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Elevated stream trace and minor element concentrations in the foreland of receding tropical glaciers

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ABSTRACT

Globally, the ongoing retreat of mountain glaciers will ultimately diminish fresh water supplies. This has already begun in watersheds with greatly reduced glacial coverage. Still unknown are the affects of glacial retreat on downstream water quality, including the threats to human and ecosystem health. In the Cordillera Blanca, retreating glaciers have exposed sulfide-rich rock outcrops, negatively affecting the quality of the glacial meltwater. This study has evaluated glacial melt stream hydrogeochemistry in the sulfide-bearing Rio Quilcay watershed ($\sim 9^{\circ}27'S$, $\sim 77^{\circ}22'W$) during the 2008 dry season. Surface water samples were collected from the upper 12 km of the watershed during the 2008 dry season. Dissolved ($0.4 \mu\text{m}$) and unfiltered acidified ($\text{pH} < 2$) Al, Co, Cu, Fe, Ni, Mn, Pb, Zn and dissolved major ions and organic C (DOC) concentrations were quantified and pH and temperature were measured in the field. Twenty of 22 stream samples had pH values below 4, generating significantly ($p < 0.01$, $\alpha = 0.05$) greater cation denudation normalized to discharge than other worldwide glacier-fed streams. Additionally, dissolved trace and minor element concentrations were comparable to acid mine drainage. Non-conservative dissolved element behaviors resulted from adsorption/desorption reactions in tributary mixing zones. At low pH values, hydrous Fe oxides acted as the dominant sorption surfaces. The poor water quality observed in Cordillera Blanca headwaters coupled with the likely exposure of additional sulfide-rich outcrops from ongoing glacial retreat may pose water quality challenges.

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1. Introduction

The rapid retreat of tropical glaciers has heightened the awareness of their importance as a major water resource, particularly during the dry season (Bradley et al., 2006; Ebi et al., 2007; Mark et al., 2010). As Andean glaciers recede, there has been an increase in seasonal discharge and in catchments with the least glacierized area and a decrease in total annual discharge (Juen et al., 2007; Mark et al., 2005). While many studies have illustrated ways in which glacier recession affects the quantity of water being discharged from retreating glaciers (Mark et al., 2005, 2010; Pelto, 1993; Schotterer et al., 2003), very little research has examined how changes in the cryosphere affect water quality, especially the behavior of potentially toxic trace and minor elements (Fortner et al., 2009; Mitchell et al., 2001, 2006). Dry season examinations, including this study, are particularly important because during this period glacial melt provides up to 40% of the total discharge in the

Cordillera Blanca (Mark et al., 2005). The dry season thus provides the greatest potential opportunity to evaluate water quality deterioration related to glacial retreat.

Water quality downstream of retreating glaciers relates both to water management practices and natural biogeochemical cycling. The biogeochemistry of glacial melt streams largely reflects the underlying geology (Anderson, 2007; Brown et al., 2006; Hodson et al., 2002). In the Cordillera Blanca, the exposure of fresh sulfide-rich lithologies by retreating glaciers (Wilson et al., 1967) is thus integral to the biogeochemistry of proglacial streams. Before water quality issues related to glacial retreat can be understood for larger-scale watersheds, or be forecasted to inform future management and mitigation, the present-day water quality in small-scale watersheds ($< 100 \text{ km}^2$) such as glacial headwaters must be examined. Therefore, this study has evaluated a proglacial Andean valley in the Cordillera Blanca, Peru. Establishing baseline stream geochemistry was the first and foremost goal of this study in order to begin characterizing water quality issues related to ongoing glacial retreat. To achieve this goal, the dry season geochemistry of trace and minor elements was examined in the proglacial Rio Quilcay from within 1 km of its glacier origins to 12 km downstream.

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The first objective was to characterize the proglacial stream hydrogeochemistry. Dominant weathering processes were identified and major cation yields were compared with yields from other glacial stream waters worldwide. Dissolved trace and minor element concentrations were also characterized to further understand proglacial water quality and ecosystem health, since dissolved element concentrations are the most bio-accessible. The second objective was to determine the downstream controls on dissolved elements in the Rio Quilcay in relation to tributary additions. Direct measurements of discharge were made at selected sites to understand major cation dilution behavior. Because not all sites had measured discharge, dissolved trace and minor elements were normalized to Na, a conservative element, to assess dilution behavior as well as to understand solute mixing behaviors as tributaries join the Rio Quilcay. Because solutes have not all mixed conservatively, the relationship of dissolved element concentrations versus pH and PHREEQC modeled saturation indices were used to assess non-conservative behaviors (e.g. sorption and coprecipitation).

Bordered by the Cordillera Blanca and Cordillera Negra, the Rio Santa watershed (5000 km²) above the Cañon del Pato is home to approximately 260,000 people (Mark et al., 2010) (Fig. 1). The population of the valley is distributed among several urban centers that include Huaraz (120,000), Caraz (23,500), Yungay (20,000) and approximately 1500 small rural settlements (INEI, 2007). Inhabitants of the region rely on the river and glacial discharge in the upper watersheds of the Cordillera Blanca for domestic consumption, livestock, irrigation for agriculture and hydroelectric power generation (Bury et al., 2010; Young and Lipton, 2006). Overall, the water quality in the Upper Santa River watershed is threatened by historical and present-day mining and increasing near-stream disposal of domestic, industrial and mining waste as well as livestock grazing (BCRP, 2009; Young and Lipton, 2006). However, regionally, baseline water quality issues associated with natural rock weathering have not been identified. What is known is that glaciers in the Cordillera Blanca have lost an average of 22.4%

of their total area between 1970 and 2003 (Racoviteanu et al., 2008). Regional proglacial groundwater reserves are also likely to be threatened by glacial retreat with several Cordillera Blanca proglacial watersheds storing water for less than 4 a (Baraer et al., 2009) and, therefore, interacting with surface water on short time-scales.

This study examined the Rio Quilcay, a glacial-fed tributary to the Upper Rio Santa in the uppermost 12 km at elevations ranging from approximately 4800 to ~3800 m.a.s.l. (Fig. 1). The study area is grazed (not heavily) by livestock and is irrigated in the lowermost reaches, but is not affected by mining (i.e. no present or past mines). The sampled region of the Rio Quilcay receives glacial melt directly and indirectly from two proglacial lakes: Cuchillacocho and Tulpacocho. Geology in this region of the Cordillera Blanca includes pyrite schists and phyllite and pyrite-bearing quartzite intruded by a central granodiorite-tonalite batholith all overlain by clastic sediments deposited during glacial retreat (Wilson et al., 1967). Sulfide-rich lithologies are prevalent especially in the north-eastern high-altitude regions of the Cordillera Blanca (e.g. the Rio Quilcay Valley) with fresh exposures resulting from glacial scour (Wilson et al., 1967). Many headwaters in the Cordillera Blanca, including the Rio Quilcay and its tributaries, have ochreous precipitates, as illustrated in Tributary C (Fig. 2).

2. Methods

In July 2008, water samples were collected from a total of 24 stream localities, seven minor tributaries, and one lake in the upper Rio Quilcay watershed (Fig. 1). Field measurements of cross-sectional area and three evenly spaced point measurements of flow using a flow meter were used to determine discharge at selected sites including above and below the confluence of the NW and NE Branch of the Rio Quilcay and at site 24, one of the lowermost sites (Fig. 3). Stream and tributary samples were collected from the thalweg to ensure mixing. Lake Tulpacocho was sampled

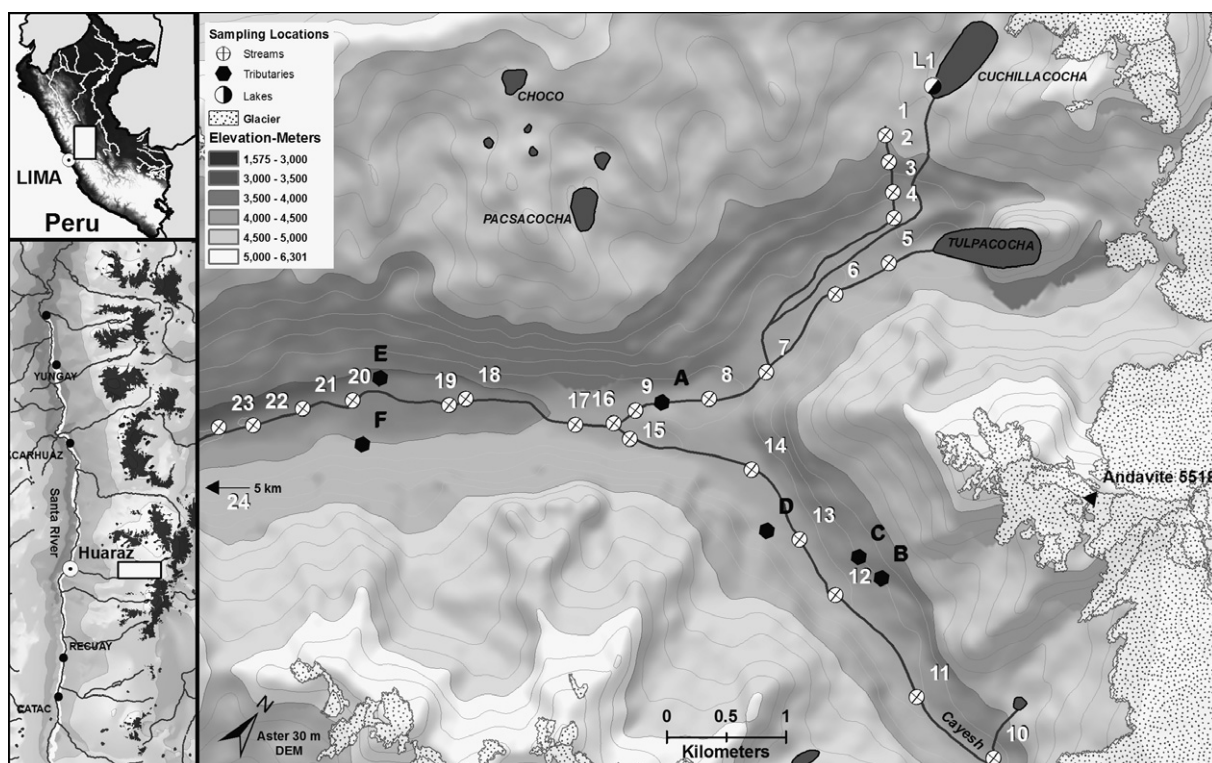


Fig. 1. Sampling locations in and along the upper 12 km of the Rio Quilcay, Cordillera Blanca, Peru. Main stream samples labeled 1–24, tributaries labeled A–F.

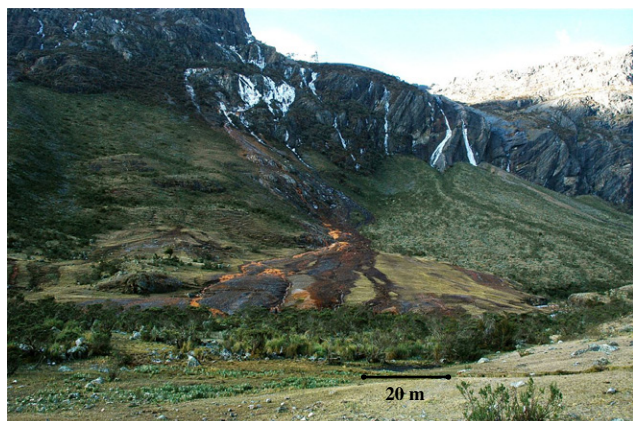


Fig. 2. Tributary C feeds the Northeast Branch of the Rio Quilcay, Peru. This tributary has abundant ochreous precipitates.

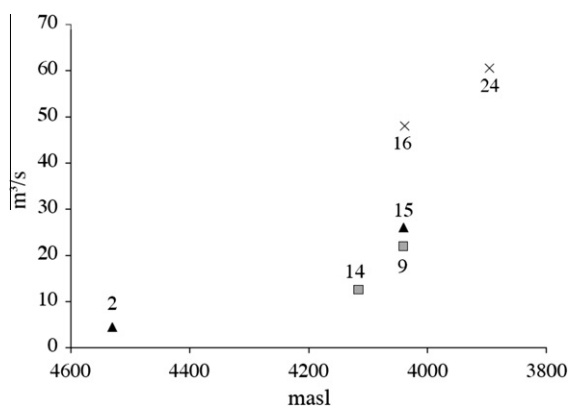


Fig. 3. Measured discharge (m^3/s) for select Rio Quilcay, Peru samples by elevation.

near its outlet into the Rio Quilcay. The pH value of each sample was measured in situ using a Thermo Orion® field meter. Samples for major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , and NO_3^-) were syringe filtered ($0.4 \mu\text{m}$) into DI washed LDPE bottles. Syringe filtered ($0.4 \mu\text{m}$), or dissolved, and unfiltered samples (Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn) were collected using trace element clean techniques modified from Shiller (2003). LDPE bottles were soaked in a 10% trace metal grade HCl bath for 1 week, rinsed with DI, filled with 10% trace metal grade HNO_3 , for 1 week, rinsed with DI, and stored with 2% v/v Optima® HNO_3 for another week. LDPE rubber-free syringes were cleaned in the same acid bath sequence and then $0.45 \mu\text{m}$ filters were pre-treated by pressing 40 mL of DI through each filter followed by 40 mL of 2% v/v Optima® HNO_3 and another 40 mL of DI. Filters were dried using a vacuum pump by connecting the filters to acid-cleaned luer valves. Additionally, streams were sampled for unfiltered acidified (Optima® HNO_3 , $\text{pH} < 2$) trace and minor elements.

Aluminum, Ca, Fe, K, Mn, Na, and Si were determined using an Optima 3000 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) using five calibration standards that bracketed the range of concentrations within the samples, excepting the three highest samples which were diluted 1:10 before analyses. Cobalt, Cu, Ni, Pb and Zn were determined on a Perkin-Elmer Sciex Elan 6000® Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) also using five calibration standards, however with no sample dilution. All element results were drift corrected. Sulfate and NO_3^- were determined using a Dionex DX-120 ion chromatograph (IC). Only SO_4^{2-} is reported because other anions fall near detection limits (DLs) in the higher elevation samples, or represent less than 5% of

the charge balance in the $\text{pH} < 4$ streams. Similarly, Hach® alkalinity titrations recorded negligible total alkalinity. Dissolved organic C (DOC) was determined using the methods of Carey et al. (2005) including a Shimadzu 5050A Total Organic Carbon analyzer equipped with a high sensitivity catalyst. Precision and accuracy were greater than 5% for all elemental analyses, with the exception of DOC (11%), based on the relative standard deviation of calibration standards rerun as check standards every 5–7 samples. Samples rerun in triplicate had element concentrations which were always within 5% of each other. DLs for all chemical constituents were calculated as three times the standard deviation of the blanks (Table 1). Only samples above DLs were used in subsequent calculations.

Saturation indices were calculated using PHREEQC (Parkhurst and Appelo, 1999) based on the dissolved concentrations of all measured constituents in the water samples and standard thermodynamic data. Saturation indices were calculated for all tributary samples and stream water samples, including samples found in mixing zones.

3. Results and discussion

3.1. Geochemical and flow conditions of the Rio Quilcay

The majority (>70%) of the stream samples had pH values below 4 (Table 1). In addition, most Rio Quilcay major cation:anion ($\text{Ca}^{2+} + \text{Na}^+ + \text{Mg}^{2+} + \text{K}^+ : \text{SO}_4^{2-}$) equivalent ratios were close to or exceed 0.75 suggesting sulfide oxidation was the dominant weathering process (Fig. 4) (Bigham et al., 1996). The exceptions were sites 1–4, the only ones with circumneutral pH values (6.9–7.5); these sites occur in the low concentration SO_4^{2-} headwaters. Regional geology included abundant pyrite schists and phyllites and lacked an evaporite source for SO_4^{2-} (Wilson et al., 1967). Additionally, SO_4^{2-} has been noted as the dominant anion in other regional glacier-fed tributaries to the Rio Santa (Mark et al., 2005). In the Rio Quilcay, bacterial mats within the stream and within some of the tributaries likely accelerated sulfide mineral oxidation and the release of cations and SO_4^{2-} (Singer and Stumm, 1970). Acid sulfate waters exist in other alpine streams overlaying similar lithologies such as the pyrite-schist Zillertal region of Austria (Bigham et al., 1996; Schwertmann et al., 1995) and Kyushu, Japan (Kawano and Tomita, 2001). Acid sulfate streams typically contain elevated concentrations of potentially harmful elements (Aström and Corin, 2000; Munk et al., 2002). In the Rio Quilcay, dissolved trace elements such as Co, Cu, Ni, Pb and Zn ranged from below detection in circumneutral conditions to concentrations greater than those observed in acid rock drainage at low pH. For example, dissolved Co, Cu, Ni, Pb and Zn occurred at maximum concentrations of 35.9 $\mu\text{g}/\text{L}$, 8.7 $\mu\text{g}/\text{L}$, 62 $\mu\text{g}/\text{L}$, 5.3 $\mu\text{g}/\text{L}$ and 435 $\mu\text{g}/\text{L}$, respectively, within the Rio Quilcay and the maximum tributary concentrations were even greater. Rio Quilcay trace and minor element concentrations were similar to maximum concentrations reported in alpine acid rock drainage at the Snake River to Deer Creek confluence, Colorado, USA (Munk et al., 2002). However, maximum Rio Quilcay dissolved Fe concentration (21.4 mg/L) was more than an order of magnitude greater than the maximum observed in Snake River (0.51 mg/L). In fact, at site 11 and Tributary C, dissolved Fe was the dominant cation (740 mg/L) representing more than 40% of the charge balance. The role of Fe in the downstream geochemical behavior of the Rio Quilcay is discussed further.

3.2. Major cation yields from the Rio Quilcay compared to other glacial streams

Major cation yields and annual specific discharge were determined for the Rio Quilcay sample sites that had measured

Table 1

Stream, Lake Cuchillacocha, and tributary geochemistry results from the upper 12 km of the Rio Quilcay, Peru. Unfiltered concentrations of Co, Cu, Fe, Mn, Ni, Pb, and Zn are given in parenthesis for samples 1–24 when more than 10% greater than filtered concentrations.

Site	pH	DOC (mg/L)	Al (mg/L)	Ca ²⁺ (mg/L)	K ⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	Fe (mg/L)	Mn (mg/L)	SO ₄ ²⁻ (mg/L)	Co (μg/L)	Cu (μg/L)	Ni (μg/L)	Pb (μg/L)	Zn (μg/L)
1	7.5	1.0	<0.2	19	0.6	3.0	1.6	<0.1	<0.1	2.9	<0.2	<0.04 (1.1*)	<0.01 (1.4*)	<0.05 (0.3)	97
2	7.5	0.9	<0.2	27	0.6	3.0	1.7	<0.1	<0.1	3.1	<0.2	<0.04	<0.01	<0.05	87
3	7.5	0.9	<0.2	25	0.6	3.1	1.7	<0.1	1.0	4.9	22.1	7.3	38.9	2.4	79
4	6.9	0.6	<0.2	18	1.0	2.5	2.4	<0.1	<0.1	2.1	<0.2	0.2 (0.4)	<0.01	<0.05	49
5	3.4	0.2	3.3	19.0	0.8	8.0	0.9	1.0 (2.9)	1.1	109	19.7	11 (12.5)	39 (45)	5.1	435
6	3.3	<0.1	3.6	19.5	0.9	8.3	0.9	1.0 (NA)	1.0 (NA)	137	18.8	10 (NA)	37	4.8 (NA)	422 (NA)
7	3.3	0.2	3.6	20.7	0.9	8.7	1.0	0.9 (1.1)	1.7	123	10.3	2.6 (14.3)	58	4.4	394
8	3.7	0.2	2.2	22.2	0.9	7.6	1.7	0.4 (0.6)	1.7	116	<0.2	<0.04	56	2.5	338
9	3.8	0.1	2.1	22.7	1.0	7.6	1.9	0.3	1.8	125	26.6	4.4 (9.1*)	52	2.2 (2.7)	333
10	3.6	0.2	1.2	2.8	<0.1	3.8	<0.2	0.2	1.7	44	34.7	4.6	12	4.7 (5.8)	32
11	3.7	0.3	6.1	12.9	0.6	5.6	0.1	21.4 (29.7)	1.2	92	30.5	6.1 (12.7*)	(58.5)	(35.8)	(444)
12	3.7	0.2	2.1	14.5	0.2	4.6	0.2	1.2 (11.3)	0.7	87	35.9	7.3	47	5.3 (16.7)	290
13	3.5	0.6	2.4	25.2	0.2	8.6	0.7	12.8 (NA)	1.4	151	27.7	8.7	59	4.2 (5.3)	347
14	3.4	0.3	3.0	26.3	0.2	9.0	0.9	10.8 (13.7)	1.3	158	25.4	7.6	51	2.7 (NA)	353
15	3.3	0.2	2.2	27.8	<0.1	3.8	<0.2	5.1 (11.5)	1.1	154	23.7	7.5	62	4.3 (7.1)	416
16	3.5	0.3	2.6	22.7	0.6	7.8	1.4	2.8 (7.2)	1.1	147	26.8	8.7	50	3.6	367
17	3.4	0.3	2.7	25.0	0.6	8.6	1.4	3.5 (5.8)	1.2	149	15.8	5.5	45	2.9 (4.3)	346
18	3.4	0.2	2.7	24.3	0.6	8.4	1.5	2.9 (4.5)	1.2	148	21.5	7.7	43	2.6 (3.4)	335
19	3.4	0.2	23.6	23.0	2.4	7.6	1.5	<0.1 (4.2)	1.2	137	18.1	6.3	47	2.9 (3.5)	379
20	3.4	0.1	2.4	22.2	0.6	7.5	1.6	2.2 (2.8)	1.0	134	20.2	7.7	29	1.4 (3.7)	228
21	3.5	0.2	2.3	22.1	0.7	7.2	1.6	1.8 (4.5)	1.0	133	17.6	6.0	39	2.0 (2.7)	310
22	3.5	0.0	2.2	16.3	0.7	6.9	1.7	1.4 (NA)	0.9 (NA)	123	33.8	16	32 (NA)	2.0 (NA)	304 (NA)
23	3.7	0.3	1.8	19.4	0.9	6.2	2.4	1.3 (3.5)	0.8	116	32.7	15	38	1.5 (2.2)	262
24	3.8	0.2	2.0	20.4	0.8	6.4	2.3	0.6 (1.3)	0.9	111	30.6	14	31	1.4 (2.4)	245
<i>L. Cuchillacocha</i>	3.1	0.2	2.5	37	0.9	17	2	7.2	1.7	266	<0.02	<0.04	<0.01	<0.05	380
Tributary A	6.8	0.7	<0.2	9	0.4	0.3	<0.2	<0.1	<0.1	12	<0.02	0.07	<0.01	<0.05	0.9
Tributary B	4.9	0.1	3.4	19	0.3	7.1	0.6	<0.1	0.6	107	8.5	7.3	59	1.9	507
Tributary C	2.9	1.1	14.2	230	0.9	61	3.7	740	13	620	323	25	510	12.2	2000
Tributary D	6.1	0.5	<0.2	4.0	0.3	0.1	1.4	<0.1	<0.1	6	<0.02	4.7	<0.01	<0.05	<0.1
Tributary E	6.9	0.7	<0.2	9	0.7	<0.1	0.8	<0.1	<0.1	8	<0.02	<0.04	<0.01	<0.05	16
Tributary F	3.6	1.0	1.1	13	0.3	3.1	1.5	0.4	0.3	59	9.6	3.6	12	<0.05	141
Detect. Lim.		0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.02	0.04	0.01	0.05	0.1
Field blanks		0.1	<0.2	<0.2	<0.1	<0.1	<0.2	<0.1	<.1	<0.2	<0.02	<0.04	<0.01	<0.05	<0.1

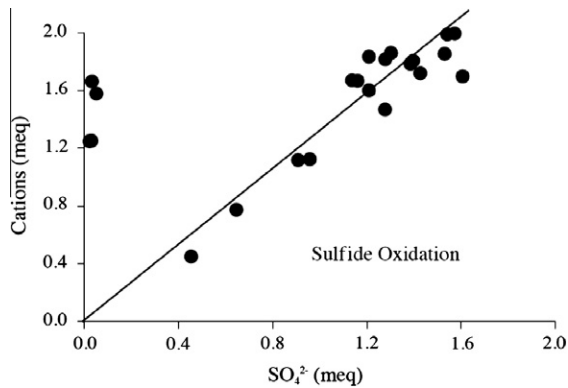


Fig. 4. Summed major cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) in equivalents versus SO_4^{2-} in equivalents for Rio Quilcay sites 1–24. Sulfide mineral oxidation occurs when >0.7 of the summed major cations are balanced by SO_4^{2-} .

discharge (Fig. 5). Because annual cation yields and discharge were estimated from dry season conditions, they may not represent total annual yields that would also include wet season measurements. However, they were likely a good estimate, given that the annual cation yields estimated from monthly samples for one year are within 15% of the annual yield estimates based on dry season months only as calculated from Mark and Seltzer (2003). Estimated annual Rio Quilcay cation yields range from $5.7 \text{ t km}^{-2} \text{ a}^{-1}$ to $37.9 \text{ t km}^{-2} \text{ a}^{-1}$. A Mann–Whitney test revealed Rio Quilcay ratios of cation:discharge were significantly greater ($U = 60$, $p < 0.05$) than those observed in other glacially fed streams worldwide (Anderson et al., 1997). The compared world glacial streams drain watersheds with a wide range of lithologies including: amphibolites, granite, gneiss, volcano-clastics, carbonates, shales, phyllites, and basalts (Anderson et al., 1997). Yet, those glacial sites in dominantly non-carbonate and sulfide-bearing lithologies had weathering yields primarily generated by carbonate dissolution followed by sulfide oxidation (Anderson et al., 1997). Yet stream samples in closer proximity to glaciers have greater sulfide oxidation than those more distal from glaciers (Anderson et al., 2000). Therefore, it is likely that both the sulfide-rich lithology underlying the Rio Quilcay and the near-glacier sample locations enhanced sulfide weathering, and generated exceptionally high cation loads.

3.3. Dominant downstream controls of Rio Quilcay geochemistry

Downstream variations in Rio Quilcay geochemistry including pH, summed major cations, SO_4^{2-} , and dissolved Fe, Al, Mn, Zn,

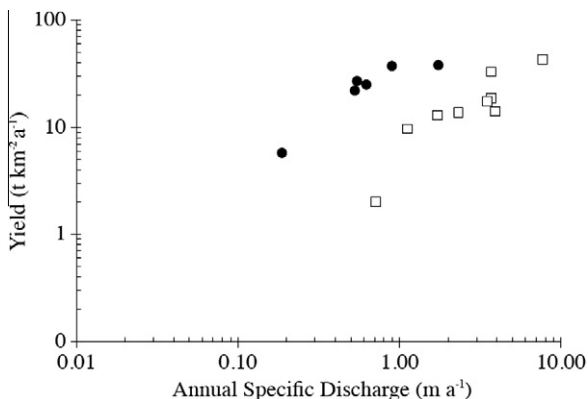


Fig. 5. Summed major cation yield from Rio Quilcay, Peru (black circles) compared with other glacial melt streams (white squares) in the United States, Canada, India, Switzerland, and Iceland (Anderson et al., 1997).

Pb, Ni, Co and Cu were related to distance downstream, over decreasing elevations (Fig. 6). In circumneutral fresh waters, concentrations of dissolved trace and minor elements are generally low (Adriano, 2001; Koski et al., 2008), as was the case for sites 1–4 in the Rio Quilcay, where dissolved Fe, Al, Co, Cu, Pb and Ni were below detection. However, these solutes occurred downstream of sites 1–4 at some of the most elevated concentrations observed in the watershed at site 5. This indicates that sulfide-weathering processes, including the release of trace and minor cations occurred rapidly. In fact, dissolved Mn and Zn concentrations increased from $<0.1 \text{ mg/L}$ and $49 \text{ } \mu\text{g/L}$ to 1.0 mg/L and $422 \text{ } \mu\text{g/L}$, respectively, or by an order of magnitude. Site 5 receives drainage from acidic (pH 3.1) Lake Tulpacocha (Table 2). Streams receiving Acid Mine Drainage (AMD) from tailings ponds have similarly low downstream pH values and increased concentrations of elements including Fe, Al, Mn and Zn (Lee et al., 2002).

Elevated dissolved Al, Fe and Cu concentrations (6.1 mg/L , 21.4 mg/L , $6.1 \text{ } \mu\text{g/L}$) were observed at site 11, 0.3 km immediately downstream of a moraine. Concentrations of these elements increased by more than four times the concentrations at site 10. Concentration gains were likely associated with glacier melt rapidly weathering minerals within the moraine (Brown, 2002). Site 12 is downstream of Tributary B and likely contributed further to the dissolved Co, Cu and Pb concentrations. Tributary C also influenced the chemical composition of the stream immediately below its inflow at site 13. In fact, Fe reached the second highest concentration reported (12.8 mg/L) and dissolved Al, Mn, Co, Cu, Ni and Zn concentrations also increased above their upstream values. Tributary C overlays a region with enhanced sulfide mineral oxidation (Fig. 2). Evidence for this includes a major cation: SO_4^{2-} equivalent ratio of 1, and abundant algal mats covered with yellow and orange precipitates (Bigham et al., 1996). In addition, dissolved Al and Zn increased an additional 270% and 160% relative to site 13–14, respectively, and after the inflow of tributary D.

Immediately downstream of the confluence of the NW and NE Branch of the Rio Quilcay (Fig. 3), all constituents occurred at concentrations intermediate between the two branches (Table 2). After the confluence of the NW and NE Branch, concentrations of major cations, SO_4^{2-} and dissolved trace and minor elements generally began to decrease while pH increased. In contrast, DOC had no apparent trend downstream of the confluence.

Low overall DOC ($<1.1 \text{ mg/L}$) concentrations observed in the Rio Quilcay and its tributaries may reflect either enhanced oxidation of DOC into CO_2 favored in acidic waters (Gennings et al., 2001), or DOC sorption on the streambed (McKnight and Bencala, 1990). The circumneutral headwaters of NW Branch of the Rio Quilcay (pH = 6.9–7.5) had greater DOC concentrations (0.9 – 1.1 mg/L) before becoming more acidic (pH = 3.3–3.8) downstream and dropping below 0.9 mg/L . In the NE Branch of the Rio Quilcay, overland Tributaries E and F had elevated DOC concentrations (0.7 mg/L and 0.9 mg/L) and served as DOC sources with observed DOC increases from site 19 to 20. The site that received acidic drainage from Lake Tulpacocha, site 5, had low DOC concentrations (0.2 mg/L), suggesting enhanced photochemical oxidation of DOC because of the low pH of the lake (Gennings et al., 2001), or possible retention of DOC on the lake floor during the dry season. In Lake Cuchilla, dissolved element concentrations were typically greater than at sites 1–4, yet DOC concentrations were low (0.2 mg/L) in spite of elevated DOC (1.1 mg/L) from tributary C, likely due to the algal growth observed at this site (Kaplan and Bott, 1982).

Among these dry season determinations, there were no correlations between the dissolved trace and minor element concentrations and DOC. However, such correlations may exist during the wet season when the landscape produces and releases particulate and dissolved organic material. For example in the Sagavanirktok

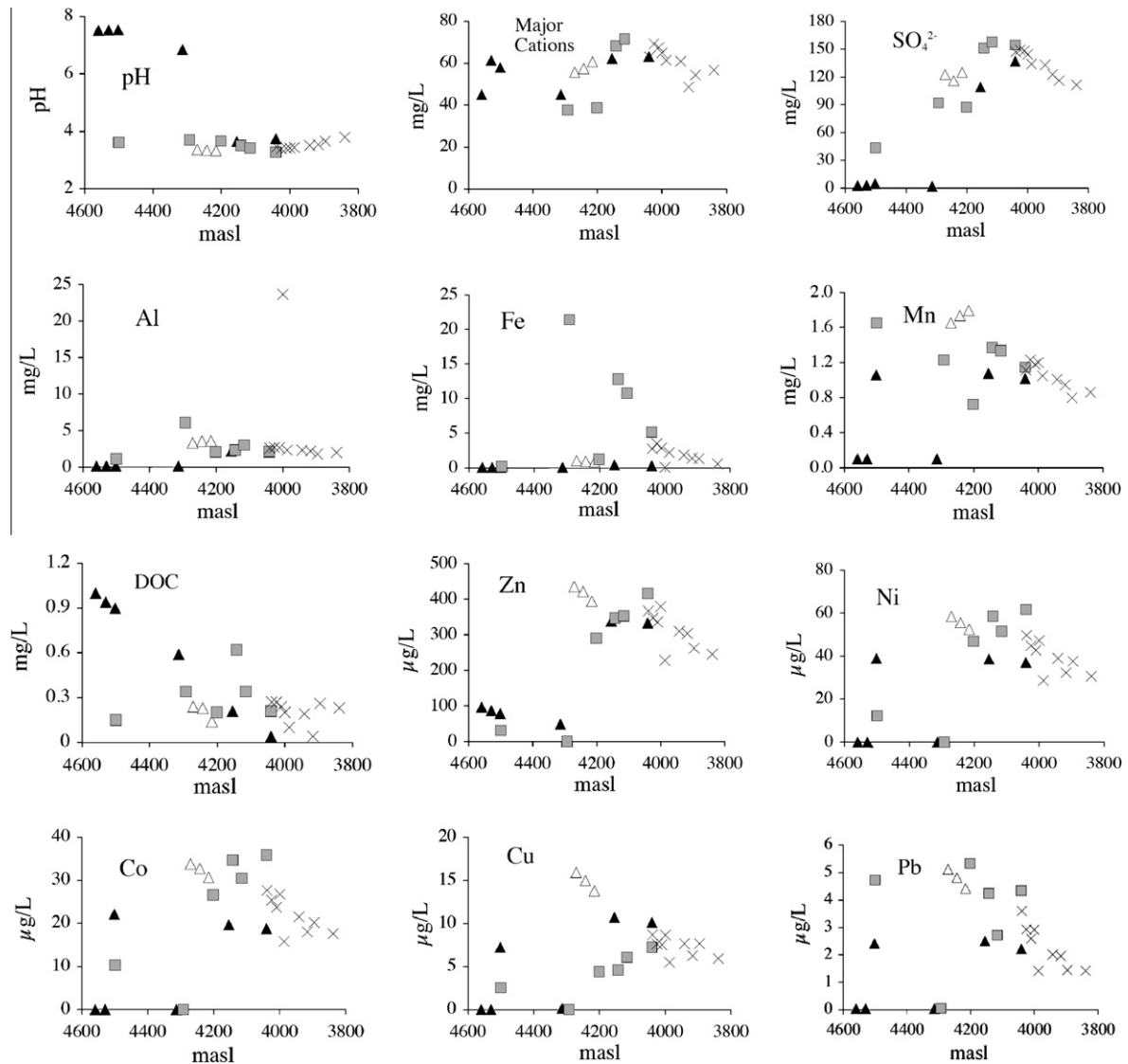


Fig. 6. Rio Quilcay geochemistry by elevation including: the Northeast branch (white squares), the Northwest branch (black triangles), and below confluence (gray circle). Summed major cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$), SO_4^{2-} , Fe, Al, Mn, and DOC in mg/L and Co, Cu, Pb, Ni, and Zn in $\mu\text{g/L}$.

Table 2

Saturation indices (SI) of Fe-compounds in Lake Cuchillacocha and the tributaries of the Rio Quilcay, Peru as calculated using PHREEQC; positive numbers indicate saturation.

Site	pH	Goethite	Hematite	$\text{Fe}(\text{OH})_3$
Lake Cuchillacocha	3.1	-3.15	-4.32	-16.84
Tributary A	6.8	5.65	13.28	-0.06
Tributary B	4.9	-0.12	1.74	-5.83
Tributary C	2.9	-3.08	-4.19	-8.79
Tributary D	6.1	3.57	9.12	-2.14
Tributary E	6.9	5.93	13.85	0.22
Tributary F	3.6	-2.78	-3.57	-8.48

River, Alaska, increases in dissolved Cu, Fe, Pb and Zn were associated with increased discharge and DOC concentrations during summer as a result of permafrost melt (Rember and Trefry, 2004). Similarly, a positive correlation in DOC concentrations vs. discharge has been observed in streams draining wetlands and alpine areas during spring rains and/or snowmelt (Boyer et al., 1997; Olivie-Lauquet et al., 2001).

Since discharge was not measured at all sites, summed major cations were normalized to Na^+ , to determine the relative role of

weathering across the study area in stream water chemistry regardless of dilution (Fig. 7). Sodium is considered a conservative tracer in aquatic environments (Chapman, 1982; Christophersen et al., 1982) including acidic streams. Major cation: Na^+ ratios in the NE Branch of the Rio Quilcay were generally greater than those observed in the NW Branch. The uppermost NE branch of the Rio Quilcay (e.g. 11, 12) had the greatest major cation: Na^+ ratios. This may reflect the low discharge at these sites allowing more time for water-rock interaction and greater cation release (Anderson et al., 2000; Lyons et al., 1998) or the greater degree of mineralization. Even above their convergence, the NE Branch had a greater cation: Na^+ ratio than the NW Branch. However, the NE Branch had an almost 20% higher flow than the NW Branch and was, therefore, expected to show greater dilution. Cation denudation was, therefore, enhanced in the NE Branch with respect to the NW Branch. There was more unconsolidated rock, bacterial mats and ochreous material observed throughout the NE Branch especially near Tributary C (Fig. 2), which had the highest solute loads of any tributary measured. Greater mineralization and/or greater exposure of sulfide minerals may also explain overall higher cation concentrations in the NE Branch than the NW Branch. The two mixed conservatively

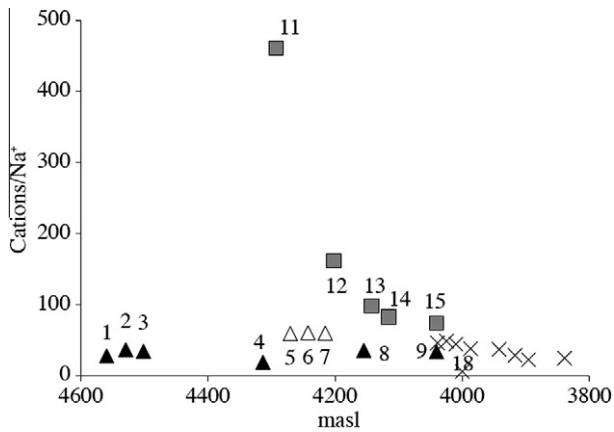


Fig. 7. Summed major cations divided by Na^+ (g:g) versus elevation for stream samples (black triangles = Northwest Branch; white triangles = Northwest Branch downstream from Lake Tulpacocha; squares = Northeast Branch; crosses = below the convergence of the Northwest and Northeast branches).

downstream of their confluence (site 16). Downstream of site 16, major cation: Na^+ ratios generally decreased. Flow had also increased by 26% from site 16 ($48 \text{ m}^3/\text{s}$) to site 24 ($60.5 \text{ m}^3/\text{s}$) and that suggests that cation dilution occurred. The somewhat lower cation: Na^+ g:g ratio (6.1) observed at site 18 possibly reflected sampling proximal to an unmeasured dilute tributary.

3.4. Non-conservative geochemical behavior within the Rio Quilcay

Although Rio Quilcay geochemistry was predominantly influenced by weathering and dilution, sorption also played a role in solute concentrations. Dissolved element concentrations were converted to the activities of their ionic species using PHREEQC and used to calculate saturation indices (SIs) (Parkhurst and Appelo, 1999) (Table 2). Negative SIs indicated undersaturation, whereas, positive SIs indicated supersaturation, and/or the formation of precipitates or salts. The PHREEQC results showed that Tributaries A, B, D and E were saturated ($\text{SI} > 0$) with respect to hydrous Fe oxides (HFOs) but undersaturated ($\text{SI} < 0$) with respect to organic C and Al and Mn oxyhydroxides. Main stream samples were undersaturated with respect to organic C, HFOs and Al and Mn oxyhydroxides. Therefore, only the SIs of the HFOs in the tributaries are reported (Table 2). Specifically, Tributary A and B were saturated with respect to hematite, Tributary D was saturated with respect to hematite (Fe_2O_3) and goethite ($\text{FeO}(\text{OH})$), and Tributary E was saturated with respect to hematite, goethite and $\text{Fe}(\text{OH})_3$. Although Tributary C had the highest dissolved Fe concentrations it was highly acidic ($\text{pH} = 2.9$), and, therefore, undersaturated with respect to HFOs. Acidic ($\text{pH} = 3.6$) Tributary F was also undersaturated in HFOs. PHREEQC modeling results suggest that stream samples were undersaturated with respect to Fe and Al oxyhydroxides, yet precipitates formed at the convergence of many of the tributaries with the stream. Because non-conservative behavior was predicted by PHREEQC, non-conservative behavior was further evaluated. Actual concentrations of trace and minor solutes measured downstream of tributary additions were compared with the concentrations that would be generated if conservative mixing occurred (Fig. 8). These estimates were based on using ratios of elements normalized to Na^+ in samples measured in the Rio Quilcay above the addition of a tributary and in the tributaries themselves to estimate concentrations downstream. As previously noted, all dissolved elements exhibited conservative mixing immediately below the confluence of the NE and NW Branch of the Rio Quilcay at site 16. However, Tributary A and E were not included because Na^+ was below detection limits ($< 0.1 \text{ mg/L}$) and could not be used to estimate conservative mixing values. Since DOC concentrations

are low ($\leq 1.0 \text{ mg/L}$), any DOC effects on the sorption behavior of trace and minor elements in the presence of abundant dissolved Fe and/or Al was considered negligible (Munk et al., 2002; Runkel et al., 1999; Schemel et al., 2007).

Since Tributary A was supersaturated in goethite and hematite and Tributary E was supersaturated in goethite, hematite and FeOH_3 , and the Rio Quilcay was not, it was very likely that Fe and possibly other trace and minor solutes were released from particulates into the Rio Quilcay downstream of those tributaries. This was especially likely given the change from circumneutral pH values of tributary A (6.8) and E (6.9) to a pH of less than 4 within the Rio Quilcay which would dissolve/desorb many trace and minor elements that were contributed from the less acidic tributaries (Lee et al., 2002).

Downstream of tributary B, measured SO_4^{2-} , dissolved Fe, Al and Mn were less than values expected for conservative mixing, while Cu, Co, Ni, Pb and Zn were greater than predicted values (Fig. 8). Water in Tributary B was predicted to be supersaturated with respect to hematite but the Rio Quilcay was predicted to be undersaturated (Table 2), suggesting that Fe and/or Fe-bearing minerals might be desorbed or dissolved in the Rio Quilcay downstream of Tributary B. However, in this case, it was unclear why measured Fe concentrations were less than predicted concentrations. As Fe desorbs in the more acidic Rio Quilcay, other trace and minor elements would be released.

Measured solutes all occurred at concentrations less than predicted downstream of Tributary C (Fig. 8). Tributary C contained the greatest overall solute concentrations and had the lowest measured pH (2.9) of any site. It was very likely that solutes sorbed to particulates as Tributary C mixed with the less acidic stream. Because SO_4^{2-} and dissolved Fe were the most substantially underpredicted (i.e. more than 50 mg/L lower than predicted), it was highly likely that the yellow and red coatings observed downstream of the addition of Tributary C contained iron sulfate precipitates. Interestingly, PHREEQC modeling results show that the tributary was too acidic for any Fe-bearing mineral to be supersaturated. Perhaps the observed streambed Fe-rich precipitates are the result of the dynamic diurnal or seasonal conditions in the stream resulting from changing flow, pH, biological activity, or light (McKnight and Bencala, 1988, 1990; Nimick et al., 2005). Hydrochemical modeling suggests that proglacial environments in the Cordillera Blanca have short periods ($< 4 \text{ a}$) of groundwater storage (Baraer et al., 2009), however, the water quality associated with groundwater dynamics is not presently understood. Ongoing monitoring of stream changes in trace and minor elements through time, space, and in relation to groundwater behavior would provide more depth to hydrogeochemical understanding.

Measured dissolved Al and Mn were greater than predicted while measured SO_4^{2-} and dissolved Fe were similar to predicted values downstream of Tributary D (Fig. 8). Measured dissolved Al, Mn, Ni, Co, Cu, Pb and Zn were all less than predicted. The circumneutral pH of tributary D favor the sorption of trace elements to Al and Mn hydrous oxides. PHREEQC results indicated that the tributary was also saturated in hydrous Fe oxides (HFOs) including goethite and hematite (Table 3). It may be that as tributary waters mix with the more acidic stream Al and Mn desorb or dissolve, while trace constituents remained sorbed to Fe oxides or to sulfides.

Measured dissolved concentrations of Fe, Ni, Cu, Co, Pb and Zn downstream of Tributary F were similar to the projected concentrations (Fig. 8). Measured dissolved Al, Mn, and SO_4^{2-} , however, were less than projected. The pH of tributary F was similar to the Rio Quilcay suggesting that HFOs remained the primary sorbants of these trace elements. Yet, because there was both more particulates and solute in the Rio Quilcay, it may be that dissolved Al and Mn in the tributary readily sorbed upon mixing with the stream.

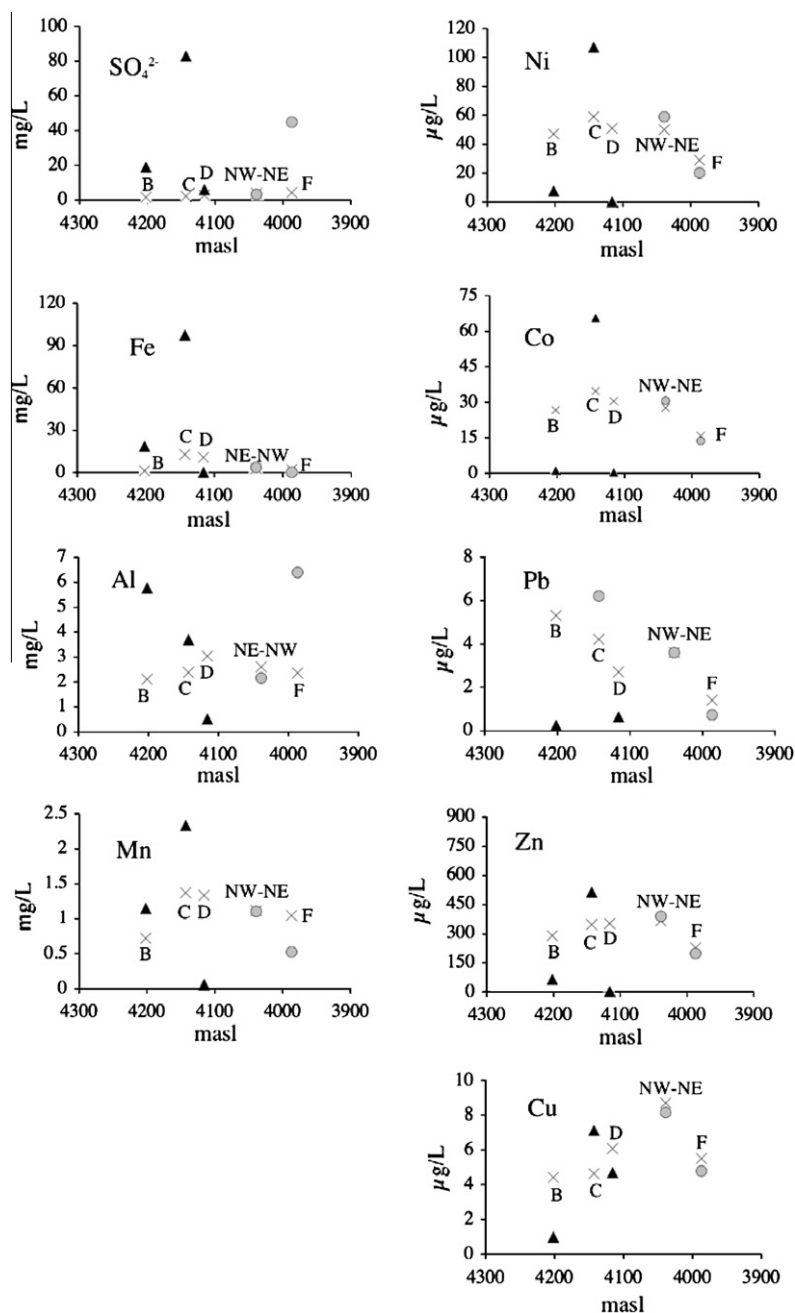


Fig. 8. Measured (crosses) and predicted (black triangles = Northeast Branch, circles = below confluence) dissolved element concentrations in the Rio Quilcay. Sites shown are downstream from tributaries B, C, D, F, and the confluence of the Northwest and Northeast branches. Predicted values are based on element:Na⁺ mixing ratios. Tributary A is not included because Na⁺ concentrations were below detection limits (DLs). Tributary E was not included because it contributed little (<1%) total flow.

Although non-conservative mixing occurred downstream of many of the Rio Quilcay tributaries, stream samples had similar (within 5%) dissolved and unfiltered concentrations of Al, Mn, Cu, Zn, Cd and Co (Table 1). These elements all typically occur in dissolved form at low pH values (Dzombak and Morel, 1990; Koski et al., 2008). Neutralization of the Isabella Mine, Tennessee, United States, Fe-rich acidic waters suggested that dissolved Pb sorbed to HFOs at much lower pH values (50% sorbed at pH = 3) than Cu, Zn, Cd and Co, which remained in solution until pH values were above 4 (Lee et al., 2002).

The amount of sorbed/precipitated Fe and Pb were quantified by subtracting dissolved element concentrations from unfiltered and acidified (pH < 2) concentrations. Fig. 9 shows the amount of Pb sorbed versus the amount of Fe sorbed in the low pH Rio Quilcay samples. The amount of Fe and Pb sorbed have a significant lin-

ear relationship ($R^2 = 0.44$, $\alpha = 0.05$, $p < 0.01$) suggesting their coprecipitation. It was unclear if Pb or Fe also related to SO_4^{2-} because unfiltered SO_4^{2-} was not quantified. However, neither sorbed Fe or sorbed Pb significantly correlated with SO_4^{2-} concentrations. In acidic conditions, SO_4^{2-} has been shown to co-adsorb more Pb, Cu and Zn than Fe alone (Webster et al., 1998). As the Rio Quilcay joins with the circumneutral Rio Santa downstream of the sample area, further dilution of the dissolved and particulate loads should occur unless there are additional inputs.

3.5. Significance for water quality

Several water quality parameters within the Rio Quilcay watershed exceeded World Health Organization (WHO), United States Environmental Protection Agency (USEPA) and Peruvian drinking

Table 3
Comparison of USEPA, WHO and Peruvian water quality standards for pH and concentrations of potentially toxic elements from Rio Quilcay and its tributaries (Cu is not included because all Rio Quilcay and tributary samples were substantially below recommendations).

Parameters	pH	Al (mg/L)	Fe (mg/L)	Mn (mg/L)	Co (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
Rio Quilcay and tributaries (this study)	2.9–7.5	<0.2–24	<0.1–740	<0.1–13	<0.2–323	<0.1–510	<0.5–12	<0.1–2000
USEPA Primary (USEPA, 2009)		–	–	–	–	–	15	–
USEPA Secondary ^a (USEPA, 2009)	6.5–8.5	0.05–0.2	0.05	0.05	–	–	–	5000
WHO ^b (WHO, 2006)	6.5–9.5	–	2	0.4	–	70	10	3000
Peru A1 ^c (PSD, 2008)	6.6–8.5	0.2	0.3	0.1	–	20	10	3000
Peru A2 ^d (PSD, 2008)	5.5–9.0	0.2	1	0.4	–	25	50	5000
Peru A3 ^e (PSD, 2008)	5.5–9.0	0.2	1	0.5	–	25	50	5000
Peru B1 ^f (PSD, 2008)	6.0–9.0	0.2	0.3	0.1	–	20	10	3000
Irrigation ^g (PSD, 2008)	6.5–8.5	5	1	0.2	50	200	50	2000
Animal consumption (PSD, 2008)	6.5–8.4	5	1	0.2	–	200	50	24,000

^a USEPA secondary standards are non-enforceable guidelines.

^b WHO has no formal recommendations for pH, Fe, or Zn, but notes that Fe concentrations above 2 mg/L may lead to elevated body burdens and that Zn in excess of 3 µg/L “may not be acceptable to consumers”.

^c Class A waters – “superficial water destined for potable water”. Class A1 – water that can be potable with disinfection.

^d Class A2 – water that can be potable with conventional treatment (e.g. decantation, coagulation, flocculation, sedimentation, filtration, disinfection).

^e Class A3 – water that can be potable with advanced treatment (e.g. chlorination, micro filtration, ultra filtration, nanofiltration, activated carbon, reverse osmosis or equivalent).

^f Class B waters – “superficial water destined for recreation”. Class B1 – primary contact (swimming, surfing, underwater fishing).

^g Irrigation for low and high stemmed vegetables.

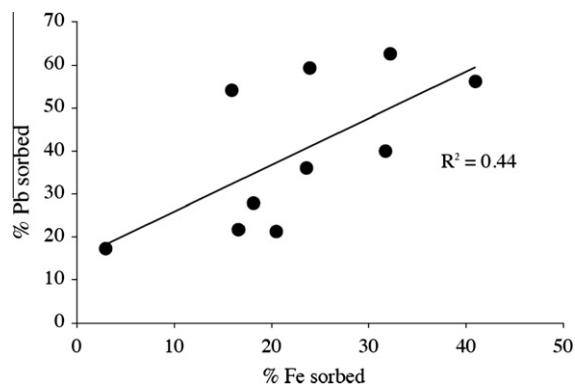


Fig. 9. Sorbed Pb versus sorbed Fe; the two are significantly correlated ($\alpha = 0.05$, $p < 0.01$).

water standards (i.e. enforceable) and recommendations for irrigation and agriculture (Table 3). The maximum Pb concentration (12.2 µg/L) measured in the Rio Quilcay exceed WHO and Peruvian drinking water (i.e. potable) standards (Peru Supreme Decree, 2008; WHO, 2006). Elevated blood concentrations of Pb adversely affect physical and mental development (USEPA, 2009). In the Rio Quilcay watershed, maximum Ni concentrations (510 µg/L) are an order of magnitude greater than WHO and Peruvian drinking water standards. This value even exceeds Peruvian guidelines for vegetable irrigation and animal consumption, both of which are managed at less than 200 µg/L (Peru Supreme Decree, 2008). High doses of Ni can cause kidney failure, lower body mass, and elevated death at birth in laboratory animals and in humans high Ni doses may cause digestive complications, headaches and weakness (WHO, 2006).

Aluminum, Fe, Mn and pH are not regulated by the United States EPA or by the WHO, yet, the Rio Quilcay values exceeded suggested limits for human consumption. For example, almost all of the Rio Quilcay sites exceeded USEPA drinking water recommendation for Fe and Mn (0.05 mg/L) and Peruvian potable water standards of 0.3 mg/L and 0.1 mg/L respectively. High Fe and Mn concentrations are known to stain clothing and other materials they touch (USEPA, 2009). High doses in drinking water are not frequently studied, however, there has been an increase in reported neurological problems associated with elevated blood Mn (Ljung and Vahter, 2007). Although Zn concentrations do not exceed any

recommended human, animal, irrigation use guidelines, the maximum Rio Quilcay watershed Zn concentration (2 mg/L) approached recommended values and should, therefore, possibly be monitored over time along with those elements that are already above standards and guidelines. Interestingly, Co is only element regulated for animal consumption under Peruvian guidelines (Peru Supreme Decree, 2008) and there are no drinking water recommendations or regulations by WHO or the USEPA (USEPA, 2009; WHO, 2006). Yet, high concentrations of Co are toxic to minnows, although toxicity is greater in softer water (Diamond et al., 1992).

Because so many water quality standards and recommendations were exceeded throughout the Rio Quilcay watershed, other sulfide-mineral rich regions in the Cordillera Blanca may face similar water quality challenges, particularly because the northeastern Cordillera Blanca has the highest concentration of mapped sulfide deposits and is covered more extensively by glaciers than the SW (Wilson et al., 1967). As the glaciers in the NW retreat, the exposure of fresh sulfide minerals and associated release of potentially toxic elements may further affect downstream water quality. The dominance of sulfide weathering in the Rio Quilcay produced higher cation yields than other world glaciers of similar discharge. In addition, the decline of glacial melt water contributions to watersheds would potentially deplete water storage in proglacial wetlands and shallow groundwater, thereby increasing stream oxidation and enhancing the release of many toxic elements. To further assess present and future water quality issues in the Cordillera Blanca, it will be necessary to increase the spatial and temporal resolution of water quality studies. This could include examining topographic, diurnal and seasonal variations in trace and toxic elements as many of these elements are sensitive to variations in light, flow patterns, biology and pH. Future studies are necessary to establish how changing flow conditions in response to glacial retreat will alter water quality. The abundance of sulfide-rich minerals in the Cordillera Blanca makes these studies especially important to this region.

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