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Earth Surface Dynamics
Discussions

Interactive comment on "Impact of sediment-seawater cation exchange on Himalayan chemical weathering fluxes" *by* M. Lupker et al.

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We thank the anonymous second referee for his insightful comments and tried to answer all of them appropriately:

#1 Comment: "My major suggestion for the authors would be to add a paragraph to discuss in what extent the adsorption of the major cations on G-B sediments can influence the accuracy of the method for determining silicate weathering flux, which is based on dissolved Ca/Na and Mg/Na ratio (e.g. Gaillardet et al., 1999). Indeed, it has been recently suggested (e.g. Tipper E., 2015 AGU conference abstract) that the selective adsorption of the major cations to river sediments can significantly fractionate the Ca/Na and Mg/Na ratio of the "measured" dissolved load relative to the Ca/Na and Mg/Na of the initially dissolved cations. In that case, using the measured Ca/Na

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and Mg/Na ratio to calculate silicate weathering rates can lead to underestimated or overestimated silicate weathering flux calculations. Considering the low proportion of adsorbed cations relative to the total dissolved cations, the answer is probably going to be that the adsorption processes in the G-B do not fractionate significantly the Ca/Na and Mg/Na dissolved ratio, but I think that this would be a good addition to the current manuscript."

#1 Answer: That's an interesting point that didn't occur to us. We have tried to address it in a separate paragraph, refereeing to AGU abstract. However, it is not clear to us where the statement found in the abstract "However, it has been proposed that Na-Ca exchange reactions with clay on mineral surfaces could account for 80% of the Na in rivers waters." comes from and if it applies to the riverine environment only or the river plus the ocean. In the case of the G&B, adsorbed Na+ on river sediments (and in the riverine environment) accounts for less than 1% of the total dissolved river load. The importance of exchange reactions for the Na budget is more important once in the oceanic environments, where sediments can re-absorb up to 15% of the riverine dissolved load by releasing adsorbed Ca2+. It is nevertheless true that the greater portion of adsorbed Ca2+ (about 6% of the dissolved load) compared to Na+ may bias the measured dissolved Ca/Na ratios and hence impact the apportionment of silicate and carbonate weathering fluxes. However, as discussed in the manuscript, we think that in the case of the G&B this bias is limited

#1 Changes in the manuscript: - §4.1 p8: Table 3 shows that only less than 1% of the dissolved riverine Na+ load but ca. 8% of K+, 6% of the Ca2+ and 3% of the Mg2+ are carried by sediments as exchangeable cations in the river system. These related fluxes are therefore typically not accounted for when the major elemental composition or river water is used in the context of determining upstream chemical weathering rates (Gaillardet et al., 1999). Although overall small, these "missing" fluxes are of a similar order of magnitude as cyclic salt corrections commonly applied to river water compositions for K+, Ca2+ and Mg2+ (e.g. Galy et al., 1999). Riverine dissolved compositions are also largely used to apportion the contribution of silicate and carbonate weathering to the total riverine Ca2+ flux. This is generally based on the total Na+ and K+ fluxes (as these are assumed to be predominantly released by silicate weathering) and estimates of the Ca/Na and Ca/K composition of weathered source rocks (Gaillardet et al., 1999). The preferential uptake of Ca2+ and K+ compared to Na+ by cation exchange in the riverine environment will affect the measured dissolved Ca/Na ratios (Ca/K being less affected as these two cations are taken up in very similar proportions). It has been suggested that these effects could be significant (Tipper, 2015). However, in the case of the Ganga-Brahmaputra the change in the measured dissolved Ca/Na ratio due to the differential uptake of Ca and Na is about 5%, which is most presumably well within the overall uncertainty of the carbonate and silicate weathering apportionment.

#2 Comment: “Page 3 Line 17: what about dolomite dissolution? G-B sediments contain more dolomite than calcite (Lupker et al., 2012) and the CoHex solution is only saturated with calcite. Would you expect any dolomite dissolution during the CEC determination experiment?”

#2 Answer: The dissolution of dolomite cannot totally be excluded. However, the fact that the total CEC determined using Co absorption measurements and determined using the sum of major cations after exchange agree (Figure 1) suggests that dolomite dissolution is negligible and does not significantly affect our measurements. We specified this in the manuscript:

#2 Changes in the manuscript: - §2.2 p3: The CoHex solution is slightly acidic and may lead to the dissolution of sedimentary carbonates during exchange. To avoid this carbonate dissolution, the CoHex solution was saturated with pure calcite before exchange (Dohrmann and Kaufhold, 2009). - §2.2 p3: which underlines that no significant amounts of other cations are released during exchange or through mineral dissolutions such as dolomite.

#3 Comment: Page 3 Line 24: did you try to make a second leaching step with Co-

Hex, on at least one sample, in order to check whether all exchangeable cations have actually been exchanged with Cobalt ions during the experiment?

#3 Answer: No this was not tested. The exchange reactions have been made using a large excess of CoHex with respect to exchangeable sites (i.e. CEC value). CoHex is also known to have a very high affinity towards exchange sites (Ciesielski et al., 1997). We therefore assumed that the conditions lead to complete exchange. As reported by Ciesielski et al. (1997) repeated extractions only marginally increased the CEC of some soils and also increased undesirable secondary effects such as dissolutions.

The other remarks have been implemented as well.

Please also note the supplement to this comment:
http://www.earth-surf-dynam-discuss.net/esurf-2016-26/esurf-2016-26-AC2-supplement.pdf

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