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Atmospheric Chemistry and Physics Discussions

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 #2

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General Comments

This manuscript reports an analysis by a productive and well-respected group of investigators that addresses a topic relevant for publication in ACP. Based on measurements of Cl- and Na+ in filter samples of freshly produced and ambient submicron marine aerosol in coastal California, the authors interpret paired measurements with an HR-AMS to differentiate "refractory" versus "non-refractory" components of ambient particulate Cl- concentrations and to estimate associated Cl- depletions. Unfortunately, as

detailed under specific comments below, several issues make the presentation rather difficult to follow and also raise concerns about the reliability and general applicability of results based on the reported approach.

- The discussion of factors that regulate the gas-aerosol phase partitioning of Cl-containing compounds is rather vague and in many respects inconsistent with current understanding based on both experimental evidence and theory as implemented in thermodynamic and numerical models.

- The term “non-sea-salt” (nss) as employed by the authors is not consistent with that traditionally used in the literature and the distinction between “nss” versus “non-refractory” in the text is often ambiguous. These are not synonymous terms.

- Several critical assumptions on which the analysis is based are either not stated or are not justified.

- The large accumulated uncertainties associated with the calculated results are mentioned in passing but not addressed quantitatively.

The broader scientific implications and relevance of this work are also unclear. The introduction mentions the importance of primary and secondary sources for particulate Cl in coastal regions but any credible investigation of associated chemical processes must consider the supermicron size fractions, which account for virtually all particulate Cl emitted from the ocean to the atmosphere and virtually all volatile Cl produced by subsequent chemical transformations. In addition, the chemical evolution of submicron size fractions is coupled with that of supermicron size fractions through interactions with the same gas phase. Because the AMS is not able to characterize the composition of supermicron particles, process-level interpretations of results with respect to Cl chemistry are inherently problematic. I encourage the authors to elaborate on how interpretations of AMS data based on the reported approach will further scientific understanding.

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Specific Comments

The title refers to a “marine environment” but, as discussed in the manuscript, the investigation focused on coastal air that was heavily impacted by urban emissions during periods of off shore flow. Consequently, the study region might be more appropriately characterized as a “polluted coastal environment” rather than a “marine environment.”

Page 2087, lines 66-79 to page 2088, line 15 and page 2088, lines 25 to 28. The discussion regarding the gas-aerosol phase partitioning of HCl and NH3 in marine air in terms of “reversible formation of ammonium chloride” is confusing. The equilibrium phase partitioning of these gases is controlled by their respective Henry’s Law and dissociation constants and associated temperature dependencies, aerosol liquid water content, and solution pH (e.g., see papers by S. Clegg and co-workers and R. Sander and co-workers and the corresponding E-AIM model and MECCA chemical scheme, respectively, both of which are available on line; among others). Using HCl as an example,

HClg $\leftrightarrow$ {HClaq} $\leftrightarrow$ {H+} + {Cl-}

Note that NH3 does not appear explicitly in the above expression. NH3 impacts the partitioning of HCl only indirectly through its influences on aerosol solution pH, hygoscopicity, and ion activities. The same is true for the impact of HCl on NH3 phase partitioning. Acids other than HCl also influence solution pH, liquid water content, and ion activities so there is no direct correspondence between the gas-aerosol phase partitioning of HCl and NH3.

In addition, based on its thermodynamic properties, HCl in marine air partitions preferentially with the less acidic supermicron-diameter size fractions of deliquesced aerosols, virtually all condensed Cl is ionized, and most particulate Cl- is typically in the form of dissolved NaCl. Conversely, NH3 in marine air partitions preferentially with the more acidic submicron-diameter size fractions, virtually all condensed NH4 is ionized, and most NH4+ is typically in the form of dissolved NH4HSO4 [e.g., Huebert et

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al., 1996, JGR; among others]. In contrast to the authors' suggestion in this section, it is evident from the above that HCl and NH3 cycling in marine air is largely decoupled and not directly related to "reversible formation of ammonium chloride." In addition, NH3 does not have a preferential "affinity" for H2SO4 versus HCl. As indicated above, NH3 partitions preferentially as a function of solution pH and, thus, the mixture of acids and bases in the system and their respective thermodynamic properties; size-resolved aerosol loadings, composition, associated hygroscopicities, and lifetimes against deposition; and physical conditions. The solubility of NH3 in circumneutral or alkaline solutions is quite low. The text should be revised accordingly.

Page 2088, lines 23 to 25. N2O5 is not an acid and, thus, does not drive acid displacement directly. Some fraction of N2O5 hydrolyzes at aerosol surfaces to produce HNO3 [e.g., Behnke et al., 1997, JGR], which can displace HCl from deliquesced aerosol. The text should be clarified.

Page 2089, lines 6 to 9. Model calculations suggest that significant atomic Cl is also produced from the photolysis of BrCl and HOCl [e.g., Keene et al., 2009, ACP].

Page 2090, lines 16 to 17. What is the rationale for characterizing the calculated concentration of nssCl as "more volatile?" Relative to what is its volatility gauged?

More generally, the authors' definition of nss is not consistent with typical usage in the literature. Nss components of marine aerosol have traditionally been inferred based on the following standard approach [e.g., Huebert et al., 1996, JGR; Savoie et al., 2002, JGR; among others] (using Cl- as an example):

nss Cl- = measured Cl- – ss Cl-

where ss Cl- is the original amount of Cl- associated with freshly produced marine aerosol prior to chemical processing. Ss Cl- is estimated from the measured concentration of a conservative sea-salt reference species (typically Na+ or Mg2+) and the corresponding ratio of Cl- to the reference species in seawater. For example:

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ss Cl- = measured Na+ * (Cl- / Na+)seawater

Based on the above approach, nss contributions would correspond to measured Cl- concentrations greater than ss Cl-. However, as discussed later in the manuscript and illustrated in Figure 9, marine aerosol is typically depleted in Cl- relative to conservative sea-salt tracers yielding negative concentrations of nss Cl- (commonly referred to as Cl- deficits relative to sea salt) based on the above relationships. Such deficits reflect losses of ss Cl- via formation and volatilization of HCl and other Cl-containing gases.

In the authors approach, measured Cl- concentrations less than ss Cl- include contributions from both ss and nss components, which is not consistent with the traditional definition of nss Cl- as detailed above. To minimize the potential for confusion, the distinction between the authors' definition of nss and the traditional usage should be explained or, preferably, alternative terminology specific to the authors' approach adopted.

Page 2091, lines 20 to 23. Earlier in this section, the authors indicate that aerosol characterized by the HR-AMS corresponds to the size range of 70- to 700-nm diameter at 55% RH. Here they indicate that the collection efficiency was quantified via comparison with non-refractory aerosol constituents sampled in parallel on filters and measured in parallel with a quadripole AMS. It would be appropriate to indicate here the size range for aerosol sampled on filters (presumably particles less than 1.1 micrometer diameter at 60% RH as noted later in the methods section). It would also be helpful to specify the size range characterized by the quadripole AMS. Were the paired data used to estimate the collection efficiency for the HR-AMS adjusted (and if so how) to account for differences in size ranges? If not, what are the implications for the inferred collection efficiency and associated results? If data from the quadripole AMS were also corrected based on an inferred collection efficiency, is it reasonable to employ those results as a reliable reference with which to estimate a collection efficiency for the HR-AMS? Finally, it would be appropriate to also mention the non-refractory constituents used in the analysis, the numbers of paired samples that were compared, and the associated

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uncertainties.

Page 2092, line 25 to 2093, line 3. It would be helpful to mention the type of filter material that was used. Also, as described in detail later in the manuscript, the authors' analysis is based on the premise that particulate Cl- measured using this approach exhibits significant negative bias due to artifact volatilization of Cl-containing compounds from samples. To my knowledge, the co-authors who generated these data (Bates and Quinn) have not previously reported artifacts of this nature involving this measurement technique. If such problems are known, it would be appropriate to describe them here since this issue is directly relevant to the authors' analysis.

Page 2093, lines 10 to 12. Are direct reactions between freshly produced and ambient particles considered to be a serious problem for this experimental design as suggested here? Don't the authors mean "... not modified by mixing with ambient particles or reactions with ambient gases ..."?

Page 2094, lines 8 to 9 and elsewhere. What it the rational for attributing the HxCl+ signal to NaCl as opposed to other chlorine-containing salts (e.g., MgCl) associated with freshly produced and subsequently dried marine aerosol? Not all Cl- in fresh marine aerosol is balanced on an equivalent basis by Na+.

Page 2095, lines 2 to 3. Presumably, the authors are referring here to signals corresponding to sea salt in ambient air as suggested by the title of the section. Later in the paragraph and in the cited Figure 2, data from both ambient air and sea sweep are mentioned. The text should be clarified.

Page 2096, lines 1 to 3. Suggest specifying the duration of the time periods that were eliminated. Comparisons among the time-series figures (5, 6, 7, And 9) indicate that the durations of eliminated periods varied among analytes and that, for a given analyte, the durations of eliminated periods were not identical.

Page 2096, lines 4 to 14 and elsewhere in the text. The characterization of particulate

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Cl associated with HCl and NH4Cl in marine aerosols as “nssCl” is misleading. Certainly, contributions for nss Cl from combustion and industrial sources may be important during periods of heavily polluted urban outflow. However, as indicated in some of the cited literature, virtually all particulate Cl (and Cl associated with volatile reaction products) in marine air was originally emitted from the ocean surface as a component of primary marine aerosol. The corresponding H+ and NH4+ in ambient marine aerosol originate from multiphase chemical transformations subsequent to aerosol production (i.e., acid displacement and NH3 condensation, respectively) but virtually all of the associated Cl does not originate from nss sources and, thus, should not be characterized as nssCl. Rather than sea-salt versus nss Cl, it appears that the authors are attempting to differentiate contributions of relatively more refractory versus relatively less refractory Cl-containing compounds in dried marine aerosol measured with a HR-AMS. The terminology here and elsewhere should be clarified.

Page 2096, lines 25 to 27. Earlier in the paragraph, the authors state that “Na35Cl+ is expected to result exclusively from the ionization of NaCl.” On line 291, they state this expectation as a fact. If this expectation corresponds to an assumption, the statement should be revised accordingly. Alternatively, if the source of Na35Cl+ has been demonstrated conclusively, a supporting reference should be added and the text clarified.

As mentioned above, not all Cl- in either fresh or aged submicron marine aerosol is balanced by Na+ on an equivalent basis. What is the rationale for assuming that “the ratio HxCl+/Na35Cl+ for sea salt chloride” results exclusively from NaCl?

Page 2097, 1ines 1-21 and Figure 3. As indicated earlier in the manuscript, the relative composition of ambient marine aerosol is not conservative with respect to seawater and, consequently, “sea-salt” mass inferred from equation 2 is unreliable. For example, in polluted coastal CA, any HCO3- associated with freshly produced submicron diameter marine aerosol would be titrated within seconds to a few minutes following injection from the ocean into the atmosphere via incorporation of acids and acid precursors from the gas phase and the CO2 titrations product would rapidly volatilize from

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the aerosol [e.g., Chameides and Stelson, 1992, JGR; among others]. Consequently, this approach does not provide a reliable estimate for the mass of inorganic sea-salt components associated with ambient marine aerosol. In addition, comparison with an assumed sea-salt mass is not necessary to support the primary point. The corresponding correlations with measured Na+ and Cl- (from which sea-salt mass was inferred from Eq. 2) are adequate for this purpose.

It should be mentioned here that some (and perhaps most) of the scatter around the slopes reflects measurement uncertainty. Adding error bars that depict these uncertainties to the data points in Figure 3 would be useful to illustrate this point.

Figure 3. Normally the dependent variable (Na35Cl+) would be plotted on the Y axis and the reference variable(s) on the X axis. Suggest reversing.

The approach used to regress the data should be specified. Since both sets of paired data are subject to significant uncertainty, the Reduced Major Axis procedure would be the most appropriate technique.

Page 2097, line 28 to page 2098 line 18, Figure 4, and elsewhere in the text. I don't follow this interpretation. The comparison between the ratios of these analytes in sea sweep versus ambient aerosol as depicted in Figure 4 indicate that, on average, (1) concentrations of Cl-containing components of sea sweep aerosol per unit volume of air measured by the AMS were relatively higher than those of ambient aerosol (consistent with data shown in Figure 2) and (2) ratios of HxCl+/Na35Cl+ in sea sweep aerosol measured by the AMS were relatively lower than those in ambient aerosol. While it is evident that the ratios tend to vary directionally in response to chemical processing, these results reveal nothing about the factors that drive this directional variability or the corresponding sources (ss versus nss) for the particulate Cl. As indicated above, chemical processing alone does not change the original source of the Cl. "Nss" is not synonymous with "non-refractory". The text should be revised.

More importantly, the authors' interpretation of these relationships appears to be based

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on the implicit but unstated assumption that the Na35Cl+ signal is conservative with respect to chemical processing and, thus, the relatively higher ratios of HxCl+/Na35Cl+ in ambient aerosol reflect "additional contributions" of nssCl (or non-refractory Cl) to the HxCl+ signal. However, the rational for this assumption is unclear and should be justified. The sea sweep data in Figure 4 indicate that freshly produced aerosol yield significant HxCl+ signals prior to chemical processing and, thus, independent of any "additional contributions" from nss sources. In addition, ambient submicron marine aerosol are typically depleted significantly in Cl- relative to freshly produced marine aerosol (e.g., Fig. 9). Consequently, it would seem reasonable to expect that the associated conversion of most NaCl to NaNO3 and Na2SO4 in ambient submicron aerosol (via acid displacement and volatile loss of HCl following incorporation of HNO3 and H2SO4, respectively) would result in proportionately lower contributions of NaCl to the Na35Cl+ signal in ambient relative to freshly produced marine aerosol. What is the rationale for assuming that the higher HxCl+/Na35Cl+ ratios for ambient aerosols were driven exclusively or even primarily by increased contributions of nss species to the HxCl+ signal as opposed to decreased contributions of ss NaCl to the Na35Cl+ signal? The entire analysis seems to hinge on this key but unjustified assumption.

Page 2098, lines 19 to 21, page 2099, lines 11 to 13, and elsewhere. If the nssCl compounds are volatile as suggested by the authors, why would they partition into the particulate phase in ambient air but evaporate from particles when sampled on a filter? I appreciate that large pressure drops can cause significant artifact volatilization of semi-volatile compounds but it appears that the data reported by the authors correspond to samples collected on quartz fiber filters (this should be specified in the methods section), which correspond to relatively low pressure drops and associated artifacts of this nature. The rationale for assuming significant losses of volatile Cl compounds from submicron aerosols sampled on a fiber filter should be supported with citations. This is another key but unjustifed assumption involved in the analysis.

As indicated above, the equilibrium phase partitioning of HCl and NH3 between the gas

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phase and submicron particles in both ambient air and samples of submicron aerosol is regulated by thermodynamics. Significant HCl may evaporate from marine aerosol sampled in bulk because the pH of the bulk mixture on a filter is typically lower than the pH of the supermicron size fractions with which most HCl partitions in ambient air. Similarly, significant NH3 may evaporate from marine aerosol sampled in bulk because the pH of the bulk mixture on a filter is typically higher than the pH of the submicron size fractions with which most NH3 partitions in ambient air. In these cases, mixing chemically distinct aerosol size fractions on a bulk filter often results in supersaturation of the sampled aerosol with respect to the gas phase leading to significant artifact evaporation of both HCl and NH3. However, these losses are driven by the thermodynamic properties of these compounds not by the volatility of NH4Cl. In addition, selective sampling of only submicron aerosol (as reported here) would have minimized divergence between the pHs of submicron aerosol in ambient air versus submicron aerosol sampled on filters and associated artifact phase changes of this nature.

Page 2099, line 11. The assumption that concentrations of submicron particulate Cl- sampled on quartz-fiber filters and analyzed by IC exhibit significant negative bias should be justified. Bates et al [2012] did not report inherent bias of this nature and I am unaware of reports by these or other investigators documenting such problems.

Page 2099, lines 23 to 25. It would be helpful to identify the periods of continental outflow on the Figure 6.

The presence of detectable nss Cl- in urban outflow is not surprising. However, the authors' analysis implies that, during some sampling periods with relatively high sea-salt concentrations (presumably under conditions of on-shore flow), (1) significant amounts of the original ss Cl- were lost from the aerosol via volatilization of HCl or other Cl-containing gases resulting in large deficits (Fig. 9) and (2) some of this lost ss Cl- was replaced by nss Cl- (e.g., Fig. 6). This result is surprising and also inconsistent with the major sources for Cl in marine air reported in some of the cited literature. Do the authors have any thoughts regarding the speciation or fate of the original ss Cl- that

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was lost from the aerosol or the speciation or origin of the nss Cl- that was incorporated into the aerosol? These results imply the possibility that the loss of ss Cl- and the incorporation of nss Cl- may have been segregated in space and or time. Is this considered a reasonable expectation?

Page 2101, line 19 to page 2102, line 14 and Figure 9. It would be helpful to remind readers that the larger gaps in the AMS results following sea sweep deployments depicted in Figure 9 relative to those depicted in Figures 5, 6, and 7 resulted in part from data removed due to the slow recovery from the high background signal for Na+. However, the durations of periods with no data depicted in Figure 9 vary a bit. For example, why are there no data in Figure 9 from the latter part of 7 June to 8 June whereas data for those periods are depicted in Figures 5, 6, and 7? This should be explained.

It would also be helpful to elaborate on the accumulated analytical uncertainties associated with these and other calculated values and the associated implications for interpreting results

The legend on Figure 9 is potentially confusing because both the “Ambient Air” and “Filter Measurements” correspond to data for ambient air. Suggest change to unambiguous terms like “Ambient – AMS”, “Ambient – Filter”, and “SeaSweep – AMS”.

Figures 5, 6, 7, and 9. Suggest reducing the number of minor ticks between each major tick on the X axis.

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