

# Replies to the referees

## Referee #1

**R1:** This study presents high concentrations of radionuclides found in cryoconite collected from two mountain glaciers in European Alps. Cryoconite is organic and inorganic sediment on glacial ice and has been studied chemically and biologically on worldwide glaciers. However, there has been still limited information on radionuclides in cryoconite. The manuscript is well-written and contains interesting analytical results, which were properly discussed in terms of natural and anthropogenic sources of radionuclides. However, I have some concerns on the discussion of the accumulation processes of radionuclides in cryoconite. I would strongly suggest to revise the points indicated below before the publication.

**Reply:** Thank you very much for the comment, we will do our best to update the manuscript considering your comments which we found appropriate and constructive.

**R1:** I would strongly suggest to divide the section of “Results and discussion” into two sections: i.e. “Results” and “Discussion”, which would present the context of this paper more efficiently.

**Reply:** if possible, we would like to maintain the current structure of the paper. We have decided to merge the two parts in order to facilitate the reading to people which is not expert in the field of radioecology. In its current structure, the paper is directly divided into “logical” sections, where data are directly discussed in relation to the glaciological context and to the many comparison that we have presented. We believe that dividing results from conclusions could make more difficult to appreciate the unique radiological features of cryoconite, in particular for people not expert in the field of radioecology.

**R1:** Use carefully the terms of “cryoconite” and “cryoconite granules”. “Cryoconite” means bulk sediment on glacier ice, but “cryoconite granules” mean spherical aggregations of the sediment. This difference is particularly important when authors discuss the resident time of substances or elements in cryoconite. In many cases in the text, cryoconite should be replace to the cryoconite granules, please check it throughout the text.

**Reply:** we agree with the reviewer, we have modified the text and in particular the section entitles “The age of cryoconite and its relationship with ice surface processes”, where we have tried to better highlight the differences between cryoconite and cryoconite granules in relation to the age issue, adding some passages about this point.

**R1:** High concentrations of  $^{210}\text{Pb}$  in the cryoconite is interesting. Authors concluded that it is a result from interaction between ice, meltwater, and cryoconite. However, this could be discussed more carefully with previous works. For example, there has been a quantitative study of accumulation of  $^{210}\text{Pb}$  in snow and ice on an alpine glacier in Europe (Gäggeler et al., 1983). The age of ice at the sampling sites in this study seems to be important to explain the high  $^{210}\text{Pb}$  concentrations. If available, it would be worth to show the exact locations of samples on the glaciers and age of ice (or estimation based on the glacial ice movement). In terms of role of organic matter or biological activity for  $^{210}\text{Pb}$  in cryoconite, there have been many studies on the process of  $^{210}\text{Pb}$  (or  $^{210}\text{Po}$ ) in organics in marine or other environments (e.g. Kim et al., 2012; Fowler et al., 2011) and also on accumulations of heavy metals in snow algal cells (Fjerdingsstad, 1973), which would help to understand why the  $^{210}\text{Pb}$  was concentrated in cryoconite. Nagatsuka et al. (2010) showed the variations in stable isotopes of Pb in different organic and mineral fractions in cryoconite, which may also be worth to discuss the accumulation process of Pb in cryoconite.

**Reply:** we thank the reviewer for having suggested the mentioned paper that we didn't know. The paper is a pioneering study about the application of  $^{210}\text{Pb}$  as a dating tool for ice core samples at a high altitude Alpine glacier. Now  $^{210}\text{Pb}$  is routinely applied by the ice core community. Assuming a constant depositional rate,  $^{210}\text{Pb}$  is more abundant in surficial (and relatively young) snow and ice, while in the deeper layers of the glaciers (which are normally older) it is less abundant because of the radioactive decay. But this is true when dealing with undisturbed and high elevation cold glaciers only, where no melt occurs and where the ice stratigraphy is preserved and not altered by excessive horizontal ice motion. When we consider temperate glaciers subjected to massive melt, this is no longer true, because  $^{210}\text{Pb}$  is mobilized by meltwater and the stratigraphic signal is destroyed. This is discussed by Gaggeler et al. (1983) themselves and by some of the cited references (Shotterer et al., 1977, Ambach et al., 1971). Considering the terminal part of the Morteratsch and Forni glaciers we need to highlight two points: 1) at both glaciers the terminal part is subjected to strong melt during summer and in fact the glaciers are experiencing a strong retreat. No net accumulation is possible there and thus the stratigraphic signal of  $^{210}\text{Pb}$  into the ice is completely destroyed by the mass loss and by meltwater percolation. 2) the regions of the glaciers where we have sampled cryoconite are located downstream of two steep icefalls. Such glaciological contexts are known for the effects on ice stratigraphy which is completely disarranged (Goodsell et al., 2002). For these two reasons we believe that the age of the ice where we sampled cryoconite doesn't have a relevant role in determining the amount of  $^{210}\text{Pb}$  found in cryoconite. We don't have the possibility to estimate the age of the ice at the sampling points, but we also believe that such information could be hardly obtained, considering that the ice stratigraphy is somewhat disturbed in those regions.

We have now included the suggested references about the role of organic matter and biological activity in the accumulation of radionuclides and about the ability of supraglacial debris in accumulating heavy metals and Pb stable isotopes.

**R1:** The accumulation process of elements in cryoconite should not rely on their radioactivity, but on the chemical or biological properties of each element regardless of radioactive or stable elements. Some statements in the text are misleading. For example, authors say that "cryoconite accumulates radioactivity" in L92, but cryoconite does not accumulate radioactivity, but may chemically accumulate the elements including radionuclides. Same in many places (e.g. L435-446). Please present it correctly.

**Reply:** we agree with the reviewer. We have modified several passages in the text where we have stated that "cryoconite accumulates radioactivity". In most cases we now have changed to "accumulate radionuclides". In addition, we have added a passage to better communicate that cryoconite doesn't accumulate radioactivity because it is affine for it, but because it presents a biogeochemical affinity for some species that are, by the way, radioactive:

*"The extreme ability of cryoconite is likely related to the presence of organic matter and extracellular polymeric substances which are affine for heavy metals, including the radioactive ones (Chuang et al., 2015; Gadd 1996; Fowler et al., 2010; Kim et al., 2011). An additional support for the importance of organic matter in this process is also given by previous studies showing that the organic fraction of cryoconite and snow algae accumulates heavy metals associated to anthropogenic atmospheric emissions, such as stable Pb (Fjordingstad, 1973, Nagatsuka et al., 2010)."*

**R1:** In conclusion, authors mentioned that cryoconite is a potentially hazardous material, however, I would think that this is an excessive statement and out of the context of this manuscript. There was only one sample that exceeded 10000 Bq kg<sup>-1</sup> in this study. Also, the limitation of legislations on the radioactivity in environmental materials should be shown and their potential risk for human health should be quantitatively discussed if authors want to use this statement. I would suggest to state the conclusion more objectively.

**Reply:** a comment from the second referee is very similar to this. We have thus decided to remove this passage from the Conclusions.

**R1:** Title: I would not be sure that cryoconite can be an efficient monitor of radioactive fallout. Use of “monitor” here is very vague. Based on the conclusion, we might detect artificial radioactive elements in cryoconite, but it seems to be difficult to know the time and amounts of their fallout. There might be more proper title for the manuscript.

**Reply:** we agree with the reviewer. The new proposed title is “*Cryoconite: an efficient accumulator of radioactive fallout in glacial environments*”

**R1:** L27 It would be worth to state the specific interaction between cryoconite and the environments.

**Reply:** we have added a sentence in the abstract to better present what we mean: “*We hypothesize that the impurities originally preserved into ice and mobilized with meltwater during summer, including radionuclides, are accumulated in cryoconite because of their affinity for organic matter, which is abundant in cryoconite.*”

**R1:** L28 Again, what is “an ideal monitor”? Need specific explanation.

**Reply:** we have now changed to “*matrix*”

**R1:** L47 Insert “on the ice surface” after “a dispersed material”.

**Reply:** done.

**R1:** L53 Insert “granules” after “cryoconite”.

**Reply:** done.

**R1:** L63 Insert the year of Meese et al.

**Reply:** done.

**R1:** L82-85 Nagatsuka et al. (2010) could also be worth to be cited here.

**Reply:** we have added the reference.

**R1:** L92 Please state properly that cryoconite doesn’t accumulates radioactivity, but accumulates radioactive elements.

**Reply:** we have changed accordingly.

**R1:** L103-116 It would be worth to add more information of the two glaciers in this study, for example, the reason why the authors selected these two glaciers for this study and difference of mass balance, glacial flow velocity or estimated age of ice at the sampling sites between the glaciers.

**Reply:** As partially explained in a previous reply, we don’t have the possibility to estimate the age of the ice where we have sampled cryoconite. The two glaciers present similar features: they are both experiencing a strong retreat as a consequence of a notably negative mass balance. We have selected them because of their size, we

know from our experience that cryoconite is more abundant in larger glaciers than in small ones. In addition, it should be mentioned that both the glaciers are relatively easy to access and are thus suited for multiple expeditions during summer, so as to construct multi-year records in the next years. We have included some passages to take into account these points.

**R1:** L127-128 Please show exact locations of the 12 samples for Morteratsch and 10 for Forni Glaciers on the map of Fig.2, and add their coordinates and altitudes in the Table S1. This is important to discuss the resident time of cryoconite on the glaciers. Also, please show the total amounts (dry weight) of cryoconite used in this study.

**Reply:** unfortunately we don't have the exact information about sample position and elevation. The regions of the glaciers where we sampled cryoconite are extremely dynamic. They are at same time experiencing a strong retreat (tens of meters per year) and subjected to ice horizontal flow (10-20 m per year, an accurate description of the Morteratsch glacier can be found in Rossini et al. (2018), for the Forni glacier we have available the information from the yearly monitoring activity carried out by the regional glaciological service). Considering the continuous evolution of the glacier surface in the sampling area we believe that knowing the exact position of the samples (which continuously changes) is not of primary importance, for this reason we have decided to highlight the region of the glaciers where we sampled cryoconite and not their exact location. We have decided not to add a table with the punctual details about samples, but we have added some passages in the section dedicated to site description, where we specify the altitude at which we have collected the samples and their mass.

**R1:** L168 "Pearson's correlation coefficient" instead of "Peason correlation"

**Reply:** adjusted.

**R1:** L179-184 This part, which presents mostly previous works, should not be in Results, but be moved to Introduction or discussion section.

**Reply:** we have now removed the passage which is already present in the introduction.

**R1:** L214 Suggest to start a new paragraph here.

**Reply:** done.

**R1:** It is very good to compare the results with those of other environmental samples. But, it would be better to compare with only studies in Europe in order to show whether cryconite accumulates the elements or not. Because the radionuclide activities can vary with geographical locations, i.e. the distance from the source.

**Reply:** we have considered worldwide data because our intention is to show a global comparison. It is true that for specific nuclear accidents (for example the Chornobyl one) the distance from the source is important. But this is not the case for other sources, such as the stratospheric fallout related to atmospheric nuclear tests. In this case the fallout is not coming from a specific source, but from a diffused source, making impossible to estimate a distance between the sampling site and radioactive source. The primary aim of our comparison is to show that cryoconite, regardless the geographic position, is the most efficient radioactivity accumulator. For this reason, we would prefer to maintain the comparison as it is. In addition, we note that if we considered only European data, we would have few data available and the comparison would be less significant.

**R1:** L254-255 Please clarify that this statement is from previous works (need references) or from this study.

**Reply:** we have modified this passage including references and more information about its novelty

**R1:** L274-278 The difference of the two glaciers is interesting and can be discussed in more detail here or later.

**Reply:** A discussion about the differences observed at the two glaciers in relation to the different organic matter content of cryoconite is now presented in section 4.5:

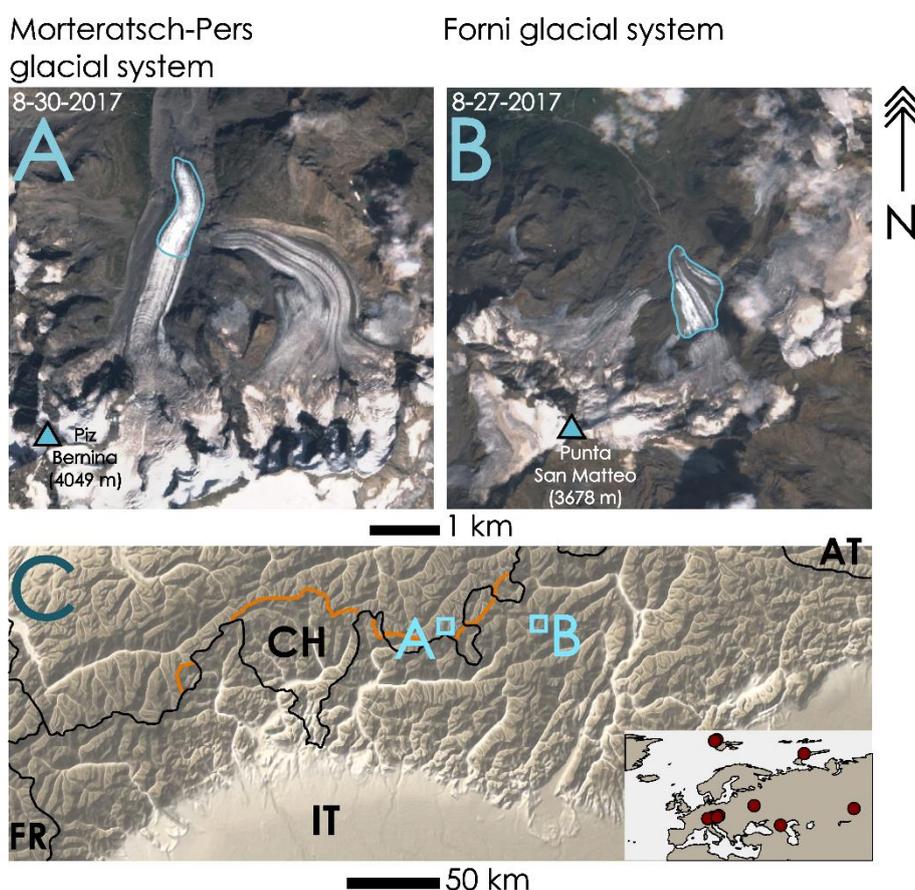
*“Another factor that should be considered to explain the stronger contamination of cryoconite from the Morteratsch glacier, is the higher concentration of carbonaceous compounds in cryoconite from this glacier, for which radionuclides are particularly affine (Chuang et al., 2015; Gadd 1996; Fowler et al., 2010; Kim et al., 2011).”*

**R1:** L304-305 Specify the time difference between “historic” and “contemporary”. It would be worth to mention the age of ice at the sampling site if available.

**Reply:** unfortunately we don't know the age of ice at the sampling sites. To avoid any misunderstanding, we have replaced the term “historic” with past.

**R1:** L324-347 and Fig.5 It would be worth to show a map showing the geographical locations of the Caucasus, Svalbard, Chernobyl, Semipalatinsk, and the glaciers of this study.

**Reply:** we have updated Fig. 1 including a large scale map where the locations cited in the present work are shown.



**R1:** L360-374 Organic carbon contents in cryoconite seems to be significantly different between the two glaciers. Please explain why.

**Reply:** we can make a hypothesis to explain the difference. Cryoconite sampled at the Morteratsch glacier has been obtained from an elevation between 2100 and 2300 m a.s.l., Forni cryoconite has been obtained from a higher elevation, between 2600 and 2800. The significant elevation difference could be an important factor to explain the difference in terms of organic carbon content. A higher elevation implies lower temperatures, a shorter summer season and thus a less pronounced biochemical activity. We have added a passage to present this hypothesis:

*“Cryoconite from the Morteratsch glacier presents a higher concentration of both organic and elemental carbon than the one from the Forni glacier (Student’s t test for organic carbon concentration:  $0.0010 < p\text{-value} < 0.0025$ ; degree of freedom = 9; t-score = 3.80; for elemental carbon concentration:  $0.01 < p\text{-value} < 0.05$ ; degree of freedom = 7; t-score = 3.11). We hypothesize that elevation has a role in explaining this difference. Cryoconite from the Morteratsch glacier have been sampled at an elevation between 2100 and 2300 m a.s.l., while samples from the Forni glacier have been collected between 2600 and 2800 m a.s.l. A higher elevation implies lower temperatures, a shorter summer season and thus a less pronounced biochemical activity, which is in accordance with the lower organic carbon content observed in cryoconite at the Forni glacier.”*

**R1:** L383-400 It is interesting that the radionuclides differ between the two glaciers. Authors discussed it with only the difference of altitude of the glaciers, but it needs to be discussed more carefully. What is the geology of the bedrock of the two glaciers? There is a significant difference of carbon contents in cryoconite, which could also affect the accumulation of radionuclides? Please discuss also the difference of age of ice of the glaciers.

**Reply:** we agree that the discussion here can be deepened here. We don’t think that geology has an important role, despite the two sites actually present different lithologies (regolith for the Morteratsch and schists for the Forni, but the elemental composition is not so different, we have unpublished data about this). Considering the previous comment, we can assume that elevation has two effects on cryoconite radioactivity. The first one is already discussed in the text, the second one is indirect and involves the different concentration of carbonaceous compounds. Cryoconite from the Morteratsch glacier have been sampled at lower altitude than Forni and for this reason it is more abundant in organic matter (see previous comment). Given the affinity for organic matter of many radionuclides this could be an important factor to explain the higher contamination observed at Forni for many nuclides. We have added a passage to take into account this second hypothesis:

*“Another factor that should be considered to explain the stronger contamination of cryoconite from the Morteratsch glacier, is the higher concentration of carbonaceous compounds in cryoconite from this glacier, for which radionuclides are particularly affine (Chuang et al., 2015; Gadd 1996; Fowler et al., 2010; Kim et al., 2011).”*

**R1:** L410 Clarify whether this text means “cryoconite” or “cryoconite granules”.

**Reply:** in the considered work the dating method is used to estimate the age of cryoconite, not of cryoconite granules. In the section dedicated to the links between cryoconite, its age and the glacial environment, we have now tried to clarify the differences between cryoconite, cryoconite granules and the respective age in relation to aggregation and dissolution processes involving cryoconite.

**R1:** L420 Again, insert “granules” after cryoconite, and check it throughout this paragraph.

**Reply:** we would like to maintain cryoconite here. We believe that the accumulation of radionuclides is something that involves cryoconite regardless its aggregation state. In the present paragraphs we have made several changes to better highlight the differences between cryoconite, cryoconite granules and age.

**R1:** L434 What is “absorption”? Explain and clarify it.

**Reply:** we agree that this is not the best term. We have thus decided to change it with “continuous accumulation”.

**R1:** L447-449 It is likely, but please explain more carefully how the organics incorporate the elements, by microbial metabolism, or by just chemical combination? Also, discuss it with the difference of organic matter contents between the two glaciers.

**Reply:** we cannot go too much in detail here because we don't have direct observations about the binding mechanism between radionuclides, organic matter and/or microbes. We have reviewed the literature about this topic which mostly focuses on the marine environment. It seems that radionuclides are preferentially bound to organic colloid and polymeric extracellular macromolecules rather than being incorporated into microbial cells (Gadd 1996; Yang et al., 2013; Chuang et al., 2015). We have already added a section where we discuss the differences observed at the two glaciers in relation to the different content of organic matter in cryoconite. We have now changed the passage as follows:

*“The extreme ability of cryoconite is likely related to the presence of organic matter and extracellular polymeric substances which are affine for heavy metals, including the radioactive ones (Chuang et al., 2015; Gadd 1996; Fowler et al., 2010; Kim et al., 2011).*

**R1:** L456 “older” is very vague. What this “old” exactly means? Does it mean the time from deposition on the glacier, or from the formation of cryoconite granules?

**Reply:** cryoconite formation is a complicated process which involves biotic and abiotic mechanisms that are only partially understood. When we talk about “old” cryoconite, without referring to granules, we mean cryoconite that formed on the glacier long time ago, regardless of its aggregation state. Cryoconite is composed by local material (englacial debris, local sediments from the moraines), by remote material (aeolian dust) and by allochthonous matter (organic matter formed at the glacier surface). Cryoconite formation is definitely a complex process that is not yet fully understood. Within this context it is important to distinguish between cryoconite and cryoconite granules, as the reviewers has correctly highlighted. A cryoconite granule can be of recent formation, but the cryoconite matter can be significantly older. In the present section when we talk about cryoconite age, we refer to the time passed since its original formation as a consequence of the processes cited above, regardless of its aggregation state. We have made many changes to this section and we hope that these points are now sufficiently clear.

**R1:** L481 Again, “makes cryoconite a “sponge” for radioactivity” is misleading expression. It is not a sponge for radioactivity, but might be a sponge for the elements including the radionuclides.

**Reply:** we have now changed: *“There is evidence to suggest that the fundamental process which makes cryoconite a “sponge” for specific impurities, including radionuclides, is the interaction between ice and cryoconite itself, through the mediation of meltwater.”*

## Referee #2

**R2:** General comments. This paper is an interesting summary of an emerging research area, that of cryoconite as a record of fallout radionuclides and a potential concentrator of impurities. I cannot comment on the nuclide analysis methods, but they seem sound and reference other publications, so I have confidence in the research team to conduct these analyses appropriately. The paper is generally well written and presents some interesting results. I particularly liked the dating hypothesis discussion, and was gratified that the authors acknowledge that this is an area that needs more work, rather than trying to sew up everything in this one paper. I found the carbon discussion a little distracting and would recommend removing this section since it didn't really contribute to the main story.

**Reply:** Thank you very much for the positive comment. Regarding the section dedicated to carbonaceous matter, we would prefer to maintain it. We agree with the reviewer that in the first draft the section have sounded a little bit disconnected from the other sections of the manuscript. Reviewer 1 has asked for a deeper discussion about the relationships between cryoconite radioactivity and organic matter, also in relation to the differences observed between the two glaciers. We have expanded these sections and for this reason we would like to maintain it.

**R2:** The figures were sometimes a little confusing, with too much colour and too much information presented simultaneously. I make some suggestions for improvement below, but would certainly recommend testing for colour-blind readers as a minimum, and improving/simplifying the labelling and shortening the captions.

**Reply:** we have modified many of the figures, enhancing the color contrast, using markers in place of colors and trying to simplify them.

**R2:** I would also suggest that the abstract is rewritten to better reflect the key findings of the paper (which I understand as): that cryoconite is an important concentrator of FRNs; that FRNs in different Alpine Glaciers are similar to each other; that Alpine glaciers are similar to other glaciers but show important differences with respect to proximity to some sources; and that FRNs could be a way of dating cryoconite, since they accumulate over time (in contrast to previous suggestions). As written now, I didn't think it represented the key findings of the paper. The distinction between local and global sources is also confusing, since most cryoconite research considers 'local' to be within catchment (when defining, for example, debris sources or microbial seeding grounds). Instead, perhaps be specific that Chernobyl impacted the Alpine Glaciers but not so much the Svalbard one. The processes description in the abstract is particularly weak and I didn't think very relevant. Use the words for your dating hypothesis instead.

**Reply:** We have modified the abstract considering the suggestions from the reviewer. Here the new version:

*“Cryoconite is rich in natural and artificial radioactivity, but a discussion about its ability to accumulate radionuclides is lacking. A characterization of cryoconite from two Alpine glaciers is here presented. Results confirm that cryoconite is significantly more radioactive than the matrices usually adopted for the environmental monitoring of radioactivity, as lichens and mosses, with activity concentrations exceeding 10,000 Bq kg<sup>-1</sup> for single radionuclides. This makes cryoconite an ideal matrix to investigate the deposition and occurrence of radioactive species in glacial environments. In addition, cryoconite can be used to track environmental radioactivity sources. We have exploited atomic and activity ratios of artificial radionuclides to identify the sources of the anthropogenic radioactivity accumulated in our samples. The signature of cryoconite from different Alpine glaciers is similar and compatible with the stratospheric global fallout and Chernobyl accident products. Differences are found when considering other geographic contexts. A comparison with data from literature shows that Alpine cryoconite is strongly influenced by the Chernobyl fallout, while cryoconite from other regions is more impacted by events such as nuclear test explosions and satellite re-entries. To explain the*

*accumulation of radionuclides in cryoconite, the glacial environment as a whole must be considered, and particularly the interaction between ice, meltwater, cryoconite and atmospheric deposition. We hypothesize that the impurities originally preserved into ice and mobilized with meltwater during summer, including radionuclides, are accumulated in cryoconite because of their affinity for organic matter, which is abundant in cryoconite. In relation to these processes, we have explored the possibility to exploit radioactivity to date cryoconite.”*

**R2:** L20: ‘extremely rich’ is too subjective

**Reply:** we have now removed “extremely”.

**R2:** L23: ‘among the most radioactive environmental matrices’ is rather vague – can you be specific?

**Reply:** we have now changed to “...cryoconite is significantly more radioactive than the matrices usually adopted for the environmental monitoring of radioactivity, as lichens and mosses...”

**R2:** L27: can you elaborate here? What specific aspects of their interaction?

**Reply:** we have now added the following passage: “We hypothesize that the impurities originally preserved into ice and mobilized with meltwater during summer, including radionuclides, are accumulated in cryoconite because of their affinity for organic matter, which is abundant in cryoconite, and in particular for extra-cellular polymeric substances.”

**R2:** P2 L33: ‘the latter of these’ instead ‘of which’

**Reply:** we have replaced with “cryoconite”.

**R2:** Suggest combining the first two paragraphs, they are very short.

**Reply:** we agree with the reviewer, done.

**R2:** L45: ‘incoherent’ is awkward, suggest replacing with ‘unconsolidated’

**Reply:** changed accordingly.

**R2:** L46: I would dispute that cryoconite requires abundant meltwater to form - it is found on ice surfaces in Antarctica with extremely limited quantities of meltwater

**Reply:** we agree, we have now removed “abundant”

**R2:** L50: please include a reference on the role of cyanobacteria

**Reply:** we have now included Langford et al., 2010.

**R2:** L53: I think this is specific to cryoconite granules – cryoconite may be present without forming granules (eg. Antarctica). I would suggest adding ‘granules’ to the end of this sentence.

**Reply:** done.

**R2:** L59: could you include some example references or a review paper here?

**Reply:** not to increase too much the number of references, we have added a quote to suited papers that had already been cited in the paper.

**R2:** Figure 1: please indicate the scale on A and B, or state the approx. hole diameter in the text

**Reply:** we have now included the scale in the two panels.

**R2:** P4 L104: could you include some example references or a review paper here?

**Reply:** not to increase too much the number of references, we have added a quote to suited papers that had already been cited in the paper.

**R2:** L106: can you tell us when it detached, rather than ‘few years’?

**Reply:** of course, it was 2015.

**R2:** L114: tell us why this is favourable for the formation of cryoconite (simply put: because there is more source material)

**Reply:** we have added the passage.

**R2:** L118: define ‘clean’ – how were they cleaned? Deionised water? Ethanol? Between samples? In what vessels were the samples stored, and how were they treated?

**Reply:** we have added the details. We used sterile disposable pipettes, sterile plastic tubes and spoons cleaned with ethanol between samples.

**R2:** L128: How were the sampling sites chosen, and how widespread were they?

**Reply:** they were extremely common, on average the distance between two adjacent deposits or holes was of few meters. We have chosen the ones where cryoconite was more abundant, we have now added this detail to the text: *“We selected the most abundant cryoconite deposits, so as to have material available for other analyses also: twelve samples have been gathered on the Morteratsch Glacier (between 2100 and 2300 m a.s.l.) and ten on the Forni Glacier (between 2600 and 2800 m a.s.l.), each one consisting in 10-40 g of wet cryoconite.”*

**R2:** L131: this is the assumption of all papers. Instead of saying that the material are not published, I would suggest rephrasing to say that accompanying gamma spectroscopy data can be found in the 2017 publication.

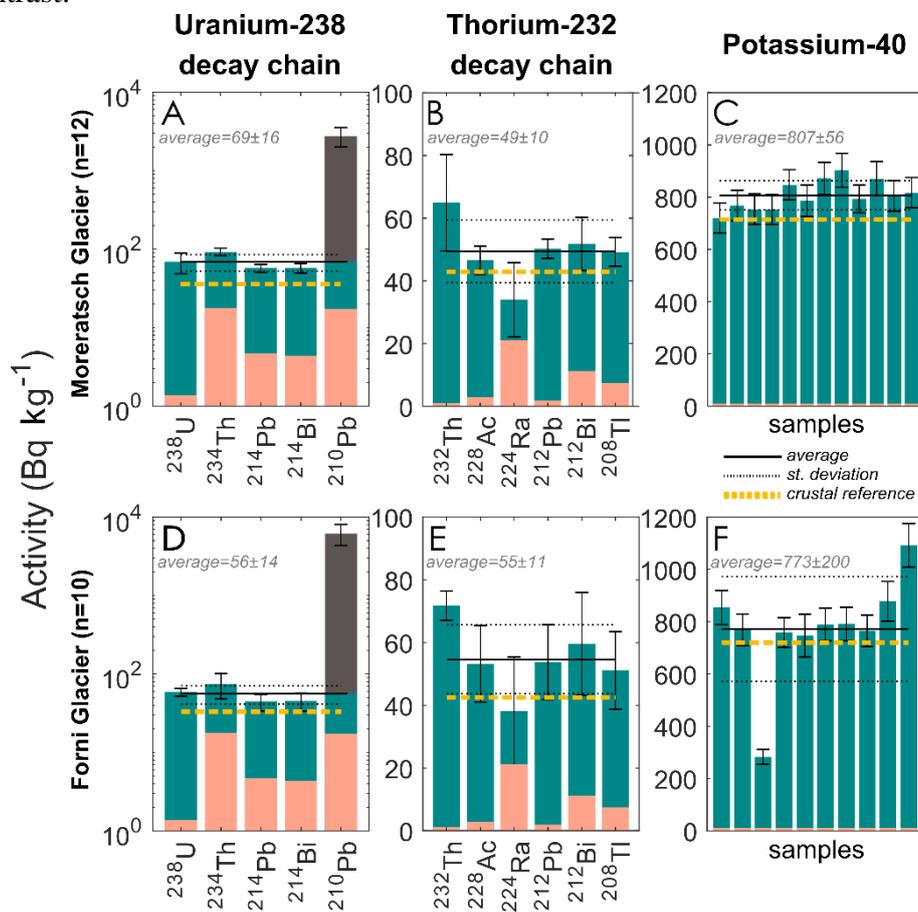
**Reply:** we agree, we have rephrased accordingly: *“Part of the data concerning gamma spectrometry applied to cryoconite from the Morteratsch samples has already been published (Baccolo et al., 2017).”*

**R2:** L172: Is the equation and description of Pearson Correlation necessary? I think the reference is sufficient, but leave this at the author’s discretion.

**Reply:** we have shortened the passage where we described the link between r and d, however we would to prefer to maintain the equation since MDS is not usually applied to correlation but to distance.

**R2:** Figure 3: Can the lines be labelled on the plot rather than in the very long caption? For example, the yellow (continental crust), black (average (mean?!)) and dashed (st dev) could be labelled instead, reducing the overlong caption. I would also check the colours for use by colour-blind readers – perhaps patterns could be used instead?

Reply: thanks for the suggestion, we have modified the couple figure-caption as it follows, adding a legend and enhancing color contrast:



**Fig. 3** Activity of the radionuclides belonging to the decay chains of  $^{238}\text{U}$  and  $^{232}\text{Th}$  and of  $^{40}\text{K}$ . The upper row (panels A-C) refers to the cryoconite samples from the Morteratsch glacier, the lower ones (panels D-F) to the samples collected on the Forni glacier. Red bars represent detection limits, green bars measured activities. The activity of  $^{210}\text{Pb}$  is divided into supported (green bar) and unsupported fractions (grey bar), considering the upper  $^{238}\text{U}$  decay chain as reference for the supported fraction. Crustal references are inferred from Rudnick & Gao (2003).

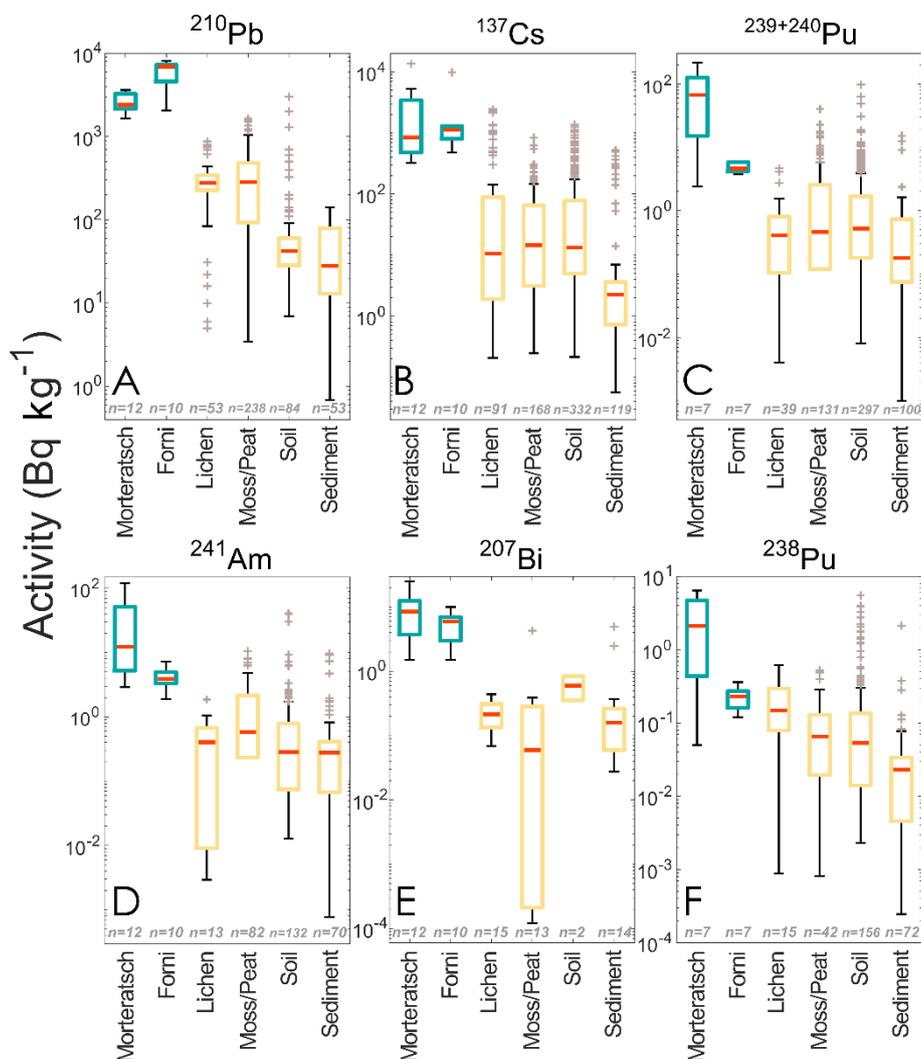
**R2:** L190: I don't understand why the difference between K40 and the UCC is not significant, but the difference between U and Th is significant, considering the scales on the activity plots. This is because this is beyond my subject area, but may be the case for other readers, so I suggest clearer explanation on the differing scales and assignation of significant differences.

**Reply:** potassium is one of the most abundant elements in Earth crust and is also the largest responsible for Earth crust radioactivity. It is a common element found in heaps of different minerals. On the contrary both Th and U are orders of magnitude less abundant and are considered trace elements. In addition, they share peculiar chemical properties, with large ionic radii and high ionic charges. Such features make the two elements incompatible with many common minerals and enhance their fractionation in rare and ancillary minerals which are found in specific lithologic contexts. For this reason, it is not surprising that dealing with K we have found concentrations similar to the Earth crust, while this is not the case for Th and U which are enriched in our samples. In Baccolo et al., 2017 we have discussed the fractionation of some elements in cryoconite. We found that elements usually associated to heavy minerals (as Th and U) are enriched in cryoconite because meltwater flow preferentially removes light minerals and enriches the heavy ones. We have added a passage to explain this point:

“These values, as seen in Fig. 3, are slightly higher than the average  $^{238}\text{U}$  and  $^{232}\text{Th}$  radioactivity of upper continental crust (UCC) reference (Rudnick and Gao, 2003), which is 34 and 43  $\text{Bq kg}^{-1}$  for  $^{238}\text{U}$  and  $^{232}\text{Th}$  respectively. The difference is probably related to the accumulation in cryoconite of heavy minerals, where both U and Th are typically enriched, because of hydraulic sorting related to meltwater flow (Baccolo et al. 2017).”

R2: Figure 4: Nice clear plot, although check the colours again.

Reply: thanks, we increased the color contrast between cryoconite and not-cryoconite samples, now the graph is:



R2: L246: This is really interesting!

Reply: thank you!

R2: L260: Include a reference

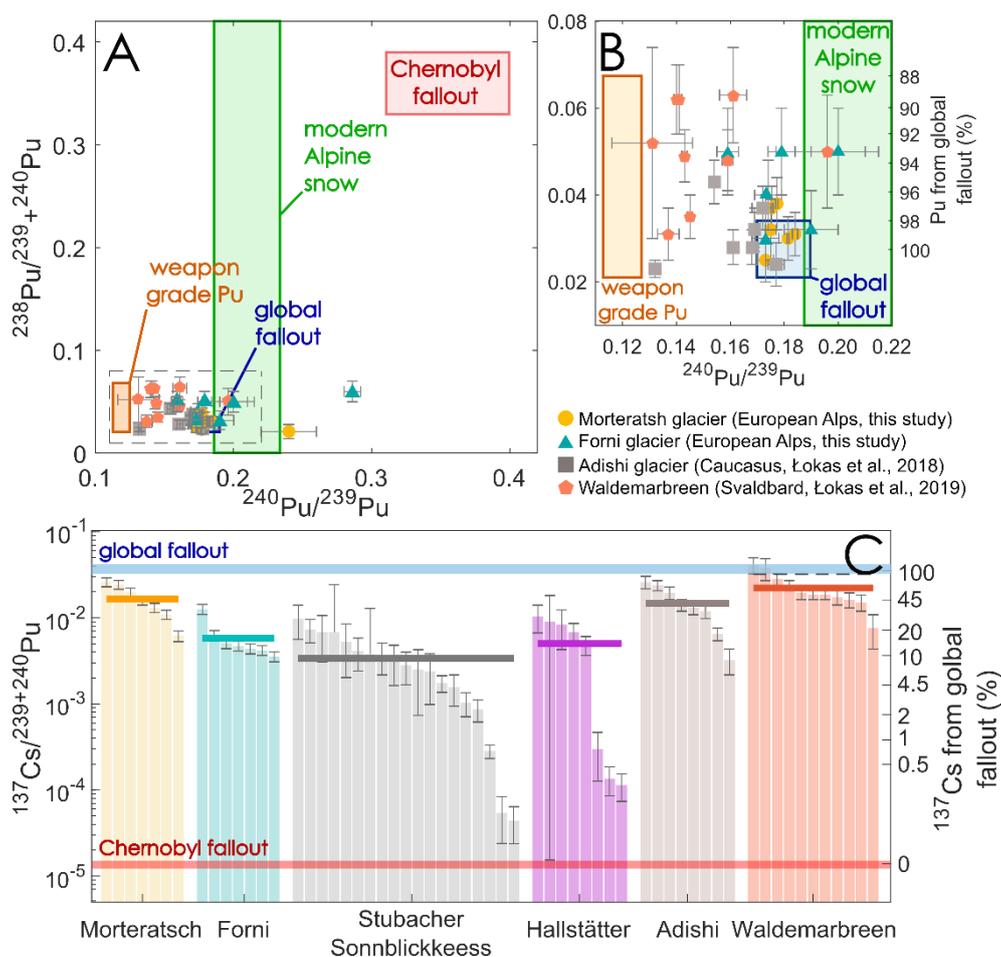
Reply: we have now added two references, Bossew et al., 2006 and Shabana & Al-Shammari, 2001.

R2: L362: Include a ref on plutonium deposition in snow here

Reply: we couldn't find the right position, maybe there's a typo with the line number.

**R2:** Figure 5 is quite baffling. I like the labelled sections, but it's unclear whether the labels refer to a whole box or a specific point. The percentage lines on the lower plot are also quite confusing – would this be better presented in a table?

**Reply:** thank you for the comment, we have exaggerated with colors.... We have better highlighted the boxes, removing the colored bands which could be somewhat confusing. In addition, we changed sample markers to help distinguishing them regardless their color. In the lower graph we have removed the labels about the percentage for each glacier, but we have decided to keep the lines corresponding to average values calculated for each glacier. We agree with the reviewer, to increase readability we have now included a table presenting the average fractions of Pu and  $^{137}\text{Cs}$  related to global fallout at the different glaciers. This is the new version of the figure:



**R2:** L360-366: include more details on this in the methods section

**Reply:** we have moved the technical details in the methods section. A full technical description of this procedure can be found in the cited literature, for this reason we have decided not to add further information here.

**R2:** Section 4.4: is this relevant to the overall story of the paper? There are many studies exploring carbon and black carbon content of cryoconite, particularly in Greenland, and I wonder if these data would be more relevant in another comparative study.

**Reply:** we have decided to maintain the section. The first reviewer suggested to better discuss the relationships existing between radionuclides and organic matter content, in particular to explain the differences observed at the two glaciers (cryoconite from Morteratsch is richer in cryoconite than Forni).

**R2:** L387: typographical error

**Reply:** corrected.

**R2:** Figure 7 is slightly confusing, could only the most important be labelled in C?

**Reply:** we agree, there are a lot of labels, but we don't know how to select only some of them. The only reasonable way would be to remove all the labels, but without labels the figure would be completely unreadable.

**R2:** L406: yes, this would be really cool! You could refer to the work of Tranter, Fountain or Bagshaw on using chloride to date hydrological age of cryoconite in Antarctica as an example if you wanted to include a comparison.

**Reply:** thanks for the advice. We have deepened the discussion about the influence of supra-glacial dynamics on the age of cryoconite. We have added the suggestion references few lines below the point suggested by the reviewer. The new extended passages now read:

*“The distribution of cryoconite on glaciers is extremely dynamic and is influenced by meteorological processes, local ice morphology, and supraglacial melting and runoff. It has been observed that within only a few days, single cryoconite holes can form, deepen and collapse, scattering cryoconite granules downstream on the glacier (Takeuchi et al., 2018). In addition, it is known that cryoconite is far from being a static sediment: cryoconite granules are in fact subjected to uninterrupted changes, such as aggregation and break-up, and their lifetime on glaciers don't exceed a few years (Takeuchi et al., 2010). In Antarctica, where cryoconite holes are usually covered by a permanent ice lid and supra-glacial hydrology is poor, the isolation age (i.e. the time period during which a single cryoconite hole have remained isolated from glacial hydrology) of single cryoconite holes has been estimated through a biogeochemical method: it never exceeds a few years (Fountain et al., 2004; Bagshaw et al., 2007). The transience of surficial glacial environments is also confirmed by glacier moss balls, whose lifespan was observed not to exceed few years (Hotelling et al., 2019). Given these evidences, we find it unlikely that a fraction of the cryoconite sampled on the surface of a small and steep glacier as the Stubacher Sonnblickkees, could form at the end of the 19<sup>th</sup> century and persist there since then without being subjected to significant compositional changes.”*

**R2:** L 431-445: This hypothesis seems sound and defensible, except the supposition that cryoconite only forms when meltwater is available (L445). I would rephrase this.

**Reply:** we have removed that passage

**R2:** L466: give examples of the legislations, or remove this sentence (it's not particularly relevant)

**Reply:** we have removed the passage

**R2:** L484: I think that rather than 'absorbs', 'binds' would be a better description, since you seem to show that the EPS sticking the granules together binds up the impurities as well

**Reply:** we agree, we have now modified with “*binds and accumulates*”

**R2:** Final sentence is not strictly relevant and a bit literary.

**Reply:** we have removed the passage

**R2:** Data availability are not shown. This must be corrected.

**Reply:** we have now included the availability statement: *“Full data are available as supplementary material.”*

# Cryoconite: ~~as an efficient monitor-accumulator for the deposition of~~ radioactive fallout in glacial environments

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**Abstract.** Cryoconite is ~~extremely~~ rich in natural and artificial ~~radionuclides~~radioactivity, but a ~~comprehensive~~ discussion about its ability to accumulate radionuclidesactivity is lacking. A characterization of cryoconite from two Alpine glaciers is ~~here~~ presented ~~and discussed~~. Results confirm that cryoconite is ~~among the most~~significantly more radioactive ~~than the environmental~~ matrices ~~usually adopted for the environmental monitoring of radioactivity, such as lichens and mosses, with-~~with a activity concentrations exceeding 10,000 Bq kg<sup>-1</sup> for single radionuclides. ~~This makes cryoconite an ideal matrix to investigate the deposition and occurrence of radioactive species in glacial environments. In addition, cryoconite can be used to track environmental radioactivity sources. We have exploited A~~atomic and activity ratios of ~~artificial radionuclidesPu and Cs radioae~~ to identify the sources of the anthropogenic radioactivity accumulated in our samples. The signature of cryoconite from different Alpine glaciers is compatible with ~~tive isotopes reveal that the artificial radioactivity of Alpine cryoconite is mostly related to the stratospheric global fallout from nuclear weapon tests and to the 1986-Chernobyl accident products~~. Differences are found when considering other geographic contexts. A comparison with data from literature shows that Alpine cryoconite is strongly influenced by the Chernobyl fallout, while cryoconite from other regions is more impacted by events such as nuclear test explosions and satellite re-entries. To explain ~~The signature of cryoconite radioactivity is thus influenced by both local and more widespread events. T~~the extreme accumulation of radionuclidesactivity in cryoconite, ~~can be explained only considering~~ the glacial environment as a whole ~~must be considered~~, and particularly the interaction between ice, meltwater, cryoconite and atmospheric deposition. ~~We hypothesize that the impurities originally preserved into~~

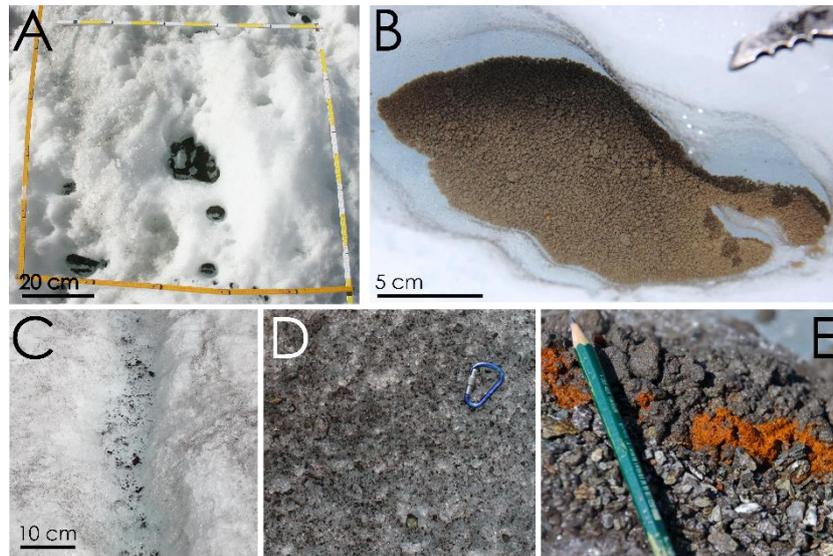
~~ice and mobilized with meltwater during summer, including radionuclides, are accumulated in cryoconite because of their affinity for organic matter, which is abundant in cryoconite. In relation to these processes, we have explored the possibility to exploit radioactivity to date cryoconite. Cryoconite is an ideal monitor to investigate the deposition and occurrence of natural and artificial radioactive species in glacial environment.~~

## 40 **1 Introduction**

Radioecological research is primarily focused on Earth surface ~~environments~~, where continuous atmospheric deposition of fallout radionuclides (FRN), both natural and artificial, are accumulated. The most common FRNs are cosmogenic nuclides, <sup>222</sup>Rn progeny and artificial products. The ~~latter-last ones~~ of which have been released into the environment since the second half of the twentieth century, as a consequence of nuclear test explosions and accidents. Hundreds of thousands of PBq were  
45 spread in the high troposphere and stratosphere from the 1940s to the 1960s, allowing for global dispersion and contamination at the Earth surface. The extent and impact of FRN deposition on the Earth surface is monitored through the analysis of different environmental matrices, which are used to reconstruct FRN deposition (Steinhauser et al., 2013) and understand their environmental mobility and distribution (Avery et al., 1996; Yasunari et al., 2011).

Among the matrices used in the study of FRNs, those that receive the greatest attention share common features: their  
50 composition is directly influenced by airborne deposited impurities; the contribution from environmental compartments other than atmosphere is limited; they are widespread, accessible and preferably easy to sample. Given these attributes, lichens, mosses and peat are commonly used to study the distribution of FRNs and establish depositional inventories (Nifontova, 1995; Kirchner and Daillant, 2002).

In recent years cryoconite began drawing attention in the field of radioactive ~~environmental~~-monitoring as an alternative  
55 environmental matrix. Cryoconite is the dark, ~~incoherent-unconsolidated~~ sediment that is found on the surface of glaciers worldwide (Takeuchi et al., 2001). It forms exclusively at the ice-atmosphere interface and in presence of ~~abundant~~ meltwater. It can be found as a dispersed material on the ice surface or as a deposit accumulated on the bottom of characteristic water-filled holes melted into ice, usually aggregated into granules (cryoconite holes, see **Fig. 1**). Cryoconite forms out of the interaction between the mineral particles present on the ice surface (both allochthonous and autochthonous),  
60 and the complex microbial communities that develop on the surface of glaciers (Cook et al., 2015). Among the microbes that are present on glaciers, cyanobacteria play a major structural role (Langford et al., 2010). During the ablation season, when liquid water is available at the surface of glaciers, cyanobacteria develop films and filaments that promote the formation of aggregates composed of mineral sediments and organic matter, resulting in cryoconite granules (Takeuchi et al., 2001). The composition of cryoconite is dominated by a mineral component accounting for 85-95 % of its mass, whereas the remnant  
65 fraction is comprised of both living and dead organic matter and is responsible for its dark colour (Cook et al., 2015). The formation of cryoconite holes is attributable to the dark colour, and thus low albedo, of cryoconite, which enhances the



**Fig. 1 Cryoconite from the Morteratsch (A) and Forni (B) glaciers. Panel C: the beginning of the melt season at the Morteratsch glacier. The ice surface has been exposed to the atmosphere after snow melting, and cryoconite is preferentially accumulating within the early meltwater channels. Panel D: the end of the melt season at the Morteratsch glacier. The ice surface has experienced months of melting and is now largely covered by cryoconite. Panel E: this cryoconite deposit (at the Morteratsch glacier) was located few meters downstream from a melting snow patch rich in Saharan dust. Cryoconite aggregates acted as a filter, retaining and accumulating dust particles.**

absorption of ~~incoming~~ solar radiation and locally increases ice melting to foster the development of holes in the ice surface. Due to its contribution to ice ~~surface~~ melting, its diverse composition, and the role in biodiversity, cryoconite has been studied by a range of disciplines, including glaciology, microbiology, biogeochemistry and ecology ([Takeuchi et al., 2001](#); [Langford et al., 2010](#); [Cook et al., 2015](#); [Ferrario et al., 2017](#); [Pittino et al., 2018a](#)). More recently cryoconite has been the subject of renewed interest due to its ability to accumulate specific substances, including anthropogenic contaminants ([Pittino et al., 2018b](#)).

To the best of our knowledge, the first evidence of the accumulation of radionuclides in cryoconite was reported in 1996 by Tomadin et al. who found high levels of anthropogenic radioactivity in cryoconite samples from the European Alps. [In 1997](#)~~The following year~~ Meese et al. analysed cryoconite formed on the surface of multi-year Arctic sea ice, measuring high radioactivity values. [Similar observations were successively reported by Cota and co-authors \(2006\) who founded unexpectedly high radioactivity burdens \(related to  \$^{137}\text{Cs}\$ ,  \$^{210}\text{Pb}\$  and  \$^7\text{Be}\$ \) in cryoconite from the surface of multi-year sea ice in the Canadian Arctic.](#) Since the~~nse early findings~~, no other studies (to our knowledge) have focused on the radioactivity of cryoconite until the presentation of an extensive characterization of samples from an Austrian glacier in 2009 (Tieber et al., 2009). That study has showed that cryoconite is contaminated not only by  $^{137}\text{Cs}$ , a common artificial radionuclide spread into the environment, but also by several other species, ~~both~~ artificial and natural in origin. The reported activity levels in this study are extremely high, ~~in some cases exceeding  $10,000 \text{ Bq kg}^{-1}$ , and~~ comparable to soil samples from nuclear incident and explosion sites ([Abella et al., 2019](#); [Steinhauser et al., 2014](#); [Abella et al., 2019](#)). Subsequent studies, carried out in different

regions of global cryosphere (Alps, Caucasus, Svalbard and Canada), have corroborated the ability of cryoconite to ~~efficiently~~ accumulate radionuclides ~~in the European Alps, the Caucasus, and the Svalbard~~ (Baccolo et al., 2017; Łokas et al., 2016, 2018, Owens et al., 2019), with radioecological consequences concerning the presence of FRNs that ~~are not limited to glaciers, but~~ extend to the pro-glacial areas (Łokas et al., 2017, Owens et al., 2019). In addition to FRNs, 95 cryoconite has also been shown to accumulate other anthropogenic contaminants including heavy metals (Nagatsuka et al., 2010; Łokas et al., 2016; Baccolo et al., 2017; ~~Łokas et al., 2016~~; Singh et al., 2017, Huang et al., 2019), artificial organic compounds (Ferrario et al., 2017; Weiland-Bräuer et al., 2017), and ~~even~~ microplastics (Ambrosini et al., 2019). However, among the species found in cryoconite, radionuclides show by far the highest concentration with respect to other environmental matrices. The considerable activity concentrations of artificial FRNs found in cryoconite, has allowed for the 100 application of cutting-edge radiological techniques, offering important insight to the sources and distribution of radioactivity deposited within the glaciated regions of the Earth (Łokas et al., 2018, 2019), and making novel contributions to the emerging field of environmental nuclear forensics (Steinhauser, 2019).

Even though the link between cryoconite and environmental radioactivity is now indisputable, several important questions remain. Firstly, is not clear why and how cryoconite accumulates ~~radioactivity radionuclides and other anthropogenic~~ 105 ~~impurities~~ and to what extent this accumulation is related to processes specific to glacial environments. Previous studies (Osburn Jr., 1963; Pourcelot et al., 2003) have focused on the role of snowmelt in accumulating radionuclides in residual snow patches during summer, suggesting that nival and melt processes could encourage local accumulation of radioactivity in a similar fashion to what has been observed in cryoconite on glaciers. Secondly, it is not fully understood where this radioactivity comes from ~~and if its signature is local, regional or even more widespread~~.

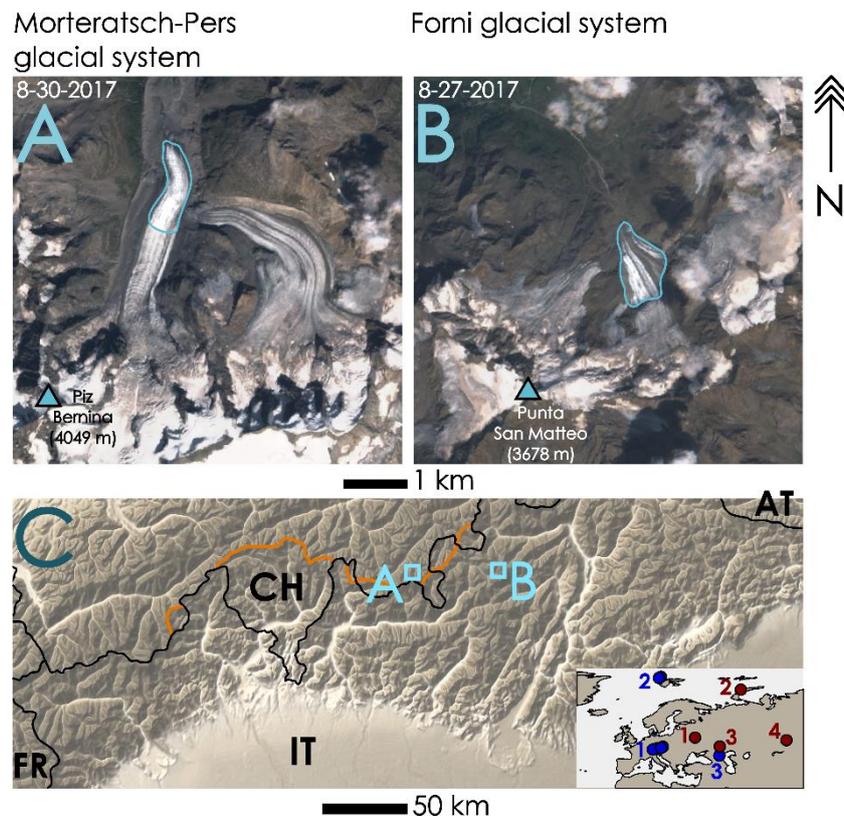
110 This paper aims to present cryoconite as a promising tool for radioecological monitoring in high latitude and high-altitude areas and sheds light on some of the open issues related to the themes explored above. Data concerning cryoconite from two ~~European~~ Alpine glaciers are presented and compared ~~in detail~~ to data from previous studies on both cryoconite and other environmental matrices used for radioactive monitoring.

## 2 Study site and sampling strategy

115 The Morteratsch and Forni Glaciers are located in the European Alps and are situated ~50 km apart (**Fig. 2**). Both glaciers are among the biggest and most studied in the Alps (Azzoni et al., 2017; Di Mauro et al., 2019). The Morteratsch is a Swiss glacier and the largest in the Bernina range, spanning an altitudinal range of roughly 2000 m and with a terminus located at 2100 m a.s.l. It has an area of ~7.5 km<sup>2</sup>, but until ~~few years ago~~ 2015 the value exceeded 15 km<sup>2</sup> due to its connection with a tributary glacier that has since detached. A similar setting characterizes the Forni Glacier, the biggest ~~glacier one of~~ 120 Ortles-Cevedale range in Italy. Forni is a north-facing valley glacier presenting a glacial tongue that was, until recently, fed by three accumulation basins. Owing to retreat of the glacier, the connections between the basins have become weaker and

the glacier is now fragmented in two ~~distinct~~ parts (Azzoni et al., 2017). The Forni glacier ranges between 2500 to 3750 m a.s.l. and is characterized by a surface area of ~10 km<sup>2</sup> considering both ice bodies. From a climatic perspective, the glaciers are similar; they are ~~both~~ characterized by a continental climate and in the last years experienced a darkening of their ablation zones because of the accumulation of impurities on the ~~ice~~ surface and the progressive emergence of detritus from medial and lateral moraines (Di Mauro et al., 2017; Fugazza et al., 2019). ~~The abundance of supra-glacial debris~~ These processes are is favourable for the formation of cryoconite, ~~and in fact these~~ two glaciers are well studied ~~Alps~~ in terms of cryoconite and its components (~~Ambrosini et al., 2019; Baccolo et al., 2017; Di Mauro et al., 2017; Pittino et al., 2018a; Ambrosini et al., 2019; Fugazza et al., 2019; Pittino et al., 2019~~). We have considered these glaciers also because of the relatively easy access, which makes them ideal sites for annual sampling campaigns.

Samples considered here were collected in summer 2015 (July and September) and 2016 (July) from the ablation zones of



**Fig. 2** The geographic setting of the present work. Satellite images (ESA Sentinel-2) of the considered glaciers (A and B). The highest peak point within the two catchments are highlighted; the blue lines define the ablation areas where cryoconite has been collected. Panel C: a wider view of the central sector of the European Alps. The black line represents national borders, while the orange line, when not coincident with the black one, the Northern-Southern Alpine watershed dividing line. In the box a map showing the sites cited in the discussion: Alpine (1), Svalbard (2) and Caucasus (3) glaciers where cryoconite have been studied from the radiological perspective (blue dots); Chernobyl (Ukraine, 1); Novaja Zemlya (Russia, 2), Semipalatinsk (Kazakhstan, 3) and Kapustin Yar (Russia, 4) nuclear testing areas (red dots).

140 ~~both the~~ glaciers (Fig. 2). Each sample represents a distinct cryoconite hole. The sampling was carried out using ~~clean sterile~~  
~~disposable~~ pipettes and ~~ethanol cleaned~~ spoons; samples were kept ~~at 0°C in sterile tubes at 0°C~~ during the field campaign  
and ~~successively~~ stored at -20°C in the EUROCOLD laboratory of the University Milano-Bicocca, until preparation for the  
geochemical analyses. ~~We selected the most abundant cryoconite deposits, so as to have material available for other analyses~~  
~~also: twelve~~ samples have been gathered on the Morteratsch Glacier (~~between 2100 and 2300 m a.s.l.~~) and ten on the Forni  
145 Glacier (~~between 2600 and 2800 m a.s.l.~~), ~~each one consisting in 10-40 g of wet cryoconite~~. Where possible, multiple  
analyses have been carried out on the same samples, but this has not been always possible. Part of the data ~~concerning~~  
~~gamma spectrometry applied to cryoconite from the Morteratsch samples~~ ~~emerging from the fieldwork on the Morteratsch~~  
~~glacier (data concerning gamma spectroscopy)~~ has already been published (Baccolo et al., 2017), ~~however the remaining~~  
~~samples and results are presented here for the first time.~~

## 150 3 Materials and Methods

### 3.1 Radioactivity measurements

The activity of natural and artificial radionuclides in cryoconite, ~~was has been~~ measured using a number of techniques. <sup>137</sup>Cs,  
<sup>241</sup>Am, <sup>207</sup>Bi, <sup>40</sup>K and <sup>238</sup>U and <sup>232</sup>Th decay chain nuclides were analysed through ~~gamma spectrometry~~ ~~seopy~~ about six months after  
sampling, full details are found in the supplementary material. Aliquots dedicated to ~~gamma spectrometry~~ ~~seopy~~ consisted in ~1 g  
155 of dry material (dried until constant weight at 50°C, 2 mm sieved) sealed in polyethylene vials. The acquisition of the  $\gamma$ -  
spectra took place at least two weeks after the sealing, to allow the secular equilibrium between <sup>222</sup>Rn and its progenies to be  
attained. Each sample ~~was have been~~ counted for one week using a customized high purity germanium well detector (Ortec).  
Details about the instrument, calibration and analytical performances are presented elsewhere (Baccolo et al., 2017).  
Aliquots dedicated to Pu analyses (~1 g of dry material) ~~were have been~~ ashed at 600° C to remove organic matter. The ash  
160 ~~was have been~~ dissolved with mineral acids and the resultant liquid samples ~~have undergone~~ ~~went~~ radiochemical separation  
and concentration of Pu. The procedure is extensively described elsewhere by Łokas and colleagues (2016). Activities of  
<sup>239+240</sup>Pu and <sup>238</sup>Pu ~~were have been~~ determined through  $\alpha$ -spectrometry after Pu co-precipitation with NdF<sub>3</sub>, using Canberra  
7401 and Ortec Alpha Duo spectrometers. After further radiochemical purification ~~procedures~~, the <sup>240</sup>Pu/<sup>239</sup>Pu atomic ratio  
was measured through MC-ICP-MS (Thermo Fisher Scientific Neptune spectrometer), in accordance with Łokas et alii  
165 (2018). <sup>238</sup>U and <sup>232</sup>Th activities ~~were have~~ not ~~been~~ directly measured but ~~were have been~~ estimated considering the total  
content of U and Th.

### 3.2 Instrumental neutron activation analysis

The Th and U composition of cryoconite ~~was has been~~ assessed through instrumental neutron activation. Samples ~~were have~~  
~~been~~ irradiated at the LENA laboratory, where a TRIGA Mark II nuclear reactor is available. The irradiation ~~lasted have~~  
170 ~~lasted~~ for six hours under a thermal neutron flux of  $2.4 \pm 0.2 \cdot 10^{12}$  neutron s<sup>-1</sup> cm<sup>-2</sup>. To determine the concentration of Th

and U in the samples, the following nuclear reactions and  $\gamma$ -emissions ~~were~~ have been exploited:  $^{232}\text{Th} (n,\gamma) ^{233}\text{Th} \rightarrow ^{233}\text{Pa}$  (analyzed emissions: 300.3 and 312.2 keV) and  $^{238}\text{U} (n,\gamma) ^{239}\text{U} \rightarrow ^{239}\text{Np}$  (analyzed emissions: 228.2 and 277.6 keV). Irradiated sample ~~was~~ have been counted for six hours a few days after the irradiation, using the same well detector applied for  $\gamma$ -spectrometry. The quantification of concentrations ~~was~~ have been carried out comparing samples and reference materials (Baccolo et al., 2017).

### 3.3 Carbonaceous content

A thermo-optical analyzer (Sunset Lab Inc. analyzer) ~~was~~ have been used for the determination of organic and elemental carbon content (OC and EC respectively), following the protocol adopted in Baccolo et al. (2017). Cryoconite samples ~~were~~ have been suspended on clean quartz fiber filters and analyzed. The mass concentration of OC and EC ~~was~~ have been obtained combining the information relative to filter superficial concentrations and the mass of cryoconite deposited on the latter, determined using an analytical microbalance (precision 1  $\mu\text{g}$ ) which ~~was~~ has been operated inside an air-conditioned room ( $T = 20 \pm 1$  °C; relative humidity =  $50 \pm 5$  %). Mass concentration of OC has been converted into organic matter content (Pribyl, 2010).

### 3.4 Statistics

To evaluate the degree of correlation between variables and samples, two multivariate statistical tools have been applied. Multidimensional scaling (MDS) has been used to appreciate the degree of correlation between the radionuclides (Diaconis et al., 2008). MDS has been applied to a similarity metric derived from the correlation matrix (Pearson's correlation coefficient) of the original data, following **Eq. 1**, where the distance  $d$  between variables  $v_1$  and  $v_2$  is obtained considering their Pearson correlation coefficient ( $r$ ) ~~. In accordance to this metric distance (van Dongen and Enright, 2012), two perfectly correlated (or anticorrelated) variables ( $r = \pm 1$ ) have a null distance, while two uncorrelated variables ( $r = 0$ ) have a maximum distance equal to 1.~~

$$d(v_1, v_2) = \sqrt{1 - r(v_1, v_2)^2}$$

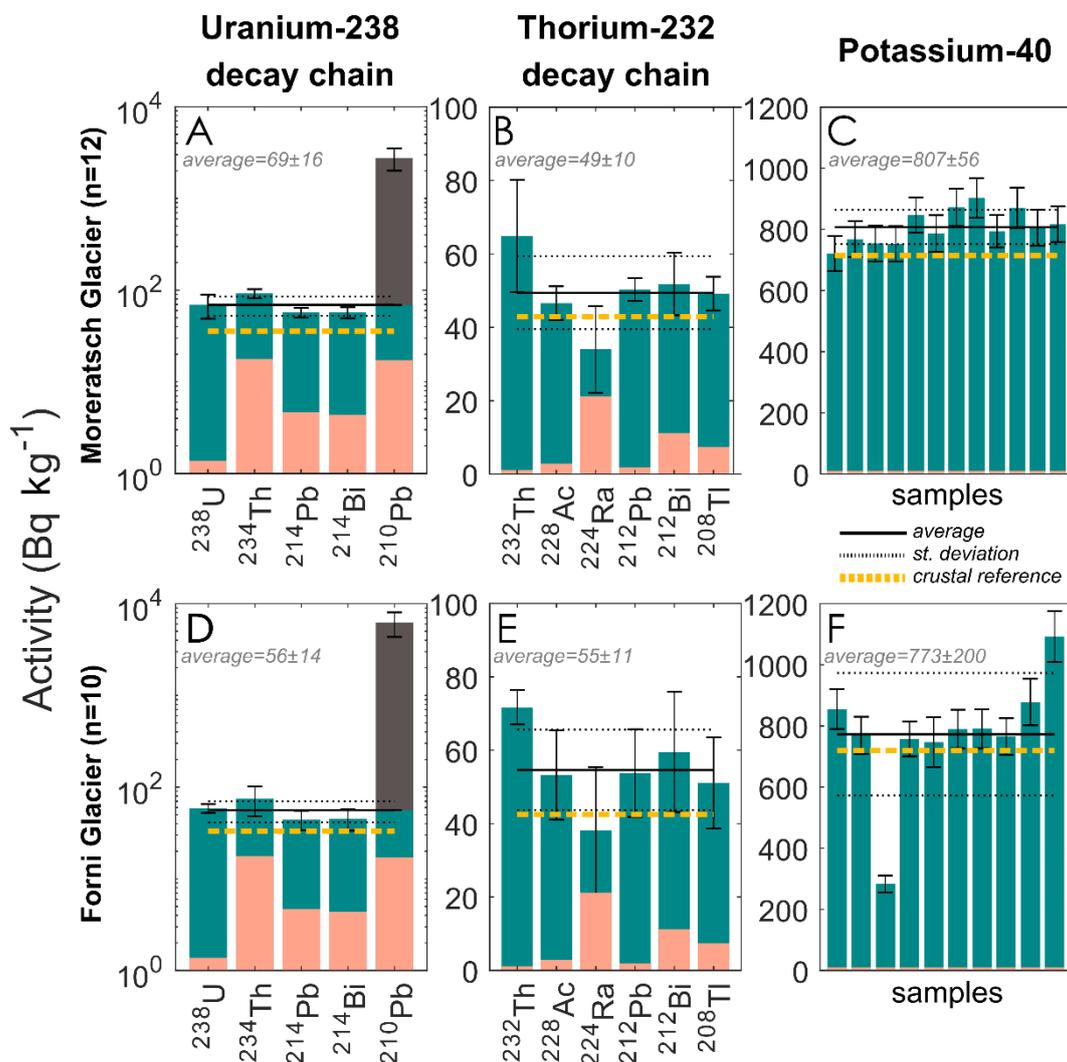
**Eq. 1**

The correlation between samples and the differences between the two glaciers have been evaluated applying the principal component method to standardized data (PCA). The first two components (which explain 65 % of the total variance) have been taken into consideration.

## 4 Results and discussion

### 4.1 Cryoconite natural radioactivity

Our ~~The ability of cryoconite to accumulate radioactivity is now recognized within a number of previous research efforts and multiple locations around the world (Baccolo et al., 2017; Lokas et al., 2016, 2018; Tieber et al., 2009).~~ results further support ~~confirm the ability of cryoconite to accumulate radioactivity and in particular FRNs. In fact only this process of accumulation, with anomalously high activities found for the majority of the analysed radionuclides. The common factor shared by the enriched radionuclides is their primary source. Only~~ FRNs, whose environmental occurrence distribution is related to atmospheric transport, are actually accumulated in cryoconite from the Morteratsch and Forni glaciers, not the lithogenic ones. This ~~feature~~ can be observed in **Fig. 3**, where the activity of lithogenic radionuclides is presented. A substantial secular equilibrium characterizes the nuclide belonging to the  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay chains, except for  $^{210}\text{Pb}$  ( $t_{1/2} = 22.3$  yr), which presents an excess with respect to the other  $^{238}\text{U}$ -related nuclides. Excluding it, the average  $^{238}\text{U}$  and  $^{232}\text{Th}$  chain activities are  $70 \pm 15$  and  $52 \pm 8$  Bq  $\text{kg}^{-1}$  respectively for the  $^{238}\text{U}$  chain (Morteratsch and Forni samples,  $\pm$  standard deviation) and  $50 \pm 10$  and  $55 \pm 10$  Bq  $\text{kg}^{-1}$  for the  $^{232}\text{Th}$  chain. These values, as seen in **Fig. 3**, are slightly comparable higher than ~~to~~ the average  $^{238}\text{U}$  and  $^{232}\text{Th}$  radioactivity of upper continental crust (UCC) reference (Rudnick and Gao, 2003), which is 34 and 43 Bq  $\text{kg}^{-1}$  for  $^{238}\text{U}$  and  $^{232}\text{Th}$  respectively. The difference is probably related to the accumulation in cryoconite of heavy minerals, where U and Th are typically enriched, because of hydraulic sorting related to meltwater flow (Baccolo et al. 2017). ~~An analogous situation concerns the primordial radioactive nuclide  $^{40}\text{K}$  ( $t_{1/2} = 1.28 \cdot 10^9$  yr). Its~~ The activity of the primordial radioactive nuclide  $^{40}\text{K}$  ( $t_{1/2} = 1.28 \cdot 10^9$  yr) in the samples from the Morteratsch and Forni glaciers ( $810 \pm 55$ ,  $770 \pm 200$  Bq  $\text{kg}^{-1}$ ) is of the same order of magnitude of  $^{40}\text{K}$  the-UCC activity, i.e. 720 Bq  $\text{kg}^{-1}$ , ~~calculated from the UCC reference~~ (Rudnick and Gao, 2003). ~~This~~ Such results points to a typical crustal origin for the ~~natural~~-lithogenic radionuclides measured in cryoconite ~~and to the absence of accumulation and/or dilution processes~~. An exception to this is  $^{210}\text{Pb}$ , which, although being a decay product of  $^{238}\text{U}$  progeny, shows activity levels two orders of magnitude higher than the other  $^{238}\text{U}$ - chain nuclides. The average activities in the samples from the Morteratsch and Forni glaciers are  $2,800 \pm 800$  and  $6,200 \pm 1,900$  Bq  $\text{kg}^{-1}$  ~~concentration of K,~~ respectively and are statistically different (Student's t test:  $t_{20} = 5.9$ ; p-value  $< 0.001$ ) (Student's t test: p value  $< 0.01$ ; degree of freedom = 20; t value = 5.9) within the two glaciers. Finding such high  $^{210}\text{Pb}$  activities in samples collected on the surface of ~~collected on the surface of~~ glaciers is not completely unexpected. It is common to observe an excess of  $^{210}\text{Pb}$  in Earth surface environments, due to its dual source. A fraction of  $^{210}\text{Pb}$  is present in materials of geologic origin because of the internal decay of  $^{238}\text{U}$  progeny (supported  $^{210}\text{Pb}$ ); a second fraction (unsupported  $^{210}\text{Pb}$ ) is found in samples exposed to the atmosphere and is attributable to the scavenging by precipitation of atmospheric  $^{210}\text{Pb}$ , produced from the decay of the gaseous  $^{222}\text{Rn}$  released into the atmosphere from rocks and soils. Given its relatively long half-life (22.3 yr), precipitated  $^{210}\text{Pb}$  concentrates in surficial environments, but typically its activity doesn't exceed tens or a few hundreds of Bq  $\text{kg}^{-1}$  in matrices strongly influenced by atmospheric deposition and rich in organic matter, for which Pb is particularly affine (Strawn and Spark, 2000).



**Fig. 3** Activity of the radionuclides belonging to the decay chains of  $^{238}\text{U}$  and  $^{232}\text{Th}$  and of  $^{40}\text{K}$ . Panels A-B-C refer to cryoconite from the Morteratsch glacier, panels D-E-F to cryoconite from the Forni glacier. Red bars represent detection limits, green bars measured activities. The activity of  $^{210}\text{Pb}$  is divided into supported (green bar) and unsupported fraction (grey bar), considering the upper  $^{238}\text{U}$  decay chain as reference for the supported fraction. Crustal references are calculated from Rudnick & Gao (2003).

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235 In **Fig. 4**, cryoconite radioactivity is compared to data concerning other environmental matrices. With respect to lichens and mosses, which are known to be efficient in accumulating radioactive atmospheric species (Kirchner and Daillant, 2002), cryoconite shows a  $^{210}\text{Pb}$  activity that is, on average, higher by one order of magnitude. Two hypotheses are made to explain the excess found in cryoconite: 1) the glaciers considered here are located in areas where the atmospheric deposition of  $^{210}\text{Pb}$  is enhanced; 2) cryoconite is more efficient at concentrating atmospherically derived radionuclides than lichens and mosses.

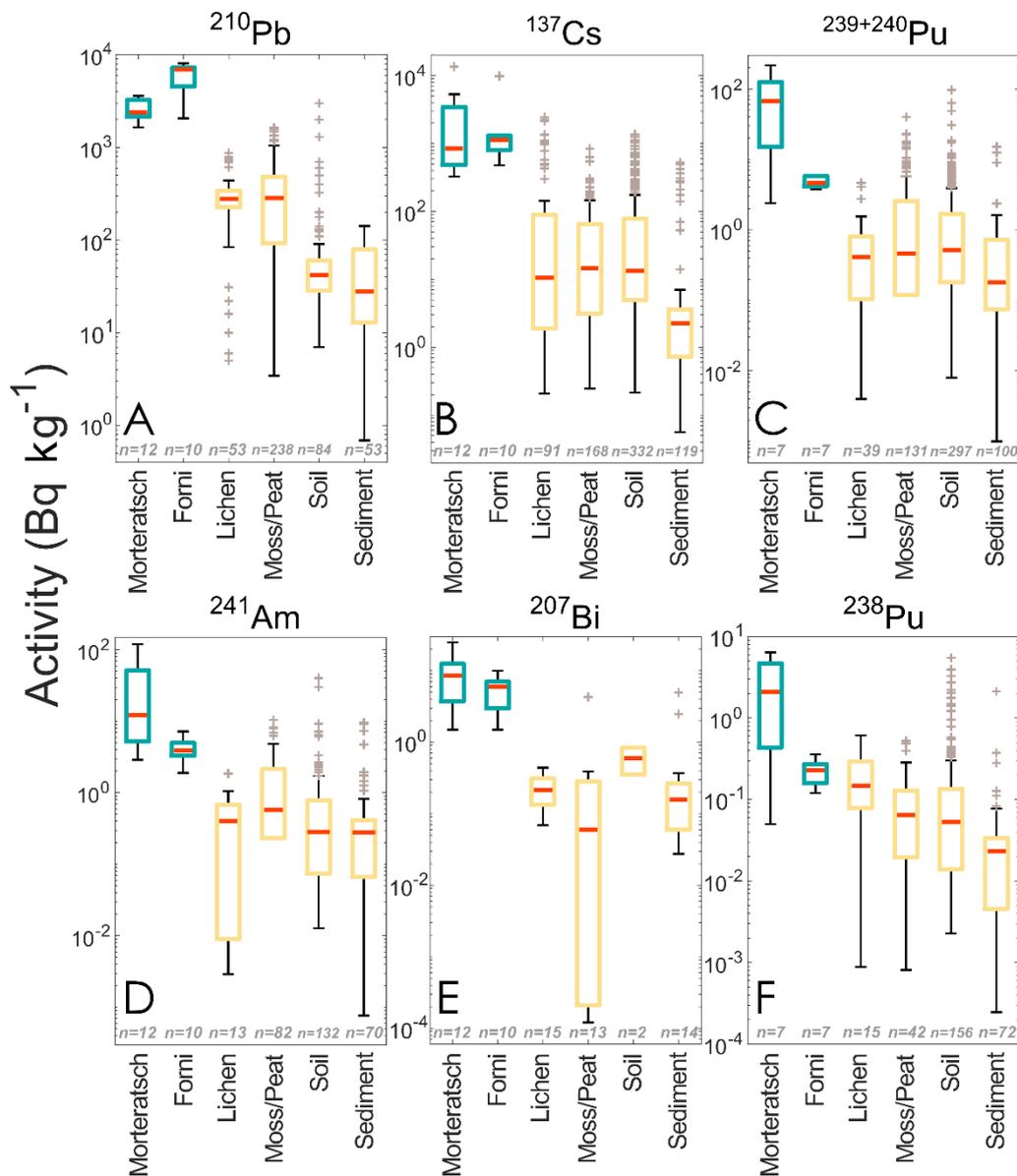
240 At the Morteratsch Glacier a comparison has been made between cryoconite and samples collected from the surface of the moraines surrounding the glacier (Baccolo et al., 2017). The moraine sediments have had a mean activity of  $145 \pm 30 \text{ Bq kg}^{-1}$  for unsupported  $^{210}\text{Pb}$ , while in cryoconite it has exceeded  $2,500 \text{ Bq kg}^{-1}$ . This evidence rejects the first hypothesis: if an

anomaly of atmospheric  $^{210}\text{Pb}$  deposition was present in the Morteratsch valley, it should impact both the ~~surface of the moraines and glacial surfaces~~ ~~surface of the glacier~~. Several studies have reported high unsupported  $^{210}\text{Pb}$  activity in cryoconite from different regions of the Earth (~~Baccolo et al., 2017~~; Łokas et al., 2016, 2018; Tieber et al., 2009; Baccolo et al., 2017), suggesting that high  $^{210}\text{Pb}$  activity is related to specific characteristics of cryoconite ~~and to interactions with processes occurring on the surface of glaciers~~.

#### 4.2 Anthropogenic radioactivity in cryoconite and other environmental matrices

In **Fig. 4**, the comparison between radioactive contamination of worldwide lichens, mosses, soils and sediments from other studies (full information in the supplementary material), is extended to all of the radionuclides that have been found in excess in cryoconite in this study. Out of all of them,  $^{210}\text{Pb}$  is the only natural occurring species while the others are anthropogenic in origin. In descending order of average activity in cryoconite, they are:  $^{137}\text{Cs}$  ( $t_{1/2} = 30.1$  yr),  $^{239+240}\text{Pu}$  ( $t_{1/2} = 24,110$  and  $6,536$  yr respectively),  $^{241}\text{Am}$  ( $t_{1/2} = 432.2$  yr),  $^{207}\text{Bi}$  ( $t_{1/2} = 31.6$  yr),  $^{238}\text{Pu}$  ( $t_{1/2} = 87.7$  yr). These nuclides have been released into the environment as a consequence of nuclear incidents and explosions and have been atmospherically transported and deposited globally. For all radionuclides, the activities measured in cryoconite are always higher than those of other environmental matrices (see **Fig. 4**). To find samples with activities comparable to the ones found in cryoconite, it would be necessary to consider sites within the vicinity of nuclear tests or incidents. The mean ratios between the activity levels found in cryoconite and in lichens for  $^{137}\text{Cs}$ ,  $^{239+240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{207}\text{Bi}$ ,  $^{238}\text{Pu}$  are 9.5, 58, 39, 35, 7 respectively, and the values are even higher when matrices less efficient in accumulating ~~radioactivity-radionuclides~~ are considered. This supports the hypothesis that cryoconite accumulates atmospherically derived artificial radionuclides more efficiently than other matrices, as already suggested by exploring unsupported  $^{210}\text{Pb}$ .

The accumulation ability of cryoconite can be observed not only for common artificial radionuclides, such as  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$ , but also for less abundant species, such as  $^{241}\text{Am}$ ,  $^{207}\text{Bi}$  and  $^{238}\text{Pu}$ .  $^{137}\text{Cs}$  is among the most common long-lived fission products from  $^{235}\text{U}$  and has been released in the environment due to commercial reactor failures and fission bomb test explosions. The plutonium isotopes 239 and 240 also originate from atmospheric weapon tests and nuclear accidents, but the relative contribution from atmospheric tests is larger, since  $^{239}\text{Pu}$  has been the most common fissile material used in fission bombs and for igniting fusion devices. Because of their widespread dispersion,  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  are the most abundant artificial nuclides found in cryoconite from the two glaciers, confirming previous results (Tieber et al., 2009; Łokas et al., 2018,2019). Their mean activities in the samples from Morteratsch and Forni Glaciers are  $2,600 \pm 3,800$  and  $1,900 \pm 2,900$  Bq  $\text{kg}^{-1}$  for  $^{137}\text{Cs}$ ,  $80 \pm 75$  and  $4.9 \pm 0.9$  Bq  $\text{kg}^{-1}$  for  $^{239,240}\text{Pu}$  (average activities and standard deviations for the Morteratsch and Forni cryoconite respectively). Less abundant nuclides are present in cryoconite with lower concentration, including  $^{241}\text{Am}$  ( $30 \pm 35$  and  $4 \pm 1.5$  Bq  $\text{kg}^{-1}$ ),  $^{207}\text{Bi}$  ( $9 \pm 7$  and  $6 \pm 2$  Bq  $\text{kg}^{-1}$ ) and  $^{238}\text{Pu}$  ( $2.5 \pm 2.5$  and  $0.22 \pm 0.08$  Bq  $\text{kg}^{-1}$ ). Despite being low, such activities are still significant and among the highest ever found in the environment ~~with respect to these nuclides~~. Typical environmental activities usually do not exceed 1 Bq  $\text{kg}^{-1}$  for  $^{241}\text{Am}$  and  $^{207}\text{Bi}$ , and 0.1 Bq  $\text{kg}^{-1}$  for  $^{238}\text{Pu}$ .



**Fig. 4** Radionuclides presenting anomalously high activities in cryoconite compared to other environmental matrices. Activity in cryoconite (green boxes) is compared to data from literature concerning the contamination in other matrices sampled in surficial environments (yellow boxes). The number of considered samples is shown in the lower part of each plot. Given the number of publications from which the displayed data were sourced, they have been listed individually in the supplementary material. All activities were corrected for decay at June 2017, with the exception of <sup>210</sup>Pb, which, being continuously produced in the atmosphere, did not require any adjustment.

(Fig. 4), and being their rarity related is due to their production mechanisms (Shabana & Al-Shammari, 2001; Bossew et al., 2006). The presence of <sup>241</sup>Am in the environment is not primarily related to direct deposition (it is present in nuclear power plant spent fuel); it is mostly produced *in situ*, from the decay of its parent nuclide (<sup>241</sup>Pu, t<sub>1/2</sub> = 14.3 yr), which has been

285 released into the environment alongside other Pu isotopes. Thanks to  $^{241}\text{Pu}$  decay, the environmental activity of  $^{241}\text{Am}$   
globally is increasing and will peak around year 2100 (Thakur and Ward, 2018).  $^{238}\text{Pu}$  is one of the rarest plutonium isotopes  
produced by commercial reactors and nuclear explosions, and its diffusion is mostly related to the atmospheric re-entry of  
satellites powered by pure  $^{238}\text{Pu}$  thermoelectric generators (Łokas et al., 2019) and to a smaller degree by the release from  
nuclear fuel reprocessing plants into marine environment (Bryan et al., 2008).  $^{207}\text{Bi}$  has been released as a consequence of a  
290 few high yield thermonuclear explosion tests (Noshkin et al., 2001) and has rarely been observed within the environment.  
Finding easily detectable activities in cryoconite for these rare radionuclides, many of which were released decades ago, is  
both surprising and unprecedented. Studies focused on them usually require the application of pre-concentration and  
separation procedures, but for cryoconite a direct measure of activity was sufficient. These results highlight the potential of  
this environmental matrix for radioecological monitoring.

295 Looking in detail at the two Alpine glaciers considered here, only the activity of Pu isotopes is significantly different  
between the two sites, with higher values found in the samples from the Morteratsch Glacier (Student's t test:  $t_{12} = 2.99$ ; p-  
value = 0.010 for both  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$ ).  $^{241}\text{Am}$  is also more abundant in Morteratsch cryoconite, but not significantly  
because of the large standard deviation (Student's t test:  $t_{20} = 2.24$ ; p-value = 0.018). The ratios between the mean activity of  
the Morteratsch and Forni samples are 15.9, 11.6 and 6.8 for  $^{239+240}\text{Pu}$ ,  $^{238}\text{Pu}$  and  $^{241}\text{Am}$  respectively.

### 300 **4.3 Sources of anthropogenic radioactivity in cryoconite**

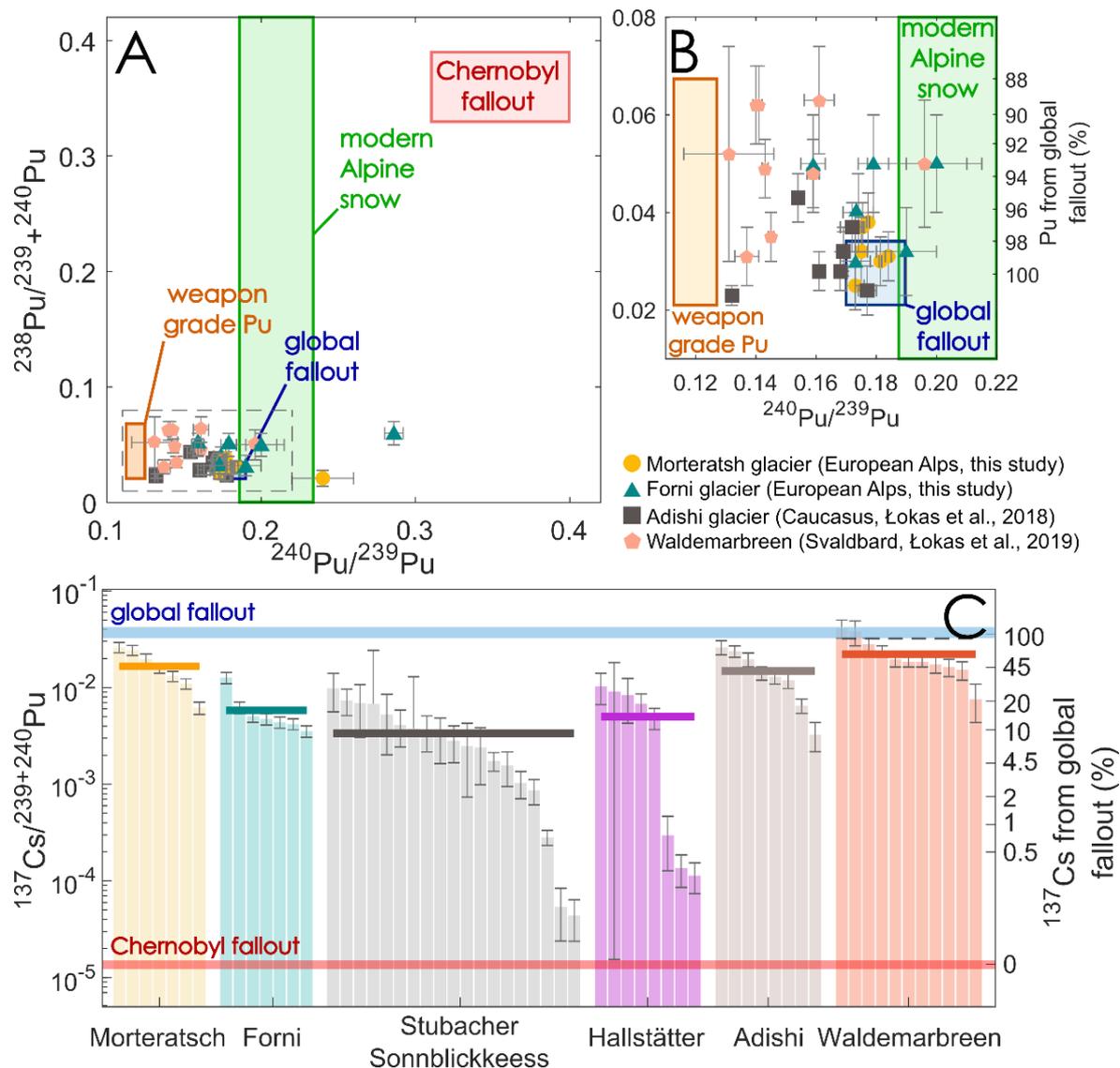
To infer the potential sources of the radioactivity found in cryoconite from Alpine glaciers, isotopic and activity ratios  
between Pu and Cs isotopes have been calculated (**Fig. 5**). The use of such ratios has been used to estimate the provenance of  
environmental radioactivity, since specific signatures are associated to different sources (Steinhauser, 2019). The atomic  
ratio  $^{240}\text{Pu}/^{239}\text{Pu}$  and activity ratio  $^{238}\text{Pu}/^{239+240}\text{Pu}$  show that the plutonium-related radioactivity of Morteratsch and Forni  
305 cryoconite is compatible with the worldwide signal from global radioactive fallout (**Tab. 1** and **Fig. 5a,b**). The latter reflects  
the composition of the stratospheric reservoir, established in the '60s as a consequence of atmospheric nuclear weapon  
testing. On average, more than 99 % of the Pu found in cryoconite from the Morteratsch glacier is from global fallout, while  
for the Forni glacier the average contribution is 95 %, suggesting a non-negligible influence from the Chernobyl accident (~5  
%).

310 By comparing the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of global fallout and of modern snow deposited in the Alps (Gückel et al., 2017), it is  
possible to further discuss the Pu sources in cryoconite. Modern Alpine snow has a slightly higher ratio than global fallout  
(0.21 vs. 0.18), probably because of the partial influence of re-suspended Chernobyl radioactive fallout, which is more  
enriched in  $^{240}\text{Pu}$  than global fallout (Ketterer and Szechenyi, 2008). Only two cryoconite samples (one from Forni and one  
from Morteratsch) show a Pu isotopic composition pointing to the Chernobyl influence. They show a ratio of  $0.286 \pm 0.006$   
315 and  $0.24 \pm 0.02$  respectively, which is even higher than the that of modern Alpine snow. The occurrence of only two samples

Glacier (sample nr.)	Geographical Location	Pu from global fallout (%)	<sup>137</sup> Cs from global fallout (%)
Morteralsch (7) <i>this study</i>	Alps	99±2	41±18
Forni (6) <i>this study</i>	Alps	95±3	12±6
Stubacher Sonnblickkees (19) <i>Tieber et al. 2009</i>	Alps	n.a.	5±4
Hallstätter (8) <i>Wilflinger et al. 2017</i>	Alps	n.a.	10±8
Adishi (8) <i>Lokas et al., 2018</i>	Caucasus	99±2	36±19
Wlademarbreen (9) <i>Lokas et al., 2019</i>	Svalbard	93±4	56±25

**Tab. 1 Data about the fraction of Pu and <sup>137</sup>Cs related to global fallout in cryoconite samples from the Morteralsch and Forni glaciers and from other glaciers. To calculate global fractions, reference ratios defined by Ketterer et al. (2008), Cagno et al. (2014), Gückel et al. (2017) and Wilflinger et al. (2018) have been used.**

320 ~~bearing-with~~ a partial Chernobyl signature can be explained by the presence of fallout particles from Chernobyl nuclear fuel in these specimens. The non-volatile constituents of nuclear fuel, such as Pu, were not scattered into the environment homogenously, as in the case of the more volatile <sup>137</sup>Cs, but as micrometric and highly radioactive particles (Sandalls et al., 1993). The presence of even one of such particles in the two samples could be sufficient to explain the anomalies. The other samples present a global signature fully compatible with global fallout and not with modern Alpine snow. This implies that Pu accumulated in Alpine cryoconite dates back to when the deposition of radionuclides was dominated by global stratospheric fallout, approximately from 1960 to 1980 (Hirose et al., 2008). The deposition of plutonium which is still 325 occurring on the Alpine snowpack, is too weak to influence the isotopic fingerprint of cryoconite. Pu activity in fresh snow ranges from 0.4 to 11.5 µBq kg<sup>-1</sup> (Gückel et al., 2017), roughly six orders of magnitude lower than the average activity of cryoconite, which is 41 Bq kg<sup>-1</sup>. This has important implications because it suggests that cryoconite is more influenced by ~~pasta-historie~~ atmospheric fallout rather than the contemporary one, at least when considering Pu. The only source that can 330 provide to cryoconite FRNs from past atmospheric deposition is ice accumulated within the period of maximum deposition



**Fig. 5** The fingerprint of cryoconite radioactivity. Panel A and B: Pu isotopic composition of cryoconite samples (panel B is an enlargement of panel A).  $^{238}\text{Pu}/^{239+240}\text{Pu}$  is expressed as an activity ratio,  $^{240}\text{Pu}$  to  $^{239}\text{Pu}$  as an atomic ratio. Panel C:  $^{137}\text{Cs}$  to  $^{239+240}\text{Pu}$  activity ratio of cryoconite. In addition to the Forni and Morteratsh glacier samples, data from the Austrian Alps (Stubacher Sonnblickkees and Hallstätter glaciers, Tieber et al., 2009; Wilflinger et al., 2018), Svalbard (Waldemarbreen, Łokas et al., 2019) and from the Caucasus (Adishi glacier, Łokas et al., 2018) are included. Reference ratios (blue square for global fallout, red square for Chernobyl fallout, yellow square for weapon grade Pu, green square for modern Alpine snow) are from literature (Ketterer et al., 2008; Cagno et al., 2014; Gückel et al., 2017; Wilflinger et al., 2018). All values are corrected for decay to June 2017. A geographic setting of the data presented here is found in Fig. 2.

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of atmospheric radioactivity, when the latter was dominated by global stratospheric fallout. The presence of  $^{207}\text{Bi}$  in cryoconite also supports this hypothesis. In the northern hemisphere  $^{207}\text{Bi}$  was produced during the explosion of the Tzar thermonuclear device in 1961 in Novaja Zemlya (Aarkrog and Dahlgaard, 1984). A few years after this event the  $^{207}\text{Bi}$

atmospheric contamination decreased until reaching non-detectable levels (Kim et al., 1997). If a considerable amount of  $^{207}\text{Bi}$  is present in cryoconite, it means that the cryoconite has had the possibility to interact with ice deposited shortly after  
345 1961.

Comparing our results with the data obtained for cryoconite collected in the Caucasus and in regions of the Arctic (Łokas et al., 2018, 2019), it is possible to see that there are variations in the radioactive signatures, pointing to secondary regional influences, despite the general features are compatible with global stratospheric fallout (**Fig. 5**). Caucasian and Arctic samples are characterized by a lower  $^{240}\text{Pu}/^{239}\text{Pu}$  atomic ratio than the Alpine samples (**Fig. 5a** and **b**). Such a signature is  
350 compatible with the influence of weapon grade Pu, depleted in  $^{240}\text{Pu}$  (Cagno et al., 2014). It has been argued that samples from the Caucasus were influenced by the debris spread from the Semipalatinsk (Kazakhstan) and Kapustin Yar (Russia) test sites, where hundreds of nuclear explosions have been carried out (Łokas et al., 2018). The effects of high latitude nuclear polygons (Novaya Zemlya) and of the re-entry of  $^{238}\text{Pu}$  powered satellites, explain the non-global fallout contribution observed in the Arctic cryoconite, which is enriched in both  $^{239}\text{Pu}$  and  $^{238}\text{Pu}$  with respect to the Morteratsch and Forni  
355 samples (Łokas et al., 2019). The latter, showing a good agreement with the global fallout reference, rule out the possibility that a fraction of the Pu found in Alpine cryoconite was produced during the Algerian atmospheric nuclear tests carried out by France in 1960s.

By studying the  $^{137}\text{Cs}$  and  $^{239+249}\text{Pu}$  activity ratio (**Tab. 1** and **Fig. 5c**), it is possible to infer the potential sources of  $^{137}\text{Cs}$ , whose activity is by far the highest among the artificial radionuclides found in cryoconite. While global fallout has been  
360 demonstrated as the main source of Pu, the same is not for  $^{137}\text{Cs}$ . On average, the  $^{137}\text{Cs}$  fraction found in the Morteratsch Glacier samples from global fallout is 41 % with respect to total  $^{137}\text{Cs}$ . For the Forni samples the value is lower (12 %). The non-global fraction of  $^{137}\text{Cs}$  found in Alpine cryoconite is attributable to the radioactive contamination released during the Chernobyl event. The Alps, and in particular the Eastern Alps, were among the most heavily impacted areas by Chernobyl fallout, where  $^{137}\text{Cs}$  was ~~one of the main~~ dominant components (Steinhauser et al., 2014). This is confirmed by the  
365 radioactive signature of cryoconite from two Austrian Alpine glaciers (~~in the~~ Eastern Alps) (Tieber et al., 2009; Wilflinger et al., 2018), whose  $^{137}\text{Cs}$  content is dominated by Chernobyl contamination (more than 90 %). Samples from the Caucasus also show a dominant Chernobyl contribution with respect to  $^{137}\text{Cs}$ , while cryoconite from Svalbard is anomalous in being characterized by a primary influence from global fallout (56 %). This is, however, not unexpected since, among the glaciers considered in **Fig. 5**, the Waldemarbreen (Svalbard) is the farthest from Chernobyl.

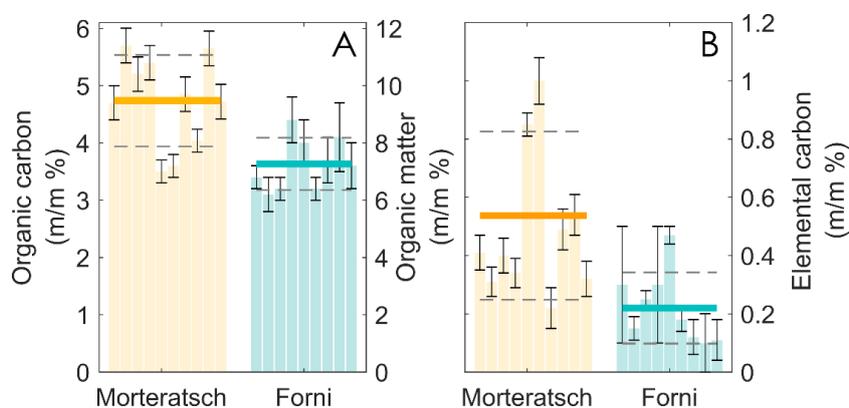
370 While Pu has a dominant global source,  $^{137}\text{Cs}$  is related both to global and Chernobyl-related fallouts. Pu, together with the other actinides, is highly non-volatile and its transport mostly takes place through the dispersion of micrometric particles from nuclear fuel, fission and activation products (Sandalls et al., 1993), while Cs is ~~more~~-volatile and its ~~atmospheric~~ mobilization during nuclear accidents requires relatively low temperatures. The Pu contamination from Chernobyl was limited to few hundreds of km from the emission site and could not be efficiently transported for long distances, while  $^{137}\text{Cs}$

375 transport was widespread, leaving a strong signature all over Europe (Steinhauser et al., 2014), as it is also supported by  
Alpine cryoconite.

#### 4.4 Carbonaceous content

380 Results of carbon analyses are ~~fully~~ presented in Fig. 6. On average ( $\pm$  standard deviation), the carbonaceous composition of  
the Morteratsch Glacier samples is  $9.44.7 \pm 1.40.7$  % m/m ~~in terms of~~ organic ~~carbon-matter~~ and  $0.50 \pm 0.25$ % m/m for  
elemental carbon. Cryoconite from the Forni Glacier contains a lower concentration of both species:  $7.23.6 \pm 0.84$  % for  
organic ~~carbon-matter~~ and  $0.2 \pm 0.2$  % for elemental carbon. ~~Organic carbon content has been converted into organic matter  
content, following the convention by Pribyl (2010). The mean estimated organic matter concentration for the Morteratsch  
Glacier is 9.4 %, while for the Forni it is 7.2 %.~~ Values about organic matter are compatible with the wider literature, where  
385 organic matter in cryoconite has been reported to vary between 2 and 18 % (Cook et al., 2015). Very limited information is  
available about the elemental and/or black carbon composition of cryoconite, despite a great deal of attention having been  
given to the carbonaceous impurities present in snow in relation to the effect on ice/snow darkening (Di Mauro et al., 2017).  
Our results show that elemental carbon is accumulated in cryoconite with respect to Alpine snow, where typical  
concentrations are ~~at least four~~ orders of magnitude lower (Jenk et al., 2006). Only contaminated urban soils present an  
elemental carbon concentration comparable to Alpine cryoconite samples (Lorenz et al., 2006). These findings support the  
390 hypotheses by Hodson (2014), who have suggested that cryoconite plays a role in extending the residence time of black and  
elemental carbon on the surface of glaciers, with implications for the accumulation of hydrophobic contaminants and for ice  
darkening.

Cryoconite from the Morteratsch glacier presents a higher concentration of both organic and elemental carbon than the one  
from the Forni glacier (Student's t test:  $t_{19} = 3.80$ ; p-value < 0.001 for organic carbon concentration - Student's t test  $t_{19} =$



395 Fig. 6 Carbonaceous content of Alpine cryoconite: organic carbon (and ~~to~~ estimated organic matter) is shown in panel A, ~~and~~  
elemental carbon in panel B. Mean values are depicted alongside standard deviations (coloured and dashed lines).

3.10; p-value = 0.003 for elemental carbon). We hypothesize that elevation has a role in explaining the difference. Cryoconite from the Morteratsch glacier have been sampled at an elevation between 2100 and 2300 m a.s.l., while samples from the Forni glacier have been collected between 2600 and 2800 m a.s.l. A higher elevation implies lower temperatures, a shorter summer season and thus a less pronounced biochemical activity, which is in accordance with the lower organic carbon content observed in cryoconite at the Forni glacier.

#### 4.5 Considering radioactivity as a whole

To analyse possible relationships between the different radionuclides, MDS and PCA have been applied on our data. The first tool has been used to represent the degree of similarity and dissimilarity between the radionuclides (Fig. 7a). In the ~~two~~ two-dimensional domain of MDS, the radionuclides are grouped within three clusters which are interpreted as: 1) artificial radionuclides; 2)  $^{238}\text{U}$ -chain nuclides; 3)  $^{232}\text{Th}$ -chain nuclides. Despite  $^{40}\text{K}$  ~~not~~ doesn't belonging to any of these groups, its distance from the  $^{238}\text{U}$ - and  $^{232}\text{Th}$  chain clusters is limited, confirming that K, Th and U in cryoconite are all associated to lithogenic components. The most isolated of the nuclides is unsupported  $^{210}\text{Pb}$ , in accordance to its peculiar biogeochemical cycle.

MDS is able to highlight the different sources of the radionuclides considered in this study: 1) the artificial radionuclides, whose presence on ~~the~~ glaciers is mostly related to stratospheric fallout; 2) the lithogenic radionuclides which are present in the mineral fraction of cryoconite; 3) and  $^{210}\text{Pb}$  which is deposited onto the glacier from the lower troposphere by precipitation. This partitioning is useful for interpreting the differences observed between the two glaciers considered here. At the Morteratsch Glacier the activity of the stratospherically derived radionuclides (Pu, Am, Bi) is higher than on Forni Glacier; for  $^{210}\text{Pb}$  the opposite is true (Fig. 7 and Supplementary Material). This pattern may be related to the altitude of the glaciers. The Morteratsch Glacier basin has a maximum altitude of 4,049 m a.s.l. and an average elevation higher than 3000 m a.s.l., while the Forni basin is delimited by peaks whose maximum altitude spans from 3200 to 3400 m a.s.l. and only occasionally exceed 3500 m a.s.l.. The lower altitude could explain the higher amount of  $^{210}\text{Pb}$  found in cryoconite from the Forni Glacier, since the maximum atmospheric scavenging of  $^{210}\text{Pb}$  occurs in the lower troposphere, below 4,000 m (Guelle et al., 1998). In contrast, the Morteratsch basin, given its high elevation, is more exposed to stratospheric fallout, perhaps explaining why the cryoconite from this glacier is highly contaminated with Pu isotopes,  $^{241}\text{Am}$  and  $^{207}\text{Bi}$ . Another factor that should be considered to explain the stronger contamination of cryoconite from Morteratsch, is the higher concentration of carbonaceous compounds in cryoconite from this glacier, for which radionuclides are particularly affine (Gadd 1996; Fowler et al., 2010; Kim et al., 2011; Chuang et al., 2015).

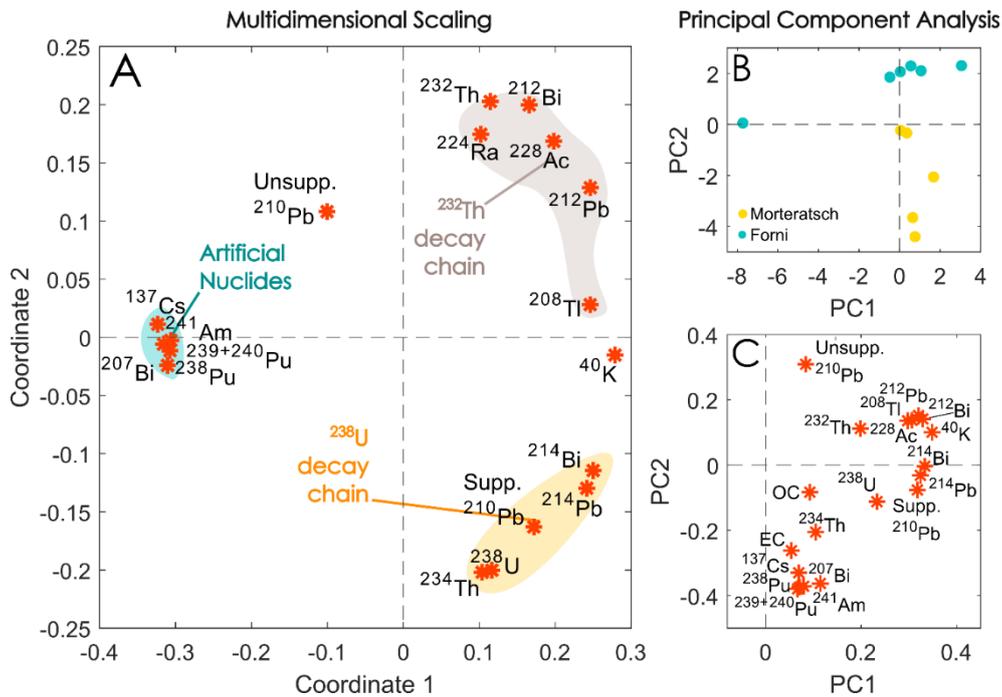


Fig. 7 Multivariate statistical analysis applied to Alpine cryoconite radioactivity data. Panel A: results from multidimensional scaling applied to the correlation matrix related to different nuclides. Panel B and C refer to scores and loadings of the first two principal components respectively, calculated through principal component analysis. OC is organic carbon; EC is elemental carbon.

Results from PCA allow for the distinction of cryoconite sampled from the two glaciers. As seen in **Fig. 7b-c**, the first two components, mostly the second one, separate the Morteratsch and Forni samples. The nuclides diagnostic for the separation in PC2 are the anthropogenic ones, which define the negative scores of Morteratsch samples, and unsupported  $^{210}\text{Pb}$ , which is linked to the positive scores of Forni cryoconite. One sample from the Forni Glacier is an outlier with respect to the others, being characterized by low concentration activity for most of the radionuclides, in particular the artificial ones.

#### 4.6 The age of cryoconite and its relationship with ice surface processes

Natural and artificial FRNs are widely used to constrain chronologies in sedimentary environments. Among the nuclides considered in this work here,  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  are commonly applied for dating, while  $^{207}\text{Bi}$  and  $^{241}\text{Am}$  have been rarely used to mark the period of maximum FRN deposition from atmospheric weapon tests (Appleby, 2008; Kim et al., 1997; Appleby, 2008). Given the high concentration of radionuclides in cryoconite, it would be interesting to assess if they could be used to estimate the age of cryoconite itself. The most important issue that makes any attempt at dating challenging, is the complete absence of a stratigraphic record in cryoconite. In studying cryoconite it is only possible to obtain a set of distinct and uncorrelated samples. Wilflinger and colleagues (2018) used  $^{210}\text{Pb}$  to infer the mixing age (intended as an approximate mean age) of cryoconite samples from an Austrian glacier, the Stubacher Sonnblickkees. To attempt the dating, an assumption was made: once cryoconite is formed, its radioactive content starts decreasing following the decay law, regardless of the

aggregation and dissolution processes that affect cryoconite granules (Takeuchi et al., 2010). Based on this hypothesis, cryoconite is viewed as a sort of pure concentrated airborne material which is ~~extremely~~ rich in atmospheric derived contaminants, as FRNs, and maintains its composition despite the dynamism of the supra-glacial environment. In Wilflinger et al. (2018) ~~A~~ highly radioactive sample of airborne sediments extracted from fresh snow, was interpreted as a sort of time-zero reference (a primordial cryoconite material), however no further details were given about this specimen. Comparing the  $^{210}\text{Pb}$  activity of cryoconite to the reference, the mixing age of the samples ~~was~~ have been thus inferred. According to this conceptual model, older cryoconite presents lower  $^{210}\text{Pb}$  activity in the light of the fact that the more time has passed from its formation, the more profound should be  $^{210}\text{Pb}$  depletion due to the exponential radioactive decay. The estimated ages ranged from a few years to more than a century (Wilflinger et al., 2018). The glacier considered by Wilflinger et al. (2018) is small (less than  $1\text{ km}^2$ ) and is undergoing significant retreat and fragmentation (Kaufmann et al., 2013). The distribution of cryoconite on glaciers is extremely dynamic and is influenced by meteorological processes, local ice morphology, and supraglacial melting and runoff. It has been observed that within only a few days, single cryoconite holes can form, deepen and collapse, scattering cryoconite granules downstream on the glacier (Takeuchi et al., 2018). In addition, it is known that cryoconite is far from being a static sediment: its granules are in fact subjected to uninterrupted changes, such as aggregation and break-up, and their lifetime on glaciers don't exceed a few years (Takeuchi et al., 2010). In Antarctica, where cryoconite holes are usually covered by a permanent ice lid and supra-glacial hydrology is poor, the isolation age (i.e. the time period during which a single cryoconite hole have remained isolated from glacial hydrology) of single cryoconite holes has been estimated through a biogeochemical method: it never exceeds a few years (Fountain et al., 2004; Bagshaw et al., 2007). The transience of surficial glacial environments is ~~also~~ furtherly confirmed by glacier moss balls (conglomerations of mineral debris, moss and organic matter forming on the surface of glaciers), whose lifespan was observed not to exceed few years (Hotaling et al., 2019). Given these evidences ~~We, we thus~~ find it unlikely that a fraction of ~~the~~ cryoconite sampled on the surface of a small and steep glacier as the Stubacher Sonnblickkees, could form at the end of the 19<sup>th</sup> century and persist there since then without being subjected to significant compositional changes.

470 We present an alternative hypothesis to link the content of FRNs in cryoconite and its formation age. Our conceptual model arises from an assumption opposite to that of Wilflinger and coauthors (2018): cryoconite is not a static material, its composition changes with time because of the processes taking place on the surface of glaciers. In light of this, the radioactive content of cryoconite is not only subjected to decay, but also to a build-up derived from ~~absorption~~ continuous accumulation. Consequently, the older the cryoconite is, the higher is its  $^{210}\text{Pb}$  content, because it has had a longer time within which to accumulate the radionuclide, which is continuously deposited on the glacier with snow and rain. We hypothesize that the build-up of radioactivity in cryoconite is derived from the interaction between ice, meltwater and cryoconite granules. During summer, ~~ice and snow melt, mobilizing their~~ radionuclide content of ice and snow melt is mobilized through melting, including unsupported  $^{210}\text{Pb}$ , which is always present in relatively recent ice (given its lifetime, it is not present at detectable concentrations in ice older than 150-200 years). The interaction between cryoconite granules and

480 meltwater containing  $^{210}\text{Pb}$ , explains why the latter is always found at high concentrations in cryoconite, regardless of the geographic context. For artificial FRNs the case is different since they are not continuously deposited on the surface of glaciers; however, they are still present in cryoconite with high activities. Each year during the melting season part of the ice dating back to the peak of atmospheric nuclear tests and to major nuclear incidents, melts out, releasing ~~the-its~~ artificial nuclide burdens which ~~isare~~ transported by meltwater. As for unsupported  $^{210}\text{Pb}$ , cryoconite granules, ~~which only forms if meltwater is available (Cook et al., 2015; Takeuchi et al., 2001),~~ retains such nuclides owing to their biogeochemical properties, and accumulate a load of artificial radioactivity even if decades have passed since its original deposition on glaciers. The ~~extreme~~ ability of cryoconite is likely related to the presence of affinity-organic matter and extracellular polymeric substances which are affine for for-heavy metals, including the radioactive ones radionuclides of organic matter and the sticky extra-cellular polymeric substances produced by cyanobacteria ( Gadd 1996; Fowler et al., 2010; Kim et al., 485 2011; Chuang et al., 2015; Gadd 1996). An additional support for the importance of organic matter in this process is also given by previous studies showing that the organic fraction of cryoconite and snow algae accumulates heavy metals associated to anthropogenic atmospheric emissions (Fjerdingstad, 1973; Nagatsuka et al., 2010; Łokas et al., 2016; Baccolo et al., 2017; Owens et al., 2019; Huang et al., 2019).

One observation might corroborate our hypothesis. Wilflinger et al. (2018) reported about high activity of  $^7\text{Be}$  ( $t_{1/2} = 53$  d) in 495 their samples, of up to  $34,000 \text{ Bq kg}^{-1}$ .  $^7\text{Be}$  is a short-lived cosmogenic radionuclide, deposited from the atmosphere with precipitation. We observed  $^7\text{Be}$  within our samples, but we could not properly quantify it because ~~six~~ months passed between sampling and  $\gamma$ -spectrometry. Finding an excess of  $^7\text{Be}$  in cryoconite, implies that, given its lifetime, the absorption by cryoconite granules took place in the weeks just before sampling and not when the cryoconite originally formed. The presence of short-lived nuclides suggests that cryoconite granules continuously accumulates radioactive species through the 500 interaction not only with meltwater but also with rain, where  $^7\text{Be}$  is always present.

According to our interpretation, cryoconite containing higher concentrations of radionuclides has formed on the glacier before should be older than the cryoconite with-presenting lower activities. Beyond this, however, we believe it is difficult to attempt a more precise dating ~~of cryoconite~~ through radioactive decay, even if it remains an interesting task. Too many processes are poorly understood to make a rigorous attempt at present, we first should understand the relationships which 505 exist between the formation of cryoconite and of cryoconite granules, ~~the~~ geometry of the glacier, the age and displacement of ice, and in particular the exchanges between ice, meltwater and cryoconite granules.

## 5 Conclusions and future perspectives

We have described the ~~capability-ability~~ of cryoconite to accumulate both artificial and natural FRNs. A comprehensive comparison against other environmental matrices revealed that cryoconite is, excluding samples from nuclear test and 510 incident sites, one of the most radioactive natural substance found in Earth surface environments, ~~with activities for single~~

~~radionuclide that can exceed 10,000 Bq kg<sup>-1</sup>, making cryoconite a potentially hazardous material with respect to many legislations.~~

515 ~~Our study is~~ focused on cryoconite samples from the European Alps but results from other regions of the global cryosphere confirm our findings, proving that the accumulation of radioactivity is not a local phenomenon, but involves worldwide glaciated areas. The ~~capability accumulation of cryoconite to accumulate~~ FRNs ~~in cryoconite~~ is so efficient that it has even allowed for a relatively easy detection of not common FRNs. ~~The high activities detected also made it possible to determine elemental and activity ratios.~~ Cryoconite is ~~thus an~~ extremely promising tool in the fields of radioecology and environmental nuclear forensics.

520 The use of diagnostic ratios ~~has~~ shed light on the sources of radioactivity found in cryoconite. ~~ResultsOur analysis revealedshow~~ that multiple sources, both regional and global, influence ~~sd its the~~ radioactive signature ~~of Alpine cryoconite~~. Pu related nuclides ~~(Pu and Am isotopes)~~ revealed a dominant source of their presence to be the global stratospheric fallout ~~from, associated with~~ atmospheric nuclear tests carried out in the second half of the 20<sup>th</sup> century. In contrast, the major contribution for <sup>137</sup>Cs ~~was is~~ determined to have come from the 1986 Chernobyl accident. The ~~capability ability~~ of recording both ~~regional and~~ planetary ~~and more regional~~ events, ~~was is~~ also suggested by a comparison with literature ~~data~~ concerning ~~eryoconite from~~ other geographic contexts. ~~Some d~~ Differences ~~were are~~ observed ~~and in terms of radioactivity signatures and they could can~~ be explained considering the impact of ~~local regional~~ events. It is important to note that currently no information exist about the radioactivity of cryoconite from the Southern Hemisphere. To build a comprehensive picture of radioactivity in the global cryosphere this is a geographic gap that it would be valuable to close.

530 There is evidence to suggest that the fundamental process which makes cryoconite a “sponge” for ~~radioactivityimpurities in glacial environments, including radionuclides~~, is the interaction between ice and cryoconite itself, through the mediation of meltwater. When glaciers melt, they release and mobilize with meltwater the radionuclides originally preserved in snow and ice layers. Due to the organic matter content and its sticky properties, cryoconite efficiently ~~absorbs binds and accumulates~~ the impurities contained in meltwater, in particular those with an affinity for organic substances, including radionuclides.

535 This study has focused strictly on the glacial environment, ignoring the fate of cryoconite once it is released by glaciers and transported into the downstream ecosystems. It is likely that owing to meltwater discharge, the radioactivity accumulated in cryoconite is promptly diluted, avoiding any health and ecotoxicological risk. However, caution should be taken considering those pro-glacial areas in close proximity to the ice, where the dilution could be limited, and some risks could exist. Given the global relevance of this phenomena, further research should focus on the extra-glacial fate of cryoconite and the contaminants contained within it.

540 ~~Half a century ago, when nuclear atmospheric testing was a common practice, no one could expect that, thanks to the unique features of glacial environments, the ultimate legacies from those activities would have been maximally concentrated on the surface of glaciers around the world.~~

### **Data availability**

Full data are available as supplementary material.

### 545 **Author contributions**

G.B. conceived the idea of this study, interpreted the data and wrote the manuscript with contributions from all the coauthors; R.A., G.B., B.D.M., A.F., R.S.A. collected the samples; G.B., E.L., P.G., M.N. performed the radioactivity measurements and outlined the potential sources of radioactivity; D.M. and P.P. determined the carbonaceous content of cryoconite; G.B., M.N, M.P. carried out neutron activation analysis; C.C., B.D., V.M., E.P. helped in the interpretation of the  
550 data; V.M. handled funding acquisition.

### **Competing interests**

The authors declare that they have no competing interests.

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