

Review of: Wonaschütz, A., et al., Hygroscopic properties of organic aerosol particles emitted in the marine atmosphere, *Atmospheric Chemistry and Physics Discussions*, 13, 11919-11969 (2013).

This paper presents results from a truly novel “in situ experiment,” where a plume of primary organic aerosol (mostly hydrocarbon like) was generated in the marine environment. Subsequent changes in the physical and chemical properties of the aerosol were quantified, with a focus on the aerosol hygroscopic properties and CCN. Different behaviors on consecutive days were observed and were likely due to dramatically different meteorology on the different days: one was sunny with lower RH while the other was foggy with much reduced solar radiation. The results are novel and will be of interest to many in the atmospheric science community. I recommend that the paper be accepted for publication after the following issues are addressed.

Overall Comments:

The writing overall is good, but there is a grammatical issue that needs to be addressed: the verb tense oscillates between present and past tense throughout the entire paper. The tense changes several times within paragraphs (and even at times within the same sentence), which is very distracting. Choose a tense and be consistent throughout.

Response: In revising the manuscript, we have paid close attention to inconsistencies in the tense, and applied many corrections. Sometimes, switching between tenses cannot be avoided, though, as there is an inherent difference between discussing what happened during the cruise or what was done to a data set (past tense) and what is visible in a figure and what conclusions are drawn (present tense). Naturally, there are grey zones between the two, but we hope that the text is more consistent now.

I think that the central points of the paper would come through more clearly if the paper were shortened. As an example, Sections 3.1 and 3.5 could be shortened substantially without taking away from the overall findings of the paper. Other sections would also benefit from copy editing to reduce wordiness and extraneous discussion (one example: pg. 11932, lines 4-7).

Response: We have re-arranged the paper according to another reviewer suggestion, thus shortening the paper and simplifying its structure. Chemical composition is now discussed in Section 3.3, the contents of Section 4 (hygroscopic properties in the context of chemical composition measurements) have been moved into corresponding sub-sections of Section 3, and Section 4 has been eliminated. We also made substantial cuts to Sections 3.1 and 3.5 (now Section 3.3).

A focus of the paper is the comparison of GFs for different particle sizes. In some cases, there are very small changes in GFs (for example: abstract, lines 17-20). A discussion of the uncertainty of the GF measurements is surely needed. Are GFs of 1.04 and 1.06 statistically different? (this comment pertains to Section 3.4 as well)

Response: We agree that the discussion of growth factor measurement uncertainty was lacking given the small changes in growth factors reported. We have added a section discussing GF uncertainty

using the results of model calculations (Brechtel and Kreidenweis 2000a, 2000b; Sorooshian et al., 2008) of growth factors. We have added a paragraph discussing growth factor uncertainties to Section 2.3. In this response, we would like to lay out this discussion in more detail than was possible in the paper: As already outlined in the manuscript, the maximum variability of RH in DMA 2 (maximum – minimum measured RH in DMA2 over the duration of a scan) permitted to accept the scan was 3% RH. However, the mean RH in DMA2 from one scan to the next rarely exceeded 1% RH. Shown below are tables of the change in growth factor (ΔGF) of particles of pure ammonium sulfate, sodium chloride, and malonic acid, for a change in RH of 1% (+/- 0.5% of the target RH shown in the leftmost column). For informative purposes, the change in GF at an RH of 42% and 50% are shown for ammonium sulfate and sodium chloride, respectively, those RH values being the lowest for which a growth factor could be calculated. Since the tables consider pure, hydrophilic inorganic and organic substances, they provide a constraint on the uncertainty of the growth factors of the ambient aerosol (likely an internal mixture of more and less hydrophilic components) measured during the campaign.

30 nm	$\Delta GF(\Delta RH = 1\%RH)$		
RH (%)	$(NH_4)_2SO_4$	NaCl	Malonic acid
40	Below efflorescence	Below efflorescence	0.010
42	0.009	Below efflorescence	
50		0.078	
70	0.016	0.025	0.021
85	0.033	0.041	0.045
92	0.066	0.095	0.087

Table 1: Modeled GF uncertainty for inorganic and organic pure particles with a dry size of 30 nm for a RH uncertainty of 1% RH

75 nm	$\Delta GF(\Delta RH = 1\%RH)$		
RH (%)	$(NH_4)_2SO_4$	NaCl	Malonic acid
40	Below efflorescence	Below efflorescence	0.008
42	0.009	Below efflorescence	
50		0.018	
70	0.018	0.025	0.018
85	0.040	0.059	0.042
92	0.093	0.162	0.090

Table 2: As in Table 1, for a dry particle size of 75 nm

150 nm	$\Delta GF(\Delta RH = 1\%RH)$		
RH (%)	$(NH_4)_2SO_4$	NaCl	Malonic acid
40	Below efflorescence	Below efflorescence	0.007
42	0.010	Below efflorescence	
50		0.025	
70	0.018	0.026	0.018
85	0.044	0.066	0.040
92	0.106	0.185	0.090

Table 3: As in Table 1, for a dry particle size of 150 nm

Specific instances of comparisons of growth factors reported in the manuscript are discussed as follows:

Abstract, lines 17-20: Comparing the increase of hygroscopic growth factors (RH = 92%, 30 nm) from 1.05 to 1.09, to the calculated change in GF of pure organic acid particles upon a change in RH from 91.5 to 92.5% (ΔGF 0.08-0.13), we find that the ΔGF of 0.04 lies well within the measurement uncertainty and is therefore not significant. The change from 1.02 to 1.1, a ΔGF of 0.08 for 150 nm

dry size, is not significant, either (ΔGF of malonic acid = 0.09). We have made the according changes in the abstract and Section 3.4 (now 3.5).

The manuscript's Table 2 is shown below, with calculations of ΔGF between the average GFs by regime: While changes in GF of 0.03 and 0.02 would without a doubt be insignificant at the higher values of RH ($\geq 90\%$) typically reported in the literature, they are significant at the RH of 40% under consideration here. As shown in the tables above, ΔGF for malonic acid for a change in RH from 39.5 to 40.5 was calculated to be 0.007. Even if the presence of a mix of organic and inorganic particles leads to a larger ΔGF , as suggested by Hersey et al. (2009), it is unlikely that this would result in a $\Delta GF > 0.02$, as indicated by the ΔGF for pure ammonium sulfate for a change in RH from 41.5 to 42.5%.

150 nm	Regime 1		Regime 2	
RH	mean	σ	mean	σ
40%	1.06	0.03	1.04	0.03
	$\Delta GF = 0.02$, significant			
70%	1.24	0.04	1.21	0.03
	$\Delta GF = 0.03$, significant			
85%	1.44	0.05	1.44	0.05
	$\Delta GF = 0$			
92%	1.66	0.12	1.60	0.10
	$\Delta GF = 0.06$, not significant			

GF plume 18th of July (Section 3.4, now 3.5) increased from 0.94 to 1.47: ΔGF over the consecutive scans is 0.53, therefore significant. RH in DMA2 shows no systematic increase that could alternatively explain the increase in growth.

References (also added to the manuscript):

Brechtel, F. J., and Kreidenweis, S. M.: Predicting Particle Critical Supersaturation from Hygroscopic Growth Measurements in the Humidified TDMA. Part I: Theory and Sensitivity Studies, *J. Atmos. Sci.* 57:1854–1871, 2000a.

Brechtel, F. J., and Kreidenweis, S. M.: Predicting Particle Critical Supersaturation from Hygroscopic Growth Measurements in the Humidified TDMA. Part II: Laboratory and Ambient Studies, *J. Atmos. Sci.* 57:1872–1887, 2000b.

Hersey, S. P., Sorooshian, A., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Aerosol hygroscopicity in the marine atmosphere: A closure study using high-time –resolution, multiple-RH DASH-SP and size-resolved C-ToF-AMS data, *Atmos. Chem. Phys.*, 9, 2543-2554, doi: 10.5194/acp-9-2543-2009, 2009.

The lack of a sea salt measurement (as Na⁺ and Cl⁻) seems to hinder the analysis. Interpretations of changes in CCN/CN are largely based on AMS measurements, which (1) are limited to < 1 μm, and (2) cannot measure sea salt (even in the fine mode). How would changing sea salt concentrations impact any of the stated conclusions, and can the size distribution data (which extend up to 20 μm) be used to constrain the contribution of sea salt to total CCN?

Response: Upcoming work by Modini et al. will deal with the contribution of sea salt to the E-PEACE background aerosol and CCN concentrations in great detail: X-ray Fluorescence (XRF) spectroscopy on aerosol collected on teflon filters is used to measure the concentration of ions heavier than Na, including Na⁺ and Cl⁻. This analysis is used together with size distributions to calculate the contribution of sea salt to CCN. Preliminary results suggest that sea salt did not contribute much to total number concentrations (<15%). Therefore, and in accordance with the wind speed range encountered during the cruise (see also response to comment #4), sea salt likely did not have a controlling influence on the GF measurements.

In particular, we do not think that our conclusions about the aging plume would be changed by detailed knowledge of sea salt concentrations: During the plume tracking events, wind speeds were low (not least, this was a necessary condition to even enable plume tracking by the ship, see also Section 2.6): 3.7 ± 0.9 m/s on 17 July and 5.4 ± 1.3 m/s on 18 July. We take into account an externally mixed sea salt mode for the GF measurements on 18 July (multi-modal fit of GF distributions, Section 3.4, now 3.5), but in all instances, it was a very minor contribution. Even at high wind speeds, sea salt would likely not have a significant influence on in-plume measurements, as plume particle concentrations were much higher than the background.

We do agree that the limitation of AMS measurements to sub-micrometer particles makes it an insufficient tool to characterize the chemical composition of the entire plume, in particular its larger particles. The plume production process itself constrains the initial composition of the particles to a degree (fresh, minimally oxidized organics). But more importantly, the paper focuses on CCN concentrations, which are most sensitive to the large number concentrations of small particles found in the secondary plume particles, and GFs measured at particle sizes that are well within, or at the lower size limit of the AMS.

Specific Comments:

1. The title is misleading – it implies that the organic particles were emitted naturally.

Response: We changed the title of the manuscript to “Hygroscopic properties of smoke-generated aerosol particles emitted in the marine atmosphere” and hope that this eliminates any ambiguity.

2. Since analysis of the plume is the focus of the paper, more detail is needed on the plume generation beyond simply citing the Russell et al. (2013) study: the paraffin-type oil chemical characteristics, aerosol/plume generation method...etc.

Response: We have added a more detailed description of the plume production process. An FTIR analysis of the pure paraffin-type oil is given in Figure 8.

3. For clarity, consider labeling the July 18 plume encounters as B1 and B2.

Response: We have made the suggested change.

4. Pg. 11931, line 13: that the background aerosol was dominated by sulfate and organics seems to be a function of the analysis methods. One would expect sea salt to be a prominent component of the background aerosol during this study. The AMS cannot measure sea salt (which is why the chloride concentration in Fig. 3 seems to have no correlation with wind speed) – this is a limitation that should be explicitly stated. (see above comment as well)

Response: We have made according changes in the wording of the opening statement of section 3.1: “AMS measurements show a background aerosol dominated, in the non-refractory sub-micrometer fraction, by sulfate and organic“. Acknowledging that sea salt is an obvious contributor to marine aerosol, we moved the discussion of its potential contribution based on wind speed and size distributions to the top of the paragraph: “AMS measurements show a background aerosol dominated, in the non-refractory, sub-micrometer fraction, by sulfate and organic (Figure 3). During Regime 1, wind speeds generally stayed below 10 m s^{-1} . In Regime 2, wind speeds were frequently higher than 10 m s^{-1} , but rarely exceeded 15 m s^{-1} . Externally mixed sea salt starts to become an important contributor to marine aerosol at wind speeds exceeding $6 - 10 \text{ m s}^{-1}$ (Ovadnevaite et al., 2012, Swietlicki et al., 2008 and references therein). While higher concentrations of particle volume in the $400 \text{ nm} - 1 \text{ }\mu\text{m}$ range (Figure 3, top panel) during Regime 2 likely have their origin in bubble bursting processes, we do not expect sea salt to have a controlling influence on the plume measurements, which were conducted at low wind speeds during Regime 1.”

AMS measurements have recently been shown to allow quantitative conclusions about sea salt (Ovadnevaite et al., 2012). The lack of a correlation of chloride with wind speed in our measurements is likely due to its non-marine, pollution sources. However, as Section 3.1 serves mostly as a backdrop to the plume measurements, we are not providing a more detailed analysis of sea salt; that will be the subject of the upcoming work by Modini et al. (see response to above comment).

Reference:

Ovadnevaite, J., Ceburnis, D., Canagaratna, M., Berresheim, H., Bialek, J., Martucci, G, Worsnop, D., and O’Dowd, C.: On the effect of wind speed on submicron sea salt mass concentrations and source fluxes, *J Geophys Res*, 117, D16, doi: 10.1029/2011JD017379, 2012.

5. Pg. 11935, lines 20-26: It is not clear why CCN concentrations would increase at the moderate S before they would increase at the higher S ? This does not seem physically possible, and the stated explanation for this behavior is very confusing.

Response: The reviewer is right that this is not physically possible. What appears as increase of CCN concentrations at moderate S before high S is a result of sequential measurements, rather than a true physical effect. We have deleted the confusing discussion from the paragraph.

6. Sections 3.4, 3.5: when contrasting the CCN results with the GF results, care must be taken to put the respective measurements in perspective. The CCN measurements are not size specific in the way that the GF measurements are. Since the GF measurements are limited to $< 300\text{nm}$, these measurements are fundamentally characterizing different regimes in the aerosol distribution – this should be mentioned (e.g., Section 3.4, first sentence mentions this comparison).

Response: We are fully aware of the limitations in comparability. We have added clarifications where this may not have been stressed enough, such as the opening sentence of Section 3.4 (now 3.5), which we changed to: “As opposed to the CCN measurements, which were not size-resolved, the GFs were measured for specific sizes, thus giving direct insight into the properties of the smaller and the larger mode particles.”

7. From the FTIR spectra (Fig. 8), it appears that in plume A3, the strong alkane peaks are gone, or are at least dominated by the hydroxyl peaks – why then is the WSOM:Org ratio still relatively low during A3 (hard to tell from the scale on Fig 7, but it appears to be ~7-20%)?

Response:

We thank the reviewer for pointing out this interesting observation. While we do not have an immediate answer, other than hydroxyl groups and WSOM not necessarily being the same thing, we decided to point it out in Section 3.5 (now 3.3): “For plume age A3, the hydroxyl peaks are a large feature. The concurrent low ratios of WSOM:Org (0.07) reflect the fact that WSOM and hydroxyl groups are not directly correlated.”

8. From Figure 7, it appears as though the grey shaded region (labeled ‘A3’) represents time in the plume and significant ‘dilute’ (background) sampling as well? Was the entire shaded region depicted in Fig. 7 used for the A3 analysis? If so, how is this justified?

Response: This was an error on our part and we thank the reviewers for pointing it out. Plume sampling period A3 according to the in-plume definition $\text{org:sulfate} > 5$ was indeed shorter than indicated by the grey shading. We have corrected the error and updated Figure 7 (now Figure 6), Figure 9 (now Figure 8) and Figure 6 (now Figure 10).

9. Figure 6: x-axis scale (i.e., horizontal scale of one hour) should be consistent for top and bottom panels.

Response: We have made the suggested change.

10. Pg. 11937, line 9: is there a statistically significant difference between GFs of 1.05 and 1.09? (see above comment)

Response: See detailed response on GF uncertainties above.

11. Pg. 11937, line 14: say "...those observed within the plume")...

Response: We have made the suggested change.

12. Pg. 11939, line 13-14: what were the WSOM and AMS org. concentrations at points A1 and A2? These should be given for comparison.

Response: We have added the maximum concentration of WSOM during A1 and of AMS org during A1 and A2. The section in the paragraph now reads: "The maximum concentrations of AMS total organic mass and WSOM during plume age A1 are $885.67 \mu\text{g m}^{-3}$ and $4.16 \mu\text{g m}^{-3}$, respectively. An interesting aspect is the increase of absolute concentrations of WSOM during A2: from $3.44 \mu\text{g m}^{-3}$ at 11:38 to $4.96 \mu\text{g m}^{-3}$ at 12:32. Since the typical background WSOM concentrations were below $1 \mu\text{g m}^{-3}$, mixing of the plume with background aerosol cannot explain this increase. Rather, it is likely that WSOM formed in the plume, potentially contributing to the observed growth of newly formed particles. In the most aged plume (A3), WSOM and AMS total organic concentrations still reach 3.4 and $48.4 \mu\text{g m}^{-3}$, respectively, showing that WSOM from SOA production largely compensated for plume dilution."

13. Pg. 11942, line 17-18 "inorganic mass fractions were very low at all particle sizes" – Clarify that this only applies to sub-1 μm particles.

Response: The sentence has been removed during editing.

14. Pg. 11927, line 3: what fraction of scans were accepted/discarded? This should be stated.

Response: 75% of the scans were accepted. We have added this information in Section 2.3.

15. Pg. 11927, line 27: is there an error in one of the diameters given: 266 nm (midpoint: 946 nm)?

Response: What we were trying to explain is the fact that due to the increase of the size bins in the distributions with increasing particle size, the smoothing over 11 size bins is a smoothing between 11.6 and 32.8 nm (total averaging width = 21 nm) for a midpoint of 21 nm, and a smoothing between 847 and 1113 nm (total averaging width = 266 nm). We arrived at the conclusion that this level of detail may be too wordy and have simplified the sentence as follows: "Since the measured masses were close to the detection limit, the size distributions were smoothed over 11 size bins, resulting in a smoothed size distribution between 21 and 946 nm."

16. Pg. 11936, line 25: delete 'ship'

Response: We have made the suggested change.

17. Pg. 11944, line 16: change 'cloud' to either 'fog' or 'aqueous'

Response: We changed “cloud” to “aqueous-phase”: “its simultaneous detection with glyoxylate only on 18 July suggests that aqueous-phase processing was an important factor on that day.”

18. Pg. 11944, line 23: see comment above on the title – saying organic particles “emitted” in the marine atmosphere is misleading and suggests they are naturally occurring

Response: In accordance with the new title, the sentence now reads: “We have shown substantial differences in hygroscopic growth and CCN activity of smoke-generated organic particles emitted in the marine atmosphere under different meteorological conditions.”