

Sources and pathways of stream generation in tropical proglacial valleys of the Cordillera Blanca, Peru



Ryan P. Gordon^{a,*}, Laura K. Lautz^a, Jeffrey M. McKenzie^b, Bryan G. Mark^c, Daniel Chavez^b, Michel Baraer^d

^a Syracuse University, Department of Earth Sciences, 204 Heroy Geology Laboratory, Syracuse, NY 13244, USA

^b McGill University, Department of Earth and Planetary Sciences, 3450 University Street, Montréal, PQ H3A 0E8, Canada

^c The Ohio State University, Department of Geography, 1136 Derby Hall, 154 North Oval Mall, Columbus, OH 43210, USA

^d Department of Construction Engineering, École de Technologie Supérieure, Université du Québec, 1100 Notre-Dame Ouest, Montréal, PQ H3C 1K3, Canada

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SUMMARY

Tropical glaciers supply approximately half of dry-season stream discharge in glacierized valleys of the Cordillera Blanca, Peru. The remainder of streamflow originates as groundwater stored in alpine meadows and other proglacial geomorphic features. A better understanding of the hydrogeology of alpine groundwater, including sources, storage zones, and the locations and magnitudes of contributions to streamflow, is important for making accurate estimates of glacial inputs to the hydrologic budget, and for our ability to make predictions about future water resources as glaciers retreat. This field study focuses on two high-elevation meadows in valleys of the Cordillera Blanca, in headwaters and mid-valley locations. Tracer measurements of stream and spring discharge and groundwater-surface water exchange were combined with synoptic sampling of water isotopic and geochemical composition in order to characterize and quantify contributions to streamflow from different groundwater reservoirs. At the headwaters site, groundwater supplied approximately half of stream discharge from a small meadow, with most originating in an alluvial fan adjacent to the meadow and little (6%) from the meadow itself; however, at the mid-valley site, where meadows are extensive, local groundwater has a large impact on streamflow and chemistry through large net contributions to discharge and turnover of surface water due to gross exchanges with groundwater. At the mid-valley site, stream discharge increased by 200 L s^{-1} (18% of average discharge) over 1.2 km as it descended a moraine between two meadows. Such valley-crossing moraines, which create significant steps in the down-valley slope, are likely locations of substantial groundwater contribution to streams.

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1. Introduction

Alpine (highland or high-elevation) watersheds are an important source of fresh water in the world, and in semi-arid regions, mountain drainages supply a vastly disproportionate share of the water used by populations downstream (Barnett et al., 2005; Kaser et al., 2010; Viviroli et al., 2007). More than 80% of the water supply in the semi-arid tropics and subtropics originates in mountain watersheds, affecting over half of humanity (Messerli, 2001). Alpine watersheds are dominated by snow and ice melt processes, which are highly impacted by global climate change (Barnett et al., 2005). Water resources preserved in glaciers and snowpack are being permanently lost due to world-wide glacier recession

(Barnett et al., 2005; Barry and Seimon, 2000; Barry, 2006; Kaser et al., 2006; Milner et al., 2009; Nogues-Bravo et al., 2007; Vuille et al., 2008). Both the timing and the total quantity of water discharging from glacierized mountain areas will be affected by continuing climate change; specifically, dry-season discharge will be reduced as water supplied by melting ice and snow diminishes, and both seasonal and inter-annual runoff will become more variable as precipitation becomes the dominant control on streamflow (Baraer et al., 2012; Barnett et al., 2005; Mark and Seltzer, 2003; Milner et al., 2009). The effects of glacier-loss on seasonal runoff variation will be felt most acutely in the tropics, because mid-latitude glaciers amplify seasonal runoff variation while tropical glaciers smooth the variation, an effect that decreases significantly as glaciers recede (Kaser et al., 2003; Kaser and Osmaston, 2002; Mark and Seltzer, 2003).

* Corresponding author. Tel.: +1 315 443 2672 (O).

E-mail address: rpgordon@syrr.edu (R.P. Gordon).

As seasonal discharge patterns shift and the hydrologic buffering capacity of meltwater released from ice and snow is lost, the storage capacity of alpine landforms has an increasing influence on seasonal and inter-annual streamflow discharge and timing (Barnett et al., 2005). Although groundwater storage in glacierized valleys is typically oversimplified or assumed to be negligible in watershed modeling studies (e.g. Caballero et al., 2004; Kaser et al., 2003), common proglacial features such as meadows, moraines, rock slides, talus slopes, and alluvial and colluvial fans may store substantial groundwater that is released to streams at different rates in different seasons, with consequences for hydrologic modeling and water resource management (Clow et al., 2003). Understanding sources of streamflow and the storage capacity of natural reservoirs in proglacial watersheds is important for alpine hydrology, and has potential impacts on the way hydrologists model alpine processes and predict future impacts of glacier recession on water resources; however, little research has explored the groundwater processes contributing to streamflow in glacierized tropical catchments.

The role of groundwater in alpine watershed hydrology has been understudied (Hood et al., 2006). Using hydrograph separation or end-member mixing analyses, several studies (Brown et al., 2006; Huth et al., 2004; Liu et al., 2004; Sueker et al., 2000) have estimated a wide range for the percent contribution of alpine groundwater to streamflow at the catchment scale. At a

more detailed scale, Caballero et al. (2002) investigated the hydrologic behavior of talus slopes and lateral moraines using salt tracer breakthrough curves in the Cordillera Real, Bolivia. A series of studies (Hood et al., 2006; Langston et al., 2011; McClymont et al., 2010, 2011; Muir et al., 2011; Roy and Hayashi, 2009) have used a variety of geophysical and more traditional hydrologic techniques to investigate groundwater storage and interactions among a number of alpine geomorphic units including proglacial lakes, moraines, talus slopes, springs, and a small meadow, all in a single watershed in the Canadian Rocky Mountains. McClymont et al. (2010) estimated the storage and residence time of a talus slope-meadow complex, suggesting future studies should investigate different types of alpine meadow complexes and their impacts on watershed runoff and water quality.

Water storage capacities and hydrologic pathways are generally unknown for the moraines, talus slopes, and unique meadows that are likely storage reservoirs in tropical glacierized catchments of the central Andes (Baraer et al., 2009, 2014; Caballero et al., 2002; Mark and McKenzie, 2007; Mark et al., 2005). As a result, proglacial hydrologic models have frequently oversimplify the contribution of groundwater to watershed budgets, either ignoring it altogether or treating it like a lumped black box, calibrated empirically (Hood et al., 2006). Interactions between groundwater and streamflow have likewise been neglected or decoupled in simulations of climate change effects on alpine hydrology (Huntington

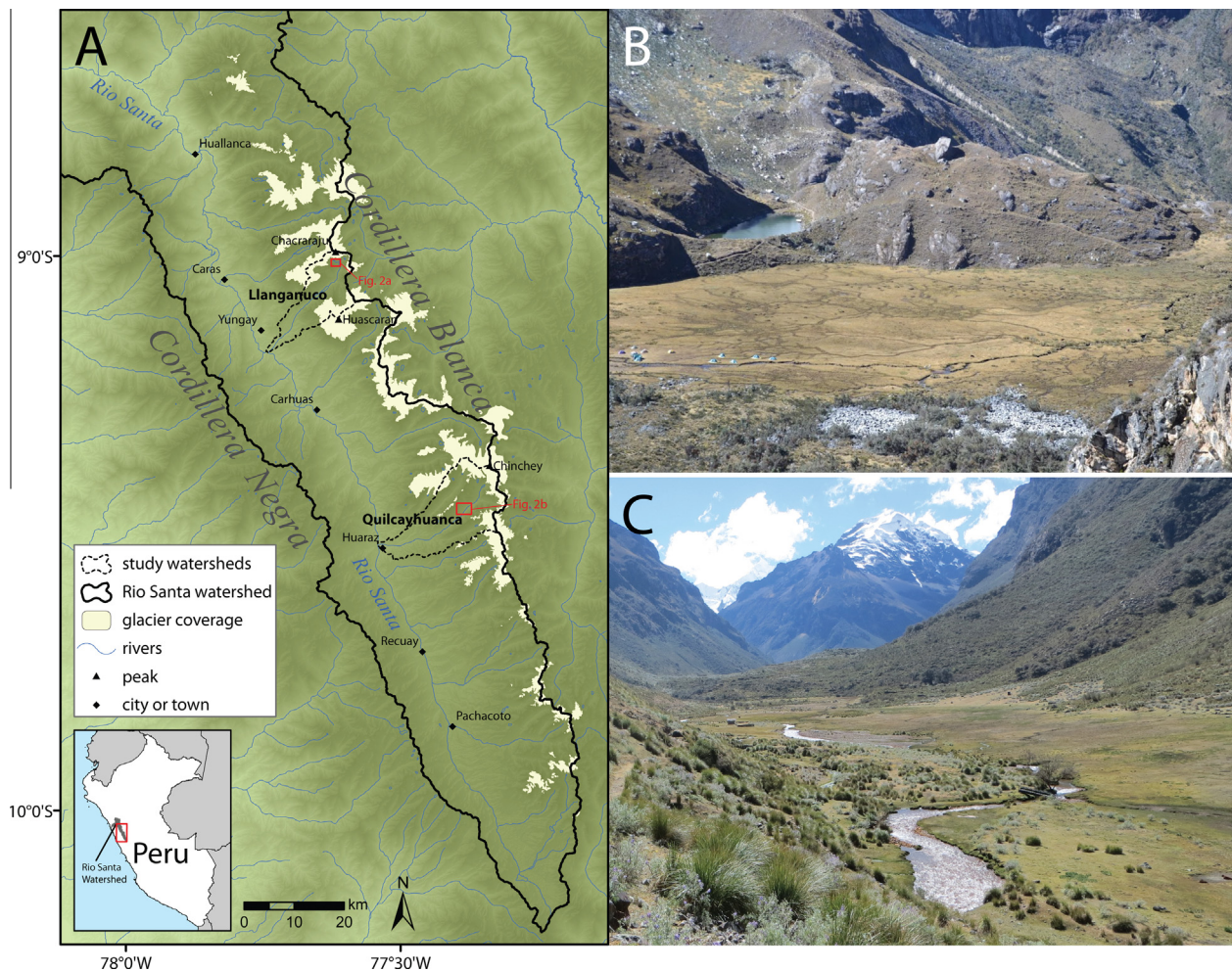


Fig. 1. (A) The Cordillera Blanca and upper Rio Santa valley, with red boxes indicating study locations in the Llanganuco and Quilcayhuanca watersheds. (B) Photograph of the studied meadow in Llanganuco, looking from west to east down from the top of the Laguna 69 fan. Water flow in the stream is from left to right. (C) Photograph of the Casa del Agua meadow in Quilcayhuanca, looking upstream (towards the east). The valley-crossing moraine can be seen on the far side of the flat pampa meadow.

and Niswonger, 2012). Studies that have estimated the relative contributions of groundwater and glacial melt to total stream discharge have done so using mass-balance and geochemical end-member mixing approaches at the basin and sub-basin scale (e.g. Baraer et al., 2009; Mark et al., 2005; Wagnon et al., 1998). This type of study is very useful in large, poorly instrumented mountain regions, but by its nature cannot quantify interactions between groundwater and surface water at a smaller scale than the identified sub-basins, such as potential recharge of proglacial aquifers by glacial meltwater and transformations in stream chemistry due to chemical weathering or hydrologic turnover. Although complex interactions between surface water and groundwater have been recognized for some time (e.g. Winter et al., 1998), the interactions between groundwater and mountain streams at the reach scale (10 m to 1 km) is a recent subject of interest (e.g. Bencala et al., 2011; Covino and McGlynn, 2007; Covino et al., 2011).

In the Cordillera Blanca, we expect that interactions between groundwater in geomorphic reservoirs and surface water in proglacial streams affect the quantity, timing, and chemistry of downstream discharge. Understanding these groundwater-surface water interactions is important for making accurate estimates of glacial meltwater contributions to the total hydrologic budget, and for our ability to make predictions about future surface water resources. In this paper, we report the results of an investigation of streamflow generation, groundwater-surface water interactions (GWSWI), and water sources in two proglacial high-elevation meadow complexes in the tropical Andes of Peru (Fig. 1). The objective of this research is to characterize the influence of high-elevation meadows and other proglacial geomorphic features on surface water quantity and quality in glacierized, tropical mountain catchments, with a focus on streamflow generation and GWSWI between streams and proglacial aquifers during the dry season (austral winter). We studied GWSWI between proglacial stream channels and shallow aquifers in wet meadows and adjacent moraine, talus, and fan features by measuring exchange rates between groundwater and stream channels and by investigating the isotopic and geochemical contributions, mixing, and transformations of source waters.

2. Site description

The Cordillera Blanca of Peru (Fig. 1) is the most glacierized tropical mountain range in the world. It is also the largest and highest mountain range in Peru, with the highest peak at Huascarán (6768 masl). In the 1970s, 723 km² of glacier area in the Cordillera accounted for 40% of Peru's glacial volume (Ames et al., 1989), but glaciers have since been retreating rapidly, and in 2010 covered 482 km² (Burns and Nolin, 2014; Mark et al., 2010). The glacierized catchments on the western side of the range supply two-thirds of the dry-season discharge of the Santa River (Rio Santa) (Mark et al., 2005), which flows to the Pacific Ocean. The Rio Santa powers multiple hydroelectric plants, representing over 4% of total Peruvian power production, which supply electricity to cities, villages, polymetallic mining operations, and heavy industry in the watershed and beyond; water from the Rio Santa is also used for small-holder agriculture in the upper basin, and to irrigate commercial agriculture operations on the arid coast (Bury et al., 2013). The upper Rio Santa basin adjacent to the Cordillera Blanca is known as the Callejón de Huaylas, with an area of 4900 km² and a population of 267,000 (Mark et al., 2010). The climate in the Callejón de Huaylas is semi-arid with a highly seasonal precipitation regime; 80% of precipitation falls in the austral summer, between October and May, and totals 800–1200 mm yr⁻¹ (Bury et al., 2011; Kaser et al., 2003). The average annual temperature, dependent

on elevation, is between 0 and 9 °C, with differences in monthly mean temperature much less than the daily variation (Kaser et al., 1990).

Glacial meltwater provides approximately half of the dry-season stream discharge in some Cordillera Blanca valleys (Mark et al., 2005), and meltwater buffers streamflow throughout the range, making it less susceptible to inter-annual variations in precipitation (Barnett et al., 2005; Mark and Seltzer, 2003; Milner et al., 2009). The remainder of dry-season streamflow is supplied by groundwater (Baraer et al., 2009, 2014). In the future, when glacier loss has reduced the influence of meltwater on streams of the Cordillera Blanca, groundwater discharge will be the single largest dry-season source of stream water for irrigation, municipalities, and hydropower generation in the Rio Santa watershed, putting livelihoods and economies at risk for water shortage (Baraer et al., 2012; Bury et al., 2011).

Many glaciers on the western side of the Cordillera Blanca are situated above low-gradient meadows or wetlands, locally called “pampas” or “bofedales” (Fig. 1B and C), and glacial meltwater typically flows via a stream network through a complex landscape of lakes, moraines, talus slopes, and fans around these meadows (Fig. 2). Kaser et al. (2003), in a study of glacial water storage in the Cordillera, noted that watersheds with “extensive, swampy plains and plateaus” appear to have additional storage capacity that complicates the effects of glaciers on discharge. Mark and McKenzie (2007) suggested that groundwater flow in the Cordillera Blanca valleys is derived from stored wet-season precipitation, and proposed that proglacial wet meadows (pampas) are likely groundwater reservoirs but require further study. The meadows are generally understood to form by paludification in low-gradient valley bottoms or from lakes dammed by moraines or rock slides (Earle et al., 2003; Squeo et al., 2006), and are ecologically characterized by a community of grass, sedge, and wetland plants in hydric soils. Meadows are underlain by organic and lacustrine deposits over buried talus, till, and bedrock. Baraer et al. (2014) investigated four glacierized valleys and identified talus slopes at the sides of meadows as key hydrologic features for groundwater recharge from the valley sides, storage through the dry season, and discharge by springs. The authors also concluded that water in buried coarse talus deposits flows beneath the meadow organic layer in confined aquifers, which occasionally connect to the meadow surface to form artesian springs.

For this study, we performed investigations at two meadow complexes in two glacierized valleys on the western side of the Cordillera Blanca, which were chosen due to their contrasts in stream discharge, meadow extent, adjacent geomorphic features, bedrock geology, and position relative to glacier termini. The first site, Llanganuco, is characteristic of the proglacial geomorphology at the headwaters of westward-flowing Cordillera Blanca valleys, and the second, Quilcayhuanca, is characteristic of the extensive mid-valley meadow systems.

The first site includes a meadow and proglacial stream system at the head of the Llanganuco valley. The meadow system (9.017°S, 77.604°W, 4370 masl) and adjacent geomorphologic features cover approximately 0.5 km² and include terminal moraine deposits, an alluvial/debris fan, rock falls, several groundwater springs at different geomorphic positions, and over 2 km of stream channel in tributaries draining two proglacial lakes (Figs. 1b and 2a). This meadow complex was chosen because of its small size and low stream discharge, the presence of terminal moraines, talus slopes, and a fan that all impinge upon the meadow margins, and the fact that the groundwater system is relatively contained in a hanging glacial cirque with a single, measurable outflow over a bedrock waterfall. Elevation of the watershed studied in Llanganuco ranges between 4340 m at the outflow and 6108 m at the peak of Chacaraju, and is 12.5 km² in area, 1.5% of which is meadow,

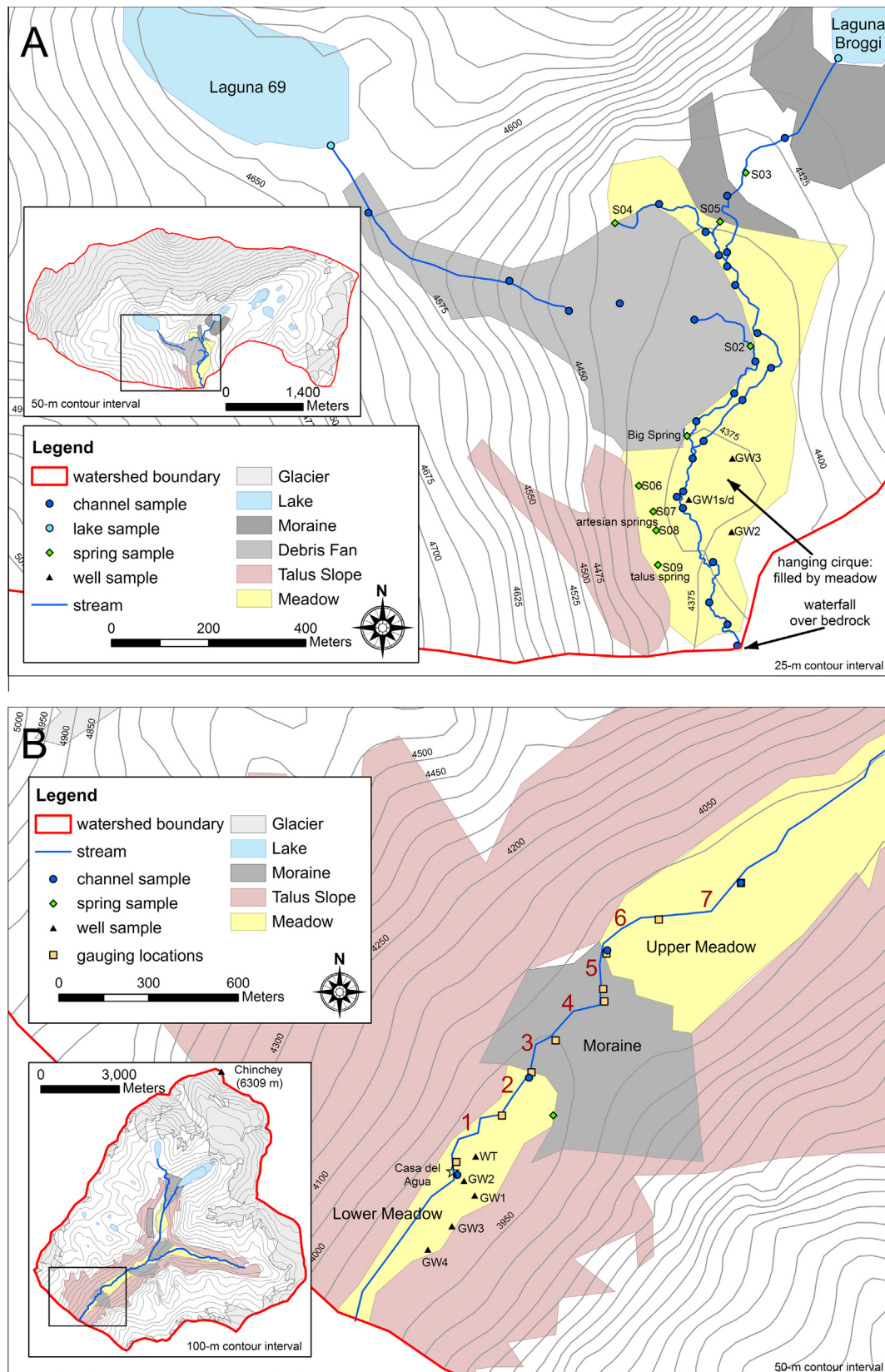


Fig. 2. Maps of water samples collected in 2012 at study sites in the (A) Llanganuco and (B) Quilcayhuanca valleys, with geomorphic units shown. In Quilcayhuanca, fluorometer locations for discharge gauging measurements and stream reach numbers are also indicated.

and 43% glacier (estimated from Quickbird-2 satellite imagery, 2003). The lowest glacier terminus is at approximately 4750 m elevation. Discharge measured at the outflow was 115 L s^{-1} during

our study. The majority of bedrock in the Llanganuco valley is granodiorite/tonalite of the Miocene Cordillera Blanca batholith (Wilson et al., 1995). Although not mapped as such due to ice cover

during the 20th Century (Wilson et al., 1995), parts of the valley above Laguna Broggi appear to be composed of the Upper Jurassic Chicama formation, a unit of marine black shales high in pyrite and other sulfide minerals, which is more commonly found on the eastern side of the Blanca (Love et al., 2004). Previous work in the Llanganuco valley suggests that glacial meltwater is a greater source of stream discharge than groundwater (Baraer et al., 2014), and modeling studies predict that the Llanganuco catchment could experience over a 60% decline in dry-season discharge if glaciers melt completely (Baraer et al., 2012).

The second study site is a 1.5-km long reach of the Quilcay stream in the middle of the Quilcayhuanca valley, upstream from a water divertment colloquially named Casa del Agua (9.465°S, 77.379°W, 3905 masl) (Figs. 1c and 2b). This site was chosen because the valley is characteristic of the long, deep, hanging valleys of the Cordillera Blanca, where a series of wet meadows contained behind valley-crossing end moraines or rock slides in the upper valley are situated above larger and more continuous valley-fill grassland with very low slope (1.5°) but steep talus-mantled valley walls. The studied stream reach at its upper end meanders through a wet meadow at approximately 3970 m elevation, and then flows through a valley-crossing end moraine, at which point it is incised in a narrow gully. After dropping ~50 m, it flows out of the moraine into a lower meadow and passes through the Casa del Agua flume. The studied watershed is 69 km² in area, with a highest point of 6309 masl at the peak of Chinchey; 3.0% of the watershed is meadow, and 26% glacier (estimated from ASTER satellite imagery, 2007). The lowest glacier terminus is at approximately 4700 m elevation. Discharge measured at Casa del Agua was 1180 L s⁻¹ during our study. Bedrock of the Quilcayhuanca valley is again primarily Cordillera Blanca granodiorite, but with substantial Chicama formation found in the upper glacierized valley, above the study site (Love et al., 2004). Quilcayhuanca was the site of a detailed study of springs and shallow meadow aquifers, conducted in 2008 and 2009, which concluded that talus slopes at the sides of the valley were a main source of groundwater recharge and storage (Baraer et al., 2014).

Conceptual models of the stratigraphy and hydrogeology of these valleys were previously developed by Baraer et al. (2014) and Chavez (2013), and this study attempts to refine these models by describing interactions between groundwater aquifers and streams. We expect groundwater-surface water interactions to be controlled by valley stratigraphy, such as preferential flow through confined units of coarse talus, as well as site geomorphology, such as breaks in channel slope and the spatial relationships between streams and meadows, moraines, fans, and talus slopes. Based on stream geomorphologic analysis (Larkin and Sharp, 1992), both valleys are expected to have substantial underflow (down-valley groundwater flow), especially where closely confined by bedrock, with important components of baseflow (lateral groundwater flow towards the stream) where steep permeable units like fans or talus slopes abut the valley bottom.

3. Methods

3.1. Dilution gauging and channel water balance calculations

Each studied stream was divided into reaches approximately 100–200 m long for dilution gauging and water balance experiments using tracers, and each section was measured and mapped using handheld GPS and aerial photography. Because the two valleys identified for this study are not continuously gauged, tracer dilution gauging is the most practical method available to directly quantify stream discharge. By performing multiple dilution tracer experiments at different scales over several reaches throughout

the study areas, we were able to calculate not only net changes in discharge over distance, but also gross losses and gains of stream water—which can occur concurrently—to and from underlying aquifers over stream reaches of interest. Tracer tests used the fluorescent dye Rhodamine WT (RWT) to label stream water and estimate changes in stream discharge and gross water gains and losses. RWT is a commonly used tracer for measuring water flow, and is considered conservative in most lotic waters (Stream Solute Workshop, 1990). Except where noted, the tracer tests were conducted with the “double-slug” (two instantaneous slug injections) channel water balance method, described in the following paragraph, after Harvey and Wagner (2000) and Payn et al. (2009). (Also see Figs. 1 and 4 of Payn et al., 2009.)

First, short mixing lengths (tens of meters) are identified upstream of the top and bottom of each stream reach based on field assessment and criteria of Day (1977). A tracer mass or slug M_D is released one mixing length above the downstream end of the reach, and tracer concentration through time, $C_D(t)$, is measured with a calibrated fluorometer (C3, Turner Designs, Sunnyvale, CA) as the tracer pulse passes the downstream end of the reach. Using the dilution gauging method (Day, 1977; Kilpatrick and Cobb, 1985), discharge at the downstream end of the reach, Q_D , is calculated from the observed tracer concentration breakthrough curve:

$$Q_D = \frac{M_D}{\int_0^T C_D(t) dt} \quad (1)$$

where T is the time at which concentration returns to zero after the tracer pulse passes. Next, a second slug of tracer, M_U , is released one mixing length above the upstream end of the reach, and its concentration is measured using a second fluorometer at the upstream end, yielding $C_U(t)$. Q_U , discharge at the upstream end of the reach, is calculated from M_U and $C_U(t)$, similar to Q_D in Eq. (1). Finally, the tracer mass M_U , after having traveled the entire reach, is observed passing the downstream fluorometer, yielding $C_{UD}(t)$. The change in discharge over the reach, or net gain, $\Delta Q = Q_D - Q_U$, is the net subsurface inflow to the stream or, if negative, the net loss or outflow of stream water to the subsurface. The recovered mass, M_{rec} , which is the mass of tracer observed at the downstream end of the reach, is calculated as

$$M_{rec} = Q_D \int_0^T C_{UD}(t) dt \quad (2)$$

The mass of tracer that is lost over the reach due to exchange of tracer-labeled water with the subsurface is $M_{loss} = M_{rec} - M_U$ (negative in sign), which allows a range for the gross loss of labeled water to be calculated. The minimum gross loss, in which all losses occur before all gains, is given by $Q_{loss,min} = Q_U M_{loss}/M_U$. The maximum gross loss, in which all losses occur after all gains, is given by $Q_{loss,max} = Q_D M_{loss}/M_{rec}$. The true value of Q_{loss} must be between these two values. The range of gross gains of unlabeled water into the stream is then simply given by the net gain minus the range of losses, $Q_{gain,min} = \Delta Q - Q_{loss,min}$, and $Q_{gain,max} = \Delta Q - Q_{loss,max}$. In this paper, ΔQ , Q_{loss} , and Q_{gain} values are variously reported as discharges (L s⁻¹), discharges as a fraction of Q (unitless), discharges normalized by reach length (L s⁻¹ km⁻¹), or discharges as a fraction of Q normalized by reach length (km⁻¹); all of these unit conventions are useful for comparing reaches with varying discharges and/or lengths (Covino et al., 2011).

The channel water balance method relies on several assumptions, including complete mixing of the tracer within stream water over the mixing lengths, steady discharge through time, and complete mass recovery (no loss of tracer) over the short mixing lengths (Harvey and Wagner, 2000; Payn et al., 2009). Schmadel et al. (2010) quantified uncertainties in the channel water balance

method due to violations of these assumptions, as well as uncertainty in data collection and measurement, and calculated mean errors of approximately 8% of Q in measurements of Q , ΔQ , and gross gains and losses, almost all of which was due to incomplete mixing of the tracer. In Llanganuco, the stream was typically deep, narrow, and sinuous as it cut through the meadow, and we therefore expect tracer mixing to be good. The stream in Quilcayhuanca was likewise judged to have good mixing potential, due to very turbulent cascading flow in mixing lengths. Tracer mixing was also subjectively assessed in the field by visually observing the mixing of pink RWT tracer along mixing lengths.

In Llanganuco, double-slug dilution gauging was conducted over nine stream reaches in the meadow (labeled A–G and X–Y in Fig. 3), and three additional single-slug dilution gauging experiments were made to measure the surface discharge from each of the two lakes and discharge from the moraine onto the meadow. A single-slug experiment is a simple dilution gauging measurement, in which one tracer mass is released and observed one mixing length downstream, yielding a single discharge measurement by Eq. (1). Experiments were conducted during the dry season on July 10–11 (reaches A–F) and July 24–25 (all others), 2012.

In Quilcayhuanca, double-slug dilution gauging was conducted over seven stream reaches (labeled 1–7 in Fig. 2B) in the upper meadow, over the moraine, and in the lower Casa del Agua meadow, all on July 16–17, 2012. Due to data loss, $C_U(t)$ for Reach 7 is unavailable, so only Q_D and $Q_{\text{loss,max}}$ can be calculated for that furthest upstream reach.

3.2. Synoptic sampling and geochemical and isotopic analyses

Synoptic sampling of glacial lake, channel, spring, and well water was performed on July 22–25, 2012 in Llanganuco (Fig. 2A) and July 26, 2012 in Quilcayhuanca (Fig. 2B), all during the dry season. Synoptic sampling within a short time interval captures the spatial variation in geochemistry among end-members and mixed waters along stream profiles. In Llanganuco, the main channel was sampled approximately every 100 m up to Lagunas 69 and Broggi, tributaries to the channel were sampled near their confluence, and water was collected from springs and groundwater wells in the meadow, and springs at the base of the moraine, alluvial fan, and talus slopes (Fig. 2A). In Quilcayhuanca, the main channel approximately every 500 m, one spring at the base of the moraine, and four groundwater wells were sampled (Fig. 2B). The wells at both sites (Table 1) were drilled during the 2012 field season using a portable, hand-operated, gasoline powered core drill, with the exception of WT in Quilcayhuanca, which had been completed using a hand auger in a previous field season. All wells were cased with 1-inch PVC pipe with a slotted screen at the bottom of the casing. All wells except WT were screened in coarse talus or sand/gravel units below the upper organic and clay layers of the shallow meadow. More information on well logs and installation can be found in Chavez (2013).

Sampled waters were measured for pH and conductivity in the field using a hand-held multi-probe (Multi 340i, WTW, Weilheim, Germany) and samples were filtered in the field using 0.45 μm nylon filters. Samples were later analyzed for the ions fluoride, chloride, bromide, nitrate, sulfate, sodium, potassium, magnesium,

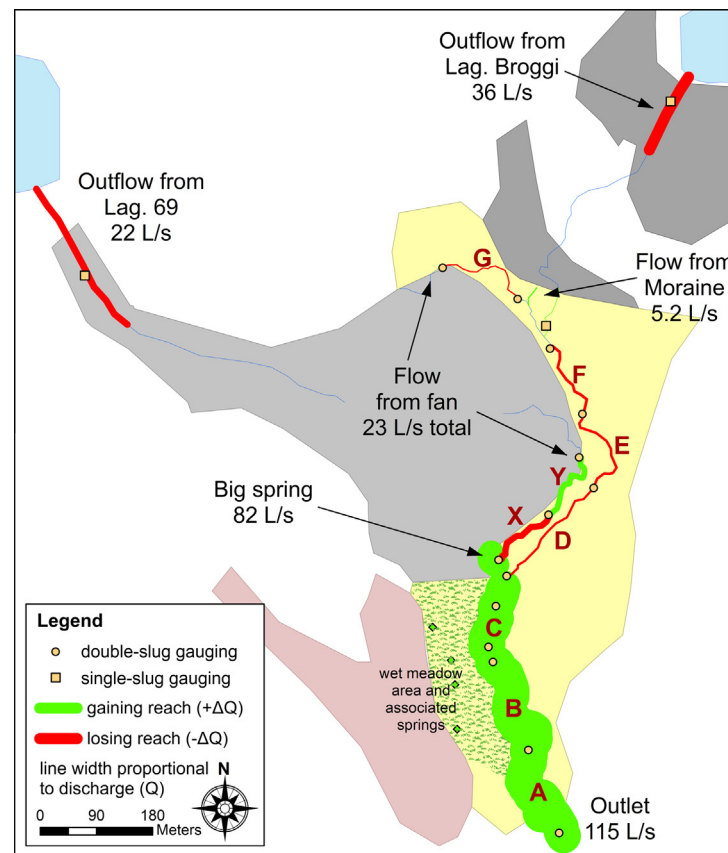


Fig. 3. Simplified map of Llanganuco showing fluorometer locations for double- and single-slug discharge gauging measurements, as well as discharge and water balance data. Reach color indicates whether the reach was gaining or losing (positive or negative ΔQ) based on water balance calculations or clear subjective observations (for single-slug reaches only). Width of the colored lines are proportional to reach discharge (Q_{av}). Surface discharge (Q) at select locations is also indicated. Geomorphic units are as described in Fig. 2a.

Table 1

Physical dimensions of boreholes and groundwater wells. More information, including well logs, can be found in Chavez (2013).

Site	Well	Well depth (m) ^a	Screen length (m)
Llanganuco	GW1s	2.51	0.61
Llanganuco	GW1d ^b	4.84	0.61
Llanganuco	GW2	2.9	0.61
Llanganuco	GW3	1.49	0.31
Quilcayhuanca	GW1 ^b	3.7	0.914
Quilcayhuanca	GW2 ^c	6.17	0.61
Quilcayhuanca	GW3 ^b	1.51	1.11
Quilcayhuanca	GW4	2.27	1.635
Quilcayhuanca	WT	Unknown	Unknown

^a Depth below ground surface to the bottom of well.

^b Not included in chemistry results due to possible contamination with wet cement during installation.

^c Well sealed after completion and sampling due to artesian flow.

and calcium by ion chromatography (Dionex ICS-2000, Thermo Fisher Scientific, Waltham, MA) and for stable isotopes of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) using a cavity ring-down spectrometer (L2130-i Water Isotope Analyzer, Picarro, Santa Clara, CA). Bicarbonate and carbonate concentrations were determined by charge balance and pH. Concentrations of fluoride, chloride, nitrate, sulfate, sodium, potassium, magnesium, and calcium in surface water samples in Llanganuco were incorporated into a principal component analysis (PCA) (Gordon et al., 2013; Hooper, 2003; Lautz and Fanelli, 2008; Mencio and Mas-Pla, 2008; Woocay and Walton, 2008). A PCA for Quilcayhuanca is not feasible, due to the number of samples being close to the number of variables.

4. Results

4.1. Stream discharge and channel water balances

The magnitude of stream discharges as well as the relative gains and losses over study reaches varied widely within sites and between the two sites (Tables 2 and 3, Fig. 3). In Llanganuco, the highest discharges were found in the lower half of the meadow (Reaches A–C), where discharge measured by dilution gauging ranged from 108 to 115 L s^{-1} with a length-weighted average (Q_{av}) of 111 L s^{-1} . Reaches A–C were gaining (positive ΔQ) from lateral subsurface inflow, with a total net gain of 7 L s^{-1} over 485 m of stream length, or 14 $\text{L s}^{-1} \text{ km}^{-1}$ (as a percentage of Q_{av} , this is 13% km^{-1}). The reaches in the upper half of the meadow (Reaches D–G), in contrast to those in the lower, had much smaller discharges (4.1–9.3 L s^{-1}) and showed net losses of stream water to the subsurface (negative ΔQ). Over the consecutive Reaches D–F, the net loss was

–2.5 L s^{-1} over 678 m with a Q_{av} of 8.2 L s^{-1} , or –53% km^{-1} . The longitudinal patterns can be seen clearly in Fig. 4A, which shows ΔQ as negative in the upper meadow and positive or near zero in the lower meadow. The other two meadow reaches (X and Y) were on a tributary to the main stem that flowed off of the Laguna 69 fan, and joined the main stem between reaches C and D (Fig. 3). Discharges in these reaches ranged from 16 to 21 L s^{-1} . Reach X was losing discharge at –71% of Q_{av} per km, similar to the nearby Reach D (–80% km^{-1}), but Reach Y was gaining a large amount of water (180% km^{-1}), mostly from a collection of diffuse springs and rivulets that were observed flowing into the channel from a very wet area at the nearby alluvial fan-meadow interface.

A detailed analysis of error in the dilution gauging method was not performed as in Schmadel et al. (2010), but multiple discharge measurements were performed at the downstream ends of reach A ($n = 3$) and C ($n = 2$) to test for repeatability. In these tests, fluorimeters were placed in different locations within the same channel cross-section, and multiple tracer releases were conducted. At both locations, the multiple measurements of discharge had low variability, with 2 standard deviation error of approximately 2% of mean discharge.

The balance of gross gains and losses in the studied reaches in Llanganuco also showed contrasts between the upper and lower sections of the meadow. Four of the five reaches that experienced net loss in the upper meadow also showed gross gains concurrent with gross losses, meaning that the reaches were exchanging water with the underlying meadow aquifer in both directions (Reaches E–G and X, Table 2, Fig. 4A and B). On the other hand, no gross losses of stream water were observed in reaches in the lower part of the meadow that experienced net gains (Reaches A–C) or Reach Y.

Contributions to the meadow streams from the adjacent geomorphic units were also highly variable in Llanganuco. We found that the majority of the stream water that exits the study area (115 L s^{-1} at the outlet) was issuing from a single spring situated at the base of the alluvial fan near the confluence of Reaches X and D, which we called the Big Spring (Fig. 3). By measuring all other flows upstream and downstream of the Big Spring, its discharge was estimated at 82 L s^{-1} . Other measurable flows from the alluvial fan into meadow channels totaled 23 L s^{-1} , including spring and surface flow at the head of Reach Y and spring flow at the head of Reach G, but excluding the Big Spring. At the very top of the alluvial fan, channel outflow from Laguna 69 was measured as 22 L s^{-1} , all of which disappears into the loose, blocky subsurface material near the top of the fan. Flow from the Broggi moraine onto the meadow was through two spring-fed channels totaling 5.2 L s^{-1} , which join the main stem above Reach F. Channel outflow from Laguna Broggi onto the moraine was measured as 36 L s^{-1} , all of which is lost to the subsurface on the upper moraine.

Table 2

Llanganuco dilution gauging and water balance results.

Reach	Description	Distance up stream (m)		Length (m)	Q (L s^{-1})			ΔQ (L s^{-1})	Q_{loss} (L s^{-1})		Q_{gain} (L s^{-1})	
		Downstream	Upstream		Downstream	Upstream	Mean		min	max	min	max
A	Lower meadow, outlet	7	208	200	115	110	113	5	0	0	5	5
B	Lower meadow	208	419	212	110	110	110	0	0	0	0	0
C	Lower meadow	457	530	73	110	108	109	2	0	0	2	2
D	Upper meadow	591	799	207	6.8	8	7.4	–1.2	–1.0	–0.9	–0.3	–0.3
E	Upper meadow	799	971	172	8.0	8.9	8.5	–0.9	–1.6	–1.7	0.7	0.9
F	Upper meadow	971	1107	136	8.9	9.3	9.1	–0.4	–1.1	–1.2	0.7	0.8
Moraine ^a	Flow off Broggi moraine				1.5							
G	Upper meadow	1208	1371	163	4.1	4.2	4.2	–0.1	–0.2	–0.2	0.0	0.0
Broggi ^a	Laguna Broggi outflow				36							
X	Alluvial fan trib	616	737	120	19	21	20	–1.7	–2.9	–3.1	1.2	1.4
Y	Alluvial fan trib	737	872	135	21	16	19	4.4	0.0	0.0	4.4	4.4
69 ^a	Laguna 69 outflow				22							

^a Single-slug gauging sites.

Table 3
Quilcayhuanca dilution gauging and water balance results.

Reach	Description	Distance up stream (m)		Length (m)	Q ($L s^{-1}$)			ΔQ ($L s^{-1}$)	Q_{loss} ($L s^{-1}$)		Q_{gain} ($L s^{-1}$)	
		Downstream	Upstream		Downstream	Upstream	Mean		min	max	min	max
1	Lower meadow	29	300	270	1200	1500	1300	−300	−1400	−18000	1100	17000
2	Lower meadow	300	472	172	1500	930	1200	550	−27	−45	580	600
3	Bottom of moraine	472	624	152	930	820	880	110	−320	−600	430	710
4	Moraine	624	840	216	820	760	790	58	−110	−140	170	200
5	Top of moraine	881	1003	122	900	1200	1100	−350	−820	−1700	460	1300
6	Upper meadow	1003	1246	243	1200	1000	1100	220	−920	−11000	1100	11000
7 ^a	Upper meadow	1246	1559	313	1000					−2400		

^a Upstream discharge not available for Reach 7.

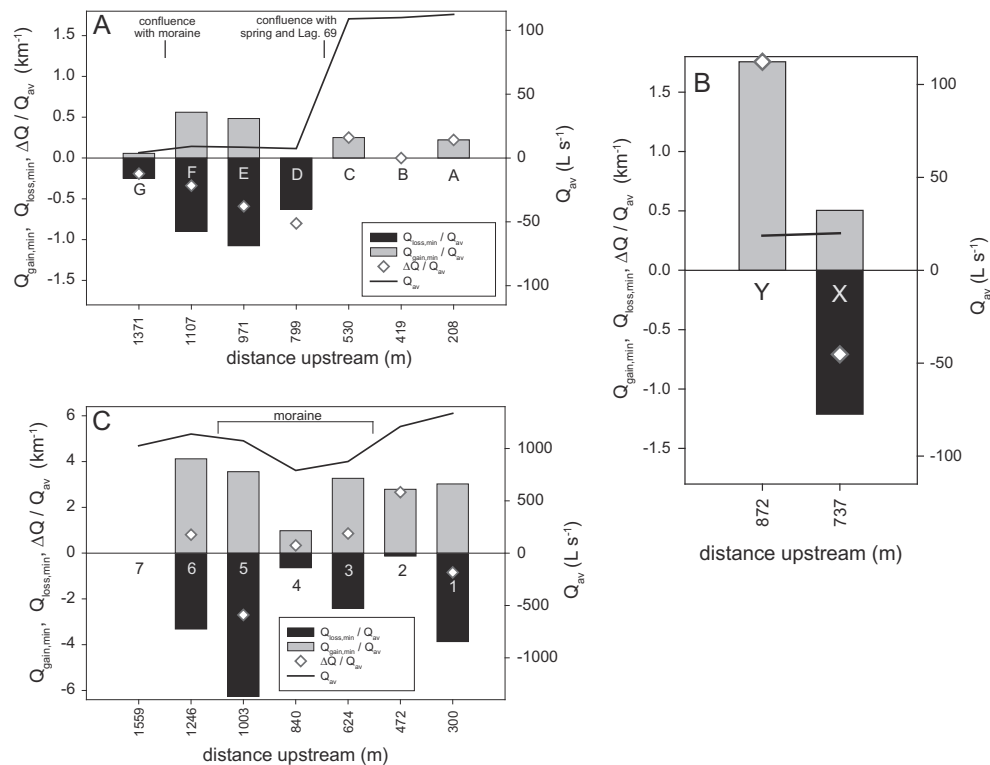


Fig. 4. Stream reach discharges and water balances for (A) Llanganuco main stem, (B) Llanganuco Laguna 69 tributary, and (C) Quilcayhuanca. Distance upstream is the distance of the top of each reach (labeled with reach letter or number) from an arbitrary point near the most down-stream part of the study areas. Q_{av} (black line) is the average of Q at the top and bottom of each reach, in $L s^{-1}$ (right axis). Bars show the minimum calculated gross gain and loss ($Q_{gain,min}$ and $Q_{loss,min}$) for each reach as a fraction of Q_{av} normalized by stream length (km^{-1}) (left axis). Diamond symbols represent the ΔQ over each reach as a fraction of Q_{av} normalized by stream length (km^{-1}) (left axis). For Reach 7 in Quilcayhuanca, only $Q_{loss,max}$ (not shown) and Q at the bottom of the reach (shown in place of Q_{av}) can be calculated.

Discharge measured in the stream in Quilcayhuanca ranged from $760 L s^{-1}$ in the middle of the moraine to $1500 L s^{-1}$ at the head of Reach 1 (Table 3). Delta- Q values varied depending on the reach position relative to the upper and lower meadows and the moraine (Table 3, Fig. 4C), but are generally of higher magnitude than the ΔQ values in Llanganuco as a percentage of Q , meaning there was more variability in streamflow with distance. Gaining reaches include Reach 6, in the upper meadow just upstream of the moraine ($81\% km^{-1}$), Reaches 4 and 3, in the middle and lower sections of the moraine (34% and $86\% km^{-1}$), and Reach 2, the first reach downstream of the moraine margin in the lower meadow ($270\% km^{-1}$). Losing reaches include Reach 5, the most upstream reach in the moraine ($-270\% km^{-1}$) and Reach 1, the most downstream meadow reach adjacent to Casa del Agua ($-84\% km^{-1}$). Normalized gross gains and losses were also larger than in Llanganuco, with the highest gross gains and losses in

the meadows (Reaches 1 and 6) and at the top of the moraine (Reach 5), and the lowest in the middle of the moraine at Reach 4 (Fig. 4). All reaches had concurrent gains and losses, but Reach 2 was the most lopsided, with a $Q_{loss,min}$ of $-27 L s^{-1}$ and a $Q_{gain,min}$ of $580 L s^{-1}$.

4.2. Geochemical and isotopic composition of waters

The chemical composition of surface and groundwater is dominated by calcium and sulfate and/or bicarbonate at both Llanganuco and Quilcayhuanca, and the general patterns look similar plotted on Piper diagrams (Fig. 5). Upstream channel samples plot high in the calcium-sulfate corner, with more downstream samples tending towards groundwater in the calcium-bicarbonate corner. A more subtle shift towards greater sodium in downstream and spring samples is also apparent. For the Llanganuco surface waters,

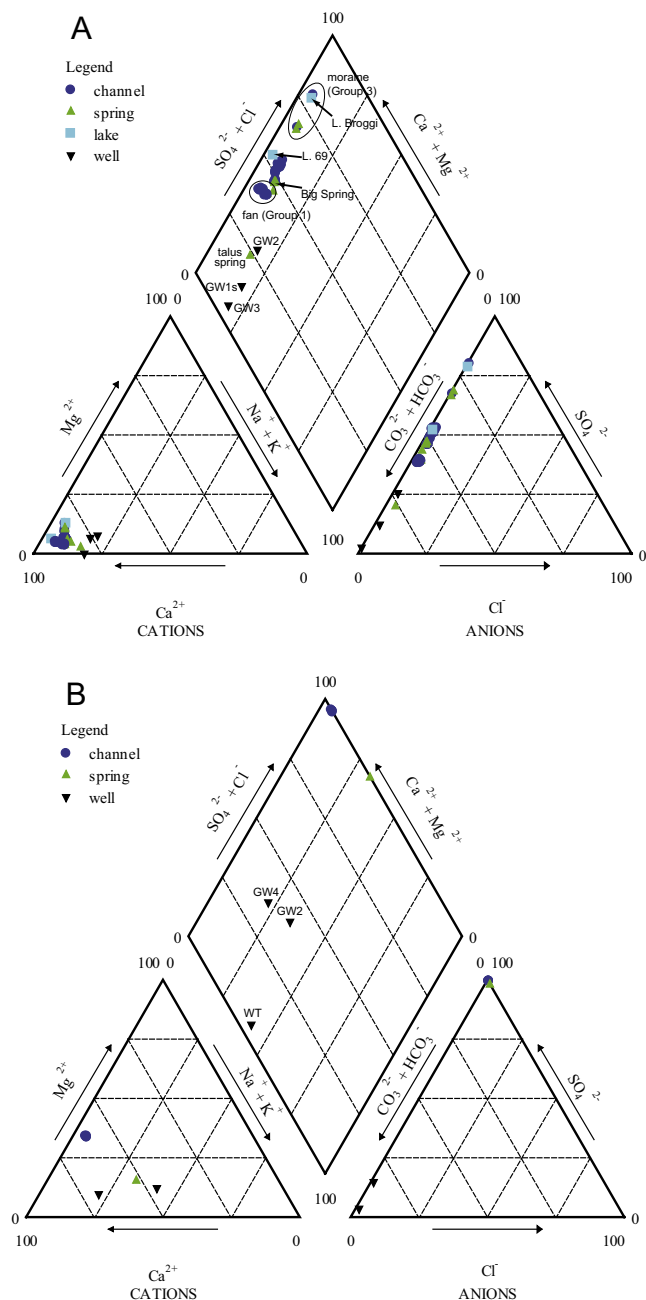


Fig. 5. Piper plots of sample geochemistry from (A) Llanganuco and (B) Quilcayhuanca. Chemistry of GW3 in Quilcayhuanca is not shown due to likely contamination of the sample.

where enough samples were taken to make meaningful correlations ($n = 41$), sulfate is strongly positively correlated with magnesium (Pearson $r = 0.97$, $p < 0.001$) and more weakly with calcium ($r = 0.63$, $p < 0.001$). Fluoride is positively correlated with both sodium ($r = 0.53$, $p < 0.001$) and chloride ($r = 0.61$, $p < 0.001$), and negatively correlated with sulfate ($r = -0.73$, $p < 0.001$), but the correlation between sodium and sulfate is weak ($r = -0.38$, $p = 0.013$). Sodium and chloride are only weakly correlated ($r = 0.46$, $p = 0.002$). Detailed chemistry data for individual samples at both study sites can be found in [Tables A1 and A2 in the Supplementary Dataset](#).

In Quilcayhuanca, which is dominated in the upper catchment by the sulfide-rich Chicama formation, sulfate values were as high as 105.1 mg L^{-1} in the stream and pH was low (~ 3.8). In Llanganuco,

the Broggi lake outlet is the most concentrated in sulfate (28.5 mg L^{-1}), but pH throughout the watershed is generally circumneutral to weakly alkaline (6.8–7.9 in stream water and up to 8.5 in springs). Laguna 69, on the other hand, is not as heavily sulfate dominated, with proportionally more bicarbonate than Laguna Broggi. The valley above Laguna Broggi is composed of Chicama formation, but none is exposed above Laguna 69, where the bedrock is granodioritic.

In Llanganuco, the concentration of sulfate drops and the concentration of sodium rises in general as water moves downstream from both lakes, and some springs and wells are enriched in sodium. Plotting sodium versus sulfate is therefore useful to elucidate dominant relationships between groups of samples ([Fig. 6A](#)). Samples fall into several groupings in [Fig. 6A](#) ([Table 4](#)). Laguna 69 is moderately high in sulfate and low in sodium, but the sodium concentration jumps up in the channel samples on the fan (Group 1), and jumps up again in the springs and channels at the fan base (Group 2). Laguna Broggi is very high in sulfate, but the concentration drops in the channel and springs as water flows over and through the moraine (Group 3). The upper meadow channel samples (Group 4, Reaches D–F) sit in a cluster in the middle of the plot, and the Big Spring and lower main channel samples (Group 5, Reaches A–C) form another cluster between the upper channel and the base of the fan. Three springs sit apart; two artesian springs (samples S07 and S08) that were found in raised mounds in the middle of the wet meadow, and a single spring issuing from the base of the talus slope to the west of the meadow (sample S09). Due to its position in the watershed and its very different chemistry, the talus spring likely has no glacial influence and is completely precipitation derived. In Quilcayhuanca, a similar plot shows that the four stream samples decrease in sulfate and increase in sodium towards the spring and well samples as they move downstream ([Fig. 6B](#)).

In order to simplify the multidimensional geochemistry and to analyze mixing and other relationships between ions and samples, a principal component analysis (PCA) was performed with the geochemical samples from Llanganuco. The groundwater wells were excluded from the PCA because their unique chemical signatures would dominate the principal components and obscure relationships among the surface water samples. The first two principal components (PC1 and PC2) explain 78% of the total variance of the data set, and the third component explains only an additional 8%, so PC1 and PC2 were retained and plotted ([Fig. 6C](#)). The first component, PC1, is positively correlated with fluoride ($r = 0.85$, $p < 0.001$), chloride ($r = 0.84$, $p < 0.001$), nitrate ($r = 0.82$, $p < 0.001$), and sodium ($r = 0.53$, $p < 0.001$), and negatively correlated with potassium ($r = -0.60$, $p < 0.001$), calcium ($r = -0.64$, $p < 0.001$), and especially sulfate ($r = -0.90$, $p < 0.001$) and magnesium ($r = -0.95$, $p < 0.001$). The second component, PC2, is positively correlated with fluoride ($r = 0.279$, $p = 0.077$), sodium ($r = 0.66$, $p < 0.001$), potassium ($r = 0.70$, $p < 0.001$), and calcium ($r = 0.53$, $p < 0.001$). In general, samples appear in similar groupings as in [Fig. 6A](#) and [Table 4](#).

The stable isotopic composition of water is reported as $\delta^{18}\text{O}$ and $\delta^2\text{H}$, relative to Vienna Standard Mean Ocean Water (VSMOW) ([Fig. 7](#)). The distribution of stable isotopic composition was relatively narrow, with $\delta^{18}\text{O}$ ranging from -17.3‰ to -14.8‰ and $\delta^2\text{H}$ from -128‰ to -108‰ . This is a small range relative to the expected seasonal variation; for example, monthly means over two years at Marcapomacocha, Peru, at a similar elevation (4477 m) to the Llanganuco meadow, range from -20.33‰ $\delta^{18}\text{O}$ and -149.7‰ $\delta^2\text{H}$ in March to -5.21‰ $\delta^{18}\text{O}$ and -24.4‰ $\delta^2\text{H}$ in August, with a precipitation-weighted mean of -16.25‰ $\delta^{18}\text{O}$ and -115.5‰ $\delta^2\text{H}$ (IAEA, 2013). All samples at both sites fall near or above the global meteoric water line (GMWL), with similar deuterium excesses (range of 10.0–13.0), and similar local slopes (lin-

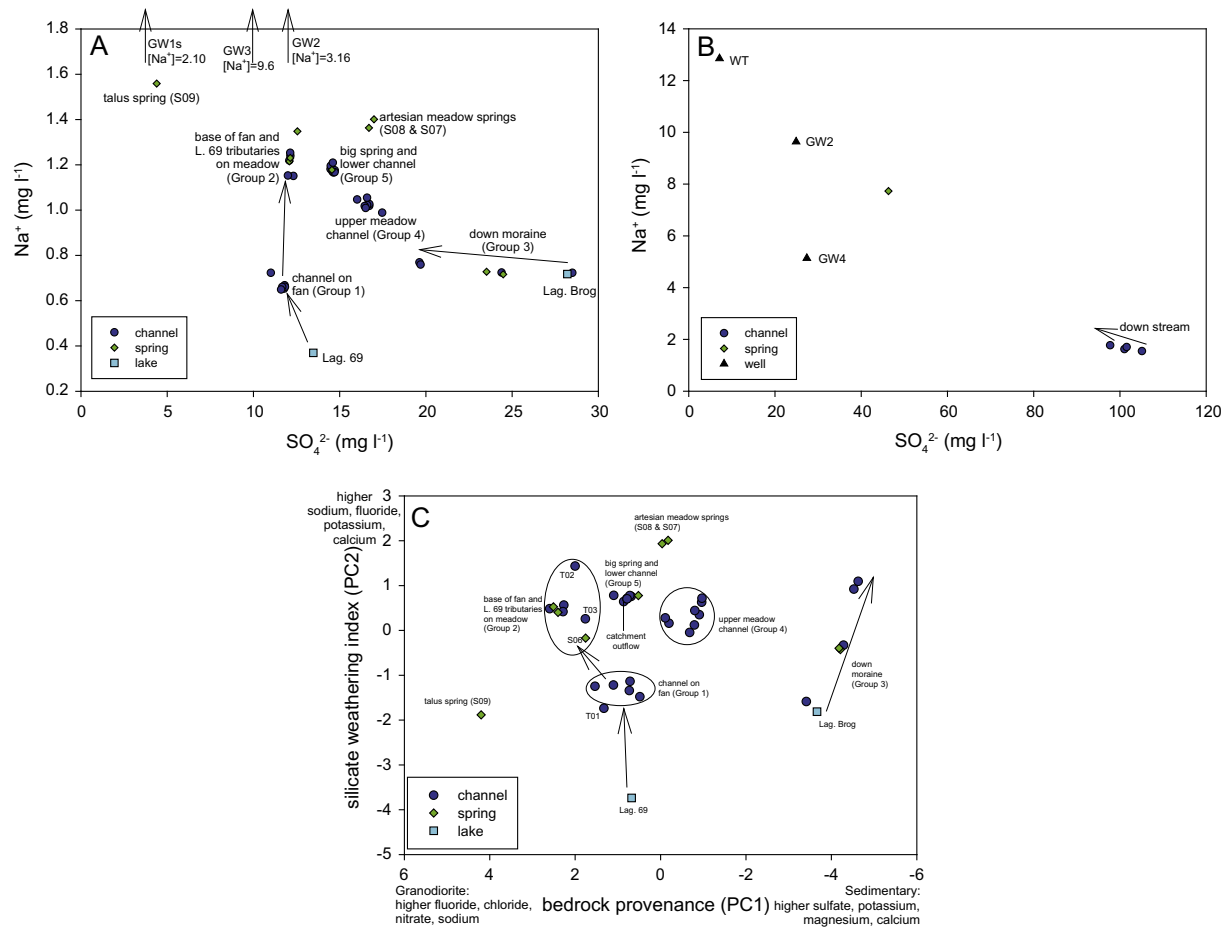


Fig. 6. Plots of selected geochemistry, including sodium versus sulfate plots for (A) Llanganuco and (B) Quilcayhuanca, and (C) a plot of the principle components PC2 versus PC1 for Llanganuco. Full sample geochemistry data can be found in [Tables A1 and A2 of the Supplementary Dataset](#).

Table 4

All water samples from Llanganuco, organized into geographic groups for ease of discussion. (See [Table A1 in the Supplementary Dataset](#) for individual sample chemistry.)

Group reference	Short description	Geographic description	Included reaches (from Fig. 4)	Samples names
Group 1	Alluvial fan	Tributary on fan downstream of Laguna 69 and upstream of spring S02	–	C18, C19, C22, T01, T05, T06
Group 2	Base of fan	Springs at base of fan and tributaries that are downstream of these springs and upstream of the Big Spring or the confluence with Group 3 channel	G, X, Y	S02, S04, T02–T04, C20, C21
Group 3	Moraine	Tributary on moraine downstream of Laguna Broggi and upstream of confluence with tributary leading from S04 (part of Group 2)	–	C14, C14A, C16, C17, S03, S05
Group 4	Upper meadow	Channel downstream of confluence with Group 3 channel and upstream of confluence with Big Spring	D, E, F	C08–C13, C15, C15A
Group 5	Lower meadow	Big Spring and channel downstream to the waterfall	A, B, C	S01 (Big Spring), C01–C07
–	Laguna Broggi	Lake to the northeast	–	L01
–	Laguna 69	Lake to the northwest	–	L02
–	Meadow springs	Springs in wet meadow to west of lower meadow channel	–	S07 and S08 (artesian), S09 (tallus), S06
–	Groundwater wells	Groundwater wells to east of lower meadow channel	–	GW1s, GW1d, GW2, GW3

ear regression slopes of 7.9 in Llanganuco and 7.6 in Quilcayhuanca), with the exception of the Laguna Broggi samples. The Laguna Broggi outlet and the channel and spring samples down the moraine (Group 3) fall below the GMWL with deuterium excess values down to 7.3, indicating evaporation effects in the lake or the series of lakes above it. In Llanganuco, groundwater from wells is the

most enriched in heavy isotopes (mean of -15‰ $\delta^{18}\text{O}$, excluding GW3), while samples near the base of the moraine and in the upper meadow are the most depleted. The majority of samples from the main channel and Big Spring fall in the middle of the plot near -16.3‰ $\delta^{18}\text{O}$. Similarly in Quilcayhuanca, all the stream samples also cluster near -16.3‰ $\delta^{18}\text{O}$, with most groundwater wells more

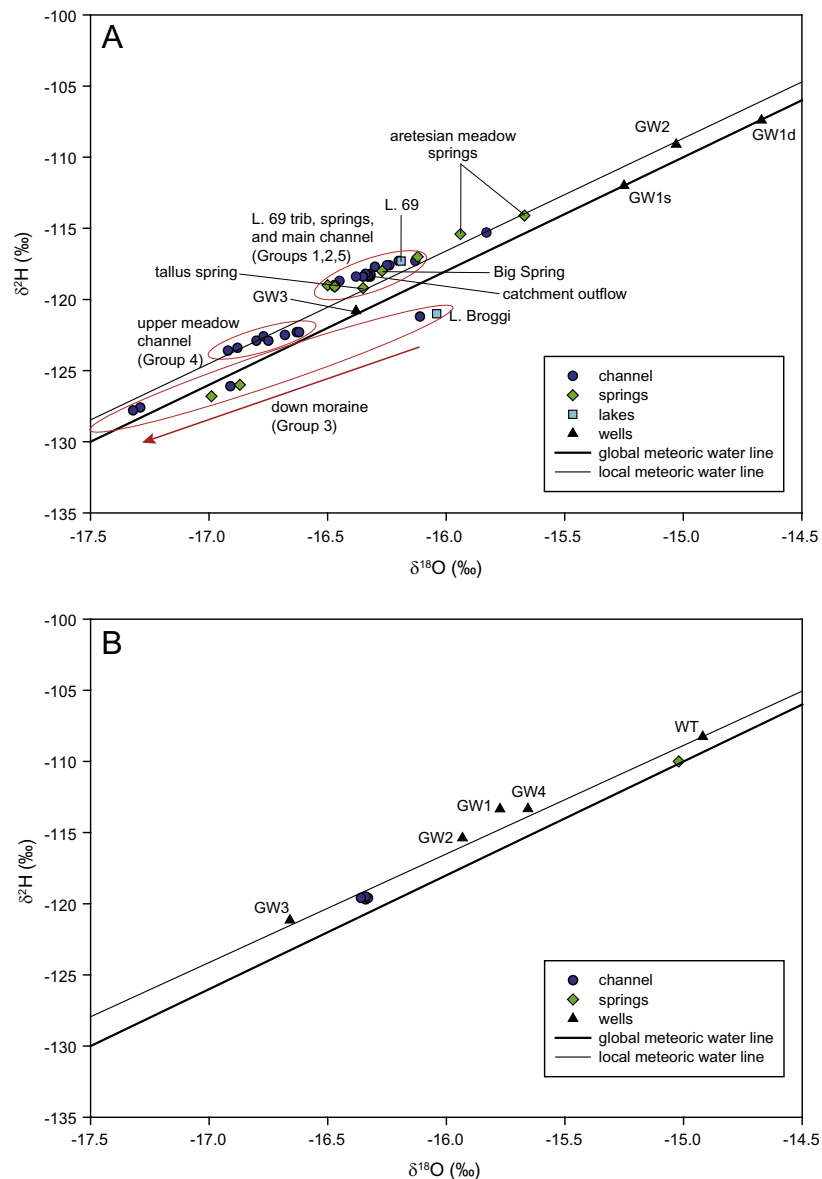


Fig. 7. Plots of stable water isotopic composition for (A) Llanganuco and (B) Quilcayhuanca. Individual sample isotopic compositions can be found in [Tables A1 and A2 of the Supplementary Dataset](#).

enriched. Detailed isotopic composition data for individual samples at both study sites can be found in [Tables A1 and A2 in the Supplementary Dataset](#).

5. Discussion

5.1. Interactions between proglacial streams and groundwater

Gains and losses of water were unequally distributed across the landscape during our study. The streams at both study sites were gaining and losing water at different rates in locations controlled by geomorphology, especially by the strongly varying slopes of geomorphic units (fan, moraines, and meadows), as we would expect from standard groundwater flow fields around breaks in topographic slope (Winter et al., 1998). Fig. 8 presents conceptual models, related to those developed by Baraer et al. (2014) and Chavez (2013), illustrating subsurface flow paths and resulting GWSWI based on our results and interpretation.

In Llanganuco, the outlets of both glacial lakes were losing water to the subsurface at the top of the alluvial fan and moraine (Fig. 3), where slopes become steep (average slopes are 12° and 7° for fan and moraine, respectively). Both channels run completely dry before they descend much of their respective units, which means that glacial lake water is recharging aquifers beneath these units. Similarly in Quilcayhuanca, there is a net loss of stream water to the subsurface as it traverses the upper reach of the moraine (Reach 5, Fig. 4C), which has an average slope of 5°. Near the bottom of these steep units, water is discharging from the subsurface and feeding streams, which was observed in Llanganuco as springs and incipient channels that appear around the bases of the fan and moraine, and measured as a positive ΔQ in Quilcayhuanca at Reach 3, the last reach in the moraine. This suggests that flow cells of groundwater move through these steep units, connecting recharge at the top with discharge at the bottom (Fig. 8).

In the meadows, stream channels closest to the margins of the fan and moraine in Llanganuco (Reach Y and the springs and channels upstream of Reach F) and at the base of the moraine in Quil-

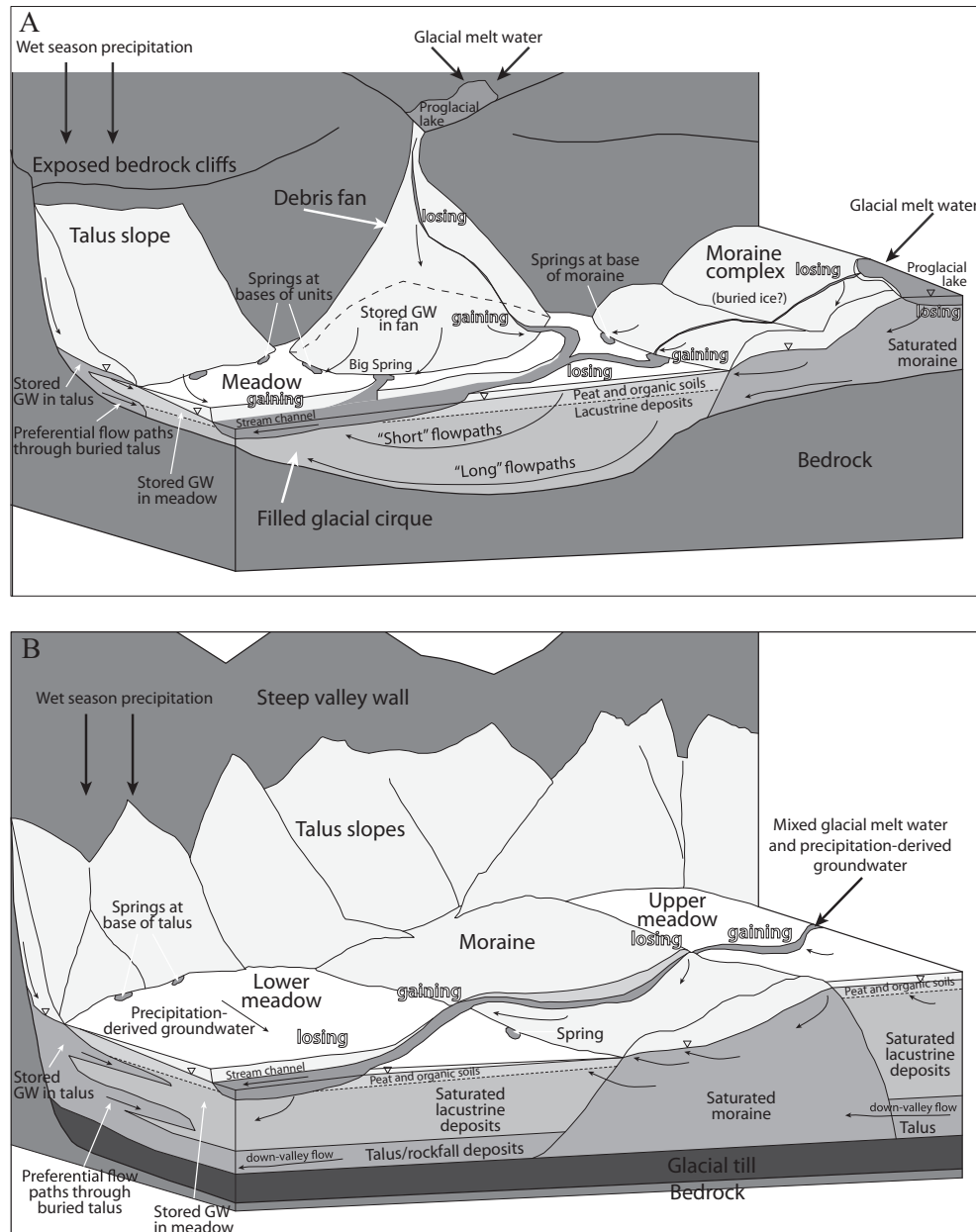


Fig. 8. Conceptual models of groundwater-surface water interactions and subsurface flowpaths (black arrows) at (A) Llanganuco and (B) Quilcayhuanca. Locations where surface water is gaining from or losing to the subsurface are indicated in outlined text.

cayhuanca (Reach 2 and the spring in Fig. 2B) are strongly net gaining; however, once a short distance away from the margins, reaches that flow through the upper portions of meadows (Reaches D-G and X in Llanganuco and Reach 1 in Quilcayhuanca) are net losing to the underlying meadow. In the lower portions of meadows, the streams are net gaining again (Reaches A-C in Llanganuco and Reach 6, at the downstream end of the upper meadow, in Quilcayhuanca), suggesting that there are groundwater flow cells through the meadows, as well (Fig. 8).

In Llanganuco especially, it is also interesting to compare the absolute fluxes of water as they vary over the catchment. Because the stream exits the study area over a bedrock outcrop and waterfall (Fig. 2A), we can be certain that we measured the total outflow from the watershed (neglecting potential fracture flow through bedrock) at 115 L s^{-1} . We found that the majority of this outflow (71%) was not flowing from the upper stream reaches through sur-

face channels, but was issuing from a single source in the Big Spring, at the base of the Laguna 69 fan and relatively far down in the catchment, which makes the source of the Big Spring especially important for understanding sources of stream water in the catchment. Other fractional components of the total outlet discharge are the upper meadow channel (6%), the Laguna 69 tributary (17%), and lateral groundwater inflow to the lower meadow channel (6%). As a result of the dramatic inflow at the Big Spring, discharge in the upper meadow channels was a small fraction of discharge in the lower reaches. Also, if its origin is assumed to be exclusively from alluvial fan groundwater, then the large Big Spring discharge makes the alluvial fan a net contributor to streamflow during the dry season; the fan aquifer receives 22 L s^{-1} of surficial water from the glacial lake, but contributes 105 L s^{-1} to the meadow channels, mostly through springs at its base. The excess surface water produced could be from wet season

precipitation (potentially mixed with glacial melt water) stored in the fan aquifer, or from glacial lake water that seeps through the lakebed and into the fan.

In contrast to the fan, the moraine in Llanganuco was a net sink of surface water during our study, receiving 36 L s^{-1} of water from the Laguna Broggi outlet, but contributing only 5 L s^{-1} to the meadow streams, and demonstrating that different aquifer units of the proglacial landscape have varying potential as stores of groundwater and as sources of streamflow during the dry season. The wet meadow along Reaches A–C (Fig. 3) contributed a small absolute amount of discharge to the total stream outflow (7 L s^{-1}). These reaches pass through the wettest part of the meadow, adjacent to the talus slope on the west side of the stream, where several springs are located at the talus margin and in spongy vegetated mounds that rise above the rest of the meadow (artesian springs). Because the center of the meadow on the eastern side of the stream was relatively dry, we assume that most of the 7 L s^{-1} came from groundwater associated with the talus slope and springs on the western side. Although the absolute contribution to discharge measured over this approximately $\frac{1}{2} \text{ km}$ of channel was small, it must be remembered that this meadow is a small example high in the watershed, and many glacial valleys of the Cordillera Blanca contain tens of kilometers of wet meadows along their streams.

The study site in Quilcayhuanca was relatively lower in its valley than the headwaters studied in Llanganuco, with a considerably larger contributing area. Predictably, absolute discharges were much larger in Quilcayhuanca as a result, but interestingly, net and gross gains and losses were also larger as a normalized fraction of total discharge, even in the lower meadow Reach 1 where head gradients were low. This situation is opposite to the general pattern found by Covino et al. (2011) of decreasing relative gross loss with increasing discharge. Gross gains and losses occurred concurrently in every measured reach, and were often up to 4 times the average discharge per km.

The net gain over 1.2 km of studied stream length was 200 L s^{-1} , which is a large proportion of the average total discharge of approximately 1100 L s^{-1} for a relatively small increase in watershed area. While it is possible that this large net discharge is partially a product of error in the dilution gauging method (Schmadel et al., 2010), other explanations are suggested by the geomorphology of the valley. Valley-fill aquifers that are constrained by bedrock, such as Quilcayhuanca, are often dominated by underflow (down-valley groundwater flow), especially where coarse deposits are overlain or confined by less permeable sediments (Larkin and Sharp, 1992). We expect that the depth of unconsolidated sediment above bedrock in the valley bottom to be shallow compared to the length of the valley meadows. Down-valley flow that may be taking place in the groundwater system beneath the upper meadow could be forced to the surface where the steep moraine impinges upon the valley aquifer, especially if the valley sediments were thicker beneath the upper meadow than the lower meadow. The large net increase in stream discharge over the moraine could therefore be due to groundwater sourced from higher up the valley coming to the surface in a relatively small, concentrated location.

The higher degree of interaction between surface and subsurface waters in Quilcayhuanca than in Llanganuco is partially due to the high gradient over the moraine at Quilcayhuanca, and possibly due to differences between the sites in subsurface hydraulic conductivity or heterogeneity. These differences may be representative of longitudinal gradients in Cordillera Blanca valleys or differences between the morphology of glacial deposits closer to or farther from modern glacial termini. We therefore expect that groundwater will have a greater impact on stream chemistry as streams flow downwards through their valleys and experience

repeated gross gains and losses of stream water from and to underlying aquifers. This process is known as fractional hydrologic turnover, which occurs when streams lose a fraction of water to the subsurface while concurrently or successively gaining a similar fraction of groundwater (Covino et al., 2011). Due to this process, stream chemistry can be influenced by groundwater chemistry and subsurface geochemical conditions over distances, even without net changes in discharge. Likewise, the influence of a single contributing end-member in the headwaters can decay with distance, as the original water is lost and groundwater from different aquifers along the length of the valley is gained in its place.

We should also note, however, that even in the headwaters of the Llanganuco valley, almost all of the water exiting the catchment spent some time in the subsurface, and half of the total outflow originated as groundwater downstream of the glacial lakes. Clearly, groundwater in both proglacial geomorphic units and wet meadows has a considerable influence on streams, but the original sources of groundwater (local precipitation or stream water lost to the subsurface up-hill), as well as groundwater residence time and age, are not always obvious or known.

5.2. Water sources, mixing and transformation

High sulfate concentrations in water proximal to glaciers have been used to trace glacial water in mixing models (Baraer et al., 2009, 2014, 2005). These high concentrations have been explained by the common occurrence of sulfide minerals in bedrock of the high glacierized peaks, and the high rates of weathering beneath glaciers and in freshly exposed till (Mark et al., 2005). The prominence of sulfide-rich bedrock has specifically been shown to negatively impact water quality in the Quilcay watershed (Fortner et al., 2011). In this study, however, it is difficult to use sulfate as an indicator of glacial contribution because of the differing influence of the Chicama formation in the study basins, which leads, for example, to Laguna Broggi having higher sulfate concentrations than Laguna 69. We therefore used plots of solutes or transformed solutes to interpret relationships between different sampled waters in the complex terrain and channel configuration of the Llanganuco site. Although similar to the sodium versus sulfate plot (Fig. 6A), the PCA plot (Fig. 6C) takes the total variation of all solutes into account, and performs better at partitioning causal relationships. For example, water flowing down and through the moraine from Laguna Broggi does not appreciably change PC1 value in Fig. 6C, while it does change sulfate concentration in Fig. 6A. PC1, which explains the most variation in the data, appears to separate the samples influenced by Laguna Broggi (the lake and Group 3 samples), with its high-sulfate Chicama signature, from the other samples with less or no Chicama influence. We therefore interpret PC1 as an indicator of bedrock provenance, with negative values indicating more Chicama influence, and positive values indicating Cordillera Blanca batholith influence. This allows PC2, orthogonal to PC1, to be relatively free of this influence. With its correlations to sodium, potassium, calcium, and fluoride, we interpret PC2 as an indicator of silicate weathering processes (Appelo, 1993), which would have a greater influence on groundwater in proportion to its contact time with silicate sediments or rock.

Mixing relationships throughout the Llanganuco catchment are difficult to determine using Fig. 6A or C, because there is a wide scatter of points instead of clear mixing lines, and because the end members of different mixing relationships are not clear. For example, the two glacial lakes have different compositions, the meadow groundwater is not chemically consistent, and the Big Spring and catchment outflow are in the middle of the plot, where they could represent varying combinations of several potential end members. However, when focusing on the downstream samples (Groups 2, 4, and 5), meadows springs, and wells, the geochemistry

supports the composition of the outlet discharge estimated above using tracer dilution data (71% Big Spring, 17% fan, 6% upper meadow, and 6% meadow groundwater); the outflow is close to the Big Spring, but shifted slightly towards samples at the base of the fan. The source of the Big Spring water itself is difficult to determine conclusively based on the geochemistry. It sits slightly apart from the other springs and channels at the base of the alluvial fan, shifted to the right in both plots towards the upper meadow samples, and may represent mixing of these two water types in the subsurface.

Other clusters of points in Fig. 6A and C appear to be controlled not so much by mixing as by transformations in geochemistry concurrent with changes in geomorphology and GWSWI discussed above. Both lakes are set apart from the channels just downstream from them, which is especially evident in the increase in PC2 from Laguna 69 to the Group 1 channels on the alluvial fan. PC2 jumps again between Group 1 and samples at the base of the fan (Group 2). The value of PC2 in surface water samples on the moraine (Group 3) also increases quickly with distance from Laguna Broggi. Substantial shifts in chemistry appear to be punctuated by changes in slope. Groundwater flowing through these units and discharging to the surface at their bases is significantly higher in silicate weathering products than channel and lake water recharging at the tops of the units. Other samples with high silicate weathering products include the well samples (not shown in Fig. 6C), the artesian meadow springs, and the talus spring (especially high in sodium), suggesting that these waters have had extended contact with silicate minerals in the subsurface (Dethier, 1986). Because of the non-conservative geochemical behavior in waters sourced from the two lakes and in samples with heavy groundwater influence, it is not possible to estimate percentages of glacial lake water in the outlet stream or springs.

The stable isotopes of water, however, do not react or change composition in the subsurface (Buttle, 1994), and the lack of local evaporation effects in the dataset (with the exception of Laguna Broggi) makes them conservative in this context. The conservative nature of the isotopic signatures makes additional conclusions about water sources and mixing possible, which are not possible with the geochemical data. The main controls on isotopic composition in the Cordillera Blanca are season, the elevation of source precipitation, and the influence of glacial meltwater (Mark and McKenzie, 2007; Mark and Seltzer, 2003). All of the samples at both sites (Fig. 7) fall within a narrow range close to the precipitation weighted mean for their approximate elevation, but variations within sites may be due to differences in the elevation of sources (the altitude effect), or possibly the season of precipitation.

In Llanganuco, the groundwater in most of the meadow wells was the most enriched (approximately -15‰ $\delta^{18}\text{O}$), suggesting that these samples represent precipitation that fell directly on the meadows, while samples from streams and springs have sources at higher elevation and are more depleted. GW3 is the outlier, and appears to be influenced by water from the upper meadow channel. Samples sourced from near Laguna 69 fall tightly together in the center of the plot, including Groups 1 and 2, the lake itself, and the talus spring, which were set apart in the geochemistry plots by substantial differences in the concentration of silicate weathering products, suggesting that all of these samples have sources with a similar average elevation, with little mixing with lower elevation groundwater during the descent from lake to meadow. It is also interesting that Laguna 69 is so similar in isotopic composition to the waters at the base of the fan, because it suggests that the observed changes in geochemistry are due in part to chemical transformations in the subsurface.

Assuming an average isotopic altitude effect of -0.325‰ $\delta^{18}\text{O}$ per 100 m (Clark and Fritz, 1997), the apparent elevation difference between the Big Spring and groundwater wells is 390 m, putting

the mean source of the spring at 4765 masl, approximately the same elevation as the glacier terminus. Using an altitude effect of -0.7‰ $\delta^{18}\text{O}$ per 100 m (measured in Cordillera Negra springs by Mark and McKenzie, 2007) the mean spring source would be at 4556 masl, on the upper reaches of the fan. Baraer et al. (2014) used an altitude effect of -0.24‰ $\delta^{18}\text{O}$ per 100 m to make similar calculations in Quilcayhuanca. The artesian meadow springs have an isotopic composition intermediate between the Laguna 69 samples and the wells, perhaps a result of mixing of these sources in the deeper meadow aquifer, although this effect is not seen clearly in the geochemistry (Fig. 6A). The most depleted samples, from the base of the Broggi moraine in Group 3, have an apparent elevation difference of 710 m above the meadow wells or 5085 masl using Clark and Fritz (1997), or 4705 masl using Mark and McKenzie (2007). Laguna Broggi itself appears to be enriched by evaporation from a similar source. Another potential source of the depleted water at the base of the moraine is permafrost or residual glacial ice that may be buried in the moraine and be contributing melt water to the moraine springs.

Samples from the upper meadow channel in Llanganuco (Group 4) are less depleted than samples from the base of the moraine, and are likely a mixture of that source and groundwater from the meadow and the alluvial fan. In the lower meadow (Group 5), however, the channel does not appear to be influenced to an obvious degree by meadow precipitation, and channel flows are primarily sourced from higher-elevation water, which supports the conclusion from our tracer dilution results (as well as Baraer et al., 2014), that meadow groundwater does not have a large influence on this stream.

In Quilcayhuanca, there was more evolution in water geochemistry observed along the channel than in the sampled reaches in Llanganuco, likely due to the greater fractional hydrologic turnover observed between the channel and subsurface (see Section 5.1). From upstream to downstream, the samples move linearly toward the groundwater and spring samples, which have less sulfate and more sodium (Fig. 6B). We must note, however, that the number of stream water samples was lower at Quilcayhuanca ($n = 4$) than Llanganuco ($n = 24$). In Quilcayhuanca, the groundwater has a more uniform composition among the wells and the spring issuing from the base of the moraine, and it alters the channel chemistry in a predictable fashion. The groundwater samples are more isotopically enriched (with the exception of GW3) than the channel samples, which cluster tightly together at -16.3‰ $\delta^{18}\text{O}$, likely due to the channel's higher elevation source. Because of the large amount of bi-directional groundwater-surface water exchange observed in Quilcayhuanca, the isotopic and geochemical influence of the stream source waters has likely been diluted by groundwater through fractional hydrologic turnover, and the sources of streamflow are probably at a higher average elevation than the isotopic composition suggests.

5.3. Groundwater and surface water as resources

Our results show that in the dry season, groundwater is an important influence on and component of streamflow. In the highest headwaters of glacierized catchments, groundwater makes up a large percentage of incipient streamflow, although it is not clear in this study what percentage of this groundwater is from stored precipitation versus recharged glacial melt. In these relatively small meadow systems, the contribution to streamflow by meadow precipitation is certainly low. However, in the mid-valley meadow systems, groundwater is more certainly derived from wet-season precipitation sources, primarily recharged through side-valley talus slopes during the wet season (Baraer et al., 2014). In these more robust valley aquifers, GWSWI are substantial and influence stream discharge rates and geochemistry.

Our results in Quilcayhuanca are compatible with the earlier conceptual model developed by Baraer et al. (2014) for that valley, in which coarse talus units at the sides of the valley are the primary groundwater recharge and storage zone. The wells drilled for this study all intersect coarse, water bearing talus units beneath shallow, low-permeability meadow units, one of which was apparently confined and pressurized (artesian) when drilled (Chavez, 2013). It is this water stored in talus units which is most likely to contribute to watershed discharge, either through springs that flow over-land into streams, or through subsurface connections between buried talus and the stream channel. Although the geometry of the connection between talus units and the moraine is unknown, it appears that water confined beneath the meadows is preferentially entering the stream where it flows through the steep moraine. The high groundwater inflow rate measured over the moraine (200 L s^{-1} net inflow over 1.2 km), combined with the occurrence of multiple moraines dispersed over tens of kilometers in Quilcayhuanca and similar valleys, suggests that groundwater contributions to streamflow are a substantial and important dry-season water resource.

Glacial recession has been hypothesized to cause increasing incidence of poor water quality (high metal concentrations and low pH) in the Cordillera Blanca, both by exposing fresh bedrock and till to weathering and by decreasing stream discharge, thereby increasing solute concentrations (Fortner et al., 2011). The GWSWI observed in this study could positively or negatively impact water quality depending on the type of interaction and the age and lithology of subsurface sediments. While large-scale flow of water through steep proglacial headwater units, as observed in Llanganuco, certainly could cause leaching of fresh sulfide minerals, we observed either no change or decreasing sulfate concentrations at that site, likely due to the older age and bedrock source of the sediments. On the other hand, shallow GWSWI through anoxic or organic-rich sediments in streambeds and banks can immobilize metals, increase alkalinity, and remove sulfate from stream water through chemical reduction (Baker et al., 2000), thereby improving water quality. Furthermore, fractional hydrologic turnover with, and net inputs from, precipitation-derived groundwater can dilute pollutant concentrations in streams, observed as sulfate concentrations that decreased downstream in Quilcayhuanca. Whether they improve or degrade it, GWSWI in proglacial streams increase the influence of subsurface conditions and geochemistry on stream water quality.

6. Conclusion

We found that groundwater is an important element in the proglacial hydrologic landscape, although the magnitude and type of impact varies from headwaters to mid-valley and between geomorphic units (moraines, fans, meadows, and talus). In general, gains and losses of water to and from stream channels are unequally distributed in the dry season, and are primarily controlled by geomorphic unit, slope, and valley position. Losses of stream water to the subsurface were observed at the upper ends of meadows and steeper geomorphic units, while gaining stream reaches were observed at the lower ends of meadows and where steep geomorphic units terminate into gently sloped meadows, leading to generalizable groundwater flow cells (Fig. 8). Glacial lake water in stream channels was observed recharging aquifers in fan and moraine units, which represented a net loss of surface water to the moraine in Llanganuco, but which was more than made up by discharging groundwater from the Llanganuco alluvial fan and the moraine in Quilcayhuanca.

In Llanganuco, groundwater supplied approximately half of stream discharge from the watershed (115 L s^{-1} total), with most

originating in an alluvial fan adjacent to the alpine meadow and little (6%) from the meadow itself. Groundwater contributions to streamflow over the moraine in Quilcayhuanca were large (discharge increased by 200 L s^{-1} or 18% over 1.2 km) compared with a small increase in watershed area. It is possible that groundwater moving down the valley in confined coarse deposits joins the stream channel where the steep moraine impinges upon the valley aquifer.

Changes in slope and geomorphic unit also punctuate changes in geochemistry, which shows evidence of influence by both conservative mixing and chemical weathering at the headwater site. Stable isotopes mainly indicate the elevation of source precipitation, which shows that meadow groundwater is a small component of the streamflow compared to higher lakes, glaciers, and precipitation in the headwater Llanganuco catchment. At the mid-valley site, stream water geochemistry trends towards the groundwater geochemical composition as water flows downstream, due to direct net inflow and hydrologic turnover.

The two study sites can be generalized to represent two points in a downstream continuum from headwaters to mid-valley in a typical Cordillera Blanca valley, if the hydrology at these two sites is assumed to be as representative as the geology and geomorphology. The headwaters are dominated by water from glacial lakes, although much of it passes through the groundwater system in steep proglacial geomorphic units, reemerging through springs at the meadow margins, rather than being transported directly in stream channels. Along these subsurface flow paths, the water acquires a geochemical signature from silicate weathering. The mid-valley systems, with their extensive stepped meadows and moraines, are dominated by net inflows from precipitation-derived groundwater and hydrologic turnover (gross gains and losses) with the underlying groundwater aquifer. In such a continuum, groundwater contributions to stream discharge increase with distance downstream, while the influence of groundwater on stream chemistry changes more subtly. High in the catchment, surface water chemistry is strongly affected by in-situ weathering in locations where large portions of streamflow enter and travel through the groundwater system, such as the debris fan at Llanganuco. In the mid-valley, stream chemistry is affected by fractional mixing as streams interact with groundwater in lower meadow systems over large distances. By the time they reach the Rio Santa at the edge of the Cordillera Blanca, streams are certainly heavily influenced by groundwater in both their total discharge and water chemistry.

There are several unknown aspects of groundwater in proglacial valleys that deserve further attention. For example, the total storage volumes and residence times of the groundwater aquifers in meadows and other units remains unknown; this information would help us understand how different aquifers might respond to reduced-meltwater scenarios, and how long the coupled groundwater-surface water system would take to adjust to different flow or precipitation regimes. More information about the details of subsurface flow paths would also constrain the influence of heterogeneity in moving water through the units studied. Further work in this area should concentrate on subsurface exploration (drilling and non-invasive geophysical methods) to map the depth to bedrock and estimate porosity and heterogeneity, leading to estimates of total storage capacity, as well as modeling of residence times or dating of water.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhydrol.2015.01.013>.

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