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Research papers

Influence of glacial sediments on the chemical quality of surface water in the Uta valley, Cordillera Blanca, Peru



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ABSTRACT

The Río Santa (Ancash, Peru) and its tributaries are an essential source of drinking and irrigation water. Its discharge relies on glacial meltwater, which is diminishing due to the rapid decrease in glacial extent. As a secondary effect, water quality can be compromised (e.g. pH < 3 and high concentrations of SO₄²⁻ and trace metals). Although this has previously been attributed to pyrite rich Chicama bedrock exposed by glacial retreat, little is known about the occurrence of Chicama fragments in Quaternary glacial sediments and its influence on water quality. This research aims at elucidating this effect by relating observed changes in water quality in streams to presence and chemical composition of morainic ridges in the Quebrada Uta in the Río Santa basin. Changes in water quality before and after contact with a morainic ridge were assessed using carbonate alkalinity titration, ion analysis and elemental analysis. Moreover, relative contributions of glacial meltwater and precipitation were assessed qualitatively using stable water isotope analysis. We used a novel method to explain the provenance of contaminated glacial sediments using a reconstruction of their source area. The mineralogical composition of a morainic ridge was strongly related to the geology of the source area indicating that mineralogical composition of tills may be predicted using this technique. Effects of glacial sediments in morainic ridges on water quality were minimal but depended on their mineralogical composition. Morainic ridges with a high content of Chicama shales tended to increase solute loads of Mg and SO₄²⁻. Additionally, isotope signatures suggest that during the dry season, moraines may act as reservoirs for precipitation-derived shallow groundwater. Clear trends in water quality were observed along the whole flow path of the Río Buín, which could potentially be explained by increased groundwater contribution downstream and shifts in dominant weathering mechanisms. Future research should focus on disentangling these various drivers of water quality in glacial catchments.

1. Introduction

Due to mass loss of glaciers, glacier-fed freshwater supplies are expected to decline globally on the long term (Jiménez Cisneros et al., 2014). Although a worldwide phenomenon, mass loss of glaciers is especially pronounced in the Andes (Rabatel et al., 2013). Due to decreasing extent of glaciers, freshwater reservoirs in the Cordillera Blanca are diminishing in size (Kaser et al. 2003; Mark and Seltzer

2003; Mark et al., 2010; Baraer et al., 2012), while glacial meltwater is an important source of water within the Río Santa watershed and parts of the coast of Peru. With 600 km², the Cordillera Blanca is the largest glaciated area in the tropics, comprising a quarter of all tropical glaciers. Its waters mainly drain into the Río Santa watershed, where it is used to maintain intensively cultivated areas and generate hydropower (Kaser et al., 2003).

Water quality in the Río Santa watershed is affected negatively both

Abbreviations: ELA, Equilibrium Line Altitude; DTM, Digital Terrain Model; AAR, Accumulation Area Ratio; LOD, Limit of detection; ICP-OES, Inductively Coupled Plasma Optical Emission Spectroscopy; XRF, X-Ray Fluorescence; PSA, Particle Size Analysis; K_{Sat}, Saturated Hydraulic Conductivity; EC, Electrical Conductivity; HDPE, High Density Polyethylene; DOC, Dissolved Organic Carbon; CRDS, Cavity Ring-down Spectroscopy; VSMOW, Vienna Standard Mean Ocean Water; VSLAP, Vienna Standard Light Antarctic Precipitation

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by anthropogenic activity such as mining and by natural sources of contamination. The latter is most notably caused by sulphide weathering occurring in the pyrite-rich Jurassic “Chicama Formation” (Fortner et al., 2011; Burns et al., 2011; Gordon et al., 2015). A case study by Fortner et al. (2011) in the Río Quilcay, a tributary of the Río Santa originating from the Quilcayhuanca quebrada (glacial valley), indicated that several water quality parameters exceeded limits for human consumption issued by the World Health Organization and Peruvian drinking water standards. Surface water pH levels of 3 to 4 are common and as a result of the ensuing enhanced heavy metal solubility, concentration limits for irrigation and agriculture are exceeded locally (Fortner et al., 2011; Bury et al., 2013).

Within this context, this study focuses on the influence of till deposits in morainic ridges on water quality in a previously unstudied and pyrite-containing glacial valley in the Cordillera Blanca. It is still unclear how exactly natural contamination from mineral sources affects the chemical quality of surface water. While the presence of upstream Chicama Formation has been identified as a source of natural contaminants due to rock weathering, a main point of debate is the effect of mineralogy of Quaternary fluvioglacial deposits on natural contamination (Fortner et al., 2011; Burns et al., 2011). Since these deposits have never been studied in detail in the Peruvian Andes, little is known about their mineralogical composition. Whereas the Chicama Formation is confined to the uppermost reaches of the Cordillera Blanca (Fig. 1), redistribution of Chicama material in the form of fluvioglacial deposits could contribute to additional natural contamination of water further downstream in catchments. Attempts to relate the presence of fluvioglacial deposits to water quality in streams intersecting these deposits remain incidental. Moreover, hydrological behaviour of these deposits remains largely unknown (Gordon et al., 2015). This study contributes to filling this gap of knowledge through measurement of chemical water quality up- and downstream of Quaternary fluvioglacial deposits combined with chemical and hydrogeological characterization of these deposits. This approach may yield insights into the effect of glacial redistribution of potentially contaminating minerals on the chemical quality of surface water in glacial systems worldwide.

In the proglacial zone highly erodible material is present which is initially water-saturated and has a high water/rock contact area. This facilitates high weathering rates and solute loads (Anderson et al., 2000). In prior studies of weathering processes in the Cordillera Blanca, sulphide weathering (due to presence of pyrite) has been identified as the dominant weathering process (Fortner et al., 2011; Burns et al., 2011; Walsh, 2013). Sulphide and carbonate weathering are the dominant weathering processes in proglacial and subglacial zones worldwide (Anderson et al., 2000). Weathering of pyrite precipitates ferric oxyhydroxides and produces SO_4^{2-} and H^+ , which rapidly decreases the pH of surface waters and may cause other compounds to dissolve (Åström and Åström, 1997; Munk et al., 2002). Buffering of acidification by CO_3^{2-} or HCO_3^- has been shown to occur in highly acidic streams (Munk et al., 2002; Fortner et al., 2011). Upon depletion of sulphides and carbonates, the role of silicate weathering increases in the proglacial zone (Tranter et al., 2005; Anderson et al., 1997; Walsh, 2013).

Gordon et al. (2015) found that moraines in the Quebrada Quilcayhuanca were in many cases connected to groundwater-bearing subsurface talus deposits, which are important aquifers in the Cordillera Blanca (Baraer et al., 2015; Glas et al., 2017). Baraer et al. (2015) found that during the dry season such talus deposits may be significant sources of groundwater, derived from preceding wet-season precipitation. This may result in addition of precipitation-derived groundwater to the outflow of the morainic complex and cause water to be less representative of pyrite weathering. The relative contribution of glacial meltwater and groundwater to the total outflow of such a deposit is difficult to infer from field assessments. However, previous studies have used end-member mixing models to derive isotope and chemical signatures of precipitation-derived groundwater and glacial meltwater in

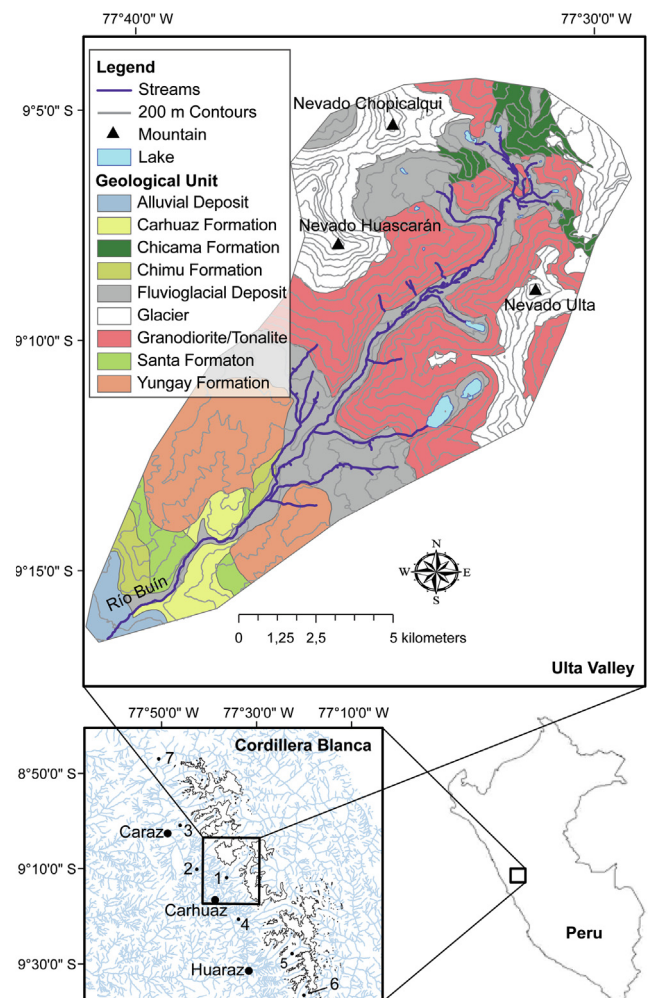


Fig. 1. Location of the Study Area, with WGS 1984 coordinates. Geology adapted from IGMM (2011). Numbers 1 – 7 indicate locations of previous studies mentioned throughout this study. 1) Río Buín (this study), 2) Río Mancos, 3) Río Lullana, 4) Marcará, 5) Río Quilcay/Quilcayhuanca, 6) Río Negro/Olleros, 7) Quitarasca.

the dry season (Mark and Seltzer, 2003; Mark et al., 2005; Baraer et al., 2009; Burns et al., 2011; Baraer et al., 2015; Gordon et al., 2015). In the Andes, differences in enrichment of heavy isotopes in precipitation are dominated by the altitude effect. Due to orographic uplift, progressive condensation of moisture from air leads to increasing depletion of heavy isotopes in rainfall with elevation (Rozanski and Araguás-Araguás, 1995). Additionally, isotope ratios in surface water may be affected by the contribution of glacial melt to total stream discharge, since glacial meltwater is depleted in heavy isotopes compared to groundwater (Baraer et al., 2015; Gordon et al., 2015; Mark and McKenzie, 2007). As such, isotopes of oxygen and hydrogen may be used to distinguish between various sources of water based on source area elevation (Burns et al., 2011; Baraer et al., 2015; Gordon et al., 2015).

Morainic ridges largely consist of subglacially eroded material but may include englacial and supraglacial material and outwash sediments deposited at the glacier margin (Boulton, 1986). Subglacial erosion rates vary throughout a glacier and depend on a multitude of factors related to glacial flow rates such as subglacial terrain. Historically, glacial flow and mass balance equations have been used to reconstruct former glacier extents and monitor glaciers over time (Rodbell, 1992; Kaser and Georges, 1997; Mark and Seltzer, 2005; Racoviteanu et al., 2008; Benn and Evans, 2010). Theoretically, the composition of a morainic ridge should correspond to the geology of its source area,

especially in areas of maximum glacial flow rate. Therefore, this study adopts a novel application of glacial mass balance equations in order to predict mineralogical composition of moraines based on the lithology of the former glacier extent. Such an approach may prove useful in the prediction of the provenance of contaminated sediments in various glacial environments. Additionally, subglacial lithology could be predicted based on the composition of currently developing morainic deposits, which may prove useful in the context of glacial retreat worldwide.

The aim of this study is to assess the influence of Quaternary glacial sediments, present in the proglacial zone as morainic ridges, on chemical surface water quality in the Quebrada Ulta. The objectives are to:

- (1) assess predictability of till composition based on a morainic ridge's position in the landscape by reconstruction of the source area of moraine complexes,
- (2) assess the influence of chemical composition of morainic ridges on the chemical quality of surface water through measurement of chemical composition of sediments and water,
- (3) assess the influence of texture and saturated hydraulic conductivity of sediments on the chemical quality of surface water
- (4) relate changes in water quality upon contact with a morainic ridge to changes in relative contribution of glacial meltwater and precipitation-derived groundwater as derived from qualitative assessment of isotope ratios of water

We expect that the composition of morainic ridges will be correlated to the subglacial geology of the extent of glaciation at the time of deposit, most notably that of the most erosive zone around the ELA (Equilibrium Line Altitude) (Benn and Evans, 2010; Dahl and Nesje, 1992). In turn we expect that changes in water quality upon contact with a morainic ridge will be related to the presence of specific minerals and compounds in the morainic ridge. This may also be expressed through differences in texture and saturated hydraulic conductivity of tills. We expect to find less deterioration of water quality in cases where the morainic ridge is connected to subsurface precipitation-derived groundwater flows. Within the context of a ubiquitous trend of glacial mass loss and adverse impacts of global warming on freshwater supplies, this study is of global relevance.

2. Methods

2.1. Research area

The Quebrada Ulta is the catchment of the Río Buín tributary to the Río Santa, situated close to the town of Carhuaz in the province of Ancash, Peru. To our knowledge no publications exist that describe the geohydrology or water quality within this catchment, while several do exist for nearby valleys such as the Quebrada Quilcayhuana (Gordon et al., 2015; Fortner et al., 2011; Baraer et al., 2012; Burns et al., 2011, Glas et al., 2017), Yanamarey (Bury et al., 2013; Baraer et al., 2012; López-Moreno et al., 2017), Llanganuco, Querococha and Pumapampa (Baraer et al., 2012).

The Quebrada Ulta ranges from approximately 3500–6750 m in altitude and is flanked by several glaciated mountaintops, among which the Nevado Huascarán, which is the highest peak of the Cordillera Blanca. The geology of the Quebrada Ulta is dominated by granodiorite and tonalite intrusives, with some outcrops of the meta-sedimentary Jurassic Chicama formation in the higher regions of the quebrada (Fig. 1). The catchment area of the Río Buín contains various fluvio-glacial, colluvial and glacial deposits (IGMM, 2011) and several glacial lakes and paleo-lakes that formed upon the retreat of glaciers. Such glacial lakes may be dammed by ice, bedrock or morainic ridges. Often several levels of morainic ridges are present within a quebrada, related to different episodes of glacial advance. This creates a staircase-like landscape with glacial lakes (or paleo-lakes) dammed by morainic

ridges at different altitudes (Iturrizaga, 2014).

The local climate is characterized by relatively large daily and small seasonal temperature variations and a distinct dry (May–September) and wet season (October–April) due to oscillation of the cloud belt of the Intertropical Convergence Zone. As a result, monthly mean temperatures remain between 5 and 10 °C throughout the year, but precipitation differs from below 50 mm per month during the dry season up to 150 mm per month during the wet season (Kaser et al., 1990). In the Quebrada Ulta, glacial cover of the Huascarán-Chopicalqui massif decreased by 18.67% between 1970 and 2003 (Racoviteanu et al., 2008). Based on previous studies in other quebradas of the Cordillera Blanca it can be expected that a decrease of glacial extent leads to reduced availability of meltwater as a source of freshwater runoff in the area (Kaser et al. 2003; Mark and Seltzer 2003; Mark et al., 2010; Baraer et al., 2012). As a consequence of local climate, mass accumulation from precipitation is mostly confined to the wet season in the highest part of the glacier (Kaser and Georges, 1997), whereas precipitation in the form of snow on the tongues of the glaciers of the Cordillera Blanca tends to melt within days (Kaser et al., 1990). This causes steep vertical gradients (Kaser and Georges, 1997).

2.2. Paleoglacier reconstruction

We test a novel method to explain the mineralogical composition of morainic ridges based on their source area, in this case the area occupied by the former glacier that created the morainic ridge (“paleoglacier”). Based on field observations and interpretation of a Digital Terrain Model (DTM) (ASTER GDEM v2, retrieved from <https://lpdaac.usgs.gov>, April 2016 and Sentinel MSI aerial photography (European Space Agency, 2016), we mapped morainic ridges. Additionally, glacial geomorphological features such as glacial trimlines were mapped using the Sentinel data and field observations. Trimlines are the demarcation lines visible between glacially eroded and non-eroded terrain, often presumed to represent the limit of a glacier's erosive zone (Benn and Evans, 2010). Geological data (IGMM, 2011), the DTM and glacial geomorphological features were used to infer paleoglacier extents and subglacial lithology. Field-mapped morainic ridges were combined into polygons representing the original moraine deposits by connecting lateral and terminal moraines. For each of these polygons a watershed was generated using ArcMap 10.4 and the AcrHydro Tools toolbox (ESRI, 2011). Watersheds were adapted manually based on a set of criteria:

- (1) the paleoglacier is confined by trimlines and lateral moraines. Trimlines indicate the ice height and thus paleoglacier extent at some point of glacial equilibrium in the past (Ballantyne, 2002).
- (2) In the upper reaches of the paleoglacier watershed, any area with a slope in excess of 60° is interpreted as cirque headwall (Meierding, 1982).
- (3) Ice height was assumed to be the same on either side of a glacier tongue.

Adapted watersheds represent a reconstructed paleoglacier extent corresponding to a specific moraine deposit. To infer the ELA, we used the widely accepted Accumulation Area Ratio (AAR) method, which requires as input the total area of the former glacial extent and a DTM, of which a fraction (typically 0.65) is assumed to represent the paleoglacier's accumulation area (Rodbell, 1992; Kaser and Georges, 1997; Mark and Seltzer, 2005; Racoviteanu et al., 2008). However, as the mass balance of tropical glaciers is steeper, we used an AAR of 0.75 as proposed by Kaser and Georges (1997). The paleoglacier polygons were used to calculate the 75% height percentile of all DTM cells within the polygons as the ELA. This was achieved by clipping the contour line of the 75% percentile height to the extent of the paleoglacier. A 500 m buffer zone was generated around the reconstructed ELA as an “ELA zone”, to represent the most erosive zone of the paleoglacier. The

Table 1
Overview of major groups of morainic ridges.

Moraine group name ¹	Estimated age (yrs BP)	Typical altitude [m]	Comments
<i>Pre-Holocene</i>			
Cojup	29 ka–4.3 myr ^a	?	
Rurec	34–21 ka ^b	3400–3800 ^a	
Laguna Baja	16 ka ^b	3800–4000 ^a	
Manachaque	11 ka ^b	4000–4300 ^{a,c}	Possibly including Younger Dryas ^c
<i>Holocene</i>			
Various groups	7–0.1 ka ^d	> 4300 ^d	Including Little Ice Age ^d

a) Rodbell (1993), b) Farber et al. (2005), c) Rodbell and Seltzer (2000), d) Solomina et al. (2007).

maximum altitude at which lateral moraines occur was used as a validation for the minimum height of the ELA (Dahl and Nesje, 1992). Both from the entire paleoglacier extent and from the ELA zone, subglacial lithology was inferred by recording the percentage occurrence of specific geological units within those polygons. This generated a dataset of 15 morainic ridge complexes with a paleoglacier extent, ELA, paleoglacier lithology and ELA zone lithology. A full procedure can be found in Appendix D.1.

Morainic ridges were dated based on relations between the altitude and the age of moraine complexes in the Cordillera Blanca from literature (Table 1). Throughout the Cordillera Blanca, various episodes of glacier advance in the past have left distinct complexes of lateral and terminal moraines throughout different quebradas. Attempts to inventory and date these have been made by various authors based on relative positioning, lichenometry, ¹⁰Be and radiocarbon dating (Rodbell, 1993; Rodbell and Seltzer, 2000; Farber et al., 2005; Solomina et al., 2007; Rodbell et al., 2008).

2.3. Sampling

To assess the influence of the composition of morainic ridges on the chemical quality of surface water, a sampling scheme was set up in which water samples were collected at contact areas of streams with proglacial tills in morainic ridges. Sampling was carried out during the dry season (between late June and mid-July 2016) to limit potential sources of surface water to glacial melt and groundwater. Water was sampled upstream and downstream of a contact zone, and proglacial till was sampled along the contact zone with the stream (distance from stream < 50 m). In case of larger moraine complexes, several till samples were collected from both lateral moraines. This sampling scheme was based on the premise that water bodies receive either direct runoff or groundwater from permeable deposits such as morainic ridges. Using rain gauges, no precipitation was recorded during the sampling period. In case springs were observed to discharge from a morainic ridge, a sample was taken of the spring water as well as two samples up- and downstream of the confluence point of the spring with a receiving stream. Since sampling was carried out in the dry season, we assume that these springs are perennial. To allow for mixing of the two water bodies, samples downstream from the confluence point were taken at a distance of at least ten times the width of the stream, but upstream of any other tributaries. In these cases, till samples were taken from as close to the spring as feasible (< 20 m). This was done in locations on various geological subunits and altitudes in the Quebrada Uta. This way, changes in water quality upon contact with a morainic ridge could be related to the composition of the morainic ridge, while minimizing influence of other processes as much as possible. The sampling scheme is depicted in Fig. 2.

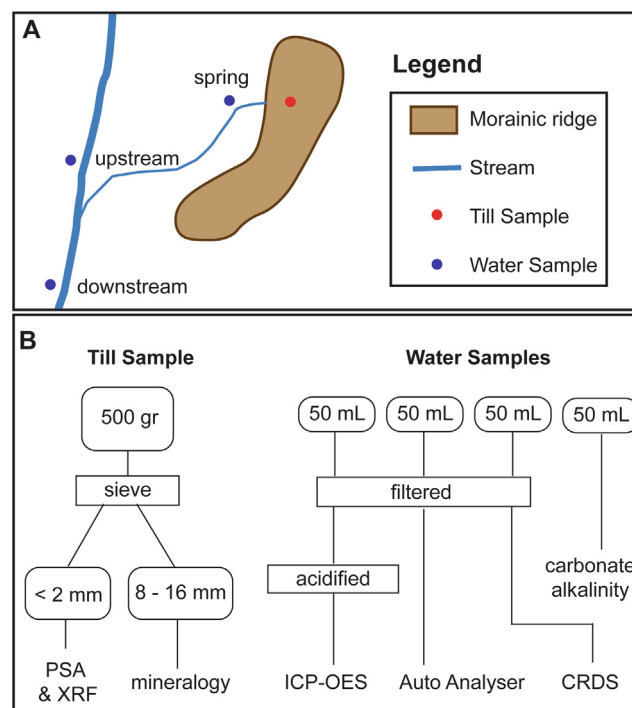


Fig. 2. Spatial overview of the sampling procedure (a) and workflow for analysis of till and water samples (b). CRDS = Cavity Ring-down Spectroscopy, PSA = Particle Size Analysis, XRF = X-ray Diffraction. ICP-OES = Inductively Coupled Plasma Optical Emissions Spectroscopy.

2.4. Parent material analysis

Proglacial till was sampled from parent materials by collecting approximately 500 g of material from below the A and B horizons in a zip lock bag. Material was sieved over a 16 mm, 8 mm and 2 mm sieve tower and all fractions were weighed.

A Niton XL3 series handheld X-Ray Fluorescence (XRF) analyser was used on milled and sieved (< 2 mm) material to quantify Ba, Mo, Nb, Zr, Sr, Rb, As, Pb, Zn, Cu, Fe, Mn, Cr, Ti, K, Ca, Al, P, Si, S and Mg concentration in tills. NIST 2709a, NIST 180–661 (National Institute of Standards and Technology) and SDAR-m2 (USGS) standard reference materials were measured to correct for measurement errors (see protocol in Appendix D.2.3). Other elements of interest such as Na, S and Mg were not suitable for analysis with the used XRF analyser and were analysed in duplicate using microwave extraction in Aqua Regia and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Optima 8300, Perkin Elmer, USA).

Particle Size Analysis (PSA) was performed on 20 g of unmilled, sieved (< 2 mm) material. Pre-treatment (removal of organic matter and iron oxides) followed Mehra and Jackson (1960) and Gee and Or (2002). After pre-treatment, soils were separated into a fraction > 63 μm and a fraction < 63 μm by wet-sieving. The fraction < 63 μm was freeze-dried and analysed with sedigraph analysis using X-ray attenuation (Sedigraph III Plus, Mircomeritics, USA). The fraction > 63 μm was analysed for particle size using a sieve tower and scale with 0.01 g precision. The GRADISTAT software designed by and described in Blott and Pye (2001) was used to calculate sand-, silt- and clay fractions of the soil material of < 2 mm from the sieve tower and sedigraph data. A protocol is available in Appendix D.2.2.1. Based on sand, silt and clay fractions, gravel content and OM content, saturated hydraulic conductivity (KSat) was determined using the SPAW Soil Water Characteristics Calculator (Saxton and Willey, 2005; Saxton and Rawls, 2006; Saxton, 2007). The equations used in SPAW can be found in Saxton and Rawls (2006).

To assess till Chicama content, the 8–16 mm fractions were

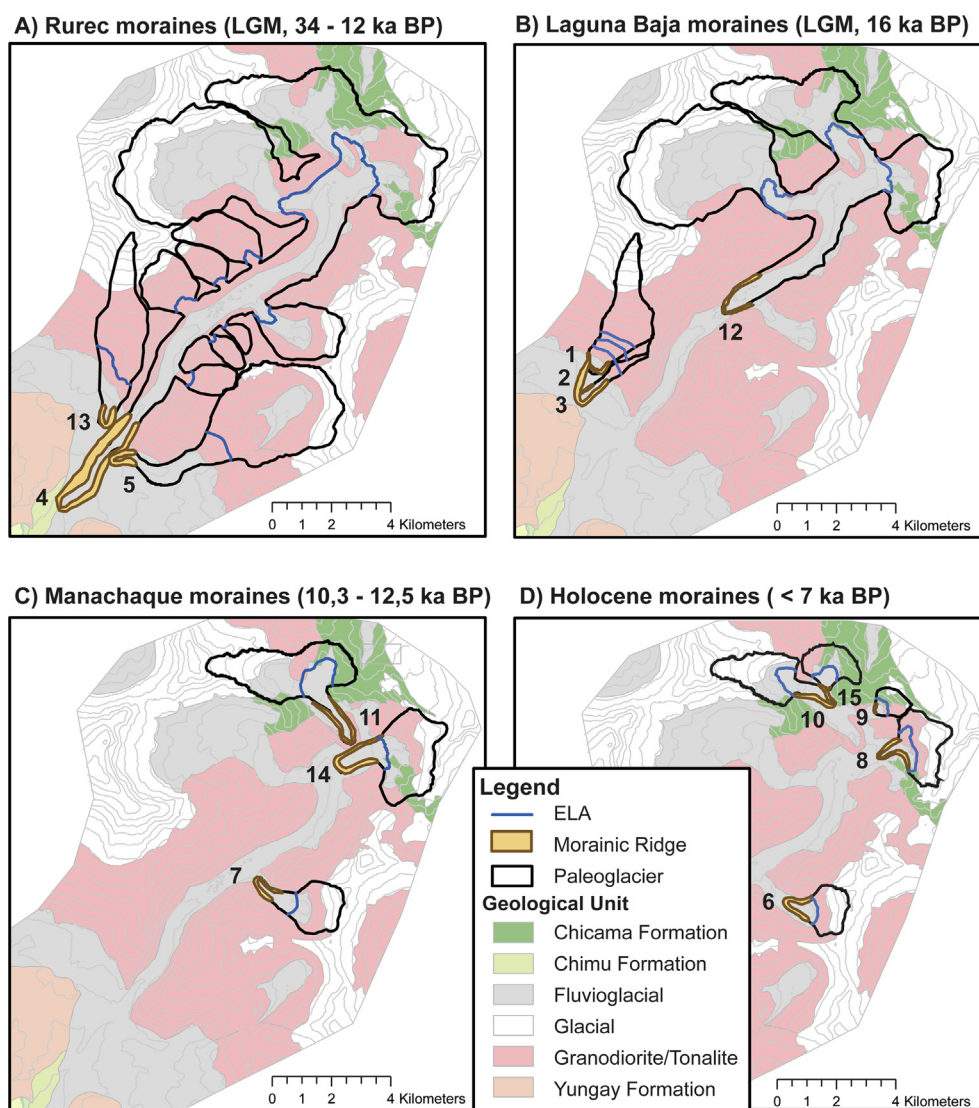


Fig. 3. Map of morainic ridges, paleoglacier extents and ELAs reconstructed using watershed analysis. It is possible that paleoglaciers in Fig. 3A (glaciers 13, 4 and 5) were connected during this stadium.

mineralogically classified using a jeweller's loupe and Streckisen's (1974) QAPF diagram after removal of clay coatings and iron oxides (see Appendix D.2.2.5).

2.5. Water analysis

For each water sampling location, temperature corrected pH and Electrical Conductivity (EC) were measured using a pH90 pH-meter and LF96 micro-conductivity meter (WTW, Germany). EC in meltwater streams in this region shows a diurnal trend due to temperature-dependent glacial melt contribution (Burns et al., 2011). Therefore, these data were detrended using a time series of logged EC data with a 15-minute interval from a meltwater stream spanning 4 days. This series was used to fit sine functions to describe diurnal variation in EC measurement. The amplitude and phase of the sine function were related with distance to glacier (Fig. D2, Appendix D.3.1). An empirical relation was set up of distance to glacier and phase and amplitude of the diurnal sine functions, so that EC data of meltwater streams could be detrended based on their distance from an active glacier (see Appendix D.3.1). Specific compound or element concentrations and isotope ratios were not detrended for diurnal variation, since compound-specific discharge relations may depend on compound-specific geochemical

processes (Nimick et al., 2003). Throughout the manuscript, detrended EC values are used for meltwater streams.

Water samples were taken in quadruplicate, using 50 mL high-density polyethylene bottles pre-rinsed with sample water. 3 out of 4 replicates were filtered using a rinsed syringe and 0.45 μm filter. 1 out of 3 filtered samples was acidified using 2 drops of 70% nitric acid.

Alkalinity titrations were conducted in the field with a field titration set. Time between sampling and titration varied from 1 to 7 days. Titration of 10 mL unfiltered, unacidified sample was conducted using HCl [0.067 M] under continuous measurement of pH. We used the USGS Alkalinity Calculator tool (USGS, 2013) to calculate total alkalinity in CaCO_3 equivalents, HCO_3^- and CO_3^{2-} concentrations applying Gran function plots as first choice (Andersen, 2002; Gran, 1950; USGS, 2013). The inflection point method was used instead in case insufficient data was available to construct a Gran function. The detection limit (LOD) was set to 1.7 μmol based on the minimum drop size and titrant concentration.

The acidified aliquot was used for ICP-OES (Optima 8300, Perkin Elmer, USA) to measure total element concentrations of major cations and trace elements (Al, Fe, Na, Ca, K, Mg, Cu, Ni, S, As, Cd, Co, Li, B, Ba, Mn, In, Sr, Ti, Be, Cr, Mo, Sb, Ga and Si). 8 mL of non-acidified sample was used to measure NO_x , PO_4^{3-} , SO_4^{2-} , Cl^- and NH_4^+ concentrations

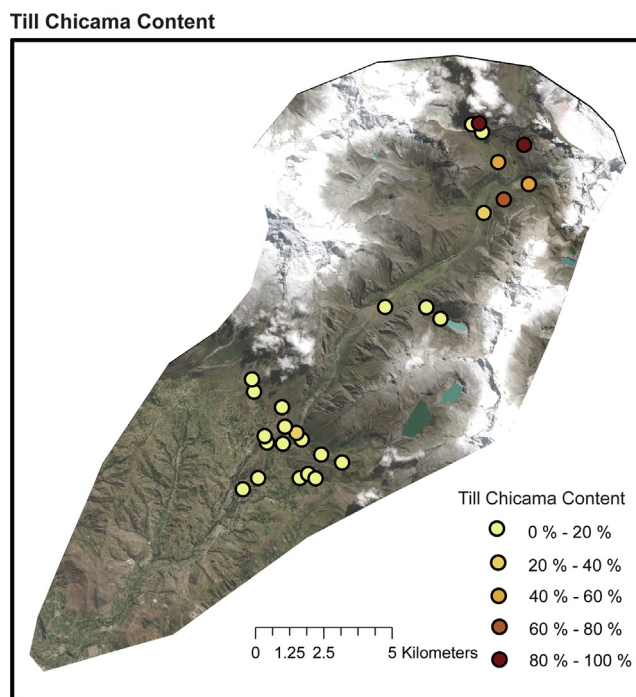


Fig. 4. Soil sampling locations coloured by percentage of Chicama shales in till, reported as % of rocks in 8–16 mm texture class. Sentinel MSI aerial photography (European Space Agency, 2016) is used as basemap.

using an Auto Analyser (San++ , Skalar, Netherlands). LODs per compound are in Table C.6. Samples below LOD were set to LOD / 2. Total dissolved C (organic and inorganic) and N (nitrogen) were measured using a TOC WVP (Shimadzu Corporation, Japan) on 15 mL of sample using 700 °C combustion catalytic oxidation. From the difference between total C and inorganic C the total amount of dissolved organic C (DOC) was calculated. The negative charge of DOC was calculated according to Oliver et al. (1983). The ion balance was calculated as the percentage difference between the total charge of anions and total charge of cations (using the elemental concentrations of the major cations) divided by the sum of positive and negative charges (Appendix D.3.2). Samples with an error in ion balance of over 15% were omitted from further analysis.

Stable oxygen and hydrogen isotope analyses of water samples were performed by cavity ring-down spectroscopy (CRDS) (L2130-I, Picarro Inc., USA). About 0.8 µl of unacidified sample water was injected into the vaporizer, converted to water vapour and transported into the cavity with synthetic air as carrier gas. Water samples were measured in replicate together with internal laboratory standards calibrated against international isotopic reference materials (Brand et al., 2014). The isotopic compositions are expressed as δ -values in per mil (‰) as follows in Eq. (1):

$$\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000 \quad (1)$$

with R_{sample} and R_{standard} as isotope ratios ($^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$) of sample and standard, respectively. Isotope values of oxygen and hydrogen were normalized to VSMOW/VSLAP. Analytical precision as determined from internal standards was better than $\pm 0.05\text{‰}$ for $\delta^{18}\text{O}$ and 0.1‰ for $\delta^2\text{H}$. No precipitation could be sampled during the fieldwork period due to complete absence of precipitation. As an alternative, isotopic signatures were compared to known Meteoric Water Lines from literature to facilitate a qualitative interpretation.

2.6. Data analysis

To assess the influence of morainic ridges on the chemical quality of

surface water, a pair-wise comparison was made between water chemical data up- and downstream of a morainic ridge. The extent to which these differences were related to till composition was assessed by correlating downstream – upstream differences to till physical and chemical data. To assess the role of the pyrite-rich Chicama formation in tills, locations were subdivided into high-Chicama tills (> 30% Chicama) and low-Chicama tills (< 30% Chicama). A comparison was made between the changes in water quality parameters between up- and downstream samples for the low-Chicama group and high-Chicama group using a two-sample test of difference of means. Afterwards, the same procedure was conducted for differences in water quality parameters in spring water among the high-Chicama and low-Chicama group. All water data (EC, pH, stable isotope ratios and compound concentrations) were tested for correlation with elevation. To assess the extent to which moraine deposits act as reservoirs for local precipitation, trends of stable isotope ratios with elevation were assessed for moraine-fed springs and meltwater streams separately and compared to known isotope ratio elevation trends in precipitation and surface water in the Cordillera Blanca (Rozanski and Araguás-Araguás, 1995; Windhorst et al., 2013; Baraer et al., 2015).

To assess relations between paleoglacier or ELA lithology and till composition, the percentage of areal cover of Chicama formation of a paleoglacier area or ELA zone was correlated to physical and chemical data of till from the corresponding morainic ridge. Additionally, correlation among individual compounds in tills was analysed and compared to till Chicama content to facilitate the identification of specific minerals in the Chicama formation responsible for observed effects on the chemical quality of surface water.

For all correlation analyses, Pearson's product-moment correlation was used for normally distributed data, Spearman's rank correlation was used in all other cases. A Student's *t*-test was used if the difference in water quality parameters was normally distributed and a Wilcoxon signed-rank test was used in all other cases. For paired differences, a two-sample *t*-test was used to test significant difference of means, or a Wilcoxon rank sum test for non-normally distributed differences. 0.05 was used as significance criterium, and *p* values of up to 0.1 were reported as tendencies. Bonferroni-Holm correction (Holm, 1979) was used on all separate analyses to correct for multiple testing. Data analysis was carried out in MATLAB R2014b.

3. Results

3.1. Paleoglacier reconstruction

Morainic ridges of various age are present in the Ulta valley (Fig. A.2), ranging from large, vegetated moraines (southwest) to younger unvegetated moraines (northeast). Trimlines are almost exclusively found along the central valley (Fig. A.4). Fig. 3a–d shows the reconstructed paleoglacier extents and corresponding ELAs for 15 selected moraines grouped by age (full data in Table C.1). Minor adaptations to the existing geological map (IGMM, 2011) are made based on observations during the field campaign (Fig. A.3).

3.2. Till composition

Tills mostly contain < 20% Chicama material, although higher concentrations are found with increasing elevation (Fig. 4). Most tills are of a very poorly sorted texture with varying saturated hydraulic conductivity (0.8 – 4.1 cm/hr). Apart from Si, tills contain approximately 6–14% Al, 0.8–9% Fe, 1–3% K, 1–2% Ca, 0.05–3.00% C, 0–1.4% S, 0–1.2% Mg and 0.02–0.27% N and small amounts of other elements. The contents of S, Mg, Fe and As in tills are positively correlated, as are Si and K (Fig. 5). Mo, Pb, Cu and Cr are mostly below detection limits and omitted from further analysis. The Supplementary material contains all till properties (Table C.3), detection limits and relative errors of measurement (Table C.2). Since errors were high for As, Mn and S,

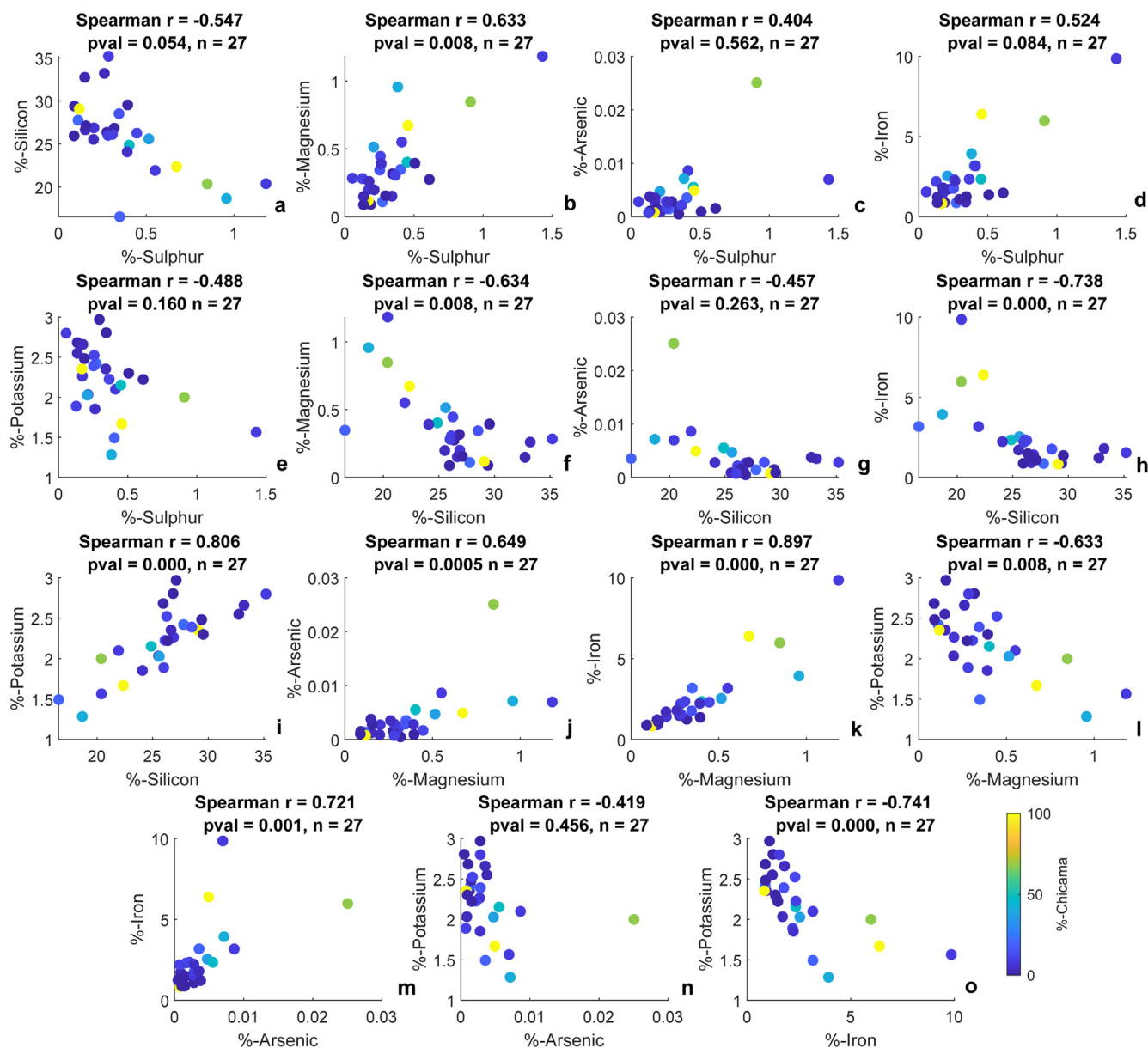


Fig. 5. Correlations between element concentrations in till samples (all in mass-%), coloured by percentage of Chicama shale in till (as % of rocks in 8–16 mm class). P-values are corrected p-values.

Table 2

Correlation (Spearman's R) matrix of till properties and paleoglacier lithology. P values are corrected p values.

	Till-Chicama [%]	Till-Ksat [cm/hr]	Till-S [%]	Till-Fe [%]	Till-As [%]	Till-Al [%]	Till-Mn [%]	Till-Si [%]	Till-K [%]	Till-Ca [%]	Till-Na [%]	Till-Mg [%]
ELA-Chicama [%]	0.799	-0.439	0.185	0.509	0.570	0.199	0.098	-0.261	-0.542	0.059	0.645	0.509
N = 14	0.008	1	1	0.817	0.431	1	1	1	0.588	1	0.165	0.818
	***	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Glacier-Chicama [%]	0.744	-0.458	0.069	0.448	0.485	0.130	-0.098	-0.011	-0.474	0.281	0.709	0.455
N = 14	0.029	1	1	1	1	1	1	1	1	1	0.059	1
	**	NS	NS	NS	NS	NS	NS	NS	NS	NS	+	NS
Till-Chicama [%]		-0.249	0.200	0.537	0.446	0.130	0.329	-0.434	-0.569	0.071	0.537	0.503
N = 27		NS	1	0.051	0.256	1	1	0.307	0.026	1	0.051	0.098
			NS	+	NS	NS	NS	NS	*	NS	+	+

= p value < 0.05, ** = p value < 0.01, *** = p value < 0.001, + = p value < 0.1, NS = not significant.

values should be interpreted with caution.

Morainic ridges consisting of Chicama-rich till were deposited by paleoglaciers from source areas and ELA zones with a higher share of Chicama material. Higher Chicama content was associated with higher

content of Fe, Mg and Na and decreased content of K (Table 2). A comparison of three till samples of both the left and right lateral moraine of the largest morainic ridge complex in the study area yielded distinctly different Chicama shale contents (1–3% vs. 8–20%).

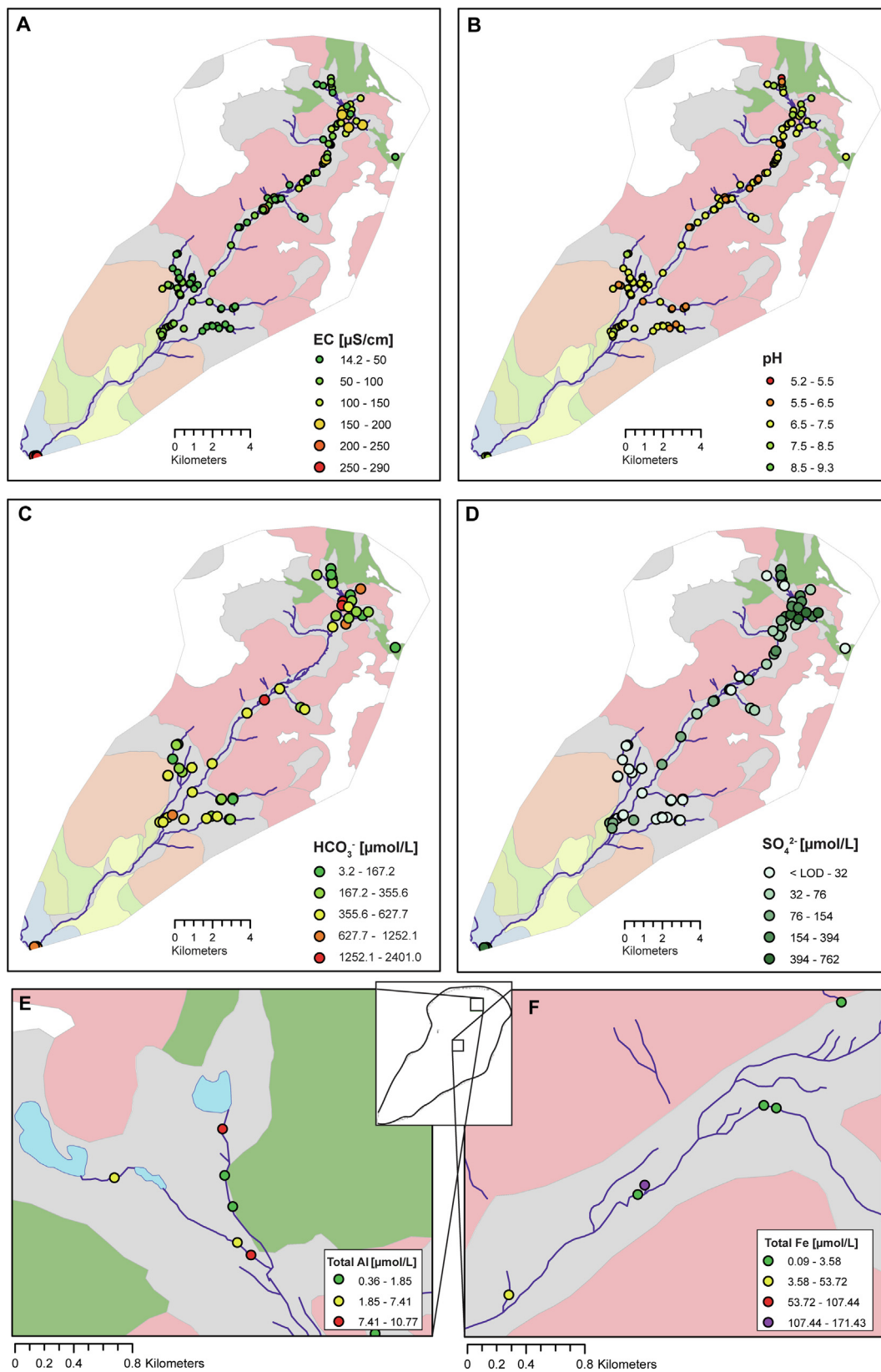


Fig. 6. Spatial patterns in surface water EC (a), pH (b), concentration of bicarbonate (c) and sulphate (d). Hazardous concentrations of aluminum (e) and iron (f) were found in specific areas. Supplementary Figs. B.2–B.20 contain similar maps for every analysed compound. Legend for the geological basemap is in Fig. 1.

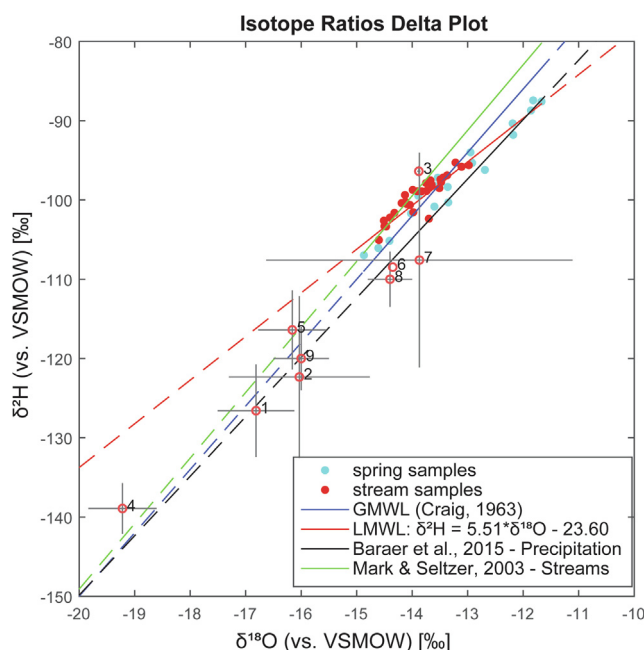


Fig. 7. Stable isotope ratios of oxygen and hydrogen, reported on the VSMOW scale. Scatterplot dots are coloured by water type. GMWL indicates the Global Meteoric Water Line established by Craig et al. (1963). Reference data are mixing lines established for stream samples by Mark and Seltzer (2003), and a Local Meteoric Water Line for precipitation samples (2006–2007) in the Cordillera Blanca from Baraer et al. (2015). LML indicates a local mixing line established by fitting a linear trend line through meltwater stream (red) and spring (light blue) samples from this study. Statistics describe correlation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for this study only. Dots with error bars represent findings from other studies cited below: Glacial Meltwater, July 2009, Quilcayhuanca (Burns et al., 2011) Groundwater (taken from springs), July 2009, Quilcayhuanca (Burns et al., 2011) Glacial Meltwater, August 2010, La Paz (Guido et al., 2016) Glacial Meltwater, March 2011, La Paz (Guido et al., 2016) Glacial Meltwater, August 2012, La Paz (Guido et al., 2016) High Elevation Streams, March 2011, La Paz (Guido et al., 2016) Shallow Groundwater, August 2012, La Paz (Guido et al., 2016) Shallow Groundwater, 2008, Cordillera Blanca (Baraer et al., 2015) Streams, 2008, Cordillera Blanca (Baraer et al., 2015). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Hydrochemistry

The most abundant anion is HCO_3^- with an average concentration of 344 $\mu\text{mol/L}$, followed by SO_4^{2-} (avg. 156 $\mu\text{mol/L}$) and Cl^- (avg. 133 $\mu\text{mol/L}$). The most abundant cation is Ca^{2+} (total Ca avg. 324 $\mu\text{mol/L}$), followed by Na^+ (total Na avg. 144 $\mu\text{mol/L}$) and total Si was 160 $\mu\text{mol/L}$ on average. Concentrations of Cr, Ga, In, Mo, Pb, Sb, As, Be, Cd, Co and Ni are generally below LOD (Table C.6) and not used for further analysis.

EC is generally below 150, with a maximum of 290 $\mu\text{S/cm}$ (Fig. 6a). pH is above 5.20 in all locations (Fig. 6b). Alkalinity (3.2–2401 $\mu\text{mol/L}$, LOD = 1.7 $\mu\text{mol/L}$, Fig. 6c) and SO_4^{2-} concentrations (< LOD – 762 $\mu\text{mol/L}$, LOD = 15 $\mu\text{mol/L}$ Fig. 6d) are highly variable. Health limits are exceeded only in few locations (Fig. 6e–f). The Supplementary material contains all concentrations and detection limits (Table C.6), used health limits (Table B.1) and maps per compound (Figs. B.1–B.19).

A delta plot of isotope values found in the Ulta valley shows correspondence with known delta plots for precipitation and surface water in the Cordillera Blanca. However, our samples show a lower slope value (Fig. 7), especially evident in meltwater streams ($\delta^2\text{H} = -27.0 + 5.2\delta^{18}\text{O}$) and less in springs ($\delta^2\text{H} = -16.4 + 6.1\delta^{18}\text{O}$). Compared to data from previous studies of isotope ratios in glacial

meltwater and shallow groundwater (Guido et al., 2016; Burns et al., 2011) our isotope values are relatively enriched and highly variable among individual tributaries (Figs. B.17 and B.18).

3.4. Effect of till composition on water quality

No generic change in compound or element concentration is found combining all downstream and upstream measurements. Changes in the chemical quality of surface do however depend on the mineralogical composition of tills in the morainic ridge. Relations between till composition and water quality parameters are presented as correlations between till properties and observed changes in water quality parameters (calculated as downstream sample – upstream sample) (Fig. 8). For 23 locations both up- and downstream water measurements and a till sample are available. Only 13 locations have alkalinity and isotope data. For 11 locations a direct measurement of a moraine-fed spring was available.

Changes in Mg concentration correlate significantly with Chicama content of tills (Fig. 8a), and change in SO_4^{2-} concentration (Fig. 8b) shows a tendency (Table C.5). Tills with a lower KSat are associated with increases in SO_4^{2-} , Fe and Mg, although only the correlation with Mg is significant and SO_4^{2-} shows a tendency (Fig. 8d–e). The hypothesized correlation between KSat and EC is insignificant (Spearman's $r = -0.12$, $p = 1$, $n = 23$). In some cases, presence of a specific compound in tills is associated with an increase of concentration of that compound in water after contact with a morainic ridge (e.g. for SO_4^{2-} , Fig. 8c), although never to a significant extent. All other relations not depicted in Fig. 8 are insignificant (Table C.5).

Higher Chicama content in tills is associated with increases in Mg and Fe and decreases in Al and heavy isotope enrichment downstream of the till deposit (Fig. 9a–e). Only the change in Mg differs significantly among low-Chicama and high-Chicama tills. Spring water originating from till with high Chicama content shows increased concentration of SO_4^{2-} , Ca, K and Mg relative to springs originating from tills with low Chicama content (Fig. 9f–i), although none of these differences are significant. All other differences not depicted in Fig. 9 are insignificant (Table C.4).

3.5. Altitudinal trends in water quality

EC and pH do not correlate with elevation ($p = 0.62$ & 0.18 , respectively), but carbonate alkalinity decreases significantly with elevation. Furthermore, concentrations of B, Na, Cl and Si decrease significantly with elevation, whereas SO_4^{2-} shows a tendency of increase with elevation (Fig. 10a–f). Other compounds show no significant correlation with elevation. Both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ show a significant negative correlation with elevation (Fig. 10g–h). Overall, $\delta^{18}\text{O}$ is given by $-11.26 - 0.0006 \cdot Z$ and $\delta^2\text{H}$ is given by $-86.82 - 0.0031 \cdot Z$, where Z is elevation in meters. Steeper declines in heavy isotope enrichment are found for spring samples than for meltwater stream samples, although only significant for $\delta^2\text{H}$ (Fig. 10g–h).

4. Discussion

4.1. Comparison with other glacial valleys in the Río Santa basin

In general, waters of the Río Buín catchment contain far lower levels of polluting solutes compared to results from previous studies in nearby tributaries of the Río Santa (Fortner et al., 2011; Burns et al., 2011). Most pH values are in the range of the global mean (7–10) for meltwater (Tranter, 2003). Trace metal contents are generally below the WHO limits, contrasting the results from Fortner et al. (2011) in the Río Quilcay catchment. Locations with low pH and high concentrations of Al, SO_4^{2-} and Fe are only observed in specific places in the northernmost tributary in the study area originating from a wetland overlying Chicama Formation containing tills and to some extent in the

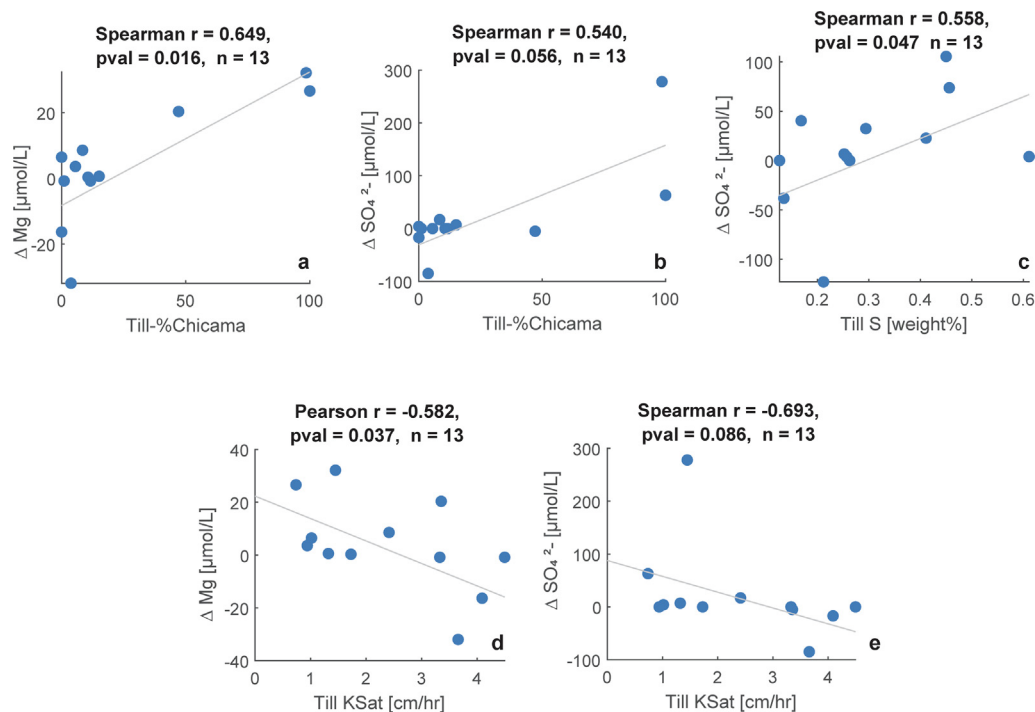


Fig. 8. Correlations between till physical and chemical properties and observed changes in water quality calculated as Δ = concentration downstream of till – concentration upstream of till. KSat = Saturated Hydraulic Conductivity. P-values are corrected p-values.

easternmost tributaries (Fig. 6). Moreover, Fortner et al. (2011) and Burns et al. (2011) report a very low alkalinity in the Quebrada Quilcayhuanca, whereas in this study HCO_3^- generally contributes more to total anions than SO_4^{2-} and other anions (Table C.6). These differences are consistent with findings of Mark et al. (2005) and Walsh (2013). Mark et al. (2005) found that the Río Buín had the second highest alkalinity (56.5 mg/L of HCO_3^-) of all tributaries to the Río Santa. Fig. 11 presents measurements of tributaries of the Río Santa from Walsh (2013) complemented with a measurement of the Río Buín (close to the confluence with the Río Santa) from this study. The negative correlation between Chicama cover and HCO_3^- (Fig. 11b) is significant, suggesting that Chicama cover is indeed related to acidification. However, previous studies have not explicitly measured $\text{CO}_3^{2-} / \text{HCO}_3^-$ ions but assumed that the sum of both is given by the difference in charge between measured anions and cations (Tranter et al., 2005; Fortner et al., 2011; Burns et al., 2011; Walsh, 2013).

Correlations between Chicama cover and both pH and SO_4^{2-} concentrations are not significant (Fig. 11a and c). It seems counter-intuitive that no clear relations exist for Chicama Formation cover and H^+ and SO_4^{2-} concentration. This can be partly explained by a case-study by Walsh (2013) using data from Mark and Seltzer (2003), which indicates that subglacial weathering of pyrite has a more profound effect on water quality than aerial exposure of pyrite-rich material in the Quebrada Quilcayhuanca. Contrary to the Río Buín catchment, in Mancos, Tabla and Olleros hot springs are present which constitute an additional input of sulphides (Walsh, 2013). Another potential explanation is local variability in pyrite content of the Chicama formation (Paragraph 4.3).

Water samples are within the -15‰ to -11.5‰ range for $\delta^{18}\text{O}$ and -110‰ to -85‰ range for $\delta^2\text{H}$ and similar to ratios found by Mark and McKenzie (2007) in the Río Buín in 2004 – 2006. These findings are comparable to results from other studies in the Cordillera Blanca (Burns et al., 2011) and the Bolivian Andes (Guido et al., 2016), although differences may exist based on valley-to-valley variation, seasonal variation (Mark and McKenzie, 2007) and year-to-year variation (Gonfiantini et al., 2001). Our minimum $\delta^{18}\text{O}$ value of -14.87‰ is comparable to the value found for the topmost snow layer of the

Huascarán glacier (Thompson et al., 1995). Burns et al. (2011) found a difference in isotopic composition between streams and springs, the latter having a slightly less negative average $\delta^{18}\text{O}$ composition. Similarly, we find that $\delta^{18}\text{O}$ is higher on average in springs than in meltwater streams ($p < 0.005$, $n = 71$).

Interestingly, we find a mixing line of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ with a lower slope value and higher intercept than earlier mixing lines established for both surface water and precipitation for the Cordillera Blanca (Mark and Seltzer, 2003; Baraer et al., 2015). This is particularly pronounced in meltwater streams and less in springs (Fig. 7). A lower slope value and higher intercept (deuterium excess) for surface water may be an indication of post-precipitation fractionation processes such as evaporation (Dansgaard, 1964). This could indicate that meltwater streams undergo evaporation along their trajectory in this catchment, whereas shallow groundwater from moraine-fed springs does not, or to a lesser extent. In contrast, previous isotopic studies of surface water in the Cordillera Blanca did not find significant effects of post-precipitation fractionation (Baraer et al., 2015; Mark and Seltzer, 2003). In general, spring water samples in the Ulta Valley are more comparable to the multi-year local meteoric water line of precipitation for the Cordillera Blanca area from Baraer et al. (2015) than water from meltwater streams (Fig. 7), indicating that morainic ridges may act as reservoirs for infiltrated precipitation.

Few studies incorporate detrending (paragraph 2.5) for temporal variations of chemical quality of water and most do not mention detrending at all (Mark et al., 2005; Fortner et al., 2011; Burns et al., 2011; Baraer et al., 2015), although variation of EC due to diurnal variations in glacial melt has been demonstrated to exist (Appendix D.3.1 and Burns et al., 2011). EC is inversely related to discharge in proglacial environments as glacial melt is usually more dilute than water from other sources (Burns et al., 2011). However, for pH, isotope ratios and specific compound concentrations, these relations may not be straightforward. Nimick et al. (2003) found widely different compound-specific relations with discharge, which could be explained to some extent by compound-specific sorption processes and geochemical alterations occurring within streams. Additionally, as glacial meltwater may differ in composition from other water sources, not all compounds

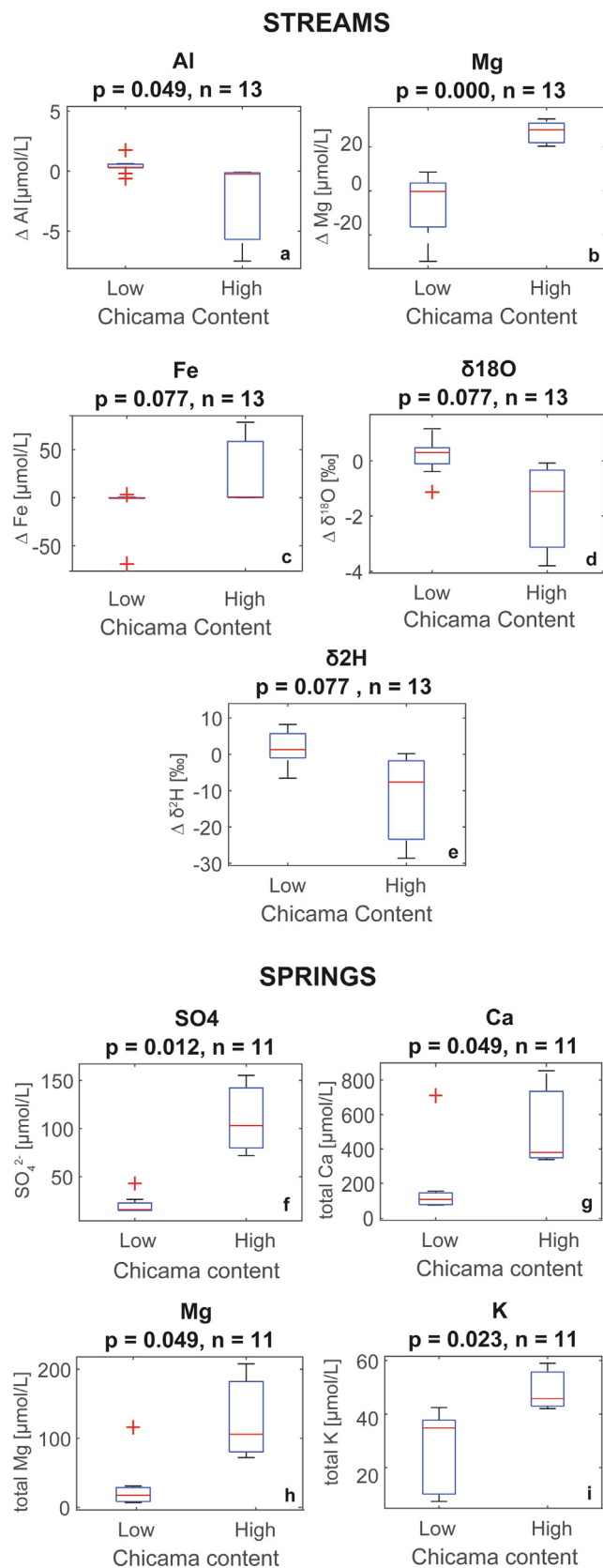


Fig. 9. a–g) Changes in water quality parameter observed upon contact with moraines with high and low content of Chicama shales. Changes in water quality were calculated as Δ = concentration downstream of till – concentration upstream of till. h–l) Difference between water quality parameters of springs between springs originating from moraines with high and low content of Chicama shales. “+”-signs indicate outliers. P-values are corrected p-values.

are suspected to vary with meltwater discharge (Burns et al., 2011; Baraer et al., 2015). Spatial differences in diurnal variation in EC throughout glacial catchments may be an interesting indication for relative glacial melt contribution.

4.2. Spatial trends of water quality in the Ulta valley

Increasing Si and HCO_3^- concentrations are observed downstream as opposed to decreasing SO_4^{2-} concentration (Figs. 10 and 12). This is consistent with theories of sequential weathering of pyrite and carbonates followed by silicates in proglacial deposits of increasing age (Anderson et al., 2000; Tranter et al. 2005; Burns et al., 2011; Walsh, 2013). These changes may also reflect variations in local geology from Chicama Formation to intrusive rocks further downstream from the active glacier zone in the Quebrada Ulta (Fig. 12). It may also indicate that streams receive increasing amounts of shallow groundwater derived from precipitation, which has been found to result in higher concentrations of Na and HCO_3^- , lower SO_4^{2-} concentrations and higher $\delta^{18}\text{O}$ compared to glacial meltwater (Baraer et al., 2015; Burns et al., 2011). Lastly, increasing B concentrations (Fig. 10b) could be related to the use of pesticides.

We found differential trends over elevation for water isotopes in meltwater streams and springs (Fig. 10g–h). A correlation between isotope signatures and elevation in precipitation and surface water is found throughout the Cordillera Blanca and may be attributed to (1) the elevation of source precipitation, known as the “rain-out effect” (Windhorst et al., 2013; Rozanski and Araguás-Araguás, 1995) and (2) a decrease in relative contribution of glacial meltwater (depleted in heavy isotopes) versus shallow groundwater (Baraer et al., 2015; Gordon et al., 2015; Burns et al., 2011; Mark and McKenzie, 2007). Especially in case of precipitation derived shallow groundwater, spring isotopic composition is expected to follow trends for $\delta^{18}\text{O}$ in precipitation against elevation, whereas (partly) meltwater derived streams may not, due to contribution of glacial melt from high source elevation (Mark and McKenzie, 2007). To test our hypothesis that moraines may act as reservoirs for precipitation derived shallow groundwater during the dry season, we compared isotope ratios and their trends against elevation in springs and streams with literature values for surface water and precipitation in Andean catchments. In Andean catchments, slope values for $\delta^{18}\text{O}$ in precipitation against elevation are typically between -0.24 and -0.17‰ per 100 m rise, and between -1.7 and -1.12‰ per 100 m rise for $\delta^2\text{H}$ (Baraer et al., 2015; Windhorst et al., 2013; Rozanski and Araguás-Araguás, 1995). Results in Fig. 10g–h indicate that overall, slope values for surface water in the Ulta Valley are much lower (-0.06‰ for $\delta^{18}\text{O}$ and -0.31‰ for $\delta^2\text{H}$). Slope values for regression lines of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ over altitude for spring water (-0.12‰ and -0.90‰) (Fig. 10g–h) are more comparable to previously mentioned findings for precipitation, albeit still low. Especially at lower elevation, springs are demonstrated to be more enriched in heavy isotopes than meltwater streams (Fig. 10g–h), also indicating that springs likely contain less meltwater than streams (Gordon et al., 2015). Apart from a significant relation with elevation, distinct spatial variability in isotope signatures is observed. Tributaries from sub-catchments with a larger degree of glaciation have relatively low $\delta^{18}\text{O}$ and $\delta^2\text{H}$ levels (Figs. B.17 and B.18), which may indicate a larger fraction of glacial meltwater with a high source elevation. Several springs originating from moraines and talus slopes show particularly positive isotope ratios (Figs. B.17 and B.18) compared to stream samples from the same altitude. One lake sample shows an anomalously high enrichment of heavy isotopes, which is attributed to high evaporation of water. Altogether, samples from moraine-fed springs are more enriched in heavy isotopes, show larger similarity to the local meteoric water line (Baraer et al., 2015) and show larger similarity to known gradients of heavy isotope enrichment over source area elevation of precipitation. This suggests that moraines act as reservoirs of precipitation during the dry season. However, isotope ratios of spring

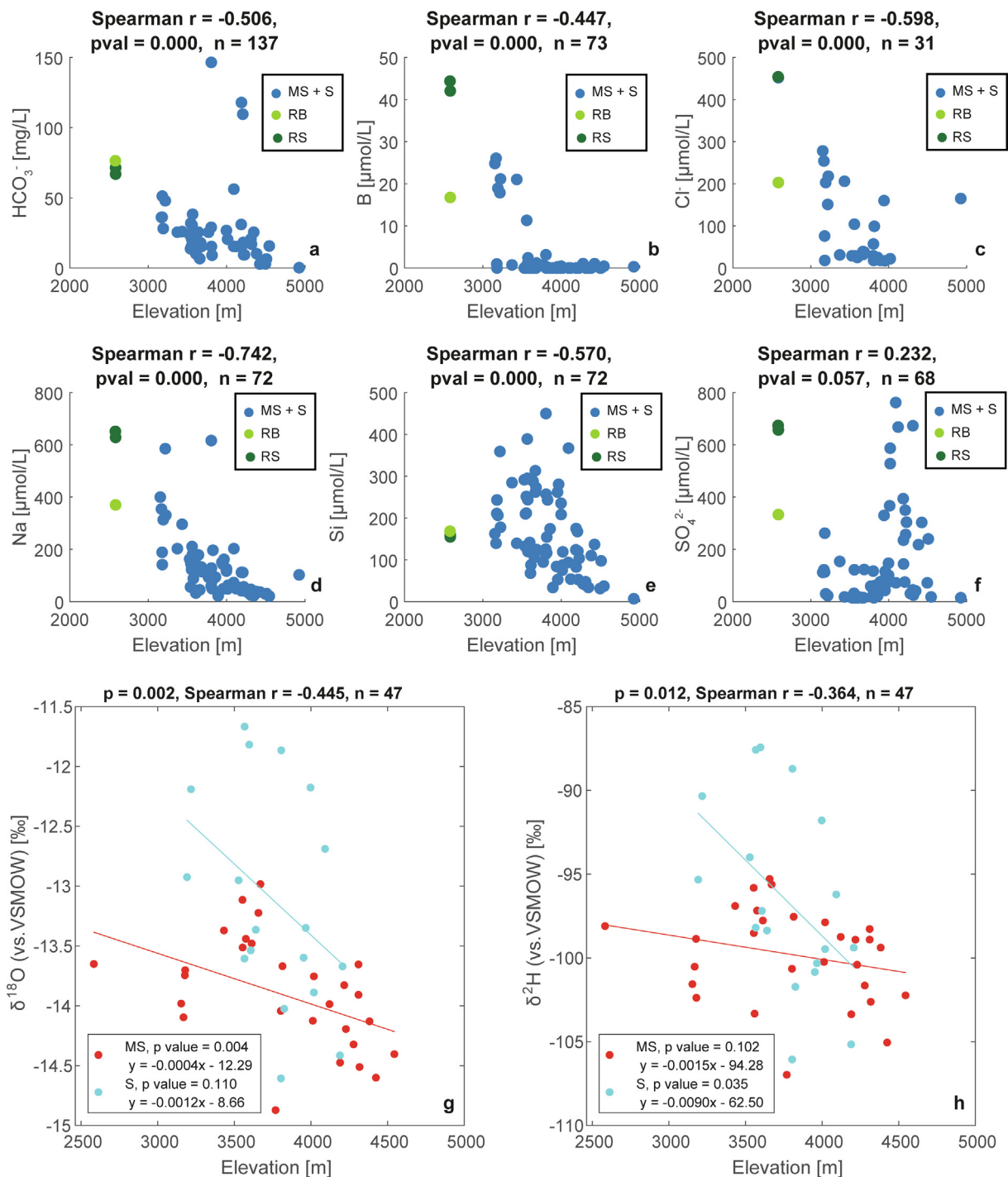


Fig. 10. Correlations between water quality parameters and elevation of water sample location. a–f) Trends in solute concentrations of meltwater streams and springs (MS + S) over elevation, Rio Santa (RS) in dark green, Rio Buin (RB) in light green. P values are corrected p-values. g–h) Correlation between elevation and isotope ratios of oxygen (g) and hydrogen (h). Red dots indicate meltwater stream (MS) samples, light blue dots indicate spring (S) samples. The reported correlation statistics in the figure titles are for both water types combined. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

water samples also show higher variability over elevation than meltwater streams (Fig. 10g–h), which indicates a substantial degree of variation in source area or in post-precipitation fractionation. Shallow groundwater from moraine-fed springs may be derived from precipitation or infiltrated glacial meltwater from various source elevations, as a result of which individual springs may have distinct isotopic signatures (Baraer et al., 2015). Possibly, groundwater recharged at high elevation contributes to springs and/or baseflows at lower elevation via

such subsurface aquifers. Tracer studies could be used to identify various pathways (Gordon et al., 2015).

4.3. Geochemistry of the Ulta valley

Mineralogical classification of rock fragments yields clear spatial distinctions between presence of intrusives and Chicama rock fragments in tills (Fig. 4), which in turn are strongly related to till source area

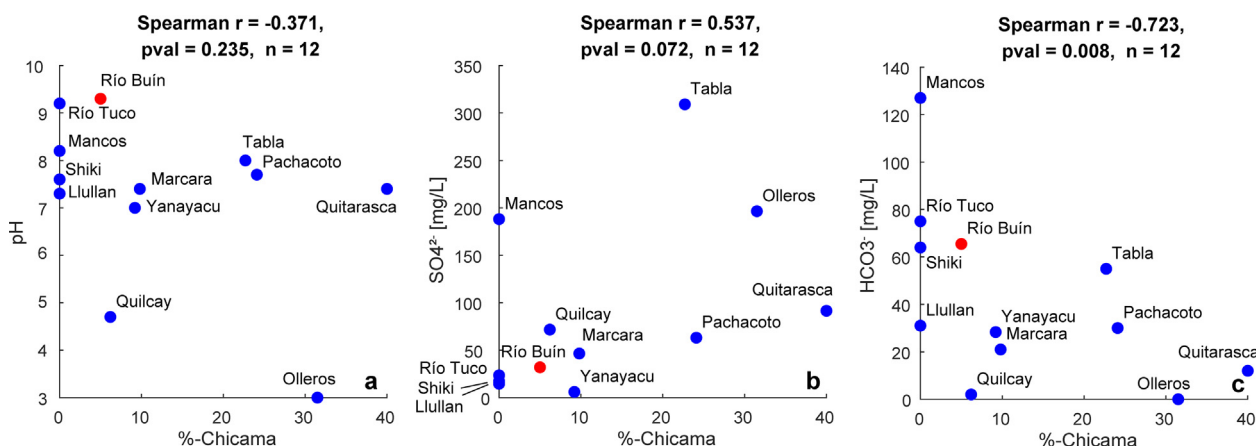


Fig. 11. % areal cover of Chicama formation plotted against several important hydrochemical parameters. a) Chicama formation & pH, b) Chicama formation and sulphate, c) Chicama and bicarbonate. Data from Walsh (2013). Río Buín, with data from this study, is indicated in red. Locations of other catchments used for comparison can be found in Fig. 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Table 2, Fig. 1). According to Petford and Atherton (1996) intrusives in the Quebrada Ulta are generally metaluminous leucogranodiorite with high contents of sodic plagioclase, which is consistent with the findings of this study. Although the Chicama formation is known to be a very heterogeneous deposit (sandstones, shales, argillites and pyrites) (Burns et al., 2011; Enay et al., 1996), the Chicama formation in the Cordillera Blanca consists mostly of dark shales with fine layers of sandstone (Smith, 1988). In the Ulta Valley, locally quartz-veins and sandstone fragments are found in till samples, although Chicama fragments are almost exclusively dark shales (Table C.2), consistent with Smith's (1988) findings.

We found a tendency for a positive correlation between till Chicama content and till Fe content but no significant correlation between till Chicama content and till S content (Table 2). This is remarkable, as Fe and S are expected to occur as pyrite (FeS_2) in Chicama shales. Possibly, high initial rates of pyrite oxidation result in high leaching rates of SO_4^{2-} (Anderson et al., 2000; Tranter et al., 2005) whereas Fe precipitates locally as ferric oxyhydroxides (Åström and Åström, 1997; Munk et al., 2002). Indeed, a significant proportion of rock fragments analysed for this study contained ferric oxyhydroxide coating (Magnússon, pers. obs). Another potential explanation is local variability in pyrite content of Chicama shales within the Cordillera Blanca. Sampled Chicama shales could contain relatively little pyrite compared to those in other sites throughout the Cordillera Blanca, although element concentrations (Fig. 5) suggest that it is present. Fig. 5 demonstrates significant, positive associations between concentrations of S, As, Fe, and Cu indicating that arsenopyrite and chalcopyrite may also be present in the Ulta valley. The presence of these sulphides was already noted by Bodenos and Ericksen (1955). Total Mg in tills also shows a tendency for a positive correlation with Chicama content (Table 2), and significant, positive correlations (almost 1:1) with till S content and till Fe content (Fig. 5). This may be an indication that apart from pyrite, Chicama shales contain considerable amounts of Mg, possibly in the form of ferromagnesian minerals. Vikre (1998) found that due to hydrothermal alterations rocks close to contact zones may have atypical composition. The presence of Mg in the Chicama Formation or in contact zones is supported by the positive correlation between till Chicama content and observed difference in Mg concentration in water samples downstream and upstream of tills (Fig. 8). To facilitate analysis of the effect of source rock composition on water quality throughout the Cordillera Blanca, local differences in the composition of Chicama shales (e.g. content of pyrite and ferromagnesian minerals) could be studied by X-ray Diffraction analysis (XRD).

4.4. Influence of glacial sediments

The lack of a clear generic effect downstream of morainic ridges compared to upstream indicates that the influence of morainic ridges on the chemical quality of surface water is likely very limited. However, pronounced differences in changes in ion and element concentrations are observable between waters that had been in contact with Chicama-rich and Chicama-poor tills (see Fig. 9). This indicates that the effect of tills on water quality depends on till composition (Chicama shale content in this case). Chicama-rich tills are associated with increased Mg concentrations, a compound that is also found in Chicama-rich tills (Fig. 5). The hypothesized increase in concentration of SO_4^{2-} in surface water after contact with a Chicama-rich moraine is visible (Figs. 8 and 9), although effects are small and generally insignificant. Despite weaker correlations, the three samples with the highest HCO_3^- content ($> 1600 \mu\text{mol/L}$) are all moraine- or talus-fed springs, although due to low discharges little effect propagates downstream of such springs. Still, this may indicate that locally moraines (and potentially talus deposits) may be important sources of HCO_3^- . No significant increases in total Fe were observed upon contact with morainic ridges. The reason for low Fe concentrations is most likely its local precipitation as oxyhydroxide (Åström and Åström, 1997; Munk et al., 2002). Similarly, trace metals associated with acid rock drainage may be adsorbed onto mineral surfaces of the streambeds at circumneutral pH (Munk et al., 2002; Schemel et al., 2007; Lee et al., 2002). Munk et al. (2002) found that 75% of dissolved trace metals were removed from streams by sorption to precipitates in a confluence zone with pH 5 – 6.3 of a highly acidic and alkaline tributary, which is similar to pH in the Ulta Valley. This indicates that high alkalinity in the Ulta Valley likely buffers potential contamination. Lastly, the difference in observed effect between Chicama-rich and Chicama-poor moraines may be related to the relative contribution of coupled pyrite oxidation and CO_3^{2-} dissolution typical of young proglacial deposits (Walsh, 2013; Tranter et al., 2005; Anderson et al., 2000). However, the occurrence of Chicama bedrock, the age of moraines and the relative importance of meltwater and precipitation-derived shallow groundwater seem to be subjected to the same altitudinal trend (Fig. 12), making it difficult to attribute observed changes in water quality over altitude to any of these potential factors.

Interestingly, no significant impacts of Chicama material in tills on EC and pH are observed. In case of pH it is possible that the relatively high abundance of HCO_3^- within the Ulta valley buffers any addition of H^+ resulting from natural weathering processes. Additionally, no significant effect of KSat on changes in EC is observed. This could also be explained by low contribution of moraine-fed springs to total water discharge.

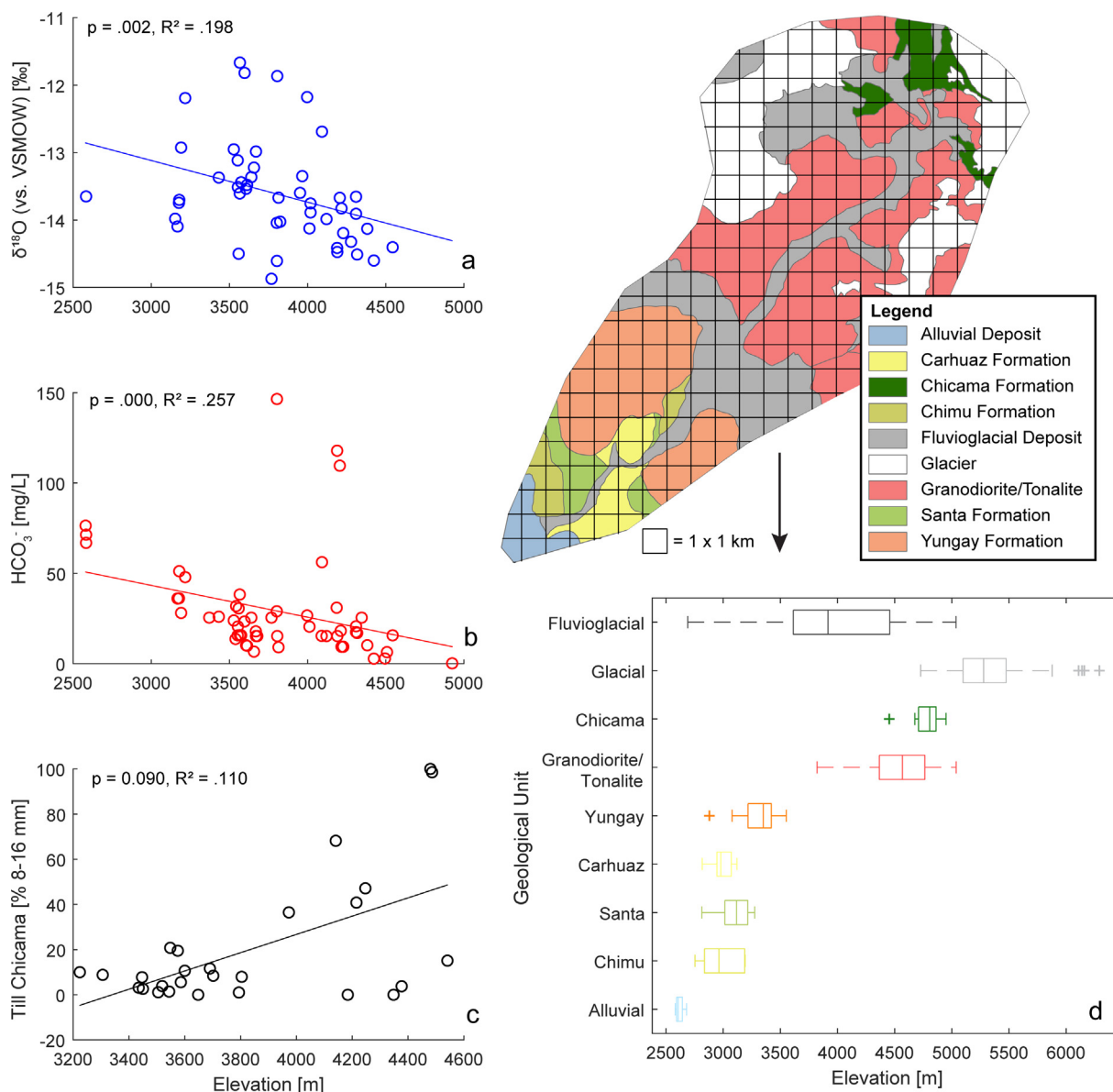


Fig. 12. Summary of main trends potentially influencing observed altitudinal variation in water quality. a) $\delta^{18}\text{O}$ of spring and meltwater stream samples over elevation. b) bicarbonate concentration of all available water samples over elevation. c) Chicama shale content of till over elevation. d) dominant geology of 1 x 1 km fishnet cell over mean elevation of fishnet cell. “+”-signs indicate outliers.

5. Conclusion

The till mineralogy is strongly correlated to paleoglacier lithology. This correlation implies that it is possible to predict the subglacial lithology from recent moraine deposits. This may be a valuable tool in assessing the impact of deglaciation of catchments worldwide. In this respect it is noteworthy that most Chicama shales occur in the higher, still glaciated areas of the Quebrada Ulta. This may result in secondary negative effects of climate change on water safety in the Río Santa catchment through deglaciation.

Morainic ridges are found to have no significant generic effect on water quality in the Ulta Valley. Instead, the changes in the chemical water quality upon contact with a morainic ridge depend on the mineralogical composition (Chicama content) of the tills present in the ridge. Higher Chicama content is associated with increases in solute load of Mg and in some cases SO_4^{2-} . Isotopic signatures of moraine-fed springs indicate that moraines are potential reservoirs for precipitation-derived shallow groundwater during the dry season. However, variable isotopic signatures among individual springs from morainic ridges

independent of elevation suggest that relative storage of precipitation-derived and glacial meltwater varies among morainic ridges (and potentially also among talus cones and other permeable deposits) and represents an important factor in the influence of morainic ridges on water quality. Our results demonstrate that local changes in the chemical quality of surface water can be traced back to the mineralogy of specific glacial tills deposits and thereby to their source area geology. This may help to identify potential sources of natural contamination and to explain spatial patterns of chemical quality of surface water in glacial catchments.

Overall, water quality in the Río Buín catchment seems higher than in other areas in the Cordillera Blanca (most notably Quebrada Quilcayhuanca and the Río Negro catchment) when compared to drinking water standards. Low provenance of Chicama Formation and high alkalinity help explain the relatively good water quality in the Río Buín catchment.

We found collinear trends in decreased presence of Chicama formation, occurrence of subglacial and proglacial weathering processes and relative quantities of meltwater and precipitation-derived shallow

groundwater with decreasing elevation. Therefore, it remains a challenge to attribute trends in chemical water quality over elevation to any specific mechanism.

CRedit authorship contribution statement

Rúna Magnússon: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Visualization. **Erik Cammeraat:** Conceptualization, Methodology, Investigation, Writing - review & editing, Supervision. **Andreas Lücke:** Investigation, Writing - review & editing. **Boris Jansen:** Investigation, Writing - review & editing, Supervision. **Anais Zimmer:** Resources, Writing - review & editing. **Jorge Recharte:** Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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