ORIGINAL ARTICLE

Acid mine drainage at Cerro Rico de Potosí I: unabated high-strength discharges reflect a five century legacy of mining

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Abstract Intensive mining and processing of Ag, Sn, Pb and Zn ores have occurred in various locations within and around the city of Potosí, Bolivia since 1545. Surface and subsurface waters, stream sediments and soils are contaminated with various ecotoxic metals in the headwaters of the economically vital, yet highly impacted, upper Rio Pilcomayo watershed. Previous studies have documented downstream trace metal contamination, however, not addressed specific sources. The AMD discharges identified in this study help link downstream pollution to primary origins. The majority of AMD would be considered high-strength due to metal concentrations and acidity orders of magnitude greater than typical AMD. Discharges from both operating and abandoned portals as well as tailings-related deposits displayed a high degree of heterogeneity with total metal concentrations ranging from 0.11 to 7480, <0.022 to 889, <0.0006 to 65.3, <0.001 to 310, 0.12 to 72,100, 0.3 to 402, <0.012 to 34.8, and 0.24 to 19,600 mg/L of Al, As, Cd, Cu, Fe, Mn, Pb and Zn, respectively. Net acidity and pH ranged from −10 to 246,000 mg/L as $CaCO_3$ equivalent and 0.90–6.94 standard units, respectively. Data were gathered during two sampling events centered around the most extreme periods of the dry and wet seasons of one water-year. Loadings to local streams were marginally greater for most metals in the wet season. If observed loadings are historically representative, Cerro Rico AMD has contributed thousands of tonnes of ecotoxic metals to the upper Rio Pilcomayo over the last five centuries. Metal and hydrogen ion concentrations in the majority of AMD sampled were several orders of magnitude above discharge limits set by the Bolivian government, yet no action has historically or contemporarily been taken.

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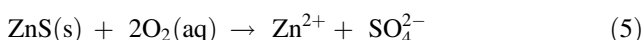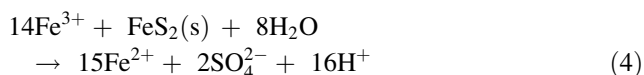Universidad Autónoma "Tomás Frías", Potosí, Bolivia
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Introduction

Historical background

Twelve years after Pizarro dethroned Atahualpa and conquered the Inca, the largest Ag deposit in the world was discovered at Cerro Rico (Rich Hill) by the indigenous nobleman Diego Huallpa. The next year the Spanish founded the city of Potosí at Cerro Rico's base with Huallpa's confidant, the Spaniard Juan de Villarroel, registering the first claim in 1545 (Wilson and Petrov 1999). Within a hundred years Potosí became one of the world's richest and most populous cities during a boom fueled by veins of up to 25% pure Ag (Wilson and Petrov 1999; Bartos 2000; Abbot and Wolfe 2003; Waltham 2005). Mining has proceeded nearly continuously over the last

five centuries and it is estimated that between 20,000 and 40,000 tonnes of Ag were produced from 1545 to 1824 and over 10,000 tonnes from 1824 to present (Lindgren 1928; Zartman and Cunningham 1995; Pretes 2002; Abbot and Wolfe 2003). Abbot and Wolfe (2003) also postulate that thousands of tonnes of Ag were produced from Cerro Rico and nearby deposits in Pre-Colombian times before and after the Incan conquest from the 10th to the 15th centuries. Ores from Potosí subsidized Spanish military expansionism while millions of forced indigenous and enslaved African laborers died premature deaths mining the depths of Cerro Rico and processing the ores found within (Galeano 1971; Tandeter 1981; Bakewell 1984). Ag, Sn, Pb and Zn have been the primary metals mined and processed in and around the slopes of Cerro Rico, sustaining the city economically for centuries. However, the environmental cost of Potosí's good fortune has been steep. Terrestrial zones have experienced extreme deforestation and associated soil loss (Godoy 1985). Local watercourses have been impacted by mineral processing effluent and unmitigated acid mine drainage (AMD).

Acid mine drainage

Economically valuable geologic deposits such as coal and metal ores are normally chemically stable under undisturbed in situ conditions. AMD forms when isolated sulfide minerals, such as pyrite (FeS_2), sphalerite (ZnS) and galena (PbS), are exposed to oxygen and water (Younger et al. 2002). Microbes such as *Acidithiobaccillus ferrooxidans* increase the rate of AMD evolution by catalyzing mineral oxidation (Younger et al. 2002). This mineral oxidation creates and mobilizes free metal, SO_4^{2-} and hydrogen ions into solution (Eqs. 1–5):

$$2FeS_2(s) + 7O_2(aq) + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{1}$$

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \tag{2}$$

$$2Fe^{3+} + 6H_2O \rightarrow 2Fe(OH)_3(s) + 6H^+ \tag{3}$$

$$14Fe^{3+} + FeS_2(s) + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$

$$ZnS(s) + 2O_2(aq) \rightarrow Zn^{2+} + SO_4^{2-} \tag{5}$$
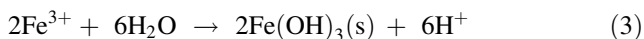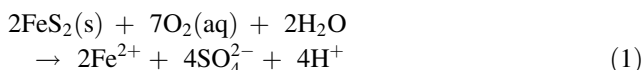
Pyrite oxidation (Eqs. 1–4) is the primary agent of AMD formation. The acidity generated by pyrite oxidation lowers the pH, increasing the solubility of many metals and allowing faster weathering of other metal sulfides. Weathering of other metal sulfides will not necessarily produce acidity, but will release metal ions to solution (Younger et al. 2002). Sphalerite oxidation (Eq. 5) is an example of these reactions which may release Zn, Pb, Ni,

Cd, Cu, As and other ecotoxic metals to solution often to be transported to discharge points such as seeps, adits or boreholes which then impact downstream environments (Younger et al. 2002).

The environmental cost of AMD has been known for centuries. The man considered to be the founder of geology as a discipline, Georgius Agricola, stated in the 16th century that "…when the ores are washed, the water which has been used poisons the brooks and streams, and either destroys the fish or drives them away" (Agricola 1556). The ecotoxic metal ions, acidity and resultant precipitates (such as iron oxyhydroxide often referred to as *ochre*) associated with AMD are a significant threat to freshwater resources and can cause fish-kills and lasting degradation of aquatic habitats (Adams and Younger 2001; Younger et al. 2002). AMD also often renders receiving watercourses unfit for use as water resources (Adams and Younger 2001).

Geologic setting

Cerro Rico de Potosí was created by volcanic eruptions of the Tertiary Age. It lies 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). Ore occurs throughout systems of veins in a conical dacitic volcanic dome rising 700 m above the city of Potosí (Zartman and Cunningham 1995). 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). The veins are enclosed in zones of metal sulfides, oxides and gangue minerals such as quartz, tourmaline, siderite and kaolinite. Silver oxides predominated in the upper altitudes of Cerro Rico while Ag sulfide ores dominate in the lower reaches (Bartos 2000). 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). Pyrite is the prime driver of AMD formation and its pervasiveness indicates that AMD will be released to the surrounding areas for decades or centuries unless remedial actions are undertaken. The polymetallic nature of the orebody indicates that this AMD would likely contain elevated concentrations of multiple metals of concern.

Legacy

The history of Potosí, like many historic mining centers, is one of cyclical boom and bust that has likely maximized AMD evolution. Many local mines have been abandoned,

flooded, dewatered and mined again multiple times (Hillman 1984), following the rise and fall of ore prices. There is evidence from Pb-contaminated lake sediments that mining and smelting for Ag production may have begun at Cerro Rico around 1000 A.D (Abbot and Wolfe 2003). However, intensive mining did not begin until Spanish conquest. Cerro Rico is considered the world's largest Ag deposit and Potosí led the world in production during the 16th and 17th centuries (Lofstrom 1970; Zartman and Cunningham 1995; Bartos 2000; Rice and Steele 2005). After an initial boom fueled by Ag oxide ores of up to 25% purity, mining lulled from approximately 1555 to 1575 until the introduction of the Hg amalgamation process (Serrano et al. 1996; Wilson and Petrov 1999). Ag production peaked in the late 16th century when there were over 600 mines on the mountain working a vertical interval of approximately 250 m (Serrano et al. 1996; Waltham 2005). Production lulled yet again from approximately 1700 to 1745 (Serrano et al. 1996). After a resurgence from approximately 1745 to 1805, production fell precipitously so that by 1825 Cerro Rico was home to more than 5,000 open mine shafts and adits, most of which were abandoned, flooded or collapsed (Lofstrom 1970). Of those shafts, only 50–60 were in use and the lower majority of the mountain was flooded (Lofstrom 1970). In the 1800s Potosí's population had fallen from a maximum of approximately 160,000 during the Ag boom of the 1600s to about 10,000 (Pretes 2002).

Resurgence of the Ag industry from 1850 to 1873 enabled by lower Hg prices (Hg was used in the amalgamation technique for processing Ag sulfides) caused the short-lived dewatering and re-start of many mines (Hillman 1984). In the latter quarter of the 1800s, Potosí's fortunes rebounded yet again with the emergence of the Sn industry as the Ag industry declined (Hillman 1984). An indication of the rich polymetallic nature of the Cerro Rico ore body, another metal, Cu, was mined and processed in the early 1900s (Miller and Singewald 1919; Cunningham et al. 1996). As of 1928, many veins in Potosí had been worked over a vertical interval of approximately 600 m (Lindgren 1928). The pinnacle of the Sn industry was in the first half of the 20th century when Bolivia was one of the top three worldwide producers during World War II (Griess 1951). Although the Sn industry was first established by the Incas, Sn only surpassed Ag in economic importance around the turn of the 20th century (Hillman 1984; Godoy 1985). At this time Sn miners dewatered and worked former Ag mines as well as alluvial deposits (*pallacos*) at the base of Cerro Rico (Bartos 2000; Waltham 2005). However, the 1985 Sn price collapse caused the closure and flooding of many Potosí mines (Waltham 2005; Younger 2007). Mineral prices have risen in recent years, leading to yet another boom cycle of dewatering and ore exploitation. In 1996,

Serrano et al. (1996) reported that over 500 shafts and adits were in operation, worked by about 5,000 miners. As of 2000, mine workings had extended to a vertical interval of 1,150 m (Bartos 2000). Currently, it is estimated that approximately 20,000 miners are either reworking old tailings and mine workings or opening new workings in deeper zones of Cerro Rico mining primarily Pb and Zn ores, and to a lesser extent, Ag and Sn ores. The repeated flooding, dewatering and mining of Cerro Rico has likely led to near-continuous production of high-strength AMD for centuries as freshly exposed sulfide minerals contact water during non-operational periods. The subsequent dewatering allows for oxygen ingress and fresh mineral exposure as the cycle is repeated.

Broad and progressive Bolivian environmental regulations became law in 1992 (BMSDP 2000). The law (Number 1333) regulates pollutant discharges of nearly all industries, sets water quality standards for receiving bodies and establishes limits for liquid discharges. However, it appears to have been largely ignored by the mining industry (Garcia-Guinea and Harffy 1998). Article 45 of the Bolivian Mining Code states that mining operations should use systems and technology compatible with environmental protection (Bocangel 2001). The Bolivian government issued and widely publicized Supreme Decree 25419, requiring all mining operations to obtain an environmental license (Bocangel 2001). Supreme Decree 25877 extended the deadline for compliance and has also met very limited success (Bocangel 2001). It is likely that, in addition to discharging AMD and mineral processing effluent out of compliance with Bolivian law, many mining facilities have not acquired an environmental license.

Previous environmental studies

Intensive mining over several centuries has devastated the aquatic environment around Potosí. Hudson-Edwards et al. (2001), Smolders et al. (2002, 2003, 2004), Miller et al. (2002, 2004) and Archer et al. (2005) documented dissolved and total ecotoxic metal concentrations orders of magnitude greater than natural background levels in Rio Tarapaya from the western edge of Potosí's city limits to ∼500 km downstream in Rio Pilcomayo. Miller et al. (2002, 2007) linked this contamination to mining activity via isotopic analysis of Pb in river sediment, however, the specific contaminant sources (i.e., AMD, mineral processing effluent, tailings dam erosion, etc.) could not be identified.

Although downstream heavy metal contamination has been fairly well documented, contamination sources have not. No peer-reviewed studies of Cerro Rico AMD or the other probable ecotoxic metal sources have been encountered in the literature. The objectives of the study were to

catalog the AMD discharges of Cerro Rico, determine the extent to which these discharges may be out of compliance with Bolivian law, and estimate metal loading rates to streams in the local watershed.

Methods

Study area

The study centered around Cerro Rico, approximately 1 km south of the city of Potosí, Bolivia. Potosí (19.585°S 65.754°W) lies in the Eastern Cordillera range of the Central Andes in the upper reaches of the Rio Pilcomayo watershed. As the entirety of Cerro Rico and immediate environs can essentially be considered a mine, all groundwater discharges noted were classified as AMD. AMD identified and characterized were from active and abandoned mine portals of Cerro Rico and seeps influenced by tailings deposits and/or the mineral-rich *pallacos* at the northwest base of Cerro Rico (Figs. 1, 2). The AMD documented in this study are those which were flowing during Potosí's dry season of July/August 2006 and wet season of March 2007 and those not intercepted for mineral processing use. Innumerable working and abandoned mine portals dot Cerro Rico, however, the majority were observed to not produce effluent. Active mine portal,

abandoned portal, and tailings-related discharges were assigned the prefixes "C", "A" and "T", respectively. Of the thirteen AMD sources identified and characterized on Cerro Rico proper, seven were from active mine portals, five were from abandoned portals and one was from a tailings deposit. Three tailings-related AMD sources were located at the northwest base of Cerro Rico.

Discharges 1A, 3A, 4T and 1–4C (Fig. 1) drain to Rio Huayna Mayu which empties into the highly polluted Ribera de la Vera Cruz, which also contains residual tailings from past mineral processing plant discharges and raw sewage from the city. Discharges 2A, 4–5A and 6C drain to Quebrada Chimborazo which shortly thereafter confluences with Rio Villacollu Mayu. Discharge 5C drains to the highly impacted Rio Jayac Mayu ("spicy river" in Quechua, the language of the Inca) which also may receive diffuse acid rock drainage (ARD) from numerous waste rock piles near its source. Discharge 7C drains to Rio Sucu/Kori Mayu which also receives AMD from the *pallacos* zones (discharges 1–3T). The *pallacos* discharges are associated with natural and anthropogenic erosion of mineral-rich material from Cerro Rico and the tailings from Sn mining of that material that ceased decades ago (Bartos 2000; Waltham 2005). These sources are also likely influenced by groundwater seepage from the San Miguel tailings deposit, which lies between Rio Sucu/Kori Mayu and the Ribera de la Vera Cruz. The Pailaviri tailings

Fig. 1 Study area and AMD discharges with respect to receiving streams, tailings deposits, greater Bolivia and South America
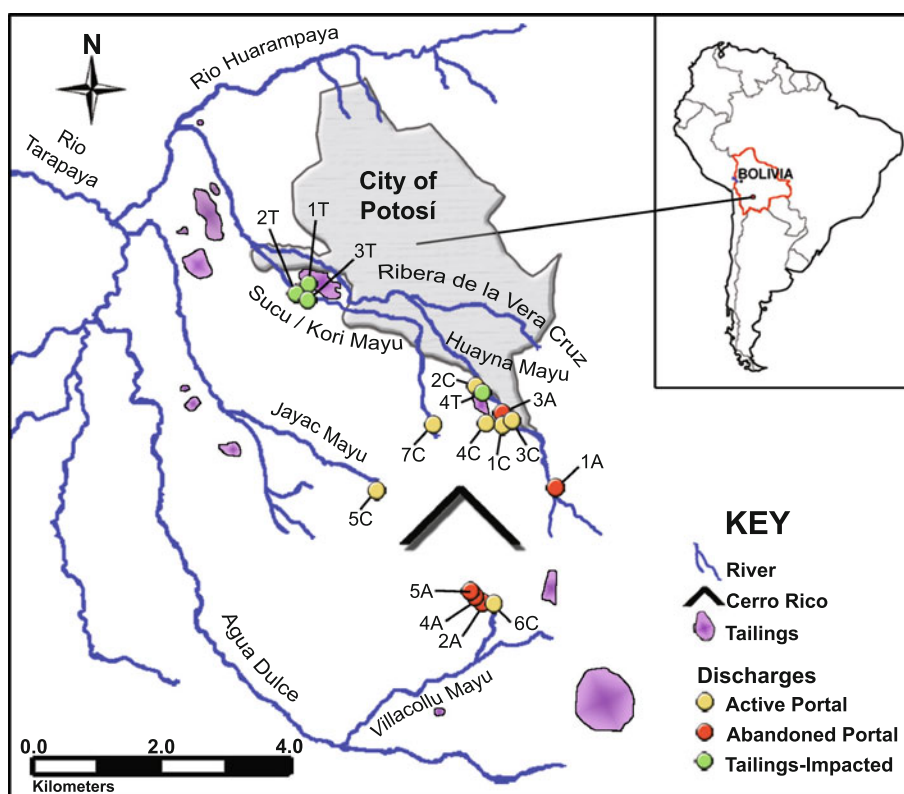
Fig. 2 AMD source 1C (*top left*), which is an active mine portal on the north slope of Cerro Rico. AMD source 1A (*top right*), which is an abandoned mine portal near the eastern base of Cerro Rico. A portion of the Pailaviri tailings deposit (*bottom*) which lies <100 m from Huayna Mayu, which confluences with the Ribera de la Vera Cruz less than 2 km from the location pictured. AMD source 4T emanates from this deposit

deposit (discharge 4T) on the slope of Cerro Rico drains to Huayna Mayu (Fig. 2). A few AMD sources (7C, 4A, 5A and 4T) were only sampled in the wet season because they were not flowing during the dry season.

Data collection

Water quality parameters and grab samples were obtained at the points indicated on Fig. 1 during the dry (July 27 to August 14, 2006) and wet (March 11–23, 2007) seasons of one water-year (Fig. 3). These intervals were chosen in an attempt to capture the groundwater level/efflux and surface water flow extremes of both seasons, when are near their minima (dry) and maxima (wet). Sampling periods were offset from the minima and maxima of the monthly average precipitation because of the common response lag of groundwater level/efflux and surface water flows to precipitation events (Eltahir and Yeh 1999).
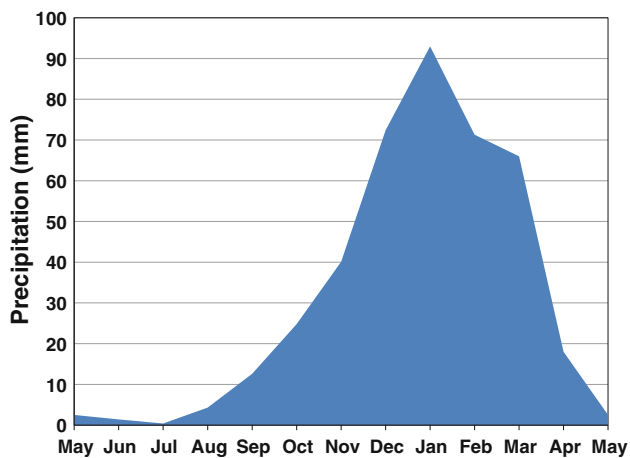
Fig. 3 Monthly average precipitation in the City of Potosí from 1958 to 2002 (BSNMH 2003)

The location of each AMD discharge was recorded with a Garmin® GPS unit. Alkalinity titrations were conducted in the field following standard methods (APHA 1998). Temperature, pH, dissolved oxygen (DO) and specific conductance (SC) were determined in the field using a properly calibrated Orion 1230 multimeter. The Orion pH probe consisted of a gel-filled epoxy body with an Ag–AgCl internal reference, wick junction and standard glass bulb. The pH was calibrated with Thermo Scientific pH 4.00, 7.00 and 10.00 standards for a three-point calibration, which is suitable for pH 2–10 (Cheng and Zhu 2005). All grab samples were taken using 125-mL HDPE containers for subsequent analysis at the University of Oklahoma Center for Restoration of Ecosystems and Watersheds (CREW) laboratories. Samples for anion analyses were stored at 4°C until filtered through 0.2 μm nylon filters and Dionex OnGuard® II H cartridges. A MetrOhm® 761 ion chromatograph unit was used to quantify SO_4^{2-} concentrations following United States Environmental Protection Agency (USEPA) method 300. Total metal samples were immediately preserved with concentrated nitric acid and stored at 4°C until microwave acid digestion. Upon collection, dissolved metal samples were immediately filtered through 0.45 μm nylon filters then preserved with concentrated nitric acid and stored at 4°C until microwave acid digestion. All microwave acid digestions followed USEPA method 3015. Digested metal samples were filtered through 0.45 μm nylon filters then analyzed via a Varian Vista-Pro® simultaneous inductively coupled plasma-optical emission spectrometer following EPA method 6010. Following USEPA methods, duplicate and/or triplicate digestions of metal samples and measurements for metals and sulfate concentrations were randomly obtained for quality assurance and control. Net acidity was calculated 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 unique waters. Hedin (2006) demonstrated an excellent relationship between calculated and measured net acidity for a diverse data set of 1,484 AMD sources.

Flow rates (Q) were obtained via two methods. When possible, flow rates were obtained by building temporary weirs and determining time to gather a known volume in a bucket or graduated cylinder. When flow rates were greater than this method would allow, discharge was estimated by determining channel cross-section, depth and velocity as approximated by floating a partially submersible object a given distance. Wet and dry season loadings were determined by multiplying total metal concentrations by their respective flow rates. Where flow rates were too low or diffuse to determine using the aforementioned methods, a conservative flow rate of 0.01 L/s based on comparative observation was assigned to enable the prudent estimation of metal loadings.

Results and discussion

Physiochemical parameters, total and dissolved metal concentrations, and SO_4^{2-} concentrations for sampled AMD are presented in Tables 1 and 2. These results are compared to various water quality criteria set by the Bolivian government in Table 3. Generally, dissolved metal concentrations were similar to total metal concentrations, indicating that the bulk of metals discharged to receiving streams from mine water discharges are in the more mobile, dissolved form. Metals and SO_4^{2-} concentrations and acidity in AMD varied by several orders of magnitude, indicating a high degree of heterogeneity within the groundwaters of Cerro Rico. Metals are not uniformly disseminated throughout Cerro Rico which is reflected by these data. The majority of AMD would be considered high-strength due to metal concentrations and acidity orders of magnitude greater than typical AMD (e.g., Younger et al. 2002; Watzlaf et al. 2004). Concentrations of contaminants in most sampled AMD were orders of magnitude out of compliance with Bolivian discharge limits and likely contributed to the aforementioned pollution downstream.

The active mine portals generally had higher metal concentrations than the abandoned and tailings-related sources (Table 2). The tailings-impacted *pallacos* discharges (1-3T) generally exhibited lower metal concentrations than the other abandoned and active mine sources. This is likely due to the increased weathering that the alluvial deposits have experienced. These deposits were created over millennia as surface rock of Cerro Rico weathered and eroded downhill. Much of the sulfides on the exposed surfaces of the alluvial deposits have likely

Table 1 Mean physical parameter measurements, net acidity and SO$_4$ concentrations, and flow rates of Cerro Rico AMD in the dry and wet season

Site	pH s.u.	DO (mg/L)	SC (µS/cm)	Net acidity (mg/L as CaCO$_3$ eq.)	SO$_4^{2-}$ (mg/L)	Q (L/s)
1C	*3.0*	*3.5*	*10,440*	*9,870 to 9.160*	–	*0.03*
1C	**3.2**	3.6	6,370	8,080 to 7,280 (7,570 to 6,860)	6,480	0.05
2C	*3.3*	*0.8*	*9,470*	*24,900 to 19,300*	–	*0.01*
2C	**3.1**	2.5	6,800	30,100 to 24,400	19,300	0.10
3C	*3.0*	*4.08*	*19,070*	*27,700 to 25,400*	–	*0.01*
3C	**3.2**	3.80	22,000	53,500 to 47,800	34,000	0.05
4C	*3.2*	*4.40*	*8,690*	*19,000 to 16,300*	–	*0.13*
4C	**3.6**	2.70	4,290	9,930 to 8,370 (10,400 to 8,850)	8,830	0.18
5C	*2.5*	*6.10*	*18,640*	*39,900 to 34,200*	–	*0.28*
5C	**3.4**	3.75	9,290	13,100 to 11,200	8,720	0.28
6C[a]	*3.3*	*2.15*	*3,160*	*2,650 to 2,190*	*3,400*	*0.17*
6C	**3.6**	7.20	3,780	3,920 to 3,350 (3,720 to 3,190)	3,270	0.08
7C	**2.1**	3.1	23,200	31,600 to 24,300 (28,800 to 22,200)	23,000	0.05
1A[b]	*3.6*	*6.63*	*1,888*	*1,250 to 1,150*	*1,320*	*0.86*
1A[a]	**4.5**	6.39	1,457	979 to 870 (461 to 455)	631	0.86
2A[a]	*2.9*	*1.33*	*7,530*	*11,100 to 9,320*	*9,180*	*0.02*
2A	**2.3**	0.10	11,300	12,500 to 10,400 (12,200 to 9,870)	8,740	0.18
3A	*3.0*	*2.91*	*14,900*	*28,100 to 25,200*	–	*0.07*
3A	**3.6**	3.00	9,230	14,200 to 12,300 (13,500 to 11,500)	10,000	0.02
4A	6.9	5.70	345	−6.61 to −6.50 (−6.51 to −6.38)	232	0.03
5A	6.9	5.55	272	−10.0 to −7.25 (−37.3 to −37.2)	257	0.06
1T	*3.0*	*2.50*	*2,820*	*1,400 to 1,350*	–	*0.26*
1T	**3.0**	3.75	2,710	1,050 to 1,020 (1,030 to 1,000)	1,730	0.72
2T	*4.2*	*4.65*	*1,115*	*78.8 to 78.4*	–	*4.6*
2T	**4.1**	1.00	1,174	83.2 to −83.1(82.3 to −82.2)	498	1.1
3T	*6.5*	*6.60*	*893*	*−46.9 to −46.8*	–	*0.10*
3T	6.4	3.79	960	−30.9 to −30.8 (−32.0 to −31.9)	322	0.33
4T	**0.9**[c]	–	54,600	246,000 to 181,000 (239,000 to 176,000)	175,000	0.03

Dry season data are italicized and wet season data are underlined. $N = 1$ except where otherwise noted. Net acidity range calculations used total and (dissolved) metal concentrations, the lower bound assuming all Fe to be trivalent, the upper bound assuming all Fe to be divalent. pH is bolded where exceeding the monthly Bolivian discharge limit

– Not determined

[a] $n = 2$

[b] $n = 3$

[c] Exact value is suspect because it is below the instrumental range

been weathered, leaving more inert material that produces AMD or ARD of lower metal concentrations and acidity. The freshly exposed sulfides within Cerro Rico are likely leading to the higher metal concentrations observed in the AMD of the active mines. Cerro Rico has been mined for centuries at irregular unsystematic intervals and many workings are interconnected due to the degree of exploration and common collapse features (Petersen 1945; Cunningham et al. 1996). The active mine portals shared the same general pH and metal concentrations as three of the abandoned portals (1–3A). The abandoned mine portals

sampled in this study are likely connected to and receive waters from active workings, thus sharing in the effect of the ongoing fresh sulfide mineral exposure and oxidation.

The seep from the Pailaviri tailings deposit (4T) produced the most acidic and metal-laden AMD identified. The pH and metal concentrations of this seep place it among other extreme examples of AMD. Dissolved As, Fe and SO$_4^{2-}$ concentrations rival those documented at Iron Mountain, which as of 1999 was reported to have the greatest concentrations of these constituents ever recorded in groundwater (Nordstrom and Alpers 1999; Nordstrom

Table 2 Mean total and (dissolved) metal concentrations determined for grab samples of Cerro Rico AMD

Site	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1C	273	0.57	12.4	2.28	0.030	1.76	796	18.3	2.92	0.211	4,000
1C	211 (196)	1.35 (0.65)	10.7 (11.2)	2.08 (2.02)	0.034 (0.032)	2.83 (2.75)	896 (795)	18.8 (17.0)	3.08 (2.86)	0.50 (0.29)	2,880 (2,780)
2C	461	29.6	7.19	4.05	0.09	10.8	6,320	402	4.26	1.40	3,050
2C	420	85.2	12.2	2.68	0.12	30.7	6,390	221	4.20	2.82	6,630
3C	752	34.4	35.9	3.93	0.13	12.9	2,580	33.6	6.36	2.53	10,800
3C	1,110	125	65.3	7.22	0.63	39.6	6,310	56.0	11.2	34.8	19,600
4C	648	40.7	21.2	2.51	0.22	84.9	3,050	84.6	1.87	1.07	4,500
4C	306 (258)	30.6 (4.66)	10.3 (11.0)	1.35 (1.84)	0.29 (0.17)	49.5 (44.0)	1,750 (1,710)	74.8 (73.7)	2.01 (1.71)	13.1 (0.61)	3,460 (2,690)
5C	1,120	180	36.2	4.03	0.43	152	6,410	51.7	2.55	17.5	10,500
5C	440	8.46	6.94	2.21	0.16	5.91	2,052	114	2.15	5.41	3,180
6C[b]	110	13.6	0.57	1.05	0.031	0.39	512	54.2	0.56	7.36	351
6C	64.1 (64.1)	15.0 (8.31)	4.73 (4.99)	0.70 (0.75)	0.049 (0.042)	0.32 (0.28)	637 (587)	43.4 (42.2)	2.26 (0.55)	6.05 (1.21)	1,140 (1,100)
7C	1,300 (1,170)	138 (125)	10.6 (11.1)	2.79 (2.66)	1.10 (1.10)	227 (232)	8,130 (7410)	9.60 (6.31)	2.83 (2.56)	5.65 (1.28)	1,170 (1,120)
1A[a]	5.76	0.030	0.17	0.14	0.002	0.037	111	13.2	0.16	0.065	574
1A[b]	25.7 (8.97)	0.94 (0.022)	0.43 (0.38)	0.079 (0.057)	0.011 (<0.001)	0.13 (0.040)	105 (14.3)	14.1 (9.94)	0.087 (0.067)	3.23 (0.22)	271 (226)
2A[b]	85.0	21.5	7.79	0.59	0.031	0.047	2,000	135	0.82	0.50	3,240
2A	77.1 (80.5)	41.5 (38.8)	9.42 (9.84)	0.73 (0.74)	0.042 (0.043)	0.13 (0.12)	2,410 (2,410)	122 (125)	0.92 (0.96)	1.46 (1.67)	3,360 (3,130)
3A	810	7.35	48.5	5.58	0.15	10.5	3,240	44.9	5.92	0.64	9,620
3A	446 (437)	8.44 (7.15)	16.5 (17.3)	2.02 (2.46)	0.14 (0.14)	29.9 (29.9)	2,140 (1920)	45.8 (46.5)	2.91 (2.60)	0.65 (0.60)	3,810 (3,050)
4A	0.11 (0.023)	<0.022 (<0.022)	<0.0006 (0.001)	<0.001 (<0.001)	<0.001 (<0.001)	<0.001 (0.003)	0.12 (0.15)	3.95 (4.09)	<0.004 (< 0.004)	<0.012 (<0.012)	0.24 (0.43)
5A	3.82 (0.052)	<0.022 (<0.022)	0.0008 (<0.0006)	<0.001 (<0.001)	0.001 (<0.001)	<0.001 (0.002)	3.12 (0.072)	0.42 (0.060)	<0.004 (< 0.004)	0.043 (<0.012)	0.26 (0.11)
1T	167	<0.022	0.72	0.33	0.006	23.6	49.1	48.5	0.29	0.17	103
1T	123 (115)	<0.022 (<0.022)	0.55 (0.64)	0.27 (0.30)	0.005 (0.007)	20.0 (20.3)	27.8 (29.0)	39.4 (40.4)	0.23 (0.25)	0.036 (0.049)	87.0 (90.3)
2T	8.12	<0.022	0.087	0.018	0.004	0.60	0.36	3.65	0.078	0.042	14.3
2T	8.27 (8.06)	<0.022 (<0.022)	0.10 (0.10)	0.022 (0.021)	<0.001 (< 0.001)	0.68 (0.68)	0.14 (0.14)	4.23 (4.08)	0.058 (0.058)	<0.012 (< 0.012)	15.5 (15.9)
3T	0.28	<0.022	0.025	<0.001	0.002	0.030	0.15	0.30	0.026	0.025	4.84
3T	0.48 (0.27)	<0.022 (<0.022)	0.035 (0.035)	<0.001 (0.002)	<0.001 (<0.001)	<0.001 (0.044)	0.13 (0.028)	0.79 (0.80)	0.022 (0.023)	<0.012 (<0.012)	6.32 (6.46)
4T	7,480 (7,390)	889 (821)	16.6 (15.1)	14.8 (8.3)	2.51 (2.56)	310 (301)	72,100 (7,0500)	96.1 (91.5)	11.4 (11.6)	24.8 (26.1)	1,660 (1,630)

Dry season data are italicized and wet season data are underlined. As, Cd, Cr, Cu, Fe, Pb and Zn concentrations are bolded where exceeding the monthly Bolivian discharge limit. Total Cr concentrations were compared to more conservative Cr(III) discharge limits because it is the more commonly prevalent species at the pH conditions noted (Stumm and Morgan 1996)

Values are in mg/L

[a] $n = 3$

[b] $n = 2$

Table 3 Bolivian discharge and receiving water body criteria

Standard	pH s.u.	Al	As	Cd	Co	Cr[a]	Cu	Fe	Mn	Ni	Pb	Zn	SO₄
Daily discharge	6–9		1.0	0.3		1.0/0.1	1.0	1.0			0.6	3.0	
Monthly discharge	6–9		0.5	0.15		0.5/0.05	0.5	0.5			0.3	1.5	
Class "A"	6.0–8.5	0.2	0.05	0.005	0.1	0.05	0.05	0.3	0.5	0.05	0.05	0.2	300
Class "B"	6–9	0.5	0.05	0.005	0.2	0.6/0.05	1.0	0.3	1.0	0.05	0.05	0.2	300
Class "C"	6–9	1.0	0.05	0.005	0.2	0.5/0.05	1.0	1.0	1.0	0.5	0.05	0.2	300
Class "D"	6–9	1.0	0.1	0.005	0.2	1.1/0.05	1.0	1.0	1.0	0.5	0.05	0.2	400

Values are in mg/L

[a] Cr (III) and Cr(VI) limits, respectively

Table 4 Seasonal AMD total metal loadings to streams draining Cerro Rico

	Dry Season				Wet Season			
	Operating	Abandoned	Tailings	Total	Operating	Abandoned	Tailings	Total
Al	38	5.6	6.9	50	31	3.7	28	63
As	5.1	0.08	[a]	5.2	2.7	0.73	2.4	5.8
Cd	1.2	0.33	0.05	1.6	0.84	0.20	0.09	1.1
Co	0.15	0.5	0.01	0.21	0.15	0.02	0.06	0.23
Cr	0.01	0.001	0.002	0.02	0.02	0.002	0.007	0.03
Cu	4.7	0.07	0.76	5.5	2.3	0.05	2.1	4.5
Fe	210	32	1.2	240	200	48	200	450
Mn	3.4	1.5	2.5	7.4	6.5	3.0	3.1	13
Ni	0.11	0.05	0.04	0.20	0.21	0.02	0.05	0.29
Pb	0.55	0.01	0.02	0.58	0.58	0.26	0.07	0.91
Zn	330	110	8.0	450	280	77	11	370

Values are in kg/day

[a] Concentrations below detection limits (<0.022 mg/L), loading inestimable

et al. 2000). Other sites with acute AMD, the Iron Duke mine in Zimbabwe and Peña de Hierro in Spain, demonstrated similar extreme elevated concentrations of Al, Cd and/or Mn as the Pailaviri seep (Williams and Smith 2000; Romero et al. 2011). Iron Mountain, Iron Duke, and Peña de Hierro are examples of the most ideal geologic settings for AMD production in the world. The Pailaviri tailings deposit must present a similar geologic setting, and thus a major environmental liability.

The AMD documented in this study are contributing to the downstream violations of Bolivian receiving body water quality limits noted in the following chapter. Class "D" is the lowest designation of Bolivian receiving water bodies in which industrial applications and navigation are the only suitable uses except in extreme circumstances (BMSDP 2000). Bolivian law states that class "D" waters must be "coagulated, flocculated, filtered and disinfected" prior to domestic use (BMSDP 2000). It is not known how or if the water bodies downstream of Potosí are designated. However, they are used for agriculture and therefore should

be rated at a minimum above class D. The introduction of AMD with concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn and SO_4^{2-} orders of magnitude greater than class "D" limits is contributing to non-compliance downstream.

All but one of the AMD discharges (4A) exceeded Bolivian monthly discharge limits to some degree and most by orders of magnitude for multiple metals. Half of the sixteen AMD discharges had higher than permissible concentrations of As, Cd, Cu, Fe, Pb and Zn. Fourteen AMD discharges had higher than permissible Zn concentrations, often by three or four orders of magnitude. Thirteen had lower than permissible pH. The data support the assertion of Garcia-Guinea and Harffy (1998) that Bolivian environmental law "has been sadly ignored where mining is concerned."

Local streams were considerably loaded with ecotoxic metals from Cerro Rico (Table 4). Active mine portals contributed the majority of metal loadings in both seasons. All metal loadings except Cd, Cu and Zn were at least

marginally greater during the wet season. Combined Al, As, Fe, Mn, Ni and Pb loadings were 26, 12, 88, 76, 45 and 57% greater, respectively, in the wet season. Tailings-related discharge loadings were much greater in the wet season when 4T was flowing. The majority of AMD discharges had concentrations of As, Cd, Cu, Pb and Zn orders of magnitude higher than those found downstream in Rio Tarapaya and Rio Pilcomayo by earlier studies (e.g., Hudson-Edwards et al. 2001; Smolders et al. 2003). Overall, the data indicate that these AMD discharges are contributing to some degree to downstream heavy metal pollution in the upper Rio Pilcomayo basin, which is further demonstrated in Strosnider et al. (2011a). If observed loadings are historically representative, AMD has contributed thousands of tonnes of ecotoxic metals to the upper Rio Pilcomayo over the last five centuries. Nonpoint source ephemeral ARD sources also exist, due to the prevalence of innumerable ancient and recent ore and tailings dumps upon and around Cerro Rico (Miller and Singewald 1919; Lindgren and Creveling 1928; Francis et al. 1981), exposure of ores near the peak with recent and ongoing surface mining, as well as the highly mineralized nature of Cerro Rico's slopes. Despite efforts to locate all AMD sources around Cerro Rico, other point sources likely exist because of the size of Cerro Rico and dynamic nature of ongoing mining. The likelihood of other AMD sources renders downstream loadings documented in this study a probable underestimate.

The relative importance of different pollution sources to the Rio Pilcomayo is unknown. Hudson-Edwards et al. (2001), Smolders et al. (2002, 2003) and Miller et al. (2002, 2004, 2007) stressed the significance of mineral processing effluent to downstream contamination. However, these studies were undertaken when the tailings load to the upper Rio Pilcomayo was much greater, before the construction of the Laguna Pampa and San Antonio tailings dams which are now the destination of most mineral processing effluent. In addition, no published peer-reviewed studies have documented the mineral processing effluent characteristics and loading rates. This study is the first to characterize AMD sources. However, the data presented in this study were the minimum required to extrapolate annual loading to downstream watercourses, and are likely an underestimate of the total loading from point AMD sources because of the probable existence of other sources. Further research, including mineral processing effluent discharge and nonpoint ARD characterization will help solidify the relative importance of the upper Rio Pilcomayo's pollution sources. This information would help establish priorities for future remediation efforts.

The extraction and export of mineral wealth has dominated the economy of Bolivia for centuries. Potosí's economy and roughly 150,000 residents remain heavily dependent upon mineral extraction and processing.

Therefore, environmental law enforcement should be carefully applied and fitting solutions presented to lessen the impact of mining operations. Measured by multiple metrics, Bolivia is one of the poorest nations in the Western Hemisphere (World Bank 2009). Hence, solutions attempted to address to the mine water pollution problems in Potosí cannot be capital-intensive. A labor-intensive solution may be desirable because of high unemployment and underemployment in Potosí, as well as the low cost of local labor.

Passive systems may be more suitable than active systems for AMD treatment in Potosí. Passive treatment uses unrefined natural materials to promote natural chemical and biological processes to improve water quality (Younger et al. 2002). Active treatment, the improvement of water quality by methods that require ongoing inputs of energy and chemical reagents, generally has higher operational costs than passive systems (Younger et al. 2002). Highly mechanized construction or operational activities are not desirable in Potosí because of logistical and supply issues. In developed nations, passive treatment systems have higher up-front costs because of greater land and construction expenses (Younger et al. 2002). However, in Bolivia depressed land and low construction costs may make passive treatment a logical solution from both long- and short-term perspectives. The chemicals, electricity and equipment needed for active treatment may make passive treatment by default the most applicable solution. In addition, passive treatment system construction and metal reclamation could provide needed employment.

The two major raw materials often required for passive treatment systems are organic substrate and limestone. Locally available limestone is suitable for passive treatment (Strosnider and Nairn 2010). Results from Santamaria et al. (2009) indicate that locally available llama dung, cattle manure, and brewery waste are suitable for use in passive treatment. Conventional hybrid active–passive treatment systems are also a more sustainable option. The passive co-treatment of Potosi's AMD with municipal wastewater is also a less conventional option that has been recently proved feasible (Strosnider and Nairn 2010; Strosnider et al. 2011b, c).

Conclusions

The AMD of Cerro Rico de Potosí can generally be categorized as high-strength, with concentrations of various ecotoxic metals often orders of magnitude greater than discharge limits. If the loadings observed are historically representative, AMD has been a prime contributor of ecotoxic metals to the upper Rio Pilcomayo over the last five centuries. Yet, no action has been taken to address

these discharges, neither historically nor contemporarily. Further studies, concerning the relative contributions of ecotoxic metal sources to the upper Rio Pilcomayo and treatability of these sources are recommended to refine remediation priorities and approaches.

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