Marine submicron aerosol gradients, sources and sinks

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Abstract

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

1. Introduction

Marine aerosols contribute significantly to the global radiative budget and consequently, changes in marine aerosol abundance and/or chemical composition have an impact on climate change through both direct and indirect effects. The Northeast Atlantic region is of particular interest due to a combination of storminess, prevailing westerlies bringing marine air masses into continental Europe, and biological activity in surface waters significantly affecting chemical composition of atmospheric particulate matter (O'Dowd et al., 2004). Organic matter (OM) has been observed in marine aerosol particles for many decades and has been linked to fractional contribution of OM transferred from the sea-surface into the tropospheric boundary layer through bubble-mediated production processes (Blanchard, 1964; Hoffman and Duce, 1977; Middlebrook et al., 1998; Oppo et al., 1999; Russell et al., 2010). There has been a significant progress in understanding marine aerosol composition, which has been identified to consist of significant amounts of organic matter (Cavalli et al., 2004; Sciare et al., 2009) both water-soluble and water-insoluble. It has historically progressed from mainly consisting of sea salt and non-sea salt sulphate (Charlson et al., 1987; O'Dowd et al., 1997) to complex primary biogenic organic mixtures and states (dissolved, particulate, colloidal or nanogel) (Cavalli et al., 2004; Leck and Bigg, 2005; Russell et al., 2010; Decesari et al., 2011) as well as secondary organic compounds like organic acids (Kawamura and Sakaguchi, 1999; Mochida et al., 2002; Turekian et al., 2003; Rinaldi et al., 2011) and recently discovered biogenic amines (Facchini et al., 2008a; Muller et al., 2009). The findings of Ceburnis et al. (2008) and Facchini et al. (2008b) independently confirmed that water insoluble organic carbon (WIOC) in marine atmosphere has primary origin while water soluble organic carbon (WSOC) is mainly secondary or processed primary (Decesari et al., 2011), however, studies of Keene et al. (2007) and Russell et al. (2010) evidenced that even WSOC can largely be of primary origin. After significant fraction of marine sea spray particles was found to contain biogenic organic matter compounds (O'Dowd et al., 2004) it became even more important to determine principal sources and sinks of marine organic matter. Tentatively, the source of biogenic marine organic matter has been linked to the ocean surface and driven by a biological activity in surface waters based on a seasonality pattern of organic matter and chlorophyll-a (Yoon et al., 2007; Sciare et al., 2009) or regression analysis (O'Dowd et al., 2008; Russell et al., 2010). Furthermore, the first quantitative estimate of submicron aerosol organic matter in oceanic environment has been performed by Ceburnis et al. (2011) using dual carbon isotope analysis that showed over 80% of organic matter in clean marine air masses is of marine biogenic origin. A pilot study based on concentration gradient method performed in marine environment by Ceburnis et al. (2008) revealed that water soluble organic matter is largely produced by secondary processes while water insoluble organic matter is of primary origin.

This study is the extension of the study by Ceburnis et al. (2008) through the combination of off-line chemical analysis of samples and the measurements of boundary layer height, expansion of the range of chemical species and extension of the timescale to consider seasonal pattern of primary production. Contrary to the above study the flux-gradient method was not attempted due to the uncertainty of the averaged coefficient of turbulent transfer derived from eddy-covariance method, but instead sea salt fluxes were estimated by the boundary layer box model.

2. Experimental methods

The flux of sea-spray aerosols has been studied previously as sea salt mass fluxes or aerosol size and number flux (O'Dowd and De Leeuw, 2007; de Leeuw et al., 2011). Apart from few studies, the flux experiments have typically focused on super-micron sized particles. Eddy covariance method for studying submicron particle fluxes was first used by Buzorius et al. (1998) estimating submicron particle fluxes and sinks and has been since applied in a variety of environments: boreal and tropical forest (Buzorius et al., 1998; Ahlm et al., 2009), ocean (Nilsson et al., 2001; Geever et al., 2005; Norris et al., 2008; Brooks et al., 2009), desert (Fratini et al., 2007) and urban (Martensson et al., 2006; Martin et al., 2009). Eddy-covariance method is typically used to study total particles fluxes. The technique has been modified into relaxed eddy-covariance method to allow studying size-segregated particle fluxes (Gaman et al., 2004) or disjunct eddy covariance method (Held et al., 2007) employing slower response instruments. It should be noted, however, that while number of sea spray particles is dominated by submicron particles, mass is dominated by super-micron sizes and not a single method is capable of measuring particles around the important boundary of 1 micrometer. None of the above techniques were suitable for studying chemically resolved fluxes, because chemical analysis typically requires long sampling time (many hours for off-line chemical analysis). Most recently, however, eddy-covariance system coupled with high resolution aerosol mass spectrometer has been used to study chemically resolved fluxes (Nemitz et al., 2008; Farmer et al., 2011), but those were largely limited to areas with relatively high concentration of species.

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

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

LIDAR measurements (Jenoptik/Lufft and Vaisala ceilometers) are continuously conducted at Mace Head and a dedicated algorithm for temporal height tracking (THT) (Haeffelin et al., 2012; Milroy et al., 2012) using the backscatter profiles measured by the LIDAR was used to identify the surface mixed layers (SML) and the decoupled residual layers (DRL), both important parameters when considering boundary layer filled by primary fluxes.

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

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

where C was the concentration measured at 30m height, H_{BL} was the measured boundary layer height averaged over the sample duration and τ was boundary layer filling time (fixed at 2 days with the uncertainty of ±1day).

The above method was critically assessed by Lewis & Schwartz (2013) who argued that the method can hardly provide information on wind speed dependence. Indeed, estimated fluxes cannot be strictly related to particular wind speed because the corresponding boundary layer filling time was not constant and the local wind speed may not have been accurate with regard to the wind speed where primary production occurred. However, the method was only used in this study to roughly estimate the fluxes without attempting to derive a parameterisation but rather to provide an estimate.

The chlorophyll satellite data (daily, 1° spatial resolution) were obtained from GlobColour (http://www.globcolour.info). They result from the merging of Medium-Resolution Imaging Spectrometer (MERIS), Moderate Resolution Imaging Spectroradiometer (MODIS), and Sea-viewing Wide Field-of-view Sensor (SeaWiFS) data, using advanced retrieval based on fitting an in-water biooptical model to the merged set of observed normalized water-leaving radiances. A thorough description of the data treatment can be found in Rinaldi et al.(2013).

2.1 Sampling strategy

Meteorological records demonstrate that on average marine westerly air masses account for over 50% of time at the station (Cooke et al., 1997; Jennings et al., 2003). The gradient measurement system PM1 samplers (Sven Leckel Ingenieurbüro GmbH) ran in parallel at a flow rate of 38 lpm. Samples were collected in clean marine conditions (wind direction $190 < WD < 300$ and Condensation Particle Counter (CPC) concentrations < 700 particles cm^{-3}) using an automated sampling system on quartz filters for the analysis of both organic and inorganic components of marine aerosol. The system operated day and night whenever the above clean marine conditions were met. Active control of the sampling conditions excluded sampling during occasional short-term spikes of CPC concentrations either due to coastal nucleation events or occasional local ship traffic. Post-sampling analysis revealed that such air masses did not have contact with land for 4-5 days (as confirmed by air mass back-trajectories) and black carbon (BC) concentration measured by an Aaethalometer (AE-16, Magee Scientific, single wavelength at 880 nm) did not exceed 50 ng m^{-3}. Such air masses have been typically spending the last 48 hours (at least) in the marine boundary layer as documented by Cavalli et al. (2004) and Ceburnis et al. (2011). The latter study quantitatively demonstrated that in clean marine air masses anthropogenic carbon species typically contributed to 8-20% of the total carbon mass which should be applicable to other anthropogenic species due to internally mixed anthropogenic aerosol far from the source. It is important to note that clean marine samples collected at Mace Head are representative of the open ocean environment considering chemical and physical similarities between open ocean and coastal (Mace Head) samples (Rinaldi et al., 2009). The marine air criteria used at Mace Head were demonstrated to be sufficient at ensuring that anthropogenic and coastal effects are minimised to guarantee a dominant, if not at times overwhelming natural marine aerosol signal as detailed in the study of O'Dowd et al.(2014).

2.2 Off-line chemical analysis and concentration gradients

Fifteen PM1 gradient samples were collected during 13 month period in clean marine conditions as listed in Table 1. The sampling strategy aimed at capturing two samples per month providing that clean marine conditions were prevailing and each sample duration lasted on average 50% of time during the calendar week.

The samples were analysed for a wide range of chemical species present in aerosol particles: sodium (a marker for sea salt (SS)), non-sea-salt sulphate ($nssSO_4$), nitrate (NO_3), ammonium (NH_4), methanesulphonic acid (MSA), total carbon (TC), oxalate (Oxa), (analytical details can be found in Cavalli et al. (2004)), water soluble organic carbon (WSOC), water insoluble organic carbon (WIOC) (Rinaldi et al., 2009), water soluble organic nitrogen (WSON), total nitrogen (TN), dimethylamine (DMA) and diethylamine (DEA) (Facchini et al., 2008a). WIOC was calculated as WIOC=TC-WSOC while WSON was calculated as WSON=TN-WSIN (water soluble inorganic nitrogen). WSOM (water soluble organic matter) was calculated as WSOC*1.8 and WIOM (water insoluble organic matter) was calculated as WIOC*1.4 (Decesari et al., 2007; Facchini et al., 2008b). Sea salt concentration was calculated as SS=Na*3.1 (Seinfeld and Pandis, 2006). The absolute concentration ranges of all measured components are summarised in Table 2.

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

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

2.3 Errors and uncertainties

The uncertainty of estimated boundary layer fluxes was dependent on the cumulative uncertainty of the measured species concentration, boundary layer height and boundary layer filling time:

$$\frac{\partial F}{F} = \sqrt{\left(\frac{\partial C}{C}\right)^2 + \left(\frac{\partial H}{H}\right)^2 + \left(\frac{\partial \tau}{\tau}\right)^2} \qquad (2)$$

where the assigned boundary layer filling time uncertainty (50%) was dominating the combined uncertainty due to relatively small concentration uncertainty (5%) and boundary layer height uncertainty (10%).

The relative uncertainty of the organic matter fractional contribution to sea spray (OM_{ss}=WIOM/(WIOM+SS)), where the variable *WIOM* appeared in both nominator and denominator and *WIOM* represented total sea spray OM, resulted in a more complicated equation of the combined propagated uncertainty of the OM fractional contribution:

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

where the ratio in front of the square root is the fractional contribution of sea salt in sea spray resulting in the fractional uncertainty of the OM fractional contribution dependent on the sea salt fractional contribution and, therefore, always smaller than the additively combined fractional uncertainty of sea salt and WIOM measurement.

The uncertainty of the fitted functional relationships obtained from the discretely measured values was presented with the 95% confidence bands which was conceptually different from the fractional uncertainties of individual values. The confidence bands also helped to define the best fitted function (e.g. linear or power law) as unrealistic fits had very low or no confidence at all. Typically, the confidence bands become narrower as the number of points increases and/or their scatter decreases. The presentation of the confidence bands provided the physical meaning of the points residing outside the confidence bands. An individual point which is outside the confidence bands suggests a higher order of the relationship or an unaccounted freak error. Several of such cases will be discussed accordingly.

3 Results and Discussions

The measurements at three different heights allow resolving the vertical concentration profiles of different chemical species and the magnitude of the sources and sinks shaping the profiles. Most of them were non-linear, but well interpretable having studied concentration and flux footprints in detail in the previous pilot study of (Ceburnis et al., 2008). It is important to note that the footprint of the measured absolute concentration was of many tens to hundreds of kilometres offshore while the footprint of the concentration gradient was within about 10km from the measurement location, i.e. coastal waters (Ceburnis et al., 2008). The surf zone emissions may have had certain influence on the concentrations of sea salt or sea-spray at the lowest level of 3m, particularly for low wind speeds, practically disappearing at higher winds (O'Dowd et al., 2014), but had little or no impact on secondary organic aerosol. The different distances of the flux footprint arise from emissions contributing to the concentration at different heights. The flux footprint of the 90% concentration difference between 3 and 10 meters is 0.2-1.2 km while the footprint of the 90% of the difference between 10 and 30 meters extends to 5 km (Figure 1, Ceburnis et al. 2008). The remaining 10% of the contribution extends well beyond 5km, perhaps 10 km distance being a safe approximation. A condensation potential could have also contributed to the concentration differences of certain species as the time required for the air parcel to cover 10 km distance is about 15 min which is more than sufficient to achieve gas-aerosol equilibrium, e.g. (Meng and Seinfeld, 1996; O'Dowd et al., 2000).

3.1 Concentration gradient profiles

3.1.1 Primary components

The concentration profile of sea salt (top left in Figure 1) was unambiguously surface sourced or primary, i.e. concentration was decreasing vertically. Some of the individual profiles were sharper than others, but all were primary with only three exceptions where the profiles were distorted at lower heights possibly partly due to measurement errors and partly due to boundary layer dynamics and changes in sea state during the sampling period (ascending and descending wind regimes). However, as it was stated earlier, surf-zone emissions could have had influenced the concentration value at the lowest level of 3 meters.

Interestingly, similar “negative gradient” concentration profiles were obtained for nitrate and oxalate. However, those profiles were slightly, but repeatedly (systematically) distorted, i.e. the concentrations of oxalate and nitrate significantly diverged from the sea salt one at the lowest sampling height of 3 meters while following the sea salt profile above 10 meters. It is well established that nitrate is produced by secondary processes and mainly manifesting itself through condensed nitric acid on pre-existing sea salt particles in the absence of anthropogenic ammonium nitrate. Sea salt particles at the lowest level were the freshest having the closest flux footprint and, consequently, adsorbed the least amount of condensable nitric or oxalic acid compared to higher levels. Similarly to nitrate, oxalic acid could have been condensing on pre-existing sea salt particles as well despite more diverse chemical pathways of oxalic acid (some of the oxalate could also be produced by oxidation of organic matter inside sea-spray particles (Rinaldi et al., 2011) and, therefore, manifesting itself as “primary” species. The concentration profile of oxalic acid was similar to that of nitrate and could indicate that a significant amount of oxalate is produced in the atmosphere aloft subsequently condensing onto primary sea spray particles due to its acidic nature.

The water insoluble organic matter (WIOM) concentration profiles were split between three main categories: production (5 profiles), removal (6 profiles) and mixed profiles (4 profiles) (bottom right of Figure 1). Given that fractional contribution of OM in primary sea spray is related to the enrichment of organic matter at the ocean surface, this range of behaviour can be interpreted in terms of the location of biologically active region relative to the flux footprint. The wind speed has been reported to have an effect on fractional contribution of OM, but quantitative effect is unclear and will be discussed in more detail in chapter 3.4. The biologically active water patches within the flux footprint (~10 km form the measurement location) were responsible whether WIOM was produced or removed from the surface layer, or a combination of both processes. Therefore, a mixed profile was pointing at the production at a longer distance from the coast and the removal close to the measurement location. Thus the removal profile was pointing both at the deposition within the flux footprint area and/or the absence of biological activity in surface waters within the flux footprint area. The WIOM production by the secondary processes cannot be completely excluded either, but we have no evidence of that. It is worth noting that the production profiles were observed in early spring (March until early May) when biological activity is high at the coast and during late summer (late July-August) when biological activity has a second maximum identified by the chlorophyll proxy (Yoon et al., 2007). In contrast, the removal profile was observed during late spring and early summer when biological activity is retreating away from the coast into the open ocean. Despite a general pattern of the evolution of biological activity presented by Yoon et al. (2007) it should be stressed that biological activity is very patchy all over the ocean including coastal areas and the phytoplankton blooms are generally governed by the availability of nutrients which themselves are supplied by ocean currents and upwelling and become unpredictable on a day-to-week time scale.

3.1.2 Secondary components

The inorganic secondary species (nssSO_4 and NH_4) are presented in top right of Figure 1 along with an aerosol neutralisation profile considering only ammonium and sulphate which will be discussed later. Ammonium profile was clearly secondary, as expected, due to ammonia being the principal gaseous neutralizing agent in the marine boundary layer. It should be noted that the concentration profile of nssSO_4 was pretty constant and did not follow that of the ammonium profile as it could be expected considering that sulphuric acid is the main acidic species in the marine boundary layer, typically neutralized by ammonium. NssSO_4 was calculated as the difference between two relatively large numbers (total measured SO_4 minus sea-salt SO_4 as inferred from a conservative tracer such as Na ion). As sea salt concentration was changing quite dramatically with height especially in moderate to high wind speed during winter, some ambiguity must be acknowledged before interpreting nssSO_4 profile. In fact, if the winter sulphate profiles were excluded from the average that would have improved the average profile. In any event nssSO_4 concentrations at three different heights were not significantly different preventing any conclusions with respect to apparently secondary nssSO_4. The uncertainty in nss-sulphate determination can be the reason of the difference with respect to the profile of ammonium. Looking at the profiles, it can be observed that marine aerosol sampled at Mace Head is more neutralized at 30 m than closer to the sea level (Figure 1 (top right) and Figure 2), even though neutralization with respect to sulphuric acid is never complete, due to scarcity of ammonia in the marine boundary layer. Figure 2 shows calculated ammonium (considering neutralisation by sulphate only as nitrate was more likely to be neutralised by sodium (causing chloride depletion) due to scarcity of ammonia in the marine boundary layer) versus measured ammonium revealing significant but consistent differences in neutralisation pattern at three different heights. The neutralization profile can be driven by the gaseous ammonia vertical profile, which we have no hint about, or can be an indication of the importance of in-cloud processes of sulphate neutralization considering also that measurements at the lowest level were somewhat perturbed due to surf-zone fluxes. In fact, if the neutralization of acidic sulphates occurred prevalently in clouds, after scavenging of gaseous ammonia into acidic droplets, this process would occur more likely at the top of the marine boundary layer, were cloud layers form, justifying the observed neutralization profile.

The secondary organic species (MSA, WSOM and WSON) are presented in the bottom left of Figure 1. The MSA exhibited a “mixed profile” with steep increase of concentration between 3 and 10 m, typical of secondary products and decreasing profile between 10 and 30 m, likely due to condensation of MSA on sea salt particles (Hopkins et al., 2008) that causes an apparently primary profile. A clear secondary profile was observed for WSOM also, reaffirming the conclusion of Ceburnis et al. (2008) on the secondary origin of WSOM. The water soluble organic nitrogen concentration pattern is presented in the bottom left of Figure 1. WSON presents a mixed profile, therefore, it is not possible to attribute it to primary or secondary formation processes unambiguously. WSON concentration in aerosol samples is generally difficult to quantify as it is calculated as the difference between the total nitrogen (TN) and the water soluble inorganic nitrogen (WSIN) – both numbers of similar magnitude. As a result, only 7 complete profiles could be derived out of 15 samples and should, therefore, be considered cautiously (8 profiles were discarded as incomplete, i.e. missing determined concentration at one or two levels). Along with WSON, aliphatic amines were analysed following Facchini et al. (2008a). WSON, DMA and DEA are minor constituents of marine aerosol, together typically accounting for 10% of secondary organic aerosol (Facchini et al., 2008a). While the magnitude of their absolute concentrations maybe misleading – amines can be important species facilitating new particle production in the marine atmosphere (Dall'Osto et al., 2012) – quantification of their concentration by offline chemical analysis is always challenging. Mostly concentrations of DMA and DEA at the lowest height were below detection limit and, therefore, no profile can be provided for these species with confidence. However, the fact that detectable concentrations were always observed at 30 m, strongly suggests a secondary origin for DMA and DEA.

The well-established aerosol chemical compounds such as nitrate, oxalate, MSA and less well established WSON were all studied for the first time using flux-gradient method. The concentration profiles of the above compounds have not demonstrated that the species were secondary, despite well-established knowledge of their secondary formation in the atmosphere aloft (boundary layer, clouds or free troposphere) (Seinfeld and Pandis, 2006; Facchini et al., 2008a; Rinaldi et al., 2011). Figure 3 is presented for elucidating an apparent "primary" profile of nitrate and oxalate which is due to aforementioned species condensing or reacting with sea spray particles. MSA by contrast has the weakest if any relationship with sea salt. Figure 3 (top left) presents the relationship between nitrate and sea salt mass which appears as linear with the exception of 2-3 outliers. The outliers likely appeared due to the presence of trace amounts of ammonium nitrate. Ammonium nitrate is generally considered as anthropogenic species and can be present in trace amounts due to pollution background. The trace amount was really small, 20-30 ng m^{-3} of nitrate only re-affirming cleanness of the marine atmosphere studied at Mace Head. Despite a strong similarity in concentration pattern of nitrate and primary sea salt it is inconceivable that a significant amount of primary nitrate can be produced (nitrate is a tracer nutrient in sea water) and, therefore, must be derived by condensation of nitric acid on pre-existing sea salt.

The relationship of sea salt and oxalate (top right plot of Figure 3) was slightly different from nitrate and somewhat similar to MSA. While oxalate can indeed condense on pre-existing sea salt particles its chemical pathways of secondary production are different and more diverse than that of nitrate as were detailed by Rinaldi et al. (2011). Oxalate can also be present in sea-spray particles via oxidation of organic matter in sea-spray and, therefore, dependent on biological activity of the ocean. As opposed to nitrate, the oxalate was not enhanced in the presence of copious amounts of sea salt particles suggesting that oxalic acid is not an ever present species in the boundary layer which would readily condense on sea salt. The same was true for MSA which showed even less of a relationship with the sea salt mass (bottom left of Figure 3). MSA production is photochemically driven and time limited considering the gradient footprint of

0.2-10 km in the coastal zone. The water soluble organic nitrogen (WSON) is a relatively less studied class of chemical compounds of which amines are the best known compounds (Facchini et al., 2008a). The observed concentrations of DEA, DMA and WSON were very similar to the ones documented by Facchini et al. (2008a) in clean marine air masses. Both WSON and the sum of dimethylamine (DMA) and diethylamine (DEA) exhibited a relationship with water soluble organic carbon (WSOC) (bottom right of Figure 3), however, only WSOC and WSON correlated at a significant level ($r = 0.58$). Note, that the sum of amines is presented in absolute concentration while that of WSON as a mass of nitrogen. The comparison between the WSON and the sum of amines suggested that the amines were likely the dominant species of WSON, but difficult to determine due to detection limit as noted above. WSOC/WSON/DEA/DMA relationship is presented in Figure 3 (bottom right) for exploratory purposes as these interrelationships have not been examined or discussed in the context of marine aerosol.

3.2 WIOM and chlorophyll-a relationship

Gantt et al. (2011) suggested that fractional contribution of organic matter in sea spray particles depends not only on the biological activity in oceanic surface waters, but also the wind speed at the point of emission. The data of this study were examined according to the approach of Gantt et al. (2011). Figure 4 presents inter-relationship between fractional organic matter contribution to sea spray (OM_{ss}=WIOM/(WIOM+SS)), wind speed using the data set of this study which were not part of the dataset used by Gantt et al. (2011) and chlorophyll-a concentration in the open ocean area area upwind from Mace Head as examined in Rinaldi et al. (2013). Open ocean region was 10x10deg or roughly 1000x1000 km upwind from Mace Head. Only WIOM was taken into account in calculating fractional contribution of OM in sea spray. Notwithstanding the fact that a fraction of measured WSOM was associated with sea spray and formed by processing primary WIOM, quantitative assessment is beyond current knowledge. Both relationships were statistically significant ($P<<0.01$) and explained 58% of the variance (top plots) suggesting an overlap. The obtained relationships agree well with the relationship reported by Rinaldi et al. (2013) based on an extended dataset (reaching 70% OM fractional contribution at 1.0 µg m^{-3}). Further, when the former relationship is coloured by the chlorophyll-a concentration in the oceanic region upfront of the measurement location at Mace Head, no apparent pattern can be discerned (bottom plot) apart from general mutual relationship. It can be concluded, that while the OM_{ss} dependence on wind speed is significant it may actually be weaker than the OM_{ss} and chlorophyll-a relationship due to inter-dependence of wind speed and chlorophyll-a – wind speed is higher in winter when chlorophyll-a concentration is at its lowest and vice versa – thereby contributing to the excessive variance of OM_{ss} and wind speed. Note that seasonal relationship between wind speed and chlorophyll is simply a coincidence. For example, the effect of wind speed could be elucidated if very low OM fractional contributions were often observed during summer or high fractional contributions during winter which was never the case with very few exceptions (only two). However, it is hardly a coincidence that the two points (top right plot in Figure 4) with rather similar chlorophyll-*a* concentration (~0.4 µg m^{-3}) residing outside the 95% confidence bands are the ones characterised with the lowest and the highest wind speed re-affirming that the effect of wind speed is real, but difficult to separate from the OM_{ss} and chlorophyll-*a* relationship. In conclusion, wind stress is the driver of primary sea spray production, but biological productivity is modifying sea spray chemical composition. Last but not least, it is important to note that the chlorophyll-a concentration is only useful as a proxy of biological activity which can affect a fraction of primary organic matter in sea spray in different ways depending on the trophic level interactions (O'Dowd et al., 2015).

3.3 Flux estimates and implications for existing sea spray source functions

The surface mixed layer (SML) height obtained from LIDAR measurements varied in the range of 846-1102 meters among the eight periods for which overlapping LIDAR measurements were available. An occasional formation of nocturnal boundary layer was ignored here due to the nature and resolution of the gradient samples. It is important to note that the boundary layer filling time constant τ is a feature of a particular low pressure system(s) arriving at the point of observation in a connecting flow. However, the sample deployment time (7 days) and the actual number of sampled hours within particular sector prevented estimating sample dependent constant τ which was set at 2 days with the uncertainty of ±1day. SML measurements were available for 10 out of 15 gradient samples. The sea salt fluxes estimated using Equation 1 (and using sea salt concentration at 30m height) ranged from 0.3 to 3.5 ng m^{-2} s^{-1} over the wind speed range of 5-12 m s^{-1}. Concurrently, estimated WIOM fluxes ranged from 0.3 to 2.2 ng m^{-2} s^{-1} over the same wind speed range and were inversely correlating with SS fluxes, i.e. highest SS flux estimates were accompanied by the lowest WIOM fluxes conforming to fractional OM considerations in Chapter 3.2.

Given the uncertainty of the estimated sea salt fluxes over the wind speed range it was necessary to compare it with the available sea spray source functions. Equally important was to cover a wide range of methods used to derive fluxes. Figure 5 presents the source functions for which submicron sea salt mass could have been calculated and include the following: Callaghan (2013), Clarke et al. (2006), Fuentes et al. (2010), Gong-Monahan (Gong, 2003), Martensson et al. (2003), Ovadnevaite et al. (2012; 2013) and the boundary layer box model estimates of this study. Clarke et al. (2006), Fuentes et al. (2010) and Martensson et al. (2003) parameterisations were derived in either laboratory conditions or in-situ surf breaking waves and coupled with Monahan and Muircheartaigh (1980) whitecap parameterisation to yield flux wind speed relationship. All of the above parameterisations were based on exploring SMPS measurement data. Gong et al. (2003) used an original Monahan (Monahan et al., 1982) parameterisation obtained in the laboratory experiment and adjusted for the size range <0.2 µm. Callaghan (2013) used in-situ whitecap measurements developing a discrete whitecap method and Gong (2003) parameterisation to obtain submicrometer sea salt mass flux and wind speed parameterisation. While the Callaghan (2013) paper proposes a new SSA source function, it pulls the whitecap parameterisation from the Callaghan et al. (2008) paper. One of the primary findings of the Callaghan (2013) work was the importance of choosing the correct whitecap timescale for the discrete whitecap method in particular. Finally, Ovadnevaite et al. (2012; 2013) and gradient method of this study used ambient measurement data (real-time AMS sea salt measurements, SMPS measurements and PM1 gradient measurements, respectively), but were completely independent of each other and different in terms of the utilised methods. It should be noted, that despite the fact that the latter methods estimated net fluxes as opposed to production fluxes measured in the laboratory experiments, deposition fluxes are typically small, in the order of 2-4% in submicron particle range (Hoppel et al., 2002). The presented parameterisations fall into two regimes as seen in Figure 4: Clarke et al. (2006), Fuentes et al. (2010), Gong (2003) and Martensson et al. (2003) parameterisations exhibit a significantly higher wind-speed dependency compared to the more recent parameterisations by Callaghan (2013) or Ovadnevaite et al. (2012; 2013). The split into regimes is even more apparent on a linear flux scale. It must be noted that up until now majority of global or regional scale models used one of the former four parameterisations (Gong, 2003; Martensson et al., 2003; Clarke et al., 2006; Fuentes et al., 2010) typically resulting in the overestimated mass concentrations (e.g. (Textor et al., 2006; de Leeuw et al., 2011). It should be also noted that the applicability of the Clarke et al.(2006), Fuentes et al. (2010) and Martensson et al. (2003) parameterisations come more questionably for higher wind speeds as the divergence between the more recent parameterisations becomes progressively greater and the slope of the dependency curve becomes unrealistically steep.

Figure 5 reiterates the conclusion made by Ovadnevaite et al. (2012) that the improvements were needed in both whitecap parameterisation, now addressed by Callaghan (2013); and the more realistic differential aerosol productivity term recently advanced by Ovadnevaite et al.(2013). It is reasonable to suggest that the laboratory experiments or the *in-situ* surf breaking waves were most likely unable to realistically replicate air entrainment by the open ocean breaking waves and consequently formed bubble plumes, resulting in unrealistic whitecap coverage and/or size distributions. The most recently developed parameterisation by Ovadnevaite et al. (2013) advanced even further by introducing Reynolds number instead of a commonly used wind speed, thereby removing the uncertainty related to the sea wave state (during rising or waning winds) and implicitly containing sea surface water temperature and salinity which have been both implicated to altering aerosol production (Martensson et al., 2003; Jaegle et al., 2011; Zabori et al., 2012).

It can be argued that the new whitecap parameterisation of Callaghan et al. (2013) coupled with Clarke et al. (2006), Fuentes et al. (2010) and Martensson et al. (2003) parameterisations would bring all of them closer to the more recent parameterisations, however, it is important to make few distinctive comments. While the Gong-Monahan parameterisation has decreased the sea salt mass flux when coupled with Callaghan (2013) whitecap parameterisation instead of the original Monahan (Monahan et al., 1982) whitecap parameterisation, the size resolved flux remains unrealistic due to the arbitrary adjusted submicron size distribution below 0.2 µm (Gong, 2003). A single mode centred at around 100nm fails to reproducing submicron size distributions observed in ambient air in stormy maritime boundary layer (Ovadnevaite et al., 2013). Similarly, Clarke et al. (2006), Fuentes et al. (2010) and Martensson et al. (2003) parameterisations, even when coupled with Callaghan (2013) whitecap parameterisation, would still predict concentrations far in excess of observed concentrations. The size resolved fluxes are crucial in predicting direct and indirect climate effects and have to be benchmarked against the ambient rather than the laboratory measurements unless both reasonably agree.

3.4 Seasonality of observed concentrations, gradients and estimated fluxes

The sampling strategy aimed at capturing two samples per month providing that clean marine conditions were prevailing and each sample lasted on average 50% of time during the calendar week. In reality, fifteen samples were collected covering full year (April 2008 – May 2009) as listed in Table 1. The observed seasonal cycle may not have been typical, but allowed to examine gradients and corresponding flux estimates associated with varying oceanic conditions throughout the calendar year.

The observed chemical species concentrations have been typical of those documented at Mace Head by Yoon et al. (2007) and Ovadnevaite et al. (2014). Sea salt concentrations and respective estimated fluxes by the box model were generally largest in winter (0.2-0.85 µg m^{-3} and 1.2-3.5 ng m^{-2} s^{-1}, respectively) and smallest in summer (0.08-0.55 µg m^{-3} and 0.3-1.1 ng m^{-2} s^{-1}, respectively) which was mainly due to the wind pattern over the North East Atlantic (Jennings et al., 2003; O'Dowd et al., 2014). However, occurrence of deep low pressure system in e.g. September 2008 with corresponding high winds resulted in high sea salt concentrations and large fluxes despite seasonal pattern suggesting otherwise. On the other hand, it has been suggested that sea salt can be replaced in primary sea spray by primary marine OM (Oppo et al., 1999; Facchini et al., 2008b) in which case sea salt fluxes estimated from observed concentrations would become smaller. Vaishya et al. (2012) showed that aerosol scattering dependence on the wind is different between contrasting seasons suggesting the effect of primary marine OM on sea spray production. However, considering the uncertainties of the estimated flux by the box model, a quantitative proof of the aforementioned effect was not possible.

The WIOM concentrations and gradients revealed a much more complex pattern. The absolute concentrations were lower in winter (0.06 - 0.19 µg m^{-3}) and higher in summer (0.1 - 0.44 µg m^{-3}) following the pattern of oceanic biological activity lately reaffirmed by Ovadnevaite et al. (2014). The seasonal variation of WIOM gradients and estimated fluxes, however, was different as the gradients depended on biological activity in the flux footprint region (0.2-10 km from the coast) while the fluxes depended both on the biological activity and wind speed dependent sea spray production in the flux footprint area. The three distinct profiles of WIOM gradients presented in Figure 3 clustered in characteristic periods. The removal gradient prevailed in late spring and early summer when biological activity was waning close to the coast. Yoon et al. (2007) demonstrated that biological activity revealed by chlorophyll proxy has been typically starting at the coast early in the season and then gradually moving off-shore and northward, thereby affecting the WIOM gradients and corresponding fluxes. The production gradient manifested itself during late summer and early spring, reaffirming conclusions made by Yoon et al. (2007) about the presence of two or more phytoplankton bloom peaks during the biologically active season. The mixed WIOM profile prevailed during autumn when biological activity was waning over the North East Atlantic, but at the same time shifting closer to the coast. The spatial resolution of satellite chlorophyll data and the large errors associated with coastal interfaces in particular (Darecki and Stramski, 2004; Gregg and Casey, 2007) prevented exploring the relationship between coastal biological activity and WIOM gradients and its fractional contribution to sea spray. Previous chapter demonstrated that open ocean biological activity revealed by the chlorophyll proxy upwind from Mace Head correlated well with the WIOM fractional contribution to sea spray validating the seasonal pattern of

WIOM gradients and fluxes. Therefore, despite WIOM gradient profiles were found dependent on biological activity in the flux footprint area (0.2-10km) that did not invalidate a relationship between WIOM and chlorophyll in the open ocean over the North East Atlantic. Recently, Long et al. (2014) demonstrated a diurnal signal in primary marine OM production suggesting that sunlight-mediated biogenic surfactants may have a previously overlooked role. Time resolution of the gradient samples (weekly) and randomness of clean sector sampling during day and night, prevented exploring the effect in this study. However, the results of this study do not contradict the above study either as the primary marine OM production would be enhanced in summer compared to other seasons following radiation pattern.

4 Conclusions

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

Acknowledgements

The work of this paper has been funded by the EPA Ireland STRIVE project EASI-AQCIS and D. Ceburnis fellowship project Research Support for Mace

Head. The European Space Agency (Support To Science Element: Oceanflux Sea Spray Aerosol) and EC ACTRIS Research Infrastructure Action under the 7th Framework Programme support are acknowledged as well. The authors would like to thank A. Callaghan from Scripps Institution of Oceanography, USA for sharing his data; Salvatore Marullo from Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Frascati, Italy and Rosalia Santoleri from Institute of Atmospheric Sciences and Climate, National Research Council, Rome, Italy for providing satellite chlorophyll data.

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Table 1. Gradient sample weekly collection time scale and the number of hours each sample was sampled during 13 month period in 2008-2009.

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

Table 2. Absolute concentration ranges of measured chemical species.

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

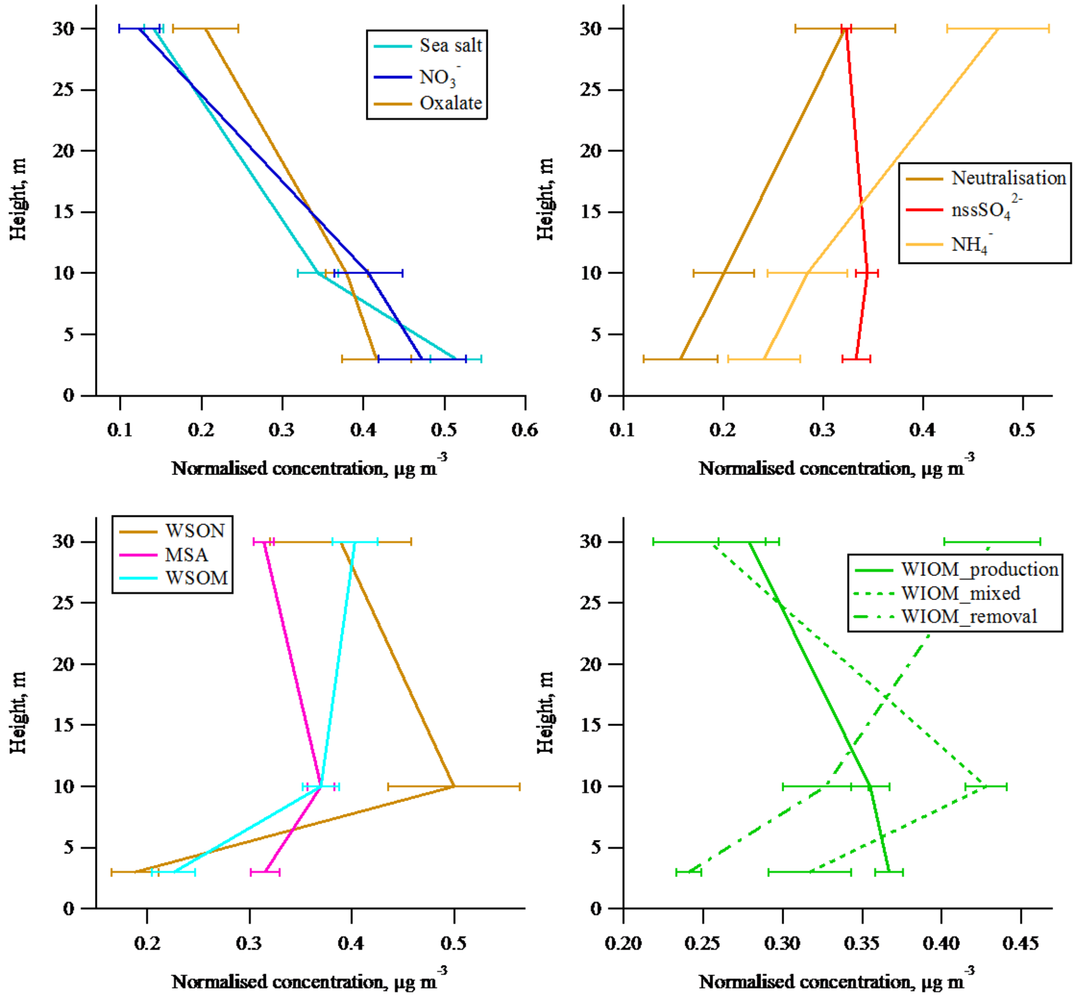

Figure 1. The gradient profiles of chemical species studied: species resembling primary production (top left); inorganic species resembling secondary production (top right); organic secondary species (bottom left) and water insoluble organic matter split into production, removal and mixed profiles (bottom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

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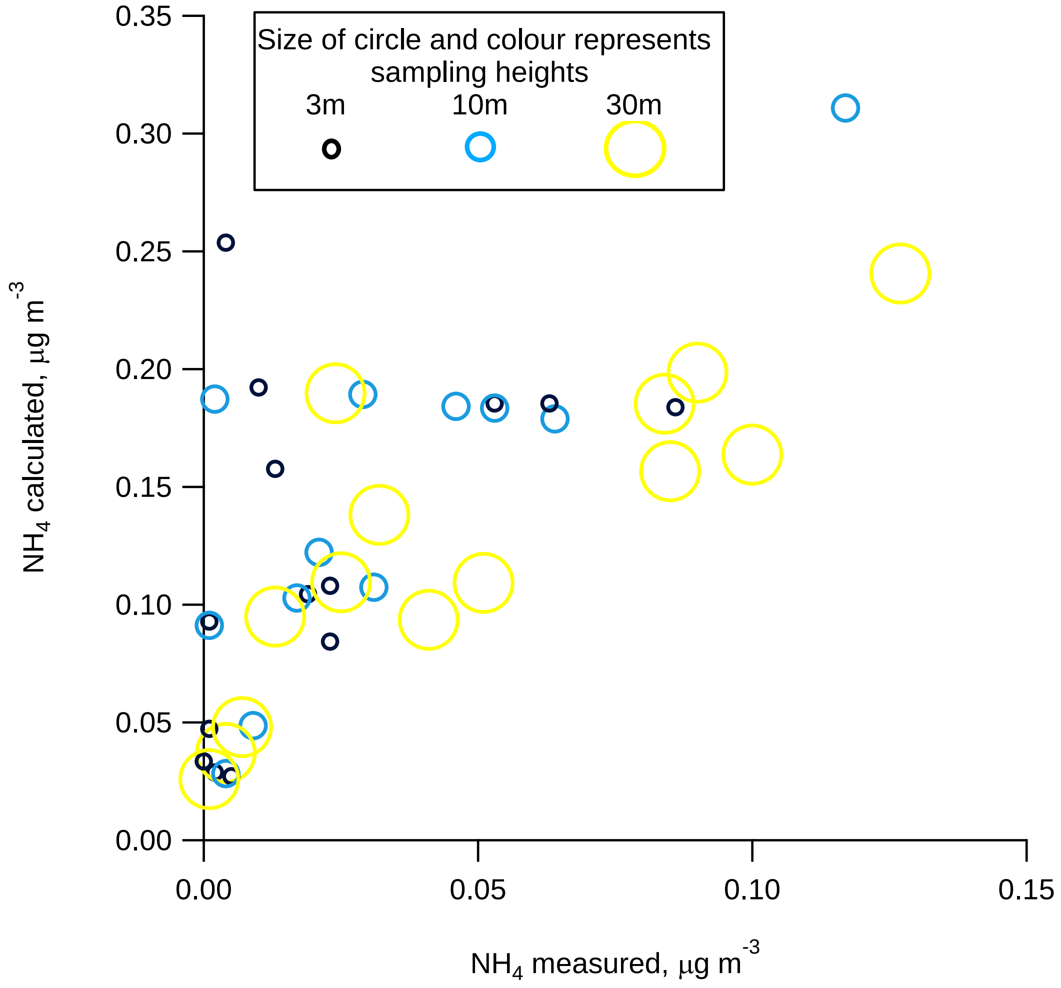

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1006 Figure 2. A scatter plot of sulphate neutralisation by ammonium with respect to

1007 sampling height.

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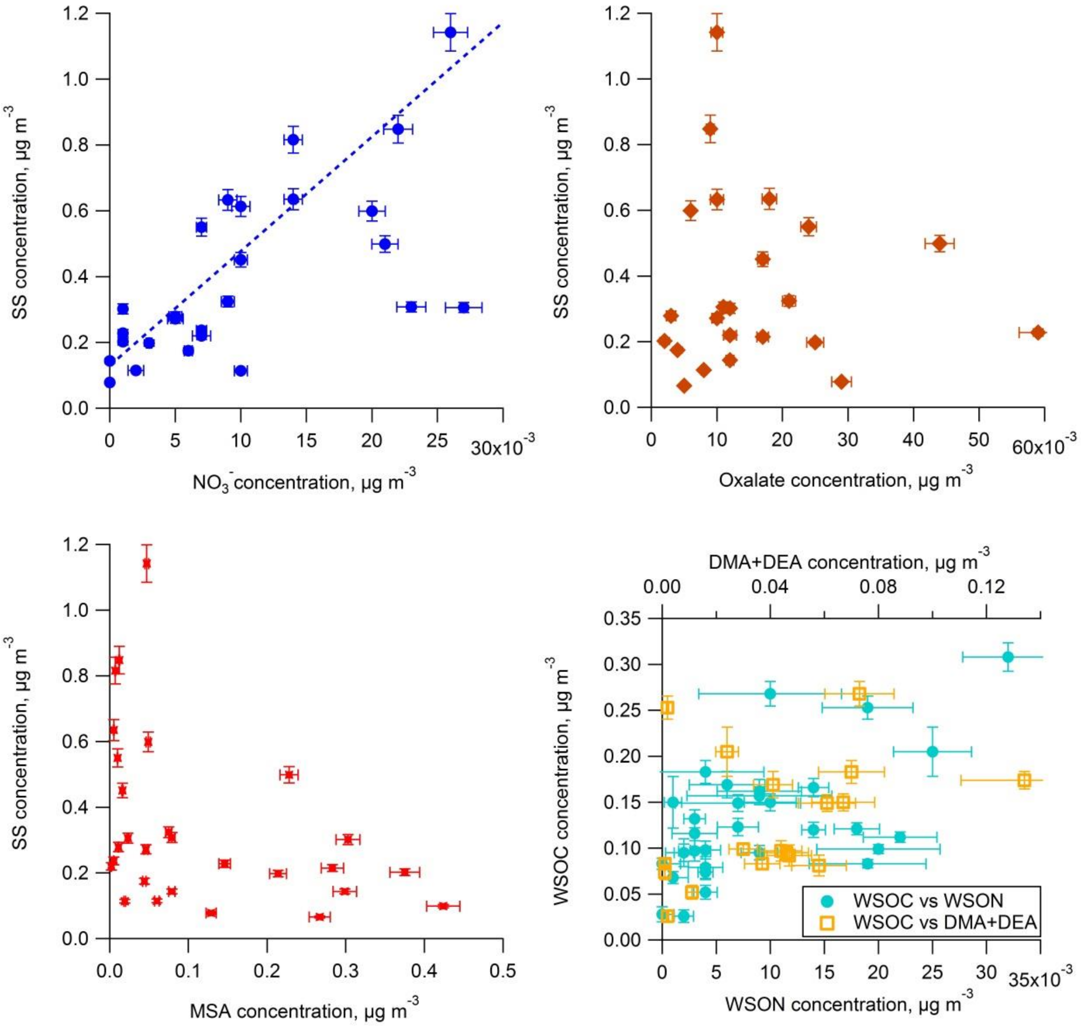

Figure 3. Plots of sea salt and secondary species which resembled primary production concentration pattern: SS vs NO_3 (top left); SS vs Oxalate (top right); SS vs MSA (bottom left) and WSOC vs WSON (also plotted as the sum of dimethylamine and diethylamine)(bottom right). Note, that WSOC and WSON concentration are presented as µg of carbon or nitrogen mass, respectively, while all other species reported in absolute species concentrations.

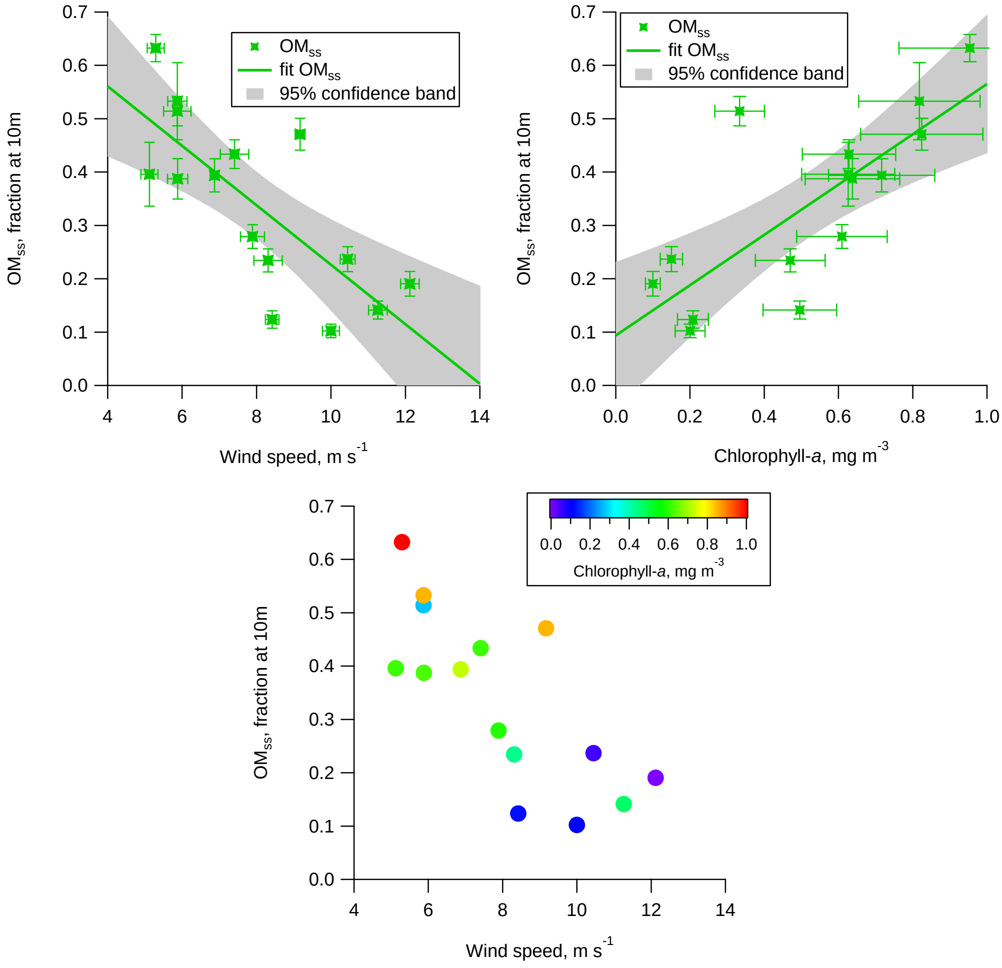

Figure 4. Effect of wind speed and chlorophyll-a concentration on the fractional contribution of organic matter (OM_{ss}): OM_{ss} vs WS (top left); OM_{ss} vs chlorophyll-a (top right) and OM_{ss} vs WS coloured by chlorophyll-a (bottom). Individual uncertainties of the flux and wind speed marked with caps while the grey area denotes 95% confidence bands of the fitted parameterisation.

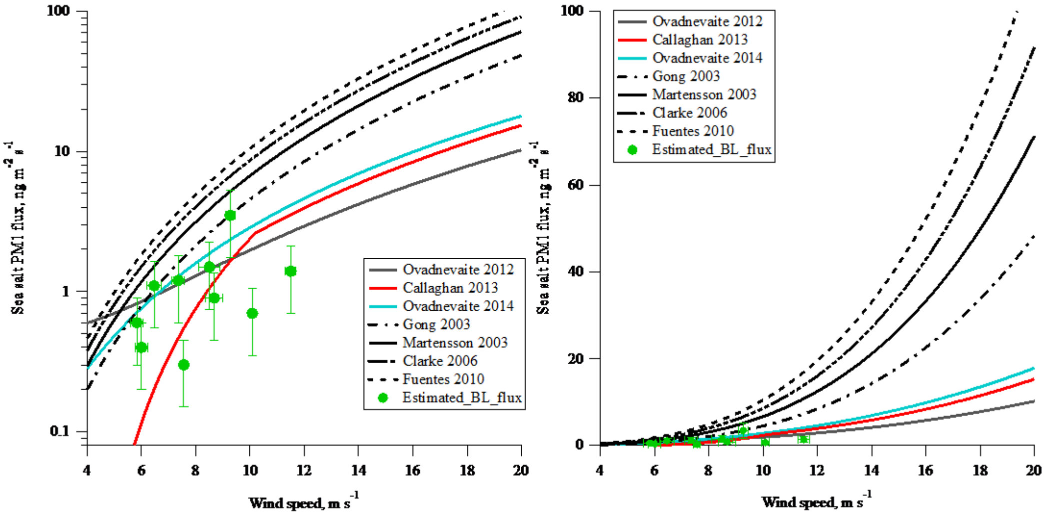

Figure 5. A comparison of the most often used and recently developed sea spray and wind speed parameterisations in log scale (left) and linear scale (right). The estimated boundary layer fluxes by the box model (green circles) were not fitted against the wind speed due to the uncertainty related to the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

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

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