Anonymous Referee #2
Received and published: 6 August 2019

Checklist of ACP review criteria:
>Does the paper address relevant scientific questions within the scope of ACP?
Yes.

>Does the paper present novel concepts, ideas, tools, or data?
New data yes, otherwise, not really. The overall approach, methods, and interpretation of the findings, including the manner in which the results are graphically presented, are very similar to what was reported in the 2018 paper by the same authors on the older (1992) Gulyia ice core. It is understandable that the methods need to be consistent to ensure a coherent continuity between the older core and the new extension. However I can't help to wonder why the authors did not simply report findings from the two C1 cores together in a single paper. There is a great deal of unnecessary duplication of information in this new paper that is not really novel, but a simple repetition of earlier work.
[Response] The work on trace elements of the 1992 Guliya ice core was done as part of a project called "Impact of Atmospheric Trace Elements on the "Third Pole" Glaciers". When this project was developed and approved by the NSF back in 2012, we did not have the 2015 Guliya ice core. In fact, we did not have the 2015 ice core by the time we had finished the analysis. And it was because of the results of the 1992 Guliya core and the publication itself showing a small increase in Cd and Pb enrichments after 1970 that we thought the 2015 Guliya core could help us to understand those enrichments.

>Are substantial conclusions reached?
Somewhat. This is not the first ice core record of trace element deposition to have been developed from central or East Asia (cf Fig. 4 in Sierra-Hernandez et al., 2018), and it shows a continuation of the same general trend in increasing trace metal deposition in the late 20th century seen in other cores, which generally agrees with what is know of regional emission trends from possible anthropogenic sources. However, the analysis of this set of cores from Gulyia ice cap was, in my view, done with exceptional care and attention to data quality compared to previous studies.

>Are the scientific methods and assumptions valid and clearly outlined?
Yes, except in the discussion of the potential role of the North Atlantic Oscillation (NAO) on the atmospheric transport of trace elements (section 3.2). This part of the paper is weak and unconvincing, and lacks clarity. See specific comments below.
[Response] We have addressed the NAO comments below.

>Are the results sufficient to support the interpretations and conclusions?
Yes, but with the same proviso as above regarding the NAO.

>Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?
Overall, yes, or adequate references to earlier publications with details are provided. However I have some doubts about the method of calculation of the "Excess" of trace elements in the ice core. See specific comments below.
[Response] We addressed the issue with the Excess concentration. Thank you for bringing this to our attention.

>Do the authors give proper credit to related work and clearly indicate their own new/original contribution?
Yes.

>Does the title clearly reflect the contents of the paper?
Yes.

>Does the abstract provide a concise and complete summary?
Yes.

>Is the overall presentation well structured and clear?
Yes, but the introduction section repeats much of the same information that was previously given in Sierra-Hernandez et al. (2018), and seems unnecessarily long and wordy to me.
[Response] Please see below.

>Is the language fluent and precise?
Yes.

>Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?
Yes, but I have some questions about the calculation of "excesses" of TEs, see specific comments below.
[Response] We address this point below.

>Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?
I recommend shortening the introduction, abbreviating the discussion in section 3.1, and dropping section 3.2 altogether. See specific comments below.
[Response] We think that while the introduction might indeed be a bit long, it is necessary to put into context the importance of trace elements, the changes in the region that could lead to increases in atmospheric toxic metals, and what we did and found in the 1992 Guliya core. We acknowledge that some of the information was already given in our previous publication, however the reader of this new manuscript might not necessarily know it and might not necessarily go back to it. We did shorten it and make it less wordy as the reviewer said. We eliminated the following paragraph
"The rapid economic growth of China has been the result of its economic reform and open policy beginning in 1978 after Mao Zedong's death and the subsequent five-year plans (FYP) implemented by the Chinese government. With their economic growth, China and India started to increase their coal consumption since ~1970 amplifying the global atmospheric emissions of CO_2 and $PM_{2.5}$"

And the following lines:
"The number of registered vehicles increased by ~400 % between 1996 (3.838 million) and 2014 (15.168 million) (Bajwa, 2015). Emissions from motor vehicles (60–70 %), industry, and the generation of ~54,000 t of solid waste per day which is either dumped or incinerated have been estimated as the principal sources of $PM_{2.5}$ and air pollution in Pakistan"

Regarding Section 3.1, we also feel that is important to discuss the similarities with the emissions from Pakistan for instance (Figure 5). While we cannot conclude that Pakistan is the dominant source, as suggested by the reviewers, it shows the reader that it is a possibility and perhaps they might look further into this. We mentioned that we also investigated the emission sectors from other countries. However, we do not show all of them as there is no similarity.

>Are the number and quality of references appropriate?
Yes.

>Is the amount and quality of supplementary material appropriate?
Yes.

Specific comments:
I reviewed an earlier version of this paper which had been submitted for consideration in another journal. I had made a number of recommendations for improving the paper, many of which were implemented by the authors in this new version. I focus below on some of the recommendations that were not followed, and on other points.
[Response] Thank you for reviewing the manuscript once again and for useful comments and suggestions both times.

In my previous review, I recommended that since the enrichment factors (EFs) were calculated using Fe as a reference element, the authors should show that Fe concentrations in the overlapping sections of the 2015 and 1992 Gulyia ice cores (i.e., for 1971-1992) are comparable. In the revised version of the paper, the authors indicate (in the Supplement) that "the Al and Fe median concentrations are 0.3 µg/g in both records during the 1971–1991 period in which both TE records overlap." However the data are not actually shown. I recommend again that these data should be presented graphically. This would show the reader if the Fe concentrations in the overlapping core sections vary in agreement. The fact that they have the same median concentrations does not necessarily imply that they do.
[Response] Done.
The plot with the Fe concentrations of the 2015 and 1992 Guliya ice cores is now shown in Figure S1.

L187-189: Results of cluster analyses of geochemical data should be treated with a great deal of caution, as they are very sensitive to data pre-treatment (example: transformations) and the choice of the clustering algorithm. See Templ et al. (2008; Applied Geochemistry 23: 2198–2213). The results presented on Fig. S4 would be more convincing if the authors could show that they can be replicated with different clustering criteria or methods.
[Response] Done.
We performed an additional cluster analysis using K-means algorithm (non-hierarchical method recommended in Templ et al. 2008) and the results are shown along with those from the hierarchical cluster analysis in Figure S5. The K-means clustering analysis forms slightly different groups, when compared with the hierarchical analysis but Pb and Zn remain in the same cluster.
We also changed the text (L189-196) to reflect the results from both cluster analyses and to clarify that this is an exploratory data analysis tool as mentioned in Templ et al. 2008. The text now reads: "A hierarchical cluster analysis using the Ward linkage method and the Euclidan distance measure, and a non-hierarchical (K-means) cluster analysis were performed with Factors 1-3 to explore the possible TEs distribution into associated groups. (Fig. S5). Both cluster analyses show that Pb and Zn are strongly associated suggesting these TEs likely have common origins."

On Fig. S1, aluminum (Al) shows consistently negative Excesses (i.e., deficits) in the older Gulyia (1992) ice core, including during the "pre-industrial" interval of reference (1650-1750). This is odd. The concentration of trace metals of crustal origin in environmental matrices (e.g., soils, ice) often have positively skewed probability distributions, but not that of major elements such as Al and Fe. Therefore I would expect the probability distribution of the Al/Fe ratio in the ice to be symmetrical, possibly normal. Hence, if the Ex(Al) shown

on Fig. S1 were calculated as per equation (2) in the paper, I would also expect that in the part of the core that corresponds to the interval of reference (1650-1750) there should be both positive and negative Ex(Al), depending on whether the Al/Fe ratio measured in any part of the core fell above or below the median Al/Fe value for the whole reference interval. In order for the calculated Al Excess to be consistently negative during this interval of reference, the measured Al/Fe ratios must be consistently lower than the reference median Al/Fe value used in the calculation, which necessarily implies that this value can't actually be the median. Something seems to be wrong here, and it may also affect the calculation of Excesses for other trace elements. Maybe there is something missing in the description of the calculation method?

[Response] We reviewed the calculations of the [TE/Fe] median during the pre-industrial period (1650-1750). We had originally obtained the median concentrations of the TEs during the pre-industrial period and then performed the ratio of those values (e.g., $[Al]_{1650\text{-}1750\ median}$ / $[Fe]_{1650\text{-}1750\ median}$). We now did the [TE/Fe] for all individual samples and then obtained the median of the ratios between 1650-1750. The plot has been changed in Fig. S2, and as the reviewer pointed out, the Al excess now show both positive and negative Excess concentration during the 1650-1750 period.

Excess concentrations for all TEs were recalculated for both the 1992 and the 2015 ice cores. Likewise, the statistical analyses were redone with the corrected Excess concentrations. The corrected Excess concentrations are slightly larger than those obtained before, however they do not change either the statistical results or the interpretation.

Fig. 2 has also been updated with the correct Excess concentrations.

Sections 3.1 and Figs. 4-5. The attribution of anthropogenically-derived trace metals deposited in the Gulyia ice core to specific regional sources is largely based on visual "curve matching" of trends between the ice-core composite EF (for Cd, Pb, Zn, and Ni) and in regional emission data. This is fair enough, and I think that there is a good case to be made that the increase in the composite EFs points to dominant sources from East Asia and/or the Indian sub-continent (which is hardly surprising). I am less convinced by the argument offered for the predominance of emissions from specific fossil fuel sources in Pakistan. The observed trend in EFs is probably the result of a mixture of emissions from various regions/sectors. Hence, there could in fact be more than one combination of regional/sector emission sources that could produce the observed trend in EF, but the only such combination that is analyzed in detail is that of emissions from Pakistan (Fig. 5). The argument offered in support of Pakistan would be more convincing if it could be shown that no other combination of regional sources can explain the observed trend in EFs. Ultimately, the "case" for the predominance of Pakistan seems to depend on the apparent "peak" in EFs around 2007, which could match a period of peak emissions in Pakistan at that time (if emission data from this region are to be trusted). Given that the factor analysis attributes only 2 % of the variance in TEs to anthropogenic sources (the rest being associated with crustal sources), the authors should refrain from over-interpreting minor features in the TE record. This is not to say that Pakistan may not be an important source of TEs to the Gulyia ice cap (it would be surprising if it were not), but I think that the relative dominance of emissions from this region is overstated.

[Response] We agree with the reviewer that the EF increasing trend might be a combination of regions and/or sectors, so we have changed the attribution of TEs to all the regions that influence Guliya (South Asia, western China, and Central Asia) throughout the discussion, abstract and conclusions.

Section 3.2.: I find the discussion of the possible influence of the NAO on atmospheric trace element deposition on Gulyia ice cap to be weak. First, the purported correspondence between high/low NAO phases and the composite index of trace metal EF on the Gulyia ice

cap (Fig. 6) is based on a subjective visual comparison, without any supporting qualitative metrics (e.g., correlation coefficients), and it is, to me, unconvincing. Second, this comparison does not offer a definitive way to discriminate or parse, in a quantitative way, the relative influences of the NAO and of anthropogenic source emissions of trace elements, such that one is left to speculate about which factor(s) were dominant at different times. Thirdly, no explicit mechanism is offered in the text to account for this purported relationship. I am assuming the interpretation is the same as that previously suggested in Sierra-Hernandez et al. (2018), i.e. stronger wintertime NAO => enhanced westerlies => more efficient transport of atmospheric trace elements from distant (European) sources in the west to the Gulyia ice cap. As I pointed out in my previous review, this is at odds with the effects of the NAO on atmospheric flow over the Tibetan Plateau in climatology publications (Mao et al., 2011; doi:10.1016/j.atmosenv.2010.10.020; Han et al. 2008; doi:10.1016/j.atmosenv.2007.12.025). Furthermore, there seems to be no clear or consistent association between predominantly low(high) NAO phases and variations in dust deposition on the Gulyia ice cap, as one might expect if the NAO-westerlies linkage was important for atmospheric particulate matter transport (Fig. 6-7 in Thompson et al., 2018). I had previously suggested that one possible way to verify if a stronger winter/spring NAO phase actually enhances east-west atmospheric transport towards the ice cap would be to compare the mean length of air parcel back-trajectories between years of low and high NAO indices. I can only offer the same suggestion again. Unless this or some other supporting evidence can be offered, I recommend that this section be excised altogether from the paper.

[Response] We agree with the reviewer (and the other reviewers) and believe it is better to eliminate Section 3.2 as comparisons between NAO and Guliya EFs are only visual, mechanisms cannot be established due to the complex atmospheric circulation over the Guliya ice cap, the changing emission sources, and the ice core dating uncertainty (1-2 years).

The Tibetan Plateau (TP) atmospheric circulation is influenced by the continental westerlies and the East Asian and South Asian summer monsoons (Schiemann et al., 2009; Yao et al., 2013; Maussion et al., 2014). During winter the westerlies are strong and dominate over the TP. During summer the monsoon alters the atmospheric circulation such that the westerlies weaken and shift northward to ~40-42°N while the northern limit of the monsoon reaches 34-35°N (Tian et al., 2007; Schiemann et al., 2009; Maussion et al., 2014). Thus, the Guliya ice cap (35°17’N) is dominated by westerlies during winter but during summer it can experience a combination of monsoonal and westerly flows due to the shift of the westerly jet to the north and the monsoon onset. Due to the location of the Guliya ice cap at the northern limit of the monsoon transition, it is difficult to establish the relationship between the Guliya EF enrichments and NAO.

We performed a running correlation between the winter NAO index and the EF composites of the 1992 and 2015 Guliya core to understand the correlation over time (see Figure 1 below). Unfortunately, with the number of data points we can only do a 5-year running mean and only coefficients > 0.8 are significant ($p = 0.05$). The NAO-EF relationship is positive before the 1970s and after 2000. However, as the reviewer says these positive visual correlations are not definitive to discriminate or parse, in a quantitative way, the influences of the NAO and those of the anthropogenic sources of TEs especially post-1970 due to the number of emission sources. At least one emission source must emit TEs to detect in the ice core, but given that there is a large number of post-1970 emission sources and they all have different trends, we cannot determine the role that NAO plays in the transport of atmospheric pollutants to the Guliya ice cap.

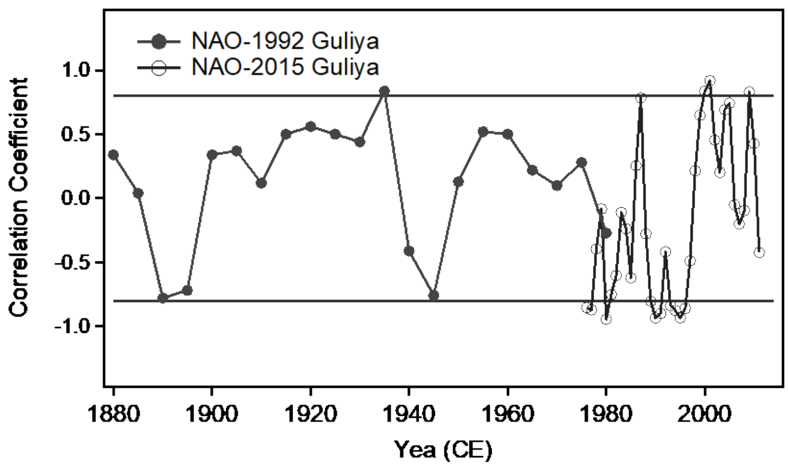

Figure 1. Five-year running correlation coefficient between the winter NAO index and the 1992 and the 2015 Guliya EF composites. The two horizontal lines show the significance level ($p = 0.05$).

As suggested by the reviewer, to verify if a stronger winter/spring NAO phase actually enhances east-west atmospheric transport towards the ice cap we looked at air parcel back-trajectories for two years, 1964 (negative NAO) and 1993 (positive NAO) (see Figure 2 below). During 1994 (positive NAO phase), the trajectories seem to go further back to the northwest compared to the 1964 winter when NAO was in a negative phase. This would suggest that the westerly jet position might be influenced by the NAO phase.

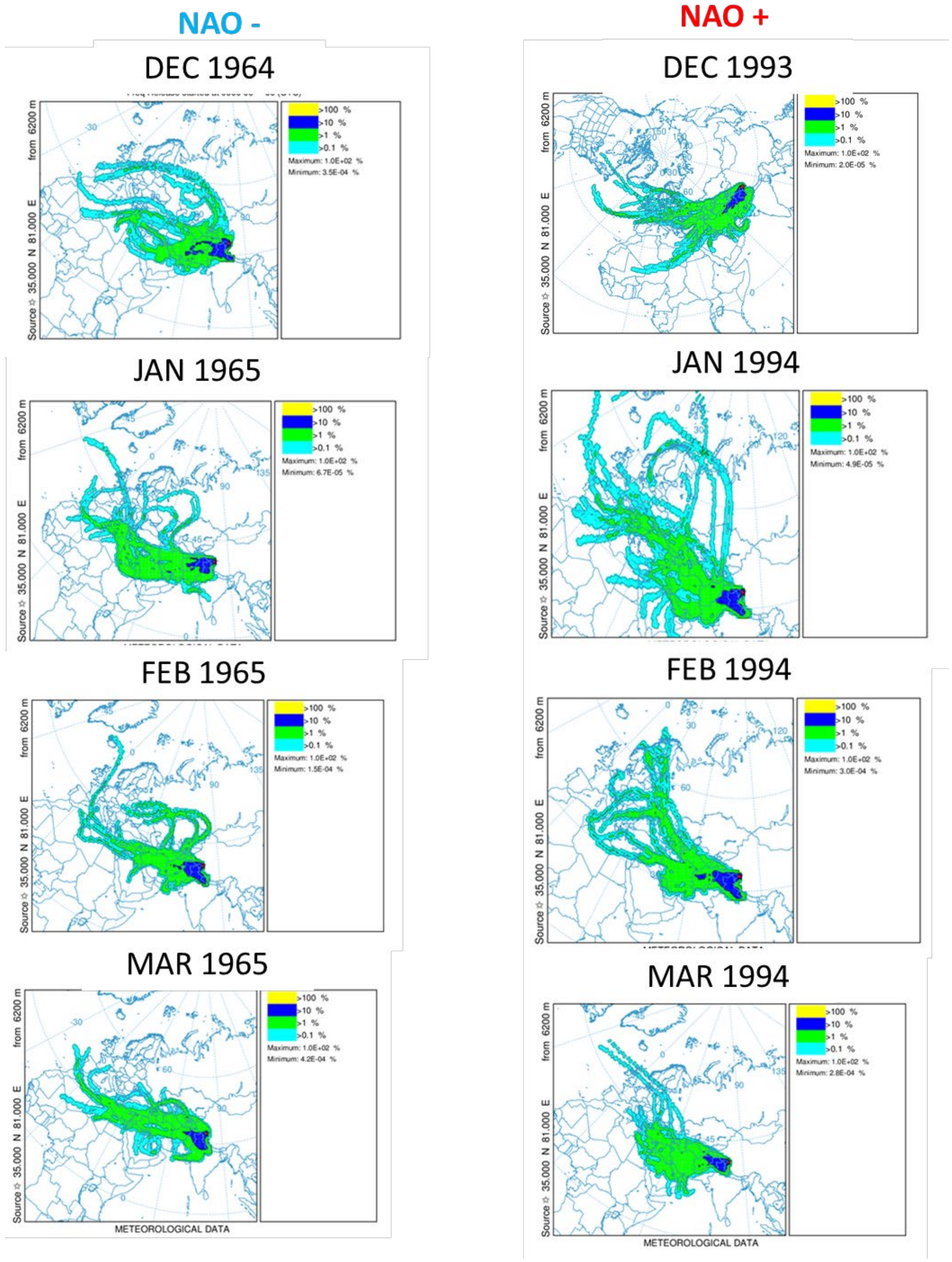

Figure 2. NOAA HYSPLIT 7-day back trajectories frequency plots for December, January, February and March for the years 1964 (negative NAO) and 1993 (positive NAO).

Minor suggested corrections:

L32-34: "TEs are also released into the atmosphere by human activities including: 1) the combustion of fossil fuels including coal, oil and its distillates (e.g., gasoline, jet fuel, diesel); 2) industrial processes such as mineral EXTRACTION [done], and metal production." L163-164: "Their EF averages increase by _10 % during 1990–2000, and during 2000–2015 by 75 % (Cd), 35 % (Pb), 30 % (Zn) and 10 % relative to the 1971–1990 period."

What does the 10 % figure refer to ? Ni ?

[Response] The 10% increase during the 1990–2000 relative to the 1971–1990 period is for all 4 TEs, and for Ni for the 2000-2015 period.

We added "for all four TEs" and "(Ni)"in the corresponding lines.

L172: " MOST of the variance (94%) is explained by both Factor 1 (73 %)...."

[Response] Done.

References

Bajwa, A., Compendium of Environmental Statistics of Pakistan. Pakistan Bureau of Statistics. 258, 2015.

Maussion, F., Scherer, D., Mölg, T., Collier, E., Curio, J., and Finkelnburg, R.: Precipitation Seasonality and Variability over the Tibetan Plateau as Resolved by the High Asia Reanalysis, J. Clim., 27, 1910-1927, 2014.

Schiemann, R., Lèuthi, D., and Schèar, C.: Seasonality and Interannual Variability of the Westerly Jet in the Tibetan Plateau Region, J. Clim., 22, 2940-2957, 2009.

Tian, L., Yao, T., MacClune, K., White, J. W. C., Schilla, A., Vaughn, B., Vachon, R., and Ichiyanagi, K.: Stable isotopic variations in west China: A consideration of moisture sources, J. Geophys. Res., 112, D10112, 2007.

Yao, T. D., Masson-Delmotte, V., Gao, J., Yu, W. S., Yang, X. X., Risi, C., Sturm, C., Werner, M., Zhao, H. B., He, Y., Ren, W., Tian, L. D., Shi, C. M., and Hou, S. G.: A review of climatic controls on $\delta^{18}O$ in precipitation over the Tibetan Plateau: Observations and simulations, Rev. Geophys., 51, 525-547, 10.1002/rog.20023, 2013.