A LEGACY OF NEARLY 500 YEARS OF MINING IN POTOSÍ, BOLIVIA: STREAM WATER QUALITY[1]

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Abstract: Silver, Ag, Sn, and Zn ores has been intensively mined and processed at Cerro Rico de Potosí, Bolivia since 1545. Acid mine drainage and processing plant effluent are prime sources of water contamination in the headwaters of the economically and ecologically vital, yet highly impacted, Rio Pilcomayo watershed. Streams receiving drainage from the slopes of Cerro Rico and surrounding landscapes were sampled during the dry (July-August 2006) and wet (March 2007) seasons of one water-year. In-stream waters contain total metals concentrations of up to 16 mg/L As, 4.9 mg/L Cd, 0.97 mg/L Co, 1100 mg/L Fe, 110 mg/L Mn, 4.1 mg/L Pb, and 1500 mg/L Zn with pH and specific conductivity ranging from 2.8-9.5 and 160-5070 μS/cm, respectively. Many of the studied water bodies are more degraded than class "D" of the Bolivian receiving water body criteria, rendering them unfit for domestic or agricultural use. However, some of these waters are currently being used for irrigation and livestock watering. The data indicate that historic and current mining activities have transformed these key natural resources into potential human and environmental health hazards.

Additional Key Words: acid rock drainage, arsenic, cadmium, iron, pyrite, aqueous geochemistry, water quality, tailings and mineral processing

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Introduction

<u>Background</u>

Mining of the largest Ag deposit in the world at Cerro Rico de Potosí, Bolivia (Miller and Singewald, 1919; Evans, 1940; Cunningham et al., 1996) began in 1545 (Wilson and Petrov, 1999) and has continued to this day, producing a lasting environmental impact in a major city. Potosí, the mining camp founded at the base of Cerro Rico, grew to become one of the world's richest and most populous cities of the 17th century (Rudolf, 1936) during a boom fueled by veins sometimes greater than 25% pure Ag (Cunningham et al., 1996; Wilson and Petrov, 1999; Bartos, 2000; Abbot and Wolfe, 2003; Waltham, 2005). However, the environmental cost of Potosí's good fortune has been steep. Terrestrial zones have experienced extreme deforestation (Godoy, 1990) and associated soil loss while local watercourses have been impacted by mineral processing effluent (Miller et al., 2004) and untreated acid mine drainage (AMD) (Strosnider et al., 2007).

Potosí lies near the headwaters of a major Bolivian watershed, the Rio Pilcomayo which flows from central Bolivia east to Argentina. Mining joins grazing pressure, farmland expansion, road construction, and urbanization as serious causes of long-term environmental degradation in highland southern Bolivia (Brandt and Townsend, 2006). Local streams are key resources in the arid, high-altitude, low-productivity landscape and Potosí has endured water shortages throughout its history (Rudolf, 1936). Contamination limits the uses of the Rio Pilcomayo and water is precious in the arid Eastern Cordillera and Chaco regions of southern Bolivia (USACE, 2004).

Water resources in and around the city of Potosí have been dramatically and continuously impacted geomorphologically, geochemically, and ecologically by human activities since the initiation of mining. First, a system of artificial lakes was constructed in the Kari-Kari region east of the city to provide drinking water and hydropower for ore processing (Rudolf, 1936). Concurrently, the Ribera de la Vera Cruz was constructed through the city with a system of 32 dams to power the waterwheels of over a hundred ore processers or *ingenios* (Rudolf, 1936; García-Guinea, 1995). *Ingenios* have continuously discharged tailings to the Ribera de la Vera Cruz until the early 2000s. AMD has likely continuously impacted local waterways since the onset of mining (Strosnider et al., 2007).

Previous studies have documented downstream geochemical and ecological impacts of mining and ore processing. 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. 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. This heavy metals pollution dramatically reduced the diversity of benthic macroinvertebrate communities downstream of the Cerro Rico mines (Smolders et al., 2003). However, no peer-reviewed studies have documented the degradation of stream water quality within the city of Potosí and on the slopes of Cerro Rico. The study presented in this paper characterizes the current water quality of the streams that drain Cerro Rico and Potosí to form Rio Tarapaya, a chief tributary of the Rio Pilcomayo system.

Methods

Study Area

The study centered around Cerro Rico, approximately 1 km south of Potosí, Bolivia (Fig. 1). 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 streams and rivers drain to Rio Tarapaya, which later combines with Rio Yocalla approximately 30 km downstream 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.
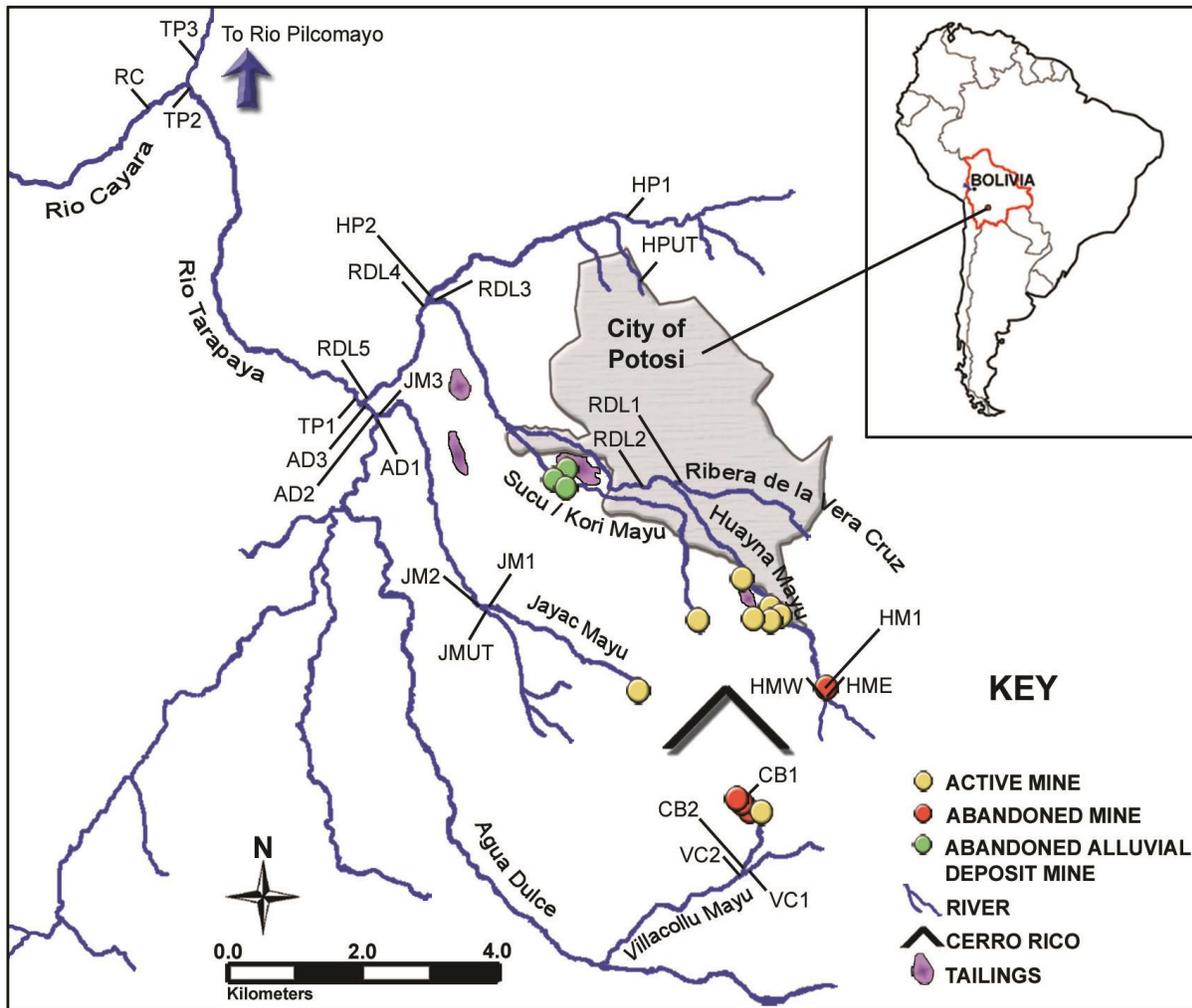
Figure 1: Study area and stream sample points with respect to AMD sources, tailings deposits and greater Bolivia and South America.

Sample Sites

The streams and rivers sampled in this study vary widely in the types of effluent they receive and the watersheds they drain, from highly urbanized to low-intensity agriculture to barren mining landscapes. Each water body and watershed is described below.

Huayna Mayu (sample sites HM1, HME, and HMW), "young river" in Quechua, is born near an abandoned mine discharge at the eastern base of Cerro Rico. Huayna Mayu runs north past abandoned brick foundries then turns west to collect drainage from AMD discharges and runoff from the Pailaviri tailings deposit (Fig. 2) on the north face of Cerro Rico. As Huayna Mayu flows through the city it also receives stormwater and wastewater until emptying into the Ribera de la Vera Cruz. During the dry season sampling period, Huayna Mayu was formed solely by an

abandoned mine discharge (HM1). In the wet season, two ephemeral tributaries to Huayna Mayu, (HMW) and (HME), joined HM1 to form Huayna Mayu.

Figure 2: A portion of the Pailaviri tailings deposit which lies within the Huayna Mayu watershed. The Pailaviri tailings are less than 100m from Huayna Mayu, which drains to the Ribera de la Vera Cruz less than 2 km from the location pictured.

The headwaters of Rio Agua Dulce, (sample sites AD1, AD2, and AD3) "sweet water river" in Spanish, lie in a sparsely populated agricultural area with little to no mining. Vilacollu Mayu (VC1 and VC2) is a tributary of Rio Agua Dulce that collects drainage from the southern slopes of Cerro Rico and Cerro Chico in the Canta Canta valley. The ephemeral stream Quebrada Chimborazo (CB1 and CB2) is formed by several AMD sources in the Chimborazo region of Cerro Rico and impacts Vilacollu Mayu before it is diverted for agricultural use in the village of Vilacollu (Choque, 2007). Rio Agua Dulce borders many farms and is slightly used for agricultural purposes along its length.

Jayac Mayu (JM1, JM2 and JM3), "spicy river" in Quechua, drains the southwestern mining district of Cerro Rico and impacts an unnamed tributary before joining with Rio Agua Dulce.

An unnamed tributary to Jayac Mayu (JMUT) is a key water resource to a few farms upstream of the confluence. A cistern has been recently constructed approximately 10 m upstream of the confluence to capture and store water from the unnamed tributary before it is impacted by Jayac Mayu. Downstream of the confluence, Jayac Mayu borders small agricultural plots (Fig. 3), but does not appear to be used for irrigation.

Figure 3: Llama and sheep grazing on a farm plot that has been prepared for planting aside a highly impacted reach of Jayac Mayu between JM2 and JM3.

Rio Huarampaya (HP1 and HP2) accepts waste and stormwater from unnamed tributaries that drain the north side of the City. It does not receive mineral processing effluent nor AMD. An unnamed tributary of Rio Huarampaya (sample site HPUT) drains wastewater and stormwater from a residential district. Rio Huarampaya runs through a small agricultural area before emptying into the Ribera de la Vera Cruz.

The Ribera de la Vera Cruz (RDL1, RDL2, RDL3, RDL4, and RDL5) runs east to west through the city past multiple active and defunct mineral processing plants. Since its

construction in the 1570's (Ruldolf, 1936; Serrano et al., 1996), tailings and other mineral processing waste had been dumped directly into this stream. However, after the construction of the Laguna Pampa tailings dam and tailings diversion chute in the early 2000s, tailings introduction has nearly ceased. The tailings diversion chute runs parallel to Ribera de la Vera Cruz until it veers towards the San Antonio tailings dam, near the Laguna Pampa tailings dam. Tailings still periodically enter the stream during rain events when the chute overflows and when mineral processing plants fail to pump their tailings to the chute. Ribera de la Vera Cruz also accepts stormwater and wastewater from the city. Despite the recent measures to limit tailings introduction, the substrate of Ribera de la Vera Cruz remains "tailings" grey. The telltale red staining from weathering pyrite is evident along the banks and in stagnant pools in the stream. In addition, the Ribera de la Vera Cruz runs less than 100 m from the San Miguel tailings deposit, a serious potential nonpoint pollutant source, and accepts AMD from springs in abandoned alluvial deposit mines.

Rio Tarapaya (TP1, TP2, and TP3) is formed by the combined flows of the Ribera de la Vera Cruz and Rio Agua Dulce. The substrate of Rio Tarapaya is visually similar to that of Ribera de la Vera Cruz and red staining from weathering pyrite is evident in stagnant portions of the river. Rio Tarapaya meets Rio Cayara at a shuttered Sn smelting facility where slag piles line the southern bank. Tailings have accumulated over the centuries in the Rio Tarapaya valley because its bed slope is much less than its tributaries.

Rio Cayara (RC) 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. However, past or present mining activity cannot be ruled out due to the near ubiquity of mining in the region.

Reference points (JMUT, HP1, VC1, and RC) were designated in reaches without in-stream tailings deposits that should not be considerably impacted by historical or current mining or mineral processing. The only reference site sampled in the dry season was JMUT, however all four were sampled in the wet season. In all, 10 locations were sampled in the dry season and 16 sites were added to those in the wet season. Sampling points (HMW, HME, VC1, VC2, CB1, and CB2) were added in the wet season because some of the streams sampled are ephemeral and were not flowing or imperceptibly flowing during the dry season. Other points of interest were

added in the wet season to expand the scope of the study (AD3, RDL1, RDL3, RDL4, HP1, HPUT, HP2, TP2, TP3, and RC).

The AMD sources, the majority of which were characterized by Strosnider et al. (2007), that impact local waterways are represented on Fig. 1. Tailings deposits (Figs. 1 and 2), innumerable ore piles that dot the slopes of Cerro Rico, tailings discharges by ore processors and tailings within stream sediments are other probable ephemeral and permanent point and non-point sources of water quality degradation.

Data Collection

Water quality parameters and grab samples were obtained at the points indicated on Fig. 1 during the dry (July-August 2006) and wet (March 2007) seasons of one water-year (Fig. 4). These intervals were chosen to capture the extremes of both seasons, when groundwater levels and surface water flow are near their minima (dry) and maxima (wet). No rain events occurred during the dry season sampling. However, two rain events influenced wet season sampling of AD3, TP1, HME, and HMW.
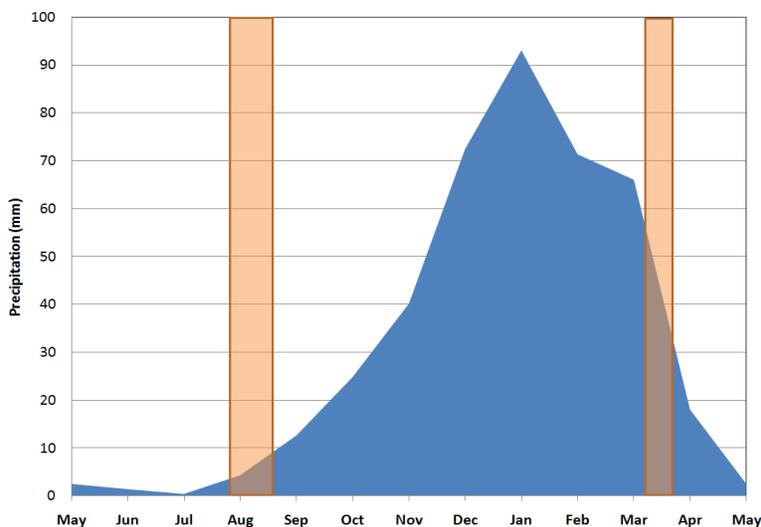
Figure 4: Sampling periods (orange) with respect to monthly average precipitation in the City of Potosí from 1958-2002 (BSNMH, 2003).

The location of each sampling 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 (SC) were determined using an Orion 1230 multi-meter. All grab samples were taken using 125-mL HDPE containers for

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later analyses at the University of Oklahoma Center for the Restoration of Ecosystems and Watersheds laboratories. Total metals samples were preserved with concentrated trace metals grade HNO_3 and stored at approximately 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 SO_4^{2-} concentrations following EPA method 300. As a field backup, SO_4^{2-} was also quantified on-site using EM QUANT® 200-1600 ppm test strips. Samples were diluted when concentrations were greater than 1600 ppm.

Results and Discussion

Physical parameters, SO_4^{2-}, and total metals concentrations for sampled AMD sources are presented in Tables 1-3. These results may be compared to various water quality criteria set by the Bolivian government and irrigation standards set by the United Nations Food and Agriculture Organization (UNFAO) and, for reference purposes, drinking water standards set by the United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) as shown in Table 4. UNFAO irrigation water guidelines are established at contaminant concentrations above which water can degrade agricultural soils and decrease crop productivity (Ayers and Wescot, 1994). UNFAO livestock drinking water guidelines are set at contaminant concentrations above which water can be toxic or unpalatable to livestock or lead to bioaccumulation, rendering livestock products unsuitable for human consumption (Ayers and Wescot, 1994). WHO drinking water guidelines and USEPA primary drinking water standards have been established to protect the public health (WHO, 2006; USEPA, 2007). The secondary drinking water standards determined by the USEPA are guidelines for contaminants that can cause adverse cosmetic or aesthetic effects, such as teeth staining, odor, and bad taste (USEPA, 2007).

Bolivian water quality standards are stringent, progressive, and comparable with those of most industrial nations. However, non-compliance with pollutant discharge criteria is rarely punished and little regulation is in effect to assure that water bodies meet their class designations. Class "A" receiving water bodies, those which are suitable for drinking without treatment or only

with bacterial disinfection, are suitable for most uses, including livestock watering and irrigation (BMSDP, 2000). Class "B" waters, only differ from Class "A" in that they require filtration and disinfection to be suitable for drinking. Class "C" waters differ from Class "B" in that they are unsuitable for the irrigation of fruits or vegetables. Class "D" is the lowest designation of Bolivian receiving water body in which industrial application 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 and that they are unsuitable for agricultural usage or animal watering (BMSDP, 2000). There is no class designation lower than "D" and it is not known how the water bodies downstream of Potosí are designated, nor if they have a designation at all. However, some are used for agriculture and therefore should be rated at a minimum above class "D".

Table 1. Physical parameter measurements. The pH is bolded if it exceeds Bolivian Class "D" requirements. SC is underlined if it exceeds the 700 µS/cm ceiling recommended for unrestricted irrigation water use by the UNFAO. Sites are indented by watershed.

Site	pH	Net Acidity[a] (mg/L as $CaCO_3$ eq.)	DO (mg/L)	SC (µS/cm)	Temp. (°C)
Dry Season					
JM1	**3.4**	-	13.4	5070	2.9
JMUT	7.3	-	9.7	534	6.1
JM2	**3.5**	-	10.6	4870	4.9
JM3	**9.5**	-	8.5	2100	9.5
AD1	8.0	-	10.0	1010	10.0
AD2	**9.4**	-	7.7	2010	10.6
HM1*	**3.6**	910	6.6	1890	8.5
RDL2	**5.0**	-	10.8	1420	7.4
RDL5	7.5	-	9.0	1160	11.7
TP1	7.7	-	8.7	1170	11.0
Wet Season					
VC1	7.7	-40	7.5	593	14.0
CB1	**4.7**	219	6.1	216	13.3
CB2	**3.1**	1406	9.4	2510	13.4
VC2	**3.6**	469	8.0	1210	12.8
JM1	**2.8**	1875	8.3	2820	13.0
JMUT	8.1	-30	8.8	160	11.8
JM2	**4.8**	311	9.4	870	12.3
JM3	**5.0**	623	6.5	1140	16.5
AD1	7.5	-49	9.5	290	14.8
AD2	6.9	-10	6.2	613	14.9
AD3	7.7	-	5.8	438	16.7
HP1	8.3	-255	5.2	1460	19.8
HPUT**	8.5	-377	4.5	1280	14.3
HP2	8.4	-320	5.7	1020	16.3
HM1**	**4.5**	625	6.4	1460	9.6
HMW	**5.4**	-	6.0	181	6.0
HME	**5.5**	-	6.0	718	5.0
RDL1	6.3	447	7.5	1290	11.3
RDL2	**3.2**	1250	9.2	2430	10.6
RDL3	**3.4**	-	6.2	2310	14.0
RDL4	**5.4**	-	6.3	1380	17.0
RDL5	6.3	158	6.1	1390	18.0
TP1	7.4	-	1.7	548	15.3
TP2	**4.9**	-	5.5	1620	18.5
RC	7.1	-180	6.4	374	15.8
TP3	**5.9**	-	5.9	1040	17.9

*n = 3; ** n = 2 (n =1 for all other sites); [a]Net acidity = total acidity – total alkalinity; - = no data available

Table 2. Dry season mean sulfate and total metal concentrations. Concentrations are bolded if exceeding Bolivian Class "D" requirements and underlined if exceeding long term use irrigation standards recommended by the UNFAO. Sites are indented by watershed.

Site	Al	As	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Zn	SO$_4^{2-}$	SO$_4^{2-}$‡
JM1	**<u>210</u>**	**<u>14</u>**	140	**<u>4.9</u>**	**0.90**	0.065	**<u>19</u>**	**<u>1100</u>**	110	**<u>82</u>**	24	**<u>0.81</u>**	**3.2**	**<u>1500</u>**	-	**4000-8000**
JMUT	0.21	<0.022	46	0.0007	<0.001	<0.001	0.007	0.44	36	0.044	23	0.009	0.040	**0.29**	-	**< 200**
JM2	**<u>220</u>**	**<u>16</u>**	140	**<u>4.9</u>**	**<u>0.97</u>**	0.071	**<u>20</u>**	**<u>1100</u>**	110	**<u>79</u>**	22	**<u>0.84</u>**	**4.1**	**<u>1500</u>**	-	**4800-6400**
JM3	**<u>19</u>**	**<u>1.1</u>**	**540**	**<u>0.41</u>**	<u>0.11</u>	0.008	**<u>2.6</u>**	**<u>44</u>**	19	**<u>10</u>**	52	0.10	**1.2**	**<u>110</u>**	-	**400-800**
AD1	0.44	<0.022	90	0.002	<0.001	0.003	0.009	0.52	41	<u>0.23</u>	57	0.017	0.041	**0.76**	-	**< 200**
AD2	**<u>17</u>**	**<u>0.86</u>**	**530**	**<u>0.38</u>**	<u>0.10</u>	0.008	**<u>2.4</u>**	**<u>37</u>**	19	**<u>9.3</u>**	52	0.094	**1.1**	**<u>100</u>**	-	**1200-1600**
HM1*	**<u>5.8</u>**	0.03	100	**<u>0.17</u>**	<u>0.14</u>	0.002	0.037	**<u>110</u>**	16	**<u>13</u>**	15	0.16	**0.065**	**<u>570</u>**	1300	**1200-1600**
RDL2	**<u>38</u>**	**<u>1.2</u>**	51	**<u>0.12</u>**	<u>0.066</u>	0.015	**<u>1.2</u>**	**<u>140</u>**	11	**<u>2.9</u>**	57	0.073	**0.26**	**<u>29</u>**	-	**400-800**
RDL5	**<u>14</u>**	**<u>1.7</u>**	100	**<u>0.10</u>**	<u>0.038</u>	0.014	**<u>0.84</u>**	**<u>67</u>**	14	**<u>2.2</u>**	65	0.041	**1.1**	**<u>32</u>**	-	**400-800**
TP1	**<u>13</u>**	**<u>1.4</u>**	140	**<u>0.12</u>**	<u>0.042</u>	0.012	<u>0.82</u>	**<u>59</u>**	13	**<u>2.9</u>**	63	0.065	**0.92**	**<u>34</u>**	-	**400-800**

‡ Sulfate ranges obtained in the field with EM QUANT® test strips; bdl = Below detection limits; * n = 3 (n =1 for all other sites); - = no data available

Table 3. Wet season mean sulfate and total metal concentrations. Concentrations are bolded if exceeding Bolivian Class "D" requirements and underlined if exceeding long term use irrigation standards recommended by the UNFAO. Sites are indented by watershed.

Site	Al	As	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Zn	SO$_4^{2-}$	SO$_4^{2-}$‡
									- - - - mg/L - - - -							
VC1	**1.3**	<0.022	74	0.002	<0.001	<0.001	0.005	1.0	13	**_3.0_**	31	0.008	<0.012	**1.5**	200	**400-800**
CB1	**3.5**	0.091	18	**_0.018_**	<0.001	0.0020	0.014	**2.7**	3.3	_0.79_	3.5	0.011	**0.33**	**_7.3_**	74	**400-800**
CB2	**_41_**	**_1.1_**	110	**_1.2_**	**_0.27_**	0.014	_0.50_	**_210_**	27	**_61_**	6.7	_0.26_	**0.33**	**_560_**	1400	**> 1600**
VC2	**_16_**	**_0.38_**	86	**_0.39_**	_0.095_	0.008	0.17	**_66_**	18	**_21_**	24	0.095	**0.13**	**_170_**	720	**800-1200**
JM1	**_71_**	**_0.25_**	92	**_0.24_**	**_0.81_**	0.020	**_6.7_**	**_180_**	78	**_110_**	13	**_0.80_**	0.24	**_64_**	2200	**>1600**
JMUT	**_15_**	<0.022	22	0.002	0.035	0.015	0.015	0.030	9.2	**_16_**	3.2	**_7.2_**	0.046	**0.37**	23	<200
JM2	**_21_**	**_0.11_**	38	**_0.63_**	**_0.22_**	0.009	**_1.7_**	**_63_**	28	**_25_**	8.3	_0.21_	**0.17**	**_160_**	440	**400-800**
JM3	**_24_**	**_0.31_**	120	**_0.58_**	_0.20_	0.020	**_1.3_**	**_79_**	45	**_27_**	19	_0.23_	**0.37**	**_140_**	640	**800-1200**
AD1	**_81_**	0.088	97	**_0.018_**	_0.053_	0.054	0.076	**_100_**	37	**_2.5_**	17	0.065	**0.18**	**_2.3_**	66	**400-800**
AD2	**_71_**	**_0.13_**	97	**_0.16_**	_0.10_	0.049	_0.40_	**_100_**	41	**_9.5_**	17	0.12	**0.26**	**_44_**	240	**400-800**
AD3	**_630_**	**_0.45_**	_930_	**_0.082_**	**_0.38_**	_0.47_	_0.91_	**_950_**	310	**_27_**	47	**_0.57_**	0.95	**_25_**	110	**400-800**
HP1	**8.1**	0.034	190	0.002	<0.001	0.004	0.015	**_7.3_**	51	_0.30_	100	0.010	0.046	0.16	6	< 200
HPUT*	**5.9**	0.053	66	**0.006**	<0.001	0.007	0.065	**_6.7_**	12	_0.34_	78	0.011	**0.22**	**_1.6_**	10	< 200
HP2	**2.6**	0.032	72	0.002	<0.001	0.006	0.033	**4.7**	35	_0.55_	57	0.005	**0.069**	0.47	230	< 200
HM1*	**_21_**	**_0.37_**	71	**_0.27_**	_0.065_	0.007	0.064	**_73_**	14	**_7.7_**	8.7	0.073	**1.2**	**_220_**	630	**800-1200**
HMW	**_190_**	**_1.8_**	65	**_0.34_**	_0.12_	0.074	_0.35_	**_370_**	34	**_11_**	9.8	0.095	**_6.1_**	**_120_**	100	-
HME	**_240_**	**_2.2_**	43	**_0.14_**	_0.13_	_0.11_	_0.69_	**_530_**	41	**_17_**	6.9	0.10	**_9.2_**	**_38_**	330	-
RDL1	**_16_**	**_0.84_**	150	**_0.23_**	_0.051_	0.009	**_1.9_**	**_40_**	14	**_5.2_**	55	0.046	**0.66**	**_38_**	420	**400-800**
RDL2	**_71_**	**_5.0_**	110	**_0.37_**	_0.16_	0.026	**_3.6_**	**_410_**	19	**_6.7_**	55	0.16	**0.52**	**_93_**	1400	**> 1600**
RDL3	**_60_**	**_4.6_**	150	**_0.39_**	_0.17_	0.022	**_3.5_**	**_330_**	24	**_10_**	53	0.15	**0.62**	**_100_**	1300	**800-1200**
RDL4	**_20_**	**_1.6_**	97	**_0.12_**	_0.059_	0.010	**_1.1_**	**_100_**	18	**_3.7_**	58	0.056	**0.35**	**_35_**	490	**400-800**
RDL5	**_19_**	**_2.1_**	180	**_0.11_**	_0.061_	0.010	**_1.2_**	**_110_**	19	**_4.2_**	58	0.079	**0.57**	**_33_**	600	**1200-1600**
TP1	**_550_**	**_0.43_**	_450_	**_0.12_**	**_0.27_**	_0.29_	_0.60_	**_650_**	200	**_18_**	47	_0.25_	0.95	**_10_**	160	**400-800**
TP2	**_36_**	**_1.8_**	180	**_0.18_**	_0.099_	0.019	**_1.4_**	**_150_**	30	**_7.2_**	50	0.097	**0.98**	**_53_**	720	**800-1200**
RC	**_14_**	<0.022	70	0.002	<0.001	0.009	0.011	**_12_**	11	_0.38_	16	0.023	0.024	0.15	110	< 200
TP3	**_24_**	**_1.2_**	130	**_0.11_**	_0.060_	0.013	_0.93_	**_92_**	20	**_4.1_**	32	0.065	**1.2**	**_30_**	420	**800-1200**

Sulfate ranges obtained in the field with EM QUANT® test strips; * n = 2 (n =1 for all other sites); bdl = Below detection limits; - = no data available

Table 4. Bolivian receiving water body criteria, UNFAO irrigation and livestock drinking water guidelines, USEPA drinking water standards, and WHO drinking water guidelines.

Standard	pH	Al	As	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Zn	SO$_4^{2-}$
								---------- mg/L ----------								
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
UNFAO[μ]	6.5-8.4	20	2.0		0.05	5.0	1.0	5.0	20		10		2.0	10	10	
UNFAO[δ]	6.5-8.4	5.0	0.1		0.01	0.05	0.1	0.2	5.0		0.2		0.2	5.0	2.0	
UNFAO[τ]		5.0	0.2		0.05	1.0	1.0	0.5	2.0		0.2		0.2	5.0	2.0	
WHO			0.01		0.003		0.05	2.0			0.4		0.07	0.01		
USEPA primary			0.01		0.005		0.1	1.3						0.015		
USEPA secondary	6.5-8.5	0.2						1.0	0.3		0.05				5	250

[α] Cr (III) and Cr (VI) limits respectively
[μ] Short term (< 20 years) of continuous irrigation usage
[δ] Long term (> 20 years) of continuous irrigation usage
[τ] Livestock drinking water standard

All streams sampled failed to meet class "D" water quality standards in the wet and the dry seasons. The introduction of AMD orders of magnitude over class "D" limits (Strosnider et al., 2007) is likely leading to non-compliance downstream. However, in some cases the failure to meet class "D" standards could be indicative of overly stringent water quality standards applied in a mineral-rich landscape where background concentrations of many of the metals tracked are naturally elevated. In fact, Cerro Rico of Potosí was dubbed "The Red Mountain" because of its color, which is due to the oxidation of Fe on its slopes, and mining abounds in the region due to the naturally elevated metals concentrations. The chosen reference reaches (JMUT, HP1, VC1, and RC) did not meet class "D" requirements and were unsuitable for irrigation and livestock despite the minimal influence that mining likely had on these systems. Generally, elevated concentrations of the less ecotoxic metals (Al, Fe, and/or Mn) place these water bodies above the various limits. However, the reference reaches are the least contaminated in the region and it is likely that these reaches could be representative of background metals concentrations. Conversely, all mining-impacted reaches had concentrations of the highly ecotoxic metals (As, Cd, Cr, Pb, and/or Zn), in addition to the aforementioned less ecotoxic metals, that place them well above WHO, USEPA, UNFAO, and Bolivian class "D" standards.

Nearly all of the waters sampled were unsuitable for irrigation according to the UNFAO, save the unnamed tributary to Jayac Mayu in the dry season. However, this unnamed tributary does not adequately dilute Jayac Mayu, which after the confluence retains concentrations of ecotoxic elements orders of magnitude greater than is acceptable for irrigation or livestock use. Overall, there is a general trend of AMD and tailings impacted waters intercepting and degrading waters that were formerly much more suitable for irrigation and livestock consumption, such as is also observed when Jayac Mayu intercepts Rio Agua Dulce, Quebrada Chimborazo intercepts Villacolu Mayu, Ribera de la Vera Cruz intercepts Rio Huarampaya, and Rio Tarapaya intercepts Rio Cayara. Oporto et al. (2007) found that Cd concentrations of 0.065-0.24 mg/L in a mining-impacted river used for irrigation 150 km northwest of Cerro Rico caused a human health risk via Cd uptake in potatoes, a crucial Andean staple. Many of the reaches sampled have higher Cd concentrations than those noted by Oporto et al. (2007), indicating that they could present a yet greater risk. The presence of 0.39 mg/L Cd in Vilacollu Mayu at VC2, which is diverted for agricultural use shortly thereafter, is an especially alarming situation. Locally grown beans, potatoes, barley, and maize (Choque, 2006) may pose a health risk as well. In addition,

indigenous populations in the region make use of tens of other plant species for natural remedies (Fernandez et al., 2003), another possible bioaccumulation route.

The rain events during the wet season sampling of AD3, TP1, HME, and HMW likely led to an increase in suspended sediment, which could explain the elevated metals concentrations that accompany uncharacteristically low SO_4^{2-} and SC within the streams at that time. However, the data from these events indicate that large quantities of metals from non-point sources may enter streams with runoff, increasing rather than diluting contaminants. These data indicate the opposite of the trend observed by Smolders et al. (2002) downstream in Rio Pilcomayo.

Between sampling points JM2 and JM3, an *ingenio* may have been discharging tailings to Jayac Mayu. Elevated pH is necessary for ore floatation processing and this is achieved by the addition of quicklime (CaO). The great increase in pH and Ca concentrations observed in the dry season in a locality where there is little natural alkalinity generating capacity and the telltale grey froth observed indicate that this tailings discharge likely exists. However, the same pattern was not observed in the wet season, indicating that this discharge may be irregular or had since ceased.

The decrease in pH from TP1 to TP2 is likely partially due to weathering of sulfide minerals present within the bed of Rio Tarapaya. No other mining influences were noted in this reach. The inefficient floatation methods applied in Potosí lead to high concentrations of unrecovered metals (metal sulfides) in tailings (Smolders et al., 2003). Rio Tarapaya has collected tailings for centuries through direct discharges from bordering *ingenios* and tailings discharges to the Ribera de la Vera Cruz within the city of Potosí. Despite the dramatic recent decrease in tailings introduction to Rio Tarapaya and the Ribera de la Vera Cruz, tailings are still evident within Rio Tarapaya and appear to be negatively influencing water quality.

Conclusions and Recommendations

Mining and ore processing are considerable contributors to water quality degradation downstream of the Cerro Rico mines. Streams and rivers that receive AMD, tailings discharges and runoff from mining areas or tailings deposits, or impacted tributaries that do so, contain concentrations of ecotoxic metals (As, Cd, Co, Pb, and Zn) that render them unusable and environmental hazards. Dilution and natural passive biogeochemical attenuation are the likely mechanisms by which metals and hydrogen ion concentrations decrease with distance from

AMD sources within the streams not heavily contaminated with tailings. However, the weathering of tailings within the bed of Rio Tarapaya appears to present a strong enough signal to override some of the effects of the natural attenuation that occurs in its tributaries.

The dynamic nature of Potosí's surface hydrology and contamination sources solicit further study. The water quality conditions related in this study represent a limited snapshot of one water-year. Strosnider et al. (2007) demonstrated that AMD was a noteworthy contributor of trace metals and acidity to local streams. The findings presented here suggest that tailings in stream sediment and tailings discharges are also sources of water quality degradation. However, due to the natural dynamic hydrology of the region inherent with the extremes of the wet and dry seasons overlying the El Niño / La Niña cycle, further study is recommended. AMD, diffuse acid rock drainage, terrestrial tailings, in-stream tailings, and tailings discharges are likely contributors to water quality degradation and should be further studied to determine remediation priorities.

Acknowledgements

Literature Cited

Abbot, M. B. and A. P. Wolfe. 2003. Intensive Pre-Incan metallurgy recorded by lake sediments from the Bolivian Andes. Science. 301: 1893-1895. http://dx.doi.org/10.1126/science.1087806.

American Public Health Association (APHA). 1998. Standard Methods for the Examination of Water and Wastewater. 20th Ed.

Ayers, R. S. and D. W. Westcot. 1994. Water Quality for Agriculture. United Nations Food and Agriculture Organization.

Bartos, P. J. 2000. The pallacos of Cerro Rico de Potosí, Bolivia: a new deposit type. Economic Geology and the Bulletin of the Society of Economic Geologists. 95: 645-654. http://dx.doi.org/10.2113/95.3.6454.

Bolivian Ministry of Sustainable Development and Planning (BMSDP). 2000. Ley del medioambiente – No. 1333.

Bolivian National Meteorology and Hydrology Service (BSNMH). 2003. Meteorologicalbulletin of the department of Potosí.

Brandt, J. S. and P. A. Townsend. 2006. Land use – land cover conversion, regeneration and degradation in the high elevation Bolivian Andes. Landscape Ecology. 21: 607-623. http://dx.doi.org/10.1007/s10980-005-4120-z23.

Choque, P. 2007. Evaluacion del grado de contaminacion minera en las aguas, de la micro cuenca Vilacollu Mayu. Masters Thesis. Universidad Autónoma de "Tomás Frías" Potosí, Bolivia

Cunningham, C. G., R. E. Zartman, E. H. McKee, R. O. Rye, C. W. Naeser, O. Sanjinés V., G. E. Ericksen and F. Tavera V. 1996. The age and thermal history of Cerro Rico de Potosí, Bolivia. Mineralium Deposita. 31: 374-385. http://dx.doi.org/10.1007/BF00189185.

Evans, D.L. 1940. Structure and mineral zoning of the pailaviri section, Potosí, Bolivia.Economic Geology. 35: 737-750. http://dx.doi.org/10.2113/gsecongeo.35.6.737.

Fernandez, E. C., Y. E. Sandi and L. Kokoska. 2003. Ethnobotanical inventory of medicinal plants used in the Bustillo Province of the Potosí Department, Bolivia. Fitoterapia. 74: 407-416. http://dx.doi.org/10.1016/S0367-326X(03)00053-4.

García-Guinea, J. 1995. Cerro Rico in-mine museum project, Potosí, Bolivia. Minerals Industry International: Bulletin of the Institution of Mining and Metallurgy 1026: 13-19.

Godoy, R. A. 1990. Mining and Agriculture in Highland Bolivia: Ecology, History, and Commerce among the Jukumanis. University of Arizona Press, Tuscon.

Hudson-Edwards, K. A., M. G. Macklin, J. R. Miller and P. J. Lechler. 2001. Sources, distribution and storage of heavy metals in the Rio Pilcomayo, Bolivia. Journal of Geochemical Exploration. 72: 229-250. http://dx.doi.org/10.1016/S0375-6742(01)00164-9.

Miller, B. L. and J. T. Singewald. 1919. The Mineral Deposits of South America. McGraw-Hill, New York.

Miller, J. R., P. J. Lechler, K. A. Hudson-Edwards and M. G. Macklin. 2002. Lead isotopic fingerprinting of heavy metal contamination, Rio Pilcomayo basin, Bolivia. Geochemistry: Exploration, Environment, Analysis. 2: 225-233. http://dx.doi.org/10.1144/1467-787302-026.

Miller, J. R., K. A. Hudson-Edwards, P. J. Lechler, D. Preston and M. G. Macklin. 2004. Heavy metal contamination of water, soil and produce within riverine communities of the Rio Pilcomayo basin, Bolivia. Science of the Total Environment. 320: 189-209. http://dx.doi.org/10.1016/j.scitotenv.2003.08.011.

Oporto, C., C. Vandecasteele and E. Smolders. 2007. Elevated cadmium concentrations in potato tubers due to irrigation with river water contaminated by mining in Potosí, Bolivia. Journal of Environmental Quality. 36: 1181-1186. http://dx.doi.org/10.2134/jeq2006.0401.

Rudolf, W. E. 1936. The lakes of Potosí. Geographical Review. 26(4): 529-554. http://dx.doi.org/10.2307/209714.

Serrano, C., Pelaez, J. and J. L. Bouso. 1996. La Ribera de la Vera Cruz de Potosí. Rocas y Minerales. 293: 49-67.

Smolders, A. J. P., R. A. C Lock, G. Van der Velde, R. I. Medina Hoyos and J. G. M. Roelofs. 2003. Effects of mining activities on heavy metal concentrations in water, sediment, and macroinvertebrates in different reaches of the Pilcomayo river, South America. Archives of Environmental Contamination and Toxicology. 44: 314-323. http://dx.doi.org/10.1007/s00244-002-2042-1.

Smolders, A. J. P., R. A. C Lock, G. Van der Velde, R. I. Medina Hoyos and J. G. M. Roelofs. 2003. Effects of mining activities on heavy metal concentrations in water, sediment, and macroinvertebrates in different reaches of the Pilcomayo river, South America. Archives of Environmental Contamination and Toxicology. 44: 314-323.

Strosnider, W. H., R. W. Nairn and F. S. Llanos. 2007, A legacy of nearly 500 years of mining in Potosí, Bolivia: Acid mine drainage source identification and characterization, Proceedings

America Society of Mining and Reclamation, 2007 pp 788-803 http://dx.doi.org/10.21000/JASMR07010788

United States Army Corps of Engineers. 2004. <u>Water Resources Assessment of Bolivia</u>.

United States Environmental Protection Agency. 2007. National Primary Drinking Water Regulations. United States Code of Federal Regulations, Part 141, Chapter 1, Title 40, Volume 22.

United States Environmental Protection Agency. 2007. National Secondary Drinking Water Regulations. United States Code of Federal Regulations, Part 143, Chapter 1, Title 40, Volume 22.

Waltham, T. 2005. The rich hill of Potosí. Geology Today. 21(5): 187-190.

Wilson, W. E. and A. Petrov. 1999. Famous mineral localities: Cerro Rico de Potosí, Bolivia. Mineralogical Record. 30: 9-36.

World Health Organization. 2006. Guidelines for Drinking-water Quality 3rd Edition.