

Detailed Response to the Editor and the Referee #2

Manuscript ID: **tc-2020-165**

Date: December 18, 2020

Title: "Osmium isotope and trace elements reveal melting of Chhota Shigri Glacier, western Himalaya, insensitive to anthropogenic emission residues "

Dear Prof. Harry Zekollari,

We would like to thank you and anonymous referee #2 for insightful comments which will certainly improve our manuscript. Below, we address each of the comments and concerns explicitly, and we assure that appropriate changes will be made in the manuscript, if we are allowed to submit a revised manuscript. We hope that we find our response acceptable to permit us to submit a revised manuscript.

Below, we address each of the comments and concerns explicitly and document the appropriate changes that will be made to the revised manuscript.

Note:

- *Referee's concerns are in italic and our response in normal font*
- *RC and AR correspond to Referee's Comment and Author's Response respectively*

RC: *First, I am very sorry that this review is so late. Second, I am even more sorry that my review is so negative. The introduction to the paper is poorly focused. The paper is trying to ascertain the level of anthropogenic pollution in the catchment via an analysis of cryoconite, moraine, coal and diesel exhaust. The conclusion is that there is little evidence of pollution, and I think that this may be because the sampling and methodology may be not fit for purpose. I could be very wrong, but the text does not provide a convincing argument that the sampling and methodology is fit to deliver the aims and objectives of the paper.*

AR: We would try to revise the introduction of the paper if required. We would like to highlight that referee 1 praised our writing style. He/she writes "In general, the manuscript is well written and easy to follow". However, if the Editor feels that it needs to re-written, we would be happy to revise the introduction accordingly. The sampling and methodology part is written explicitly, and in fact, Referee 1 states "The authors seem quite confident and I have nothing to report on the methodology". I think the referee's questions the use of cryoconite to deliver the aims and objective of the paper. We would like to highlight that there are numerous papers (e.g. Owen et al., 2019; Baccolo et al., 2017; Lokas et al., 2016; Singh et al., 2013) that have used cryoconite (a mixture of dust, soot, and microbes) and achieved similar goals. For example, algae in cryoconite holes and mats on the ice surface can significantly decrease the albedo compared to clean ice (Figure 6, Yallop et al., 2012). Therefore, many factors are contributing to reduced albedo, and in turn melting, yet little is known about the interplay between dust, soot, and biology in the ablation zone. So, we don't see why the referee is not convinced. Nothing is new in the methodology, all aspect of the study from sampling and analytical is very well established.

RC: *First, which pollutants are you most interested in and why have you selected these?*

AR: As we stated, we are interested in metal impurities that get deposited along with other emission impurities including organic carbon (Sarwar et al., 2020). As stated earlier, the idea of my dissertation work was to characterize organic and inorganic impurities that are present in the CSG cryoconites. In this study, we only focused on inorganic (metal) impurities, whereas, Sarwar et al.,

2020 reported organic impurities. We would like to highlight that each individual metal species comes from a specific anthropogenic source or a mixture of many sources. For example, Os is mostly derived from catalytic converters, whereas Cd is derived from coal. All these metal impurities can be tagged to a specific anthropogenic source. However, our intention was not to identify the contribution of individual anthropogenic sources, but to look into the overall presence of anthropogenic particles, and then dive into possible sources. We selected these metals as they are widespread anthropogenic pollutants, and not to track their individual biogeochemical cycling.

RC: *Second, how will you know if these pollutants are above naturally occurring levels on your glacier?*

AR: This was already included in the manuscript, and perhaps referee 2 overlooked Figure 4. Trace metal enrichment exceeding the local background value (see Figure 4 in the original manuscript) provide the first-order evidence for the presence of any anthropogenic pollution in any pristine environment. Enrichment factor calculation (Figure 4) is a routine standard procedure to discriminate between natural and anthropogenic (metal) pollutants. To be more confident, we also used osmium isotopes ($^{187}\text{Os}/^{188}\text{Os}$) to quantify anthropogenic sources. Please see Figure 11a and its associated discussion in Section 4.2. As such we consider the presentation of the submitted paper already covers the referees question.

RC: *Third, why should cryoconite be polluted relative to the local rock you sample? What assumptions do you make and have you tested any of them?*

AR: By definition, cryoconite is a mixture of dust, soot (anthropogenic particles), and microbes and they are regarded as a sink for the natural and anthropogenic sources in a glaciated environment (Baccol et al., 2017, Lokas et al., 2016, Owen et al., 2019, Sing et al., 2013). Since anthropogenic sources have a very high amount of metal concentration, even a small contribution from such a source could be visible in the cryoconite, unless the signal is completely overwhelmed by the local signature. Moreover, $^{187}\text{Os}/^{188}\text{Os}$ crustal signature is around 1.4 whereas anthropogenic signature can be as low as 0.16. We would like to emphasize this variability is huge, and to an isotope geochemist, even a third decimal place variability in the Os isotope is acceptable. We looked into multiple geochemical evidences such as inter-elemental relationship (e.g., Figures 6, 7, 8, 12) and in the osmium isotope space (Figures 10, 11a). All these data conclusively show the absence of the anthropogenic signal in any of the cryoconite sediments. Based on all the geochemical evidence we have concluded that the CSG surface is essentially free of anthropogenic particles. Our claim is further supported by our one more recent paper (Sarwar et al., 2020) where we looked into ^{14}C activity and activation energy of OC. As such we consider the presentation of the submitted paper already covers the referees question, particularly given that the entire paper discusses multiple geochemical evidence, modelling, and quantitative assessments.

RC: *Fourth, how much variability is there in the pollutant content of coal and diesel? Are your samples representative of the pollutants being deposited on the glacier from these sources?*

AR: This is a good question. Cryoconite does not represent snow and ice—the main components of glaciers. So of course the obvious question is why not just measure the metal and its isotopic composition (e.g., $^{187}\text{Os}/^{188}\text{Os}$) of snow and ice. While it will be truly ideal to know ice and snow composition, these analyses are extremely logistically challenging in this environment. One could melt ice and snow, further collect the material on a quartz filter (e.g. Wientjes et al., 2012), or bring back 10s of liter of melted ice and snow meltwater back to the laboratory. Also, once we filter ice and snowmelt water, the anthropogenic particles can be much smaller than the pore size of a typical quartz filter and there will be a chance of chemical fractionation. Therefore, for the time being, we

carried out the study in cryoconite debris, as our objective was to find out the presence and absence of anthropogenic particles in CSG, and these samples very well suit our objective.

Coming back to the other question about concentration variability in coal and diesel. At this moment, we cannot assess the pollutant content variability of coal and diesel in CSG since these particles were absent in CSG. Our intention was to only use coal and diesel compositional range as end-member compositions to deconvolute source end-member of Os using the three-component isotope mixing model. However, since all geochemical evidence pointed towards the absence of any fossil fuel source, we did not use coal and diesel compositions as source end-member composition. Moreover, we also had ancillary datasets on the distribution of OC activation energy, ^{14}C activity, and radiogenic isotopes of $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ in these samples that conclusively demonstrate that $98.3 \pm 1.6\%$ and $1.7 \pm 1.6\%$ of the OC in western Himalayan glaciers are derived from biomass and petrogenic sources, respectively, and there is negligible fossil fuel component. Therefore, based on all organic and inorganic tracers we concluded that there is no fossil fuel signature in CSG. We agree that there will be a lot of chemical heterogeneity in the coal and diesel samples, but, since we did not use them in the mixing model or talked about spatial variability, we can negate the concern.

RC: *Fifth, why aren't you using sequential extraction, rather than analysis of whole rocks only, to look for evidence of trace metal pollution. Cryoconite has a large mineral component from melt out debris and local aerosol. Don't you have a problem of signal to background to contend with? Whole rock digestion will bias your results to a comparison of these minerals to the rock samples you collected from the moraine.*

AR: This is a very good question and we understand the concern. Again, we would like to iterate that measuring $^{187}\text{Os}/^{188}\text{Os}$ on leachates is analytically very challenging. Therefore, we relied on fine fractions ($<63\mu\text{m}$) with the assumption that would contain long-range transported Os particles. Wherever it was possible, we did sequential extraction. For example, on the same set of samples, we have used a sequential extraction procedure (RPO analysis), which involves continuous sample heating, which leads to the release of CO_2 . Each fraction was cryogenically purified, trapped and flame sealed into a glass tube for detailed C-isotope analysis. The CO_2 concentration in the carrier gas was continuously measured at a resolution of 1 second by an infrared gas analyzer. Each RPO fraction collected is graphitized with the radiocarbon abundance determined via Accelerated Mass Spectrometry whereas a 10% split of each RPO fraction was used for stable isotopes ($\delta^{13}\text{C}$) analysis using a dual-inlet Isotope Ratio Mass Spectrometer (IRMS). A detailed description of the sequential extraction procedure can be found in Sarwar et al., (2020). The sequential extraction procedure (RPO technique) also revealed the absence of anthropogenic particles, namely fossil fuel sources. Thus we acknowledge the concern, but, based on all geochemical evidence, we are certain that our reached conclusion is robust.

RC: *Finally, you need to be very clear about why and for what purpose you are using the isotopes you employ. It is unclear from the introduction why do include these data. Where I am is that I am unsure about the conclusions you reach, given the lack of justification of the methodology and sampling you have undertaken.*

AR: We do not agree with the referee's comment since we explicitly mentioned the scope of the osmium isotopes in source identification in environmental studies and why we selected it (Page# 3 lines 1-13 in the original manuscript). Similarly, we have also discussed the significance of different size fractions of local moraine in the methodology section to fix the local crustal and windblown signal (Page# 5 lines 24-26 original manuscript). What perhaps needs to be added in the methodology section is about the selection of coal and engine exhaust samples. We will therefore add a line in section 2.4.2 as "coal and diesel engine exhaust samples were selected to

represent anthropogenic emission source end-member.” As for as referee’s concern about our conclusion, we would like to mention that our outcome is simply based on the absence of anthropogenic signals. Given that there is no or limited anthropogenic emission residues, therefore, the glacier melting behavior will not be likely affected by anthropogenic emission residues as reported in other parts of the Himalaya and globe.

We hope that after these responses, the manuscript we will be allowed to carry out a detailed revision of the manuscript, followed by submission in *The Cryosphere*.

Yours Sincerely,

Sarwar Nizam & Indra Sen
Department of Earth Sciences
Indian Institute of Technology Kanpur
Kanpur, U.P., India

References

Baccolo *et al.* 2017. Cryoconite as a temporary sink for anthropogenic species stored in glaciers. *Sci Rep.*, **7**, 9623.

Lokas *et al.* 2016. Accumulation of atmospheric radionuclides and heavy metals in cryoconite holes on an Arctic glacier. *Chemosphere*, **160**, 162-72.

Owens *et al.* 2019. Extreme levels of fallout radionuclides and other contaminants in glacial sediment (cryoconite) and implications for downstream aquatic ecosystems. *Sci Rep.* **9**, 12531.

Singh *et al.* 2013. Atmospheric deposition studies of heavy metals in Arctic by comparative analysis of lichens and cryoconite. *Environ. Monit. Assess.*, **185**, 1367–1376.

Wientjes *et al.* 2012. Carbonaceous particles reveal that Late Holocene dust causes the dark region in the western ablation zone of the Greenland ice sheet. *J. Glaciol.* **58**(210), 787-794.

Yallop *et al.* 2012. Photophysiology and albedo-changing potential of the ice algal community on the surface of the Greenland ice sheet. *ISME J.* **6**, 2302–2313.