Review of “Composition of 15-80 nm particles in marine air”

This paper discusses a combined TDCIMS and HTDMA approach to understanding aerosol composition and hygroscopicity for marine aerosol in the relatively pristine environment of Mace Head, Ireland. The TDCIMS data in the ~50 nm size range has the potential to be a very useful addition to the understanding of sea spray aerosol < 100 nm. While TDCIMS is a promising technique for marine aerosol analysis, the paper needs further lab test to quantify instrumental issues, does not sufficiently justify its conclusions, makes very broad claims without sufficient support from the data (in particularly in light of instrumental limitations), and does not consider related work. Specifically, the paper is missing discussion of much of the most recent sea spray aerosol literature, a great dealt of which directly relates to particles in this size range. With some new lab calibrations/quantification and further analysis/justification the manuscript could be publishable in the future. However, as is there are significant shortcomings to this manuscript and it is not publishable in the current form.

Major Points

- At a number of points in the manuscript the authors discuss a differential in sensitivity where sensitivity to nitrate > sulfate > chloride. A rough value of 100x greater sensitivity is given for ammonium nitrate > ammonium sulfate, but no quantitative value is given for the sensitivity of sulfate versus chloride (other than stating “TDCIMS sensitivity to sulfate was likely slightly higher than to chloride”). The authors do not discuss the sensitivity to sodium nitrate, which is likely the form of the nitrate in sea salt particles (through the traditional chloride displacement mechanism). Given the emphasis that the authors place on Cl^-/SO_2^- ratios and other rationalizations as to how the sulfate is from 1 source (nucleation) and chloride from another (sea salt) this needs to be addressed more rigorously and is a major deficiency in the paper. An example of why this is needed is that chloride/sulfate ratios of 1-3 compared to a seawater ratio of 17:1 (chloride/sulfate) are used as justification for the sulfate coming from nucleation. However, if the instrument is more sensitive to sulfate a value is needed to clearly show that this difference is not due to differing sensitivities. The sulfate might not be as enhanced as the paper indicates in part due to the temperature of the heating element (in this case 600 C). NaCl has a boiling point of ~1400 C and very likely won’t be volatilized to a great extent at 600C this at least it might partially explain the relative sulfate enhancement. If calibration data exist showing that Cl is being efficiently volatilized at 600C (or at least is of similar magnitude to sulfate as suggested) it would greatly strengthen the authors’ case. Without a more quantitative justification that the sulfate is truly substantially enhanced a key finding of the paper is not sufficiently supported. Overall, more quantitative discussion of sensitivities to different species is needed.
- In the abstract, discussion, and conclusions sections that authors discuss nucleation events involving sulfuric acid and organics, which are attributed to biological sulfur sources. Considering the instrumental limitations regarding chloride vs. sulfate (discussed above) further information is needed to substantiate these claims. Perhaps the authors could use satellite chlorophyll to show that there was sufficient biological activity to generate enough DMS to lead to the nucleation and growth. Also there is a bit of a discrepancy between the abstract where the authors claim the growth is due to sulfuric acid and in the paper where it is attributed to organics (which is in line with the literature). This should be made consistent. Since a mode of primary OC-sulfate particles from wave breaking

have been observed with a lower kappa than salts,[1-4] further evidence is needed that these events are from nucleation than is presented.

- The authors in this work do not discuss a great deal of the recent literature regarding sea spray aerosol generation, including publications from the groups of Keene, Bigg, Prather, Fuentes, Bates, Quinn, Facchini, Leck, etc. Many of these groups are leaders in the fields of marine aerosol research and not a single paper is referenced from any of them. This lack of discussion does not place the work in the appropriate context and is a significant shortcoming. Examples of issues that should be addressed including the following.
    - Bigg and Leck have argued that no NaCl is present in particles less than 200-300 nm, a direct contradiction to this work. While the authors' observations agree with Clarke, it is important to at least discuss how these findings fit into the hotly debated topic of < 200 nm particle composition.[5] Numerous other papers from this group discuss particles in this size range with electron microscopy.[6]
    - Facchini has shown that water soluble organic material grows in substantially at smaller sizes.[7] Since the instrument has limited abilities to see organic material (WIOM), the potential for this WIOM to play a role in the lower GF more should be discussed. Further discussion of the organic components as studied through NMR and other techniques is important to discuss with the lack of organic information from this work.[8,9]
    - Prather and the CAICE center have shown that there are different populations of particles within sea spray aerosol that could also explain many of the findings in this paper. In Prather et al. 2013, 3 different populations of particles are shown for sea spray aerosol (OC (with sulfate), SS-OC, and SS).[3] At ~60 nm particles ranged from mostly SS-OC to mostly OC under different seawater conditions[2] and these two types had vastly different Kappa values which could explain the GF's observed.[1] Since these particles were produced and sampled in a matter of seconds and no evidence for nucleation in the sealed ocean-atmosphere wave apparatus was observed the possibility that primary OC-sulfate could be contributing to this lower GF mode should be considered.
    - Fuentes has shown a range of kappa values under different seawater conditions, which would likely lead to different growth factors as well. This could explain the range of GFs without aging or nucleation as the paper suggests.[4,10]
- In the discussion the authors assert that they are observing a progression of fresh sea salt to aged that has a lower hygroscopicity. This possible explanation is not well supported beyond stating there is a lower GF mode. First, as sea salt particles age they likely take up nitric acid and displace chloride, which will only serve to increase their hygroscopicity. One possible explanation is that with decreasing pH a phase separation occurs with a concentrated organic layer forming on the outside of the particle that lowers the GF as suggested in Ault et al last year.[11] The more likely explanation though is that the relative proportions of different primary particles formed through bubble bursting has changed.[6] Sea spray aerosol particles from regions with different seawater composition can easily have greater primary organic or salt/organic mixtures that would lead to a second mode. Both an active mode and a less active mode have been observed simultaneously under many seawater conditions as f(size).[3] Further justification of why the "aged" salt-containing particles have a lower GF and are aged versus coming from different seawater should be added.

Minor Points

- Why is no positive TD-CIMS spectrum shown? It would be helpful to support the negative spectrum given in figure 2.
- In section 3.3.3 “time series presented in Fig. 3” are referenced, however Fig 3 is of GF data. This should be corrected/clarified.
- A little bit more information regarding the 50% uncertainties for mass should be given in the methods section.

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