Hydrochemical evaluation of changing glacier meltwater contribution to stream discharge: Callejon de Huaylas, Peru

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Abstract Discharge measurements, precipitation observations and hydrochemical samples from catchments of the Callejon de Huaylas watershed draining the Cordillera Blanca to the Rio Santa, Peru, facilitate estimating the glacier meltwater contribution to streamflow over different spatial scales using water balance and end-member mixing computations. A monthly water balance of the Yanamarey Glacier catchment shows elevated annual discharge over December 2001–July 2004 compared to 1998–1999, with net glacier mass loss in all months. Glacial melt now accounts for an estimated 58% of annual mean discharge, 23% greater than 1998–1999. At Lake Querococha, below Yanamarey (3.4% glacierized), a hydrochemical end-member mixing model estimates that 50% of the streamflow is derived from the glacier catchment. Average concentrations from the Rio Santa leaving the Callejon de Huaylas (8% glacierized) are modelled as a mixture with 66% deriving from glacierized tributaries of the Cordillera Blanca as opposed to the non-glacierized Cordillera Negra end member.

Key words Cordillera Blanca; end-member mixing; hydrological balance; Peru; tropical glaciers; water resources

INTRODUCTION

Extensive recent glacier recession throughout the Andes is a concern for regional water resources (e.g. Ribstein et al., 1995; Thompson, 2000; Seltzer, 2001; Ramirez et al.,
While glaciers comprise only one component of the hydrological budget, they are critically important in buffering streamflow, especially in the tropical regions that are dominated by highly seasonal precipitation (Barry & Seimon, 2000). The quantification of the hydrological impact of melting glaciers to water supply on a regional scale has been limited by a fundamental lack of water quality and discharge observations. Most work has focused on small individual glacier catchments, where detailed glacier mass balance and stream discharge data exist over relatively short time intervals and permit quantitative estimates of the volumetric contribution to streamflow made by glacier mass loss. For instance, over half of the mean annual discharge from Yanamarey Glacier (<1 km²) of the Cordillera Blanca was supplied from net ice mass loss from glacier recession (Hastenrath & Ames, 1995). Likewise, the small Chacaltaya Glacier, Bolivia (<0.06 km²), could disappear within a decade, causing an estimated 30% loss of stream discharge (Ramirez et al., 2001).

An important challenge, given limited observations of precipitation and historic discharge, is to apply the results from smaller catchments to larger regional-scale watersheds. Government institutions are often not able to maintain streamgauge monitoring, leaving instrumentation and data to private hydroelectric companies. Where data have been recovered in Peru and Bolivia, analyses indicate that glacier meltwater augments stream discharge, and diminishes the contrasts between tropical wet and dry seasons (Tamayo, 1996; Kaser et al., 2003; Mark & Seltzer, 2003). In another approach, integrated modelling combining climatic, hydrological, and hydraulic parameters has been applied to simulate runoff from glacierized and non-glacierized sub-basins of a 95-km² Andean watershed (Caballero et al., 2004). This approach can provide practical guidance for estimating flow to hydroelectric systems, while relying on critical assumptions and fine-tuning parameterizations using site-specific discharge records. Environmental tracers provide an important alternative method to bridge the gap where lack of empirical data on other components of the hydrological cycle (e.g. evapotranspiration and groundwater) limits volumetric estimates of glacier meltwater impact—either inter-seasonally or over longer time periods.

Relative end-member contributions to regional streamflow (e.g. melting glacier ice, precipitation, groundwater) were estimated with a volumetric mixing model. This method has been used in alpine glacier settings, utilizing the dissolved ionic species and stable isotopes (e.g. Sharp et al., 1995; Singh et al., 1995; Laudon & Slaymaker, 1997). This technique holds good promise in the context of quantifying the impact of melting Andean glaciers to water resources. In a 1999 case study, glacier meltwater had a significant impact on the seasonal and interannual runoff and streamflow in the Rio Santa draining the Cordillera Blanca, Peru. Hydrological balance computations combined with volumetric end-member mixing models using stable isotopes have shown that glacier melt contributes 30–45% of total annual discharge from the Yanamarey and Uruashraju glacier catchments, with contributions in the dry season approaching 100% (Mark & Seltzer, 2003). These catchments are small (1.5–3.5 km²), at high elevation (>4600 m), and >65% glacierized. Based on the results from the Yanamarey–Querococha tributary valley (<10% glacierized), hydrochemical mixing estimates were scaled up to predict 10–20% of the total annual discharge in the Callejon de Huaylas section of the Rio Santa, which drains a 5000 km² area that also has <10% glacier ice coverage.
In this paper, a preliminary analysis of water samples collected in July 2004 from the Callejón de Huaylas is presented, and the hypothesis that changing degrees of glacierization can be traced downstream by using hydrochemistry on a regional scale in the tropics is tested. The purpose of the research is two-fold: (a) to revisit the Yanamarey–Querococha watershed sampled by Mark & Seltzer (2003) to evaluate changes in meltwater contribution after five years; and (b) to sample different stream water end-member sources to the Rio Santa over a regional scale to consider hydrochemical variations as related to glacier meltwater. The research is an initial survey to augment hydrochemical information from this data-poor region with additional samples from different end-member sources during the dry season that will guide future research.

STUDY AREA

The Andean Cordillera Blanca of Peru is the most glacierized mountain range in the tropics, and spans 120 km along the South American continental divide (Fig. 1). The majority of glacierized watersheds within the Cordillera Blanca discharge towards the southwest, flowing via the Rio Santa to the Pacific Ocean. Starting from Lake Conococha, the Rio Santa flows northwest over 300 km, draining a total watershed of 12,200 km². The hydroelectric power plant at Huallanca (1800 m a.s.l.) delimits the upper Rio Santa watershed to an area of 4900 km² that is referred to as the Callejón de Huaylas, which receives surface runoff from both the glacierized Cordillera Blanca on the east, and non-glacierized Cordillera Negra on the west.

Historical discharge records are available for ~40 years in some tributary streams that enter the Rio Santa. Monthly average discharge from these gauged tributary streams entering the Callejón de Huaylas is higher during the months of October–April, reflecting closely the seasonality of precipitation typical of the outer tropics (Mark & Seltzer, 2003). More than 80% of precipitation falls between October and May, and the austral winter months of June–September are known as the dry season. In contrast, temperature remains relatively constant, with an annual variation of air temperature much smaller than the diurnal variation (Kaser et al., 1990).

The glacierized Cordillera Blanca has undergone an overall reduction in glacier volume throughout the 20th century. The Glacier Inventory of Peru (Ames et al., 1989) lists the total area of glaciers in the Cordillera Blanca as 723 km², based on aerial photography from 1962 and 1970. The total count of glaciers inventoried is 722, meaning the average glacier size was ~1 km². A recent survey using 1990 satellite imagery has shown a reduction in total glacierized area that is now estimated to be less than 600 km² (Georges, 2004).

The Yanamarey Glacier catchment (YAN) covers 1.3 km² between the elevations of 4600 and 5300 m in the southern Cordillera Blanca, 75% of which is covered by glacier ice (based on 1997 imagery). The catchment is representative of small glaciers in the Cordillera Blanca, and the recession in recent years has been very extensive (Gomez, 2004). The outflow of the catchment is from a small proglacial lake that has formed in the bedrock during recent glacier recession (Fig. 1). There is very little vegetation (mosses and grasses) and poor soil development over the loosely consolidated alluvium and till. The bedrock in the region is metamorphosed...
sedimentary rocks (quartzite and hornfels), draping off the central granodioritic batholith that forms the core of the Cordillera Blanca (Wilson et al., 1967). Glacial meltwater entering the lake is transmitted directly to the outlet stream without a significant lag due to lake storage (mean residence time of ~11 days). Runoff from the catchment is mixed with non-glacierized streams that flow into Lake Querococha, defining a larger watershed (58 km², 3.4% glacierized) that drains to the Rio Santa. Yanamarey Glacier has discontinuous observations of precipitation and other glaciological variables (Hastenrath & Ames, 1995; Mark & Seltzer, 2003). In collaboration with IRD, the division of glaciology and water resources at INRENA, Huaraz, constructed a weir and installed an automatic stage recorder in 2001. Continuous discharge data and monthly total precipitation have been recorded since construction.
METHODS

Glacier catchment hydrological balance

Based on Mark & Seltzer (2003), a basic water-balance model with monthly mean discharge from YAN and total monthly precipitation was used to compute a change in glacier storage over the span of most recently available data (December 2001–July 2004). The model holds that the total volume of water discharging from a catchment is equal to the volume of water entering the catchment plus a change in storage. It is assumed that the primary outflow consists of the total discharge leaving the proglacial lake ($Q_t$), from the stage recorder, whereas the only input is precipitation ($P$) falling over the watershed. Precipitation was measured from a totalizing gauge located at the southern glacier margin (4764 m) during monthly visits to the site when the stream stage recording data were also retrieved. Losses from the system include evaporation and/or sublimation ($E$) and groundwater recharge ($Gw$). The change in storage is considered to be a loss or gain of glacier ice volume ($\Delta g$), where a loss (negative $\Delta g$) of glacier volume contributes positively to $Q_t$. Thus the final balance is:

$$Q_t = P - E - Gw - \Delta g$$  \hspace{1cm} (1)

Measurements of $Q_t$ (m$^3$ s$^{-1}$) were converted to a depth measure (mm) to compare with linear measurements of the other variables by multiplying by the number of seconds in the respective interval of time between measurements (approximately one month), and normalizing by the area of the glacier watershed as determined from a digital elevation model of the area. Likewise, $P$ is a total depth falling between the same measurement dates. A uniform distribution of precipitation falling over the 1.3 km$^2$ catchment is assumed. Observations from two other totalizing gauges in the catchment located within 100 m altitude to the monitored gauge revealed nearly identical precipitation values. The data lack significant distinction to compute an altitudinal gradient, confirming the spatial consistency of the data. Loss to the groundwater system is not considered significant because the glacier watersheds consist primarily of relatively impermeable bedrock. The water-balance model can be re-arranged to isolate the glacial meltwater contribution to stream discharge as the change in the storage term ($\Delta g$):

$$\Delta g = P - E - Q_t$$  \hspace{1cm} (2)

A lack of empirical data in this study precludes explicit monthly quantification of $E$. Generally, $E$ is small compared to other parameters in glacial watershed balance equations, and no attempt is made to estimate it, assuming it to be zero. In previous work, annual energy balance calculations from the Zongo Glacier, Bolivia were cited (Wagnon et al., 1999), to estimate that evaporation and sublimation might account for about 20% of total ice volume loss (Mark & Seltzer, 2003). This larger total volume of ice ablated annually from the catchment increases the change in storage term, equivalent to ~10% greater proportion of the total discharge in YAN (see Table 3 in Mark & Seltzer, 2003). Hence, this simplification ($E = 0$) is justified as it will likely yield a conservative estimate of the contribution of glacier melt to streamflow.

Regional hydrochemical sampling and analysis

Surface water samples were collected within the Callejon de Huaylas watershed during 2–12 July 2004, to characterize the hydrochemistry of stream water flowing from both
glacierized and non-glacierized catchments. Samples were taken at points defining larger catchment areas downstream from the YAN glacier catchment, as well as from a variety of tributary streams flowing to the Rio Santa from the Cordillera Blanca and Cordillera Negra. Individual sampling sites were chosen to maximize spatial coverage, but were fundamentally constrained by practical considerations of access and available water. There are few actively flowing streams with good access from the Cordillera Negra during the dry season that were not deemed too polluted by human activity to sample.

Using average concentrations of major cations and anions, a simple end-member mixing model was used to analyse the relative percentage of source waters deriving from streams with various amounts of glacierized area on different spatial scales, following the procedures outlined by Hounslow (1995). The chemical composition of a mixture of two waters lies along a straight line in the Piper diagram joining the two end-member compositions (Piper, 1944). The relative amount of each end member contributing to the mixture is inversely proportional to the distance along the line from the end member.

Water samples were collected in new 175 ml Nalgene bottles using standard procedures; these were subsequently stored in cool, dark locations. Upon return to North America, all samples were stored at 4°C. Direct current plasma spectroscopy (Beckman SpectraSpan-V) was used to analyse for: Ca$^{2+}$, Na$^+$, Mg$^{2+}$ and K$^+$. Concentrations of SO$_4^{2-}$ and Cl$^-$ were measured using ion chromatography with a Dionex DX500 chromatography system. Carbonate alkalinity (sum of charged carbonate species, CO$_3^{2-}$ and HCO$_3^-$) was calculated as a residual from the charge balance equation (Drever, 1997).

In the YAN–Querococha watershed, water was sampled at the stage-recording weir at YAN, as well as at three additional sites below YAN (Fig. 1). The sample at Q2 demarcates a 24 km$^2$, 7.8% glacierized sub-catchment downstream of YAN that mixes with effluent from non-glacierized catchment Q1 (19 km$^2$) in Lake Querococha. The Piper plot mixing model estimates the proportion YAN is contributing to discharge from Lake Querococha at Q3, defining the 58 km$^2$ watershed with 3.4% glacierized coverage.

Water samples were also collected from throughout the Callajon de Huaylas to capture hydrochemical variability during the middle of the austral winter dry season. The Rio Santa was sampled at four locations between the source at Conococha and the hydroelectrical plant at Huallanca, and from tributary streams to the Rio Santa from both the Cordillera Blanca and Cordillera Negra. Sample locations were selected from streams in a wide variety of settings, all within relatively easy access from the principal roadway. During the dry season, precipitation and stream discharge are typically at a minimum, maximizing relative contributions from groundwater and glacier melt components. Averaged values of cation and anion concentrations from the glacierized and non-glacierized end-member streams plotted on a Piper mixing model estimate the relative contribution of each to the averaged Rio Santa water.

Sample sites were located with a Garmin handheld GPS receiver. Spatial data were compiled using GIS (ArcGIS version 9.0), including a 30-m digital elevation model derived from 1:25 000 and 1:100 000 topographic maps and 1997 Landsat TM images. From these base layers, glacier coverage, watershed area and hydrography were digitized.
RESULTS

Changes in glacier catchment hydrological balance

There is a change in the annual hydrological balance regime at YAN from 1998–1999 to 2001–2004 as modelled from observed precipitation and discharge (Fig. 2). Whereas the glacier experienced a positive mass gain during January–April 1999, the balance remained negative at the monthly scale over the entire measurement period December 2001–July 2004. Averaged storage changes in 1998–1999 indicated that glacier melt from Yanamarey contributed $35 \pm 10\%$ of the annual discharge (error estimate accounts for precipitation and runoff uncertainty, Mark & Seltzer, 2003). The average value is $58 \pm 10\%$ over the last three years. There is also an increase in total mean discharge: over the hydrological year 1998/99, mean $Q_t = 230$ mm; from 12 January to 8 April mean $Q_t = 410$ mm. Peak annual discharges have increased ~50% in magnitude, and now occur coincidentally with peak precipitation, instead of during the early wet season as shown in 1998/99. Measurements of Yanamarey Glacier show continuous and dramatic recession over the same period. The terminus recession has been monitored regularly by INRENA since 1948, and multi-decadal rates have accelerated four-fold from 5 m year$^{-1}$ (1948–1977) to 20 m year$^{-1}$ (1977–2003).

![Average Monthly Precipitation (1981-2004)](image)

**Fig. 2** The hydrological balance at YAN from 1998 to 2004. There is a gap in years from the original study and when the new weir with continuous stage recorder was constructed. The inset shows the mean monthly precipitation measured in the catchment over all monitored years. The dark bar indicates the rainfall for July 2004, registering 46 mm (almost four times the mean of 12 mm).

Regional hydrochemical variations in the Callejon de Huaylas

Concentrations of major cations and anions were measured in water samples from 28 locations in the YAN–Querococha watershed and throughout larger Callejon de...
Table 1 Site names, date of sample, and concentrations of major cations and anions (mg L\(^{-1}\)) for water samples, separated by regional groupings with averages used in mixing models and the standard deviation (SD) in parentheses.

<table>
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<th>Site name</th>
<th>Cations (mg L(^{-1}))</th>
<th>Anions (mg L(^{-1}))</th>
<th>Alkalinity*</th>
<th>Cl(^-)</th>
<th>SO(_4^{2-})</th>
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<td>Na(^+)</td>
<td>K(^+)</td>
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*Carbonate alkalinity was calculated by charge balance. Concentrations of zero are used when actual calculated values are negative. Of note is that this condition only occurs for samples where the SO\(_4^{2-}\) values are very large, thereby indicating a slight charge balance error in these cases.

Huaylas watersheds (Table 1). A Piper diagram depicts a hydrochemical mixing between end members YAN and Q1 (Fig. 3). The mixed member coming from Querococha, Q3, falls at a distance inversely proportional to the concentration of each end-member contribution, such that ~50% is derived from YAN, and ~50% from the non-glacier stream Q1. Similarly, Q2 is closer to YAN, and is thus proportionately
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Fig. 3 Piper plot of major ion chemistry from the YAN–Querococha watershed. Q3 is on a mixing line between the glacial snout and Q1, with a relative contribution of 50% from each end member. The size of each symbol is proportional to TDS (scale bar in mg L⁻¹).

Fig. 4 Piper plot of major ion chemistry from the averaged end members in the Callejon de Huaylas watershed. The Rio Santa is on a mixing line between the glacierized Cordillera Blanca tributaries and non-glacierized Cordillera Negra tributaries, with a relative contribution of 66% from the Cordillera Blanca. The size of each symbol is proportional to TDS (scale bar in mg L⁻¹). Averages and individual samples are presented in Table 1.
more concentrated with glacier melt (67% from YAN). Another Piper diagram (Fig. 4) features a mixing line between end-member point averages from the glacierized Cordillera Blanca tributary streams ($n = 15$) and from the non-glacierized Cordillera Negra tributaries ($n = 4$). The mixed member averaged from the Rio Santa samples ($n = 5$) falls along the mixing line in-between the end members, but closer to the Cordillera Blanca tributaries average, such that 66% of the Rio Santa discharge is derived from the glacierized Cordillera Blanca catchments.

**DISCUSSION**

**Evaluating YAN–Querococha hydrological balance**

A simplified hydrological balance to estimate glacier mass balance is justified due to the lack of surface-based observations, but involves many complications (e.g. Fountain *et al.*, 1999). Without energy balance measurements and restricted to single totalizing precipitation gauges for the entire catchment, it was not possible to quantify spatially variable precipitation inputs and evaporation. Moreover, the total change in storage considered for the glacier watershed actually contains long-term storage of water coming from glacier ice, firn and snow. Much work has been devoted to investigating the seasonal patterns of meltwater storage in glaciers in different extra-tropical regions (e.g. Tangborn *et al.*, 1975; Östling & Hooke, 1986; Hodgkins, 2001), and further investigation differentiating the impact of seasonal storage should be conducted on tropical glaciers.

The results of the hydrological balance indicate that for July 2004 (normally the dry season), there was a diminished contribution from melting ice (compared to the July 1998 and July 1999 data, which showed close to 100% contribution to $Q_t$ from icemelt in the hydrological mass balance model). For the July 2004 hydrological balance, 45% of the total discharge is estimated to come from icemelt, due in part to the anomalously high rainfall registered for this year.

Precipitation ($P$) naturally varies inter-annually, and the simplified model of net mass watershed balance is sensitive to $P$. If $P$ were anomalously high or low, then the model would provide unrealistic estimates of glacier melt. However, $P$ values for the years modelled here are not anomalous. From the beginning of measurements in 1981, the mean annual $P$ measured at the totalizing gauge near Yanamarey Glacier (4764 m) is 1560 mm. The values for 1998/99, 2001/02, 2002/03 and 2003/04 are 1800, 1596, 1905 and 1578 mm respectively.

Overall, the changes in magnitude and timing of peak annual discharge, combined with the constantly negative glacier storage term, indicate that Yanamarey Glacier is rapidly melting and augmenting $Q_t$. The impact of this glacier melt over the larger spatial scale of the Querococha catchment, and in the larger Callejon de Huaylas, is also notable in the results from the hydrochemical mixing model discussed below. A continued regime of negative mass balance puts the existence of these small glaciers (<1 km$^2$) in jeopardy.

During 1998/99, mixing models indicated Q3 was comprised of 30% of YAN annually; YAN, in turn, was estimated to be 35% glacier melt. Thus ~10.5% of the total annual discharge at Q3 was from melting glacier ice. In July 2004, Q3 is closer to YAN on the Piper plot, implying ~50% of Q3 discharge volume coming from YAN,
which in turn is now ~60% glacier melt. Likewise, ~30% of the discharge volume at Q3 is estimated to be from melting ice. Q2, lying even closer to YAN on the mixing line, is estimated to be ~40% glacier melt by the same reasoning. These estimates represent one relatively dry month. However, monthly isotopic measurements taken previously at Q3 (Mark & Seltzer, 2003) imply much diminished discharge variability given the scale of the watershed and the stabilizing presence of Querococha (second largest lake in the Cordillera Blanca). This estimate is thus considered to be good evidence of enhanced glacier melt contribution to streamflow on a larger scale.

Evaluating the contribution of glacier melt to Rio Santa discharge

The use of simplified mixing models based on the solute chemistry of meltwater has been well established in glacier hydrology as a method to separate subglacial and englacial components of discharge (e.g. Collins, 1978). The method is contingent on the assumption that the end members mix conservatively (Sharp et al., 1995). Rather than deciphering members of englacial and subglacial waters routing through a glacier, this study focuses on the fate of waters leaving the glacier catchment and mixing downstream. With an independent constraint on the meltwater contribution within the catchment based on a water balance model, one can attribute the downstream change in chemistry to dilution with other source waters. This simplified mixing model is justified for making some first-order quantitative estimates of meltwater impact to stream discharge, given the lack of any other data.

The simple mixing model presented herein relies on averaging hydrochemical properties to define end members, and plotting them to consider relative contributions to the Rio Santa. Moreover, this work presents a snapshot in time, as this preliminary sample set was taken over a few days. A more definitive test will involve gathering measurements over a full hydrological year, and include actual discharge measurements.

The regional geology is another factor that will affect the end-member mixing model for the Rio Santa. The present analysis assumes that both the Cordillera Blanca and Cordillera Negra have distinct, homogeneous geological signals in their runoff water. The geology of the Cordillera Blanca is variable; for example, the Yanamarey catchment has much higher sulphate concentrations in runoff water than the other catchments, due to bedrock with increased volumes of sulphur-bearing minerals such as pyrite (FeS₂). There is also an observable increase in sulphate downstream in the Rio Santa that is related to increased travel times, drainage densities and water–rock contact time (Dethier, 1986). Nevertheless, the mixing model employed here is enhanced by using multiple species in relative concentrations. Graphical analysis using a Piper plot provides a useful tool as it is designed to show the essential chemical character of water according to relative concentrations of several dissolved constituents (Piper, 1944). Individual sampling sites were selected to maximize spatial coverage, minimizing the effects of anomalies.

Despite the limitations and assumptions, the estimate of relative contributions to the Rio Santa obtained in this study provide a valuable and unprecedented quantification of glacier meltwater impact. Drawing on the analogue YAN–Querococha watershed, where meltwater contribution was derived by area of glaciariation from the hydrochemical mix (Fig. 3), one can estimate the glacier meltwater impact.

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CONCLUSIONS AND FUTURE WORK

Ongoing and rapid glacier recession of the Yanamarey Glacier was found to have enhanced discharge at the expense of catchment storage. The glacier now appears to be in continual negative mass balance, as observed in a simplified hydrological balance model. Seasonal stream runoff will likely become more variable in the future, as peak discharge coincides with highly seasonal peak precipitation. To the extent that this glacier is representative of other small glaciers, the most predominant class of glaciers inventoried in the Cordillera Blanca (Ames et al., 1989), short-term increases in stream discharge with critical long-term loss of storage are likely to be widespread over the region. Furthermore, glacier melt provides a very significant proportion of runoff to the Rio Santa that is also likely to diminish if glaciers continue to melt. In future years, it will be of interest to study changes in river discharge and water chemistry with increasing glacier recession. It will be important to maintain continual hydrochemical observations throughout the year to capture seasonal variations, and also improve the data sampling to include more chemical species and direct measurement of alkalinity.

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