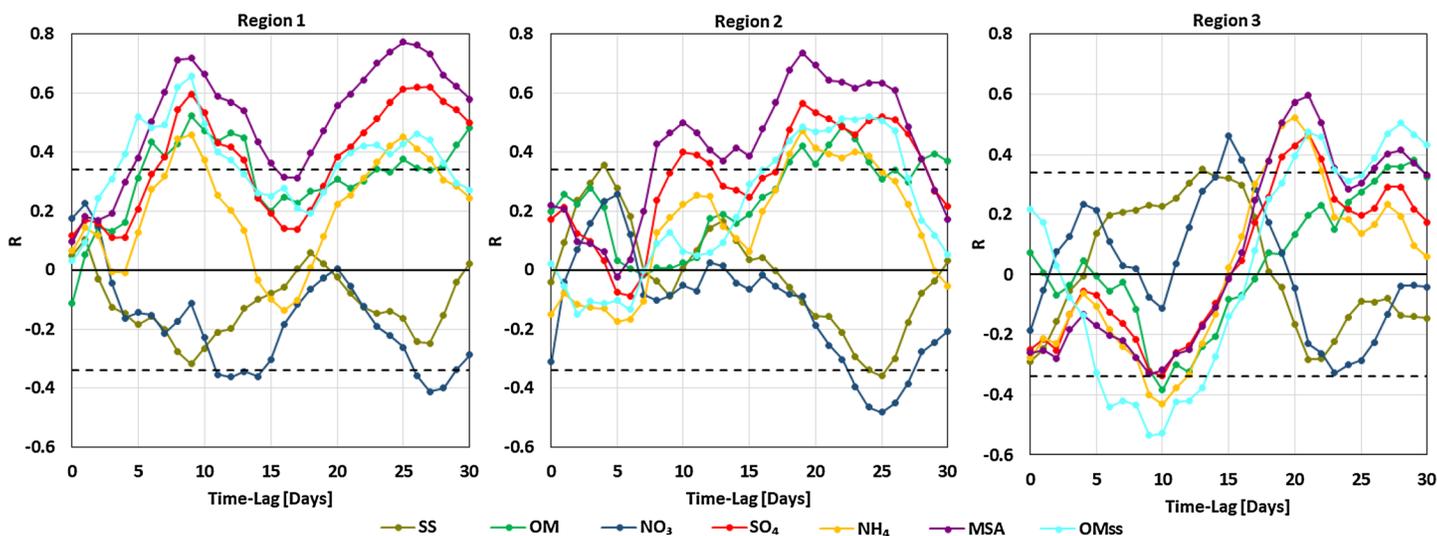
negligible in the submicrometer clean marine aerosol (Watts et al., 1990). As expected, SS also does not correlate with CHL in none of the regions.

### 3.2.2. Particle Number Concentration

A significant correlation between particle number concentration, in both Aitken and accumulation modes, and surface CHL concentration has been found (Figure 4). Generally, the shape of the correlation as a function of the delay time for particle number concentration follows the one already presented for the chemical composition. In Region 1, the correlation increased to significant levels (95%) after about 1 week, with the first maximum at time lag 10 days and a second between 20 and 25 days. Over Region 2, the correlation reaches its maximum value after 20 days, with a reduction in the number of pixels in accumulation mode. As already discussed for the chemical composition, the correlation is lower in Region 3, with significant values after 20 days, but only for the Aitken mode.

### 3.2.3. Cloud Condensation Nuclei

In agreement with aerosol chemistry and particle number concentration, there is a significant correlation between the number of CCN and CHL in the three regions (Figures 5 and S9), with a correlation versus



**Figure 3.** Correlation coefficient as a function of time lag between mean CHL concentration at different selected regions and the main aerosol chemical components. The black dashed lines represent the critical level of significant correlation at 95% confidence limit.

delay time shape broadly similar to the ones already described in the previous paragraphs. The correlation is stronger with increasing supersaturation level which agrees with the higher correlation observed between CHL and Aitken mode particle concentration, as smaller particles require higher supersaturation to be activated.

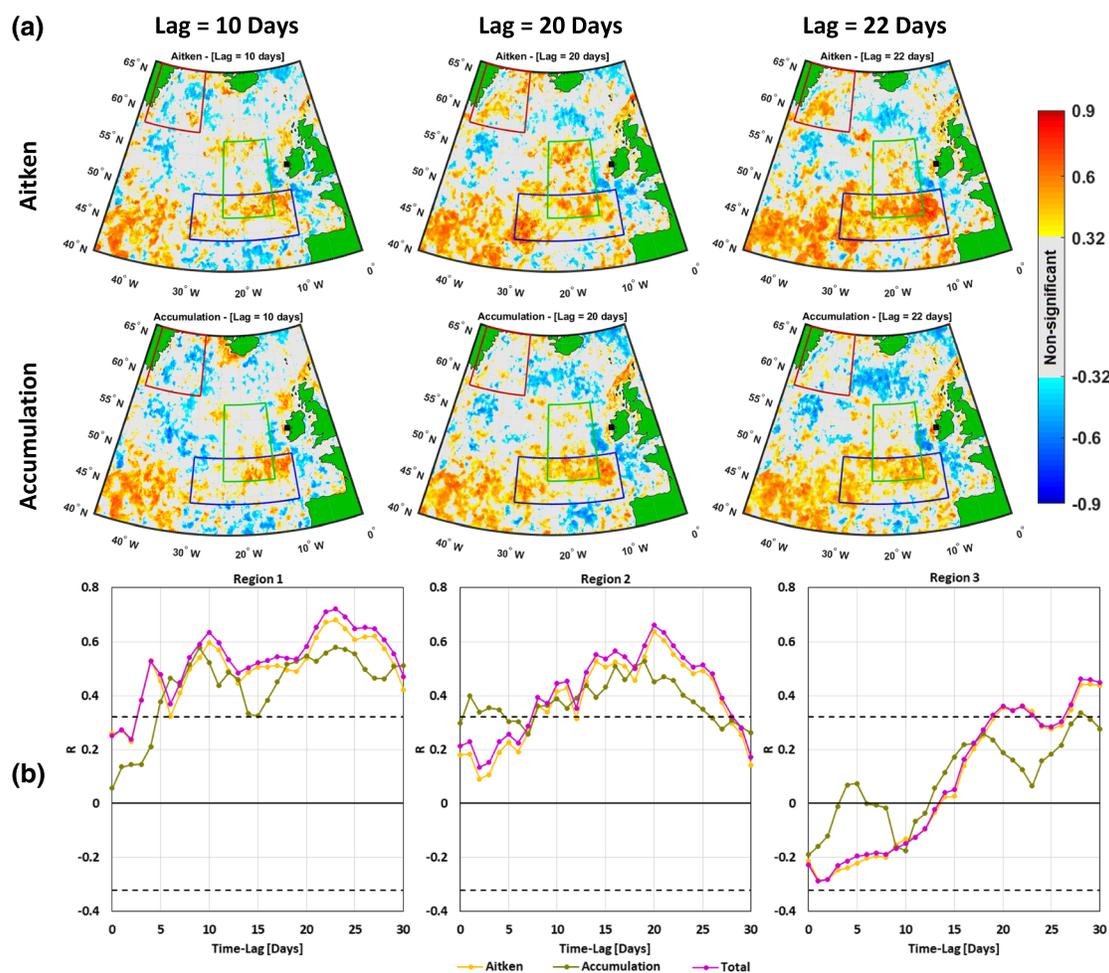
Differently from what observed for CCN concentration, the CCN fraction ( $CCN/N$ ), calculated as the ratio between CCN and total particle number concentration ( $20 < D_p < 500$  nm), shows no significant dependency on CHL over the NA (Figure 5b). This result agrees with Quinn et al. (2014), who showed that the fraction of total particles that activate to form CCN at a given supersaturation is independent of CHL. This lack of correlation suggests that, during the study period, phytoplankton activity influenced the CCN pool more by controlling the particle number concentration than by affecting the CCN properties of single marine aerosol particles. Ovadnevaite et al. (2011) showed that the CCN fraction of SSA increases as a function of organic enrichment. Consequently, the present results suggest that phytoplankton-regulated new particle production was more important than sea-spray primary production, for the CCN budget, during the observation period. This is reasonable considering that the campaign was performed in late summer when photochemistry is maximized by high solar radiation and sea-spray production is at its yearly minimum, due to the seasonal minimum of wind speed (WS) (Ovadnevaite et al., 2014; Rinaldi et al., 2010).

### 3.2.4. Ice-Nucleating Particles

SSA particles can act as ice nucleating particles (INPs) in clouds. In particular, the attention of the scientific community is oriented toward the organic fraction as responsible for the ice nucleation ability of SSA (McCluskey, Hill, Sultana, et al., 2018; Wilson et al., 2015). The correlations between CHL and  $nINP$  measured by the DFPC ( $T_A = -22^\circ\text{C}$ ,  $S_W = 1.01$ ) were investigated (Figure 6) for both the  $PM_{10}$  and  $PM_{10}$  size intervals, revealing that  $nINP_{PM_{10}}$  was positively correlated with CHL concentration by applying the time-lag approach.

$nINP_{PM_{10}}$  was statistically significantly correlated after 17 (16) days for Region 1 (2) and at 18 days for Region 3. A lack of a clear relationship between  $nINP_{PM_{10}}$  and CHL is found in this study (Figure S10). This suggests that different particle types, with different relations with CHL, are responsible for the INP properties of fine and coarse marine aerosols, as already pointed out by McCluskey et al. (2017). In detail, submicron INPs are linked to phytoplankton exudates enriching submicrometer SSA particles, while the ice nucleation properties of the coarse fraction depend on the presence of cells or cell fragments.

It is worth pointing out that a previous publication (McCluskey, Hill, Sultana, et al., 2018) already discussed the relation of the present INP data set and surface CHL concentration. Said paper concluded that there was no evidence of a significant correlation between  $nINP$  and CHL over a region roughly resembling Region 2, up to 14 days of delay time. The choice of the delay time interval (0–14 days) was based on Rinaldi



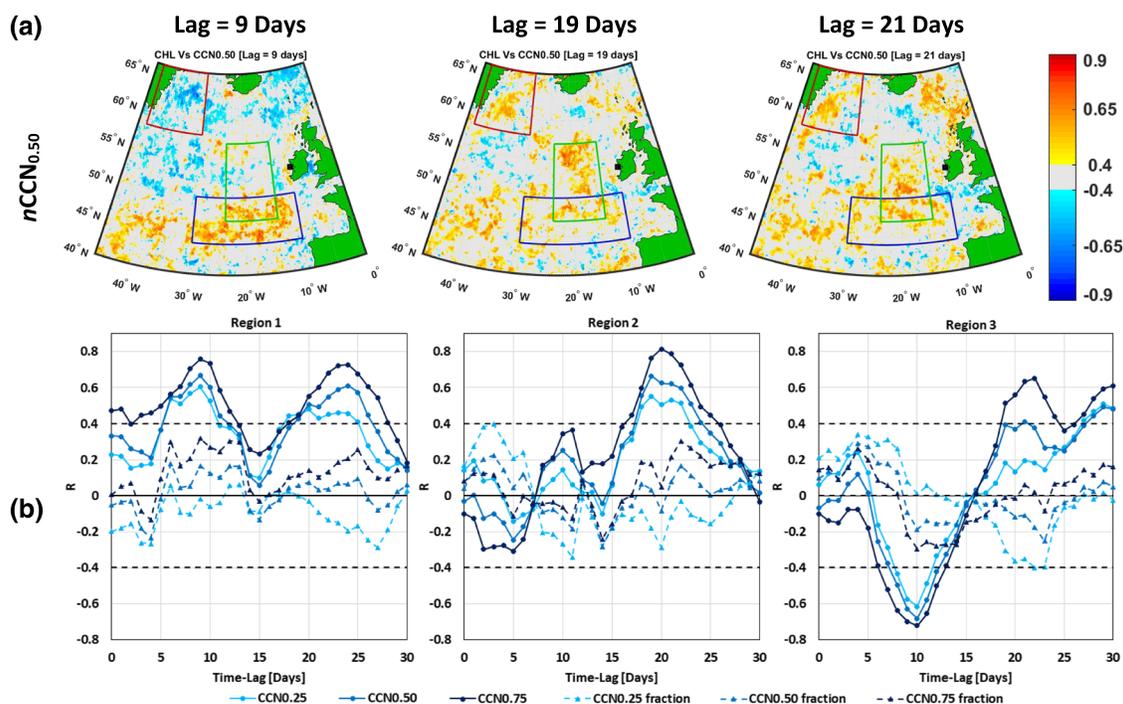
**Figure 4.** (a) Examples of correlation coefficient spatial distribution between Aitken and accumulation modes particle number concentration sampled at MHD and CHL concentration over the North Atlantic Ocean for 10 days (left), 20 days (middle), and 22 days (right) time lag, considering only clean marine air masses. (b) Correlation coefficient as a function of time lag between mean CHL concentration at different selected regions and the different modes of particle number concentration. The black dashed lines represent the critical level of significant correlation at 95% confidence limit.

et al. (2013) which showed the best correlation between CHL concentration and  $OM_{SS}$  occurring with a lag of 8 days. The present work extends the delay time interval up to 30 days and shows how  $nIPN_{PM1}$  correlates with CHL concentration with broadly the same behavior as all the previously considered marine aerosol properties.

### 3.3. Potential Source Contribution Function

An independent attempt at aerosol source identification was carried out by combining the high-resolution aerosol chemical composition and particle number concentration data with 5 days air mass BTs, following the PSCF approach (Chang et al., 2011). PSCF allows a probabilistic geographical source attribution for high-resolution aerosol data, showing the pixels associated with the highest concentrations (defined in this work as above the median), which evidence the most probable source regions. The PSCF maps (Figure 7) showed generally consistent features between all the considered aerosol chemical components and number size distribution modes. The most probable source regions of the biogenic aerosol species measured at MHD during the campaign, according to PSCF, were the oceanic region immediately to the west of Ireland and the Northwest oceanic region between Greenland and Iceland.

The results of the PSCF analysis are generally in agreement with those of the previously presented spatio-temporal correlation analysis. In order to facilitate the comparison between correlation maps and PSCF ones, in Figure 8, we have evidenced each pixel that has both a PSCF value higher than 0.5, and a

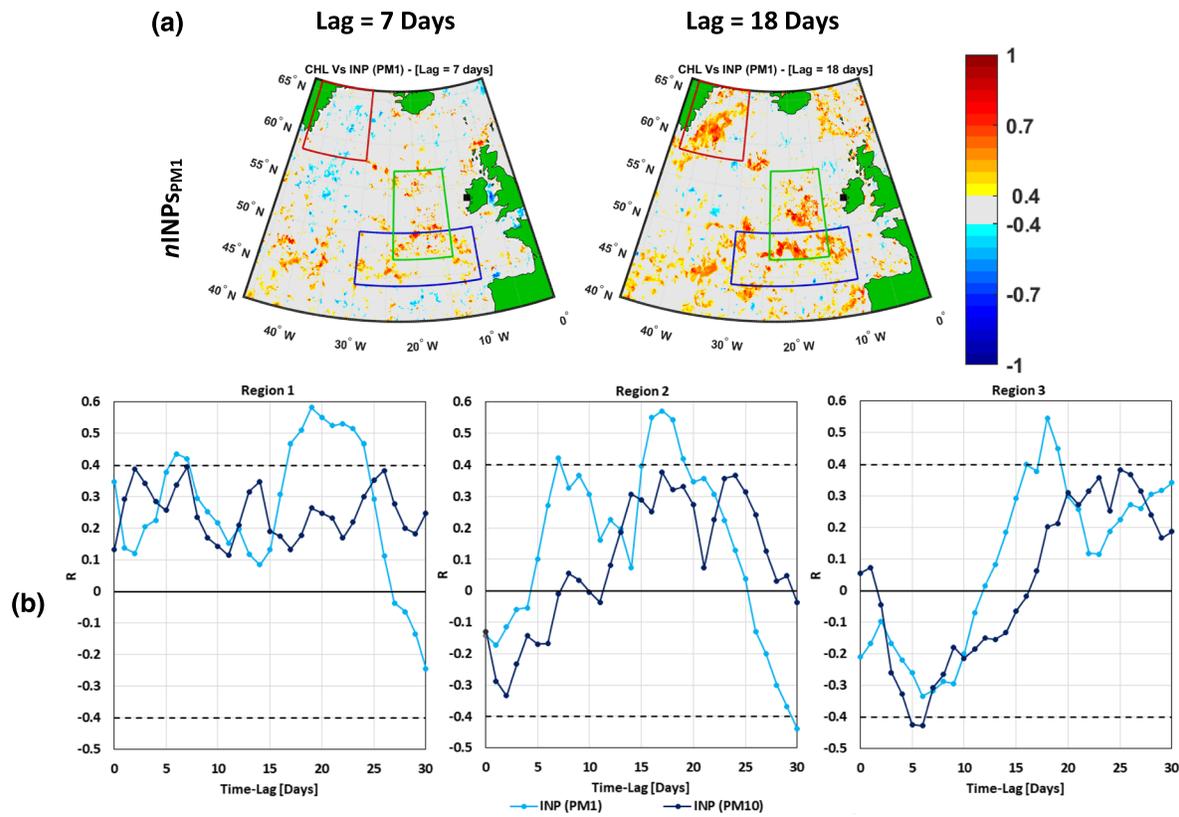


**Figure 5.** (a) Examples of correlation coefficient spatial distribution between CCN number concentration at 0.50% supersaturation and CHL concentration over the North Atlantic Ocean for 9 days (left), 19 days (middle), and 21 days (right) time lag, considering only clean marine air masses. (b) Correlation coefficient as a function of time lag between mean CHL concentration at different selected regions and the concentration of CCN and the CCN fraction at different supersaturations. The black dashed lines represent the critical level of significant correlation at 95% confidence limit.

significant and positive correlation between aerosol properties and surface CHL concentration, considering every delay time between 8 and 25 days. The ocean region broadly corresponding to Region 2 is clearly indicated as the main source region of the biogenic marine aerosol sampled during the campaign. The combined analysis also suggests that the region between Greenland and Iceland (matching broadly Region 3) likely exerts some influence on marine aerosol sampled at MHD, in particular for  $\text{SO}_4^{2-}$ , MSA, OM, and Aitken mode particles, while this is less evident for accumulation mode sized particles. We can argue that the contribution of this source region on the aerosol population sampled at MHD is lower than that of Region 2, likely because of the long distance from the receptor site. PSCF only evidences spots of high probability for Region 1 and, accordingly, only a few sparse spots are evidence by the combined analysis (Figure 8), apart for accumulation mode sized particles. This agrees with the previously evidenced low number of BTs connecting Region 1 to MHD, suggesting that the generally well-spread correlation between marine aerosol properties and CHL observed for this Region is likely not entirely due to a cause-effect relation. For this reason, Region 1 will not be considered further on in the text. This does not exclude that Region 1 may have an effect on marine aerosol reaching MHD in other periods/seasons or over different time scales, as pointed out by O'Dowd et al. (2015).

### 3.4. Effect of Meteorology on Marine Aerosol Properties

In order to evaluate the importance of oceanic biochemistry in determining the observed marine aerosol properties with respect to other relevant atmospheric parameters, we evaluated the relationship between aerosol properties and the main meteorological variables over the NA ocean. The fifth generation of ECMWF atmospheric reanalysis data (ERA5) accessed from the Copernicus Climate Change Service (<https://cds.climate.copernicus.eu/>) was analyzed to perform a spatio-temporal correlation analysis between in situ aerosol properties and meteorological parameters over the western NA Ocean domain, similar to that done with CHL. A max delay time of 5 days was considered in this case, as no meteorological effect can reasonably go back more than 5 days before aerosol sampling time.



**Figure 6.** (a) Examples of correlation coefficient spatial distribution between the number concentration of INPs for particulate matter less than  $1 \mu\text{m}$  and CHL concentration over the North Atlantic Ocean for 7 days (left) and 18 days (right) time lag, considering only clean marine air masses. (b) Correlation coefficient as a function of time lag between mean CHL concentration at different selected regions and the concentration of INPs. The black dashed lines represent the critical level of significant correlation at 95% confidence limit.

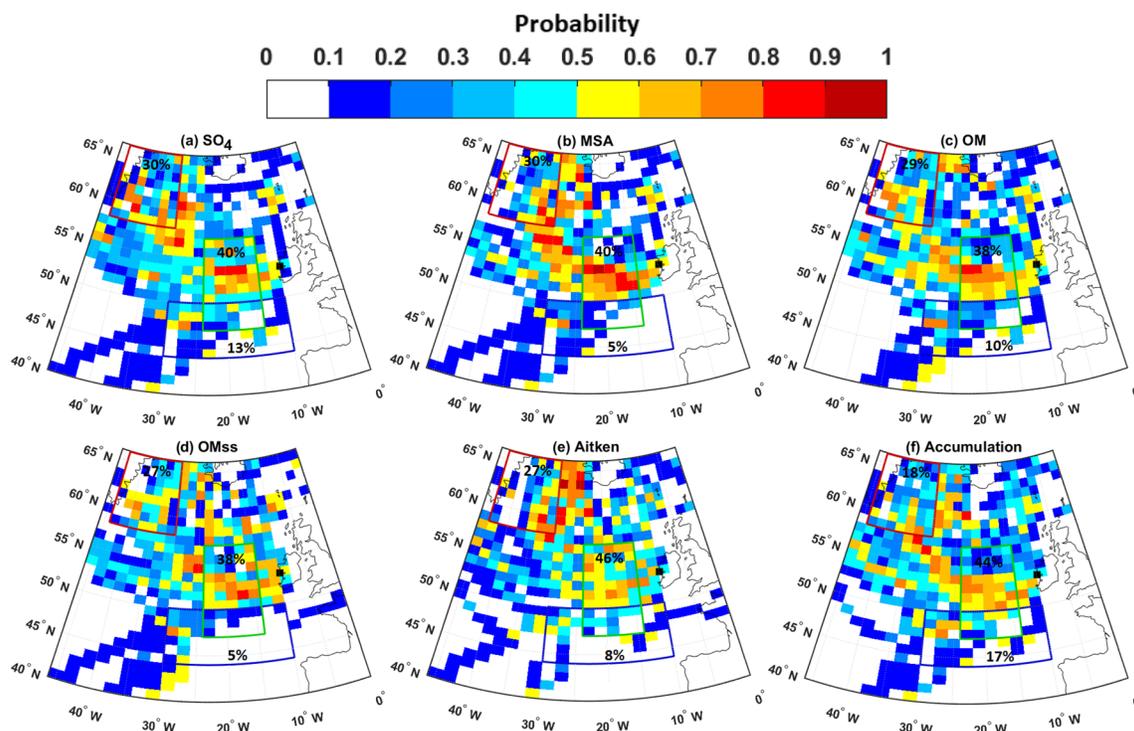
The correlation coefficients between clean marine aerosol properties and the daily mean time series of SST, net surface solar radiation (SSR), and WS over Region 2 are listed in Table 2, together with the correlation coefficients observed between aerosol properties and CHL in that region to facilitate the comparison.

Over Region 2, the main identified source of biogenic aerosol during the campaign, no meteorological parameter correlated with aerosol parameters better than CHL (apart SS and  $n\text{INPs}_{\text{PM10}}$  that do not correlate with CHL). In other words, although meteorological conditions can affect the atmospheric concentrations of marine aerosols (both in terms of mass and number), which will ultimately control the number of CCN and INPs, the strongest driver of the aerosol properties during the study period was marine biological activity traced by CHL.

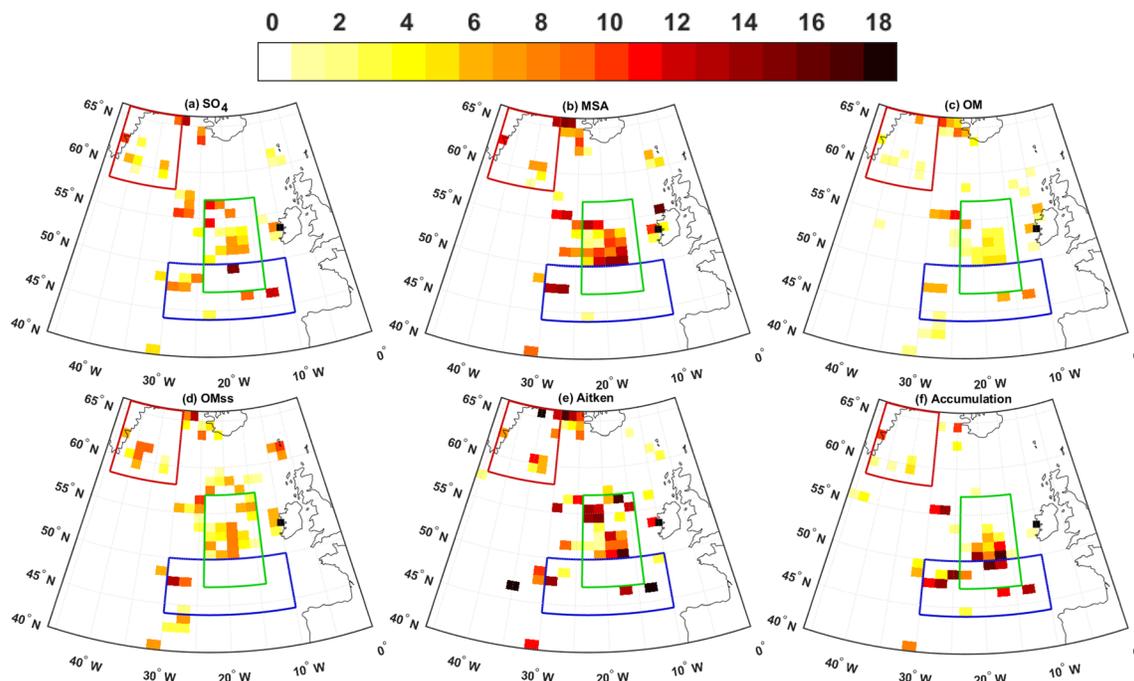
In detail, our results show a significant positive correlation between solar irradiance and both MSA and  $\text{SO}_4^{2-}$ , as expected for DMS photo-oxidation products. Toole and Siegel (2004) suggested that the net biological production and concentration of DMS in the upper mixed layer is directly proportional to the ultraviolet radiation dose at the surface and to seasonally varying variables such as temperature and solar flux. Our results are supported by Becagli et al. (2013) and Vallina and Simo (2007), who showed a strong correlation between DMS concentrations and the solar radiation dose in the upper mixed layer of the open ocean.

A significant negative correlation was observed between  $\text{OM}_{\text{SS}}$  and WS. Previous studies, focused on SSA, interpreted the inverse  $\text{OM}_{\text{SS}}$ -WS relationship as a result of the surface microlayer disruption occurring at high WS, leading to reduced organic enrichment in SSA (Gantt et al., 2011; Rinaldi et al., 2013). Considering that we cannot apportion the observed OM, which may also be contributed by secondary sources (see section 4), we recognize that this correlation may also represent the increase of SS emissions with increasing WS.

The concentration of particle numbers in various modes is positively associated with solar irradiance, thereby demonstrating the significance of processes of secondary aerosol formation during the study period.



**Figure 7.** Potential source contribution function plots for clean marine (a) sulfate, (b) methanesulfonic acid, (c) organic matter, (d) organic enrichment, and (e and f) particle member concentration in the Aitken and accumulation modes. The sources of high concentrations are defined above the median values during the period 31 August to 21 September 2015. The percent of grids that have high probability  $\geq 0.5$  inside each of the three marked regions are inserted.



**Figure 8.** Spatial distribution of the aerosol sources identified by merging the results of the spatio-temporal correlation with CHL and of PSCF for (a) sulfate, (b) methanesulfonic acid, (c) organic matter, (d) organic enrichment, and (e and f) particle member concentration in the Aitken and accumulation modes. The color scale reflects how many times a given pixel has PSCF  $\geq 0.5$  and significant correlation coefficient by running time lag from 8 to 25 days.

**Table 2**  
Daily Correlation Coefficients Between Clean Marine Aerosol Studied Variables and Meteorological Variables Over the Evidenced Source Area (Region 2) in the NA Ocean

Parameter	Samples number	SST (°C)	SSR (J m <sup>-2</sup> )	WS (m s <sup>-1</sup> )	CHL (mg m <sup>-3</sup> )
SO <sub>4</sub> <sup>2-</sup>	<i>n</i> = 35 <i>Rc</i> = 0.33	0.36	0.45	-0.35	0.57
MSA			0.49		0.74
OM			0.35		0.42
OM <sub>SS</sub>	0.39		0.49		
NH <sub>4</sub> <sup>+</sup>	0.47				
SS	0.40				
N <sub>20-100nm</sub>	<i>n</i> = 38 <i>Rc</i> = 0.32		0.45		0.64
N <sub>100-500nm</sub>			0.40		0.45
N <sub>20-500nm</sub>			0.46		0.66
<i>n</i> CCN <sub>0.25</sub>	<i>n</i> = 25 <i>Rc</i> = 0.40		-0.41		0.55
<i>n</i> CCN <sub>0.50</sub>		0.67			
<i>n</i> CCN <sub>0.75</sub>		0.77			
<i>n</i> INP <sub>SPM1</sub>	<i>n</i> = 25 <i>Rc</i> = 0.4	0.43	0.54		
<i>n</i> INP <sub>SPM10</sub>			0.56	0.52	

*Note.* Consideration is given to the time lag which maximizes the correlation within 5-days corresponding to the aerosol transport duration. Correlations with CHL are also shown at the same time lag in spatial correlation maps for comparison with meteorological data. The presented values are significant at 95% confidence level. *Rc* is the critical correlation coefficient, and *n* is the number of samples.

#### 4. Discussion

A combined approach based on spatio-temporal correlation analysis between in situ aerosol data and high-resolution satellite ocean color data, BT analysis, and PSCF on the NA Ocean domain allowed us to identify the marine regions with the highest probability of being a source of the biogenic aerosol measured at MHD, during summer 2015. The spatio-temporal correlation analysis and PSCF are totally independent one from the other, yet their results are clearly consistent for at least one region within the considered domain.

The main source of marine aerosol was the oceanic region facing directly MHD station, roughly within the grids 47°–57°N and 14°–30°W (broadly corresponding to Region 2), as pointed out in previous works. Within this oceanic region, the influence of phytoplankton patterns on marine aerosol properties is clear, as shown in the previous section.

The region between the eastern coast of Greenland and Iceland can probably be considered as a second source region, clearly of minor impact on the sampling site. This latter source region was never evidenced in previous studies based on multiyear CHL correlation, suggesting that the influence of this region may be lower in other periods of the year. The two considered marine regions are characterized by different patterns in the seasonal cycle of surface CHL as indicated by Lacour et al. (2015), who bio-regionalized the NA Ocean into six clusters based on 17 years of ocean color data. Region 2, in our study, represents the overall subpolar gyre with high phytoplankton biomass during June to September, while Region 3 is represented by two clusters characterized by less spatial coherence than the others and with blooming starting early in May. Allan et al. (2015) evidenced that the Eastern coast of Greenland is a hotspot for new particle formation during summer (July and August) due to emissions of iodine from sea-ice associated algal species. The above results may suggest that such particle source can affect the aerosol population also at high distance and at lower latitudes. This may be an interesting topic for future studies.

Analyzing the “correlation versus time-lag” profiles presented in Figures 3, 4b, and 5b by hierarchical cluster analysis to highlight similarities and differences between them (Table S1), it is evident that MSA and SO<sub>4</sub><sup>2-</sup> (in this order) are the aerosol components with the highest similarity with the total particle and Aitken mode trends. This evidences that SMA components are the most important contributors to the total particle number during the study period. This finding is also supported by the correlation analysis reported in Table S2 and Figures S11 and S12. The analysis shows that particle number, in the two considered modes, correlates best with the main tracers of SMA (MSA and SO<sub>4</sub><sup>2-</sup>), while no correlation is observed with SS (tracer of PMA). The fact that CHL tracks better the atmospheric concentration of smaller particles than accumulation mode sized ones suggests that biological activity emissions have an important impact on new particle

formation. This has been already pointed out, for different marine environments, by other studies (Dall'Osto et al., 2017; Dall'Osto et al., 2018). Wex et al. (2016), Quinn et al. (2017), and Sanchez et al. (2018) obtained similar results over different ocean regions, linking marine CCN to SMA production. In the present study, we are not able to partition OM into its primary and secondary components; however, the correlation with  $\text{SO}_4^{2-}$  (Table S2) suggests a significant secondary contribution during the study period.

Table S1 shows that the profile similarity between accumulation mode particle and CCN concentrations decreases with increasing supersaturation. As already discussed, this reflects the major role of Aitken particles to the CCN pool at higher supersaturation, when also smaller particles can activate and is also reflected by the results of the correlation analysis (Table S2). Contextually, the CCN correlation profile follows quite well the general profile of OM at low supersaturations, while the similarity with OM decreases with increasing supersaturation. The same is true also for  $\text{SO}_4^{2-}$ , even though with a lower dependency on the supersaturation. This reflects the major role that chemistry can play in particle activation at low supersaturation, indicating that also the organic fraction can play a potential role in cloud formation, particularly at low supersaturation.

The evidenced link between surface CHL and submicrometer INPs proves the potential climate relevance of SSA, even during periods dominated by secondary aerosols. Indeed, the ice nucleation activity of marine aerosol has been related to the organic content of SSA (DeMott et al., 2016; McCluskey, Hill, Humphries, et al., 2018; McCluskey, Hill, Sultana, et al., 2018; McCluskey, Ovadnevaite, Rinaldi, et al., 2018; Wilson et al., 2015), while no ice nucleation ability is attributed in literature to secondary (organic or inorganic) particles. Supporting our findings, a relation between algal blooming and ice nucleating properties of SSA has already been reported in the literature (McCluskey et al., 2017; Wilbourn et al., 2020).

Previous studies pointed out the relationship between the yearly cycle of marine biological activity, as observed by CHL concentration and net primary productivity, and marine aerosol properties over the NA Ocean (Cavalli et al., 2004; O'Dowd et al., 2004; O'Dowd et al., 2015; Rinaldi et al., 2013; Yoon et al., 2007). In particular, Rinaldi et al. (2013) tried to deconvolute the different time scales of the signals generating the  $\text{OM}_{\text{SS}}$  versus CHL correlation over the Eastern NA Ocean. They concluded that, although the seasonal signal (variability over 1 year) played a major role, the observed correlation was also contributed by both short-term fluctuations (i.e., subseasonal scale) and interannual variability (i.e., time scale greater than 1 year). The former was demonstrated to contribute for time scales of 60 and 90 days, while no statistically robust conclusion could be derived for faster fluctuations (1 month or less). The present work demonstrates that a relationship between phytoplankton activity and the main aerosol physicochemical and cloud-relevant properties can be observed also on a short time scale (1–2 months). This correlation is not driven by the seasonal pattern and shows that short time scale variations in the oceanic biological activity affect aerosol properties quickly, with a delayed response of the order of 10–20 days. This delay coincides roughly with the time necessary to pass from the blooming to the decaying phase of an algal bloom (Lehahn et al., 2014) and has been previously related to the release of SSA-transferable OM in surface seawater (O'Dowd et al., 2015; Prather et al., 2013).

These results are broadly similar to those by O'Dowd et al. (2015) which reported a peak in the correlation at 24-day delay time for  $\text{OM}_{\text{SS}}$ , but with a correlation coefficient frequency distribution that was very similar between time lags of 8, 16, and 24 days. It may also be worth considering that O'Dowd et al. (2015) used a multiyear data set, while the present study is focused on 2 months of intensive measurements, representative of late summer. This can explain some of the observed discrepancies as it can be expected that biological and biochemical processes at the sea surface occur at different velocities, in different seasons, depending on biotic (e.g., type of phytoplankton and stress conditions) and abiotic (e.g., SST, radiation, and WS.) conditions. On the other hand, the discrepancy with the results of Rinaldi et al. (2013), which reported maximized correlation at 8-day time lag, can mainly be explained by the different time resolution of the data: 8-day integrated offline samples against daily observations. In fact, the time resolution of the observations has an impact on the results of the correlation analysis, as shown by O'Dowd et al. (2015).

## 5. Conclusions

This work highlights the relationship between the NA Ocean biological activity and physicochemical/cloud relevant properties of atmospheric aerosol particles measured at the remote coastal location of MHD during late summer 2015.

The combined approach followed in this study, merging in situ aerosol data, satellite retrieved CHL fields, and BTs, allowed for the identification of the main source region of biogenic marine aerosol sampled at MHD during the campaign. Such region is comprised between 47°–57°N and 14°–30°W, facing directly MHD, and presents a clear lagged correlation between all the main aerosol physicochemical properties and surface CHL concentration. A second potential source region, of minor impact, was also suggested in the seawaters between the eastern coast of Greenland and Iceland.

These spatial and temporal relationships demonstrate that the marine biota influences aerosol properties under a variety of aspects, from chemical composition to number concentration and size distribution, up to the most cloud-relevant properties (CCN and INP concentration). Furthermore, during the study period, CHL was the most influential parameter, explaining the majority of the observed variance in aerosol properties, while a lower contribution from meteorological parameters was observed. Consequently, the oceanic biological activity can be considered the strongest driver of marine aerosol properties over the NA Ocean, at least in the conditions represented by the present study.

On multiyear scales, the fractional contribution of organics in SSA was reported to be mostly related to marine biology as traced by CHL concentration and net primary production. In the present study, we show that the same occurs on a shorter time scale of the order of 1–2 months, and that all the main aerosol components follow the same trend (apart SS). A better knowledge of these short time scale interactions may lead to a significant improvement in understanding of the ocean-atmosphere-cloud system, which contributes to large uncertainty in radiative forcing of the climate.

#### Data Availability Statement

The data used in the analysis are published in a digital Mendeley repository accessible through <https://doi.org/10.17632/65kypkcyxf.1>.

#### Acknowledgments

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