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Correspondence/Rebuttal

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Rebuttal to Correspondence on "Changes in Droplet Surface Tension Affect the Observed Hygroscopicity of Photochemically Aged Biomass Burning Aerosol"

In a comment on our publication "Changes in Droplet Surface Tension Affect the Observed Hygroscopicity of Photochemically Aged Biomass Burning Aerosol",[1] Raatikainen and Laaksonen raise an interesting discussion regarding surfactant partitioning. The commenters posit that including surfactant partitioning in the analysis (though under a different set of assumptions than put forth in the article) negates surfactant effects and thus has little to no impact on calculated hygroscopicity. We thank the commenters for their analysis and believe that this discussion is valuable to the community but we must respectfully highlight concerns regarding their partitioning analysis to this work.

The authors cite three key papers in the development of the partitioning model.[2−4] In all three papers, model surfactants are used with known inorganic mixtures to model the nature of surfactant partitioning. These partitioning models thus impose a lower-bound limit to surface tension effects of known compounds. The assumptions in these models must therefore be examined before application to complex systems.

The commenter's model is subject to a number of assumptions.[4] We have included a short list of the questionable assumptions and concerns as to why they may not be applied to biomass burning systems.

(1) *Equilibrium is established between different phases within the droplet solution systems and with respect to the surroundings, and no kinetic effects influence solution properties or droplet growth activation.*

(2) *Dry particles are spherical, such that the volume-equivalent diameter equals the selected electrical-mobility diameter and no mobility shape-factor is applied.*

Some recent studies have definitively shown that biomass burning particles are not spherical[eg.5] These studies are in agreement with our own soon to be submitted work. APM and TEM analysis show effective densities and particle morphologies that show the spherical assumption for these particles is incorrect. For a shape factor >1, the mobility diameter derived volume is greater than the true volume of the particle, for example, ref 6. Additionally, a nonspherical particle will have a different surface area than a spherical particle which could have profound effects on the kinetics of, for example, species dissolution in the droplet, the volume of a (potentially surface-active) film on the particle, and/or any assumptions of the droplet surface during droplet formation.

(3) *All components in the dry particle mixtures and aqueous droplet solutions have zero excess mixing volumes.*

This is an ideal thermodynamic assumption that may not necessarily be applied to nonideal organic-water interactions.

(4) *All dry particle components are infinitely soluble in the aqueous droplet solutions.*

(5) *All species in solution are fully dissociated.*

Dinar et al.,[7] experimentally calculated the dissociation of SRFA, a model for HULIS, at ∼20%, much less than full dissociation. While not all models for HULIS may behave the same, a 100% dissociation is of concern.

(6) *Droplet solution surface tensions are limited to the estimated minimum values at the approximate ternary critical micelle concentrations (cmcs).*

The commenter's model sets the lower-limit of surface tension using this assumption. The authors of Prisle et al.[3] themselves note that "ternary solution cmcs and minimum surface tensions will in general depend on both surfactant and salt solutes." This lower-limit is a fine assumption but the comments should reflect that the model calculations use it.

(7) *The partitioning equilibrium conserves total molar amounts and volumes of the individual droplet components.*

(8) *The molar ratios of droplet species other than surfactant are fixed.*

While this assumption is fine for a binary or ternary system of known composition, it may not be correct for the complex aerosol system that is biomass burning.

9) *Only 10% of the organic particulate material is assumed to be surface active in the commenter's model.*

While we agree that 100% of the organics being surface active is a bit high, the commenters offer no justification for why 10% is realistic.

To summarize, the article "Changes in Droplet Surface Tension Affect the Observed Hygroscopicity of Photochemically Aged Biomass Burning Aerosol"[1] aimed to offer a possible explanation for why sub- and supersaturated biomass burning hygroscopicity measurements differed. Furthermore, we put forth that majority of aerosol contained water-soluble surface active organic HULIS. We concluded that, by explicitly assuming all of our organic material was surface active, accounting for surface tension could reconcile these two measurements of hygroscopicity. If it was not explicitly stated, we would like to stress that our calculation is an upper-limit of surface tension effects. Moreover, this upper-limit is able to reconcile discrepancies in sub- and supersaturated data sets.

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Notes

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We again thank the commenters for their interest in our article. We highly regard their work in the field but believe their analysis offers a low-end limit to the importance of particle surface tension in hygroscopicity while we offer observations in the higher-end limit. The truth is likely between the two and we believe both limits should be known so the best estimations of biomass burning aerosol to the global CCN budget can be determined.

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