Authors' response letter

Manuscript Title: Laboratory-generated primary marine aerosol via bubble-bursting and atomization
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MS No.: amt-2009-73

We would like to thank the reviewers for their interest in this paper and their constructive comments. We would also like to apologize to the editor for the length of our response letter, but we wanted to address appropriately all the comments on our manuscript. In our response letter we will address the general comments about bubble path length implications raised by both reviewers and the rest of the comments will be addressed separately for reviewers #1 and #2.

Response to reviewer 1 and 2 concerning bubble path length implications:

- Reviewer's #1 comment: The shallow tank, short bubble path length (few cm), and limited time for bubble plume evolution are not representative of conditions in the surface ocean in which plumes typically extend to 1 or more m depth.
- Reviewer's #2 comment: Many laboratory generating systems use small tanks, therefore, short bubble path and lifetime. Bigger tanks like the ones used by Keene et al. (2007) or Facchini et al. (2008) would ensure longer bubble path and life time. A possibility that the bubble path could explain differences between the results of different studies should be seriously considered.

Response:
We disagree with reviewer's #1 statement. In our work we have used a small-scale physical model that, although not providing the real bubble path length, is a valid and useful system to reproduce the dynamic behavior of oceanic bubble plumes. Small-scale physical models with a varied range of plume depths, including depths<10-15 cm are generally used to study the formation and hydrodynamic evolution of bubble plumes in order to understand the process occurring in oceanic conditions (e.g. Leifer and de Leeuw, 2007, Hwang et al., 1990; Cipriano and Blanchard, 1981). This type of small-scale systems is also applied to study the properties of laboratory-generated marine aerosol proxies (Sellegri et al., 2006; Hultin et al., 2009; Mårtensson et al., 2003). We believe that the real bubble lifetimes can only be achieved in large-scale plunging water jet systems. This type of systems, however, given its large sample volume requirement, is not suitable for ex-situ laboratory works with a limited amount of sample, as it is the case of the present work. We have analyzed the implications of the short bubble lifetimes regarding the surfactants adsorption and found that equilibrium adsorption is reached in a timescale much shorter than the bubble lifetime in small-scale models. Thus, we consider our experimental system is valid for the analysis of the influence of organic matter on the particle properties.

In the present response and supplementary material (see attached file) we provide an analysis and discussion regarding the bubble lifetimes that can be achieved in small-scale models in comparison to the real conditions, along with an analysis of surfactants adsorption on the rising bubbles.

The shallowness of plumes generated by small-scale plunging water jets systems is a limitation imposed by the reduced inertial forces associated to plunging water jets of small dimensions. Near oceanic full-scale models in large tanks are required to generate water jets with velocities close to those expected in breaking wave events (Chanson et al., 2002), and thus, produce bubble plumes with depth penetrations >1m. The use of full-scale systems implies design complexity and operational limitations, due to the large amount of sample required in this type of experimental designs. This type of systems is suitable for experiments with an in situ source of seawater, as in the case of Facchini et al. 2008, which allows the use of a large amount of sample for water recirculation. For ex situ laboratory work, where a limited amount of sample is available (as it is the case of the seawater experiments with organics in our work) small-scale hydrodynamic models are usually applied to replicate the physical process leading to bubble plume formation by water impingement (Sellegri et al., 2006; Mårtensson et al., 2003).

In order to increase the lifetime of the bubbles in small-scale laboratory generators, in some recent works the bubbles have been produced from spargers situated at the bottom of deep tanks (1 m depth) (e.g, Keene et al., 2007). This technique provides longer bubble paths at the expense of reproducing the real physical process of bubble formation by water impingement. Although this type of systems allows a longer bubble path length, it is not clear if the use of such a technique provides bubble lifetimes representative of real bubble plumes, as certain glass frits produce large bubbles with characteristic high velocities.

In the supplementary material attached to this letter we compare the expected oceanic lifetimes with those achieved in current small-scale laboratory studies. As the bubble residence depth depends on the wind speed (Graham et al., 2004), in order to evaluate the case with the shortest possible bubble lifetime in the ocean, we have considered a minimum cloud residence depth of 0.65 m, defined as the depth where the majority of bubbles reside, for a minimum low wind speed of 5 m/s, necessary to induce breaking waves (Graham et al., 2004). Our calculations of lifetimes for oceanic bubbles <2 mm yield residence times from 8 s for bubbles with 2 mm diameter to 8 minutes for 60 microns bubbles for a wind speed of 5 m/s (depth 0.65 m, Graham et al., 2004), and from 12 s for bubbles with 2 mm diameter to 12 minutes for bubbles of 60 microns, for a wind speed of 5.8 m/s (depth 1 m, Graham et al., 2004). This calculation is consistent with measurements that indicate that the lifetime of bubble clouds in breaking wave events is usually on the order of minutes in field conditions (Hwang and Teague, 2000; Lamarre and Melville, 1994; Johnson, 1986). Lewis and Schwartz (2004) showed that the time for isolated bubbles to rise 1 meter length in water with surfactants ranges from 9 min for a 60 microns bubble diameter to 5.7 seconds for 2 mm bubble size. These rise times are increased in oceanic conditions due to hindrance effects existing in oceanic bubble swarms.

According to our calculations, in the work of Keene et al. (2007) only the bubbles above 1 mm present lifetimes of the order of those produced at a wind speed of 5 m/s. As the majority of the oceanic bubbles present sizes below 1 mm diameter, with a maximum near 100 microns (Deane and Stokes, 2004), we can conclude that none of the compared systems provides bubbles residence times of the order of those expected in real conditions even in the most conservative case of 5 m/s wind speed. For wind speeds above this minimum (see Figure 1, 1 meter depth for wind speed 5.8 m/s), the bubble lifetimes in all the compared laboratory systems are far below the expected oceanic lifetimes.

Our comparison indicates that the oceanic lifetimes are much longer than the bubble residence times that can be achieved with any of the small-scale systems currently used, (i.e. small tanks with spargers or plunging jets and tanks with spargers at one meter depth). In the case of the work of Keene et al., 2007, although the tank has a depth of 1-1.3 meters, the bubble lifetime indicated by the authors is relatively short (7-15 s), compared with the mean bubble lifetimes in Tyree et al., 2007 (5 s for 32-39.5 cm). The high mean bubble velocity in Keene et al., 2007, (≈10 cm/s) indicates that large bubbles were produced in their system. According to Clift et al. (1978) and Lewis and Schwartz (2004) this velocity would be characteristic of bubbles with diameters between 400 μm and 1 mm.

In the evaluated works with deep tanks and spargers, it was assumed that the use of realistic bubble paths implies replicating the real bubble residence times (Keene et al., 2007), and that short times of the order of wave periods (≈1-5 s) could be considered as representative of bubble lifetimes (Tyree et al., 2007), without considering the implications of bubble size and the specific velocities of the oceanic bubbles. Our analysis suggests that providing longer bubble paths in systems with glass frits as bubble generators does not imply reaching the oceanic bubble lifetimes, as the bubble residence time depends not only on the bubble path, but also on the rise velocity, which is a function of the size of the generated bubbles (Lewis and Schwartz, 2004). Glass frits have been shown to produce larger bubbles than plunging water jets, although the size of the bubbles depends on the filter pore size (Sellegri et al. 2006) and the flow conditions employed (Ruzicka et al., 2003). It would require a considerable extension of the tank dimensions with glass frits in order to replicate the characteristic oceanic bubble lifetimes. For instance, achieving the calculated oceanic residence times for bubbles<2 mm at 5 m/s wind speed, with the glass sintered filter of our system at the stable plate homogeneous regime, would require a tank with a depth >2.5 meters. These dimensions would imply operational limitations to the performance of this work. The use of spargers in the heterogeneous flow regime (i.e. large superficial gas velocities) would increase the void fraction and this could retard the bubble motion by hindrance (Ruzicka et al., 2003). This, however, would imply the production of increasing bubble sizes, less representative of oceanic bubbles, which would also lead to high mean bubble velocities, so it is unclear if this flow regime would be effective for replicating the realistic bubble lifetimes and bubble spectra.

Our conclusion is that only large-scale plunging water jets are suitable systems to replicate the realistic bubble lifetimes. The available evidence suggests that the optimum system to this purpose would be the generation of a large-scale plunging water jet in large volume tanks (>100 liters) as those employed by Facchini et al. (2008). This would allow the recirculation of high water flows (e.g. 20 lpm, Facchini et al. , 2008) and the generation of deep plumes with high speed water jets (>6 m/s, Chanson et al., 2002). These high speed jets can be produced by adjusting the nozzle diameter and height over water. As both the void fractions and the size of the bubbles generated by large-scale plunging jets are expected to be representative of those of oceanic plumes (Chanson et al., 2004), the generation of plume depths >1m by a plunging water jet of these characteristics would ensure the provision of bubble lifetimes of the order of those for real plumes. This type of generator is, nevertheless, only useful when large amounts of sample are available, thus they are only appropriate for in situ measurements with seawater. Due to the characteristics of our experiments, specifically regarding the limitations in the production of organic-enriched seawater with phytoplackton cultures, this type of large experimental system is not suitable for our study. We opted for a small-scale experimental configuration as physical models of reduced dimensions have been demonstrated to be useful to study the process of formation and evolution of oceanic bubble plumes and aerosol properties on a scaled basis (Leifer and de Leeuw, 2007, Hwang et al., 1990; Cipriano and Blanchard, 1981, Sellegri et al., 2006; Hultin et al., 2009; Mårtensson et al., 2003).

Implications associated to the shorter bubble lifetimes in small-scale systems with respect to the real conditions would be related to the characteristic time for adsorption of organics on the bubbles surface. In order to explore this aspect we have modeled the kinetics of adsorption of surfactants by a rising bubble in the conditions of our study to determine the characteristic time for adsorption equilibrium to be reached. The results of this calculation, which have been included in the supplementary material attached to this letter, indicate that a time of the order of milliseconds is needed for the bubbles to attain equilibrium in the T.rotula exudate solution (supplementary material, Figure 3). The bubble residence times in our system (>0.3 s, supplementary material, Figure 1) are considerably longer than the estimated characteristic time for adsorption, which means that the reduced bubble lifetime in a small-scale system is not a limiting factor to organic adsorption kinetics. In our experiments the bubble surface excess is not expected to be transport limited as equilibrium surface coverage is rapidly established, thus the experimental system employed should be valid for this type of study. It should also be taken into account that the concentration of organic matter in the tank will evolve to a distribution characterized by the highest concentration near the surface, as a result of the diffusion of surfactants to the air-water interface (Stefan and Szeri, 1999), thus, the shallow bubble plumes produced in our study spend their lifetime in the relevant region for organics adsorption.

The results of this analysis suggests that differences in the properties of the particles produced from seawater with organics due to the use of different systems would not depend on the bubble path, as adsorption equilibrium would be rapidly attained. Nevertheless, divergences between different experimental studies are expected with respect to the concentration of organics in the seawater, as this would affect the equilibrium surface excess on the bubbles interface, and to the bubbles size and number, which would affect the total amount of organic matter scavenged and transported to the subsurface near the bubble-bursting region (Stefan and Szeri, 1999).

We would like to thank the reviewers for bringing to our attention these important aspects of the work as a discussion and analysis on the raised matter have not been previously addressed in the literature. We consider that the supplementary material as well as the above discussion should be included in the manuscript.

Responses to reviewer's #1 comments:

General comments:

1. Reviewer's comment: The production experiments were conducted using artificial seawater devoid of organics and thus ignored the potentially significant influences of organics on bubble plume dynamics and aerosol production.

Answer:

The authors recognize the importance of the presence of organics for the aerosol production and that the use of organics-enriched seawater would have provided a broader picture of the effect of the aerosol generation mechanism on the particle size distribution. A limitation in instrumentation availability made impossible to conduct all the set of measurements with organics. However, the objective of the present work is not specifically an evaluation of the effect of organics on the particle production, but the comparison of the influence of different laboratory generation systems on the properties of the generated particles. We conducted the production experiments with artificial seawater and found that the mechanism employed affects the size distribution, thus, it is logical to assume that this will also occur in experiments with seawater enriched in organics, besides the potential effect that the organic matter can exert on the aerosol production.

2. Reviewer's comment: The rationale for selecting the data subsets that were compared is unclear and does not, in my view, provide an objective context for evaluating behavior.

Answer:

We disagree with the reviewer on this point. It is well known that the typical oceanic bubble spectrum shows the described power law shape. Certainly, we could provide the reviewer with an extensive list of literature references confirming this (for a review on oceanic measurements, see Lewis and Schwartz, 2004). Of course, as the bubble number depends on the position where the measurements are made, if a diverse range of oceanic bubble spectra are plotted for comparison with our results, there will be cases presenting more or less divergence in bubble number with respect to our plunging-water jet measurements. However, that does not modify our conclusion that the plunging water jet bubble spectra resembles best the bubble spectra power-law shape compared with the other systems employed in this study. In the text of our manuscript we state that our conclusion is related to the comparison of the shape of our bubble spectra and the oceanic profile (bubble spectra power-law shape with exponent from 0.8 to 5), without allusion to the bubble number, as this characteristic is known to be dependent on the position for the measurement. This finding is not specific to the conditions of our work, as this was already found by Sellegri et al. (2006). We find that reviewer #1's statement is in contradiction with Reviewer #2's comment in this regard, as Reviewer #2 appropriately points out the fact that our results confirm Sellegri et al. (2006) findings. Furthermore, similar bubble spectra to the one obtained in our work was obtained by Hultin et al. (2009) and Cipriano and Blanchard (1981) with plunging water jets of different geometries. We suggest including references of these works in our manuscript in order to support our conclusions and indicate the divergence in bubble number that exists between the available oceanic bubble spectra.

Regarding the aerosol production experiments the reviewer indicates that the results in this work are not broadly applicable, and bases this argument on a comparative analysis presented in Hultin et al. (2009). We disagree with this statement as our results are not in contrast with such a comparison:

- Hultin et al. (2009) provides a comparison of laboratory particle size distributions from different works in the literature, obtained with different aerosol generation mechanisms and diverse artificial and natural seawater samples.
- Hultin et al. indicate that some similarities are found between some of (but not all) the measurements conducted with natural seawater, however they do not draw any conclusion from this comparison as they literally state "the use of different mechanisms complicates the picture". There is not any available evidence indicating that the differences between the existing laboratory-generated particle size distributions are mainly due to the seawater sample employed. On the contrary, there is previous evidence that both the generation mechanism and the seawater sample employed have an effect on the primary particle production (Sellegri et al., 2006).

Specific comments:

1. Reviewer's comment:
[..] it would also be helpful to consolidate all relevant experimental conditions used to generate the reported data into a single table.

1. Answer:
A table with the experimental conditions will be included.

2. Reviewer's comment:
Page 2282, starting on line 2. The abstract requires revision based on the points raised below.

2. Answer:
We agree with the reviewer that the abstract requires adjustment on the statement related to the simulation of the ambient marine aerosol, as direct comparison between the laboratory primary aerosol and ambient aerosol is difficult due to secondary processes affecting the real aerosol. Regarding the statement that mentions that the plunging water jet produces the most realistic bubble spectra, we suggest to support this statement by indicating that this result confirms previous findings in the literature (i.e. Sellegri et al., 2006).

3. Reviewer's comment:
Page 2283, lines 3-5. While the production of primary marine aerosol is the dominant natural source for atmospheric aerosols globally, available evidence indicates that the corresponding burden of non-water mass is similar to that of naturally produced mineral aerosol [e.g., Andreae and Rosenfeld, 2008, Earth-Sci Rev.]. In the literature, "loading" is often used in the context of a burden rather than a flux. To minimize the potential for confusion, this distinction should be clarified in the text.

3. Answer:
Agreed; the text will be clarified.

4. Reviewer's comment:
Page 2283, line 13. The upper size limit for "sea-salt droplets" produced by breaking waves at the ocean surface is typically much greater than 10 microns diameter [..]The text should be corrected.

4. Answer:
Agreed; the text will be amended in order to mention that marine aerosol contains particles greater than 25 microns, as defined by Lewis and Schwartz, 2004. Very large particles are produced at the sea surface but the residence times of particles with r_{80}>25 microns are too short to play a role in atmospheric processes except in hurricanes.

5. Reviewer's comment:
Page 2284, lines 6-9. Here and elsewhere in the text, use of the term "sea-salt particles" is ambiguous. A general term such as "aerosols in near-surface marine air" would be a more appropriate descriptor. This section implies that the composition of aerosols in marine air at a given location can be interpreted directly in terms of biological processes in the underlying ocean at that location. Citations should also be added to identify the "field experiments" mentioned here.

5. Answer:
The term suggested by the reviewer is too long. We suggest replacing sea-salt particles by -sea spray-, which can be defined as sea salt enriched with organics. Citations of field experiments will be added.

6. Reviewer's comment:
Page 2284, lines 9-12. This statement suggests that all biogenic organic matter associated with marine aerosol in productive marine regions originates via direct emission from the surface ocean. [..]Clearly this is not the case. The text should be clarified.

6. Answer:
Agreed; the text will be modified as to avoid confusion.

7. Reviewer's comment:
Page 2285, lines 1-4. What is a "typical marine aerosol size distribution signature?" This term should be defined or an appropriate citation added. [..] size-resolved production fluxes are not directly comparable to size-resolved concentrations in ambient air. In addition, Sellegri et al. [2006] and Tyree et al. [2007] did not characterize the supermicron size fractions, which dominate the mass production flux and dry mass concentration of ambient marine aerosol and, as such, the cited distributions should not be described as "typical" of ambient.

7. Answer:
We define as typical marine aerosol size distribution the bimodal distribution defined by O'Dowd et al. (1997). We recognize that the ambient aerosol is not directly comparable with primary aerosol measurements and thus, it could not be said that the marine aerosol distribution is reproduced in the referred laboratory works. The text will be modified according to reviewer's comments.

8. Reviewer's comment:
Page 2286, line 2. The authors should clarify that sea salt dominates the non-water mass fraction of bulk marine aerosol. Typically, water dominates total mass in all size fractions of marine aerosol and organics often dominate the non-water mass of the smaller size fractions.

8. Answer:
Agreed; The text will be clarified.

9. Reviewer's comment:
Page 2286, lines 3. O'Dowd et al. [2007] is not included in the references.

9. Answer:
This work was already included in the list of references.

10. Reviewer's comment:

Page 2286, line 5. To minimize the potential for confusion, the authors should clarify that this statement refers to ambient submicron marine aerosol (to distinguish from freshly produced submicron marine aerosol).

10. Answer:
Agreed; The text will be corrected.

11. Reviewer's comment:
Page 2287, section 2.1. It would be helpful to specify additional details such as (1) the orientation for the indicated dimensions of the tank (length, width, depth), (2) the range in flow rate of bubble air, and (3) the ranges in flow rate and velocity of the water jet.

11. Answer:
A table will be included with all the relevant parameters defining the experimental conditions. Orientation of the tank dimensions will be provided in the text.

12. Reviewer's comment:
In addition, bubble plumes in the surface ocean are typically 1 m or more in depth and the organic enrichment of the primary marine aerosol increases with length of the bubble path. The authors should point out the difference between their experimental design (i.e., bubble paths of 0.05 to 0.13 m and no organics) relative to conditions more typical of the surface ocean and discuss the potential implications for interpreting results.

12. Answer:
A response to this comment has been provided in answer 1 to General comments to both reviewers. Differences between the experimental system and real conditions regarding the bubble path length will be indicated in the text, along with associated implications.

13. Reviewer's comment:
The text (line10) indicates that bubbles were generated and the chamber was swept with "zero air", which is commonly defined as air from which both particles and reactive trace gases have been removed. The text and the figure should specify how reactive gases were removed.

13. Answer:
We define zero air as air from which both particles and hydrocarbons have been removed. A charcoal filter was placed upstream of the HEPA filter to remove hydrocarbons. This element will be included in the schematic of the experimental set up.

14. Reviewer's comment:
Page 2287, lines 17-20. Did the authors test the assumption that a bubble plume produced by a single jet is representative of that produced by the same flow divided into eight jets? Some evidence suggests that this key assumption may not be valid [see for example Hoque and Aoli, 2008, Appl. Ocean Res.]. This issue and the associated implications for data interpretation should be addressed in the manuscript.

14. Answer:
We applied hydrodynamic scaling between the single and multiple water jet systems, thus our assumption is solidly based on experiments than show that systems with hydrodynamic similitude present equivalent air entrainment and bubble production (Chanson et al., 2004). Supporting this assumption is also the fact that the bubble spectra obtained in other works with different geometries are similar to those obtained in this work (Hultin et al. 2009, Sellegri et al., 2006). We scaled the multiple water jet system with respect to the single water jet system by applying Froude similitude with undistorted scale (Chanson et al., 2004). With this scaling procedure the ratio of occurring forces (Froude number) in the hydrodynamic system and the inflow conditions (ratio of height over water to nozzle diameter) are equal in both systems. This similitude between plunging water jet generators implies equal void fractions and normalized bubble spectra (Chanson et al., 2004). Description of the scaling procedure and derived assumptions will be included in the text.

15. Reviewer's comment:
Page 2288, line 1. For experiments involving the sintered glass or diffuser, did 3 LPM correspond to the flow rate of bubble air, bubble air plus sweep air, or only sweep air? Presumably, for the water jet, this air flow was exclusively sweep air.

15. Answer:

The flow of 3 lpm corresponds to the sweep airflow. This will be specified in the text.

16. Reviewer's comment:

Figure 1 indicates that sweep and bubble air were pushed into the tank and sample air simultaneously pulled from the tank. Was pressure maintained by precisely balancing the flow rates into and out of the tank or was the system operated under slight positive pressure and configured with a one-way exhaust valve in addition to the sampling lines. No such regulating device is shown in Figure 1. Since the analytical instruments require specific flow rates of sample air, presumably, some of the sample air must have been vented. If so, the vent should probably be added to the figure. Although specified in the text, it would be helpful to also define the major acronyms (BMS, CCD, MFC, etc.) in the legend.

16. Answer:

The system was operated with positive pressure and a vent was placed at the outlet of the tank to regulate the flow directed to the instruments. This will be added to the experimental system schematic. Acronyms will be defined in the Figure caption.

17. Reviewer's comment:

Page 2288, lines 1-5. How and where was RH measured? Suggest adding to Figure 1.

17. Answer:

The RH was measured at the outlet of the tank with a Rotronics HygroClip SC05 sensor. This sensor will be added to the experimental set-up schematic.

18. Reviewer's comment:

Page 2288, line 5 to 20. Was the system blanked by analysis of sweep air in the absence of bubbles? If so, the results should probably be briefly mentioned. If not, how did the authors verify that the background was sufficiently clean?

18. Answer:

Blank measurements were conducted before the experiments by measuring the particle counts in the sample air flow from the tank headspace in the absence of bubbles. Experiments were initiated when the particle counts in the blank air were zero.

19. Reviewer's comment:

The term "natural seawater" is misleading. The manuscript reports no experiments that were conducted using authentic natural seawater. It appears that all experiments were based on artificial seawater and that some experiment involved artificial seawater modified via addition of DOC produced by phytoplankton cultures grown under controlled conditions. The text should be corrected.

19. Answer:

The reviewer misinterprets how the samples were prepared. Certainly, the organics-enriched samples were prepared with natural seawater from the Tiree passage (Scotland) and this is described in the methods section. Algae were grown in this natural seawater and DOC was measured after removing algal cells. Only the samples devoid of organics were prepared with artificial seawater. Although this is explained in the methods section, we will indicate this more clearly in the abstract, figures and throughout the text to avoid confusion about the origin of the samples.

20.Reviewer's comment:

Page 2289, line 16. It would be helpful to briefly discuss the representativeness of organic-enriched artificial seawater produced in this way. Is it reasonable to expect that the physical and chemical characteristics of aerosols generated by bubbling air through these solutions were similar to those produced naturally at the ambient ocean surface?

20. Answer:

As mentioned in the previous response, the organics-enriched samples were prepared with natural seawater where living phytoplankton were grown. This allows us to assume that the samples are representative of naturally organic-enriched seawater.

21. Reviewer's comment:

Page 2289, line 17. Was this procedure used to analyze the artificially generated organic material, the artificial seawater before enrichment with OC, and/or the artificial seawater after enrichment with OC?

21.Answer:

The procedure was used to analyze the OC in the natural seawater samples after enrichment with organic matter.

22. Reviewer's comment:

Pages 2289 and 2290, Section 2.3. At what position (X, Y, Z) relative to the glass filter, diffuser, and jet was the BMS positioned for the various experiments? Why were these particular locations chosen? Later in the paper, the authors report that bubble size spectra generated with the water jet varied spatially within the tank but there is no mention of such variability for plumes generated with the other approaches or of variability as a function of depth. Were these evaluated? It would be helpful to briefly summarize in this section the specific locations within the tank at which bubble plumes were characterized for each production mechanism.

22. Answer:

The bubble spectra measurements were conducted along three longitudinal axis at positions 110 mm, 55 mm and 0 mm with respect to the tank center. The longitudinal axis selected were the one through the center and the two symmetrical axis at 47 mm from the center. These positions were arbitrarily selected, within the limitations imposed by fitting the bubble spectrometer camera into the tank. The depth for conducting all the measurements was 4 cm below the water surface. This analysis was only conducted for the plunging-water jet system.

23. Reviewer's comment:

Given the very short distance between the bubble sources (5 to 13 cm below the surface for the glass filter and diffuser; 7 to 10 cm for the jet or jets) and the BMS (3 to 8.5 cm below the surface) coupled with the time delay between production and equilibration of the bubble plume [e.g., Lamarre and Melville, 1991, Nature], are these results considered representative of open ocean conditions? Some discussion regarding this important issue would seem warranted. Why was artificial rather than nature seawater used to characterize bubble plumes? Earlier in the manuscript (page 2284 lines 4-6 and page 2286 lines 10 to 15), the authors point out the potential the importance of organics in bubble plume dynamics and aerosol production. Did the authors characterize bubble plumes in seawater modified via addition of DOC? If not, why not?

23. Answer:

We recognize that organics could affect the bubble spectra, but these measurements were not conducted due to limitations on instrumentation availability. When comparing our measurements and oceanic data we found similarities between our OC-free bubble spectra and the oceanic bubble spectra in the literature. Recently, Hultin et al. (2009) measured the bubble spectra generated with natural seawater using a plunging water jet system, which is very similar in shape to that obtained in this work with organics-free artificial seawater. This might indicate that the effect of organics on the bubble spectra might be low compared to the effect exerted by the electrolytes in the solution, which are also known to affect the bubbles spectra (Xu et al., 2009).

A discussion about the bubble path length implications has been presented in the general comment at the beginning of this letter.

24. Reviewer's comment:

Page 2289, line 25. Does the measured size range cover the full relevant size range of the bubble population within the tank? Most studies report upper limits for the bubble size distribution in the open ocean that are much greater than 1.1 mm diameter [e.g., see Lewis and Schwartz, 2004].

24. Answer:
We believe that our measurements cover the relevant size range for comparison with the oceanic bubble spectra, since although the bubble spectra extends up to several mm diameter in size the majority of the bubbles exists in the submilimetric range (Deane and Stokes, 1999; Lewis and Schwartz, 2004).

25. Reviewer's comment:

Page 2290, line 8. It would be helpful to specify the numbers of individual spectra that were averaged over 2 minutes.

25. Answer:
Agreed; The number of frames recorded will be specified in the text.

26. Reviewer's comment:

Page 2290, lines 10-13, and Figure 1. Most of the reported data for bubbles produced by the jet correspond to the BMS positioned at 110 mm from the center. Implications of the different positions of the BMS relative to the jet should be discussed here.

26. Answer:
Agreed; The text will be modified according to the reviewer's comment.

27. Reviewer's comment:
Page 2290, line 15. Suggest clarifying that only that "lower end of the aerosol size distribution" was measured.

27. Answer:
Agreed; The text will be clarified.

28. Reviewer's comment:

This section should also describe how the aerosols were transferred from the tank to the instruments. What were the measured or calculated transmission efficiencies as a function of size? It appears that the different experimental set ups were associated with different air fluxes. For example, those employing the glass filter and diffuser involved bubble rates of 5 to 10 LPM plus (presumably) 3 LPM of sweep air, plus 5% by volume of dry air whereas those employing the water jet corresponded to 3 LPM of sweep air plus 5% by volume of dry air. Did the apparent variability in the velocity of sample air through the lines influence transmission efficiency?

28. Answer:
We calculated the transmission efficiencies from the tank to the instruments as a function of size. Such analysis showed that most particle losses (up to 75% loss) occurred in the size range below 20 nm, as a result of diffusion. The sample flow through the line directed to the instruments was kept constant for all the experiments, as the excess flow was vented at the tank outlet. The section of tubing from the tank outlet to the vent, which is the part in which differences in the velocity could affect particle losses, was too short to produce significant differences in the total particle losses.

29. Reviewer's comment:

Page 2292, last few lines. Since organics influence surface tension and thus bubble plume dynamics, is there any evidence to support the implicit but unstated assumption that bubbles produced in OC-free, artificial seawater are representative of those in the surface ocean? If not, what are the implications for interpreting results?

29. Answer:
We do not make explicitly nor implicitly the assumption attributed by the reviewer. We have not tested the effect of organics on the bubble spectra in our work, thus we do not assume that bubbles produced in OC-free seawater are representative of bubbles produced in water with organics. When comparing our measurements and oceanic data we found similarities between our OC-free bubble spectra and the oceanic bubble spectra in the literature. Recently, Hultin et al. (2009) measured the bubble spectra generated with natural seawater using a plunging water jet system, which is very similar in shape to that obtained in this work with organics-free artificial seawater. This might indicate that the effect of organics on the bubble spectra might be low compared to the effect exerted by the electrolytes in the solution, which are also known to affect the bubbles spectra (Xu et al., 2009).

30. Reviewer's comment:

Page 2293, lines 1-2, and Fig. 2. It would be helpful to depict and discuss the measured variability around these average distributions in the context of evaluating whether or not the differences in mean distributions were significant. Also, here and elsewhere in the text, applying the term "aeration" to only the sintered glass and diffuser is ambiguous. The jet also introduced air into the test solutions.

30. Answer:
The low variability observed in our size distribution measurements allowed us to conclude that the differences in these size distributions are due to the different mechanisms employed. Error bars will be included in the particle size distributions. The text will be corrected regarding the term –aeration-.

31.Reviewer's comment:

Page 2293, line 19-20 and Fig. 4. The presentation seems out of order. Discussion of spatial variability in the bubble plume produced by the jet (as depicted in Figure 5) and the associated implications should preceded comparison of the plume produced by the jet with those produced by other methods.

31. Answer:
Agreed; the text will be reorganized to describe the section on bubble plume evolution before the comparison between the experiments.

32. Reviewer's comment:
Page 2293, lines 24-28 and Fig. 4. Since bubble size distributions vary systematically as a function of depth [Lewis and Schwartz, 2004; and references therein] and age [Lamarre and Melville, 1991], it is not clear how a size distribution measured at 0.03 to 0.085 m depth can be directly compared with and interpreted in the context of older (on average) plumes measured at depths ranging from 0.5 to 7.3 m [Vagle and Farmer, 1992] and from 0.4 to 1.5 m [de Leeuw and Cohen, 2002]. This issue and associated implications for interpreting results should be addressed in the manuscript.

32. Answer:
We consider that the plunging water jet system employed in this work is a physical model which allows the study of the behavior of microplumes, which can be related to real bubble plumes on a scaled basis (Leifer and de Leeuw, 2007). This comment is addressed at the first response to general comments in this letter

33. Reviewer's comment:

The terms for distance from the center of the tank and power-law exponents that are specified in the legend for Figure 4 should be defined in the caption. Here and elsewhere, to what does the plus sign preceding the distance from the center of the tank refer?

33. Answer:
Agreed. The caption of the Figure will be modified according to the reviewer's comment. The plus sign refers to the coordinate position at which the measurement was conducted with respect to the center of the tank. Coordinates with respect to the tank center are indicated in Figure 5(a).

34. Reviewer's comment:

Why is the average distribution for the sintered glass at 10 LPM rather than at 8.4 for 5.2 LPM shown? Similar question for the diffuser. It appears that the distributions which diverged to the greatest degree from that for plunging water are depicted in the plot. What is the rationale for this?

34. Answer:

We disagree with the reviewer that the plots included in the figure were those that diverged most from the plunging jet results. Furthermore, the conclusion reached about the divergence of the bubble spectra generated by these two systems with respect to the oceanic profile is the same, independently of the curves chosen for comparison. The reviewer will find in Figure 2(a) in the original manuscript that the plots for the diffuser present a similar shape at different flows. Regarding the glass frit experiments, Figure 2(b) shows that all of these spectra diverge from the power law shape characteristic of the oceanic profile.

35. Reviewer's comment:

Why are size distributions for the jet that correspond to "quiescent" conditions (110 mm from the source) rather than "acoustic" conditions (at the source) compared with distributions for the sintered glass and diffuser that were apparently (based on Fig. 1) measured directly over the source? The size distribution for the plunging jet at the source (Fig 5) appears to be more similar to those for the sintered glass (at 5.2 LPM) and diffuser (at 8 LPM) than to the corresponding "quiescent" distribution for the plunging jet. Were distributions for the sintered glass and diffuser also measured away from the source under, presumably, more "quiescent" conditions? If so, those distributions would probably be more appropriate for comparison with those measured away from the jet. If not, the comparisons seem invalid since initial bubble plumes from any source evolve over time (and, in this case, over space). It appears that this analysis is based on the implicit but unstated and unjustified assumption that bubble plumes generated by jets evolve temporally whereas those generated by other methods do not.

35. Answer:

We agree that it would be appropriate to plot the measurements by distinguishing between quiescent and acoustic conditions for this comparison. We suggest representing the acoustic oceanic measurements along with our measurements in the tank center and the quiescent measurements in different figures. Although this representation provides a clearer comparison between measurements it does not modify our conclusion that the diffuser and glass frit spectra do not present the power-law shape characteristic of the oceanic profile.

We did not conduct bubble spectra measurements for the spargers at different positions in the tank. The reason for this is that we aimed to explore the bubble plumes evolution using a physical model that reproduces the physics of bubble formation (i.e. water impingement) in order to find any correlation in the behavior of the small-scale plumes and those in real conditions. While some spatial dispersion of the bubbles is expected in the bubble columns generated by the spargers, we do not consider that a correlation can be established between mechanisms that do not resemble the real physics of bubble formation and the oceanic process.

36. Reviewer's comment:

Why are bubble size distributions reported by Vagle and Farmer [1992] and de Leeuw and Cohen [2002] plotted whereas those reported by Dean and Stokes [2002] (cited later in the manuscript) or others [e.g., Bowyer, 2001, JGR; Terrill et al, 2001, JGR; Medwin and Breitz, 1989, JGR; Walsh and Mulhearn, 1987, JGR; among others] are not. An intercomparison of all such data would indicate a much greater range in variability than suggested in Figure 4 and the associated text.

36. Answer:

We disagree with the reviewer's statement on this point. In the associated text we indicate that the comparison of our results and the real measurements is based on the bubble spectra profile and not the bubble number, where divergence exists between oceanic spectra due to the dependence of the measurements on the sampling position. The divergence in the oceanic bubble number measurements does not modify our conclusion that the plunging water jet bubble spectra resembles best the oceanic profile, in comparison with the other systems employed in this work. Some of the bubble spectra suggested by the reviewer will be included in the plot in order to illustrate the reader about the possible divergence between oceanic measurements.

37. Reviewer's comment:

- Both Vagle and Farmer [2002] and de Leeuw and Cohen [2002] report size distributions over ranges of depths and wind velocities. Which subsets of those data are depicted in Figure 4 and why were they selected?

37 Answer:
These bubble spectra were selected arbitrarily from the extensive list of works in the literature that demonstrate that the oceanic bubble spectrum presents a power law shape. Details of the subset selected (wind speed and depth) will be included in the text.

38. Reviewer's comment:

Why are the size distributions reported by Vagle and Farmer [2002] and de Leeuw and Cohen [2002] truncated at _600 _m? Should not be full size distribution be depicted in Figure 4?

38. Answer:
We compared the data from the literature in the size range corresponding to our measurements. The complete set of data can be included in this plot.

39. Reviewer's comment:

Finally, if organics are important in bubble plume dynamics as suggested the manuscript, it would seem more appropriate to compare bubble plumes in the open ocean with those generated in natural (as opposed to artificial) or in artificial seawater amended with addition of DOC. I don't understand for ignoring the influence of organics in this component of the analysis.

39. Answer:
The objective of the present work is not specifically evaluating the effect of organics on bubble production, but the comparison of different laboratory generation systems. We recognize that the use of organics-enriched seawater would have provided a broader picture on the effect on the bubble spectra. Bubble spectra measurements with organics were not conducted due to limitations with instrumentation availability. In any event, available evidence suggests that the effect on the bubble spectra shape maybe be dominated by the presence of salts and not the organic matter. Hultin et al. (2009) recently measured the bubble spectra generated with natural seawater using a plunging water jet system, which is very similar in shape to that obtained in this work with organics-free artificial seawater. This might indicate that the effect of organics on the bubble spectra might be low compared to the effect exerted by the electrolytes in the solution, which are also known to affect the bubbles spectra (Xu et al., 2009).

40. Reviewer's comment:

The primary conclusion that the authors draw from Figure 4 (lines 26-28) is, in part, a function of the data subsets that were selected for plotting. A broader comparison would have yielded a considerably more ambiguous result. This important point should be stated explicitly and considered in the context of subsequent data interpretation.

40. Answer:
We strongly disagree with this reviewer's comment. We find that this statement is also in contradiction with reviewer's #2 comments:

- The conclusion related to bubble spectra measurements reached in this work is that the plunging water jet system produces a bubble spectra which resembles the shape of the oceanic profile (i.e. power law profile with exponent from 0.8 to 5). Our statement is not based on a comparison in terms of absolute bubble number, as the bubble number depends on the depth at which the measurement is made.
- Our conclusion confirms previous findings by Sellegri et al. (2006), (as pointed out by Referee 2).
- Other works with plunging water jets have found similar results regarding the bubble spectra shape (e.g. Hultin et al., 2009, Cipriano et al., Sellegri et al.). In these works an analogous reasoning to ours is applied to evaluate the bubble spectra generated by their system. Specifically, in the work of Hultin et al. (2009), their bubble spectra shows a power law profile with an exponent value of 2 and they literally state that their generator "is adequate for producing marine particles, as the bubble generator can produce bubbles in a realistic manner".

41. Reviewer's comment:

Figure 5, caption and corresponding text on page 2294. The dashed lines and the power-law exponents should be defined.

41. Answer:
We disagree on this point; the power law exponents are clearly referred to the bubble spectra shape defined in the text. The dashed lines are a guide to the eye and do not need definition.

42. **Reviewer's comment:**
More generally, did the bubble plumes generated with sintered glass and the diffuser vary at 55 and 110 mm from the center of the tank? Presumably, like those for the water jet, these plumes also evolved over time with distance from the source.

42. Answer:
A reply to this comment has been included in response 35.

42. **Reviewer's comment:**

Page 2295, lines 5-10. Based on the above, this statement seems a bit strong. The reasonable correspondence may suggest that the plume evolved with distance from the source within the tank but it is certainly not a definitive indication that it reached a specific state comparable to an aged plume in the surface ocean. What are the implications of this relationship for the aerosol generation experiments in which 8 jets, as opposed to a single jet, were used to produce bubbles?

42. Answer:
We disagree with the reviewer's statement. As we have worked with a physical model, it is obvious that our statement refers to analogies with respect to the real system on a scaled basis. In the literature we find works where small-scale systems are used to analyze the evolution of shallow bubble plumes and correlate the behavior with real plumes (e.g. Leifer and de Leeuw, 2007, Hwang et al., 1990; Cipriano and Blanchard, 1981). As the multiple water jets system is scaled with respect to the single water jet, it is logical to think that the particle production is scaled also with respect to the single jet system and that this allows comparisons of the bubble spectra with particle production.

43. **Reviewer's comment:**

Figure 6. The legend should clarify that the size distributions correspond to particles less than 830 nm dry diameter. The larger sizes that dominate the mass flux and concentration were not characterized. It appears that the upper end of the plotted size distributions for all but the atomizer are truncated at sizes smaller than 830 nm. Why is this? Since each data point represents the average of 6 scans, it would be helpful to include the corresponding error bars to provide an indication of variability.

43. Answer:

Agreed. The legend will be clarified. The experiments for the atomizer were conducted with different settings in the DMPS system and the size range scanned was 9-830 nm. Error bars in the particle size distribution curves will be added.

44. Reviewer's comment:

Page 2295, line 23, and Table 1. Should mode 4 be 341 nm as in the text or 340 nm as in the Table?

44. Answer:

Dpg of Mode 4 should be 340 nm as in the table.

45. Reviewer's comment:

Page 2295, line 26. The terminology here is confusing. Mode 4 aerosol generated with sintered glass have a dpg of 253 not 340 nm.

45. Answer:

The text will be corrected.

46. Reviewer's comment:

Page 2296, lines 1-4. What is the basis for speculating on the importance of "splashing" as a source for mode 4 aerosol? In the absence of direct evidence, the statement as written seems overly strong. As mentioned in the preceding section of the manuscript, variability in the characteristics of bubble rafts (extent, thickness, etc.) also influences primary aerosol production. It is not clear how the relative influences of these and perhaps other factors could be differentiated based on data presented in the manuscript.

46. Answer:

Our speculation on the effect of splashing or foam on the particle size distribution is based on observation. More splash-up and foaming activity were distinctively observed with the plunging water jet system than with the rest of generators. The characteristics of the size distribution for this system might be partially due to these processes. Although to a lesser extent than bubble bursting, sea spray generation by splash can also occur (Foltescu et al., 2005). Foaming was also observed when using the glass frit system. Coincidentally, the mode 4 in the aerosol distribution of this system was more dominant than in the case of the non-foaming experiments with the diffuser. This suggests that foaming can have a role on the formation of the fourth lognormal mode. However, we agree with the reviewer that other processes may be involved and that this should be stated in the text.

47. Reviewer's comment:

Page 2296, line 26 through page 2297, line 8. I don't understand the logic here. As indicated above, submicron aerosols in ambient marine air are not representative of freshly produced aerosols at the ocean surface. The mass of dry submicron aerosol associated with on-shore flow at Mace Head is dominated throughout the year by nonsea-salt sulfate most of which originates from combustion sources over Europe [e.g., Savoie et al. [2002, JGR].

47. Answer:
We agree with the reviewer that comparison between primary aerosol and ambient aerosol cannot be made in a direct manner due to the secondary organic processes that can affect the ambient aerosol properties. We consider however, interesting to provide the reader with a representation of an ambient aerosol distribution, pointing out in the text that the existence of these secondary processes leads to a difficult comparison between the primary and the ambient aerosol distributions.

48. Reviewer's comment:

Page 2298, starting on line 11. It would be helpful to provide readers with some indication of how the DOC concentrations used in this experiment compare to the range of those in ambient surface seawater.

48. Answer:
The DOC concentration used is in the range of that of organic-enriched seawater in areas with high biological activity. References will be included in the text.

49. Reviewer's comment:
Because the generator is a closed system, surfactant organics in the artificial seawater will be depleted over time via aerosol production and removal. Did the authors evaluate this potential complication in the experimental design via time-series measurements? How long could the system be operated before the depletion of surfactant organics began to influence aerosol characteristics? It would be helpful to mention in the methods section the duration of experiments and the frequency at which solutions were replaced.

49. Answer:

Time series of particle size distribution measurements did not reveal any significant changes during the duration of the experiments (1 h). The longest experimental times were those needed to obtain humidograms (about 5 hours). Due to the limited amount of organics-enriched sample, it could not be replaced during the duration of the experiment. In order to test if the changes in the concentration due to bubbling could modify the aerosol properties, some of the measurements were replicated, but no significant changes were found in the properties of the aerosol generated.

50. Reviewer's comment:

Also, in a closed system, the delivery of organics to the surface by rising bubble can lead to the development of thick layers or organic foam that attenuate aerosol production. Did the authors observe evidence for such behavior? Were bubble rafts and/or foam more prevalent in the experiments involving OC-amended seawater?

50. Answer:
We observed more foaming activity in the experiments with organics, but we did not appreciate the formation of thick layers of organic foam.

51. Reviewer's comment:

Page 2301, lines 1-4. I don't understand this point. Bubble clouds produced by any mechanism are influenced by wake effects. Such influences are not limited to "aeration" methods.

52. Answer:
We disagree with this statement. We have not considered that wake effects are limited to spargers, but that the wake effects are more important between bubbles generated in line, as it occurs for the case of the spargers, than in bubble clouds. Interactions between bubbles depend on the characteristics of the bubble swarms, which depend on the mechanism of generation and the operating conditions. Wake effects are

more pronounced between bubbles which are generated vertically as a train of bubbles, as occurs for low superficial gas velocity in spargers at the steady state homogeneous regime, which are the conditions used in our work (superficial gas velocity =0.03 m/s) (Ribeiro and Mewes, 2007). In bubble clouds as the ones produced by plunging water jets, the wake effects are compensated by the hindrance exerted by surrounding bubbles. As the void fraction in a plunging water of the dimensions of this work is expected to be <0.02 (Chanson et al., 2004) it was assumed that the velocity of the bubbles is close to the terminal velocity of an isolated bubble. A detailed description regarding these assumptions can be found in the supplementary material.

53. Reviewer's comment:

Page 2301, lines 11-13. The description of QP is unclear. For sintered glass and diffusers, bubbles are generated by forcing compressed air through a porous medium not a single "pore".

53. Answer:
We believe that the reviewer misinterprets the definition of Qp. In spargers, air is forced through the pores of the plate. Qp is the mean air flow per pore, calculated considering the plate porosity, plate area and total flow rate. Description of Qp calculation will be added to the text (see supplementary material for details). Vb and x are the bubble volume and the space between bubbles, respectively.

54. Reviewer's comment:
Page 2302, lines 1-12 and Figure 10. It appears that this analysis is based on the implicit but unstated assumption that bubbles produced by a jet are not subject to wake effects whereas those produced by "aeration" are subject to wakes. What evidence supports this assumption? In a cloud, bubbles influence and are influenced by surrounding bubbles regardless of their mechanism of production.

54. Answer:
We disagree with the reviewer's statement. The interaction between bubbles depends on the mechanism of production and conditions of operation. Wake effects are more pronounced in bubbles which are generated vertically as a train of bubbles, as occurs for low superficial gas velocity in spargers at the steady state homogeneous regime, which are the conditions in our work (superficial gas velocity =0.03 m/s) (Ribeiro and Mewes, 2007). At these conditions hindrance due to surrounding bubbles is negligible and only wake effects are considered as interactions between trailing bubbles. In bubble swarms, as those formed by the plunging water jet system, wake effects are compensated by hindrance. The void fraction in a plunging water of the dimensions of this work is expected to be <0.02 (Chanson et al.), thus, it was assumed that the velocity of the bubbles is close to the isolated bubble terminal velocity. A detailed description regarding these assumptions can be found in the supplementary material.

55. Reviewer's comment:
Why is QP used in the equation but Q is used in the figure?
55. Answer:
Qp and Q are different flows in our analysis. Qp is the mean flow per pore and Q is the total flow through the porous media. We used the total flow Q as a reference to define the different cases in the Figure. This will be specified in the legend.

56. Reviewer's comment:

Page 2302, lines 4-6. Which of the reported depths for jet plume penetration and the sintered glass location were used in this calculation? The Methods section indicates ranges of 7 to 10 cm and 5 to 13 cm, respectively. In addition, presumably, the distance from the bottom of the jet plume to the surface corresponds to the approximate maximum rising distance for bubbles produced by the jet. Should not this analysis be based on the average or median rising distance for a "typical" bubble in the plume? How sensitive are the results to these distances?

56. Answer:

We used a distance of 10 cm for this calculation in order to compare the effect of the velocity in the two compared systems. Another case with different distances can be included in order to illustrate the effect of the distance on the analysis. In any case, according to the adsorption kinetics calculations, the differences in the bubble lifetimes in these two systems do not affect the bubble organic enrichment (see response 1 to general comments to reviewers). The different number of bubbles generated by the multiple water jet system with respect to the glass frit (estimated to be about double amount) might explain the differences observed in the hygroscopicity and CCN measurements between these two systems. A higher number of bubbles imply more transport of organic matter to the subsurface (Stefan and Szeri, 1999), which implies higher local organic concentration near the bubble bursting region. Further work with the same system and different bubble production should be conducted in order to clarify this aspect.

56. Reviewer's comment:

Page 2302, line 24 through end of manuscript. The summary and conclusions require revision based on the above comments.

57. Answer:

The conclusions will be modified based on the comments of the reviewer and the responses provided in this letter.

<u>Responses to reviewer's #2 comments:</u>

General comments:

1. Reviewer's comment:

The statement that the best generating technique was found to be impingement of water jets is not unique. Previous paper by Sellegri et al. clearly demonstrated it back in 2006. Therefore, I would rather say that this paper confirms previous findings with some additional data which should be clearly stated.

1. Answer:

We agree with the reviewer that a similar finding related to the optimum bubble spectra simulation was previously reported in the work of Sellegri et al (2006). Although we have summarized the experiments that were conducted in such a study in our manuscript, we agree that more emphasis could be made on comparing correspondences between our findings and this previous work.

On the other hand, we would like to point out that there are significant additional features in our work with respect to Sellegri et al. (2006) study. Some of these are the analysis on the relationship between water/air flows and bubble spectra, the comparison with an atomizer as aerosol generator, the analysis of the spatially-resolved bubble spectra of the water jet bubble cloud and the comparative study of the CCN and hygroscopicity properties of the aerosol produced by different mechanisms. Furthermore, a novel key characteristic of our work is that we use marine organic matter produced by real phytoplankton, as marine organic proxy, while in previous works SDS and oleic acid have been used as organic proxies (Sellegri et al., 2006, Tyree et al., 2007)

Specific comments:

1. Reviewer's comment:

The abstract stated that laboratory measurements were compared with ocean measurements. I did not see any ocean measurements performed in this study and the title is solely about laboratory experiments. If it were literature data (looks like of Sellegri et al.) that should be clearly stated.

1. Answer:

Agreed. It will be clarified that this comparison is made with data from the literature.

2. Reviewer's comment:

Page 2283 O'Dowd et al. (1997) has been misinterpreted in that wind speed above 4m/s produces droplets up to 10um. It is, indeed, very good review paper, which demonstrated that sea salt particles produced by wind stress can be as large as 50um.

2. Answer:
Agreed. The text will be corrected.

3. Reviewer's comment:
Page 2284 lines 6-15 Authors claim that data from field experiments (please name them) provided evidence for the presence of significant concentrations of biogenic organics, which is interpreted as primary. While such evidence is compelling it is important to state that organic matter in oceanic aerosols certainly is not all primary, but a significant fraction of it is secondary. Turekian et al. (2003, JGR), Ceburnis et al. (2008, GRL) and Facchini et al. (2008, GRL and ES&T) are just a few late papers demonstrating that. MSA, depending whether it is considered as organics or a separate intermediate compound nevertheless is secondary marine species as well.

3. Answer:

Agreed. Comments about other sources of organic matter in marine aerosol will be added to the text according to the reviewer's comments.

4. Reviewer's comment:

Page 2286, line 16 refers to natural seawater. The reader founds only artificial seawater made of inorganic salts and artificial seawater + synthesized biogenic organic material which was explicitly in the form of DOC. Natural seawater contains both DOC and POC with some intermediate colloidal matter (Facchini et al. 2008).

4. Answer:
The reviewer misinterprets how the samples were prepared. The organics-enriched samples were certainly prepared with natural seawater from the Tiree passage (Scotland) and this is described in the methods section. Algae were grown in this natural seawater and DOC was measured after removing algal cells as described in the text. Only the samples devoid of organics were prepared with artificial seawater. Although this is explained in the section method we will indicate this clearly in the abstract, figures and throughout the text to avoid confusion about the origin of the samples.

5. Reviewer's comment:

Page 2287 There is inconsistency with tank dimensions. Tank capacity looks like 12 l according to dimensions. It was filled with 6 l of water, which corresponded to 13cm water level, which should have been half of the tank, but then the height of the tank would be 26cm (it is 21cm in dimensions). I guess it was typo error somewhere.

5. Answer:
Agreed. The error in tank dimensions will be amended.

6. Reviewer's comment:

Line 19. 8 water jets were mentioned, but no total flow was given. Figure 3 mentions flow rates of 1.0-5.0 lpm, which dividing into 8 jets would yield as little as 0.125 lpm – surprisingly low plunging water flow rate. What was the velocity of water jets?

6. Answer:

A table with the most relevant experimental parameters will be added to the manuscript, including the flow and velocity data. The velocity of the multiple water jets at the water surface is 1.11 m/s, as a small nozzle diameter was used for generating the water jets.

7. Reviewer's comment:
Page 2289 Again the term "natural seawater" is used which was rather artificial seawater + biogenically synthesized organics.

7. Answer:
See answer 4.

8. Reviewer's comment:

Thalassiosira Rotula should be written with rotula in small cap. No information is given in terms of viability of the culture at the time of separating DOC nor the length of growth
cycle.

8. Answer:
We can provide more details on this aspect. Monitoring of algal growth was done by measuring in vivo chlorophyll-a fluorescence every 2 days using a Turner Trilogy fluorometer. This is a measurement of cell viability and growth through the proxy of increasing chlorophyll a fluorescence. Harvesting of the DOC commenced at the point when the cultures in vivo chlorophyll-a measurement peaked (a common point for each culture approximating to the entry point to the stationary phase). The actual growth time to this point varied for each of the different cultures: growth times for the 20L batch cultures varied between 23-31 days (at 15˚C with 12:12 L:D).
These details will be included in the experimental section.

9. Reviewer's comment:

DOC and TN analyses mentioned, but not clear to what purpose. In Page 2298 DOC concentration of 512 uM was mentioned. Was there any particular reason to choose it? In any case that info should be moved to Experimental section.

9. Answer:
The DOC analysis was conducted in order to characterize the concentration of organics in the seawater used for the study. The DOC concentration used is in the range of that of organic-enriched seawater in areas with high biological activity. Adequate references will be included in the text.

10. Reviewer's comment:

Page 2292. There is a long consideration about the shape of particles, ranging from cubic to spherical. How relevant is that without giving details at which RH the aerosol size distribution measurements were performed (except HTDMA at 10%)? Having a mixture of inorganic salts, namely magnesium salts, even at lower than 40% RH there is more than monolayer of water, which would change a cubic shape closer to sphere.

10. Answer:
We consider that, as the reviewer points out, these particles are highly hygroscopic and a monolayer of water might exist at the RH for size selection in the DMA. However, it is not clear to what extent the water absorbed by the particles at this RH (30-40%) can induce a change from cubic to spherical shape. Although the onset of particle morphology change for sea salt particles has been observed to occur at 45% RH,

particle rounding does not take place until 65% RH is reached (Wise et al., 2009). For this reason, we suggest including error bars in order to account for the uncertainty in the particle shape. These error bars will be included in Figure 6 of the manuscript.

11. Reviewer's comment:

Page 2295 What was the criterion to decide on "optimum" number of lognormal modes? Was it an error minimization between composite and measured size spectrum, correlation between the two or just common sense? I guess the latter would not be sufficient.

11. Answer:

The best fit to the lognormal distribution and decomposition into lognormal modes was done using a Least Square Method algorithm.

12. Reviewer's comment:

Page 2303, lines 19-21 I don't quite understand a conclusion that comparison of plunging-water jet system produced aerosol size distributions with that of Sellegri et al. real world aerosol size distributions indicates the superiority of water jet system. Was it not exactly that demonstrated by Sellegri et al.? In any event I am not sure if one can unambiguously argue that laboratory generated primary aerosol spectrum should agree with the ambient spectrum which is clearly a combination of primary and secondary processes (both may have biogenic origin). Certainly, same issue applies to Sellegri et al. results.

12. Answer:

We agree with the reviewer that comparison between primary aerosol and ambient aerosol cannot be made directly due to the secondary organic processes that can affect the ambient aerosol properties. We consider however, interesting to provide the reader with a representation of an ambient aerosol distribution, pointing out in the text that the existence of these secondary processes leads to a difficult comparison between the primary and the ambient aerosol distributions.

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Supplementary material

Manuscript Title: Laboratory-generated primary marine aerosol via bubble-bursting and atomization
Authors: Fuentes E., Coe, H., Green, D., de Leeuw, G. and McFiggans, G.
MS No.: amt-2009-73

1. Estimation of bubble lifetimes in laboratory scaled systems

We will assume that the bubbles generated by a vertical plunging water jet and spargers in seawater reach their terminal velocity rapidly after formation, as it has been shown that bubbles generated in solutions of NaCl and surfactants attain their terminal velocity in less than 1 cm (Krzan and Malysa, 2009). The rise velocity of isolated bubbles whose surface is covered with surfactants can be estimated as (Batchelor, 1967):

$$U_0^2 = \frac{4}{3}\frac{D_b(\rho - \rho_g)}{\rho C_{d0}} \qquad (1)$$

$$C_{d0} = \frac{12}{\mathrm{Re}_0}\left(1 + 0.104\,\mathrm{Re}_0\right) \qquad (2)$$

where U_0 is the rise velocity, D_b is the bubble radius, ρ is the water density, ρ_g is the air density, Re_0 is the bubble Reynolds number and C_{d0} is the drag coefficient.

The bubble rise velocity in bubble clouds is affected by hindrance and wake effects exerted by surrounding bubbles (Simonnet et al., 2007). In bubble clouds, wake effects are frequently compensated by hindrance effects and the terminal velocity of bubbles is defined as a function of the velocity of the isolated bubble and the global gas void fraction (Richardson and Zaki, 1954; Ribeiro and Mewes, 2007):

$$U_{wj} = U_0(1-\alpha)^{n-1} \qquad (3)$$

where n is the Richardson-Zaki exponent, which is a function of the Reynolds number and α is the void fraction. For the determination of the Richardson-Zaki exponent we will use the parameterization of Richardson and Zaki (1954), which has been shown to be valid for bubble swarms for Re<300 and Morton number<3.9 10^{-10} (Sankaranarayanan et al., 2002).

Void fractions generated by a plunging water jet with the dimensions used in this work are expected to be <0.02 (Chanson et al., 2004), thus we will assume that the velocity of the bubbles generated by the plunging water jet is equal to the terminal velocity of an isolated bubble.

Several flow regimes as a function of the superficial gas velocity are defined in the behavior of bubbly flows generated by injecting air through spargers (Ruzicka et al., 2003). In the homogeneous regime, non-coalescing and almost spherical bubbles are generated continuously from the orifices of the sparger plate. For low flow conditions, in the stable plate homogeneous regime, the void gas fraction increases linearly with the superficial gas velocity because of negligible hindrance effects between bubbles (Ruzicka et al, 2003). The gas superficial velocity in our measurements with the glass sintered filter is 0.03 m/s, thus we can assume that the flow conditions correspond to this linear section of the homogeneous regime (Ribeiro and Mewes., 2007). This flow regime is characterized by the formation of in-line trailing bubbles, whose motion is affected by wake effects which cause the train of bubbles to rise faster than single bubbles in still water (Zhang and Fan, 2003). The ratio between the rise velocity of a trailing bubble U_{gf} and the rising velocity of an isolated bubble U_0 is given by Zhang and Fan (2003):

$$U_{gf}/U_0 = 1 + \frac{C_{d0}}{2}\left[1 - \exp\left(\frac{\mathrm{Re}_0}{x/D_b}\right)\right] \tag{4}$$

$$C_{d0} = \frac{12}{\mathrm{Re}_0}\left(1 + 0.104\,\mathrm{Re}_0\right) \tag{5}$$

where x is the distance between the trailing bubbles.

The distance between the bubbles can be estimated from the number of bubbles in the bubble column generated from a pore on the plate, which depends on the air flow through the porous media:

$$x = \frac{h(1 - D_b N_b)}{hN_b - 1} \tag{6}$$

$$N_b = \frac{Q_p}{V_b U_{gf}} \tag{7}$$

where Q_p is the mean air flow through a pore, N_b is the number of bubbles per unit length in the bubble column over a pore, V_b is the bubble volume, and h is the distance from the porous plate to the water surface. The air flow per pore is determined as $Q_p = QA_p/(A\varepsilon)$, where Q is the total air flow through the plate, A is the area of the porous plate, ε is the plate porosity, and A_p is the mean pore area. We will adopt the definition of trailing bubbles rise velocity indicated by equation (4) to calculate terminal velocities of bubbles generated by the glass sintered filter (U_{gf}) in the conditions of our study.

The bubble lifetimes calculated by using equations (1) to (7) for the multiple water jet system (bubble path 7 cm) and the glass frit (bubble path 5 cm) are illustrated in Figure 1, along with the mean residence times indicated in the works of Tyree et al. (2007) (bubble path 32-39.5 cm) and Keene et al. (2007) (bubble path of 100-130 cm).

For comparison, the lifetime of oceanic bubbles, calculated using equations (1) to (3), by considering characteristic cloud residence depths of 0.65 m and 1 meter and a void fraction of 0.2, has also been included in Figure 1. In breaking wave events a minimum void fraction of 0.2 near the water surface is expected (Lamarre and Melville, 1991). As the bubble residence depth depends on the wind speed (Graham et al., 2004), in order to evaluate the case with the shortest possible bubble lifetime in the ocean we have considered a minimum cloud residence depth of 0.65 m, defined as the depth where the majority of bubbles reside, for a minimum wind speed of 5 m/s, necessary to induce breaking waves (Graham et al., 2004). Although we have analyzed the bubble size range above 60 μm, it should be considered that the critical bubble diameter (i.e., diameter below which bubbles reduce their size and dissolve before reaching the surface) is 80 μm and 100 μm for initial depths of 0.65 m and 1 m, respectively (Lewis and Schwartz, 2004). Above these critical sizes, the change in the bubble diameter from ≤1 meter depth to the surface is <10% (Lewis and Schwartz, 2004), thus, we will assume that the bubble size is not modified on the way to the surface.

Our calculations of lifetimes for bubbles <2mm yield residence times from 8 s for bubbles with 2 mm diameter to 8 minutes for 60 microns sizes at 5 m/s wind speed (0.65 m depth), and from 12 s for bubbles with 2 mm diameter to 12 minutes for bubbles of 60 microns, for a wind speed of 5.8 m/s (1 m depth). This calculation is consistent with measurements that indicate that the lifetime of bubble clouds in breaking wave events is usually on the order of minutes in field conditions (Hwang and Teague, 2000; Lamarre and Melville, 1994; Johnson, 1986). Lewis and Schwartz (2004) estimated rise times, for isolated bubbles with absorbed surfactants at 1 meter depth, from 9 min for 60 microns bubble diameter to 5.7 seconds for 2 mm bubble size (Figure 1). These rise times are increased in oceanic conditions due to hindrance effects existing in oceanic bubble swarms.

According to our calculations, in the work of Keene et al. (2007) only the bubbles above 1 mm present lifetimes of the order of those produced by a wind speed of 5 m/s. As the majority of the oceanic bubbles present sizes below 1 mm diameter, with a maximum near 100 microns (Deane and Stokes, 2004), we can conclude that none of the compared systems provides bubbles residence times of the order of those expected in real conditions at a wind speed of 5 m/s. For wind speeds above this minimum (e.g. Figure 1, wind speed 5.8 m/s) the bubble lifetimes in the laboratory systems are far below the oceanic lifetimes.

In the case of the work of Keene et al., 2007, although the tank provides a bubble path of 1-1.3 meter, the bubble lifetime indicated by the authors is relatively short (7-15 s), compared with bubble lifetimes in Tyree et al. (2007) (5 s for 32-39.5 cm). The high mean bubble velocity in Keene et al., (2007) (≈10 cm/s) indicates that large bubbles were produced in their system. According to Clift et al. (1978) and Lewis and Schwartz (2004) this velocity would be characteristic of bubbles with diameters between 400 μm and 1 mm. This comparison indicates that providing longer bubble paths in systems with glass frits as bubble generators does not imply reaching the oceanic bubble lifetimes, as the bubble motion in seawater depends primarily on its size (Lewis and Schwartz, 2004), and large rapid bubbles are usually produced by glass frits (Sellegri et al. 2006).

Our conclusion is that only large-scale water jets are suitable systems to replicate the realistic bubble lifetimes. The available evidence suggests that the optimum system to this purpose would be the generation of a large-scale plunging water jet in large volume tanks (>100 liters) as those employed by Facchini et al. (2008). This would allow the recirculation of high water flows (e.g. 20 lpm, Facchini et al. , 2008) and the generation of deep plumes with high speed water jets (>6 m/s, Chanson et al., 2002). These high speed jets can be produced by adjusting the nozzle diameter and height over water. As both the void fractions and the size of the bubbles generated by large scale plunging jets are expected to be representative of those of oceanic plumes (Chanson et al., 2004), the generation of plume depths >1m by a plunging water jet of these characteristics would ensure producing bubbles with lifetimes of the order of those for real plumes. This type of generator is, nevertheless, only useful when large amounts of sample are available, thus they are appropriate for in situ measurements with seawater. Due to the characteristics of our experiments, specifically regarding the limitations in the production of organic-enriched seawater with phytoplankton cultures, this type of large experimental system is not suitable for our study. We opted for a small-scale experimental configuration since physical models of reduced dimensions have been demonstrated to be useful for studying the process of formation and evolution of oceanic bubble plumes and aerosol properties on a scaled basis (Leifer and de Leeuw, 2007, Hwang et al., 1990; Cipriano and Blanchard, 1981, Sellegri et al., 2006; Hultin et al., 2009; Mårtensson et al., 2003).

2. Adsorption kinetics and characteristic time for adsorption equilibrium

In this section we will analyze the evolution of the surface excess of surfactant at the interface of a bubble rising in a T. rotula algal exudate solution in order to estimate the time required for the bubbles to attain adsorption equilibrium. For the analysis we will use the approach employed by Morgan et al. (1992), which is based on the boundary layer theory for bubble adsorption developed by Levich (1962). This approach considers mass transport by convection induced by the hydrodynamic flow and diffusion from the subsurface in equilibrium with the bulk solution to the bubble surface. According to Levich (1962), the diffusion boundary layer around a bubble is defined as the region in which mass transport by diffusion is more important than convection. Considering the diffusive flux equal to the convective flux around the bubble, the thickness of such boundary layer is defined by as:

$$\delta = \left(\frac{DD_b}{2U} \right)^{1/2} \tag{8}$$

where D is the diffusion coefficient, D_b is the bubble diameter and U is the bubble rise velocity.

The diffusion coefficient for large organic molecules in water can be calculated by using the Stokes-Einstein equation (Young et al., 2004):

$$D = 9.96x10^{-8}\frac{T}{\eta_w \bar{V}_{org}^{1/3}} \tag{9}$$

where D is the diffusion coefficient (cm^2/s), T is the temperature (298 K), η_w is the water viscosity (cP) and V_{org} is the molar volume of the organic compound. The molar volume was estimated by using a molecular weight of 1.89 kDa as derived from Langmuir isotherm measurements conducted with T.rotula exudates (Fuentes et al., 2009) and a density of 1550 kg/m^3, which is the average density of humic-like substances (Dinar et al., 2006).

Since convection effects dominate beyond the boundary layer thickness, the concentration at and beyond the boundary layer may be taken to be constant and equal to the bulk concentration. The surface excess Γ change can be expressed as a function of flux to the interface by considering Fick's law as (Morgan et al., 1992):

$$\frac{\partial \Gamma}{\partial t} = \frac{D(c_0 - c_s)}{\delta} \tag{10}$$

where c_0 is the concentration of organics in the bulk solution and c_s is the concentration of organics in the subsurface. Assuming that the bubble interface is in equilibrium with the subsurface following a Langmuir isotherm, the solution of this differential equation yields (Morgan et al., 1992):

$$t = \frac{\delta}{Dc_0}\frac{\Gamma_{eq}}{\Gamma_\infty}\left[\Gamma - \Gamma_{eq}\ln\left(1 - \frac{\Gamma}{\Gamma_{eq}}\right)\right] \tag{11}$$

where t is the time, Γ_{eq} is the equilibrium surface excess and Γ_∞ is the saturation surface excess.

This equation can be integrated if the equilibrium adsorption isotherm of the surfactants on study is known. For surfactant concentrations in the liquid bulk phase below the critical micelle concentration, the interfacial surface excess Γ at a constant temperature can be described by the Gibbs isothermal adsorption equation (Gibbs, 1928):

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d\ln c_0} \qquad (12)$$

where σ is the equilibrium surface tension at the air water interface.

Neglecting interactions of the surfactant molecules within the absorption layer, one can describe the adsorption of surface active materials at an interface using the Langmuir isothermal equation (Langmuir, 1917):

$$\Gamma_{eq} = \Gamma_{\infty}\frac{c_0}{c_0 + a_L} \qquad (13)$$

where a_L is the Langmuir parameter (concentration at half surface coverage). This equation is a good approximation for the equilibrium relationship between the surface excess Γ_{eq} at the interface and the surfactant concentration in the liquid phase. A relationship between the interfacial tension and the surfactant bulk concentration can be obtained by combining the Gibbs and Langmuir isotherms, which gives as a result the Langmuir-Szyskowski isothermal equation (Dukhin et al., 1995):

$$\sigma = \sigma_0 - RT\Gamma_{\infty}(1 + 1/a_L \ln c) \qquad (14)$$

where σ is the equilibrium surface tension at the air water interface and σ_0 is the surface tension of pure water. Measurements of surface tension of T.rotula exudate at the air/water interface conducted by axysimmetric shape analysis with a pendant drop instrument are illustrated in Figure 2 (Fuentes et al., 2009). Fitting the experimental data to the Langmuir-Szyskowski adsorption isotherm yields values of Γ_{∞} and a_L of 3.6E-6 mol/m^2 and 3.75 mol/m^3, respectively (Fuentes et al., 2009).

The evolution of the surface excess concentration with time can be derived by using equation (11), with the values of equilibrium surface excess Γ_{eq} obtained from the Langmuir isothermal equation (13). The approach to equilibrium for T. rotula exudate at the concentration of this study is illustrated in Figure 3. We find that the time required for adsorption equilibrium of a rising bubble is lower than 0.3 ms, which is rapid on the timescale of our experiments (>0.3 s, Figure 1). The time to reach equilibrium decreases with increasing bubble size as a result of the higher transport by convection associated to the higher velocity of large bubbles. In our experiments, the bubble surface excess is not expected to be transport limited as equilibrium surface coverage is rapidly established.

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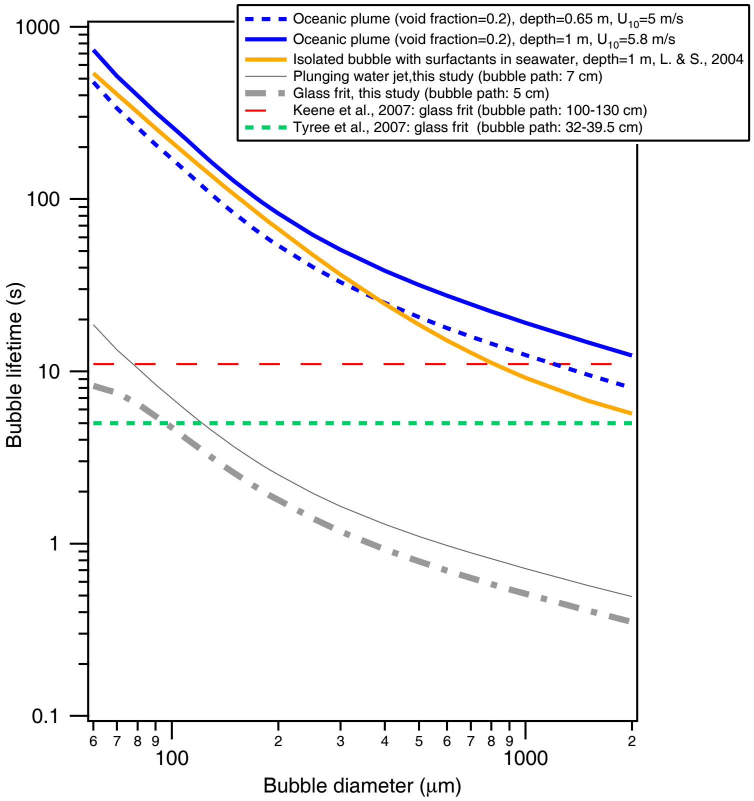

Figure 1. Comparison of estimated lifetimes of bubbles generated by the plunging-water jet (eq. 1) and the glass sintered filter (eq.4) in this study with lifetimes in the laboratory systems of Keene et al. (2007) and Tyree et al. (2007), and oceanic plumes lifetimes at a breaking wave event at 5 m/s and 5.8 m/s wind speeds at 10 m above the surface (U_{10}) . Estimation of lifetimes of isolated bubbles with surfactants in seawater by Lewis and Schwartz (2004) are included for comparison

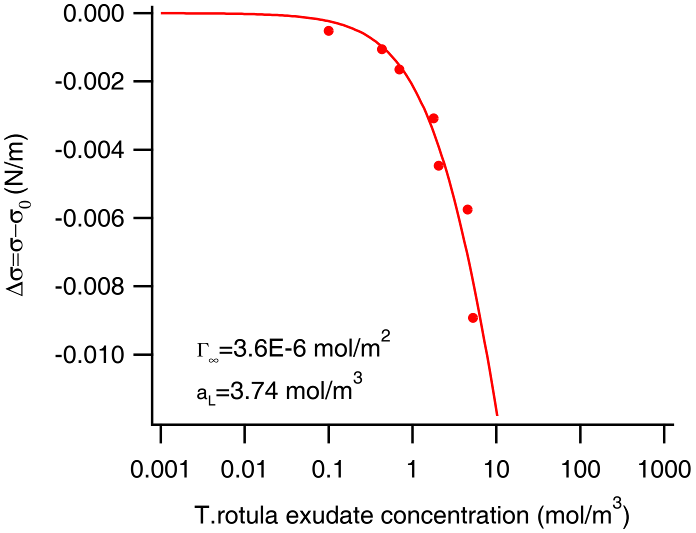

Figure 2. Langmuir-Szyskowski isotherm for T.rotula exudate at 20˚C (Fuentes et al., 2009)

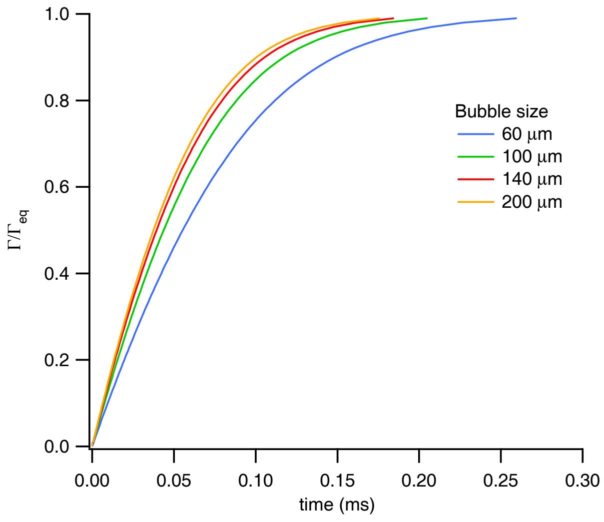

Figure 3. Prediction of Γ/Γ_{eq} ratio as a function of time for bubbles in a solution of T.rotula with DOC 512 µM.