Response to comments by E. Wolff

We thank Eric Wolff for the valuable and helpful comments. We believe that addressing the issues is considerably improving our manuscript.

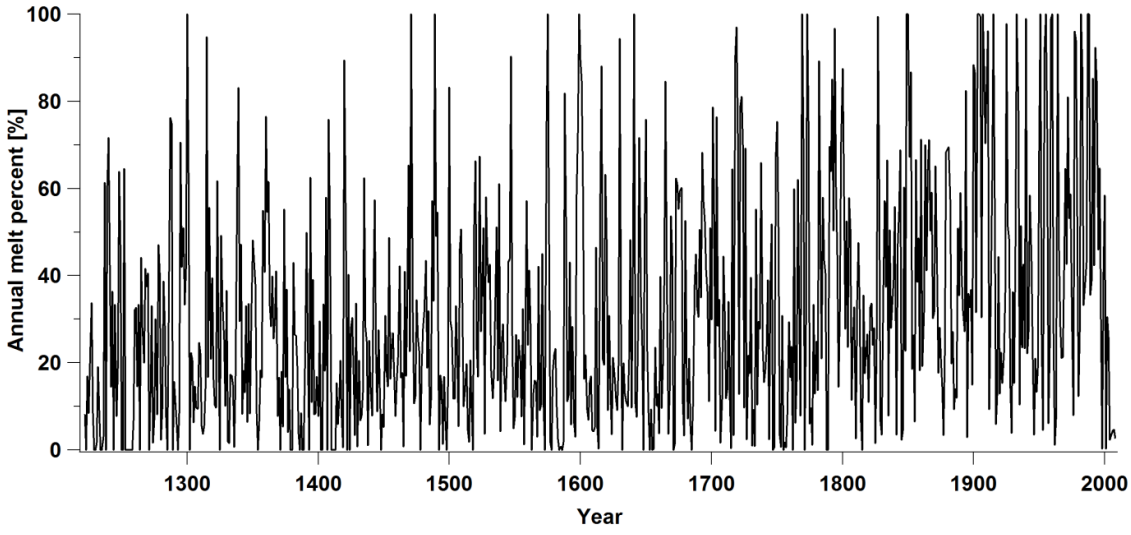
Please see our reply to each comment below.

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

This paper presents ionic chemistry data covering 800 years from an ice core in Svalbard. This is a good time period to study as it allows recent anthropogenic changes to be assessed in the light of a long period that was at least not influenced by industrial emissions. Svalbard has an interesting location, within the Arctic but influenced by different air masses compared to the more-studied Greenland records. The paper shows some intriguing trends and correlations, and will certainly become publishable. It does require some further work, mainly in two areas: firstly there are some general points that need drawing out a bit more, and secondly the authors should be a little more precise in some of their statements about what their data show (which will lead to greater caution in the conclusions).

There are two worrying general aspects of this study. The first concerns the issue of melt in the core. The high amount of melt in Svalbard cores has long been a concern, with the potential to disrupt and confuse records. I would like first to consider the issue of how much melt does occur in the ice. According to Fig S3 in the supplement and the middle panel of Fig 3, the annual melt percent is up to 1%, and when I saw this I thought the authors had been lucky and might not have a problem. However I then looked at data from Kekonen et al for the previous core near this location and found typical melt percents of more than 50%. This leads me to suspect that Fig S3 actually plots melt proportion (ie values not of 1% but of up to 100%). This should be corrected, and is such an important melt proportion that it needs much more discussion.

The melt percent in Figures 3 and S3 was corrected and is now given in %.



Given this very high amount of melt, I don't feel the authors can be entirely confident in dismissing the role melt could have played in the profiles they observe. They need to discuss it more. Firstly, the paper needs to present the temperature context of the core: what is the mean

annual temperature and the seasonal range? What is the profile of temperature in the ice itself (i.e. is this a temperate glacier, important for knowing whether melt is purely a surface phenomenon, or whether water is also present and moving at depth)? Really the only evidence given here is the reference to previous papers suggesting movement by only 2-8 annual layers, which would justify trusting decadal values – but the authors really need to expand on this, and indicate whether their data can be used to support that previous inference. The observation of low correlations between melt percent and concentration does not seem to me to be evidence that melt is not important: it is by no means obvious why you would expect a correlation. As an example, if melt occurs in a layer you may expect some (but not all) ions to move downwards out of the layer, but that doesn't allow you to predict a low concentration in the layer because you don't know what is being transported into the layer from above. It would be surprising if the eventual balance of ions in and out should depend on the amount of melt in just the single layer.

On the issue of melt therefore I suspect there will be no proof that it has not affected the profiles significantly, but it does need to be discussed more and left on the table as a concern.

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. There are only few direct air-temperature measurements from Lomonosovfonna. Mean near-surface temperature estimated by Soviet expeditions was -12.5°C at 1020 m a.s.l. (Pohjola et al. 2002:" Effect of periodic melting on geochemical and isotopic signals in an ice core from Lomonosovfonna, Svalbard"). The seasonal temperature range at Lomonosovfonna is unknown, but the long-term 1961-1990 instrumental record at the lower-altitude Svalbard airport (27 m a.s.l.) shows an average DJF temperature of -15°C and JJA temperature of 4.2°C with an annual average of -6.7°C (Nordli et al., 2014: "Long-term temperature trends and variability on Spitsbergen: the extended Svalbard Airport temperature series, 1898-2012"). 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. We attribute the discrepancy between the annual air temperature at the low elevation Svalbard airport (-6.7°C) and the mean borehole temperature to the input of energy by the release of latent heat during refreezing of melt water. 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.

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).

A second issue concerns the existence of a second set of data from a core of the same length from nearby (Lomo97). In Fig 3, the Lomo97 (grey) lines look very different from the new data, even after a long averaging, and especially for NH4+ and Na. Especially for NH4+ (compare grey and green in top panel), one's conclusion about anthropogenic versus natural variability would be quite different from Lomo97 than from Lomo09. The authors cannot therefore avoid commenting on the comparison. Is the difference due to analytical issues or is there really enough spatial variability to explain such different concentrations and variability (rendering conclusions less robust)?

The preindustrial (before 1859) concentrations of NH_4^+ at both sites are close to the detection limits of the analytical methods. In addition, NH_4^+ is prone to contamination during samples preparation and analysis. We therefore assume that the discrepancy is due to contamination and analytical issues. During our sample preparation steps we minimize NH_4^+ contamination from lab air by melting ice samples in a N_2 atmosphere.

Three observations indicate that the Lomo09 NH_4^+ concentrations are robust: 1) The preindustrial Lomo09 values are generally lower than those of Lomo97 and therefore contamination seems unlikely, 2) the Lomo09 preindustrial ion balance is close to zero, and 3) the 300 year records of NO_3^- and NH_4^+ from Holtedahlfonna (Beaudon et al., 2013) are in reasonable agreement with the Lomo09 data (Figure 3).

The concentrations of all sea salt constituents (Na^+, Cl^-, K^+, Mg^{2+}) are higher by a factor of 1.5 in Lomo09 than in Lomo97, whereas NO_3^-, SO_4^{2-}, and MSA show similar levels (period 1222-1997). Since also the annual accumulation rate is a factor of 1.6 higher at Lomo09 this suggests slightly different humidity source regions or air mass trajectories.

The ion balance is now included in Figure S2.

Sampling: Prior to analyses ice samples were melted in a N_2 atmosphere to reduce contamination from the laboratory air.

Three observations indicate that the Lomo09 NH_4^+ concentrations are robust: 1) The preindustrial Lomo09 values are generally lower than those of Lomo97 and therefore contamination seems unlikely, 2) the Lomo09 preindustrial ion balance is close to zero (Figure S2), and 3) the 300 year records of NO_3^- and NH_4^+ from Holtedahlfonna (Beaudon et al., 2013) are in reasonable agreement with the Lomo09 data (Figure 3).

I now discuss a range of more detailed issues that occur in the text:

Page 24674, line 14: I am not sure that the shape of the trends alone is sufficient to define the source region for Svalbard. There surely must be data about where air masses to Svalbard originate that would more usefully define the source region?

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.

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 characterized by Artic Haze episodes, in contrast to summer months when North Atlantic air masses prevail (Tunved et al., 2013).

Page 24676, line 15-18. For MSA-sea ice correlations in the Antarctic, I am surprised you don't cite papers by Curran et al or Abram et al.

Studies from Arctic and Antarctic ice cores found positive (Becagli et al., 2009; Legrand et al., 1997), but also negative correlations of MSA and sea ice extent (Rhodes et al., 2009; Sharma et al., 2012); see also the review on MSA and sea ice in Antarctica by Abram et al. (2013).

Abram, N. J., Wolff, E. W. and Curran, M. A. J.: A review of sea ice proxy information from polar ice cores, Quaternary Science Reviews, 79, 168-183, 2013. doi:10.1016/j.quascirev.2013.01.011.

Section 3.1. The order in which this is written is a little strange. You start with the nitrate-MSA correlation, the jump over to MSA-sea ice correlations, and then jump back (page 24678) to nitrate. I think this could be re-ordered in a way that makes it easier to follow.

We changed the order as suggested.

Section 3.1. The idea you are presenting is that MSA is controlled partly by winter sea ice and partly by nitrate fertilisation. This is intriguing, but I struggled to see how you thought the two influences interact, and I think you overstate your case on both counts:

***The correlation between MSA and nitrate looks interesting, but breaks down completely between 1300 and 1400. This should be acknowledged. *The relationship between MSA and sea ice is then tricky to assess in isolation: if you are suggesting that the main features of MSA are explained by nitrate until 1900, then it is only the residual (after accounting for that) which you would expect to correlate with sea ice. I'd have to say that, apart from the period from 1900, I don't really see much correlation.**

***The idea seems to then be that low ice extent after 1900 draws MSA away from its link to nitrate. In fact you need a really strong effect as the extra (industrial nitrate) should be fertilising the ocean strongly, increasing MSA by your hypothesis, but instead MSA drops way below its long term mean. In contradiction to that idea, ice extent is quite low from 1500-1600, with no apparent effect on MSA.**

Taken together I think your story is not quite straight, and needs to be presented in a less definite way.

We agree that the nitrate/MSA break correlation breaks down between 1300 and 1400, and we acknowledge that fertilization effect is a hypothesis. However, we do not totally agree that the low sea ice extent from 1500-1600 is a strong argument against our hypothesis. The skill of reconstruction of sea ice extent decreases before AD 1600 and the data are much more uncertain.

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

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

Page 24679, line 12. Although I don't think nitrate is of marine origin, your correlations show only that nitrate does not derive mainly from sea spray. After all, we all agree MSA is of marine origin, but that also has a very weak correlation with sodium. Therefore your statement in line 14 "not the ocean" is a bit too broad.

Yes, the correlation does only show that NO_3^- is not derived from sea spray. Because of the high solubility of nitrate in water, outgassing of HNO_3 from the ocean is unlikely.

Because of the high solubility of nitrate in water, outgassing of HNO_3 from the ocean is unlikely.

Page 24680, section 3.2. I already pointed out that the two Lomo cores have very different patterns. In line 26, you state that the Holte05 core shows the same increasing trend as Lomo09: however in that case you need also to point out the strongly different patterns in the 1700-1800 period.

The NH_4^+ record of another Svalbard core from Holtedahlfonna, spanning the last 300 years, shows a differing pattern prior to 1800 but a similar strong increasing trend as the Lomo09 record from the 18th century on (Beaudon et al., 2013) (Fig. 3).

Page 24681, line 20. While Lomo and Belukha ammonium are similar in the 20th century they appear uncorrelated before that (what is the correlation before 1900?) I don't feel you can just ignore that and claim that the same source controls both of them.

It looks more as if they may see the same industrial source, but a different pre-industrial source (or at least a different influence on transport from the source), doesn't it (as also for nitrate)?

Indeed NH_4^+ concentration trends between Lomo and Belukha agree less before ~1500. In this part, dating uncertainty of both records increases. Furthermore, NH_4^+ levels in the Lomo are very low before ~1800. The strongest argument for a similarity of the pre-industrial sources is the pronounced common NH_4^+ increase at the Lomo and Belukha site above background values already from the 18th century on, long before the industrialization. Thus, we think it is justified to state that they do have the same pre-industrial source as described in the manuscript.

Changes in manuscript (Chapter 3.2.): "The trend in the Lomo09 NH_4^+ record is similar to that in the ice core from Belukha glacier in the Siberian Altai with increasing concentrations already from around 1750 and very low concentrations between 1680 and 1750 (Eichler et al., 2009) (Figure 6). Before ~1500 NH_4^+ concentration records agree less, which could be explained by increasing dating uncertainty.