

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

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#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

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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 adsorbed (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<sup>+</sup>) 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  $K_v$  is approximately constant across sampling locations (and similar to the Amazon); however, I can only see how Eq. 2 applies to the exchange of Ca<sup>2+</sup> for Mg<sup>2+</sup>. Is this same equation (or a similar one) used to calculate the probable fluxes for Na<sup>+</sup> and K<sup>+</sup>? Or is the fact that the proportion of adsorbed cations is constant across Al/Si ratios somehow used to then calculate

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probable Na<sup>+</sup> and K<sup>+</sup> exchange fluxes? Regardless, I think the authors should spell C2 out this calculation (particularly as it applies to Na<sup>+</sup> and K<sup>+</sup>) 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<sup>2+</sup> is desorbed in seawater. The most probable exchange fluxes are therefore simply calculated assuming that the same proportion of Ca<sup>2+</sup> 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<sup>2+</sup> and Mg<sup>2+</sup> 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

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assuming that 82% of the total Ca<sup>2+</sup> exchangeable flux is effectively exchanged for Na<sup>+</sup>, Mg<sup>2+</sup> and K<sup>+</sup>. This estimation suggests that ca. 23 (±4) 10<sup>9</sup> mol of Ca<sup>2+</sup> are desorbed from the sediments in the Bay of Bengal while 27 (±8) 10<sup>9</sup> mol Na<sup>+</sup>, 5 (±2) 10<sup>9</sup> mol K<sup>+</sup>, and 8 (±3) 10<sup>9</sup> mol Mg<sup>2+</sup> 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 Ca<sup>2+</sup> 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

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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  $\text{Na}^+$  load but ca. 8% of  $\text{K}^+$ , 6% of the  $\text{Ca}^{2+}$  and 3% of the  $\text{Mg}^{2+}$  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 of 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  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (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  $8.0 (\pm 0.9)$  . . . 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  $0.23 \pm 0.01$  (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  $8.0 \pm (0.9)$  (assuming uncertainties are normally distributed, which is not totally true). Taking only the uncertainty on the Al/Si ratio into

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account yields an average CEC of  $8.0 \pm (0.7)$ . 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.

Please also note the supplement to this comment:

<http://www.earth-surf-dynam-discuss.net/esurf-2016-26/esurf-2016-26-AC1-supplement.pdf>

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Interactive comment on Earth Surf. Dynam. Discuss., doi:10.5194/esurf-2016-26, 2016.

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