# A LEGACY OF NEARLY 500 YEARS OF MINING IN POTOSÍ, BOLIVIA: ACID MINE DRAINAGE SOURCE IDENTIFICATION AND CHARACTERIZATION[1]

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**Abstract:**  Intensive mining and processing of silver, lead, tin and zinc 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 heavy metals.  Acid mine drainage and processing plant effluent are primary contaminants in the headwaters of the economically vital, yet highly impacted, Rio Pilcomayo watershed.  Previous studies have documented downstream heavy metal contamination.  The acid mine drainage sources documented in this study help to link downstream pollution to primary origins.  Selected acid mine drainage sources, from both operating and abandoned mines contributing to local streams, contained total metal concentrations of 0.284-977 mg/L Al, 0.03-191 mg/L As, 0.025-50.68 mg/L Cd, 0.03-161 mg/L Cu, 0.15-7,320 mg/L Fe, 0.3-438 mg/L Mn, 0.03-15.0 mg/L Pb and 1.46-11,760 mg/L Zn, with pH and specific conductance ranging from 2.46-6.39 and 893-19,070 μS/cm, respectively.  Data were gathered during the dry season with flows ranging from nil to 4.59 L/s.  Metals concentrations and pH values in all mine drainage sources sampled are several orders of magnitude above compliance with Bolivian environmental law.

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

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# Introduction

## 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 Spainard Juan de Villarroel, registering the first claim April 21, 1545 (Wilson and Petrov, 1999).  Within a hundred years Potosí became one of the world's richest and most populous cities during a Ag boom fueled by Cerro Rico veins of up to 25% pure metal (Wilson and Petrov, 1999; Bartos, 2000; Abbot and Wolfe, 2003; Waltham, 2005).  Mining proceeded nearly continuously over the last five centuries and it is estimated that between 20,000 and 40,000 metric tons of Ag were produced from 1545 to 1824 and nearly 10,000 metric tons 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 metric tons 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 wars in Europe while millions of forced indigenous and slave African laborers died premature deaths mining the depths of Cerro Rico and processing the ores found within (Galeano, 1971; Tandeter, 1981; Bakewell, 1984).  In addition, the environmental cost of Potosí's good fortune has been steep.  Terrestrial zones have experienced extreme deforestation and soil loss while local watercourses have been impacted by mineral processing effluent and 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 ores, such as pyrite, sphalerite and galena, 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 and hydrogen ions into solution, often to be transported to discharge points such as seeps, adits or boreholes which then impact downstream environments.

The environmental cost of AMD has been known for years.  The man who is considered 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, 2000; Younger et al., 2002).  AMD also often renders receiving watercourses unfit for use as water resources (Adams and Younger, 2000).

## Geology

Cerro Rico of Potosí was created by volcanic eruptions of the Tertiary Age (Fig. 1).  It lies within a Neogene-Quaternary volcanic-plutonic complex stretching for approximately 800 km along the Eastern Cordillera of the Central 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 Ag and base 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 "predominates greatly in the ores" according to Lindgren (1928). The Sn mineral, cassiterite, is found finely disseminated through pyrite (Petersen, 1945). Pyrite is the prime source 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.
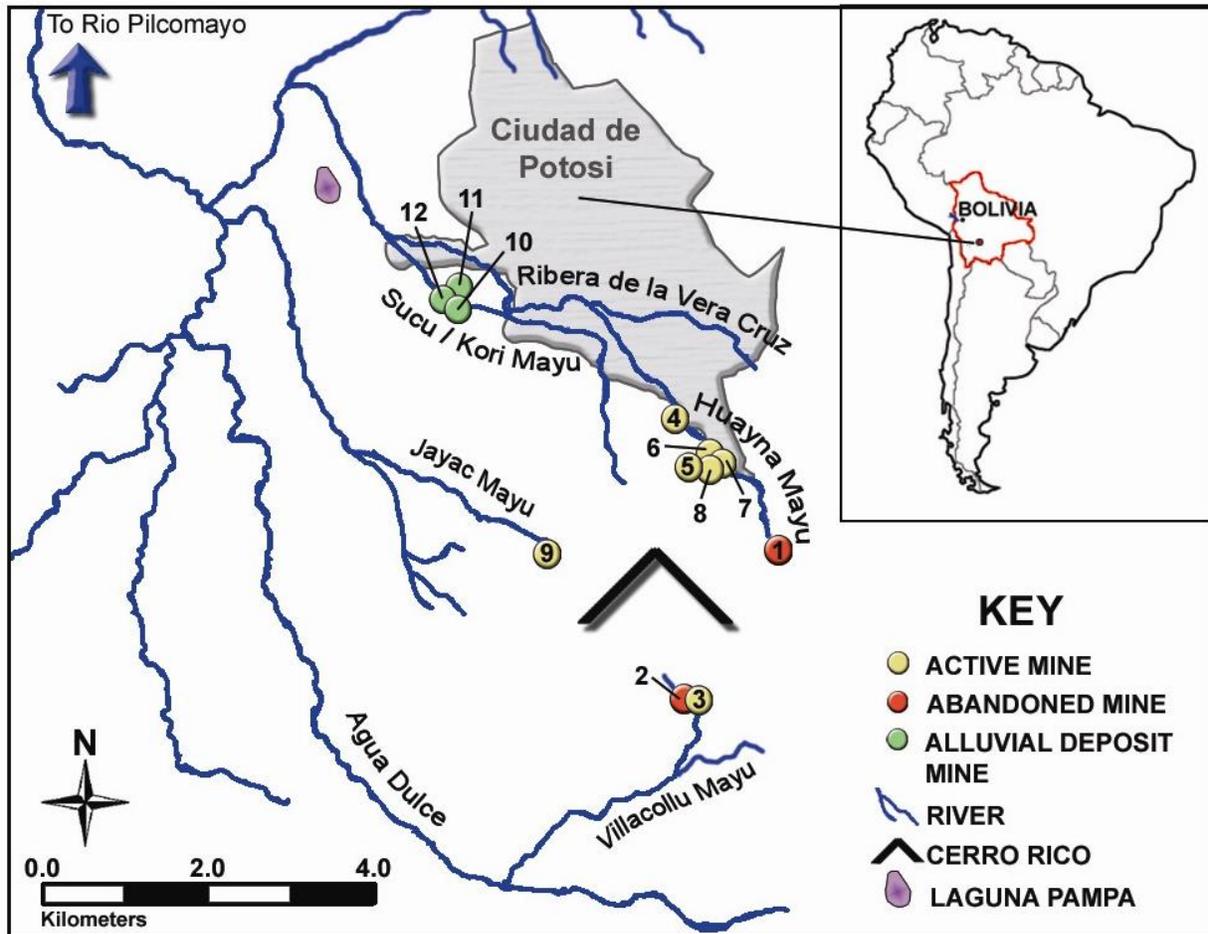


Figure 1. Study area and numbered AMD sources sampled with respect to receiving streams, greater Bolivia and South America

Potosí's Mining History and 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). There is evidence from Pb-contaminated historical lake sediments that mining and smelting for Ag production began at Cerro Rico around 1000 A.D (Abbot and Wolfe, 2003). 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). 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 (Waltham, 2005). However, eventually Ag market prices fell and ore quality decreased 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 caved in (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 as Ag mining became less profitable (Pretes, 2002).

Resurgence of the Ag industry from 1850-73 enabled by lower Hg prices (Hg was used in the amalgamation technique for processing Ag sulfides) caused the dewatering and re-start of many mines (Hillman, 1984). In the latter half of the 1800s, Potosí's fortunes rebounded yet again with the emergence of the Sn industry as the Ag industry declined (Hillman, 1984). 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 Sn 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, *in press*). Ag, Pb, Sn and Zn prices have risen in recent years, leading to yet another boom cycle of dewatering and ore exploitation. As of 2000, mine workings had extended to a vertical interval of 1,150 m (Bartos, 2000). 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.

Mining and mineral processing technology applied in Potosí has generally lagged behind contemporary methods. In the 19th century, human porters were used to remove ore in Potosí while railcars and steam power were used in Europe (Lofstrom, 1970). Through the 20th century poorly maintained and operated equipment and facilities were a hallmark of Bolivian mining (Godoy, 1985). Currently, the mining cooperatives on Cerro Rico tend to maximize labor by utilizing manpower over machinery (Waltham, 2005). Pneumatic drills and dynamite are used to drill and blast. Hand-powered winches transport the ore through vertical intervals. Ore is manually shoveled into ore carts that are often pushed by laborers out of the mines. The sorted ore is then again manually shoveled onto ore trucks for transport to local processing plants.

Outdated mineral processing methods used in Potosi have led to the release of tons of heavy metals to the local landscape and waterways. At first, Incan smelting technology was applied to process the Ag oxide cap of Cerro Rico with small charcoal-fueled clay furnaces (*huayras*) (Abbott and Wolfe, 2003). During this period, thousands of active huayras illuminated the slopes of Cerro Rico (Bakewell, 1984). Abbott and Wolfe (2003) documented the diffuse Pb deposition from these operations in nearby lake sediments. It is likely that other ecotoxic heavy metals common within Cerro Rico ores, such as As and Cd, were dispersed into the local environment during this period as well. In 1572, Hg amalgamation replaced smelting as the primary Ag extraction process as mine workings moved deeper into Cerro Rico where Ag sulfide

ores predominate (Bartos, 2000; Abbot and Wolfe, 2003). Amalgamation involves the mixing of Hg with pulverized ore to form denser Hg-Ag amalgam (Miller et al., 2004). The amalgam is heated to vaporize the Hg, leaving condensed Ag. From the 1570s to the 1810s, roughly 220,000 kg/year of Hg was mined and used in Peru, which included Bolivia at the time (Brading and Cross, 1972). Of this, the majority went towards the amalgamation process in Potosí (Brown, 2001). Wasteful use of Hg in amalgamation processes has been documented and estimates suggest that 0.85-4.1 kg of Hg was lost to the environment for every kg of Ag produced (Lofstrom, 1970; Nriagu, 1993). Hg and other heavy metals associated with mining waste were released into the local atmosphere and waterways (Nriagu, 1993; Miller et al., 2004). Nriagu (1993) has suggested that total discharge of Hg from ore processing in Peru, which then included Bolivia, was approximately 196,000 tons. As Cerro Rico was the primary colonial mine and Hg consumer, it can be assumed that the majority of that 196,000 tons was associated with mining at Potosí.

Local streams receive froth flotation effluent and pyrite-rich tailings from local mills as well as AMD from the extensive mine shafts within Cerro Rico and large tailings piles around the mountain called *sucu* (Bocangel, 2001; Miller et al., 2004). Currently, most ore processing facilities within Potosí are outdated flotation systems using disproportionate amounts of reagents (Bocangel, 2001). Aside from tremendous anthropogenic alterations in local groundwater hydrology, surface waters in Potosí bear no semblance to the pre-mining landscape. Twenty ponds were built close to an artificial channel that crosses Potosí east to west, the Ribera de la Vera Cruz, constructed in 1575 (Brading and Cross, 1972) (Figure 1). The Ribera still crosses Potosí with metal-laden effluent and its water is used by multiple ore processing facilities producing Pb, Ag, Zn, and Sn (Gioda et al., 1998; Bocangel, 2001). These facilities currently discharge sulfurous solids, cyanide, and elevated levels of heavy metals (Bocangel, 2001).

An additional canal has been recently built to shunt ore processing effluent west of the city into Laguna Pampa, an inadequately constructed tailings impoundment that is over-capacity and posing a possible failure hazard. Over the centuries and until the last few years, nearly all tailings were discharged directly into the Ribera de la Vera Cruz. Mining activities, pre-Laguna Pampa, were estimated to annually release approximately 360,000 tons of mining related sludge to Ribera de la Vera Cruz (Smolders et al., 2002). Despite the new tailings canal and tailings impoundment, 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. The current state of Laguna Pampa, and slow pace of construction on a new tailings impoundment, could necessitate the reintroduction of tailings to the Ribera de la Vera Cruz within the next year.

Broad and progressive Bolivian environmental legislation 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 effluent out of compliance with Bolivian law, many mining facilities have not acquired an environmental license.

Previous Studies

Intensive mining over several centuries has devastated the environment around Potosí. Potosí is near the headwaters of a major Bolivian watershed, the Rio Pilcomayo which flows from central Bolivia east to Argentina. Contamination limits the uses of the Rio Pilcomayo and water is precious in the arid western Cordillera Real and Chaco regions of southern Bolivia (USACE, 2004). Immediately downstream of Cerro Rico near the western edge of Potosí's city limits, Hudson-Edwards et al. (2001) found dissolved metals concentrations orders of magnitude above background levels (Table 1). However, the pH was 10.3, which limited the solubility of metals species and indicates that local mineral processing plants were discharging directly to local streams at the time. Near the same location, Smolders et al. (2003) found dissolved metals concentrations similar to that found by Hudson-Edwards et al., (2001). Total metals concentrations were found by Smolders et al. (2003) to be orders of magnitude greater than the dissolved levels (Table 1). Miller et al. (2002 and 2004) documented severe contamination of water and sediments up to 200 km downstream of Cerro Rico. Miller et al. (2002) linked this contamination to mining activity via isotopic analysis of Pb in sediment. Smolders et al. (2002 and 2004) sampled dissolved ions and suspended solids over 500 km downstream at Villa Montes to find vast differences in pollution levels between the rainy (December – March) and dry (May – September) seasons. This study found that in the rainy season, when heavy erosion from uncontaminated sources dilutes the metals concentrations of suspended solids, suspended solids averaged 23.6 g/L with Zn, Cu, Pb and Cd levels of 139, 23.9, 35.3 and 0.55 mg/kg dry weight, respectively (Smolders et al., 2002). In the dry season, when mining related effluent contributes a higher proportion of flow, suspended solids averaged 0.011 g/L with Zn, Cu, Pb and Cd levels of 19327, 1107, 1495 and 12.4 mg/kg dry weight, respectively (Smolders et al., 2002). This heavy metals pollution dramatically reduced the diversity of benthic macro-invertebrate communities downstream of the Cerro Rico mines (Smolders et al., 2003). However, the environmental effects of mining on the lower Rio Pilcomayo are lessened by the dilution of both dissolved and suspended heavy metal ions and compounds by uncontaminated waters and sediment (Smolders et al., 2002). Smolders et al. (2002) posit that a maximum of 0.3% of the sediment reaching Villa Montes is mining related.

Primary human exposure pathways in the region are likely through ingestion and inhalation of airborne particulates and contaminated water, agricultural produce and fish consumption (Smolders et al., 2002; Miller et al., 2004). Downstream communities rely on river water for irrigation, washing and occasional cooking and drinking (Garcia-Guinea and Harffy, 1998; Archer et al., 2005). Little study has been undertaken to quantify contaminant levels in humans. However, human hair and urine As concentrations in some downstream Rio Pilcomayo communities exceed published values for non-occupationally exposed subjects (Archer et al., 2005). Concentrations of Cd, Pb and Zn in some local agricultural soils exceed recommended guidelines for agricultural usage (Miller et al., 2004). Increased local human exposure risks are present because rural communities in the region have been found to consume 56 plant species for medicinal purposes (Fernandez et al., 2003). Distant consumers could be at risk as well because contaminated irrigation water is used extensively to grow vegetables for sale in greater Bolivia (Miller et al., 2004). The lower Rio Pilcomayo is also a major fishery. The sábalo (*Prochilodus platensis*) fishery in the lower Pilcomayo is the most important commercial fish in Bolivia

according to Payne and Harvey (1989).  However, heavy metal concentrations in sábalo are below international threshold values (Smolders et al., 2002).

Table 1.  Aqueous metals concentrations in downstream grab samples taken in previous studies in and downstream of Potosí.

| Site | Type | pH | As | Cd | Cu | Pb | Zn | Season | Source |
|------|------|----|----|----|----|----|----|--------|--------|
| | | | | | - - - - - mg/L - - - - - | | | | |
| Potosí | dissolved | 10.3 | 0.065 | 0.01 | 0.3 | 0.041 | 0.035 | dry-1998 | H-E |
| Potosí | dissolved | NR | NR | 0.00076 | 0.014 | 0.0285 | 0.238 | dry-1999 | S |
| Potosí | totals | NR | NR | 0.0592 | 0.304 | 1.399 | 6.021 | dry-1999 | S |
| El Molino | totals | NR | 12.8 | NR | NR | NR | NR | dry-2003 | A |
| El Molino | totals | NR | 2.74 | NR | NR | NR | NR | wet-2004 | A |
| Rio Tarapaya | dissolved | NR | NR | 0.005 | 0.013 | 0.056 | 0.601 | dry-1999 | S |
| Rio Tarapaya | totals | NR | NR | 0.315 | 1.709 | 2.291 | 12.416 | dry-1999 | S |
| Tasapampa | totals | NR | 0.272 | NR | NR | NR | NR | dry-2003 | A |
| Tasapampa | totals | NR | 0.113 | NR | NR | NR | NR | wet-2004 | A |
| Tuero Chico | totals | NR | 0.154 | NR | NR | NR | NR | dry-2003 | A |
| Tuero Chico | totals | NR | 0.199 | NR | NR | NR | NR | wet-2003 | A |
| Sotomayor | totals | NR | 1.213 | NR | NR | NR | NR | dry-2003 | A |
| Sotomayor | totals | NR | 0.421 | NR | NR | NR | NR | wet-2003 | A |
| Villa Montes | dissolved | 8.77 | 0.03 | <0.01 | <0.02 | 0.025 | 0.016 | dry-1998 | H-E |
| Villa Montes | dissolved | NR | NR | 0.00039 | 0.0022 | 0.0007 | 0.017 | dry-1999 | S |
| Villa Montes | totals | NR | NR | 0.00077 | 0.017 | 0.0198 | 0.186 | dry-1999 | S |

H-E = Hudson-Edwards et al., 2001
S = Smolders et al., 2003
A = Archer et al., 2005
NR = Not reported


Although downstream heavy metals contamination has been fairly well-documented, contamination sources have not.  This study was executed to characterize one of the sources of heavy metals pollution to the upper Rio Pilcomayo to better understand the relationship between downstream pollution and upstream sources.  The dry season was chosen for the study to establish baseline AMD flow rates and physical and chemical parameters.

## **Methods**

Study Area
   The study centered around Cerro Rico, approximately 1 km south 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.  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.  The sampled AMD sources drain to streams that reach Rio Tarapaya, which later combines with Rio Yocalla approximately 30 km downstream to become the 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.

AMD sources identified and sampled were from active and abandoned mine portals of Cerro Rico and mineral-rich *pallacos* at the Northwest base of Cerro Rico (Figures 1-2).  The sources documented in this study are those which were actively producing AMD during Potosí's dry season of July 2006 and those not intercepted for mineral processing use.  Innumerable working and abandoned mines dot Cerro Rico, however many are reported to not produce AMD.  Mines likely to be producing drainage near the base of Cerro Rico were visited in this field study.  The majority of those mines were not actively draining at the time.  Of the eight AMD sources sampled on Cerro Rico proper, six were from active mines.  Discharge sites 1 and 4-8 drain to Rio Huayna Mayu which empties into the highly polluted Ribera de la Vera Cruz, which contains raw sewage from the city, AMD and processing plant effluent before the junction.  Sites 2 and 3 drain to Rio Villacollu Mayu which empties into the relatively pristine Rio Agua Dulce.  Site 9 drains to the highly impacted Rio Jayac Mayu ("spicy river" in Quechua, the language of the Inca) which also receives diffuse AMD from numerous waste rock piles near its source.  The *pallacos* AMD sources (sites 10-12) are associated with natural and anthropogenic erosion of mineral-rich material from Cerro Rico and the Sn mining of that material that ceased decades ago (Bartos, 2000; Waltham, 2005).  These sources may also be influenced by polluted groundwater seepage from the San Miguel tailings dump.  Rio Sucu / Kori Mayu receives drainage from the *pallacos* AMD sources and soon thereafter empties into the Ribera de la Vera Cruz.



Figure 2.  AMD sources 1 (left) and 8 (right).  Source 1 is an abandoned mine near the eastern base of Cerro Rico.  Source 8 is a functioning mine on the north slope of Cerro Rico.

Water quality parameters and samples were obtained at AMD sources at the mouths of working and abandoned mines in July and August of 2006.  The location of each sample point

was recorded with a Garmin® GPS unit. Acidity and alkalinity titrations were conducted in the field following standard methods (APHA, 1998). Temperature, pH, dissolved oxygen (DO) and specific conductance were determined using a properly calibrated Orion 1230 multimeter. All grab samples were taken using 125-mL HDPE containers for later analyses at the University of Oklahoma Center for the Restoration of Ecosystems and Watersheds laboratories. Total metals samples were preserved with concentrated nitric acid and stored at 4 °C until microwave acid digestion following EPA method 3015. Digested metals samples were filtered through 0.45 μm nylon filters then analyzed via a Varian Vista-Pro® simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES) following EPA method 6010. Samples for anion analyses were stored at 4 °C until filtered through Dionex OnGuard® II H cartridges and 0.2 μm nylon filters. A MetrOhm® 761 Compact ion chromatograph (IC) unit was used to quantify sulfate concentrations following EPA method 300.0. As a field backup, sulfate was also quantified on-site using EM QUANT® 200-1600 ppm test strips. Samples were diluted when concentrations were greater than 1600 ppm.

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.

### Results and Discussion

Physical parameters, sulfate and total metals concentrations for sampled AMD sources are presented in Tables 2 and 3. These results may be compared to various water quality criteria set by the Bolivian government and, for reference purposes only, the US Environmental Protection Agency (EPA) in Table 4. Concentrations of contaminants in sampled AMD sources were orders of magnitude out of compliance with Bolivian discharge limits and contributed to the aforementioned pollution downstream.

Table 2. Mean physical parameter measurements from AMD sources around Cerro Rico

| Site | pH | Net Acidity[a] (mg/L as $CaCO_3$ eq.) | DO (mg/L) | Sp. Cond. (μS/cm) | Temp. (°C) | Q (L/s) |
|---|---|---|---|---|---|---|
| 1 (n = 3) | 3.56±0.08 | 911 | 6.6±1.2 | 1888±72 | 8.4±0.3 | 0.86 |
| 2 (n = 2) | 2.90 | 7656 | 1.3 | 7530 | 7.2 | 0.02 |
| 3 (n = 2) | 3.23 | ND | 2.2 | 3160 | 1.8 | 0.17 |
| 4* | 3.30 | ND | 0.8 | 9470 | 4.4 | † |
| 5* | 3.15 | 11375 | 4.4 | 8690 | 2.7 | 0.13 |
| 6* | 3.02 | ND | 2.9 | 14920 | 10.0 | 0.07 |
| 7* | 3.02 | ND | 4.1 | 19070 | 5.0 | † |
| 8* | 2.97 | ND | 3.5 | 10440 | 5.0 | † |
| 9* | 2.46 | ND | 6.1 | 18640 | 5.5 | 0.28 |
| 10* | 6.39 | 43.2 | 6.6 | 893 | 12.3 | 0.10 |
| 11* | 2.96 | 1344 | 2.5 | 2820 | 13.1 | 0.26 |
| 12* | 4.20 | 63 | 4.7 | 1115 | 12.4 | 4.59 |

† Flow rates not detectable  ND = Not determined  * n = 1  [a]Net acidity = total acidity – total alkalinity, alkalinity and acidity titrations necessary for net acidity were performed once

Table 3. Mean sulfate and total metal concentrations determined for grab samples of AMD sources around Cerro Rico

| Site | Al | As | Ca | Cd | Co | Cr | Cu | Fe | Mg | Mn | Na | Ni | Pb | Zn | $SO_4^{2-}$ | $SO_4^{2-}$‡ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | mg/L | | | | | | | |
| 1 (n = 5) | 4.88 ±0.16 | 0.03 ±0.01 | 104 ±2.2 | 0.17 ±0.02 | 0.139 ±0.004 | 0.053 ±0.000 | 0.037 ±0.004 | 107 ±6.9 | 16.8 ±0.36 | 13.4 ±0.63 | 15.6 ±0.41 | 0.165 ±0.006 | 0.073 ±0.009 | 616 ±29 | 1323 | 1200-1600 |
| 2 (n = 3) | 72.4 ±1.9 | 21.4 ±0.97 | 130 ±1.5 | 7.77 ±0.04 | 0.591 ±0.003 | 0.031 ±0.001 | 0.047 ±0.001 | 2449 ±100 | 34.3 ±0.36 | 146 ±7.7 | 10.1 ±0.28 | 0.817 ±0.022 | 0.51 ±0.019 | 3500 ±175 | 9184 | 4000-8000 |
| 3 (n = 3) | 99 ±5.9 | 14.4 ±5.67 | 210 ±2.5 | 0.54 ±0.05 | 1.073 ±0.01 | 0.033 ±0.002 | 0.41 ±0.021 | 595 ±94 | 52.8 ±0.91 | 58.6 ±1.70 | 6.63 ±0.19 | 0.585 ±0.010 | 7.78 ±4.79 | 380 ±6.1 | 3395 | 2400-3200 |
| 4* | 389 | 30.2 | 44.0 | 7.33 | 2.49 | 0.087 | 11.0 | 7200 | 512 | 438 | 15.5 | 4.34 | 1.46 | 3330 | ND | 24000-32000 |
| 5* | 581 | 45.2 | 477 | 19.5 | 1.92 | 0.243 | 92.7 | 3680 | 234 | 92 | 38.6 | 2.07 | 1.20 | 4950 | ND | 12800-19200 |
| 6* | 686 | 8.0 | 21.4 | 50.7 | 4.03 | 0.142 | 10.2 | 3850 | 86.4 | 46.9 | 9.9 | 5.72 | 0.63 | 10200 | ND | 9600-12800 |
| 7* | 641 | 33.4 | 116 | 37.6 | 3.82 | 0.129 | 12.5 | 3140 | 62.7 | 35.2 | 27.5 | 6.18 | 2.50 | 11800 | ND | 12800-19200 |
| 8* | 231 | 0.58 | 76.3 | 12.7 | 2.00 | 0.031 | 1.80 | 874 | 31.1 | 19.7 | 16.0 | 2.98 | 0.21 | 4400 | ND | 9600-12800 |
| 9* | 977 | 191 | 68.8 | 38.3 | 2.61 | 0.401 | 161 | 7320 | 25.6 | 54.6 | 13.2 | 2.36 | 15.0 | 11500 | ND | 24000-32000 |
| 10* | 0.284 | BDL | 95.8 | 0.025 | BDL | BDL | 0.03 | 0.15 | 32.0 | 0.30 | 43.4 | 0.026 | 0.028 | 4.86 | ND | 400-800 |
| 11* | 134 | BDL | 251 | 0.69 | 0.344 | 0.296 | 24.8 | 56.7 | 65.7 | 51.0 | 41.7 | 0.297 | 0.05 | 108 | ND | 1600-3200 |
| 12* | 6.68 | BDL | 115 | 0.089 | 0.018 | 0.016 | 0.59 | 0.36 | 37.1 | 3.62 | 43.1 | 0.10 | 0.047 | 14.2 | ND | 400-800 |

‡ These sulfate ranges were obtained in the field with EM QUANT® sulfate test strips
BDL = Below detection limits
ND = Not determined
* n = 1
Mean and standard deviations include two field duplicates taken at site 1 and one each at sites 2 and 3.

Table 4. Bolivian discharge and receiving body criteria with respect to US EPA drinking water standards

| Standard | pH | Al | As | Ca | Cd | Co | Cr | Cu | Fe | Mg | Mn | Na | Ni | Pb | Zn | SO$_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | mg/L | | | | | | | |
| Bolivian discharge[δ] | 6-9 | | 1.0 | | 0.3 | | 1.0/0.1[α] | 1.0 | 1.0 | | | | | 0.6 | 3.0 | |
| Bolivian discharge[μ] | 6-9 | | 0.5 | | 0.15 | | 0.5/0.05 | 0.5 | 0.5 | | | | | 0.3 | 1.5 | |
| Bolivian class "A" | 6.0-8.5 | 0.2 | 0.05 | 200 | 0.005 | 0.1 | 0.05 | 0.05 | 0.3 | 100 | 0.5 | 200 | 0.05 | 0.05 | 0.2 | 300 |
| Bolivian class "B" | 6-9 | 0.5 | 0.05 | 300 | 0.005 | 0.2 | 0.6/0.05[α] | 1.0 | 0.3 | 100 | 1.0 | 200 | 0.05 | 0.05 | 0.2 | |
| Bolivian class "C" | 6-9 | 1.0 | 0.05 | 300 | 0.005 | 0.2 | 0.5/0.05[α] | 1.0 | 1.0 | 150 | 1.0 | 200 | 0.5 | 0.05 | 0.2 | |
| Bolivian class "D" | 6-9 | 1.0 | 0.1 | 400 | 0.005 | 0.2 | 1.1/0.05[α] | 1.0 | 1.0 | 150 | 1.0 | 200 | 0.5 | 0.05 | 0.2 | 400 |
| US EPA primary | | | 0.01 | | 0.005 | | 0.1 | 1.3 | | | | | | 0.015 | | |
| US EPA secondary | 6.5-8.5 | 0.05 | | | | | | 1.0 | 0.3 | | 0.05 | | | | 5 | 250 |

[α] Cr (III) and Cr (VI) limits respectively
[δ] Daily discharge limits
[μ] Monthly average discharge limits

The active mines generally had higher total metals concentrations than the abandoned and alluvial deposit sources (Table 3). This is likely due to the presence of fine sulfurous solids in the drainage, probably from blasting and drilling within the mines. The alluvial deposit sources generally exhibited lower metals 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 migrated downhill. Much of the sulfides on the exposed surfaces of the alluvial deposits have likely been weathered, leaving more inert material that produces AMD of lower metals concentrations and acidity. The freshly exposed sulfides within Cerro Rico are likely leading to higher metals concentrations in the drainage of the active mines. Because Cerro Rico has been mined for centuries and many mines are interconnected due to the degree of exploration, the abandoned mine workings sampled in this study may be connected to and receive waters from active mines, thus sharing in the effect of fresh sulfide mineral exposure.

Many of the AMD sources documented in this study would likely result in violations of Bolivian receiving body water quality limits (Table 4). Class "A" receiving water bodies, those which are suitable for drinking without treatment or only with bacterial disinfection, have stringent water quality requirements (BMSDP, 2000). 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. 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 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 effluent orders of magnitude over class "D" limits is likely leading to non-compliance downstream.

All of the sources exceeded discharge limits to some degree and most by orders of magnitude. Six out of the twelve sources had higher than permissible Pb concentrations. Seven of the sources contained higher than permissible As and Cu concentrations. Nine of the sources contained higher than permissible Cd concentrations. Ten of the sources had higher than permissible Fe concentrations. Eleven of the sources had higher than permissible Zn concentrations and lower than permissible pH. For example, AMD source 2 discharged As, Cd, Fe and Zn concentrations 21.4, 25.9, 2449 and 1166 times greater than daily discharge limits. The data support the assertion of Garcia-Guinea and Harffy (1998) that Bolivian environmental law "has been sadly ignored where mining is concerned."

The AMD sources documented in this study contained elevated concentrations of the same heavy metal elements documented by earlier studies downstream. The majority of AMD sources had concentrations of As, Cd, Cu, Pb and Zn orders of magnitude higher than those found downstream. This indicates that these AMD sources are contributing to some degree to downstream heavy metals pollution in the upper Rio Pilcomayo basin.

The relative importance of pollution sources to the Rio Pilcomayo is unknown. Hudson-Edwards et al., (2001) and Smolders et al., (2003) stress the significance of mineral processing effluent in downstream contamination. However, these studies were undertaken when the tailings load to the upper Rio Pilcomayo was much higher, before the construction of the Laguna Pampa tailings dam. In addition, no published peer-reviewed studies have documented mineral processing effluent characteristics and quantity. This study is the first to characterize AMD sources. However, the dry season data presented in this study is insufficient to extrapolate

annual loading to downstream watercourses. The Smolders et al. (2002) study highlighted the need for both dry and rainy season data. It is likely that AMD flows are greater and metals concentrations lower in the rainy season, yet mass loads may be higher. Further research, including mineral processing effluent and rainy season AMD characterization and quantification will help solidify the relative importance of the Rio Pilcomayo's pollution sources. This information could help establish priorities for future remediation efforts.

## Conclusions and Recommendations

The extraction and export of mineral wealth has dominated the political economy of Bolivia for centuries, however, the importance of mining has declined somewhat in recent decades (Griess, 1951; Hillman, 1984). However, Potosí's economy and roughly 150,000 residents are still 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. Bolivia is currently the second poorest nation in the Western Hemisphere. Therefore, solutions attempted to address to the mine water pollution problems in Potosí can not 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 have 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. Also, passive treatment system construction and metal reclamation could provide needed employment for Potosínos.

In 2000, Younger demonstrated passive treatment system feasibility on the slopes of Chacaltaya and Huayna Potosí, near La Paz, a setting nearly identical to the Cerro Rico de Potosí (Younger, in press). Limestone gravel and llama dung were set in a series of tanks receiving a continuous flow of AMD from the abandoned Milluni mine. The average pH rose from 3.2 to 6.3 and metals were taken out of solution even though the experiment ran through the coldest time of year when reaction rates are lowest (Younger, in press). There are documented limestone and dolomite deposits around Potosí (Zartman and Cunningham, 1995; Deconinck et al., 2000; Kamenov et al. 2002). The Cayara® lime plant on the outskirts of Potosi currently accepts limestone of 85-92% calcite from local sources, which indicates that high quality limestone for passive treatment is available. Llama dung is readily available around Potosí as domesticated llama herds roam nearby valleys and mountainsides. Other carbon sources for sulfate reducing bacteria are also available, including domestic sewage and waste sugar cane from lowland regions Northeast of Potosí. However, the ubiquity of Al in high concentrations within the AMD around Potosí precludes the application of anoxic limestone drains and limits the useful life of reducing and alkalinity producing systems.

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Action is necessary to address the uniformly non-compliant AMD sources documented in this study. They are contributing to previously-documented downstream pollution. To determine the extent to which they are responsible, rainy season data must be collected. If environmental laws are to be enforced, care should be taken to ensure that the fragile mineral extraction and processing industries vital to Potosí can continue operation. Passive treatment may prove a suitable solution to the unique circumstances presented in the "Villa Imperial" (Imperial City) of Potosí.

## Acknowledgements

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