Impact of sediment-seawater cation exchange on Himalayan chemical weathering fluxes

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Abstract. Continental scale chemical weathering budgets are commonly assessed based on the flux of dissolved elements carried by large rivers to the oceans. However, the interaction between sediments and seawater in estuaries can lead to additional cation exchange fluxes that have been very poorly constrained so far. We constrained the magnitude of cation exchange fluxes from the Ganges-Brahmaputra River system based on cation

15 exchange capacity (CEC) measurements of riverine sediments. CEC values of sediments are variable throughout the river water column as a result of hydrological sorting of minerals with depth that control grain-sizes and surface area. The average CEC of the integrated sediment load of the Ganges-Brahmaputra is estimated ca. 6.5 meq/100g. The cationic charge of sediments in the river is dominated by bivalent ions Ca^{2+} (76%) and Mg^{2+} (16%) followed by monovalent K^+ (6%) and Na^+ (2%) and the relative proportion of these ions is constant among all

20 samples and both rivers. Assuming a total exchange of exchangeable Ca^{2+} for marine Na^+ yields a maximal additional Ca^{2+} flux of 28 x 10^9 mol/yr of calcium to the ocean, which represents an increase of ca. 6 % of the actual river dissolved Ca^{2+} flux. In the more likely event that only a fraction of the adsorbed riverine Ca^{2+} is exchanged, not only for marine Na^+ but also Mg^{2+} and K^+, estuarine cation exchange for the Ganga-Brahmaputra is responsible for an additional Ca^{2+} flux of 23 x 10^9 mol/yr, while ca. 27 x 10^9 mol/yr of Na^+, 8 x 10^9 mol/yr of

25 Mg^{2+} and 4 x 10^9 mol/yr of K^+ are re-absorbed in the estuaries. This represents an additional riverine Ca^{2+} flux to the ocean of 5% compared to the measured dissolved flux. About 15% of the dissolved Na^+ flux, 8% of the dissolved K^+ flux and 4% of the Mg^{2+} are reabsorbed by the sediments in the estuaries. The impact of estuarine sediment-seawater cation exchange appears to be limited when evaluated in the context of the long-term carbon cycle and its main effect is the sequestration of a significant fraction of the riverine Na flux to the oceans. The

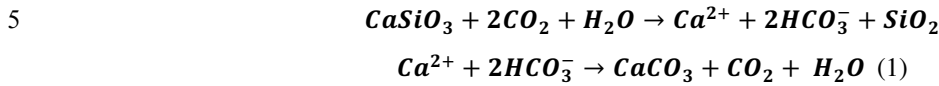
30 limited exchange fluxes of the Ganges-Brahmaputra relate to the lower than average CEC of its sediment load that do not counterbalance the high sediment flux to the oceans. This can be attributed to the nature of Himalayan river sediment such as low proportion of clays and organic matter.

1 Introduction

Chemical weathering on the continents is a primary source of dissolved elements delivered to the oceans. The

35 flux of weathering products, mainly exported through the world rivers, exerts a first order control on oceanic biogeochemical cycles. On geological time scales, silicate weathering also represents a carbon sink that balances mantle and metamorphic CO_2 input to the atmosphere thereby affecting the global climate (Walker et al., 1981). During silicate weathering by acid derived from atmospheric CO_2, Ca ions are released and are transported along

with bicarbonate ions to the oceans, where they are eventually precipitated as carbonates. This mechanism transfers carbon from the atmospheric to the geologic reservoir following the Ebelman-Urey reaction (Ebelmen, 1845; Urey, 1952):

$$CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$$
$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \quad (1)$$

Quantifying the weathering flux exported to the oceans is therefore crucial to assess the role of weathering in the global carbon cycle and further compare it to other mechanisms that control atmospheric CO_2 content on geological time scales. It is further highly relevant to a broader understanding of oceanic geochemical cycles.

Modern continental weathering fluxes have largely been derived from the study of dissolved elements exported by rivers (Gaillardet et al., 1999). However, most of these fluxes do not account for elements delivered to the oceans through cation exchange, when river sediments are transferred through estuaries and towards the ocean. 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 surrounding water chemical composition that the suspended sediment undergoes in a fluvial system occurs in estuaries across the salinity gradient. In the riverine environment, sediment surfaces are mainly occupied by adsorbed Ca^{2+} species, which is the dominant dissolved cation in rivers. When transferred to the oceans, the Ca^{2+} adsorbed on sediment surfaces is partially exchanged for Na^+, Mg^{2+} and K^+ (Sayles and Mangelsdorf, 1977) that are more abundant in ocean waters. These exchange reactions represent an additional source of Ca to the oceans and a potential sink for Na, Mg and K. These estuarine exchange reactions cannot be directly compared to additional weathering fluxes from the chemical weathering of sediments in seawater that has recently been suggested (Jones et al., 2012) as the processes are different. Chemical weathering in the presence of seawater involves the formation of secondary minerals (Jones et al., 2012), which is not the case of exchange reactions.

For the Amazon, Sayles and Mangelsdorf (1979) estimated that cation exchange fluxes remained under 10% of the dissolved flux for the major elements Na, Mg, Ca and K. On a global scale, first order estimates suggest that cation exchange can account for an extra Ca^{2+} flux to the ocean ranging from 5 to 20% of the riverine dissolved flux (Berner and Berner, 2012; Berner et al., 1983; Holland, 1978). Nevertheless, these exchange fluxes to the oceans have received little attention and are currently poorly constrained. Global estimates mainly rely on the upscaling of the Amazon data from Sayles and Mangelsdorf (1979) and the magnitude of these fluxes has so far not been assessed for other major river systems.

In an effort to refine the weathering budget of the Himalayan range and its implications for the long-term carbon cycle, we evaluate the exchange flux delivered to the oceans by the Ganga and Brahmaputra (G&B) Rivers. The G&B is the largest river in terms of sediment export, with a total suspended and bedload sediment flux of ca. 10^9 t.yr^{-1} transported from the Himalayan range to the Bay of Bengal – BoB (RSP, 1996). The high sediment to dissolved load ratio of the G&B of ca. 11 (Galy and France-Lanord, 2001), more than double the world average

(ca. 5, Milliman and Farnsworth (2011)), could potentially yield significant cation exchange fluxes that need to be properly quantified. Raymo and Ruddiman (1992) proposed that Himalayan weathering generated a major uptake of atmospheric carbon during Neogene potentially triggering the Cenozoic climate cooling. This suggestion was moderated based on the observation that Himalayan silicates are mostly alkaline and therefore generate a flux of alkalinity linked to Na and K ions that cannot lead to precipitation of carbonate in the marine environment (France-Lanord and Derry, 1997; Galy and France-Lanord, 1999). Nevertheless, cation exchange on sediment surfaces at the river-ocean transition can potentially exchange Na^+ for Ca^{2+}, strengthening the subsequent carbonate precipitation. Earlier studies on the carbon budget of Himalayan weathering used a rough approximation of this process (France-Lanord and Derry, 1997), and in order to better evaluate the carbon budget of Himalayan silicate weathering, it is necessary to assess the importance of cation exchange fluxes based on the specific physico-chemical properties of G&B suspended sediments.

2 Samples and Methods

2.1 Sampling

Sediments used in this work were sampled at the mouth of the Ganga and Brahmaputra Rivers as well as their confluence in Lower Meghna in Bangladesh during monsoon seasons between 2002 and 2010 (Figure 1). These sample locations integrate all Himalayan tributaries and therefore cover the entire sediment flux exported by the G&B basin. These sampling locations are also located upstream of the Ganga-Brahmaputra estuary and can therefore be considered as true riverine samples. Suspended sediments were sampled along depth profiles in the center of the active channel in order to capture the full variability of transported sediments (Lupker et al., 2011). Bedload samples were dredged from the channel as well. Sediments were filtered at 0.2 µm within 24h of sampling and freeze dried back in the lab. Sediment contact with anything else than river water was prevented to avoid biases in the composition of bound cations due to so called "rinsing effects" (Sayles and Mangelsdorf, 1977). The major element composition of sediments was determined by ICP-OES after $LiBO_2$ fusion at SARM-CRPG (Nancy, France).

2.2 Cation Exchange Capacity determination

The cation exchange capacity (CEC) is defined as the amount of cations bound to mineral surface charges that can be reversibly exchanged. In this work, cation exchange capacity was measured by displacing the adsorbed ions with Cobalt-Hexammine ("CoHex", $Co(NH_3)_6^{3+}$). CoHex is a stable organometallic compound that effectively displaces major cations while maintaining the pH of the sample constant (Ciesielski et al., 1997; Orsini and Remy, 1976). 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). Between 1 and 2g of sediments where reacted with 30 ml of a calcite-saturated CoHex solution for 2 hours. After centrifugation, the remaining cobalt concentration in the supernatant was determined by spectrometric UV absorbance measurements (Aran et al., 2008), which by difference with the initial cobalt concentration of the solution, yields a first estimate of the total CEC of the sediments (CEC_{UV}). 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. The sum of the released cations provides a second determination of the total CEC of the sediments ($CEC_{\Sigma cat}$). No systematic differences between CEC_{UV} and $CEC_{\Sigma cat}$ are observed (Figure 2), which underlines that no significant amounts of other cations are released during exchange or through mineral dissolutions such as dolomite. Repeated measurements showed that the reproducibility of both measurements is better than 10 %. Freeze-drying the sediment samples prior to CEC analyses did not affect their CEC behaviour since different splits of sediments conserved in river water until exchange and splits subsequently freeze-dried showed similar CEC values within uncertainty.

3 Cation Exchange Capacity of Himalayan sediments

3.1 Total cation exchange capacity

The CEC of river sediments in the Ganga, Brahmaputra and lower Meghna are reported in Table 1. The CEC of sediments is correlated to the sediment sampling depth. Surface sediments have generally a higher CEC than coarse bedload sediments. This is further illustrated by the positive correlation between CEC and the Al/Si ratio of sediments (Figure 3). Al/Si is well correlated to grain size, which is controlled by hydraulic mineral sorting of sediments within the water column (Bouchez et al., 2011; Lupker et al., 2012; Lupker et al., 2011). The variable Al/Si ratio of sediments in the water column is to a first order the result of binary mixing between Si-rich, coarse-grained quartz bottom sediments and Al-rich phylosilicates and clays that are relatively enriched in surface sediments. Surface sediments also have a higher surface area favouring adsorption compared to bedload samples (Galy et al., 2008). Sediments from the Ganga show higher CECs for a given Al/Si ratio compared to sediments from the Brahmaputra. Ganga sediments also have a higher surface area (Galy et al., 2008), which can be attributed to a higher abundance of mixed layer and smectite clays of Ganga sediments relative to the Brahmaputra (Heroy et al. 2003; Huyghe et al., 2011). Additionally, the CEC of surface sediments may also be enhanced because of the higher organic matter content of river surface samples (Galy et al., 2008) that can provide additional exchange capacity (e.g. Thompson et al., 1989; Turpault et al., 1996). The variable CEC of sediments in the water column and amongst river reaches can therefore be tentatively summarized as resulting from the mineralogical and grain-size control on the surface area and organic matter loading of the sediments (Malcolm and Kennedy, 1970).

3.2 Nature of adsorbed cations

Figure 4 shows the molar fraction of each major cation adsorbed onto the sediments delivered to the Bay of Bengal. Ca^{2+} and Mg^{2+} are the dominant adsorbed cations in river water with 76 % and 16 % of the total exchangeable cations, respectively. Na^+ and K^+ account respectively for 1 % and 7 % of the total adsorbed species. However, in contrast to total CEC, the nature of the exchangeable cations is not dependent on the Al/Si ratio of the sediments and is constant amongst all samples. The partitioning of exchangeable cations bound to the riverine sediments is therefore not controlled by grain-size or mineralogical sorting in the water column. These exchangeable compositions are also very similar for Ganga, Brahmaputra and Lower-Meghna sediments and for samples collected over different years.

The composition of sediment exchangeable cations is to a first order imposed by the dissolved composition of the river water transporting these sediments. For the two most abundant adsorbed cations, the binary Ca/Mg exchange

is commonly described as an exchange isotherm with an equilibrium constant K_v (Sayles and Mangelsdorf, 1979), such that:

$$\frac{X_{Ca}}{X_{Mg}} = K_v \cdot \left(\frac{a_{Ca}}{a_{Mg}}\right)^p$$

5   (2)

where X_{Ca} and X_{Mg} are the fraction of adsorbed cations, a_{Ca} and a_{Mg} the cation activity in the river water and p a constant. The chemical composition of the river water directly in contact with the sampled sediments has not been systematically measured. However, the constant composition of exchangeable cations for sediments sampled at

10   different seasons suggests that a first order determination of K_v can be made using the average dissolved composition of the Ganga, Brahmaputra and Lower Meghna (Galy and France-Lanord, 1999). The equilibrium constant, K_v, for sediments of the Ganga, Brahmaputra and lower Meghna is relatively similar (between 1.7 and 2 for p = 1) despite the use of average dissolved river water compositions that do not take into account for the compositional variability of these rivers (Galy and France-Lanord, 1999; Singh et al., 2005). Using a p value of

15   0.76 as found in Amazon sediments (Sayles and Mangelsdorf, 1979), the calculated K_v ranges from 2.1 to 2.5, also in agreement with the equilibrium constants found on the Amazon (Table 1). These very similar constants show that the behaviour of Himalayan sediments with respect to the cation exchange composition is very similar to the sediments transported by the Amazon. These similarities most probably stem from the first order resemblance of the mineralogical composition of both rivers (Garzanti et al., 2011; Martinelli et al., 1993).

20   **3.3 Exchangeable flux to the Bay of Bengal**

In order to derive the flux of exchangeable cations that can be delivered to the Bay of Bengal by Himalayan sediments it is necessary to take into account the variability of the CEC of sediments with the water depth. The average CEC of sediments exported to the BoB can be constrained using the average Al/Si ratio of the sediments owing to the linear correlation between CEC and Al/Si (Figure 3). Lupker et al. (2011) constrained the average

25   Al/Si of Ganga sediments in Bangladesh to 0.23. Changes in the Al/Si ratio of sediments during transport are mainly the result of sequestration of quartz rich sediments in the subsiding floodplain. In the case of the Ganga, the sequestrated flux is limited and the Al/Si ratio of sediments in Bangladesh is close to that inferred for the Himalayan crust. The major immobile element content (Al, Si and Fe) of Brahmaputra sediments is very similar to that of Ganga sediments (Lupker, 2011) suggesting that the parent material has a very similar composition.

30   Furthermore, the constricted morphology of the Brahmaputra floodplain does not favour high sedimentation fluxes in the floodplain. We therefore suppose here that the average Al/Si of the Brahmaputra is very similar to that of Ganga sediments.

Using an Al/Si ratio of 0.23 ($\pm$0.01) yields an average total CEC of 8.0 ($\pm$0.9), 4.2 ($\pm$1.2) and 6.5 ($\pm$1.3) meq/100g

35   for Ganga, Brahmaputra and lower Meghna sediments respectively. The average lower Meghna CEC deduced from the regression through the analysed sediments is very similar to the ca. 6.0 ($\pm$1.1) meq/100g CEC that would be expected from the mixing of 550×10^6 t/yr of Ganga sediments and 590×10^6 t/yr of Brahmaputra sediments

(RSP, 1996). For a combined Ganga and Brahmaputra sediment flux of 1.14×10^9 t/yr, the total exchange capacity of the sediments amounts to 74.1 ($\pm$14.8) $\times 10^{12}$ meq/yr. The maximum exchangeable flux is reported in Table 2. During exchange with seawater, river sediments mainly lose Ca^{2+} to the ocean while adsorbing Mg^{2+}, Na^+ and K^+ (Sayles and Mangelsdorf, 1979, 1977). Assuming a total exchange of Ca^{2+} (the dominant cation in riverine water)

5   for Na^+ (the dominant cation in seawater) during the transfer of sediments to the ocean yields a maximum exchange flux of 28 ($\pm$6) $\times 10^9$ mol/yr Ca^{2+} to the Indian Ocean, while 56 ($\pm$12) $\times 10^9$ mol/yr Na^+ are adsorbed onto the sediments. These additional Ca, and lower Na fluxes to the ocean are not accounted for by modern dissolved riverine fluxes.

10   However, Sayles and Mangelsdorf (1979; 1977) showed that only a fraction of adsorbed Ca^{2+} is exchanged during prolonged contact of sediments and clays with seawater and that these cations are not only exchanged for Na^+ but also partially for Mg^{2+} and K^+. In their experiments, the authors found that ca. 82% of the adsorbed riverine Ca^{2+} is exchanged for Na^+, Mg^{2+} and K^+ in respective molar proportions of 58%, 32% and 10%. For the estimation of the most probable flux of cations exchanged by Ganga-Brahmaputra sediments upon entry in the Indian Ocean,

15   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

20   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 ($\pm$4) $\times 10^9$ mol of Ca^{2+} are

25   desorbed from the sediments in the Bay of Bengal while 27 ($\pm$8) $\times 10^9$ mol Na^+, 5 ($\pm$2) $\times 10^9$ mol K^+, and 8 ($\pm$3) $\times 10^9$ mol Mg^{2+} are reabsorbed (Table 3). The main exchange reaction is therefore still the exchange of riverine Ca^{2+} for marine Na^+, but non-negligible amounts of K^+ and Mg^{2+} are fixed in the marine environment by the sediments.

3.4 Comparison with Ganga-Brahmaputra dissolved fluxes

30   To evaluate the importance of cation exchange fluxes to the ocean we compare the maximum and probable exchange fluxes derived above to the dissolved flux exported by the G&B. Galy and France-Lanord (1999) estimated that the G&B export an annual molar flux of 183×10^9 Na^+, 59×10^9 K^+, 462×10^9 Ca^{2+} and 187×10^9 Mg^{2+}. These estimates are close to the fluxes estimated from the GEMS / Water program (UNESCO) and show the dominance of the Ca^{2+} flux, largely derived from carbonate dissolution. Assuming a total replacement of

35   adsorbed Ca^{2+} with seawater Na^+, the maximum cation exchange flux would be +28 ($\pm$6) $\times 10^9$ mol/yr Ca^{2+} and -56 ($\pm$12) $\times 10^9$ mol/yr Na^+ to the dissolved flux. This would increase by ca. 6% the riverine Ca^{2+} flux and decrease by 32% the Na^+ flux (Figure 5). However as discussed earlier, total cation exchange is not expected and a more probable exchange flux can be determined from Sayles and Mangelsdorf (1979) work on the Amazon. This more probable estimate suggests that the cation exchange flux represents an addition of ca. 5% of the dissolved Ca^{2+}

flux and a subtraction of 16% of the dissolved Na^+ flux, 8% of the dissolved K^+ flux and 4% of the dissolved Mg^{2+} flux (Table 3, Figure 5). The main effect of estuarine cation exchange for the Himalayan weathering budget is therefore a moderate but significant decrease of the overall Na^+ flux to the Indian Ocean since about one sixth of the riverine flux is reabsorbed. The increase in riverine Ca^{2+} and decrease in K^+, Mg^{2+} fluxes remain limited.

4 Discussion

4.1 Magnitude of cation exchange fluxes

The exchange fluxes of G&B sediments are in the order of few percent of the riverine dissolved fluxes exported to the Bay of Bengal. Despite the fact that the G&B sediment flux is of the same order of magnitude as that of the Amazon River (Milliman and Farnsworth, 2011), the cation exchange flux of the G&B appears lower by a factor 3 to 5 depending on the element, compared to that determined for the Amazon by Sayles and Mangelsdorf (1979). This difference can be attributed to the lower average CEC value of ca. 6 meq/100g of the G&B sediments compared to the ca. 22 meq/100g of Amazon sediments, (Sayles and Mangelsdorf, 1979) that compensates for the high sediment yield of the Himalayan system. The overall low CEC of G&B sediments also limits the relative importance of cation exchange on the dissolved fluxes. Even though the suspended to dissolved load ratio of the G&B is almost 3 times higher than that of the Amazon River (ca. 4, Milliman and Farnsworth (2011)) the effect of cation exchange are comparable with an increase of ca. 4 to 5% of the Ca^{2+} dissolved flux and a decrease of 4 to 8 % of the Mg^{2+} and 6 to 8% of the K^+ dissolved fluxes (Sayles and Mangelsdorf, 1979). The effect of riverine Na^+ re-adsorption is more substantial with a decrease of ca. 16% for the G&B compared to the 6% determined for the Amazon, but this can mainly be attributed to the high dissolved Na flux of the Amazon. If a CEC value of world average river sediments of 18 meq/100g is retained (Berner and Berner, 1996; Holland, 1978), the total riverine cation exchangeable flux would also be higher by a factor of ca. 3 and yield an additional Ca^{2+} flux in excess of 15 to 18 % compared to the actual dissolved Ca^{2+} flux. This difference highlights the importance of assessing the average CEC on a river-by-river basis.

The relatively low CEC values of G&B sediments can be linked to the dominance of physical erosion in the Himalayan system that does not favour the formation of high area clay minerals (smectite) and leads to the export of clays dominated by illite and overall coarse-grained material with low surface areas (Galy et al. 2008). CEC exchange fluxes can be expected to scale with the magnitude of sediment fluxes, which means that the underestimation of modern dissolved chemical weathering fluxes is greatest in the most active areas with highest dissolved fluxes (West et al., 2005). However, it seems unlikely that this scaling is linear since active erosion processes do not necessarily favour high surface area mineral formations and hence limit the overall CEC of exported sediments. We would therefore expect the CEC flux over dissolved flux ratio to decrease with increasing erosion or sediment yield. 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.

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"

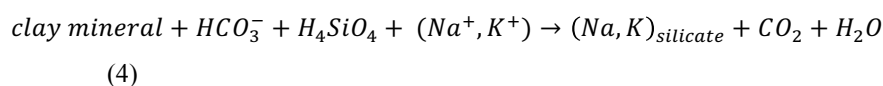
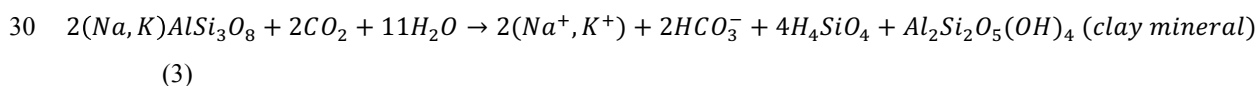
10   fluxes are of a similar order of magnitude as cyclic salt corrections commonly applied to river water compositions for K^+, Ca^{2+} and Mg^{2+} (e.g. Galy et al., 1999). Riverine dissolved compositions are also largely used to apportion the contribution of silicate and carbonate weathering to the total riverine Ca^{2+} flux. This is generally based on the total Na^+ and K^+ fluxes (as these are assumed to be unambiguously 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

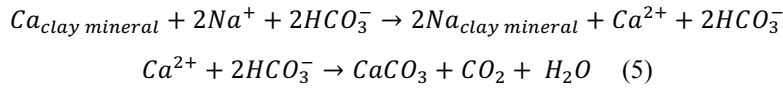
15   of Ca^{2+} and K^+ compared to Na^+ by cation exchange in the riverine environment will affect the measured dissolved Ca/Na ratios (Ca/K being less affected as both cations are taken up in very similar proportions). It has been suggested that these effects could be significant (Tipper, 2015). However, 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.

20   **4.2 Effect of cation exchange on the long-term carbon budget of Himalayan erosion**

The effect of continental weathering on the long-term carbon cycle is mainly dictated by dissolved fluxes derived from Ca-silicate weathering following the Ebelmen-Urey reaction (eq. 1) because it can directly lead to precipitation of carbonate. This reaction stabilizes half of the alkalinity flux used to dissolve the initial silicates and release the other half as CO_2 to the ocean and atmosphere. Silicate-derived Mg fluxes are also similarly

25   efficient as they are exchanged for Ca during oceanic crust alteration or consumed during Mg-rich calcite precipitation (Berner and Berner, 2012). In contrast, it is generally assumed that on the long-term, the uptake of CO_2 by Na^+ or K^+ silicate weathering (eq. 3) is balanced by the CO_2 release during the formation of new Na and K silicates on the seafloor during reverse weathering reactions (eq. 4) (MacKenzie and Garrels, 1966).

30    $$2(Na,K)AlSi_3O_8 + 2CO_2 + 11H_2O \rightarrow 2(Na^+,K^+) + 2HCO_3^- + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4 \; (clay\ mineral)$$
(3)
$$clay\ mineral + HCO_3^- + H_4SiO_4 + (Na^+,K^+) \rightarrow (Na,K)_{silicate} + CO_2 + H_2O$$
(4)

35   In such case case, Na and K silicate weathering do not participate in the long-term carbon budget of continental erosion. Alternatively, cation exchange reaction allows exchange of Na^+ or K^+ for Ca^{2+} and may subsequently lead to $CaCO_3$ precipitation and long term carbon sequestration (eq. 5) (Berner, 2004; Berner et al., 1983; MacKenzie and Garrels, 1966; Michalopoulos and Aller, 1995).

$$Ca_{clay\ mineral} + 2Na^+ + 2HCO_3^- \rightarrow 2Na_{clay\ mineral} + Ca^{2+} + 2HCO_3^-$$
$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \quad (5)$$

Assuming annual exchange fluxes as discussed above (Table 3), 27×10^9 mol/yr Na^+ and 5×10^9 mol/yr K^+ would be exchanged for 16×10^9 mol/yr Ca^{2+} which can ultimately precipitate as $CaCO_3$. This is substantial but remains relatively marginal compared to the total flux of silicate derived alkalinity of the Ganga-Brahmaputra that is estimated to be around 270×10^9 mol/yr (Galy and France-Lanord, 1999). 60 to 65% of this silicate alkalinity is balanced by Na^+ and K^+, which corresponds to 160 to 175×10^9 mol/yr of HCO_3^-. Therefore, about 10% of the alkalinity linked to Na-K silicate weathering could finally lead to carbonate precipitation through cation exchange. Hence the total flux of silicate weathering derived alkalinity that can precipitate as $CaCO_3$ is 55 to 62×10^9 mol/yr. This estimate remains highly speculative since the extent and magnitude of reverse weathering reactions are currently poorly quantified.

These fluxes may be substantial but are still limited when compared to the ca. 300×10^9 mol/yr C storage associated to the organic carbon burial fluxes of the modern Himalayan system (Galy et al., 2007), which remains the main forcing of the carbon cycle from Himalayan erosion. It should nevertheless be kept in mind that our estimates are formulated based on the Himalayan system at present. On longer time scales, the variability in both sediment (Goodbred and Kuehl, 2000) and weathering fluxes (Lupker et al., 2013) mean that the relative importance of cation exchange fluxes in the global weathering budget has likely varied and hence should be treated carefully. Finally, it's worth mentioning that these estimates of weathering impact on the carbon cycle do not take into account the role of chemical weathering through sulfuric acid (Galy and France-Lanord, 1999; Turchyn et al., 2013) that is known to also contribute to the weathering budget of Himalayan erosion and does counteract long-term carbon sequestration (Calmels et al., 2007).

5 Conclusions

The Ganga-Brahmaputra is the highest sediment point source of sediment to the oceans with an export of about 1 billion tons of sediments every year. The high average sediment concentration suggests that the cation exchange fluxes of this system may be significant or at least need to be quantified in order to derive robust weathering flux estimates. The flux of exchangeable cations has been quantified in this study based on CEC measurements of riverine sediments. These measurements show that the CEC of sediments is strongly variable within the water column, which is linked to sediment sorting effects and variable mineralogical composition with depth. Contrary to the total CEC, the nature of adsorbed cations is remarkably constant amongst all samples with the dominance of divalent cations Ca^{2+} and Mg^{2+}. The equilibrium constants between adsorbed cations and river water composition of the Ganga-Brahmaputra are also very close to the ones derived for sediments from the Amazon in a previous study.

Based on the sediment flux of the Ganga-Brahmaputra and assuming a total exchange of adsorbed riverine Ca^{2+} for marine Na^+ we estimated that estuarine cation exchange could increase the dissolved Ca^{2+} flux to the ocean by 6 % at most. Taking more realistic estimations based on a partial exchange of riverine Ca^{2+} for marine Na^+,

Mg^{2+} and K^+ yields an increased Ca^{2+} flux of ca. 5%, while the equivalent of 15% of the dissolved Na^+ flux, 8% of the dissolved K^+ flux and 4% of the Mg^{2+} are reabsorbed by the sediments in the estuaries. Estuarine sediment-seawater cation exchange is therefore mainly a riverine Na^+ sink. In the context of the long-term carbon budget of Himalayan erosion, cation exchange increases the pool of Ca^{2+} that can participate to $CaCO_3$ storage. This additional flux is however limited to ca. 10% of the Ca-Mg silicate derived flux. In spite of the very intense particle flux associated to physical erosion of the Himalaya, the cation exchange process occurring in the estuarine zone does not change significantly the estimate of the impact of silicate weathering on long term carbon sequestration. It is likely limited by the relatively coarse nature and low surface area of Himalayan sediments that lead to an overall low CEC.

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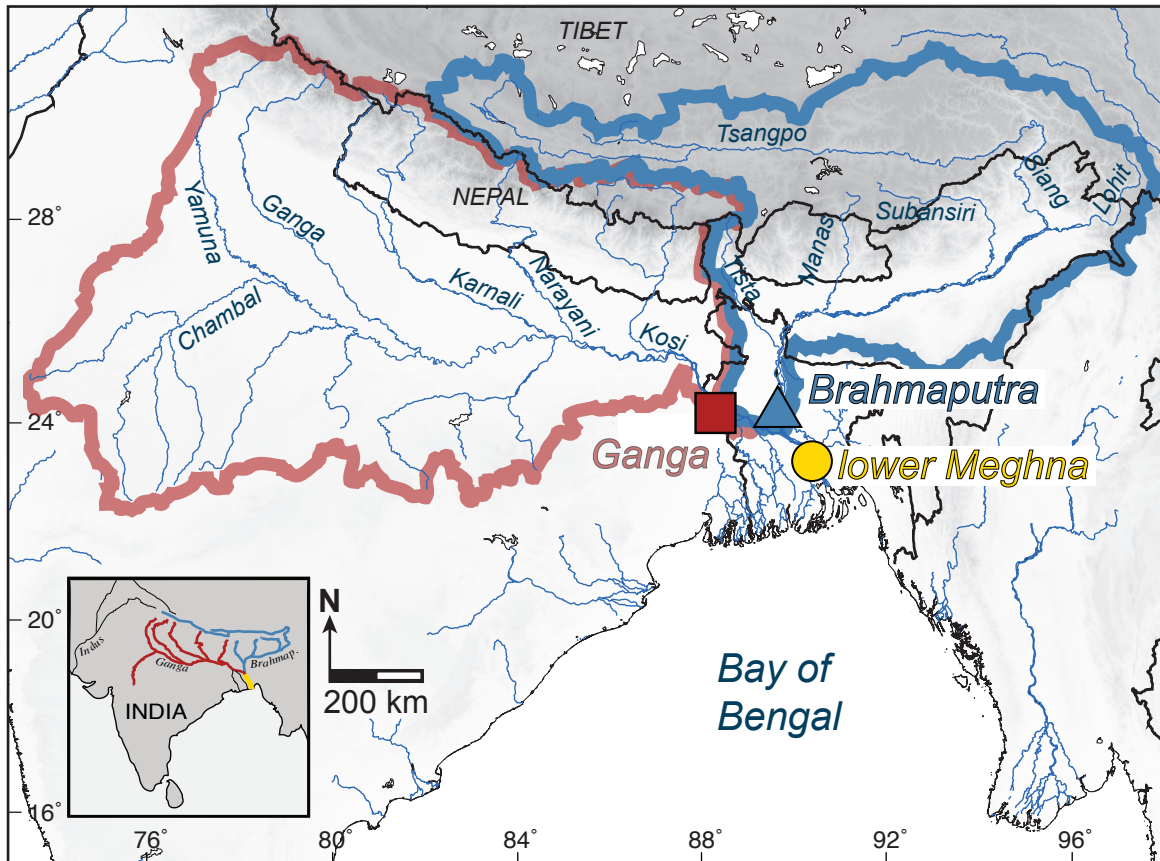


Figure 1: Map of the Ganga and Brahmaputra basins (respectively delimited in red and blue) and sampling locations of sediments used in this study on the Ganga River, the Bramaputra River and the lower Meghna River, which is the confluence of both rivers.

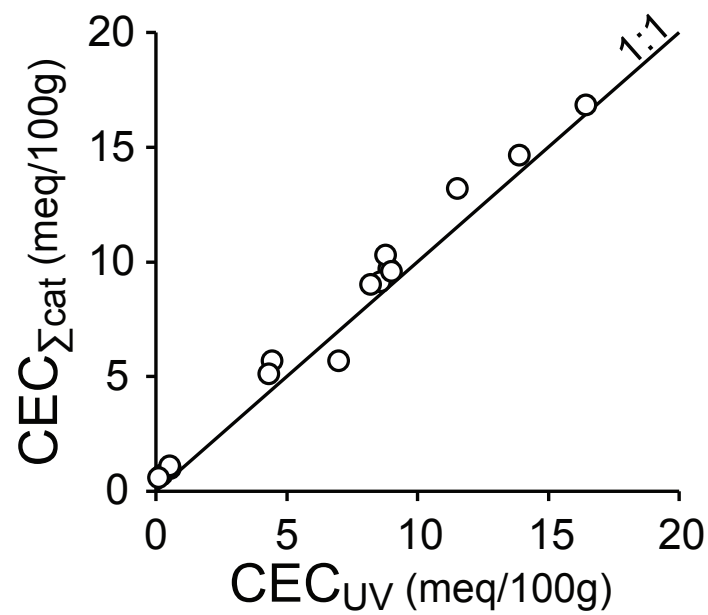



Figure 2: Total CEC determined by the sum of cations (Ca^{2+} + Mg^{2+} + Na^+ + K^+) released after sediment exchange with a CoHex solution ($CEC_{\Sigma cat}$) as a function of the total CEC determined based on the absorption of cobalt ions from the CoHex solution after exchange (CEC_{UV}). For each sample $CEC_{\Sigma cat}$ and CEC_{UV} where determined on the same CoHex solution.

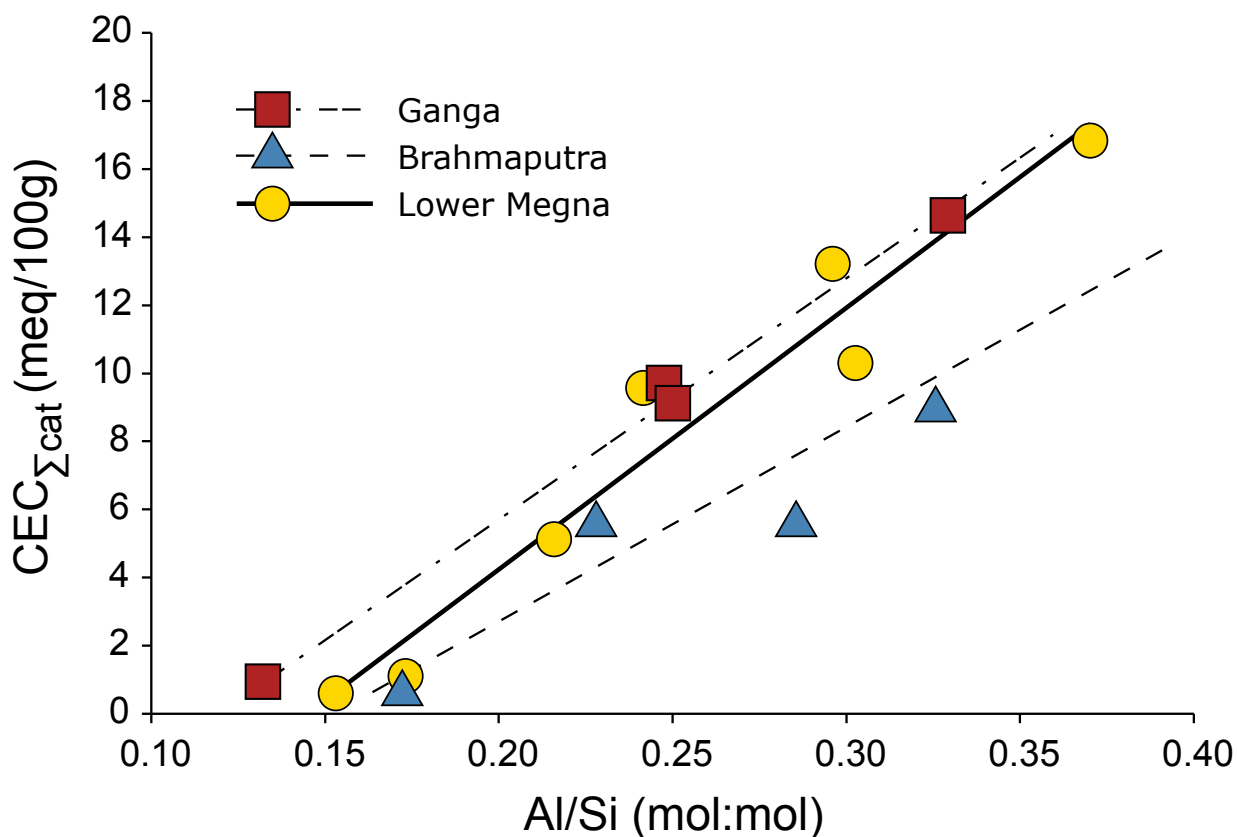



Figure 3: CEC of sediment samples from the Ganga, Brahmaputra and lower Meghna Rivers as a function of Al/Si that is used here as a proxy for grain size and sediment sorting in the river channel.

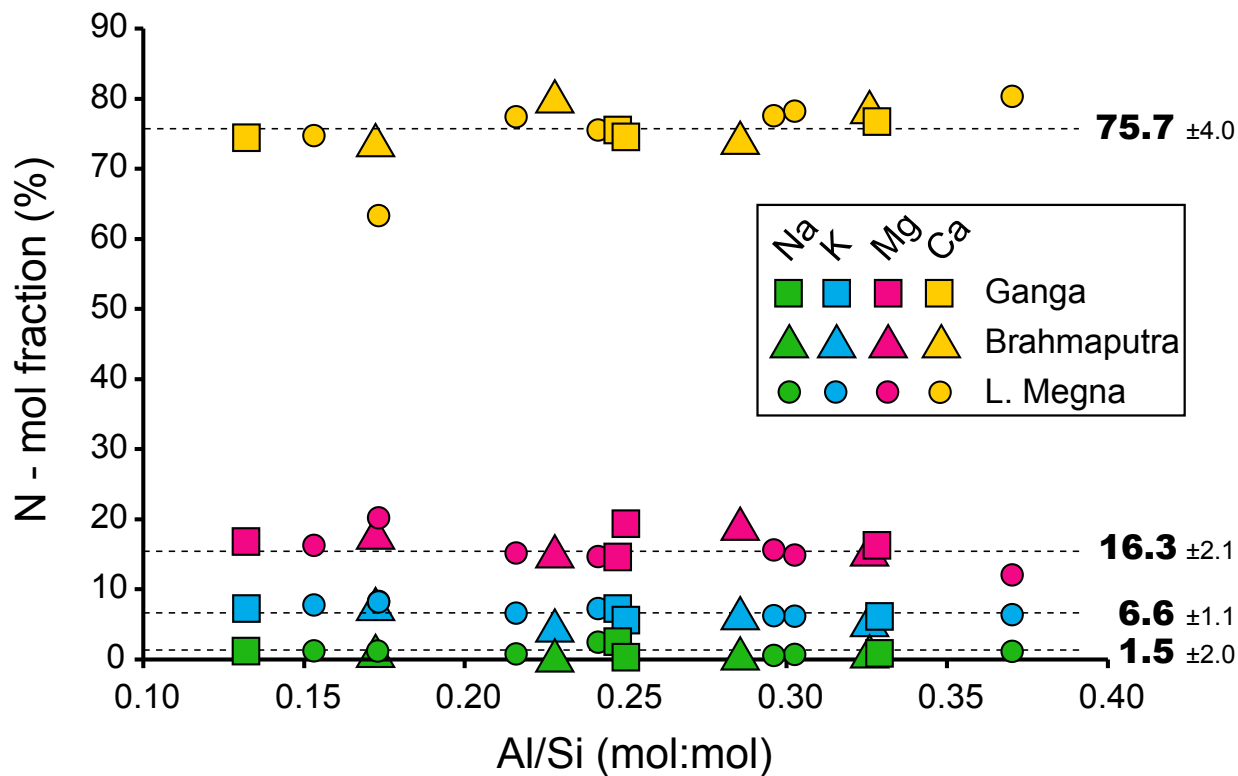
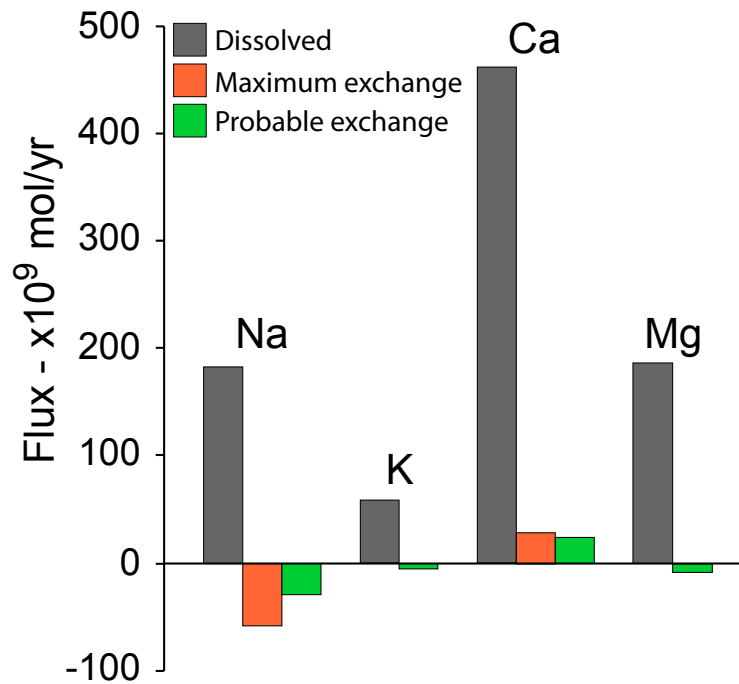



Figure 4: Molar fraction of major cations absorbed to sediments in the Ganga, Brahmaputra and lower Meghna Rivers as a function of Al/Si.

5   **Figure 5:** Maximum cation exchange fluxes (for a complete exchange of riverine Ca^{2+} for Na$^+$) and more probable exchange fluxes (partial exchange of riverine Ca^{2+} for Mg^{2+}, K$^+$ and Na$^+$) based on exchange data of Sayles and Mangelsdorf (1977; 1979) of G&B sediments. These exchange fluxes are compared to the total dissolved fluxes exported by the G&B as estimated by Galy and France-Lanord (1999).

Sample n°	River	Sample type	Water depth	Sampling date	Latitude	Longitude	Al/Si	CEC$_{UV}$	CEC$_{\Sigma cat}$	Na	K	Ca	Mg	X$_{Na}$	X$_K$	X$_{Ca}$	X$_{Mg}$	Kv (p=1)	Kv (p=0.76)
			m		°N	°E	mol:mol			meq/100g				mol:mol					
BR8221	Ganga	Bedload	12	01.09.2008	24.0599	89.0232	0.132	0.54	1.00	0.01	0.04	0.78	0.18	0.01	0.07	0.74	0.17	1.6	2.1
BR715	Ganga	Suspended	3	17.08.2007	24.0550	89.0313	0.247	8.90	9.71	0.13	0.37	7.71	1.50	0.02	0.07	0.76	0.15	1.9	2.4
BR1027 (n=7)	Ganga	Bedload	12	08.07.2010	24.0527	89.0248	0.250	8.57	9.13	0.02	0.27	7.02	1.83	0.00	0.06	0.75	0.19	1.4	1.8
BR8222	Ganga	Suspended	0	01.09.2008	24.0599	89.0232	0.328	13.90	14.65	0.06	0.47	11.65	2.47	0.01	0.06	0.77	0.16	1.7	2.2
average										*0.05*	*0.29*	*6.79*	*1.49*	*0.01*	*0.07*	*0.75*	*0.17*	*1.7*	*2.1*
BR8206	Brahmaputra	Bedload	10	31.08.2008	24.3712	89.7640	0.172	0.23	0.71	0.00	0.03	0.55	0.13	0.00	0.08	0.74	0.18	1.8	2.2
BR207 (n=7)	Brahmaputra	Suspended	1	15.07.2002	24.3848	89.7971	0.228	6.98	5.69	0.02	0.13	4.67	0.88	0.01	0.04	0.80	0.15	2.4	2.9
BR8204	Brahmaputra	Suspended	1	31.08.2008	24.3704	89.7639	0.286	4.44	5.70	0.02	0.18	4.38	1.12	0.01	0.06	0.74	0.19	1.7	2.1
BR8210	Brahmaputra	Suspended	0	31.08.2008	24.7973	89.7973	0.326	8.20	9.03	0.04	0.22	7.30	1.46	0.01	0.05	0.79	0.16	2.2	2.7
average										*0.02*	*0.14*	*4.22*	*0.90*	*0.01*	*0.06*	*0.77*	*0.17*	*2.0*	*2.5*
BR8230	lower Meghna	Bedload	17	03.09.2008	22.5878	90.7599	0.173	0.51	1.10	0.05	0.05	0.76	0.24	0.08	0.08	0.63	0.20	1.3	1.6
BR8226	lower Meghna	Suspended	16	03.09.2008	22.5872	90.7622	0.216	4.32	5.13	0.02	0.18	4.12	0.81	0.01	0.07	0.77	0.15	2.1	2.6
BR8227	lower Meghna	Suspended	10	03.09.2008	22.5876	90.7615	0.303	8.77	10.31	0.04	0.33	8.35	1.59	0.01	0.06	0.78	0.15	2.1	2.7
BR724	lower Meghna	Bedload	11	19.08.2007	23.4563	90.2555	0.153	0.11	0.60	0.00	0.02	0.47	0.10	0.01	0.08	0.75	0.16	1.9	2.3
BR721	lower Meghna	Suspended	10	19.08.2007	23.4598	90.2540	0.241	9.00	9.57	0.12	0.37	7.60	1.48	0.02	0.07	0.76	0.15	2.1	2.6
BR8202	lower Meghna	Suspended	1	29.08.2008	23.4263	90.2516	0.296	11.51	13.21	0.04	0.43	10.60	2.14	0.01	0.06	0.78	0.16	2.0	2.5
BR723	lower Meghna	Suspended	0	19.08.2007	23.4597	90.2534	0.370	16.43	16.86	0.10	0.56	14.08	2.12	0.01	0.06	0.80	0.12	2.7	3.4
average										*0.05*	*0.28*	*6.57*	*1.21*	*0.02*	*0.07*	*0.75*	*0.16*	*2.0*	*2.5*

Table 1: Sample number, location, chemical composition (Al/Si) and exchange data of sediments used in this study. The total CEC determined through cobalt absorption (CEC$_{UV}$) is given along with total CEC determined from the sum of major cations released during exchange (CEC$_{\Sigma cat}$). Molar fractions occupied by the major cations on the river sediments are indicated as X$_{Na}$,

X_K, X_{Ca} and X_{Mg}. The exchange coefficient for a binary Ca-Mg exchange in an average Ganga, Brahmaputra and lower Meghna river water composition is given for a p-exponent value of 1 and 0.76 as in Sayles and Mangelsdorf (1979), see text for more details. Samples BR1027 and BR207 are average values of n = 7 replicates each.

River	Average CEC	Sediment flux	Total exchangeable	Na exchangeable	K exchangeable	Ca exchangeable	Mg exchangeable
	meq/100g	Mt/yr	1e12 meq/yr			1e12 meq/yr	
Ganga	8.0 (±0.9)	550	44.0 (±5.0)	0.7 (±0.7)	2.9 (±0.6)	33.3 (±4.2)	7.2 (±1.2)
Brahmaputra	4.2 (±1.2)	590	24.8 (±7.1)	0.4 (±0.4)	1.6 (±0.5)	18.8 (±5.5)	4.0 (±1.3)
lower Meghna	6.5 (±1.3)	1140	74.1 (±14.8)	1.1 (±1.1)	4.9 (±1.3)	56.1 (±11.6)	12.1 (±2.9)

Table 2: Sediment fluxes (RSP, 1996), average CEC of the sediments and exchangeable flux of major cations bound to

10   **the river sediments.**

			Ganga	Brahmaputra	lower Meghna
Na	Total exchangeable	$\times 10^9$ mol/yr	0.7 (±0.7)	0.4 (±0.4)	1.1 (±1.1)
	Riverine dissolved flux		128	55	183
	Total ex. - % of dissolved		0.5%	0.7%	0.6%
	Probable exchange		-15.8 (4.4)	-8.9 (±2.5)	-26.6 (±7.3)
	Prob. ex. - % of dissolved		12%	16%	15%
K	Total exchangeable	$\times 10^9$ mol/yr	2.9 (±0.6)	1.6 (±0.5)	4.9 (±1.3)
	Riverine dissolved flux		29	29	58
	Total ex. - % of dissolved		10%	6%	8%
	Probable exchange		-2.7 (±0.7)	-1.5 (±0.4)	-4.5 (±1.5)
	Prob. ex. - % of dissolved		9%	5%	8%
Ca	Total exchangeable	$\times 10^9$ mol/yr	16.7 (±2.1)	9.4 (±2.8)	28.1 (±5.8)
	Riverine dissolved flux		252	211	463
	Total ex. - % of dissolved		7%	4%	6%
	Probable exchange		13.7 (±2.2)	7.7 (±1.2)	23.0 (±3.7)
	Prob. ex. - % of dissolved		6%	4%	5%
Mg	Total exchangeable	$\times 10^9$ mol/yr	3.6 (±0.6)	2.0 (±0.7)	6.1 (±1.5)
	Riverine dissolved flux		93	94	187
	Total ex. - % of dissolved		4%	2%	3%
	Probable exchange		-4.5 (±1.2)	-2.5 (±0.7)	-7.6 (±2.1)
	Prob. ex. - % of dissolved		5%	3%	4%

Table 3: Total exchangeable flux of major cations bound to the sediment in river water and most probable exchange

fluxes taking place during interaction of G&B sediments with seawater based on the measured total exchangeable

cations and the effective exchange proportions of Sayles and Mangelsdorf (1977; 1979). These fluxes are compared to

the riverine dissolved fluxes as given by Galy and France-Lanord (1999).