
Appendix A. Sampling and analytical methods

A.1 Field sampling

River waters were sampled from the surface of river channels and filtered through 0.22 μm PES filters. Waters were collected in pre-cleaned HDPE bottles with one sample acidified to a pH of ~2 using doubly distilled concentrated HNO₃ for analysis of cations and Li isotopes and one sample unacidified for analysis of anions. Bed sand samples were collected from the river bank and collected in plastic zip-lock bags. Upon return from the field the sediment samples were dried in an oven at ~40ºC (generally ~48 hours), and water samples were stored in a cold room (~5ºC). Details of the catchments sampled, and sample locations are given in Supplementary Data Table A1.

A.2 Analytical methods

All analytical procedures were conducted at the Department of Earth Sciences, University of Cambridge, UK.

A.2.1 Sample preparation

No preparation was needed prior to Li and the other element concentration determinations on the water samples. Prior to Li isotopic analyses, river waters containing ~4 ng Li were dried down on a hot plate and refluxed with concentrated aqua regia at 100ºC for 24 hours to eliminate organic matter. The samples were then evaporated to dryness and taken up in 0.7N HCl to be loaded on to the ion-exchange column.

River bed sediments were ground to a homogenous powder using an agate pestle and mortar, and baked at 950ºC for 8 hours in ceramic crucibles to destroy organic matter. Approximately 20 mg of the sample was then dissolved in a mixture of concentrated HNO₃, HCl and HF (1:1:1) in Savillex® screw-top beakers on a hotplate at 110ºC. Post dissolution (typically a few hours) the samples were dried down and taken up in 6N HCl. If fluoride residues were present the sample was refluxed with concentrated HNO₃ until a clear solution
was obtained.

A.2.2 Determination of Li and water major element concentrations

Major element compositions of the river waters (Supplementary Data Table A2) were measured using inductively coupled plasma optical emission spectrometry (ICP-OES) on an Agilent 5100. Calibration standards with matrices similar to Alaknanda waters were made using pure mono-elemental standards. Repeat analyses of the SLRS-5 river water standard indicates external reproducibility within ±5% (2σ). Anions were determined by ion chromatography (Dionex™) with the Dionex™ Combined Five Anion Standard (ThermoFisher), (F, SO₄, NO₃, Cl) and repeat analyses of river water standard LGC6025 at appropriate dilutions indicates an external reproducibility of better than 4% (2σ). Carbonate alkalinity as $\text{HCO}_3^-$ was calculated from the difference between the sums of charge on cations and anions.

The concentrations of Li in river waters and sediments (Supplementary Data Table A3) were measured by ICP-MS on the Thermoscientific Element XR. The samples were calibrated against in-house matrix matched standards and external reproducibility was determined by the analysis of secondary standards. The measurement of SLRS-5 yielded Li concentrations of 0.43±0.06 ppb (2σ, n=6), in the range of published values ranging from 0.33-0.50 ppb (Heimburger et al., 2013; Yeghicheyan et al., 2013). Digested rock standards yielded Li concentrations of 5.1±0.3 ppm (2σ, n=5) for BHVO-2, 50.0 ppm (n=1) for SCo-1 and 36.8 ppm (n=1) for SDC-1, which have recommended Li concentrations of 5.0, 48 and 37 ppm respectively (USGS).

A.2.3 Li isotopic analysis

Li isotopes were analysed following Bohlin et al. (2018) (Supplementary Data Table A3). Samples containing ~4 ng of Li were loaded onto high aspect ratio columns packed with the macro-porous cation exchange resin AGMP-50 (BioRad) and eluted with 0.7N HCl. Li elutes in 12 ml, and 1 ml pre- and post-cuts were collected and measured for their Li concentration to ensure quantitative recovery of Li within the 12 ml cut. Following elution the Li cuts were dried down on a hot plate and refluxed with concentrated double distilled HNO₃ to remove potential organic matter sourced from the columns. Following refluxing the samples were dried down and taken up in 2% HNO₃ ready to be analysed for their isotopic composition.

Li isotopic analysis was conducted by multi-collector inductively coupled mass
spectrometry (MC-IC-MS) on the Thermoscientific NEPTUNE Plus, utilising $10^{13}$ Ω amplifiers on the Faraday collector cups (Bohlin et al., 2018). The samples were analysed at 0.4V on $^7$Li corresponding to a Li concentration of 0.4 ppb. Lithium samples are normalised to NIST SRM 8545 L-SVEC and a sample-standard bracketing method was used. $\delta^{7}$Li values were calculated following

$$
\delta^{7}\text{Li} \ (%o) = \left[ \frac{\left( \frac{^7\text{Li}}{^6\text{Li}} \right)_{\text{sample}}}{\frac{^7\text{Li}}{^6\text{Li}}} + \frac{\left( \frac{^7\text{Li}}{^6\text{Li}} \right)_{\text{LSVEC1}}}{2} - 1 \right] \times 1000
$$

Long term external reproducibility of the instrumental method was determined from the repeat analysis of secondary standards Li6-N and Li7-N (Carignan et al., 2007) yielding values of $-8.18 \pm 0.39\%o$ ($2\sigma$, $n=42$) and $30.30 \pm 0.39\%o$ ($2\sigma$, $n=43$) respectively (Bohlin et al., 2018). The full reproducibility of the method is $0.40\%o$ determined from the separation and measurement of seawater yielding a value of $31.27 \pm 0.40\%o$ ($2\sigma$, $n=30$). BHVO-2 was processed through the columns 6 times yielding a $\delta^{7}$Li value of $4.76 \pm 0.29\%o$ ($2\sigma$).

### Appendix B. Atmospheric and hydrothermal input to the dissolved Li budget

The dissolved load of rivers has several source inputs apart from dissolution of silicate rock, including dissolution of carbonate rock, evaporites and input from rain and hydrothermal fluids from hot springs. There are no mapped salt deposits in the Alaknanda basin, although the hot springs access NaCl-rich fluids. Carbonate rocks have low Li concentrations and despite their faster dissolution kinetics contribute minimally to the Li budget (e.g. Kisakürek et al., 2005; Millot et al., 2010; Dellinger et al., 2015). Rain and hot spring inputs are traditionally corrected for using the dissolved Cl concentration as a conservative tracer of these sources, as evaporites are rare in Himalayan rocks. Previously the lowest Cl concentration in each tributary basin has been taken as rain input and Cl in excess of this value is presumed to be due to concentration of solutes via evaporation or from hydrothermal fluid input (e.g. Bickle et al., 2005). The input from rain is corrected following

$$
Li^* = Li_{river} - \left[ \left( \frac{Li}{Cl} \right)_{\text{rain}} \times Cl_{\text{basin min}} \right]
$$
where $L_i^*$ is the corrected Li concentration of the river, $L_i$ is the measured Li concentration of the river, $C_{\text{Cl\,min}}$ the lowest measured Cl concentration within the tributary basin and $L_i/C_{\text{Cl\,rain}}$ is the Li/Cl ratio of rainfall. There are currently no published data on Li concentrations of Himalayan rain, and the few global studies that have been made on atmospheric inputs show a large range with Li/Cl ratios ranging from close to seawater such as $4.3 \times 10^{-5}$ in the Lesser Antilles (Clergue et al., 2015), to values as high as $3.1 \times 10^{-3}$ in Central and western France (Millot et al., 2010). For the corrected concentrations in this paper the average value (excluding anomalously high values $> 10^{-3}$) of $2.0 \times 10^{-4}$ is used (Supplementary Data Table B1). Using this ratio the rainfall contribution to the dissolved Li ranges from less than 1% for the TSS, HHCS and HHCS-LHS combined catchments, 5% for LHS catchments and 13% for OLHS catchments. Assuming rain has $\delta^7\text{Li} = 20\%$, corrections to the Li-isotopic ratios are all less than 1‰ (Supplementary Data Table B2).

In the Alaknanda catchments, Cl in excess of rain (allowing for evapo-transpiration) has previously been presumed to be supplied by hot springs. Analyses of the $\delta^7\text{Li}$ compositions of Himalayan hot springs are not available. In general, hot springs are associated with low $\delta^7\text{Li}$ and high Li concentrations (e.g. Pogge von Strandmann et al., 2016). Chatterjee et al., (2017) cite hot spring Li/Cl ratios from the Alaknanda catchment with Li/Cl molar ratios between $10^{-3}$ and $3.6 \times 10^{-2}$ (average $2.1 \times 10^{-2}$). Correction assuming Cl in excess of that supplied by rain is supplied from hot springs with a Li/Cl ratio of $10^{-3}$ reduces Li

Figure B1 - $L'_i$ versus $\Delta^7\text{Li}_{f-S}$ with solid symbols corrected for rain inputs assuming rain has minimum Cl of rivers in that catchment and open symbols assuming all Cl is from rain.
concentration by less than 5% except for the OLHS samples (correction about 50%) and AK429 and AK431 from the LHS (correction about 20%). Assuming that the hotspring component has $\delta^7\text{Li} = 5\%$, the corresponding corrections to $\delta^7\text{Li}$ are less than 1% except for the LHS samples AK429 and AK431 (8 and 4%) and the OLHS samples which are up to ~36%. Hot springs are mainly found in the upper reaches of the Alaknanda and Dhauli Ganga and it seems more likely that the higher Cl concentrations in the LHS and OLHS are the result of concentration by evapo-transpiration. Correcting all the samples assuming that all the Cl is derived from rain decreases Li concentrations by less than 2% and $\delta^7\text{Li}$ by less than 0.2% in the TSS, HHCS, HHCS-LHS combined and the mainstem Alaknanda sample, less than 8% and $\delta^7\text{Li}$ by less than 1% in the LHS samples and less than 20% and $\delta^7\text{Li}$ by less than 2% in the OLHS samples. The implications of such shifts in Li concentrations and isotopic ratios on the calculated $N_D$ and $K_{net}$ values are illustrated on Fig. B1.

Appendix C. Calculation of the $f$ factor

The volume fraction of dissolved rock which is re-precipitated as clay minerals, the “$f$ factor”, is calculated with the assumption that all the aluminium (Al) in the dissolving mineral is re-precipitated, as Al is sparingly soluble in surface waters

$$f = \frac{(\text{Volume}/\text{mol Al})_{\text{clay mineral}}}{(\text{Volume}/\text{mol Al})_{\text{primary mineral}}}$$  \hspace{1cm} (C1)

The mineral compositions are given in Supplementary Data Table C1 and $f$ factors in Supplementary Data Table C2.

Appendix D. The volumetric partition coefficient, $K_V$

The partitioning of Li between forming clay minerals and water at low temperatures is largely unknown. Few experimental studies have been performed between clay minerals and fluid at temperatures below 50°C (Berger et al., 1988; Vigier et al., 2008; Decarreau et al., 2012), and fluids are often extremely concentrated (hundreds of ppm Li) compared to the natural weathering environment (~ppb Li). Further, few field-based studies have separated weathering products from bulk sediments. The order of magnitude in the value of partition coefficients can however be estimated using Li concentrations of natural clays (Tardy et al., 1972; Garçon et al., 2014) and relating these to the global average dissolved river Li concentration of 0.0018 ppm (Misra and Froelich, 2012). This calculation yield values of $K_V$ in the order of $10^3$ to $10^6$ (Supplementary Data Table D1).
Based on experimental studies at 75-90°C and Li fluid concentrations ranging from 2 to 200 ppm, Decarreau et al. (2012) derived an empirical relationship relating the partition coefficient by mass \((K_d)\) to the temperature and Li concentration of the solution:

\[
\log K_d = \frac{-1319}{T_K} + 5.5Li_f^{-0.0806}
\]

where \(T_K\) is the temperature in degrees Kelvin and \(Li_f\) is the concentration of Li in the water from which the clays precipitate (ppm). To obtain a volumetric partition coefficient used in the reactive transport model, \(K_d\) is multiplied by the densities of the solid and fluid phases following:

\[
K_v = K_d \frac{\rho_s}{\rho_f}
\]

where \(\rho_s\) and \(\rho_f\) are the densities of the solid clay minerals and fluid respectively, taken as 2.7 and 1.0 g/cm\(^3\). Using this expression for the global average riverine Li concentration of 0.0018 ppm and a temperature of 25°C \(K_v\) is 1.4x10\(^5\), in the range of values calculated from natural samples. These estimated values are considerably higher than the \(K_d\) of 0.95-22 (\(K_v\) of 2.6-59.4) obtained in the experimental study which derived equation D1 (Decarreau et al., 2012). The large differences are a consequence of the difference in temperature and fluid Li concentration between the natural weathering environment and the experimental conditions.

**Appendix E. Solutions for \(K_{net}\) and \(N_D\) from sample Li’ and \(\Delta^7Li_{f-s}\) compositions**

Supplementary Data Table E1 gives input parameters to the reactive transport model and the calculated values of \(K_{net}\) and \(N_{D Li}\). Li’ is the rock normalised Li concentration (\(Li_f/Li_s\)), Li’\(_0\) and \(\delta^7Li_{i-0}\) the initial Li’ and \(\delta^7Li_f\) at the start of the flow path (\(z’=0\)), \(K_{net}\) is the calculated net volumetric partition coefficient of Li and \(N_{Di}\) the calculated Damköhler number. The value of \(K_{netLi}’\) indicates whether more Li is being incorporated into clays than is being dissolved (value higher than 1). The value of \(K_{net}\) is calculated using equation 14 (main text), which is then inserted into equation 11 to solve \(N_{Di}\). Alternatively, both \(K_{net}\) and \(N_{Di}\) of samples can be read graphically from the reactive transport grid (Figure 5).
Appendix F. Data from Himalayan catchments, the Strengbach Catchment and the Ganges Floodplain

Figure F1 illustrates Himalayan rivers sampled by Kisakürek et al. (2005) in Nepal and springs and streams from the Strengbach catchment (Lemarchand et al., 2010) in the Vosges mountains plotted on the reactive transport grid calculated as Fig. 5 (main text), with Δ= -17‰ and upper grid starting composition with Li₀’ = \(2.35 \times 10^{-5}\) and Δ\(^{7}\)Liₚ = 17‰. Δ\(^{7}\)Liₚ of samples from the study by Kisakürek et al. (2005) is calculated from bed sediment analyses. Δ\(^{7}\)Liₚ of samples from the Strengbach catchment are calculated using the composition of Brezouard granite (Li = 19.3 mmole/Kg, δ\(^{7}\)Li = 0.3‰). Note that, with the exception of the HHCS samples from the Dudh Khosi, the majority of the samples plot below Δ\(^{7}\)Liₚ = 17‰. The wider scatter in the Kisakürek et al. (2005) dataset likely reflects seasonal variations as these samples were collected in both the pre- and post-monsoon when hydrological conditions are markedly different, and a broader geographic spread of these samples.

Figure F1 - River and spring analyses from the Nepal Himalayas (Kisakürek et al., 2005) and Strengbach catchment (Lemarchand et al., 2010) plotted on the reactive transport grid. Samples from Alaknanda catchment shown with open symbols.
Figure F2 illustrates the downstream evolution of $\delta^7\text{Li}$ in the Ganga mainstem compiled from analyses by Bagard et al., (2015), Huh et al., (1998), Manaka et al., (2017) and Pogge von Strandmann et al., (2017). Distance downstream is relative to Rishikesh. Location of confluence with Yamuna and downstream location of Farakka are marked.

Figure F3 illustrates Ganga mainstem samples and tributaries in the floodplain plotted on the reactive transport grid with $\Delta = -21\%$ and the input water composition for the upper grid with $\text{Li'} = 1.5\times10^{-4}$ and $\Delta^7\text{Li}_{f-s} = 21\%$. The composition of the bedrock source for all floodplain samples is taken as the average of bedload samples at Harding Bridge with $\text{Li} = 20$ ppm, $\delta^7\text{Li} = 0.4\%$ (Dellinger et al., 2014) which are similar to bedsands at Srinagar (sample AK416, $\text{Li} = 22$ ppm, $\delta^7\text{Li} = 2.1\%$).
Figure F3 - Ganga mainstem and tributaries plotted on reactive transport grid. Data from Bagard et al., (2015), Huh et al., (1998), Manaka et al., (2017) and Pogge von Strandmann et al., (2017). Open symbols are samples from Alaknanda catchments.

References


