Supplemental Materials: Spatiotemporal Drivers of Hydrochemical Variability in a Tropical Glacierized Watershed in the Ande

1 Uncertainty Analysis

Perturbed horizontal hydraulic conductivity (KSATH), vertical hydraulic conductivity (KSATV), porosity, and van Genuchten water retention curve parameters were implemented in the model to produce uncertainty distributions for stream discharge, groundwater chemistry, and stream chemistry. Initially the model was manually calibrated to obtain a narrow range of potential values for each parameter. An upper and lower bound was assigned to each parameter to span the range of possible values based on calibration results and values reported in literature (Table S1).

	Parameter	Range assigned (Literature values)	Notes and References
Horizontal hydraulic conductivity	1.1E-07 to 9.5E-07 ((2.5E-08 to 2.5E-06))	Unconsolidated glacial and fluvial sediments (Dominico and Shwartz, 1990)	
Vertical hydraulic conductivity	3E-08 to 7E-07 (5.5E-08 to 5.5E-06)	Anisotropy=2	
Posority	0.1 to 0.55 (0.1-0.3) (0.3-0.65)	Unconsolidated sediments Fractured bedrock (Earle S., 2018)	
Alpha	0.1 to 0.5 (0.01 to 0.7)	Unconsolidated sediments (Porebska et al., 2006)	
Beta	1 to 2.5 (1 to 3.6)	Unconsolidated sediments (Porebska et al., 2006)	

Table S1: Select parameters perturbed for the ensemble run, the range of values based on literature in parentheses, and the range of values assigned.

Latin hypercube sampling method was used to randomly sample parameters from uniform distributions for each parameter, and the model was run for 20 random sets of parameters. The ensemble of 20 model runs with perturbed soil hydraulic properties, including saturated horizontal hydraulic conductivity (KSATH), saturated vertical hydraulic conductivity (KSATV), porosity, and Van-Genuchten water retention curve parameters, is shown in figure S-1 in gray lines. The calibrated simulation of stream concentrations at the outlet are represented in red lines, which match reasonably well with measured concentrations in the stream during the 2015 and 2016 field campaigns.

Major ion concentrations also reasonably match observed concentrations at different sampling points along the stream. The simulated Na+ concentrations at SW-1, SW-2, and SW-3 sampling points (Figure 2a) are shown in Figure S2.

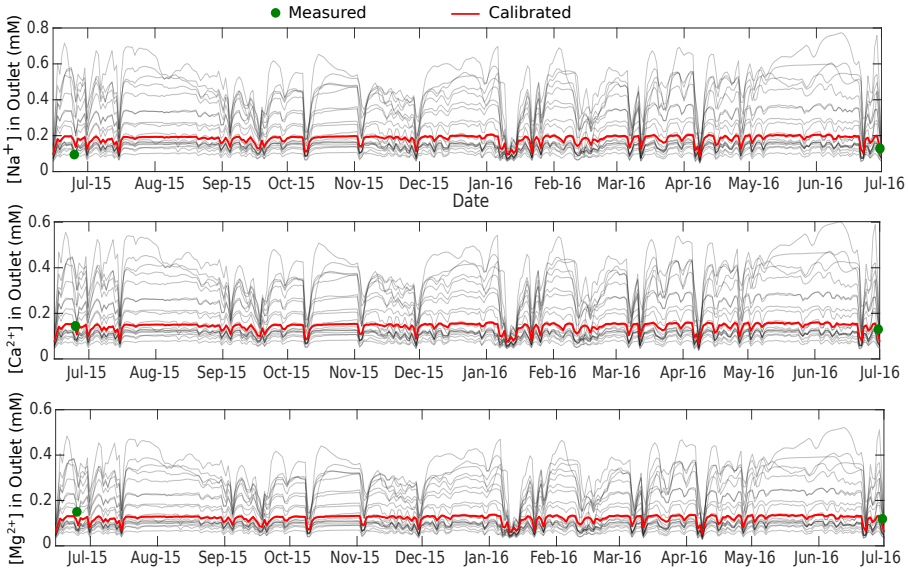

Figure S1: Calibrated simulations of stream concentrations for Na^+, Ca^{2+}, and Mg^{2+} at the outlet, shown in red lines, compared to the measured stream concentrations at the SW-4 site (Figure 2a). Gray lines show the ensemble of simulated concentrations at the outlet with a range of soil hydraulic properties.

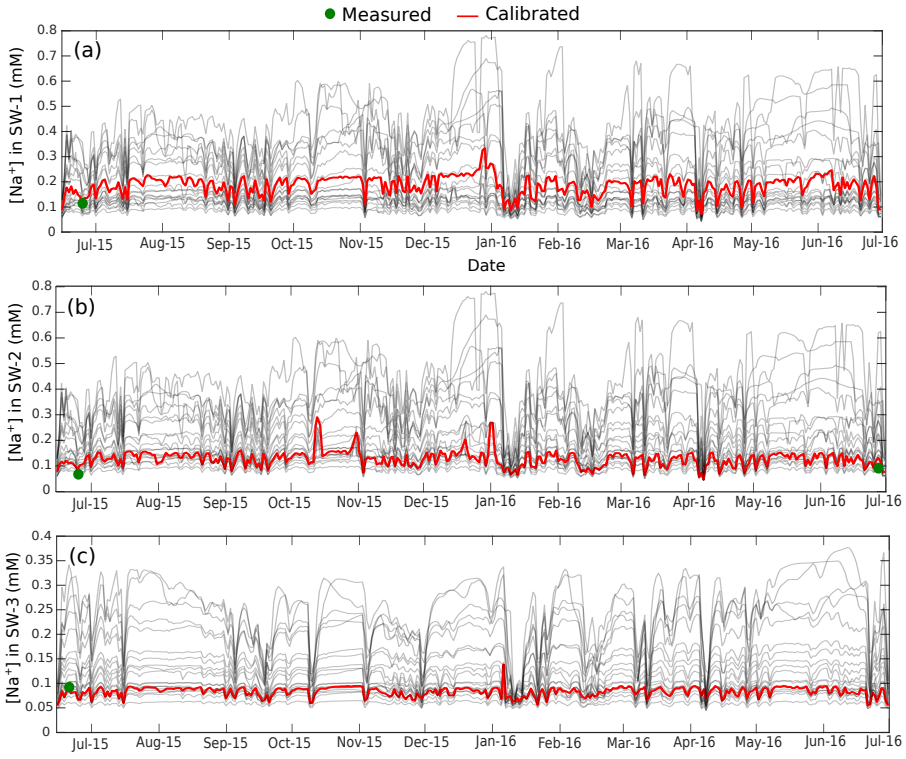

Figure S2: Simulated and measured Na^+ concentrations in a) sampling site SW-1, b) sampling site SW-2, and c) sampling site SW-3

2 Clibrated Parameters

Table S2 shows the calibrated parameters with and without hydrochemical constraints.

	KINFV (m/s)		KSATV (m/s)		KSATH (m/s)		Porosity		α (1/m)		β (-)	
Ice-covered	2.07E-7	1.64E-7	4.56E-8	5.36E-8	6.71E-7	7.56E-7	0.461	0.296	0.863	0.412	1.06	1.038
Sparsely Vegetated	1.43E-7	1.74E-7	4.63E-8	4.85E-8	4.63E-7	5.85E-7	0.459	0.296	0.585	0.437	1.063	1.038
Grassland	1.23E-7	1.87E-7	4.02E-8	5.27E-8	4.02E-7	5.27E-7	0.493	0.297	0.488	0.469	1.066	1.039

Table S2: Calibrated parameters without (Saberi et al., 2019) and with hydrochemical constraints. Parameters include hydraulic conductivities for vertical infiltration (KINFV), vertical saturated flow (KSATV), horizontal saturated flow (KSATH), porosity, residual soil moisture, and shape parameters (α and β) for the Van Genuchten moisture retention curve: $\theta = \theta_{res} + porosity \times \left(\frac{1}{1+|\alpha\psi|^{\beta}}\right)^{(1-\frac{1}{\beta})}$, with water content θ and pressure head ψ.

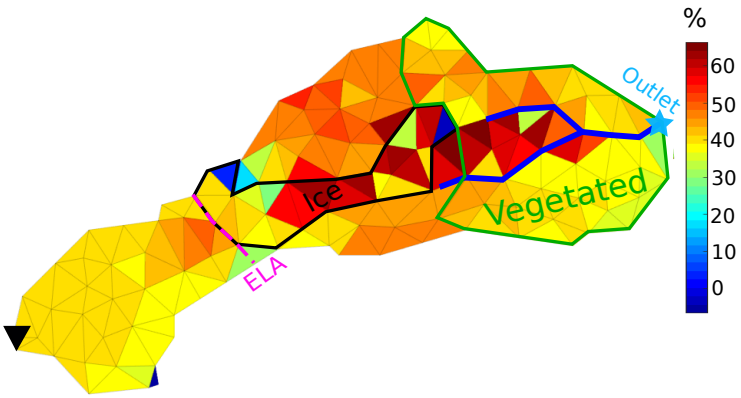

Figure S3: Percent change in the Na+ concentrations in groundwater by mineral dissolution over the entire watershed. The black triangle shows the peak of Volcan Chimborazo (6280 m a.s.l.). The dashed pink line represents the ELA at 5050 m a.s.l. The black outline indicates the glacierized grid cells below the ELA, in which glacier melt is applied in model. The green outline identifies the vegetated part of the watershed. The blue line shows the stream line and the blue star represents the outlet. Vegetated areas are shown in Figure 2a.