Referee 1 response:

We are very grateful to our colleague Jeremy Caves for his constructive review of the manuscript. We tried to address all his comments and suggestions as highlighted hereunder. A reviewed manuscript with highlighted changes is appended to this submission.

#1 Comment: "I am somewhat confused as to precisely where these cation exchange fluxes occur. On page 2, 2nd paragraph, the authors explain that these fluxes occur in estuaries as river water is transferred to the ocean. However, should not these exchange fluxes be potentially occurring along the entire length of the river system, as tributaries with somewhat different dissolved and adsorbed chemistries contribute water and sediment to the main trunk? Or is the chemical difference between river water and seawater so substantial that this is where the largest cation exchange fluxes are expected? I understand that the authors sampled between the mouths of the Ganges and Brahmaputra and also in the Lower Mengha; however, is the Lower Mengha considered an estuary or still primarily freshwater? A more specific explanation, linked to the hydrology of the GB and Lower Mengha, would greatly help the reader follow the precise mechanism and setting in which these exchange fluxes occur."

#1 Answer: Cation exchange is supposedly occurring over the entire length of the river network but also in the landscape and soils that are being eroded. Any change in surrounding water chemistry will lead to a change in the adsorbed cation composition load. However, these changes within the river network are likely small and limited. The best argument to support this is given by the observation that the fraction of cations that are absorbed (Figure 4) does not change significantly between rivers and date of sampling even though the chemical composition of the water at the time of sampling was likely slightly different. The most drastic change in water chemistry occurs during transfer of the sediments to seawater as the concentration of dissolved cations (mainly Na^+) changes by several orders of magnitude. This occurs several tenth of km of the sampling site on the Lower Meghna which is still in the fresh water zone.

#1 Changes in the manuscript: We have modified the manuscript so as to make it clearer that the major cation exchange occurs across the salinity gradient in the estuary and that all river samples are considered as purely riverine:

- *§1 p2: Sediments in an aqueous solution such as river or oceanic water reversibly adsorb cations in equilibrium with the surrounding environment. The nature of these adsorbed cations evolves with changes in the chemical composition of the surrounding solution. The most radical change in the surrounding water chemical composition that the suspended sediment undergoes in a fluvial system occurs in estuaries across the salinity gradient.*
- *§2.1 p3: These sampling locations are also located upstream of the Ganga-Brahmaputra estuary and can therefore be considered as true riverine samples.*

#2 Comment: "I do not follow how the probable exchange fluxes are calculated. I understand that the authors used Eq. 2 to show that Kv is approximately constant across sampling locations (and similar to the Amazon); however, I can only see how Eq. 2 applies to the exchange of Ca2+ for Mg2+. Is this same equation (or a similar one) used to calculate the probable fluxes for Na+ and K+? Or is the fact that the proportion of adsorbed cations is constant across Al/Si ratios somehow used to then calculate probable Na+ and K+ exchange fluxes? Regardless, I think the authors should spell C2 out this calculation (particularly as it applies to Na+ and K+) more clearly since these probable fluxes are the primary point of the paper."

#2 Answer: The CEC measurements on the sediments allow us to constrain the amount of cations that are bound to the sediments within the riverine environment. However, it is known (Sayles and Mangelsdorf, 1977; 1979) that not all Ca^{2+} is desorbed in seawater. The most probable exchange fluxes are therefore simply calculated assuming that the same proportion of Ca^{2+} as observed in the Amazon is exchanged in the case of the G&B. We think this is a reasonable assumption as the exchange characteristics of G&B and Amazon sediments are very similar. This similarity of exchange characteristics is derived from the calculation of the exchange coefficient K_v for both the Amazon and the G&B. The calculation of K_v using eq. 2 is done for the equilibrium between Ca^{2+} and Mg^{2+} because these are the dominant species adsorbed in the riverine environment and hence the deduced K_v is more robust.

#2 Changes in the manuscript: The calculation has been clarified and table 3 is now more explicit.

- *§3.3 p6: For the estimation of the most probable flux of cations exchanged by Ganga-Brahmaputra sediments upon entry in the Indian ocean, we assume that the exchanged proportion measured by Sayles and Mangelsdorf (1979; 1977) on Amazon sediments also applies here. This is a reasonable assumption as the aforementioned studies highlight that the nature of exchange reactions (i.e. the relative proportions of cations exchanged during transfer to the ocean) is very similar among the different samples studied, irrespective of sampling location within the Amazon basin, composition or grain-size. Furthermore, we showed in the previous section that the equilibrium constant K_v between different cations in solution and adsorbed to the sediments sampled in the Ganga, Brahmaputra and lower Meghna is in the same range as the equilibrium constant found on Amazon sediments suggesting a similar behavior of these two river systems with respect to cation exchange. A reasonable estimate of the effective exchanged flux in the G&B estuary can therefore be made assuming that 82% of the total Ca^{2+} exchangeable flux is effectively exchanged for Na^+, Mg^{2+} and K^+. This estimation suggests that ca. 23 (±4) $\times 10^9$ mol of Ca^{2+} are desorbed from the sediments in the Bay of Bengal while 27 (±8) $\times 10^9$ mol Na^+, 5 (±2) $\times 10^9$ mol K^+, and 8 (±3) $\times 10^9$ mol Mg^{2+} are reabsorbed (Table 3).*

#3 Comment: "One change that might make this manuscript more widely accessible would be to address whether measurements such as presented here should be more widely made as part of river sampling campaigns. For example, it appears as if the methodology presented here is widely applicable and could be more widely implemented. Though the authors conclude that these exchange fluxes have a relatively limited importance when compared with the long-term carbon cycle, some of the corrections here (ie, 5% of the Ca2+ flux) are of a similar magnitude to corrections for precipitation and cyclic salts (see, for example, Appendix Tables in Torres et al. (2015)). Thus, it would be helpful to note whether this method should be more broadly applied, given that many other corrections to weathering data are being made that are similar in magnitude to the one presented here. Perhaps globally the effect of cation exchange negates the correction for atmospheric inputs of divalent cations?"

#3 Answer: This is a good point and we have tried to incorporate these comments in a paragraph and also expanding on the global significance of CEC fluxes:

#3 Changes in the manuscript:

- *§4.1 p8: …Accordingly, the relative importance of CEC fluxes compared to dissolved fluxes is probably limited for most large fluvial systems. Notable exceptions that would require a more precise quantification of CEC fluxes include rivers draining volcanic areas, as these areas are known to export high surface area and smectite-rich sediments e.g. (Chen, 1978). Organic-rich rivers should also be considered, as the presence of organic matter may yield a high overall CEC (e.g. Thompson et al., 1989; Turpault et al., 1996) susceptible of altering the dissolved fluxes more significantly. In any case it is important to stress that these future evaluations should take into account the variable CEC of sediments with sampling depth so as to correctly evaluate the integrated CEC of a river system. The evaluation of estuarine exchange processes may also be important to better understand the delivery of trace elements to the ocean (e.g. von Blanckenburg and Bouchez, 2014) or for possible isotopic fractionation of light elements during exchange.*
- *§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 Ca^{2+} and 3% of the Mg^{2+} 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^+, Ca^{2+} and Mg^{2+} (e.g. Galy et al., 1999).*

#4 Comment: "Finally, it does not appear that errors have necessarily been fully propagated, and the authors should check that their reported errors are accurate. For example, on page 5, 2nd full paragraph, the authors write that the "average total CEC is 8.0 (±0.9)… for the Ganga, Brahmaputra, and lower Mengha." These numbers are calculated using the linear regressions on Figure 3, though it does not appear that the uncertainty on these regressions is accounted for in these errors. Since the authors do go to the trouble of reporting errors, it would be appropriate if the full range of errors were accounted for."

#4 Answer: The determination of the average CEC of the different rivers is based on the regressions between Al/Si and the measured CEC as shown in Figure 3. The average Al/Si ratio of the G&B is estimated to be 0.23 ± 0.01 (see text and Lupker et al., 2011). The calculated average CEC takes into account the uncertainty on the average Al/Si ratio of the sediments as well as the uncertainty on the regression between Al/Si and CEC itself.
e.g. for the CEC data of the Ganges, using R for the regression and prediction at a 68% confidence interval we obtain an average CEC of 7.976 (+0.892 -0.911), which we rounded to 8.0 ± (0.9) (assuming uncertainties are normally distributed, which is not totally true). Taking only the uncertainty on the Al/Si ratio into account yields an average CEC of 8.0 ± (0.7). Most of the uncertainty is hence carried by the uncertainty on the average Al/Si ratio.

This uncertainty was propagated through the calculations and was better reported in the manuscript and in table 3. However, this uncertainty has not been further propagated to the calculations of possible carbon sequestration as the uncertainty carried by the assumptions would be very difficult to quantify and are certainly larger than the uncertainty on the estimate of the total estuarine CEC fluxes. Propagating uncertainties to carbon fluxes would give, in our opinion, a false impression of precision and accuracy on a very speculative point of the manuscript.

The remarks from the annotated manuscript have been implemented as well.

Referee 2 response:

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

<u>#1 Comment:</u> "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 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."

<u>#1 Answer:</u> 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 Ca^{2+}. It is nevertheless true that the greater portion of adsorbed Ca^{2+} (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

<u>#1 Changes in the manuscript:</u>

- *§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 Ca^{2+} and 3% of the Mg^{2+} 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^+, Ca^{2+} and Mg^{2+} (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 Ca^{2+} 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 Ca^{2+} 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.*

<u>#2 Comment:</u> "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?"

<u>#2 Answer:</u> 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:

<u>#2 Changes in the manuscript:</u>

- *§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.*

<u>#3 Comment:</u> Page 3 Line 24: did you try to make a second leaching step with CoHex, on at least one sample, in order to check whether all exchangeable cations have actually been exchanged with Cobalt ions during the experiment?

<u>#3 Answer:</u> 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.

Editor's response:

We'd like to thank the editor for considering our manuscript and spend the time to provide additional comments.

We have implemented all minor comments and these are not detailed here. We appended a revised manuscript to this revised submission so that changes that were made to the manuscript can be tracked and evaluated.

#1 Comment: "3.18: do you have to monitor potential addition of Ca^{2+} to the solution as a result of adding the calcite?"

#1 Answer: Non-reacted (non-exchanged) CoHex solution was used as base line or reference for the measurement of exchanged cations so that the initial concentration in Ca^{2+} is accounted for.

#1 Changes in the manuscript:

- *§2.2 p3: Additionally, major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) released by the sediments during exchange were determined by atomic absorption spectrometry at SARM-CRPG on the same solution, using a non-reacted CoHex solution as reference.*

#2 Comment: 6.30-34: This seems like a very important finding. Higher solid:dissolved ratio (i.e. more turbidity) does not necessarily mean more CE. You make this point in the next paragraph too, but I wonder if it could be more clearly drawn out (and worthy of pointing out in the abstract).

#2 Answer: It has been added to the abstract

#2 Changes in the manuscript:

- Abstract p1: The limited exchange fluxes of the Ganges-Brahmaputra relates to the lower than average CEC of its sediment load that do not counterbalance the high sediment flux to the oceans. This can be attributed to the nature of Himalayan river sediment such as low proportion of clays and organic matter.