

Interactive comment on “A spatial framework for assessing current conditions and monitoring future change in the chemistry of the Antarctic atmosphere” by D. A. Dixon et al.

Anonymous Referee #1

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Comments to the paper:

Dixon, D.A. et al., A spatial framework for assessing current conditions and monitoring future change in the chemistry of the Antarctic atmosphere.

General Comments

The paper is concerning the discussion of the spatial trend of a large number of chemical compounds and elements along three traverses in the Byrd – South Pole – Taylor Dome West/East Antarctica Sector. The paper contains a large and relevant analytical work, able to produce a qualitatively and quantitatively exhaustive data set in such a large Antarctic area. This data set can be used as a “reference record” of the current

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chemical composition of this Antarctic sector in monitoring possible future changes. For these reasons, surely the manuscript deserves the publication on The Cryosphere Discussion journal. On the other hand, the paper seems to be too descriptive, too long, and some criticisms and observations have to be made on the data statistic treatment and on their annual or seasonal significance. 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. In particular, the discussion is too focused on showing the effect of the glaze/dune areas and to their inability to preserve reliable chemical records. This is correct but, once this fact is demonstrated, 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. In this regard, Authors sometimes confuse sources and transport processes. For instance, “upper” and “low” atmosphere cannot be considered sources (with the possible exclusion of nitrate). Besides, the marine source (mainly, primary sea salt and secondary biogenic compounds) is sometimes incorrectly called “sea spray”. As concerning the transport processes of chemical compounds over Antarctica, Authors coarsely distinguish between “upper atmosphere” (in the stratosphere) and “low atmosphere” (in the PBL or free troposphere) transport. In my knowledge, the only relevant stratospheric transport to Antarctica are related to nitrate (for which is really important the stratospheric source, by photochemical reactions, together with the lightning in the free troposphere at mid-latitudes) and emissions from explosive volcanic events (mainly H₂SO₄ from oxidation of SO₂). Background volcanic emissions (degassing, little events, fumaroles) and the majority of natural and anthropic (with the exception of some gases such as CFC, N₂O etc..) sources emit particulate and gases into the PBL and the low troposphere and their transport processes are usually confined in the first few thousands of meters. The relationship between snow concentrations and altitude is not depending, in my opinion, from transport processes in the stratosphere, but from accumulation

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rate at the site and from the kind of atmospheric scavenging (wet or dry deposition). For components characterized by prevalent dry deposition (mainly dust elements, but also sea spray and biogenic compounds in internal sites of Antarctica), their concentration in the snow surface will be inversely correlated to accumulation rate, showing higher concentrations in sites at high altitudes and low temperatures. On the contrary, for sea spray and biogenic compounds in the coastal site, mainly scavenged by wet deposition, changes in amount or composition of snow events control their concentrations in the snow cover. 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). In addition, 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. In this way, 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. In this regard, I'd prefer that results from firn samples, even if their number is very lower than superficial samples, are discussed with higher detail. Indeed, annual averaged values (and their standard deviations) are here used just to enlighten the effects of the glaze/dune areas. Another relevant criticism (but here I well understand the Authors difficulty) is the lack of reliable accumulation rates along the traverses, because accumulation is fundamental in interpreting the temporal and spatial trends of chemical snow components, especially scavenged by dry deposition. I know that the dating of superficial snow is impossible and the dating of firn samples is a hard task, but Authors should be aware that accumulation rates obtained by a compilation of net surface mass balance data are just indicative and the same accumulation rate is attributed to large areas. As a consequence, the result of the comparison between concentrations and fluxes has to

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be carefully considered. In this way, the Authors statement that flux calculation does not significantly change the spatial trend is difficult to share. EOFs evaluation is an important tool of the multi-variate statistical analysis if its application to the data fits two main objectives: 1. a significant reduction of the variable number, leading to an easier interpretation of the spatial (or temporal) trends of the variables enclosed in the same EOF; 2. the inclusion in every EOF of a homogeneous group of components with the same origin or similar transport processes. Unfortunately, these goals were not fully achieved. In some cases, Authors show and discuss a EOFs number comparable with the single variables; in other cases (ion and trace-element EOFs), the first (more significant) EOFs include a large number of chemical compounds having different sources of transport processes (for instance, dust, sea spray and biogenic marine markers). 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. The first EOF of the physical properties is fully expected, because the relationships among $\delta^{18}O$, temperature, altitude and accumulation rate are well known, and deserves little attention. The relationship between back-scattering and grain size, in order to identify glaze/dune areas is more interesting and could be discussed in a deeper way. For instance, 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. For these reasons, in my opinion, the manuscript could be accepted for publication on The Cryosphere Discussion Journal after major revisions accordingly to the comments and suggestions.

Specific Comments

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Abstract

Lines 21-22 page 886. 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.

Lines 24-25 page 886. 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.

Introduction

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).

Methodology

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

Chemistry Quality Control

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).

Flux vs. concentration

This section is crucial in understanding the spatial trends of the chemical compounds or of the EOF factors along traverses passing through regions with very different ac-

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cumulation rate. Indeed, for internal Antarctic sites, many chemical components are deposited on the snow surface by dry deposition processes (for instance, dust components and, partially, sea-salt and biogenic compounds). Therefore, their concentration in the snow is inversely correlated to accumulation rate. I know that sample dating is a very hard task for short firn cores and it is not possible for superficial samples, but Authors should be aware that the compilations of net surface mass balance data can be used just as an indication of the accumulation rate and are compiled on annual basis (and cannot be used for summer samples, neither representative of the entire summer season). The results of their "flux correction experiment" should be carefully considered, especially for seasonally-characterized components (such as sea spray). Analogous prudence should be devoted in interpreting the role of the accumulation in the EOFs. In conclusion, I accept that fluxes are not evaluated (by difficulties in obtaining reliable accumulation rates), but I cannot accept the statement that flux correction is not significant.

Physical EOFs.

The relationships between $\delta^{18}\text{O}$, 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 glazed and mega dune areas. EOFs higher than 3 (at maximum) have no significance and their trends should be deleted in the plots.

Seasonality of samples.

The seasonal pattern of Na is more complex and could include contributions from the frost flower source in the sites closest to the coastline. The sentence should be improved and the references updated. The comparison of the ion concentration in the superficial (summer) samples with that calculated as averaged value in the firn samples seems to be too simplistic in order to evaluate the effect of the glaze-dune areas. Indeed, we have to remember that superficial snow samples probably are related to

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single summer snow precipitation and they not represent even all the summer period. In fact, just the uppermost 2 cm were collected in every site. Therefore, it is very hard to reliability compare the data. As a result, for instance, the Na trend shows a high variability. Its pattern in the ITASE 02 confirms the Authors statement, but ITASE 03 shows Na concentration near the mean also in non glazed/dune areas and this occurs also in several sections of the 06-07 ITASE traverse. Besides, we have to consider that summer snow concentrations are low in summer but, as demonstrated by aerosol measurement, some sea spray spikes could occur also in this season. As concerning sulphate, the pattern in the ITASE 03 and ITASE 06-07 glazed/dune areas are opposite. 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. 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.

Major ions

Authors do not justify the different pattern of Ca in glaze/dune areas with respect to the Na trend. If K is affected by analytical uncertainties, the description of its spatial trends could be removed. Different ions have different seasonal pattern and not necessary higher concentrations in the glaze-dune areas are unexpected. Biogenic sulphate, for instance, has summer maxima and it is correct that superficial snow samples have higher concentration than the mean of the firn samples. For MSA and nitrate, superficial snow samples have larger concentration than the mean of firn samples by their summer maxima and, especially, since they are not preserved in the snow when accumulation is low (as it occurs in the central Antarctica), by re-emission processes.

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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.

Major ion EOF

Unfortunately, EOF analysis cannot separate components with different sources and/or different transport processes, such as sea spray and biogenic components (all included in the same EOF; for instance, the ITASE 02 EOF-2). That makes difficult the discussion of the EOFs trend and, indeed, Authors often come back to the description of the single-compound trends. In addition, some EOFs contain just one element. EOFs with a low explained variance should be removed in the plots.

Lines 25-26 page 898. 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).

Lines 1-5, page 899. Authors should distinguish between sources and atmospheric transport. In my knowledge, just nitrate has relevant atmospheric sources (in the stratosphere, by solar irradiation of N-cycle compounds, and in the troposphere, by lightning at low, medium latitude). 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. Besides, the main transport processes in Antarctica occur via troposphere (at different altitudes, depending on the deposition site) and not in the stratosphere. In addition to nitrate, only sulphate (and other volcanic emissions, including HCl) is mainly transported in the stratosphere, if explosive eruptions inject gases and particulate at high altitudes. Therefore, 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. Differences in snow chemical composition in west or east Antarctica are probably re-

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lated 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.

Line 15, page 899. ITASE-02 EOF 1 includes mainly nitrate (together with physical parameters); EOF 2 captures both sea spray (Na, Mg and just a part of sulphate) and marine biogenic (non sea salt sulphate – dominant in the sulphate budget in summer – and MSA), mixing primary and secondary marine sources, which have different sources and, usually, different atmospheric (tropospheric) transport (note that the biogenic emissions cannot be named “sea salt ions”). Therefore, the double peak structure in the spatial profile could be explained by the different contributions of primary and secondary marine components as distance from the sea and altitude change. EOF 3 includes just Ca (probably the non sea salt fraction related to dust). The limitations of the ITASE-02 EOFs are present also in the ITASE-03 EOFs: EOF 1 captures the majority of ions and EOF 2 just nitrate. Therefore, ITASE 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

Line 4, page 900. Atmospheric transport of dust occurs both in the PBL (local sources) and in the high troposphere (long range transport from continental areas around Antarctica).

Along this section, too much attention is spent in enlightening the effect of glaze-dune

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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.

Trace elements.

Even in this section, too much relevance (in my opinion) is spent in pointing out that glaze/dune areas are not suitable for a reliable interpretation of the spatial trends along the traverses. Authors should give more attention to the positive information from non-glaze/dune areas. Besides, the section is hard to read, with some repetitions and discussion on not-significant measurements (such as Mg, by problems related to the sample storage) that could be removed. The discussion should be focused just to the elements useful as relevant markers (source, transport, climate or environmental markers). All the section requires a re-organization and should be shortened.

Similarly to the ion EOFs, even trace-element EOFs are not fully able to separate elements with the same origin and/or transport. In all the traverses, EOS 1 contains the majority of the chemical species. Some source markers are distributed in more than one EOFs. For instance, dust elements are present both in ITASE -02 EOF 1 and EOF 2 (could this pattern due to the different composition of dust originated from local source areas (Transantarctic Mountains, for instance) or coming from continental areas around Antarctica by long-range transport?). On the other hand, some EOFs contain just one element. 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.

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.

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Cs, S, Mg and K measurements by ICP-MS. It is correct that the first measurements of the spatial trend of total Cs concentration are underlined by the Authors, but I'd like that the environmental and/or climatic relevance of this finding is discussed. 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 ¹³⁷Cs isotope? Besides, 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.

Bi high concentrations. 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. With the exception of the very high values at SP (contamination from anthropic activities?) and, at a lower extent, in the glaze-dune areas, the Bi mean concentrations here measured are 2-4 times higher than those in the coastal areas and this difference could be justified by the lower accumulation rate in the traverse sites. In the same way, 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).

Trace element enrichment factors

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. The discussion on Mg enrichment includes storage

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problems and could be very shortened or removed.

Volcanic contribution

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 (both nss-sulphate and MSA contribute to the S budget). In this way, the volcanic contribution to the elements could be really over-estimated (especially for background volcanic emissions). 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. 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.

Conclusions

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

Interactive comment on The Cryosphere Discuss., 5, 885, 2011.