Quantification of Coastal New Ultra-Fine Particles Formation from In situ and Chamber Measurements during the BIOFLUX Campaign


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Environmental Context. Secondary processes leading to the production of ultra-fine particles by nucleation are still poorly understood. A fraction of new particles formed can grow into radiatively active sizes, where they can directly scatter incoming solar radiation and, if partly water soluble, contribute to the cloud condensation nuclei population. New particle formation events have been frequently observed at the Mace Head Atmospheric Research Station (western Ireland), under low tide and sunny conditions, leading to the hypothesis that new particles are formed from iodo-species emitted from macroalgae.

Abstract. New particle formation processes were studied during the BIOFLUX campaign in September 2003 and June 2004. The goals were to bring new information on the role of I2 in new particle formation from seaweeds and to quantify the amount of I2 emitted and new particles formed by a given amount of seaweed. These two goals were achieved by using a simulation chamber filled with selected species of seaweeds from the Mace Head area and flushed with particle-free atmospheric air. It was found that total particle concentrations and particles in the 3–3.4 nm size range produced in the chamber are positively correlated with gaseous I2 concentrations emitted by the seaweeds, with a typical source rate of 2800 particles cm−3 ppt−1 (I2) in the 3–3.4 nm size range. In fact, I2 and particle concentrations are also both directly positively correlated with the seaweed mass (64 300 particles cm−3 formed per kg of seaweed, and 24 ppt of I2 per kg of seaweeds) until saturation was reached for a seaweed biomass of 7.5 kg m−2. From the chamber experiments, the flux of 3–3.4 nm particles was calculated to be 2.5 × 1010 m−2 s−1 for a seaweed loading of 2.5 kg m−2 (representative of a typical seaweed field density), decreasing to 1 × 1010 m−2 s−1 for a seaweed loading of 1 kg m−2. At a seaweed loading of 2.5 kg m−2, the growth rate of particles produced in the chamber was calculated to be 1.2 nm min−1. The source rates and growth rates determined from the chamber experiments were used in conjunction with seaweed coverage in and around Mace Head to produce local emission inventories for a meso-scale dispersion model. Comparison of the resulting aerosol size distributions from the model simulations and those observed exhibited good agreement suggesting that the chamber fluxes and growth rates are consistent with those associated with the tidal emission areas in and around Mace Head.


Introduction

The global impact of atmospheric particles cannot be evaluated if their sources, both natural and anthropogenic, are not understood. Natural atmospheric aerosols can be produced through both primary and secondarily processes. Sources of primary particles, such as sea spray and desert dust have been extensively studied and are usually correlated with the wind speed and their production mechanisms are quite well understood. However, secondary processes leading to the production of ultra-fine particles by nucleation are still poorly understood. A fraction of new particles formed can grow into radiatively active sizes where they can directly scatter incoming solar radiation, and if partly water soluble, contribute to the cloud condensation nuclei (CCN) population. New
particle formation events have been frequently observed at the Mace Head Atmospheric Research Station (western Ireland), under low tide and sunny conditions, leading to the hypothesis that new particles are formed from iodo-species emitted from macroalgae.\[1,2\] To confirm this hypothesis, it has recently been shown in laboratory studies that ultra-fine iodine-containing particles are produced by algae exposed to scrubbed atmospheric air enriched with ozone.\[3\]

One of the main objectives of the scientific community concerned with this topic is to be able to predict the number of new particles formed by secondary processes, in order to evaluate their impact on a larger scale. Detailed models have been developed in order to simulate new particle formation from a certain amount of gaseous precursors that, under sunny conditions, will be oxidized into condensable species.\[3\] However, significant uncertainties still remain, both on the nature of the nucleating species and on the emission rate of their precursors. Several chemical mechanisms implying iodo-compounds have been suggested to explain the formation of new particles in the coastal atmospheric of western Ireland. Iodine was observed to be released from seaweeds mainly as CH$_2$I$_2$, and in sometimes significant fractions of CHBr and CHCl$_2$.\[4,5\] In conjunction with these observations, it was found that new particles were formed from CH$_2$I$_2$ in the presence of UV radiation and O$_3$.\[1,6\] Analysis, by mass spectrometry, of the new particles formed during these experiments show that they were composed of iodine oxides and oxy-acids. CH$_2$I$_2$ readily photolyses at ambient light levels, and I$_2$ becomes the main gaseous species after a few minutes.\[6\] Depending on the uptake of I$_2$ in the models, I$_2$ is not converted to the particulate phase and remains in the gas phase until it is photolyzed\[6\] or it becomes the major component of the final aerosol (uptake of 1).\[6\] Recent works show that I$_2$ is present at levels of the order of 10 ppt in the coastal atmosphere of Mace Head, most likely emitted from macroalgae at low tide and that concentrations of this magnitude could be significant in terms of contributing to the new particle formation process.\[7\] However, it is not yet elucidated if I$_2$ is directly emitted from seaweeds by liquid-to-gas transfer, or if it is formed by oxidation of I$^-$ by H$_2$O$_2$ upon stress on the seaweed during low tide atmospheric exposure.\[13\]

The goal of this paper is two-fold: (1) to elucidate the relationship between I$_2$ and new particle formation from seaweeds; and (2) to quantify the source rates of new particles formed in the vicinity of Mace Head and nearby biologically-active regions. We present the results of two measurement campaigns (Quantifying coastal BIOgenic aerosol and gas FLUX: BIOFLUX) on the coastal site of Mace Head and its surroundings, conducted during September 2003 and June 2004. During BIOFLUX, a simulation chamber was built to quantify I$_2$ emissions along with new particle formation and growth rate from selected species of seaweeds, representative of the area, under atmospheric conditions. A mobile lab equipped with particle size distribution analyzers was used to study in situ new particle formation at high-density seaweed locations in order to relate chamber and in situ measurements, by the mean of a mesoscale transport model Regional Atmospheric Modelling System (RAMS). New particle size distributions were simultaneously measured at the Mace Head Atmospheric Research station (53.33\'N, 9.90\'W, 5 m above sea level) and, with the mobile laboratory, from several locations in the coastal areas of western Ireland which are believed to have a higher particle formation activity than Mace Head.

**Experimental**

The Mace Head Atmospheric Research Station,\[8\] located at the west coast of Ireland, shows evidence of frequent nucleation events and particle growth cases.\[9,10\] These particle formations are usually observed when tides are low and sunshine is available. The simulation chamber was filled with seaweed collected from the Mace Head region. The chamber was 2 m $\times$ 1 m $\times$ 1 m in dimension and was made of the Perspex with a 50% UV radiation transmittance. The chamber was operated in two modes, one without flow through and another with flow of ambient coastal air scrubbed of background aerosols but not scrubbed of gases. Chamber particle size distributions were measured using a nano-SMPS (Scanning Mobility Particle Sizer for nano-particles composed of a 3085 TSI short column and a 3025 TSI CPC). Gasseous molecular iodine was collected using a denuder sampling technique based on the specific reaction between starch and iodine.\[9,10\] An ethanolic starch solution (2 mg mL$^{-1}$) was used to coat to the inner surfaces of brown glass tubes (inner diameter 6 mm, outer diameter 9 mm, length 50 cm). In order to produce a uniform starch coating of the inner denuder walls, four 0.5 mL aliquots of the coating solution were slowly instilled into the pre-cleaned rotating denuder. During the coating procedure the denuder tubes were dried by flushing N$_2$ at a flow rate of 0.5 L min$^{-1}$. Finally, the denuders were sealed with polypropene end-caps. For the chamber experiments, a volumetric air flow of 500 mL chamber air per minute was sucked through the denuder tubes. The sampling time varied between 15 and 30 min. Once the sampling was completed, the open endings of the tubes were again sealed with PP-caps. In the laboratory, the iodine–amylose complex was eluted and extracted from the denuder walls with 4 mL of a TMAH-solution (TetraMethylAmmonium Hydroxide, 5% by weight) at 90°C for 3 hours. Afterwards, the solution was diluted to 1% TMAH, with adding 200 ppb Tellurium as an internal standard and the iodine concentration was finally determined by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS, HP 4500, Agilent, USA).

The Mace Head atmospheric research station is equipped with a twin-CPC (3010 and 3025 TSI CPC) which detects particles with different cut-off diameters (3 nm and 10 nm respectively) thus give information on newly formed particles. Also, a Scanning Mobility Particle Sizer (SMPS) is operated continuously at the station for the measurement of the aerosol size distribution between 8 and 300 nm in diameter. The Mobile lab (Helsinki Polytechnic, Finland),\[11\] was equipped with a nano-SMPS and an Electrical Low Pressure Impactor (ELPI, Dekati). The nano-SMPS was set to measure particle sizes from 3 to 50 nm with a time resolution of 30 s and the ELPI measured particle sizes from 7 nm to 10 $\mu$m with a 1 s resolution averaged to the same 30 s time resolution. It was possible to compare the number of particles smaller than 10 nm measured by the nano-SMPS in the mobile laboratory with the number of particles smaller than 10 nm inferred from the twin CPC at the Mace Head station, when the mobile laboratory was at the Mace Head research station.

**Results**

**New Particles from Seaweeds in the Simulation Chamber**

Two genera of seaweeds widely found in the Mace Head tidal area were tested, (1) Laminaria sp. and (2) Fucus sp. Both Laminaria and Fucus seaweed species produced particles in the simulation chamber with no distinguishable difference. In the first experiment, no flow-through of coastal particle-free air was applied to the chamber (except the 1 LPM needed
for sampling, which was assumed to be negligible relative to the 2 m³ chamber). Under these conditions, up to $5 \times 10^6$ 3–3.4 nm particles cm⁻³ were produced. The newly formed particles grew very rapidly to sizes of 50 nm where concentrations in this size range were of the order of 250 000 particles cm⁻³ after 30 min. Particle formation during this experiment was typical of a series of nucleation pulses where there is a large burst of 3–3.4 nm particles followed by rapid growth and where the formation of new particles stops shortly after the initial pulse (Fig. 1a). After growth of the new particles to larger sizes, another nucleation pulse follows. This pattern can be explained either by an increase in the condensation sink of the formed aerosol to a level which shuts off nucleation or by a rapid consumption of O₂ to shut off the production of the nucleating species, or by a combination of both of these processes. The condensation sink due to pre-existing particles during new particle formation events is calculated using the full distribution of the Aitken, accumulation and coarse modes inferred from the SMPS distribution (10 nm < $D_p$ < 266 nm) complemented by the particles concentration measured with the last 6 stages of the ELPI (266 nm < $D_p$ < 10 μm). Calculation of the condensational sink was performed according to [12]

$$CS = 2\pi \times D \times \beta(i) \times d(i) \times N(i),$$

where D is the diffusion coefficient depending on density and molecular volume of the condensable species OIO, $\beta$ is a coefficient depending on the Knudsen number and a sticking coefficient of 1, the particle diameter is d and N the number of aerosols of diameter d.

After clear evidence of nucleation pulses from local seaweed under atmospheric conditions, a steady-state experiment was setup to evaluate this phenomenon in more detail and as a function of seaweed biomass. The chamber was filled with a given amount of seaweeds, then the lid of the chamber was closed and a flow rate of 800 L min⁻¹ was applied to the chamber outlet, letting in ambient atmospheric air through the particle-filtered inlet. Hence, the mean residence time being 2 min 30 s, temperature and relative humidity inside the chamber are close to ambient conditions ($T = 16.7 \pm 0.4^\circ{C}$ and $RH = 69.3 \pm 1.6$ over the measurement period). A steady state was reached within a few min when new 3 nm particles were continuously produced (the wave pattern was not observed when a constant flushing of 800 L min⁻¹ was applied). After the steady state was reached, sampling of the particles and gas phase molecular iodine concentration were performed for about 15 min. The same procedure was repeated for several different amounts of seaweeds. Size distributions of particles as a function of time are shown Fig. 1b. For 16 kg of seaweeds, the total and 3–3.4 nm particle concentrations were $1 \times 10^7$ and $1.2 \times 10^6$ particles cm⁻³ respectively. Nanoparticles were continuously produced whatever the amount of seaweed, irrespective of the condensation sink present within the chamber. In fact, for the highest chamber content of seaweed, the condensation sink was as high as 0.7 s⁻¹ and new particles were still produced in significant quantities.

For each amount of seaweed biomass there corresponds a steady state number of particles produced and steady state gaseous I₂ concentration resulting. We found that total particle concentrations and 3–3.4 nm particles concentrations produced in the chamber are positively correlated with the gaseous I₂ concentrations emitted by the seaweeds (Fig. 2a). The rate of new 3–3.4 particle production is of 2800 cm⁻³ ppt⁻¹. In fact, we also found that I₂ and particle concentrations are both directly positively correlated to the seaweed mass until saturation is reached at approximately 15 kg (or 7.5 kg m⁻²) of seaweed (Fig. 2b). For densities of seaweeds lower than 7.5 kg m⁻², the relation between seaweed and 3–3.4 nm particle is linear, with a concentration of 64 300 particles cm⁻³ resulting from each kg of seaweed present in the chamber. Similarly, concentrations of 24 ppt of I₂ per kg of seaweed biomass was observed. After 7.5 kg m⁻² of seaweed, a limiting factor is preventing either I₂ or the nucleating species from being produced in the chamber. Possibly either the ozone-induced release of volatile precursor compounds from the seaweed (e.g. I₂) or the formation of

![Image](image-url)
condensable iodine vapours by subsequent gas phase reactions of iodine species with ozone is already limited by the ozone concentration at the higher seaweed masses. Also, it is possible that after a certain level of seaweed the flushing air is not penetrating into the seaweed mass with the same efficiency (the flow is going over the surface of seaweed but not through it). From these results, we suggest that ozone induce the emission of I$_2$ from seaweed (e.g. either directly by the oxidation of iodide at the plant–air interface or indirectly involving H$_2$O$_2$ chemistry) as a first step, than I$_2$ is photolysed, forming I followed by the reaction of I with ozone to iodine oxides that condense.

On average, we picked up between 1 and 5 kg of seaweed per m$^2$ in the field, hence, the most representative of real atmospheric conditions in the chamber are for a seaweed content of 5 kg (the chamber has a 2 m$^2$ floor area). The growth rate of new particles can be calculated from the chamber experiment for this most representative seaweed density (2.5 kg m$^{-2}$) typical of the area. The size distribution of particles measured in the chamber show an exponential decrease with increasing $D_p$ (Fig. 3a), illustrating the fact that the bigger the particle, the more time it spent in the chamber, and the more chances it had to be flushed hence the less concentrated it is. The exponential distribution is in fact in agreement with the theoretical residence time distribution of a continuously stirred tank reactor (CSTR). For such a reactor the residence time distribution of particles of a given concentration $C_{t=0}$, given the 2 m$^3$ volume and 800 L min$^{-1}$ flow rate would be as shown Fig. 3b. By fitting Fig. 3a, and Fig. 3b, we obtain Fig. 3c, i.e. the residence time corresponding to each particle size bin. Larger particles have spent more time in the chamber, the relationship between
their size and residence time is their growth rate. The growth rate is observed to be constant with size and is calculated to be of $1.2 \text{ nm min}^{-1}$.

This implies that 3 nm particles have only spent 20 s in the chamber before they reach the next size bin (they are sampled during the size bin width of 0.4 nm). Concentrations of 3–3.4 nm particles are 500 000 cm$^{-3}$ for 5 kg (2.5 kg m$^{-2}$) of seaweeds, which corresponds to a flux of new particle formation of $2.5 \times 10^{10}$ m$^{-2}$ s$^{-1}$.

Consequently, for the range of 1–5 kg m$^{-2}$ seaweed density, we expect the production areas to release between $1 \times 10^{10}$ and $5 \times 10^{10}$ particles m$^{-2}$ s$^{-1}$. It is important to note that these experiments have been performed under closely realistic atmospheric conditions of typical light levels and ambient O$_3$ (34 ppb) concentrations. The main deviation from true atmospheric conditions was the 50% reduction in light intensity (which does not seem to significantly influence the system) and the removal of background aerosol. These close-to-real atmospheric conditions were required in order to quantify realistic I$_2$ and new particle production from seaweeds.

If the particle production events observed regularly over these coastal areas are driven by seaweeds activity during low tide, we should be able to apply the chamber-derived source rates and growth rates to all regions around the coast. In the following sections, we evaluate whether this is feasible to an acceptable degree of accuracy through comparison with growth rates of newly formed particles measured at the nearby strong source region Mweenish.

**New Particle Growth Rate from Mweenish**

The Mace Head atmospheric station is located about 100 m from the tidal zone and surrounded by rocky areas where seaweeds are relatively less abundant compared with spots nearby (Fig. 4). As a result, it is believed that areas of higher seaweed density nearby, such as the Mweenish area, have greater potential in terms of particle formation. Mweenish is located to the south east of Mace Head and is characterised by multiple source regions in all wind sectors except for the northerly sector. In particular, prevailing westerly winds advect air over multiple tidal emission regions. This is illustrated on Fig. 4 by the wind sectors calculated over the minimum tide height 2-hour period for three case study days (27, 28 and 29 September). The Helsinki Polytechnic mobile lab was mobilised to sample particle size distributions from Mweenish.
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Nucleation bursts were detected at Mweenish and are presented for three consecutive days (Fig. 5). 30 min averages of the particle size distribution over 2 hours around low tide (Fig. 6) show that, with constant wind direction and speed, the particle mode is stable at diameters between 5 and 6 nm. Particles from 3 to 10 nm detected at the sampling site have been produced at various distances covering the source region. During a particle formation event, particle number concentrations of all sizes increase with the surface of seaweed exposed to the atmosphere, and reach a maximum at low tide (Fig. 6). With the exception of 27 September, we observe a ‘characteristic’ size distribution representative of the tidal area and wind direction, with only the intensity of this size distribution evolving with tidal height. On 27 September, an increase in the mean size is observed from 1130 hours to 1200 hours, which would correspond to a slight change of wind direction from NW to N, hence bringing to Mweenish larger particles from further away. No growth of the newly formed particles is observed when the wind speed and direction is stable and is characteristic of being a fixed distance from a point, or multiple point sources.

At maximum particle concentrations, we can suppose that the largest seaweed area is exposed, which is confirmed by a synchronization with the minimum tidal height. During the low tide period, the largest particles measured at the sampling site...
site are originating from the farthest spot of air-exposed seaweed. From the time needed to advect over this distance, and noting the largest particle size observed, we can infer a growth rate. Because on 27 and 29 September, more distant sources can contribute to the size distribution observed, we chose to focus 28 September as a case study: the wind direction is purely west and no other source than the immediate coastline could contribute to the new ultra-fine particles observed. On 28 September, the largest diameter for which particle concentrations were significantly increased during nucleation compared to background level is 14.2 nm (Fig. 6). The 25th percentile and 75th percentile of the wind speed are calculated to be 6.2–7.2 m s$^{-1}$, respectively, for the period corresponding to the maximum seaweed exposure around low tide. From Fig. 4, 14.2 nm particles have traveled between 5 and 6 km before reaching the sampling site, which took between 12 and 16 min. Hence, the growth rate is estimated to be between 0.8 and 1.2 nm min$^{-1}$, which corresponds to the lower side of what has been measured in the chamber for a 2.5 kg m$^{-2}$ of seaweeds density (1.2 nm min$^{-1}$). However, the path length of the particles up wind of the sampling site is not evenly and fully represented by seaweed fields of 1 to 5 kg m$^{-2}$ density (Fig. 4). If we estimate that in this area, about half of the path way is covered by seaweed fields, this growth rate would correspond to a mean 1.25 kg m$^{-2}$, to compare with the 2.5 kg m$^{-2}$ in the chamber. Hence, the growth rate of particles produced in the chamber is consistent (within a factor two underestimated) with the growth rate of particles that would have been produced by the seaweed fields around Mweenish and transported there.

**New Particle Emissions from the Coastal Area around Mweenish**

In this section we test if the new particle formation rate measured in the chamber is also realistic in comparison with the ambient observations at Mweenish. A mesoscale transport model (RAMS) was used to simulate particle concentration that would be found in Mweenish, based on the new particle fluxes measured in the chamber and the seaweed field around the area.

The RAMS (http://www.atmet.com/, verified November 2005)$^{131}$ model is a parallel mesoscale model allowing the simulation of meteorological fields with horizontal scale spanning from one km to a thousand km. It includes nested grids. Many investigations on regional pollution with an online coupling of emission codes which can be associated to chemical mechanism, were previously made using RAMS model.$^{114–117}$ For this study, simulations have been performed using three nested grids simultaneously to take the synoptic and local circulation into account. Grid1 covers the region with a horizontal resolution of 25 km. Grid2, the intermediate domain, has a resolution of 5 km, and Grid3 consists of the experimental domain with a resolution of 1 km (17 meshes). We used a time step of 10 s and 35 levels in the vertical dimension (the same in the three grids) with 15 levels from surface to 1500 m, which ensures a fine description of the boundary layer. However, the boundary layer contains an initial surface mixing layer of 100 to 300 m, into which the emissions are initially confined.$^{118}$ The meteorological fields have been initialized and nudged every 6 hours by ECMWF (European Center for Medium-Range Weather Forecasts) database. The simulation starts on 27 September 2003 at 00:00 UTC and ends 28 September 2003 at 13:00 UTC. The observed and simulated values of the speed and the direction of wind, the temperature and the humidity are in good agreement. An aerosol inventory (source map) is introduced as an input in RAMS (Fig. 7) and the emission at each time step is activated. This source map was built by calculating the source rate of each km$^2$ from (1) the flux of particles from (1) the flux of particles and (2) the percentage of seaweed density, and the spatial repartition of the intertidal zones on the western side of the measurement area (from Fig. 4), used as source input in Regional Atmospheric Modelling System for the 28 September simulation. Mace Head is at coordinates 0.0.

![Fig. 7. Local emission inventory, in number of 3–3.4 nm particles m$^{-2}$ s$^{-1}$, calculated from the new particle flux measured in the chamber for a 5 kg m$^{-2}$ seaweeds density, and the spatial repartition of the intertidal zones on the western side of the measurement area (from Fig. 4), used as source input in Regional Atmospheric Modelling System for the 28 September simulation. Mace Head is at coordinates 0.0.](image-url)
The vertical extension of the new particle plume can also be simulated with RAMS. Figs 9a and 9b illustrate the vertical dispersion of the total particle concentrations for the two transects shown on Fig. 8. The vertical extension of the new particle plume is enhanced when the coastline rises above the sea level (section B), but, in general, the plume rapidly reaches 300 m (in less than 4 km) and 600 m after 10 km. These simulations are in agreement with the LIDAR observations performed during PARFORCE (PARticle FORMation and fate in the Coastal Environment, 1998–1999, Mace Head).[18]

From the growth rate and traveling speed, each size bin of particle can be spatially associated to a source distance. Hence the size of the particles at Mweenish can be simulated by keeping in memory the distance at which they have been produced. This can be done by entering in the source map a different tracer for each grid sector, and calculating their growth during transport using the growth rates of 0.5 nm min⁻¹ (if about half the distance is on average covered by seaweed fields). The zero-distance particles (within the grid sector where Mweenish is situated) are considered to be 3–4.4 nm sized particles. Modeled and measured size distributions are shown Fig. 10 where quite close agreement is seen using the chamber fluxes and growth rates applied to the observed seaweed biomass concentration in the area, if higher seaweed densities are used for the simulations (5 kg m⁻² and 7.5 kg m⁻² instead of the usual 2.5 kg m⁻²). A better agreement is achieved when the intertidal area density is higher (7.5 kg m⁻²). The seaweed fields density being typically lower than 7.5 kg m⁻², this confirms that the fluxes of 3–3.4 nm particles derived from our chamber experiment might be slightly underestimated. However, the shape of the new particle size distribution could be relatively well simulated based on the hypothesis that all particles were produced by the seaweed field.

To summarize, growth rates, new particle formation rates and new particle size distributions measured in situ at Mweenish, although slightly higher, are consistent with (1) the growth rate and new particle formation rate simulated in the chamber with seaweeds, and (2) the spatial repartition of the seaweed fields relative to the sampling site. In an attempt to evaluate the role of these high-density seaweed fields in the coastal particle productions, we used a mobile van that allowed us to detect new particle production on a larger spatial scale.

**Spatial Extension of New Ultra-Fine Particle Production in the Coastal Area**

The hypothesis of new particle formation from high productivity spots around Mace Head was mentioned during QUEST (Quantification of Aerosol Nucleation in the European Boundary Layer) airborne measurements [20] in April 2002. Airborne particle concentration measurements using condensation particle counters show that nano-particles were...
formed over Mweenish and Roundstone area (North of Mace Head), Co Galway, whereas the Mace Head station simultaneously showed no particle formation. Fig. 11 is showing the respective I2 concentrations at two different locations around Mace Head, which have different seaweed surroundings (with north-easterly winds, the bridge location is downwind of a larger seaweed field than MRI-Mweenish). These results, also compared with the chamber I2 concentrations, indicate that I2 concentrations are a function of the seaweed field density. Considering the I2-to-new particle concentrations pointed out in this work, they would confirm the QUEST observations that Mace Head is experiencing less intense new particle formation events than its surroundings during the prevailing westerly winds. Simultaneous measurements of ultra-fine particles in Mace Head and Mweenish have been performed during BIOFLUX, which can help us address this matter. Previously, a classification of the new particle formation events at Mace Head according to 4 wind sectors was performed.\(^{[21]}\) Type I events are locally produced particles observed during clean marine wind sector; type II events show particles produced locally and from more distant sources transported by northerly winds; during type III events, distant sources produce new particles in more polluted air masses coming from the south and south-eastern sector, and finally no event is observed for type IV, when the wind sector is north-east. Comparison of the particle formation intensity observed in Mace Head with its intensity in Mweenish was performed over a number of days during the BIOFLUX campaign (on 14, 25, 26, 27 and 30 September and 1 October 2003). Table 1 shows for the different wind sectors the comparison of particle <10 nm number concentration for both sites under different environmental conditions (low tide occurrence, wind speed and direction and condensational sink).

Particle formation is more intense in Mweenish compared to Mace Head when the wind sector is of type I (western marine air masses), which is consistent with the lack of high-density seaweed areas west of Mace Head. Particle formation is more intense in Mace Head compared to Mweenish when the wind sector is of types III and IV (south–south-east): there is an immediate production zone

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**Fig. 10.** Particle size distribution calculated from the Regional Atmospheric Modelling System simulation of each size bin of particles corresponding to a distance from Mweenish to the source map shown in Fig. 7, and a growth rate of 0.5 nm min\(^{-1}\), and comparison with the measured size distributions at Mweenish around 12 UTC.

**Fig. 11.** Comparison of I2 mixing ratios for two different locations around Mace Head and in the seaweed chamber for two types of seaweed (Laminaria and Fucus).
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</table>

*At Mweenish but also 20 km down wind (Gilsink).*

south-east of Mace Head. Intense new particle formation (up to 1 million particles cm<sup>-3</sup>) occurs in Mace Head, even though the air masses originating from sectors III and IV are usually polluted (condensation sink ranging from 0.002 to 0.006 s<sup>-1</sup>). When the wind sector is north (type II), it happened that both Mace Head and Mweenish experienced strong particle formation events (on 26 and 27 September). These observations show that particle formation events are consistent with the location of seaweeds fields influenced by wind direction during sampling. They corroborate airborne measurements showing that particle production was more intense in Mweenish than in Mace Head during clean marine western winds,[2] which are the most frequent wind directions observed in the area. New particle formation can be detected irrespective of wind direction and environmental condition (polluted on 25 September and 1 October, and cloudy/rainy on 14 September), provided that sampling is performed downwind of a seaweed field during low tide.

Also shown on Table 1 are the ambient concentrations of I<sub>2</sub> measured over 15 to 30 min at Mweenish, sampled in the same place as the corresponding 3–4 nm concentrations. Concentrations of I<sub>2</sub> varied from 20 to 100 ppt during low tide, in agreement with the concentrations measured in the simulation chamber from the seaweeds representative density of 2.5 kg m<sup>-2</sup> (75 ppt). Denuders were placed less than 2 m from the seaweed field where the dispersion and dilution of I<sub>2</sub> would be low and comparable with that seen in the chamber measurements. The relationship between I<sub>2</sub> and ultra-fine particle concentrations is not so clear. For the cases presented, the highest concentration of I<sub>2</sub> (100 ppt) corresponds the lowest ultra-fine particle concentration (400 cm<sup>-3</sup>), and the highest particle concentrations (213 000 cm<sup>-3</sup>) were sampled, whereas I<sub>2</sub> was at an average level (34 ppt) for a nucleation event. In fact, it is not a surprise not to be able to relate the local I<sub>2</sub> concentration with the total concentration of particles smaller than 10 nm, since we have shown earlier that the whole history of seaweed field repartition on the wind trajectory should be taken into account. This suggests that the dynamics of air masses, wind direction and seaweed repartition are major parameters necessary to predict a new particles concentration at a given location.

### Summary and Conclusions

The goals of this paper were to investigate the relationship between I<sub>2</sub> and new particle formation and to provide the first quantitative estimate of the flux of coastal new particles as a function of exposed seaweed biomass.

In a 2 m<sup>3</sup> simulation chamber filled with various amounts of seaweeds, we showed that under near-real atmospheric conditions (natural UV light, ambient O<sub>3</sub> level and particle-free flushing un-scrubbed air), new particle formation was occurring at high rates (up to 1 million particles cm<sup>-3</sup>), in proportion to high I<sub>2</sub> concentrations (up to 400 ppt) with a ratio of 2800 particles cm<sup>-3</sup> ppt<sup>-1</sup>. I<sub>2</sub> is produced proportionally to the amount of seaweeds, up to a maximum seaweeds level of 7.5 kg m<sup>-2</sup>. Above this level of seaweeds, I<sub>2</sub> and subsequent new particles formed start to be produced with a lower efficiency, presumably due to a lack of O<sub>3</sub> reaching the seaweed surface or available for oxidation. At an *in situ* representative seaweed content, new particles were formed at a rate of 2.5 × 10<sup>19</sup> m<sup>-2</sup> s<sup>-1</sup>, whereas the CS was about 0.015 s<sup>-1</sup>. In fact, for seaweeds densities in the range of what is usually found in the area, new particle concentrations were found to be linearly proportional to the amount of seaweeds, which provides a relatively simple parameterization of the new particle formation in the coastal area of western Ireland.

This parameterization could be tested against *in situ* measurements using a mobile laboratory around Mace Head. The seaweeds mass-to-new particle flux relationship measured in the chamber was applied to the intertidal zone map of the area, fed as a source map in a mesoscale model (RAMS), and compared with real atmospheric particle size distributions. Simulations were in agreement with the measurements, in terms of total particle concentrations, within a factor 5. In the non-spatially-homogeneous environment of coastal areas, growth rates could not be calculated on the real atmospheric measurements with the usual method of tracking the temporal
evolution of the nucleation mode from 3 to 25 nm. Instead, ambient growth rates were calculated from the largest new particle detected and the farthest new particle intertidal zone, under stable wind speed and direction conditions. This average growth rate of 0.8–1.2 nm min\(^{-1}\) about twice higher than the growth rate measured in the simulation chamber if the seaweed field was composed of 2.5 kg seaweed m\(^{-2}\) over about half of the total area (0.5 nm min\(^{-1}\)). When a 0.5 nm min\(^{-1}\) growth rate is introduced in the meso-scale simulation of particle growth over the coastal area, we obtain simulated size distributions in fairly good agreement with the observed size distributions.

New particle formation depends on the balance between the source rates and sinks of condensable precursor gases. However, in these chamber experiments, we found a direct link between the amount of seaweeds and new particle production that would integrate both parameters into a simple relationship. This relationship has been found to be realistic regarding the amount and size of new particles formed at Mace Head and its surroundings. In fact, in this area, because new particle formation occurs with high intensities also in polluted air masses (types III and IV), we suggest that the condensable iodo-compound sources are so important that they are the one parameter determining the intensity of new particle formation.

Acknowledgements

This work was supported by Irish Research Council for Science and Engineering Technology (IRCSET) and European Commission under the QUEST contract. For the RAMS modeling, computer resources were provided by CINES (Centre Informatique National de l’Enseignement Supérieur) project amp2107. The authors also wish to thank the computer team of the laboratoire de Météorologie Physique de l’Université Blaise Pascal (France); A.M. Lanquette, S. Banson and Ph. Cacault.

References