

A spatial framework for assessing current conditions and monitoring future change in the chemistry of the Antarctic atmosphere

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Author Comments to Anonymous Referee 1

1) The discussion of the trends of single chemical or physical components and of the EOFs is often carried out with an excessive detail, giving relevance also to elements or EOFs with a low significance.

A1) The EOF sections have been completely revised and shortened.

2) the discussion is too focused on showing the effect of the glaze/dune areas and to their inability to preserve reliable chemical records.

A2) The discussion of glaze/dune areas throughout the manuscript has been significantly shortened.

3) I'd like that the discussion is focused on the sections of the traverses where the snow deposition is sufficiently unperturbed to give reliable information on the spatial and, for the firn samples, temporal trend of chemical components that can be used as markers of sources and transport processes.

A3) Much of the discussion does indeed focus on the unperturbed sections of the traverses i.e. the non-glaze/dune areas. However, the authors cannot presently discuss the temporal trends of chemical components because these core data are not yet dated. A Doctoral student is in the process of dating these records and will publish temporal results in the near future.

4) Authors sometimes confuse sources and transport processes. For instance, “upper” and “low” atmosphere cannot be considered sources.

A4) The text has been changed to indicate that “upper” and “lower” atmosphere are not considered sources, but rather “transport pathways from specific sources”.

5) Besides, the marine source (mainly, primary sea salt and secondary biogenic compounds) is sometimes incorrectly called “sea spray”.

A5) The manuscript does not contain the phrase “sea spray”, however, we have changed all instances of the “sea salt ions” reference to “marine-source ions”.

6) Authors coarsely distinguish between “upper atmosphere” (in the stratosphere) and “low atmosphere” (in the PBL or free troposphere) transport.

A6) We have updated the text to clearly define between “stratosphere”, “upper-troposphere”, and “lower-troposphere” transport pathways.

7) The relationship between snow concentrations and altitude is not depending, in my opinion, from transport processes in the stratosphere, but from accumulation rate at the site and from the kind of atmospheric scavenging (wet or dry deposition).

A7) We agree with the reviewer that these processes certainly play a role. However, there are also other processes to take into account, such as atmospheric circulation, transport pathway, and distance from source. Determining which of these is the dominant process affecting concentration is not always possible. However, it is worth bearing in mind that, as stated in the text, “it would not be accurate to correct these surface snow chemical concentration data for flux because we do not know when the precipitation occurred, or its volume.”

8) One of the most relevant features of the spatial profiles is the presence of large glaze-dune areas along at least two of the three transects. The Authors correctly discuss this aspect but, anyway, this fact highly reduces the possibility to have a reliable interpretation of the spatial trends of the chemical compounds (especially in the ITASE 03 and part of ITASE 06-07 traverses).

A8) We respectfully disagree with the second part of this comment. The first ~600km of the ITASE-03 traverse are free of glaze/dune features. When combined with the ITASE-02 traverse, this makes for a significant transect of West and East Antarctica.

9) the statistic significance of the trends is weakened by the consideration that the superficial snow samples were collected in the uppermost 2 cm snow cover.

A9) The statistic significance may be weakened, but these samples are collected over a significant area of East and West Antarctica and are therefore still providing us with valuable information.

10) samples cannot be representative of the whole year, but are likely related to a single snow events occurred in summer. Therefore, due to the large variability of the snow deposition in Antarctica, their chemical composition can be hardly compared with mean values from firn sections analysis or multi-annual record reported in literature.

A10) The reviewer is correct in stating that 2cm surface samples cannot be representative of a whole year, we are well aware of this fact. However, we feel that the reviewer has not understood the rationale for the comparison with multi-year min, max, and mean values. We compare the surface samples to multi-year values for a number of reasons...

1) to assess whether the surface concentrations are unusually high (i.e. whether contamination may have occurred); 2) to determine whether the surface values fall within the high- or low-range of the multi-year values; 3) to give us some idea of the seasonality of the samples (i.e. to reassure us that the surface samples are in fact representative of summer precipitation based upon the established seasonality of specific chemical species such as SO₄ and Na).

11) annual averaged values (and their standard deviations) are here used just to enlighten the effects of the glaze/dune areas.

A11) The reviewers statement is not quite true, see the three reasons listed in the previous response (A10).

12) the result of the comparison between concentrations and fluxes has to be carefully considered. In this way, the Authors statement that flux calculation does not significantly change the spatial trend is difficult to share.

A12) We understand the reviewers apprehension of the concentration-flux comparison with the flux calculated from a compilation of net surface mass balance data and we also agree that this is not the ideal method. However, it is the best we can do with the data we have and therefore, we feel it is worth including in the manuscript. We have added a statement to section 2.2 to make this fact clear.

13) I'd like suggest to the Authors trying to carry out ion and trace-element EOFs calculation without the physical parameters, which could create unwanted correlations (via accumulation or altitude or distance from the sea, for instance). Just EOFs with the highest significance (high percentage of the explained variance) should be shown in the figures and discussed. When a single EOF contains just one parameter (that is correct, anyway), the discussion of the spatial trend of the chemical components is more suitable than that of the related EOF.

A13) We feel that it is necessary to include the physical parameters in each EOF because one of our primary goals is to elucidate any associations that may exist between the chemistry and physical parameters. However, at the reviewer's suggestion we have reduced the discussion to only the first few (strongest) EOF modes and have adjusted the EOF figures accordingly.

14) more discussion could be made on the possibility to distinguish glazed from mega-dune areas. I suppose that the conservative properties of the mega-dune fields are higher than those in highly glazed areas.

A14) All of the points mentioned in the reviewers comment are discussed in some detail in the conclusions section (4) of the manuscript. We have added more discussion regarding the differentiation of glazed and dune areas.

15) Chemical records are precluded in the glaze/dune areas since snow deposition is not preserved and not because chemical concentrations are higher than in other areas.

A15) Sentence changed to reflect reviewers comment.

16) Superficial samples are probably related to single summer precipitation events and their chemical composition cannot be reliably compared with other annual or multi-annual records. The Authors statement is true only for the mean value measured on samples collected by snow pits or firn cores.

A16) This comment has already been addressed – see (10 & A10 above).

17) In the introduction, Authors report a lot of information on sampling and chemical analysis. Such information should be moved in the "Methodology" section or in a dedicated "Sampling and Analysis" section. Repetitive information has to be removed (in particular, those concerning the traverse information, reported also in the "Sample time periods" section).

A17) Created a "Sampling and Analysis" section and removed repetitive information.

18) The description of the sub-sampling and de-contamination procedures should be shortened and summarized.

A18) The descriptions have been shortened and summarized.

19) This section should be summarized simply referring to the Table 2 and avoiding the list of the ion MDL percentage. Authors could just say for which ions the MDL percentage is higher than the optimal value (i.e., for instance, higher than 10 % the real-sample mean values).

A19) This section has been summarized.

20) Flux vs. concentration...

A20) This comment has been addressed (see comments 7 & 12 above).

21) The relationships between d18O, temperature and elevation are well known. More interesting is the relationship between backscatter and grain-size. The results of this relationship should be deepened, even in the tentative differentiation of glaze and mega dune areas.

A21) This comment has been addressed (see comment 14 above).

22) EOFs higher than 3 (at maximum) have no significance and their trends should be deleted in the plots.

A22) This comment has been addressed (see comments 1 & 13 above). However, we respectfully disagree with the reviewers comment that “EOFs higher than 3 have no significance”. Often, a large percentage of a single (or a few) chemical timeseries will be represented by an EOF mode greater than 3. The EOF mode may have a small percentage variance explained relative to the EOF as a whole, but the signal within the EOF mode can still have meaning for the respective chemical timeseries.

23) Seasonality of samples...

A23) This comment has been addressed (see comment 10 above).

24) Finally, calcium does not show any trend supporting the Authors statement, showing summer values always lower than the averaged firn values also in the glaze/dune areas.

A24) Calcium does not exhibit a distinct seasonal signal in Antarctic cores and therefore is not useful as a seasonal indicator (see Dixon et al., 2011. International Journal of Climatology for a discussion of the calcium signal in multiple Antarctic ice cores).

25) These different patterns could demonstrate that the difference between summer samples and mean value, in characterizing glaze/dune areas, is not as reliable as Authors say. Anyway, I'm convinced that glaze/dune areas are not able to preserve reliable snow record, but this fact is hardly demonstrated by the concentration trends. In these areas, the simple observation of the presence of blue-ice, sastrugi and wind redistribution features directly suggests that they are not a conservative environment. I'd suggest to revise the section accordingly.

A25) The reviewer is neglecting the fact that we use multiple lines of investigation to identify glaze/dune areas – not just the difference between surface snow concentrations and min-max-mean firn section values. We use the backscatter and grainsize parameters in combination with the surface snow chemistry to identify glaze/dune areas.

26) Authors do not justify the different pattern of Ca in glaze/dune areas with respect to the Na trend.

A26) This comment has been addressed (see comment 24 above).

27) If K is affected by analytical uncertainties, the description of its spatial trends could be removed.

A27) We have removed the discussion of potassium spatial trends.

28) Besides, MSA trend in the 06-07 ITASE traverse is hard to understand, the superficial (summer) samples have concentrations lower than annual averaged firn values also in non glaze/dune areas.

A28) We have added additional discussion regarding the ITASE-06/07 MS trend.

29) EOFs with a low explained variance should be removed in the plots.

A29) This comment has been addressed (see comments 1, 13 & 22 above).

30) Which is the difference between “aerosols” and “particles”? I'd suggest: chemical components can reach Antarctica as gases, aerosols (dry deposition) and snow precipitation (wet deposition).

A30) An aerosol can be defined as a system of solid or liquid particles suspended in a gaseous environment. Lines 25-26 on page 898 have been modified accordingly.

31) Authors should distinguish between sources and atmospheric transport.

A31) This comment has been addressed (see comment 4 above).

32) Chloride originates mainly from sea spray but, in summer, it is subjected to exchange reactions between NaCl and sulphuric and nitric acids, giving gaseous HCl. This compound has different transport pathways with respect to sea spray.

A32) Cl is also found in the stratosphere, primarily in the form of HCL. The source of the HCl in the stratosphere is industrial chlorine compounds (see Crutzen & Arnold, 1986. Nature 324, 651 - 655; doi:10.1038/324651a0).

33) in my opinion, the distinction between “upper-atmosphere” (i.e. “stratosphere” for the Authors) and “lower-atmosphere” is not suitable to enlighten the differences in source location and atmospheric transport of chemical compounds.

A33) This comment has been addressed (see comment 6 above).

34) Differences in snow chemical composition in west or east Antarctica are probably related to differences in altitude and distance from the main sources (especially from the coastline) of the deposition sites and to the dominant transport processes (including the height of the air masses carrying on aerosols and clouds). Besides, differences in snow concentration of chemical components mainly scavenged from the atmosphere by dry deposition are controlled by accumulation rate. Authors should revise their statements in this way or cite updated references.

A34) Lines 1-5, page 899, paragraph has been updated as per the reviewers comment.

35) EOF analysis seems to be not able to reduce the component number by grouping components with the same sources or transport processes and a discussion on the sea salt, biogenic, dust and atmospheric compounds could be made by using directly the chemical markers, instead of EOFs. Besides, EOFs with scarce significance should be removed from the figures. I'd like that Authors try to reduce the parameters in the EOF analysis (maybe, removing physical parameters from the chemical EOF data-set) in order to possibly obtain better EOF results.

A35) This comment has been addressed (see comments 1, 13, 22 & 29 above).

36) Atmospheric transport of dust occurs both in the PBL (local sources) and in the high troposphere (long range transport from continental areas around Antarctica).

A36) We agree with the reviewers comment but also wish to point out that the dominant transport pathway of dust into West Antarctica is via the lower troposphere, as explained in Dixon et al., 2011 – International Journal of Climatology. We have updated Line 4, page 900 to reflect both transport pathways.

37) Along this section, too much attention is spent in enlightening the effect of glaze-dune areas. Once it is stated that these areas are not suitable for a reliable interpretation of the spatial record of snow chemical composition (I completely agree with this statement), I'd prefer that the discussion is focused on the traverse parts in which the chemical signature is significant.

A37) This comment has been addressed (see comments 2 & 3 above).

38) Trace elements... All the section requires a re-organization and should be shortened.

A38) All comments regarding this section have been addressed above. Additionally, the section has been reorganized and shortened.

39) Trace elements... The main information is related to the (expected) inverse relationship between dust-element concentration and accumulation rate (EOF 2), so demonstrating that snow concentration of dry-deposited elements is accumulation-rate dependent.

A39) The reviewers point has been added to the relevant section.

40) First two sentences of the 3.4 Section. The simple analysis of summer samples (possibly related to just one or few snow events) cannot justify a reliable comparison with multi-annual mean values, especially for components with a sharp seasonal pattern. The sentences should be changed accordingly.

A40) This comment has been addressed (see comment 10 above).

41) Could the Authors say which new information the total Cs concentration in the snow is able to give, with respect to the measurement of the ^{137}Cs isotope?

A41) The relevance of the total Cs measurement is discussed in detail at the beginning of section 4 in the manuscript. We also added that total Cs concentration may be useful as a new proxy indicator for crustal dust.

42) Authors underline the first determination of total S, Mg and K snow concentrations by ICP-MS measurements. Even in this case, no discussion on the significance of these measurements is made. I expect that all S is soluble, but the insoluble fraction of Mg and K (other than Ca) could give useful information on the crustal vs. sea spray contribution of these elements.

A42) The reviewer is quite correct in his expectation, the significance of the S, Mg, and K measurements is as stated: S is soluble and both Mg and K have a significant insoluble fraction. The text has been updated accordingly.

43) I agree with the Author hypothesis that Bi mainly originates from volcanic emissions and it is transported on Antarctica by long-range transport in the high-troposphere – stratosphere. But I think that its relatively high concentration in the plateau areas is probably correlated to the lower accumulation rates, with respect to the coastal regions, because it is dry-deposited on the snow surface.

A43) We respectfully disagree with the reviewer on this point because the Bi vs. Distance profiles (Fig.7b) do not show an increase from West to East Antarctica - as would be the case if concentrations were associated with dry deposition and accumulation rate. Rather, what we observe is the Bi concentrations uniformly high across Antarctica.

44) differences in seasonal accumulation rates (and not a supposed “upper-atmosphere, i.e. stratosphere, transport) could explain the higher (with respect to west-Antarctica) east-Antarctica Na and Sr concentrations in summer, with respect to the pattern of the multi-year mean (higher concentrations in west-Antarctica, closer to the coastline). In my opinion, the stratospheric transport of sea spray or dust over East-Antarctica is not significant (if really it occurs).

A44) It seems the reviewer is confused on this point. In the paper we state that "Na and Sr have a dominant lower-atmospheric transport pathway and are primarily deposited outside of the summer season."

45) I'd suggest calculating the enrichments relative to the Earth's upper crust only after correction for sea-water contributions and discussing just the elements that are enriched after the sea-water correction.

A45) We agree... removed discussion of EF(c) from text and now refer only to nssEF(c).

46) The discussion on Mg enrichment includes storage problems and could be very shortened or removed.

A46) We agree... discussion on Mg enrichment has been removed.

47) This section is potentially interesting but the volcanic global background contribution is very hard to evaluate and results have to be carefully considered. The estimation that 10-15% of S comes from volcanic sources seem to be very high for summer samples, with a very large biogenic contribution

A47) Two references are provided for this estimate of S. We are aware that the global volcanic background must be carefully considered and therefore we conservatively present the range of possible contributions based upon the referenced values of 10-15% (min and max) of S.

48) The contribution of the Erebus plume is still more difficult to evaluate, because its contribution cannot be considered as (spatially and temporally) homogeneously distributed. Authors are requested to discuss these topics.

A48) We understand that the Erebus plume is not homogeneously distributed. However, for the sake of the calculation we must make the assumption - Changed text to: "For the sake of the following calculation we are assuming the Erebus plume is homogeneous over Antarctica, which is likely an oversimplification."

49) Due to the large uncertainty in evaluating the volcanic fraction, just elements with significant (i.e., higher than 20%, for example) contributions should be here discussed.

A49) We agree. Shortened discussion in text accordingly.

50) Discussion has to be changed following the previously reported suggestions. Besides, the description of the future planned work could be shortened.

A50) The discussion has been changed. However, we respectfully disagree with the second part of the reviewers comment, the future work section is already short (just one small paragraph).

We wish to thank the anonymous reviewer for the many comments which help to improve our manuscript