

Response to Reviewer 1:

General comments:

This manuscript presents a detail examination of chemical compounds, mainly depletion of sulfate and chlorine relative to sodium with respect to freshly emitted sea salt aerosol, in aerosols that arrived at Concordia in central Antarctica, as well as acidic gases (HCl and HNO₃) in air based on their multiple year-round records of samplings. Both bulk and size- segregated depletion of chloride and sulfate are reported with a major goal of determining the origin of sea salt aerosols reaching the high plateau. To achieve that, the authors have introduced a novel method to remove biogenic sulfate contamination to the sulphates containing in the aerosols. Their approach has been successfully applied to the raw dataset and the conclusion derived indicating rough similar contribution of sea salt aerosols from both sea-ice and open ocean emission during polar winter is well consistent with previous model findings. Together with a back-trajectory result, they further confirm that a larger sulfate to sodium ratio would be observed when air masses had travelled a longer time over sea ice than over open water. Moreover, their novel data seem to show that small sub-micron sized SSA has much larger sulfate depletion than larger ones which is likely to indicate different sized SSA could face quite different preferential production mechanisms as predicted previously.

The second major part of the manuscript is about chlorine depletion in aerosols. Their multi-year data clearly show a maximum depletion occurring in spring which is associating with high level of sea salt amount. The interpretation of the spring peak in chloride depletion has been discussed carefully, in associating with concentrations of nitrate, acidic sulphur in aerosols, as well as nitric acid and HCl in gas phase.

In general, this is a novel and deepening study of aerosol depletions for chlorine and sulphate at a central Antarctica site. It is well written and with huge scientific implications for our understanding of the sea salt ice records taken from inland Antarctica. It deserves a publication in ACP with a minor revision (see my specific comments shown below).

Specific comments:

P12: In terms of the chlorine depletion mechanisms, only two controlling factors (e.g. nitrate and sulphate) are highlighted in the manuscript. Given the fact that the largest chlorine depletion occurs in spring and is associating with highest SSA load, a season seeing the highest BrO in coastal sites of the Antarctic, then the manuscript would benefit if the authors could discuss the potential role of halogen, here mainly bromine in influencing chlorine release from SSA. Particularly, chloride can be liberated via heterogeneous reaction through $\text{HOBr(g)} + \text{Cl}^- \rightarrow \text{BrCl}$ (e.g. see Abbatt et al., 2012). Though at inland sites like Concordia, this process is not important due to the relatively low inorganic bromine species (a few pptv, see their paper of Legrand et al., 2016), however, at coastal sites during bromine explosion events in spring, the boundary layer HOBr concentration could be as high as (or even higher than) HNO_3 . Apart from this process, BrONO_2 hydrolysis reaction (via heterogeneous reaction on wet surface) has been found dominating nitric acid formation in high latitude. For instance, a global model (pTOMCAT) with a detailed bromine chemistry included clearly showed that when BrONO_2 hydrolysis is included, about 60-80% atmospheric NO_x in high latitudes will be removed (Fig. 12c of Yang et al., 2005) indicating BrONO_2 hydrolysis could efficiently convert NO_x to HNO_3 in mid- to high latitude (not in low latitude due to high OH and low BrO there). Does this process play a role, either directly or indirectly, in affecting chlorine depletion? Can bromine be ruled out completely as a role in HNO_3 formation and chlorine depletion? If not, then a discussion should be given.

Concerning the direct role of HOBr on the release of chloride from sea-salt, its level even in spring at the coast is limited to 1 pptv or so (Legrand et al., 2016). For comparison the HNO_3 level at Concordia reaches 0.5 nEq m^{-3} (i.e., $\sim 11 \text{ pptv}$) and more than 1 nEq m^{-3} in November-December (i.e., more than 22 pptv). Concerning coastal regions, in samplings made on denuder tubes at DDU, Legrand et al. (2016) reported mass ratios of Br/NO_3 of 0.2 in summer and close to 1-2

in winter. Checking these data we calculate a mean ratio of 0.7 for spring (September/October). That leads to a molar ratio of 0.5. Since HOBr represents at the east coast a quarter of the total inorganic bromine (Legrand et al., 2016, Figure 14), we can conclude that, at least in East Antarctica, the role of HOBr cannot be ruled out but is certainly not dominant. We have introduced this discussion in the text:

“Several previous studies discussed the nature of chemical species (nitric acid, sulfuric and methanesulfonic acid) involved in the de-chlorination of sea-salt aerosol in Antarctica but no overall picture yet emerged. Chloride can also be released from the reaction of gaseous HOBr with sea-salt aerosol (Abbatt et al., 2012). The HOBr level at Concordia was investigated by Legrand et al. (2016) who reported mixing ratios close to 1 pptv in spring. For comparison, the HNO₃ level at Concordia reaches 0.5 nEq m⁻³ (i.e., ~11 pptv) in October and more than 1 nEq m⁻³ in November-December (i.e., more than 22 pptv), suggesting that HOBr does not significantly contribute to the chloride depletion over the high Antarctic plateau in spring and summer. At coastal regions, in samplings made on denuder tubes at DDU, Legrand et al. (2016) reported a bromide to nitrate mass ratio of 0.2 in summer and close to 1-2 in winter (a mean ratio of 0.7 being observed for September/October). That leads to a bromide to nitrate molar ratio of 0.5. Since, at that site, HOBr represents around a quarter of total inorganic bromine trapped together with nitric acid on denuders (Legrand et al., 2016), we can conclude that, at least in East Antarctica, the contribution of HOBr in the chloride depletion of sea-salt aerosol cannot be totally ruled out, but it is certainly not a dominant process.”

Concerning the role of bromide chemistry on nitric acid formation, though this is an interesting aspect, we feel that this point is out of the scope of this paper. At this point, we also would like to emphasize that indeed p-TOMCAT modelling including bromide chemistry suggests that at high latitude BrONO₂ photolysis is an important pathway for the production of HNO₃, but we have to consider that the Antarctic continent also experiences a major release of NO_x from the snowpack, a process that is not considered by the model.

P24, Figures 6/7: My second concern is again about the chlorine depletion in section 3.1. If the acidic replacement is indeed dominating chlorine release, then it could be possible to see a nearly 1:1 linear scatter relationship between chlorine depleted and $[H^+]$ derived. The $[H^+]$ can be derived from the two major acidic species (nitrate and sulphate without SS_SO_4). Equally, a scatter plot between the ratio of r and ratio of $[H^+]/[Na^+]$ is also indicative to whether the replacement process is working. This examination can be made both for seasonal depletion data shown in figure 7 as well as for size-dependent depletion shown in figure 6. Instead of using $[H^+]$, a sum of $[NO_3]/M_{NO_3} + 2X[SO_4]/M_{SO_4}$ can also be used in the scatter plot. here M_{NO_3} and M_{SO_4} are molecular weight of NO_3 and SO_4 respectively.

We understand (and agree) what you means but Figure 7 was designed to discuss this point: may be it was not clear enough that in Figure 7 we expressed concentrations of chloride depletion and acidic components in molar units (“All concentrations are here expressed in molar units (in $nEq\ m^{-3}$)”). We now specify this important point both in the figure caption and in the text. Furthermore, the relationship between chloride depletion and H^+ needs to be at least equal to 1 but can exceed one (and it is what is observed in late summer in Figure 7). This point is now emphasized before discussing the respective role of nitrate and sulfur species (that on a molar basis the sum of acidic species always exceed the chloride depletion):

“Figure 7 also indicates that, on a molar basis, the sum of acidic species always exceeds the chloride depletion. Whatever the time period, acidic sulfur particles are always present in large enough amounts to replace chloride in small sea-salt particles (Fig. 7a).”

Technical corrections:

P2L32: add ‘mass’ between ‘sodium’ and ‘ratios’: *OK Done*

P8L10: remove ‘to’ before ‘due to’ *OK Done*

P8L20: ‘Fig.6’ should be ‘Fig. 7’? *Sorry, in fact it is Figure 8 here. Corrected*

P8L18: 'larger' here should be 'smaller'? *Sorry, we refer to supermicron (not submicron) particles and larger is correct. Corrected.*

P9L19: remove the extra 'and' in 'or/and and too high' *OK Done*

P12L3. A reference is needed to 'high dust levels that neutralized HNO₃ and H₂SO₄. *OK, we add a reference (Usher et al., 2003)*

P12L29: change 'part' to 'parts' *OK Done*

In most of figures, change NO₃ to NO₃⁻, SO₄ to SO₄⁼, Na to Na⁺. *OK Done.*

P22 figure 4: It would be good to add 'r' line to high light the 'relative depletion factor. *It is possible but we feel that this figure is already heavy and is mainly dedicated to show (1) the timing of the recovery of nitric acid in the gas phase versus the increase of nitrate on aerosol, (2) to compare calculated chloride depletion in HV and observed HCl in denuder tubes. Anyway r values are already show in Figure 2 (together with chloride depletion).*

P24 figure 6. Please add a line of total sulphate derived based on MAS (without SS_SO4). *It is possible but we feel that this figure is already heavy and is mainly dedicated to show on which particles nitrate is staying. Anyway examples of the size distribution of sulfate are shown in Figures 8 and 9.*

P25 figure 7b: is the number '0.64' in '(0.64-3.5 μm)' actually 0.46? why there is a gap between 0.46 to 0.64 μm ? same question in P6 L25. *It is an arbitrary cut but it show more clearly the difference between small and large particles.*

P28: what do the two dash lines represent for?

OK we now specify in the figure caption: "The two horizontal dashed lines (in blue) refer to the R value in seawater (0.25, upper line) and in strongly fractionated sea-salt aerosol as observed in winter at the coast (0.07, lower line)."