

## ***Interactive comment on “Separating refractory and non-refractory particulate chloride and estimating chloride depletion by aerosol mass spectrometry in a marine environment” by I. Nuaaman et al.***

### **Anonymous Referee #1**

Received and published: 8 February 2015

This paper covers measurements of sea salt using the Aerodyne AMS aboard the RV Atlantis during CalNex. Measurements of sea salt, while highly desirable, have tended to be notoriously difficult on the AMS, with various groups getting mixed results as to the quantitative capabilities. By comparing ambient data with that from the Sea Sweep, the authors here present a methodology to not just quantify submicron seasalt mass, but also the amount of chloride depletion within the sea salt.

This is certainly a very interesting piece of work and will no doubt make a contribution

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to the general technical development of AMS measurements in marine environments and also the atmospheric measurements from CalNex. The paper isn't without its flaws; there are a number of issues I would like to see addressed (below). What I would consider the most important would be that the paper refocus slightly to place a greater emphasis on the atmospheric findings and to deal with the subject of surface ionisation, or rather the lack of in this work, as this has proved a major technical hurdle in the past. However, these should be straightforward to address and given that the paper is generally well-written, I don't foresee any reason why it can't be published otherwise.

#### General comments:

This paper is very technical in nature and as such, risks being more suited to AMT rather than ACP. For the sake of being more applicable to general atmospheric science, I suggest that a greater emphasis be placed on the interpretation of the ambient results. For example, did the periods of high Chloride displacement detected coincide with periods of high tracers of certain pollutants, e.g. NO<sub>z</sub>?

The methodology proposed here has quite a number of similarities with Ovadnevaite et al. (2012). While this paper is referred to many times, it would be of great benefit to the reader if the authors could include a section systematically detailing the specifics of how their proposed technique compares with this and why (this is touched on in section 3.5, but it would be more informative to cover it during the methodology section and in more detail). In this context, it would also be worth comparing against the earlier work of Allan et al. (J. Geophys. Res.-Atmos., 109, D23S24, doi:10.1029/2003JD004208, 2004).

The lens transmission efficiency and the collection efficiency of the AMS probably deserve more discussion than they get, which are both fundamental issues when it comes to quantification. Specifically, the authors should refer to any data they have on how well their system conforms to the nominal performance and what fraction the 'submi-

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cron' fraction represents of the total sea salt mass (or at least, the amount getting through the cutoff of the ship's inlet system). The authors should also really include a more in depth discussion on the collection efficiency as well; anecdotally, attempts to quantify sea salt aerosol have been met with mixed results and it has been suggested that the phase of the particles (resulting from the inlet relative humidity) may be a factor, meaning that sea salt particles can have a different (presumed lower) CE compared to the accumulation mode (nominally 0.5) under dry conditions. Ovadnevaite et al. (2012) used an inlet without any drying and the sampling humidity used here should be specified (while the humidity of the ship inlet system is specified, it is not clear whether this humidity is maintained to the instrument).

A recurring problem with AMS measurements of sodium and potassium is surface ionisation (as opposed to electron ionisation), which produces large but non-quantitative signals. The mass spectrum in figure 1 would imply that this isn't a problem here, but the authors should confirm that they believe this is the case. They should also say if any special tuning was needed to remove this problem.

As regards the fraction of chloride displacement, no discussion is given here to the nitrate concentrations, which would seem pertinent because nitrate from  $\text{NaNO}_3$  is detectable by the AMS, albeit potentially with a different sensitivity to  $\text{NH}_4\text{NO}_3$ . The authors should comment on whether this could be reconciled with the measured chloride displacement and whether there is any insight into the different types of nitrate detectable.

Specific comments:

P2088, L13: The formation of  $\text{NH}_4\text{Cl}$  being dependent on the neutralisation of sulphuric (and also nitric) acid is more than a 'reported' phenomenon. This has a firm basis in the thermodynamic properties of the components and can be predicted using established models such as E-AIM (e.g. Clegg et al., J. Phys. Chem. A, 102, 2155-2171, 1998).

P2089, L12: 'Submicron' and 700nm would be considered contradictory. A clarification

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should be given.

P2093, L25: The authors need to be more specific than 'metal ions', as this would encompass sodium, potassium, magnesium etc. Where were these metals coming from?

P2095, L5: Mineral silicates would be expected to be far too refractory for the AMS to detect (more so than sea salt), so where was the  $\text{SO}_2^+$  signal coming from? If this was from silicone tubing, this should be stated.

P2095, L17: The alternation frequency of the chopper should be stated, as this can affect the relative signals for slow-vaporisation species.

P2095, L24: Was the decay of the background signals exponential? If so, the decay constants (expressed as an e folding time or half-life) should be reported. If not, more detail should be given on how the authors class 'complete disappearance'.

P2103, L27: As regards regular calibrations, would it be sufficient to used nebulised sea salt if a future user did not have access to a sea sweep? Was this tried as part of this work?

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 2085, 2015.

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