Answer to Referee Margit Schwikowski

We would like at first thank the reviewer for her comments. In the following our answers are made in italic.

This manuscript presents an ice core record of sulfate from a glacier on Mount Elbrus covering the time period 1774-2009. Generally, it is well written and structured and mostly scientifically sound (see comments below). The high-quality data set fills a gap, since it is the first sulfate record from South-Eastern Europe. Regional data on pre-industrial to industrial concentration changes of major aerosol components are essential to constrain emission estimates used in modelling the aerosol effect on climate. I therefore expect that this record will have an impact. The manuscript definitely deserves publication, after taking into account the comments and suggestions listed in the following.

Specific comments: There is very little information about the ice core itself. The coordinates are just given in the abstract and the length in the introduction. I suggest adding a short paragraph about the Elbrus ice core, including some additional information, e.g. name of the glacier, ice thickness, ice temperature, and net accumulation rate. In the abstract it is called a deep ice core, but that is relative. More important is if it reached bedrock or not. In addition, it would also be good to summarize briefly previous work published on this core.

Thanks for this comment, we added a paragraph with more information on the drill site, the ice core and previous works done on this ice core, as follows "A deep ice core was drilled to bedrock (182.6 m, i.e. 142.1 meter water equivalent (mwe)) in 2009 on the western plateau of Mt. Elbrus (43°21'N, 42°26'E; 5115 m above sea level) in the Caucasus, Russia (Fig. 1). Glaciological settings of the drill site are detailed in Mikhalenko et al. (2015). In brief, the surface of the glacier plateau is about 0.5 km^2, and the surface snow accumulation at the drill site is about 1.5 mwe yr^{-1}. Ice-penetrating radar measurements made in 2007 and 2009 revealed a maximum glacier thickness of 255 ± 8 m at the central part of the plateau, and minimum values of ~60 m near the western border of the glacier. Borehole measurements indicated temperatures of -17°C at 10 m depth and -2.4°C at 181.8 m depth. Occasionally melting of surface snow can occur, however, the thickness of the infiltration ice layers, which do not form every year, does not exceed 10 mm. After the overall presentation from Mikhalenko et al. (2015), two other studies of the ELB ice core were dedicated to black carbon (Lim et al., 2017) and water stable isotope composition on the 126 m upper layers (Kozachek et al., 2017). "

Use the term South-Eastern Europe instead of Central Europe for the source area of emissions detected in the Elbrus record.

OK done through the text.

You observe a stronger thinning with depth of the winter layers compared to the summer layer. This is interesting. Is it due to a change of precipitation seasonality or is it an artefact caused by diffusion of chemical tracers or even different flow behaviour of summer and winter layers?

We assume that the reviewer refers here to Figure 1 (mean summer and winter sample length). The initial aim of this figure was to illustrate the fact that we adapted the depth resolution of the ice sampling (from 10 cm at the top to 2 cm at the bottom) to the decrease of annual thickness with depth, in view to minimize the lost of temporal resolution. In fact this aspect is particularly important in the companion paper that deals with changes of the frequency of sporadic dust events over time. In the revised version this figure has been reworked to illustrate the thinning of summer, winter, and annual layers with depth.

As now shown, indeed the winter layer thickness decreases more than the summer ones but only in the lowest part of the core (below 155 mwe, see Figure 1d). Already observed in

Alpine small-scale glaciers we assume that this effect is likely due to more wind erosion of winter than summer snow layers upstream the drill site. Note also that no changes in the seasonal precipitation contributions were observed at least over the last 100 years for which the seasonal precipitation was reconstituted for this ice core (Kozachek et al., 2017). The text in the manuscript in section 2.1. was revised accordingly. "The large decrease of the net snow accumulation in winter below 155 m (Fig. 2), likely due to more wind erosion of winter than summer snow layers upstream the drill site as already observed at other high altitude glacier sites (e.g. Preunkert et al., 2000), leads to a more pronounced loss of resolution in these winter layers compared to the surface layers (12 samples per winter near the surface and 1-2 samples per winter at 157 m depth)."

Dating of the core: This is so central for the interpretation and it was extended compared to the previous publication (Mikhalenko et al., 2015). I therefore suggest including a depth-age figure with the 14C dating points to give an idea about the thinning (can this be fitted with a glaciological flow model?). Also the volcanic horizons used to anchor the counted layers should be shown. You evoke basal melting to explain why the deepest ice is so young. Does this mean, the glacier is not frozen to bedrock at the drilling site? This has implications on the thinning. Please clarify.

Thanks for encouraging us to add a figure, since we were not sure whether the new results are important enough to add a figure or not. We now added a figure (Fig.5) reporting the entire annual layer counting, the most prominent identified time horizons, the ^{14}C data, and a ice flow fit based on the Nye law.

Our speculation on melting was meant in the sense to not exclude that this might had happened in the past, since Mikhalenko et al. (2015) proposed that in present time basal melting might occur below ice thicknesses of more than 220 m at the Elbrus site possibly due to a heat magma chamber. If ever this heat magma chamber had an increased energy in the past this underlying heat source could have melted the lowest ice layers, without influencing significantly above situated ice layers still having negative temperatures.

The manuscript was revised accordingly: "From the observed temperature gradient in the borehole ELB site, Mikhalenko et al. (2015) calculated a heat flux at the bottom glacier that is presently 4-5 times larger than the mean value for the Earth's surface, possibly due to a heat magma chamber of the Elbrus volcano, leading to potential basal ice melting when ice thicknesses exceeds 220 m. Though the ice at the drill site and upstream is at present frozen to bedrock, we can not exclude that in the past, assuming a more active heat chamber due to the eruption of 50 ± 50 CE (located 1.6 km away from the Eastern Elbrus plateau), a temporary basal ice melting had occurred at the drill site. If so, that may explain the young age of basal ice at the volcanic crater site compared to other non-volcanic mountain glaciers."

I am not convinced by the equidistant binning of the summer and winter layers to obtain monthly values. This requires the absence of seasonality in precipitation and snow preservation. Precipitation data from nearest meteorological stations show strong seasonality (Kozachek et al., 2017). Since the monthly data are not really discussed, accept for showing the seasonality of chemical tracers in Fig. 6, I suggest deleting this part and the figure.

We agree and the figure with monthly resolution was skipped. In addition we revised the text accordingly (see paragraph 2.2) and the figure caption of old figure 2 (now figure 3).

Figure 3. ELB ice chronology at depth intervals of 166.2 to 168.5 m (top), 154.4 to 156.5 m (mid), and from 99.8 to 107.3 m (bottom), based on the ammonium and succinate stratigraphy. Vertical red lines denote yearly dissection based on identification of winter layers (see Sect. 2.2). For the two oldest time-periods (1773-1782 and 1850-1859), each sample was 2 cm long whereas for the most recent time period (1925-1934) one sample was on average 4 cm long.

Note that, though being not coherent with the intra seasonal precipitation distribution (see Kozachek et al., 2017), we here assumed that the accumulation is equally distributed within summer and winter seasons. "

Identification of annual layers and attribution of summer and winter layers: You use two criteria for that (ammonium and succinate). To which of the two do you give priority when the two signals do not agree? How does the attribution of summer and winter layers presented in this manuscript agree with the one based on the stable isotope record of the same core (Kozachek et al., 2017)?
As now specified in the text, it is required that at least one of the criteria is fulfilled and the value of the other is below or close to the limit (< 10% above). "Requiring that at least one of the criteria is fulfilled and the value of the other is below or close to the limit (< 10% above) the annual counting was found to be very accurate dating (a 1-year uncertainty) over the last hundred years when anchored with the stratigraphy with the Katmai 1912 horizon (Mikhalenko et al., 2015)."
Kozachek et al. (2017) compared the dating derived from examination of the annual cycle of ^{18}O with the dating obtained with the ammonium-succinic criteria, and found a discrepancy of 2 years at a depth of 126 m (at the end of the examined water isotope profile). The text in paragraph 2.2 was changed as "A good agreement (a 2-year discrepancy) was also found when comparing this dating with the chronology achieved by annual layer counting of the water stable ^{18}O isotope back to 1900 (Kozachek et al., 2017). Though the annual counting becomes less evident prior to 1860, Mikhalenko et al. (2015) reported an ice age of 1825 at 156.6 m depth, what is still consistent with the presence of volcanic horizon at around 1833-1940 such as Coseguina (1835)."

14C-dating: Was the AMS equipped with a gas ion source? You used a rather old version of Oxcal. I suggest using an updated version.
Yes the AMS was equipped with a gas source. The Oxcal version used (4.3) is to our knowledge the actual one (see https://c14.arch.ox.ac.uk/oxcal.html), but the reference we used (Bronk Ramsey, 1995) refers to the overall introduction of Oxcal. In the revised version, we added the reference of Bronk Ramsey (2009), which deals with new features of Oxcal 4.
we reworded the sentences as "After cryogenic extraction of the CO2 content, radiocarbon analyses were done at the accelerator mass spectrometer facility at the Curt-Engelhorn-Center Archaeometry (CEZA) in Mannheim equipped with a Gas Interface System (GIS) (Hoffmann et al., 2017). Calibration of the retrieved 14C ages was done using OxCal version 4.3 (Bronk Ramsey, 1995, Bronk Ramsey, 2009)."

Ion balance: Use the same unit (either ppb or uEq/L) in the text and in Figure 4.
OK done

Attribution of dust sources: This part of the manuscript is not convincing to me. What is the argument to relate high Ca concentrations to Saharan dust and low Ca concentrations to sources in the Middle East?
The argument is given in the paper from Kutuzov et al. (2013) as well as in the companion paper as now referenced in the text.

The plots in Figure 5 show a large scatter and low correlation coefficients, so I wonder if the ion ratios you discuss are significantly different. For the ions with strong anthropogenic influence this correlation analysis is anyway not meaningful without splitting the data set in

the pre-industrial and industrial periods. To me this part of the manuscript is weak, distracts from the main message, and could be omitted.
We agree with you and the whole discussion on the origin of dust (including old Table 2 and old Figure 5) was removed.

Important is to estimate the amount of sulfate originating from dust and correct for that when discussing anthropogenic sulfate. Attribution of sulfate related to mineral dust: Instead of arbitrarily introducing a Ca level to identify dust events, I propose to look at the pre-industrial Ca to sulfate correlation. If both are highly correlated, you can use this ratio to correct for mineral dust sulfate in the industrial period.
Thanks for this very important comment. We agree and follow your suggestion. This part was totally reworked and new dust-free sulfate figures are shown.
"As discussed in section 3, large dust events significantly enhanced the sulfate level of the ELB ice. Since, as detailed in Kutuzov et al. (this issue), their occurrence have changed over the past with more frequent events after 1950, we have examined to what extent they contribute to the sulfate trend. It is difficult to accurately directly correct sulfate concentration from the large dust event contribution since the amount of sulfur trapped by the alkaline material during atmospheric transport towards the site would be very different from event to event. For instance, Kozak et al. (2012) reported non-sea-salt-sulfate to non-sea-salt calcium mass ratios in aerosol collected in the eastern Mediterranean ranging between 0.25 (in case of direct arrival at the site of air mass from the Sahara) to 1.15 (when mineral dust passed through polluted sites located in the Balkans and Turkey before arriving at the site). Instead of corrected sulfate values for the large dust events, we therefore have reported in Figure 8 individual values of total sulfate and sulfate calculated after having removed from the average samples suspected to contain large amount of dust ($SO_4^{2-}{}_{red.}$ values). The influence of large dust events on the long-term SSA winter trend is rather insignificant and if existing (i.e. effect of < 10 ppb) remaining limited to two decades around 1870 and the recent decade (2000-2010) (Fig. 9). Remaining negligible prior to 1850, the large dust event effect on the summer trend gradually increases after 1950, reaching often 100 ppb after 1960. This change of large dust events results from change in the occurrence of drought in North Africa and Middle East regions (Kutuzov et al., this issue).
In addition to the enhanced frequency of large dust events after 1950, the calcium background concentrations (i.e., $Ca^{2+}{}_{red.}$) also change over time with an increase from 68 ± 21 ppb prior to 1900 CE to 194 ± 61 ppb after 1960 CE. As discussed by Kutuzov et al. (this issue), this change may result from changes in precipitation and soil moisture content in Levant region (Syria and Iraq). In view to discuss the free-dust sulfate changes with respect to anthropogenic emissions, we make an attempt to correct the sulfate record from this increase of the background level of dust. To do so, we examined in Figure 10 the relationship between calcium and sulfate concentration in individual summer samples corresponding to pre-industrial time (1774-1900 CE). Although being poor (R^2=0.32), the correlation suggests a mean slope of the linear SO_4red-Cared relationship close to 1. The use of this value to correct sulfate from background dust emissions would lead to an overestimation of the sulfate dust contribution. Indeed, as seen in Figure 10, there are numerous samples that contain more sulfate than what is expected with respect to the presence of pure calcium sulfate (gypsum, see the blue line reported in Figure 10), likely to due the presence of sulfate as ammonium sulfate or sulfuric acid. To correct sulfate from the background dust contribution we here have used a sulfate to calcium ratio close to 0.63 (see the red line drawn as the lower envelope of the relationship in Figure 10) and subtracted this contribution from the $SO_4^{2-}{}_{red.}$ values by using the $Ca^{2+}{}_{red.}$ values."

I recommend adding a map with the Elbrus site, outlining the dust and SO2 emission source areas.
OK, done: we show a map (Figure 1) where countries can be easily identified and dust emission are reported.

Table 5 is mentioned in the text, but does not exist.
Sorry (it was a typographic error: Table 3)

Discussion of outliers: This is hard to follow without seeing the raw data (which should be shown anyway). Can some of the outliers be explained by volcanic events? It is strange that you don't see a signal of the largest eruption in the last centuries (Tambora, 1815) and the largest eruption in the Northern Hemisphere in the last centuries (Laki, 1783).
In the revised version we introduce a raw data figure (now Fig. 7). Well we were also surprised by the lack of evidence for Laki and Tambora.

Comparison with emission estimates: You stress in the manuscript the importance to distinguish between summer and winter sulfate values and trends (to me the trends look similar). And then you compare this with emission estimates, which are annual values (I guess). This is inconsistent. You need to include the total anthropogenic sulfate record, which would also be very valuable for comparison with data sets from other ice cores, which are not resolved in summer and winter values. In addition, you give the impression that SO2 emissions in winter are much lower than in summer. The opposite is the case. The major factor producing the difference in summer and winter values at high-alpine sites is the reduced vertical atmospheric transport in winter (and not the variation in source area). You need to explain this in the manuscript.
Indeed the winter and summer trends appears quite similar at ELB. This contrasts to the case of CDD for which the model EMEP simulations confirmed the finding of a clear difference between summer and winter. We cannot discuss further that since we don't have EMEP simulations for the ELB ice core. Anyway in the revised version we also report annual means and discuss as follows: "Since available at all three sites, we compared in Figure 11 the annual long-term trends of dust-free sulfate from ELB, CDD, and BEL. The ELB and CDD annual values were calculated as arithmetic mean from 5 yr-SSA winter and summer records, whereas the BEL annual data refer to 5 year averaged raw data. Examination of the three annual records reveal three major differences between the three sites: (1) an impact of anthropogenic emissions already significant in 1910-1930 at CDD but neither at ELB nor at BEL, (2) a maximum of the anthropogenic perturbation which is reached in 1970-1980 at CDD and later at the two other sites (10 years after at ELB, and a few years after at BEL), and (3) a far less pronounced re-decrease at the beginning of the 21th century at ELB compared to CDD. The re-decrease of sulfate over the very recent decades is somewhat stronger at BEL than at ELB. Using data from Smith et al. (2011), available at http://sedac.ciesin.columbia.edu/data/set/haso2-anthro-sulfur-dioxide-emissions-1850-2005-v2-86, we report in Figure 12 emissions of SO_2 from countries located nearby the ELB site: Georgia, Azerbaijan, Syria, Irak, Turkey, Russian, Iran or located further north (Ukraine) and west (Bulgaria). In these countries SO_2 emissions became significant after 1930 and reached maximum in the late 80's or later (for Turkey and Iran). This feature clearly differs from the situation at CDD where emissions from countries located around the site (France, Italy, Spain, Switzerland and Germany) were already significant in 1930 and exhibited a maximum between the early 70's and the early 80's (Figure 10). For BEL, Eichler et al. (2009) demonstrated the importance of emissions from eastern Europe for the dust-free sulfate annual record at that site.

Finally, we tentatively examine the cause of the recent decrease of sulfate, focusing on the summer season for which the most relevant source regions are limited to countries located nearby the site. As discussed by Kutuzov et al. (this issue), 10 day backward air mass trajectories calculated for the ELB site using the NOAA HYSPLIT-4 model suggest that, in summer, air masses arriving at ELB mainly originate from the nearby Georgia, Azerbaijan, Syria, Irak, and from Turkey, South Russian, and North of Iran. As previously discussed by Fagerli et al. (2007), the CDD site in summer is mainly influenced by emissions from France, western Germany, Italy and Spain. Consistently with SO_2 emission changes, the recent sulfate decrease is more pronounced at CDD than ELB with a recovered 2005 level (316 ppb) close to the 1950 one (296 ppb) (Figure 13). At the ELB site this is not the case, here the 2005 level (380 ppb in 2005) is found to be still almost two times higher than the one of 1950 (227 ppb in 1950). An intermediate pattern is seen at BEL, likely due to a weak impact of countries like Turkey that significantly contribute to the ELB record but not the BEL one, and a more strong contribution of emissions from Russian at BEL (see also Eichler et al., 2009) than at ELB."

Considering the SO2 emission source areas you identified it is strange that you just compare the Elbrus record with the CDD record from the Alps. I strongly recommend to include the sulphate record from Eastern Europe (from Belukha ice core, Eichler et al., EST 2012).
Thanks to rise this important question. We agree and now compare ELB, CDD, and Belukha records (see our answer above and the new Figure 11).

Figure 1. I don't see the point of showing the mean summer and winter sample length. This should not be so different from the sample resolution.
OK this aspect is very important for the discussion made in the companion paper of the enhanced frequency of sporadic large dust events after 1950. So we remove this to the companion paper and reworded the old figure 1 (showing now annual, half-year summer and winter ice thickness).

Technical corrections
Title: seems too long and a bit cumbersome. Suggestion: Reconstruction of anthropogenic sulfate trends from Elbrus ice core, Caucasus.
OK we changed it: The Elbrus (Caucasus, Russia) sulfate ice core record: reconstruction of past anthropogenic sulfur emissions in south-eastern Europe".

Abstract L. 18: After having examined. . . Rephrase and give the results: dust contribution to sulfate concentrations was identified and subtracted to focus on anthropogenic sulphate (not sulfur).
OK, this sentence has been reworded.

P2L4: Replace Andreae et al., 2015 with a newer estimate e.g. from IPCC.
Well we prefer to cite this reference, which highlighted for the first time this aspect instead of an updated report (we don't discuss further this aspect later in the paper).
P2L8: "impact" instead of "disturb". Ok, we changed to "impact"

P2L13-15: The Altai and Kamchatka are not part of Europe.
We correct: In Eurasia…"

P2L16-19: ice cores have been investigated . . .to examine.
Ok done.

P3L12: Give more details how ice cores were decontaminated (by removing xx cm from the outside of the core. . .)
Ok the section was revised as following: "Ice cores were subsampled and decontaminated at -15°C using the electric plane tool methodology described in Preunkert and Legrand (2013). In brief, in a first step ice samples were cut with a band saw. After that, all surfaces of the cut samples were decontaminated by removing ~ 3 mm with a pre-cleaned electric plane tool under a clean air bench."

P3L17:loss
Ok done

P3L29: Give details, which fluid was used.
Ok we added the name of the drilling fluid: "During the drill operations, an incident occurred at the depth of 31 m and a fluid (Havoline XLC, Texaco company) was poured in the hole to liberate the drill device."

P4L7: For the ammonium seasonality earlier work should be cited (Maupetit et al., Atmos. Environ., 1995; Eichler et al., JGlac., 2000):
OK done

P6L14-15: Replace "disturb the chemistry" by changes the chemical composition Table 1: Include 14C lab sample reference number.
Ok disturb was replaced, and in fact the "Sample name" we gave in Column 1 of Table 1 is the 14Csample name used in the 14C lab. The column was renamed.