Marine submicron aerosol sources, sinks and chemical fluxes

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Abstract

Aerosol physico-chemical fluxes over NE Atlantic waters were quantified through the parallel deployment of micrometeorological eddy covariance flux system and an aerosol chemistry gradient sampling system. Fluxes of primary components, specifically, sea salt (SS), water insoluble organic carbon (WIOC) and a combined sea spray are presented in the context of seasonality of marine aerosol sources and sinks. The chemical gradients of secondary aerosol components, specifically, nitrate, ammonium, oxalate, amines, methanesulfonic acid (MSA) and water soluble organic nitrogen (WSON) were examined in great detail. A strong power law relationship between fluxes and wind speed has been obtained for primary sea salt and sea spray while water insoluble organic matter (WIOM) followed a linear dependency. The power law relationship between sea salt flux (F_{SS}) and 10m height wind speed (U_{10}) ($F_{SS}=0.0011U_{10}^{3.15}$) compared very well with existing parameterisations but highlighted the divide between parameterization derived from ambient observation versus laboratory measurements. The observed seasonal pattern of sea salt production 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 wind dependent fluxes 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. The latter study evaluated the first wind speed dependent fluxes, but those remained uncertain due to the absence of parallel eddy covariance measurements and a limited sampling period. Considering a significant seasonal cycle of marine organic matter is important to study chemical fluxes on a full year basis to capture the variability in aerosol sources and sinks.

This study is the extension of the study by Ceburnis et al. (2008) through the combination of eddy covariance measurements in parallel with the off-line chemical analysis of samples, expansion of the range of chemical species and extension of the timescale to evaluate fluxes as a function of season.

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 fluxes 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-flux 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. For the approach to work one needs neutral or near-neutral boundary layer stability conditions persisting for sufficient timescales to allow sampling over many hours. The biggest caveat is whether representative averaging over many hours can produce meaningful results. The approach was previously demonstrated to work in urban environment (Valiulis et al., 2002) as well as in a relatively clean marine environment (Ceburnis et al., 2008). This study is the continuation of the latter

study adding full scale eddy-covariance system and expanding the number of chemical species studied.

A new set-up to study gradient chemical fluxes 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) while the eddy covariance system installed at the 22 meter height.

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.

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 Eddy-covariance system

Eddy-covariance measurements of micrometeorological parameters, water vapour (H_2O) and CO_2 fluxes were undertaken in parallel (Keane-Brennan, 2011) which provided micrometeorological measurement data for calculating gradient fluxes. The flux package comprised a Solent sonic anemometer (Gill Windmaster Pro) to provide 3-D wind fields at 10 Hz. The sonic anemometer was mounted 2 meters out from the sea-facing side of the 22 m tower and a turbulent flow around the tower (Buzorius et al., 1998). Flux data were averaged for 30 min for further analysis and more details on flux data can be found in

Geever et al. (2005) and Keane-Brennan et al. (2011). Half-hourly flux data were further averaged to match the periods of gradient samples. The undertaken strategies allowed a complete analysis of the source and sink fluxes as a function of wind speed and oceanic biological activity and provided a quantification of both primary and secondary inorganic and organic aerosol species cycling in the marine boundary layer.

2.4 Flux-gradient method

First-order closure turbulent flux parameterisation, often known as a gradient transport theory, *K*-theory or flux-gradient similarity method, can be expressed according to Stull (1988) as following:

$$F = -K_z \left.\frac{dc}{dz}\right|_z \qquad (1)$$

where F is the flux, K_z is the turbulent-transfer coefficient; dc/dz is the concentration gradient.

Thus having K_z value and the measured concentration gradient it is possible to calculate fluxes of chemical species. The approach, however, would only allow calculating the net flux and does not allow distinguishing between upward and downward fluxes in high time resolution as is typically done with the eddy covariance system. The K_z parameter can be calculated from the eddy covariance (EC) measurements using high frequency data of vertical wind velocity using the formula: $\sigma=\sqrt{(2K_z/t)}$ (where σ is the standard deviation of vertical wind velocity, K_z is the turbulent-transfer coefficient, and time is the unit time (1s)) which follows from diffusivity fundamentals (e.g. (Reible, 1998)) applied to the vertical wind speed. K_z had to be averaged over about 50 to 140 hours to represent the sampling period of a particular concentration profile. The averaged K_z values were compared with eddy covariance data and presented in Figure 1 to check whether the averaged K_z values were consistent with the high time resolution measurements. The dependence of K_z values on horizontal wind speed were very similar pointing to the fact that K_z values were consistently distributed around the mean and the mean average representing gradient samples was statistically meaningful. The variance of K_z values around the mean provided the partial

uncertainty in flux calculations. It is worth noting that the power law coefficient of the averaged K_z(WS) dependence was very similar to the one given by Ceburnis et al. (2008) (1.97 and 2.07 respectively). A similarity between the relationships obtained by Ceburnis et al. (2008) from 2002 EC data and this study period (2008-2009) suggests that the dynamics of the boundary layer did not change significantly over time at this geographical location, thereby providing a confidence that the K_z values can be reliably derived from the horizontal wind speed measurements if the K_z values cannot be estimated directly. A tight relationship between K_z and horizontal wind speed and the absence of a diurnal cycle of K_z is typical in wind shear generated turbulence environment like marine sector at Mace Head. Consequently, the above relationship between horizontal wind speed and the coefficient of turbulent transfer would only apply to the marine sector and Mace Head location. The scatter of K_z values over a short or long period of time was mainly due to gustiness as presented in Figure 2 where the K_z and wind speed relationship was coloured by normalised standard deviation of the horizontal wind using random subset of data. All elevated values of K_z were accompanied by high values of the standard deviation of the horizontal wind speed. Therefore, K_z values were all meaningful and must have been included in the mean average to represent fast turbulent eddies.

It is important to know the thickness of the surface layer as it is here that fluxes are considered to be constant and gradients adhere to similarity theory. Another caveat is the formation of internal boundary layers (Stull, 1988). Detailed measurements performed during NAMBLEX campaign at Mace Head (Heard et al., 2006) provided strong evidence that the internal boundary layer had little impact on the measurements made on the main tower if they were conducted above 7-10 m (Coe et al., 2006; Norton et al., 2006), which would include two out of our three sampling points. Norton et al. (2006) showed that the internal boundary layer was typically limited to below 10m and never propagated to the top of the tower in marine sector, consequently, having small effect on our measurements at 10 m and 30m. Coe et al. (2006) concluded that over a wide range of aerosol sizes there was no impact of the inter-tidal zone or the surf zone on measurements made at 7 m above ground level or higher.

2.5 Errors and uncertainties

The flux-gradient method based on the Equation 1, involves several variables, necessitating a calculation of the combined propagated uncertainty. Specifically, not only it involved two independently measured concentrations at two heights, but the uncertainty of the subtracted blank concentration (pre-fired but not exposed filter) and the uncertainty of the K_z value. The combined fractional uncertainty of an individual flux was calculated by the following Equation:

$$\delta q = \sqrt{\left(\frac{\partial q}{\partial x_1}\delta x_1\right)^2 + \cdots + \left(\frac{\partial q}{\partial x_n}\delta x_n\right)^2} \qquad (2)$$

where x_i are the independent variables and δx_i are the fractional uncertainties of the independent variables.

The uncertainty of individual concentrations (C) (provided in Table S1) and the gradient (G) was calculated by the following Equations:

$$\delta C = \sqrt{(\delta C_{meas})^2 + (\delta C_{blank})^2} \qquad (3)$$

$$\delta G = \sqrt{(\delta C_{10})^2 + (\delta C_{30})^2} \qquad (4)$$

where C_{meas}, C_{blank}, C_{10} and C_{30} were measured, blank and concentration at 10 and 30 meters, respectively.

The relative uncertainty of the corresponding fluxes was calculated by the following Equation based on multiplication of measured quantities ($F=G*K_z$):

$$\frac{\delta F}{F} = \sqrt{\left(\frac{\delta G}{G}\right)^2 + \left(\frac{\delta K_z}{K_z}\right)^2} \qquad (5)$$

where G and K_z are corresponding gradients and coefficient of turbulent transfer, respectively. Note that the flux uncertainty is dominated by the gradient uncertainty, because the uncertainty of turbulent transfer coefficient would be actually smaller than presented in Eq. 5 due to being an average of over a hundred of half-hourly values.

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:

$$\frac{\delta OM_{ss}}{OM_{ss}} = \frac{SS}{(SS+WIOM)}\sqrt{\left(\frac{\partial WIOM}{WIOM}\right)^2 + \left(\frac{\partial SS}{SS}\right)^2} \qquad (6)$$

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, or corresponding fluxes, shape 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 or the flux 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 3) 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 above, surf-zone emissions could have had influenced the concentration value at the lowest level of 3 meters and, therefore, this level was not used in the flux calculations of primary sea spray species.

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 3). 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

435 The inorganic secondary species ($nssSO_4$ and NH_4) are presented in top right of
436 Figure 3 along with an aerosol neutralisation profile considering only ammonium
437 and sulphate which will be discussed later. Ammonium profile was clearly
438 secondary, as expected, due to ammonia being the principal gaseous neutralizing
439 agent in the marine boundary layer. It should be noted that the concentration
440 profile of $nssSO_4$ was pretty constant and did not follow that of the ammonium
441 profile as it could be expected considering that sulphuric acid is the main acidic
442 species in the marine boundary layer, typically neutralized by ammonium.
443 $NssSO_4$ was calculated as the difference between two relatively large numbers
444 (total measured SO_4 minus sea-salt SO_4 as inferred from a conservative tracer
445 such as Na ion). As sea salt concentration was changing quite dramatically with
446 height especially in moderate to high wind speed during winter, some ambiguity
447 must be acknowledged before interpreting $nssSO_4$ profile. In fact, if the winter
448 sulphate profiles were excluded from the average that would have improved the
449 average profile. In any event $nssSO_4$ concentrations at three different heights
450 were not significantly different preventing any conclusions with respect to
451 apparently secondary $nssSO_4$. The uncertainty in nss-sulphate determination can
452 be the reason of the difference with respect to the profile of ammonium. Looking
453 at the profiles, it can be observed that marine aerosol sampled at Mace Head is
454 more neutralized at 30 m than closer to the sea level (Figure 3 (top right) and
455 Figure 4), even though neutralization with respect to sulphuric acid is never
456 complete, due to scarcity of ammonia in the marine boundary layer. Figure 4
457 shows calculated ammonium (considering neutralisation by sulphate only as
458 nitrate was more likely to be neutralised by sodium (causing chloride depletion)
459 due to scarcity of ammonia in the marine boundary layer) versus measured
460 ammonium revealing significant but consistent differences in neutralisation
461 pattern at three different heights. The neutralization profile can be driven by the
462 gaseous ammonia vertical profile, which we have no hint about, or can be an
463 indication of the importance of in-cloud processes of sulphate neutralization
464 considering also that measurements at the lowest level were somewhat perturbed
465 due to surf-zone fluxes. In fact, if the neutralization of acidic sulphates occurred
466 prevalently in clouds, after scavenging of gaseous ammonia into acidic droplets,
467 this process would occur more likely at the top of the marine boundary layer,
468 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 3. 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 3. 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 5 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 5 (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 5) 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 5). 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 5), 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 5 (bottom right) for exploratory purposes as these interrelationships have not been examined or discussed in the context of marine aerosol.

3.2 Chemical fluxes

3.2.1 Sea salt flux

The individual concentration profiles had to be fitted first in order to calculate gradients and then fluxes using Equation 1. The concentration gradient is a derivative of the concentration as a function of height. The lowest level at which concentration was measured was at 3 meters and may have been affected by surf-zone fluxes as discussed in detail by Ceburnis et al. (2008). Therefore, only the concentrations measured at 10 and 30m were used in calculating primary fluxes in order to reduce surf-zone related uncertainty in calculated fluxes. This approach yielded "linear gradients" and constant fluxes. It is important to note that for comparison purposes K_z values were adjusted for 10m wind speed from Figure 1 given well established relationship between K_z values and the horizontal wind speed as well as good agreement between EC and gradient samples. Sea salt (SS) and sea-spray (SS+WIOM) flux dependence on the wind speed is presented in Figure 6. The uncertainty parameters of all the fitted flux-wind speed relationships are summarised in Table 3. The obtained relationship was the power law very similar to the one obtained by Ceburnis et al. (2008), but this time it was quantified separately for sea salt and sea-spray. The relationship of sea-spray flux was stronger; however, inherent uncertainty had to be considered. The K_z values were calculated explicitly and, therefore, the uncertainty of the flux was down to the uncertainty of the gradient which in turn was dependent on the accuracy of the chemical analysis. The uncertainty of the individual sea salt fluxes was calculated as a combined propagated uncertainty of the two concentrations (10 and 30m height) and the uncertainty of K_z values. The uncertainty of the fitted relationship was presented as the 95% confidence bands. Typically, the confidence bands would narrow constraining the relationship as

the number of points increase and/or their scatter decreases. The power law exponent of SS and sea spray (3.15 & 3.4) source function were very similar to SS source function obtained by Ovadnevaite et al. (2012) who obtained power law exponent of 2.7 using high resolution measurements with aerosol mass spectrometer. The maximum sea salt flux calculated by flux-gradient method was 2-3 ng m^{-2} s^{-1} at the maximum average wind speed of 11-12 m s^{-1} while the mass flux range presented by Ovadnevaite et al. (2012) was 15-20 ng m^{-2} s^{-1} at 25 m s^{-1} hardly in need of extrapolation to even higher wind speed. However, quantitatively both studies (this study and Ovadnevaite et al. (2012)) agreed well for a given wind speed of e.g. 10 m s^{-1}, 1.67 and 1.97 ng m^{-2} s^{-1}, respectively. Only two of the individual fluxes lay outside the 95% confidence bands suggesting that the linear flux-gradient method is not the ideal one - it is an approximation after all. It is suspected that the necessitated long averaging time of the sample was an important reason behind it as well.

3.2.1 Organic matter flux

The corresponding chemical flux of WIOM was calculated and presented in Figure 7 (left). All uncertainty considerations are the same for the sea salt and sea-spray fluxes. There was one important difference, however; the WIOM fluxes turned out to be positive only at relatively strong wind speed exceeding 7 m s^{-1} while all WIOM fluxes below this value were negative (with consequential large intercept), pointing at the removal or deposition of WIOM. Note, that the negative fluxes corresponding to lower wind speed were obtained from removal profiles introduced previously in chapter 3.1.1. That does not mean that the production flux becomes negative at low wind speed, but rather reflects observations when the production flux at very low wind speed in the gradient footprint area is smaller than the deposition flux of WIOM generated tens to hundreds kilometres away. Therefore, the resulting negative WIOM flux at low wind speed occurred due to the absence of biological activity in the flux footprint area (within ~10 km from the measurement location). Another possibility is that there is no measurable concentration increase in WIOM mass at wind speeds below 7 m s^{-1} resulting in the negative flux as WIOM is being removed from the surface layer due to the largely absent source.

The WIOM flux was best fitted to the linear function (all other functional forms were associated with uncertainties far larger than the coefficient values) and there were reasons why it might be so. The WIOM content in sea spray depends on two processes: (1) fractional contribution of OM to sea spray as a function of biological activity and/or organic matter concentration and physico-chemical state in sea water; and (2) sea spray production flux as a function of wind stress or wave state. The two processes are independent and combine differently during different seasons. For example, during summer the fractional contribution of OM is typically higher, but the sea spray flux is typically lower while during winter the production flux would typically be high (due to deeper low pressure systems generating higher wind speeds), but the fractional contribution of OM would be the lowest.

The water soluble organic matter exhibited the removal gradient throughout the study period which allowed studying a seasonal pattern of a sink and a dependence on meteorological parameters. Individual WSOM concentration profiles were first fitted to power law using concentrations at all three heights and then the resulting fluxes were calculated by the Equation 1 at 10 meter height. The reason why all three heights were used is that WSOM concentration profiles pointed to a well-established removal profile with the surf-zone having minimal if any impact. The removal rate dependence on the wind speed is presented in Figure 7 (right) and attempted to fit to the power law. It turned out that the WSOM removal rate or sink was dependent on the wind speed, but with the large uncertainty and, therefore, declared unreliable. Due to the large uncertainty of the individual fluxes the actual removal rate was uncertain too, but worth noting that the removal rate of WSOM was opposite in sign to WIOM production flux.

3.3 A comparison with the other flux-wind speed relationships

Given the uncertainty of the derived sea salt flux and wind speed parameterisation it was important to compare it with other available source functions. Equally important was to cover a wide range of methods used to derive fluxes. Figure 8 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 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 flux-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 9: 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), Ovadnevaite et al. (2012; 2013) and this study. Note, that all the latter parameterisations were based on ambient measurement data. 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). Figure 7 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.

The most significant limitation of the flux-gradient method is that it allowed calculating fluxes up to moderate wind speed only. It is extremely rare that the average wind speed above 15 m s^{-1} would be sustained over a week period. Therefore, the sea spray source function method proposed by Ovadnevaite et al.

(2012; 2013) has to be considered as the more useful source function covering wind speed range of up to 26 m s^{-1}. 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.

3.4 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 9 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 9) 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.

3.5 Seasonality of observed concentrations, gradients and 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 fluxes 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 fluxes were generally the largest in winter (0.2-0.85 µg m^{-3} and 0.9-2.5 ng m^{-2} s^{-1}, respectively) and the smallest in summer (0.07-0.5 µg m^{-3} and 0.1-0.6 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. Therefore, sea salt fluxes should be considered independent of the season and dependant on the wind speed. 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. This is at least partially reflected in the differences between sea salt and sea spray fluxes and the larger respective sea spray flux uncertainties. Also, the stronger sea salt and wind speed power law relationship compared to pure sea salt relationship presented in Ovadnevaite et al. (2012) suggests that the smaller sea salt fluxes during summer may be due to the aforementioned replacement effect and may have constrained the relationship to the higher power. Furthermore, 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 flux-gradient method, a quantitative proof of the aforementioned effect was not possible.

The WIOM concentrations and fluxes 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 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, fluxes 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 fluxes 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. However, 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.

3.6 Boundary layer filling time

The boundary layer filling time helps to understand a conceptual relationship between the species concentration and its corresponding flux. The calculated sea salt fluxes allowed an estimation of an important parameter called boundary layer filling time τ according to the following equation:

$$F_{eff} = \frac{C \times H_{MBL}}{\tau} \qquad (4)$$

where F_{eff} is the effective flux; C is the concentration; H_{MBL} is the height of marine boundary layer.

The boundary layer filling time for each sampling period was calculated using the measured boundary layer height (day or night providing clean sector condition were met), calculated sea salt flux (Figure 6) and the absolute sea salt concentration at 30m level assumed as representative of the well mixed boundary layer. 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

841 resolution of the gradient samples. The corresponding filling time range was
842 calculated as 0.9-5.1 days with the median value of 1.8 days. Similar values of
843 the time constant to reach equilibrium concentration in the boundary layer taking
844 into consideration particle sizes were obtained by Hoppel et al. (2002) and the
845 value of 2 used by Ovadnevaite et al. (2012) in calculating the sea salt mass flux
846 based on sea salt concentration measurement. It is important to note, however,
847 that the filling time constant is a feature of a particular low pressure system
848 arriving at the point of observation in a connecting flow. Moreover, the flux-
849 gradient method is independent of the filling time and pretty insensitive to
850 precipitation which would mainly affect the absolute concentration value not
851 used in this study (concentration gradient was used instead). All other things
852 equal, the absolute concentration in the well mixed boundary layer would
853 continuously increase at a given flux eventually reaching steady state. Figure 10
854 helps to visualise various relationships between the four parameters: sea salt
855 concentration, sea salt flux, wind speed and boundary layer filling time. The
856 shortest filling time was obtained for the periods of the highest flux when the
857 absolute concentration was at its lowest. Clearly, the strongest winds could not
858 be sustained over the long periods of time to achieve a proportionally high
859 absolute mass concentration.
860 The longest boundary layer filling times should be attributed to the series of
861 well-defined low pressure systems without significant precipitation and the
862 calculated flux should be representative of the entire region of concentration
863 footprint which is many tens to few hundred kilometres upwind from Mace Head
864 (Ceburnis et al., 2008).
865

866 ## 4 Conclusions

867 Marine aerosol sources, sinks and chemical fluxes were studied over the entire
868 year by the gradient method. The chemical fluxes of primary species, such as sea
869 salt, and more generally sea-spray were found to show strong power law
870 relationship with the wind speed. The power law exponent of sea salt mass
871 source function was 3.15 which was fractionally higher than the generally
872 considered cubic power law relationship. The flux versus wind speed relationship
873 of WIOM was found to be linear resulting from a dependence on the biological
874 activity in oceanic waters as supported by the linear dependence of fractional

contribution of organic matter on chlorophyll-a concentration and the power law relationship of sea spray production. 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 corresponding fluxes highlighted complex interactions between biological activity, especially in the flux footprint area, and wind driven sea spray production. The marine boundary layer filling time was found to be variable in the range of 1 to 5 days linking species concentration, flux and wind speed. The obtained sea salt mass flux and wind speed parameterisation compared very well with other parameterisations which used carefully selected ambient measurement data. The comparison with the range of available flux-wind-speed parameterisations revealed significant advances in the development of the sea spray source function for the benefit of global climate models.

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1228 Table 1. Gradient sample weekly collection time scale and the number of hours
1229 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

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1232 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

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Table 3. Uncertainty of the fitted parameters (± one standard deviation) of derived parameterisations in Figures 7-8.

Parameterisation	Linear coefficient	Power coefficient
Sea salt vs U_{10} $F_{SS}=0.0011U_{10}^{3.15}$	0.0011±0.0014	3.15±0.55
Sea spray vs U_{10} $F_{sea\ spray}=0.0007U_{10}^{3.4}$	0.0007±0.001	3.4±0.6
WIOM vs U_{10} $F_{WIOM}=-0.73+0.10U_{10}$	0.10±0.03	Intercept -0.73±0.28

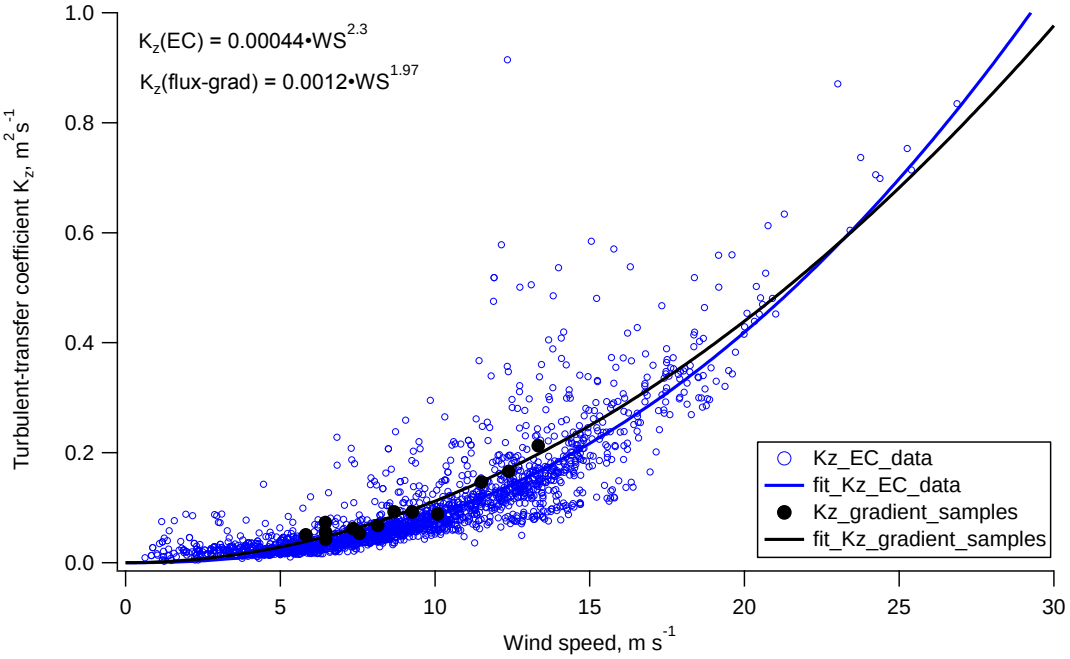
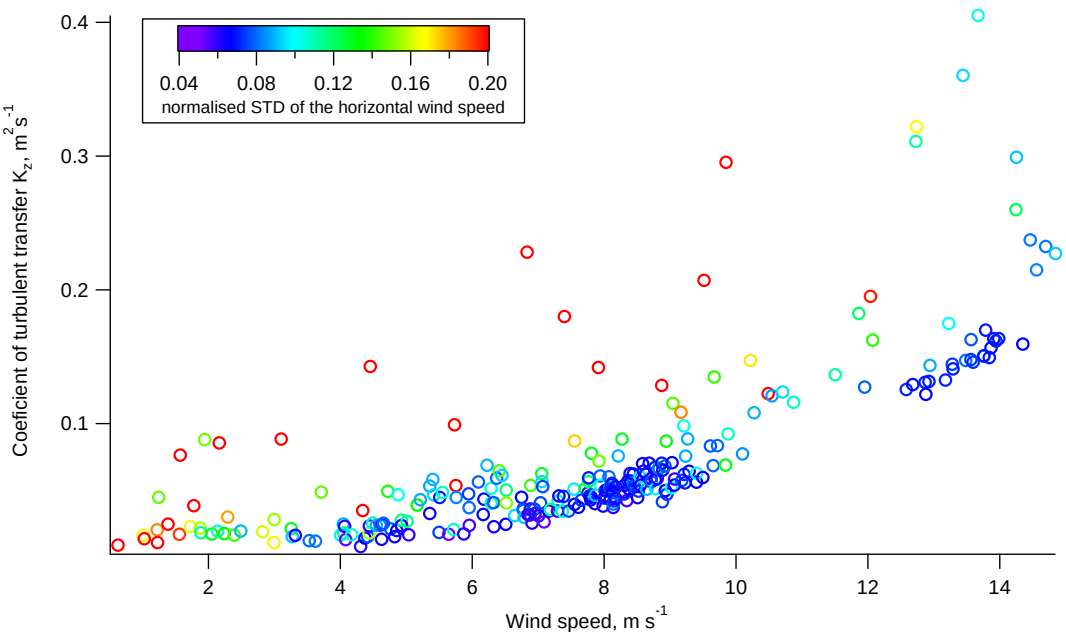


Figure 1. A relationship between the coefficient of turbulent-transfer K_z (eddy diffusivity) and the horizontal wind speed in clean marine air over the whole sampling period. 30 min data from eddy covariance system (blue open circles) and averaged eddy covariance data for the duration of gradient samples (black circles) were both fitted by power law relationship.



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1252 Figure 2. A dependence of the coefficient of turbulent-transfer K_z on the
1253 horizontal wind speed and normalised standard deviation of horizontal wind
1254 speed during April 2008 (a randomly chosen subset of data).

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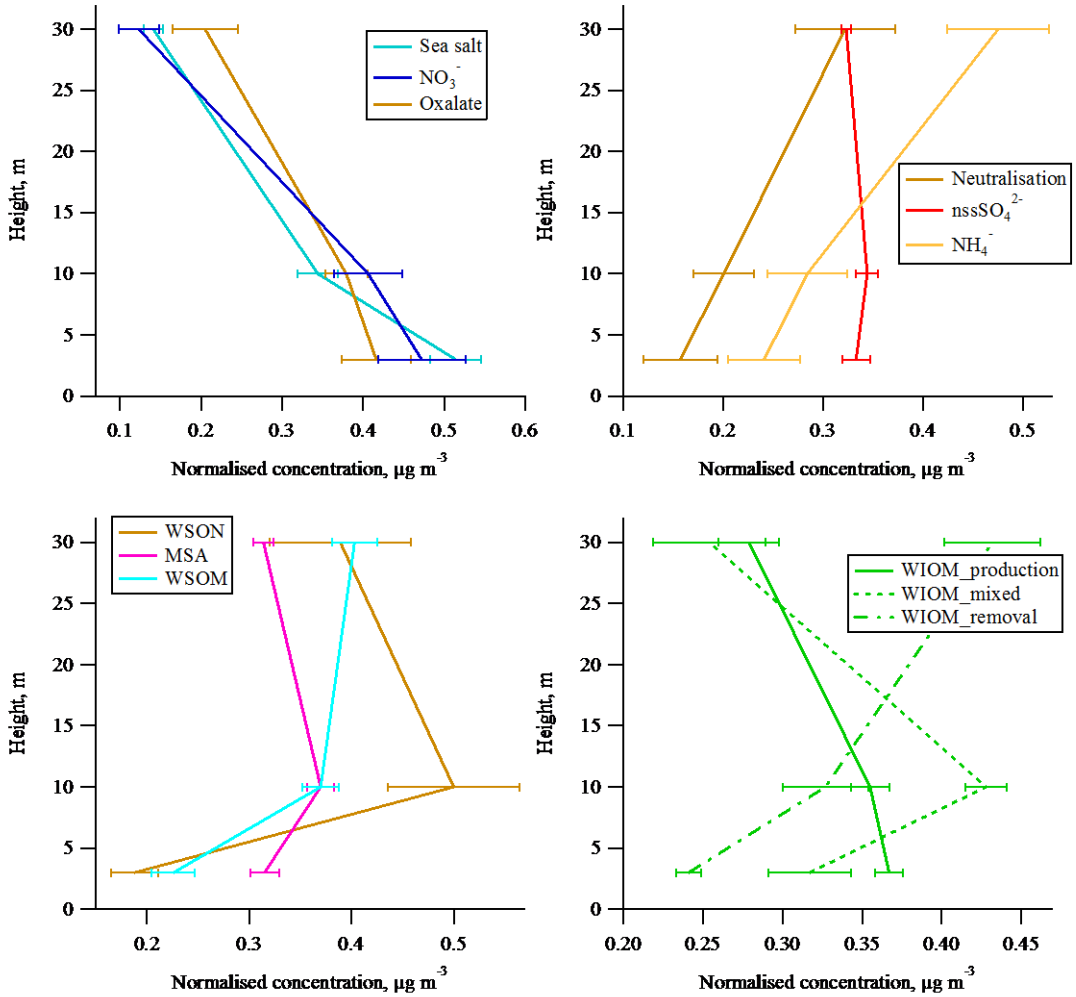


Figure 3. The gradient profiles of chemical species studied: species resembling primary production (top left); inorganic species resembling secondary production (top right); organic secondary species (bottom left) and water insoluble organic matter split into production, removal and mixed profiles (bottom right).

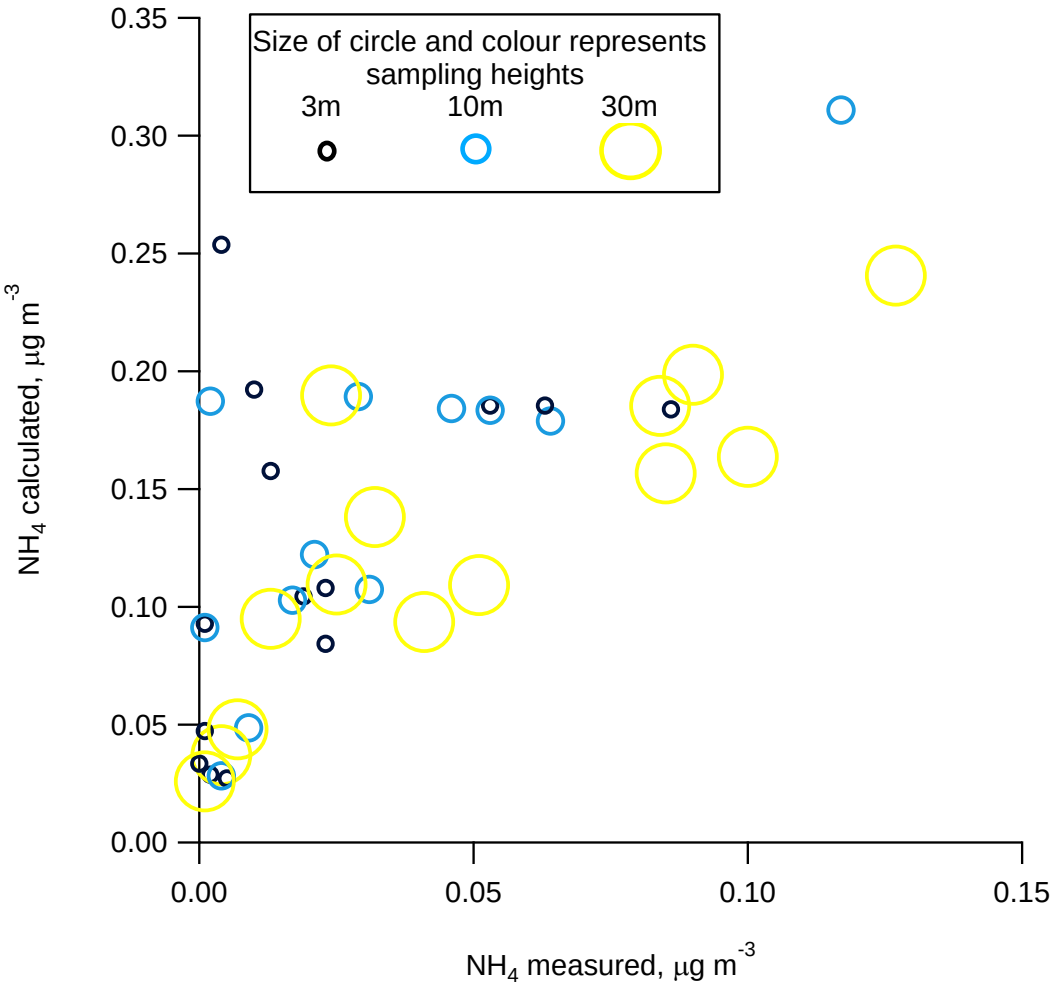
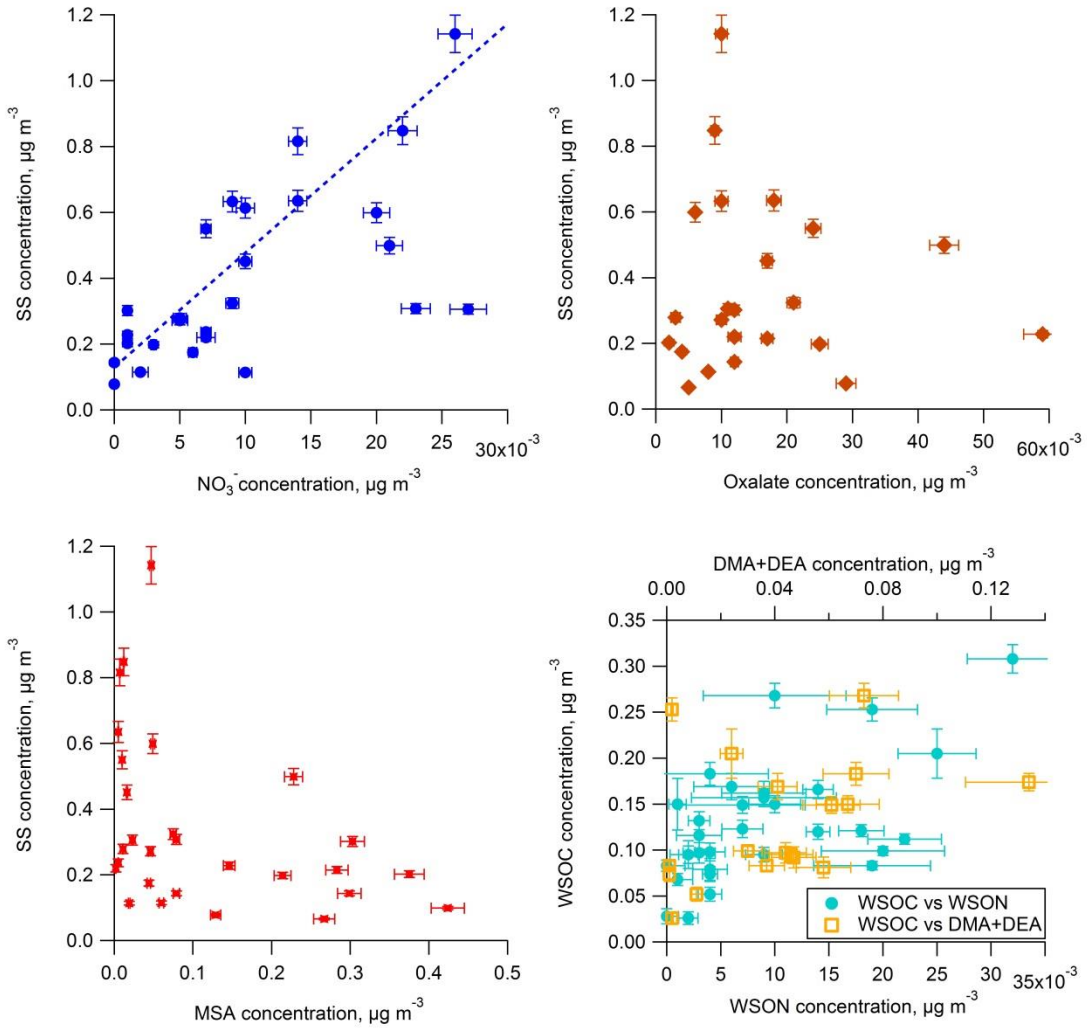


Figure 4. A scatter plot of sulphate neutralisation by ammonium with respect to sampling height.



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1273 Figure 5. Plots of sea salt and secondary species which resembled primary
1274 production concentration pattern: SS vs NO_3 (top left); SS vs Oxalate (top right);
1275 SS vs MSA (bottom left) and WSOC vs WSON (also plotted as the sum of
1276 dimethylamine and diethylamine)(bottom right). Note, that WSOC and WSON
1277 concentration are presented as µg of carbon or nitrogen mass, respectively, while
1278 all other species reported in absolute species concentrations.

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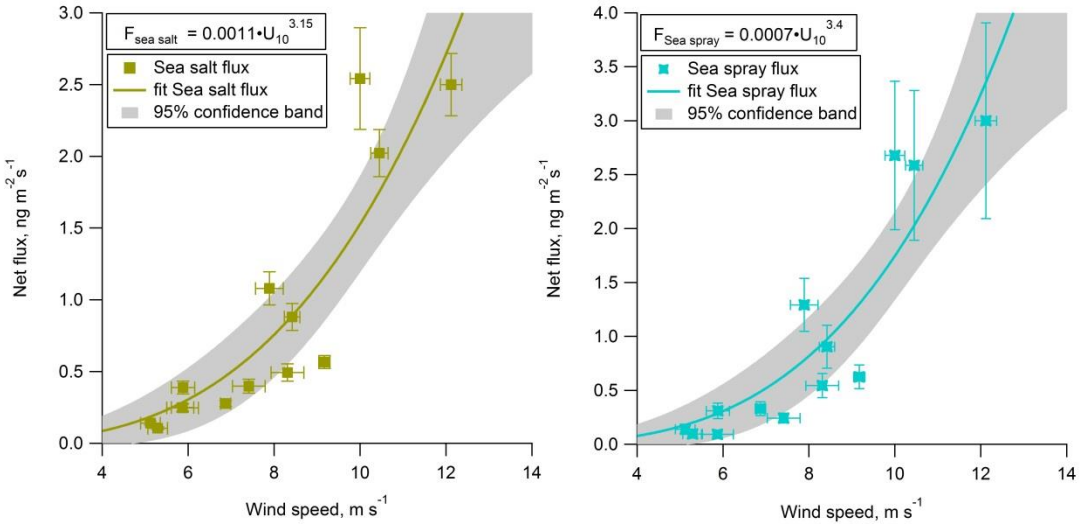

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1282 Figure 6. Sea salt and sea spray net production flux versus wind speed.
1283 Individual uncertainties of the flux and wind speed marked with caps while the
1284 grey area denotes 95% confidence bands of the fitted parameterisations.

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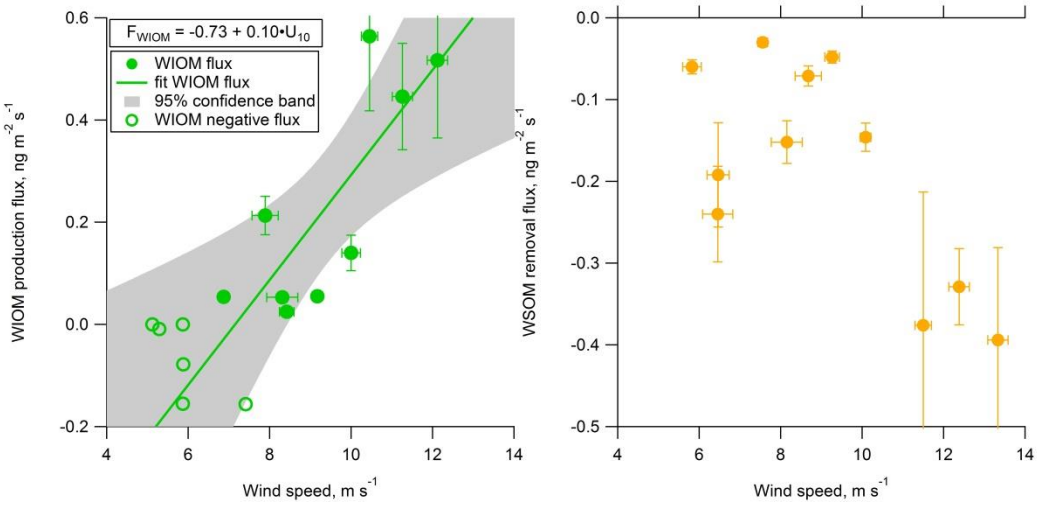

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1288 Figure 7. Water insoluble organic matter net production flux versus wind speed
1289 (left) and the dependence of the WSOM removal rate on wind speed (right).
1290 Individual uncertainties of the flux and wind speed marked with caps while the
1291 grey area denotes 95% confidence bands of the fitted parameterisations. WSOM
1292 relationship was not parameterised due to large uncertainties.

1293

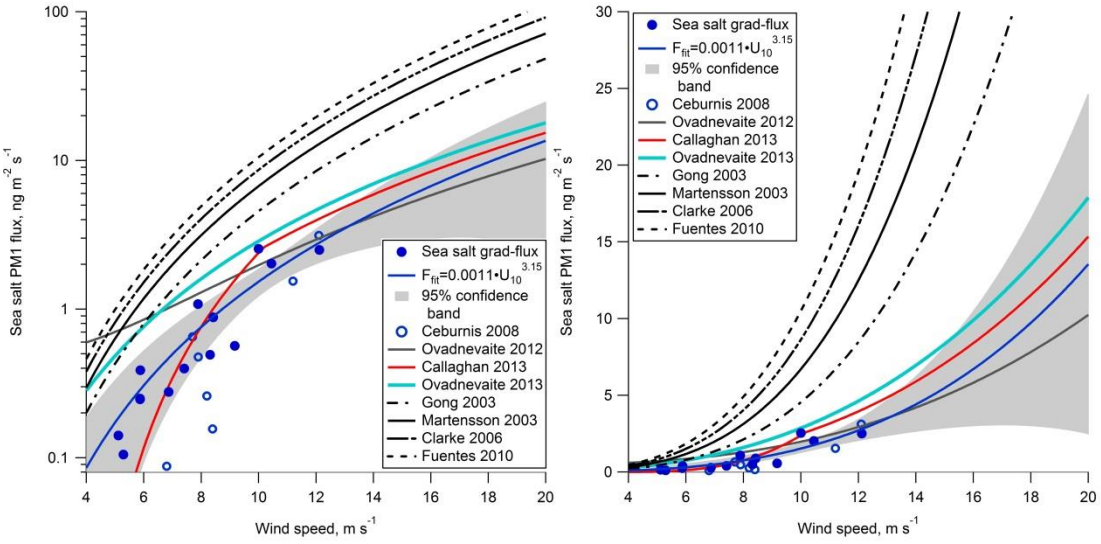

Figure 8. A comparison of the most often used and recently developed sea spray and wind speed parameterisations in log scale (left) and linear scale (right). The grey area denotes the 95% confidence bands of the flux-gradient fitted relationship.

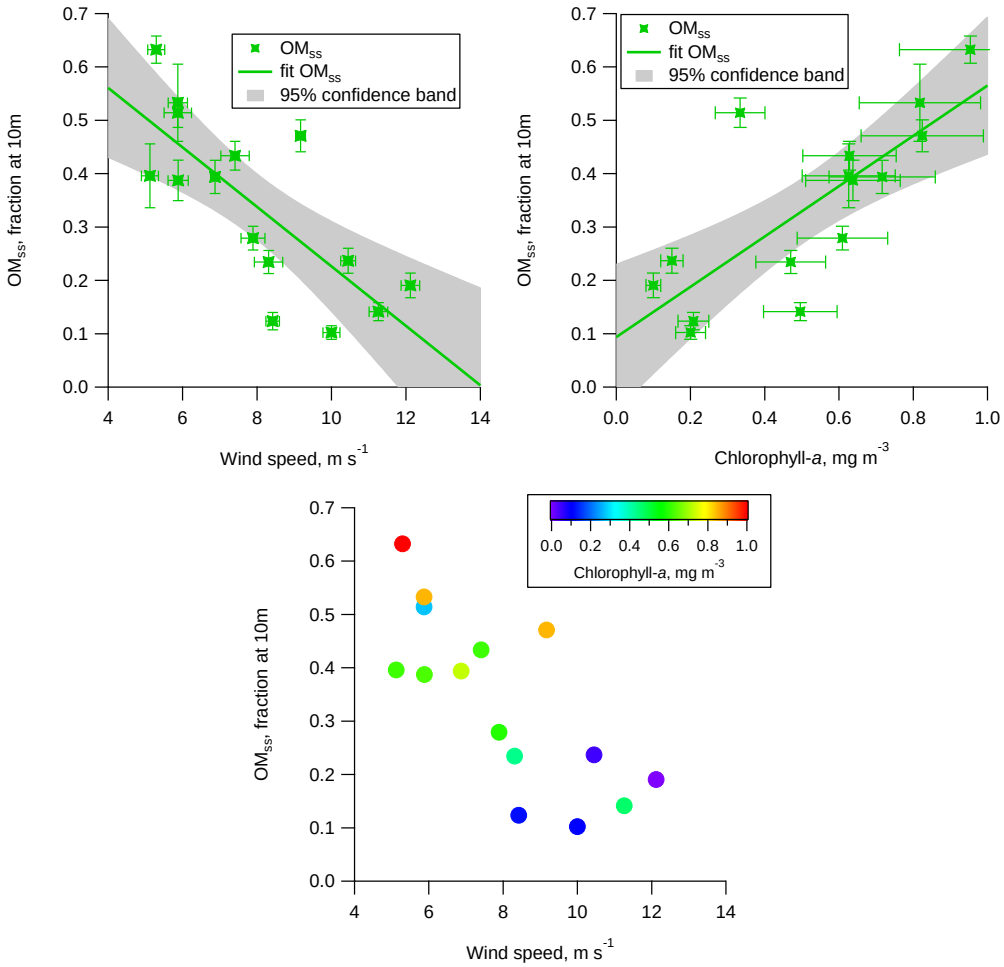

Figure 9. Effect of wind speed and chlorophyll-a concentration on the fractional contribution of organic matter (OM_{ss}): OM_{ss} vs WS (top left); OM_{ss} vs chlorophyll-a (top right) and OM_{ss} vs WS coloured by chlorophyll-a (bottom). Individual uncertainties of the flux and wind speed marked with caps while the grey area denotes 95% confidence bands of the fitted parameterisation.

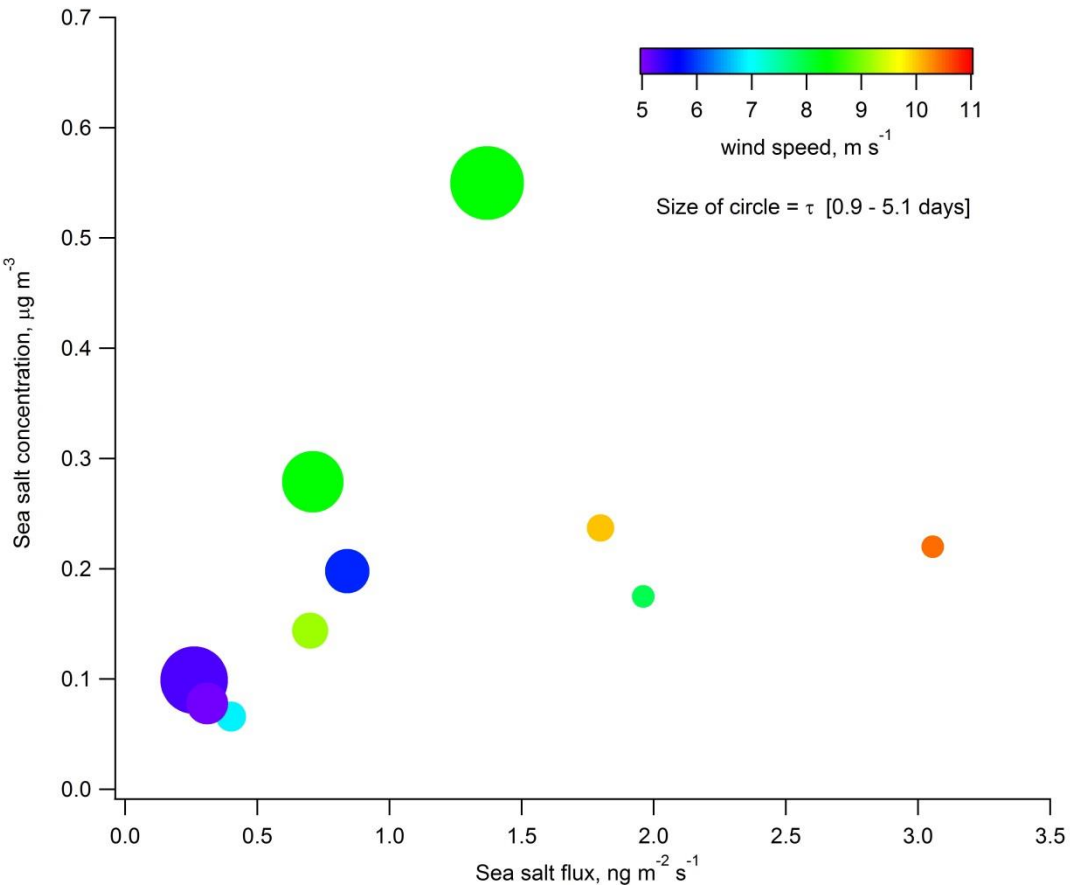

Figure 10. A relationship between sea salt absolute concentration (y-axis), sea salt flux (x-axis), wind speed (colour) and boundary layer filling time (marker size).

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%