Response to comments by Michel Legrand

We thank Michel Legrand for the valuable and helpful comments. We believe that addressing the issues raised by Michel Legrand will considerably improve our manuscript.

Please see our reply to each comment below.

Note: All reviewer comments are in bold. All author responses are in normal format (blue) and changes in the manuscript in italics (red).

1. As for any ice core extracted from Svalbard, the large presence of melted snow layers rise the question to what extend the chemical ice core signals can be here safety related to atmospheric chemistry change. This crucial point needs to be addressed furthermore in the manuscript. As it stands, it is claimed in the abstract and the conclusion that this question is discussed in the paper but in fact it is only indirectly discussed when the common feature of nitrate and MSA is discussed in section 3.1 (see my other comments below). Since the effect of melt would differ from one chemical species to another one, I strongly suggest addressing more carefully this point as follows:

Put your Figures S1 and S2 (only available in the supplementary material) in the main text, for S1 please report not only 18O and sodium but also melt, nitrate, ammonium, and MSA.

We agree with this comment. As indicated by Figures 3 and S3, melt does occur regularly at Lomonosovfonna in summer and we will include a corresponding discussion in the manuscript. Measured borehole temperatures in the upper 42 m (between -1.7°C and -4.3°C) at the Lomo09 drill site are in good agreement with the average borehole temperature at the Lomo97 drill site of -2.8°C with a nearly isothermal profile (Van de Wal et al. 2002:" Reconstruction of the historical temperature trend from measurements in a medium-length borehole on the Lomonosovfonna plateau, Svalbard"). No liquid water was seen during drilling. Lomonosovfonna is therefore not a temperate glacier. Because of the strong seasonal T cycles we assume that meltwater formed in summer refreezes within deeper layers. Since ice lenses are formed, the percolation to deeper layers is hindered as supported by the well-preserved tritium and ^{210}Pb signals. Though runoff of melt water for the strongest melt events in the 20th century cannot totally be excluded (see Moore et al., 2005), it is assumed to be much reduced in the period of interest before 1859, for which the melt percentage was generally lower.

We changed Figures S1 and S2 by including nitrate, ammonium, and MSA, but left them in the Supplement. Referee 3 suggested adding a Figure with the raw concentration data of MSA, Na^+, NO_3^- and NH_4^+ and annual averages of melt on a time scale into the main text (see responses to Referee 3). Since we do not discuss the raw data in the manuscript we preferred not to include Figures S1 and S2 into the main text. Please note that melt cannot be resolved on a depth-scale since it was calculated as annual melt percent.

Abstract: Changes in melt at the Lomonosovfonna glacier are assumed to have a negligible effect on the decadal variations of the investigated compounds.

Drilling site and meteorological settings: Measured borehole temperatures in the upper 42 m (between -1.7°C and -4.3°C) at the Lomo09 drill site are in good agreement with the average borehole temperature at the Lomo97 site of -2.8°C with a nearly isothermal profile (Van de Wal et al. 2002). Previous studies indicate that summer melt water in the study area is refrozen mostly within the previous winter's snow, and the remainder within the next two to three lower annual layers (Samuelson, 2001). Percolation length was found to be up to 8 years only in the warmest years during the 20th century (Kekonen et al., 2005; Moore et al., 2005).

Page 24675: The average annual melt percent of the Lomo97 core was 41% (Pohjola et al., 2002) compared to 31% of the Lomo09 core. We thus assume that the maximum percolation lengths in the Lomo09 core do not exceed the eight annual layers determined for the Lomo97 core. As a

conservative estimate we used the 10-year-average record of melt percent in the PCA to examine the influence of melt on the NH_4^+ and NO_3^- records.

The melt percent is the only parameter that has a high loading in PC5. This suggests that on the considered decadal time scale the influence of melt on the ion concentration averages is negligible, which is in agreement with Pohjola et al. (2002) and Moore et al. (2005).

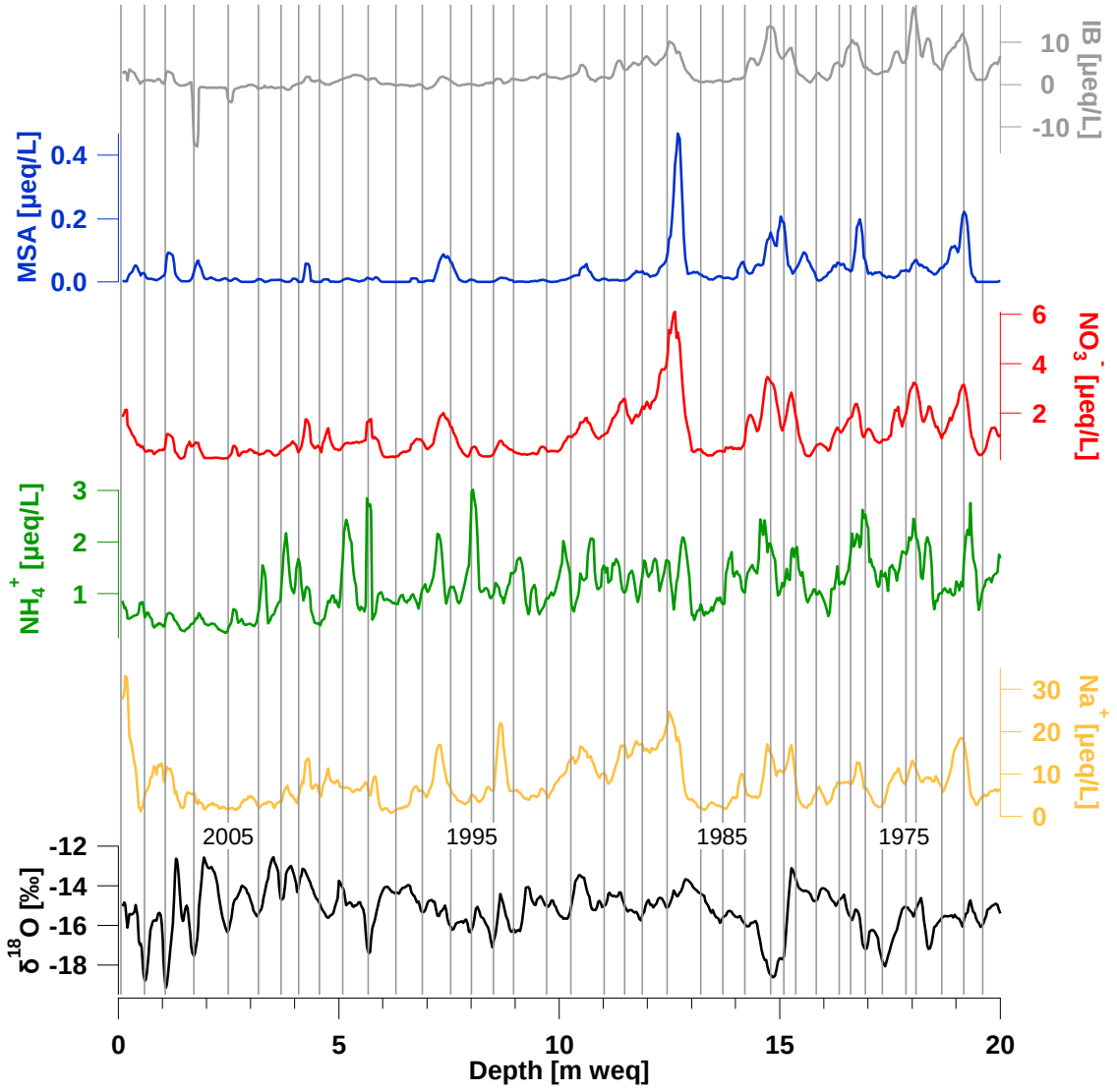

Figure S1 Example for annual layer counting (ALC) for the core section between 0 and 20 m weq using the records of $\delta^{18}O$, Na^+, NH_4^+, NO_3^-, and MSA. Data are five-point-moving averages to facility identification of the annual cycles. Grey vertical lines indicate the single counted years; numbers within the graph give the resulting year. IB is the ion balance (sum of anions-sum of cations).

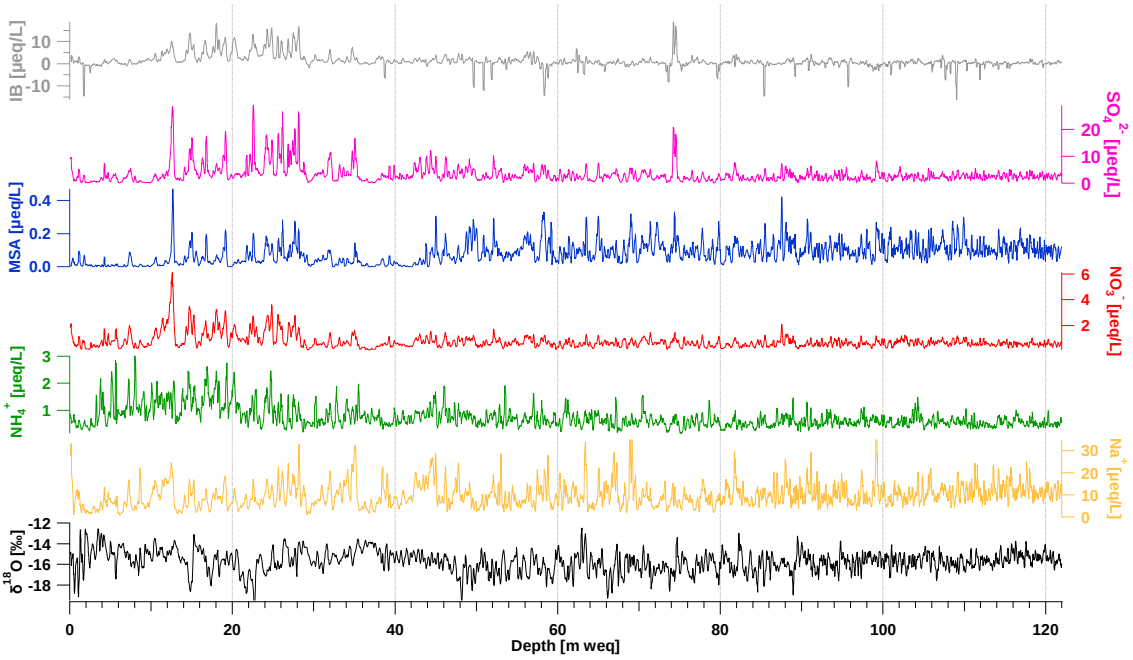

Figure S2 Raw data of $\delta^{18}O$ and of concentrations of Na^+,NH_4^+, NO_3^-, MSA, and SO_4^{2-} of the Lomo09 ice core versus depth. IB is the ion balance (sum of anions-sum of cations). Data shown are 5-point-moving-averages for better visibility especially for the IB.

Please explain how your vertical lines (annual layer counting) were identified (at the first glance on the basis of 18O but did the sodium profile really useful?).

The annual layer counting in the Lomo09 was performed using the seasonality of the $\delta^{18}O$ record and, where it was critical to identify single years, additionally the Na^+ record was used which shows higher values in summer due to more open water that can lead to sea spray formation. It was possible to count years down to a depth of 79.86 m weq which was attributed to the year 1749 AD. Below that depth it was difficult to identify the annual cycles. The annual layer counting was supported by reference horizons and ^{210}Pb dating as detailed in the manuscript.

Where are located other ions compared to sodium at such a seasonal scale? Did the delocalization due to melt differs from MSA to nitrate?

In this study the focus was on decadal variations, except for annual layer counting for the dating. The seasonality is different for instance for sodium and ammonium see above Figure 1, but we cannot rule out that melt influenced the observed seasonal variations. We do not see any difference in delocalisation in MSA and nitrate, and again this would not be relevant on the decadal time scales considered here.

Could you calculate the ionic balance to evaluate the acidic character of snow layers and melted snow layers that may have influenced the remobilisation? Please comment.

The ion balance shows a surplus of anions between 10 to 30 m weq, which is explained by anthropogenic input of acidic aerosols (we did not analyse H^+ which is therefore missing in the ion balance). Below 30 m weq the ion balance is balanced (close to zero), except for the acidic layer at 78 m weq which is the volcanic layer from the Laki eruption. We do not see remobilisation of MSA from acidic to less acidic layers (see Figure S1), since the diffusion process is hindered by the formation of ice lenses. And again this would also not be relevant on the decadal time scales considered here.

2. The discussion of data in terms of sources (natural and anthropogenic) is rather vague, often based on comparison with other smoothed records extracted at other places in the northern hemisphere to identify sources or source regions. What are missed in the manuscript, that may help the reader to follow the comparison with various records (Altai, Alps, Greenland), are air mass back trajectories calculated for winter and summer at your site using HYSPLIT and the NCEP reanalysis for instance.

Such analyses were already done by Eichler (GRL, 2009) for Altai in Siberia, by Kahl (JGR, 1997) for Summit in central Greenland or Fagerli (JGR, 2007) for the Alps (here with the EMEP transport-chemistry model). They need to be done for Svalbard as well. Such information would then strengthen (or not) your argument based on correlations between records that may be sometimes coincidental.

Kahl, J. D. W., Martinez, D. A., Kuhns, H., Davidson, C. I., Jaffrezo, J. L., and Harris, J. M.: Air mass trajectories to Summit, Greenland: A 44-year climatology and some episodic events, J. Geophys. Res. Oceans, 102, 26861–26875, doi:10.1029/97jc00296, 1997.

Fagerli, H., M. Legrand, S. Preunkert, V. Vestreng, D. Simpson, and M. Cerqueira, Modeling historical long-term trends of sulfate, ammonium, and elemental carbon over Europe: A comparison with ice core records in the Alps, J. Geophys. Res., 112, D23S13, doi:10.1029/2006JD008044, 2007.

Several publications deal with source identification for pollutants in Svalbard based on transport modelling and trajectory analysis. Hirdman et al. (2010a and b) identified Eurasia as source region, whereas Tunved et al.(2013) showed that there is a strong seasonality of dominating source areas, with Eurasia dominating during the autumn and winter period and dominance of North Atlantic air during the summer months. Concerning the sources for Greenland and the Alps: It is mentioned on page 24669 L.17 onwards that emissions from North America and Europe reach Greenland. It is mentioned on page 24674 L.13 that Western Europe mainly influences the Alps.

Hirdman, D., Sodemann, H., Eckhardt, S., Burkhart, J. F., Jefferson, A., Mefford, T., Quinn, P. K., Sharma, S., Ström, J. and Stohl, A.: Source identification of short-lived air pollutants in the Arctic using statistical analysis of measurement data and particle dispersion model output, Atmospheric Chemistry and Physics, 10, 669–693, 2010a.

Hirdman, D., Burkhart, J. F., Sodemann, H., Eckhardt, S., Jefferson, A., Quinn, P. K., Sharma, S., Ström, J. and Stohl, A.: Long-term trends of black carbon and sulphate aerosol in the Arctic: changes in atmospheric transport and source region emissions, Atmospheric Chemistry and Physics, 10, 9351–9368, 2010b. doi:10.5194/acp-10-9351-2010

Tunved, P., Ström, J. and Krejci, R.: Arctic aerosol life cycle: linking aerosol size distributions observed between 2000 and 2010 with air mass transport and precipitation at Zeppelin station, Ny-Ålesund, Svalbard, Atmospheric Chemistry and Physics, 13(7), 3643–3660, doi:10.5194/acp-13-3643-2013, 2013.

Our finding is in agreement with results from transport modelling and trajectory analysis, identifying Eurasia as source region for Svalbard (Hirdman et al., 2010a and b). Eurasian pollution dominates especially during the autumn and winter period characterised by Artic Haze episodes, in contrast to summer months when North Atlantic air masses prevail (Tunved et al., 2013).

Sometimes your conclusions drawn when comparing different records are a bit subjective. I here take the example of the nitrate change and your comparison with Altai, the Alps and Greenland. My conclusion is very different from your. When discussing source regions of concern for anthropogenic NOx emissions you pointed out the similarity between your record and the one from Altai indicating that both records show a strong anthropogenic trend followed by a decrease after 1980 that contrasts with Alpine and Greenland records showing persisting high values after 1980. From that you concluded that the main source region for anthropogenic emissions at your

site is Eurasia. First, it has be recognized that Greenland ice archives anthropogenic emissions from North America and Eurasia (polluted air masses from these two regions being advected in winter in the Arctic basin and transported over Greenland and lower latitudes in spring). Note that for Greenland you can also report in your Figure 4, in addition to Geng et al. (2014) the record from Savarino and Legrand (which, as your ice core, extend back to 1200 AD). For the Alps, the main source region is western Europe (see Preunkert et al., 2003 or Preunkert and Legrand, 2013, for nitrate records).

Savarino, J., and M. Legrand, High northern latitude forest fires and vegetation emissions over the last millenium inferred from the chemistry of a central Greenland ice core, J. Geophys. Res., 103, 8267-8279, 1998.

Preunkert, S., and M. Legrand, Towards a quasi-complete reconstruction of past atmospheric aerosol load and composition (organic and inorganic) over Europe since 1920 inferred from Alpine ice cores, Clim. Past, 9, 1403-1416, doi:10.5194/cp-9-1403-2013, 2013.

Preunkert, S., Wagenbach, D., and M. Legrand, A seasonally resolved Alpine ice core Record of Nitrate: Comparison with Anthropogenic Inventories and estimation of Pre-Industrial Emissions of NO from Europe, J. Geophys. Res., 108, D21, 4681, doi : 10.1029/2003JD003475, 2003.

Second, comparing Altai and your record my conclusions are different from you: whereas your nitrate level drops after 1980, this change is far less pronounced in the Altai record. I think you may have difficulties to fit your recent nitrate decrease with recent change of nitrogen oxide emissions. Furthermore, the Altai record clearly shows that anthropogenic emissions do not dominate preindustrial sources, and since a large variability is obvious for these natural sources in your Figure 4 (reported below), you cannot use the small decrease seen after 1980 as a sign of decreasing anthropogenic emissions there. In fact, except after 1980 your record is more similar to the Greenland one with a rather low preindustrial level compared to the strong post 1940 increase at the opposite to the record at Altai where clearly natural sources can be as high as anthropogenic emissions.

The Greenland nitrate record published by Savarino and Legrand (1998) covers only the time prior to 1980 AD. This record does therefore not help to identify if there was a decrease after 1980. Nevertheless we will include this record in Fig. 4 since it extends further back in time than the record from Geng et al. (2014) if we can get access to the data.

In the Siberian Altai record from Belukha ice core the decrease from 1980 to 2000 is similar to the decrease at Lomonosovfonna, but the record ends in 2001. At Lomonosovfonna the decrease continues until 2009 which is the end of that record. The nitrate trend in the Siberian Altai fits well with NOx emissions as discussed in Eichler et al. (2009) where the Eastern European NOx emissions are shown. The anthropogenic nitrate peak is larger than the preindustrial peak (6 µeq/L compared to 5 µeq/L, 10-year averages). We will change the colours in Fig. 4 to make this more visible.

For Europe the record from Mt. Blanc also did not show a nitrate concentration decrease before 1995 (Preunkert and Legrand, 2013) in agreement with the record from Colle Gnifetti which we show in Fig. 4.

Overall we think that the NOx emissions trends in North America, Western Europe and Eastern Europe were significantly different to distinguish the impact of these source areas on the corresponding nitrate records.

The Siberian Altai core ends in 2001, explaining why the continuation of the decrease seen at Lomonosovfonna is not recorded there. The nitrate trend in the Siberian Altai fits well with NOx emissions as discussed in detail in Eichler et al. (2009) where the Eastern European NOx emissions are shown.

Section 3.1: Whereas I found the idea to explain positive correlation between nitrate and MSA innovative and interesting, I would suggest to be more careful in your conclusion drawn by examining your 3 hypothesis (line 23-25, page 24678). I am not sure that you can discard an effect of melt as you did it, based on examination of correlation since the redistribution of nitrate may be different from the one of MSA. Please also recognize that the good correlation between nitrate and MSA works for the periods around 1480, 1560, and 1680 but fails for the peak of MSA seen around 1350 (see Figure 5).

The correlation analysis is based on 10-year-averages, so we think that melt effects can really be excluded as outlined above. We agree that the nitrate/MSA correlation breaks down between 1300 and 1400, and we acknowledge that fertilization effect is a hypothesis. MSA is influenced by both factors, fertilization by nitrate input and sea ice extent (shows maximum in 1350).

The only exception is the period at about 1350 when the correlation breaks down.

We therefore propose the fertilizing effect to be the dominant cause for the high correlation of NO_3^- and MSA in pre-industrial times.

In discussing MSA, I always like to see the sulphate record (especially during the pre-industrial time). I am sure that the record is available since you used it for the dating purpose. It would have been also interesting as additional (back-up)

We added the raw sulphate data in Figure S2 in the Supplement, see above.

Section 3.2: same comments as for nitrate: when comparing Altai and Svalbard: Fig 6 first indicates me that Svalbard and Greenland pre-industrial ammonium level are similar but are both one order of magnitude lower than at Altai, clearly pointing out the importance of continental biospheric emissions in Siberia compared to Greenland and Svalbard located far away from continental emissions.

We do not totally agree with this statement. Preindustrial ammonium levels are lower in Greenland than in Svalbard and there is no increase after the 1750s visible in the Greenland record. The difference in order of magnitude between Siberia and Svalbard is already explained in the paper as different distance to source.

Minor points:

Page 24668, line 23: I don't think that you can claim that PAN is efficiently wet deposited (PAN is not very soluble in acidic water).

We agree. PAN will be deleted.

The major source for bio-available nitrogen in the Arctic is the deposition of reactive atmospheric nitrogen that is present primarily as nitrate (NO_3^-) and ammonium (NH_4^+) (Björkman et al., 2013; Kühnel et al., 2011).

Page 24668, line 25: Replace "in general" by "at a global scale"

Will be changed.

Page 24670, line 16-18: I agree with your statement for nitrate but I don't see how possible is a migration of ammonium in a cold archives (without melting). At the opposite I am surprised that you don't mention previous studies having shown migration of MSA in snow and ice.

We do not discuss migration of ammonium, but the potential relocation by melting. The focus is here more on the loss processes or in general on the preservation of nitrate and ammonium in ice cores and the reliability of the records. We think that migration is not so relevant for our study, since we discuss decadal variations as already mentioned above.

Page 24672, line 7: Please note that nitrate is not at all totally present in the aerosol phase.

We agree that nitrate is mainly present as HNO_3 with a shorter lifetime, but also for HNO_3 wet and dry deposition should be reduced.

…aerosol related species…

Page 24668, line 24: What do you mean by "Values were not blank corrected" ? Either skips it or explains how blank are done, report if they are significant or not

We skipped this sentence since the procedure blanks are not relevant for the measured concentrations (e.g. 0.06 µeq/L for NH_4^+).