

Uncovering Hidden Carbon Reservoirs: The geochemistry of Himalayan groundwaters

Giovanni Bernardi

2024-2025

Abstract

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

Contents

Abstract	i
1 Introduction	1
2 Study Area	5
3 Materials and Methods	7
3.1 Field Sampling	7
3.2 Major and Trace Element Analysis	7
3.3 Isotope Analysis	7
3.4 Cyclic and Evaporite Correction	7
4 Results	9
5 Discussion	10
5.1 Step 1: Rearrange for D	10
5.2 Step 2: Solve for t Using D	11
5.3 Conclusion	11

Acknowledgements

List of Tables

Nomenclature

1 Introduction

Silicate weathering, whereby silicate minerals are dissolved by carbonic acid sequesters atmospheric CO₂ over long (10⁷ year, check) timescales, influencing 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 (Knight et al, 2024) The dissolution kinetics of the largely silicate rocks in these catchments are sensitive to temperature and runoff. Silicate weathering in the Himalayas as a result of their uplift and erosion in the Cenozoic is therefore thought to have contributed significantly to the global cooling over the past 40 million years (Raymo and Ruddiman, 1992; West et al, 2005). 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].

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 can also reveal 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 solved using the chemical weathering products of spring waters from a highly monitored Himalayan catchment. This will not only provide a better understanding of the field based reaction rates of silicate mineral dissolution reactions, 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).

What makes the Himalayas unique is also what makes them difficult to model, namely

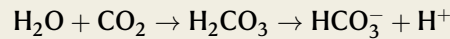
the monsoon system that characterises the region. The monsoon system is characterised by a strong seasonal reversal of winds, which brings heavy rainfall to the region during the summer months, and dry conditions during the winter. The monsoon system brings a large amount of water in the form of precipitation to the region, which reacts with the CO_2 in the air to make carbonic acid. This subsequently reacts and dissociates with the silicate minerals, drawing down atmospheric CO_2 (see some section with the full equations).

Work done by Andermann et al. (2012) on the Melamchi catchment in Nepal shows that the discharge of the river is highly seasonal. Anticlockwise hysteresis loops of precipitation against discharge (include basic schematic) suggest that there is a delay 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 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. Residence time of groundwater can hence be used to quantify this delay and nature of its origin (McGuire et al, 2005).

Box 1

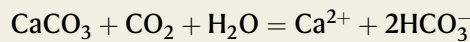
Chemical Weathering

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.

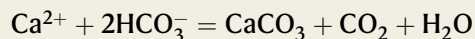


Carbonic Acid Weathering of Carbonate - Net Zero

Short Term [timescale]:

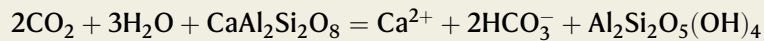


Long Term [timescale]:

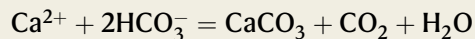


Carbonic Acid Weathering of Silicate - Net CO_2 drawdown

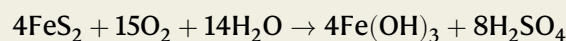
Short Term [timescale]:



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.

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.

2 Study Area

- What is the lat long extent of the study area?

85.441 - 85.601 E, 27.822 - 28.157 N

- What is the elevation range of the catchment?
- What is the area that the river drains? How do you calculate that (i.e. DEM)?
- What is the geology of the area?
- What is the climate of the area? what is it influenced by? i.e. monsoon, etc.

Bookhagen and Burbank (2010) identify two main climatic influences in the Himalayas: the monsoon system and the westerlies. The westerly winds, typical of this latitude, are responsible for the dry season in the Himalayas. The monsoon system is further divided into the East Asian and Indian Monsoon systems, which interact with each other.

The high elevation of the High Himalayas creates a barrier that affects atmospheric circulation. Bookhagen et al. (2005b) suggest that the Tibetan Plateau's high elevation generates a low-pressure cell near the surface, altering atmospheric circulation patterns. This is one explanation for the monsoon, though other studies present differing views (see Bookhagen and Burbank, 2010 for a discussion).

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.

- What is past literature on rainfall in monsoon season?
- What about clouds and fog? Especially when you are here?
- What are the annual mean temperatures at different elevations?
- What is the lapse rate like?
- What is the vegetation like?
- What is the land use like?

- Make sure to insert a description of the catchment: catchment, Area, mean slope, mean elevation, elevation range, land cover type, geology, Lat Long range

Catchment	Area	Mean Slope	Mean Eleva- tion	Elevation Range	Land Cover Type	Geology	Location Range
	(km ²)	(%)	(m)	(m)			(DD)
	325			786 - 5697			85.441 - 85.601 E 27.822 - 28.157 N

Table 1: Catchment characteristics of the study area.

3 Materials and Methods

3.1 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 HNO_3 to give a pH of ~ 2 , keeping the cations in solution. Samples were titrated with a Hach digital titrator with 0.05M HCl to calculate the alkalinity of the water following the Gran Method (Gran, 1952).

3.2 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.

3.3 Isotope Analysis

3.4 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:

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

Where $[Cl]_{river}^*$ 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:

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

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:

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

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.

4 Results

Need to propagate Monte Carlo Uncertainty
results/tables yo

5 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

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

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

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

$$L = q \cdot t$$

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

$$R = \frac{1}{\alpha} \cdot k \cdot A \cdot X$$

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

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

5.1 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 :

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

5.2 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:

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

5.3 Conclusion

The expression for t is:

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

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