

# Journal of Geophysical Research: Atmospheres

## RESEARCH ARTICLE

10.1002/2013JD021330

**Key Points:**

- AMS measurements revealed seasonal trend in marine aerosol chemical composition
- Chemical aerosol signatures were associated with the origin of marine air masses
- Evolution of organic oxidation is determined by marine organic composition

**Supporting Information:**

- Readme
- Text S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4

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**Citation:**

Ovadnevaite, J., D. Ceburnis, S. Leinert, M. Dall’Osto, M. Canagaratna, S. O’Doherty, H. Berresheim, and C. O’Dowd (2014), Submicron NE Atlantic marine aerosol chemical composition and abundance: Seasonal trends and air mass categorization, *J. Geophys. Res. Atmos.*, 119, 11,850–11,863, doi:10.1002/2013JD021330.

Received 7 DEC 2013

Accepted 21 SEP 2014

Accepted article online 24 SEP 2014

Published online 18 OCT 2014

## Submicron NE Atlantic marine aerosol chemical composition and abundance: Seasonal trends and air mass categorization

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**Abstract** Three years of continuous Aerosol Mass Spectrometry measurements at the Mace Head Global Atmosphere Watch research station revealed seasonal patterns in the chemical composition of submicron NE Atlantic marine aerosol as well as distinct chemical signatures associated with marine air masses of different origin (i.e., polar, Arctic, or tropical). Concentrations of secondary inorganic aerosol species and both primary and secondary organic compounds were closely related to oceanic biological activity and ranged from low median mass concentrations during winter to high median values during summer as follows:  $0.025\text{--}0.9 \mu\text{g m}^{-3}$  for nonsea-salt sulfate (nss-sulfate),  $0.025\text{--}0.4 \mu\text{g m}^{-3}$  for organic matter,  $0\text{--}0.09 \mu\text{g m}^{-3}$  for methanesulfonic acid (MSA). Sea-salt concentrations illustrated an opposite pattern with the highest median value being observed during winter ( $0.74 \mu\text{g m}^{-3}$ ) and lowest during summer ( $0.08 \mu\text{g m}^{-3}$ ). Maritime polar air masses typically featured the highest concentrations of sea salt and marine organics, particularly enhanced under primary organic plumes during periods of high biological activity. MSA and nss-sulfate were more prominent in tropical air masses. The oxidation of organic matter increased with increasing ozone concentration and wintertime (low biological activity) organic matter displayed a different fragmentation pattern from that of summertime organic compounds.

### 1. Introduction

The marine aerosol is an important part of the natural aerosol and often dominates the total aerosol burden in remote locations. However, the exact chemical and physical properties of marine aerosol are still not well quantified, especially in terms of the organic aerosol component and its seasonal and regional variation. The sources of marine aerosol range from the primary aerosol production, sea spray, to secondary particle formation resulted from dimethyl sulfide (DMS) oxidation or marine volatile organic compounds (VOC) [O’Dowd and De Leeuw, 2007]; the different marine aerosol sources also affect their chemical and physical properties. Sea spray composition varies depending on the season and biological activity. During periods of low biological productivity, sea spray aerosol consists mainly of sea salt, but it could be dominated by organic compounds during the periods of high productivity, e.g., in the northeast Atlantic Ocean [O’Dowd *et al.*, 2004]. Likewise, the secondary aerosol production and its properties would depend on the season and temperature [Seinfeld and Pandis, 2006], and the availability of DMS and marine VOC.

The importance of the marine aerosol at the global scale has been documented in many studies [Gantt and Meskhidze, 2013; Leck and Bigg, 2005; Monahan *et al.*, 1983; O’Dowd and De Leeuw, 2007; Ovadnevaite *et al.*, 2011b; Russell *et al.*, 2010; Schmale *et al.*, 2013; Sciare *et al.*, 2009; Vignati *et al.*, 2010]. Moreover, the considerable marine source contribution to the aerosol loading observed in one of Europe’s megacities [Crippa *et al.*, 2013] and to continental polluted air masses at Mace Head [Ceburnis *et al.*, 2011] have been recently reported.

Marine aerosol plays a significant role in both direct and indirect climate effects by affecting the aerosol scattering [Bates *et al.*, 2006; Kleefeld *et al.*, 2002; Vaishya *et al.*, 2011] and cloud formation [Andreae and Rosenfeld, 2008; O’Dowd *et al.*, 1999; Ovadnevaite *et al.*, 2011a]. Therefore, understanding marine aerosol sources, chemical composition, and its seasonal changes is essential for climate models [Gantt and Meskhidze, 2013]. Changes in marine aerosol composition are related to the seasonal changes in marine biological

activity [Cavalli *et al.*, 2004; O'Dowd *et al.*, 2004; Sciare *et al.*, 2009; Yoon *et al.*, 2007]; moreover, specific organic species have been attributed to marine organics [Facchini *et al.*, 2008b; Fang *et al.*, 2002; Mochida *et al.*, 2002; Russell *et al.*, 2010]. Medium-term and long-term studies with detailed regional chemical characterization are still lacking.

Recently, high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) data have revealed new and unique features about marine aerosol chemical composition such as the plume-like behavior of marine organics [Ovadnevaite *et al.*, 2011b], dependence on air mass origin [Dall'Osto *et al.*, 2010], and mass spectral fingerprints [Ovadnevaite *et al.*, 2011b; Schmale *et al.*, 2013].

In this work a unique data set consisting of continuous 3 year HR-ToF-AMS measurements of marine aerosol at the Mace Head Atmospheric Research Station is examined in detail. The high time resolution aerosol mass spectrometer data are used to understand the effect of season and air mass origin on the chemical composition of the marine aerosol.

## 2. Methods

### 2.1. Location

The measurements were undertaken at the Mace Head Global Atmosphere Watch research station, located on the west coast of Ireland and facing westward to the northeast Atlantic. More detailed station information is summarized in O'Connor *et al.* [2008] and O'Dowd *et al.* [2013]. The measurements reported in this study spanned a period from 1 January 2009 to 30 June 2011. Considering that marine atmosphere can be potentially perturbed by anthropogenic pollution, especially in the Northern Hemisphere, the data in this study were strictly filtered to select only the cleanest maritime air masses, using a strict and conservative black carbon (BC) concentration criteria (hourly BC concentrations  $<15 \text{ ng m}^{-3}$ ). An analysis of the Mace Head representativeness of clean maritime air masses can be found in the recent study by O'Dowd *et al.* [2013]. Essentially, there are three maritime air masses encountered at Mace Head, namely maritime polar (*mP*), maritime tropical (*mT*), and maritime Arctic (*mA*). A detailed air mass classification for Mace Head can be found in the study by Dall'Osto *et al.* [2010], and trajectories representing air masses during this study are shown in Figure 1. Although all three masses are maritime, they possess different meteorological characteristics (details are presented in the supporting information) and are influenced by specifically different source regions.

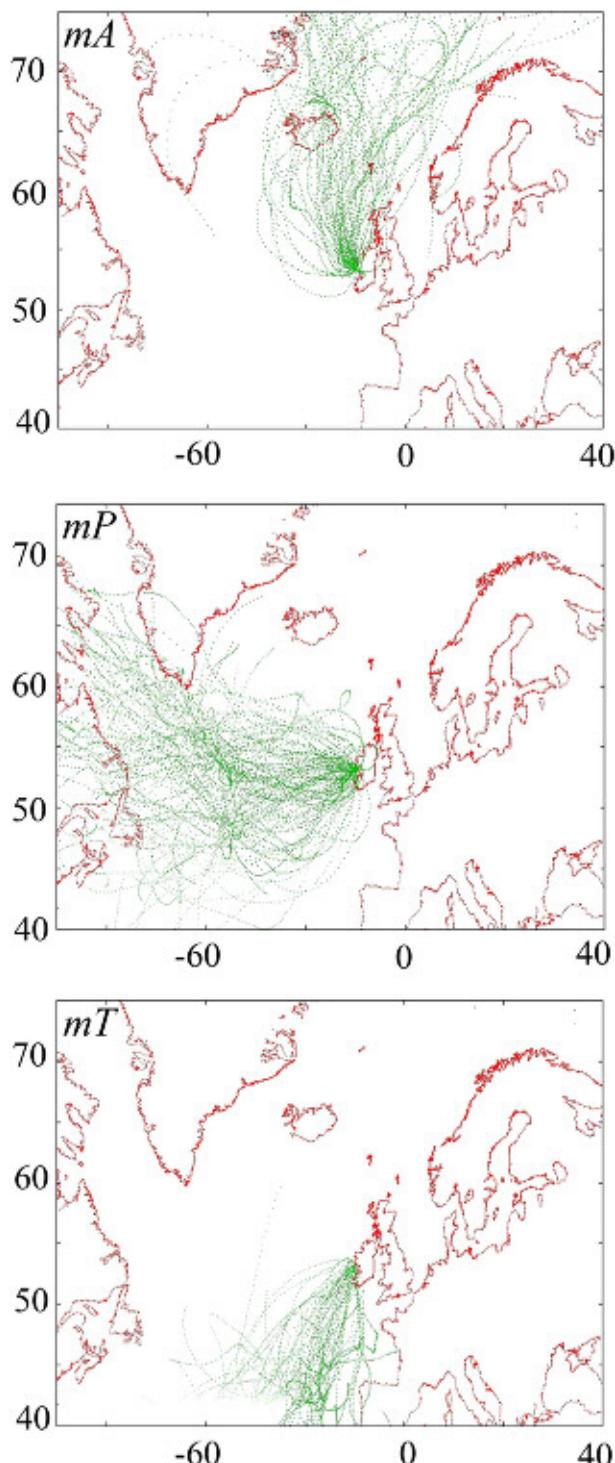
### 2.2. Clustering of the Air Mass Back Trajectories

Air mass back trajectories were calculated using Hybrid Single-Particle Lagrangian Integrated Trajectory, a transport and dispersion model developed by the NOAA Air Resources Laboratory [Draxler and Rolph, 2014]. The back trajectories were calculated every 6 h for an arrival height of 100 m and length of 96 h. The individual back trajectories were then clustered using a nonhierarchical clustering algorithm based on the work of Mattis [2002] and Dorling *et al.* [1992]. The methodology used in this study is described in more detail in Tripathi *et al.* [2010]. The cluster analysis yielded an optimal number of 11 clusters for Mace Head. These clusters were then further combined to marine air mass types, as illustrated in Figure 1 for *mP*, *mT*, and *mA* air masses considered in this study.

### 2.3. Aerosol Chemical Composition Measurements

The characteristic chemical composition of submicron aerosols in different marine air masses was derived from the high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) [DeCarlo *et al.*, 2006] measurements. The HR-ToF-AMS was routinely calibrated according to the methods described by Jimenez *et al.* [2003] and Allan *et al.* [2003]. The HR-ToF-AMS was connected to the main community sampling system while retaining an isokinetic flow. The main sampling system was constructed from a 100 mm diameter stainless steel pipe with the main inlet at 10 m above ground level. The performance of this inlet is described in Kleefeld *et al.* [2002].

The HR-ToF-AMS measurements were performed at a time resolution of 5 min and a vaporizer temperature of  $\sim 650^\circ\text{C}$ . The net overall particle transmission and detection efficiency, expressed as the collection efficiency (CE), are dependent on the particle composition. Therefore, a composition-dependent CE [Middlebrook *et al.*, 2012] was applied for the measurement periods discussed in this study, and consequently, the CE in this



**Figure 1.** Classification of marine air mass back trajectories: (top) Trajectories assigned to maritime arctic air mass; (middle) maritime polar air mass; (bottom) maritime tropical air mass. The back trajectories were calculated every 6 h, and the length is 96 h.

followed by a Differential Mobility Analyzer configured to pass 300 nm monodisperse particles from the nebulized polydisperse flow, and fed directly into the AMS inlet. The high-resolution mass spectrum was measured and analyzed using the standard high-resolution AMS data analysis tool (PIKA v1.10h). The main ions

study ranged from 0.45 to 0.97. In supporting tests, good agreement was found between the online aerosol mass spectrometer (AMS) nss-sulfate measurements and those obtained by offline ion chromatography PM<sub>2.5</sub> filter measurements (presented in Figures S1 and S2 in the supporting information). Corrections due to relative humidity were not applied here as RH was always < 80% in the sampling line in front of the AMS inlet.

Since the air mass back trajectories were obtained every 6 h, the higher time resolution HR-ToF-AMS data were selected accordingly, that is, 1 h average around the time of the air mass back trajectory was calculated and used in this study, assuming that this average represented the time of the appropriate trajectory.

#### 2.4. Methanesulfonic Acid Calibration and Measurements

It is commonly considered that the HR-ToF-AMS quantitatively measures only nonrefractory aerosol composition, namely, organics, sulfate, nitrate, and ammonium; however, with careful calibration, it is also capable of quantifying nonrefractory methanesulfonic acid (MSA) and refractory sea salt at 650°C. Methanesulfonic acid is one of the largest identified contributors to the marine organics [Facchini *et al.*, 2008a]. In the AMS, quantification of MSA is complicated by the fact that MSA fragments to several organic ions as well as to inorganic sulfate-containing ions such as SO<sup>+</sup> and SO<sub>2</sub><sup>+</sup> which can also have large contributions from inorganic aerosol sulfate species. Indications that the MSA fragmentation pattern could be instrument dependent [Zorn *et al.*, 2008] complicate its quantification further.

The fragmentation pattern of MSA was explicitly calibrated for the HR-ToF-AMS used in this study. The HR-ToF-AMS was calibrated using 0.02% aqueous solution of MSA (Sigma-Aldrich, ≥99.5%) dissolved in deionized water. The 4 mM solution was nebulized with a TSI atomizer (model 3076),

contributing to the MSA fragmentation pattern were  $\text{CH}_3^+$  (m/z 15.02),  $\text{CHS}^+$  (m/z 44.98),  $\text{HSO}_2^+$  (m/z 64.97),  $\text{CH}_3\text{SO}_2^+$  (m/z 78.98), the parent ion  $\text{CH}_3\text{SO}_3\text{H}^+$  (m/z 95.99), and ions contributing to the sulfate spectrum:  $\text{SO}^+$  (m/z = 47.96) and  $\text{SO}_2^+$  (m/z = 63.96). Since many of these fragments can come from sources other than the MSA, only the ions  $\text{CH}_3\text{SO}_2^+$  and  $\text{CH}_3\text{SO}_3\text{H}^+$ , almost exclusively of MSA origin, were selected for the MSA quantification. The ratio between the ion intensity and the total MSA concentration was found; moreover, the contribution of MSA ions to inorganic sulfate fragments was subtracted by scaling to typical organic MSA ions in order to allow for more accurate quantification of nss-sulfate concentrations. The fragmentation pattern dependence on the AMS vaporizer temperature was analyzed as its importance was indicated in the previous study by Zorn *et al.* [2008]. We found 2% variation in signal intensity within the AMS vaporizer temperature range from 550°C to 650°C; however, the significant changes can occur if the vaporizer is operated at lower temperature regimes [Zorn *et al.*, 2008].

## 2.5. Sea-Salt Measurements

Though sea salt is considered to be a refractory species and thus assumed not to be measurable by the AMS, recent studies [Ovadnevaite *et al.*, 2012; Schmale *et al.*, 2013] have shown that sea salt can, indeed, be measured and even quantified with the HR-ToF-AMS. The sea-salt measurement method by the HR-ToF-AMS is described in detail in Ovadnevaite *et al.* [2012]. Where detailed intercomparison with a filter method, showing a very good and quantitative agreement between AMS and filter measurements ( $R^2 = 0.87$ ), is presented. The same scaling factor of 51 was used here as the measurements cover the same period as in Ovadnevaite *et al.* [2012].

## 2.6. Nonsea-Salt Sulfate Calculations

Nonsea-salt sulfate (nss-sulfate) and sea-salt sulfate can both contribute to the measured sulfate concentrations; therefore, the contribution of the nss-sulfate was evaluated by subtracting the sea-salt sulfate concentration (7.7% of total sea salt, measured by HR-ToF-AMS) [Ovadnevaite *et al.*, 2012] from the total sulfate concentration. However, these corrections were substantial only for cases of low sulfate and high sea-salt concentrations during winter months and were insignificant during the high biological activity, high sulfate, and low sea-salt concentration cases.

## 2.7. Neutralization of Nss-Sulfate Particles

A neutralization of nss-sulfate particles is calculated from the ratio between  $\text{NH}_4^+$  measured by HR-ToF-AMS and  $\text{NH}_4^+$  required to fully neutralize nss-sulfate. A ratio of 1 indicates fully neutralized nss-sulfate in the form of ammonium sulfate, and values higher than 1 indicate that nitrate or chlorine neutralization should be included. During this study neutralization ratios greater than 1 were not observed.

## 2.8. Ozone Measurements

Ozone ( $\text{O}_3$ ) measurements were acquired every 10 s using a commercial UV spectrometer (Model 49C, Thermo Electron Inc., CO, USA) and recorded as hourly averages. The instrument was calibrated every 3–6 months against a primary UV photometer [Sweeney and Stacey, 1992]. The instrument was also regularly validated by a system and performance audit conducted by the World Calibration Centre for surface ozone [Zellweger *et al.*, 2005], and the performance of the instrument was consistently judged to be good.

## 3. Results

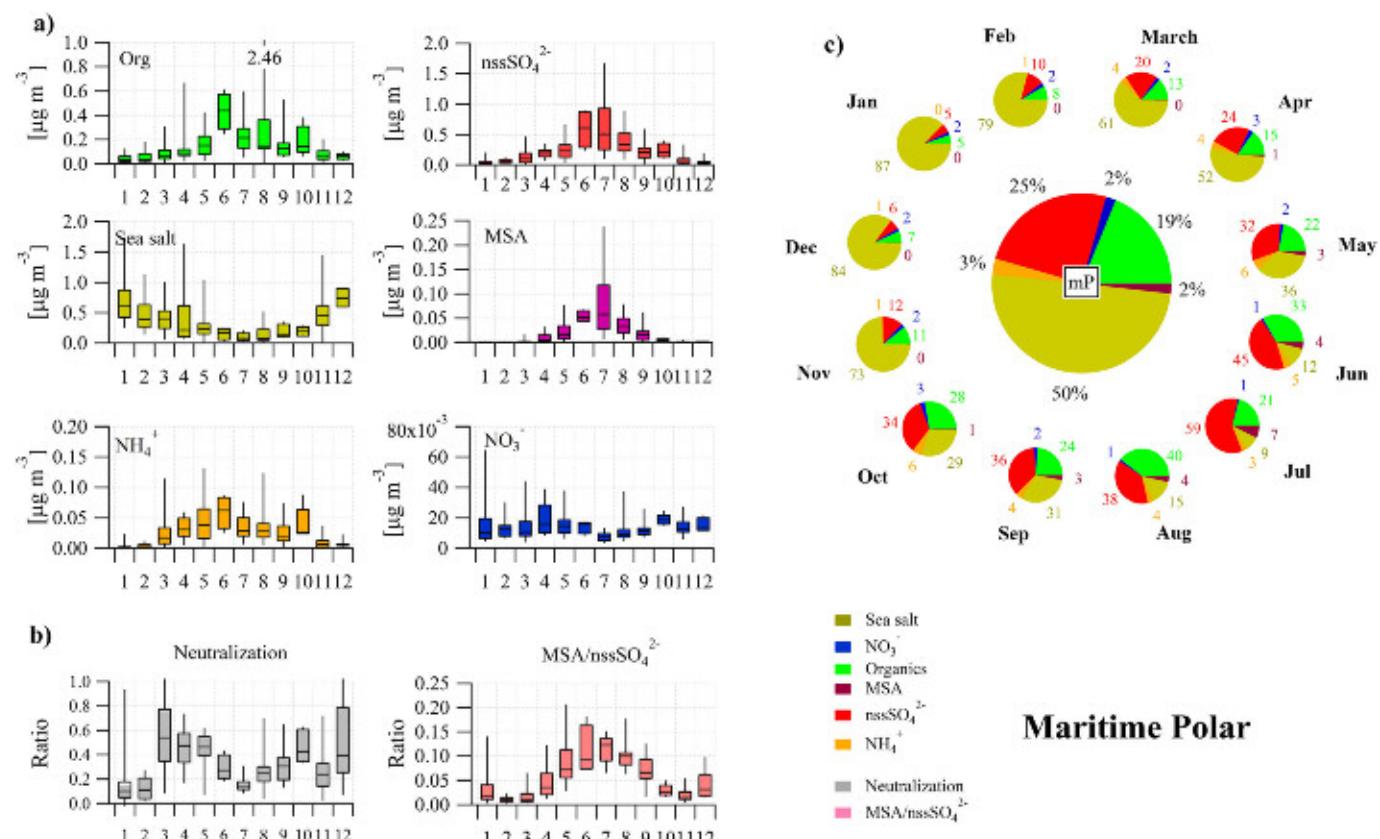
Speciated aerosol mass concentrations and fractional contributions to the total aerosol mass concentration are presented in Table 1. The results are segregated into two out of four seasonal periods: summer (June, July, and August) and winter (December, January, and February). The maritime polar air mass has the highest organic contribution during summer and the highest sea-salt concentration during winter. On the other hand, aerosol advected in the maritime tropical air mass contains higher contributions from nss-sulfate, consistent with the previous study by Dall'Osto *et al.* [2010]. Table 1 also illustrates that the standard deviations are often larger than the average mass concentrations themselves, indicating that mass concentrations were not normally distributed. For this reason, further detailed monthly variations of chemical compounds are presented by medians and percentiles rather than the average values. The number of air mass occurrences for every month and the data used for the averages and medians are presented in the supporting information (Figure S3).

**Table 1.** Chemical PM<sub>1</sub> Particle Composition During Periods of High (Summer) and Low (Winter) Biological Activity in Different Marine Air Masses ( $\mu\text{g m}^{-3}$ )<sup>a</sup>

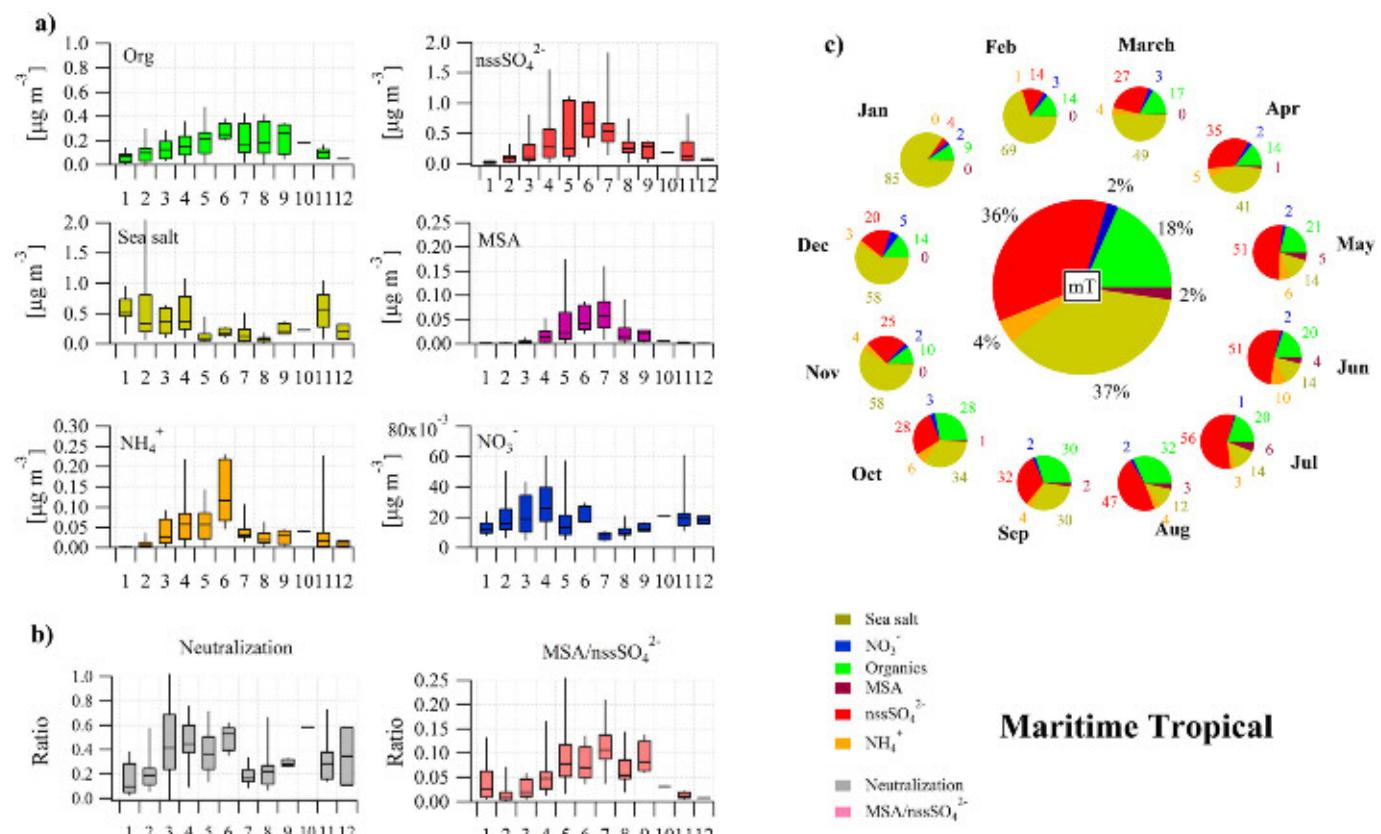
		mP					mT					mA				
		N	Mean	Median	SD	%	N	Mean	Median	SD	%	N	Mean	Median	SD	%
Summer	Org	59	0.36	0.2	0.45	34	43	0.21	0.19	0.13	24	30	0.22	0.22	0.12	24
	nss-SO <sub>4</sub> <sup>2-</sup>		0.46	0.37	0.32	44		0.45	0.36	0.33	52		0.43	0.34	0.37	48
	SS		0.13	0.08	0.11	12		0.11	0.09	0.10	13		0.16	0.11	0.14	18
	MSA		0.05	0.04	0.04	5		0.04	0.03	0.03	5		0.04	0.02	0.04	4
	NO <sub>3</sub> <sup>-</sup>		0.01	0.01	0.01	1		0.01	0.01	0.01	1		0.01	0.01	0.01	1
	NH <sub>4</sub> <sup>+</sup>		0.04	0.03	0.02	4		0.04	0.03	0.05	5		0.04	0.03	0.02	4
	Total		1.05					0.86					0.90			
Winter	Org	77	0.05	0.03	0.04	7	29	0.09	0.08	0.07	13	23	0.04	0.04	0.02	15
	nss-SO <sub>4</sub>		0.05	0.03	0.04	7		0.08	0.06	0.07	11		0.04	0.04	0.02	15
	SS		0.62	0.59	0.33	84		0.50	0.43	0.45	72		0.18	0.12	0.25	66
	MSA		0.00	0	0.00	0		0.00	0	0.00	0		0.00	0	0.00	0
	NO <sub>3</sub>		0.01	0.01	0.01	1		0.02	0.02	0.01	3		0.01	0.01	0.00	4
	NH <sub>4</sub>		0.00	0	0.01	0		0.01	0	0.01	1		0.00	0	0.00	1
	Total		0.73					0.70					0.27			

<sup>a</sup>Averaging period is 1 h. Percentage contribution is calculated from the averages.

Figures 2–4 reveal a general seasonal pattern in all air masses: concentrations of organics, sulfate, methanesulfonic acid, and ammonium increase during the summer season. This trend coincides with the marine biological activity, or productivity, trend and strongly points to a significant biogenic source for the aerosol in question. While generally the ammonium is considered as originating from anthropogenic sources,



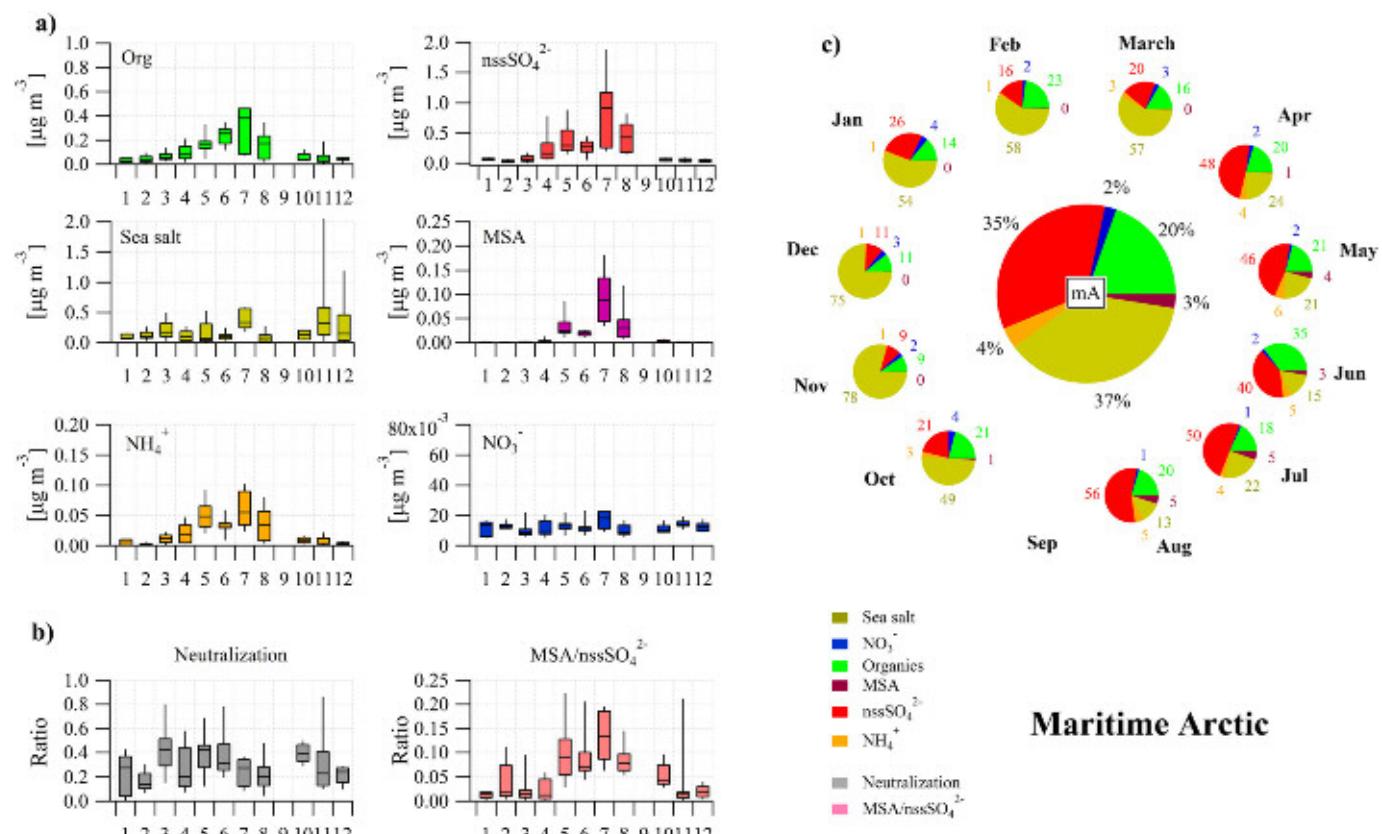
**Figure 2.** Chemical representation and seasonal pattern of the maritime polar air mass. (a) The seasonal pattern of the marine aerosol chemical composition: lines represent median concentrations, boxes represent 25–75% percentile, and whiskers demonstrate 0–100% percentile for all compounds during maritime polar air mass. (b) Left: neutralization of nss-sulfate particles and right: MSA to nss-SO<sub>4</sub><sup>2-</sup> ratio; (c) Average chemical composition of the marine aerosol in maritime polar air mass (pie chart in the center), small pie charts show monthly variations.



**Figure 3.** Chemical representation and seasonal pattern of the maritime tropical air mass. (a) The seasonal pattern of the marine aerosol chemical composition: lines represent median concentrations, boxes represent 25–75% percentile, and whiskers demonstrate 0–100% percentile for all compounds during maritime tropical air mass. (b) Left: neutralization of nss-sulfate particles and right: MSA to nss-SO<sub>4</sub><sup>2-</sup> ratio. (c) Average chemical composition of the marine aerosol in maritime tropical air mass (pie chart in the center), small pie charts show monthly variations.

the seasonal pattern registered here is in agreement with isotopic studies that show ammonium contributions from marine sources [Felix *et al.*, 2013; Jickells *et al.*, 2003]. Sea-salt mass concentration, in contrast, increases during winter months and has the lowest values during summer. Higher winds during winter months are typical for the North Atlantic Ocean [Rinaldi *et al.*, 2013] and result in higher sea spray concentrations due to the power law sea spray-wind speed relationship [Monahan *et al.*, 1983]. The sea-salt seasonality pattern follows previous observations by Vaishya *et al.* [2012], which have shown a high positive correlation coefficient of 0.88 between the aerosol scattering coefficient and wind speed. Figures 2a, 3a, and 4a show the median (lines), 25–75% percentile (boxes), and 0–100% percentile (whiskers) for all compounds during maritime polar (Figure 2a), maritime tropical (Figure 3a), and maritime arctic (Figure 4a) air masses. The largest median concentrations for sulfate, MSA, and organics are observed in June and July. Elevated plume-like concentrations are also observed for organics as previously reported by Ovadnevaite *et al.* [2011b]. The plumes with high organic aerosol mass concentrations correspond to the points in the whisker plot that are much larger than the median. The organic mass concentrations associated with the plumes are significant during the whole period of high biological activity and stood out, in particular, in August, with hourly concentrations reaching up to  $2.46 \mu\text{g m}^{-3}$ . Of all compounds, MSA shows the most pronounced seasonality with systematically higher median concentrations occurring in July for all three marine air masses. Maximum median concentrations are observed in maritime Arctic aerosol (Figures 2a, 3a, and 4a). Minimum concentrations of more or less zero were observed during the winter.

Overall, ammonium concentrations follow the nss-sulfate pattern, but the neutralization of nss-sulfate varies slightly with seasons (Figures 2b, 3b, and 4b). Nevertheless, nss-sulfate in marine air masses arriving to Mace Head is never fully neutralized to ammonium sulfate and ranges from a pure sulfuric acid to ammonium bisulfate state. Since there is always a lack of ammonium, sulfate neutralization is taken into account first as



**Figure 4.** Chemical representation and seasonal pattern of the maritime arctic air mass. (a) The seasonal pattern of the marine aerosol chemical composition: lines represent median concentrations, boxes represent 25–75% percentile, and whiskers demonstrate 0–100% percentile for all compounds during maritime arctic air mass. (b) Left: neutralization of nss-sulfate particles and right: MSA to nss- $\text{SO}_4^{2-}$  ratio. (c) Average chemical composition of the marine aerosol in maritime arctic air mass (pie chart in the center), small pie charts show monthly variations.

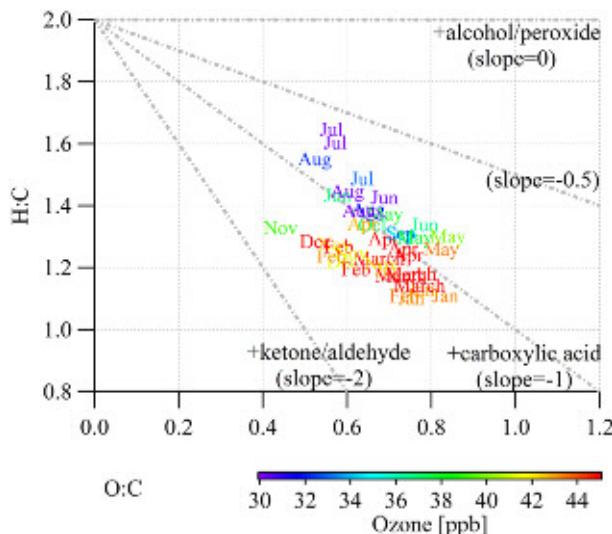
sulfuric acid would always be neutralized first before nitric or other acids. The ratio of measured versus calculated ammonium represents the availability of ammonia to neutralize the existing sulfuric acid; a ratio of 1 indicates fully neutralized sulfate, and all values below 1 indicate the range between the ammonium bisulfate and pure sulfuric acid. The median value of this ratio varies between 0 and 0.6, with the highest values being observed during spring and autumn, indicating higher neutralization to ammonium bisulfate during these periods (Figures 2b, 3b, and 4b) and a dominance of more acidic aerosol during summer. While marine aerosol in *mP* (Figure 2b) and *mT* (Figure 3b) indicate quite similar neutralization patterns, *mA* (Figure 4b) particles have a lower degree of neutralization and weaker variation with seasons.

Nitrate does not show any seasonal pattern, which is actually anticipated due to the absence of marine sources of the particulate nitrate combined with the stringent “clean marine air” sampling criteria deployed. It typically ranges around or below  $20 \text{ ng m}^{-3}$  and along with low BC concentrations indicates very negligible anthropogenic contribution.

The ratio of MSA to nss- $\text{SO}_4^{2-}$  also reveals a seasonal pattern with the highest values being observed during summer (Figures 2b, 3b, and 4b). July median values of the ratio range between 0.11 and 0.13, which is comparable to 0.1 ratio presented by *Crippa et al.* [2013]. Although the latter study was performed in the megacity Paris, the authors were able to separate nss-sulfate of marine origin from that of anthropogenic origin. The comparison with this study is relevant, especially considering the lack of MSA measurements in  $\text{PM}_{1}$  size range. Moreover, the comparison with  $\text{PM}_{2.5}$  particles would not be appropriate due to the preferable MSA condensation on larger particles.

The ratio is higher in colder air masses (*mP* and *mA*) than warmer air masses (*mT*) and is in line with the latitudinal dependence of MSA to nss- $\text{SO}_4^{2-}$  ratio [Berresheim *et al.*, 1995; Campolongo *et al.*, 1999]. For example,

## Maritime Arctic



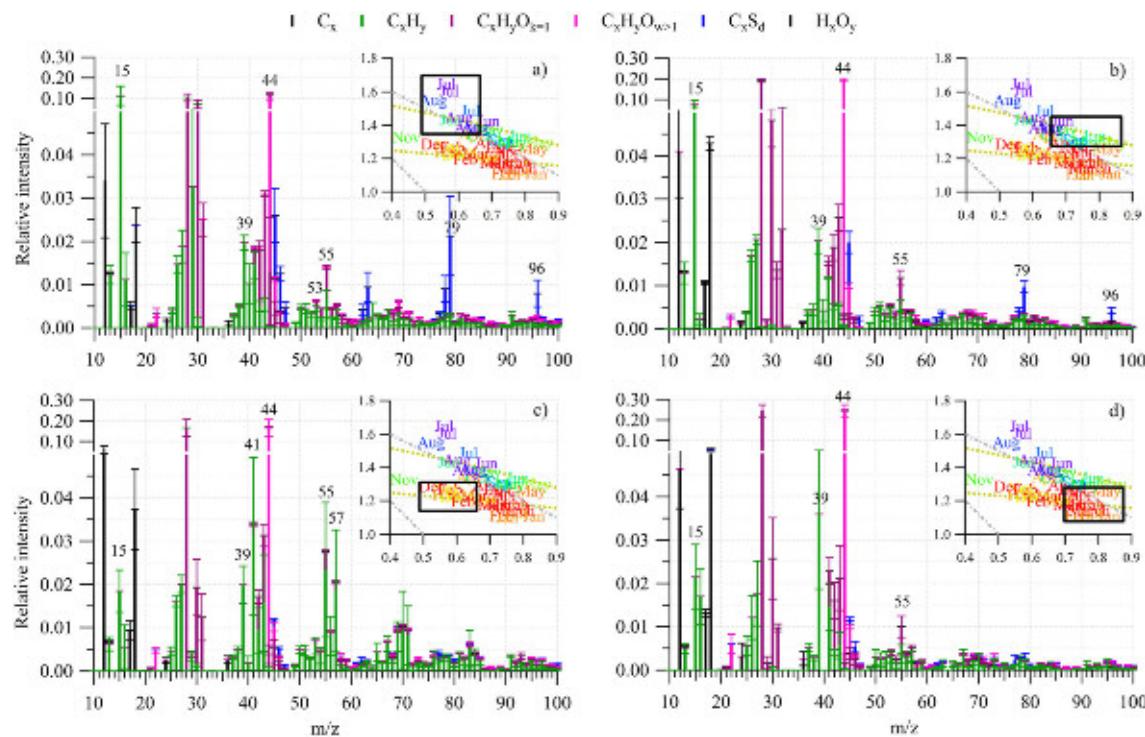
**Figure 5.** Van Krevelen diagram for the marine organic matter. Color scale represents the ozone concentration, data include all three maritime air masses, and abbreviations indicate the averages for the particular month of the year. Grey lines represent functionalization reactions of the organic species [Heald et al., 2010] reproduced from Ng et al. [2011].

and 37%, accordingly, in the  $mT$ ). Organic matter contribution is on the order of 18–20%. Monthly aerosol chemical composition averages (small pie charts in Figures 2c, 3c, and 4c) highlight the predominant sea-salt contribution during the winter season and nss-sulfate during summer (Figures 2c, 3c, and 4c). During August, organic matter dominates the  $mP$  aerosol particle composition and makes up to 40% of the total particle mass (Figure 2c), illustrating the significant contribution from the marine organic plumes. MSA's contribution is highest during summer months and contributed up to 7% of  $PM_1$  aerosol mass in July (maritime polar air mass (Figure 2c)).

Figure 5 shows the evolution of the oxygen to carbon atomic ratio (O:C) and hydrogen to carbon atomic ratio (H:C) of marine organic aerosol in a Van Krevelen diagram [Heald *et al.*, 2010]. Increasing O:C values indicate a history of more oxidation, and smaller H:C values indicate species with a greater degree of unsaturation. The degree of saturation, in the context of organic chemistry, indicates the availability and the proportion of multiple C–C bonds, e.g., unsaturated organic compounds which would contain double or triple bonds, while saturated ones would contain only single bonds. Oxidation reaction would replace hydrogen in C–H bond and thus increase the oxidation state of the organic molecule. Elemental ratios between oxygen and carbon as well as hydrogen and carbon can provide some insights into organic composition [Aiken *et al.*, 2007]. The O:C (H:C) ratios obtained with the HR-ToF-AMS have an absolute average error of ~30% (~10%) and precision of ~5% [Aiken *et al.*, 2007]. Changes of these ratios (presented as Van Krevelen diagram [Heald *et al.*, 2010]) would reflect an aerosol chemical evolution process primarily driven by oxidation. The Van Krevelen diagram cross plots the hydrogen to carbon atomic ratio (H:C) and the oxygen to carbon ratio (O:C) where the most oxidized species lie at the lower right [Heald *et al.*, 2010]. The marine organics shown in Figure 5 are less oxidized and more saturated during the summer months (June, July, and August) in comparison to the spring, winter, or autumn months. The higher degree of oxidation is observed concurrently with higher ozone concentrations, and the correlation between them is ~0.6 (color coding in Figure 5). Other oxidants such as OH, which depend mainly on solar radiation, possess opposite seasonal trends with higher values during summer and lower values during winter. The trends of these oxidants are similar to the seasonal patterns of other marine aerosol species such as MSA and nss-sulfate that result mainly from OH oxidation. Taken together, these observations indicate that oxidation of primary marine organic species is dominated by O<sub>3</sub> rather than OH. It is well known that ozone reacts with unsaturated organic compounds, and previous studies have shown that marine organic species contain unsaturated aliphatic chains [Decesari *et al.*, 2011; Donaldson and George, 2012]. The fact that the highest observed H:C ratio in Figure 5 is lower than 2 (~1.6–1.7; saturated organic compounds would have H:C > 2) indicates that the marine organics in this study contain

the highest median of the ratio during the warm period is 0.12 and 0.13 in  $mP$  and  $mA$ , respectively, while the highest median in  $mT$  was 0.11. A similar trend is observed for the 25–75% percentiles: maximum of 0.16 and 0.17 is observed in  $mP$  and  $mA$ , respectively, and 0.13 in  $mT$ .

The overall average aerosol chemical composition (the large pie charts in Figures 2c, 3c, and 4c) indicates the differences between the three marine air masses. Sea salt clearly dominates the maritime polar air mass aerosol composition (50%) and is followed by nss-sulfate (25%) and organic matter (19%); ammonium (3%), MSA (2%), and nitrate (2%) are minor components (Figure 2c). The nss-sulfate contribution is comparable to that of sea salt in the maritime Arctic (Figure 4c) and tropical (Figure 3c) air masses (35% of nss- $\text{SO}_4^{2-}$  and 37% of sea salt in the mA and 36%



**Figure 6.** Typical mass spectra of the organic matter measured during different periods of the year reflected in Figure 5; the inserts (zoomed replicas of Figure 5) denote periods of interest marked in black; (a) the mass spectrum of the organic matter averaged over summer period (highest H:C and the lowest O:C ratios, July and August periods); (b) the mass spectrum typical of transitional periods (April and September); (c) the mass spectrum of winter organics (December and February); (d) the most oxidized mass spectrum (H:C ~ 1.2 and O:C ~ 0.8) typical of the spring time organics (March and May). Error bars represent standard deviations.

unsaturated carbons that would be capable of reacting with ozone. Moreover, the slope of the Van Krevelen diagram in Figure 5 (approximately  $-1.5$ ) is consistent with the addition of a mixture of carboxylic and keto/aldehyde functionalities as expected for products of the reaction of unsaturated carbon bonds with ozone. The Van Krevelen slope observed in the winter is shallower than in summer and has a value approximately  $-0.6$ . The shallower slope could result from net addition of both COOH and OH/OOH functional groups without fragmentation, and/or the addition of COOH groups with fragmentation [Ng *et al.*, 2011]. Figure 5 indicates that during both seasons, primary marine organic matter is likely to be processed to carboxylic acids and eventually become indistinguishable from other sources of secondary organic matter [Jimenez *et al.*, 2009].

The high-resolution mass spectra of marine organic matter are dominated by the fragments at  $m/z$  39 ( $C_3H_3^+$ ),  $m/z$  53 ( $C_4H_5^+$ ),  $m/z$  43 ( $C_2H_3O^+$ ),  $m/z$  55 ( $C_3H_3O^+$ ), and  $m/z$  44 ( $CO_2^+$ ). These spectra are comparable to those observed during primary marine organic “plume” events [Ovadnevaite *et al.*, 2011b]. The contribution from the  $m/z$  44 (the mass fraction of  $m/z$  44 relative to all organic  $m/z$  fragments) varies with the degree of oxidation—the highest contribution of  $m/z$  44 is observed for the organics with the highest O:C ratio. The  $m/z$  44 contribution, which is a signature of carboxylic acid groups in AMS measurements, increases with increasing oxidation; it contributes  $\sim 14\%$  to the least oxidized spectrum during summer months (Figure 6a), which is consistent with the highest sea spray production and is in agreement with  $\sim 16\%$  registered during organic plume events [Ovadnevaite *et al.*, 2011b]. Effective oxidation and less efficient primary production of sea spray aerosol results in higher  $m/z$  44 contribution ( $\sim 20\%$ ) during early spring and autumn (Figure 6b) with the highest contributions ( $\sim 27\%$ ) registered in late spring (Figure 6d).

The summertime high-resolution mass spectra show a contribution from MSA fragments (e.g.,  $m/z$  15, 45, 46, 63, 78, 79, and 96) that are all associated with different CH, CHS, and CHSO fragments. They are more intense during the periods of high biological activity but nonplume organic (July and August, Figures 6a and 6b).

In addition to a different slope in the Van Krevelen diagram, the wintertime organic matter has a different mass spectral fragmentation pattern that is dominated by hydrocarbon series such as  $C_nH_{2n-1}$ ,  $C_nH_{2n}$ , and  $C_nH_{2n+1}$  (Figure 6c). The  $C_nH_{2n+1}$  and  $C_nH_{2n-1}$  hydrocarbon fragments (e.g.,  $m/z$  15, 43, 57, and 71 and

m/z 41, 55, 69, and 83, respectively) indicate a notable contribution from refined anthropogenic hydrocarbons; however,  $C_nH_{2n+1}$  and  $C_nH_{2n-1}$  along with  $C_nH_{2n}$  (m/z 42, 56, 70, and 84) could also arise from the aliphatic halides ( $C_nH_{2n}X^+$ , where X could be fluorine, chlorine, bromine, and iodine) [McLafferty and Turecek, 1993]. The  $C_nH_{2n}$  class of fragments is not typical for the anthropogenic hydrocarbon organic aerosol [Zhang *et al.*, 2011].

#### 4. Discussion

The continuous and extensive 3 year HR-ToF-AMS data set obtained and analyzed in this study enabled the most detailed definition of northeast Atlantic marine aerosol composition seasonal patterns and cycles to date. The seasonal cycles observed here are consistent with the previous studies done at Mace Head [Cavalli *et al.*, 2004; O'Dowd *et al.*, 2004; Yoon *et al.*, 2007]. An increase in nss-sulfate, MSA, and organic matter is observed during midsummer, and low concentrations of these species are observed during winter. Sea salt has an opposite seasonal time trend. On the other hand, no seasonal pattern was observed for submicron nitrate concentration as compared to Yoon *et al.* [2007] who registered an increase in concentration of the coarse nitrate during summer.

Over and above the previous studies, the current study's data set also enabled the identification of distinct organic fingerprints during periods coinciding with different levels of primary biological productivity and different air mass source regions. Significant variations in chlorophyll *a* (chl *a*) concentrations with latitude are characteristic of the North Atlantic Ocean [Siegel *et al.*, 2013]; however, it seems that observed changes in marine aerosol concentration and composition are not as prominent. Organic matter dominated the marine aerosol composition in *mP* air masses, and the highest sea-salt concentrations (absolute and relative) were also registered in the maritime polar air masses during the winter season when winds were high. The *mT* air masses, which were characterized by higher temperatures and oxidative potential, had the highest contributions of secondary nss-sulfate. Maritime arctic aerosol was characterized by different seasonal patterns due to the shorter period of biological activity in these air masses.

Entrainment of air from the free troposphere (FT) could have had some impact on the measurements here, but the most likely effect for typical clean background FT was to dilute absolute aerosol concentrations while maintaining the marine aerosol chemical signature. While entrainments of pollution or biomass burning plumes can contribute to the measured organic matter (OM), the dual isotope approach [Ceburnis *et al.*, 2011] revealed that nonmarine OM contributes less than 20% of the total OM mass observed at Mace Head in the marine sector. In our analysis, we expect negligible contributions of these nonmarine OM sources by applying more confined filtering criterion for the cleanliness of the air mass (hourly BC concentrations  $< 15 \text{ ng m}^{-3}$  instead of  $50 \text{ ng m}^{-3}$  used in Ceburnis *et al.* [2011] study). This is consistent with the fact that the OA mass spectral signatures shown in Figure 6 are more similar to those of marine organic plumes [Ovadnevaite *et al.*, 2011b] than to mass spectral signatures of anthropogenic OA.

The seasonal evolution of the oxidation and saturation of organic matter can be explained by the peculiar composition of the primary marine organic matter. Numerous studies on organic biomarkers in oceanic waters [Rontani *et al.*, 2007; Volkman *et al.*, 1998; Volkman and Tanoue, 2002; Zabeti *et al.*, 2010] have indicated that predominant particulate organic carbon consists of long unsaturated aliphatic chains, lipids, fatty acids, and similar organic compounds originating from algae, bacteria, and viruses associated with them. Moreover, similar compounds were also found in the aerosol phase during biologically active periods and were attributed to the primary marine sources [Facchini *et al.*, 2008b; Fu *et al.*, 2013]. The presence of these compounds is, indeed, consistent with the mass fingerprints and H:C and O:C features observed in this study, especially during the high biological activity months (June, July, and August) as well as during marine organic plumes. Susceptibility of unsaturated compounds to ozone oxidation is also reflected in the changes of marine organics with the predominant m/z 44 contribution (a signature of carboxylic acid groups in the AMS) and the highest O:C ratios being observed during elevated ozone concentrations. These results point to carboxylic acid as being the likely final oxidation product of primary marine organics. However, the question of where the oxidation occurs—in water [Rontani, 2001; Rontani *et al.*, 2007] or airborne sea spray—still remains open. Both pathways are possible, but the high correlation (0.96–0.98) between the hydrocarbon type and oxygenated organics observed in this and previous study by Ovadnevaite *et al.* [2011b] indicates a fast and efficient oxidation; otherwise, the correlation would have been distorted by different oxidation conditions occurring in the ambient air.

Organic matter observed during the period of low biological activity shows different mass spectral features. Since biological activity is significantly diminished during the cold period, the concentration of the particulate organic matter reduces as well. Therefore, organics contributing to the aerosol composition during that period could arise from old dissolved organic carbon existing in the ocean throughout the year [Bendtsen *et al.*, 2002; Flerus *et al.*, 2012; Repeta and Aluwihare, 2006; Schmitt-Kopplin *et al.*, 2012]. Oxidation processes of dissolved organic matter likely differ from those of particulate organic matter. The organic concentrations in the marine aerosol were very low during winter months and ranged  $\sim 50 \text{ ng m}^{-3}$ ; therefore, an anthropogenic contribution—small by absolute measure—could have been more significant in relative terms. Concentration levels  $\sim 50 \text{ ng m}^{-3}$  and low enrichment of organics in sea spray during the period of low biological activity were quite comparable to some other marine aerosol studies [Chang *et al.*, 2011; Shank *et al.*, 2012] that postulated low contribution from primary marine organics.

The plume-like behavior of primary marine organics shows an advantage of long- to medium-term studies over the short-term campaigns as there would always be a risk of presenting a partial information if measurements do not coincide with the right bloom conditions. The organic features observed during the period of low biological activity could mimic those of the organics produced during the period of high biological activity when localized phytoplankton blooms are not observed. These distinct differences in chemical composition of the marine organic aerosol can result in different aerosol scattering and cloud condensation nuclei (CCN) activation efficiencies ranging from suppression [Fuentes *et al.*, 2011] to enhancement [Ovadnevaite *et al.*, 2011a].

The pronounced seasonal pattern of MSA to nss-sulfate ratio was opposite to the expected dependency of this ratio on the temperature: the ratio should decrease with increasing temperature if only the competition between the two Dimethyl sulfide (DMS) oxidation branches (MSA versus sulfate) is considered [Seinfeld and Pandis, 2006]. DMS reacts with OH in two pathways: (1) addition of OH and (2) abstraction of H by OH. The first pathway dominates at low temperatures, and second pathway at high temperatures (crossover point approximately 280 K). MSA is produced in both pathways, but it is preferentially formed in the first pathway due to the fact that intermediate radicals,  $\text{CH}_3\text{SO}_2$  and  $\text{CH}_3\text{SO}_3$ , break up thermally to yield  $\text{SO}_2$  (perhaps also  $\text{SO}_3$ ) which can be oxidized by OH to  $\text{H}_2\text{SO}_4$ . At lower temperatures these radicals do not break up but form MSA and DMSO, which in the aqueous phase may also form MSA. The Mace Head trend showed that the ratio increased with increasing temperature (summer months). Similar seasonal patterns were observed in other studies [Ayers *et al.*, 1991; Legrand and Pasteur, 1998] and were postulated to be due to changes in oxidants and relative humidity. Since the relative humidity did not show a pronounced seasonality at Mace Head (supporting information, Figure S4), we explain the observed trend by changes in particle size distribution and especially different proportions between submicron and supermicron modes observed in summer versus winter seasons. Previous studies [Vaishya *et al.*, 2011] have shown that wintertime light scattering is dominated by large particles, while light scattering during summer months is mainly caused by the smaller particles. Rinaldi *et al.* [2011] have suggested that MSA, in contrast to nss-sulfate, partitions almost equally between the submicron and supermicron aerosol modes. Therefore, the higher abundance of supermicron particles would relatively reduce submicron MSA concentration in winter if compared to the summer month when supermicron particle mode is less prominent. While particular attention was paid to select the cleanest maritime air masses, we cannot safely exclude the higher relative contribution of nss-sulfate originated from anthropogenic or volcanic emissions, which would also affect the MSA to nss-sulfate ratio in the same way.

## 5. Conclusions

Continuous medium-term marine aerosol studies revealed the different chemical composition of the particles in three maritime air masses ( $mP$ ,  $mT$ , and  $mA$ ):  $mP$  air mass aerosol was dominated by sea salt (50%), while contribution from nss-sulfate was comparable to that of sea salt in the  $mT$  and  $mA$  air masses (35%–36% and 37% accordingly). The yearly average contribution from organic matter was quite similar in all three air masses (18–20%), but primary marine organic plumes were observed exclusively in the maritime polar air mass in August, with monthly organic contribution as high as 40%. The length of the high biological activity period was different for the specific air masses, with the shortest being observed in the maritime arctic air mass. The general seasonal pattern was such that the highest concentrations of nss-sulfate, organics, MSA, and ammonium were observed during summer, and the highest sea-salt concentrations were observed during winter. In addition to the seasonal variability of the aerosol chemical composition, the ratio of MSA to nss-sulfate also

showed a pronounced seasonal pattern that could not be explained by the temperature-driven competition between MSA and sulfuric acid oxidation. The nss-sulfate aerosol was never fully neutralized to ammonium sulfate but rather existed in the form of ammonium bisulfate or pure sulfuric acid. This partial neutralization will have further implications for the marine aerosol chemistry (e.g., aerosol reactivity and/or partitioning of gaseous species). The mass spectra of the marine organic matter exhibited different fragmentation patterns and degrees of oxidation as a function of season. Periods of high biological activity (summer) were characterized by marine organic aerosol species that were less oxidized and more saturated. Organic aerosol observed during seasons with low primary marine aerosol production (spring, autumn, and winter), however, were more oxidized and contained more unsaturated material, presumably caused by ozone oxidation. The question of where the oxidation occurred—in the water or airborne sea spray—still remains open.

#### Acknowledgments

This work was supported by the Science Foundation Ireland (grant 08/RFP/GEO1233), HEA-PRTLI4 Environment and Climate: Impact and Responses programme, European Commission IP EUCAARI, EPA-Ireland, European Space Agency (Support To Science Element: Oceanflux Sea Spray Aerosol), EC ACTRIS Research Infrastructure Action under the Seventh Framework Programme. The ozone measurements at Mace Head are supported by the Department of Energy and Climate Change (DECC; award GA0201). Special thanks to Phillip O'Brien (EPA-Ireland) for collecting back trajectories and Gerard Spain (NUI Galway) for facilitating ozone measurements. Please contact the corresponding author to access the data published in this manuscript.

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