

Hidden Time:
Interpreting the geochemistry of Himalayan
groundwaters

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Abstract

This is the abstract. Feel free to add anything insightful... or not :). Hello!

Contents

Acknowledgements

Thanks Babe

List of Tables

Nomenclature

Add geology eg HHCS Silicate Weathering

All the variables

1 Introduction

Silicate weathering, whereby silicate minerals are dissolved by carbonic acid sequesters atmospheric CO₂ over long (10⁵ year) timescales, influences global climate regulation. The Himalayan mountain range spans more than 590,000 km², and is the source of major rivers, including the Ganges, Brahmaputra, and Indus.

In highly erosive regions where the supply of silicate minerals far exceeds the weathering rate, silicate weathering reactions are thought to be sensitive to climate (Stallard & Edmund 1983 JGR, West et al, 2005) The dissolution kinetics of the largely silicate rocks in these catchments are sensitive to temperature and runoff because the weathering reactions have not gone to completion. Silicate weathering in the Himalayas as a result of their uplift and erosion in the Cenozoic may have contributed significantly to the global cooling over the past 40 million years (Raymo and Ruddiman, 1992; West et al, 2005, Kump et al, 2000 Ann Rev Earth Sci). Thus, it is this sensitivity to climate as well as their large size that makes them important to study, from both a scientific and practical perspective. More recent models have proposed silicate weathering is more sensitive to the hydrological cycle, than to temperature [cite]. There are a range of flow paths with different residence times, and rock is exhumed through these flow paths with a much longer time constant than the water in the flow paths.

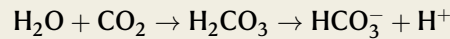
However, there remain a number of unknowns in the weathering fingerprints of these catchments, namely the residence time of the water, flow path direction and length, rate of reaction, and extent to which equilibrium is reached. Understanding residence time in particular is important because the geochemical reactions that are used to quantify weathering (and the biogeochemical ones too) are time-dependent. Residence time will also reflect the variety of flow routes within a catchment, and help to constrain hydrological models. In this contribution the flow paths and residence times of water will be investigated using the chemical weathering products of spring waters from a highly monitored Himalayan catchment. This will not only provide better constraints on reaction rates of silicate mineral dissolution reactions in the field, but also a greater understanding of the role of hydrology in providing a climate-sensitive negative feedback between atmospheric CO₂ and silicate mineral dissolution. An added benefit will also be provided via a greater understanding of Himalayan water supplies which are essential for billions of people (Ives

and Messerli, 1989).

Box 1

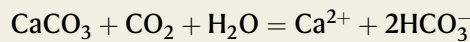
Chemical Weathering

As water passes through the subsurface, it interacts with rock. This causes the addition of solute species to water, and the formation of stable secondary minerals through the dissolution of primary minerals formed at different pressure and temperature. Dissolved CO_2 derived from the atmosphere present in rainfall makes it slightly acidic. This acidity is further increased by the presence of decomposition of organic matter and CO_2 production from organic activity in the soil.

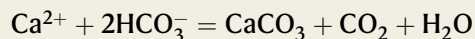


Carbonic Acid Weathering of Carbonate - Net Zero

Short Term [timescale]:

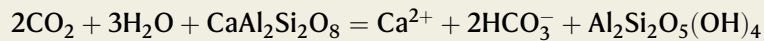


Long Term [timescale]:

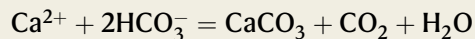


Carbonic Acid Weathering of Silicate - Net CO_2 drawdown

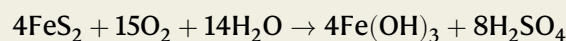
Short Term [timescale]:



Long Term [timescale]:



The rate of weathering is dependent on the mineralogy of the rock. Different minerals weather at different rates (from Shand et al, 1999: quartz > albite > mafic silicates > anorthite > carbonates), so the most reactive minerals will contribute disproportionately to the solute load of the water. [Something about Tipper 2006 and carbonates during monsoon?? somewhere]. Note that here, only the weathering of carbonic acid is considered. Sulfuric acid is also often considered a big player in weathering, but its impact is not considered in this study because the pyrite deposits required for its formation are not present in lithological studies of the Melamchi region [follow up].



Mineral reactions are also time-dependent, so the longer that water spends in contact with the rock, the higher the degree of completion of a chemical reaction [can mention incongruent dissolution whereby only part of the mineral dissolves?]. Current models of silicate and carbonate weathering (the two dominant lithologies considered) do not generally consider underground flow paths in their carbon flux estimates (Gaillardet et al, 1999 and others). Hence, a potentially underestimated part of the carbon cycle is this underground weathering.

2 Literature Review

What makes the Himalayas unique is also what makes them difficult to model, namely the monsoon system. This is characterised by a strong seasonal reversal of winds, which brings heavy rainfall to the region during the summer months, and dry conditions during the winter.

Andermann et al. (2012) show that anticlockwise hysteresis loops of precipitation against discharge (include basic schematic) suggest that there is a 3 month lag in the response of the river to precipitation. The delay in river discharge is a topic of debate. Bookhagen and Burbank (2010) suggest it may be due to the response of glaciers at higher elevations, while Andermann et al. (2012) propose that at lower elevations, it is more likely due to groundwater storage of precipitation in the fractured basement. Also important to note is that catchments with little glacial input show the same delay. Residence time of groundwater can hence be used to quantify this delay and nature of its origin (McGuire et al, 2005).

Weathering regimes can be classified as either transport-limited or kinetically limited. West et al. (2005) distinguishes the two regimes by the rate of erosion in the catchment. In low erosion rate settings, weathering is transport-limited due to limited mineral supply. Weathering here is therefore proportional to the material eroded. In high erosion rate settings, weathering is kinetically limited due to an abundant mineral supply. Rapidly eroding catchments like Melamchi are therefore likely kinetically limited. Field evidence supports this claim, with landslides being frequent during the monsoon (Baniya et al., 2010).

In the present study, spring and rain samples from the Melamchi catchment are used as a case study to investigate the weathering rates in a rapidly eroding catchment. The sample dataset consists of 372 samples spanning four field campaigns over three years (2021-2024), as well as more recent year-long bi-weekly timeseries data from stream and spring samples in sites across the catchment. [See map] As Tipper et al, 2006 writes, studying small catchments gives the opportunity to attribute large changes in water chemistry to seasonal climate changes like the monsoon. (More in Area)

This study considers major and trace ion concentrations, alkalinity, and radiogenic strontium isotopes from the Melamchi catchment. This study shows that there are systematic

variations in the chemical composition of the water along and away from the ridge. These can be explained through lithological differences and chemical weathering respectively. Estimation of the carbon flux in the groundwater yields *****?. Residence time calculations determined using rate constants close to equilibrium give ages of 10-25 years. This is in agreement with previous studies which calculated residence times using gas ages (Atwood et al [expand on this]). Previous studies have linked residence time to topography, such that areas with a small topographic gradient evolve to a larger residence time and vice versa. (McGuire et al, 2005). A similar relationship is found in this study.

So far, papers modelling the evolution of weathering have not considered catchment-based data due to the non-ideal setting. This study aims to bridge that gap by applying simplified models to a highly monitored catchment. The hope is that this approach will help to give a first-order estimation on parameters that are not easily obtained with the chemistry of a system alone. This report aims to join together studies looking at the same problem from different disciplines.

3 Study Area

The Melamchi Khola catchment (85.441 - 85.601 E, 27.822 - 28.157 N) study area ranges from 790 to 5700 m a.s.l. (metres above sea level). The Melamchi River is a tributary of the larger Indrawati River and runs through the catchment draining an area of 325km². The geology of Melamchi Khola is characterised by banded gneiss, feldspathic schist and laminated quartzite alternating throughout. Notably there are pegmatite veins in the northernmost Golphu formation. The overall geology is therefore largely comprised of silicate metamorphic rock.

There are two main climatic influences in the Himalayas: the monsoon system and the westerlies (Bookhagen and Burbank, 2010). The westerly winds typical of this latitude are responsible for the dry season in the Himalayas. The source of precipitation during the Indian Summer Monsoon (ISM) affecting Melamchi is the Bay of Bengal, due to the strong pressure gradient that changes the westerly winds to southerly winds. This temperature gradient reverses in the winter, when the oceans are warm and the High Himalaya is cold. The Melamchi Khola catchment receives over 80% of its rainfall during the monsoon. The seasonal variation in rainfall is thought to relate to different hydrological regimes, whereby river discharge and precipitation are 'coupled' when there is a significant enough amount of water to recharge the groundwater system. (Illien et al, 2021) The seasonal variation in precipitation therefore also translates to a variation in runoff, whereby this is twelve times stronger during the monsoon than during the dry season (Sharma, 1997).

Annual mean temperatures in the Melamchi Khola Catchment range from 24°C at base elevation to 8°C at highest elevation sampled (3200 m a.s.l.). The area is characterised by a high erosion rate. "One-off" landslide events transport as much as four times the flux of sediment deposited in the valley in a year (Chan Mao Chen et al, 2023). These events are thought to be increasing in frequency over recent years as a result of climate change, increasing the erosion rate in these areas (Adhikari et al, 2023).

Catchment	Area	Mean Slope	Mean Elevation	Elevation Range	NDVI during Sampling	Geology	Location Range
	(km ²)	(%)	(m)	(m)			(DD)
Melamchi	325	20	2400	786 - 5697		HHCS	85.441 - 85.601 E
Khola							27.822 - 28.157 N

Table 1: Catchment characteristics of the study area.

4 Materials and Methods

4.1 Field Sampling

Two types of water body were sampled in the field: springs and rain. Springs were sampled from the closest identified source in the study area, and rain was collected in a rain gauge. Both were measured in the field for temperature, pH and TDS on a Hanna Instruments HI-991300 and and EXTECH DO700. The field measurements were done at the source for the springs, and back at base for the rain before titrating, 24 hours within having been collected. Six aliquots were collected for each spring for anion, cation, titration, DIC, isotope and archive purposes respectively. Rain samples had a smaller yield and so only three aliquots were collected, for ion, isotope and archive purposes. Both water body types were filtered through a 0.2 μ m PES membrane in a filtration unit prior to bottling. Cation and archive samples were acidified with concentrated HNO₃ to give a pH of \sim 2, keeping the cations in solution. Samples were titrated with a Hach digital titrator with 0.0625M HCl to calculate the alkalinity of the water following the Gran Method (Gran, 1952).

4.2 Major and Trace Element Analysis

Ion concentrations were measured in Cambridge once back from the field. Cation concentrations were determined using a Agilent Technologies 5100 Inductively-Coupled Plasma Optical Emission Spectrometer (ICP-OES) using a calibration line made from a Nepalese spring stock solution. Anion concentrations were determined using a Dionex ICS-5000 Ion Chromatograph against the Battle-02 standard calibration line. Associated uncertainties range between 5-10% for cations and 10-15% for anions.

4.3 Sr Isotope Analysis

Samples were dried down to provide at least 1 μg of Sr. Samples were then dissolved in aqua regia (3:1 HNO_3 : HCl) to remove any additional organic matter. Once dried down again, they were added to 30 μl teflon columns with Eichrom SrSpec[®] resin pipetted in. Once washing the column three times with Milli-Q[®] water, it was primed with 3N HNO_3 . The sample was centrifuged then loaded onto the column avoiding any solids. The column was then washed a total of three times with 3N HNO_3 to remove cations. Lastly the column was eluted to a beaker with Milli-Q[®] water to collect the Sr. Once dried, the samples were ...

$$D_w = L \cdot \phi \cdot k \cdot M_{in} \cdot f$$

4.4 Cyclic and Evaporite Correction

Rain input is a significant factor in the chemical composition of rivers (Drever, 1997). Spring water is corrected for rain input according to the average concentration for the closest rain sample collected in this field season.

To remove the contribution of the rain the following formula is used for any element X:

$$[X]_{\text{rain-corrected}} = [X]_{\text{river}} - (Cl_{\text{river}} - Cl_{\text{river}}^*) \frac{[X]_{\text{rain}}}{[Cl]_{\text{rain}}}$$

Where $[Cl]_{\text{river}}^*$ is calculated by subtracting the concentration of chloride in the rain from that in the river (Tipper et al, 2006). Cl^* is taken to be zero if the concentration of chloride in the rain is greater than concentration of river. Evapotranspiration is not considered by this model, because of studies like Andermann et al (2012) which show that it plays a minor role, accounting for less than 10% of the hydrological budget in the Himalayas. They agree with Bookhagen and Burbank

In those cases where Cl^* is not zero then, a primary rain correction is simply:

$$[X]_{\text{rain-corrected}} = [X]_{\text{river}} - [X]_{\text{rain}}$$

Once the samples have been corrected for rain input, the remaining $[Cl]^-$ is assumed to be derived from evaporites encountered in the flow path.

Hence, the sample with the highest $[Cl]^-$ is used to correct the ions in a similar fashion to how the most dilute sample was used above:

$$[X]_{\text{evaporite-corrected}} = [X]_{\text{rain-corrected}} - \frac{[X]}{[Cl]_{\text{highest-Cl}}} * [Cl]_{\text{rain-corrected}}$$

This ensures that all chloride in the corrected sample is removed. The correction uses ionic ratios from the most concentrated water source, which acts as a proxy for the sediment imparting its signature. In this way, the correction does not affect samples which do not have high Cl (and hence do not have a large evaporite contribution), but does decrease the concentration of ions for those that do.

5 Results

Need to propagate Monte Carlo Uncertainty
results/tables yo

6 Discussion

Andermann et al, 2012

They also talk about a model Look at response time, being inversely proportional to hydraulic diffusivity. They assume length scales of 0.5-5km, and typical values of time to be about 45 days.

They are looking at very large discharges, order 5000 m³/s

Also want the Maher and Chamberlain rate constant explanation compared to normal data

Want to input the beginning steps of the derivation from Maher and Chamberlain, 2014's model. Eg the solution to a heterogeneous irreversible advection reaction equation

$$C = \frac{C_0}{1 + D} + C_{eq} \cdot \frac{D}{1 + D}$$

$$D = \frac{\cdot D_w}{q}$$

$$D_w = \frac{L \cdot}{T_{eq}}$$

$$L = q \cdot t$$

$$T_{eq} = \frac{C_{eq}}{R \cdot f}$$

$$R = \cdot k \cdot A \cdot X$$

$$k = 8.7 \cdot 10^{-6} \text{ mol/m}^2/\text{yr}$$

$$k = 8.7 \text{ mol/m}^2/\text{yr}$$

6.1 Step 1: Rearrange for D

Multiply through by $(1 + D)$:

$$C \cdot (1 + D) = C_0 + C_{eq} \cdot D$$

Distribute C :

$$C + C \cdot D = C_0 + C_{eq} \cdot D$$

Group terms involving D :

$$C \cdot D - C_{eq} \cdot D = C_0 - C$$

Factor D :

$$D \cdot (C - C_{eq}) = C_0 - C$$

Solve for D :

$$D = \frac{C_0 - C}{C - C_{eq}}$$

6.2 Step 2: Solve for t Using D

Now substitute D into:

$$D = \frac{\tau \cdot t \cdot \phi \cdot R \cdot f}{C_{eq}}$$

Rearranging for t :

$$t = \frac{D \cdot C_{eq}}{\tau \cdot \phi \cdot R \cdot f}$$

Substitute D :

$$t = \frac{\left(\frac{C_0 - C}{C - C_{eq}} \right) \cdot C_{eq}}{\tau \cdot \phi \cdot R \cdot f}$$

Simplify:

$$t = \frac{(C_0 - C) \cdot C_{eq}}{(C - C_{eq}) \cdot \tau \cdot \phi \cdot R \cdot f}$$

6.3 Conclusion

The expression for t is:

$$t = \frac{(C_0 - C) \cdot C_{eq}}{(C - C_{eq}) \cdot \tau \cdot \phi \cdot k \cdot M_{in} \cdot f}$$

Where:

- C_0 : Initial concentration.
- C : Current concentration.
- C_{eq} : Equilibrium concentration.
- τ : Characteristic timescale.
- ϕ : Porosity.
- R : Reaction rate term.
- f : Scaling factor.

References

Remember to add a box explaining Sr isotopes in the Appendix

Hello