

Review of “A physical based framework for modeling the organic fractionation of sea spray aerosol from bubble film Langmuir equilibria”
Burrows et al., 2014 – ACPD.

This paper represents one of the more thought-out studies of the processes involved air-sea interaction physics in recent years, and represents a true application of our current understanding of the physics and thermodynamics governing air-sea interaction processes. Therefore, though, I am compelled to press harder on the author(s) to correct what I see are, in some cases, major errors and deficiencies. Were they to do this satisfactorily, this paper would represent a truly substantial advancement in air-sea interaction studies that for once begins to confront the complexities that are generally brushed aside in previous studies. I hope the authors are willing to make the necessary effort to do this, because this is an important piece of work & I want to be confident when I cite this in the future.

General Statements

I think the authors did a good job distilling information regarding compounds considered relevant proxies for ocean surface active material.

The uncertainties of the method must be truly enormous; and some attempt to convey their bounds is absolutely necessary.

First Major Point

There is growing evidence that the organic mass fraction of nascent aerosol is emphatically *not* correlated with Chl *a*, and pointing more towards the hypothesis that the ocean is everywhere capable of saturating the available bubble surface area (i.e. the ocean is surface-area limited), yielding pretty much uniform mass fractions.

- 1) Long et al. (2014) showed, using dynamic surface tensiometry, significant surface activity in productive & oligotrophic seawater. This suggests that surface active material is present in large quantities in seawater independent of Chl *a* or ocean trophic state. For example, as a minimum, using the method of Joos and Rillaerts, (1981), and an approximate diffusion coefficient of $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, a change in surface tension of -0.4 mN m^{-1} , and a surface age of 4 seconds (thus setting the lower bounds), the theoretical concentration of oleic acid in oligotrophic seawater is on the order of $1 \times 10^{-5} \text{ M}$. While it is recognized that this is unlikely for such a short lived species, this would also imply that the concentration of less surface-active material could be higher. Please let me know if this need to be clarified.
- 2) Both Keene et al. (2007) and Quinn et al. (2014) show enrichment factors & mass fractions above the modeled values in oligotrophic water, and more similar to those predicted by Long et al. (2011).

These points together suggest that the ocean may be uniformly capable of saturating bubble surfaces regardless of location or biological activity. The main mechanistic effect,

as pointed out by this paper, would be in the relative contribution of different chemical species.

Second Major Point

While the presence of surfactant material on the water surface does impact bubble residence times, there is extensive literature suggesting that the SML does *not* exist appreciably behind breaking waves, or at highly energetic sea states.

For example, from Wurl et al. (2011),

“For obvious reasons, the SML is temporarily disrupted in the presence of breaking waves, dispersing SML material into the bulk water. In both and field experiments, surface films appear to reform within seconds after disruption.”

In the presence of breaking waves, dispersed SML materials adsorb rapidly to the surface of the rising air bubbles, and therefore, bubble plumes may be the most important transport vector for surface-active material to the SML.”

I also point the author to the 1st chapter in Donelan et al. (2002) and the references cited therein. These as well as in many other places in Donelan et al. (2002) indicate observation of the SML, or “sea slicks” as they are oft referred, breaking up under conditions of relatively minimal strain. As well, the surface divergence associated with a bubble plume detraining is also sufficient to break apart an SML.

Thus, the active hypothesis in the Atmos. Sci. community that the SML has an appreciable impact on either the process of particle formation or composition is, in my opinion, broadly invalid. Rather – and the author points this out nicely, though without acknowledging the full consequence of the statement – the SML is made up of material generally transported to the surface via bubbles; and that the SML has to regenerate after a wave breaks. I think the appropriate interpretation is that both the SML and particle OM enrichment are nearly independent consequences of interactions between bubbles and surface active material in the ocean.

Third Major Point

While it appears that the calculation of 0.05 ms equilibrium time for adsorption by Fuentes et al. (2010) is numerically sound, that time is likely several orders of magnitude too fast. There is some good literature on competitive adsorption equilibrium for surfactant mixtures at much higher concentrations that seem in the ocean, and their results are nowhere near equilibrium (few examples... Fritz and Schlünder, 1981; Mulqueen et al., 2001a, 2001b). It is not clear what the implications for this might be for your model since the time scales for bubble surfaces in the ocean are much greater than 0.05 ms. But, for competitive adsorption, the use of a thermodynamic equilibrium model is likely insufficient to truly capture the partitioning of individual surfactants on bubble surfaces on the relevant time scales in the ocean. If surfactant-surfactant, or surfactant-ion interaction is important, then the equilibrium model is most definitely insufficient. Given the presence of divalent ions and ionic surfactants in the ocean (e.g. oleic acid, decanol, etc.), and the known tendency of surface active material to form aggregates in seawater, the interactions between surfactants are likely very important. I note that the authors do address this uncertainty in statement, and it is likely outside of our ability to constrain it, given the current body of knowledge.

First Minor Point

Is it not precarious to use a model that drives its ocean biology with Chlorophyll as a primary metric to study the potential for Chl *a* as a proxy for ocean OM? Or am I misinterpreting how the model was employed? Please correct me if I'm wrong.

Also, to my knowledge, the processes controlling OM composition in the surface ocean are still highly uncertain, and it is unlikely that a climate-model based incantation of the surface ocean is doing an adequate job.

Second Minor Point

The authors regularly fail to acknowledge the work by Keene et al. (2007) who clearly demonstrated that high OM mass fractions could be achieved in low-chlorophyll waters. If the authors have some reason for excluding these results, it would be good to provide a justification.

Specific Comments:

P5379-L7: Note, the assumption that Chl *a* was a good proxy for organic aerosol fraction was, in the case of Long et al. (2011), not motivated by observations at tower-based sites. Rather, it was motivated by its potential use as a proxy for surface active material production, and as an observable ocean quantity reflective of microbiology.

P5379-L21-22: This should be reworded to emphasize that DOC is an operationally defined quantity.

P5382-L27: What is a low concentration for humate? Is this a correct statement? It is my understanding that on continental shelves and in proximity to terrestrial runoff, humate concentrations can be quite high.

P5388-L8: It is not clear why $N_{\text{bub}}=2$ is done. Is it possible to coat two sides of a bubble surface with surfactant? Perhaps if a bubble was created by dilation of a preexisting film, this could happen. If it is the authors' intent to suggest that one side of the film is made of SML material, I point them to the 'Second Major Point' above. If they wish to have a more detailed discussion about this, I will be glad to do so.

P5389-L3-5: I think this assertion is far too simplistic. Please see, among others, Lhuissier and Villermaux (2011) and Brenner and Gueyffier, (1999) for a detailed description of the process of film droplet production.

P5405-L23-28: I disagree with this statement. The observations are quite limited. Also see the statement in the 'First Major Point' above.

Fig 3: Are the units correct for the y-axis? The concentrations of surfactant seem a bit high relative to ocean concentrations.

Fig. 10: If possible, you might consider adding the error bars for the lines showing Long et al. (2011) results. They were pretty large.

Technical comments:

Several of the figures are difficult to read. Primarily, the fonts are blurry unless zoomed in quite a bit. Also, the figures' subtitles are placed in an odd way. Panel labels designating a letter (e.g. in Fig. 4: a) Stearic Acid) should be above the appropriate figure and left justified. I found it a bit confusing otherwise. While I was able to rationalize which figure was referenced, without taking time, I misinterpreted the figures.

The paper wanders a bit in some places. For example, Fig. 17 is cited before Figs. 14, 15 & 16. Also, some of the text is a bit wordy & not clear or easy to follow.

References:

Brenner, M. P. and Gueyffier, D.: On the bursting of viscous films, *Phys. Fluids*, 11(3), 737, doi:10.1063/1.869942, 1999.

Donelan, M. A., Drennan, W. M., Saltzman, E. S. and Wanninkhof, R.: Gas transfer at water surfaces., edited by M. A. Donelan, W. M. Drennan, E. S. Saltzman, and R. Wanninkhof, American Geophysical Union, Washington, USA., 2002.

Fritz, W. and Schlünder, E. U.: Competitive adsorption of two dissolved organics onto activated carbon—I: Adsorption equilibria, *Chem. Eng. Sci.*, 36(4), 731–741, doi:10.1016/0009-2509(81)85088-9, 1981.

Joos, P. and Rillaerts, E.: Theory on the determination of the dynamic surface tension with the drop volume and maximum bubble pressure methods, *J. Colloid Interface Sci.*, 79(1), 96–100, doi:10.1016/0021-9797(81)90051-5, 1981.

Keene, W. C., Maring, H., Maben, J. R., Kieber, D. J., Pszenny, A. A. P., Dahl, E. E., Izaguirre, M. A., Davis, A. J., Long, M. S., Zhou, X., Smoydzin, L. and Sander, R.: Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface, *J. Geophys. Res.*, 112(D21), doi:10.1029/2007JD008464, 2007.

Lhuissier, H. and Villermaux, E.: Bursting bubble aerosols, *J. Fluid Mech.*, 696, 5–44, doi:10.1017/jfm.2011.418, 2011.

Long, M. S., Keene, W. C., Kieber, D. J., Erickson, D. J. and Maring, H.: A sea-state based source function for size- and composition-resolved marine aerosol production, *Atmospheric Chem. Phys.*, 11(3), 1203–1216, doi:10.5194/acp-11-1203-2011, 2011.

Mulqueen, M., Datwani, S. S., Stebe, K. J. and Blankschtein, D.: Dynamic Surface Tensions of Aqueous Surfactant Mixtures: Experimental Investigation, *Langmuir*, 17(24), 7494–7500, doi:10.1021/la010782p, 2001a.

Mulqueen, M., Stebe, K. J. and Blankschtein, D.: Dynamic interfacial adsorption in aqueous surfactant mixtures: Theoretical study, *Langmuir*, 17(17), 5196–5207, 2001b.

Quinn, P. K., Bates, T. S., Schulz, K. S., Coffman, D. C., Frossard, A. A., Russell, L. M., Keene, W. C. and Kieber, D. J.: Empirical constraints on modeling the organic matter enrichment in nascent sea spray aerosol, *Nat. Geosci.*, (Accepted), 2014.

Wurl, O., Wurl, E., Miller, L., Johnson, K. and Vagle, S.: Formation and global distribution of sea-surface microlayers, *Biogeosciences*, 8(1), 121–135, doi:10.5194/bg-8-121-2011, 2011.