Evidence of atmospheric nanoparticle formation from emissions of marine microorganisms

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Key Points:
- Atmospheric particle clusters are formed at the air-sea interface above non-tidal seawaters
- Clusters are correlated to iodine emissions but not to DMS oxidation products, while amines contribute to the cluster growth
- Iodine is correlated to biological seawater tracers other than Chl a while amines are linked to Chl a

Supporting Information:
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5
- Supporting Information S1

Correspondence to:
K. Sellegri,
K.Sellegri@opgc.cnrs.fr

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Evidence of atmospheric nanoparticle formation from emissions of marine microorganisms

K. Sellegri[1], J. Pey[2,3], C. Rose[1], A. Culot[1], H. L. DeWitt[2], S. Mas[4], A. N. Schwier[1], B. Temime-Roussel[2], B. Charriere[5,6], A. Saiz-Lopez[7], A. S. Mahajan[8], D. Parin[4], A. Kukui[9], R. Sempere[5], B. D'Anna[10], and N. Marchand[2]

[1]Laboratoire de Météorologie Physique, CNRS-UMR6016, Université Blaise Pascal, Aubière, France, [2]Aix-Marseille Université, CNRS, LCE UMR 7376, Marseille, France, [3]Now at Geological Survey of Spain (IGME), Zaragoza, Spain, [4]Centre d'Ecologie Marine Expérimentale MEDIMEER, UMS 3282 OSU OREME, Université de Montpellier, CNRS/IRD, Sète, France, [5]Aix-Marseille Université, Mediterranean Institute of Oceanography (MIO), Université de Toulon, CNRS/IRD UMR 7294, Marseille, France, [6]Centre de Formation et de Recherche sur les Environnements Méditerranéens, CNRS UMR5110, Perpignan, France, [7]Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rocasolano, CSIC, Madrid, Spain, [8]Indian Institute of Tropical Meteorology, Pune, India, [9]Laboratoire de Physique et de Chimie de l'Environnement et de l'Espace, CNRS-UMR6115, Orléans, France, [10]Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Université Lyon 1, CNRS, UMR5256, Villeurbanne, France

Abstract Earth, as a whole, can be considered as a living organism emitting gases and particles into its atmosphere, in order to regulate its own temperature. In particular, oceans may respond to climate change by emitting particles that ultimately will influence cloud coverage. At the global scale, a large fraction of the aerosol number concentration is formed by nucleation of gas-phase species, but this process has never been directly observed above oceans. Here we present, using semicontrolled seawater-air enclosures, evidence that nucleation may occur from marine biological emissions in the atmosphere of the open ocean. We identify iodine-containing species as major precursors for new particle clusters' formation, while questioning the role of the commonly accepted dimethyl sulfide oxidation products, in forming new particle clusters in the region investigated and within a time scale on the order of an hour. We further show that amines would sustain the new particle formation process by growing the new clusters to larger sizes. Our results suggest that iodine-containing species and amines are correlated to different biological tracers. These observations, if generalized, would call for a substantial change of modeling approaches of the sea-to-air interactions.

1. Introduction

The CLAW (Charlson, Lovelock, Andreae, Warren) hypothesis [*Charlson et al.*, 1987] proposes a biological regulation of climate described by the following feedback loop: in response to an increase of temperature, seawater phytoplankton emit dimethyl sulfide (DMS) which oxidizes to form particles that serve as cloud condensation nuclei (CCN), thus modifying the cloud reflectivity and albedo, and finally resulting in a decrease of the Earth's global temperature. The past three decades of field, laboratory, and modeling studies have failed to provide evidence of the CLAW hypothesis [*Quinn and Bates,* 2011]. One possible reason, among several others, is that DMS oxidation products are not the species determining the formation of new particle clusters. New particle formation, initiated from the nucleation of aerosol clusters from gaseous precursors, is an important and complex atmospheric process that generates a large number of aerosols [*Merikanto et al.*, 2009]. New particle formation (NPF) has been widely observed in many environments. In particular, marine coastal areas display the highest NPF rates [*Kulmala et al.*, 2004] as a result of daytime low tide macroalgae exposure to ambient air [*O'Dowd et al.*, 2002a]. However, over open oceans, which represent 71% of the Earth's surface, nucleation has not been directly evidenced, although it is commonly integrated into global modeling exercises. The only experimental evidence of the occurrence of NPF over open oceans was recently presented from ambient measurements performed at the Mace Head station (Ireland), from the detection of aerosol already grown to 20 nm [*O'Dowd et al.*, 2010]. While iodine-containing species released by macroalgae were identified to form the main precursor to new particles over tidal coastal zones [*O'Dowd et al.*, 2002a; *O'Dowd et al.*, 2002b; *McFiggans et al.*, 2004], dimethyl sulfide (DMS) oxidation products are commonly proposed as the main species driving secondary aerosol number production and influencing the number of cloud condensation nuclei (CCN) over open oceans [*Charlson et al.*, 1987; *Fitzgerald,* 1991]. Thus, DMS is the only biologically driven species included in global

modeling exercises [*Boucher et al*., 2003; *Bopp et al*., 2003], even though it is recognized that other CCN sources are necessary to explain observations [*Ayers and Gras,* 1991; *Sorooshian et al*., 2009]. One hypothesis, proposed by *Leck and Bigg* [2005], was that the CCN concentration over oceans is primarily determined by the concentration of particles made of surface microlayer microcolloidal aggregates that collapse upon condensation of acidic gases. The chemical analysis of open ocean new particle formation events, similar to the ones reported by *O'Dowd et al.* [2010] in the 15–85 nm size range, revealed a correlation between organic species (benzoic acid, in particular) and the increase of the particle number concentration in the 10–60 nm size range [*Lawler et al*., 2014a]. The nature and origins of the organic compounds of the Aitken mode particles in the clean marine atmosphere remain largely unknown. Here we address three key issues related to the role of marine emissions on climate by isolating the air-seawater interface from the ambient atmosphere and simultaneously analyzing the atmospheric and seawater composition. First, we address the question of the occurrence of nucleation over nontidal marine zones. Second, we screen for the chemical precursors responsible for the new cluster formation and their early growth to larger sizes. Third, we investigate the potential biological origin of these natural marine emissions.

2. Materials and Methods

From 5 to 23 May 2013, three moored mesocosms (A, B, and C) enclosed a large volume of oligotrophic seawater sampled in the Bay of Calvi (Corsica, France). They were simultaneously filled with 2.26 m^3 of filtered ($<$1000 μm) subsurface (1 m) sampled several meters above the sea bottom and thus exclude the presence of any large planktonic organisms. These three mesocosms (1.2 m diameter and 3 m height) were made of two transparent, UV-stabilized, 200 μm thick vinylacetate mixed polyethylene films separated by a reinforcing nylon mesh. The 1.9 m^3 headspace of the mesocosms was closed using 56% UV transparent ETFE domes and continuously flushed with filtered air, while letting in an additional flow of nonfiltered ambient air (Figure S1). The residence time distribution of particles entering or formed in the mesocosm headspace shows an average 20 min and a 10ile of 70 min. The seawater in two mesocosms (B and C) was enriched with different levels of nutrients (see supporting information for more information), whereas mesocosm A remained unperturbed and was used as the control mesocosm. Seawater biogeochemical properties were monitored over the course of the experiments. Chlorophyll a (Chl *a*) concentrations increased significantly in the enriched mesocosms compared to the control (Figure 1e) and allowed for the study of marine emissions under different levels of phytoplankton biomass, although it has to be emphasized here that the increase of Chl *a* levels in mesocosms B and C is not the result of a natural phytoplanktonic bloom. The atmospheric composition of the headspace of the mesocosms was characterized for its gas-phase chemical composition using a Ionicon High Resolution Proton Transfer Time of Flight Mass Spectrometer, its particulate-phase chemical composition using an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer for particles larger than 70 nm and the aerosol number size distribution using a TSI Scanning Mobility Particle Sizer (SMPS). During a 7 day subperiod, the concentration of particles with a diameter larger than 1 nm was monitored using an Airmodus Particle Size Magnifier (PSM) coupled with a TSI Condensation Particle Counter (CPC 3010). The particle cluster and sub-10 nm particle (1–10 nm) concentrations were deduced from the combination of the SMPS and PSM-CPC. We use the term "particle clusters" hereafter as a definition of convenience for the concentration of clusters and nanoparticles comprising the 1–10 nm size range. Details on the instrumental setup and data analysis can be found in the supporting information.

3. Results

3.1. Evidence of Nucleation of New Particle Clusters From Nontidal Seawater Emissions

Results showed that enhanced number concentrations of total particles and 1–10 nm particle clusters, in particular (72 ± 19% of the total particle number concentration), were detected in the mesocosm's headspace compared to ambient air (Figure 1a), indicating that nucleation occurred from seawater emissions. The main reasons explaining larger particle clusters' concentrations in the mesocosm's headspace than in ambient air are likely due to (1) the lower aerosol condensational sink in the mesocosm headspace due to constant flushing with particle-filtered air and (2) because the sea-to-air emissions of particle cluster precursors are confined within the mesocosm headspace while they are immediately diluted when emitted to the ambient air. Particle clusters' formation was detected every day in the control mesocosm (A), while they were formed only on 1 day in each enriched mesocosm (on 19 May in B and on 17 May in C). This last observation implies that particle clusters' formation was not driven by the total biomass reflected by Chl *a* levels (Figure 1e). A

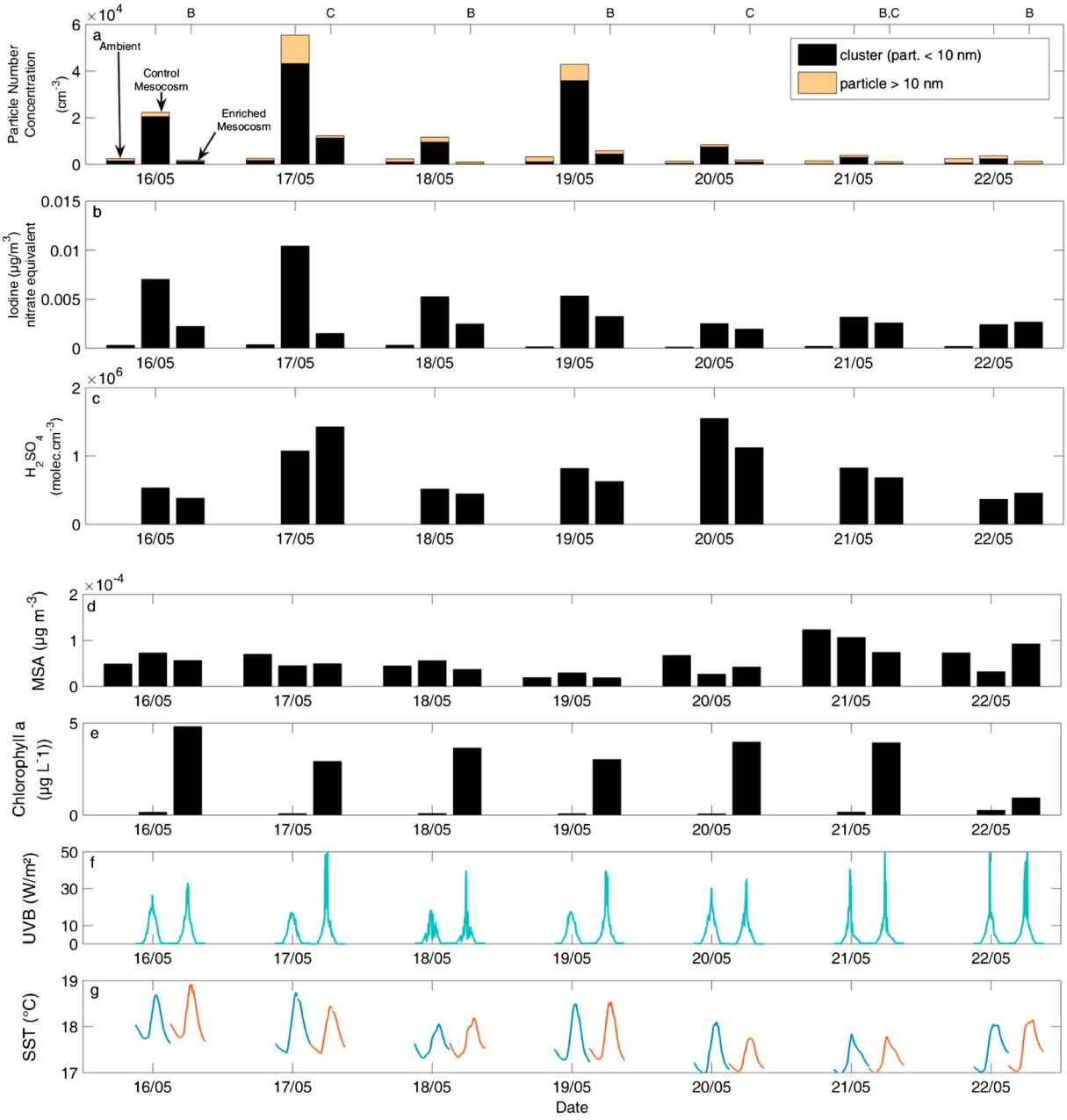

Figure 1. Daily averages in the ambient air, the control mesocosm (A), and the enriched mesocosms (either B or C or both) of (a) total and particle clusters (cm^{-3}); (b) iodine-containing species concentrations based on the abundance of the following fragments I^+, CH_3I^+, I_2^+, IO^+, and HOI^+; (c) estimated H_2SO_4 concentrations in the gas phase (see supporting information); (d) Methanesulfonic acid (MSA) concentrations, corrected from ambient concentrations for the mesocosm headspace; and (e) Chl *a* concentrations, between 16 and 22 May. Daily variation of (f) UVB received ($W\,m^{-2}$) and (g) sea surface temperature (SST) in the control and enriched mesocosms. Measurements were performed in mesocosm B on 16, 18, 19, 21, and 22 May and in mesocosm C on 17, 20, and 21 May 2013.

high day-to-day variability in the particle clusters' concentrations was found, with a daily average in the range of $1.1–4.0 \times 10^4$ particle clusters cm^{-3} during the first part of the 7 day period (16–19 May), decreasing to daily particle clusters' concentrations in the range of $2.3–7.8 \times 10^3$ for the last 3 days. Measurements show that the observed daily variability is not clearly linked to the availability of UVB radiation (Figure 1f), which should increase photochemical reactions leading to higher concentrations of low-vapor pressure products nor to the water surface temperatures (Figure 1g). A clear diurnal variation of the particle clusters' concentration was observed (Figures 2a and 2b), with high concentrations during daytime and nearly no particle clusters observed during nighttime. Interestingly, the particle clusters' production lasted over the majority of the

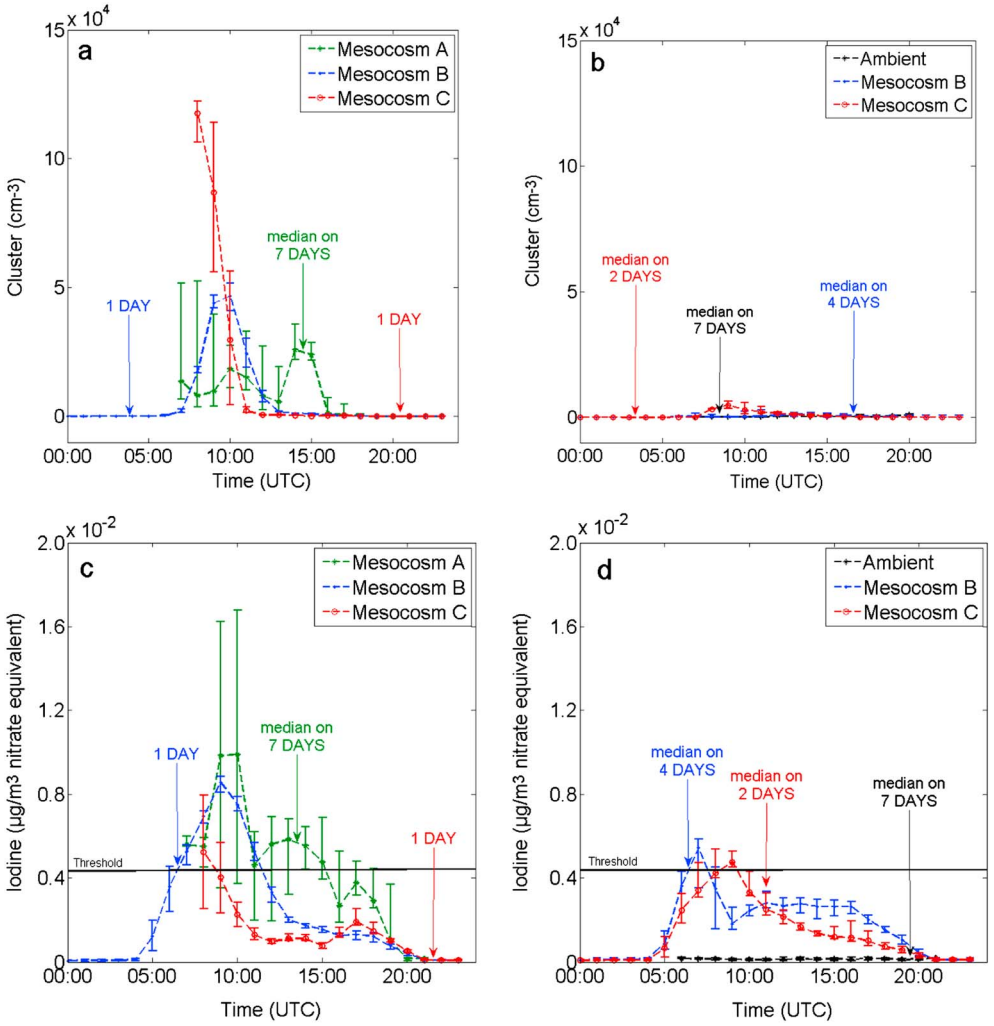

Figure 2. (a) Hourly median of particle clusters' concentrations (cm^{-3}) for nucleation days in mesocosms A, B, and C. (b) Hourly median of particle clusters' concentrations (cm^{-3}) for nonnucleation days in mesocosms B and C and the ambient atmosphere. (c) Hourly median of iodine-containing species concentrations ($\mu g\, m^{-3}$) for nucleation days. (d) Hourly median of iodine-containing species concentrations ($\mu g\, m^{-3}$) for nonnucleation days.

day (from 8:00 UTC to 19:00 UTC) in the control mesocosm (A), while it was more intense but over a shorter time period in the enriched mesocosms B and C (8:00–13:00 UTC and 8:00–11:00 UTC, respectively).

During new particle formation periods, aerosol size distributions show a constant profile for particles smaller than 20 nm, with an exponential decrease of concentrations with increasing size in all mesocosms (Figures S1 and S2 in the supporting information), indicating the achievement of a quasi-steady state of a permanent particle production. The calculated formation rates (Table S1) are high (daily averages from 25 to 2127 $cm^{-3}s^{-1}$) in comparison to those reported in the literature for ambient air (median values ranging from 0.7 to 34 $cm^{-3}s^{-1}$ over seven European sites) [*Manninen et al.*, 2010], although below rates that can be achieved in marine tidal areas (up to 10^4–10^5 $cm^{-3}s^{-1}$) [*O'Dowd et al.*, 2002a].

In order to survive coagulation losses, the newly formed particle clusters must rapidly grow to larger sizes by condensation of additional vapors. Combining the residence time distribution in the mesocosm with the particle size distribution during steady state conditions (see supporting information) allows for the calculation of growth rates (GR) of nucleated particles between 1 nm and 10 nm (GR_{1-10}) that ranged from 2.9 nm h^{-1} to 9.5 nm h^{-1}, whereas GR_{10-15} ranged between 3.4 nm h^{-1} and 106.9 nm h^{-1} (Table S1). These GR are higher than the ones reported from ambient measurements over open oceans for larger particles [*O'Dowd et al.*, 2010], although lower than those that can be measured in marine tidal zones [*Dal Maso*

et al., 2002; *Manninen et al*., 2010]. GR also followed a daily cycle with three maxima: at the highest radiation level (13:00–14:00 UTC) but also in the early morning and late afternoon (Figure S3).

3.2. Screening for New Particle Clusters' Chemical Precursors

Existing correlations between particle clusters' concentrations and chemical species detected both in the particulate and the gas phases were screened to identify potential precursors to the high particle clusters' concentrations observed. When considering the 24 species measured in the gas phase, including DMS (Figure 1d) and estimated H_2SO_4 (see supporting information), no significant correlations (at the 98% confidence level, with R^2 above 0.4) were found in any mesocosm ($N = 150$, 299, and 218 points for mesocosms A, B, and C, respectively). We calculated that kinetic-type binary homogeneous nucleation of H_2SO_4 concentrations would lead to average nucleation rates ranging from 0.52 to 11.7 $cm^{-3}s^{-1}$ and is not expected to significantly contribute to the nucleation rates observed in the mesocosms. Thus, if sulfuric acid was involved in the nucleation process, it would need the presence of a third species, such as amines, which could enhance the expected nucleation rate by an order of magnitude [*Almeida et al*., 2013]. However, no linear correlations were found to be significant between estimated H_2SO_4 (Figure 1c), or any oxidized VOC proxy, and the particle clusters' concentrations. The production of methanesulfonic acid (MSA) within the mesocosm headspace can be an indicator of potential oxidation of DMS within the residence time of the experiment and was calculated by subtracting the ambient MSA concentrations from the mesocosm dilution-corrected MSA concentrations. We found that MSA was indeed produced within the mesocosm headspace (Figure 1d), indicating the probable oxidation DMS in the mesocosm headspace within the residence time of the experiment. However, as mentioned, the lack of correlation between estimated H_2SO_4 concentrations and particle cluster concentrations allows excluding DMS (and other H_2SO_4 sources, if any) as the source of new particle clusters under our experimental conditions.

The chemical analysis of the particulate phase was only made on particles larger than 70 nm, therefore on particles larger than those formed in the mesocosm headspace. However, aerosols from the nonfiltered ambient air entering the mesocosm headspace (Figure S1) probably served as a seed for condensing vapors analogous to those vapors forming new particles. Considering the fragments and main identified groups of chemical compounds found in the particulate phase (including halogenated compounds (bromine, chlorine, and iodine) and amines, see supporting information) correlations with new particle clusters' number concentrations were found to be significant in the control mesocosm A only for the total iodine-containing species concentrations (i.e., the sum of masses corresponding to I^+, CH_3I^+, IO^+, HOI^+, and I_2^+ in the HR-AMS spectrum) (at the 98% confidence level and with an R^2 above 0.4; $R^2 = 0.575$, and $N = 192$), each of the oxides fragments (IO^+ and HOI^+) and the CHO_1 family ($C_xH_yO_z$ where $x \geq 1$, $y \geq 0$, and $z = 1$) ($R^2 = 0.466$), for the overall period of measurements. The correlation with iodine-containing species concentrations was not found in ambient air, where these compounds are depleted compared to the mesocosm headspace. Iodine-containing species concentrations were also correlated with particle clusters in the enriched mesocosm B ($R^2 = 0.664$, and $N = 373$). Only iodine-containing species concentrations presented significant correlations with particle clusters' concentrations on a day-to-day basis (5 days out of 7 showed significant correlations in mesocosm A). Using nighttime and early morning measurements, it was possible to quantify a delay of 1 h and 20 min between the onset of the iodine-containing species concentration increase (at 5:40 UTC, i.e., 40 min after solar radiation increase on average) and the particle clusters' concentration increase (at 7:00 am UTC on average). This delay is likely the result of the iodine-containing species gas-phase condensation onto preexisting particles during the first part of the day after sunrise, until the gas-phase iodine-containing species production rate surpasses its condensation rate onto preexisting particles, then allowing new particle clusters' formation.

As depicted in Figures 2c and 2d, the day-to-day variability of iodine diurnal patterns was not as strong as that for particle clusters' concentration. The experiment revealed lower iodine-containing species concentrations in the enriched mesocosms when compared to the control mesocosm and that iodine-containing species concentrations were not detected in the ambient atmosphere. We observed a clear diurnal cycle in all three mesocosms with a maximum between 7:00 and 10:00 (UTC) and near-zero concentrations during the night. Iodine-containing species concentrations daily variations showed higher concentrations during nucleation days compared to nonnucleation days. In the control mesocosm, iodine-containing species concentrations showed a main emission peak in the morning, an additional peak during the afternoon and another one in the early evening, which can be related to similar features observed in the particle clusters daily variation

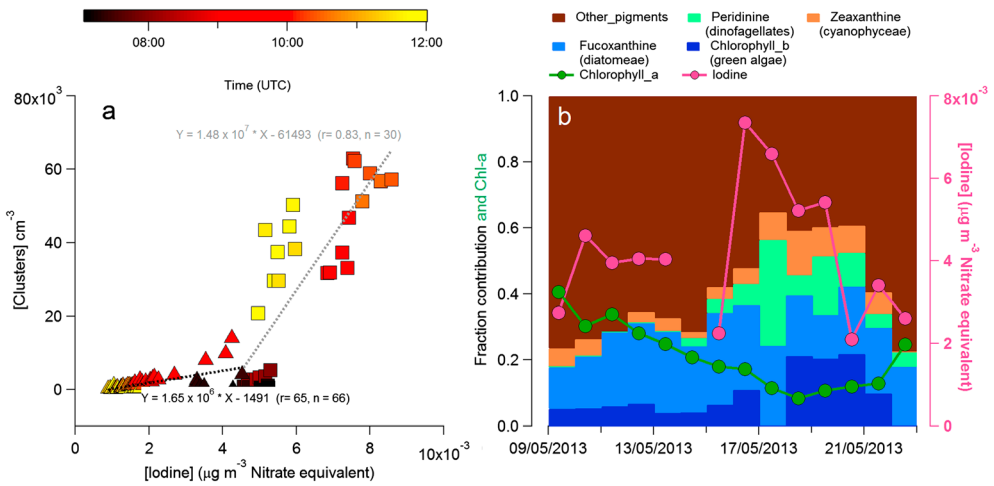

Figure 3. (a) Correlation between iodine concentrations ($\mu g\ m^{-3}$) and particle clusters' number concentrations (cm^{-3}) on 19 May in the enriched mesocosm B and linear regression for iodine concentrations above (squares) and below (triangles) the threshold value (0.004–0.005 $\mu g\ m^{-3}$). (b) Pigments and Chl *a* detected in the mesocosm A seawater daily samples and iodine concentration in the atmospheric particulate phase.

(Figure 2a). Correlation between iodine-containing species and particle clusters' number concentrations on 19 of May in mesocosm B (Figure 3a) suggests a threshold (~0.004 $\mu g\ m^{-3}$ nitrate equivalent for iodine) from which the particle clusters' number concentration increase sharply, indicating the production of late generation products of lower volatility than the first generation products. Enriched mesocosms generally displayed daily iodine-containing species concentrations below that threshold, except on the nucleation days. On 19 May in mesocosm B, we calculate a particle clusters yield of 1.5×10^7 particle clusters cm^{-3} $(\mu g_{iodine}/m^3)^{-1}$ above the iodine-containing species concentration threshold and a particle clusters' yield of 1.65×10^6 particle clusters cm^{-3} $(\mu g_{iodine}/m^3)^{-1}$ below the iodine-containing species concentration threshold. In mesocosm A, particle clusters' yields vary from 1.2×10^6 particle clusters cm^{-3} $(\mu g_{iodine}/m^3)^{-1}$ on 17 of May to 1.4×10^7 particle clusters cm^{-3} $(\mu g_{iodine}/m^3)^{-1}$ on 16 May, with a medium yield of 2.8×10^6 particle clusters cm^{-3} $(\mu g_{iodine}/m^3)^{-1}$.

3.3. Relevance of the Processes Evidenced for Open Ocean Conditions

New particle formation events were never unambiguously and directly detected (at the lowest particle sizes) under open sea conditions in past studies, yet the fluxes of particle clusters that we computed inside the mesocosms exceeded 200 $cm^{-3}s^{-1}$ and led to particle clusters' concentrations up to 20 times higher than ambient concentrations. We identified a clear positive correlation between the new particle clusters' production rate and iodine-containing species found in the particulate phase. These observations indicate that iodine-related species emitted by the seawater could be direct precursors or be oxidized to form precursors to the formation of new particles in the open ocean atmosphere, at least if similar iodine-containing species concentrations as observed in these experiments were reached. Concentrations of iodine were higher inside the mesocosms than in the ambient air (23 times higher in the control mesocosm (A) on average), which, as already stated, is likely due to a lack of dilution of the emissions inside the mesocosms in comparison to the ambient air, allowing concentrations of iodine to reach the threshold observed. As the gas-phase reactive iodine-containing species were below instrument detection limits, a gas-phase iodine chemistry box model coupled to a coagulation module was used to quantify the gas-phase flux of iodine-containing species and the concentrations of total inorganic iodine compounds (I_y) necessary to generate iodine oxide clusters at similar levels to those observed during the experiments. The gas-phase iodine chemistry box model, which is a zero-dimensional version of the Tropospheric Halogen chemistry Model (THAMO) [*Saiz-Lopez et al.*, 2005; *Mahajan et al.*, 2010], includes a complete list of inorganic iodine compounds detected in the marine atmosphere. In the box model, the clusters are considered to be made up of iodine oxides. Recent laboratory studies have shown that I_2O_3 and I_2O_4 form via the recombination of IO and OIO, or OIO with itself, respectively [*Saunders and Plane*, 2006; *Saiz-Lopez et al.*, 2012]. These higher oxides then act as monomers for the subsequent coagulation steps. At low gas-phase concentrations (<0.8 parts per thousand by volume (pptv) of I_y), the model predicts that no appreciable levels of particle clusters are formed. Above this threshold, clusters

containing iodine readily form and a concentration of ~2 pptv of I_y is necessary to replicate the maximum particle clusters' concentrations observed during the experiments. Although atmospheric total inorganic iodine compounds have never been measured, typical total I_y loadings have been modeled to range from 1.5 to 4 pptv in the open ocean marine boundary layer (MBL) [*Saiz-Lopez et al.*, 2005], which correspond to the levels of I_y estimated in the mesocosm headspace above the threshold. Past studies suspected I_2 of being the main precursor of new particle formation in coastal areas [*Saiz-Lopez et al.*, 2005]. *Lawler et al.* [2014b] measured I_2, with concentrations ranging from 0.02 parts per thousand (ppt) to 1.67 ppt in a semiremote site in the eastern Atlantic, which would also be higher than the threshold of gas-phase iodine-containing species calculated by the model. Therefore, our results suggest that the levels of gas-phase iodine-containing species present in the mesocosms headspace—although more concentrated than the normal Mediterranean atmosphere during this time of the year (May) corresponding to low levels of microorganisms in the seawater—can be achieved in the ambient atmosphere over other seas and oceans under different levels of biological activity, as measured/predicted in the literature. Thus, nucleation observed in the mesocosms related to iodine can occur in the ambient atmosphere.

3.4. Relationships to the Biochemical Composition of the Seawater

Recent laboratory experiments and modeling predictions have suggested that abiotic precursors would contribute to the majority of the observed global iodine oxide (IO) budget [*Carpenter et al.*, 2013; *Prados-Roman et al.*, 2015] (typical daytime MBL levels are ~1 pptv), one of the main iodine oxidized compounds leading to particulate iodine. In addition to potential ocean abiotic iodine sources, we further show that among all biological parameters monitored in the seawater during the experiment (see supporting information), a significant correlation was found in the control mesocosm between iodine-containing species concentrations and some phytoplanktonic pigments (peridinin, chlorophyll *b*, and zeaxanthin) but not with the total autotrophic biomass (Chl *a*) (Figure 3b). This result explains that nucleation was not promoted in the enriched mesocosms B and C, which both show higher levels of Chl *a* and lower levels of peridinin, chlorophyll *b*, and zeaxanthin than in the control mesocosm A. In this particular case, the addition of nutriments to artificially create phytoplanktonic blooms might alter biological equilibria and hinder our ability to extract applicable relationships between biogeochemical properties of seawater and the properties of marine aerosols. This newly found correlation between iodine-related emissions and these biological proxies should be further explored in ocean regions with high concentrations of phytoplanktonic species related to these biological proxies as they may represent a significant source of atmospheric particle clusters' formation. We also find that total VOCs emitted in the mesocosms and the presence of amines in particles larger than 70 nm is well correlated with Chl *a*, and that GR_{1-10} is strongly correlated to gas-phase trimethylamine (TMA) ($R^2 = 0.8$, and $N = 80$). TMA is very volatile and would need to be associated with acids to be stabilized in particle clusters. A lower level of confidence correlation ($R^2 = 0, 462$) is indeed found between GR_{1-10} and gas-phase CO_2H (carboxylic acid). This would indicate that the most condensable biologically driven organics participate in the growth of nucleated particles below 10 nm. Thus, the best conditions for persistent new particle formation events in the open ocean atmosphere would be the concomitant presence of iodine-containing species emissions for particle clusters' formation, a low preexisting particle condensation sink, and condensable gases of biological origin related to Chl *a* to promote particle cluster subsequent growth at larger sizes. These findings would be in line with the fact that the only open ocean new particle formation events observed so far are typically associated with polar marine air masses passing throughout biologically rich waters [*O'Dowd et al.*, 2010] and that increased particulate concentrations of hydrocarbons and nitrogen-containing organics were observed during the growth period of these open ocean new particle formation events [*Dall'Osto et al.*, 2012]. Levels of ambient-corrected dimethylamine DMA particulate concentrations in the mesocosm headspace (average daily concentrations ranging from 0.86 to 3.25 ng m^{-3}) are slightly lower than the range of concentrations reported by *Facchini et al.* [2008] in Atlantic Ocean marine air masses during high biologic activity (DMA = 10 (2–24) ng m^{-3}) and slightly higher than concentrations reported by *Müller et al.* [2009] in Cape Verde during an algal bloom period (0.10–1.40 ng m^{-3}).

4. Conclusions

The complex mechanisms existing between bioorganisms population types, gas-phase emissions, and nucleation are not completely elucidated from these experiments. However, this study shows a clear relationship between biologically driven iodine-containing species emissions from nontidal seawaters and new particle clusters' formation in the atmosphere. After they form, these particle clusters grow to larger sizes in the

presence of a number of Chl *a*-related organic precursors. Finally, these results suggest that a biological activity modification in future climate scenarios might modulate the atmospheric nucleation frequency and the chance for newly formed particles to grow to larger sizes. This could ultimately influence cloud cover, inducing a subsequent change in radiation reaching the sea surface and hence a potential feedback loop between biological activity and climate.

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