Dear Dr. Legrand,
My apologize for such a long time for the open discussions of your manuscript. Your manuscript did undergo an unusual experience, which is certainly unpleasant for you as well as for us. Two referees had accepted our invitation to review your manuscript in April. But both of them failed to submit their reports in early July when the open discussions should be closed normally for your manuscript. It took a few weeks more for me to contact them and to nominate other potential referees. Although I found another two referees agreeing to review your manuscript, unfortunately the report from one referee was missing again by the initial and extended deadlines. While promising to submit the review report soon, one referee said in his/her personal email to me that the paper is good but tough to get through and it's taken longer than expected. Actually, I share the same feeling with that referee when reading your manuscript.

Now we have gotten two review reports. While both referees admire import value of your data and significance of your work, one of them rates a low value of the quality of your manuscript especially in presentation. I agree with the referee (Referee 3) in that the manuscript needs to be focused more on the analysis of chemical processes. Actually, another referee (Referee 1) also suggested that additional chemical process be considered for chlorine depletion relative to sodium with respect to freshly emitted sea salt aerosols.

I noted that the sulfate aerosol issue has been intensively addressed by a companion paper of this manuscript (Legrand et al., 2017), which was also published in ACPD. Therefore, you may refer to that paper for the filtering of biogenic sulfate aerosols and, as suggested by the referee, focus more on the ionic chemistry involved in sulfate depletion relative to sodium with respect to the composition of sea water.

I also agree with the referee in that the discussions on implications for ice core stud- ies (Sect. 3.3) should be skipped over if these discussion help little to explain your measurement and analysis results presented in the preceding sections.
In summary, I think that your manuscript needs substantial revisions based on the comments from the referees. You are welcome to submit the revised manuscript if you think that all the issues they raised can be well addressed. Your manuscript will be sent to the referees for further review, and the final decision can be made then.
If you have any questions, please do not hesitate to contact me. C2
Sincerely,
Jianzhong Ma
Reference: Legrand, M., Preunkert, S., Weller, R., Zipf, L., Elsässer, C., Merchel, S., Rugel, G., and Wagenbach, D.: Year-round record of bulk and size-segregated aerosol composition in central Antarctica (Concordia site) Part 2: Biogenic sulfur (sulfate and methanesulfonate) aerosol, Atmos. Chem. Phys. Discuss., 2017, 1-39, 10.5194/acp- 2017-305, 2017.

Answers to the Editor

Thank you very much for your comments. We have now three reviewers and two of them are very positive, both considering the paper as well written and important for atmospheric chemists as well as the ice core community (reviewer 1: "It is well written and with huge scientific implications for our understanding of the sea salt ice records taken from inland Antarctica."), reviewer 4 (for instance "This paper provides constraints to some long-standing questions regarding the source of anomalies in the ratio of Na to Cl in snow, whether and by how much Cl in aerosols is depleted in the continental Antarctic and in ice and the factors driving it."). In our response, we carefully considered all points raised by reviewer 1 and reviewer 4.

Concerning reviewer 3, we have carefully addressed the questions he raised on the poor discussion we had of the ionic balance and have now reported the mean ionic balance of aerosol (Table 1).

We cannot, however, follow two of the proposed changes.

First, it is clearly not realistic to mix the two manuscripts. Indeed in our response the reviewer 3 we argued that: "*The topics of the two papers are totally different: part one is dedicated to the origin of sea-salt and its degree of fractionation over Antarctica, part 2 focuses on the understanding of the behaviour of biogenic sulfate and MSA.*

Part 1: is 17 pages of text (including references), 1 table, and 13 figures, Part 2: is 22 pages, 5 Tables, and 12 figures. Mixing the two papers (even considering the overlaps in section *“sites, sampling and methods”, and possible mixing 2 figures together), the resulting paper would be far too long and we feel this is not realistic.”*

Second, we don’t agree with the suggestion to remove the section on ice core implications. Indeed, as argued in our answer: *“The ice core data can, in no way, here support the atmospheric observations discussed in this study simply because, as clearly mentioned, post depositional effects modified the original atmospheric signal. On the contrary, as clearly introduced in the paper, the atmospheric studies described in this paper are needed to better understand ice core signals. The reviewer 1 clearly highlighted this point: “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.”*
Also the title of this paragraph is very explicit: “Implications for ice core studies” and not the reverse. From our experience some previous papers also ended with a discussion on “implications for ice core”: see for instance the JGR paper “Preunkert, S., Jourdain, B., Legrand, M., Udisti, R., Becagli, S., and Cerri, O.: Seasonality of sulfur species (dimethyl sulfide, sulfate, and methanesulfonate) in Antarctica: Inland versus coastal regions, J. Geophys. Res., 113, D15302, doi:10.1029/2008JD009937, 2008. »

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 HNO_3) 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 that 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 cholrine release from SSA. Particularly, chloride can be liberated via heterogeneous reaction through $HOBr(g)+Cl^{-} \rightarrow BrCl$ (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 BrONO2 hydrolysis is included, about 60-80% atmospheric NOx in high latitudes will be removed (Fig. 12c of Yang et al., 2005) indicating $BrONO_2$ hydrolysis could efficiently convert NOx 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., ~11 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 HNO_3 *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 $BrONO_2$ *photolysis is an important pathway for the production of* HNO_3*, 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, them 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 $[NO_3]/M_{NO3}+2X[SO_4]/M_{SO4}$ can also be used in the scatter plot. here M_{NO3} and M_{SO4} 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 HNO_3 and H_2SO4. *OK, we add a reference (Usher et al., 2003)*
P12L29: change ‘part’ to ‘parts’ *OK Done*

In most of figures, change NO3 to NO_3^-, SO4 to $SO_4^=$, 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).”

Answer to Referee #3

We would like to first thank the reviewer for their comments which have emphasised to us that we needed to explain better some underlying concepts. We hope these additional explanations will answer most of the comments

The manuscript presents multi-year measurement results of seal salt aerosols and associated ion composition as well as HCl and HNO3 acid gases in the central Antarctic site. With these data, the authors examine the chloride depletion relative to sodium with respect to freshly emitted sea salt aerosols and the sulfate depletion relative to sodium with respect to the composition of sea water. The seasonal variability of such depletion, the role of acidic sulfur aerosol and nitric acid in the depletion, and the contribution sea-ice and open ocean emissions to the sea salt aerosols load are investigated. The reported data are valuable and such kind of study should be a welcome addition to the literature on Antarctic environmental and atmospheric chemistry research. On the other hand, the manuscript appears to be not well written and some discussions are ambiguous without a clear clue to follow. Especially there is a lackness of in-depth analysis based on the fundamental chemistry. In my opinion the quality of this manuscript is not high enough to be published in ACP for its current version. Below are my comments in detail.

We note that, in the quick report, our paper was evaluated as "good" for the aspect "scientific quality" and "data presentation".

What does the authors mean in the term of "acidic sulfur aerosol" (e.g., in P1, L22)? The authors also define nitrate as "acidic compounds" (P6, L26-28). Do they refer to HNO3 in aerosols? Note that SO4= and NO3- should be taken as neutral, instead of acidic, ions in water solution. They calculated the acidic sulfur component as the sum of non-sea-salt sulfate plus MSA after subtracting the amount of ammonium (P6, L27- 28). What does the residual mean in acid-base equilibrium chemistry? The authors should have investigated the balance status between cations and anions in measured aerosols before analyzing the chlorine depletion by so called replacement reactions. Figure 7 and related discussions (P7, L10-17) provide some information. However, only when the full set of ions have been taken into account and, if possible, neural compounds (e.g., CaSO4 , Na2SO4, (NH4)2SO4, and NaNO3) diagnosted, the dis-placement process could be understood clearly. Note that there is a neutralization order for the ions in a solution, e.g., SO4= > NO3- for anions and Ca2+ > Na+ for cations. From Figure 7c, one cannot see whether the displacement had happened or not. Only by investigating NO3-, Na+ and other associated ions in the aerosols, the role of HNO3 in the displacement might be seen. Note that partitioning of HNO3 be tween gaseous and aerosol phases depends not only on the acidity of liquid aerosols but also atmospheric temperature.

OK we understand that we made an assumption that readers are familiar with polar atmospheric chemistry and central Antarctic ice core chemistry. So before presenting the calculations of acidic sulfur we remedy that by presenting, as recommended by the reviewer, the ionic balance of aerosol at Concordia. This should indicate very clearly that, apart from the sea salt components, the main cation associated with nitrate and sulfate is H+ :

"An examination of the role over time of chemical species possibly involved in aerosol de-chlorination is reported in Fig. 7, the amount of chloride loss being compared on a molar basis to the main atmospheric acidic components. The mean ionic composition of aerosol collected in spring at Concordia is reported in Table 1. It shows that, apart from sea-salt components, aerosol present at Concordia in spring/summer consists of sulfate (1.2 nEq m^{-3}), nitrate (0.08 nEq m^{-3}), MSA (0.05 nEq m^{-3}), and ammonium (0.18 nEq m^{-3}). Other non-

sea-salt components (nssK$^+$, nssCa^{2+}, and oxalate) remain at the level of 0.01 nEq m^{-3} or less (Table 1). From that, we have calculated the acidic sulfur component as the sum of non-sea-salt sulfate plus MSA after subtracting the amount of ammonium."

Table 1. Mean chemical composition of aerosol collected at Concordia from October to December (2006-2015). Values in bold and in parenthesis refer to the non-sea-salt components of aerosol. All concentrations are expressed in nEq m^{-3}.

Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	$CH_3SO_3^-$	$C_2O_4^{2-}$
0.47	0.18 (**0.18**)	0.02 (**0.01**)	0 .11	0.02 (**<0.01**)	0 .08	0.08 (**0.08**)	1.25 (**1.19**)	0.05 (**0.05**)	0.015 (**0.015**)

Concerning your remark that "From Figure 7c, one cannot see whether the displacement had happened or not.":
Indeed, because only a small fraction of total nitrate is on sea-salt particles and figure 7c shows the gas phase fraction which (independently of sea-salt) increases from spring to summer with the recovery of the photochemistry and NOx emissions from the snowpack.

For Section 3.2 of the manuscript, neither the terms of SO4, biogenic sulfate, ssSO4, nssSO4 and MSA and are well defined, nor their measuring (or calculating) methods clearly introduced.

We think that the readers of Atmospheric Chemistry and Physics are already familiar with most of this terminology, and for example know that SO4 is sulphate. The method of calculation of nssSO4 was already defined on Page 2, line 16. The calculation of ssSO4 was already defined on Page 9, line 6. We think that the wording "biogenic sulphate" would be understood by the readers of ACP. We indeed missed spelling out MSA, and it is now done in the revised version in the introduction: "They also pointed out that, even when examining the chemical composition of particles deposited on the top stages of the impactor, there can be a significant underestimation of the degree of fractionation of sea-salt particles due to a residual presence of biogenic sulfate, as indicated by the presence of MSA (methanesulfonic acid). »
Adding this last sentence, we also clarify what is biogenic sulfate (see below).
Measurements are detailed in section 2, calculations are presented in this section. Please tell us if we need to do more but this seems sufficient for readers with any familiarity with the topic, and the justification for these calculations for those less familiar can easily be found in the cited references.

It is difficult for me to follow the discussions as the assumption (e.g., the relationship between biogenic sulfate and MSA in P8, L22-25) has not been fully based one fundamental atmospheric chemistry and physics. There is a doubt that the regression results from small particles can be applied to large ones.

We do not understand the argument for such a statement that, in any case, is not supported by observations. This point was already discussed in the text and we have included another sentence (mentioning that this has been previously discussed and published by Jourdain et al., 2007): "For the 5 lowest stages (smallest particle sizes) of the impactor, we find that the ratio of nssSO$_4$/MSA is reasonably constant (red dots in Fig 8e (or Fig 9e) falling on a straight line through zero). This then supports the assumption that in winter the size distributions of biogenic sulfate and MSA are the same and that the nssSO$_4$/MSA ratio is constant over the entire size distribution (see also Legrand et al., this *issue). The similarity of the nssSO_4/MSA ratio over the entire size distribution was already pointed out by Jourdain et al. (2007). «*

The authors refers to a companion paper: "Legrand, M., Preunkert, S., Weller, R., Zipf, L., Elsässer, C., Merchel, S., Rugel, G., and Wagenbach, D: Year-round (2006-2015) record of bulk and size-segregated aerosol composition in central Antarctica (Concordia site) Part 1: Sulfur derived aerosol (MSA and sulfate), this issue" (note that both companion papers are labelled as "Part 1").
Thanks for identifying this typographic error.

Considering that sulfate aerosol is a large and important part of this manuscript, I would suggest the paper not to be separated into two parts.

This suggestion is unrealistic. The topics of the two papers are totally different: part one is dedicated to the origin of sea-salt and its degree of fractionation over Antarctica, part 2 focuses on the understanding of the behaviour of biogenic sulfate and MSA.
Part 1: is 17 pages of text (including references), 1 table, and 13 figures, Part 2: is 22 pages, 5 Tables, and 12 figures. Mixing the two papers (even considering the overlaps in section "sites, sampling and methods", and possible mixing 2 figures together), the resulting paper would be far too long and we feel this is not realistic.

Sulfate depletion relative to sodium has been attributed to sea-ice related emissions due to precipitation of mirabilite (Na2SO4.10H2O) during freezing of seawater. As both sulfate and sodium will loss with the deposition of mirabilite, how the depletion of sulfate relative to sodium occurs should be explained quantitatively in detail.

This aspect is introduced and well referenced in the introduction (lines 10 to 21), and it is now a well recognized process. It is obvious that because there is much more sodium than sulfate in sea salt, precipitation of mirabilite removes proportionally more sulfate, leading to a depletion; we do not feel this needs to be explained again.

The manuscript needs to be concise and formulas (1), (3), (4), (6), and (7) and associated descriptions can be moved to the Supplement.

Since theses calculations address two very different processes: equation 1 to 4 refer to calculations for summer (chloride depletion), whereas equations 5 to 7 to sulphate depletion in winter, they have to appear in the corresponding paragraph dedicated to summer and winter, respectively. Mixing them in a supplement would be more confusing, and we do not feel this would help the reader.

The authors use the p-TOMCAT model to confirm their conclusion on the source of sea salt aerosols (P10, L11-23). But the model and its simulation results have not been well evaluated and introduced in this manuscript. These discussions (P10, L11-23) provide no more convincing information than the backward trajectory analysis described in previous paragraph.

As discussed in these lines, these model simulations were evaluated against observations in the cited previous papers. We feel that these previous works have to be reported here since the present paper clearly assesses (on a far more robust basis) previous observations. The advantage of the p-TOMCAT simulations compared to back trajectories is that they quantitatively assess the source of sea salt aerosol while the back trajectories merely assess the source of air masses.

I do not think that Sect 3.3 should be included in this manuscript as it appears to provide no strong support to explain the observational results of this study.

We disagree. The ice core data can, in no way, here support the atmospheric observations discussed in this study simply because, as clearly mentioned, post depositional effects modified the original atmospheric signal. On the contrary, as clearly introduced in the paper, the atmospheric studies described in this paper are needed to better understand ice core signals. The reviewer 1 clearly highlighted this point : "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."

Also the title of this paragraph is very explicit: "Implications for ice core studies" and not the reverse. From our experience some previous papers also ended with a discussion on "implications for ice core": see for instance the JGR paper "Preunkert, S., Jourdain, B., Legrand, M., Udisti, R., Becagli, S., and Cerri, O.: Seasonality of sulfur species (dimethyl sulfide, sulfate, and methanesulfonate) in Antarctica: Inland versus coastal regions, J. Geophys. Res., 113, D15302, doi:10.1029/2008JD009937, 2008.

Anonymous Referee #4

The authors address a pressing topic; sea salt, its size distribution in aerosols and co-located gas phase measurements over annual cycles. The interpretation of sea salt records in Antarctica is relevant to sea ice distribution patterns recorded in glacial records. This manuscript contributes significantly to this discussion, demonstrating that approximately half the sea salt aerosol load comes from open ocean versus sea ice. The relationship of sea salt, aerosol acidification and the production of HCl and HNO3 is also examined by considering denuder measurements of acid gases and their effect on aerosol characteristics. The authors argued that HCl emission from surface snow or differences in the lifetime of HCl versus sea salt transported from the coast drove differences observed between denuder and aerosol measurements. These results are novel and intriguing. This paper provides constraints to some long-standing questions regarding the source of anomalies in the ratio of Na to Cl in snow, whether and by how much Cl in aerosols is depleted in the continental Antarctic and in ice and the factors driving it. These points are all strong and convincing. Arguments about sea salt and biogenic sulfate however, are less well-rounded: likely this is because detail is provided in a separate manuscript dealing with sulfate and sulfate to sodium ratios. The manuscript is strong, but some sections, particularly with respect to sulfate and sulfate to sodium ratios need additional attention prior to publication.

Portions of this manuscript associated with interpretation of sulfate needs additional description (that perhaps can be found in the accompanying paper on sulfur-derived aerosol) to be fully understandable. Page 8 line 24 refers to quantifying biogenic sulfate using MSA and the relationship between MSA and sulfate on particles with a diameter <0.46 microns. This assumes that all non sea salt sulfate in aerosols <0.46 microns in diameter is biogenic. Is this because anthropogenic sulfate is negligible and volcanic sulfate is absent in the Antarctic interior? A previous study in the Arctic demonstrated that MSA in for aerosols <0.49 microns correlated with the presence of fine particles rather than with biogenic sulfate (Rempillo et al., 2010). In that study the surface of <0.49 micron aerosol, rather than biogenic sulfate, were the dominant factor affecting MSA formation. The authors need to demonstrate why anthropogenic and volcanic sulfate are not factors in MSA formation at this continental Antarctic site. Line 23 on page 8 ".. we therefore have corrected the concentrations of sulfate present on the upper stages of the impactor for the (nss rather than biogenic contribution)".

Thank you for this comment: Yes, at these high southern latitudes, anthropogenic and volcanic sources can be neglected with respect to DMS oxidation. Such a statement was drawn from model approaches (Gondwe et al., 2003), sulfur isotopic measurements (Patris et al., 2000) and examination of MSA to nssSO4 (Minikin et al., 1998). Furthermore, indeed this point is discussed in the accompanying paper. It is concluded that, even for the low winter levels of nssSO4 (6 ng m^{-3}), its presence is mainly attributed to long-range transport of marine biogenic emissions from mid-latitude, the non-biogenic sulfate level remaining limited to 1 ng m^{-3}. But we have considered your comment and in section 3.2., we first refer to sea-salt sulphate and non-sea-salt sulphate modes, then we refer to the accompanying paper arguing that we can assume that non-sea-salt sulfate present in winter there mainly originates from marine biogenic emissions, and finally use the wording "biogenic sulfate".

Gondwe, M., Krol, M., Gieskes, W., Klaassen, W., and de Baar, H.: The contribution of ocean-leaving DMS to the global atmospheric burdens of DMS, MSA, SO_2, and NSS SO_4, Global Biogeochem. Cycles, 17(2), 1056, doi:10.1029/2002GB001937, 2003.

Minikin, A., Legrand, M., Hall, J., Wagenbach, D., Kleefeld, C., Wolff, E., Pasteur, E. C., and Ducroz, F.: Sulfur-containing spacies (sulfate and methanesulfonate) in coastal Antarctic aerosol and precipitation, J. Geophys. Res., 103, 10,975-10,990, 1998.

Patris, N., Delmas, R. J., and Jouzel, J.: Isotopic signatures of sulfur in shallow Antarctic ice cores, J. Geophys. Res., 105(D6), 7071-7078, doi:10.1029/1999JD900974.

On page 10 how were the values of 40% and 60% of travel time within the boundary layer determined? This is not evident from the examples of air mass back trajectories provided in Figure 11. Is there a reference or data to support a boundary layer of ~600 m for open ocean and over sea-ice in the Antarctic at this time of year? The discussion suggests a quantified analysis that is not shared with the reader which makes this section less convincing.

You are right, our wording concerning 600 m was confusing. Also Figure 11 only shows the location of the trajectories and not the altitude. The altitude of the trajectories is provided by trajectories calculations but not shown here. So we reworded the paragraph as follows: "The temporal variability of sea-salt aerosol reaching Dome C, its level and composition with respect to the sulfate relative to sodium fractionation, were examined in the light of air masses reaching the site, as shown by calculated 10-day backward trajectories. The model was run every 6 h in backward mode for three different altitudes (0, 250, and 500 m above ground level, agl) for time periods corresponding to impactor run sampling. It is seen that when air masses arriving at Dome C have spent more than two days (up to 4 days) over oceanic sectors their mean sodium concentrations reach 47 ± 21 ng m^{-3} against 12 ± 5 ng m^{-3} when air masses have spent less than 0.5 days over oceans. Some typical examples of 10-day backward trajectories corresponding to strong, mid and weak sulfate relative to sodium fractionations are reported in Fig. 11. Backward air mass trajectory calculations also document the altitude of trajectories (not shown) and we calculated the time that air masses reaching Dome C were traveling below 600 m elevation over oceans, distinguishing between sea-ice and open ocean areas. The elevation of 600 m asl corresponds to the middle of the boundary layer whose the thickness over oceanic regions is typically 1000-1500 m. Selecting the impactor runs corresponding to sampling time periods over which the 10-day backward trajectories indicate more than one day of travel over the ocean, we find an overall decreasing trend of R (i.e. a stronger sulfate depletion relative to sodium) when air masses arriving at Dome C (0 m agl) have a longer contact with sea-ice than with open-ocean ($R^2 = 0.4$). For example, from 9 to 23 September 2006, air masses reaching Concordia had travelled more than two days over oceanic sectors, with 40% and 60% of travel time below 600 m elevation over sea-ice and open-ocean boundary, respectively. The corresponding R value is low (R = 0.1, Fig. 11a), consistently suggesting a very significant contribution of sea-ice-related processes to the sodium level. At the opposite, from 28 August to 3 September 2008 (Fig. 11d), air masses arriving at Dome C have only travelled 5% of time below 600 m elevation over sea-ice (95% over open-ocean). Intermediate situations, from 26 July to 9 August 2007 (Fig. 11b) or 28

August to 11 September 2009 (Fig. 11c) are characterized by R values close to 0.15 and 20-25 % of travel time below 600 m elevation over sea-ice (75-80% over open-ocean).”

Line 30 on page 10 is confusing “A slight increase of the sulfate depletion in particles smaller than higher than one micron. . ..”

We agree: this sentence is confusing and add nothing with respect to the preceding sentence. So we removed it.

Year-round records of bulk and size-segregated aerosol composition in central Antarctica (Concordia site) Part 1: Fractionation of sea-salt particles

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Abstract. Multiple year-round records of bulk and size-segregated composition of aerosol were obtained at the inland site of Concordia located at Dome C in East Antarctica. In parallel, sampling of acidic gases on denuder tubes was carried out to quantify the concentrations of HCl and HNO_3 present in the gas phase. These time-series are used to examine aerosol present over central Antarctica in terms of chloride depletion relative to sodium with respect to freshly emitted sea-salt aerosol as well as depletion of sulfate relative to sodium with respect to the composition of seawater. A depletion of chloride relative to sodium is observed over most of the year, reaching a maximum of ~20 ng m^{-3} in spring when there are still large sea-salt amounts and acidic components start to recover. The role of acidic sulfur aerosol and nitric acid in replacing chloride from sea-salt particles is here discussed. HCl is found to be around twice more abundant than the amount of chloride lost by sea-salt aerosol, suggesting that either HCl is more efficiently transported to Concordia than sea-salt aerosol or reemission from the snow pack over the Antarctic plateau represents an additional significant HCl source. The size-segregated composition of aerosol collected in winter (from 2006 to 2011) indicates a mean sulfate to sodium ratio of sea-salt aerosol present over central Antarctica of 0.16 ± 0.05, suggesting that, on average, the sea-ice and open ocean emissions equally contribute to sea-salt aerosol load of the inland Antarctic atmosphere. The temporal variability of the sulfate depletion relative to sodium was examined at the light of air mass backward trajectories, showing an overall decreasing trend of the ratio (i.e. a stronger sulfate depletion relative to sodium) when air masses arriving at Dome C had travelled a longer time over sea-ice than over open-ocean. The findings are shown to be useful to discuss sea-salt ice records extracted at deep drilling sites located inland Antarctica.

Keywords: Sea-salt aerosol, hydrochloric acid, sea-salt fractionation, chemistry (chemical composition and reactions)

1. Introduction

The understanding of the atmospheric budget of sea-salt aerosol at high latitudes is important for several reasons. In these regions, sea-ice-related processes such as frost flowers (Wagenbach et al., 1998; Rankin et al., 2000) or blowing snow (Yang et al., 2008; Jones et al., 2009) could represent an important sea-salt aerosol source with respect to the common sea-salt emissions from open-ocean. If correct, that offers the possibility to reconstruct the sea-ice conditions in the past by studying sea-salt ice core records (Rankin et al., 2002). Sea-salt aerosol emitted from open-ocean and by sea-ice related processes represents a large atmospheric source of halogens (Sander et al., 2003) that, if activated, can contribute to the chemical reactivity of the atmosphere over these high latitude regions (see Simpson et al. (2007) and Abbatt et al. (2012) for reviews). The chemical composition of sea-salt aerosol varies, depending on the emission process involved. In particular, the sulfate to sodium mass ratio (R) of sea-salt aerosol emitted by the open ocean is similar to that in seawater (0.25) whereas sea-ice-related emissions lead to a strong depletion of sulfate relative to sodium (R well below 0.25) in aerosol, due to precipitation of mirabilite ($Na_2SO_4.10\ H_2O$) during freezing of seawater (Wagenbach et al., 1998). At coastal Antarctic sites in winter, where the sea-ice surface was shown to be the dominant source of sea-salt aerosol, Wagenbach et al. (1998) reported R values close to 0.07 at Neumayer (NM, 70°S 85°W) and 0.10 at Dumont d'Urville (DDU, 66°S 140°E). These estimations were done by examining the relationship between the non-sea-salt sulfate ($nssSO_4^{2-}$) content calculated by using the seawater ratio of sulfate to sodium ($nssSO_4^{2-} = SO_4^{2-} - 0.25\ Na^+$) and sodium in bulk aerosol samples. A study of the size-segregated aerosol composition performed at DDU has shown that sea-salt aerosol present in super micron modes is depleted in sulfate relative to sodium (R close to 0.13) from May to October (Jourdain and Legrand, 2002). This more direct quantification of the sulfate depletion relative to sodium in aerosol with respect to seawater confirmed the importance of sea-ice related processes as a source of sea-salt in winter at the Antarctic coast.

At inland Antarctic sites, the estimation of the sulfate depletion relative to sodium by direct examination of the bulk aerosol composition becomes far more difficult due to low sea-salt concentrations and high biogenic sulfate content, as discussed by Weller and Wagenbach (2007) for Kohnen (75°S, 0°E) and Jourdain et al. (2008) for Concordia. At Concordia, the size-segregated aerosol composition was studied over the course of winter 2006 using a 12-stage impactor (Jourdain et al., 2008) and over the years 2005-2007 using a 4-stage impactor (Udisti et al., 2012). These two studies identified significant sulfate depletion relative to sodium during a few winter marine events. They also pointed out that, even when examining the chemical composition of particles deposited on the top stages of the impactor, there can be a significant underestimation of the degree of fractionation of sea-salt particles due to a residual presence of biogenic sulfate, as indicated by the presence of MSA (methanesulfonic acid).

In addition to the sea-salt fractionation discussed above, related to the presence of sea-ice in winter, the more commonly observed release of chloride from sea-salt particles (Graedel and Keene, 1995) is also taking place in summer in coastal

Antarctica. This is suggested by values of the chloride to sodium mass ratios (r) in bulk aerosol filters that are lower than the seawater reference value of 1.8 (Wagenbach et al., 1998, Jourdain and Legrand, 2002; Legrand et al., 2016). For inland Antarctica, bulk aerosol composition also revealed r values lower than 1.8 in summer (Hara et al., 2004; Cunningham and Zoller, 1981; Tuncel et al., 1989). It remains however difficult to quantify how much of the chloride loss had occurred in the atmosphere or on sea-salt accumulated on the bulk filter (an acid-induced sampling artefact). More reliable quantification of the chloride loss can be made by sampling aerosol using an impactor for which interactions between sea-salt particles and gaseous acids or acidic aerosols are far more limited than on a bulk aerosol filter. In this way, using a 12-stage impactor, Jourdain and Legrand (2002) and Kerminen et al. (2000) reported chloride loss in summer at the coastal Antarctic sites of DDU and Aboa, respectively. The few impactor data available for inland Antarctica (Jourdain et al., 2008; Udisti et al., 2012) have been discussed with respect to sulfate to sodium depletion in winter but not with respect to the chloride loss.

The release of chloride from sea-salt is in the form of HCl for which atmospheric measurements are very rare in Antarctica. Using denuder tube sampling, a few measurements were done at the coastal site of DDU (Jourdain and Legrand, 2002). However, as discussed by Barrie et al. (1994), the denuder tube sampling of HCl in the marine boundary layer, where a large amount of particulate chloride is present, remains difficult and the reliability of such data needs to be carefully examined. Hara et al. (2004) reported HCl data obtained by deploying at the coastal site of Syowa a sampling line made by a PTFE filter and alkaline impregnated filters for which a sampling artefact is also possible. Finally, the examination of the ionic composition (anions versus cations) of South Polar snow layers clearly suggested the presence of HCl in the atmosphere in summer at inland Antarctic sites (Legrand, 1987).

Here we report on year-round atmospheric observations of sea-salt aerosol done at the Concordia site located on the high east Antarctic plateau since 2006. The 10-year record (2006-2015) of bulk aerosol is complemented by a study of the size-segregated aerosol composition conducted by running a 12-stage impactor. Initiated in 2006, the impactor samplings were done continuously over three years (2009-2011). Impactor data are used in this paper for accurately quantifying the contribution of sea-ice related emissions to the sea-salt budget over inland Antarctica and are also essential for discussing biogenic sulfur aerosol as done in the accompanying paper from Legrand et al. (this issue). Gaseous acidic species were also sampled year-round since 2009 at Concordia using coated denuder tubes. Results for HCl are of interest here to discuss the atmospheric budget of chloride in these remote regions. Some of the findings are also discussed with respect to interpretation of deep ice core chemical records.

2. Sites, Sampling, and Analyses

As summarized in Fig. 1, samplings of various gases and atmospheric aerosol were initiated in 2006 at the inland site of Concordia (75°06'S, 123°20'E, 3233 m asl, located 1100 km away from the nearest coast of East Antarctica). Aerosol was sampled at a flow rate of 0.834 m^3 STP (standard temperature and pressure conditions of 298 K and 1013 hPa) min^{-1} on circular quartz filters (Gelman Pallflex Tissuquartz 2500QAT-UP, 15 cm diameter), denoted as HV (high volume) in Fig. 1.

Forty one filters were collected in 2006 and 405 filters from January 2008 to January 2016. In 2006, each weekly sampling was interrupted over one or two days whereas since 2008 the weekly sampling was most of the time conducted continuously (Fig.1). A piece of each filter (10 cm^2 of a total surface of 150 cm^2) was extracted with 10 mL of ultra pure Milli-Q water. Twelve times per year a field blank was achieved. Given the weekly sampling time, a large air volume was sampled (~ 8000 m^3) permitting the blank values to remain well below 1 ng m^{-3} (0.17 ± 0.25 ng m^{-3} for chloride, 0.17 ± 0.15 ng m^{-3} for sodium, 0.4 ± 0.3 ng m^{-3} for sulfate, 0.05 ± 0.05 ng m^{-3} for nitrate, and zero for MSA). Note that due to an error made in the field, different filters were used in 2007 leading to high sodium blank values. These data were therefore not considered in this paper (Fig. 2).

In addition to bulk HV aerosol samplings, a multiple year-round study of size-segregated aerosol composition has been carried out at Concordia using 105 discontinuous samplings done between March 2006 and January 2012 using a small deposit area impactor, similar to the one developed by Maenhaut et al. (1996), and equipped with a 20 µm cut-off diameter inlet. At each run of the impactor a blank of the deposit was done. A sampling interval of 2 weeks was applied with a flow rate of 0.54 m^3 h^{-1}. In 2006 and 2007 eight run per year were done, whereas a more continuously sampling (25 runs per year) was done from 2009 to 2012 (Fig. 1). With a sampled air volume of 160 m^3 and using a 9 mL extraction water volume, the blank values of the deposit remain well below 1 ng m^{-3} (0.22 ± 0.18 ng m^{-3} for chloride, 0.17 ± 0.12 ng m^{-3} for sodium, 0.08 ± 0.06 ng m^{-3} for sulfate, 0.06 ± 0.04 ng m^{-3} for nitrate, and zero for MSA). All data were blank corrected.

Finally, 261 samplings of acidic gases including HCl and HNO_3 were done at Concordia between January 2009 and March 2014 using a gas sampling line of 3 annular denuder tubes placed in series and coated with Na_2CO_3 (Jourdain and Legrand, 2002; Legrand et al., 2012). Over the first year, a sampling interval of 2 to 3 days was applied in summer and winter, respectively. From 2010 to 2016 the sampling became more continuous (Fig. 1) and the sampling time was increased to 6 days both for winter and summer. At each denuder tube run, two tubes were used as blanks to evaluate the contamination during coating and drying of the tubes. With a sampling interval of 6 days and a flow rate of 0.6 m^3 hr^{-1} (i.e. a total air sampled volume of ~ 80 m^3) and extraction of tubes with 5 mL of ultra pure Milli-Q water, the blank values correspond to atmospheric concentration in the range of 0.1 to 0.4 ng m^{-3} for nitrate. For chloride, the blank values were far more significant (up to 30 ng m^{-3} in 2009) and showed a large variability (± 10 ng m^{-3}). These samplings were discarded from the record and, as seen in Fig. 3, there are far more nitrate than chloride data in 2009. The situation improved when a more continuous sampling was applied and since mid-2012 chloride blank values remained most of the time limited to less than 1 ng m^{-3} (reaching occasionally 1 to 4 ng m^{-3}). These blank values were subtracted from raw data.

To characterize the origin of air masses reaching the Concordia region, 5- and 10-day backward trajectories were computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (Stein et al. (2015), available at: http://ready.arl.noaa.gov/HYSPLIT.php). Meteorological data from Global Data Assimilation Process (available at ftp://arlftp. arlhq.noaa.gov/pub/archives/gdas1) were used as input, and the model was run every 6 h in backward mode for three different altitudes (0, 250, and 500 m above ground level, agl).

3. Discussions

3.1. Chloride relative to sodium fractionation in aerosol

To evaluate the magnitude of the chloride to sodium fractionation of aerosol collected at Concordia with respect to the seawater composition, we calculate the chloride to sodium mass ratio (r). The uncertainties of r are related to the accuracy of the determinations of sodium and chloride that are determined by the ion chromatography accuracy (5%) and the standard deviation of blank filter values (σ_{blank}), as follows:

$$\Delta r^2 = (\Delta Cl/Na)^2 + (Cl\ \Delta Na/Na^2)^2 \qquad (1)$$

with $\Delta Cl^2 = (0.05Cl)^2 + \sigma_{blank}^2$

and $\Delta Na^2 = (0.05Na)^2 + \sigma_{blank}^2$

As discussed in Sect. 2, HV blank values lead to a σ_{blank} of 0.15 ng m^{-3} for sodium and 0.25 ng m^{-3} for chloride.

We also calculated the depletion of chloride relative to sodium for aerosol ($Cl_{depletion}$) with respect to the composition of fresh sea-salt aerosol as follows:

$$Cl_{depletion} = k_{Cl/Na}\,(Na^+) - (Cl^-) \quad (2)$$

With $k_{Cl/Na}$ being the ratio in fresh sea-salt aerosol.

In summer, as discussed by Legrand et al. (2016), sea-salt aerosol reaching central Antarctica essentially originates from the open-ocean and in applying equation (2) we have assumed a $k_{Cl/Na}$ value of 1.8 (i.e. the seawater value). The uncertainties in calculating the chloride depletion relative to sodium are calculated as:

$$\Delta(Cl_{depletion})^2 = (1.8\ \Delta Na)^2 + (\Delta Cl)^2 \qquad (3)$$

In winter, when sea-ice related processes act as sources of sea-salt aerosol, the precipitation of mirabilite on the sea-ice surface which causes a loss of sulfate relative to sodium, also causes a loss of sodium relative to chloride, leading to a $k_{Cl/Na}$ value slightly higher than 1.8 (Wagenbach et al., 1998). A mass balance calculation, done by assuming that the totality of sulfate (i.e. 0.25 Na) has been removed by mirabilite precipitation, permits estimation of an upper limit of the subsequent enrichment of chloride relative to sodium with a $k_{Cl/Na}$ value reaching 2.2 (Legrand et al., 2016). As discussed in sect. 3.2, from May to October a variable degree of sulfate depletion relative to sodium was observed on sea-salt particles present at Concordia. We therefore have assumed that over this period the $k_{Cl/Na}$ value can range between 1.8 and 2.2 ($k_{Cl/Na} = 2.0 \pm 0.2$). In winter, the uncertainties in calculating the chloride depletion relative to sodium therefore include uncertainties in the $k_{Cl/Na}$ value, as follows:

$$\Delta(Cl_{depletion})^2 = (k_{Cl/Na}\ \Delta Na)^2 + (Na\ \Delta k_{Cl/Na})^2 + (\Delta Cl)^2 \qquad (4)$$

With $k_{Cl/Na}$ being equal to 2.0 and $\Delta k_{Cl/Na}$ equal to 0.2.

The r values in bulk aerosol show a large departure from 1.8 in summer with values remaining far lower than 1.8 (close to 0.1 from November to April, Fig. 2). In winter, monthly mean values reach a maximum of 1.2 ± 0.3 in July (not shown) but, as seen in Fig.2, a few weekly samples exhibit r values that significantly exceed 1.8. The grand average r value over the year is about 0.7.

The calculated chloride depletion relative to sodium on bulk aerosol has an annual mean of 8.4 ± 15 ng m^{-3}, remains close to 4 ± 1.6 ng m^{-3} from January to September and increases in spring (21 ± 9 ng m^{-3} in October, 26 ± 12 ng m^{-3} in November, and 9 ± 2.6 ng m^{-3} in December, Fig. 4a). We cannot however rule out that these values are overestimated due to an acid-induced remobilization of chloride on the HV filters. The comparison of HV data with those available on the impactor (for which the above mentioned artefact is strongly limited) in 2009 and 2010 indicates a similar timing of the maximum of the chloride depletion (October-November, Fig. 5) but lower values than on the HV filters (18 ± 9 ng m^{-3} against 36 ± 15 ng m^{-3}, not shown), suggesting that the chloride depletion calculated from HV data is overestimated. On an annual basis (2009-2010), the difference between HV and impactor samplings is relatively lower with a chloride depletion calculated on the HV filters of 10.4 ± 14 ng m^{-3} against 7.4 ± 7 ng m^{-3} on the impactor runs, likely due to the fact that the HV sampling artefact would be important only when acidic species are abundant in spring/summer. From that, we estimate that the overestimation of the chloride depletion calculated on the HV filter sampling is on an annual average close to 40% but reaches 100% in spring.

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 HNO_3 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.

Based on 12-stage impactor data, Kerminen et al. (2000) found that in January 1998 at the coastal site of Aboa, H_2SO_4 particles account for slightly more of the observed de-chlorination than HNO_3 whereas Jourdain and Legrand (2002) attributed most of the de-chlorination to HNO_3 with little effect of the sulfur compounds at DDU (end of November to mid December 2000). Rankin and Wolff (2003) also showed that at coastal Halley station nitrate was reasonably well-correlated with sodium on the stages of an impactor associated with smaller sea-salt aerosol, suggesting an important role for nitrate in reacting with sea-salt there.

Until now no impactor data were available to discuss species involved in the chloride loss over central Antarctica. The presence of nitrate on HV filters seen during later winter/spring (Fig. 4d) when nitric acid concentrations become large (Fig. 4f), suggests a significant role of nitric acid in acidifying sea-salt particles over the Antarctic plateau. That is clearly confirmed by the examination of the size-segregated composition of aerosol (Fig. 6) showing the presence of nitrate mainly on sea-salt particles (and to a far lesser extent on sulfuric acid submicron particles).An examination of the role over time of chemical species possibly involved in aerosol de-chlorination is reported in Fig. 7, the amount of chloride loss being compared on a molar basis to the main atmospheric acidic components. The mean ionic composition of aerosol collected in spring at Concordia is reported in Table 1. It shows that, apart from sea-salt components, aerosol present at Concordia in spring/summer consists of sulfate (1.2 nEq m^{-3}), nitrate (0.08 nEq m^{-3}), MSA (0.05 nEq m^{-3}), and ammonium (0.18 nEq m^{-3}). Other non-sea-salt components ($nssK^+$, $nssCa^{2+}$, and oxalate) remain at the level of 0.01 nEq m^{-3} or less (Table 1). From that, we have calculated the acidic sulfur component as the sum of non-sea-salt sulfate plus MSA after subtracting the amount of ammonium. This examination was done for both small (0.09 to 0.46 µm diameter, Fig. 7a) and large (0.64 to 3.5 µm diameter, Fig. 7b) particles. We also report the temporal evolution of the observed chloride concentration (in grey) and of the chloride fraction that was lost (in blue) after emission. The sum of these two fractions corresponds to the amount of chloride that was originally present as sea-salt, as estimated from the observed sodium concentration and the relevant $k_{Cl/Na}$ value for freshly emitted sea-salt aerosol (see equation 2). Finally, we report the time evolution of nitric acid collected in denuder tubes (Fig. 7c). The first feature revealed by Fig. 7 is that the maximum of the chloride loss (in blue in Figs. 7a and 7b) takes place from mid/end October to mid/end November. That coincides with the period at the end of winter when there are still important sea-salt concentrations reaching Concordia (see the sum of grey and blue fractions in Figs. 7a and 7b) before the decrease by late-November/early-December and the overall increase of both submicron sulfur particles (in green in Fig. 7a) and gaseous nitric acid (in red in Fig. 7c). Although this applies to the absolute amounts of chloride lost, the percentage of chloride that is lost (see blue versus the sum of blue and grey in Figs. 7a and 7b) remains low (down to 20%) in September but generally exceeds 50% (up to 100%) in November and during the rest of summer. That clearly suggests that the amount of chloride release from sea-salt depends on the sea-salt load and of the availability of acidic species to replace chloride on sea-salt aerosol. Fig. 7 also indicates that, as reported in many previous studies (see Graedel and Keene (1995) and references therein), the fraction of chloride lost with respect to emission (i.e., the blue compared to the sum of blue and grey in Fig. 7) is larger on small particles (Fig. 7a) than on large particles (Fig. 7b).

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). A quite different picture emerges for larger particles with a competition between gaseous nitric acid and acidic sulfur compounds (Fig. 7b). Only during full summer conditions is there enough acidic sulfur present on large particles, whereas in October/November there is insufficient sulfur and nitric acid becomes important in replacing chloride. Note that later in summer, when acidic sulfur species become abundant enough in large particles, they become the dominant displacement agent rather than nitrate, despite the relatively high concentrations of nitric acid (Fig. 7c). This suggests that sea-salt aerosol is able to scavenge (mainly smaller) acidic sulfate particles, which then react to displace chloride. HNO_3 has less affinity for acidic particles, and might even itself be displaced from particles where it had already reacted.

As seen in Fig. 3, HCl exhibits typical concentrations remaining below 10 ng m^{-3} in winter and a well-marked maximum in spring with values reaching 40 to 60 ng m^{-3} in October and November. Given that the chloride depletion calculated for HV filters is overestimated, its comparison with HCl concentrations measured on denuder tubes in 2013-2015 (Fig. 4g) suggests that, in spring and summer, HCl could be around a factor two more abundant than the amount of chloride lost by sea-salt aerosol (Fig. 4e and 4g). Several causes can be invoked to explain this difference. First, HCl may be more efficiently transported to Concordia than sea-salt aerosol, implying a longer atmospheric lifetime of HCl than sea-salt aerosol. Examination of HCl and sea-salt gradients between the coast and inland Antarctica tends to support this assumption. Sea-salt aerosol decreases by more than one order of magnitude from the coast (200 ng m^{-3} and 400 ng m^{-3} of sodium at DDU in winter and summer respectively, Legrand et al., 2016) to Concordia (3 ng m^{-3} and 15 ng m^{-3} of sodium in summer and late winter, respectively, Figs. 4b and 4d) whereas HCl summer concentrations only decrease from the coast (~50 ng m^{-3} at Syowa, Hara et al., 2004; ~100 ng m^{-3} at DDU, Jourdain and Legrand, 2002) to 20-40 ng m^{-3} at Concordia (Fig. 4g). However, such a relatively weak gradient of HCl concentrations between the coast and inland Antarctica could also be accounted for by an HCl reemission from the snowpack. The existence of HCl reemission from the snowpack was suggested by the observation of a trend of chloride levels in the upper meters of the snowpack, particularly at sites characterized by very low snow accumulating rates (less than 3 g H_2O cm^{-2} yr^{-1}) like Concordia and Vostok (Legrand and Delmas, 1988; Legrand et al., 1996), whereas the phenomenon is strongly reduced at sites with higher snow accumulation rates (5 to 10 g cm^{-2} yr^{-1}) like Dronning Maud Land (Weller et al., 2004) or the South Pole (Legrand et al., 1996). A more direct evidence of the remobilization of HCl after its deposition in snow came from the observed presence of ^{36}Cl in the surface snow at Vostok (Delmas et al., 2004), due to a broad peak starting in 1940 and ending nearby the surface instead of the expected peak in 1950-1960 related to atmospheric nuclear tests having taken place in the late 1950s to the early 1960s. This process could result from HCl formed in the atmosphere being deposited and re-emitted, allowing HCl effectively to hop inland through several steps thus increasing its apparent lifetime. Alternatively it could also arise from reactions between acid and sea salt occurring in the snowpack itself, allowing new production of HCl that augments that occurring in the atmosphere. The fact that the grand average r value in aerosol at Concordia (0.7) is only slightly higher than the average (0.58, Röthlisberger et al., 2003) observed in snow between 10 m and 50 m depth (i.e., covering the last 1000 years) at Dome C (see Sect. 3.3) would suggest that post-depositional emissions may be largely of already produced HCl rather than new production in the snowpack. Since, however, the r value of 0.7 is likely underestimated due to an acid-induced remobilization of chloride on the HV filters, we cannot ruled out that a significant fraction of chloride is also lost due to HCl chemical production in the snow.

3.2. Sulfate relative to sodium fractionation in winter

In addition to the above-discussed depletion of chloride relative to sodium that mainly occurs in spring-summer, another fractionation process that mainly takes place in winter is a sulfate depletion relative to sodium with respect to the seawater composition. We have quantified this process by examining the sulfate to sodium (R) ratio in sea-salt aerosol collected on the 12 stage impactor. At the coast, as done by Jourdain and Legrand (2002), R values can be directly derived from the examination of the sulfate and sodium present in supermicron particles (diameter particles larger than 1.7 μm). However, at

Concordia the separation of the non-sea-salt and sea-salt sulfate modes is less straightforward than at coastal sites. Confirming several previous Antarctic studies, Legrand et al. (this issue) concluded that non-sea-salt sulfate present in winter there mainly originates from marine biogenic emissions. As seen in Fig. 8, there is still a small contribution of biogenic sulfate on particles having a diameter larger than 0.46 µm where the main fraction of sea-salt aerosol is present, and conversely, we can note the presence of fine sea-salt aerosol.

To evaluate the sulfate depletion relative to sodium of sea-salt aerosol reaching Concordia in winter, we therefore have corrected the concentration of sulfate present on the upper stages of the impactor for the biogenic contribution. This biogenic sulfate fraction can be estimated from the MSA concentrations and using the observed relationship between sulfate and MSA on small particles (diameter of less than 0.46 µm). The effect of the small amount of sodium present on small particles on this relationship was examined by subtracting from sulfate the sea-salt fraction. This is done by assuming a sulfate to sodium ratio of sea-salt aerosol ranging between 0.25 (if no fractionation with respect to the seawater composition is assumed) and 0.07 (if the sulfate depletion relative to sodium is very large, as seen at the coast). Figs. 8 and 9 indicate that uncertainties related to the assumed value of sulfate to sodium ratio of sea-salt aerosol have only a weak effect on the derived slope (denoted $k_{nssSO4/MSA}$) of the linear relationship between sulfate and MSA on the small particles (see the vertical bars reported in Figs. 8e and 9e). It is here important to emphasize that the $k_{nssSO4/MSA}$ values are systematically changing over the course of winter, showing higher values (16 ± 4.4, see Fig. 9 for instance) at mid-winter (June/-August) and lower values (8 ± 2.4, see Fig. 8 for instance) in late winter (September-October). The corresponding increase of the MSA to non-sea-salt ratio (from 6% to 13%), already seen at the coast by Legrand and Pasteur (1998), is discussed in Legrand et al. (this issue) for Concordia in terms of source regions of biogenic sulfur aerosol over the course of the year.

For the 5 lowest stages (smallest particle sizes) of the impactor, we find that the ratio of $nssSO_4/MSA$ is reasonably constant (red dots in Fig 8e (or Fig 9e) falling on a straight line through zero). This then supports the assumption that in winter the size distributions of biogenic sulfate and MSA are the same and that the $nssSO_4/MSA$ ratio is constant over the entire size distribution (see also Legrand et al., this issue). The similarity of the $nssSO_4/MSA$ ratio over the entire size distribution was already pointed out by Jourdain et al. (2007). This allows us, for each impactor run, to calculate the sea-salt sulfate ($ssSO_4$) present on larger particles as follows:

$$ssSO_4 = SO_4 - k_{nssSO4/MSA}\,MSA \qquad (5)$$

$k_{nssSO4/MSA}$ being the slope of the linear relationship observed between $nssSO_4^{2-}$ and MSA on the 5 lower stages of the impactor, where most of biogenic sulfate is present.

The uncertainties in calculating $ssSO_4$ are related to the accuracy of the determinations of sulfate and MSA as well as the uncertainties of the calculated value of $k_{nssSO4/MSA}$:

$$\Delta(ssSO_4)^2 = (k_{nssSO4/MSA}\,\Delta MSA)^2 + (MSA\Delta\, k_{nssSO4/MSA})^2 + (\Delta SO_4)^2 \qquad (6)$$

Uncertainties in the estimate of R values of sea-salt aerosol were then calculated as follows:

$$\Delta R^2 = (\Delta ssSO_4/Na)^2 + (ssSO_4 \text{ x } \Delta Na/Na^2)^2 \qquad (7)$$

Results of the calculated R values of each impactor run are reported in Fig. 10 together with an estimate of the uncertainties. On a total of fifty runs, it was possible to evaluate R values on forty ones leading to a mean R value of 0.17 ± 0.05. As seen in Fig. 10, missed R values were due to either too low sodium, as in June/July 2007, or/and too high MSA, as in October 2009. Discarding two R values for which the error exceed 0.05 (0.22 ± 0.06 in October 2009 and 0.27 ± 0.13 in September 2010), the average R value becomes 0.16 ± 0.05, suggesting that on average the sulfate depletion relative to sodium of sea-salt aerosol reaching Concordia in winter corresponds to a similar sea-salt fraction emitted from the open ocean (R=0.25) and from the sea-ice related processes ($R \approx 0.07$).

The temporal variability of sea-salt aerosol reaching Dome C, its level and composition with respect to the sulfate relative to sodium fractionation, were examined in the light of air masses reaching the site, as shown by calculated 10-day backward trajectories. The model was run every 6 h in backward mode for three different altitudes (0, 250, and 500 m above ground level, agl) for time periods corresponding to impactor run sampling. It is seen that when air masses arriving at Dome C have spent more than two days (up to 4 days) over oceanic sectors their mean sodium concentrations reach 47 ± 21 ng m^{-3} against 12 ± 5 ng m^{-3} when air masses have spent less than 0.5 days over oceans. Some typical examples of 10-day backward trajectories corresponding to strong, mid and weak sulfate relative to sodium fractionations are reported in Fig. 11. Backward air mass trajectory calculations also document the altitude of trajectories (not shown) and we calculated the time that air masses reaching Dome C were traveling below 600 m elevation over oceans, distinguishing between sea-ice and open ocean areas. The elevation of 600 m asl corresponds to the middle of the boundary layer whose the thickness over oceanic regions is typically 1000-1500 m. Selecting the impactor runs corresponding to sampling time periods over which the 10-day backward trajectories indicate more than one day of travel over the ocean, we find an overall decreasing trend of R (i.e. a stronger sulfate depletion relative to sodium) when air masses arriving at Dome C (0 m agl) have a longer contact with sea-ice than with open-ocean ($R^2 = 0.4$). For example, from 9 to 23 September 2006, air masses reaching Concordia had travelled more than two days over oceanic sectors, with 40% and 60% of travel time below 600 m elevation over sea-ice and open-ocean boundary, respectively. The corresponding R value is low (R = 0.1, Fig. 11a), consistently suggesting a very significant contribution of sea-ice-related processes to the sodium level. At the opposite, from 28 August to 3 September 2008 (Fig. 11d), air masses arriving at Dome C have only travelled 5% of time below 600 m elevation over sea-ice (95% over open-ocean). Intermediate situations, from 26 July to 9 August 2007 (Fig. 11b) or 28 August to 11 September 2009 (Fig. 11c) are characterized by R values close to 0.15 and 20-25 % of travel time below 600 m elevation over sea-ice (75-80% over open-ocean).

A chemistry transport model, p-TOMCAT (parallelized-Tropospheric Offline Model of Chemistry and Transport), that includes open-ocean and blowing-snow sources was developed by Levine et al. (2014) to simulate sea-salt levels in Antarctica. Tested against atmospheric sea-salt observations, the model confirmed the importance of sea-ice-related sea-salt emissions in winter at both coastal and central Antarctica. Recently, a more accurate comparison of model simulations and observations was done for the central site of Dome C (Legrand et al., 2016) on the basis of a 4-year record of bulk aerosol (2008-2011) at Concordia. We here discuss these 2008-2011 simulations with our observations. In summer, values close to 5 ng m^{-3} of sodium were simulated, consistent with our 2006-2015 observations (Fig. 4b). In winter, simulations indicated higher sodium concentrations (~ 15 ng m^{-3}) from June to September. As seen in Fig. 4 b, whereas the 2006-2015 record also suggests a winter sodium maximum close to 15 ng m^{-3}, it has to be noticed that the maximum is observed slightly later (in October and November). The model also suggests that a similar fraction of winter sea-salt aerosol at Concordia comes from open-ocean and sea ice. As above discussed, based on 38 impactor runs done in winter from 2006 to 2011, the observed R values (0.16 ± 0.05) suggests that, on average, the sea-ice and open-ocean contributions are similar at that season, consistent with the p-TOMCAT 2008-2011 simulations.

The mean mass size distribution of sodium is reported in Fig. 12 showing, that whatever the season, 80% of the sodium mass is present on particles whose diameter ranges between 0.3 and 2.6 μm, the distribution peaking between 1 and 1.6 μm diameter. These observations are consistent with those from Udisti et al. (2012) showing a maximum between 1.1 and 2.1 μm diameter. However the finding of a larger size mode in summer (around 1-2 μm diameter) than in winter (submicrometric mode) is not here confirmed by our data.

Interestingly, as seen in Fig 13, in winter the sulfate depletion relative to sodium is less important in particles of which the diameter is larger than 1.6 μm diameter. Note that very rare are the cases for which such an examination of the sulfate depletion versus the size can be conclusive with respect to error uncertainties in the estimated R values; only sampling corresponding to a high sea-salt load permits that. If confirmed such a larger depletion of sulfate relative to sodium on the smaller than on the larger particles reaching Concordia in winter suggests that the process related to sea-ice involved in the production of sea-salt aerosol in winter produces more small particles than the more common open-ocean bubble bursting process. This is also in the line with the observation made by Legrand et al. (2016) of a larger presence of sub-micron sea salt particles in winter than in summer at the coastal East Antarctic site of Dumont d'Urville, also broadly captured by model simulations, suggesting that the mechanism of sea-salt aerosol formation via sublimation of blowing salty snow particles, as formulated in Yang et al. (2008), is reasonable.

3.3. Implications for ice core studies

This multiple-year round size-segregated aerosol studies conducted in central Antarctica provides a more statistically reliable estimate of the respective contribution of sea-salt emissions from the open ocean and sea-ice surface than previous studies based on a few impactor runs for which uncertainties induced by the difficulty to separate sea-salt and biogenic sulfate were not accurately quantified. It is found that under present-day climatic conditions, a similar fraction of winter sea-salt aerosol at Concordia comes from open-ocean and sea-ice. Given the much larger extension of sea-ice, particularly during winter, around Antarctica during the last glacial maximum (Gersonde et al., 2005), it seems likely that the fraction of sea-salt aerosol from sea-ice was much increased at that time.

Both sea-salt aerosol and HCl present in the lower atmosphere of central Antarctica are expected to be efficiently trapped in freshly deposited snow there. In the present-day (2006-2015) aerosol at Concordia, we observe an annual mean level of sodium of 6.9 ± 11 ng m^{-3} and of chloride of 4.7 ± 15 ng m^{-3}, the corresponding grand average of r being close to 0.7 and the chloride depletion to 8.4 ng m^{-3}. The calculation of the chloride depletion was done by using equation (2) and by assuming a $k_{Cl/Na}$ value of 1.9 (i.e. 1.8 in summer and 2.0 in mid-winter, see Sect. 3.1). As discussed in section 3.1, if considering a sampling artefact leading to an overestimation of the annual mean lost of chloride by 40% due to acidification of HV filters, the chloride depletion would be close to 6 ng m^{-3} and the r value to 0.86. In the present-day atmosphere at Concordia, the mean annual level of HCl (16 ± 12 ng m^{-3}, see Sect. 3.1) makes this gaseous species the dominant chloride species (three times more abundant than chloride present in the aerosol phase). The ratio of total chloride (aerosol plus HCl) to sodium of 3 in the present-day atmosphere is actually considerably lower than the value of ~8-10 in surface snowpack at Dome C (Röthlisberger et al., 2003), suggesting that initially HCl is more easily deposited than aerosol chloride. However, this atmospheric chloride partitioning between gas and aerosol phase is subsequently modified after deposition as suggested by the observed decreasing trend of r values from 8-10 nearby the surface to less than one below 4-5 m below the surface (Legrand and Delmas, 1988; Röthlisberger et al., 2003). In ice deposited under present-day conditions (from 0 to 8 kyr BP) at Concordia, the mean sodium and chloride levels are of 22 and 15 ppb, respectively, and a mean r value of 0.67 is reported by Röthlisberger et al. (2003) for this time period. From this similarity of the r values in ice deposited between 0 and 8 kyr BP and in present-day atmospheric sea-salt aerosol, and as previously mentioned in Sect. 3.1, we can conclude that most of HCl initially present in snow deposited at the site was lost to the atmosphere and chloride archived in snow is mainly related to sea-salt aerosol as it reaches the site.

In the ice deposited during the last glacial maximum (LGM, from 18 to 23 kyr BP), from the observation of a r value of 1.73, Röthlisberger et al. (2003) suggested that the de-chlorination of sea-salt aerosol was suppressed in the atmosphere at that time due to high dust levels that neutralized HNO_3 and H_2SO_4 (Usher et al., 2003). Due to reduced snow accumulation rate during the colder climate of the LGM with respect to present-day conditions, we may expect that any HCl initially trapped in snow was efficiently reemitted to the atmosphere. The examination of the r value in the LGM ice would therefore be related to the state of sea-salt aerosol reaching Concordia at that period. As discussed in Sect. 3.1, a $k_{Cl/Na}$ value of 1.8 and of 2.0 in summer and winter, respectively, adequately described the present-day freshly emitted sea-salt aerosol. If we assume a similar $k_{Cl/Na}$ value of 1.9 for glacial conditions than for present-day conditions, the observed 175 ppb of chloride and 100 ppb of sodium in ice deposited between 18 and 23 kyr BP (Röthlisberger et al., 2003) correspond to a lack of chloride relative to sodium of ~15 ppb. This value is likely underestimated since the expansion of sea-ice area in winter that reached a factor of two with respect to present-day (Gersonde et al., 2005) would lead to a higher value of $k_{Cl/Na}$ value of freshly emitted sea-salt in winter, possibly up to 2.2. If we assume $k_{Cl/Na}$ value of 2.0 for glacial conditions (i.e. 1.9 in summer and 2.1 in mid-winter), a lack of chloride relative to sodium of ~27 ppb is obtained (against 27 ppb in ice deposited between 0 and 8 kyr BP). Because atmospheric concentrations at Dome C are expected to be related to the deposition flux rather than the snow concentration, the ~50% lower snow accumulation rate at the LGM suggests that the absolute depletion in the atmosphere was about a factor of 2 lower in the LGM than the Holocene. However there was a much reduced percentage loss (r value of 1.74 suggests 13% loss, compared to r value of 0.58 for the late Holocene representing 70% loss).

As seen in Figs. 4d and 4f, to-day, most of the nitrate is present in the Dome C atmosphere as nitric acid. The vast increase in nitrate concentration in Dome C ice in cold periods, extremely well-correlated with calcium (e.g., Legrand et al., 2000; Wolff et al., 2010), at least suggests the possibility that nitrate may have been mainly attached to dust aerosol, with an absence of nitric acid over the polar plateau. This is difficult to assess, because much of the nitrate over the plateau today is secondary, created by photochemistry occurring in the snowpack (Savarino et al., 2007; Davis et al., 2008), and it is not known whether such photochemistry occurred or not during the LGM. A partial neutralisation of acidic sulfur aerosol by dust could also be envisaged.

However, this simple interpretation is hard to reconcile with measurements of the acidity of melted ice (CO_2 free measurements, Legrand et al., 1982), which revealed no significant difference in ice deposited during the LGM ($[H^+] = 1.9 \pm 0.4$ µEq L^{-1}) and the present-day climatic conditions ($[H^+] = 2.1 \pm 0.5$ µEq L^{-1}) (Legrand, 1987). This is not consistent with a simple change in acidity over Antarctica as the main reason for the relative absence of de-chlorination of sea-salt during the LGM, although it does not rule out a reduction of acidity over some parts of the travel path or some parts of the year. In particular, we can imagine that, if sea-ice was greatly extended, the proportion of sea-salt arriving in winter would be even more important and perhaps shifted earlier in the spring, at a time when sulfate aerosol and nitric acid concentration is much reduced.

It therefore seems possible that the estimated factor 2 reduction in the absolute amount of chloride depletion might be due to a reduced overlap between the period of high sea salt and the period of high nitrate and acidic sulfur aerosol, combined with a possible partial neutralisation of nitric acid. However the much greater reduction in the percentage loss (which is what leads to r values close to that of sea-salt) requires another explanation, which is suggested by Fig. 7. Where grey bars extend above the sum of green and red, this can be taken to imply that chloride depletion is mainly limited not by the availability of sea-salt, but by the availability of nitric acid and acidic sulfur particles. During the LGM the sea-salt flux in Dome C ice (taken as a measure of the sea-salt aerosol concentration) was increased by a factor ~2. The flux of $nssSO_4^{2-}$ remained almost constant (Wolff et al., 2010). The correlation of nitrate with calcium suggests that more nitrate was transported as aerosol, making it hard to assess the gaseous component alone, but Fig. 7 suggests that nitrate is anyway low during the months when sea-salt is high. This implies that the acidic aerosol and gas available for reaction with sea salt during the months when sea salt is highest was at best similar to today (and probably lower), while the amount of sea salt was much higher. This would explain a modest reduction in the absolute value of Cl depletion and a much lower percentage depletion.

4. Concluding remarks

Load and composition of sea-salt aerosol at inland East Antarctica are established from multiple year-round records of bulk aerosol samplings, and for the first time in central Antarctica, the size-segregated composition of aerosol. These aerosol records are complemented, also for the first time over the high plateau, by multiple year-round sampling of gaseous HCl and HNO_3 acids. It is shown that, except in mid-winter, a depletion of chloride relative to sodium takes place throughout the year, reaching a maximum of ~20 ng m^{-3} in spring when, following winter, there are still large sea-salt amounts and acidic components start to recover. Acidic sulfur particles are always present in large enough amounts to replace chloride in small sea-salt particles whereas for larger particles gaseous nitric acid competes with acidic sulfur compounds. We find that HCl is around twice more abundant than the amount of chloride lost by sea-salt aerosol, suggesting that reemission from the snow pack represents an additional significant HCl source over the Antarctic plateau. These atmospheric data on the chloride depletion with respect to sodium in aerosol and the amount of chloride present as HCl in the gas phase are shown to be useful in discussing the aging of sea-salt in the past as inferred from ice core chemical records. Impactor runs done in winter (from 2006 to 2011) indicate a mean sulfate to sodium ratio of sea-salt aerosol present over central Antarctica of 0.16 ± 0.05, suggesting similar contribution of sea-ice and open ocean emission to the sea-salt load over inland Antarctica. It is shown that the sulfate depletion relative to sodium is larger when air masses arriving at Dome C had travelled a longer time over sea-ice than over open-ocean.

Data availability

Data on aerosol (bulk and size-segregated composition) and gaseous nitric and hydrochloric acids at Concordia can be made available for scientific purposes upon request to the authors (contact: michel.legrand@univ-grenoble-alpes.fr or Suzanne.Preunkert@univ-grenoble-alpes.fr).

Acknowledgements

National financial support and field logistic supplies for the summer campaign were provided by the Institut Polaire Français-Paul Emile Victor (IPEV) through program n°414 and 903 and the Agence Nationale de la Recherche through contract ANR-14- CE01-0001-01 (ASUMA). This work was initiated in the framework of the French environmental observation service CESOA (Etude du cycle atmosphérique du Soufre en relation avec le climat aux moyennes et hautes latitudes Sud, http://www-lgge.obs.ujf-grenoble.fr/CESOA/spip.php?rubrique2) with the financial support of INSU (CNRS). We thanks the three anonymous reviewers for their helpful comments.

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Table 1. Mean chemical composition of aerosol collected at Concordia from October to December (2006-2015). Values in bold and in parenthesis refer to the non-sea-salt components of aerosol. All concentrations are expressed in nEq m^{-3}.

Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	$CH_3SO_3^-$	$C_2O_4^{2-}$
0.47	0.18	0.02	0 .11	0.02	0 .08	0.08	1.25	0.05	0.015
	(**0.18**)	(0.01)		(<0.01)		(**0.08**)	(**1.19**)	(**0.05**)	(0.015)

Figures

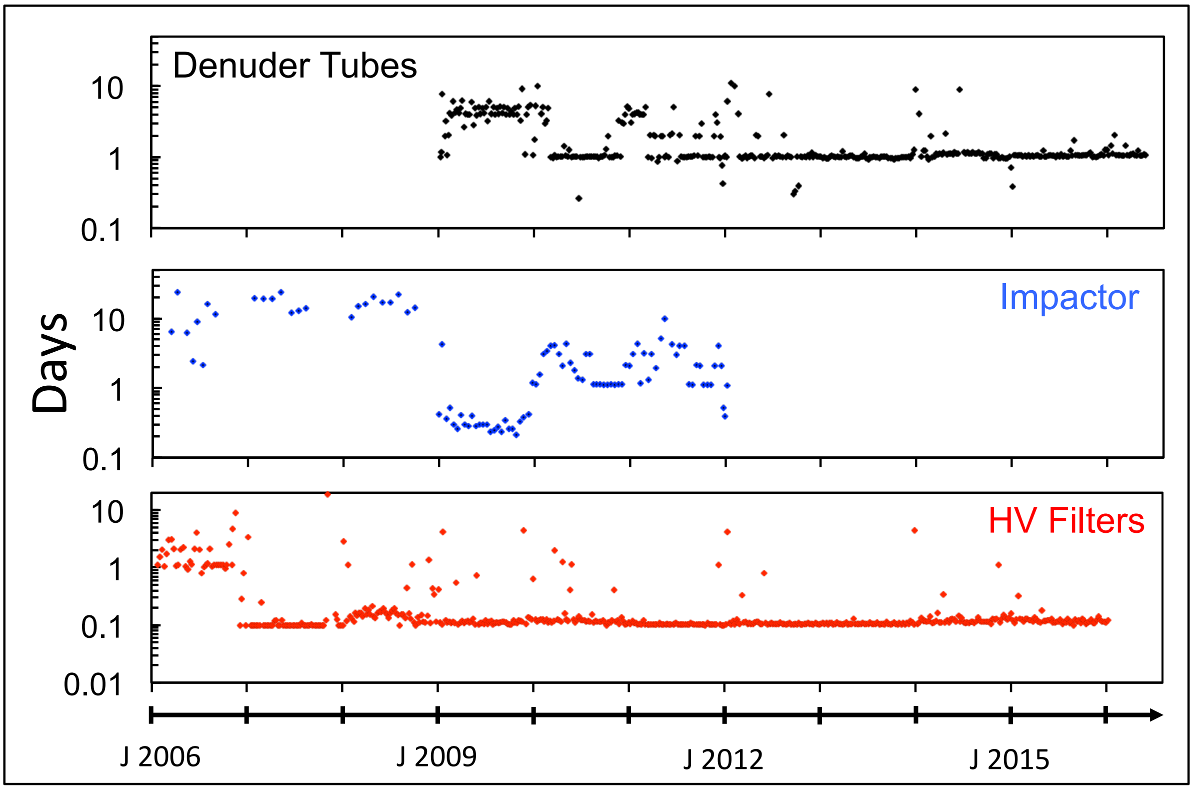

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Figure 1. Time (in days, logarithmic scales) spent between two successive samplings for acidic gases (denuder tubes), size-segregated (12-stage impactor) and bulk (HV filters) aerosol composition at Concordia (2006-2015) (Sect. 2).

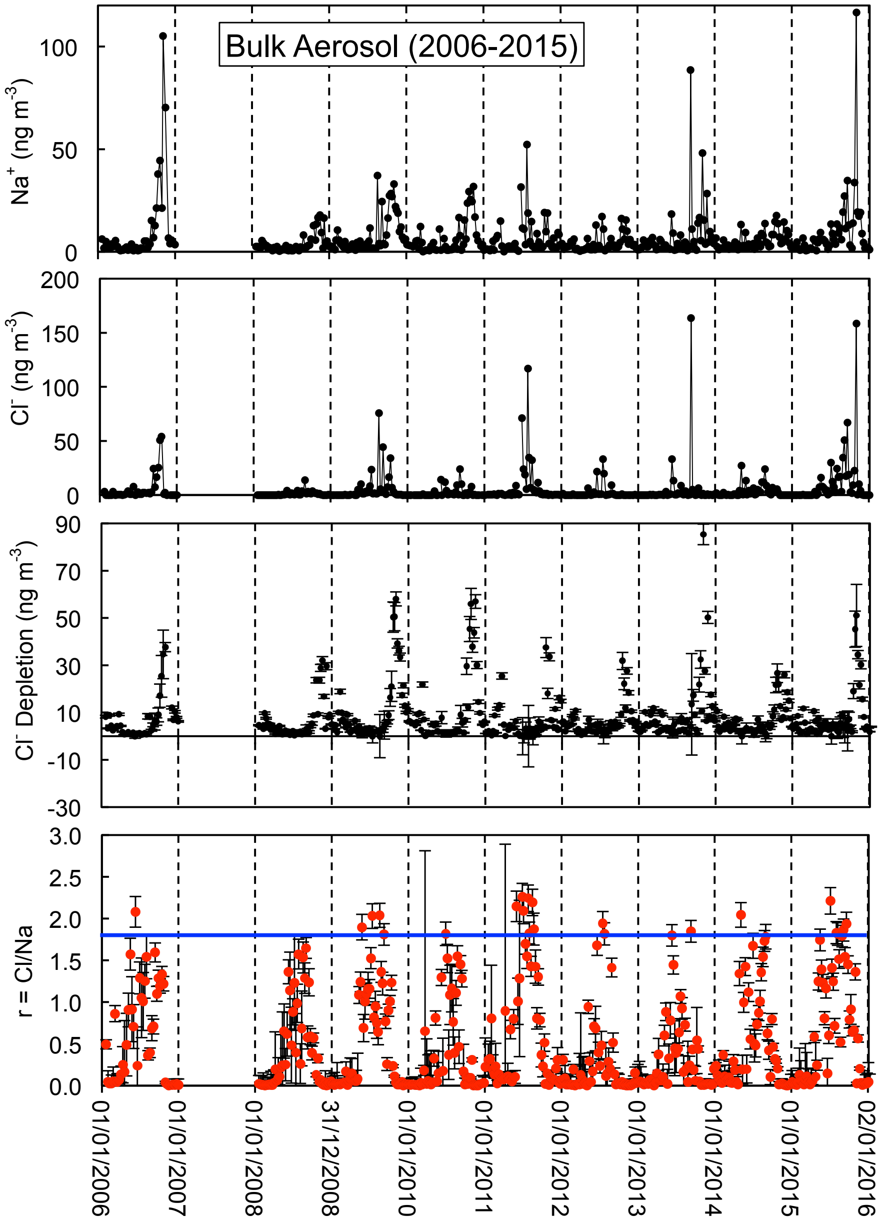

Figure 2. Weekly bulk aerosol concentrations of sodium and chloride and the calculated chloride depletion relative to sodium with respect to the composition of freshly emitted sea-salt aerosol (equation 2) and the mass Cl/Na ratio (r). Vertical bars refer to uncertainty in calculating r (equation 1) and the chloride depletion value (equations 3 and 4). The horizontal blue line refers to the r seawater reference value (1.8).

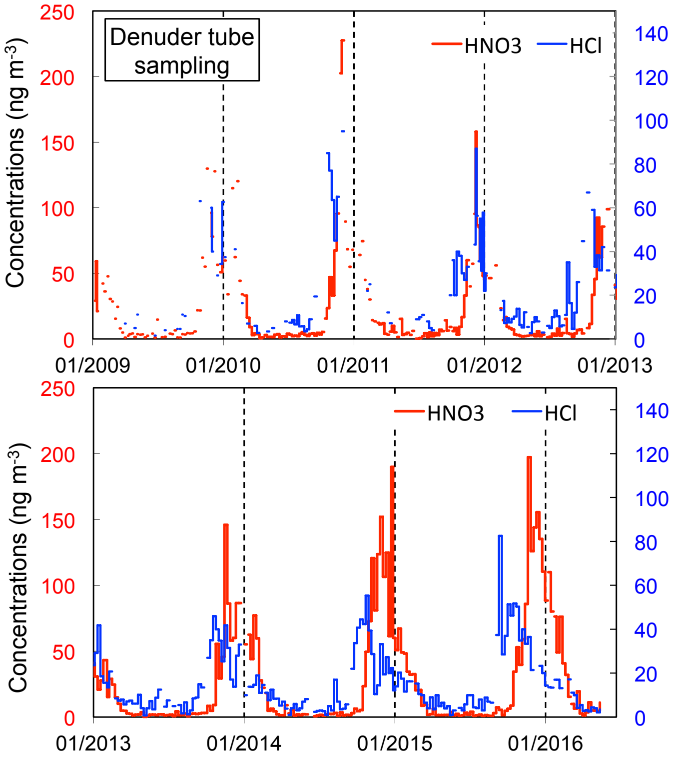

Figure 3. Year-round records of HCl and HNO_3 sampled on denuder tubes at Concordia from January 2013 to May 2016.

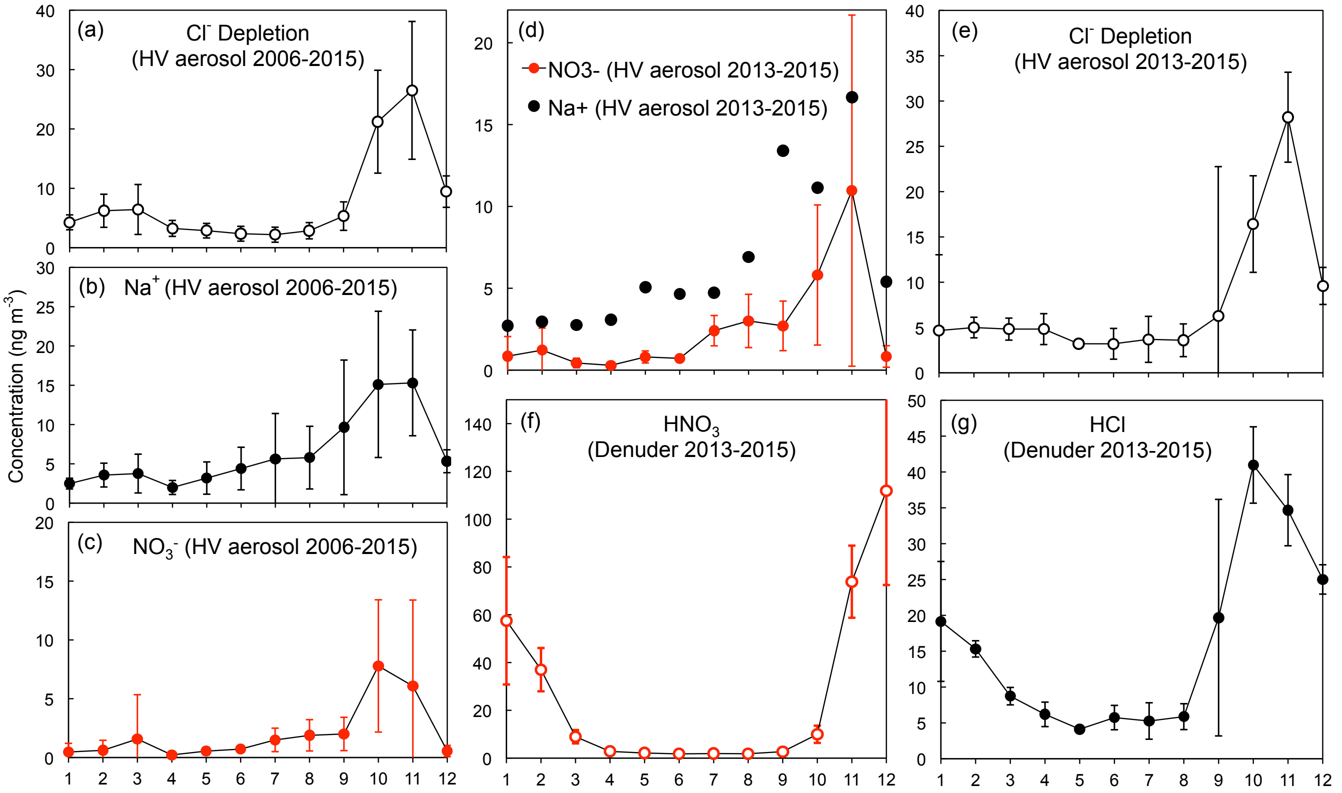

Figure 4. From (a) to (c): Monthly mean Cl^- depletion relative to Na^+ with respect to the composition of freshly emitted sea-salt aerosol (a), concentrations of Na^+ (b) and NO_3^- (c) in bulk aerosol. From (d) to (g): Monthly mean Na^+ and NO_3^- concentrations (d) and Cl^- depletion relative to Na^+ with respect to the composition of freshly emitted sea-salt aerosol (e) in bulk aerosol (2013-2015) together with concentrations of HCl (g) and HNO_3 (f) sampled on denuder tubes over the same time period. Vertical bars refer to the year-to-year variability.

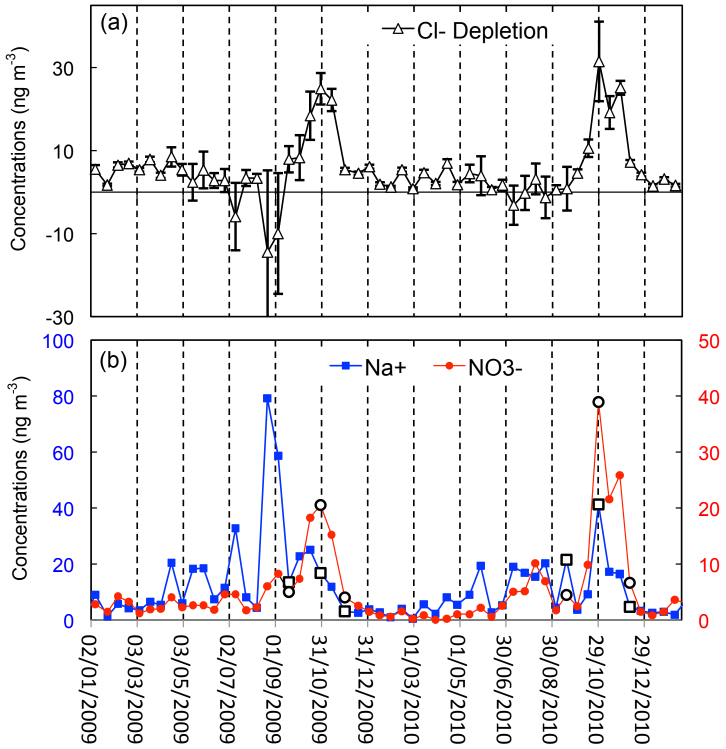

Figure 5. (a) Cl^- depletion relative to Na^+ with respect to the composition of freshly emitted sea-salt aerosol (equation 2) and (b) concentrations of Na^+ and NO_3^- in aerosol collected on the 12-stage impactor in 2009 and 2010 (biweekly sampling). Vertical bars refer to uncertainty in calculating the chloride depletion (equations 3 and 4).

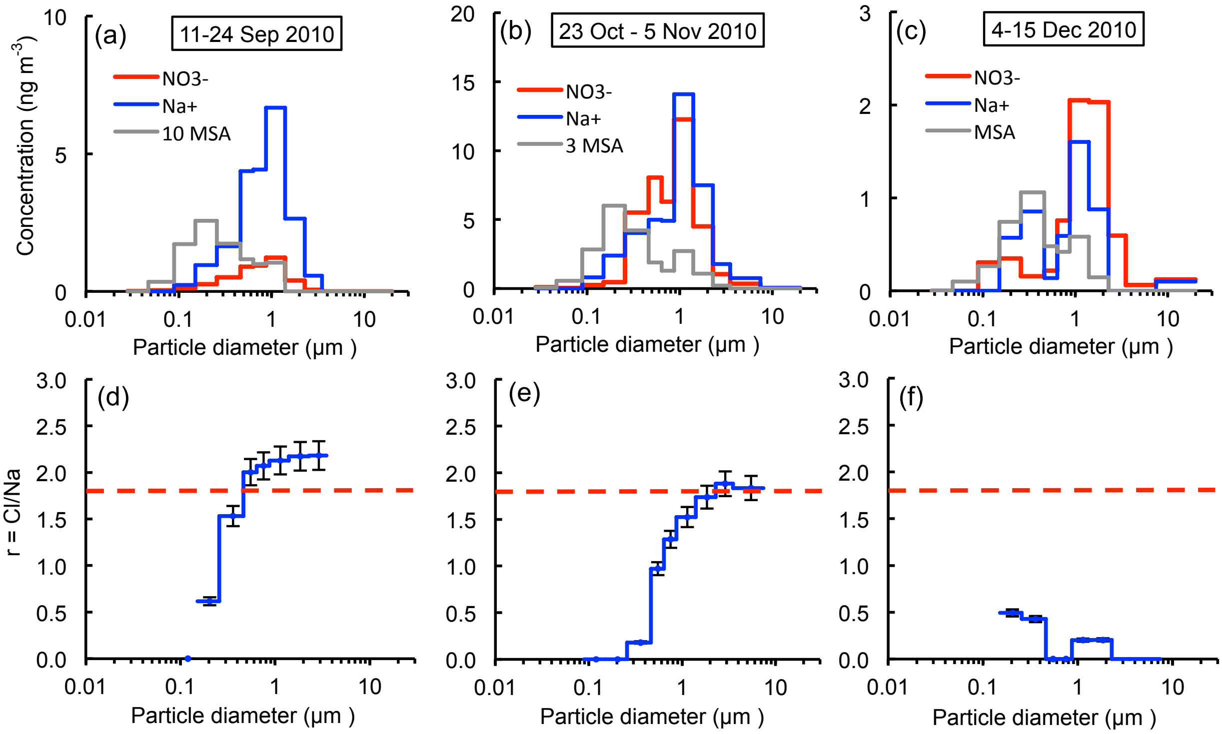

Figure 6. From (a) to (c): Size-segregated aerosol composition (nitrate, sodium, and MSA) from September to December 2010 at Concordia. In (a) and (b), MSA levels were multiplied by a factor of 10 and 3, respectively. From (a) to (c), the levels of HNO_3 simultaneously sampled on denuder tubes were enhanced from 3.5 ± 1 ng m^{-3} to 40 ± 7 ng m^{-3}, and 80 ± 1 ng m^{-3} (see Sect. 3.1). From (d) to (f), the corresponding r values as function of the aerosol size.

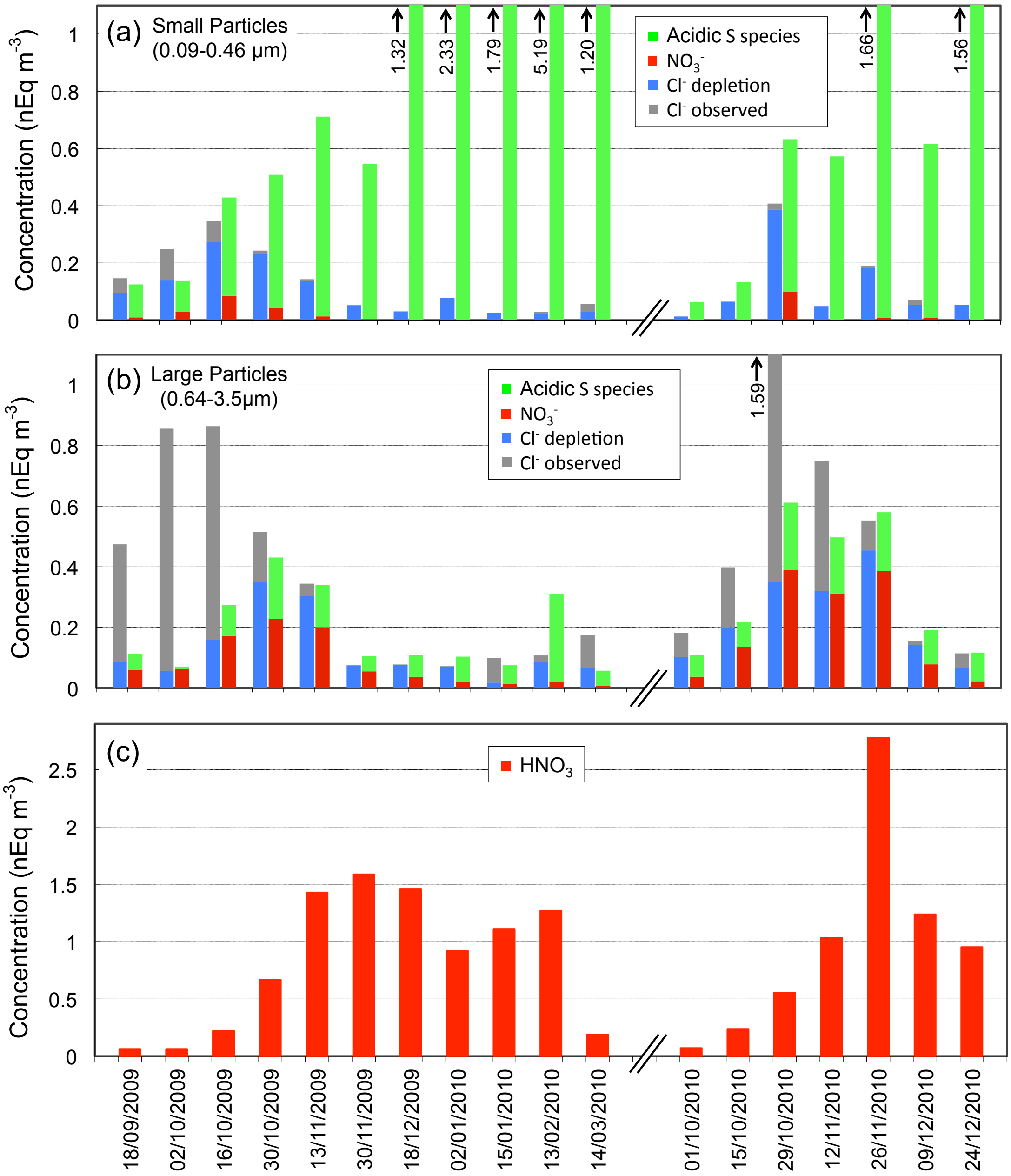

Figure 7. Acidic compounds and chloride depletion relative to sodium from October to December in 2009 and 2010. (a) and (b): Observed chloride (grey) and estimated loss of chloride (in blue, equation 2) versus nitrate (in red) and acidic sulfur species (in green, see Sect. 3.1) in small (a) and large particles (b). (c): HNO_3 sampled on denuder tubes over the same time period. All concentrations are here expressed in molar unit (in nEq m^{-3}).

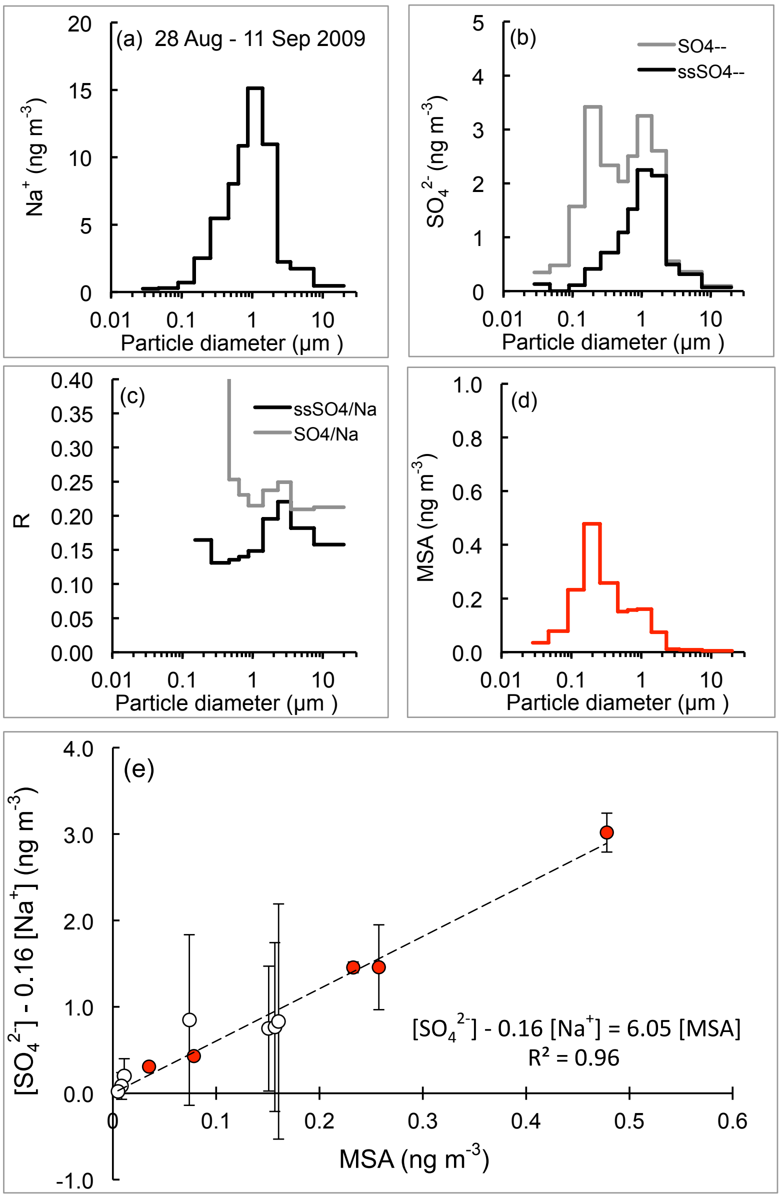

Figure 8. From (a) to (d) : Mass size distribution of Na$^+$ (a), SO$_4^{2-}$ (b, grey curve), and MSA (d) of the aerosol sampled at Concordia 28 August to 11 September 2009. Also plotted is the sulfate to sodium mass ratio (R) (c, grey curve). The black lines on the panels of sulfate and sulfate to sodium ratio (R) refer to values of sea-salt sulfate calculated after having subtracting the biogenic contribution estimated from MSA (see panel e). (e): Relationship between biogenic sulfate and MSA observed on the 12 stages of the impactor, the red points referring to values on the smaller particles (below 0.5 µm diameter). The vertical bars denote uncertainties in calculating the biogenic contribution by assuming a sulfate to sodium ratio in sea-salt aerosol ranging between 0.07 and 0.25 (0.16 ± 0.09) (Sect. 3.2).

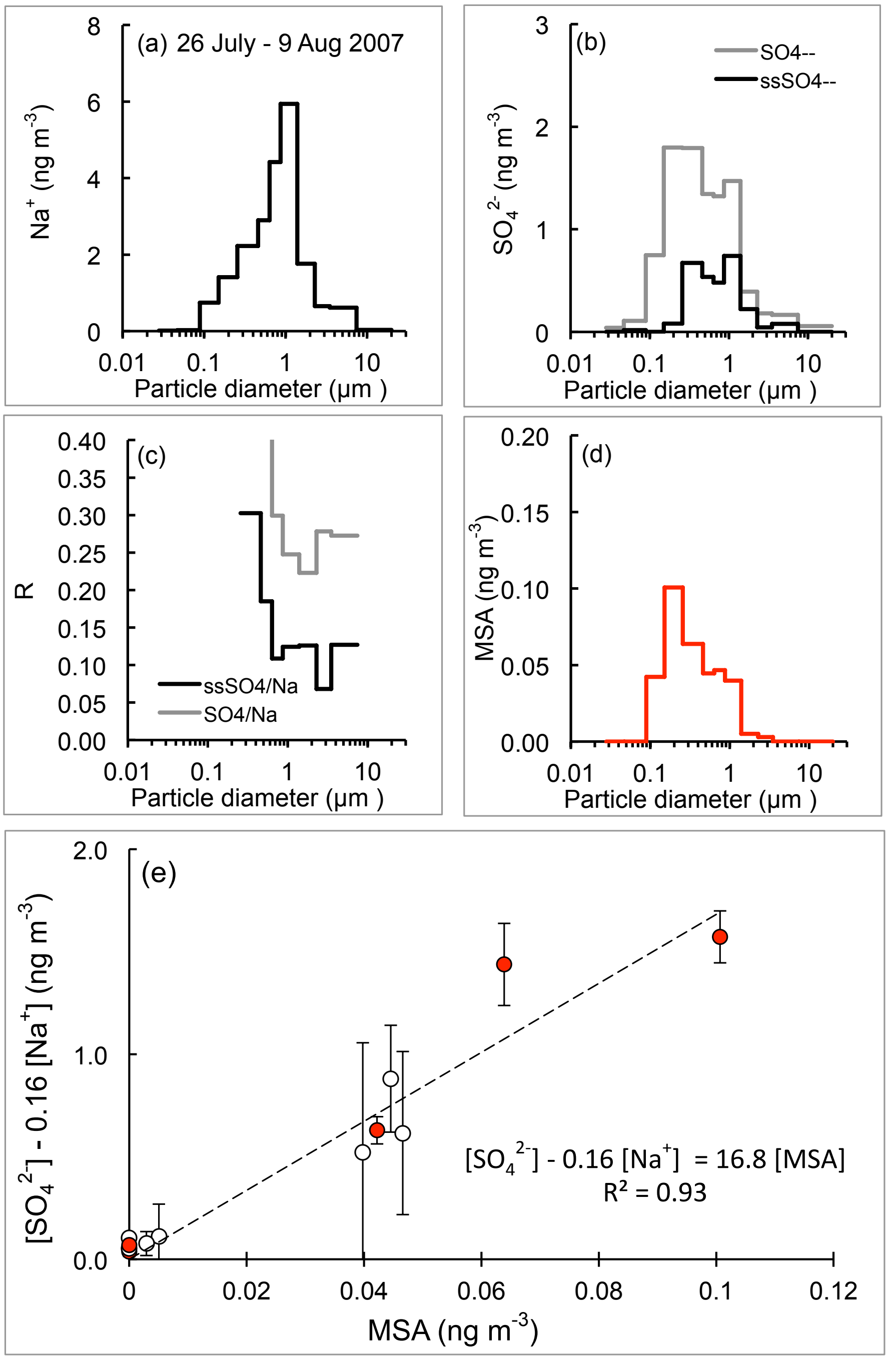

Figure 9. Same as Fig. 8 for aerosol collected between 26 July and 9 August 2007.

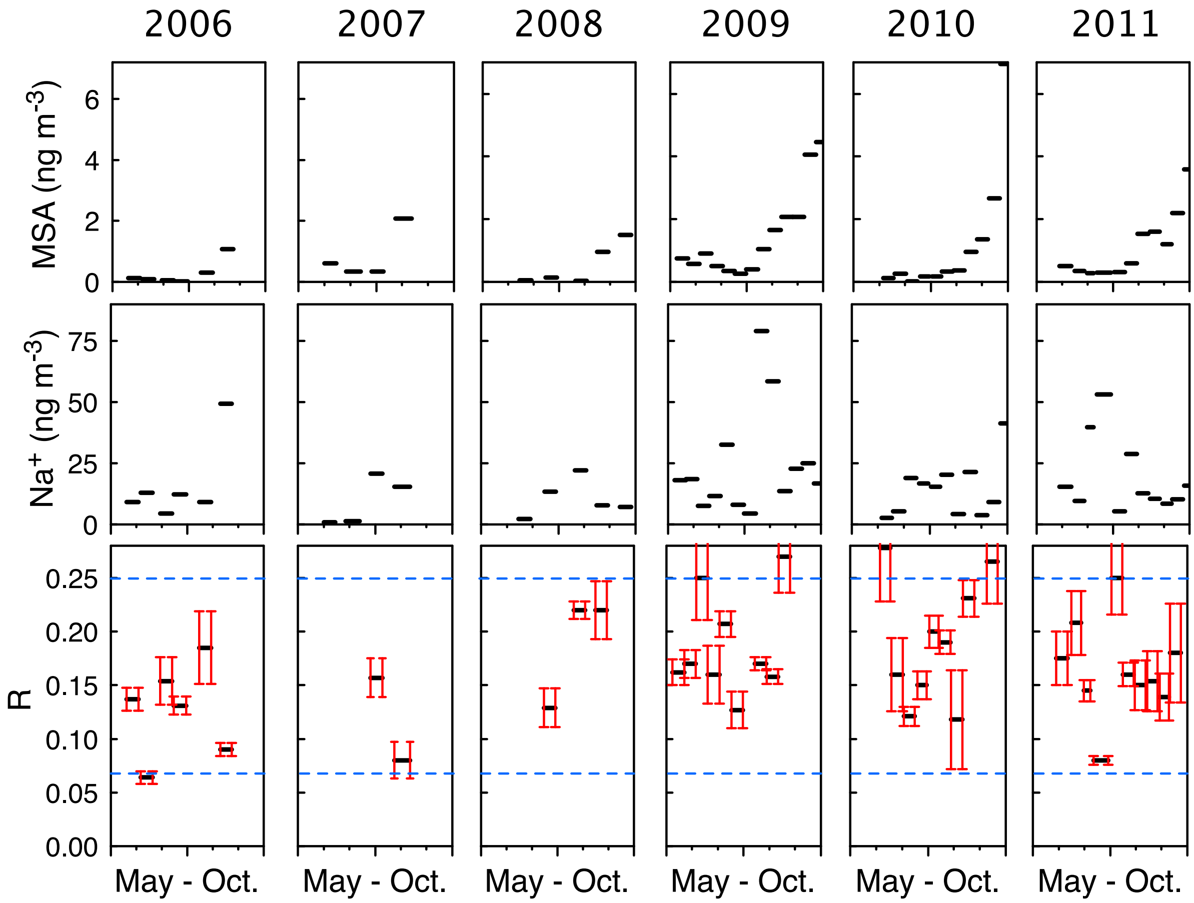

Figure 10. Year-round winter composition of aerosol collected on the 12-stage impactor sampler. MSA and sodium refer to the total concentration (i.e. the sum of concentrations observed on the 12 stages). R is the sulfate to sodium mass ratio of sea-salt aerosol. R values were derived from sulfate and sodium present on the impactor stages having collected most of sea-salt (from 0.5 to 2 µm diameter, see examples reported in Fig. 8 and 9) and for which sulfate concentrations have been corrected from its biogenic fraction (equation 5). Vertical bars refer to uncertainties related to the estimation of R (equation 7). 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).

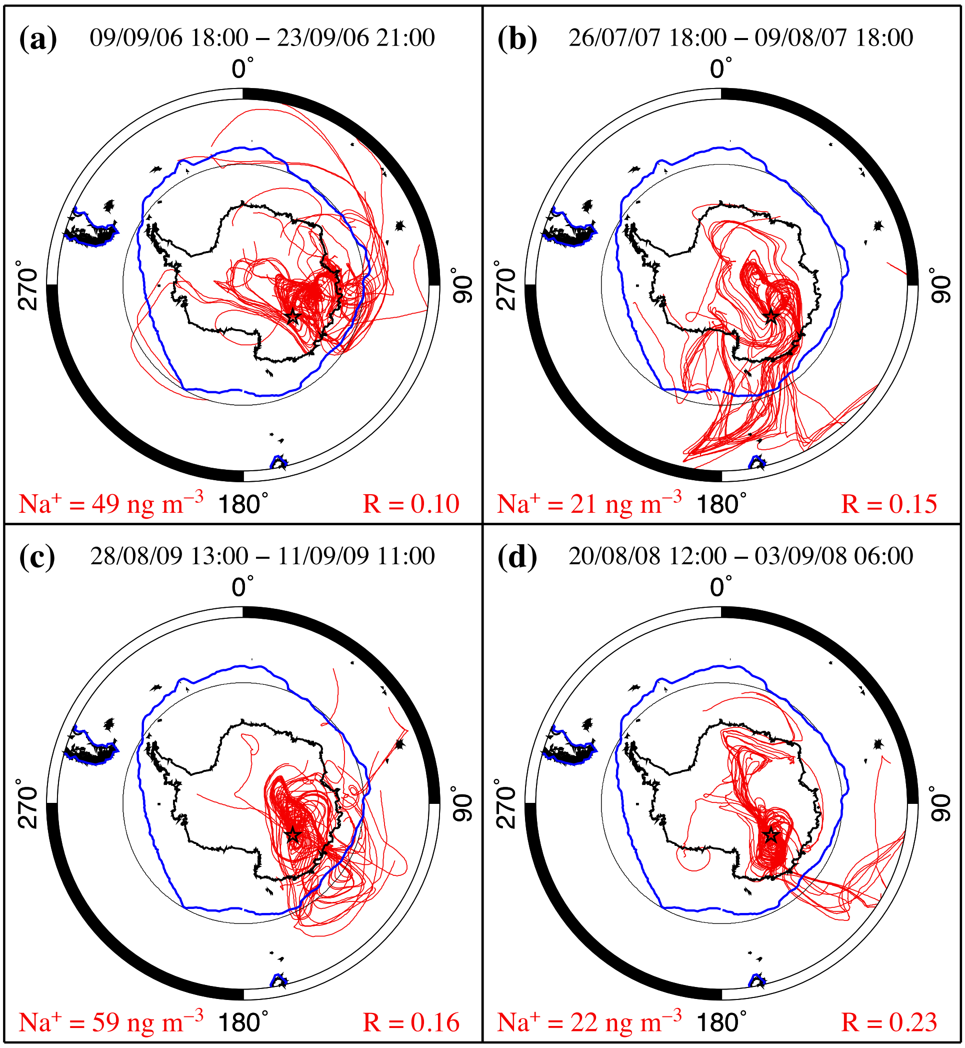

Fig. 11. Examples of 10-day backward trajectories corresponding periods of aerosol sampled by using the 12 stage impactor and for which a strong to moderate and weak sulfate depletion relative to sodium was observed (see Fig. 10). Note that trajectories arriving at 250 m and 500 m agl (not shown), revealed similar data. All lines correspond to arrivals at 0 m agl. The blue line refers to the mean location of the sea-ice edge end of winter (August) over the period 1981–2012 NOAA_OI_SST_V2 data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, http://www.esrl.noaa.gov/psd). In each case, we report in red the sodium concentration and the sulfate to sodium mass ratio (R) related to sea-salt particles (see Fig. 10).

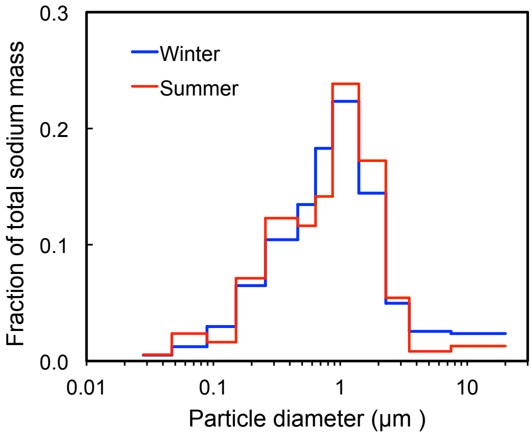

Fig. 12. Mean size-segregated mass of sodium (expressed as fraction of the total sodium mass) in winter (May-October, 55 samples) and summer (November-April, 40 samples).

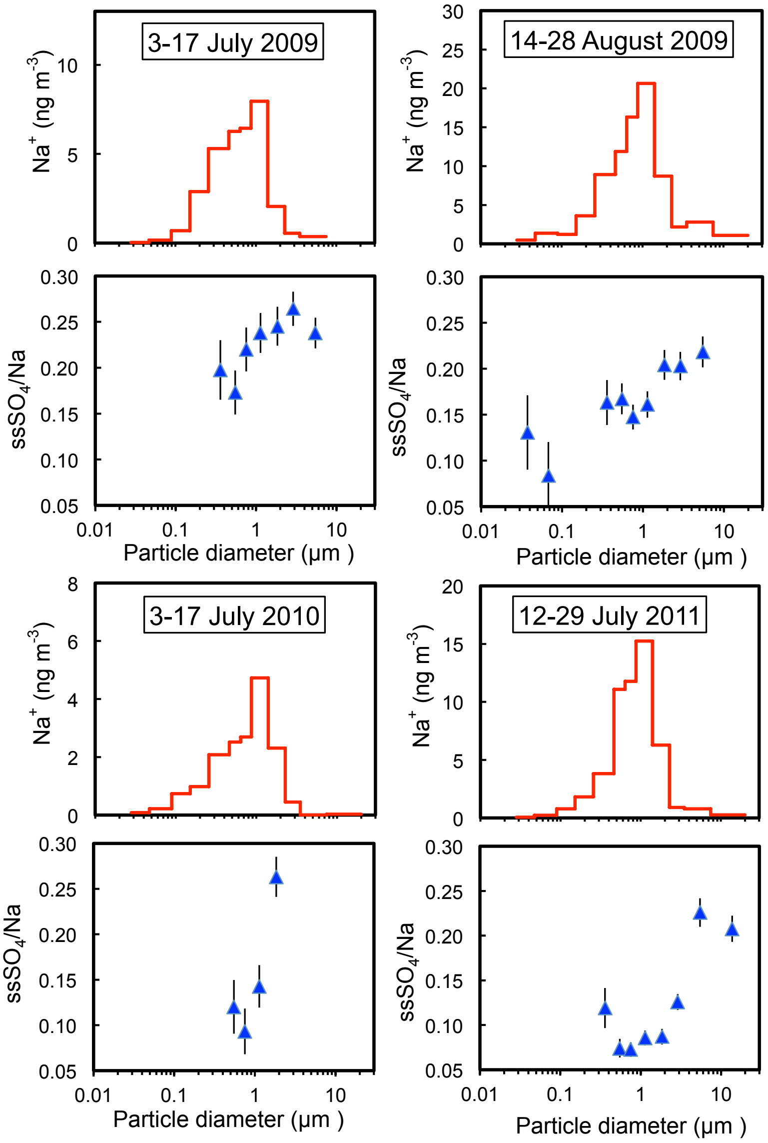

Fig. 13. Size distribution of sodium and sea-salt sulfate to sodium (R) ratio in 4 winter aerosol samples collected at Concordia. The vertical bars refer to uncertainties in calculating R.