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Overall I think Sierra-Hernandez and others present a comprehensive and interesting follow-up of the 1992 Guilya ice core and highlight some important trends in trace metals that have taken place since then. In general I only have minor comments and suggestions. The largest remaining question in my mind is how an NAO index is mechanistically related to higher EFs, so an explanation of that would be helpful.

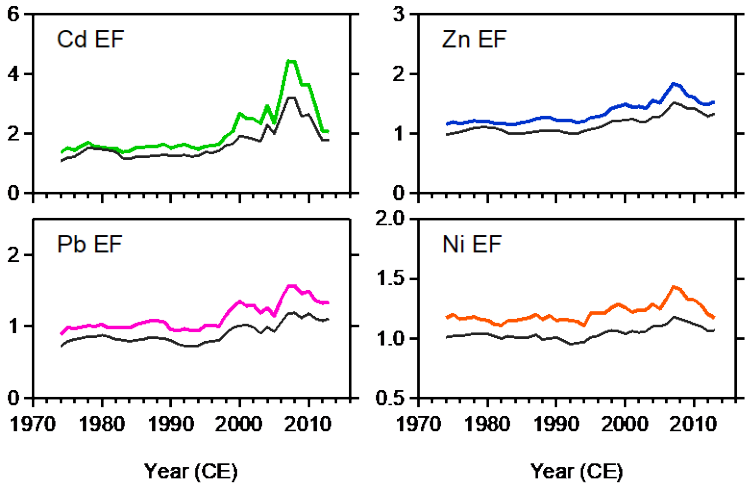
Line 56- What is the "new Silk Road"?
[Response] It is an initiative proposed by President Xi Jinping formally called the Belt and Road Initiative to modernize and build new railways, ports, pipelines, power grids and highways to connect China with the west. This has been added accordingly.

Line 65- Is this percentage (50-60%) meant to imply this is how much emissions can be attributed to motor vehicles?
[Response] Yes, we have changed it to "(estimated to be ~60–70 % of the total air emissions)". There was also a typo and it should be 60-70 % and not 50-60 %.

Lines 93-95- If more anthropogenic sources have emerged, then what new developments have taken place and are in use in this manuscript to attribute possible sources?
[Response] New comprehensive emission inventories of air pollutants have been developed since the 1970s and 1980s to regulate their emissions. In particular, we use the Emissions Database for Global Atmospheric Research (EDGAR v4.3.2) which compiled a comprehensive dataset of air pollutants between 1970 and 2012 and is used in this manuscript to attribute possible sources along with emission inventories from the U.S. Energy Information Administration, and the British Petroleoum (BP) Statistical Review of World Energy. In our previous publication (Sierra-Hernandez, 2018), the TE ice core record stopped at 1991, and thus the increases observed between 1975 and 1991 were not possible to compare with emission inventories since the time interval was too short. With this new Guliya core drilled in 2015, we now have a 40-year timeseries of TEs that can better show temporal trend similarities with emission inventories.
A description of these new developments is now included in the text.

Lines 139-140- Fe is an interesting choice. Why not something else like Al? Or Ti?
[Response] In our previous publication (Sierra-Hernandez, 2018) we used Fe as a crustal element. To be consistent, we continue to use Fe as a crustal element in this new ice core record. In lines 143-145 we explain that "Fe was chosen as the crustal reference due to its stability and high abundance in soil and rocks (Wedepohl, 1995), its high concentration both in the ice core samples and the PSAs, and the ability of the ICP-SFMS to measure Fe with high accuracy and precision". We added the following text in lines 149-152: "Additionally, Fe is highly correlated with Al ($r = 1$), and also with Ba ($r = 0.98$). Like in Sierra-Hernandez (Sierra-Hernández et al., 2018), EFs calculated using Al and Ba as crustal references had no significant differences compared to EFs relative to Fe which all together shows that the choice of Fe as a crustal TE to calculate EFs did not affect the results."

Here is the comparison between EF relative to Fe (color curves) with EFs relative to Al (black curves)



Lines 150-152- What is defined as "pre-industrial" in this case? Before what time period?
[Response] We consider the pre-industrial period to be the period before the Industrial Revolution in Europe (~1780). Similar to our previous publication (Sierra-Hernandez, 2018), we used the period 1650-1750 as pre-industrial to be more conservative due to the time scale uncertainty of the ice core.
We have clarified this in the text accordingly.

Lines 192-194- I understand the difference between EF and Excess calculations, but why would some elements have significant trends for EF but not Excess? This needs some additional explanation.
[Response] For all our statistical tests we used the datasets at full resolution. However, the Mann-Kendall trend tests were performed with the annual dataset. The problem with the Excess concentration was that by averaging the values within one year, large negative values skewed the final results to negative numbers.
The tests have been re-done using the full resolution EF and Excess concentration datasets. The updated results show that both EFs and Excess concentrations of Bi, Cd, Ni, Pb, Tl, and Zn show significant increasing trends. Changes were made in the manuscript accordingly.

Lines 224-225- Since the EDGAR database excludes biomass burning and land use change, is it possible that some of the observed trends could be attributed to these processes? I know it will be hard to make these estimations without quantitative data, but these could be potentially significant.
[Response] The EDGAR database does include some anthropogenic biomass burning activities such as domestic combustion and agricultural waste burning excluding only large-scale biomass burning. We have added a Biomass Burning section (Sect. 3.1.2) to discuss domestic combustion and agricultural waste burning.
It is possible that the TE trends observed in the Guliya ice core can be attributed to large-scale biomass burning and land use change. Recent increases in wildfires in the Himalayas have been detected in Central Tibet possibly due to recent warming (You et al., 2018). This is mentioned in Sect. 3.1.2.

Lines 303-305- A brief mechanistic explanation about how a positive NAO index actually results in higher EFs would be useful.
[Response] We have eliminated Section 3.2. Please see the full response regarding this in the responses to Reviewer #2.

Lines 310-313- However, I think it's important to note that the drop from 1940-1970 is also when there is a gap/transition in the data. Neither coal nor oil consumption estimates extend fully back

through this period. And while coal production is still reasonably high, it does start to decline. This is not to say that I don't believe the NAO is having an impact, but I think it's important to highlight that there are some gaps in the data.
[Response] Yes, we agree that the gaps in the inventories are important and should be noted. As described above the NAO discussion has been eliminated, therefore these inventories are not shown/discussed anymore.

Lines 337-336- This is an interesting development and would seem to be a reversal of coal consumption declines since 2009 as previously noted in line 320. Was the decline in 2009 a temporary slow down then?
[Response] Yes, it is a temporary slow-down between 2009 and 2013. This Figure has been eliminated.

Figure 5- The second y-axis on the right needs a label.
[Response] Label has been added. The Figure was moved to the Supplement as Fig. S6

Figure 6- Why is the 1992 core plotted as a 5-year running median while the 2015 core is a 5-year running mean?
[Response] The 2015 Guliya EF composite z-scores were plotted as 5-year running means in Fig. 6 to keep consistency with the previous figures of the manuscript. Since Section 3.2 has been removed, there is no Figure 6 anymore.

References
You, C., Yao, T., and Xu, C.: Recent Increases in Wildfires in the Himalayas and Surrounding Regions Detected in Central Tibetan Ice Core Records, J. Geophys. Res.: Atmospheres, 123, 3285-3291, 10.1002/2017jd027929, 2018.

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.

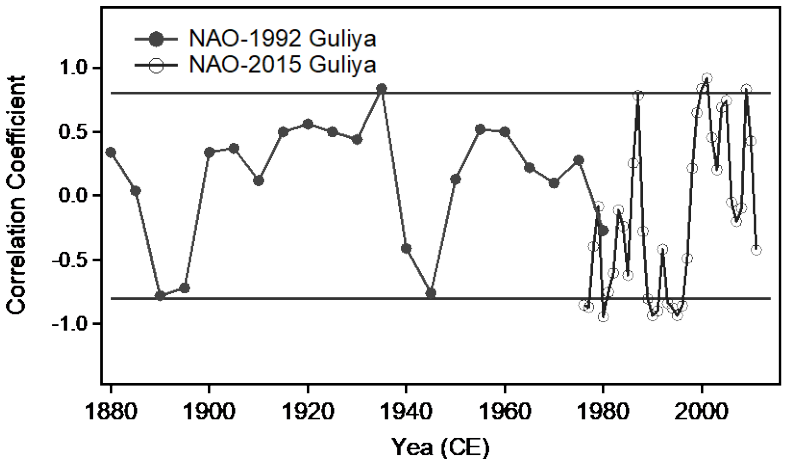


Figure 1. Five-year running correlation coefficient between the winter NAO index and the 1992 and the 2015 Guliya EF composites. The two horizontal lines show the significance level ($p = 0.05$).

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.

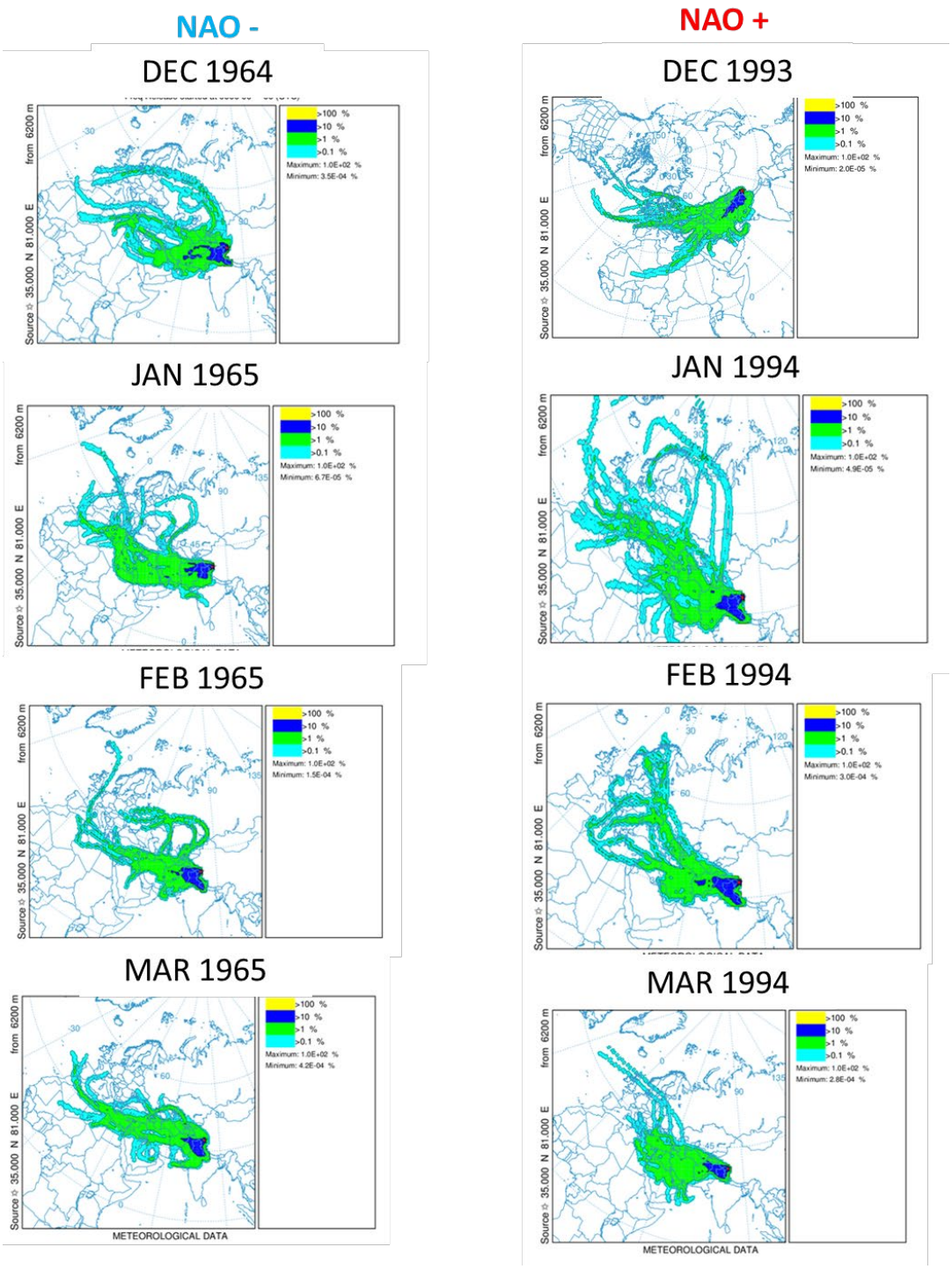


Figure 2. NOAA HYSPLIT 7-day back trajectories frequency plots for December, January, February and March for the years 1964 (negative NAO) and 1993 (positive NAO).

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
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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.

Anonymous Referee #3
Received and published: 10 August 2019

The work of Sierra-Hernández et al. describes trace metal analysis of an ice core from the Guliya ice cap in northwestern Tibet that represents deposition from 1971 to 2015. This extends the metals deposition record from that location that previously ended at 1991. The authors demonstrate increased deposition of several trace metals in the 21st century, with some starting to decrease more recently. Trends in deposition are related to industrial activities in the region and to climate. The measurements are made with good analytical rigor, but some of the trends and source attribution could be more convincing. I recommend the changes detailed below be made to the manuscript prior to consideration for publication in ACP.
[Response] Thank you. Following the recommendations by this and the other reviewers we changed the source attribution. Please see our responses below.

General comments
The Authors use two different metrics to assess enrichments of metals, enrichment factor (EF) and excess concentration. The rationale for using two metrics (i.e. the unique information provided by each) is not provided. It would be useful to provide additional information of this type in Section 2.3. Where different trends were observed for each metric (e.g. lines 191-194, Figure 2), the authors should explain the reasoning and implications of these differences.
[Response] The EFs calculated relative to the PSA are particularly small since the composition of the PSA is a much closer representation of the crustal background of the ice samples compared to those obtained using the UCC (upper continental background by Wedephol). Thus, to further demonstrate that these "small" increases are significant, we used a second metric which is the Excess concentration. The excess concentration provides the TE concentration difference between TE deposition after and before the pre-industrial period. For the pre-industrial period we use the 1992 Guliya ice core data comprised between 1650 and 1750. We added a brief explanation in Section 2.3 accordingly.

The difference in trend observed between EF and Excess concentration was due to an error in the Mann-Kendall trend test. Here it is the response to Reviewer #1 to this issue:
For all our statistical tests we used the datasets at full resolution. However, the Mann-Kendall trend tests were performed with the annual dataset. The tests have been re-done using the full resolution EF and Excess concentration datasets. The updated results show that both EFs and Excess concentrations of Bi, Cd, Ni, Pb, Tl, and Zn show significant increasing trends.
The problem with the Excess concentration was that by averaging the values within one year, a large negative value skewed the final results to negative numbers.

Section 3.2 relating the North Atlantic Oscillation (NAO) to enrichments on the Guliya ice cap is very qualitative and speculative. Although it seems reasonable that some relationship exists with the NAO, there is no quantitative analysis provided. The authors mention that correlation was observed in previous studies (lines 303-305). Was there any correlation observed here? It seems a stretch to conclude that the source of enrichments for several trace metals is related to a specific industry in Pakistan (i.e. line 330).
[Response] We have eliminated Section 3.2. Please see the full response regarding this in the responses to Reviewer #2.
We agree with this reviewer (and reviewer #2) that the EF increasing trend might be a combination of regions and sectors, so we have changed throughout the discussion, abstract and conclusions the attribution of TEs to all the regions that influence Guliya (South Asia, western China, and Central Asia).

Specific comments

Line 46: Suggest not using an acronym for five-year plan since the term is used only three times in the manuscript.
[Response] Done.

Lines 55-59: Although the sampling site is given with reference to Xinjiang Province, this area is not labeled on the map in Figure 1(a). This should be added.
[Response] Done.

Lines 125-133: The quality assurance/quality control of the sample analysis is comprehensive and well-described, demonstrating the quality of the presented data.
[Response] Thanks for the comments.

Lines 140-141: Please provide a brief description of the PSA used here along with the reference to the previous study.
[Response] A description has been added accordingly.

Lines 165-167: What about Pb deposition post-2008? The first part of the sentence refers to both Pb and Cd, while the final part of the sentence describes only Cd. Please clarify.
[Response] The final part of the sentence has been changed and it now reads "The 1992 Guliya TE records show that enrichments of Pb and Cd begin ~1975 while the 2015 Guliya record shows they continue to rise into the 21st century until ~2008 when they started to decrease."

Line 252: Statistical information for the significant positive correlations should be provided.
[Response] Done. The significance is $p < 0.001$, and it has been added in the corresponding line.

Line 530: Typo in first word of the caption.
[Response] Done.

21st Century Asian air pollution impacts glacier in northwestern Tibet

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Abstract. Over the last four decades, Asian countries have undergone significant economic development leading to rapid urbanization and industrialization ~~in the region~~. Consequently, fossil fuel consumption has risen dramatically worsening the air quality in Asia. Fossil fuel combustion emits particulate matter containing toxic metals that can adversely affect living organisms, including humans. Thus, it is imperative to investigate the temporal and spatial extent of metal pollution in Asia. Recently, we reported a continuous and high-resolution 1650–1991 ice core record from the Guliya ice cap in northwestern Tibet, China showing ~~a~~ contamination of Cd, Pb and Zn during the 20th century. Here, we present a new continuous and high-resolution ice core record of trace metals from the Guliya ice cap that comprises the years between 1971 and 2015, extending the 1650–1991 ice core record into the 21st century. Non-crustal Cd, Pb, Zn and Ni enrichments increased since the 1990s relative to the 1971-1990 period reaching a maximum in 2008. The enrichments of Cd, Pb, Zn, and Ni increased by ~75 %, 35 %, 30 %, and 10 %, respectively during the 2000–2015 period relative to 1971–1990. ~~Our analysis suggests that emissions from Pakistan's fossil fuel combustion (by road transportation and the manufacturing and construction industries) became the dominant source of Cd, Pb, Zn, and Ni deposited on Guliya between 1995 and 2015. However, it is possible that emissions~~ The observed TE enrichments likely originated primarily from fossil fuel combustion and biomass burning with likely contributions from industrial processes, and agricultural activities from South Asia (Pakistan, Afghanistan, India, Nepal), Central Asia, ~~Afghanistan, India, Nepal,~~ and the Xinjiang province in western China ~~have also impacted Guliya during the 21st century~~. ~~The enrichments of Cd, Zn, and Ni declined after 2008 likely due to a coal consumption decrease in Pakistan at that time.~~ This new record demonstrates that the current emissions in Asia are impacting remote high-altitude glaciers in the region and that mitigation policies and technologies should be enforced to improve the air quality as economic development continues in most Asian countries.

1 Introduction

Atmospheric trace elements (TE), including toxic metals (e.g., Hg, Pb, Cd) have dramatically increased since the 19th century due to human activities (Pacyna and Pacyna, 2001; Tian et al., 2015). Some TEs are highly toxic and harmful to an array of animals, plants and humans. Atmospheric TEs can originate from natural sources/processes in the environment such as windborne dust, wildfires, sea-spray aerosols, volcanic activity, and from vegetation (Nriagu,

1989a, b). TEs are also released into the atmosphere by human activities such as: 1) the combustion of fossil fuels including coal, oil and its distillates (e.g., gasoline, jet fuel, diesel), 2) biomass burning (e.g., wood, dung, agricultural waste); ~~2~~3) industrial processes such as mineral extraction, and metal production;~~ 3~~4) agriculture practices that include the use of fertilizers and pesticides; and ~~4~~5) waste disposal (Pacyna and Pacyna, 2001; Christian et al., 2010; Zhang et al., 2014; Chen et al., 2015; Singh et al., 2018). These activities, especially high temperature processes, emit~~-~~ fine (< 2.5 μm) particulate matter ($PM_{2.5}$) ~~which can~~ containing toxic metals such as As, Cd, Pb, and Zn (Richaud et al., 2004; Xu et al., 2004; Reddy et al., 2005; Alves et al., 2010; Christian et al., 2010) that due to its small size, ~~$PM_{2.5}$~~ can reside in the atmosphere for over a week, thereby allowing it to be transported and deposited far from its initial sources (e.g., onto remote glaciers) (Pacyna and Pacyna, 2001; Marx and McGowan, 2010).

Since the 1970s, Asian countries such as China, India, Pakistan, Nepal, Bangladesh and others have undergone significant and rapid economic growth, leading to considerable urbanization and industrialization in the region. Consequently, fossil fuel consumption has risen dramatically in most of these countries worsening the air quality. In particular, China and India, the second and fifth largest economies in the world according to the International Monetary Fund, are respectively the largest and third largest emitters of both CO_2 and $PM_{2.5}$~~.~~

~~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 $PM_{2.5}$~~ (Crippa et al., 2018; EDGARv4.3.2, 2017).

In 1999, the Chinese government implemented the "Western Development" policy in the 10th five-year plan~~FYP~~ to improve the quality of the environment in the east and to transfer energy (West to East energy program) and mineral resources from the west to the rest of the country (Lai, 2002; Chen et al., 2010; Dong and Yang, 2014). For this purpose, the necessary infrastructure (e.g., airports, railways, highways, water infrastructure, power lines) was built. As a result, energy consumption (Jianxin, 2016) and atmospheric emissions (Liu et al., 2015) have been increasing significantly in western China.

In particular, the Xinjiang Uygur Autonomous Region, situated in an arid region of northwestern China, has become important for the Western Development implementation because of its location on the new Silk Road, a project to modernize and build new infrastructure to connect China with the West, and its large reserves of oil, gas, and coal (Chen et al., 2010; Dong and Yang, 2014; Fridley et al., 2017). Three mountain ranges shape the topography of this province: the Altai on the northern border, Tien Shan in the center, and the western Kunlun Mountains, where the Guliya ice cap is located (see below), along the southern border with Tibet (Fig. 1a).

Pakistan, to the southeast of Xinjiang, gained its independence in 1947 after which its population rose very rapidly becoming the world's sixth most populated country by 2003 (UN, 2017). Although Pakistan's economic growth has been much lower than that of China and India, urban Pakistani cities are among the most polluted in the world (WHO, 2016) due to the high population growth, industrialization and a significant increase in motor vehicles that lack emission controls and use low quality gasoline/diesel. ~~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 (Colbeck et al., 2010; Sánchez-Triana et al., 2014).~~

For the year 1995, Pacyna and Pacyna (2001) estimated that non-ferrous metal production was the largest source of As, Cd, Cu, In, and Zn, ~~while~~ coal combustion was a major source of Cr, Hg, Mn, Sb, Se, Sn, and Tl, and oil combustion was ~~the~~ a major source of Ni and V, both worldwide and in Asia. For the same year, these authors estimated that leaded gasoline was the ~~major~~ primary source of Pb worldwide as well as in Asia. However, changes in emissions of atmospheric TEs have occurred during the 21st century in Asia due to the following: 1) China and India emerged as the fastest growing economies and most populated countries in the world (UN, 2017); 2) developing countries such as Pakistan, Nepal and Bangladesh have significantly increased their national economic activities since the 1980s–1990s; 3) temporal and regional variations in the implementation of control emission technologies and air quality standards (often higher concentrations than those recommended by the World Health Organization); 4) leaded gasoline was banned in 2000 in China, India, and Nepal and in 2002 in Pakistan, while it is still consumed in Afghanistan. Therefore, it is imperative to study the spatial and temporal effects of these new pollution sources and their resulting impacts on the environment.

Atmospheric emission estimates are associated with large uncertainties due to inaccurate statistical information, the lack of field data, and limited temporal and spatial coverage of observations. Thus, natural registers of past environmental conditions such as glaciers, which are influenced only by deposition of atmospheric species, are essential for reconstructing time series of atmospheric metal depositions (Hansson et al., 2015; Cooke and Bindler, 2015; Gabrielli and Vallelonga, 2015; Marx et al., 2016) that can be further used by modelers to reconstruct past emissions and project future atmospheric contamination trends.

Recently, we obtained a 350-year (1650–1991) high-resolution TE record (Sierra-Hernández et al., 2018) using an ice core drilled in 1992 from the Guliya ice cap located in northwestern China, specifically in Tibet's Kunlun Mountains (35° 17.37' N; 81° 29.73' E; 6200 m a.s.l.) (Thompson et al., 1995) (Fig. 1a). Outside of the Arctic and Antarctica, the glaciers in the Kunlun Mountains, along with those in Tibet and the Himalayas, are the largest reservoir of ice on the globe and are commonly referred to as the "Third Pole". This glacial region is the source for numerous rivers in Asia which provide water to hundreds of millions of people. The 1992 Guliya TE record showed that long-distance emissions from coal combustion in Europe were likely deposited on the ice cap between 1850 and 1940 (Sierra-Hernández et al., 2018). Additionally, Pb, Cd, and Sn enrichments were detected between 1975 and 1991. The origin of these more recent enrichments could not be determined as more anthropogenic sources have emerged, especially in this region.

Here, we use a new ice core retrieved from Guliya in 2015 to extend the 1650–1991 TE records into the 21st century (1971–2015) and to determine the impacts of the recent emission changes in Asia on the western Kunlun Mountains glaciers. New emission inventories of air pollutants, in particular the Emissions Database for Global Atmospheric Research (EDGAR v4.3.2) which compiles a comprehensive dataset of air pollutants between 1970 and 2012, are used

here to attribute possible sources. This study fills a temporal and spatial gap in the investigation of atmospheric toxic trace metals in Northwestern China where atmospheric emission data are limited.

2 Methodology

2.1 Guliya cores

In 2015, two ice cores (309.73 m and 72.40 m long) were extracted from the plateau of the Guliya ice cap (6200 m a.s.l), in close proximity to the 1992 drilling site. The timescale was constructed by annual layer counting using three fixed horizons at 2015 (surface of the glacier), at 1992 corresponding to the surface of the 1992 core (at 6 m in the shallow core), and at 1963 (at 10.9 m in the shallow core determined by beta radioactivity from the Arctic thermonuclear tests). Annual layers were determined using both cores by matching the signals of at least three different parameters (Cl^- and Na^+, dust and Ca^{2+}, SO_4^{2-}, and $\delta^{18}O$). Dating uncertainties are estimated at 1–2 years between the fixed points and may be the result of the very low annual accumulation (~230 mm water equivalent) and surface-alteration processes such as snow redistribution through wind. Details of the drilling operation, the ice cores, and the timescale can be found in Thompson et al. (2018).

2.2 Sample preparation and ICP-SFMS analysis

The preparation of the samples and their analysis were performed following the same procedures adopted for the 1992 Guliya core samples (Sierra-Hernández et al., 2018). Briefly, 159 ice samples comprising the years 1971 (11 m) to 2015 (0.06 m) were cut from the 309.73 m long-deep ice core. To ensure the analysis of 3–4 samples $year^{-1}$, the sample resolution was adjusted between 4.5 and 11 cm accordingly. The samples were rinsed three times with nanopure water (18.3 MΩ) in a class-100 cleanroom and placed in acid pre-cleaned LDPE containers (Nalgene) to melt. Once melted, samples were transferred into acid pre-cleaned LDPE vials where nitric acid (HNO_3, Optima for Ultra Trace Element Analysis, Fisher Scientific) was added to obtain a 2 % (v/v) acidified sample. The samples were then stored in the cleanroom for a 30-day period during which the acid leaching process took place. At the end of the 30-day period, the samples were immediately analyzed or stored at –32 °C.

Twenty-nine TEs (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Li, Mg, Mn, Mo, Na, Nb, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, U, V, and Zn) were measured in the samples by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) (Element 2) (Sierra-Hernández et al., 2018; Beaudon et al., 2017). Trace elements were quantified using linear calibration curves constructed from external standards analyzed before and after the samples.

Detection limits, procedural blanks, and accuracy results are presented in Table S1. Detection limits correspond to three standard deviations of the concentration of 10 blank measurements (2 % optima HNO_3 aqueous solution) and fluctuate between 0.01 pg g^{-1} for Bi to 0.2 ng g^{-1} for Fe and 0.4 ng g^{-1} for Na (Beaudon et al., 2017; Sierra-Hernández et al., 2018). To verify that the sampling and decontamination procedures did not add TEs to the ice core samples, procedural blanks were made with nanopure water and analyzed with the ice core samples (Uglietti et al., 2014). Their TE concentrations are considered negligible for all TEs, apart from Nb (9 %), as they were lower than 2 % of the

corresponding median concentration. The accuracy of the ICP-SFMS was determined each day of analysis using a 20-fold dilution of a TMRain-95 certified solution (Environment Canada). The obtained TE concentrations fell within the uncertainty limits in the certificate of analysis.

2.3 Non-crustal contribution

Enrichment Factors (EF) and Excess concentrations are used to assess the crustal and non-crustal (e.g., anthropogenic) origins of each TE.

The EF is obtained following Eq. (1)

$$EF = [TE\ /\ Fe]_{ice} / [TE\ /\ Fe]_{PSA} \quad (1)$$

where $[TE\ /\ Fe]_{ice}$ corresponds to the ratio of a particular TE concentration to that of Fe in an ice sample and $[TE\ /\ Fe]_{PSA}$ is the respective ratio in dust samples used as potential source area (PSA). Eight dust samples were collected during the 1992 and 2015 Guliya field expeditions and are used here as PSAs. For details about the ~~Guliya~~ collection sites, the preparation and analysis of the PSA samples, and EFs derived from PSAs, the reader is referred to Sierra-Hernández (2018). Briefly, approximately 0.1-0.5 g of PSA sample was added to an acid pre-cleaned LDPE container with ultrapure water. The solution was mixed by agitation and settled ~2 minutes. For the ICP-SFMS analysis, 10 ml of supernatant was used and prepared like the ice samples.

Similar to the previous Guliya TEs study, Fe was chosen as the crustal reference due to its stability and high abundance in soil and rocks (Wedepohl, 1995), its high concentration both in the ice core samples and the PSAs, and the ability of the ICP-SFMS to measure Fe with high accuracy and precision (Uglietti et al., 2014). Additionally, Fe is highly correlated with Al (r = 1) and with Ba (r = 0.98). EFs calculated using Al and Ba as crustal references showed no significant differences to EFs relative to Fe which indicates that the choice of Fe as a crustal TE to calculate EFs did not affect the results (Sierra-Hernández et al., 2018).

The EFs relative to the PSA are particularly small since the composition of the PSA is a much closer representation of the crustal background of the ice samples compared to those obtained using the upper continental background (Wedepohl, 1995). Therefore, Excess concentration is also used here as in our previous publication (Sierra-Hernández et al., 2018) to further corroborate the EF increases observed.

Excess concentrations are calculated following Eq. (2)

$$Excess = [TE]_{ice} - \left([TE/Fe]_{pre-industrial} \times [Fe]_{ice}\right) \quad (2)$$

$[TE]_{ice}$ and $[Fe]_{ice}$ are the concentrations of a particular TE and of Fe in the sample; $[TE/Fe]_{pre-industrial}$ is the median of the TE concentration to the Fe concentration ratio during the pre-industrial period (1650-1750). The pre-industrial period corresponds the oldest part of the 1992 Guliya record (Sierra-Hernández et al., 2018) between 1650 and 1750, ~30 years before the Industrial Revolution began in Europe. The Excess concentration provides the TE concentration difference between TE deposition after and before the pre-industrial period.

To be consistent with our previous Guliya TEs publication, a TE will be considered of non-crustal origin (enriched) when increases in EF and Excess concentration are significantly different from its background (pre-industrial levels), using both a two-sample t-test for averages and the Mann–Whitney test for medians ($p < 0.01$).

2.4 Statistical analysis

All statistical analyses, including factor analysis, cluster analysis, Mann–Whitney tests for medians, two-sample t-tests for averages, and Mann–Kendall trend tests, were performed using Minitab 17 and 18. The Mann–Whitney test and the two-sample t-test were applied to the entire data set and subdivided into three groups: 1971–1990, 1990–2000, and 2000–2015.

3 Results and discussion

The time series of Cd, Pb, Zn, Ni, and Al concentrations, Excess concentrations and EFs are presented as 5-year running means in Fig. 2. The concentrations show high variability between 1971 and 1990 that decreases after 1990 perhaps as a result of the decreasing frequency of dust storms in the region (Thompson et al., 2018).

The Excess concentrations and EFs of Cd, Ni, Pb, and Zn increase after ~1990 and continue to increase more rapidly and significantly after 2000. Their EF averages increase by ~10 % for all four TEs during 1990–2000, and during 2000–2015 by 75 % (Cd), 35 % (Pb), 30 % (Zn), and 10 % (Ni) relative to the 1971–1990 period.

A comparison between the 1992 and the 2015 Guliya TE records is discussed in the Supplement (Fig. S1-S2). The 1992 Guliya TE records show that enrichments of Pb and Cd begin ~1975 while the 2015 Guliya record shows they continue to rise into the 21st century until ~2008 when the Cd enrichment started to decrease. In addition to these TEs, the 2015 record exhibits clear increases in Zn and Ni EFs since the 1990s into the 21st century, and similar to Cd, they decrease after 2008. The Zn enrichment began to increase after 1975 similar to Pb and Cd; however, the signal may have been overwhelmed by its crustal component in the 1992 core record rendering it undetectable.

A factor analysis method was ~~used~~ performed to assess the shared variability among TEs to determine possible common sources (Sierra-Hernández et al., 2018). ~~Much~~ Most of the variance (94%) is explained by both Factor 1 (73 %) and Factor 2 (21 %) (Table S2). Similar to the 1992 TE results, TEs of crustal origin (e.g., Al, As, Ba, Fe, Mg, Mn, Ti, and V) fall into Factor 1. In Fig. ~~S2~~ S3 the time series of Factor 1 scores are compared with the ice core concentrations of dust particles ($\rho = 0.20$, $p = 0.2$) and with the typical crustal TEs, Fe and Al. Water-soluble TEs (e.g., Na, Sr), which are deposited in the form of salts (evaporites) or carbonates, contribute to Factor 2 (Sierra-Hernández et al., 2018) (Table S2). This is shown in the Factor 2 time series (Fig. ~~S3~~S4) which has significant ($p < 0.001$) correlations with the ions Cl^- ($\rho = 0.83$), NO_3^- ($\rho = 0.84$), SO_4^{2-} ($\rho = 0.90$), Na^+ ($\rho = 0.92$), NH_4^+ ($\rho = 0.62$), K^+ ($\rho = 0.84$), Mg^{2+} ($\rho = 0.86$), and Ca^{2+} ($\rho = 0.75$) (Thompson et al., 2018).

Factor 3 explains 2 % of the variance and is loaded in Cd, and to a lesser extent in Bi, Cu, Mn, Ni, Pb, Sn, Tl, and Zn. Although 2 % represents a low variance possibly within the background noise, it could still have a physical

significance (Moore and Grinsted, 2009). In order to determine if Factor 3 is physically explainable, its time series scores are plotted with the EFs of Cd, Pb and Zn in Fig. 3.

Factor 3 was found to be significantly ($p < 0.01$) correlated with the EFs of the following 12 metals: Cd ($\rho = 0.92$), Zn ($\rho = 0.92$), Pb ($\rho = 0.80$), and Ni ($\rho = 0.80$) shown in Fig. 2, and Ag ($\rho = 0.62$), Bi ($\rho = 0.60$), Co ($\rho = 0.50$), Cr ($\rho = 0.60$), Cu ($\rho = 0.51$), Mn ($\rho = 0.63$), Sn ($\rho = 0.74$), and Tl ($\rho = 0.64$). This indicates that Factor 3 explains the EFs of the aforementioned metals. ~~To distribute the TEs into associated groups, a~~ A hierarchical cluster analysis using the Ward linkage method and the Euclidan distance measure, and a non-hierarchical (K-means) cluster analysis ~~was~~ were performed with Factors 1-3 to explore the possible distribution of TEs into associated groups. ~~using the Ward linkage method and the Euclidan distance measure~~ (Fig. ~~S4~~S5). ~~The~~ Both cluster ~~analysis~~ analyses show~~s~~ that Pb and Zn are strongly associated~~, with Cd, Bi, and Mn~~ suggesting these TEs likely have ~~a non-crustal~~common origins.

3.1 21st Century anthropogenic sources

The Mann–Kendall trend test was used to detect TEs with sustained and significant increasing trends in EF and Excess concentration during the 1971–2015 period. The trend test indicated that Bi, Cd, Ni, Pb, Tl, and Zn, which are loaded in Factor 3, have significant increasing EF and Excess concentration trends~~ but only Cd, Ni, Pb, and Zn have additionally significantly increasing trends in Excess concentration~~. The EFs obtained here using PSAs are much smaller than those calculated using the upper continental crust average (Wedepohl, 1995) and also smaller than those from ice cores with lower dust loads compared to Guliya. Thus, it is necessary to determine which of the TEs mentioned above were significantly more enriched during the 2000–2015 period. For this purpose, two different tests were used, the Mann–Whitney test and the two-sample t-test ($p < 0.0005$). Both tests showed that the EFs and Excess concentrations for ~~all four~~the metals, Cd, Zn, Pb, and Ni, are significantly higher during the 2000–2015 period than during the 1971–1990 period. Thus, the following sections will specifically focus on these four TEs and their possible sources.

Back-trajectory frequency distributions were determined to establish the origin of air parcels reaching the Guliya ice cap. Back trajectories (7 days) were calculated daily for the 1992–2015 period for winter (December–January–February) (Fig. 1b) and summer (June–July–August) (Fig. 1c) using the HYSPLIT model from the National Oceanic and Atmospheric Administration. During winter, Guliya is strongly influenced by air parcels mostly from western Xinjiang (China); from Central Asia, which consists of the former Soviet republics of Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan, and Uzbekistan; from Afghanistan and Pakistan in South Asia; and to a lesser extent from the Middle East, Northern Africa, and both Eastern and Western Europe. In summer, westerly and southerly (monsoonal) flows, and even occasional northerly flows, influence Guliya, such that the entire Xinjiang region in addition to Central Asia and the northern regions of Afghanistan and Pakistan, lies within the back trajectories area. Air parcels from other Southern Asian countries, such as India and Nepal, can also reach Guliya during summer.

Trace element enrichments in the Guliya core could reflect changes in emissions, atmospheric circulation, and/or post-depositional processes. Post-depositional processes (e.g., seasonal surface melting, percolation and refreezing of meltwater) do not significantly affect the stratigraphy of the Guliya core (Thompson et al., 2018). The Guliya borehole

temperatures were between –8°C and –12°C from the surface to ~15 m depth confirming that the ice is cold (Thompson et al., 2018) and that overprinting of the TE records due to meltwater percolation is unlikely to occur. Thus, the enrichments observed in the Guliya record indicate increasing emissions in specific source regions and/or changes in atmospheric circulation.

To determine the origin of the Guliya Cd, Pb, Zn, and Ni enrichments, we examine the most important emission sources of atmospheric TEs from the determined regions of influence: Central Asia, South Asia (Afghanistan, Pakistan, and India), and Xinjiang (China). We also use $PM_{2.5}$ emission estimates, which very likely contain toxic metals such as Cd, Pb, Ni, and Zn, using the EDGAR (Emissions Database for Global Atmospheric Research) v4.3.2 air pollutant dataset (1970–2012) (EDGARv4.3.2, 2017; Crippa et al., 2018). The EDGAR dataset provides total $PM_{2.5}$ and also $PM_{2.5}$ by emission sector for all countries.

In the EDGAR database, the total $PM_{2.5}$ corresponds to emissions from all human activities except large-scale biomass burning and land use, land-use change, and forestry (EDGARv4.3.2, 2017; Crippa et al., 2018). To better understand the possible emission sources, here we divided the EDGAR $PM_{2.5}$ emission sectors into ~~four~~ five source categories in accordance with the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC, 2006). These source categories include: 1) fossil fuel combustion which comprises the emission sectors: power generation and combustion in the manufacturing, transportation, and residential sectors, 2) biomass burning which includes biofuel combustion in the manufacturing, transportation, and residential emission sectors as well as agricultural waste and field burning, ~~2~~3) industrial processes which include the emission sectors: mineral, chemical, and metal industry and other production industry (note: this category does not include any type of fossil fuel combustion used by these industries), ~~3~~4) agriculture which includes the emission sectors: manure management, rice cultivation, direct soil emission, manure in pasture/range/paddock, and other direct soil emissions, and ~~4~~5) waste which includes the emission sectors: waste incineration and solid waste disposal on land.

~~From 1980 to~~ In 2012, fossil fuel combustion was the primary source of the total $PM_{2.5}$ emissions in ~~Afghanistan, Pakistan, India, Nepal, and~~ China, Kazakhstan, and Kyrgyzstan ~~primarily originated from the fossil fuel combustion emission sectors~~ (~~80–95~~60–80 %), followed by biomass burning (~20–35 %), industry ~~source category~~ (~~5–20~~2–10 %), agriculture ~~source category~~ (~~9~~1–3 %), and waste ~~source category~~ (<1 % for China, no $PM_{2.5}$ emissions estimated for waste incineration for the other countries in the EDGAR database). While biomass burning was the primary $PM_{2.5}$ source in Afghanistan, Pakistan, and Nepal (~80–90 %) and in India, Tajikistan, Uzbekistan, and Turkmenistan (~50–60 %) followed by fossil fuel combustion (~2–15 % and 20–30 %, respectively) and industrial activities (< 2 % and ~2–15 %, respectively) (EDGARv4.3.2, 2017; Crippa et al., 2018). Regarding Xinjiang in particular, numerous studies have estimated coal combustion as a major source of atmospheric Cd, Pb, Zn, and Ni followed by smelting processes as a source of Cd, Pb, and Zn (Li et al., 2012; Shao et al., 2013; Cheng et al., 2014; Tian et al., 2015), and by oil combustion as a source ~~for~~ of Ni (Tian et al., 2012) and biomass burning as a source of Cd, Pb, and Ni (Cheng et al., 2014; Tian et al., 2015). Thus, in the following sections we focus on the ~~three~~ largest TE and $PM_{2.5}$ source categories: fossil fuel combustion (Sect. 3.1.1), biomass burning (Sect. 3.1.2), metal production (Sect. 3.1.~~2~~3), and the agricultural sector (Sect. 3.1.~~3~~4).

3.1.1 Fossil fuel combustion

In the regions that influence Guliya, two distinct trends in fossil fuel consumption ~~and total $PM_{2.5}$~~ emissions are discernible. Firstly, a steady increasing trend since the 1970s is observed in the Xinjiang province, Afghanistan, Pakistan, India, and Nepal (Fig. 4a). Secondly, a decline after the 1990s is observed in Central Asian countries due to the collapse of the Soviet Union (Fig. 4b). India and Xinjiang (China) became the largest consumers of both coal and oil in the region during the 21st century, with coal as their primary energy source (Fig. 4). The third largest consumer of coal and oil in the region during the 21st century is Kazakhstan despite its decreased consumption after the 1990s. ~~Interestingly, for each individual country, total $PM_{2.5}$ emissions generally follow coal consumption as shown in Fig. 4.~~

Significant positive correlations ($p < 0.001$) were found between the Guliya EFs of Cd, Pb, Zn, and Ni and coal consumption in Xinjiang, India, China, and Pakistan; oil consumption in Xinjiang, India, China, Pakistan, and Turkmenistan; and total $PM_{2.5}$ emissions from China, India, Pakistan and Afghanistan. These positive correlations were expected since these records show generally increasing trends as shown in Fig. 4. Although Pakistan's fossil fuel consumption is 1–2 orders of magnitude lower than that of Xinjiang and India, the Guliya TE enrichments closely resemble Pakistan's coal consumption between 2005 and 2015. Both records peaked in 2008 after which they began to decrease suggesting Pakistan's coal consumption could be one of the sources of anthropogenic TEs observed in the Guliya core.

To further investigate the role of fossil fuel combustion in Pakistan and in the other regions, we examined $PM_{2.5}$ emitted by the different sectors comprising fossil fuel combustion. The most interesting outcome is the temporal correspondence between the Guliya TE enrichments and Pakistan's $PM_{2.5}$ emissions ~~from fossil fuel combustion~~ associated with road transportation and manufacturing and construction (M-C) industries, which are the two largest fossil fuel combustion $PM_{2.5}$ emission sectors in Pakistan (Fig. ~~5~~S6). The enrichments of Cd, Pb, Zn, and Ni have two maxima, one in 2000 when $PM_{2.5}$ emissions from road transportation peaked, and the other in 2008 when $PM_{2.5}$ emissions from the M-C industries peaked. After 2008, TE enrichments (except for Pb) and $PM_{2.5}$ emissions (road transportation and M-C industries) decreased (Fig. ~~5~~S6). ~~These temporal similarities suggest that the TE enrichments detected in the Guliya ice core after 1995 may have primarily originated from the combustion of fossil fuels in Pakistan by road transportation (since 1995) and by the M-C industries (since 2004).~~

Although Pakistan's oil and coal consumption is much lower than that in Xinjiang and India~~'s~~, Pakistan is home to some of the most polluted cities in the world (WHO, 2016) due to the lack of emission controls and air quality standards (Colbeck et al., 2010; Sánchez-Triana et al., 2014). These cities include Peshawar, Rawalpindi, Lahore, Faisalabad, and Pakistan's capital, Islamabad (Rasheed et al., 2014; WHO, 2016; Shi et al., 2018), all located in northern Pakistan from which air parcels have been shown to strongly influence the Guliya site throughout the year. Air parcels from Xinjiang and India, on the other hand, only reach Guliya during summer (Fig. 1c). Thus, fossil fuel combustion emissions from Xinjiang and India but also from Pakistan ~~which further suggests that Pakistan is the likely dominant geographical origin of the~~contribute significantly to the Guliya TE enrichments observed. Nepal's and Afghanistan's fossil fuel consumption have also been increasing and even though it is ~10-100 times lower than those

of Xinjiang, India or Pakistan, they are within the high percentage (5-15 %) region of back trajectory frequencies. Thus, fossil fuel emissions from both Nepal and Afghanistan can also reach Guliya. Although fossil fuel consumption has declined in Central Asia since the 1990s, their emissions have also likely contributed to the TE enrichments detected in Guliya since Central Asia is in the high frequency region of the Guliya back trajectories.

3.1.2 Biomass Burning

Total $PM_{2.5}$ emissions from biomass burning have been increasing since 1970 in Pakistan, India and Nepal at a constant rate, and in Afghanistan, Tajikistan, Uzbekistan, and Turkmenistan since ~1995 (Fig. 5). In China, they reached a maximum in 1990 after which they slightly decreased probably due to the increase of fossil fuel consumption. The Guliya TE enrichments do not resemble the biomass burning $PM_{2.5}$ emission trends for any country except for Turkmenistan's that peaks in 2007, one year before the Guliya EF maximum, and then it decreases similarly to the Guliya TE enrichments. The residential sector is the largest contributor of biomass burning $PM_{2.5}$ emissions in China, India, Nepal, and Pakistan followed by agricultural waste burning, conversely, in Central Asia and Afghanistan the burning of agricultural waste is the largest contributor of biomass burning $PM_{2.5}$ followed by the residential sector (EDGARv4.3.2, 2017; Crippa et al., 2018).

Households in developing countries particularly in rural areas of Asia, widely use traditional biomass burning, characterized by its low efficiency and by the lack of emission controls, for heating and cooking (Gumartini, 2009; Chen et al., 2017; Weyant et al., 2019). In 2012, 4513 Gg of $PM_{2.5}$ from biomass burning and 2534 Gg of $PM_{2.5}$ from fossil fuel combustion from all the countries of interest here (except China) were emitted to the atmosphere (EDGARv4.3.2, 2017; Crippa et al., 2018). Some studies have found higher TE contents in $PM_{2.5}$ emitted from coal combustion than from biomass burning (except for Zn) (Steenari et al., 1999; Ross et al., 2002; Richaud et al., 2004). However, biomass, like fossil fuels, is a complex mixture of organic and inorganic matter and the TEs contents in its $PM_{2.5}$ emissions depend on the type and origin of the biomass and on its burning conditions (Christian et al., 2010; Vassilev et al., 2013). Thus, while $PM_{2.5}$ from biomass burning is almost twice that from fossil fuel combustion, we can only conclude that biomass burning emissions from Central Asia, South Asia and Xinjiang likely have significantly contributed, like fossil fuels, to the TEs enrichments detected in the Guliya ice cap.

Large-scale biomass burning events, excluded in the EDGAR database, can be another source of atmospheric TEs. In the regions of interest here, fire activity and its emissions decreased in Central Asia and in northwest China between 1997 and 2016. However they increased in India (including northwestern India) and in Nepal, both of which are in the high percentage back trajectory frequency of Guliya (Fig. S7) (van der Werf et al., 2017; You et al., 2018). Thus, emissions from the increased fire activity in India and Nepal probably contribute to the enrichments observed in the Guliya ice core.

3.1.3 Metal production

Like fossil fuel consumption, metal production has increased in Asia since the 1980s (Fig. ~~S5~~S8) being China, India and Kazakhstan the most important non-ferrous metal producers in the region and in the world (BGS, 2015). In China,

most of the non-ferrous metal production is located in the coastal regions while all Ni production is located in the western region of China (Gansu, Xinjiang, Chongqing, Yunnan, and Liaoning provinces). Gansu, just east of Xinjiang, produces 95 % of the total Ni production in China (Yanjia and Chandler, 2010). The Guliya TE enrichment trends do not resemble those of metal production in China, Pakistan, India nor Kazakhstan (Fig. ~~S5~~S8). Thus, although these important metal production sources are relatively close to Guliya, they are likely not the primary source of the Guliya TE enrichments.

$PM_{2.5}$ emissions by industrial processes contribute ~~~ 20 %,~~ 10 % of the total $PM_{2.5}$ emissions in China, and ~~5~~ 2 % to the total $PM_{2.5}$ emissions in India, Pakistan, and Kazakhstan. Pakistan's $PM_{2.5}$ emissions by industrial processes peaked in 2008 similarly to the Guliya TE enrichments, but they remained relatively stable after ~~that~~ 2008 while the Guliya TE enrichments decreased (Fig. ~~S5~~S8). Thus, while the increasing emissions from metal production could also influence the TE depositions observed in Guliya, the metal production temporal trends and the industrial $PM_{2.5}$ emissions suggest they are not the main sources of the Guliya TE enrichments.

3.1.~~3~~ 4 Agricultural activities

Emissions from agricultural activities are an important source of atmospheric $PM_{2.5}$ worldwide (Lelieveld et al., 2015; Bauer et al., 2016). Fertilizers and pesticides can be a direct (aerial spreading) or indirect (soil exposed to wind erosion) source of toxic metals such as As, Cd, Cu, Cr, Pb, Ni, Zn, and others to the atmosphere (Nriagu and Pacyna, 1988; Nriagu, 1989b). In particular, fertilizers derived from phosphate rocks contain heavy metal impurities such as Cd and Pb that can contaminate agricultural soils (Mortvedt, 1995; Roberts, 2014). While consumption of phosphate fertilizers decreased in Central Asia in the 1990s, it has been increasing in China, Pakistan, India, and Nepal since the 1970s (Fig. ~~S6~~S9). The Guliya TE enrichments resemble neither the phosphate fertilizer consumption records in these countries nor their $PM_{2.5}$ emissions from agricultural activities (Fig. ~~S6~~S9). ~~Thus~~However, emissions associated with agricultural activities in western China, Pakistan, India, and Nepal are likely becoming more important sources of atmospheric TEs since they have been increasing recently and they originate in the back trajectory high frequency regions for Guliya.~~even though agricultural activities and their emissions have also been increasing since the 1970s, their depositions at the Guliya ice cap are likely overwhelmed by those from fossil fuel combustion in Pakistan.~~

~~3.2 Atmospheric circulation~~

~~In our previous Guliya TEs study (Sierra-Hernández et al., 2018), we observed a positive correlation between the North Atlantic Oscillation (NAO) index and the EFs at Guliya suggesting non-crustal depositions originated from regions to the west. Likewise, Thompson et al. (2018) determined possible positive linkages between NAO and the 2015 Guliya ice core temperature and snowfall proxies. Fig. 6 presents a comparison of the 1992 and 2015 Guliya EF composites with the winter (DJF) NAO index and with coal production/consumption from Europe, and Pakistan between 1800 and 2015. The extended Guliya EF composite shows two periods of enrichment: ~ 1850–1940 and 1970–2015. We suggested that the former originated from coal consumption in Europe, which alongside the U.S. was a major coal consumer at the time. The TE enrichment dropped to pre-industrial levels during 1940–1970 coinciding with a negative NAO phase. This drop occurred at a time when atmospheric emissions in Europe reached a maximum~~

~~(Pacyna and Pacyna, 2001) suggesting that atmospheric circulation (NAO) had a stronger influence over Guliya than the emission source(s) intensity. Post 1970s enrichments in both the 1992 and the 2015 Guliya records occur during positive phases of NAO. Emissions control devices were introduced in Europe ~ 1970 decreasing their $PM_{2.5}$ emissions (Pacyna et al., 2007; Pacyna and Pacyna, 2001) and consequently atmospheric emissions of TEs; however, TE enrichments continue to increase in the Guliya ice core record. This divergence can be explained by changes in either emission source intensity and/or atmospheric circulation, and indeed changes in both emission intensity and atmospheric circulation have occurred post 1990s.~~

~~TEs enrichments start to decrease in 2009 while the NAO entered a slightly negative phase between 2010 and 2014. Similarly, coal consumption has decreased in Pakistan since 2009, in Kazakhstan since 2012, and in Afghanistan since 2011 while in Xinjiang it continues to increase. In addition, the Chinese government implemented the 12th FYP (2011 - 2015) that included policies to mitigate heavy metals emissions, implement air quality standards on $PM_{2.5}$, and increase renewable energy consumption which likely explains the decrease of smoke and dust particles emitted in Xinjiang since 2014 (Fig. 4). The decline in coal consumption in the region, the Chinese mitigation policies and the slightly negative NAO could all have led to a decrease in EFs and Excess concentrations. However, the winter NAO index has also been slightly negative in other years (e.g., 1919, 2000) without affecting the enrichments detected in the Guliya core. Therefore, the slightly negative NAO phase between 2010 and 2014 probably did not play a significant role in the Guliya TE enrichments decrease after 2009~~

Although practically all human activities that emit $PM_{2.5}$ and toxic metals have been increasing in South Asia and in Northwest China, it is very likely that emissions from ~~Pakistan's~~ fossil fuel combustion and biomass burning have dominated the Guliya Cd, Pb, Zn, and Ni enrichments during the 21st century~~,~~. ~~and more specifically oil combustion by road transportation since 1995 and the subsequent significant rise of coal combustion in 2004, likely mostly consumed by the M-C industries.~~ Emissions from other sources such as ~~(~~industrial processes, agriculture activities, waste disposal, and land-use change~~)~~ have also likely been deposited on the Guliya ice cap. ~~from Pakistan and other regions (Central Asia, Xinjiang, Afghanistan, Northwest India and Nepal) have also likely been deposited on the Guliya ice cap but to a lesser extent.~~ Although economic activities in Central Asia have declined since the 1990s, emissions from their different sectors also probably contribute to the TE enrichments observed in Guliya during the 21st century.

China is investing ~~$62 billion~~heavily in global infrastructure projects like the Belt and Road Initiative (New Silk Road), the Western Development policy, and the Pakistan-China Economic Corridor (PCEP) that could potentially increase the emission of atmospheric toxic TEs. These projects were established~~established in 2013~~ to improve the ~~economy of Pakistan and to facilitate~~ economic connectivity with the West and with other countries in the region by modernizing and building new airports, railways, highways, water infrastructure, and power lines. ~~Until 2015,~~ In Pakistan~~'s~~ energy was generated mostly from oil, gas, and hydropower until 2015. After the establishment of the PCEP, five coal-fired power plants were built and have been operational since 2017. Three ~~more~~ additional plants are expected to open ~~during~~ in 2019 and ~~others~~ more are currently under construction (CPEC, 2019). These developing projects and ~~Moving~~ the shift to coal-generated power ~~will further increase the total coal consumption in Pakistan~~

~~which in turn~~ could have severe environmental and human health impacts in the region if mitigation actions are not taken.

4 Conclusions

A new continuous, high-resolution ice core record of trace elements covering the 1971–2015 period was extracted from the Guliya ice cap in Northwestern Tibet, China. This new record extends our previous 1650–1991 Guliya record well into the 21st century making it, the first and most up to date ice core-derived archive of trace metal contamination in the Third Pole region. Since the dust concentrations in the Guliya ice cores are extremely high in comparison to other ice cores from the Third Pole as shown in Sierra-Hernandez et al. (2018), we also used EF and Excess concentrations to differentiate between crustal and non-crustal origins in this new record. Increases in EF and Excess concentrations of Cd, Pb, Zn, and Ni are observed since the 1990s, reaching a maximum in 2008. The enrichments of Cd, Pb, Zn, and Ni increased by ~75 %, 35 %, 30 %, and 10 %, respectively, during the 2000–2015 period relative to 1971–1990. Comparisons between the Cd, Pb, Zn, and Ni enrichments from the Guliya records and fossil fuel consumption, metal production, phosphate fertilizer consumption, and $PM_{2.5}$ emissions from Xinjiang (China), Afghanistan, Pakistan, India, Nepal, and Central Asia suggest that the metal enrichments detected in Guliya originate primarily from fossil fuel combustion and biomass burning in these regions and secondarily from industrial processes and agricultural activities. ~~(road transportation and the manufacturing and construction industry) in Pakistan between 1995 and 2015. The post-2008 Cd, Zn, and Ni decline likely reflects a coal consumption decrease in Pakistan at that time. It is likely that emissions from Xinjiang, Afghanistan, India, Nepal, and Central Asia, are also impacting Guliya during the 21st century, however their contribution is overwhelmed by that of fossil fuel combustion emissions from Pakistan.~~ This new Guliya ice core record demonstrates that the current emissions in Asia are impacting remote high-altitude glaciers in the region. Therefore, mitigation policies and technologies should be enforced by the governments of Central and South Asian countries to improve the air quality in the region as most Asian countries continue to develop.

Data availability.

Supplement. The Supplement is available online

Author contributions. R.S.H. wrote the paper, performed all the data analysis, interpreted the data, and ran the daily HYSPLIT back trajectories; R.S.H. and E.B. prepared the ice core samples and conducted their ICP-MS analysis; E.B. created the maps for Fig. 1. All authors contributed to the study design, data interpretation, revision and edition of the manuscript. P.G. oversees the ICP-MS lab. L.G.T. planned the drilling operation and led the field expedition in which both L.G.T. and P.G. contributed to the ice core processing in the field.

Competing interests. The authors declare no competing financial interests.

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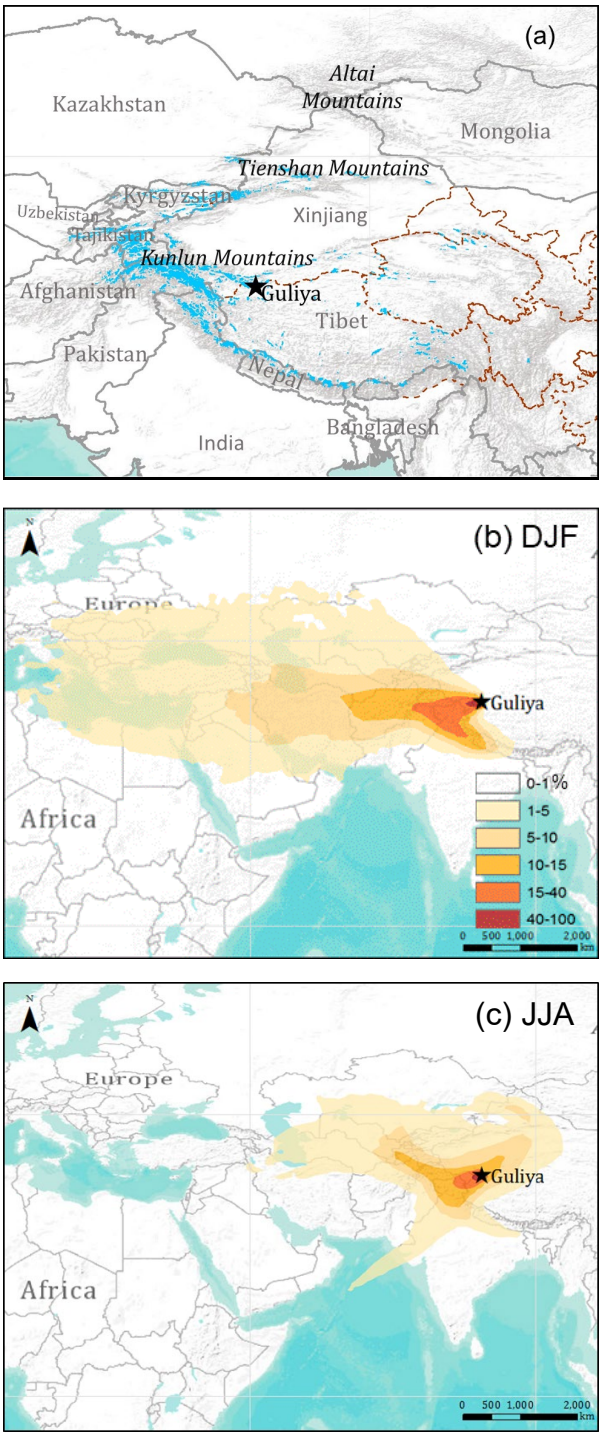
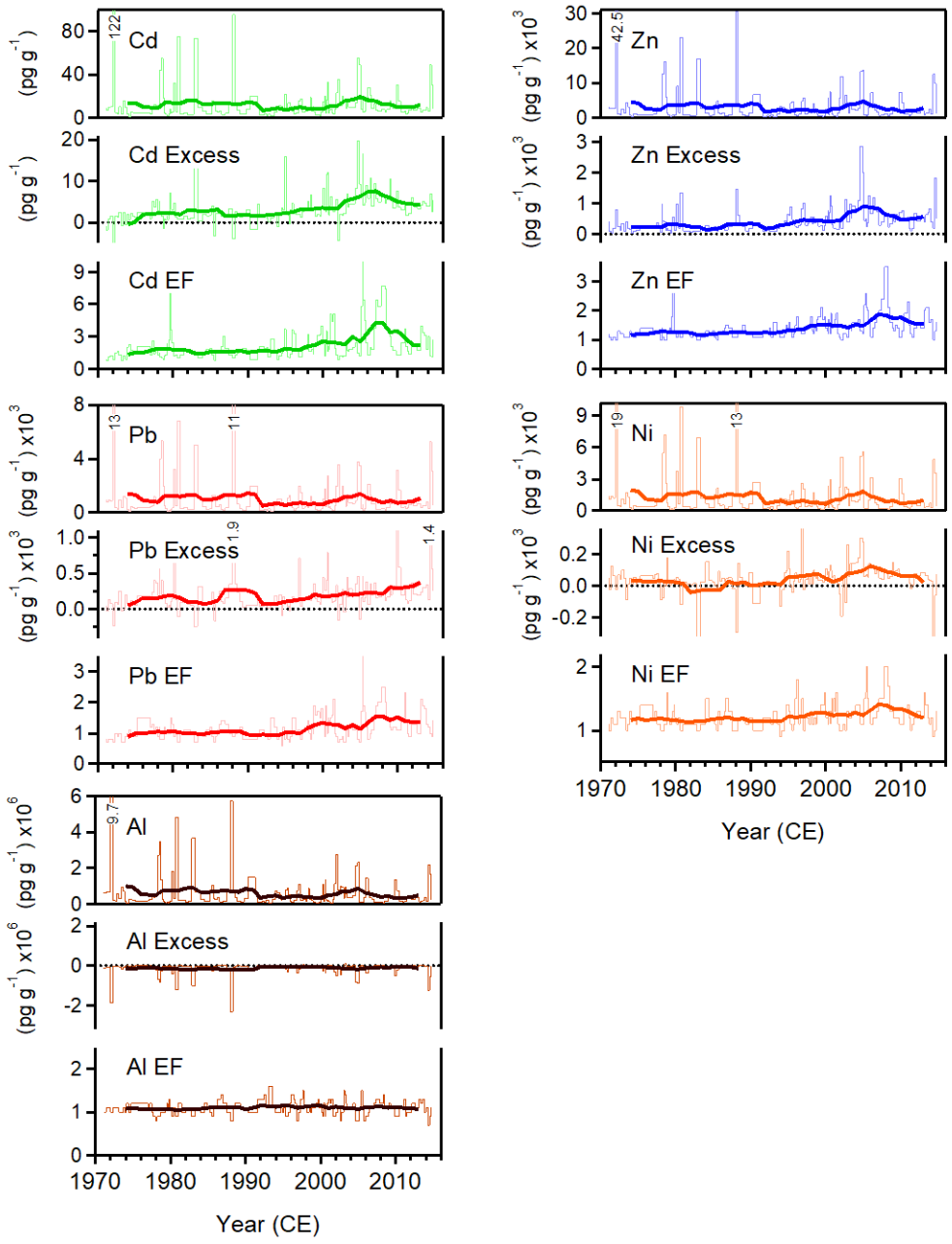


Figure 1. Maps showing the location of the Guliya ice cap (star) and the three mountain ranges of the Xinjiang province (a), and seasonal NOAA HYSPLIT 7-day back trajectories frequency plots for December, January, and February (b); and June, July, and August (c) for the 1992–2015 period (Rolph et al., 2017; Stein et al., 2015).



626

627 **Figure 2**. Cd, Pb, Zn, Ni, and Al 5-year running means (thick lines) of concentrations, Excess concentrations, and
628 EFs between 1971 and 2015. Thin lines show the sample resolution.

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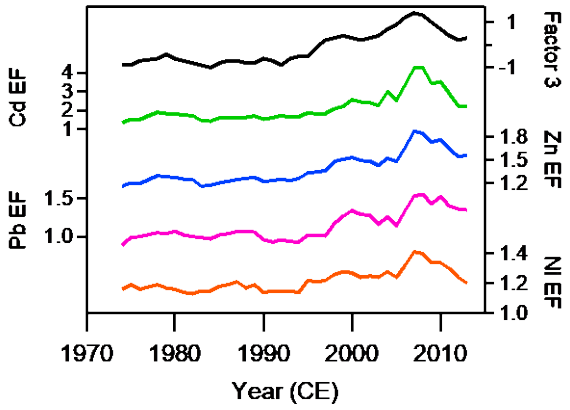

630

631 **Figure 3.** Comparison of 5-year running means of Factor 3 scores with Cd, Zn, Pb, and Ni EFs between 1971 and
632 2015.

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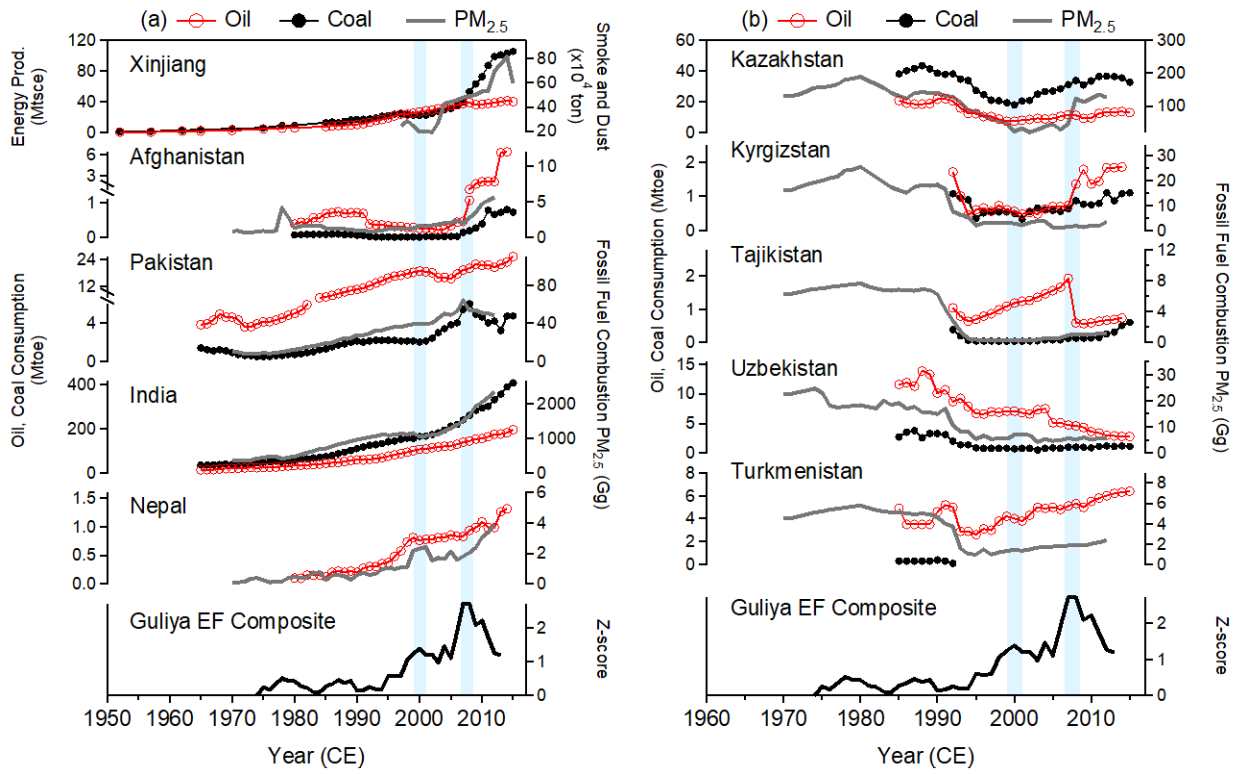


Figure 4. Oil and coal consumption in: (a) Xinjiang, as coal energy production in million tonnes of standard coal equivalent (Jianxin, 2016); in million tonnes of oil equivalent (Mtoe) in Afghanistan (EIA, 2019), Pakistan (BP, 2016), India (BP, 2016), and Nepal (coal ≤ 0.1 Mtoe) (EIA, 2019). (b) Central Asian countries: Kazakhstan (BP, 2016), Kyrgizstan and Tajikistan (EIA, 2019), and Uzbekistan and Turkmenistan (BP, 2016). $PM_{2.5}$ emissions from ~~anthropogenic~~ fossil fuel combustion sources (EDGARv4.3.2, 2017; Crippa et al., 2018) shown in both panels for all countries except Xinjiang (China). Smoke and dust emissions from Xinjiang (Ning, 2016) are shown since no $PM_{2.5}$ data was available. The Guliya EF composite (average of Cd, Pb, Zn, and Ni EF z-scores) is shown at the bottom of each panel for comparison. The two Guliya maxima at 2000 and 2008 are shown as shaded bars.

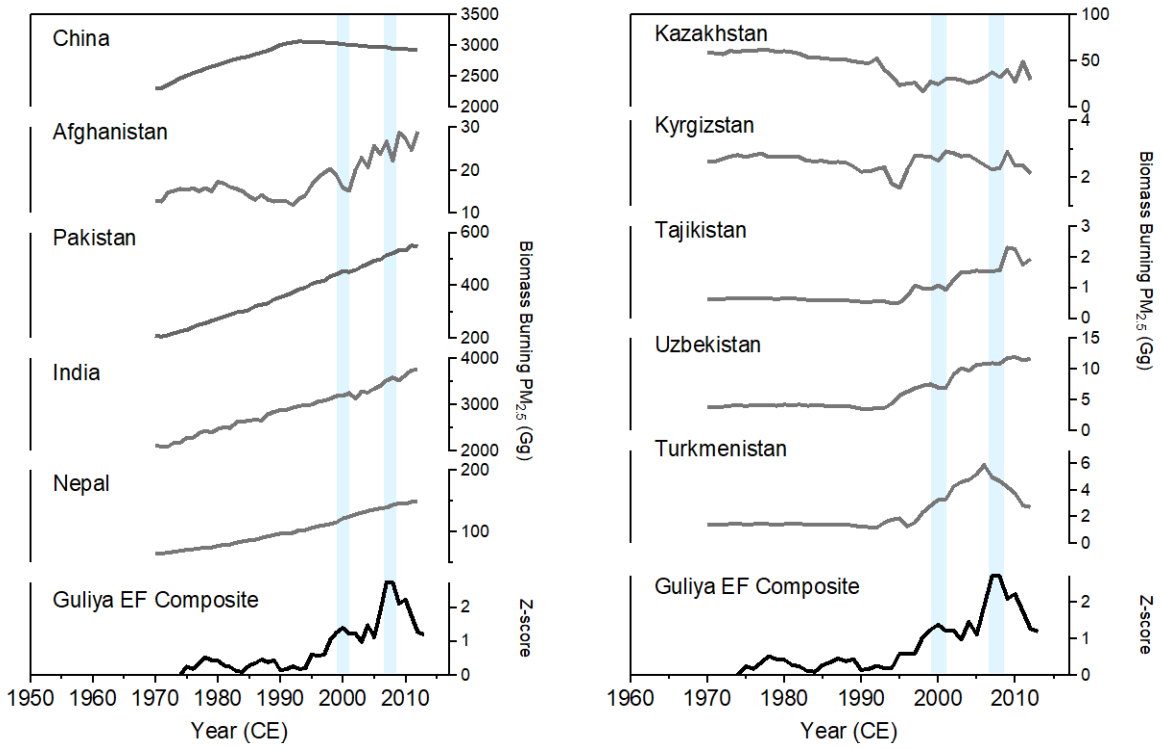
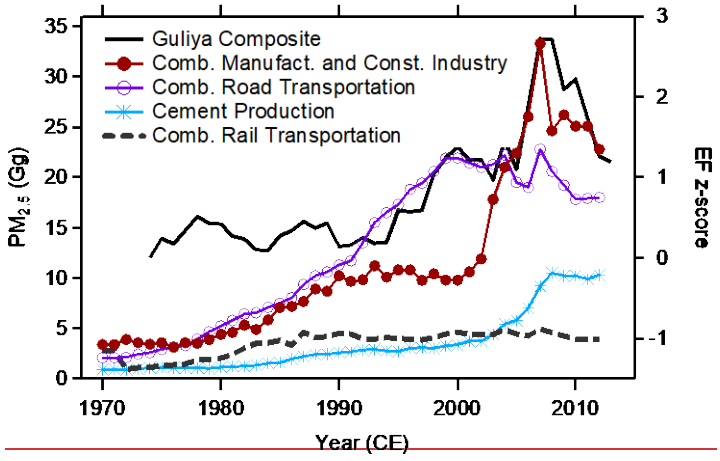
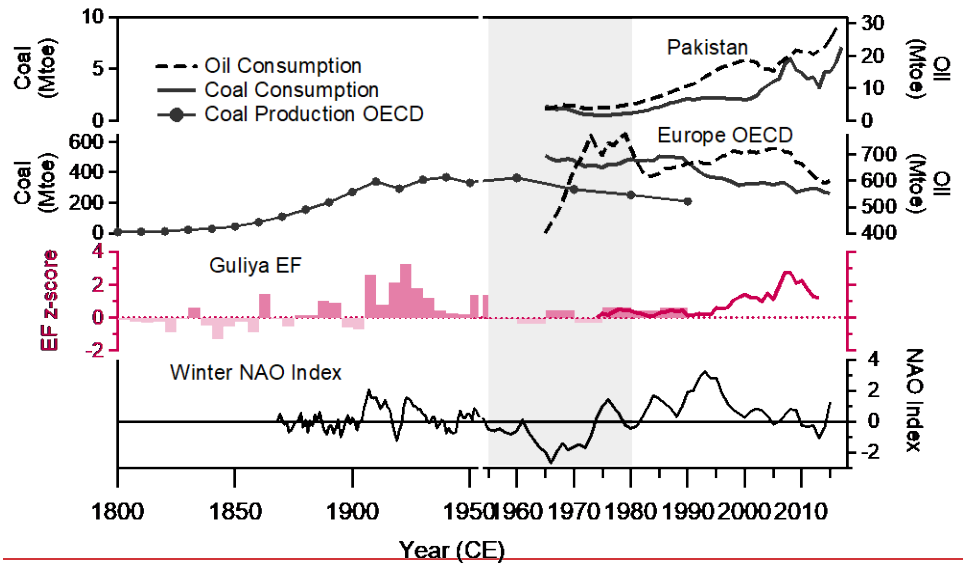


Figure 5. $PM_{2.5}$ emissions from biomass burning sources (EDGARv4.3.2, 2017; Crippa et al., 2018) shown in both panels for all countries. The Guliya EF composite (average of Cd, Pb, Zn, and Ni EF z-scores) is shown at the bottom of each panel for comparison. The two Guliya maxima at 2000 and 2008 are shown as shaded bars.



~~**Figure 5.** Larges emitter sectors of $PM_{2.5}$ in Pakistan between 1970 and 2012: fossil fuel combustion in manufacturing and construction industries, fossil fuel combustion by road transportation, cement production, and fossil fuel combustion by rail transportation . The Guliya EF composite (average of Cd, Pb, Zn, and Ni EF z-scores) is shown for comparison.~~



~~**Figure 6.** Comparisons of the Guliya EF composite (average of Cd, Pb, Zn, and Ni EF z-scores) from the 2015 Guliya core with the winter NAO index shown as 5-year running mean . The 1992 Guliya EF composite (average of Cd, Pb, and Zn EF z-scores) is shown as 5-year medians and the 2015 Guliya EF composite is a 5-year running mean. The light gray band (1955–1980) highlights the period of negative NAO. Pakistan's and Europe coal and oil consumption (1965–2017) are shown for comparison. Europe's coal production (1800–1990)~~

Supplement of

21st Century Asian air pollution impacts glacier in northwestern Tibet

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Table S1. Limit of detection (LOD), procedural blank (TE concentrations of the water used to make the artificial ice core and of the ice from the artificial ice core), accuracy, and blanks average. LOD corresponds to three times the standard deviation of the concentration of 10 measurements of ultrapure water (18.3 MΩ). The concentrations of the Reference Material (TMRain-95) are reported as total concentrations accounting for the dilution factor of ~20.

		Procedural Blank		Accuracy	
Trace Element	LOD	Ultrapure water	Artificial ice core	TMRain-95 Found	TMRain-95 Certified
Ag (pg g^{-1})	0.1	0.5 ± 0.1	1 ± 0.01		
Al (ng g^{-1})	0.03	0.6 ± 0.6	0.9 ± 1.2	2 ± 0.9	2 ± 0.9
As (pg g^{-1})	0.8	3 ± 0.7	4 ± 1	1126 ± 153	1070 ± 250
Ba (pg g^{-1})	2	27 ± 11	32 ± 19	762 ± 59	730 ± 150
Bi (pg g^{-1})	0.01	0.03 ± 0	0.04 ± 0.03	802 ± 13	630 ± 260
Cd (pg g^{-1})	0.1	0.9 ± 0.5	1 ± 0.2	468 ± 14	480 ± 120
Co (pg g^{-1})	0.2	0.3 ± 0.1	1 ± 0.5	227 ± 10	220 ± 37
Cr (pg g^{-1})	1	3 ± 3	7 ± 5	770 ± 37	790 ± 170
Cs (pg g^{-1})	0.1	1 ± 0.3	2 ± 0.5		
Cu (pg g^{-1})	1	21 ± 4	27 ± 5	6305 ± 101	6200 ± 930
Fe (ng g^{-1})	0.2	0.1 ± 0.2	0.4 ± 0.3	24 ± 10	24 ± 4
Ga (pg g^{-1})	0.5	2 ± 2	3 ± 3		
Li (ng g^{-1})	0.04	0.8 ± 0.3	0.7 ± 0.1	0.3 ± 0.2	0.4 ± 0.08
Mg (ng g^{-1})	0.02	0.2 ± 0.1	0.2 ± 0.1		
Mn (pg g^{-1})	1	4 ± 5	5 ± 2	6013 ± 77	6100 ± 780
Mo (pg g^{-1})	0.2	0.5 ± 0.2	1 ± 0.1	174 ± 7	170 ± 100
Na (ng g^{-1})	0.4	1 ± 0.7	2 ± 0.7		
Nb (pg g^{-1})	0.2	5 ± 2	10 ± 6		
Ni (pg g^{-1})	0.8	3 ± 0.6	3 ± 0.8	845 ± 35	800 ± 170
Pb (pg g^{-1})	0.3	0.43 ± 0.2	0.8 ± 0.5	281 ± 5	290 ± 93
Rb (pg g^{-1})	1	18 ± 18	25 ± 16		
Sb (pg g^{-1})	0.1	0.1 ± 0.03	0.1 ± 0.01	322 ± 7	350 ± 100
Sn (pg g^{-1})	4	2 ± 0.5	2 ± 0.7		
Sr (pg g^{-1})	5	285 ± 133	296 ± 132	1729 ± 58	1700 ± 260
Ti (pg g^{-1})	10	21 ± 26	31 ± 24		
Tl (pg g^{-1})	0.02	0.03 ± 0.01	0.05 ± 0.02	330 ± 6	330 ± 72
U (pg g^{-1})	0.03	0.07 ± 0.01	0.09 ± 0.02	262 ± 5	250 ± 60
V (pg g^{-1})	1	4 ± 4	7 ± 5	678 ± 39	640 ± 120
Zn (pg g^{-1})	3	8 ± 4	5 ± 1		

Table S2. Loadings and communalities of each Trace Element (TE) of the first three factors for the entire concentration data set (1971–2015).

TE	Factor 1	Factor 2	Factor 3	Communality
Ag	0.92	-0.29	0.16	0.95
Al	0.96	-0.24	0.07	0.99
As	0.83	-0.50	0.02	0.94
Ba	0.85	-0.47	0.07	0.96
Bi	0.94	-0.25	0.15	0.97
Cd	0.79	-0.30	0.50	0.97
Co	0.96	-0.26	0.08	0.99
Cr	0.96	-0.26	0.08	0.99
Cs	0.95	-0.25	-0.02	0.97
Cu	0.93	-0.32	0.10	0.98
Fe	0.96	-0.25	0.06	0.99
Ga	0.96	-0.26	0.06	0.99
Li	0.79	-0.56	0.01	0.95
Mg	0.80	-0.57	0.05	0.96
Mn	0.84	-0.43	0.18	0.92
Mo	0.41	-0.85	0.08	0.90
Na	0.09	-0.96	0.03	0.93
Nb	0.94	-0.28	-0.02	0.96
Ni	0.95	-0.28	0.10	0.99
Pb	0.93	-0.24	0.24	0.97
Rb	0.94	-0.32	-0.01	0.99
Sb	0.78	-0.57	0.04	0.93
Sn	0.82	-0.36	0.30	0.89
Sr	0.20	-0.95	0.07	0.94
Ti	0.79	-0.58	0.04	0.96
Tl	0.92	-0.35	0.11	0.98
U	0.82	-0.50	0.08	0.93
V	0.95	-0.29	0.07	0.99
Zn	0.94	-0.24	0.21	0.99
Variance (%)	72.6	21.4	2.1	
Cum. Variance (%)	72.6	94.0	96.1	

Guliya's 1650–2015 trace element records

In Thompson et al. (2018), we showed the high reproducibility between the 1992 and 2015 Guliya $\delta^{18}O$ profiles. This reproducibility is also observed in the TE records (Figure S1). Likewise, the Al and Fe concentrations show good agreement during the 1971–1991 period in which both TE records overlap (~~not shown~~Fig. S1) with median concentrations ~~are~~ of 0.3 µg g^{-1} in both records ~~during the 1971–1991 period in which both TE records overlap~~.

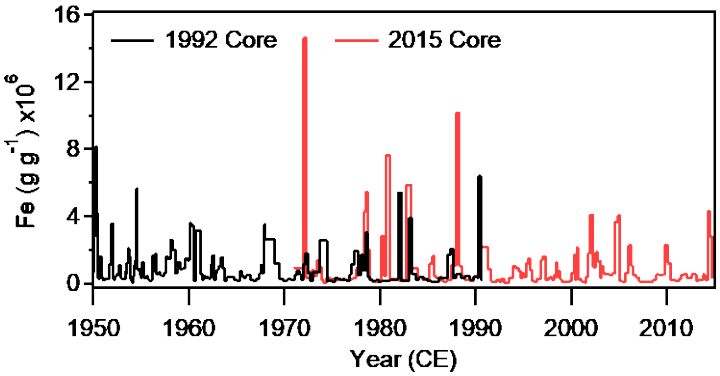


Figure S1. Comparison of Fe concentrations at full resolution in the 1992 and the 2015 Guliya ice cores.

Figure ~~S1~~ S2 displays 5-year median concentrations and EFs of the 1992 (1650–1991) and 2015 (1971–2015) cores for TEs that showed post-1850s enrichments (Pb, Cd, Zn, and Al for comparison). The 5-year median concentrations of Cd, Pb, and Zn are slightly higher in the 2015 record than the 1992 time series for the 1971–1991 period. For example, the Cd median concentrations are 5 and 6 pg g^{-1} in the 1992 and 2015 records, respectively. The difference in concentrations between the 1992 and the 2015 records is not significant (Mann–Whitney test: $p < 0.0005$ for medians) and may be due to spatial variability of ice layers between the two boreholes. Similarly, during the 1971–1991 period, the EFs in the 2015 record are slightly higher than in the 1992 record. This might result from the natural signal to noise ratio differences between the two records. Despite the slight EF differences between the two records during the 1971–1991 period, the reproducibility of TEs allows determination of temporal trends from pre-industrial times (~1650) into the 21st century (2015) using the 1992 and the 2015 TE records.

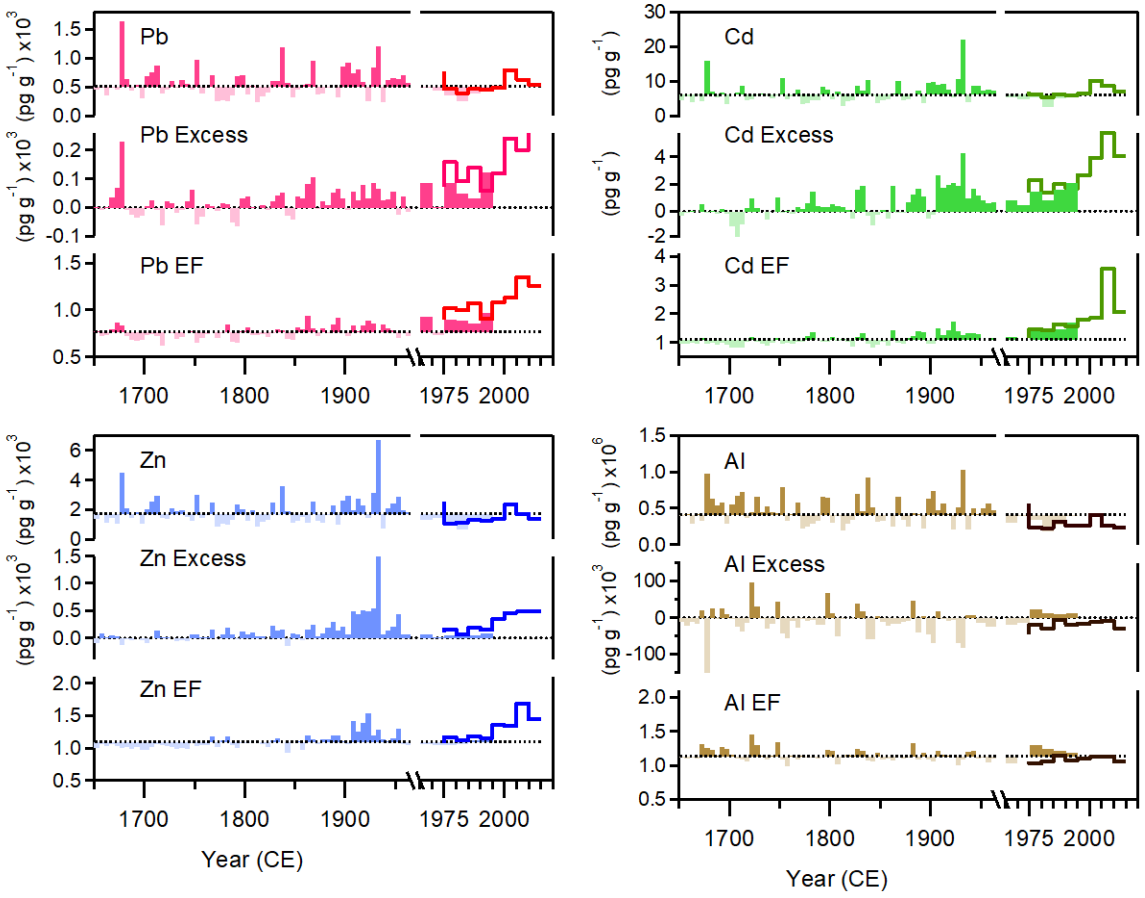


Figure ~~S1~~S2. Pb, Cd, Zn, and Al shown as 5-year median concentrations, excess concentrations and enrichment factors (EF) from the 1992 Guliya ice core (1650–1991) and the 2015 Guliya ice core (1971–2015; thick line). The horizontal dotted lines show the 1650–1991 concentration and EF medians for the 1992 core.

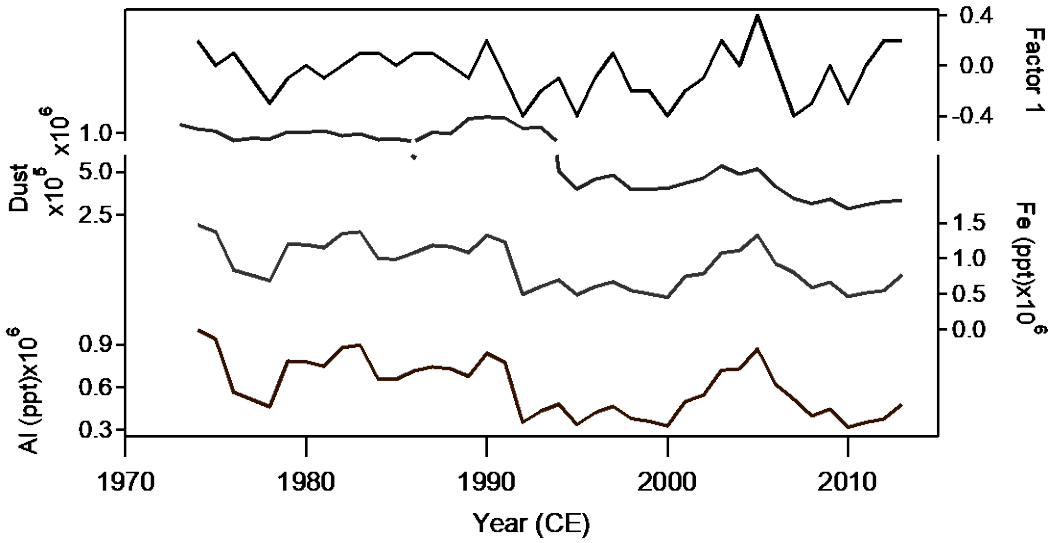


Figure ~~S2~~S3. Comparison of Factor 1 scores (crustal contribution), dust concentrations (particles ml^{-1}) (Thompson et al., 2018), and concentrations of the typical crustal TEs Fe and Al. All data are presented as five-year running means.

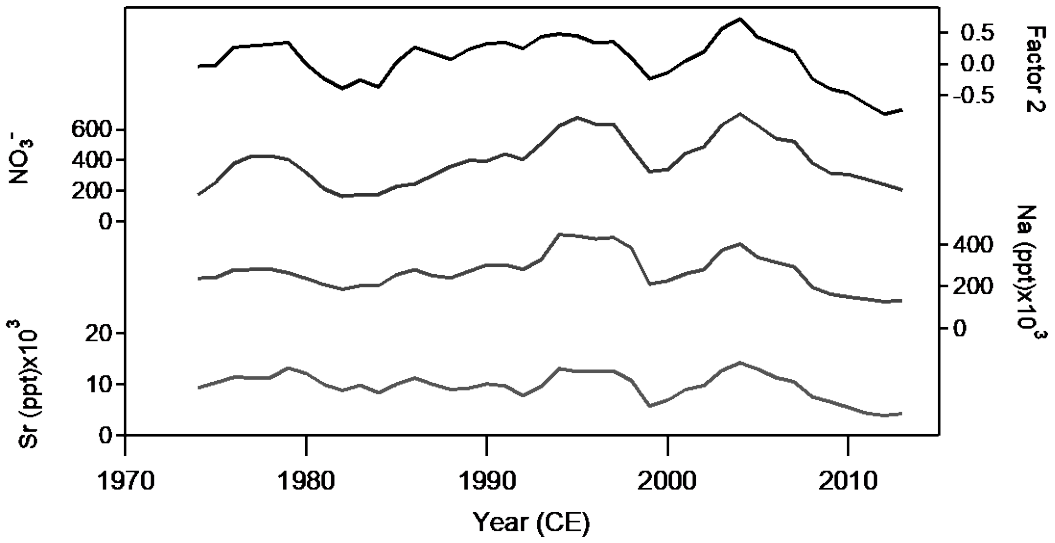
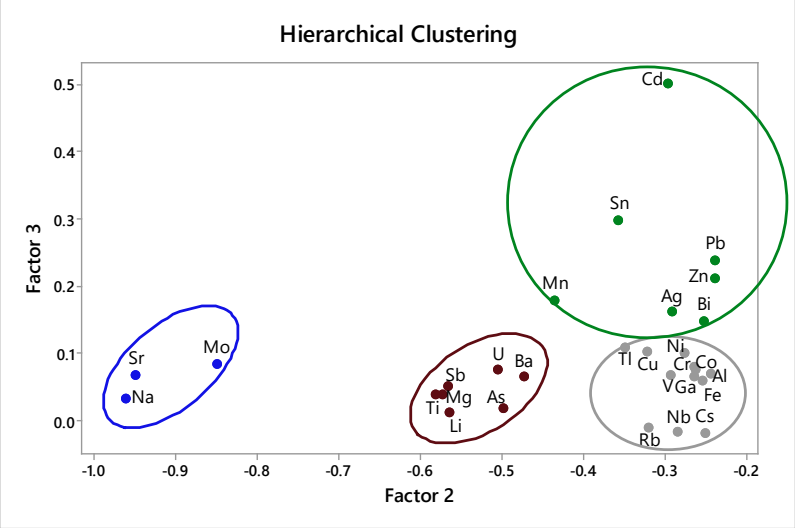


Figure ~~S3~~S4. Comparison of Factor 2 scores (evaporitic contribution), NO_3^- ion concentrations (Thompson et al., 2018), and TEs concentrations of sodium (Na) and strontium (Sr). All data are presented as five-year running means.



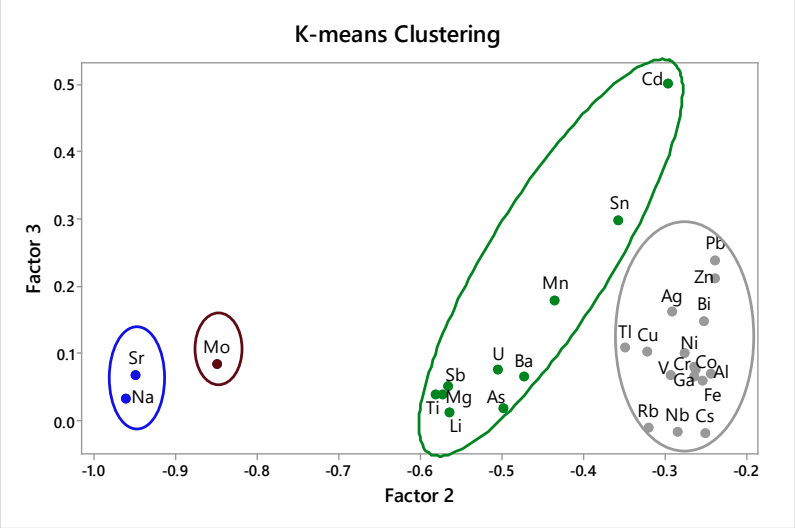


Figure ~~S4S5~~. Hierarchical and non-hierarchical (K-means) cluster analysis extracted from the first three factors during the 1971–2015 period.

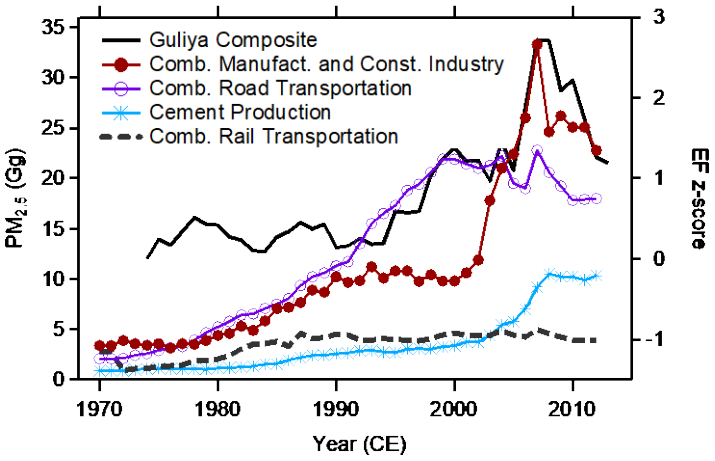


Figure S6. Largest emitter sectors of $PM_{2.5}$ in Pakistan between 1970 and 2012: fossil fuel combustion in manufacturing and construction industries, fossil fuel combustion by road transportation, cement production, and fossil fuel combustion by rail transportation (EDGARv4.3.2, 2017; Crippa et al., 2018). The Guliya EF composite (average of Cd, Pb, Zn, and Ni EF z-scores) is shown for comparison.

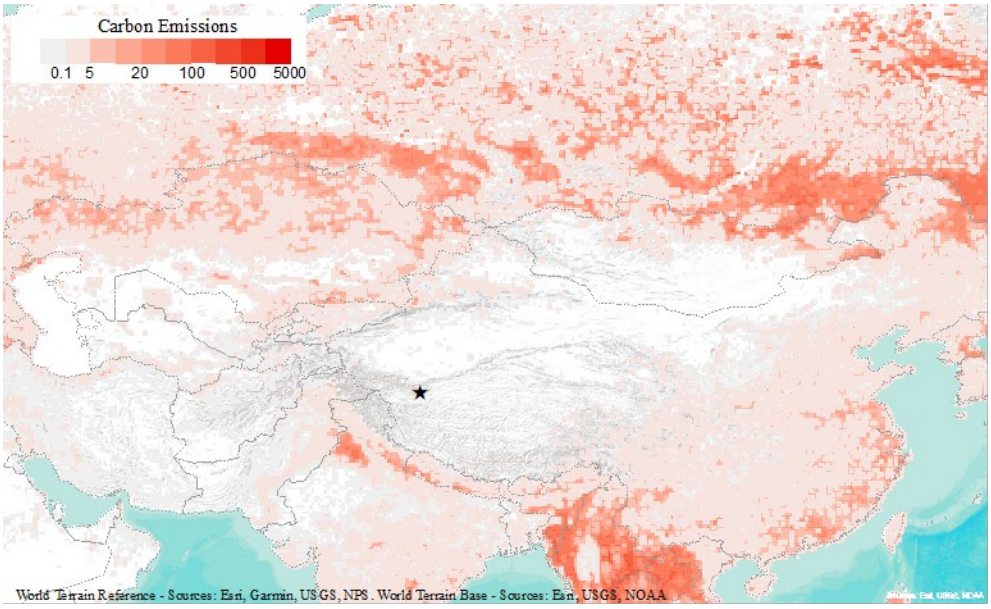
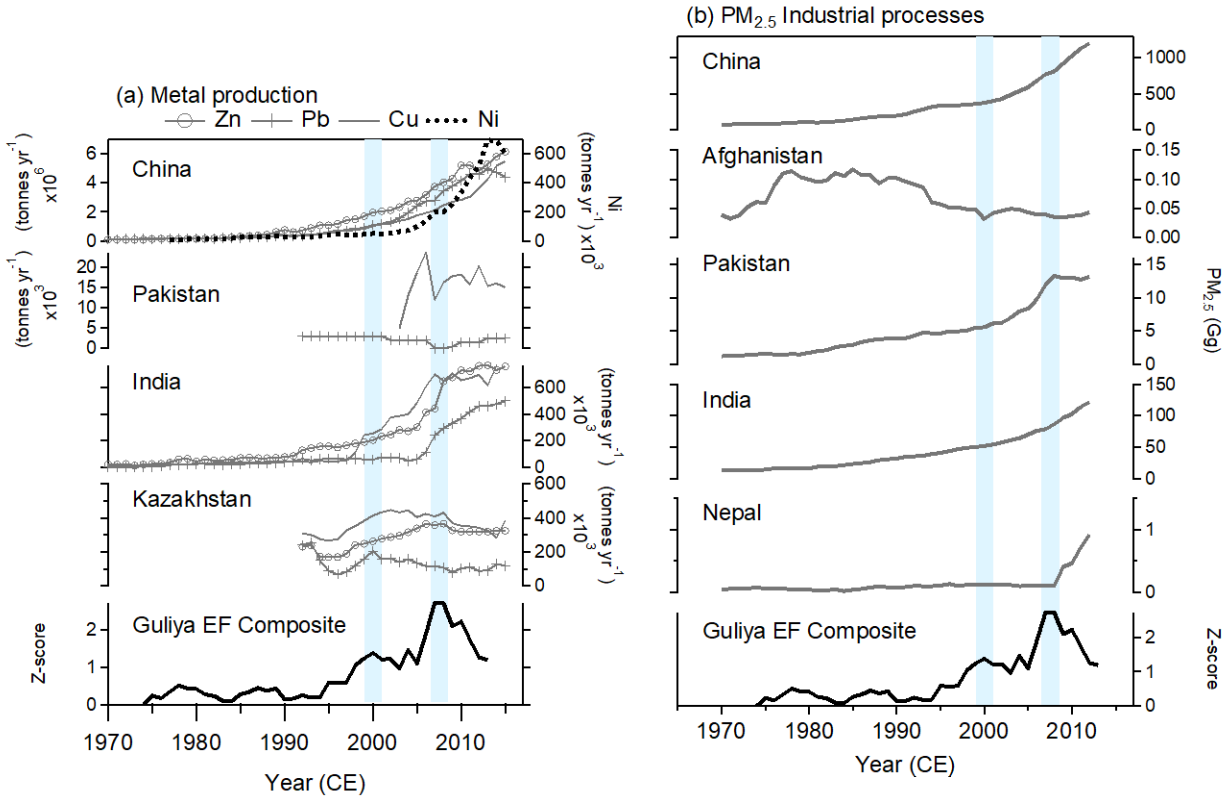


Figure S7. Annual carbon emissions (g C m^{-2} $year^{-1}$) from fires averaged over the 1997–2016 period (van der Werf et al., 2017). The Guliya ice cap location is indicated in the map with a star.



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111 **Figure ~~S5~~S8**. (a) Metal production in China (Zn, Pb, Cu, and Ni), Pakistan (Pb, Cu), India (Zn, Pb, Cu) and
112 Kazakhstan (Zn, Pb, Cu) (BGS, 2015) and (b) $PM_{2.5}$ from industrial processes (including the production of cement,
113 lime, chemicals, and metal production). The Guliya EF composite (average of Cd, Pb, Zn, and Ni EF z-scores) is
114 shown at the bottom of each panel for comparison. The two Guliya maxima at 2000 and 2008 are shown as shaded
115 bars.

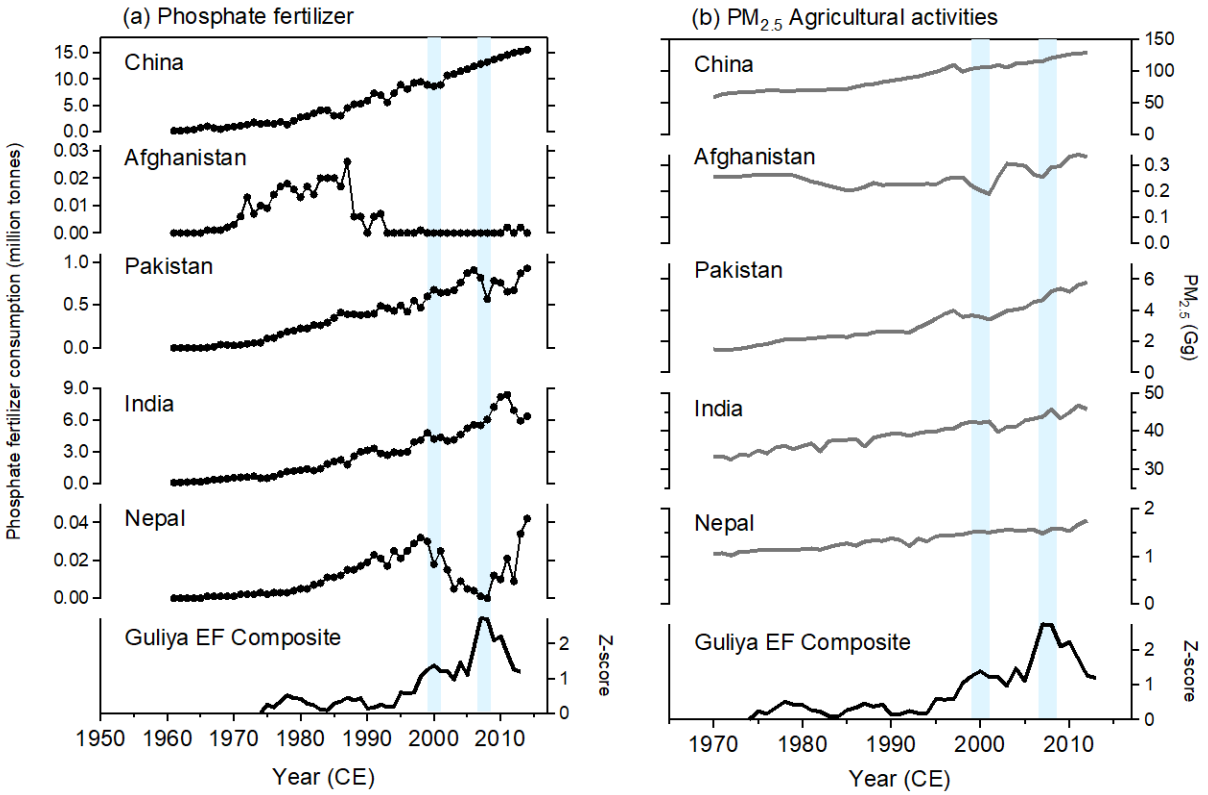

Figure ~~S6~~S9. (a) Phosphate fertilizer consumption (FAO, 2019) and (b) $PM_{2.5}$ from agricultural activities (including direct soil emission, rice cultivation, and manure management) (EDGARv4.3.2, 2017; Crippa et al., 2018). The Guliya EF composite (average of Cd, Pb, Zn, and Ni EF z-scores) is shown at the bottom of each panel for comparison. The two Guliya maxima at 2000 and 2008 are shown as shaded bars.

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