Detailed response to comments of Referee 1 in the interactive discussion

Reviewer 1

The manuscript from Moradi and colleagues offers an interesting overview on the export of trace elements from a high-mountain catchment subject to intense acidic rock drainage. The topic is of high relevance at locations where permafrost degradation, under predisposing geological settings, enhances solute concentrations in river networks. I found the attempt of providing solute fluxes from the rock glacier novel and worthwhile, and the conceptual model of a possible explanation of solute mobilization from rock glaciers an interesting hypothesis.

We thank Stefano Brigenthi for his time and effort in providing insightful and valuable feedback. We are pleased that he acknowledges the novelty of our research approach.

Comment 1
Despite the significance of the topic, I found the storyline of the manuscript weak. In my opinion, the major flaw is the attribution of the solute export from the entire catchment and from the rock glacier to permafrost ice melt occurring in this landform. Several studies highlighted that the intense solute export at high elevations is mostly related to more complex and indirect processes than the ice melt itself. These include: the exposure of new ice-free areas to air and water, the abundance of freshly ground mineral surfaces (e.g., provided by rock glacier movement and grinding), periglacial processes and related rock fracturing and thawing/freezing, temperature increase, decline of the water table, and concentration-effect from low discharge. All these processes occur also nowadays, and can provide a huge mobilization of solutes. Although permafrost ice can be particularly enriched in solutes including trace elements, the melt of this ice cannot be inferred as the sole driver of solute export from rock glaciers. Physically, it is very unlikely, if not impossible, that most of the solute export from the permafrost ice melt occurs during early summer, i.e., when most of discharge is generally composed of the snowmelt component and the 0°C isotherm is well above the permafrost table. Therefore, I suggest the authors to build a different storyline, where the permafrost ice melt from water films is included among the potential processes involved in the solute export from the rock glacier, and wider landform- and catchment-scale processes are included among potential drivers.

We fully agree that the intense export of solutes in general reflects a complex sequence of coupled processes including those listed by the referee (e.g. exposure of new ice-free areas to air and water, abundance of freshly ground mineral surfaces, rock fracturing, freezing/thawing, temperature increase). However, for the rock glacier system in this study, we have strong experimental and observational arguments that allow us to conclude that the recorded solute fluxes essentially reflect the mobilization of elements which were leached over a long but unknown period of time from the host rock and have been subsequently stored and accumulated in the rock glacier ice. Therefore, the mobilized fluxes reflect the final stage of a highly complicated sequence of processes. Based on the comments of both referees, it is evident that our discussion paper was not clear enough and we concede the need for additional and more in-depth discussion to conclusively demonstrate that this is a valid and plausible interpretation of our data. In contrast, by no means we intended to postulate that permafrost degradation occurs in early summer when the 0 °C isotherm is well above the permafrost table. Therefore, we intend to strongly revise the introduction and discussion sections when preparing an update version of our manuscript as described in detail in various responses to comments of both referees. Thereby, we will follow the arguments presented in the following paragraphs.

First, while the original mobilization of the solutes is due to chemical weathering, the high solute concentrations and solute fluxes itself are strongly affected by the storage in the ice. This has been demonstrated for many sites similar to the Val Costainas system in the Eastern Alps, where the presence of ice such as in intact rock glacier is needed to explain the high concentrations of toxic solutes (e.g. Ni, Mn, Al, F; Wanner et al., 2023). Within this work, there are data from long-term laboratory flow-through experiments and field studies in alpine streams originating from intact rock glaciers. Based on these laboratory experiments, even during a typical water residence of several months within the low permeable base layer (Jones et al., 2019), the pyrite content of the paragneisses frequently occurring in the affected catchments and the pyrite oxidation rate are both too low for generating toxic solute concentrations on the same order of magnitude as those observed at the field sites. Accordingly, the enrichment of toxic solutes originally mobilized by chemical weathering (which is indeed heavily controlled by the rock surface exposed to water and air and hence by freezing/thawing cycles and rock fracturing) in rock glacier ice over time is essential to generate the high concentrations of toxic solutes observed today (see also extended discussion on pyrite content and pyrite oxidation rates in Wanner et al., (2023). The strong relevance of the storage for the enrichment process in rock glacier ice has also been demonstrated by Nickus et al. (2023). Therein, the authors reported for a very similar geological setting, high concentrations of the same elements (e.g., Ni, Zn, Mn) at the top of a frozen rock glacier core as those showing high concentrations in the streams originating from such rock glaciers.
Second, based on the arguments provided above, the presented toxic element fluxes reflect the quick export of ice melt from the rock glacier observed after hydraulic events such as snowmelt and heavy rainfall (Fig. 8). In this context, we would like to emphasize that we relate the recorded element fluxes to the export of ice melt and not

to ice melt itself. We make this subtle difference because we fully agree with the referee, that owing to the low temperature, ice melt rates are low in early summer. Consequently, instead of claiming that ice melt rates are high in early summer, we propose that the export of ice melt is high during this period (see also response to Comment 2 below). A possible explanation for this is that some leftover (e.g. isolated) meltwater may remain unfrozen during wintertime (e.g. in the base layer), which is then hydraulically exported during snowmelt and heavy precipitation events. We agree that this point could be emphasized and clarified in an updated version of the manuscript (please see also our response to Comment 5 of Referee 1). Therefore, we agree that high fluxes of toxic elements in early summer are surprising but we strongly disagree with the statement that "it is very unlikely, if not impossible, that most of the solute export from the permafrost ice melt occurs during early summer". This is because we have four datasets (the first two are fully independent from each other) that show that this observation is true: (i) manual flux measurements of Ni and Zn near the rock glacier outlet (Fig. 7a,b), (ii) manual flux measurements of Ni and Zn 5 km downstream of the rock glacier (Fig. 7c,d), (iii) automated flux measurements of Ni and Zn at the downstream location (Fig 8), and (iv) concentration measurements at the downstream monitoring location revealing very high concentrations in early July (Fig. 5a, Table S1, Electronic Appendix). All of these datasets show that the fluxes of Ni and Zn strongly increase after termination of the snowmelt and reach in most cases maximum values in early summer. Furthermore, we would like to emphasize that, contrary to what the referee argues, the observation that the fluxes of Ni and Zn at the downstream monitoring location AP10 are essentially the same as near the rock glacier outlet (Fig. 7) demonstrates that fluxes of toxic elements recorded for the entire catchment at the downstream monitoring location can be well attributed to the export from the small rock glacier at the origin of the catchment. Therefore, while the enrichment of toxic elements in the ice is due to the long-term coupling between chemical weathering and accumulation, the mobilization follows the hydraulic export of meltwater from the rock glacier ice (see also response to comment 2 below). Moreover, owing to the kinetically-limited nature of the pyrite oxidation reaction, we consider it impossible that short-term chemical weathering alone could cause solute flux peaks within a few hours or days after hydraulic events (Fig. 8). More specifically, this also explains why in the investigated Val Costainas catchment, the export of solutes, as inferred from the lack of white Al-sulfate precipitates (basaluminite) along the stream (Wanner et al., 2023), was much less in the last century when the permafrost degradation rates and hence the mobilization of temporary stored solutes were lower. In this context, it is unclear what the referee means with the statement that "all these processes occur also nowadays, and can provide a huge mobilization of solutes". Unfortunately, no data or studies are referenced here. We interpret it in a way that the referee encourages us to consider chemical weathering to account for the solute production on a shorter timescale without enrichment and storage in the ice. We outlined in the last two paragraphs why we consider it alone not being able to account for the enrichment and export of toxic solutes in the Val Costainas system and provided the data and evidence that underpins our reasoning.

Comment 2
In my opinion, the work would also benefit from more investigations on the seasonal dynamics of solute export, building on what found by other studies. For example, (1) can the series of both years be normalized based on the days elapsed from the snow cover end? (2) What is the hydrological/hydrochemical response to rain events, dilution or rather enrichment of solutes? (3) Can the period of permafrost degradation be identified based on the data on discharge and chemistry? (4) What is the relation between sulfate export and metal export? (5) Does a seasonal shift of carbonate/sulfate prevalence occur in the streams, or is this rather a stable ratio?

We thank the referee for these suggestions. Compared to other studies, we have chosen to systematically record element fluxes and not just element concentrations. The reason for this choice was that, unlike solute concentrations, solute fluxes are independent of the degree of dilution caused by snowmelt and precipitation, which cannot be precisely quantified. For the studied system, tracking element fluxes is particularly useful because Ni, Zn, Al, and Mn are almost exclusively mobilized from the rock glacier at the origin of the stream (see arguments for this in our reply to Comment 1 of Referee 2). Tracking of the fluxes thus allows to assess the mobilization process from the rock glacier. To the best of our knowledge, this discussion paper is the first to systematically track element fluxes in high-alpine streams originating from rock glacier affected by acid rock drainage (instead of tracking concentrations). Accordingly, we cannot really compare our findings regarding solute fluxes to other studies because they do not exist. To address the comment, however, we will make this point clearer by updating Section 5.1 when preparing an updated version of this discussion paper. At the moment this section (lines 382-421) discusses why tracking fluxes is useful but does discuss that it has never been done so far in a systematic way for such systems. To further emphasize that flux measurements are more useful to track element mobilization from rock glaciers than solute concentrations, below we provide additional information regarding the measured solute concentrations, also to address the four specific suggestions the reviewer made in this particular comment.

(1) It is an interesting idea to normalize the years based on the days elapsed from the snow cover end. The first discharge and flux peaks (highlighted in blue in Fig. 8) can be certainly explained by a similar number of days elapsed since the end of the snow cover (5 days). For the remainder of the monitoring period, however, the flux curves recorded for the two years look so different (Fig. 8) that we do not see any value of performing such additional evaluation. Instead, the visually observed temporal correlations between precipitation events and discharge as well as flux peaks (yellow bars in Fig. 8) proof that there is strong hydraulic export of toxic elements

after each rainfall event, which is independent of the time elapsed from the end of the snow cover. If you just recorded concentrations, then this may be masked by dilution caused by these rainfall events (see next point).

(2) The plots below (Figs. R1and R2) demonstrate that the response of solute concentrations recorded at various locations along the stream to snowmelt and rainfall depends on the location in is thus not as clear as that of the solute fluxes. This is because of the competing behavior of the increased mobilization in the rock glacier (causing an increase in concentration) and increasing dilution (causing a decrease of the concentration). Because the flux data provides much more information and because the scope of the manuscript is on fluxes, we do not see an additional value in adding an extended discussion on the response of solute concentrations to rainfall events (although the seasonal evolution of the concentrations is already discussed in detail on lines 314-324 with a particular emphasis on the contrasting seasonal pattern for the different monitoring locations to demonstrate that use of concentration date for gaining insight into processes in the rock glacier is limited). The strong correlation of the seasonal flux evolution with snowmelt and precipitation as well as the lack of correlation between solute concentrations and these hydraulic events at the rock glacier springs (Fig. R1), in our opinion, very strongly demonstrates that flux measurements are more useful to track the mobilization process of toxic solutes in the rock glacier than solute concentrations.
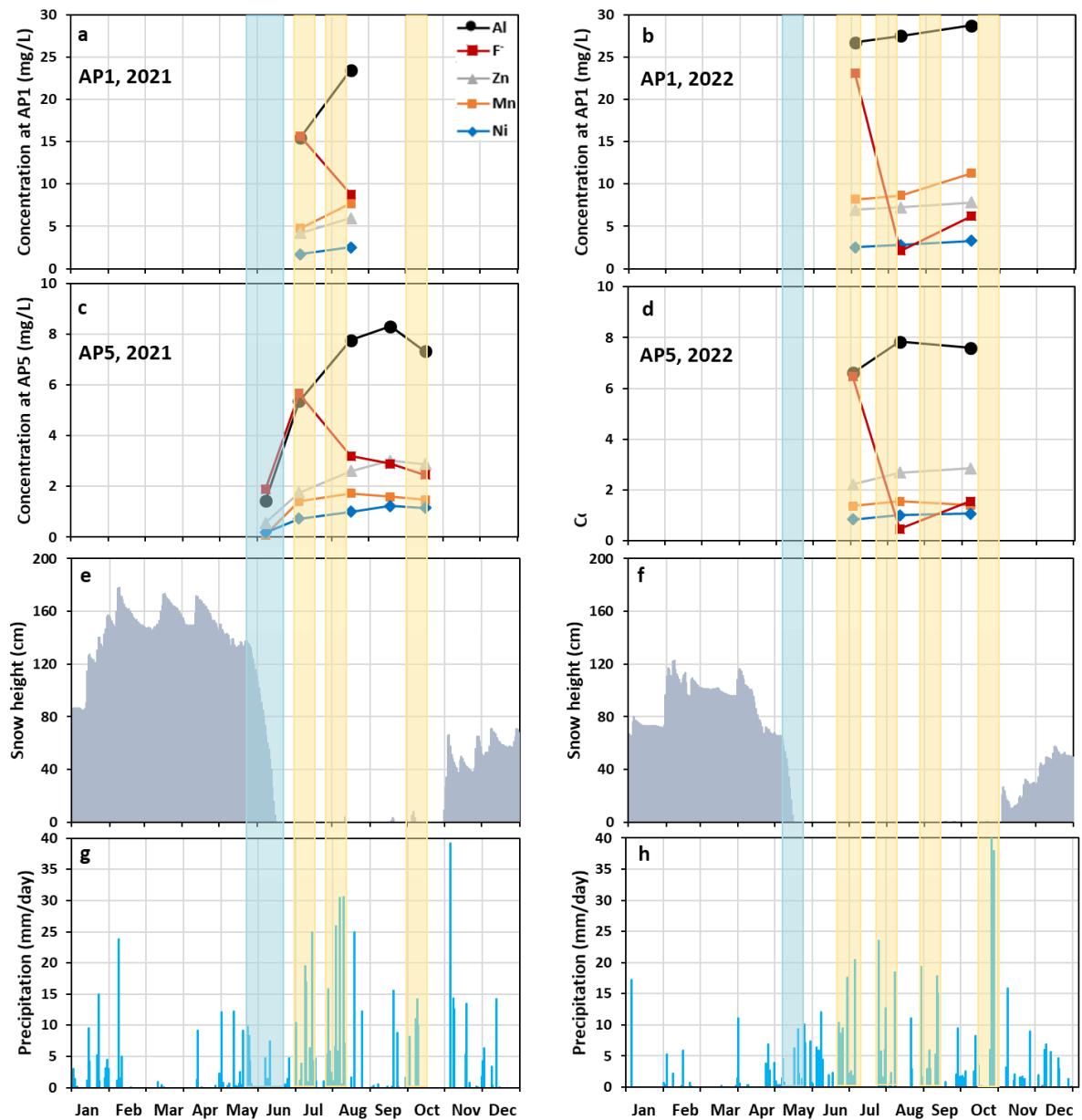
Fig. R1: Seasonal variation of the concentrations of Al, F⁻, Zn, Mn, and Ni at the rock glacier spring AP1 and the upstream discharge monitoring location AP5 (Fig. 1). (a), (b) Concentrations of samples taken at AP1 in 2021 and 2022, respectively. (c), (d) Concentrations of samples taken at AP5 in 2021 and 2022, respectively. (e), (f): Snow height recorded in 2021 and 2022 at the Murtaröl snow station, located some 15 km Northwest of AP10 at an altitude of 2359 m a.s.l. (SLF, 2023). (g), (h): Rainfall recorded in 2021 and 2022 at the Santa Maria weather station, located some 6.5 km North of AP10 at an altitude of 1388 m a.s.l. 375 (MeteoSwiss, 2023). The light blue bars show the snowmelt period and the yellow bars highlight major rainfall events. There is no obvious correlation between snowmelt/rainfall and solute concentrations at the source area, i.e. at AP1 and AP5.
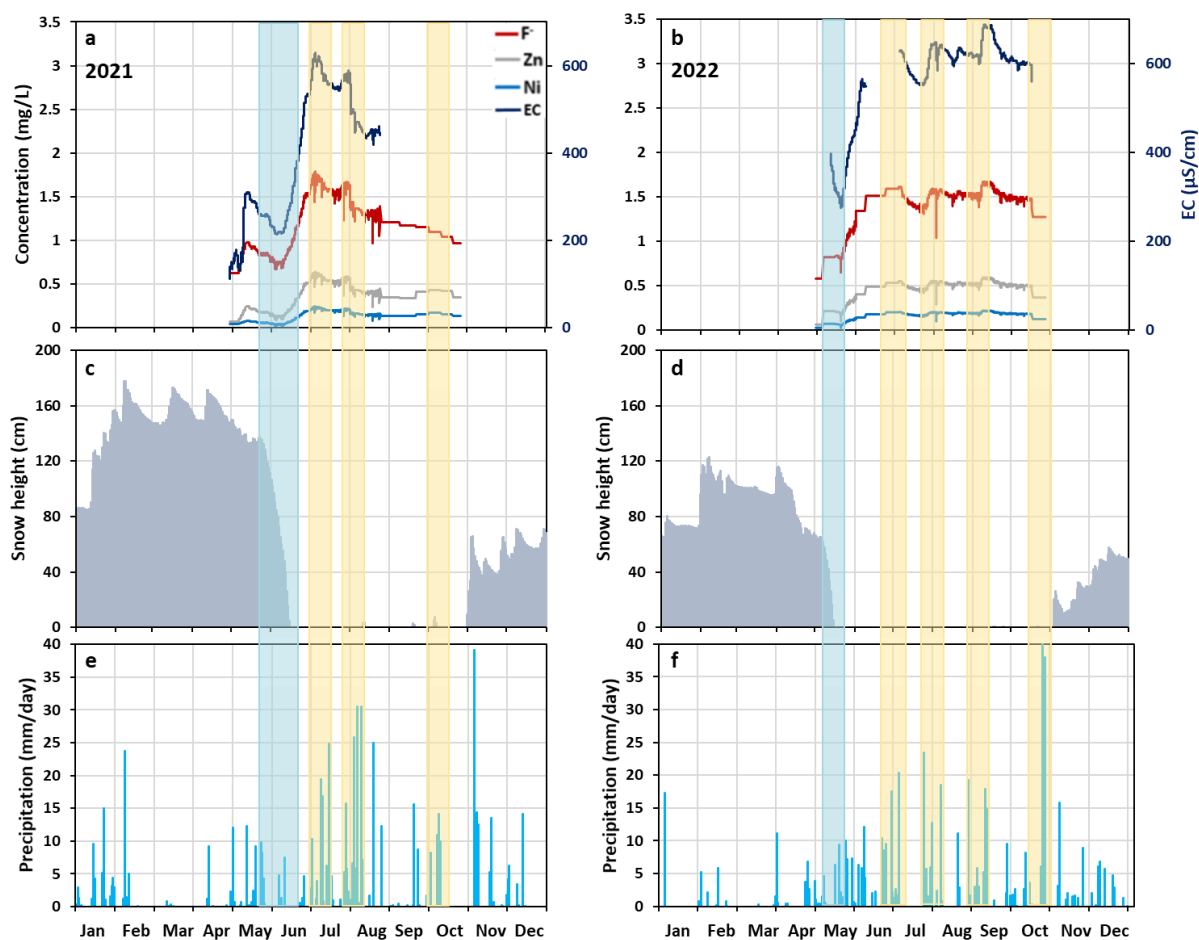
Fig. R2: Seasonal evolution of the EC and the concentrations of F⁻, Zn, and Ni at the downstream monitoring location, AP10, in the year (a) 2021 and (b) 2022. (c), (d): Snow height recorded in 2021 and 2022 at the Murtaröl snow station, located some 15 km Northwest of AP10 at an altitude of 2359 m a.s.l (SLF, 2023). (e), (f): Rainfall recorded in 2021 and 2022 at the Santa Maria weather station, located some 6.5 km North of AP10 at an altitude of 1388 m a.s.l 375 (MeteoSwiss, 2023). The light blue bars show the snowmelt period and the yellow bars highlight major rainfall events. As, the EC data was not reliable for the following periods: 1–14. May 2021, 29. Aug–30. Oct 2021, 1–20. May 2022, 7. Jun–7. Jul 2022, and 21–30. Oct 2022, a linear interpolation of the chemical analysis of the biweekly samples (Table S1, Supplement) was employed for the mentioned periods to estimate the seasonal evolution of the solute concentrations.

(3) Based on the arguments provided in Wanner et al. (2023), in this discussion paper, and in our response to Comment 1 of Referee 1, the recoded fluxes (product of discharge and solute concentrations) of Zn and Ni are proportional to the amount of ice melt being exported from the rock glaciers. As discussed in Section 5.3 (lines 520-585), it may be even possible to quantify the exported amount if the solute concentrations at the surface of the frozen rock glacier core were known. To what degree the estimated amounts of exported ice melt reflect current permafrost degradation and how much is inherited from past degradation for instance during a previous summer remains unclear, and requires further investigation (we agree that this point needs to be more discussed in an updated version of the manuscript). In contrast to solute fluxes, it is highly challenging to use solute concentrations to identify periods with accelerated permafrost degradation. For instance, at the rock glacier spring AP1, the highest concentrations were measured in mid October 2022 (e.g. 29 mg/L Al, 6 mg/L F, 8 mg/L Zn, 11 mg/L Mn, and 3 mg/L Ni, Fig. 6), when the average temperature at the weather station located at ca. 1388 m a.s.l. was only 5 °C (Fig. 9), implying that it was only slightly above zero at the rock glacier at 2600 m

a.s.l. and that very little ice melt was produced on that day. In contrast, the solute concentrations at this location were lowest in July when the exported fluxes were high in both years (Fig. 6b, d) and when the temperature was almost 10 °C higher (Fig. 9). It follows that it is very challenging to track permafrost degradation from solute concentrations. In the studied system where the export of toxic solutes is very high, only at the downstream monitoring location the concentrations of Zn and Ni showed maximum values at roughly the same time as the recorded fluxes (in July of both years as shown on Fig. 8). Once again, the reason why concentrations are not as useful as fluxes is that they are affected not only by the release of the elements from their source, but also by an unknown degree of dilution caused by snowmelt, rainfall and merging streams and groundwater with low solute concentrations.

(4) and (5): The figure below (Fig. R3) demonstrates that all samples collected at the various locations during the two monitoring years plot on the 1:1 correlation between the sum of the concentrations of cations and the concentrations of sulfate. As discussed in detail in Wanner et al. (2023), this demonstrates that the interaction of sulfuric acid inherited from the oxidation of sulfides such as pyrite and the paragneiss host rock components in the rock glacier strongly dominates the composition throughout the entire year and along the entire stream segment we have monitored. The lack of seasonal variations of this ratio (even at 5 km downstream) is caused by the very strong chemical signal emerging from the rock glacier at the origin of the stream.
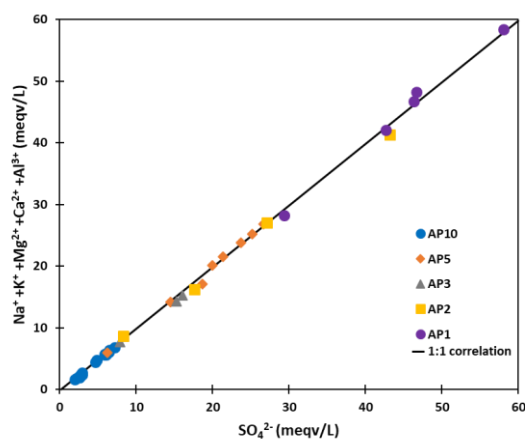
Fig. R3: Sum of the equivalents of major cations (Tables S1-5) at various monitoring locations of the stream during the two monitoring years vs. corresponding SO_4^{2-} concentrations. The 1:1 correlation demonstrates that sulfate strongly dominates the composition throughout the entire year and along the entire segment of the monitored stream.

Comment 3
I kindly ask the authors to also reshape the contents of paragraphs, to build a more linear and streamlined story. Also, some parts should be moved to their appropriate section. E.g., the calculations and results of the ice melt contribution with mixing models partly belong to the Methods and Results sections.

We thank the referee for this suggestion and we will carefully assess how to reshape the structure of the manuscript when preparing an updated version of the discussion paper. As described in our replies to Comments 1 and 2 of Referee 1, we do not see any value in completing switching the focus of the manuscript to an extended discussion on the seasonal behavior of solute concentrations. Accordingly, the main scope of the manuscript will remain the same. However, we intend to strongly revise the introduction and discussion sections to demonstrate that our interpretations and conclusions are valid (Comment 1 of Referee 1). Upon reshaping the structure of the manuscript, we will also take into account the suggestion of Referee 2 asking to remove Section 5.3 (lines 520-579) on the quantification of the ice melt contribution (Comment 22 of Referee 2).

Comment 4
Introduction: This part needs to be restructured according to a streamlined flow. What are rock glaciers, why are they hydrological significant, what is the quality of their waters, potential reasons behind the intense export of solutes from intact rock glaciers, aim of the study.

We thank the Referee for this suggestion and we will carefully assess how to restructure the introduction to more clearly convene this information. Nevertheless, in the current version, all topics mentioned by the Referee are already addressed: In the first paragraph of the "Introduction", explanations on RGs, and their role as fresh water storage with respect to climate change are given (lines 34-52). In the third paragraph (lines 80-92), we discussed about their water quality, solute export and the reason behind it. Finally, the aim of the study is explicitly stated in the last paragraph (lines 94-106).

Comment 5
Introduction: The internal structure of rock glaciers is incomplete. According to Wagner et al. (2020; 2021), below the active layer and the permafrost area, an unfrozen and thick layer of fine sediments represents the aquifer of the rock glaciers, transiently storing water and releasing it to springs as baseflow/groundwater. This should be also considered in the discussions. See also review paper from Hayashi (2020), and Harrington et al. (2018).

Thank you for pointing out this error. The base layer (BL) is an unfrozen layer of fine sediments below the frozen core (sediment-ice mixture) characterized by low permeability and flow rates with an average residence time of about 7 months (Jones et al., 2019). We will update the description of the rock glacier structure accordingly (lines 39-42). In the discussion part (Fig. 10), the base layer is already considered in the current version of the discussion paper. Nevertheless, we agree that the role of the base layer in generating the high solute fluxes in early summer needs to be discussed in more detail. A potential add-on to our conceptual model (Fig. 10) is that ice melt from the frozen rock glacier core enriched in toxic elements may reside in the unfrozen base-layer during wintertime. If the base layer is hydraulically flushed during snowmelt, then such hypothesis could well explain the high fluxes right after snowmelt (Fig. 8). We will carefully assess whether such discussion as well as an update version of the conceptual model should be added when preparing an updated version of the manuscript.

Comment 6
Introduction: Also, the difference between intact and relict is not well described (see e.g., discussed in Colucci et al., 2019):
Intact = ice + movement (active) OR ice and no movement (inactive)
Relict = no ice or little ice remnants (pseudorelict)

The referee is right that this definition is missing and that the manuscript will benefit from it. We will add it when preparing an updated version.

Comment 7
Methods: In my opinion, this part needs some streamlining too. When did you start field activities? What is the frequency of field campaigns at different locations? What did you do during each campaign (sampling + discharge measurements)?

We provide this information in Section "3.1 Sampling of streamwater", lines 159-168. We specifically state the monitoring period, the frequency of sampling at all the monitoring locations, and the description of how and what we sampled are all provided in detail. Additionally, in the next section "3.2 Discharge measurements", lines 170-172, the period and the frequency of the discharge measurements are provided as well.

Comment 8
Methods: The description of the salt dilution method can be shortened or moved to supplementary materials. Also, how did you ensure a good mixing of the salt? Did you ensure a downstream distance between injection and recording of at least 15-20 times the channel width?

We will follow the recommendation and move the description of the salt dilution method to the Electronic Appendix. As described on lines 182-185, all aspects mentioned by the Referee were taken into account to ensure reliable discharge measurements. In particular, we mixed the salt in a 30 L barrel prior to adding the properly dissolved salt to the stream. Furthermore, we did ensure that the downstream distance between adding salt and the location of the probes is at least 15-20 times the channel width. To ensure proper mixing and verify the accuracy of the discharge measurement, we systematically repeated the discharge measurement by slightly changing the distance between the salt input and measurement location as well as the added amount of salt.

Comment 9
Results: I am a bit sceptic about the linear fitting between EC and trace element concentrations (Figure 4). I am not sure that the seasonal behaviour of trace elements follows the same pattern as those of elements (and this is something revealed also by Figure 6). I suggest the authors to provide the EC and discharge series in a first plot, before providing those reconstructed for the other solutes. This would better allow comparing the seasonal patterns of EC in parallel to those of trace elements, and proof the validity of transforming EC series in Ni/Zn/F series.
Also, is this relation EC – Ni/Zn/F different at different locations?

The correlations shown in Figures 4a-4c are defined by more than 20 samples collected during two subsequent monitoring years and covering a concentrations range varying by a factor of more than three for all solutes. Thus, in our opinion, these figures demonstrate that for the concentration ranges observed at this monitoring location (which are high compared to other sites described in the literature) the EC data can be used to estimate the concentration for these solutes. However, to increase clarity, an additional validation is provided in the updated version of Figure 5, now showing that the concentrations of Ni, Zn, and F estimated based on EC measurements and the correlations shown on Figures 4a-c are very close to the actual concentrations measured on the biweekly collected water samples (Fig. R4),

Nevertheless, we agree that the EC data should be provided for the downstream monitoring location (AP10) because they are used to determine the fluxes. A useful option is to plot it on top of Figure 5 as shown below (Fig. R4). The seasonal evolution of discharge for both monitoring years is shown in Figure 8. In our understanding, the same data should not be shown more than once. Therefore, we prefer to keep the discharge curves in Figure 8 because it is crucial to show the correlations between solute fluxes, discharge as well as snowmelt and rainfall events.

In the discussion paper, we only present a correlation between EC and solute concentrations for the downstream monitoring location AP10, because only there the EC data was recorded continuously and subsequently used to estimate the solute concentrations. Moreover, for the other sites located much closer to the rock glacier, the number of samples is much lower (5 to 8 instead of 39 at AP10, see Tables S1-S5, Electronic Appendix). Of course, we could derive such additional correlations, but we do not see any value because the concentration measurements performed on actual samples are much more accurate for quantifying the solute fluxes reported in Figure 7.
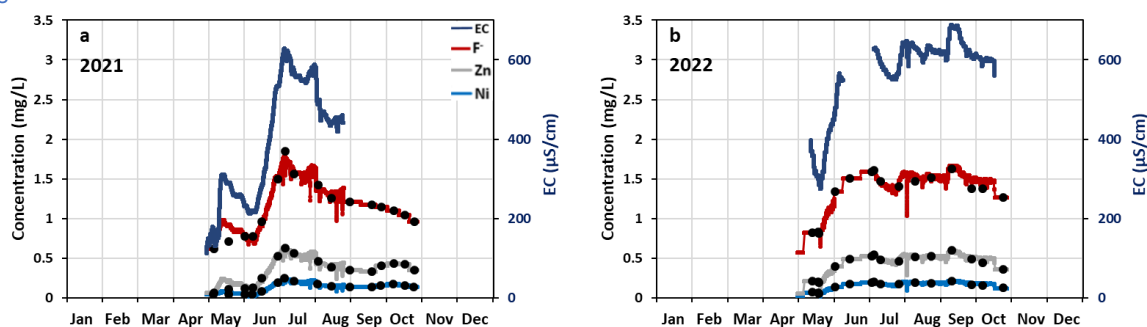
Fig R4: Seasonal evolution of the EC and the concentrations of F⁻, Zn, and Ni at the downstream monitoring location, AP10, estimated based on the electrical conductivity data and the correlations shown in Figure 4, (a) 2021, (b) 2022. The black filled circles on each curve show the actual concentration of the same element measured from the bi-weekly water analysis (Table S1, Supplement). As, the EC data was not reliable for the following periods: 1–14. May 2021, 29. Aug–30. Oct 2021, 1–20. May 2022, 7. Jun–7. Jul 2022, and 21–30. Oct 2022, a linear interpolation of the chemical analysis of the biweekly samples was employed for the mentioned periods to estimate the seasonal evolution of the solute concentrations.

Comment 10
Results: For Figure 6, when looking at the points here, increasing trends of elements generally occur from June to October (and this behaviour agrees with what observed in other studies). This contrasts with Figure 5a, where concentrations peak during early July! Still for figure 6, since a little number of samples was collected, it would make sense to normalize the series based on a chronological driver (e.g., calendar day). For example, some works highlighted that the number of days elapsed from the end of snow cover is a good predictor of hydrochemical behaviour of RG spring (Brighenti et al., 2021; Bearzot et al., 2023; Munroe et al., 2023)…worth an attempt for all locations, and both solute concentrations and fluxes?

Figure 5 shows seasonal evolution of the element concentration at the downstream location, AP10, while Figure 6 shows this variation at the two upstream locations, AP1 and AP5. As we discussed on lines 397-406, the concentration of the elements at these three locations show contrasting behavior because, owing to strong difference in catchment size, the degree of dilution is strongly different. In contrast, when comparing fluxes of Ni and Zn the values are very similar because these are not affected by the (unknown) degree of dilution. This confirms once again that tracking solutes fluxes is more useful than tracking just concentrations. Owing to the strongly contrasting behavior of element concentration at the downstream and upstream monitoring location (decreasing vs. increasing trend), normalizing the concentration against days elapsed since the end of the snow cover will not make the pattern similar. Thus, as already pointed out in our reply to Comment 2 of Referee 1, we do not see any value to perform such additional assessment.

Comment 11
Results: The rating curve presented in Figure 3. From what I know, EC/water height normally follow a cubic/exponential relationship, and polynomial curves can return unreliable overfitting of the transformations. As such, the red point should not be excluded since it represents a reliable condition of low-flow.

We assume that here the referee refers to the water height/discharge relation and not to the relationship between EC and water height. Evaluating water height/discharge relation and rating curves of many gauging stations of the Swiss Federal Office for the Environment showed that the shape of the rating curve depends strongly on the hydraulic conditions at the measuring cross-section (unpublished consulting report). These hydraulic conditions depend mainly on the geometry and the friction of the measuring cross-section. Hence, it does not necessarily have to be followed by a cubic, exponential or a polynomial function. If the geometry changes with increasing

water table height considerably, also the rating curve can change its shape. The Federal Office for the Environment uses polynomial functions, but for most gauging stations, they use more than one function, because hydraulic conditions change with increasing water table several times. The fact that one polynomial function fits well in our case, is thanks to the suitable hydraulic conditions at the measuring cross-section.

Regarding the red point, we are convinced that it should not be used for the correlation. The reason is that the hydraulics during winter time are completely different than during the rest of the year. This is because of the presence of ice and the much smaller width of the stream at very low discharge rates. Moreover, we have realized that the water table measurement corresponding to our discharge measurement of March 23, 2021, was affected by a wooden installation protecting the inlet of a local hydropower plant during wintertime, which is located 20 m downstream of the location of the probe. Therefore, we will address the comment by removing the red point when preparing an update version of the manuscript. Please note that during our May to October monitoring period, the discharge was never as low as measured on March, 23 2021. Therefore, excluding the data point does not affect any of the flux estimates reported in the discussion paper. Moreover, as suggested by Reviewer 2 (Comment 17), we intend to move Fig. 3 and Section "4.1.2." to the Electronic Appendix.

Comment 12
Discussion: Why do you state that Ni and Zn behave conservatively, just because they are strongly correlated with EC? White coatings were also demonstrated to be enriched in Nickel (Thies et al., 2018), for example, and some precipitation along the stream is supposed to occur given the shifts in pH, isn't it?

The linear correlation between EC and the concentrations of Ni and Zn is only one argument to postulate that they behave conservatively. If the two elements would quickly sorb to basaluminite (white coating), then the ratio between their concentrations and the total dissolved solid concentrations would depend on the residence time in the stream (more sorption at higher residence time). This would lead to seasonally varying ratios between EC and element concentrations and hence to an overall poor correlation between EC and these concentrations such as discussed for Mn. In addition, as it is demonstrated in Fig. R5 below, the Ni/Zn ratio (ca. 0.39) along the stream is very constant as manifested by very similar correlation coefficients between the concentrations of these two solutes, confirming their conservative behavior. A much more important argument for the conservative behavior of Ni and Zn, however, is that the fluxes recorded at the upstream and downstream monitoring locations compare quite well for specific days (Fig. 7). This demonstrates that very little Ni and Zn is lost along the stream and that the fluxes recorded at the more accessible downstream location are useful to track the fluxes exported from the rock glacier at the source of the catchment (see discussion on this topic on lines 407-410).

The Referee is right that basaluminite precipitation (white coating) occurs along the stream (see description of the site on lines 125-132 as well as Figure 2, where the stream segment with basaluminite precipitation is highlighted) and that basaluminite may be enriched in Ni. For the studied system in Val Costainas, we have reported a Ni content in basaluminite of 1261 ppm (Wanner et al., 2023). This accumulation reflects a long-term but unknown time during which Ni sorption occurs. Based on the arguments provided above, however, basaluminite does not operate as a sufficiently efficient Ni sink to significantly affect the Ni flux along the stream, at least not between the two monitoring locations.
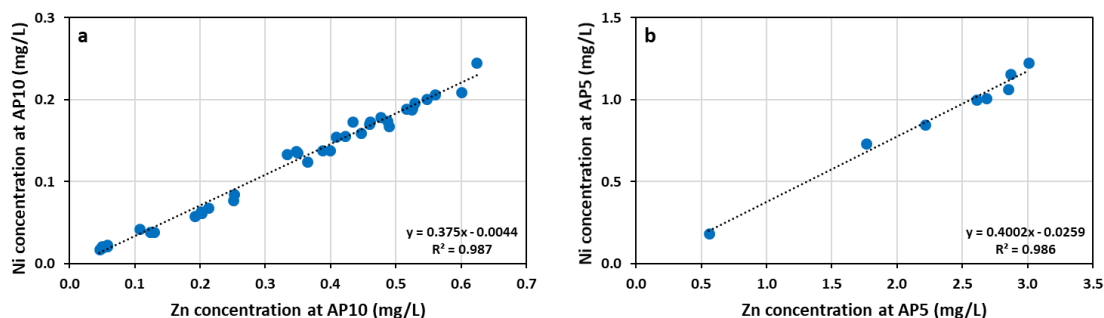
Fig. R5: Concentrations of Ni and Zn recorded at (a) AP10 and (b) AP5 (Tables S1 and S2). The correlation between the two solutes is excellent and the Ni/Zn ratio at both locations is very constant throughout the entire monitoring period (0.37-0.40), demonstrating the conservative behavior of these two solutes.

Comment 13
Discussion: Agreed that the RG has a strong influence on the export of solutes at AP10, there is no reason to infer that the ice melt is the sole phenomenon involved in this export. Since several hypotheses exist on the solute export from active rock glaciers, and since your work does not investigate the chemical conditions of the RG ice in Val Costainas, I suggest to reshape your figure according to all these hypotheses. I find your hypothesis interesting, and I believe it should be valorised. But this is only a hypothesis and should be contextualised with several others that can be found in the literature.

We do not claim at all that ice melt is the sole phenomenon for the export of toxic solutes (see responses to comments 1 & 2 above). As already postulated in the previous study (Wanner et al., 2023), the strong export of solutes observed today reflects the last stage of a complicated sequence of coupled processes. In fact, it is clearly described on lines 88-93: "The adverse water quality of rock glacier springs is often caused by acid rock drainage (ARD) where the weathering of pyrite produces sulfuric acid and therefore promotes the leaching of toxic elements from the crystalline host rocks (Wanner et al., 2018, 2023). After mobilization, the elements are temporally stored and enriched in the rock glacier ice (Nickus et al., 2023). As a consequence, today the climate-change induced accelerated melting of rock glaciers leads to a quick and focused export in summer when ice melt production rates are high (Wanner et al., 2023)".

In our point of view, so far the postulated conceptual model (Fig. 10) is the best explanation for the recorded dataset although our conceptual model could be extended by additionally addressing the possible role of the base layer in storing melt water over wintertime (see our reply to Comment 5 of Referee 1). We acknowledge though that we did not sufficiently discuss alternative explanations for the strong export of solutes from rock glaciers provided in other publications. This will be added when preparing an updated version of the discussion paper.

Comment 14
Discussion: It sounds impossible that the export of ice melt occurs during the entire summer! Studies highlighted that permafrost thawing can occur only during late summer (Williams et al., 2006; Colombo et al., 2019), when the 0°C isotherm reaches the permafrost table. During this period, some hydrochemical effect may be detected according to Brighenti et al. (2021). Can you build on these studies and provide evidence of the occurrence of this period? For instance, if I look at figure 11, a short period of solute boosting in September/October of both years might be identified as a window of solute export from RG ice melt? What are the others peaks related to? Snowmelt pulses, intense rainfall events? Is there any correlation between rainfall amount and solute export? What is the delay between a rain event and enhanced solute export?

As pointed out in our response to Comment 1 of Referee 1, we would like to emphasize that we relate the recorded element fluxes to the export of ice melt and not to ice melt itself. We make this subtle difference because we fully agree with the referee, that permafrost thawing mainly occurs in late summer. Consequently, instead of claiming that ice melt rates are high in early summer, we propose that the export of ice melt is high in this period. A possible explanation for this is that some leftover (e.g. isolated) meltwater from the previous summer may remain unfrozen during wintertime. A possible location where ice melt from the frozen rock glacier core enriched in toxic elements may "survive" is the unfrozen base layer of the rock glacier (see our reply to Comments 5 and 13 of Referee 1).

Based on the recorded element fluxes reflecting mobilization of elements from the rock glaciers (Fig. 8), we do not see a particular point in time towards the end of summer where accelerated export of solutes occurs. Accordingly, the hypotheses of (Brighenti et al., 2021) is not necessarily true for the catchment studied here. Instead, the events with increased solutes fluxes in September and October the Referee is referring to are caused by strong rainfall events as described in detail on lines 355-365 and highlighted with yellow bars in Figure 8.

Comment 15
Discussion: Building on striking difference between the two years, can you summarize what will it happen to solute export and concentrations under a changing climate?

The differences between the two monitoring years are because of strong differences in the amount of snowmelt and rainfall events. It is correct that we report huge differences. As mentioned on lines 609-613, we expect to see a trend of increasing solute export until it reaches a maximum. However, two years of monitoring is not sufficient to provide a meaningful quantitative assessment by how much the export of solutes will increase in future. To obtain a better estimate of the future behavior, we continue our monitoring effort and we are confident to provide a robust answer to this question in a few years.

Comment 16
Discussion: In my opinion, the high solute fluxes recorded during early summer cannot be explained by the melt of permafrost ice. Instead, these can be related to the higher amount of water in contact with rock clasts. A limited amount of weathering can occur relatively quickly during the freshet, when snowmelt infiltrates and interacts with the sediments of the entire catchment! During this period, given the amount of water involved and the wide area which is interested in the phenomenon, even a small weathering intensity or export of already weathered solutes can translate in a relatively high solute export, just because of this discharge-effect.

Based on the use of the exclamation mark, the referee seems to have very strong evidence that chemical weathering between water and the rock glacier sediments is so efficient to plausibly explain the high fluxes observed in early summer (e.g. on July 9, 2021: ca. 120 kg of Al and F, 40 kg of Ni, 35 kg of Mn and 20 kg of Ni were exported from the rock glacier on a single day and the corresponding concentrations at the rock glacier

spring AP1 were ca. 15 mg/L of Al and F-, 5 mg/L of Mn, 4 mg/L of Zn and 2 mg/L of Ni, 1354 mg/L; Figs. 6, 7; Table S5). The same applies regarding the observation that solutes fluxes peak within only a few days after each rainfall event. We would be very interested to see concrete experimental evidence that such immediate and strong mobilization can be caused solely by chemical weathering. If such evidence could be provided, then we would be more than happy to revise our interpretation, if not, then the comment has no real meaning because then it would represent an unproven and not justified statement. In our understanding, so far there is no conclusive evidence that in natural acid rock drainage scenarios (i.e. without the presence of ore bodies) such strong and immediate mobilization can happen without the presence of ice.

It is well known that pyrite oxidation is a kinetically-limited reaction (e.g. Williamson and Rimstidt, 1994), which means that it does not happen instantaneously. For silicate minerals like chlorite and feldspars, representing the main source for the high concentrations of major cations such as Mg (e.g. 234 mg/L on July 9 2023 at AP1) as well as trace elements (e.g. Al: 15 mg/L on the same day) (Wanner et al., 2023), kinetic limitations are even more important because their dissolution rate is several orders of magnitude lower than that of pyrite (see compilation of mineral reaction rates by Palandri and Kharaka, 2004). The observation that weathering of pyrite-bearing paragneiss does not happen instantaneous, at least not within a few days, was recently confirmed by a column experiment where the interaction of powdered paragneiss from two similar locations in the Eastern Alp with deionized water at a water to rock ratio of roughly 1:1.5 and at room temperature lead to dissolved solute concentrations after 4 months that were roughly two orders of magnitude lower than those observed downstream of intact rock glaciers where ice is present. Given that the pyrite content in the paragneiss of the Eastern Alps is rather low (e.g. Wanner et al., 2023) and that mineral reaction rates decrease with decreasing temperature (e.g. Lasaga, 1984) we consider it very unlikely that the observed chemical signal is solely caused by chemical weathering. Instead, as pointed out in our response to Comment 1 of Referee 1, it very likely requires the accumulation and enrichment of solutes leached by chemical weathering in the rock glacier ice.

Comment 17
Discussion: Also, the different concentrations and fluxes at different RG springs can be almost fully explained with a different catchment size. If the RG aquifer is generally located mostly in the mid-lower part of RGs, not surprisingly the lowermost spring AP1 is perennial (it receives water from the entire aquifer) and the others are intermittent (they receive water from only a part of the aquifer, horizontally and vertically).

We fully agree that the perennial nature of the lowermost spring could be an effect of the larger catchment size. Owing to the larger overall discharge, we thus agree that the highest solute fluxes at this spring could as well be explained by the larger catchment size. Regarding the control on the solute concentrations, however, we disagree with the referee. These are controlled by the interplay of chemical weathering, the release of interimely stored solutes in the rock glacier ice, and dilution caused by snowmelt and rainfall. Owing to the higher discharge caused by the larger catchment, the dilution effect is highest at the lowermost spring whereas the weathering rates (i.e. in mol per kg water per s) is roughly the same assuming that the mineralogy of the host rock, grain size distribution, and the temperature are the same. Nevertheless, despite the higher degree of dilution, the concentrations at this spring are at least 3-4 times higher than in those located further upstream. Accordingly, at a constant weathering rate, the release of previously stored elements from the rock glacier ice must be higher in the vicinity of this lowermost spring. As pointed out in our discussion paper, this could be due to the higher export of ice melt (line 503-510).

Comment 18
PDF, Tittle: the paper did not investigate the ice melt dynamics...see main comments

We agree that we need to reconsider the title. As pointed it out in our reply to Comment 1 of Referee 1, the recorded element fluxes reflect the export of ice melt, which does not necessarily occur at the same time as the ice melt itself. We thus strongly consider to remove this part of the title and describe the subtle difference between ice melt and its export more precisely in the discussion. This will be done when preparing an updated version of the manuscript.

Comment 19
PDF, line 12: since this is not a work dedicated to management, I suggest not stressing too much the limits for drinking water. Instead, I suggest to stress the issues related to drinking water and environmental concern (the limits are also surpassed for environmental quality standards!) not in the aims but, instead, in a dedicated section or part of a final paragraph

Comparing the solute concentrations with the drinking water limits helps the readers to understand the adverse water quality. However, it is a good suggestion to stress the issue related to the environmental quality standards as well as to present an additional paragraph on environmental issues. Since the exceedance of drinking water limits represent an important motivation for carrying out our monitoring efforts, however, we consider it important to mentioned this already in the introduction.

Comment 20
PDF, line 13: I would suggest a more general sulfide-bearing minerals here (pyrite is not the only one...)

It can be more generalize, as you mentioned. However, pyrite (FeS2) is a very important source for sulfuric acid because it is the most abundant sulfide and it has a metal to sulfide ratio of 2:1, causing the strong production of sulfuric acid (e.g. Bigham and Nordstrom, 2000). Consequently, it is safe to assume that it represents the main source of sulfate and consequently the main weathering agent (Wanner et al., 2018, 2023). Nevertheless, we will address the comment by stating "sulfide-bearing minerals such as pyrite" when preparing an updated version of the manuscript.

Comment 21
PDF, lines 17-18: this is definitely not true. Several studies suggest that the cause of enhanced solute export should be mostly attributed to ongoing weathering (see main comments). Inferring ice melt dynamics just from chemical tracers may induce strong biases in the conclusions of a research

The main cause of enhanced solute dissolution is indeed the weathering process. It is all about rock-water interaction. There is nothing against it in the current manuscript. We only emphasize that these solutes are temporally stored in the ice and are finally exported from their source area after melting and the infiltration of water into the system causing their hydraulic export. In our opinion, only such coupled sequence of processes can cause such a strong correlation between solute fluxes with rainfall events and snowmelt (Figure 8). An extended reply is provided in our response to Comments 1 and 16 of Referee 1.

Comment 22
PDF, line 19: I would be more general in this aim: to investigate the influence of thawing rock glaciers in downstream water quality...

We agree that aims and scope of the manuscript need to be revised. In our response to Comments 33 and 34 of Referee 1 it is described how we intend to reformulate them.

Comment 23
PDF, line 19: rock glaciers do not melt. The permafrost ice melts, rock glaciers thaw

Thank you for spotting this error; it should read "RG ice melt". This will be corrected.

Comment 24
PDF, line 22: located five km downstream from the rock glacier front

We agree that this information should be added here. We will do that when preparing an updated version of the manuscript.

Comment 25
PDF, lines 31-32: a conceptual model of accumulation and release of toxic elements from rock glaciers, to be validated in future studies

We agree that we should add something like this in the abstract. This will be done when preparing an updated version of the manuscript.

Comment 26
PDF, lines 33-34: but this is not demonstrated in your work, nor in other works

As written on line 33-34, we do not claim to have conclusively demonstrated that monitoring solute fluxes allows to estimate ice melt export rates. Instead we say that we *argue* that this opportunity exists and that future research should further test such approach. As detailed in the manuscript as well as in our reply to various comments of Referee 1, we are confident that our data allows to make such an open hypothesis. We would have no problem if it falsified in the future based on experimental data and field observations, but at the moment, in our opinion, it is consistent with all our observations.

Comment 27
PDF, lines 47-50: this can be shortened a bit

We agree. This will be done when preparing an update of the manuscript.

Comment 28
PDF, lines 55-61: geophysical methods are not part of the manuscript. Please shorten this part and only provide information relevant to your storyline

The geophysical methods are mentioned in this paragraph to show the limited knowledge in the estimation of ice melt contribution to the downstream discharge. As suggested in the manuscript, using the strong chemical signal

of solute export forms an interesting opportunity to get novel insights about the export of ice melt and permafrost degradation. In our opinion, it makes a lot of sense to list existing methods and their limitations in order to propose new approaches. Nevertheless, as we intend to narrow down the focus of the manuscript, we likely remove this part (see our reply to Comment 22 of Referee 2).

Comment 29
PDF, line 76: see also Brighenti et al., 2023, where a discussion on natural tracers for intact rg springs is discussed

We thank the Reviewer for pointing this out and we will refer to this publication when updating the manuscript.

Comment 30
PDF, line 78: see also Liaudat et al., 2019; Brighenti et al., 2019

We thank the Reviewer for pointing this out and we will refer to this publication when updating the manuscript.

Comment 31
PDF, line 88: sulfide-bearing minerals like pyrite

We agree. Accordingly, we will change it to "sulfide-bearing minerals such as pyrite".

Comment 32
PDF, line 91: note that these authors attributed the enrichment of solutes in some layers of the ice core to volcanic activities and metallurgy, i.e., not to bedrock weathering. The latter process was considered as a persistent but minor driver for solute concentrations in the RG ice!
Line 92: see also Del Siro et al., 2023

We admit that we did not sufficiently explain how our conceptual model differs from those of others. Such discussion will be added when preparing an updated version of the manuscript. In our opinion, we agree that atmospheric deposition as proposed in Nickus et al., (2023) and Siro et al. (2023) could contribute to some degree to the formation of sulfuric acid due to the emission of sulfur oxides from industrial activity (e.g. metallurgy) as well as during volcanic degassing (via e.g. acid rain). However, we consider it quite challenging to relate the high fluxes of major elements like Mg and Ca, also observed in our study area based on the very concentrations in the rock glacier springs (Table S5, Electronic Appendix), to such industrial or volcanic sources. Based on our previous experimental work (Wanner et al., 2023) but also based on a systematic monitoring of all rock glaciers springs in Austria only showing enrichment of Ni, Zn, Mn, Al and sulfate in pragneissic geological setting (Wagner et al., 2019), we consider it safe to assume that most of the solute fluxes reported in our study originate from rock weathering. If atmospheric deposition would be relevant, rock glacier springs in other geological settings would also show elevated concentrations of these elements, but at least in Austria, this was not the case (Wagner et al., 2019).

Comment 33
PDF, lines 96-97: this sentence is really strong, and needs at least some references to research that clearly demonstrated it! I am not aware of any study, though, even though something has been HYPOTHESIZED WITHOUT ANY EVIDENCE and, of course, needs to be demonstrated

The sentence summarizes the conclusions and implications of our previous study (Wanner et al., 2023). We agree though that we should present them as hypotheses that we want to test with the current study and not as a proven fact. We will update the manuscript accordingly.

Comment 34
PDF, lines 101-106: Please change this part by providing the aims of your work, and if applciable some research hypothesis. This part should build on the knowledge gaps outlined in the rest of the introduction.

The aims and scope of the discussion paper are provided in the previous sentence:

"To test this approach and to further assess the consequences of accelerated rock glacier melt on the stream water quality, we have initiated a detailed monitoring of a high alpine catchment in the Central Eastern Alps in Switzerland"

In contrast, the sentences the referee is commenting on provides an outlook for the remainder of the paper to motivate the reader to move on. Nevertheless, we agree that we should more clearly describe that the scope of this manuscript is to test the hypotheses that tracking solute fluxes may provide insights into the export of ice melt from rock glacier by setting up a flux monitoring similar as that described here (see our response to Comment 33 of Referee 1).

Comment 35

PDF, line 126: and other compounds, right?

Based on our previous study (Wanner et al., 2018, 2023) where we applied synchrotron-based high-energy X-ray diffraction and infrared spectroscopy, basaluminite is clearly the dominating phase of the white precipitates. The referee, however, is right in the sense that basaluminite can be enriched in trace elements like As, and Ni (max. 1500 ppm). Moreover, the precipitates typically show a significant silica concentration on the order of 0.5 to 2.5 wt% and it has been postulated that Si occurs as an individual SiO_2 phase and not as a trace element in basaluminite (Caraballo et al., 2019). Since the scope of the discussion paper is not on the white precipitates, we suggest to not add a detailed discussion on their composition and structure.

Comment 36
PDF, line 130: "white coatings occur" to not confound with precipitation/rainfall

Thank you for mentioning this; we agree that should be changed to "basaluminite precipitation" to avoid confusion with precipitation/rainfall.

Comment 37
PDF, line 134: very nice figure! the km scale has a reverse order? 2- 0 instead of 0-2

Thank you for spotting this, we will correct it.

Comment 38
PDF, line 145: do you have a picture of the entire catchment to show?

We do have one (see below). This picture will be added to the Electronic Appendix:

Fig. R6: Picture showing the upper part of the monitored catchment where flow direction of the stream is roughly from South to North (Fig. 2).

Comment 39
PDF, lines 148-151: this part belongs to study area

We agree, this can be moved to the very end of the "Site description" section, line 133 (See also our reply to Comment 8 of Referee 2)

Comment 40
PDF, line 168: one drop is not a specific amount...please provide the mL added or state that HNO3 was added until pH reached a certain value.

We agree, we will clarify that HNO_3 was added until the sample had a pH between 2 and 3.

Comment 41
PDF, line 191: why?

It is explained a few words earlier that "during wintertime, the discharge of the stream is very low, and the stream is periodically covered by snow and an ice layer rendering the readings of the probe unreliable." In our opinion, that answers the question, which means that the answer is already provided in the current version of the discussion paper.

Comment 42
PDF, line 194: how much? for how long? Can the data missing be identified in the figures?

Each data loss and unreliable data record of the probe is specifically mentioned in the caption of the related figures (Figs. 4 and 8). In our opinion, the answer to this question is thus already provided in the current version of the discussion paper.

Comment 43
PDF, lines 196-202: this method is unclear...how did you get the fitting parameter? what are the units of all parameters?

The referee is correct, this information was missing and will be added when preparing an updated version of the manuscript. The units of the parameters are as follows:
Q_t is the discharge at time t is in L/s, Q_0 is the discharge at time 0 in L/s, t is the time between Q_0 and Q_t are in seconds, and a is the fitting parameter (L^{-1}), which was achieved by the following formula:

$$a = \frac{log Q_0 - log Q_t}{0.4343\,t}$$

Comment 44
PDF, line 242: this was not described in methods

It is the relative discharge contribution AP5/AP10 normalized by the ratio of the two catchment areas (AP5: 1.33 km^2; AP10: 9.41 km^2). In our opinion, the relevant method here is the discharge measurement, which is described on lines 170 to 185. Moreover, the two catchment areas are provided in caption of Fig. 1 as well as on lines 150-151. In contrast, we do not think that taking a simple ratio needs to be necessarily explained in the method section.

Comment 45
PDF, lines 250-251: Since a figure of raw series of EC and Q at AP10 is missing, and would be esstential to validate the EC/metals relationships, I suggest to transform this table in a figure with different boxes corresponding to Discharge and EC at different locations.

We admit that the raw data regarding EC is not provided in a useful format although the raw EC data (and raw water table and discharge data) is provided as an excel file that can be downloaded (https://zenodo.org/doi/10.5281/zenodo.10558549). Accordingly, we plan to answer this comment by plotting the raw EC data on top of Figures 5,a,b (see Figs. R2, R4) and by adding the discharge measurement used for the corresponding correlation to Table S1, Electronic Appendix (The EC data is already provided in this particular table). In this context we like to emphasize we did not establish a EC vs. concentrations relationship for AP5 as described in our reply to Comment 9 of Referee 1.

Comment 46
PDF, Figure 3: normally the discharge-height are based on a power/exponential relationship...accordingly, the red point makes more sense than the blue points at high water table values...

Please see our response to Comment 11 of Referee 1. The red point shows the limitation of the probe to record the water table in winter time where part of the stream might be frozen, there might be snow cover, see comment 41. Furthermore, considering the width of the stream where the probe is installed, it is reasonable that up to a certain water height the record is not reliable.

Comment 47
PDF, line 277: there is no reason of comparing the observed values against drinking water standards. This belongs to the discussions section

We disagree. To put the measurements into perspective, we consider it helpful for the reader to list the limits in the same table. In contrast, we do not consider it useful to provide the measurements in two different tables once without and once with the limits. As pointed out in our response to Comment 19 of Referee 1, we plan to add a paragraph to the Discussion to discuss environmental issues in more detail.

Comment 48

PDF, Table 2: SO_4^{2-}...according to the EU legislation, a standard limit of 250 mg/L exists for sulfates...perhaps you can use this standard if sulfates are not covered by Swiss regulation?

Thank you for suggesting using the EU standard limit for sulfate. We agree that this information is useful so we will add the EU limit for sulfate to this table. Interestingly, the same limit was in place in Switzerland until 2017 before it was removed.

Comment 49
PDF, Figure 4: Similarly to Figure 3, I am not sure about the relationship type between EC and Ni/Zn. What does it happen to your outcomes if exponential relationship is applied? Does the linear model return the best fit when compared with other types of relationships?

In our understanding, the EC should linearly correlate with total dissolved solid concentrations (Rusydi, 2018). It follows that if the ratio between solute concentrations of a series of water samples remains the same, linear correlations should be observed between EC and individual solute concentrations, at least for a specific concentration range. Based on the correlations shown in Figs. 4a,b this appears to be the case for Ni and Zn. In fact, the plots below demonstrate that at AP10 the concentration of SO_4, representing the solute with the highest concentrations, shows strong linear correlations with our solutes of interest (Ni, Zn). This demonstrates that the corresponding concentration ratios (Ni/SO_4 and Zn/SO_4) remained very constant during the two monitoring years. Based on the arguments listed above and the good linear correlations between EC and the concentrations of Ni and Zn (Fig, 4a,b), for us it does not make sense to apply an exponential relationship, also because there is no physical reason for doing so.
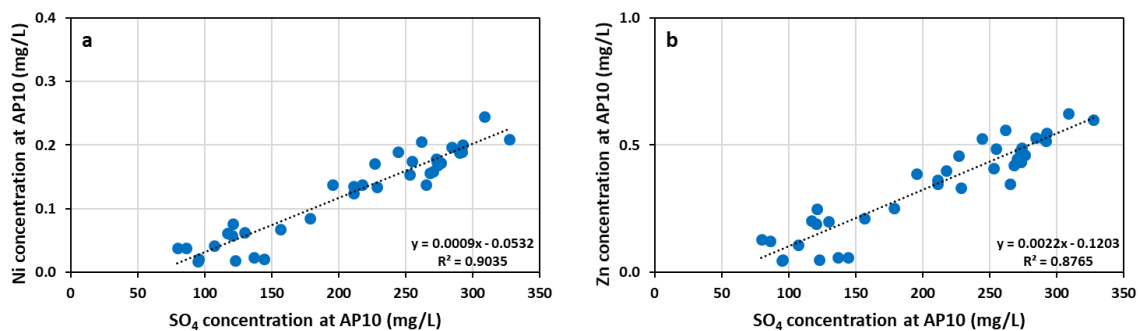
Fig. R7. Concentrations of SO_4 at AP10 plotted vs. those of (a) Ni and (b) Zn (Tables S1 and S2). The linear correlations are excellent indicating that the Ni/SO_4 and Zn/SO_4 ratios were very constant throughout the entire monitoring period.

Comment 50
PDF, Figure 5: the curves in a) appear unrealistic to me. Are you sure that concentrations peak during early summer, i.e., when most of snowmelt dilution occurs? Again, a raw figure on the EC and Q series at AP10 can help strenghtening these outcomes...

We are very sure about the concentration peaks in early summer because they are independently confirmed by the chemical analyses of the bi-weekly collected water samples (Table S1, Electronic Appendix). To emphasize this, the interpolated seasonal evolution of the measured concentrations are plotted in the Figure below (Fig. R8). For the updated version of the manuscript, we will add these actual measurements to the curves shown on Fig. 5 (see Fig. R4). The raw data of EC and Q will be presented in a condensed way in Table S1, Electronic Appendix (see our response to Comment 45 of Referee 1).
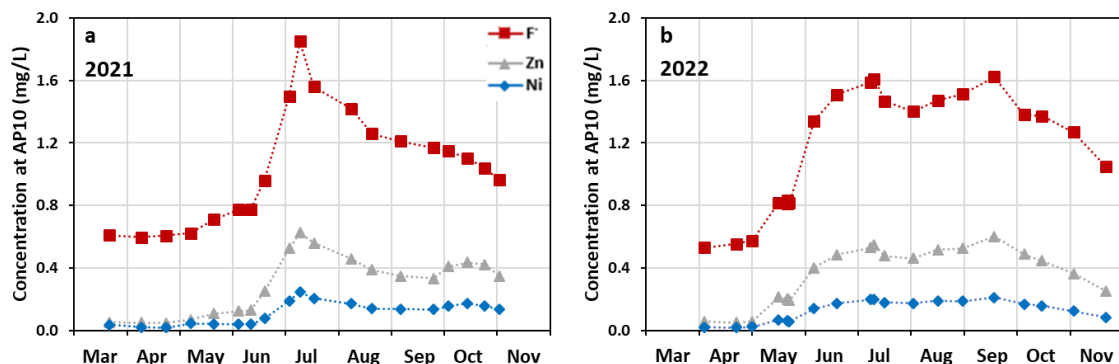
Fig. R8: Seasonal evolution of the concentrations of F⁻, Zn, and Ni at the downstream monitoring location, AP10, obtained from interpolation of biweekly water analysis (Table S1), (a) 2021, (b) 2022.

Comment 51
PDF, Figure 6: when looking at the points here, increasing trends of elements generally occur from June to October (and this behaviour agrees with what observed in other studies). This contrasts with Figure 5a, where treneds peak during early july!

Please see our response to Comment 10 of Referee 1.

Comment 52
PDF, line 385: a huge amount of literature warns about the conservative behaviour of solutes, particularly in glacial, periglacial, and permafrost environments!

As extensively discussed on lines 381-421, our interpretation regarding conservative vs. reactive behavior in the stream is based on our extended dataset consisting of seasonal concentration and flux measurements along the stream and not on literature review (see our Response to Comment 12 of Referee 1). In total, we have presented 47 water analyses, 18 flux measurements (plus numerous flux estimates based on the EC and water table data from AP10) and as outlined in our responses to various comments of Referee 1 we are convinced that we have well justified our interpretation.

Comment 53
PDF, line 388: the key point, in my opinion, is that there are some elements that are strongly related to the ionic strenght, and others not. The relation with EC might be related to the fact that anions are dominated by sulfates (i.e., proxy for sulfide oxidation)...in any case, the ocurrence of conservative behaviour does not imply that EC and TE are correlated, unless you can proof it with literature

As discussed in our response to Comment 12 of Referee 1, our interpretation of the conservative behavior of Ni and Zn is only subordinately based on the correlations between EC and solute concentrations. A more important argument for the conservative behavior of Ni and Zn is that the fluxes recorded at the upstream and downstream monitoring locations compare quite well for specific days (Fig. 7). This demonstrates that very little Ni and Zn is lost along the stream and that the fluxes recorded at the more accessible downstream location are useful to track the fluxes exported from the rock glacier at the source of the catchment (see discussion on this topic on lines 407-410).

In addition, we would like to emphasize that on the lines the referee is commenting on, we link the reactive behavior of Al and Mn inferred from the flux measurements at the up- and downstream monitoring location to the poor correlations between EC and these concentrations. In contrast, here we do not use the poor correlation to infer that these elements behave reactively.

Comment 54
PDF, line 408: these elements were found highly concentrated in white coatings of other rock glacier springs...Thies et al., 2018

Please see our response to Comment 12 of Referee 1.

Comment 54b
Line 409: but both concentrations and fluxes decrease when moving downstream...

While it is true the concentrations of Ni and Zn strongly decrease when moving downstream, the fluxes remain quasi-constant (Fig. 7). Together with the constant Ni/Zn ratio along the stream, this demonstrates their conservative behavior (Fig. R5, Comment 12 of Referee 1).

Comment 55
PDF, lines 428-429: this sentence needs references or to be supported by further evidence

We agree that this very important statement should be discussed in more detail. Therefore, we will add some of the arguments provided in our response to Comment 1 of Referee 1 when preparing an updated version of the manuscript.

Comment 56
PDF, line 436: water.

As explained in detail in Section 5.2 (lines 423-516, including Figure 10 and its caption), water from snowmelt and rainfall event enters the rock glacier systems and causes the hydraulic export of meltwater, enriched in solutes and reflecting the long-term accumulation of products from acid rock drainage.

Comment 57
PDF, lines 444-446: can you build more on this? Did other works suggest this process? This is interesting...the temperature may control the ice melt, whereas the water seeping into the systems exports the solutes...can you build a little bit more on this?

To the best of our knowledge, we are the first to report the simultaneous occurrence of solute flux and discharge peaks as well as the strong correlation between annual discharge rates and annual solute fluxes This is because, to our knowledge, solutes fluxes in such settings have not been systematically monitored so far. Therefore, we are also the first to try to provide an explanation for this observation. As discussed in our responses to Comments 1 and 5, however, we plan to expand on this by additionally discussing that part of the exported ice melt could reflect permafrost degradation from the previous summer that somehow "survived" at the origin of the stream (e.g. in the unfrozen base layer of the rock glacier) when preparing an updated version of the manuscript. Moreover, we plan to provide a discussion about how our conceptual model (Fig. 10) differs from those of others (see reply to Comment 32 of Referee 1).

Comment 58
PDF, Figure 9: this part belongs to results

Thank you for this suggestion. The flux and discharge curves are already provided in the results section. Accordingly, their comparison with the temperature data, in our opinion, should be part of the discussion because it shows that water infiltration into the system has a more direct effect on solute export than temperature variations. Alternatively, we could add the temperature curves to Figure 8, which is first referred to in the results section, and move Figure 9 to the Electronic Appendix because with such update all data would have been plotted on Figure 8 already. We will make a final decision on this point when updating the manuscript.

Comment 59
PDF, line 520: this paragraph mostly belongs to methods (mixing models) and to results. Please provide in the discussion only the information which is relevant for your storyline
Figure 11: This part belongs to results

Please see our response to Comment 3 of Referee 1.

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