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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "A physically-based framework for modelling the organic fractionation of sea spray aerosol from bubble film Langmuir equilibria" *by* S. M. Burrows et al.

S. M. Burrows et al.

susannah.burrows@pnnl.gov

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Response to reviewer 3:

We thank the reviewer for the thorough, thoughtful and constructive comments on our manuscript, which pushed us to think more deeply about certain aspects of the proposed parameterization. Our detailed responses to the reviewer's comments follow. Reviewer comments are in italic font and our responses are in non-italic font.

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.

We have already attempted to convey the range of uncertainties in presenting multiple sensitivity cases that address uncertainties in the surface activities of the compound classes. Information about uncertainties in the underlying ocean biogeochemistry model can be gleaned from Doney et al. (2009). However, a detailed exploration of all the uncertainties is a large project that is beyond the scope of the current paper.

To address the reviewers' concerns on this point, we have significantly expanded the discussion of uncertainties in the discussion section, including adding the following text:

"Additionally, our model is limited by the predictive capabilities of ocean biogeochemistry models, which currently have a limited ability to accurately predict the exact location and timing of phytoplankton blooms (Doney et al., 2009). While the model has some difficulty in exactly reproducing the location and timing of phytoplankton blooms, the patchiness of the active phytoplankton blooms is a realistic qualitative feature. These blooms can be extremely localized, as can also be seen in satellite-derived maps of chlorophyll. This leads to highly localized distributions of the lipid-like class and of OM fraction in our model (Fig. 6 and Fig. 7)."

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 1x10-10 m2s-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 x 10-5 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.

We regard highly the work by Quinn et al. (2014) and Long et al. (2014). Both of these studies were published around the time that our ACPD manuscript was submitted or afterwards. We will address each of these in turn, and we will address Keene et al. (2007) later in our response.

Long et al. (2014)

We agree with the comment that “surface-active material is present in large quantities in seawater independent of Chl a or ocean trophic state”, and this is reflected in our model.

L14 report that artificial sea spray aerosol production rates during the WACS campaign were higher during daytime than during nighttime for biologically productive waters

(high Chl-a), but were constant over the diel cycle (and low) for biologically unproductive waters. However, the total organic mass fraction was similar in both productive and unproductive waters. This suggests that there are differences in the surface chemistry of biologically-productive waters and unproductive waters that can lead to differences in the aerosol production process, even in the absence of changes in the overall organic mass fraction.

Comparison to Quinn et al. (2014)

When looking broadly at published in situ observations of ambient marine aerosol, many studies have found much lower OM fractions observed for fine-mode sea spray aerosol measured in biologically inactive regions and periods compared to the most biologically-active regions and periods (e.g., Barker and Zeitlin, 1972; Hoffman and Duce, 1977; Oppo et al., 1999; O’Dowd et al, 2004; Yoon et al., 2007; Sciare et al., 2009; Ovadaneite et al., 2011; Miyazaki et al., 2011). Since so many studies are in agreement on this point, we feel that ignoring them in favor of the hypothesis that OM fractions in marine aerosol are constant in all times and places equally requires a strong justification.

Instead, we believe that our model offers a mechanism that can satisfactorily explain both sets of observations. In the following, we will show that our model is in agreement with the results of Quinn et al. (2014; hereafter Q14).

The revised manuscript will include several new figures that enable a closer comparison with experimental results: an expanded version of Figure 7 that includes model estimates of the organic mass fraction in May, in addition to the February and August panels already included, an expanded and improved version of Figure 12, including seasonal cycles for all the highlighted ocean regions, and a new figure comparing seasonal cycles in the model with coastal measurements and shipboard measurements (including Q14) in the northwestern North Atlantic, the northeastern North Atlantic, and coastal California and the North Pacific. We will also add a new subsection specifically discussing the Q14 measurements.

The main disagreement between Q14 and our model is that the model predicts that the organic mass fraction is generally higher in regions with higher chlorophyll (ca. 0.2 at the high-Chl-a station and ca. 0.05 at the low-Chl-a station), while Q14 report similar average OM fractions in both regions ([5.6 ± 1.7]% and [5.9 ± 1.9]%, respectively). Given the natural variability of observed mass fraction, however, a larger number of samples would likely be required to detect the relatively small gradient in the organic mass fraction predicted by our model in that region.

On the other hand, the mean enrichment factors during WACS were in fact higher for low-Chl-a samples than for high Chl-a samples, and this difference was statistically significant ($p<0.001$ by a t-test calculated from the values presented in Supplementary Table S1 of Q14), which is consistent with stronger organic enrichment in biologically active waters. Sub-1.1 um enrichment factors in generated aerosol were reported by Q14 to be 1500 ± 460 at Station 1 (high Chl-a) and 2600 ± 900 at Station 2 (low Chl-a); our model predicts enrichment factors in the range 1000–5000 in this region in August (Fig. 7 of ACPD manuscript).

Q14 also presents a second dataset originating from the CalNex field campaign, in coastal waters off the coast of California. Because our model is not designed to simulate coastal processes, and because there may be factors other than ocean biogeochemistry at work, such as runoff from land, and ship pollutants, that field study is less appropriate for comparison with our model.

Nevertheless, we note that our model's predicted OM fraction is within the variability of the CalNex observations, and is similar to the model's prediction in the WACS region (this will be apparent in the new figure comparing model and observations). We also note that the model OM fractions in both the WACS and CalNex regions lack the clear seasonal signal that is present in the model's OM fraction in the North Atlantic and Arctic regions, which are upwind of Mace Head, Ireland.

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 associate 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.

We agree that the literature shows that the surface microlayer is dynamic, although we do not think that the dynamic nature of the surface microlayer and its disruption by waves necessarily negates the relevance of the SML under relatively calm ocean conditions.

However, our parameterization currently does not require an assumption that the SML exists, it only assumes that the ocean-atmosphere interface is coated by organics to the same extent as bubble interiors. Both the interior and exterior surfaces of the bubble film are assumed to be in equilibrium with concentrations in near-surface waters. The ratio of the coating of the bubble film's exterior surface to its interior surface is controlled by the parameter nbub, which can be appropriately viewed as an adjustable parameter within the model.

We will revise the manuscript to clarify this point, by adding the following text:

"The parameter nbub is an adjustable parameter that represents the number of sides of the bubble film that are covered with the areal fraction j_{bub}. The smallest physically meaningful value, $n_{bub} = 1$, implies that only the bubble interior is coated. We assume $n_{bub} = 2$, which implies that the coverage of the interior and exterior films of the bubble are equivalent (Figure 2). Values of $n_{bub} > 2$ would imply an enriched microlayer, which is possible under calm conditions."

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.

We concur that surfactant interactions with other molecules, and the formation of aggregates, are significant uncertainties, as we pointed out in the manuscript. We were unable to address these mechanisms within this initial formulation of the parameterization because of the limited current understanding of these processes. However, we are actively working on approaches to incorporate understanding of these processes in the future.

The fundamental question of whether an equilibrium model is an appropriate choice is an important one. Bubble rise times are on the order of tens of seconds, so even if the time scale estimated by Fuentes et al. is four orders of magnitude too fast and the true equilibrium time is 0.5 s instead of 0.05 ms, it would still be much faster than bubble rise times. Krzan et al., (2007) studied the formation of a steady-state adsorption profile on single rising bubbles for several organic surfactants (C5 – C16). In most cases, the time to reach equilibrium was less than 1 s, which as noted above is much shorter than typical bubble rise times in the ocean.

Mulqueen et al. 2001a,b is an excellent pair of papers of which we were previously unaware, and we thank the reviewer for bringing them to our attention. These papers show experiments and theoretical analysis of experiments in which, with single surfactants, equilibrium was reached on time scales between 2 – 24 s, but in binary mixtures where the less-surface-active component dominates, it occupies the surface more rapidly, and is only gradually replaced by the more surface-active component as it slowly desorbs, leading to a much slower equilibrium time on the order of 100 s. In the example presented in Fig. 8b of Mulqueen et al. (2001b), assuming that equilibrium was reached after only 10 s (instead of >100 s) would result in a 20% overestimate of the fractional surface coverage (0.48 vs. 0.4). However, it would result in a large error in the partitioning of the surface coverage, which after 10 seconds would be about equal between the two surfactants, whereas at equilibrium the more surface-active component entirely out-competes the less-surface-active component, which is barely present on the surface. This suggests that where the equilibrium assumption is not valid, it will result in greater errors in the chemical speciation at the surface than in the total surface coverage.

However, these experiments were performed for adsorption on a still surface, in a situation where molecular diffusion was the only mechanism for transport to the surface. In the case of a rising bubble plume, molecules can encounter surfaces much more efficiently because the bubble plume itself creates small-scale turbulence that increases the frequency of contact far beyond molecular diffusion alone, so adsorption time scales should be shorter. For larger particles (such as marine colloids) interception and impaction are also important. As a result, time scale analyses from stationary systems are not directly applicable to adsorption in a bubble plume. From both theoretical considerations and experimental evidence, it is clear that the actual kinetics of adsorption on bubble plumes depends in a complex way on the chemical nature and bulk concentration of surfactants, and on the size distribution and rise times of bubbles.

The relevance of the kinetics of adsorption on bubble plumes in this context deserves further study. However, since time scales for surfactants reaching equilibrium on bubble surfaces are frequently shorter than bubble rise times, we believe an equilibrium assumption is a reasonable first approximation, until the limitations of this assumption are more fully understood and a more detailed approach is possible. Furthermore, if equilibrium is approached but not fully achieved, the relationship of surface coverage and bulk concentration may still be approximately represented by a Langmuir isotherm curve (with appropriately adjusted parameters). This is supported, e.g., by calculations of the kinetics of the surface coverage of bubbles with surfactants (transferred to the

bubble surface by convective diffusion) as a function of the length of time for which the bubble is exposed to the solution. Results of such detailed kinetic calculations have shown that for bubbles exposed to n-octanol solutions for periods several times shorter than the equilibration time, the relationship between bulk concentration and surface coating is still similar to a Langmuir isotherm, but with a larger value of $C_{1/2}$ (Jachimska et al., 2001). In other words, to a first approximation, assuming equilibrium when the exposure time of the bubble is in fact somewhat shorter than the time required to reach equilibrium would result in the surfactant appearing to be somewhat less strongly adsorbing than it is in reality.

Since bubbles in the ocean span a range of sizes and penetration depths, and ocean surfactants are a complex mixture of species, it will likely not ever be possible to directly simulate the full complexity of these systems in complete chemical detail, but the fidelity of global simulations may ultimately be improved by identifying and incorporating the key processes and variables, particularly those that vary between seasons or ecosystems. We believe our approach offers a path to incorporate a more detailed and mechanistic understanding of the key factors influencing the geographic and seasonal variability of sea spray chemistry, but with a small enough number of variables that it is tractable for implementation in an Earth System modeling context.

To address the reviewer's comment, we will replace the statement that equilibrium is achieved quickly (as estimated by Fuentes et al., 2011) with a short section discussing these issues in more detail:

"It is unclear how rapidly adsorption equilibrium is reached on bubble surfaces in the ocean. Estimates differ widely, for example, Fuentes et al. (2011) estimated an equilibration time scale of less than 0.05 ms for bubbles in a sample of filtered algal exudate, while Krzan et al. (2007) measured adsorption of several organic surfactants on single rising bubbles and observed equilibration to occur in less than 1 s in most cases. The rise velocities in seawater of bubbles with radii greater than 700 μm are in the range 22-35 cm s^{-1} (Patro et al., 2002). Bubble plumes formed by breaking waves penetrate to depths of at ca. 20–30 cm or more (Melville, 1996; Deane and Stokes, 2002), so if equilibrium is reached within less than one second, the exposure time will be sufficient to reach or nearly reach equilibrium for many ocean bubbles. Furthermore, if equilibrium is approached, but not fully achieved, the relationship of surface coverage and bulk concentration may still be represented by a Langmuir isotherm curve (using appropriately adjusted parameters) with fidelity sufficient for application in an Earth System Model. This is supported by calculations of the kinetics of convective-diffusive transport of surfactants to bubble surfaces, and subsequent adsorption (Jachimska et al., 2001).

Because the time scales of surfactant equilibrium in the ocean are similar to or less than bubble rise times in many cases, the assumption of equilibrium is a reasonable and useful first approximation for the purpose of representing bubble adsorption in Earth System models. Further investigation is required to determine under which conditions the assumed Langmuir equilibrium ceases to be a satisfactory approximation, particularly in regards to the equilibrium between competing surfactants (Mulqueen et al., 2001b,a).“

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.

The POP/BEC ocean model is not driven with chlorophyll, rather, chlorophyll is predicted as a diagnostic variable. Prognostic variables in the model include phytoplankton concentrations and semi-labile DOC. We will improve clarity on this point by adding a sentence to the section “Aims and Approach” (in bold font, with the context reproduced here):

Nevertheless, we will show that this approach – applying a well-established basic sur-

face chemistry theory to marine biogeochemistry model output – is capable of reproducing important features of the observed patterns in the SSA organic mass fraction. In particular, it approximately reproduces the increased OM fraction during strong seasonal blooms associated with high Chl a, e.g., in the North Atlantic. **This is significant because the model chlorophyll is not directly used to calculate the OM fraction, in contrast to other parameterizations of the OM fraction that are computed using chlorophyll.**

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.

This is in fact one of the major limitations of our approach. In order to improve understanding of processes and to represent the system in more detail than is possible using a single proxy variable, it is imperative to use a process-based model. Global biogeochemistry models qualitatively and broadly capture many important features of ocean biota and chemical composition, yet they still struggle to accurately reproduce, for instance, the precise location and timing of phytoplankton blooms (Doney et al., 2009), much in the same way that weather prediction models struggle to reproduce the exact location and timing of precipitation events and are nevertheless useful.

We are also actively working toward improving the predictive capability of the CESM biogeochemistry model and have recently submitted a related paper (Ogunro et al., 2014, submitted) that focuses on the oceanic organic concentration.

In response to the reviewers' comments, we have added a sentence to the discussion that points out this limitation and provides a reference for the skill of the CESM ocean biogeochemistry model:

“Additionally, the model's predictive capability is limited by the predictive capabilities of ocean biogeochemistry models, which currently have a limited ability to accurately predict the exact location and timing of phytoplankton blooms (Doney et al., 2009)."

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.

We did not intentionally exclude Keene et al. (2007) from the discussion, but we did focus more on field observations than on laboratory experiments involving sea spray generation. We made this choice in part because laboratory experiments have given contradictory results, and the reasons for this are not yet clearly understood (as summarized in the recent review by Gantt and Meskhidze et al., 2013). However, we are happy to correct this oversight and include K07 in our discussion.

We fully agree that high OM enrichments can be produced from low-chlorophyll waters, and our model is in agreement with K07 on this point. A linear parameterization of OC fraction as a function of chl-a, based on measurements at high-chl-a and at low-chl-a, likely underestimates the amount of OC emitted in intermediate chl-a waters, as was nicely shown by Long et al. (2011) using a Langmuir adsorption-based argument.

To address the referee's comment, we will add a new subsection specifically discussing the K07 measurements, including the following paragraph:

"Keene et al. (2007; hereafter K07) measured the chemical composition of aerosol generated, using a glass frit system, from low-chlorophyll water (Chl-a=0.055) from the Sargasso Sea. The aerosol produced in that had a median enrichment factor for soluble OC of 387, and the OC fraction for the smallest particles produced (0.13 um) was ca. 80%. Using the ``medium'' values of size-resolved aerosol composition reported in K07, we calculate an OC/(OC+inorganics) fraction of 0.26 for 0.75-um particles, and 0.076 for 1.34-um particles. Figure 10 shows that in grid points with Chl-a=0.055, our model predicts submicron OM fractions ranging up to a maximum of about 0.15 (OC

fraction = 0.24, assuming OM:OC = 1.8). This value is in reasonable agreement with the K07 results."

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.

In response to the reviewer's comment, we have revised this sentence to:

"Chl a has been used as a basis for global atmospheric model parameterizations primarily because it is a globally available proxy for ocean biological activity. It is also moderately predictive of the organic aerosol fraction at sites . . ."

The motivation for the use of Chl a as a proxy for surface active material by Long et al. (2011) has already been pointed out later in the same paragraph (p. 5379, l. 24-26).

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

Following the reviewer's suggestion, we have reworded this sentence to read:

"Almost all of the marine OC mass is dissolved organic matter (DOM), which is operationally defined as the portion of marine organic matter that will pass through a filter..."

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.

This sentence contained an error in which “surface concentration” was erroneously substituted for “surface chemistry”. After correcting this error, the sentence reads:

“However, less emphasis will be placed on these classes, because their **surface activity**is generally low.”

P5388-L8: It is not clear why Nbub=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.

It was indeed our intention to suggest that one side of the film is covered with SML material, as discussed in the response to the “second major point”. We note that it is not necessary that enriched concentrations of surfactants be present throughout the top 20-100 microns for this to occur. It only requires the formation of a monolayer on the ocean’s air-water interface, which should form on timescales that are shorter than many bubble rise times and much shorter than the time between waves under even relatively calm conditions, as noted above. We have revised the text to clarify this.

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.

This is indeed a simplification of a very complex process, and we are only asserting that this is a possible partial explanation. However, there is empirical evidence that larger bubbles have thicker films and also produce larger film drops upon bursting from the experiments on film drop production by D. Spiel (1998). We will revise this sentence to make clear the relationship between bubble size, film thickness, and film drop size:

“It may also account in part for the size distribution of the organic mass fraction: since

smaller film drop particles are more frequently produced from the thinner films of smaller bubbles (Spiel, 1998), they would be expected to have a higher organic enrichment than larger particles produced from the thicker films of larger bubble (Oppo et al., 1999; Facchini et al., 2008; Gantt et al., 2011).

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

This sentence did not clearly reflect our intended meaning.

The original sentence read: “The link between Chl a and surface active DOM has been well-established by observations and experiments.”

We will amend this sentence to: “Many studies have identified links between ocean surfactant concentrations and biological activity, which sometimes manifest as a correlation between ocean concentrations of surfactants and Chl a.”

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

The units are correct. The strongest surfactants are the lipid-like group, which we assume has concentrations largely below 6 [μmol C] L^{-1}, which equates to about 0.3 μmol L^{-1} or 95 μg L^{-1} oleic acid. The protein-like group has concentrations in the range . The referee notes that surface pressures measured by Long et al. (2014) indicate that “the theoretical concentration of oleic acid in oligotrophic seawater is on the order of 1 x 10^{-5} M”. Lipids are not shown directly in Fig. 3, however, since their enrichment is so strong that they would appear far to the right of the figure and including them would render the proteins and polysaccharides difficult to display on the same axis.

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

After corresponding with Dr. Long on this point, we have elected not to include this uncertainty range, because it is not readily available in a closed analytical form, and also because it would clutter this figure, which already has a large information density.

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.

Following the reviewer's suggestion, we have worked to improve the readability of the figures' axis labels and subtitles.

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.

To improve readability and organization of the text, we have added some subsection headings in the Results section. We have also revised the wording in some parts of the paper to improve readability, and corrected the ordering of the figures.

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