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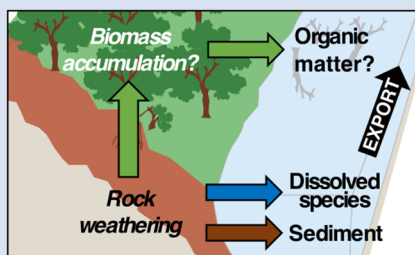
A global imbalance in potassium and barium river export: the result of biological uptake?

Q. Charbonnier^{1,2*}, J. Bouchez¹, J. Gaillardet^{1,3}, E. Gayer¹, S. Porder⁴



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Abstract



The role of biological cycling on the chemistry of rivers remains poorly understood. In an attempt to close this knowledge gap, here we examine the difference between the elemental supply to catchments through rock degradation and the corresponding elemental riverine export, for two non-nutrient elements lithium (Li) and sodium (Na) and two nutrients-like elements potassium (K) and barium (Ba), in 20 of the largest world river catchments. Overall, the riverine export of K and Ba are lower than their estimated release by catchment scale rock degradation, while the two fluxes match for Li and Na. Barium isotope constraints lending support to this observation, we take this difference between these two element groups as a suggestion of the influence of biological uptake of rock-derived nutrients on river chemistry.

Nevertheless, the magnitude of riverine K depletion cannot be reconciled with a pervasive growth of the biota on continents, nor with an “occult” export of organic material that would go unnoticed by common sampling protocols. One plausible explanation for this conundrum could lie in the complex partitioning of elements amongst soil, biota, and dead organic matter. As a consequence, our study emphasises the need for further work aiming at deciphering the cycle of rock-derived nutrients in the Critical Zone.

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Introduction

The Earth surface hosts a suite of complex interactions between the lithosphere, the hydrosphere, the atmosphere, and the biosphere which all occur in the “Critical Zone” (CZ) between un-weathered rock and the atmosphere (Riebe *et al.*, 2017). Chemical weathering within the CZ regulates atmospheric CO₂ over million year timescales, influences soil formation, and releases rock-derived nutrients to ecosystems, thereby profoundly influencing life on Earth (Gaillardet *et al.*, 2018).

As the CZ cannot be sampled in its totality, river chemistry is an integral tool for large scale studies of the CZ processes. River loads of base cations (Na⁺, K⁺, Mg²⁺, and Ca²⁺) and dissolved silica (SiO₂) are commonly used to derive catchment scale weathering fluxes and associated CO₂ consumption (Bouchez and Gaillardet, 2014). This approach assumes some balance between the production of major solutes by rock weathering and their riverine export. However, this assumption is falsified if processes exist in the CZ that transiently store base cations. In particular, the biological uptake of the major rock-derived nutrients Ca, Mg, K, and Si is almost always assumed to be in balance with their release during organic matter degradation in soils (Viers *et al.*, 2014). Were this assumption violated, river chemistry would not faithfully record chemical weathering processes and rates. An apparent deficit of rock-derived nutrients in the river load, together with shifts in their isotope signatures, has

been reported for a range of bio-utilised elements such as K, Mg, Ca, P and Ba in streams (von Blanckenburg *et al.*, 2021) as well as in the Amazon (Charbonnier *et al.*, 2020), suggestive of imbalance in the export of rock-derived nutrients. Such deficit might be due to changes in the size of the biological reservoir with time beyond the typical observational time scale of a few years; or might occur if the transport of unsampled river particulate organic matter constitutes a significant pathway of rock-derived nutrient export from the catchment.

Here we show that data from the largest world rivers provide evidence for a global imbalance in the river export of cations, and examine the role potentially played by the biota as an “embezzler” of nutrient river fluxes (Fig. 1). We achieve this goal through the comparison of estimates of rock-derived nutrients supply to the CZ through rock weathering – along with their isotopes – against their actual riverine export.

A Global Imbalance in Rock-Derived Nutrient Riverine Export from the Critical Zone

We quantify the catchment scale budgets between rock degradation by chemical weathering and subsequent riverine export for some of the world largest rivers, for a series of elements: lithium (Li), sodium (Na), potassium (K), barium (Ba). Large rivers

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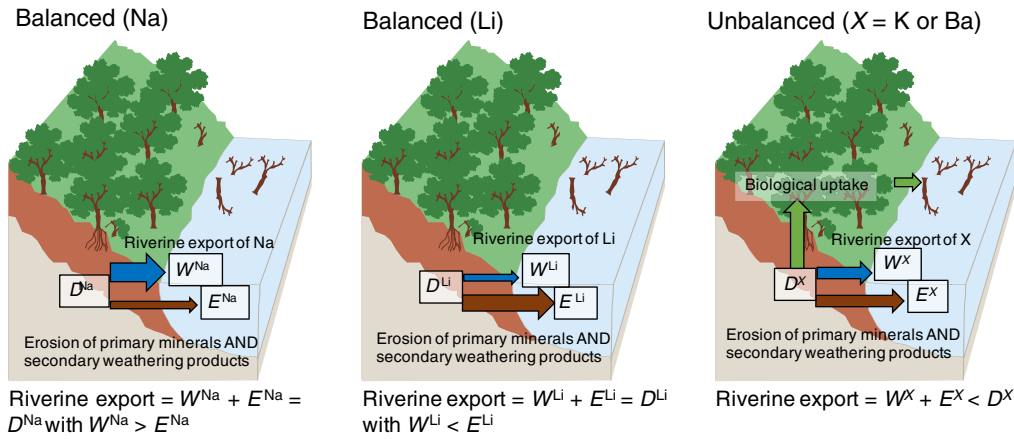


Figure 1 Conceptual sketch of the catchment scale mass budgets, for $X = Na, Li$ (non-nutrients) and for nutrient/nutrient-like elements ($X = K$ and Ba). This approach aims to quantify the catchment scale (im)balance between the supply of a rock-derived nutrient X through rock degradation (D^X) and the summed dissolved and solid riverine export (W^X and E^X , respectively). The difference in the “solubility” translates into a difference in the size of the W^X and E^X arrows.

draining significant portions of the continents offer unique access to first order, global information on the cycle of elements. The set of large rivers considered here encompasses various geological, geomorphological, and climatic contexts. Detail on sample locations and analytical methods is provided in the [Supplementary Information](#), together with a full derivation of the mass balance equations used to quantify the river mass budget.

Briefly, in this approach inspired from previous work such as [Gaillardet et al. \(1999\)](#), we establish the equation: bedrock = dissolved load + particulate load, for some silicate-derived soluble elements (*i.e.* partitioned between the dissolved and residual particulate phases of weathering) such as here lithium, sodium,

potassium and barium, as well as for insoluble elements (such as aluminium, samarium and thorium) that are only transported in the particulate form ([Fig. 1](#)). Graphically, data for different elements and rivers can then be plotted in a diagram representing the fraction of the soluble element X transported in the dissolved load, against the relative depletion factor of this soluble element in the particulate load (compared to bedrock), as in [Figure 2](#). A balanced river mass budget is manifested as data points lying on the down sloping diagonal in [Figure 2](#), whereas depletion of X in the total river export (be it a deficit in the river dissolved or solid load) translates into data points below this diagonal. Critically, partitioning of X between the dissolved and solid river exports does not have any influence on the results of the river

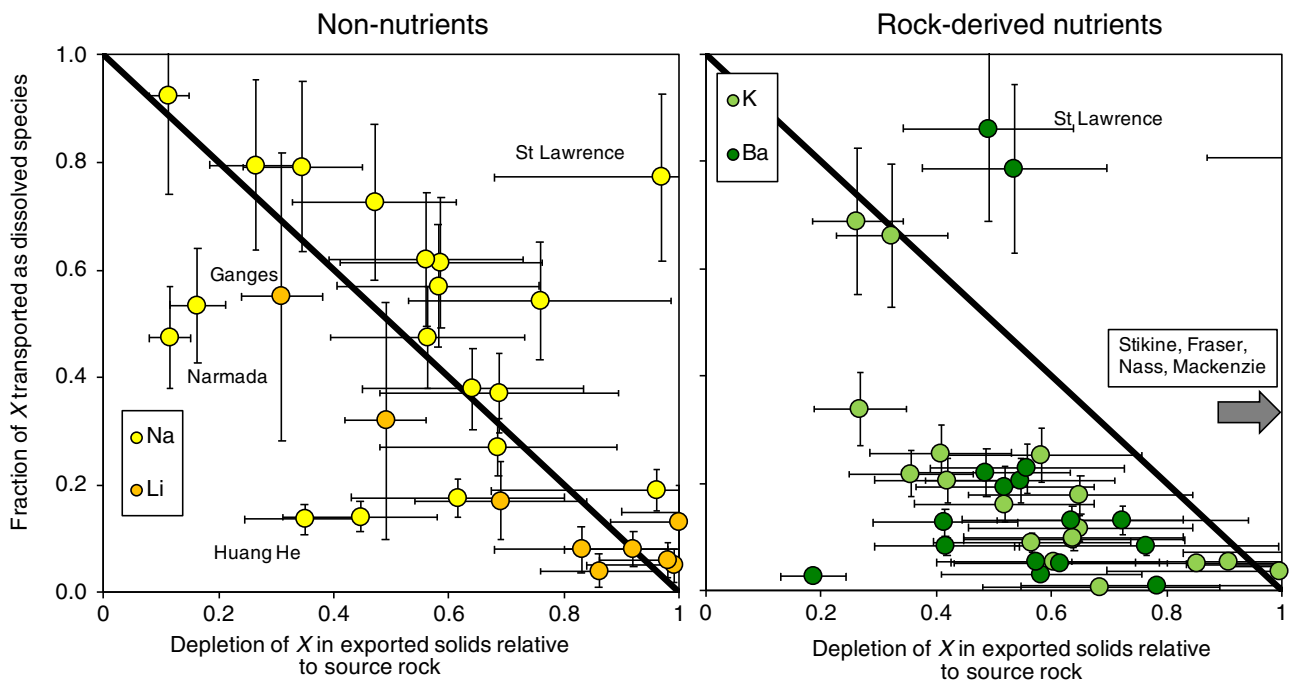


Figure 2 Comparison between the relative dissolved export of an element X and its depletion in river solids compared to source rock for $X = Na, Li, K,$ and Ba for some of the world largest rivers. A catchment scale balance between river export and supply by rock degradation is represented by the diagonal line. The root mean square deviation from the trend of a balanced budget (diagonal line) is much higher for Ba and K (0.51 and 0.35, respectively) than for Na and Li (0.14 and 0.11, respectively). Detail about calculations is provided in the [Supplementary Information](#).

mass budget, as it does not move data points away from or closer to the diagonal. Rather, this analysis is only sensitive to whether the overall elemental riverine export reflects the abundance of this element in the rock weathered.

In the world's largest rivers, for the two non-nutrient elements sodium (major element, Na) and lithium (trace element, Li), the supply to the CZ by rock degradation is balanced by the combined dissolved and solid riverine export (Figs. 2, 3). Such agreement was already noticed based on Li isotopes by Dellinger *et al.* (2015). Such balance is remarkable as the formation of river solids and solutes in soils by chemical weathering operate over different timescales, implying that at any time varying soil formation and erosion should lead to significant imbalance in river mass budgets. In other words, this observation suggests that the formation of secondary weathering phases in the CZ, such as clays or (hydr)oxides in soils, is balanced by their export as river solids, and that consequently no significant net accumulation of a Li-bearing secondary phase within the global CZ is occurring.

Conversely, the major rock-derived nutrient potassium (K; group 2 in the classification of Marschner *et al.*, 1996)

and the minor, nutrient-like element barium (Ba; Bullen and Chadwick, 2016) show a widespread imbalance between supply to the CZ and riverine export fluxes by rivers (Fig. 2), consistent with previous studies on headwater catchments (von Blanckenburg *et al.*, 2021) and in the Amazon (Charbonnier *et al.*, 2020). Collectively, these results suggest that Ba and K sourced from silicate weathering are fractionated between a "residual" reservoir in the CZ and the total riverine export.

Accumulation of secondary phases of weathering within the CZ could explain this deficit. However, in such a scenario our data would reflect the formation and accumulation of specific, Ba- and K-hosting phases not exported by rivers, at least not in the same way as Na and Li. These Ba- and K-bearing phases could be of inorganic nature. In fact, the K and Ba river mass budget equations used here are relative to the insoluble element thorium (Th), meaning that the observed imbalance suggests the formation of high Ba/Th and K/Th reservoirs within the CZ, whereas the river export is lower in Ba/Th and K/Th compared to source silicate rocks. Given the insoluble and non-nutrient nature of Th, such enriched Ba and K components can hardly derive from the scavenging into classical secondary

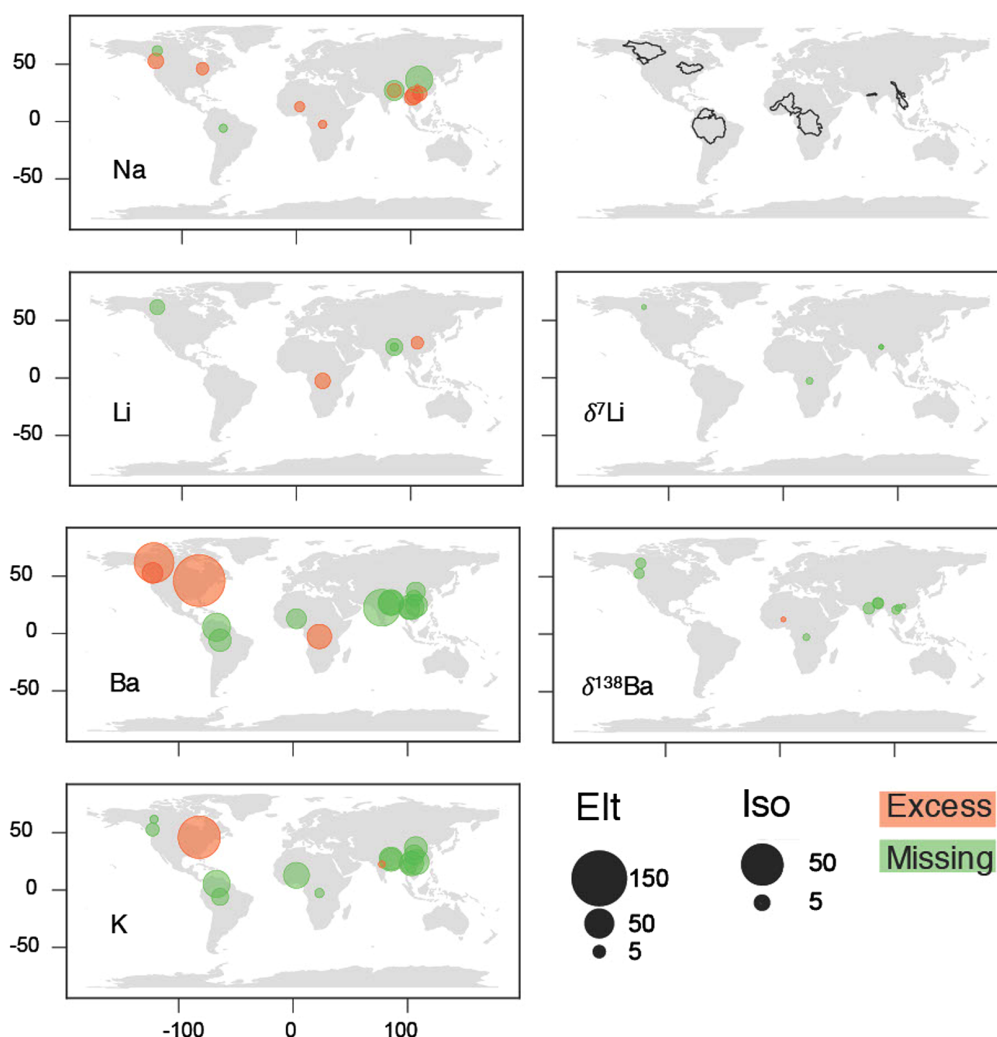


Figure 3 Quantification of catchment scale elemental and isotope (im)balance for the world largest rivers using river mass budgets. The upper right map indicates the studied river catchments. Elemental imbalance ("Elt") is expressed in percentage, and the isotope imbalance ("Iso") is expressed as the isotope difference quantified in Equation 5-8. Due to the mass difference between Ba and Li, the magnitude of isotope fractionation is much larger for Li than for Ba, resulting in larger numbers for the isotope imbalance. To make the numbers for both isotope systems comparable, we multiply each of the "raw" numbers for the isotope imbalance (as quantified by Eq. 5-8) by the ratio between the mass of the element (e.g., 137.32 for Ba) and the difference of mass of the two isotopes used (e.g., 138 – 134 = 4 for Ba).

soil phases. Even though iron oxides can be characterised by higher Ba/Th ratios than silicate minerals (Gong *et al.*, 2019), such phases should be exported from the CZ together with other secondary phases of weathering. Further, K does not show such enrichment in iron oxides (Gong *et al.*, 2019), showing that the positive relationship between the magnitudes of Ba and K imbalance (Fig. S-4) cannot derive from a global retention of iron oxides in soils. This analysis argues for a role of organic phases in the Critical Zone in producing the observed global K and Ba imbalance.

Furthermore, the Ba river export by most large rivers is characterised by an isotope signature heavier than that of the Ba input to the CZ by rock degradation (see [Supplementary Information](#); Fig. 3). This either means that heavier-than-thought Ba is released to the CZ during rock degradation, or that a Ba component enriched in the light isotope is missing. Regarding the first possibility, recent work suggests that the weathering of black shales delivers heavy Ba isotope signatures (Charbonnier *et al.*, 2022). Nevertheless, such a heavy Ba flux is associated with an elemental excess of Ba (Charbonnier *et al.*, 2022), which is observed only for the Mackenzie Basin in the present global dataset. Furthermore, no relationships between dissolved Ba isotopes and sulfate content or osmium isotopes (two tracers of black shale weathering) emerge (not shown). Therefore, an isotopically light reservoir of Ba must exist in the global CZ. As suggested above, this isotopically light Ba reservoir could reflect the formation of secondary weathering products and their retention in soils (Gong *et al.*, 2019), or biological uptake (Bullen and Chadwick, 2016).

Barium adsorption onto river sediments, although able to account for variations in dissolved Ba isotopes (Bridgestock *et al.*, 2021), cannot influence the results of river mass budgets, which sum together the signatures of the dissolved and solid river loads leading to an isotope neutral effect for the processes partitioning the elements between the different river phases. Finally, formation and retention of secondary weathering products in soils should result in a strong Li isotope imbalance, as the light isotope of Li is preferentially incorporated in these phases (Pogge von Strandmann *et al.*, 2012). As this is contradictory to our observations (Fig. 3), we are left with biological uptake as the only explanation for the relatively heavy Ba isotope composition in our global river dataset.

Testing for the Role of Biological Uptake in Deleting the River K and Ba Exports

Taken at face value, the depleted river export of rock-derived nutrients might reflect their locking within biological materials through two categories of phenomena. First, (1) the corresponding biological material could be exported from catchments as particulate organic carbon that is not adequately sampled. For example, Abbe and Montgomery (2003) have shown that significant river transport of woody debris would not be properly accounted for by traditional methods used for sampling large rivers. Another possibility for such “hidden” export of particulate organic matter is tree logging by human activities. Alternatively, (2) accumulation of biological material within the catchment as above or underground biomass or as litter would also result in an imbalance, at least over the timescale over which the data used for the river mass budget are collected. Below, we show how the results of our investigations are difficult to reconcile with these scenarios.

First of all, basins characterised by the strongest negative imbalance in the river mass budgets of rock-derived nutrients are not characterised by the strongest logging activities (see

[Supplementary Information](#)). Therefore to test for scenario (1) above, that is one of a “ungauged organic flux”, we estimate the amount of river particulate organic carbon (C) that would be needed to account for the observed imbalance in K (Fig. S-5) by using a typical K/C mass ratio for plant material of 0.0012 (Charbonnier *et al.*, 2020). For a given catchment, the inferred missing flux of river particulate organic C is more than two orders of magnitude higher than the river export of particulate organic carbon estimated by Galy *et al.* (2015) (Fig. S-5). It seems unrealistic that 99 % of the biogenic particulate organic carbon is exported through poorly- or non-sampled episodic and/or coarse vegetation debris in large river systems for this K/C ratio (a ratio the validity of which will be further discussed).

The likelihood of organic matter accumulation within catchments as an explanation for the global imbalance in catchment scale mass budgets (a “growing organic pool” scenario, labelled as (2) above) can first be appraised using a back-of-the-envelope calculation. Using typical K concentrations in rocks and plants and estimates of organic matter stocks in biomass and soils (see [Supplementary Information](#)), we calculate that an annual 0.1–0.2 % increase in the biomass can explain the observed imbalance in K catchment scale mass budgets. Although the time scale over which the observed catchment scale imbalance is established remains elusive, we note that if such an increase in biomass or organic matter were sustained over 30 yr – a period over which we believe constraints on the global land carbon pools are reasonable – this would result in an overall biomass growth by 3.5–8.0 %, which has not been reported (Friedlingstein *et al.*, 2020).

Overall, the results of the first order calculations presented above challenge the biological uptake role in deleting the global river exports of K and Ba. However, we also note that some degree of decoupling might exist between biological uptake and riverine export of rock-derived nutrients. In particular, biological activity is known to exert an indirect control on the distribution of rock-derived nutrients and their isotopes amongst the different CZ compartments (Bullen and Chadwick, 2016). For example, the top layer of soils accumulates a sizeable reservoir of nutrients that are readily accessible for the biota, a feature known as “bio-lifting” (Jobbágy and Jackson, 2004). If these top-soil horizons were disproportionately contributing to the global river particulate carbon export, such enrichment leading to elevated nutrient-to-carbon ratios in exported organic matter would require revision of the K/C ratio used above, possibly to a level where the scenarios explored above would become plausible. Clearly, further work is needed to pinpoint how life might (a) transiently divert rock-derived nutrients released by rock weathering from river export, and (b) partition rock-derived nutrients amongst the CZ compartments.

Implication for the Study of Critical Zone Processes from River Chemistry

The global balance of riverine Li and Na and the global imbalance of riverine K and Ba, supported by isotopic observations, raises the possibility that nutrient-like elements are “diverted” from the riverine export, and may constitute a tangible influence of biological uptake on riverine export of rock-derived nutrients.

Nonetheless, comparison between the depleted flux of riverine K and Ba cannot be reconciled with reasonable figures for globally growing biomass, or for unsampled biogenic river components, indicating that the exact distribution of rock-derived nutrients amongst the various CZ compartments constitutes a critical knowledge gap. Overall, contrasting patterns between riverine exports of nutrient and non-nutrient elements



suggest that major river cations are likely “less conservative” than previously thought. As a consequence, the way geochemical processes are deduced from river chemistry might warrant reconsideration.

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Additional Information

Supplementary Information accompanies this letter at <https://doi.org/10.7185/geochemlet.2214>.



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