Coastal Iodine Emissions: Part 2. Chamber Experiments into Particle Formation from Laminaria digitata-Derived and Laboratory-Generated I2
Coastal Iodine Emissions: Part 2. Chamber Experiments into Particle Formation from *Laminaria digitata*-Derived and Laboratory-Generated I$_2$

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Laboratory studies into particle formation from *L. digitata* macroalgae were undertaken to elucidate aerosol formation for a range of I$_2$ (0.3-76 ppb$_v$) and O$_3$ (<3-96 ppb$_v$) mixing ratios and light-levels ($E_{PAR} = 15$-235 µmol photons m$^{-2}$ s$^{-1}$). No clear pattern was observed for I$_2$ or aerosol parameters as a function of light-levels; however, aerosol mass fluxes (assuming I$_2$O$_4$ gas-to-particle conversion) and particle number concentrations were correlated ($R^2$=0.7 and 0.95, respectively) with I$_2$ mixing ratios for low O$_3$ mixing ratios (<3 ppb$_v$). Additional experiments into particle production as a function of laboratory-generated I$_2$, over a mixing ratio range of 1-8 ppb$_v$, were conducted under moderate O$_3$ mixing ratios (~24 ppb$_v$) where a clear, 100-fold or greater, increase in the aerosol number concentrations and mass fluxes was observed compared to the low-O$_3$ experiments. A linear relationship between particle concentration and I$_2$ was found, in reasonable agreement with previous studies. Scaling the laboratory relationship to aerosol concentrations typical of the coastal boundary layer suggests a I$_2$ mixing ratio range of 6-93 ppt$_v$ can account for the observed particle production events. Aerosol number concentration produced from I$_2$ is more than a factor of 10 higher than that produced from CH$_2$I$_2$ for the same mixing ratios.
Introduction

The release of volatile iodine organic compounds and of molecular iodine (I$_2$) into the marine boundary layer (MBL) has been linked to the rapid production of large numbers of new, ultrafine, aerosol particles$^{1-4}$. The nucleation and growth events have been observed to occur most frequently in coastal areas under conditions of solar irradiation and low tide. Initial studies on the dominant aerosol precursor focused on the release of CH$_2$I$_2$ by shore biota$^2$, 5, 6; however, it was later shown that the dominant iodine source is more likely to be I$_2$$^{7,8}$. In fact, McFiggans. (2004)$^7$ found that the iodine flux from I$_2$ was three orders of magnitude higher than that from CH$_2$I$_2$, due to a higher photolysis rate for I$_2$. Photo-chemically produced iodine atoms react rapidly with ozone to produce iodine monoxide radicals (IO) which subsequently self-react to form iodine dioxide radicals (OIO) and I$_2$O$_4$. A fraction of the newly formed I$_2$O$_4$ may then form new particles while reaction with IO may form I$_2$O$_3$ which again may react with O$_3$ to form I$_2$O$_5$$^{7,9-11}$. Modelling studies have also suggested that OIO or I$_x$O$_y$ molecules may co-nucleate or co-condense with other molecules such as H$_2$SO$_4$ and/or low-volatility organic compounds$^{12,13}$. Most previous laboratory studies have focused on the common kelp Laminaria (L.) digitata which is prone to high I$_2$ emission rates when exposed to oxidative stresses$^{14,15,16,17,18,19}$. Field-chamber experiments (using scrubbed marine air) have shown a linear correlation between new particle formation and I$_2$ mixing ratios from Laminaria and Fucus species$^{20}$ in the vicinity of Mace Head, located on the Irish – Atlantic coastline$^{21}$. This work extends previous studies$^{22,23,24}$ into particle production from I$_2$ emissions from a number of different seaweed species in that it specifically focuses on aerosol formation for a wide range of I$_2$ mixing ratios from a strong I$_2$ emitter, L. digitata, under a wider range of conditions (i.e. various light levels and ozone mixing
ratios), followed by the quantification of aerosol production from laboratory-generated I_2, for moderate ozone mixing ratios.

This report comprises Part 2 of a two-part study – Part 1 focuses on I_2 emission rates from *L. digitata* under various environmental conditions and is reported in *Ashu-Ayem et al.*, (2012).

**Experimental Section**

Experiments were carried out in an atmosphere simulation chamber comprising a cylindrical FEP bag housed inside a 2 m long enclosure. The chamber volume was 2.2 m^3 and its surface area was approximately 10 m^2. A photolysis light source, comprising an externally-mounted 2 kW xenon lamp (Rige Lighting), produced a circular collimated beam above the chamber. The lamp spectrum (400 to 850 nm, \( \lambda_{\text{max}} = 550 \text{ nm} \)) provided simulated Photosynthetically Active Radiation (PAR) spectrum leading to an I_2 chamber photolysis rate of 0.0075±0.0010 s^{-1}. Ozone was added using an Ozone Lab model OL80W/FM ozone generator. An incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) system was the principle tool for analyzing the gas phase composition of the chamber. The IBBCEAS comprised two optical cavities across the length of the chamber: a blue channel (420 to 460 nm) for IO and a green channel (520 to 560 nm) for I_2 and OIO. Reference spectra for IO and OIO were obtained from *Spietz et al.* and *Bloss et al.* respectively, and convoluted to this particular instrument function. O_3 was monitored using a UV absorption monitor (2B Technologies model 202) with a sampling rate of 1 L min^{-1}. 


A nano scanning mobility particle sizer (n-SMPS), comprising a Thermo Systems Inc. (TSI) model 3776 condensation particle counter with a TSI model 3085 differential mobility analyzer, was operated continuously to measure particle sizes from 3nm to 20nm while a TSI model 3034 scanning mobility particle sizer (SMPS) was used in conjunction with the n-SMPS to measure particle size ranges a further 20 nm – 500 nm. The SMPS was only available for the third set of experiments. The n-SMPS and SMPS were operated with a time resolution of 20 s and 120 s respectively.

Repeated measurements in the chamber in the absence of *L. digitata* showed zero or close to zero particles, zero I₂, and levels of O₃ around the detection level of the instrument. Two types of static experiments were conducted on *L. digitata*: (1) iodine emission and subsequent particle formation from five replicas were examined under “low” (15 μmol photons m⁻² s⁻¹), “medium” (100 μmol photons m⁻² s⁻¹) and “high” (235 μmol photons m⁻² s⁻¹) irradiances and under very ozone mixing ratios (< 3 ppbᵥ); and (2) iodine emissions and particle formation under low (15 μmol photons m⁻² s⁻¹) irradiances but with ozone mixing ratios of the order of ~94 ppbᵥ. It should be noted that “high” light conditions here corresponds to 15% of the upper light limit that algae would be exposed to under real-world conditions. A third set of experiments were conducted on a range of mixing ratios of laboratory-generated I₂ under flow-through conditions and ozone mixing ratios ~24 ppbᵥ. For the *L. digitata* experiments, algae were placed in a 33 L tray filled with natural seawater which and were allowed to acclimatise over 10 minutes after which the seawater was gradually drained over the following 10 minutes (i.e. to mimic an outgoing tide). A complete description of experimental methodologies can be found in Ashu-Ayem *et al.*, (2012)
Results & Discussion

Particle Formation Under Different Light Conditions and Low O₃, *L. digitata* samples were exposed to irradiances of $E_{PAR}= 15, 100$ and $235 \mu$mol photons m$^{-2}$ s$^{-1}$, labelled “low”, “medium” and “high” light conditions, respectively under static-chamber flow conditions. Experiments were performed at each light-level using five replicate *L. digitata* specimens to account for potential high variability in I$_2$ emission rates as previously observed$^{23}$ (See Table 1 in Ashu-Ayem et al., (2012), and Supplementary Information for full experimental summary).

Particle formation was observed in all experiments when exposed to light and low-O₃ air. A characteristic strong particle burst, $\sim$10-30 s after the start of the experiment, and peaking at concentrations ranging from $2.6 \times 10^4$ cm$^{-3}$ - $3.9 \times 10^7$ cm$^{-3}$, corresponding to a range I$_2$ mixing ratios from 5.3 – 76.3 ppbv, was observed. Figure 1 illustrates the evolution of the aerosol size distribution, O₃, I$_2$, and IO mixing ratios, the aerosol condensation mass flux (determined by the increase in nSMPS-derived volume, taking an I$_2$O$_4$ density of 2.5 g cm$^{-3}$), and number concentration. For medium light levels, I$_2$ mixing ratios of 1.1 - 20.2 ppbv, led to particle concentrations of $7 \times 10^3$ cm$^{-3}$ - $3.9 \times 10^6$ cm$^{-3}$, while for high light levels, particle concentration ranged from $2.1 \times 10^6$ cm$^{-3}$ - $3.8 \times 10^7$ cm$^{-3}$ for I$_2$ mixing ratios of 4.1-36.8 ppbv. The condensable mass flux for the low, medium and high light-level experiments ranged from $2.4 \times 10^{-10}$ µg cm$^{-3}$ s$^{-1}$ - $1.7 \times 10^{-7}$ µg cm$^{-3}$ s$^{-1}$, $2.3 \times 10^{-10}$ µg cm$^{-3}$ s$^{-1}$ - $1.7 \times 10^{-8}$ µg cm$^{-3}$ s$^{-1}$ and $2.5 \times 10^{-9}$ µg cm$^{-3}$ s$^{-1}$ - $5.3 \times 10^{-7}$ µg cm$^{-3}$ s$^{-1}$, respectively. Full details are tabulated in Table S1 in Supplementary Material.
The experiments in this study did not reveal and clear pattern between biomass, light-levels and either I₂ mixing ratios (as discussed in Part 1 of the study) or particle concentration. However, for the low and medium light-level experiments, a high correlation coefficient, fitted in log—log space, was found between mass flux and I₂ mixing ratio ($R^2=0.7$ and 0.95, respectively). Similarly high correlations were found for number concentration and I₂ mixing ratio ($R^2=0.83$ for low light-levels and 0.98 for medium light-levels). For the highest light-level, $R^2$ for mass flux as a function of I₂ mixing ratio was -0.02, in stark contrast to the low and medium light levels. From the 5 high light-level replicates, two concurrent samples (#12 and #13) stand out in that they are associated with relatively high biomass, quite low I₂ mixing ratios, and the highest mass flux. Variability in I₂ emissions could explain the low I₂ mixing ratios resulting from moderate to high amounts of biomass; however, the aerosol condensation flux yield for the corresponding I₂ mixing ratios is 1-2 orders of magnitude higher in these samples compared to all others (specifically, the ratio of mass flux over I₂ mixing ratio for these two samples ranges from $2.8 \times 10^{-8}$ $\mu$g cm$^{-3}$ s$^{-1}$ ppb$^{-1}$, while the ratio for the other samples ranges from $4 \times 10^{-11}$ to $5 \times 10^{-9}$ $\mu$g cm$^{-3}$ s$^{-1}$ ppb$^{-1}$). Such ratios are equivalent to those observed in the later O₃ – rich experiments.

It should be noted that the air in the chamber prior to each replicate had an O₃ mixing ratio that was at or below detection limit of 3 ppb; however, particle formation still proceeded. Therefore, O₃ was present in sufficient concentrations to produce significant quantities of aerosol, although still at or below detection limits. It is thought that either O₃ was produced by trace amounts of VOCs and NOx entering the chamber from laboratory air or direct entrainment of O₃ from laboratory air. We
suggest that samples #12 and #13 were potentially influenced by slightly elevated O$_3$ mixing ratios resulting in significant increases in aerosol yield, thus also explaining the low I$_2$ mixing ratios for relatively high biomass abundance. In fact, peak O$_3$ values recorded above the detection limit were 3-4 times higher for these two particular cases compared to the other samples (even spiking at 18 ppb$_v$). In light of the suspicion relating to comparability of the replicate #12 and #13 experiments in terms of O$_3$ upper mixing ratios, we have removed these cases from further analysis. The remaining three data lead to a $R^2$=0.98 for a log-log fit, indicating minimal scatter across these remaining samples. The remaining low, medium and high light-level datasets were grouped together, excluding sample #12 and #13, for an overall analysis and the inter-relationships between mass flux and concentration, as a function of mixing ratio, are shown in Figure 2. The mass flux versus I$_2$ mixing ratio exhibited a correlation of $R^2$=0.72, while the number concentration exhibited a correlation of $R^2$=88 with mixing ratio. Further investigations are required to address the variability in I$_2$ emission rates from *L. digitata*, as discussed in more detail in Part 1, *Ashu-Ayem et al.*, (2012).

**Particle Formation Under Low Light Conditions and High O$_3$.** An experiment composed of five replicates (replicates #21 - #25 - See Table 2 in Part 1) was also carried out. All algal specimens were of similar age and weight as those in the low light - low O$_3$ experiment (see Table S.1) Experimental conditions were kept the same as those of replicates #16 - #20 (i.e. low light) except for O$_3$ mixing ratios of 92-96 ppb$_v$. As in the previous experiments under low O$_3$, mixing ratios, the resulting I$_2$ mixing ratio varied enormously from sample to sample with no correlation between biomass being observed. This, in turn, led to variability in the characteristics of the
resultant aerosol number concentration and mass flux. For the general collection of replicates, a higher rate of aerosol mass flux was observed under high O$_3$ conditions, perhaps resulting from a combined O$_3$ influence on both increased I$_2$ emissions resulting from potential oxidative stress of the algae along with increased particle production through oxidation processes; however, it is not possible to distinguish between the two processes since oxidative stress was not quantified in this experimental set up.

A typical particle size distribution evolution associated with this experiment is shown in Figure 3 where the experiment was observed to yield concentrations of particles of $3.5 \times 10^7$ cm$^{-3}$ associated with I$_2$ mixing ratios of 17 ppb$_v$. In each of the replicates, an initial peak was observed followed by a second and stronger peak shortly after a steep rise in I$_2$ and IO mixing ratios. This can be seen in Figure 3, where the initial, and less intense peak was observed at ~11:40 am and the subsequent, stronger, peak was seen at ~12:10 pm. The maximum particle number concentration occurs at $4.2 \times 10^7$ cm$^{-3}$; however, the true concentration is expected to be higher as the growth rate of newly formed particles is so rapid that the mode diameter rapidly grows past the upper diameter detection limit of the nSMPS.

The overall particle number concentration increased from between $1 \times 10^4$ cm$^{-3}$ and $1 \times 10^7$ cm$^{-3}$ during the low ozone mixing ratio experiment to greater than $1 \times 10^7$ cm$^{-3}$ during the high O$_3$ mixing ratio experiment, although due to the rapid modal growth out of the measurement size range, no quantitative relationship can be derived. The mass flux ranged from $8.2 \times 10^{-8}$ μg cm$^{-3}$ s$^{-1}$ to $1.2 \times 10^{-6}$ μg cm$^{-3}$ s$^{-1}$, compared to $2.3 \times 10^{-10}$ μg cm$^{-3}$ s$^{-1}$ to $1.7 \times 10^{-7}$ μg cm$^{-3}$ s$^{-1}$ for a the low O$_3$, low light experiment.
This indicates at least 2 orders of magnitude more aerosol mass production in the presence of abundant ozone mixing ratios.

The effects of exposure of *L. digitata* to O$_3$ and the subsequent enhancement in the particle number concentration by several orders of magnitude have been reported in previous studies 9, 15, 17; however, what remains unclear in these experiments is if exposure to O$_3$ leads to an increased I$_2$ net production rates (*P* > 0.05; see Table 1 and 2 in Part 1) in experiments with higher O$_3$ mixing despite the specimens being in similar light conditions (15 µmol photons m$^{-2}$ s$^{-1}$), although there is a trend of higher net production rates if normalised to biomass weight. For this set of experiments, there was no conclusive statistical link between particle number concentration and I$_2$ mixing ratios; however, particle concentrations were generally higher for the high ozone mixing ratios. The lack of a statistical link, as suggested above, may be due to the rapid growth of the nucleation mode out of the nSMPS detection range.

IO trends tracked generally that of I$_2$, however, mixing ratios were typically two orders of magnitude lower. OIO, a by-product of the IO-IO self-reaction, is not detected despite having being considered the main precursor of iodine oxide aerosol particles. The interactions between I$_2$, IO and OIO are discussed in Part 1 of the study where the lack of detectable OIO (detection limit 30 ppt$_v$) is attributed to fast reactions between OIO and I atoms under the mixing ratio conditions in the chamber.

**Particle Production as a Function of I$_2$ Mixing Ratio.** In order to further study the role of I$_2$ in particle formation, a set of experiments were conducted under laboratory generated and controlled I$_2$ mixing ratios and a moderate O$_3$ mixing ratio of 24 ppb$_v$, 
regarded as representative of tropospheric conditions. The experiments were carried out with a “flow through” configuration of 225 L min$^{-1}$ applied to the chamber where light intensity was fixed at 100 μmol photons m$^{-2}$ s$^{-1}$ and I$_2$ mixing ratios varied from 1 ppbv to 8 ppbv (see Table 1). The flow-through experiment did not comprise continuous supply of O$_3$ and I$_2$, more so, O$_3$ concentrations were set to 24 ppbv in the chamber and then a pulse of I$_2$ was introduced. Controlled I$_2$ mixing ratios were generated by evaporating I$_2$-methanol solutions of known concentrations to dryness, followed by heating the I$_2$ residue in a stream of nitrogen into the chamber.

In each experiment, on mixing I$_2$ and O$_3$ in the photolysis chamber, both mixing ratios were rapidly reduced due to combined photolysis, oxidation and subsequent formation and growth of the aerosol. For each replicate the total particle number concentration increased rapidly initially, reaching its peak after about 10 minutes from the inception of photolysis and then rapidly decayed. Figure 4 illustrates the general evolution of the aerosol number concentrations in relation to the gas species mixing ratios over time. For the example shown in Figure 4, the initial ozone mixing ratio was 24 ppbv, and after the introduction of I$_2$ into the chamber, I$_2$ peaked at 6.6 ppbv while simultaneously IO peaked at 0.1 ppbv. Tens of seconds later, particle production was observed and after about five minutes, a peak concentration of $9 \times 10^7$ cm$^{-3}$ was observed. By the time the peak aerosol concentration was observed, both I$_2$ and IO mixing ratios had reduced by a factor of 2. I$_2$ decayed more rapidly than IO. For the other experiments, I$_2$ ranged from 1.0 ppbv to 8.1 ppbv and the total aerosol concentration ranged from $2.5 \times 10^6$ cm$^{-3}$ to $1.1 \times 10^8$ cm$^{-3}$, respectively, while 3 nm particle concentration ranged from $8.9 \times 10^4$ cm$^{-3}$ to $3.7 \times 10^6$ cm$^{-3}$, respectively.

Comparison of the condensing mass flux and number concentration, over the range of I$_2$ mixing ratios overlapping (i.e. 1-8 ppbv) in the low ozone experiment and the
moderate ozone experiment, illustrates generally 2-3 orders of magnitude greater mass flux in the moderate ozone experiment (see Figure 5).

The total particle number concentration, as well as the 3 nm particle concentration increased linearly as the initial I\textsubscript{2} mixing ratio was increased. The linear fit (in linear space) between I\textsubscript{2} and total particle concentration is shown in Figure 4 and was found to be \( N_{\text{tot}} \text{ (cm}^{-3}\text{)} = 1.34 \times 10^{7} \text{ I}_{2} \text{ (ppb\textsubscript{v})} \) while the linear fit between 3 nm particle concentration and I\textsubscript{2} was found to be \( N_{3\text{nm}} \text{ (cm}^{-3}\text{)} = 4.69 \times 10^{5} \text{ I}_{2} \text{ (ppb\textsubscript{v})} \). The total particle concentration as a function of IO was also seen to increase linearly with increasing IO.

The correlations between I\textsubscript{2} and particle concentrations, shown in Figure 6, were \( R^2 = 0.7 \) for both the total and 3 nm particle concentrations, with more scatter having been observed for lower values of I\textsubscript{2}. During the course of the present study, other species such as HOI may have been preferentially formed at different mixing ratios but not detectable by IBBCEAS methods and may contribute a “missing” component in the cycle. The relationship between particle concentration and I\textsubscript{2} in this study is compared to that from Sellegri \textit{et al.}, (2005), extending up to 400 ppt\textsubscript{v}, along with the relationship between particle concentration and CH\textsubscript{3}I\textsubscript{2} mixing ratios reported by Burkholder \textit{et al.}, (2004) and Jimenez \textit{et al.}, (2003). While the I\textsubscript{2} mixing ratios in this study are higher than Sellegri \textit{et al.} comparison of both relationships indicates a greater particle concentration generated by Sellegri \textit{et al.} at low I\textsubscript{2} mixing ratios, but relatively similar concentrations at high I\textsubscript{2} mixing ratios. Both this study and that of Sellegri \textit{et al.} illustrate at least an order of magnitude higher aerosol yield from I\textsubscript{2} compared to that from CH\textsubscript{3}I\textsubscript{2}, consistent with differences in photolysis lifetimes.
Comparison to Ambient Measurements. Results arising from the flow-through chamber studies reported here can be directly compared to field measurements of coastal, iodine-driven, new particle production events \(^2,^3\). While the concentrations in the laboratory are significantly higher than observed in the field, they can be extrapolated down to lower concentrations in order to estimate the \(I_2\) mixing ratios required to produce observed particles in coastal events such as those at Mace Head. Over the period from 1\(^{st}\) May 2010 to the 1\(^{st}\) August 2010, 28 typical clean air coastal production events were analysed and were found to have a total particle concentration range between \(7.8 \times 10^4\) cm\(^{-3}\) - \(1.2 \times 10^6\) cm\(^{-3}\) and a peak 3 nm particle concentration range of \(4.3 \times 10^3\) cm\(^{-3}\) - \(9.4 \times 10^4\) cm\(^{-3}\). Scaling the relationships between particle concentration and \(I_2\) downward to observed concentrations in the field points to a coastal boundary layer \(I_2\) mixing ratio of 6-93 ppt. Values in this range are in line with a previous studies by Saiz-Lopez and Plane (2004) who found that the nucleation events observed at Mace Head (\(N_{n_{nm}} = 5 \times 10^4\) cm\(^{-3}\)) could be produced by the daytime photolysis of 10 ppt, \(I_2\), typical of the daytime mixing ratios observed at low tide during the measurement period.

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References


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**Table 1** Summary of experiments preformed with mixing ratios of I₂ and O₃ in a 2200 Litre chamber with a purge flow of 225 L min⁻¹.
FIGURE 1. (Top) Typical particle size distribution evolution (Sample #19) over time for *L. Digitata* in chamber without flow-through for low light conditions. (Bottom) Particle concentration, mass flux, I$_2$ mixing ratio and O$_3$ mixing ratio.

FIGURE 2. Condensation mass flux and particle concentration as a function of I$_2$ mixing ratio. Low, medium and high light-level data are colour coded.

FIGURE 3. (Top) Particle size distribution evolution for *L.digitata* (Replicate #25) in chamber without flow-through with low light conditions and an initial mixing ratio of 95.8 ppb of O$_3$. (Bottom) Particle concentration, mass flux and I$_2$, IO, I$_2$ and O$_3$ mixing ratios.

FIGURE 4. (Top) Aerosol size distribution evolution for laboratory-generated I$_2$ flow-through experiment CH1. (Bottom) Particle concentration, I$_2$, IO, and O$_3$ mixing ratios for flow-through experiment CH1.


FIGURE 6. Particle concentration as a function of I$_2$ and CH$_2$I$_2$ for this study and previous studies. The mixing ratio range associated with previous studies is shown by horizontal lines on top of graph.
FIGURE 1. (Top) Typical particle size distribution evolution (Sample #19) over time for L. Digitata in chamber without flow-through for low light conditions.
(Bottom) Particle concentration, mass flux, I₂ mixing ratio and O₃ mixing ratio.
FIGURE 2. Condensation mass flux and particle concentration as a function of I₂ mixing ratio. Low, medium and high light-level data are colour coded.
FIGURE 3. (Top) Particle size distribution evolution for *L. digitata* (Replicate #25) in chamber without flow-through with low light conditions and an initial mixing ratio of 95.8 ppb of O$_3$. (Bottom) Particle concentration, mass flux and I$_2$, IO, I$_2$ and O$_3$ mixing ratios.
FIGURE 4. (Top) Aerosol size distribution evolution for laboratory-generated I$_2$ flow-through experiment CH1. (Bottom) Particle concentration, I$_2$, IO, and O$_3$ mixing ratios for flow-through experiment CH1.
FIGURE 6. Particle concentration as a function of I₂ and CH₂I₂ for this study and previous studies. The mixing ratio range associated with previous studies is shown by horizontal lines on top of graph.
**Supplementary Table S1. Laminaria Experiments Summary**

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