Hydroclimate and bedrock permeability determine young water fractions in streamflow across the tropical Andes mountains and Amazon floodplain

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Abstract

The role of topography on water transit times and pathways through catchments is unclear, especially in mountainous environments — yet these environments play central roles in global water, sediment, and biogeochemical fluxes. Moreover, the vast majority of intensively monitored catchments are located in northern latitudes. As a result, the interplay between water transit, topography and other landscape characteristics is particularly underexplored in tropical environments. Here we present the results of a multi-year hydrologic sampling campaign (twice-monthly and storm sampling) to quantify water transit in seven small catchments (<3 km²) across the transition from the Andes mountains to Amazon floodplain in southern Peru. We use the stable isotope composition of water ($\delta^{18}$O$_{H_2O}$) to calculate the fraction of streamflow comprised of recent precipitation (“young water fraction”) for each of the seven small catchments. Mean unweighted young water fractions ($F_{yw}$) are 3–10 % in the Andes, 15–23 % at mid-elevation and 3–4 % in the foreland floodplain. Weighting the $F_{yw}$ calculation by volume of streamflow and precipitation yield $F_{yw}$ of 7–47 %. Across these catchments, topography does not exert a clear control on water transit; instead stream $F_{yw}$ is controlled by a combination of hydroclimate and bedrock permeability. Mid-elevation sites are posited to have the highest $F_{yw}$ due to less permeable bedrock, poorly developed soils and more frequent and intense rainfall. The data presented here allow us to explore relationships between topography, bedrock permeability, hydroclimate and stream baseflow $F_{yw}$ — particularly highlighting the role of bedrock permeability and hydroclimate in determining water transit times in a tropical mountain setting.
1. Introduction

As water moves from rainfall to river runoff, it is stored in soil and rock for variable amounts of time. The length of time it takes for rainfall to exit a catchment in streams and rivers, known as the water transit time, exerts an important control on biogeochemical and ecohydrologic processes. While water is within a catchment, it reacts with soil and rock, acquiring solutes (Gibbs, 1970; Drever, 1988), and it interacts with ecosystems, sustaining photosynthesis and transpiration (Allen et al., 2019; Rempe and Dietrich, 2018). Water transit times also influence the availability of freshwater resources and the potential for environmental hazards such as flooding.

Mountainous regions play particularly important roles in the global water cycle, receiving outsized amounts of precipitation and acting as “water towers” that store and gradually release water for drier downstream areas (Barnett et al., 2005; Immerzeel et al., 2020; Meybeck et al., 2001; Viviroli et al., 2007). The impacts of climate change on the water cycle (Scanlon et al., 2018; Wilusz et al., 2017), especially diminished snowpack and warming across altitudinal gradients in mountainous regions, emphasize the importance of understanding water transit times in mountainous systems. Beyond serving as water towers, mountains have high erosion rates, exposing fresh mineral surfaces to chemical weathering processes that control the geological carbon cycle (Gaillardet et al., 1999; Hilton and West, 2020). Mineral weathering reactions in mountainous environments are modulated by a balance between water transit and mineral supply and reactivity (Ameli et al., 2017; Berner, 1978; Maher, 2010, 2011; West et al., 2005). Understanding the linkages between hydrology, erosion and the carbon cycle depends on quantifying water transit in mountainous environments. Finally, mountainous regions control the export of sediment and nutrients to rivers downstream, playing important roles in water quality and regional biogeochemistry.

Despite their global hydrological importance, much is not understood about water transit times in mountain systems. Global data suggest that streamflow in mountainous catchments carries less young water than in more gently sloping catchments (Jasechko, 2016; Lutz et al., 2018), potentially because of long water flow paths through fractured bedrock (e.g., Muñoz-Villers et al., 2016). Yet the relationships between topography and young water fractions are weak, and few studies have tested these ideas across the dramatic topographic gradients of major mountain ranges. Moreover, other studies have suggested complex relationships between topography and water transit times, with other factors including watershed organization and area, as well as bedrock permeability and subsurface structure, also playing important roles (Asano et al., 2002; McGlynn et al., 2003; McGuire et al., 2005; Tetzlaff, Seibert, McGuire, et al., 2009; Tetzlaff, Seibert, & Soulsby, 2009; Asano & Uchida, 2012; Hale et al., 2016; Hale & McDonnell, 2016; Rempe and Dietrich, 2018; Scanlon et al., 2018; Wilusz et al., 2017).
Altogether, it remains unclear to what extent mountain regions affect fluid transit times, and for what reasons.

To address this problem, we collected a four-year time series (2016–2019) of approximately fortnightly stream and precipitation samples from seven small (< 3 km²) catchments in southern Peru. The study catchments are within the Madre de Dios region in southern Peru, which includes the transition from the eastern Andes mountains (3472 m) to Amazon foreland floodplain (214 m; Fig. 1) and a gradient in catchment slopes from 37–3 °. We present a systematic evaluation of the movement and retention of water within these varied tropical landscapes, focusing on isotope-derived stream young water fractions. Because stable isotopes of precipitation vary with time, and the stable isotope composition of water is conservative during transport through catchments, a comparison of time series of stable O or H isotopes in rainfall and stream water can be used to infer transit time (McGuire & McDonnell, 2006). The most general and robust interpretive framework uses isotope time series to calculate the stream young water fraction, which is the fraction of streamflow that fell as precipitation within the prior 2-3 months (Kirchner, 2016a, b). We build a stable isotope dataset and analyze the young water fractions across a range in topography (3472–214 m) and slopes (37–3 °) rarely seen in other studies, allowing us novel insight into the effect of mountains on water transit. Moreover, we provide stable isotope constraints on water transit in tropical lowlands, where little information of this kind has been reported previously.

2. Data and methods

2.1 Study area and sampling design

In this study, we carried out detailed hydrochemical monitoring at seven small (areas ranging from 0.03–3.00 km²) catchments spanning the transition from the eastern flank of the Andes Mountains to the Amazon foreland floodplain (Fig. 1; Table 1). The small catchments (SC) in this study are referred to by their sampling point elevation in meters, followed by “-SC”. Two small catchments (3472-SC and 3077-SC) are in the high Andes mountains, underlain by fractured shale bedrock, with mean slopes ranging from ~25–35 °. Two mid-elevation small catchments (2432-SC and 1540-SC) are in the similarly steep mid-elevation Andes, with one (1540-SC) underlain by a granitic intrusion. One small catchment is situated in the foreland fold and thrust belt at the foothills of the Andes (609-SC), underlain by uplifted Andean sediments, with a mean slope of 20.8 °. Two of the small catchments are situated on fluvial terraces in the
foreland floodplain (276-SC and 214-SC), with the bedrock at these sites comprised of weathered sediments from the Andes. These catchments have much lower slopes, averaging 3–4 °. We also consider stable isotope data from two nested mesoscale catchments studied in Clark et al., 2014 (dashed white line in Figure 1B-D). The catchments from Clark et al., 2014 are referred to by their mean elevation in meters, followed by “-Clark”: 3195-Clark (mean slope 26 °; mean area 49 km²) and 2805-Clark (mean slope 28 °; mean area 164 km²). Site 3195-Clark drains Andean shales and site 2805-Clark drains Andean shales and the same granitic intrusion that underlies 1540-SC (Figure 1D).

The seven small streams were sampled approximately bi-weekly beginning in April 2016. In addition to stream sampling, precipitation was collected at sites 3077-SC, 1540-SC, 609-SC, 276-SC and 214-SC. For sites 3472-SC and 2432-SC we calculated approximate precipitation oxygen isotope values by linearly interpolating between nearby precipitation samples collected at higher and lower elevations, supported by the observation that in this region precipitation isotopes have a linear relationship with elevation (Ponton et al., 2014). Precipitation was collected in a bucket left out between each sampling trip, with a layer of oil to prevent evaporative loss. Point discharge was manually measured each time a sample was taken. For sites 3077-SC and 609-SC, continuous discharge was measured in 2019 and 2020 with WL16 Global Water Level Loggers. Rainfall amount data are from tipping bucket and Vaisala rain gauges maintained by the Andes Biodiversity and Ecosystem Research Group, a manual rain gauge maintained by the Los Amigos Biological Station, and rain gauges operated by the Servicio Nacional de Meteorología e Hidrología del Perú (SENAMHI).
Figure 1. (a) Digital Elevation Model (DEM, from ALOS 30m data) of the Andes mountains and Amazon floodplain in southern Peru. White circles indicate sampling locations. (b−d) show the area within the black rectangle in (a), with small catchments from this study delineated by solid red lines, and catchments from Clark et al., 2014 by dashed white lines. (b) shows elevation of Andean sites, (c) Landsat imagery, and (d) geology, using data from INGEMMET.
Table 1. Characteristics of small catchments from this study and mesoscale catchments from Clark et al., 2014. TMCF = tropical montane cloud forest, UPRF = upper rainforest, TRF = tropical rainforest.

<table>
<thead>
<tr>
<th>Sites, this study</th>
<th>Location</th>
<th>S</th>
<th>W</th>
<th>Area (km²)</th>
<th>Mean slope (°)</th>
<th>Geology</th>
<th>Vegetation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3472-SC</td>
<td>Carretera Manu near Ajanaco</td>
<td>13.20617</td>
<td>71.61168</td>
<td>0.395</td>
<td>24.7</td>
<td>Sandia Fm. - shale</td>
<td>Puna</td>
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<td>Wayqecha Biological Station</td>
<td>13.19255</td>
<td>71.58795</td>
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<td>San José Group - shale</td>
<td>TMCF</td>
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<tr>
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<td>Carretera Manu near Pillahuata</td>
<td>13.15969</td>
<td>71.59378</td>
<td>0.0287</td>
<td>29.5</td>
<td>San José Group - shale</td>
<td>TMCF</td>
</tr>
<tr>
<td>1540-SC</td>
<td>Carretera Manu near San Pedro</td>
<td>13.06454</td>
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<td>0.613</td>
<td>36.9</td>
<td>Granite Intrusion</td>
<td>UPRF</td>
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<td>609-SC</td>
<td>Villa Carmen Biological Station</td>
<td>12.89614</td>
<td>71.41826</td>
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<td>20.8</td>
<td>Paucartambo Fm.</td>
<td>Bamboo</td>
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<tr>
<td>276-SC</td>
<td>Los Amigos Biological Station</td>
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<td>0.377</td>
<td>4.5</td>
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<td>TRF</td>
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<td>214-SC</td>
<td>Explorer’s Inn Tambopata</td>
<td>12.82955</td>
<td>69.27132</td>
<td>3.00</td>
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<td>Fluvial terrace (Quaternary)</td>
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<th>Sites, existing dataset</th>
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<th>Area (km²)</th>
<th>Mean slope (°)</th>
<th>Geology</th>
<th>Vegetation</th>
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<td>71.58917</td>
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<td>27.5</td>
<td>Sandia Fm., San José Group</td>
<td>Puna, TMCF, UPRF</td>
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<tr>
<td>2805-Clark</td>
<td>Kosñipata River at San Pedro</td>
<td>13.06028</td>
<td>71.54444</td>
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<td>29.9</td>
<td>Sandia Fm., San José Group, Granite Intrusion</td>
<td>Puna, TMCF, UPRF</td>
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2.2 Analytical techniques and data analysis

Samples were analyzed for stable isotopes of water ($\delta^{18}O$ and $\delta^2H$), with results reported here using permille notation relative to the Vienna Standard Mean Ocean Water standard. The stream oxygen or hydrogen isotope composition is referred to as $\delta^{18}O_{\text{stream}}$ and $\deltaD_{\text{stream}}$ and precipitation oxygen and hydrogen isotope composition as $\delta^{18}O_{\text{precip}}$ and $\deltaD_{\text{precip}}$. The analyses were carried out via two Los Gatos Research Liquid Water Isotope Analyzers (LGR) (Caltech and Lawrence Berkeley National Lab) and a Picarro L2130i Cavity Ring Down Spectrometer (Chapman University). The internal error of isotope measurements on the Picarro was 0.1 ‰ or better for $\delta^{18}O$ and 2 ‰ or better for $\deltaD$. On the LGR at Lawrence Berkeley National Lab the internal error was 0.1 ‰ or better for $\delta^{18}O$ and 1 ‰ or better for $\deltaD$. On the LGR at Caltech the internal error was 0.3 ‰ or better for $\delta^{18}O$ and 1 ‰ or better for $\deltaD$. Long-term accuracy on certified isotope standards was within one standard deviation of the known isotopic values.

Young water fractions were calculated for each small catchment following Kirchner (2016a, 2016b). Stream and precipitation oxygen isotope data were fit with Equation (1):

$$C(t) = a_s \times \cos (2\pi f t) + b_s \times \sin \sin (2\pi f t) + k$$  

(1)

where $C$ is the concentration of a tracer in stream or precipitation, $t$ is time, $f$ is the frequency of the interval, $a$ and $b$ are the cosine and sine coefficients and $k$ is the vertical shift. The fit to stream and precipitation isotope data was performed with and without stream discharge and rainfall amount weighting. The young water fraction was then calculated using Equations (2-4), where:

$$\text{Amplitude, } \delta^{18}O_{\text{Stream}} = \sqrt{a_s^2 + b_s^2}$$  

(2)

$$\text{Amplitude, } \delta^{18}O_{\text{Precipitation}} = \sqrt{a_p^2 + b_p^2}$$  

(3)

$$\text{Young water fraction (\%)} = \frac{\text{Amplitude, } \delta^{18}O_{\text{Stream}}}{\text{Amplitude, } \delta^{18}O_{\text{Precipitation}}}$$  

(4)

A Monte Carlo simulation was performed to assess the uncertainty associated with the young water fraction calculations, using resampling with replacement to generate 10,000 stream and isotope datasets, and then applying equations (1–4) to each dataset. In order to assess the differences in young water fraction distributions between sites, a null dataset was generated using all of the stream and precipitation isotope data across all of the sites, by subtracting each individual isotope value from the site-specific mean isotope value. We then applied the same Monte Carlo resampling routine and equations (1–4) to the null dataset. Stream baseflow indices were calculated for sites 3077-SC and 609-SC using the Matlab HydRun hydrograph analysis package (Tang and Carey, 2017).

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3. Results

3.1 Oxygen and hydrogen isotopes in streamflow and precipitation

The \( \delta^{18}O_{\text{stream}} \) and \( \delta^{18}O_{\text{precip}} \) values follow an orographic trend across the transition from high Andes mountains to foothills (3472-SC to 609-SC), with the highest elevation streams showing the most isotopic depletion (Fig. 2, 3b). Along this same mountain-to-foot hill transition, \( \delta^{18}O_{\text{precip}} \) and \( \deltaD_{\text{precip}} \) display a marked seasonal cycle (amplitude \( \delta^{18}O_{\text{precip}} \sim 4–5 \%e \) that is slightly greater in the Andes mountains than the foothills or foreland floodplain (Table 2; Figs. 2b, 4c–d).

![Boxplots of stream (a) and precipitation (b) \( \delta^{18}O_{\text{H2O}} \). Sites 3195 and 2805 are mesoscale catchments from Clark et al. (2014).](https://doi.org/10.5194/hess-2022-188)

Figure 2. Boxplots of stream (a) and precipitation (b) \( \delta^{18}O_{\text{H2O}} \). Sites 3195 and 2805 are mesoscale catchments from Clark et al. (2014).
Figure 3. (a) $\delta^{18}O$ and $\delta D$ of stream and precipitation. (b) mean $\delta^{18}O_{\text{stream}}$ as a function of catchment elevation at sampling point for the small catchments, and mean catchment elevation for the mesoscale catchments. Circles represent stream isotope data from this study, squares are mesoscale catchments from Clark et al. (2014) and diamonds are precipitation.

Relative to the $\delta^{18}O_{\text{precip}}$ inputs, $\delta^{18}O_{\text{stream}}$ values are damped. The degree of isotope dampening and therefore the amplitude of the $\delta^{18}O_{\text{stream}}$ seasonal cycle varies between the small catchments situated from mountain-to-foothill (Fig. 4a–b). The seasonal amplitude of $\delta^{18}O_{\text{stream}}$ values is smallest within the Andes mountains (3472-SC, 3077-SC, 2432-SC) and foreland floodplain sites (276-SC and 214-SC) and highest for the mid-elevation mountain (1540-SC) and mountain foothills sites (609-SC) (Fig. 2a, 4a–b). Of the two mesoscale catchments, 3195-Clark has a smaller amplitude in $\delta^{18}O_{\text{stream}}$ than 2805-Clark. Dual isotope space ($\delta^{18}O_{\text{H}_2\text{O}}$ and $\delta D_{\text{H}_2\text{O}}$) reveals no significant deviation from the local meteoric water line (Fig. 3a), indicating no significant evaporative signal in the stream waters.
Figure 4. $\delta^{18}O_{\text{stream}}$ (a and b) and $\delta^{18}O_{\text{precip}}$ (c and d) for the duration of the study period (2016−2019), plotted by day of year. $\delta^{18}O_{\text{stream}}$ from small catchments is denoted with circles, and the mesoscale catchment data is denoted with squares. $\delta^{18}O_{\text{precip}}$ is denoted with diamonds. Panels (a) and (c) show sites in the Andes and mountain foothills; panels (b) and (d) show the foreland floodplain sites.
<table>
<thead>
<tr>
<th>Sites, this study</th>
<th>Location</th>
<th>n, stream samples</th>
<th>δ(^{18})O(_{\text{stream}}), avg</th>
<th>Amplitude δ(^{18})O(_{\text{stream}})</th>
<th>n, precip samples</th>
<th>δ(^{18})O(_{\text{precip}}), avg</th>
<th>Amplitude δ(^{18})O(_{\text{precip}})</th>
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<tr>
<td>3472-SC</td>
<td>Mountain</td>
<td>55</td>
<td>-13.8</td>
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<td>-</td>
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<td>Mid-elevation mountain</td>
<td>62</td>
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<tr>
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<td>-6.6</td>
<td>0.17</td>
<td>15</td>
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<th>δ(^{18})O(_{\text{stream}}), avg</th>
<th>Amplitude δ(^{18})O(_{\text{stream}})</th>
<th>n, precip samples</th>
<th>δ(^{18})O(_{\text{precip}}), avg</th>
<th>Amplitude δ(^{18})O(_{\text{precip}})</th>
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<td>3195-Clark</td>
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<td>60</td>
<td>-13.7</td>
<td>0.42</td>
<td>-</td>
<td>5.29</td>
<td>-</td>
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<tr>
<td>2805-Clark</td>
<td>Mountain/mid-elevation mountain</td>
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<td>-12.1</td>
<td>0.96</td>
<td>-</td>
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</table>

Table 2. Stream and precipitation stable water isotope data from this study and Clark et al., 2014. ‘-’ indicates where samples were not collected. For sites without precipitation collection, δ\(^{18}\)O\(_{\text{precip}}\) was linearly interpolated by elevation from the nearest sites.
3.2 Young water fractions

Young water fractions ($F_{yw}$) vary between the catchments across the mountain-to-floodplain transition. Figure 7 shows calculated $F_{yw}$ values for each catchment, with violin plots reflecting ranges generated using Monte Carlo simulation. 3472-SC, 3077-SC and 2432-SC have mean unweighted $F_{yw}$ between 3 and 11 %. Mesoscale catchment 3195-Clark, draining approximately 50 km$^2$ of Andean shales, has a mean $F_{yw}$ of 8 %, roughly averaging the $F_{yw}$ seen in the three small Andean catchments. At mid-elevation, 1540-SC, which drains granitic intrusions, has a mean unweighted $F_{yw}$ of 23 %. The second mesoscale catchment, 2805-Clark, which drains a 165 km$^2$ area including Andean shales and granitic intrusions, has a mean unweighted $F_{yw}$ of 18 %. 609-SC, in the foothills of the Andes and underlain by colluvium, has a mean unweighted $F_{yw}$ of 15 %. On the foreland floodplain, 276-SC and 214-SC located on fluvial terraces, have mean unweighted $F_{yw}$ of 3 and 4 %, respectively. For comparison, the null dataset, generated from a compilation of isotope data from all sites, yields $F_{yw}$ of 7 %. In addition to changes in the mean values across the Andes-Amazon gradient, the Monte Carlo distributions change, with wider distributions for the mid-elevation catchments and tighter distributions in the high Andes and Amazon lowland catchments.
Figure 5. $\delta^{18}O_{\text{stream}}$ (solid circles) and $\delta^{18}O_{\text{precip}}$ (open diamonds) from twice-monthly sampling campaigns in each small catchment. The size of the solid circles corresponds to the flow quantile that the $\delta^{18}O_{\text{stream}}$ is from. Data in (a−c) are from small catchments in the mountains, (d) is from the mid-elevation mountain small catchment, (e) is from the foothills small catchment and (f) is from the foreland floodplain small catchment.
4. DISCUSSION

4.1 Hydroclimate and permeability controls on stream young water fractions

All else being equal, catchment topography is expected to control water transit times; steeper flow paths should produce shorter transit times (e.g., following Darcy’s Law), while greater relief may generate longer flow paths and consequently longer transit times. Yet, despite much effort to demonstrate such effects, past work has shown no systematic relationship between catchment topography and isotope-based young water fractions, including in regional studies and across global compilations (e.g., Tetzlaff et al., 2009b).

Similarly, in our results, we find no simple relationship between catchment topography and $F_{yw}$ across the Amazon-Andes gradient studied here (Fig. 8). While unweighted $F_{yw}$ is low (mean values $<$5 %) in both of our lowland catchments (276-SC and 214-SC), the other catchments from mountain to foothills show a wide range of unweighted $F_{yw}$, from 3–23 %, with no apparent relationship to either slope angle or flow path length (Fig. 8a, b). There is, however, some coherent pattern in $F_{yw}$ across these catchments that may help to explain the decoupling of $F_{yw}$ and topography at least across these sites, and perhaps more generally.

Specifically, the small catchments in the high Andes Mountains (3472-SC, 3077-SC and 2432-SC) all have low $F_{yw}$, with unweighted means between 3–10 % and relatively tight distributions, while the mid-elevation small catchments show a much wider spread, tending toward much higher $F_{yw}$ values (Fig. 7). The $F_{yw}$ values inferred from the mesoscale catchments studied by Clark et al. (2014) are consistent with the patterns from the small catchments. The mesoscale catchment in the high Andes, underlain entirely by shale bedrock, has a similar $F_{yw}$ to that of the high elevation small catchments (unweighted mean value $<$10%). In contrast, the mesoscale catchment that spans across the high- to mid-elevations (2805-Clark) has an unweighted mean $F_{yw}$ of 19%, consistent with a mixture of older water from upstream, high-permeability shale-dominated portions of the study region and younger water from low-permeability granitic areas. Overall, our data point to low and tightly distributed $F_{yw}$ in the high mountains, but higher and more broadly distributed $F_{yw}$ in the mid-elevations.

We attribute the low $F_{yw}$ observed in the high mountain sites to high permeability of the fractured shale bedrock. Fractures create conduits for fluid flow that can be magnified by dissolution of reactive minerals, such as the sulfides that are relatively abundant in the Paleozoic shale underlying our Andes Mountains catchments. Previous studies of stream hydrochemistry in the region have emphasized the importance of sulfide mineral oxidation as a primary weathering process (Burt et al., 2021; Torres et al., 2016), and pyrite...
oxidation is known to generate porosity and permeability in shale bedrock (Gu et al., 2020). In our conceptual model of water transit, the combination of pore-scale chemical weathering and regional stresses create a fractured subsurface that is conducive to long fluid flow paths, leading to overall low young water fractions in Andean streams.

The mid-elevation catchments differ in two respects that we think can explain the distinct transit times inferred for these streams. The increased spread in estimated $F_{yw}$ for the catchments between 3000 and 500m coincides with a shift to a flashier hydroclimate, with more rainfall events of higher magnitude at the mid-elevations compared to either the high Andes or the Amazon lowlands (Fig. 6a; also see Clark et al., 2016). Correspondingly, the stream hydrograph at 609-SC is much flashier than at 3077-SC (Fig. 6b; these are the two catchments with a semi-continuous discharge record). A comparison of stream baseflow indices for sites 3077-SC and 609-SC shows a higher baseflow index for site 3077-SC ($BFI = 0.77$) and lower baseflow index for site 609-SC ($BFI = 0.64$). We interpret the first-order shift in $F_{yw}$ values from the high Andes (where baseflow indices are high) to the mid-elevations (where baseflow indices are lower) as being related to this change towards a stormier climate, suggesting a primary role for hydroclimate forcing in determining transit times in these mountainous catchments. An important role for precipitation and discharge regimes has emerged from other recent transit time studies focused on single catchments with higher temporal resolution data collection (Gallart et al., 2020; von Freyberg et al., 2018; Stockinger et al., 2016). Although we see some slight variability in the amplitude of $\delta^{18}O_{stream}$ as a function of discharge in our results (Fig. 5), we lack data across the range of discharge that would be needed for robust quantitative analysis of this effect. Higher frequency sampling across gradients such as those in the Andes, though daunting given the logistical challenges of this environment, would be an interesting target for future work.

Superimposed on the overall differences that characterize the mid-elevation catchments, the $F_{yw}$ in 1540-SC stands out as especially high (Fig. 8; mean $F_{yw}$ estimate $>50\%$ when amount-weighted). Unlike the other catchments in our study that are characterized by sedimentary bedrock, this catchment is underlain by a granitic intrusion (Clark et al., 2014). We attribute the especially high $F_{yw}$ in this part of the study region to the low permeability of this granite bedrock, which prevents water from infiltrating deeply and leads to rapid, surficial flow paths over the steep topography. Altogether, then, we interpret the highly variable transit times across the Andean catchments as being related principally to a combination of hydroclimate and bedrock permeability, with these factors outweighing the influence of catchment topography.
Figure 6. (a) Precipitation return interval for rain gauges near sites 3077-SC, 1540-SC, 609-SC and 276-SC. (b) Stream runoff records for sites 3077-SC and 609-SC, showing baseflow indices for both sites.
Figure 7. Unweighted (a) and weighted (b) stream young water fractions for all catchments and a null dataset. 3195-Clark and 2805-Clark are the mesoscale catchments from Clark et al., 2014.
4.2 Implications for the role of mountains in modulating water, erosional, and biogeochemical fluxes.

The role of mountains as water towers, and particularly the response of these freshwater resources to climate change, depends in part on water transit times through mountain catchments. In revealing the importance of hydroclimate for transit times, our results suggest that shifting precipitation regimes may be important in determining not just how much precipitation falls over mountain regions (or indeed the balance of snow and rain), but also the fate of precipitation as it makes its way through mountain catchments. If our spatial comparison of catchments across the Andes-Amazon region translates to temporal trends, then a flashier rainfall regime in the future might be expected to produce a wider range of transit times including higher young water fractions in streams draining mountainous terrain. In this sense, our results are consistent with recent studies suggesting that catchments can amplify rainfall variability (Müller Schmied et al., 2020). The implications for downstream flooding and the buffering of droughts may warrant further consideration.

The hydrology of mountainous catchments may play important geological roles, too. River discharge, and particularly discharge variability, exerts a primary control on erosion (e.g., Tucker and Bras, 2000). Longer transit times may dampen the relationship between precipitation variability and the river incision that drives mountain erosion; systematic relationships between topography and water transit times could therefore either dampen or amplify erosional efficiency of a given precipitation regime. Catchment hydrology has also been invoked as central to the role of mountain building in the global carbon cycle over geologic timescales (Maher and Chamberlain, 2014). This argument depends on both the exposure of fresh minerals for chemical weathering by rapid erosion, as well as systematic changes in hydrologic flow paths associated with mountain building. However the mountainous sites within this study display a wide range of values in $F_{yw}$ (from ~3–23 %; Figure 8), with no systematic relationship between topography and $F_{yw}$. Although a global compilation of stream $F_{yw}$ shows a general negative correlation between topographic relief and $F_{yw}$ (Jasechko et al., 2016), that relationship is notably weak — and the $F_{yw}$ from the small catchments studied here emphasize how other environmental factors (hydroclimate, catchment architecture) play important roles in determining the $F_{yw}$ of streamflow. Moreover, when comparing across the high Andes and Amazon lowlands, there is remarkably little difference in $F_{yw}$ despite dramatic differences in topography: catchments with average slope angles of ~5° and ~35° have similar $F_{yw}$ ~5 %. This result argues against a systematic shift in water transit times associated with mountain building, but rather a variable response modulated by climatic and geologic factors — although our results do point to a wider range in $F_{yw}$ associated with mountains than lowlands, at least for the tropical setting of the Andes-Amazon system.
While our results, and especially the Fyw of lowland catchments, may be specific to the Andes-Amazon setting, we expect the hydroclimatic and geological effects that we document here to be more generally relevant in other mountainous regions, too. Orographic controls on precipitation tend to force the highest precipitation, as well as the most intense rainfall, along mountain fronts and at mid-elevations. In addition to the Andes, similar patterns have been shown in the Himalaya (Bookhagen and Burbank, 2006) and the European Alps (Napoli et al., 2019) and models predict complex spatial patterns of orographic precipitation that depend on several factors including climatic variables (e.g., (Barros and Lettenmaier, 1994; Roe and Baker, 2006) The dependence of catchment transit times on hydroclimate, as we find in the Andes and as reported in other recent work (von Freyberg et al., 2018; Gallart et al., 2020), suggests that orographic effects on rainfall regime may be a primary determinant of hydrologic processes in major mountain ranges. Similarly, we expect fractured bedrock, and associated high permeability, to be generally characteristic of mountain systems as seen in our work and other studies (e.g., Muñoz-Villers et al., 2016; Moon et al., 2017), though our results also highlight how the geological complexity of mountains – such as the presence of a granitic intrusion in our study area of the Andes – can introduce heterogeneity. Full understanding of the role of mountainous regions in water, sediment, and geochemical cycles will depend on evaluating the role of these multiple factors in determining hydrological behavior.
Figure 8. Circles represent small catchments from this study, triangles represent mesoscale catchments from Clark et al. (2014). In panels (a-c), dashed circles and triangles indicate volume weighted young water fractions; solid circles and triangles are unweighted young water fractions. (a) shows $F_{yw}$ as a function of mean catchment flow path length, (b) shows $F_{yw}$ as a function of mean catchment slope, (c) shows $F_{yw}$ as a function of catchment elevation at sampling point for the small catchments, and mean catchment elevation for the mesoscale catchments. (d) Compares weighted mean $F_{yw}$ to unweighted mean $F_{yw}$. 

\[
\text{Weighted mean } F_{yw} = \frac{\sum (F_{yw} \times \text{catchment area})}{\sum \text{catchment area}}
\]

\[
\text{Unweighted mean } F_{yw} = \frac{\sum F_{yw}}{\sum \text{catchment area}}
\]
5. Conclusions

We collected stream and precipitation samples for analysis of O and H stable isotope ratios in rainfall and stream water at seven streams and four rainfall stations spanning the Andes-Amazon gradient over a period of four years. Samples were collected approximately twice monthly for most sites. The stream young water fraction varied significantly between sites. Highest elevation sites 3472-SC, 3077-SC and 2432-SC displayed young water fractions between 3–10%. Mid-elevation small catchments (1540-SC and 609-SC) displayed the higher young water fractions of 15–23%. Catchments in the foreland floodplain had low young water fractions, ranging from 3–4%.

We suggest that the low young water fractions observed in Andean catchments are a result of long flow paths in fractured shale. High young water fractions observed at mid-elevation sites result from a combination of a stormier climate, and in the case of 1540-SC, granitic bedrock with poorly developed soils and low permeability, meaning that water moves through the catchment faster. In the lowlands, low permeability clay terraces and low relief together generate low young water fractions. Thus a combination of topography, climate, and bedrock properties conspire to determine water transit in this setting. Our results emphasize the complexity of the role of mountainous regions in the hydrological cycle and potentially help to explain why it has been difficult to identify a simple topographic control on young water fractions at the global scale. Accounting for the multiple factors that control water transit will be important for fully understanding the role of mountain water towers in water, sediment, and carbon fluxes.
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Code/Data availability
Stream and precipitation water isotope data are provided as a table. The Matlab code for young water fraction analysis and Monte Carlo simulation is available from E. Burt upon request.

Author contribution
EB and AJW designed the study with input from DHCR and AJCQ. EB, DHCR and AJCQ carried out the hydrochemical monitoring. EB analyzed the samples and did the data analysis with input from AJW. EB and AJW wrote the manuscript.

Competing interests
The authors declare no competing interests.
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