WATER QUALITY IMPACTS FROM IN-STREAM MINE TAILINGS IN RIO TARAPAYA, POTOSÍ, BOLIVIA[1]

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Abstract: Although recent construction of tailings dams has dramatically decreased solids discharge rates, pyrite-dominated polymetallic sulfide mine tailings persist as the primary in-stream substrate of the upper Rio Pilcomayo, a crucial water resource in the arid Southeastern Bolivian highlands. Rio Tarapaya is a primary tributary of the upper Rio Pilcomayo that drains Potosí, Bolivia, where intensive hard rock mining and ore processing has occurred for five centuries. In conjunction with standard water quality testing, field leach tests were performed on saturated sediment within the active channel as well as unsaturated sediment deposited on the banks of the Rio Tarapaya during high-flow events. Results indicate that weathering of in-stream tailings is contributing to deleterious concentrations of various ecotoxic metals. Of special concern is the mobilization of metals and acidity with increases in water level, such as occurs at the onset of the rainy season. The highly seasonal, arid climate provides for long periods of mineral oxidation followed by large precipitation events which mobilize weathered oxidation products. The reactivity of the millions of tonnes of in-stream tailings in Rio Tarapaya suggests that the upper Rio Pilcomayo will remain severely degraded for the foreseeable future and remediation will continue to be a daunting task.

Additional Key Words: acid rock drainage, sewage, aqueous geochemistry, water quality, and mineral processing

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Introduction

Background

The upper Rio Pilcomayo is a crucial water resource of relatively arid Southeastern Bolivia, in one of the poorest nations in the Western hemisphere (World Bank, 2009). The upper Rio Pilcomayo has been severely impacted by intensive hard rock (Ag, Pb, Sn, and Zn) mining for centuries, starting with the onset of Ag mining of the world's largest Ag deposit, Cerro Rico de Potosí, in 1545. Silver oxide ores were mined from 1545-1575, followed by Ag-sulfide mining from 1575 until the late 1800s transition to Sn mining which dominated until 1985 (Strosnider et al., *in press-a*). Since 1985, Cerro Rico has been surface mined for Ag-oxide ores and subsurface mined for Ag, Pb, Sn and Zn sulfide ores (Strosnider et al., *in press-a*). Historic and ongoing tailings discharges are among point-source acid mine drainage (AMD) from active and abandoned mines as well as nonpoint diffuse acid rock drainage from waste rock piles, ore piles, and tailings deposits/dams as sources of ecotoxic metals to the upper Rio Pilcomayo (Strosnider et al., *in press-a*).

Until the construction of tailings dams in 2004, Potosi's *ingenios* (ore processing facilities) continuously discharged tailings to the Ribera de la Vera Cruz, which empties into Rio Tarapaya at the outskirts of Potosí (Fig. 1). Rio Tarapaya is a chief tributary of the upper Rio Pilcomayo. Mining activities prior to 2004 were estimated to release approximately 370,000 tonnes/yr of mining-related sludge to the Ribera de la Vera Cruz (Smolders et al., 2003). As tailings discharge rates necessarily tracked mining activity, and mining proceeded at considerably higher rates at sustained intervals over previous centuries (Strosnider et al., *in press-a*), it can be induced that at least a few hundred million tonnes of tailings have been discharged to Rio Tarapaya via the Ribera de la Vera Cruz over the past five centuries. Despite the new tailings canal and tailings impoundments, some processing effluent still regularly enters the Ribera de la Vera Cruz, often washed in during rain events from an overflowing tailings canal and/or poorly designed floatation ponds or purposely released to avoid costs associated with pumping tailings to the dams (Strosnider et al., *in press-b*). The substrate of Rio Tarapaya is dominated by tailings due to the near-continuous discharges of tailings from Potosí and from events such as the hydropower dam failure in 1626, which caused extreme destruction over two hours as an increasingly polluted torrent of ore, tailings, amalgam and Hg rushed down the Ribera de la Vera

Cruz through Rio Tarapaya (Serrano et al., 1996; Hudson-Edwards et al., 2001; Gioda et al., 2002; Strosnider et al. *in press-b*).

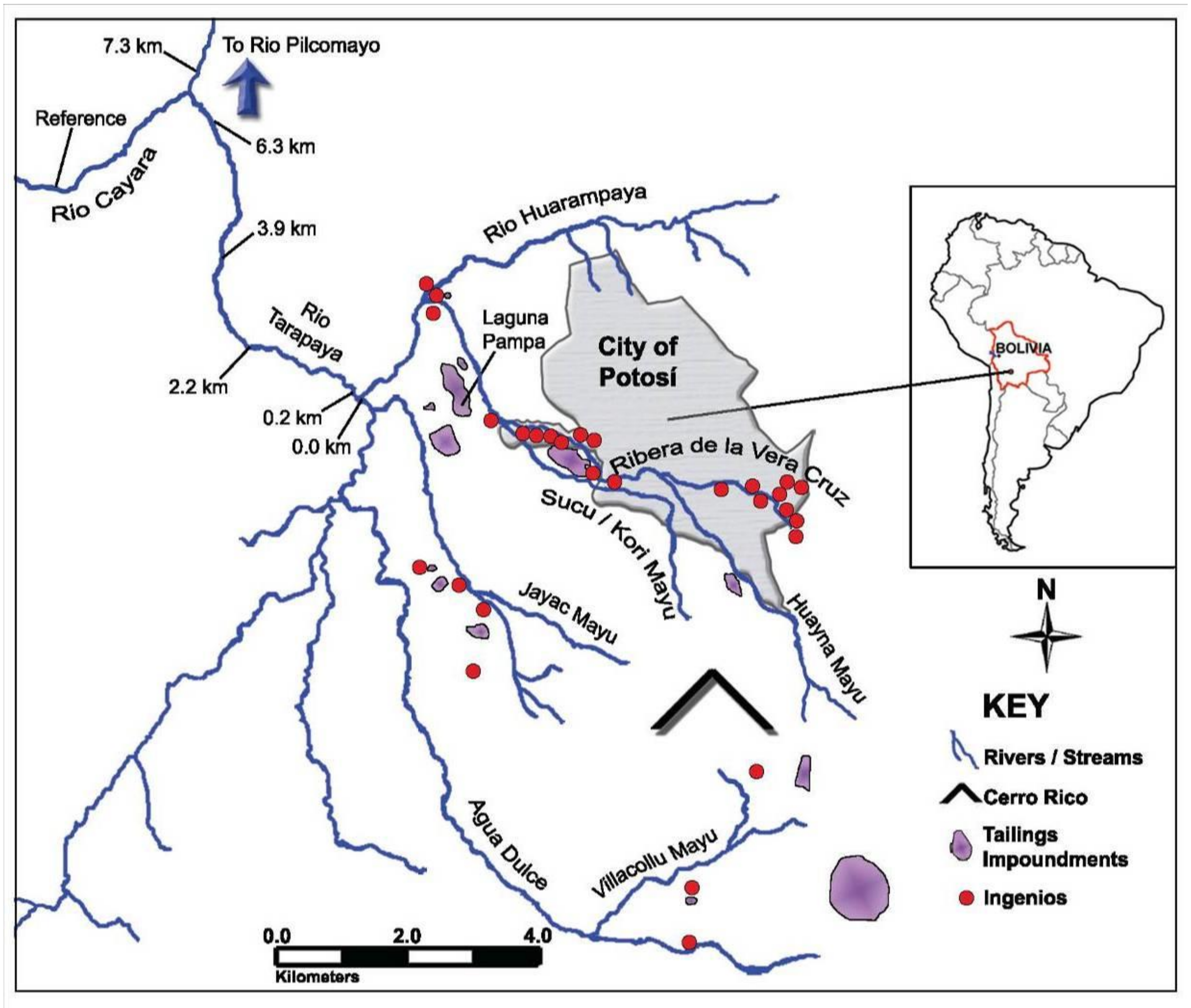

Figure 1: Location of each sampling location with respect to Potosí, mineral processing plants, and tailings impoundments.

Multiple studies have documented the combined negative effects of historic and current ore extraction and processing on the upper Rio Pilcomayo. Researchers have documented severe contamination of waters and sediment from the slopes of Cerro Rico up to 500 km downstream (Hudson-Edwards et al., 2001; Miller et al., 2002, 2004, 2007; Smolders et al., 2002, 2003, 2004; Strosnider et al., *in press-b*). In the most recent study, Strosnider et al. (*in press-b*) documented total Al, As, Cd, Fe, Mn, Pb, and Zn concentrations of 13-550, 0.43-1.8, 0.11-0.18, 59-650, 2.9-18, 0.9-1.2, 10-53 mg/L, respectively, in Rio Tarapaya. Smolders et al. (2003) found the benthic macroinvertebrate community species richness to dramatically reduce with increasing proximity to Potosí. Downstream waters have degraded agricultural lands upon which they were applied and present a human health risk via multiple exposure vectors because they are used for irrigation, livestock watering, and various domestic uses (Miller et al., 2004, 2007; Archer et al., 2005; Strosnider et al., *in press-b*).

Recent studies have stressed the importance of historical and ongoing tailings discharges from Potosí in the degradation of the upper Rio Pilcomayo (Hudson-Edwards et al., 2001; Miller et al., 2002, 2004, 2007; Smolders et al., 2002, 2003, 2004). Metal sulfide-rich tailings from the *ingenios* of Potosí dominate the bed material of the upper Rio Pilcomayo near Potosí (Hudson-Edwards et al., 2001). Hudson-Edwards et al. (2001) found concentrations of various ecotoxic metals orders of magnitude greater than background levels in the tailings deposited downstream of Potosí. In a stretch of Rio Tarapaya just downstream of Potosí, Strosnider et al. (*in press-b*) noted pH decrease and metal concentration increase that indicated the weathering of tailings within the sediment may be having a negative influence on water quality. These pyritic sediments can oxidize rapidly to produce iron oxide and gypsum crusts in high-channel deposits (Hudson-Edwards et al., 2001). Smolders et al. (2004) noted characteristics of metal sulfide weathering and dissolution of evaporitic salts from the bed material of the upper Rio Pilcomayo as well. In column studies, Kossoff et al. (2011) found that 50-95% of Cd and 50-60% of Zn could be leached from Potosí's tailings over 20 years of simulated weathering. The weathering of the tailings also created strongly acidic conditions ($\text{pH} \approx 2$) (Kossoff et al., 2011). In addition, a considerable fraction of metals can be immediately released from the tailings upon wetting, as they are partially composed of soluble metal sulfates (Kossoff et al., 2011). Although tailings discharges have been greatly diminished since 2004, the substrate of the upper Rio Pilcomayo remains dominated by millions of tonnes of tailings deposited over the last five centuries. The transport and reactivity of these tailings remain a dominant factor in the water quality of the upper Rio Pilcomayo.

The United States Geological Survey (USGS) field leach test (FLT) can estimate which constituents are water reactive, soluble, mobilized and made bioavailable via leaching (Hageman, 2007). The FLT was originally developed to predict and compare leachate geochemistry from historical metal-mining dumps (Hageman and Briggs, 2000). The FLT delivers similar results to the more commonly applied SPLP (synthetic precipitation leaching procedure) (Hageman, 2007). The FLT, often with slight variations, has been applied to a variety of contemporary and historical mine waste materials such as exposed open pit ore faces, waste rock, and tailings impoundments in Sardinia, Italy (Da Pelo et al., 2009); waste rock, smelting slag, and tailings deposits in multiple states of the USA (Piatak et al., 2004; Hammarstrom et al., 2005; Hageman, 2007; Seal et al., 2008); and tailings-impacted river sediment in Zimapán, Mexico (Espinosa et al., 2009). The goal of the following study was to use the FLT in conjunction with standard water quality characterization to determine the possible impacts of in-channel tailings in the upper Rio Pilcomayo watershed.

Methods

Study Site

The study focused upon the water quality and tailings-dominated substrate of Rio Tarapaya (19.55°S 65.82°W), from the outskirts of Potosí to its confluence with Rio Cayara (Fig. 1). Potosí lies in the Eastern Cordillera range of the Central Andes in the upper reaches of the Rio Pilcomayo watershed. The Rio Pilcomayo is a chief tributary of the Rio de la Plata system, a crucial water resource for south-central and southeastern South America. Rio Tarapaya combines with Rio Yocalla approximately 30 km downstream of Potosí to become Rio Pilcomayo. The Rio Pilcomayo flows in a general southeasterly direction down the Eastern Cordillera range and through the semi-arid Chaco Plains. Eventually, the Rio Pilcomayo forms Argentina's northern border with Paraguay before it diffuses, and partially disappears beneath the surface, into a wide alluvial fan that empties into the Rio Paraguay at Asunción, Paraguay.

Sampling locations framed a reach of Rio Tarapaya starting at Rio Agua Dulce (sample point 0.0 km on Fig. 1) before its confluence with the Ribera de la Vera Cruz and ending after Rio Tarapaya confluences with Rio Cayara. Rio Agua Dulce is impacted by the AMD and tailings - influenced Jayac Mayu, which drains AMD from the Western slope of Cerro Rico and runs by a few *ingenios* which are likely discharging to it (Strosnider et al. *in press-b*). The second sample point (0.2 km) was approximately 0.05 km downstream of the confluence of Rio Agua Dulce and the Ribera de la Vera Cruz. The Ribera de la Vera Cruz, whose bed is dominated by tailings, receives the untreated municipal wastewater, stormwater, and *ingenio* discharges of Potosí proper along with the AMD discharged on the Northern and Eastern slopes of Cerro Rico (Strosnider et al. *in press-b*). Sample point "2.2 km" was located within a steep canyon in Rio Tarapaya near the "Puerta del Diablo" landmark cave. Sample point "3.9 km" was located just

Figure 2: Sampling point “7.3 km” after the confluence of Rio Tarapaya and Rio Cayara (top). The black slag from the Sn-smelter can be seen at the center left of the image circled in blue. Sampling point “6.3 km” as seen from a nearby bridge (bottom). The telltale red tint of pyrite weathering can be seen along the banks of each reach, with a vivid example circled in red.

after Rio Tarapaya exits the canyon of “Puerta del Diablo” and consists of a lower gradient braided channel. Sample point “6.3 km” is in a similar setting that borders a lime (CaO) processing plant (Fig. 2). Sample point “7.3 km” was approximately 0.17 km after Rio Tarapaya’s confluence with the unimpacted Rio Cayara (Fig. 2). A slag heap from a Sn-smelter that operated briefly in the 1980s is centered at this confluence and runs along the East bank of

Rio Tarapaya. Tailings dominated the bed material of the entire reach of Rio Tarapaya sampled. The reference reach, Rio Cayara (Fig. 3), is an important water resource in a productive agricultural watershed, which is nearly the same size as that of Rio Tarapaya, in which no evidence of mining was observed although cannot be ruled out because of the ubiquity of mining in the region (Strosnider et al. *in press-b*).

Figure 3: The reference reach in Rio Cayara with respect to the farming community which makes use of it for irrigation, animal watering, and household consumption.

A Garmin GPS unit was used to record the coordinates of each sampling location. Low-water channel sediment (LS) and high-water sediment (HS) samples were taken at each sampling location. LS are perennially below the water-line of the river. HS lie above the water surface during the dry season yet are reworked by the river during high flow events in the wet season. In addition, water samples and water quality parameters were taken/recorded at each sampling location. Sampling occurred August 4, 2008 at the height of the dry season (BSNMH, 2003).

Geology

Cerro Rico de Potosí and the study reach of Rio Tarapaya lie within a Neogene-Quaternary volcanic-plutonic complex stretching for approximately 800 km along the Eastern Cordillera of the Andes (Zartman and Cunningham, 1995; Kamenov et al., 2002). The catchment is underlain by volcanic and sedimentary rock that are intruded by adamellites, quartz porphyries and dacites (Smolders et al., 2004). The bed material of Rio Tarapaya is dominated by the milled ores and waste rock (tailings) discharged to its tributaries over the past five centuries (Hudson-Edwards et al., 2001).

The ores of Cerro Rico formed as argentiferous magma crystallized into cassiterite-rich veins formed in Ordovician slate, dacitic tuff and tuff breccia, and other dacitic stock (Griess, 1951; Brading and Cross, 1972; Rice and Steele, 2005). Veins are enclosed in metal sulfides, oxides and gangue minerals such as quartz, tourmaline, siderite and kaolinite. Host rock is pyritized near the veins and pyrite is the predominant associated mineral with the sulfide ores and country rock (Lindgren, 1928; Lindgren and Creveling, 1928; Petersen, 1945; Wilson and Petrov, 1999). Other metal sulfides common in the veins of Cerro Rico are stannite, arsenopyrite, galena, marcasite, wurtzite, sphalerite, chalcopyrite, stibnite, jamesonite and tetrahedrite among others (Hudson-Edwards et al., 2001), the weathering of which produces the highly acidic polymettallic AMD that enamanates from the mine portals, ore piles and tailings deposits of Cerro Rico noted by Strosnider et al. (*in press-a*).

Material Collection

LS and HS samples were collected at each location noted in Fig. 1 from the top 0.1 m of sediment. LS samples were spaced linearly ¼, ½, and ¾ across the active channel perpendicular to the direction of flow. Each LS sample was a three-part linear composite centered upon the sampling location with equal parts sediment gathered at the sampling location and 0.2 m to each side perpendicular to the direction of river flow (Fig 4). HS samples were collected below bankfull discharge stage and above the active channel, 25 m up- and down-stream of the central LS sampling location (and the in-stream sediment sampling location). HS up- and down-stream samples were taken on opposite sides of the river than the central sampling location. The side of the river sampled twice was randomized. Each HS sample was a three-part linear composite centered upon the sampling location with equal parts sediment gathered at the sampling location and 0.5 m to each side parallel to the direction of river flow. Three three-part linear composite samples were taken from an unsaturated zone of the Laguna Pampa tailings dam, Potosí's primary tailings dam. All sediment samples were gathered with a steel shovel that was decontaminated between sites into sealed Whirlpack® bags.

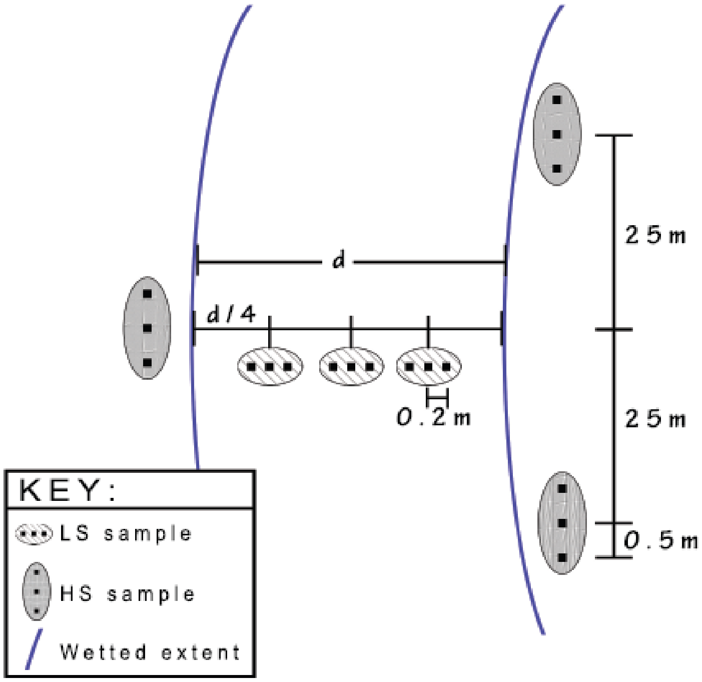

Figure 4: HS and LS sampling plan (not to scale).

Field Leach Test Methodology

FLT methodology followed that established, validated and accepted by the USGS (Hageman, 2007) with minor alterations due to the unique circumstances present in Bolivia. The FLT can determine the readily soluble, and therefore potentially bioavailable, constituents in solids leached by water (Hageman, 2007). The USGS has adopted the FLT as a surrogate for the USEPA SPLP (synthetic precipitation leaching procedure) because of similarity of results (Hageman, 2007).

Due to time constraints, all composite samples were dried at 105°C until constant mass. After drying, each composite sample was homogenized then sieved through a 2.0 mm stainless steel sieve, retaining the < 2.0 mm fraction. 125 mL of nanopure deionized water was added to 6.25 g of the sieved sediment in 125 mL HDPE bottles. The FLT bottles were agitated for 5 min on an Omron HSCA MH-4AIII shaker table at 300 rpm to ensure uniform shaking. Six control blanks, which consisted of the nanopure deionized water without any substrate, were exposed to the same agitation prior to sampling. After agitation the contents were allowed to settle for at least 10 min prior to sampling. Unfiltered samples for anion analysis were withdrawn with 60 mL Luer-Lock syringes. Dissolved metal samples were withdrawn from the FLT bottles with 60 mL Luer-Lock syringes and filtered through 0.45 µm nylon filters.

River Water Sample and Data Collection

Water quality parameters were recorded and samples were collected 50 m upstream of each sediment collection point. A properly calibrated Orion 1230 multimeter was used to determine pH, dissolved oxygen (DO) and temperature. Field alkalinity titrations were conducted in triplicate in accordance with standard methods (APHA, 1998) and Hach Method 8203 (Hach, 2006). Anion, total metal, and dissolved metal samples were taken from the estimated thalweg of the river at the sampling point. Dissolved metal samples were immediately filtered through 0.45 µm nylon filters.

Sample Analysis

Dissolved and total metal samples were stored in 60 mL HDPE bottles and immediately preserved with concentrated trace metal grade nitric acid in the field and stored at 4°C until microwave acid digestion following EPA method 3015. Total metal samples were filtered through 0.45 µm nylon filters after digestion. Digested metal samples were analyzed via a Varian Vista-Pro® simultaneous inductively coupled plasma optical emission spectrometer following United States Environmental Protection Agency (EPA) method 6010 at the University of Oklahoma Center for Restoration of Ecosystems and Watersheds laboratories. Anion samples were stored in 30 mL HDPE bottles at 4°C until filtered through Dionex OnGuard® II H cartridges and 0.2 µm nylon filters at the University of Oklahoma Center for Restoration of Ecosystems and Watersheds laboratories. A MetrOhm® 761 compact ion chromatograph unit was used to quantify anion concentrations following EPA method 300. Following EPA methods, duplicate and/or triplicate digestions of metals samples and measurements for metal and anion concentrations were randomly taken for quality assurance and control.

Data Analysis

Acidity was calculated with dissolved metal concentrations following a modified version of that presented by Younger et al. (2002), which accounted for the acidity from the substantial Cd^{2+}, Cu^{2+} and Zn^{2+} concentrations present in these waters. To facilitate the calculation of means and standard deviations, values below detection limits were assigned one half the value of the detection limit (Miller and Miller, 1986).

Results and Discussion

River Water Quality

Although pH was variable throughout the reach, it appeared to be decreasing overall with distance from Potosi (Table 1). Strosnider et al. (*in press-b*) also noted decreasing pH from the 0.2 km to 6.3 km sampling stations in the wet season (March 2007). Alkalinity was relatively stable from the city limits of Potosi (0.2 km) to the 3.9 km sampling station. The dramatic increase in alkalinity and Ca concentrations at 6.3 km may be due to the operations of the lime (CaO) plant that borders Rio Tarapaya just upstream of the 6.3 km mark (Table 3). Concentrations of ecotoxic metals, such as Al, As, Cd, Pb, and Zn were generally orders of magnitude greater than Bolivian receiving water body criteria and UNFAO (United Nations Food and Agriculture Organization) irrigation and livestock drinking water guidelines (Ayers and Westcot, 1994; BMSDP, 2000). Strosnider et al. (*in press-b*) and Smolders et al. (2003) found metal concentrations of similar magnitudes within the same stretch, which also generally exceeded Bolivian receiving water body criteria and UNFAO standards. In general, the impacted reach's ecotoxic metal and sulfate concentrations were orders of magnitude greater than the reference (Table 2). As the pH of Rio Tarapaya is buffered by the $Ca(OH)_2$ associated fresh tailings discharges and municipal wastewater it receives, most metals of interest were in the solid phase (totals). However, conditions appear to be limiting solubility but not transport as total metal concentrations remained highly elevated throughout the impacted reach. Contributors to Rio Tarapaya's total metal load are solid-phase metals from the fine sulfurous solids in tailings discharges as well as oxidation products of AMD and weathered in-stream tailings.

Table 1. River water physiochemical parameter measurements and calculated acidity.

	pH	SC	DO	T	Alkalinity	Acidity
	s.u.	µS/cm	mg/L	°C	mg/L as $CaCO_3$	
Reference	9.04	288	10.4	7.9	50	0.5
0.0 km	8.77	-	7.4	10.6	134	27.0
0.2 km	7.78	1308	7.8	11.5	223	4.7
2.2 km	8.60	1415	7.8	12.9	240	3.8
3.9 km	8.33	1382	7.6	12.5	206	3.7
6.3 km	6.69	517	7.7	12.3	360	33.0
7.3 km	7.77	840	8.7	10.5	97	6.6

Table 2. FLT and river water anion concentrations.

	F^-	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
			mg/L			
Tailings Dam	<0.20	2.0	<0.50	0.75	<0.75	134
High Sediment						
Reference	<0.20	4.1	<0.50	0.50	<0.75	15
0.0 km	<0.20	4.7	0.56	2.3	<0.75	166
2.2 km	<0.20	2.4	<0.50	4.9	<0.75	87
3.9 km	<0.20	2.7	<0.50	0.38	<0.75	257
7.3 km	<0.20	4.1	<0.50	0.65	<0.75	452
Low Sediment						
Reference	<0.20	<0.30	<0.50	<0.50	<0.75	1.1
0.0 km	<0.20	0.34	<0.50	<0.50	<0.75	15
0.2 km	<0.20	0.34	<0.50	<0.50	<0.75	14
2.2 km	<0.20	0.36	<0.50	<0.50	<0.75	15
3.9 km	<0.20	0.40	<0.50	<0.50	<0.75	14
6.3 km	<0.20	0.52	<0.50	<0.50	<0.75	26
7.3 km	<0.20	0.34	<0.50	<0.50	<0.75	9.0
River Water						
Reference	<0.20	15	1.1	1.3	<0.75	76
0.0 km	<0.20	43	<0.50	14	<0.75	946
0.2 km	0.79	82	4.7	<0.50	<0.75	364
2.2 km	0.60	82	4.9	<0.50	<0.75	428
3.9 km	<0.20	72	4.8	0.49	<0.75	457
6.3 km	<0.20	61	4.7	0.81	<0.75	721
7.3 km	<0.20	40	4.3	<0.50	<0.75	311
Control						
FLT Blanks	<0.20	<0.30	<0.50	<0.50	<0.75	<0.75

Table 3. FLT and river water major metal/metalloid concentrations. Underlined river concentrations are total concentrations. All other values are dissolved concentrations.

	Al	As	Ca	Cu	Fe	Mg	Mn	Pb	Zn
					mg/L				
Tailings Dam	0.048	<0.022	60	0.003	0.061	3.3	0.063	<0.011	0.054
High Sediment									
Reference	0.084	<0.022	8.6	0.007	0.072	0.33	0.014	<0.011	0.014
0.0 km	0.050	0.023	61	0.004	0.10	4.3	0.051	<0.011	0.042
2.2 km	0.050	<0.022	32	0.006	0.022	2.3	0.40	<0.011	1.4
3.9 km	0.67	<0.022	83	0.14	0.98	8.3	3.4	0.013	16
7.3 km	8.1	0.029	122	0.55	20	15	1.9	<0.011	17
Low Sediment									
Reference	0.064	<0.022	1.6	0.002	0.034	0.08	0.003	<0.011	0.015
0.0 km	0.070	<0.022	7.6	0.006	0.079	0.13	0.011	<0.011	0.032
0.2 km	0.039	<0.022	3.0	0.002	0.048	0.26	0.032	<0.011	0.075
2.2 km	0.021	0.025	3.0	0.004	0.034	0.16	0.051	<0.011	0.19
3.9 km	0.037	<0.022	3.6	0.004	0.049	0.20	0.028	<0.011	0.057
6.3 km	0.098	<0.022	5.3	0.006	0.17	0.69	0.16	<0.011	1.6
7.3 km	0.041	<0.022	2.2	0.002	0.028	0.13	0.010	<0.011	0.029
River Water									
Reference	0.055	<0.022	37	0.001	0.057	3.4	<0.0002	<0.011	0.080
	0.54	<0.022	38	0.003	0.52	3.7	0.039	<0.011	0.63
0.0 km	0.052	<0.022	391	0.039	0.015	26	7.7	<0.011	8.3
	7.5	1.7	397	0.65	35	31	10	1.5	70
0.2 km	0.15	0.022	126	0.05	0.22	12	1.3	<0.011	0.59
	12	3.1	139	0.94	90	15	2.7	2.1	26
2.2 km	0.14	0.028	183	0.025	0.050	14	1.3	<0.011	0.30
	22	4.0	191	1.5	116	17	3.5	3.0	38
3.9 km	0.11	0.032	152	0.083	0.040	14	1.3	<0.011	0.37
	12	2.7	168	0.89	83	16	3.2	1.8	32
6.3 km	0.065	0.023	233	0.013	6.0	21	4.5	0.029	8.8
	174	23	264	11	661	30	9.8	20	148
7.3 km	0.082	<0.022	115	0.014	1.0	9.6	1.1	<0.011	1.5
	6.0	1.3	123	0.55	40	11	1.5	1.4	24
Control									
FLT Blanks	0.026	<0.022	<0.0005	<0.001	0.025	<0.0004	<0.0002	<0.011	0.011

Table 4. FLT and river water minor metal/metalloid concentrations. Underlined river concentrations are total concentrations. All other values are dissolved concentrations.

	Ag	Ba	Cd	Co	Cr	Ni	Sb	Sn
	mg/L							
Tailings Dam	<0.0016	0.012	0.0030	0.001	0.0077	<0.004	0.014	<0.018
High Sediment								
Reference	<0.0016	0.023	0.0006	<0.001	<0.001	<0.004	<0.012	<0.018
0.0 km	<0.0016	0.027	0.0010	<0.001	<0.001	<0.004	<0.012	<0.018
2.2 km	<0.0016	0.021	0.0078	0.003	<0.001	<0.004	<0.012	<0.018
3.9 km	<0.0016	0.0096	0.060	0.034	<0.001	0.026	<0.012	<0.018
7.3 km	<0.0016	0.019	0.054	0.030	0.0030	0.035	<0.012	<0.018
Low Sediment								
Reference	<0.0016	<0.0004	0.0007	<0.001	<0.001	<0.004	<0.012	<0.018
0.0 km	<0.0016	0.022	0.0019	<0.001	<0.001	<0.004	<0.012	<0.018
0.2 km	<0.0016	<0.0004	0.0007	<0.001	<0.001	<0.004	<0.012	<0.018
2.2 km	<0.0016	<0.0004	0.0010	<0.001	<0.001	<0.004	<0.012	<0.018
3.9 km	<0.0016	<0.0004	0.0007	<0.001	<0.001	<0.004	<0.012	<0.018
6.3 km	<0.0016	0.014	0.011	0.003	<0.001	<0.004	<0.012	<0.018
7.3 km	<0.0016	<0.0004	<0.0006	<0.001	<0.001	<0.004	<0.012	<0.018
River Water								
Reference	<0.0016	0.028	0.0007	<0.001	<0.001	<0.004	<0.012	<0.018
	<0.0016	0.050	0.0009	<0.001	<0.001	<0.004	<0.012	<0.018
0.0 km	0.0032	0.099	0.11	0.018	<0.001	0.016	<0.012	<0.018
	0.014	0.20	0.24	0.074	0.005	0.085	0.10	0.020
0.2 km	<0.0016	0.073	0.0036	0.011	<0.001	0.017	0.015	<0.018
	0.038	0.56	0.098	0.030	0.011	0.063	0.25	0.040
2.2 km	<0.0016	0.10	0.0022	0.009	<0.001	<0.004	0.019	<0.018
	0.040	0.75	0.13	0.036	0.016	0.078	0.33	0.058
3.9 km	<0.0016	0.014	0.0033	0.009	<0.001	0.013	0.015	<0.018
	0.036	0.39	0.11	0.031	0.010	0.061	0.21	0.039
6.3 km	0.0019	0.035	0.028	0.034	<0.001	0.025	0.017	<0.018
	0.042	3.1	0.68	0.087	0.11	0.35	0.98	0.26
7.3 km	<0.0016	0.028	0.0076	0.008	0.005	<0.004	<0.012	<0.018
	0.026	0.14	0.073	0.019	0.005	0.030	0.21	0.027
Control								
FLT Blanks	<0.0016	<0.0004	<0.0006	<0.001	<0.001	<0.004	<0.012	<0.018

Sediment

The tailings dam material and HS and LS samples from the contaminated reach released sulfate, chloride and nitrate as well as a wide variety of metals and metalloids during the FLT. This indicates the presence of weakly bonded metal-sulfate, -nitrate, and -chloride salts in congruence with the findings of Kossoff et al. (2011). These salts are easily dissolved and mobilized via wetting. Sulfate, the primary anionic product of sulfide mineral weathering, is the dominant anion of the tailings dam, HS and LS leachate. However, the data indicate Ca and Mg sulfates likely dominate the soluble fraction of the substrates, although Al, Fe, Mn and Zn were leached in relatively high concentrations in HS 3.9 and 7.3 km samples.

Subsequent reactions of the products of sulfide weathering are the likely cause of the greater ratios of sulfate to As, Fe, Mn, Cd, Zn and Pb in the FLT leachate. It is likely that ionic Fe released via sulfide weathering in the tailings was followed by oxidation to form Fe oxyhydroxides, which are stable under aerobic circumneutral conditions such as are present in the waters of Rio Tarapaya and the FLT (Carroll et al., 1998; Younger et al., 2002). Arsenic, Cd, Zn, and Pb will strongly sorb to Fe oxyhydroxides and remain under these conditions (Carroll et al., 1998; Younger et al., 2002; Mohan and Pittman, 2007; Wilkin, 2008; Strosnider et al., 2011). Sulfate released by metal sulfide weathering would be primarily associated with soluble compounds, such as metal sulfates.

Reference sediment was much less reactive than that of Rio Tarapaya and the tailings dam. Rio Tarapaya HS and LS and tailings dam FLT sulfate and Cd, Fe, Mn, Zn concentrations were generally greater (often at an order of magnitude) than reference reach FLT. Reference FLT As, Co and Pb concentrations were below detection limits but were leached in measureable amounts from some Rio Tarapaya HS and LS samples.

Rio Tarapaya HS was much more reactive than LS, supporting the hypothesis of Hudson-Edwards et al. (2001) and Smolders et al. (2004) that the onset of the rainy season is a crucial time in the mobilization and transport of ecotoxic metals downstream. The marked increase in metal concentrations at the beginning of the wet season in the Rio Pilcomayo noted by Smolders et al. (2004) is likely due to the dissolution of reactive salts in the HS.

Rio Tarapaya HS FLT metals and sulfate concentrations generally increased with distance from the tailings source (Potosí). Tailings dam FLT Al, Cd, Fe, Mn, Zn and sulfate concentrations were also less than HS FLT at 3.9 and 7.3 km. This is likely due to downstream tailings having more time to weather and produce the highly soluble metal sulfate salts than newer tailings at the tailings dam. Hudson-Edwards et al. (2001) noted total concentrations of various ecotoxic metals in the bed material of the Rio Pilcomayo to decrease in concentration with distance from Potosí. While this is the case for the total metal content of the bed material at a large scale, it appears that the reactivity of the bed material increases with distance at the small scale (≤ 7.3 km from Potosí).

Conclusions and Recommendations

Tailings on the banks and in the saturated sediments of Rio Tarapaya are contributing to downstream heavy metals contamination. Therefore, illicit tailings discharges should cease. Even if tailings discharges are brought to an end, the reactivity of the millions of tonnes of tailings that have been dumped into Rio Tarapaya over the past five centuries suggests that the upper Rio Pilcomayo will remain severely degraded for the foreseeable future and remediation will continue to be a daunting task.

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