1 **Response to referee comments of the manuscript bg-2012-631**

2 <u>Anonymous Referee #1</u>

3 We thank referee 1 for the effort invested in reviewing our discussion paper and are glad that he/she
4 found the data worth of publication. We consider that some key points have been misunderstood
5 and thus we would like to review these key aspects before addressing the general and specific
6 comments. In a revised version of the manuscript we have clarified better our approach and
7 objectives. Many of the comments of Referee #1 were related to the following 4 points and thus
8 there are references to them in our specific responses (Note that the text in italics refers to literal
9 comments by the referee and text in blue contains literal quotations from the revised manuscript):

10 **[1]** Our work was not a manipulation experiment, nor did we use an experimental design that is
11 readily amenable to analysis using traditional ANOVA statistics. Ours is a regional-scale study of a
12 boreal catchment with two groups of sampling locations (streams and riparian soils) in which flow-
13 weighted concentrations (see **[2]**) of base cations (BC) and silica (Si) were calculated. The goal of our
14 study was to better understand the relationship between solute concentrations in riparian zones (RZ)
15 of different landscape elements common to the Scandinavian boreal forest and the streams draining
16 those forests. Our design enables us to look at the strength of relationship between riparian zone
17 and stream chemistry from the headwaters to higher order streams and hence to gain insight into
18 the strength of the relationship between soil and surface water chemistry across a range of stream
19 orders. Our use of the term 'sample' refers to the physical bottles of water that were collected and
20 taken from the field. We do not wish to imply that these bottles of water correspond to a
21 statistician's sample. The use of the term 'site' to refer to the stream and riparian sampling locations
22 followed the published literature for the same catchment where our work was conducted (See for
23 example Ågren et al., 2007; Lyon et al., 2011; Grabs et al., 2012; Wallin et al., 2012). That is the
24 Krycklan Catchment Study (KCS) (http://www.slu.se/en/faculties/s/about-the-
25 faculty/departments/department-of-forest-ecology-and-management/research/krycklan-catchment-
26 study-new/). The revised manuscript includes a first mention as sample collection locations and then
27 they are referred to as sites ("Both the stream and RZ sample collection locations will be referred to
28 as sites hereafter").

29 **[2]** The Riparian Flow-Concentration Integration Model (RIM) has been used here as a conceptual
30 approach to calculate flow-weighted concentrations of BC and Si from RZ to streams and therefore
31 comparisons of modelled and observed values or model calibrations were not intended. Applying
32 RIM at the catchment scale usually requires calibrating its parameters on stream water chemistry
33 and flow data. However, when RIM is applied at the scale of a soil profile, as in our study, hydraulic
34 parameters [obtained from groundwater level-discharge relationships (see Page 747 Lines 14-25 and
35 Page 748 Lines 7-12 in the discussion paper)] and concentrations can be measured in-situ and no
36 calibration is needed. Our method is a modification of the routines presented in Grabs et al. (2012).
37 We believe the calculations were well described in the original manuscript and follow a published
38 method that can be read in the given references (see Page 742 Lines 14-21 in the discussion paper). A
39 conceptual figure that explains the RIM concept has been added to the revised version of the
40 manuscript (see also below Fig. 1, an extended figure of the one presented in the revised
41 manuscript). For detailed information about the RIM concept see also Bishop et al. (2004), Seibert et
42 al. (2009), and Grabs et al. (2012). The few allusions of RIM as a model that we had in the original

version of the manuscript have been removed in the revised version to avoid misunderstanding. The way in which the RIM approach calculates flow-weighted concentration (or fluxes) for RZ is analogous to the way in which flow-weighted concentrations (or fluxes) are calculated in streams or rivers. ("RIM takes point measurements of chemical concentration at a series of depths and then performs an interpolation to provide a continuous estimate of chemical concentration at all depths in the RZ. This chemical concentration profile is then multiplied by an estimated lateral discharge profile to derive volume weighted concentration or flux estimates for an entire RZ profile. Conceptually, RIM is very similar to the process of estimating riverine fluxes in which point measurements of chemical concentration are interpolated through time to provide a continuous chemical time series which is then multiplied by a continuous flow record to estimate fluxes. While RIM integrates over depth, riverine flux estimation integrates over time"). In summary, the product of concentration and flow weight (flow weights are dimensionless and proportional to the incremental lateral specific groundwater discharge rates) is integrated below a modelled groundwater level in a daily basis to obtain daily flow-concentrations. The sum of all daily flow-concentrations divided by the sum of all daily flow-weights results in an annual flow-weighted concentration. If the annual flow-weighted concentration was multiplied by the total specific discharge (see **[3]**) one would obtain an annual flux (export). Because we assumed the specific discharge to be the same in all sampling sites (stream and riparian) (see **[3]**), the fluxes would be all proportional to the flow-weighted concentrations calculated here. Consequently, mass balances in headwaters between riparian zones and streams are valid assuming that the flow-weighted mass of BC and Si at the outlet of the headwater stream should be equal to the flow-weighted mass of BC and Si leaving the soils at the edge of the aquatic-terrestrial compartments, i.e. the RZ (which is what we calculated using the RIM approach). That means we investigated whether streams were conservative representatives of what comes out from riparian zones. However we decided to use the term "net fluxes" instead of "mass balances" in the revised manuscript to avoid misunderstandings.

[3] Discharge was measured at one of the stream sampling sites (C7) and the areal-specific discharge was calculated as measured discharge divided by the area of the subcatchment where the discharge was measured (C7) and then assumed to be the same all over the catchment. That means that flow in the other subcatchments (i.e. at the other stream sampling sites) can be estimated by prorating based on their relative areas, i.e. by multiplying the areal-specific discharge from C7 by the catchment area drained by the specific stream. This is a well-known and common practice in catchment science and hydrology. The uncertainties of using this method were well-described in the original manuscript (see Page 746 Lines 9-17; Page 758 Lines 23-28; Page 759 Lines 1-3) and supported by many published studies that used the same approach in the same catchment where our work was conducted, i.e. KCS (Ågren et al., 2007; Björkvald et al., 2008; Köhler et al., 2008; Wallin et al., 2010). We have also added in the revised manuscript two new references as examples of studies that have used this approach elsewhere (Bayley et al., 1992; Landre et al., 2009). There is work in progress in KCS to measure discharge at more subcatchments but unfortunately this was not started in 2008 and 2009 when our study was conducted and the prorating of specific discharge was the best approach with the available data.
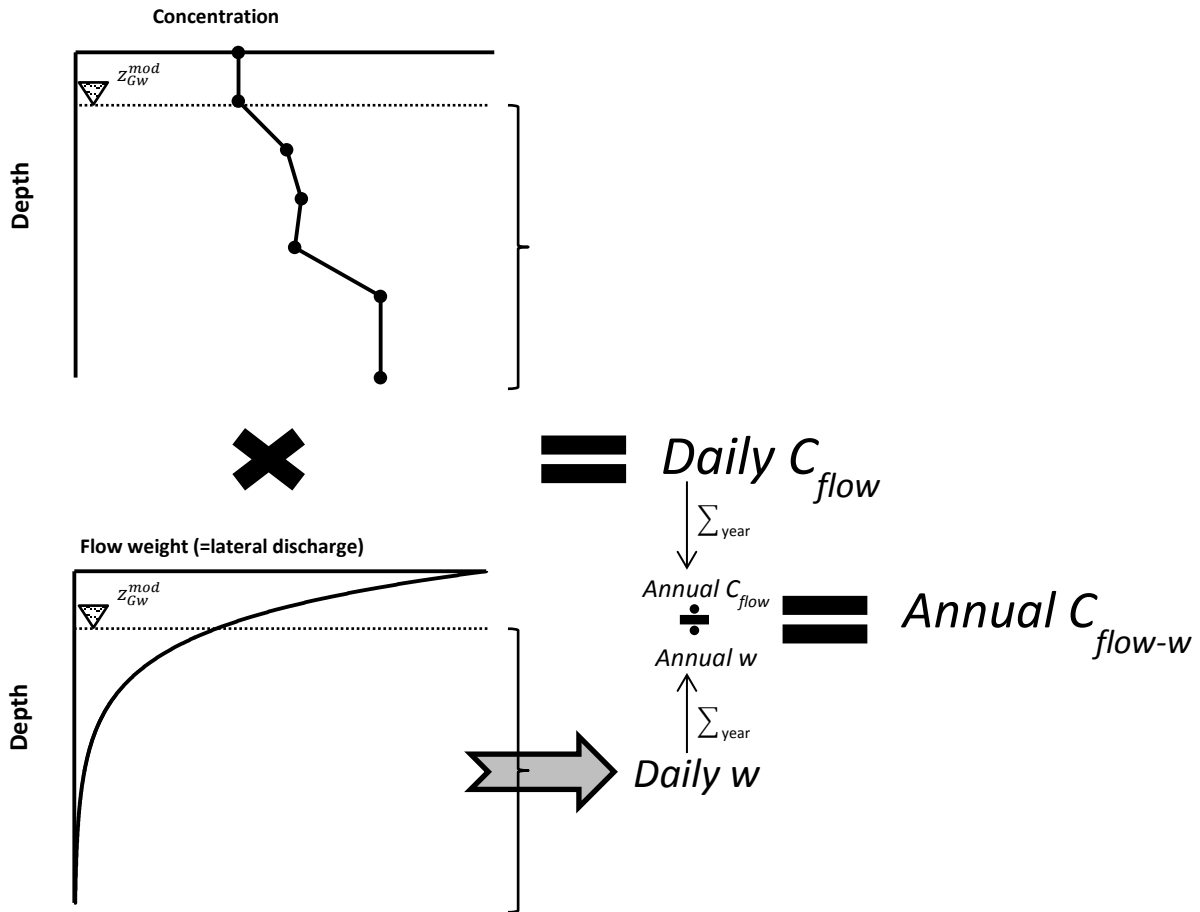
83

Fig 1. "Schematic representation of how the RIM approach was applied to calculate annual flow-weighted concentrations (C_{flow-w}) from riparian soil profiles. The product of concentrations and flow-weights is integrated below the modelled groundwater table (z_{Gw}^{mod}) in a daily basis to obtain daily flow-concentrations (C_{flow}). Daily flow-weights (w) are obtained by integrating flow-weights below (z_{Gw}^{mod}) in a daily basis. Annual C_{flow-w} is the result of dividing the summation of daily C_{flow} by the summation of daily w over a year".

[4] For clarification, we have rephrased the focus and objectives of the paper in the revised form of the manuscript, which states as follow at the end of the introduction section: "Here we present a two-year study of flow-weighted concentrations of BC and Si from RZ and streams in a boreal landscape in northern Sweden. This is the first application of RIM to study BC dynamics in forest soils and streams. The studied systems range from first order headwater streams in till soils to catchments of third and fourth order streams underlain by silty sediments. The main objective of the study was to better understand relationships between BC and Si in RZ soils and adjacent surface waters. Specific objectives were to: (1) identify temporal and spatial trends in BC concentrations in RZ draining different landscape element types, (2) identify spatial differences in BC flow-weighted concentrations from streams dominated by different landscape element types, (3) investigate whether RZ element concentrations represent flow-weighted concentrations in headwater streams, and (4) test the sensitivity of riparian flow-weighted concentrations to changes in groundwater levels as potential effects of forest management and climate change." Moreover, a conclusion section that gathers the most important findings in relation to the objectives and suggestions of future investigations have been added at the end of the revised manuscript.

3

General comments

Overall, the manuscript addresses base cation concentrations in forested catchments, including selected riparian zones and streams. Identifying catchment contributing areas, such as upslope forests and riparian zones, is important to assess the roles of forest harvesting and climate change on to streamflow and water quality in boreal and temperate biomes. In this regard, data contained in the manuscript may be worthy of publication; but not in its current format. For example, I am not convinced the adequate statistical design was used in the study. Granted, you have a partially nested catchment study, but I am left to wonder what your experimental units were and how they were stratified across sub-catchments. There are at least four levels of site cited in the text, including riparian zone, stream, wetness, and soil; with no mention of experimental units. If each riparian zone is a 'site' then the study is not replicated. It also seemed like comparisons among riparian zones, streams, wetness, and soil types were all trying to be haphazardly attempted with a limited dataset. I believe testable hypotheses, with the appropriate statistical design needs to be clearly stated, around which the paper should focus. This includes consistency in statistical terminology.

We believe our study goals to be very different to those of McLaughlin (2009). He established lysimeters transects at 25 cm depth in two riparian zones in differing forest types. We performed a regional survey of riparian zones in different boreal landscape elements so as to better understand the linkages between streams and their catchments. To do this, we established single lysimeters arrays at a range of depths in a number of near-stream sites throughout the Krycklan catchment. For better or worse, our study cannot be appropriately analysed using traditional ANOVA models. We hope that we have clarified this point. The objectives of the paper have been reformulated and stated clearly in the revised form of the manuscript (see **[4]**). The statistical terminology in the original manuscript could have misled the interpretations of the reviewer. In the revised version of the manuscript we have been very careful with the statistical terminology. We have conducted a new statistical analysis that calculates the contribution to the variance in campaign concentrations of riparian site classes, depth, and sampling campaign, i.e. spatial and temporal components ("Spatial and temporal trends in BC and Si concentrations were investigated following the approach presented by Futter et al. (2011) to partition variation between different sources. A series of analyses of variance (ANOVAs) were performed so as to estimate the relative contribution of riparian site class, riparian site, depth in the profile, and sampling campaign to the total variation in BC and Si campaign concentrations. The fraction of total variation ascribed to each component was equal to the sum of squares for that component divided by the total sum of squares from the ANOVA."). We elected not to perform any assessments of ANOVA significance due to the difficulties in unambiguously identifying the appropriate statistical design. In principle, a survey such as the one we present can be analysed as a multi-dimensional repeated measures design with missing values in which there are repeated measurements (1) for each chemical analysis, (2) over depth in the soil profile, (3) over time, and (4) among lysimeters. We believe that the appropriate assignment of probability values in such an analysis is a research question for statisticians and lies outside the scope of the biogeochemical data and analyses presented here. See also **[1]**.

We also believe our dataset is not limited but extensive. We are not aware that a similar dataset exists for stream and especially riparian zones.

146 *I also believe the methods require more in-depth description because I was confused as to the focus of*
147 *the paper. For example, were you trying to calibrate RIM for base cations in riparian zones or using it*
148 *as a guide to understand riparian zones and identify uncertainties for future studies? Given that this*
149 *was the first application of base cations using RIM, I wonder why (1) few data were presented that*
150 *compare modeled versus measured concentrations and fluxes, (2) only a pedestrian view of the model*
151 *description was presented, and (3) statistical and conceptual bases of the assumptions were not*
152 *thoroughly described and tested? These are particularly important given that discharge estimates*
153 *from one stream were used to calculate flow-weighted base cation concentrations for all riparian*
154 *zones and streams.*

155 We were not trying to calibrate RIM but more to use it "as a guide to understand riparian zones and
156 identify uncertainties" as the reviewer points out. The objectives and focus of the paper have been
157 reformulated and stated clearly in the revised form of the manuscript (see **[4]**). All the limitations of
158 the RIM approach had been honestly discussed in the original manuscript (see section "5.3
159 Uncertainties in the riparian flow-weighted concentration estimations" in the discussion paper). See
160 also **[2]** and **[3]**.

161 We believe no more description of the methodology is needed as a large proportion of the methods
162 follow the cited literature (see Bishop et al., 2004; Seibert et al., 2009; Grabs et al., 2012). However
163 we have taken into account the reviewer comment by introducing a new figure that conceptualizes
164 the calculations using the RIM approach in the revised manuscript and adding a few lines in the
165 introduction that compare the way of calculating fluxes with RIM as analogous to the traditional
166 calculation of fluxes in streams or rivers ("RIM takes point measurements of chemical concentration
167 at a series of depths and then performs an interpolation to provide a continuous estimate of
168 chemical concentration at all depths in the RZ. This chemical concentration profile is then multiplied
169 by an estimated lateral discharge profile to derive volume weighted concentration or flux estimates
170 for an entire RZ profile. Conceptually, RIM is very similar to the process of estimating riverine fluxes
171 in which point measurements of chemical concentration are interpolated through time to provide a
172 continuous chemical time series which is then multiplied by a continuous flow record to estimate
173 fluxes. While RIM integrates over depth, riverine flux estimation integrates over time"). We have also
174 introduced two new equations to get more explicit understanding of the calculations. Moreover we
175 have incorporated a small section of that gather all the information regarding the sampling
176 procedure at the beginning of the methodology section in the revised manuscript that may help the
177 reader.

178 *Finally, the manuscript requires major restructuring. For example, I suggest an overall objective with*
179 *hypothesised conditions and how they were addressed in the study to be clearly articulated in the*
180 *Introduction. The Discussion is primarily a revisiting of the Results without any discussions of model*
181 *calibration/corroboration with field data or applying results to intensified forest harvesting or climate*
182 *change, although these were important reasons justifying the study in the Introduction. There are*
183 *also a number of occasions in the Discussion where a concept is mentioned once then dropped; I was*
184 *left to wonder what point was being made.*

185 The objectives and focus of the paper have been reformulated and stated clearly in the revised form
186 of the manuscript (see **[4]**) and no model calibration/corroboration was intended. See **[2]**.

187 The restructuring of the manuscript also includes a revised version of the old section "5.6
188 Implications for surface water quality and further investigations" which now stands as "5.6 Potential
189 implications for surface water quality". Here we have related results with intensified harvesting and
190 climate change. We have narrowed the discussion to changes in groundwater levels potentially
191 caused by forest management and climate change but no other specific changes. Moreover, we have
192 added in the revised manuscript a new section named as "6. Concluding remarks and further
193 investigations" that repeats the main results and interpretations to help the reader, which also
194 contains suggestion for future research.

195 **Specific comments**

196 **Abstract**

197 *Page 740 Lines 9-22: why not use "organic" versus "mineral" deposits as the riparian types to*
198 *compare and then use the number of each type as your plots?*

199 The spatial comparison between riparian sampling sites was presented in the result section "4.1.1
200 Spatial variation" and discussed in the discussion section "5.1.1 Spatial variation". This has been
201 slightly modified by introducing the new analysis described in lines 130-136 of this response
202 document.

203 *Line 13-16: if Mg/Ca ratio provides a distinct upslope mineralogical signal, why is this not part of the*
204 *study. Also, in the Results and Discussion, you talk about stream Mg/Ca being similar to soil solution*
205 *in the riparian zones. Which was is it, or is it both and upslope and riparian contributions cannot be*
206 *detected based on the current study design? Were Mg/Ca stable throughout the sampling period?*
207 *Define "good". This is a subjective term, where one person's interpretation may differ from another's.*
208 *What data support the predictability of the model?*

209 Upslope data were not available and the upslope mineralogical signal is our interpretation of the
210 results. We used the Mg/Ca ratio to investigate homogeneity within a catchment comparing stream
211 and soil water. Changes in Mg/Ca ratio could indicate ion-exchange reactions but in our study we
212 observed a temporal and spatial stability in the Mg/Ca ratio. There was only one riparian sampling
213 site that deviated from the general pattern, and this site also presented a different mineralogy.
214 Because the ultimate origin of these elements is weathering reactions from minerals we believe the
215 water is imprinted by a mineralogical signal. In our study we show that this signal is not changed
216 through the riparian zone by ion-exchange reactions because a near equal Mg/Ca ratio was seen in
217 the streams. We did not use other element ratios due to the following reasons: K is a more dynamic
218 element that is easily released taken up by plants and Na might be influenced by salt rich rain
219 episodes. Mg/Ca ratios were stable throughout the sampling period as could be seen in Figure 6 in
220 the discussion manuscript. We also argue for the use of the Mg/Ca ratio in the revised manuscript
221 ("We used the Mg/Ca ratio to investigate homogeneity within the catchment. Changes in Mg/Ca
222 ratio could potentially indicate ion-exchange reactions but our results showed temporally and
223 spatially stable ratios in all riparian sites and depths (Fig. 7), with the exception of site R9. The fact
224 that this site also had a different mineralogy indicates that the riparian soil solution is strongly
225 imprinted by a mineralogical signal [...]. Water of mineral soil origin supports the transmissivity
226 feedback concept (Rodhe, 1989; McDonnell et al., 1998; Laudon et al., 2004; Bishop et al., 2011) in
227 which upslope 'old' or 'pre-event' water (i.e. groundwater) is the main source of RZ [...].The near-

228 constant Mg/Ca ratio and stability in the stream sites indicate that the mineralogical signal is
229 subsequently maintained in the surface waters of the catchment in all flow conditions (Fig. 7). We
230 interpret these stable patterns as a result of distinct mineralogical upslope signals integrating the
231 chemical erosion signals of biological and chemical weathering that are not changed through the RZ
232 by ion-exchange reactions").

233 We agree; "good" is probably a subjective term and the sentence has been changed to "Flow-
234 weighted concentrations of Ca, Mg, and Na in headwater streams were represented by the
235 corresponding RZ flow-weighted concentrations, which were estimated using the Riparian Flow-
236 Concentration Integration Model (RIM) approach. Stream and RZ flow-weighted concentrations
237 differed for K and Si suggesting a stronger biogeochemical influence on these elements including K
238 recirculation by vegetation and retention of Si within the RZ." The terms 'predictions' and 'model'
239 have been removed as they were confusing.

240 *Lines 20-24: do these data mean more riparian influence at larger streamflow? How is this*
241 *differentiated from upslope contribution? Could it be that near-surface soil in the upslope areas*
242 *contribute to chemical dilution during rapid runoff? Also, what about surface flow through riparian*
243 *zones?*

244 That is related with the explanations in Page 761 Line 15-26 but the sentence has been removed
245 from the abstract in the revised manuscript to avoid misunderstanding. See also previous response.

246 Overland flow through riparian zones was discarded and had been extensively discussed in the
247 manuscript (Page 760 Lines 5-20).

248 *Lines 22-24: I am not convinced that results as presented justify this conclusion.*

249 This is not a conclusion but a suggestion of future research and follows the guidelines for authors in
250 Biogeosciences ("The abstract […] provides future directions where research could focus on in the
251 near future" in http://www.biogeosciences.net/submission/manuscript_preparation.html). However,
252 as both reviewers suggested removing it we have done so.

253 *You may want to synthesise lines 13-20 into a hypothesis.*

254 The objectives and focus of the paper have been reformulated and stated clearly in the revised form
255 of the manuscript (see **[4]**).

256 **Introduction**

257 *Page 741 Line 4: define "good"*

258 The sentence has been rephrased and a reference has been added ("The RZ is important for habitat
259 function (Gundersen et al., 2010) as well as in…").

260 *Lines 6-8: do you mean more upslope contributing area?*

261 In this case by saying "recharge" we meant "upslope" so it has been changed in the new version of
262 the manuscript.

263 *Line 10: what does the riparian zone buffer?*

264   They buffer acidity. This has been added in the revised manuscript.

265   *Line 15-17: I am not sure what you mean by a third paradox. Please explain what this means.*

266   This sentence has been removed in the revised manuscript as it was confusing and needed further
267   explanations not relevant for the study.

268   *Lines 19-25: So what? Is this going to be the riparian process studied? If so, make this transition to the*
269   *above paragraph.*

270   The transition between paragraphs has been reformulated according to the suggestion.

271   *This page needs to be re-structured. You may want to point out that riparian zones provide multiple*
272   *ecosystem services, such as (1) pollutant adsorption (inorganic and organic), (2) nitrogen retention,*
273   *(3) acidity buffering, and (4) organic matter transfer to streams.*

274   We believe all of those points were made in the original version of the manuscript (see Page 741
275   Lines 10-13 of the discussion paper) but this has been stressed in the revised manuscript by adding
276   that they are important ecosystem services ("The RZ also influences stream organic carbon dynamics
277   much more than upland soils (Dosskey and Bertsch, 1994; Köhler et al., 2009) and provides important
278   ecosystem services in vulnerable headwaters (Ågren and Löfgren, 2012). It can act as a buffer of
279   acidity (Löfgren et al., 2011), or sink for inorganic nitrogen (Fölster, 2000; Petrone et al., 2007; Futter
280   et al., 2010) and retain organic pollutants (Bergknut et al., 2011) or metals such as aluminium
281   (Pellerin et al., 2002; Ross et al., 2008).").

282   *Page 742 Lines 1-13: Olsson et al. (1993) was a field study, was it not?*

283   We believe Olsson et al. (1993) used a modelling approach in their study.

284   *Line 9: what is the "transmissivity feedback mechanism"?*

285   This concept has been explained better in the new version of the manuscript ("In boreal forest till
286   soils, strong increases in saturated hydraulic conductivities towards the soil surface can cause
287   dramatic increases in the lateral flow movement to the stream as precipitation or snowmelt events
288   cause the groundwater table to rise and soil water to enter the stream via highly conductive
289   superficial soil layers in the RZ. This phenomenon is known as the 'transmissivity feedback
290   mechanism' (Rodhe, 1989; Bishop, 1991; McDonnell et al., 1998; Bishop et al., 2011). The
291   transmissivity feedback mechanism results in a large mobilization to the stream of 'old' or 'pre-event'
292   water during rainfall or snowmelt events (Laudon et al., 2004).") The given references in the text
293   provide further information (see also Bishop et al., 2004).

294   *Lines 14-21: is RIM a conceptual or mathematical model? Why study this? What is the importance of*
295   *base cations and their potential depletion? I suggest framing questions in terms of concerns about*
296   *base cation depletion and coupling (integrating) upslope and riparian zones as contributing source*
297   *areas.*

298   With the RIM version that we have used, a mathematical implementation of a concept allows us to
299   calculate flow-weighted concentrations from riparian zones (see also **[2]**). The transitions between
300   paragraphs in the introduction section have been corrected in the revised manuscript.

Line 26: why is this first mention of Si? Why is it different from base cations?

Si is presented before in the text in the revised manuscript ("The behaviour of Silica (Si) in boreal forest soils and streams is similar to that of BC (Oni et al., 2013). However, unlike BC, Si in boreal forest soils and streams is derived almost exclusively from mineral weathering"). It is introduced in the study because BC and Si dynamics are similar and the ultimate source of both BC and Si is weathering. The difference is that for Si weathering is the only source while BC might come from deposition. The deposition of BC in the area studied is low and therefore BC and Si dynamics are closely link together.

Page 743: Lines 1-5: if this is the first attempt to model base cations, why is model performance not included? I think that should be the first objective.

It is the first application of the RIM concept/approach to BC but not an attempt to model them. See also **[2]**. The objectives and focus of the paper have been reformulated and stated clearly in the revised form of the manuscript (see **[4]**).

An overarching objective is needs, with your hypothesised conditions, and how your study addressed hypotheses.

The objectives and focus of the paper have been reformulated and stated clearly in the revised form of the manuscript (see **[4]**).

Study area

Page 743 Lines 20-21: ": : :forest (87%), wetlands (9%), and lakes (1%) are not land uses, but site types or cover types.

We agree and have changed to cover types as suggested.

Lines 23-26: is straightening channels a limited impact?

The impact of straightening the channels is unknown and would merit further research out of the scope of our manuscript. We have changed the sentence in the revised manuscript so it is not implicit that straightening is a limited impact ("Although Krycklan has remained rather pristine, human activities have influenced the catchment similarly to other forests in the region. Many headwater streams in Northern Sweden were straightened and deepened to improve drainage and forest productivity during the early 20th century (Dahlström, 2005)").

Page 744 Lines 2-4: any information on annual timber removals?

The central part of the catchment (around 25 % of the total and where most of the riparian sites are located) is not harvested at all. From the rest, 1 % is harvested per year on average.

Lines 9-10: where are these located? Scots pine, Norway spruce, and birch make up 100% by your designation, so how can there be peatlands?

The percentages were given as tree volume percentages (see Page 744 Line 6 of the discussion paper) and therefore make up 100%. Their locations were also clearly stated (see Page 744 Lines 7-9).

337 *Lines 13-15: If rivers and incised, should this not be relative to stream water height?*

338 We do not understand what the referee meant here and therefore we cannot provide an adequate
339 answer.

340 *What do you mean be "Riparian Observatory"?*

341 We mean a network of lysimeter arrays. The sentence has been rephrased for better understanding
342 ("A network of lysimeter arrays (hereafter referred to as Riparian Observatory in Krycklan; ROK) was
343 established in 2007 to obtain a better understanding of the RZ influence on stream water.").

344 *Line 25: OK, so you have nested catchments, what was the design for your study? Why are there no*
345 *characteristics of the riparian zones?*

346 See **[1]**, **[2]** and **[4]**.

347 We did not present all the riparian zone characteristics because they were presented in Grabs et al.
348 (2012). Our manuscript includes already much information already presented in that study and we
349 do not want to be too redundant. However, more information describing the riparian sampling sites
350 organic characteristics has been added to the revised manuscript ("Ten of the instrumented sites
351 were located in till soils, two in the sediment part of the catchment and one in the transition
352 between sediment and till (Fig. 1). [...] Most of the riparian sampling sites located in till soils and the
353 transition site had a thick peat layer (≥ 30 cm), whereas the sites located in the sediment area had
354 very shallow organic horizons over mineral soils").

355 *Lines 26-28: why was sampling only conducted twice during spring?*

356 Thomas Grabs and collaborators did a tremendous work installing the riparian sampling sites and
357 sampling them in 8 occasions, for which reason we have a tremendous dataset to work with now.
358 The sampling of these sites is time (and therefore money) consuming and many logistical constraints
359 prohibit the sampling to be carried out as many times as we wish. During spring most of the sites are
360 inaccessible and during winter the snow and the darkness prevent the sampling. We aspire to do this
361 in the future.

362 **Study design**

363 *Page 745 Study design: what are your hypotheses and statistical design – i.e., experimental units,*
364 *random or fixed effects, balanced or unbalanced?*

365 Our focus is on flow-weighted concentrations of BC from riparian zones and streams to get an
366 understanding of the terrestrial and aquatic compartments and the link between them. See also **[1],**
367 **[2]**, and **[4]**. Also, the heading of this section has been changed in the revised manuscript from "study
368 design" to "methodology" to avoid misunderstanding.

369 *What are the upslope/riparian zone proportions in the catchments?*

370 This is a work in progress and the exact proportions are unknown. Preliminary estimations indicate
371 that the RZ proportions could be between 10-20% in the upper till part of the catchment and below
372 5% in the lower silty sediment areas.

373 *Lines 15-19: why not use groundwater if that contributes mostly to streamflow?*

374 The soil layers that contribute mostly to streamflow are those immediately below the groundwater
375 table because of the "transmissivity feedback mechanism" (see above explanation of this concept in
376 lines 285-293 of this response document). Soil water samples were collected at 5 different depths
377 below the soil surface at the different riparian sampling sites (15 cm, 30 cm, 45 cm, 60 cm, and 75
378 cm). The groundwater tables that we measured and subsequently modelled were not below 75 cm in
379 any of the sites (90th percentiles; see figure 4 and figure 5 of the original manuscript). Thus, the layers
380 that mostly contributed to the streamflow were all covered by our sampling routine.

381 *Lines 23-26: why annual if spring runoff differences occurred between years? How does RIM calculate*
382 *flow-weighted averages? Why not use volume-weighted from the volume of water in the lysimeters?*

383 A conceptual figure that explains the calculations has been added to the revised version of the
384 manuscript. See also **[2]**.

385 *Page 746: Lines 1-5: I am not sure what is meant here. Why were fluxes not calculated and what*
386 *about including mass balances?*

387 This section has been rewritten in the revised manuscript for better understanding. The way in which
388 the RIM approach calculates flow-weighted concentration (or fluxes) is analogous to the way in
389 which flow-weighted concentrations (or fluxes) are calculated in streams or rivers. If the annual flow-
390 weighted concentration was multiplied by the total specific discharge one would obtain an annual
391 flux (export) but we decided give values of flow-weighted concentrations. See also **[2]** and **[3]**.

392 *Lines 10-12: why only stream C7 and I am not convinced your assumption is valid.*

393 Unfortunately C7 was the only site with valid measured discharge. There is work in progress that
394 intend to measure discharge at some of the other subcatchments and this will hopefully improve
395 future research. In the meantime, this assumption is the best approximation that we had, which has
396 been implemented in several published articles for the same catchment. Some of these references
397 are Ågren et al. (2007); Björkvald et al. (2008); Köhler et al. (2008); Wallin et al. (2010). See also **[3]**.

398 *Lines 13-18: where were uncertainties estimated from and how were they transferrable to your*
399 *study? Combined, the total error may be large. Have the referenced studies used discharge*
400 *measurements for one sub-catchment to apply to others?*

401 The uncertainties and the references studies are from the same catchment.

402 *Lines 20-23: how was specific discharge measured? What were the experimental units?*

403 Areal-specific discharge is not measured but calculated as measured flow divided by the area of the
404 subcatchment where the flow was measured and then assumed to be the same all over the
405 catchment. See also **[3]**.

406 *Page 747 Lines 210: again, define experimental units. Why scale and not just code as missing values?*
407 *What is the certainty of the scaling factor?*

408 For a given time, a single concentration value is needed at every depth in order to perform our
409 calculations with RIM (see **[2]**). When, during a sampling occasion, a concentration could not be

410 measured at a certain lysimeter one can still use the concentrations measured at its replicate to
411 estimate a full concentration depth profile. This can be done by either direct linear interpolating
412 using the single lysimeter concentration value as campaign concentration or by first estimating a
413 value for the 'missing' lysimeter to obtain an estimated campaign concentration and then linearly
414 interpolating. This latter procedure was preferred by Grabs et al. (2012) (the Biogeosciences
415 publication in which our work is based on) because it better preserved the general shape of
416 concentration-depth solute profile and ensure that the small differences that could exist between
417 the measurements of two lysimeters located at a given depth are taking into account. This was
418 applied to dissolved organic carbon (DOC) concentrations and applying the same procedure also in
419 this study not only makes the results more comparable to those obtained by Grabs et al. (2012) but it
420 is expected that the procedure works even better for BC and Si as they exhibited considerably less
421 temporal variability than DOC (Grabs et al. 2012).

422 The use of the scaling factor had surely very little effect in the final results because: (1) we calculated
423 also potential maximum and minimum flow-weighted concentrations which within range include the
424 small differences that could result in the average flow-weighted concentration calculated using single
425 lysimeter values when only one was available instead of scaling factors, and (2) the variability in
426 concentrations for most depths, sites and elements was low as explained in the original manuscript
427 (Figures 4 and 5; Page 740 Lines 12-17; Page 751 Lines 23-27; Page 757 Lines 2-3; Page 759 Lines 5-
428 11).

429 *Lines 13-17: what does 'binned' mean? A justification for using discharge from one stream to scale all*
430 *riparian zones and streams is needed.*

431 Data binning is a data pre-processing technique used to reduce the effects of minor observation
432 errors. The original data values which fall in a given small interval, a bin, are replaced by a value
433 representative of that interval, often the central value (Wikipedia). It is a form of quantization. For
434 more information about this method see Grabs et al. (2012). We believe justifications to used specific
435 discharge were clearly stated in the original manuscript (see Page 746 Lines 7-17; Page 758 Lines 22-
436 28; Page 759 Lines 1-3). See also **[3]**.

437 *Lines 22-24: if you are calling riparian zones sites, then there is no replication in the study.*

438 The use of the term 'site' to refer to the stream and riparian sampling sites followed the published
439 literature for the same catchment where our work was conducted (See for example Ågren et al.,
440 2007; Lyon et al., 2011; Grabs et al., 2012; Wallin et al., 2012). That is the Krycklan Catchment Study
441 (KCS). The revised manuscript includes a first mention as sampling sites and then they are referred as
442 sites. See also **[1]**.

443 *Page 748 Lines 1-11: Justifications for the assumptions are needed.*

444 This procedure follows the same assumptions and routine presented in Grabs et al. (2012). The
445 shallowest depth in which we measured soil water chemistry was 15 cm. One could make many
446 different assumptions but we choose constant concentrations between the shallowest measurement
447 and the soil surface. This cannot be proven wrong or true. We believe it does not need further
448 justification, it is reasonable and used a published method.

449 *Lines 13-24: How do the model numbers compare to those collected from the field?*

450 That was not intended. See also **[1]**, **[2]** and **[4]**.

451 *Page 749 Line 13: what are 1.96 standard deviations?*

452 Those are the 95 % confidence intervals.

453 *Line 15: why are riparian zones and streams both referred to as site?*

454 They both refer to sampling sites. The use of the term 'site' to refer to the stream and riparian
455 sampling sites followed the published literature for the same catchment where our work was
456 conducted (See for example Ågren et al., 2007; Lyon et al., 2011; Grabs et al., 2012; Wallin et al.,
457 2012). That is the Krycklan Catchment Study (KCS). The revised manuscript includes a first mention as
458 sampling sites and then they are referred as sites. See also **[1]**.

459 *Page 750 Lines 5-15: what was the experimental design for riparian zones? Do they not consist of*
460 *different soil characteristics? There are no replicates as presented. Maybe consider 'organic' versus*
461 *'till'?*

462 We used the same riparian zones presented in Grabs et al. (2012). Literally from Grabs et al. (2012):
463 "The sites were located based on an initial terrain analysis of 1m resolution airborne light detection
464 and ranging (LiDAR) data and subsequent field visits to distribute sites across a range of potentially
465 different wetness conditions. Ten sites were placed in the till part, two in the sedimentary part, and
466 one site was placed at the transition between the till and the sedimentary part of the catchment.
467 Placing the majority of the sites in the till part was motivated by a detailed riparian soil survey. Data
468 from the survey showed that sedimentary riparian soils were mineral soils with no or only very
469 shallow organic horizons, while most till riparian soils had thick peat horizons." We obviously did not
470 repeat this information in our original manuscript but summarized in Page 745 Lines 3 to 5:
471 "Locations were selected to cover a wide range of wetness conditions and soil types by using terrain
472 analysis of 1 m-resolution airborne light detection and ranging (LiDAR) in conjunction with detailed
473 field reconnaissance". For more information, please read Grabs et al. (2012).

474 **Results**

475 *Lines 19-23: These should be your 'treatments'. Perhaps soil type as main effect and then dry, humid,*
476 *and wet as co-variates. Also, this is the third mention of site in the paper. I have become confused as*
477 *to what you are trying to compare.*

478 See **[1]**, **[4]** and lines 119-143 of this response document.

479 *Page 751 Lines 4-15: you may want to present these data by soil type and then, if applicable, how*
480 *moisture regime influenced within soil types.*

481 We believe that is what we did (see Page 751 Lines 4-15). The order in which the data are presented
482 has been inverted in the revised version of the paper so now it comes first the comparison between
483 till and sediment soils.

484 *Lines 10-11: does no clear pattern mean they behaved the same way?*

485 This sentence has been removed in the revised manuscript.

486 *Lines 23-28: why not look at sampling depth separately as opposed to lumped per riparian zone?*

487 Sampling depth was used in the analysis described in lines 130-136 of this response document
488 showing little effect on the variance of BC and Si campaign concentrations. However, it is clear that
489 some sites presented an increase in concentrations towards the bottom of the profile (see Figures 4
490 and 5 and Page 751 Lines 8-10 of the original manuscript).

491 *Line 28: what was K higher then?*

492 The temporal variation of K was higher than the temporal variation of the other BC and Si. This is
493 indicated in the revised version of the manuscript.

494 *Page 752 Lines 1-3: how were statistics conducted? If comparing riparian zones, then no replication*
495 *exists and you cannot conduct ANOVA.*

496 We agree that we cannot conduct an ANOVA and that analysis was discarded in the revised
497 manuscript. A new analysis was performed in order to test spatial and temporal factors in riparian
498 soil water concentrations ("Spatial and temporal trends in BC and Si concentrations were
499 investigated following the approach presented by Futter et al. (2011) to partition variation between
500 different sources. A series of analyses of variance (ANOVAs) were performed so as to estimate the
501 relative contribution of riparian site class, riparian site, depth in the profile, and sampling campaign
502 to the total variation in BC and Si campaign concentrations. The fraction of total variation ascribed to
503 each component was equal to the sum of squares for that component divided by the total sum of
504 squares from the ANOVA."). We elected not to perform any assessments of ANOVA significance due
505 to the difficulties in unambiguously identifying the appropriate statistical design. In principle, a
506 survey such as the one we present can be analysed as a multi-dimensional repeated measures design
507 with missing values in which there are repeated measurements (1) for each chemical analysis, (2)
508 over depth in the soil profile, (3) over time, and (4) among lysimeters. We believe that the
509 appropriate assignment of probability values in such an analysis is a research question for
510 statisticians and lies outside the scope of the biogeochemical data and analyses presented here.

511 *Lines 5-8: I am not sure what is meant here. If similar, how can they differ?*

512 Instead of "similar" we have wrote "close to" in the revised manuscript. We believe they are similar
513 (see Figure 6 in the discussion paper) and there is no ecological significance although we detected a
514 statistical difference due to the high statistical power (see Page 757 Lines 18-27; Page 758 Lines 1-20;
515 Table 3). This has been explained better in the revised manuscript ("The nominally significant
516 difference that was detected between the RZ and stream Mg/Ca ratios (Table 4) can be attributed to
517 the high statistical power (n=1424) but we suggest that there is no environmental significance
518 because the difference between the slopes is lower than the analytical error and the true statistical
519 significance is almost certainly less due to lack of independence of measurements").

520 *Lines 13-15: How were soils sampled for mineralogy? Is there any other soil chemical and physical*
521 *characteristic data available?*

522 A new section with sampling procedures has been added at the beginning of the methodology
523 section in the revised manuscript that gathers all sampling methods including mineralogy ("In August
524 2008, soil pits representative of the existing ROK sites were excavated for characterizing mineralogy

of the different landscape element types. X-ray diffraction (PANalytical X'Pert Pro PW3050/60) and Fourier Transformation infrared spectroscopy (FTIR, Perkin Elmer spectrum 100) were used for mineralogical identification and quantification following the procedure described in Niedermayr et al. (2013).").). Other physical data are available but they are now in preparation for another manuscript.

Lines 20-23: what is mean by "The dilution was small in forested subcatchments: : :"?

When looking at Figure 7, the dilution is given by the slope of the relationship between concentrations and discharge: the steeper the slope the more dilution. This is stated in the text in the revised form of the manuscript ("The dilution of element concentrations with increasing flow (indicated by the steepness of the slopes in the Fig. 8 plots) was small in forest subcatchments (Fig. 8a) whereas a stronger dilution effect was noted in wetland dominated sites (Fig. 8b)").

Page 753 You should present data for RIM-calculated flow-weighted concentrations at different depths and compare to field measurements.

This is not what RIM does. See **[1]**, **[2]** and **[4]**.

Lines 1-28: too much detail is presented and I suggest presenting data from soil type.

With respect we disagree with this suggestion and we would like to keep the information as it is.

Lines 18-28: this information belongs in Discussion

This part contains both descriptive information and some explanations that we believe need to come together. The second reviewer did not suggest specific changes here and we would like to keep it as it is.

Page 754 Lines 13-15: what about the headwaters from where your streamflow measurements were taken?

We do not understand what the referee meant with this question and therefore we cannot provide an adequate answer.

Line 27: what was the source of silt; glacio-fluvial or till? If deposited by till, they would be the same Quaternary deposit.

The source is glacio-fluvial (see Page 744 Lines 15-18 in the discussion paper).

Page 755 Lines 1-8: You don't have all the required data to calculate mass balances because you have only measured riparian soil solution and stream water. There are no inputs (mineral weathering and atmospheric deposition) or flux from uplands into riparian zones.

Mass balances in headwaters between riparian zones and streams are valid assuming that the flow-weighted mass of BC and Si at the outlet of the headwater stream should be equal to the flow-weighted mass of BC and Si leaving the soils at the edge of the aquatic-terrestrial compartments, i.e. the RZ (which is what we calculated using the RIM approach). That means we investigated whether streams were conservative representatives of what comes out from riparian zones. However we decided to use the term "net fluxes" in the revised manuscript to avoid misunderstandings. See also **[2]**.

561 *Lines 10-11: what do you mean by "too high" and "too low"?*

562 We meant higher and lower so it has been change accordingly in the revised manuscript.

563 *Lines 12-23: too much detail is presented and results are not necessarily justified by the experimental*
564 *design. For example, if you are calling riparian zone "sites" then there is no replication to test for*
565 *differences.*

566 See **[1]**, **[2]** and **[4]**.

Discussion

568 *Page 756 Lines 4-9: why are dry, humid, etc. barely discussed? These types of data should be*
569 *presented in the Results.*

570 Here we discussed the data/results that were presented in section 4.1.1 (Page 750 Lines 19-23 and
571 Page 751 Line 21 of the discussion paper). Section 4.1.1 has been modified in the revised version of
572 the manuscript following a previous suggestion.

573 *Lines 13-14: Highest concentrations of what?*

574 We meant highest concentrations of BC and Si. This has been added in the revised version of the
575 manuscript.

576 *Lines 15-20: So what? How does this relate to forest harvesting or climate change effects in*
577 *headwater vs. lowland catchment locations?*

578 We have narrowed this discussion in the revised manuscript to changes in groundwater levels
579 potentially caused by forest management and climate change but no other specific changes. This is
580 done in section "5.6 Potential implications for surface water quality". The new section "6. Concluding
581 remarks and further investigations" includes effects in headwater vs. lowland catchment locations
582 according to suggestion ("The high flow-weighted concentrations in RZs located in sedimentary soils
583 were attenuated by large order streams that contain water from the upper part of the catchment.
584 This indicates that headwaters may be more vulnerable to upslope changes. The importance of
585 headwaters for management strategies has been already reported (Bishop et al., 2008), especially in
586 relation to pH (Ågren and Löfgren, 2012)").

587 *Lines 19-20: I don't understand the meaning of this sentence.*

588 "The PLS analysis confirmed the importance of landscape element type as controls of BC and Si". The
589 PLS analysis (see Page 754 Lines 20-27 of the discussion paper) confirmed that high concentrations of
590 BC and Si found in riparian zones and streams located in the sediment area of the catchment are
591 explained by the landscape element types ("The catchment, and the boreal region as a whole, can be
592 conceptualized as a series of different landscape element types (Oni et al., 2013). In the Krycklan
593 region, relevant landscape elements include open water, bedrock, upland forest till soils, upland
594 peat, and lowland sediments which are primarily forest-covered but also support the small amount
595 of arable land found in the Fennoscandic boreal"), as it is speculated in previous Lines 13-18 of the
596 same Page 756.

597 *Page 757 Lines 1-3: What is meant by "remarkable"? Most of the Discussion is a very generic*
598 *interpretation of the results relative to your site and other studies conducted in boreal regions.*

599 "Remarkable" has been changed by "worth of comment" in the revised version of the manuscript.
600 The discussion is relative to boreal regions because that is the focus of the manuscript, as it is already
601 stated in the title.

602 *Lines 4-7: what about mineral weathering vs. decomposition for K?*

603 That is a good question. We discarded mineral weathering as the reason of the peak in K because this
604 peak did not occur in Ca or Mg, which would be expected to weather before K. K release in logging
605 residues is common and we have added a reference about it in the revised manuscript (Turkey,
606 1970).

607 *Lines 20-22: One could argue weathering rates vary across riparian zones.*

608 This is true but we did not argue with that.

609 *Page 758 Lines 1-5: you should be able to come up with relative measures by comparing Mg/Ca ratio*
610 *to that in the literature.*

611 The literature that we included to compare ratios referred to the same catchment. However this has
612 been removed in the revised manuscript because it was not relevant.

613 *Lines 5-13: Why and what is "transmissivity feedback concept"? Your sample size is not 1,424; that is*
614 *the number of water samples you analyzed or predicted. You have not defined a statistical design to*
615 *test for power. The sample size would be based on the number of experimental units (i.e., plots),*
616 *which have not been identified.*

617 Transmissivity feedback concept has been explained better in the new version of the manuscript ("In
618 boreal forest till soils, strong increases in saturated hydraulic conductivities towards the soil surface
619 can cause dramatic increases in the lateral flow movement to the stream as precipitation or
620 snowmelt events cause the groundwater table to rise and soil water to enter the stream via highly
621 conductive superficial soil layers in the RZ. This phenomenon is known as the 'transmissivity feedback
622 mechanism' (Rodhe, 1989; Bishop, 1991; McDonnell et al., 1998; Bishop et al., 2011). The
623 transmissivity feedback mechanism results in a large mobilization to the stream of 'old' or 'pre-event'
624 water during rainfall or snowmelt events (Laudon et al., 2004)."). The given references in the text
625 provide further information (see also Bishop et al., 2004).

626 We believe that the reviewer misunderstands our point. We argue that there is no meaningful
627 difference between Mg/Ca ratios in the RZ and the stream. We are not attempting to make any
628 inferences about environmental significance on the basis of a tabulated p-value. The reviewer
629 correctly states that our true n is probably less than 1424 due to potential spatial and temporal
630 autocorrelation between measurements. However, the statistically valid n and associated p are
631 irrelevant to our assertion that there is no environmentally meaningful difference between the
632 Mg/Ca ratios in the RZ or the stream. We have modified the paragraph accordingly ("The nominally
633 significant difference that was detected between the RZ and stream Mg/Ca ratios (Table 4) can be
634 attributed to the high statistical power (n=1424) but we suggest that there is no environmental

significance because the difference between the slopes is lower than the analytical error and the true statistical significance is almost certainly less due to lack of independence of measurements").

Lines22-25: what are the ranges and potential causes of uncertainty?

We believe section "5.3 Uncertainties in the riparian flow-weighted concentration estimations" provides an honest and extended discussion of causes and implications of all uncertainties and no further discussions are needed.

Lines 26-27: why? No statistical justification for this has been made. How did your C7 streamflow estimates compare with those from the referenced studies? C7 is a headwater; where were the other studies located? C7 may not represent all headwaters and certainly not lowland catchments.

The reference studies are from the same catchment. See **[3]**.

Page 759 Lines 1-2: why is using flow-weighted concentrations for a number of riparian zones based on streamflow from one stream better than volume-weighted concentrations from the individual tension lysimeters? What are the associated errors with your method?

With the RIM approach we calculated flow-weighted concentrations coming out from the whole riparian profile by integration of the measurements at different depths. See **[2]** and **[3]**. We have associated errors/uncertainties that were discussed in section "5.3 Uncertainties in the riparian flow-weighted concentration estimations".

Lines 8-9: this is important enough to provide basic statistics in a table.

This was presented in Page 753 Lines 12-18 in the original manuscript and in a table in the supplement.

Lines 14-22: how did measured vs. modelled concentrations compare? What were the fluxes and how did they compare to modelled results?

Here we meant observed vs. modelled groundwater tables which are compared in Figure 3 in the discussion paper.

Lines 23-28: these are predicted values, which may not be consistent with field studies and based on the data presented, there is no way to compare. Would more variation in R7 be important in forest catchment management? Why can underestimation be attributed to Zmod, Gw?

Here we meant observed vs. modelled groundwater tables which are compared in Figure 3 in the discussion paper. The importance for forest catchment management was discussed in section "5.6 Implications for surface water quality and further investigations" which has been improved in the revised manuscript and stands now as "5.6 Potential implications for surface water quality" as indicated above. The underestimation in flow-weighted concentrations in the riparian sampling site R7 (comparing the corresponding headwater stream) is attributed to underestimation in modelled groundwater tables (compared to observed groundwater tables) because when using the RIM approach (see **[2]**) the flow weighted-concentrations are depended on the measured soil water concentrations where the groundwater table varies: if the groundwater table was higher the flow-weighted concentrations would be lower because the concentrations increase with depth (see Figure

672 4 and Figure 5; see also section "4.4.1 Flow-weighted concentrations in riparian sites and
673 sensitivity/uncertainty analyses" of the discussion paper).

674 *Page 760 Line 5-7: I think many assumptions have been violated in your study.*

675 This comment is too general and vague and it cannot be responded without specifics.

676 *Lines 8-17: how does this relate to previous field studies?*

677 Overland flow has been discarded in other studies in the catchment because it has not been
678 observed (Kevin Bishop, personal communication) (see Laudon et al. 2007; Grabs et al. 2012). In any
679 case, this would be relevant only for riparian sampling sites with shallow groundwater tables but not
680 for the dry sites.

681 *Line 15: this could be stored water that is mobilised during rain events.*

682 This has never been seen in the area (Kevin Bishop, personal communication). See previous
683 comment.

684 *Lines 25-28: what is good? You presented no measured base cation flux from field to compare*
685 *modelled results. Riparian zones are not always near saturation, especially in headwater catchments.*
686 *Constant concentration in sallow soil assumption is not valid because base cation concentrations in*
687 *surface soil horizons are quite variable spatially and temporally.*

688 The sentence in which "good" was written has been removed in the revised manuscript because it
689 was confusing. We did not intend to compare measured vs. modelled fluxes. Data on groundwater
690 tables are provided for all 13 riparian sampling sites (see Figure 4 and Figure 5 of the discussion
691 paper).

692 We agree that base cations can vary in surface soil horizons but with the available data we cannot
693 quantify it. The shallowest depth in which we measured soil water chemistry was 15 cm. One could
694 make many different assumptions but we choose constant concentrations between the shallowest
695 measurement and the soil surface. This cannot be proven wrong or true with the available data for
696 the current study. Even though, we decided to provide an honest discussion of this limitation (see
697 Page 760 Line 21-28; Page 761 Lines 1-5 of the discussion paper).

698 *Page 761: Line 1: why would this occur and what is its importance?*

699 This could occur by rain or melt water dilution or by tree uptake. The importance was discussed (see
700 Page 761 Lines 1-5 of the original manuscript).

701 *Lines 2-5: no calibration or validation of RIM was reported; therefore you cannot validly test*
702 *uncertainty.*

703 We did not use a calibrated/non-calibrated model but a conceptual approach to calculate flow-
704 weighted concentrations. Please, see **[2]**.

705 *Lines 7-12: those are not mass balances, but only a model predicted concentration. Because no field*
706 *and model data comparisons were made, nothing has been demonstrated.*

Mass balances in headwaters between riparian zones and streams are valid assuming that the flow-weighted mass of BC and Si at the outlet of the headwater stream should be equal to the flow-weighted mass of BC and Si leaving the soils at the edge of the aquatic-terrestrial compartments, i.e. the RZ (which is what we calculated using the RIM approach). That means we investigated whether streams were conservative representatives of what comes out from riparian zones. However we decided to use the term "net fluxes" in the revised manuscript to avoid misunderstandings. See **[2]**.

We did not use a calibrated/non-calibrated model but a conceptual approach to calculate flow-weighted concentrations. Please, see **[2]**.

Lines 13-15: if Mg/Ca signal is indicative of mineral dominated soils, it could be from groundwater originating upslope. This cannot be separated from riparian zones based on the data presented in the paper. Also, do all riparian zones transport water and base cations to streams?

"…it could be from groundwater originating upslope". We agree and that is what we indicated in several parts of the discussion paper (Page 740 Line 15; Page 757 Line 15; Page 757 Line 21-22, Page 758 Line 7-8; Page 758 Line 18-20). That is one of the main results of the manuscript. We were expecting differences in the Mg/Ca ratio at different flow conditions but as Figure 6 of the original manuscript shows, the Mg/Ca in the stream is stable. It can be argued that at low flow the water partly bypass the RZ and therefore the signal in the streams is groundwater. If the signal is the same at low and high flow that supports our interpretation of groundwater originating upslope at all flow conditions. These ideas have been added in a new conclusion section in the revised manuscript ("We conclude that a characteristic but comparable constant upslope signal that integrates deposition, plant uptake, and weathering is maintained through all the RZ and subsequently imported to the stream waters. This is supported by: (1) the temporal stability in the concentrations of BC and Si, (2) the remarkably stable Mg/Ca ratio in the riparian soil and stream waters, and the (3) homogeneous mineralogy in the catchment. Future work should investigate upslope conditions to confirm these findings").

The locations of the riparian sampling sites were selected to cover a wide range of wetness conditions and soil types and taking into account that they were contributors of flow to streams. This was based on LiDAR in conjunction with expert knowledge. See also Grabs et al. (2012).

Lines 15-19: no comparisons were made to evaluate model performance in estimating flow-weighted concentrations. Was the flux higher because of larger depth of runoff? What about snowmelt. Large precipitation events following dry periods? What about possible base cation depletion?

We did not use a model but a conceptual approach to calculate flow-weighted concentrations. Please, see **[2]**.

We do not have data to argue about base cation depletion. The advantage of have a short time scale is that we can neglect base cation depletion, which occurs in a longer temporal scale. In the revised version of the manuscript there is a mention to base cation depletion in the introduction ("Several studies have predicted declines in soil BC pools caused by more intensive biomass removal associated with more intensive forest harvesting (Olsson et al., 1993; Akselsson et al., 2007; Klaminder et al., 2011b). […]These factors may cause serious problems in Scandinavian forest till soils where BC-enriched waters contribute relatively little to total BC fluxes into the streams because their

location in the lower part of the soil profile is often associated with low hydraulic conductivity (Nyberg, 1995).") This supports the importance of base cation studies. There is another mention to base cation depletion in the new concluding remarks section ("The role of BC pools linked to organic matter-rich RZ in buffering acidification could not be investigated with the data presented here. It could be significant and should be studied in the future. This is especially important in the long-term because many studies have predicted depletion in BC pools associated with forest harvesting (Sverdrup et al., 2005; Belyazid et al., 2006; Akselsson et al., 2007)"). This provides future directions of research. Our results provide new insight knowledge in relation to BC.

Lines 19-27: what is the importance to intensified forest harvesting and climate change?

We have narrowed the discussion to changes in groundwater levels potentially caused by forest management and climate change but no other specific changes. This was discussed on section "5.6 Implications for surface water quality and further investigations" and it has been improved in the revised manuscript ("Increasing runoff following harvesting has been observed in many distant parts of the world including Sweden (Sørensen et al., 2009; Futter et al., 2010), Canada (Kreutzweiser et al., 2008), and China (Zhang et al., 2012). The effects include elevation in groundwater levels (Bosch and Hewlett, 1982), which has been also associated to changes in precipitation regimes related to climate change (Hongve et al., 2004). Our results show low sensitivity in BC concentrations in RZ water entering the stream to changes in groundwater levels (Fig. 9), although in general they would be lower, potentially leading to episodic acidification because acid neutralizing capacity (ANC) would decrease").

Page 762 Lines 1-8: your comparison used model predictions and was not calibrated or compared to field-based measurements. Seeing this is the first attempt to incorporate base cations into RIM, you may want to focus the paper on either model calibration or its use to identify key ecosystem uncertainties requiring additional research. In either case, I have issues with how the flow-weighted concentrations were calculated and not compared to volume-weighted base cation concentrations or their fluxes.

We did not use a model but a conceptual approach to calculate flow-weighted concentrations. Please, see **[2]**.

Lines 9-13: is water transport from riparian zones diffusive or advective? I think nothing has really been supported because no field data are presented to compare model flowweighted Mg/Ca ratio or upslope contributing area.

Due to the type of soils that the catchment have is very hard to imagine that diffusive flow exists. Hydraulic conductivities in this type of soils are relative to advection flow (Nyberg, 1995). Advection transport and negligible diffusion is one of the original assumptions of the RIM concept (please see Seibert et al., 2009).

We did not use a model but a conceptual approach to calculate flow-weighted concentrations. Please, see **[2]**.

Page 763 Lines 13-14: I disagree because riparian zone contribution to streamflow and chemistry has been studied since the 1970s. The problem has been lack of acceptable methods to partition catchment source areas of streams.

787 "New" has been changed to "This differs from" in the revised version of the manuscript to avoid
788 misunderstanding. The problem of acceptable methods exists and therefore that support our study
789 and the contributions that it provides.

790 *Lines 23-24: you have measured flow for only one stream, which was in the headwaters and may not*
791 *be applicable to larger order streams.*

792 Please see **[3]**.

793 *Lines 26-28: I am not sure what you are trying to say here.*

794 This part has been rewritten in the revised manuscript ("The observed mismatches at some sites
795 could be explained by the aforementioned uncertainties in the calculations. On the other hand,
796 compounds like organic carbon are affected to a larger extent than BC by heterogeneous factors such
797 as temperature, water content or topography (Köhler et al., 2008; Winterdahl et al., 2011a; Grabs et
798 al., 2012) and might show more variation within RZ").

799 *Page 764: Lines 1-2: what about weathering rates? Temperature, water content, and topography*
800 *affects base cations too.*

801 See previous response. We agree, temperature, water content and topography affects base cations
802 too and this has been stated in the revised manuscript, but these factors are more important for
803 organic carbon.

804 *Lines3-8: I would argue the non flow-weighted concentrations are not as dangerous to use as those*
805 *produced from a non calibrated model.*

806 We did not use a calibrated/non-calibrated model but a conceptual approach to calculate flow-
807 weighted concentrations. Please, see **[2]**.

808 *Lines 10-14: what about other areas of the boreal region?*

809 We do not specifically refer to boreal regions but to Swedish and Chinese sites. We have added
810 another reference to a boreal catchment in Canada in the revised version of the manuscript that
811 takes into account this comment (Kreutzweiser et al., 2008).

812 *Lines 15-24: although concentrations may be lower in surface soil solution, fluxes may be higher*
813 *because of more runoff.*

814 Definitely, but the important for the acidity is the concentrations. This is the reason why we decided
815 to give flow-weighted concentrations instead of fluxes. The acid neutralizing capacity (ANC) can be
816 easily simplify as the sum of the concentrations of base cations minus the sum of the concentrations
817 of strong anions. If the concentrations of base cations are lower the ANC is lower and therefore the
818 acidification status is affected. These ideas have been included in the revised version of the
819 manuscript (see lines 759-766 of this response document).

820 *Lines 27-28: why would boreal catchments be vulnerable to forest management? What are some of*
821 *the possible forest management influences?*

822 The importance for forest catchment management was discussed in section "5.6 Implications for
823 surface water quality and further investigations" which has been improved in the revised manuscript
824 and stands now as "5.6 Potential implications for surface water quality" as indicated above (see lines
825 756-766 of this response document).

Tables

827 *Table 1: what is the cut-off for peat proportion of catchment that does not influence base cations?*
828 *Why are not riparian zone characteristics presented?*

829 We do not understand the first question and therefore we cannot provide an adequate answer.

830 We did not present all the riparian zone characteristics because they were presented in Grabs et al.
831 (2012). Our manuscript includes already much information already presented in that study and we
832 do not want to be too redundant. However, more information describing the riparian sampling sites
833 organic characteristics has been added to the revised manuscript ("Ten of the instrumented sites
834 were located in till soils, two in the sediment part of the catchment and one in the transition
835 between sediment and till (Fig. 1). [...] Most of the riparian sampling sites located in till soils and the
836 transition site had a thick peat layer (≥ 30 cm), whereas the sites located in the sediment area had
837 very shallow organic horizons over mineral soils").

Figures

839 *Figure 1: it is doubtful that discharge from C7 can be assumed to resemble that in higher order*
840 *catchments. Why not stick to the sub-catchments in the insert of Fig. 1? Measured streamflow from*
841 *C7 may be easier to swallow for estimating flow-weighted concentrations in the riparian zones and*
842 *streams.*

843 Please see **[3]** and the many other responses to the use of discharge from sampling site C7.

844 *Figure 2: why are there inconsistencies between measured and modelled groundwater tables during*
845 *winter and spring (and sometimes into summer)? This may be important to your conclusions.*

846 The referee probably refers to Figure 3. Yes, there are inconsistencies and they were broadly
847 discussed in the discussion paper (see Page 759 Lines 12-28; Page 760 Lines 1-4).

848 *Figure 4: you may want to provide summary of 'mineral' versus 'organic' riparian soils. Were soil*
849 *characteristics at R11 and R14 different from the other riparian zones?*

850 This information was presented in Grabs et al. (2012). We have included a small summary in the
851 methodology section of the revised manuscript (see lines 350-354 of this response document).

852 *Figure 7: are these measured or modelled concentrations? I thought discharge was measured at only*
853 *one stream (C7)?*

854 They are measured concentrations (specified in the revised manuscript). Yes, discharge was
855 measured only at stream sampling site C7, which was then use to calculate areal-specific discharge,
856 which was assumed the same in all sampling sites and that is what is plotted in the Figure. See **[3]**.

Figure 8: why different scales on the x-axis? Comparisons would be easier to make if the scales were the same.

We agree and have changed accordingly to the suggestion.

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985   <u>Anonymous Referee #2</u>

986   We thank referee 2 for his constructive comments that will improve the quality of the paper (Note
987   that the text in italics refers to literal comments by the referee and text in blue contains literal
988   quotations from the revised manuscript).

989   **General comments**

990   *This paper explores the flow of base cations and Si in riparian zone and stream environment in a*
991   *Swedish boreal forest. This is done by using the Riparian Flow-Concentration Integration Model (RIM)*
992   *and actual measurements in the field. The topic is interesting and important in view of the impact of*
993   *forest management methods and climate change on riparian zones and hence water quality.*
994   *However, the actual purpose of using the model for estimating the concentrations of base cations in*
995   *riparian soil and stream water is not clear, but perhaps it's assume that this is common knowledge.*
996   *The paper is interesting and a lot of data has been collected. However, the manuscript is long and*
997   *slightly disorganised and need some restructuring. A massive amount of references are collected for*
998   *some sections while others are missing references completely.*

999   We are glad that the reviewer found our study interesting. A conceptual figure has been added to the
1000   new version of the manuscript to clarify how we have performed the calculation using the RIM
1001   approach. We would like to point out that the RIM has been used here as a conceptual approach to
1002   calculate flow-weighted concentrations of base cations and silica from riparian zones to streams and
1003   therefore comparisons of modelled and observed values and model calibrations were not intended.
1004   The few allusions of RIM as a model that we had in the original version of the manuscript have been
1005   removed in the revised version to avoid misunderstanding. The way in which the RIM approach
1006   calculates flow-weighted concentration or fluxes is analogous to the way in which flow-weighted
1007   concentrations or fluxes are calculated in streams or rivers. This has been clarified in the revised
1008   manuscript ("RIM takes point measurements of chemical concentration at a series of depths and
1009   then performs an interpolation to provide a continuous estimate of chemical concentration at all
1010   depths in the RZ. This chemical concentration profile is then multiplied by an estimated lateral
1011   discharge profile to derive volume weighted concentration or flux estimates for an entire RZ profile.
1012   Conceptually, RIM is very similar to the process of estimating riverine fluxes in which point
1013   measurements of chemical concentration are interpolated through time to provide a continuous
1014   chemical time series which is then multiplied by a continuous flow record to estimate fluxes. While
1015   RIM integrates over depth, riverine flux estimation integrates over time.").

1016   The objectives and focus of the paper have been reformulated and stated clearly in the revised form
1017   of the manuscript ("Here we present a two-year study of flow-weighted concentrations of BC and Si
1018   from RZ and streams in a boreal landscape in northern Sweden. This is the first application of RIM to
1019   study BC dynamics in forest soils and streams. The studied systems range from first order headwater
1020   streams in till soils to catchments of third and fourth order streams underlain by silty sediments. The
1021   main objective of the study was to better understand relationships between BC and Si in RZ soils and
1022   adjacent surface waters. Specific objectives were to: (1) identify temporal and spatial trends in BC
1023   concentrations in RZ draining different landscape element types, (2) identify spatial differences in BC
1024   flow-weighted concentrations from streams dominated by different landscape element types, (3)
1025   investigate whether RZ element concentrations represent flow-weighted concentrations in

headwater streams, and (4) test the sensitivity of riparian flow-weighted concentrations to changes in groundwater levels as potential effects of forest management and climate change.").

Some restructuring has been carried out in the new version of the manuscript. For example a new conclusion section that repeats the main results and interpretations and contains suggestion for future research has been added as well as a new subsection in the methodology that gathers all sampling procedures (see further comments/responses).

With no further specifications of where in the manuscript references are missing we cannot provide an answer but some new references have been added to the new version of the manuscript (Ågren and Löfgren, 2012; Bayley et al., 1992; Bishop et al., 2008; Futter et al., 2011; Gundersen et al., 2010; Hongve et al., 2004; Kreutzweiser et al., 2008; Landre et al., Landre et al., 2009; Niedermayr et al., 2013; Nyberg, 1995; Oni et al., 2013; Turkey, 1970).

I always find it difficult to discuss ions in natural waters without involving organic matter in the discussion since it is one of the main factors influencing the chemistry of stream and soil water. How do you reason around this. Is it possible to model the base cation chemistry without taking organic matter into account?

As mentioned above, base cations and silica were not modelled but their flow-weighted concentrations calculated with a previously used approach. For the final implications to acidity, presence of organic matter needs to be considered but we do not have the necessary data. A new sentence in the new conclusion section mention the link to organic matter ("The role of BC pools linked to organic matter-rich RZ in buffering acidification could not be investigated with the data presented here. It could be significant and should be studied in the future.").

Why is the Mg/Ca ratio important, clarify

Upslope data were not available and the upslope mineralogical signal is our interpretation of the results. We used the Mg/Ca ratio to investigate homogeneity within a catchment comparing stream and soil water. Changes in Mg/Ca ratio could indicate ion-exchange reactions but in our study we observed a temporal and spatial stability in the Mg/Ca ratio. There was only one riparian sampling site that deviated from the general pattern, and this site also presented a different mineralogy. Because the ultimate origin of these elements is weathering reactions from minerals we believe the water is imprinted by a mineralogical signal. In our study we show that this signal is not changed through the riparian zone by ion-exchange reactions because a near equal Mg/Ca ratio was seen in the streams. We did not use other element ratios due to the following reasons: K is a more dynamic element that is easily released taken up by plants and Na might be influenced by salt rich rain episodes. Mg/Ca ratios were stable throughout the sampling period as could be seen in Figure 6 in the discussion manuscript. We also argue for the use of the Mg/Ca ratio in the revised manuscript ("We used the Mg/Ca ratio to investigate homogeneity within the catchment. Changes in Mg/Ca ratio could potentially indicate ion-exchange reactions but our results showed temporally and spatially stable ratios in all riparian sites and depths (Fig. 7), with the exception of site R9. The fact that this site also had a different mineralogy indicates that the riparian soil solution is strongly imprinted by a mineralogical signal [...]. Water of mineral soil origin supports the transmissivity feedback concept (Rodhe, 1989; McDonnell et al., 1998; Laudon et al., 2004; Bishop et al., 2011) in which upslope 'old' or 'pre-event' water (i.e. groundwater) is the main source of RZ [...].The near-

constant Mg/Ca ratio and stability in the stream sites indicate that the mineralogical signal is subsequently maintained in the surface waters of the catchment in all flow conditions (Fig. 7). We interpret these stable patterns as a result of distinct mineralogical upslope signals integrating the chemical erosion signals of biological and chemical weathering that are not changed through the RZ by ion-exchange reactions").

To make the "study design" easier to digest it might be a good idea to start with a sampling section of some kind, which would make it easier to find how all the samples were attained and stored, treated and analyzed. As it is now, you'll get new information about sampling in several places which makes things confusing.

"Study design" has been changed to "Methodology" in the revised manuscript. We agree with this suggestion. Now a subsection explaining the sampling is presented at the beginning of the methodology section.

As I understand it, one of the major purposes of this paper is to link the riparian soil water chemistry to the stream water chemistry in the nearby stream. Is it then wise to keep the riparian sites R1 and R2 in the study when there is no data collected from the stream C8?

That is true. However, one of our analyses consisted of investigating spatial and temporal variation in base cations and silica among the riparian sampling sites (with no consideration of the streams in this case) so we would like to keep these two sites.

Is it possible to merge study area and study design into one section and maybe rearrange them and shorten them a bit?

"Study design" has been changed to "Methodology" in the revised manuscript as it is indicated above. We believe "study area" and "methodology" sections should come separately as the former describes an existing research catchment and instrumented sampling sites that have been used in the past or will be used in the future and the latter describes specific operations, adaptations and calculations used by us in this study. Probably the longest part of the methodology describes the flow-weighted concentration calculations for riparian zones, which also include a repetition of the routines presented by Grabs et al. (2012). We believe this thorough description is necessary as the concept might be complex to understand.

Both the result and discussion are quite extensive and it would be nice with a conclusion to wrap it all up and repeat the most important findings.

We agree and a new section with conclusions has been included in the revised version of the manuscript.

Supplementary material First table: Is there a reason why the lysimeters are not listed in order?

Riparian sampling sites were sorted here as they were sorted in the table presented in page 4 in the supplement: that is from riparian zones located in small headwaters to riparian zones located in larger subcatchments downstream.

Specific comments

P740 L2 Reformulate sentence…major factor in controlling…

The sentence has been reformulated in the revised manuscript according to suggestion.

P740 L22 This is a nice sentence/intention, however it seems a little farfetched to mention in the abstract since the study don't really provide new information about the vulnerability of RZ to changes induced by changes in forest management and climate change. Maybe it woud fit better in a possible Conclusions section.

This is a suggestion of future research and follows the guidelines for authors in Biogeosciences ("The abstract […] provides future directions where research could focus on in the near future" in http://www.biogeosciences.net/submission/manuscript_preparation.html). However, as both reviewers suggested removing it we have done so.

P741 L4 Habitat function

We agree and have changed accordingly in the revised manuscript.

P741 L15 This sentence by itself doesn't really explain much. Please elaborate or remove.

The sentence has been removed as suggested in the revised manuscript.

P742 L8 Is this really an appropriate reference in this case?

We agree, that is not the most appropriate reference, and therefore it has been changed accordingly. The new reference is "Nyberg (1995)" in the revised manuscript.

P745 L16 If the stream C8 was omitted from the study, is it wise to keep the R1 and R2 sites?

Unfortunately no data were available for C8. We would like to keep R1 and R2 because one of our analyses consisted of investigating spatial and temporal variation in base cations and silica among the riparian sampling sites.

P745 L8 Are the soil depths measured from the mineral top soil surface or does it include the O-layers?

Soil depths include the O-layers. This information has been included in the revised version of the manuscript. For some of the sites, the thickness of the O-horizon was larger than 30 cm (R2, R5, R6, R7, R8, and R10). See also Grabs et al. (2012) for more information about the sites.

P746 L25 Shold the base cations have charge or not? Be consistent?

We agree and have changed accordingly in the revised manuscript.

P756 L11 This is the first mention of SiO2, please be consistent.

We agree and have changed accordingly in the revised manuscript.

P762 L5 SiO2?

We agree and have changed accordingly in the revised manuscript.

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