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Marine submicron aerosol sources, sinks and chemical fluxes

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Abstract

The objectives of the study were to quantify seasonality in aerosol physico-chemical fluxes over NE Atlantic waters through the parallel deployment of micrometeorological eddy covariance flux system and an aerosol chemistry gradient sampling system. Fluxes of primary components (sea salt, water insoluble organic carbon and a combined sea spray) and secondary aerosol components (nitrate, ammonium, oxalate, amines, methanesulfonic acid and water soluble organic nitrogen) are presented in the context of seasonal marine aerosol sources and sinks. A strong power law relationship between fluxes and wind speed has been obtained not only for primary sea salt and sea spray, but also for secondary water soluble organic matter. The power law relationship between sea salt flux (F_{SSS}) and 10 m height wind speed (U_{10}) ($F_{SSS} = 0.0011 U_{10}^{3.15}$) compared very well with existing parameterisations using different approaches.

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 has been observed in marine aerosol particles for many decades and has been linked to enrichment of sea-spray by biogenic matter 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 ever 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 who found that 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 were quite uncertain due to the absence of the 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 was an extended effort of the one used by Ceburnis et al. (2008) by combining the eddy covariance measurements with the off-line chemical analysis of samples for a wide range of chemical species during an entire year (spring 2008 to spring 2009).

2 Experimental methods

The flux of sea-spray aerosol 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 introduced by Buzorius et al. (1998) allowed studying 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 (Mårtensson 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.

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). The set-up comprised PM_1 samplers installed at three different heights and the eddy covariance system installed at 22 m height.

The LIDAR measurements (Jenoptik and Vaisala ceilometers) are continuously conducted at Mace Head since 2008 and a specially developed temporal height tracking (THT) algorithm (Haeffelin et al., 2012; Milroy et al., 2012) was used to separating surface mixed layer (SML) and the decoupled residual layer (DRL), both the important parameters in considering boundary layer filling by primary fluxes.

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 included three PM_1 samplers (Sven Leckel Ingenieur-büro GmbH) running in parallel at 3, 10 and 30 m heights with the flow rate of 38 lpm. Samples were collected in clean marine conditions (wind direction $190 < WD < 300$ and $CPC < 700$ particles cm^{-3}) using an automated sampling system on quartz filters for the analysis of both organic and inorganic components of marine aerosol. Active control of the sampling conditions excluded sampling during occasional short-term spikes of CN 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 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 h (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 ensuring that anthropogenic and coastal effects were minimised to guarantee a dominant, if not at times overwhelming natural marine aerosol signal as detailed in the study of O'Dowd et al. (2013).

2.2   Off-line chemical analysis and concentration gradients

Fifteen PM_1 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 at least 50 h per calendar week.

The samples were analysed for a wide range of chemical species present in aerosol particles: sodium (a marker for sea spray salts (SSS)), 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. Sea salt concentration was calculated as SSS = Na·3.1 (SSS stands for sea spray salts to distinguish from sea spray).

Concentration gradients of various chemical species were obtained by linear fit of the concentration profile (except WSOC). 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. 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 di-viding 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 vari-ances around the mean value. 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 increas-ing concentration with height, or positive gradient, was common of species produced by secondary processes in the atmosphere aloft or within the marine boundary layer.

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 pro-vided 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 m out from the sea-facing side of the 22 m tower and a turbulent flow (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 sec-ondary 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:

$$F = -K_z \left. \frac{\mathrm{d}c}{\mathrm{d}z} \right|_z \tag{1}$$

where F is the flux, K_z is the turbulent-transfer coefficient; $\mathrm{d}c/\mathrm{d}z$ 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 t is time). K_z had to be averaged over about 50 to 140 h to represent the sampling period of a particular concentration profile. The averaged K_z values were compared with eddy covariance data and presented in Fig. 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 normally distributed and the mean average representing gradient samples was statistically meaningful. 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

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the horizontal wind speed measurements if the K_z values cannot be estimated directly. However, 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

5   as presented in Fig. 2 where the K_z and wind speed relationship was coloured by normalised standard deviation of the horizontal wind. 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.

10   It is important to know the thickness of the surface layer as it is in this layer that fluxes are considered constant and gradients adhere to similarity theory. Another caveat is the formation of internal boundary layers. 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

15   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 limited to below 10 m and never propagated to the top of the tower in marine sector. 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

20   measurements made at 7 m above ground level or higher.

3 Errors and uncertainties

The flux-gradient method based on the Eq. (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

25   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:

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

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

The Eq. (2) was valid in most cases, but did not apply for calculating the uncertainty of the organic matter enrichment factor ($OM_{ss} = OM/(OM+SSS)$), where the variable OM appeared in both nominator and denominator. The partial derivatives resulted in the following Equation of the combined propagated uncertainty of the OM enrichment factor in sea spray:

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

where the ratio in front of the square root is the impoverishment factor of sea spray (opposite of OM enrichment) resulting in the fractional uncertainty of the OM enrichment factor dependent on the sea spray impoverishment factor 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.

4 Results and discussions

The measurements performed at three different heights allowed to resolve vertical concentration profiles of different chemical species. Different sources and sinks with corresponding fluxes can 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 10 km from the measurement location, i.e. coastal waters (Ceburnis et al., 2008). The surf zone emissions may have and had certain influence on the concentrations of sea salt or sea-spray at the lowest level of 3 m, but had little or no impact on secondary organic aerosol.

4.1 Concentration gradient profiles

4.1.1 Primary components

The concentration profile of sea salt (top left in Fig. 3) was unambiguously primary, i.e. concentration was decreasing vertically. The individual sea salt concentration profiles are presented in Fig. 4. Some of those 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 sampling period (ascending and descending wind regimes). However, as it was stated above, surf-zone emissions could have had influence on the concentration value at the lowest level of 3 m and, therefore, this level was not used in 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 systematically distorted, i.e. the concentrations of oxalate and nitrate significantly diverged from the sea salt one at the lowest sampling height of 3 m while following the sea salt profile above 10 m. 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. Since the source of the secondarily produced chemical compounds is in the atmosphere aloft the concentration profile was distorted close to the ground by deposition of sea spray particles around 1 µm which have provided large condensation sink for nitric acid. 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, removal and mixed profiles (bottom right of Fig. 3). Given that enrichment of organic component in primary aerosol is related to 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 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 while pointing at the deposition within the flux footprint area was actually telling about the absence of biological activity in surface waters within the flux footprint area and not necessary that the WIOM was produced by the secondary processes which cannot be completely excluded either. 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

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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 upwellings and become unpredictable on a day-to-week time scale.

4.1.2 Secondary components

The inorganic secondary species ($nssSO_4$ and NH_4) are presented in top right of Fig. 3 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 must be noted that the concentration profile of $nssSO_4$ was pretty constant and did not follow that of the ammonium profile which 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, some ambiguity must be acknowledged before interpreting $nssSO_4$ 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 (Fig. 3 (top right) and Fig. 5), even though neutralization with respect to sulphuric acid is never complete, due to scarcity of ammonia in the marine boundary layer. 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 sulphuric acid neutralization.

The secondary organic species (MSA, WSOM and WSON) are presented in the bottom left of Fig. 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 Fig. 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. 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 tropo-sphere). However, the gradient method also revealed important features with the potential of quantifying their production rates. 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. Figure 6 (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–$30\,\mathrm{ng\,m^{-3}}$ of nitrate only re-affirming cleanness of the marine atmosphere studied at Mace Head.

Similar relationship was observed for oxalate (top right plot of Fig. 6), but there were many more outliers from linear pattern. 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 Fig. 6). MSA production is photochemically driven and time limited considering the gradient footprint of 0.2–$5\,\mathrm{km}$ 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). Both WSON and the sum of dimethylamine (DMA) and diethylamine (DEA) exhibited a relationship with water soluble organic matter (WSOM) (bottom right of Fig. 6), however, only WSOM and WSON correlated at a significant level ($r = 0.58$). The comparison between the absolute amounts of WSON and the

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sum of amines suggested that the amines were likely the dominant species of WSON, but difficult to determine due to detection limit as indicated above.

4.2   Chemical fluxes

4.2.1   Sea salt flux

The individual concentration profiles had to be fitted first in order to calculate gradients and then fluxes using Eq. (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 m 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 30 m 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 10 m wind speed from Fig. 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 (SSS) and sea-spray (SSS + WIOM) flux dependence on the wind speed is presented in Fig. 7. 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 30 m 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 sea salt and sea spray (3.15 and 3.4) source function were very similar to sea salt source function

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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.

4.2.2 Organic matter flux

The corresponding chemical flux of WIOM was calculated and presented in Fig. 8 (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, pointing at the removal or deposition of WIOM. It suggested that WIOM fluxes in the gradient footprint zone at low wind speed were lower than deposition fluxes and that the bulk of WIOM was produced outside the gradient footprint zone. According to the discussion above it is possible that 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 the wind speed 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 line and there were reasons why it might be so. The WIOM content in sea spray depends on two processes: (Eq. 1) enrichment of OM in sea spray as a function of biological activity and/or organic matter concentration and

physico-chemical state in sea water; and (Eq. 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 enrichment 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 enrichment 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 Eq. (1) at 10 m 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 Fig. 8 (right) and fitted to the power law. It turned out that the WSOM removal rate or sink was dependent on the wind speed with a power law coefficient of 2.2. Due to the uncertainty of the individual fluxes the actual removal rate is rather uncertain as well, but the removal rate of WSOM is similar in magnitude, but opposite in sign to WIOM. Hence, it is possibly suggesting that a significant fraction of WSOM is in fact the processed primary WIOM as has been already proposed (Rinaldi et al., 2010; Decesari et al., 2011).

4.3 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 9 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), Mårtensson et al. (2003), Ovadnevaite et al. (2012, 2013) and this study. Clarke et al. (2006), Fuentes et al. (2010) and Mårtensson 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 PM_1 gradient measurements, respectively), but were completely independent of each other and different in terms of the utilised methods. The presented parameterisations cluster in a distinct pattern in Fig. 9: Clarke et al. (2006), Fuentes et al. (2010), Gong (2003) and Mårtensson et al. (2003) parameterisations are all significantly above the recently developed parameterisations by Callaghan (2013), Ovadnevaite et al. (2012; 2013) and this study. Note, that all the latter parameterisations used carefully explored ambient measurement data. The clustering 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; Mårtensson et al., 2003; Clarke et al., 2006; Fuentes et al., 2010) always resulting in the overestimated mass concentrations. Figure 8 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 real-world 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.

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 Mårtensson et al. (2003) parameterisations would bring all of them closer to the other clustered 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 100 nm 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 Mårtensson et al. (2003) parameterisations, even when coupled with Callaghan (2013) whitecap parameterisation, would still be significantly above the ambient measurement based parameterisations and/or predicting unrealistic size resolved fluxes. 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 $15\,\mathrm{m\,s^{-1}}$ 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 reliable covering wind speed range of up to $26\,\mathrm{m\,s^{-1}}$ in a well-defined low pressure system. Every proposed source function can only be reliable

over the wind speed range it was derived from. An extension of the source function albeit practical may introduce significant errors outside the derivation range as evident in Fig. 9 – the extended flux-gradient relationship rapidly diverged above the uppermost experimentally estimated fluxes.

5   WIOM and chlorophyll *a* relationship

Gantt et al. (2011) suggested that organic matter enrichment 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 10 presents a relationship between organic enrichment in sea spray ($OM_{ss} = OM/(OM + SSS)$) and the wind speed using the data set of this study and the former study of Ceburnis et al. (2008) which were not part of a dataset used by Gantt et al. (2011). The relationship is pretty clear and the data of Ceburnis et al. (2008) follow the same pattern (top left plot). However, when OM_{ss} is plotted against Chlorophyll *a* concentration a statistically significant linear dependence ($OM_{ss} = 0.094 + 0.47 \cdot Chl$, $r = 0.77$, $P \ll 0.01$) has emerged (top right plot) suggesting that the organic matter enrichment in sea-spray can be largely explained by the chlorophyll-a concentration alone without invoking wind speed and agrees well with the relationship presented by Rinaldi et al. (2013) based on an extended dataset (reaching 70 % OM enrichment at $1.0\,mg\,m^{-3}$). 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). Considering altogether it is, however, possible that the OM_{ss} dependence on the wind speed can be important over much wider range of conditions and using larger datasets as in Gantt et al. (2011). It can be concluded, that while the OM_{ss} dependence on wind speed cannot be excluded it may be weaker than the OM_{ss} and chlorophyll *a* relationship due to inter-dependence of wind speed and chlorophyll *a* – the wind speed is higher in winter when chlorophyll *a* concentration is at its lowest and vice versa. It is hardly a

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coincidence, however, that the two points with rather similar chlorophyll *a* concentration ($\sim 0.4\,\mathrm{mg\,m^{-3}}$) 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 enrichment and chlorophyll *a* relationship. 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 primary organic matter enrichment in sea spray in different ways depending on the trophic level interactions.

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:

$$F_{\mathrm{eff}} = \frac{C \times H_{\mathrm{MBL}}}{\tau} \tag{4}$$

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, calculated sea salt flux (Fig. 7) 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 m among the eight periods for which overlapping LIDAR measurements were available. The corresponding filling time range was calculated as 0.9–5.1 days with the median value of 1.8 days. Similar values of the time constant to reach equilibrium concentration in the boundary layer taking into consideration particle sizes were obtained by Hoppel et al. (2002) and the value of 2 used by Ovadnevaite et al. (2012) in calculating the sea salt mass flux based on sea salt concentration

measurement. It is important to note, however, that the filling time constant is a feature of a particular low pressure system arriving at the point of observation in a connecting flow. Moreover, the flux-gradient method is independent of the filling time and pretty insensitive to precipitation which would mainly affect the absolute concentration value not used in this study (concentration gradient was used instead). All other things equal, the absolute concentration in the well mixed boundary layer would continuously increase at a given flux eventually reaching steady state. Figure 11 helps to visualise various relationships between the four parameters: sea salt concentration, sea salt flux, wind speed and boundary layer filling time. The shortest filling time was obtained for the periods of the highest flux when the absolute concentration was at its lowest. Clearly, the strongest winds could not be sustained over the long periods of time to achieve a proportionally high absolute mass concentration.

The longest boundary layer filling times should be attributed to the series of well-defined low pressure systems without significant precipitation and the calculated flux should be representative of the entire region of concentration footprint which is many tens to few hundred kilometres upwind from Mace Head (Ceburnis et al., 2008).

7   Conclusions

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

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a potential to estimate their production rate in the marine boundary layer. The marine boundary layer filling time was found to be variable in the range of 1 to 5 days which is the important parameter considering the dynamics in the marine boundary layer. 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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Table 1. Gradient sample weekly collection time scale during 13 month period in 2008–2009.

10–15/4/2008	30/6–7/7/2008	11–18/12/2008
24–29/4/2008	14–22/7/2008	14–21/1/2009
29/4–7/5/2008	22–29/08/2008	25/2–4/3/2009
27/5–6/6/2008	8–18/9/2008	4–11/3/2009
25/6–3/6/2008	30/9–10/10/2008	5–12/5/2009
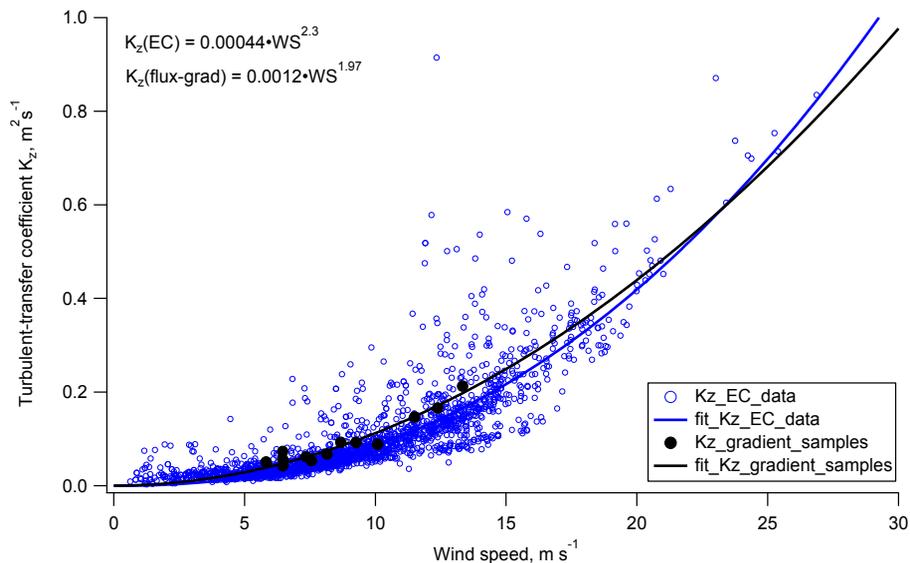
Figure 1. A relationship between the coefficient of turbulent-transfer K_z and the horizontal wind speed in clean marine air over the whole sampling period. 30 min data from eddy covariance system (blue open circles) and averaged eddy covariance data for the duration of gradient samples (black circles) were both fitted by power law relationship.
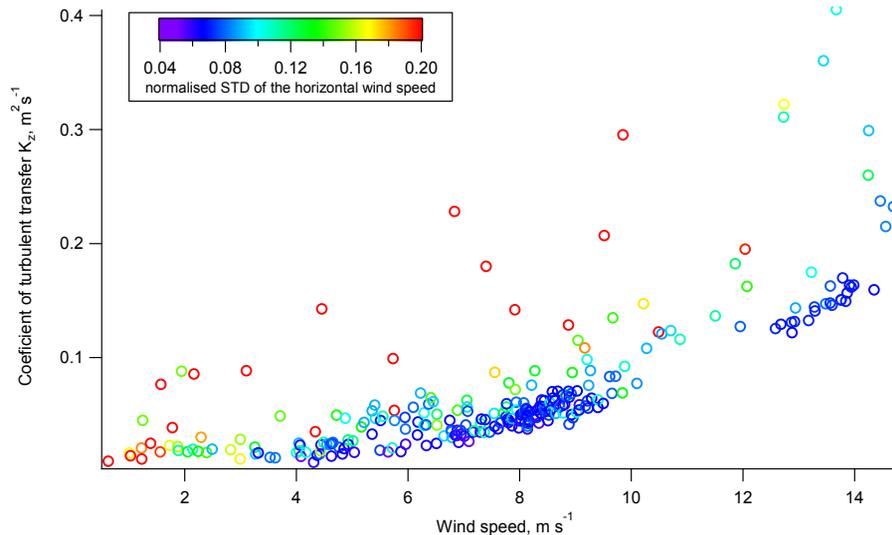
Figure 2. A dependence of the coefficient of turbulent-transfer K_z on the horizontal wind speed and normalised standard deviation of horizontal wind speed during April 2008.

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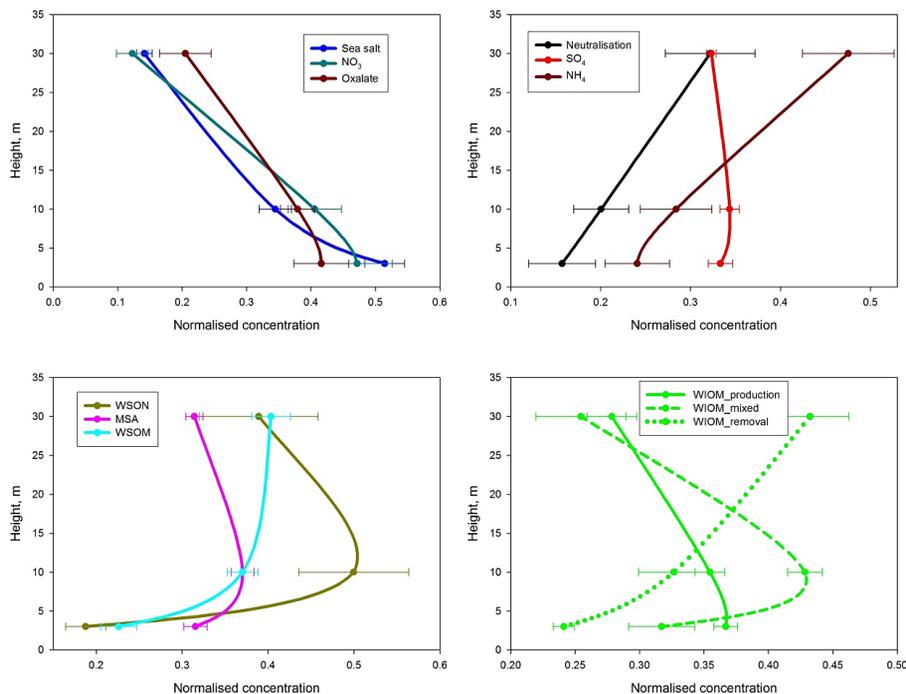
Figure 3. The gradient profiles of chemical species studied: species resembling primary production (top left); inorganic species resembling secondary production (top right); organic secondary species (bottom left) and water insoluble organic matter split into production, removal and mixed profiles (bottom right).
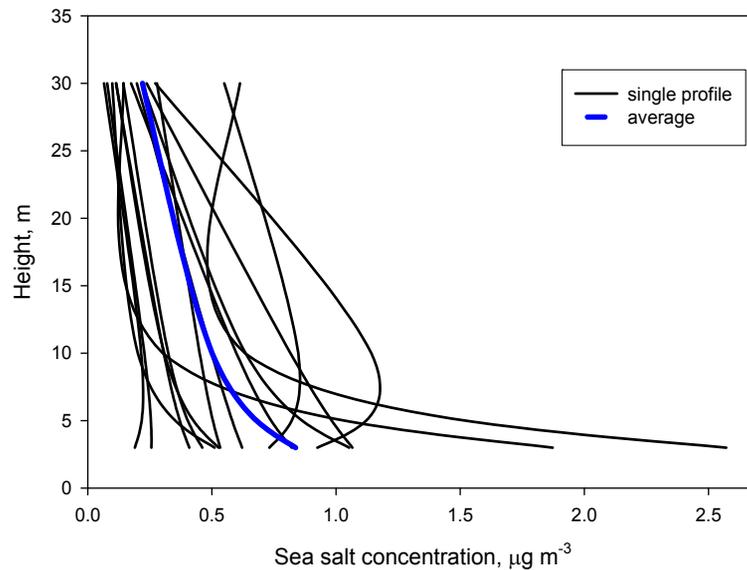
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Figure 4. The individual and the averaged sea salt concentration profiles.
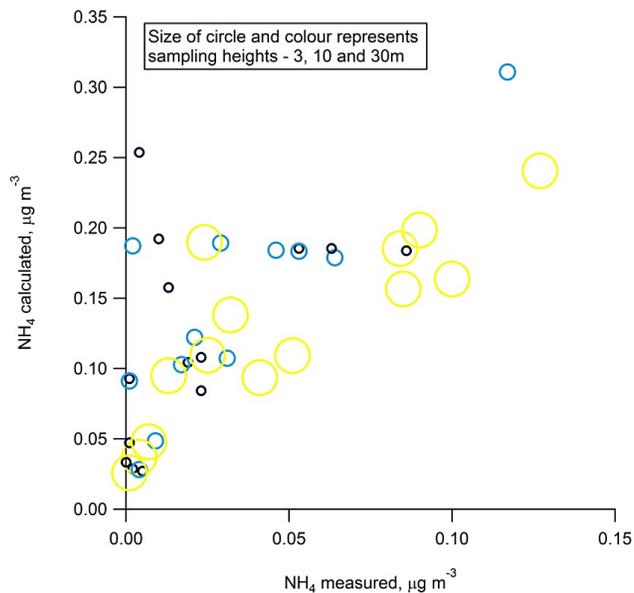
Figure 5. A scatter plot of sulphate neutralisation by ammonium with respect to sampling height.
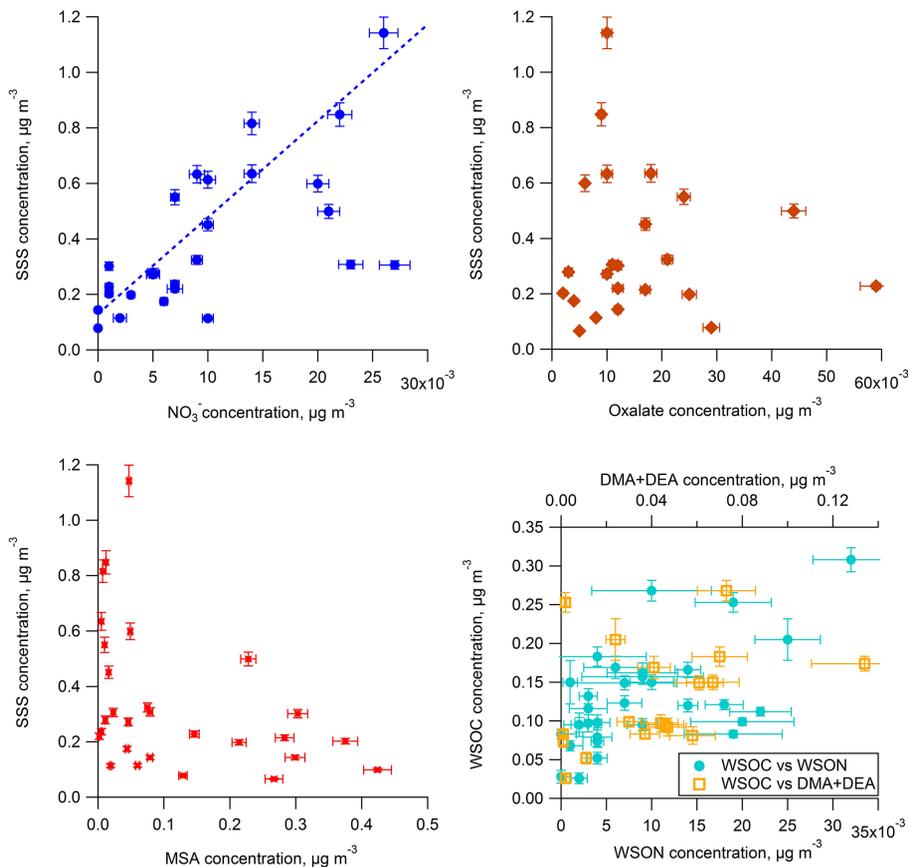
Figure 6. Plots of sea salt and secondary species which resembled primary production concentration pattern: SSS vs. NO$_3$ (top left); SSS vs. Oxalate (top right); SSS vs. MSA (bottom left) and WSOC vs. WSON (also plotted as the sum of dimethylamine and diethylamine) (bottom right).
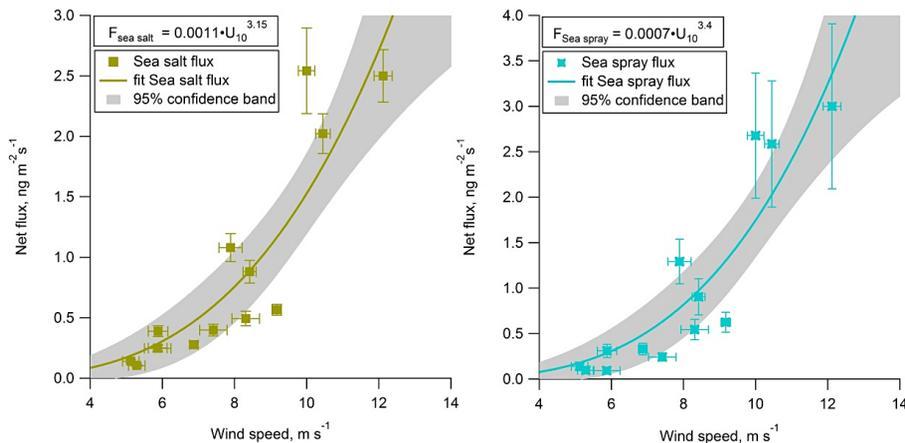
Figure 7. Sea salt and sea spray net production flux versus wind speed. Individual uncertainties of the flux and wind speed marked with caps while the grey area denotes 95 % confidence bands of the fitted parameterisations.
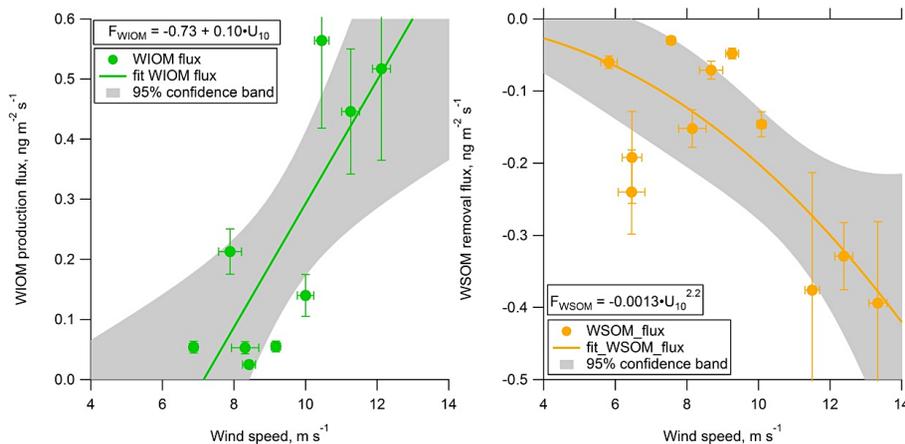
Figure 8. Water insoluble organic matter net production flux versus wind speed (left) and the dependence of the WSOM removal rate on wind speed (right). Individual uncertainties of the flux and wind speed marked with caps while the grey area denotes 95 % confidence bands of the fitted parameterisations.
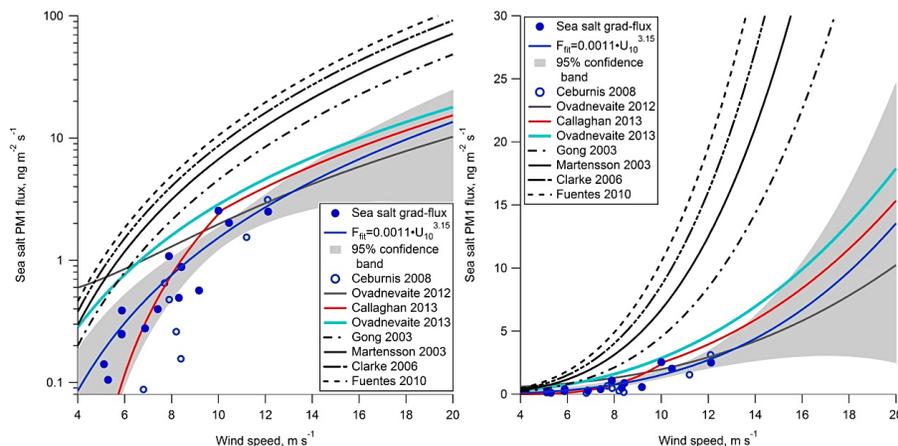
Figure 9. A comparison of the most often used and recently developed sea spray and wind speed parameterisations in log scale (left) and linear scale (right). The grey area denotes the 95 % confidence bands of the flux-gradient fitted relationship.
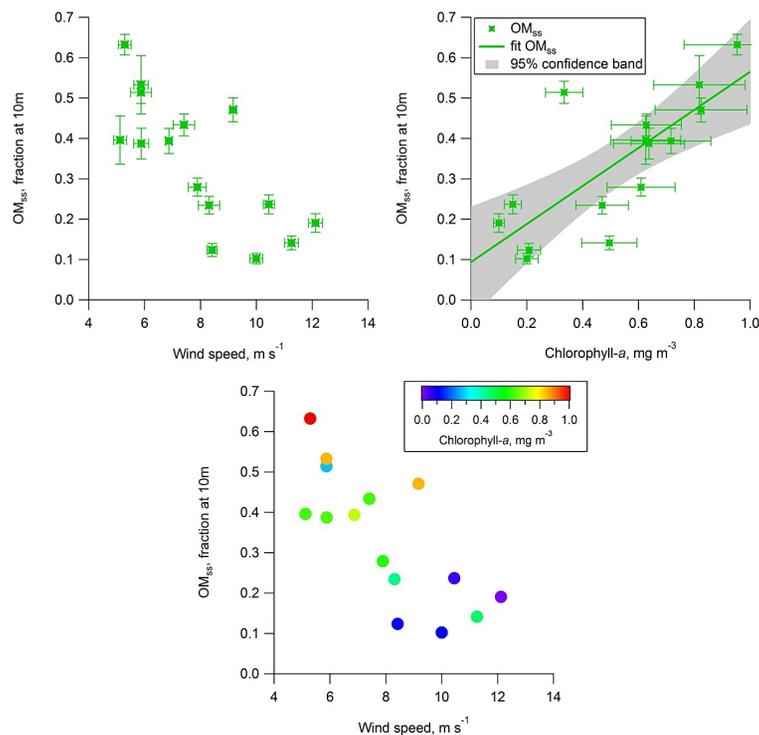
Figure 10. Effect of wind speed and chlorophyll-a concentration on the organic matter enrichment OM_{ss}: OM_{ss} vs. WS (top left); OM_{ss} vs. chlorophyll a (top right) and OM_{ss} vs. WS coloured by chlorophyll a (bottom). Individual uncertainties of the flux and wind speed marked with caps while the grey area denotes 95 % confidence bands of the fitted parameterisation.
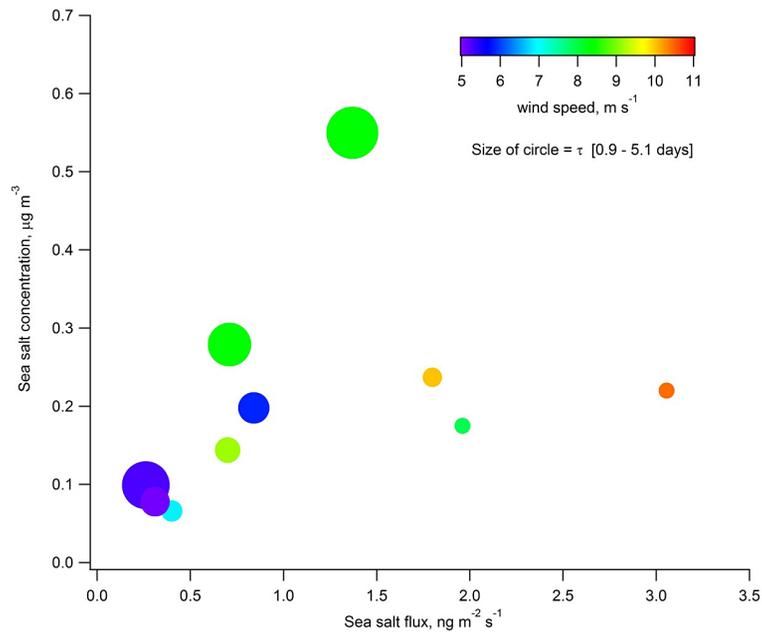
Figure 11. A relationship between sea salt absolute concentration (*y* axis), sea salt flux (*x* axis), wind speed (colour) and boundary layer filling time (marker size).

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