ACID MINE DRAINAGE IMPACTS ON IRRIGATION WATER RESOURCES, AGRICULTURAL SOILS, AND POTATOES IN POTOSÍ, BOLIVIA[1]

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Abstract: Intensive metal mining has occurred for nearly 500 years in the high altitude, arid desert of Potosí, Bolivia. Acid mine drainage (AMD) discharges have contaminated local water resources, rendering them unsuitable for agricultural and domestic use. However, due to water-limited conditions, many agricultural areas in the region make use of AMD-contaminated streams, with elevated trace metal concentrations, for irrigation. This study investigated the effects of AMD contaminated surface water irrigation sources upon the soils and crops to which they have been applied. Soil, water, and potato samples were gathered from four agricultural locations affected by AMD and one reference site. The AMD-influenced irrigation waters had trace metal concentrations that exceeded United Nations Food and Agriculture Organization (UNFAO), Canadian, and Australian guidelines for irrigation water. These waters had pH of 2.75 - 8.55, specific conductance of 150 - 2,900 µS/cm, 1.8 - 99 mg/L Cl^- and 32 - 2000 mg/L SO_4^{2-}. Total metals determined concentrations in irrigated waters were in the range of 0-35 mg/L Cu, 0-0.33 mg/L Pb, 0.43-110 mg/L Fe, 0.09-1180 mg/L Zn, 0.05-54 mg/L Mn, and 0-11 mg/L Cd. Agricultural soils contained total metal concentrations in the range of 5-520 mg/kg Cu, 12-670 mg/kg Pb, 12000-34000 mg/kg Fe, 99-3200 mg/kg Zn, 260-4200 mg/kg Mn, and 1-18 mg/kg of Cd. The Cu, Pb and Zn concentrations were greater in the exposed soils than in reference soils. Trace metal concentrations in the exposed soils exceeded Dutch, Canadian, and German guidelines. The levels of Cd, Pb, and Zn in potatoes exceeded commercially-sold vegetable guidelines. The agricultural products produced in this region may represent a potential health risk to subsistence farmers and other consumers.

Additional Key Words: acid rock drainage, farming, potatoes

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Introduction

Intensive mining activity has occurred in Potosí, Bolivia since the early 1500's from the time of Spanish colonization until the present day. Currently, rural inhabitants work in two principal economic activities: mining and agriculture. In many cases, inhabitants are involved in both sectors, the extent of which depends upon market conditions. Natural resources have been seriously damaged by contamination from mining activities, affecting the region's agricultural productivity and putting human health at risk. Acid mine drainage (AMD) containing elevated concentrations of trace metals is being discharged from mines into streams. Water from these streams is used to irrigate local agricultural produce. Soil, flora and fauna have been affected by the mining discharges. Local harvests produced for both animal and human consumption may present potential health risks.

AMD and processing plant effluent are primary contaminants in the headwaters of the economically vital, yet highly impacted Pilcomayo River watershed (Strosnider et al., 2007). Polluted streams decrease surface water resources available for drinking and irrigation purposes in the arid, high altitude and low productivity landscape of Potosí. Impacted indigenous populations who rely on the river for drinking water, irrigation, and fishing are exposed to elevated levels of toxic metals (Hudson-Edwards et al., 2003). Of specific concern is human exposure via the consumption of potatoes, the primary staple in this region. In a nearby watershed under similar stresses, Cd concentrations in potato tubers irrigated with mining impacted streams were found to be greater than those irrigated with spring water (Oporto et al. 2007). Considering common potato intakes rates, Oporto et al. (2007) determined these concentrations present a human health risk.

This paper examines trace metals concentrations in four AMD impacted agricultural areas around Potosí, and a reference site. The principal objective is to report these trace metal concentrations for irrigation water, agricultural soil, and potato tubers, and determine if there is a possible risk to inhabitants.

Methods

Four AMD-impacted agricultural systems were identified as well as an un-impacted reference site (Fig. 1). All sample sites are located around the city of Potosí, and are within the Pilcomayo River watershed. Irrigation water, soil and potato samples were collected at each site from July 27, 2008 to August 1, 2008. Water samples were taken upstream from the irrigated crops. Each site was geo-referenced using a Garmin GPS unit. Water samples were stored in 60-mL HDPE containers, and kept at approximately 4°C until analysis for total metals, dissolved metals, and anions. Conductivity, pH, dissolved oxygen, and temperature field measurements were obtained using an Orion 1230 multi-meter. Alkalinity titrations in the field were conducted following standard methods (APHA, 1998). Anion samples were filtered through Dionex OnGuard II H cartridge and 0.2 µm nylon filters, and measured by a MetrOhm 761 compact ion chromatograph (IC) following EPA method 300. Prior to preservation, dissolved metal samples were filtered through 0.45 µm nylon filters. Nitric acid was added to preserve total and dissolved metal samples. Acid microwave digestions of total and dissolved metals followed EPA method 3015.

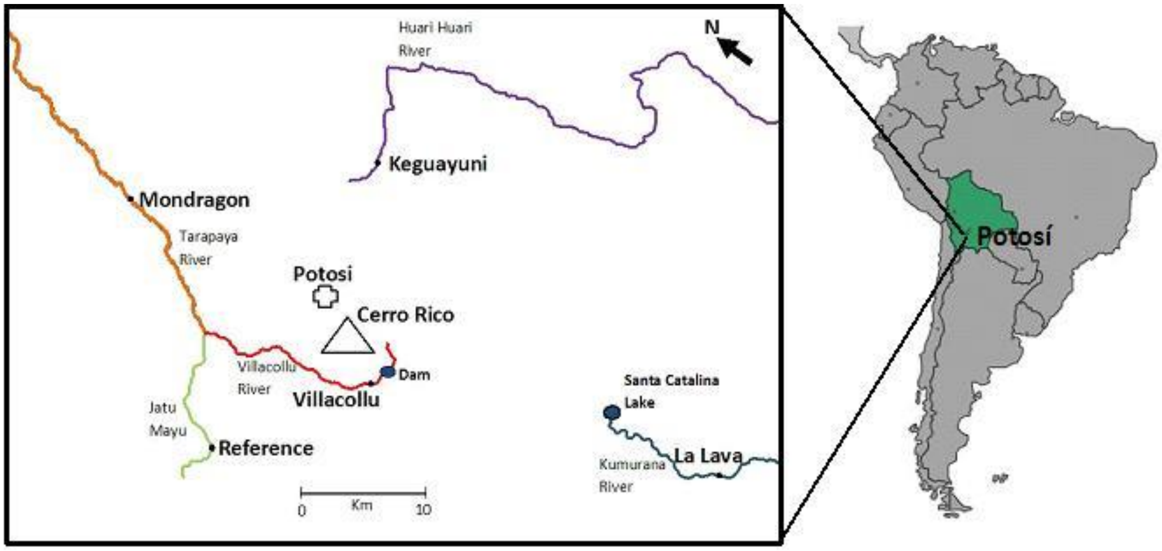

Figure 1. Map showing the location of the five sampled communities around Potosí, Southern Bolivia.

Soils were sampled from agricultural fields in which the aforementioned water samples were used in the irrigation process. Soil samples were composed of a five-part composite for a total of 500 g. Approximately 100 g were taken from the four corners and center of a measured 23 x 23 m agricultural field. Three composites were obtained per site. The depth of sampling was determined by the detection of crop roots approximately from 15 to 20 cm soil depth. Soil samples were dried, sieved and homogenized, and then 1 g of dry sample was digested following EPA method 3050B.

Potato (*Solanum* sp.) tubers were randomly collected from each irrigated field. Approximately 150 g of potatoes were sampled per area delimited. The potatoes were cleaned, cut unpeeled into small chips, dried, crushed, homogenized, and 1 g was digested using hot plates following EPA method 3050B. Digested water, soil, and potato samples were analyzed by a Varian Vista-Pro simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES) following EPA method 6010.

Site Description

Reference site water samples were taken from the river Jatu Mayu (Big River) located in the Comunidad Ingenio at 3558 m above sea level on the west side, approximately 20 km from the city of Potosí. A furrow irrigation system is applied on these soils. In this area potato and haba beans are the primary crops. People from this community live principally from the consumption and commercialization of their agricultural produce. The soil samples in this site were located around S 19°35'51.51", W 65°53'34.15" about 0.16 km from the village. Jatu Mayu confluences approximately 100 m downstream with the Jachuy Mayu (Small River) which converges 5 km downstream with the Tarapaya River.

Mondragón water samples were taken from the Tarapaya River. For centuries, this river has received the untreated municipal wastewater of Potosí, AMD from Cerro Rico (the principal mountain that has been mined) and ore processing plant effluent (Strosnider et al. 2008). Although Miller et al. (2004) reported that Tarapaya River water was not used for irrigation in Mondagón, fields were found where this was the case. Water is siphoned from the river to a furrow irrigation system in the fields that were sampled. Potato is the primary crop in this area at 3268 m above sea level. Maize and other cereals are also cultivated and used principally for domestic consumption instead of commercial purposes. Mondragón 1, 2, and 3 soil samples were located at S 19°25'45.59" W 65°47'15.81", S 19°25'46.25" W 65°47'17.04", and S 19°25'47.45" W 65°47'16.95", respectively, about 0.4 km from the center of the village. Mondragón is a small community located approximately 26 km to the north of the city of Potosí, and is composed of a population of 176 according to the INE (National Institute of Statistics) 2002.

The Villacollu River is dammed for irrigation control just 3 km from where multiple active and abandoned mines of the Chimborazo region of Cerro Rico drain to it (Choque, 2007; Strosnider et al. 2007). The irrigation canal was sampled at the toe of this dam (Fig. 1). Soils at

Villacollu (4027 m above sea level) have been cultivated with potatoes, haba beans, and other seasonal crops of the region. These sites were located 10 km to the south of the City of Potosí, and 0.74 km southeast of the Villacollu community. Site Villacollu 3 (S 19°39'5.92" W 65°46'15.43") had been fallow for two years at the time of sampling, but it was irrigated with waters from the Villacollu River. The Villacollu community is composed of approximately 70 families, of which approximately 70% labor in the mining industry due to its close proximity to the production centers of Cerro Rico (Choque, 2007). The community's agricultural production is generally for their own consumption (Choque, 2007).

The La Lava site was sampled downstream on the Juckucha River which is named the La Lava River at this location (3530 m above mean sea level). This river is impacted by several abandoned mine drainages, drainage from an active mine, ore processing plant effluent, and mine tailings runoff. Three soil samples were taken at S 19°53'18.94" W 65°38'37.85", approximately 40 km to the south of the city of Potosí. Potato and haba beans are the principal produce in this area. Some crops are irrigated with water from small natural springs in the area. Water from the La Lava River had not been used for irrigation for a couple of years due to noticeable contamination and previous crop failures experienced when using the degraded river for irrigation. Intermittent conflict has occurred between miners and farmers who claim rights to a clean irrigation water source. Approximately 50 families from this community are affected by the contamination of this stream.

Although Keguayuní was sampled during the dry season, it is irrigated during the wet season with water emanating directly from an active mining operation. Water samples were collected approximately 300 m inside the mine at 3919 m above sea level. These fields are located at 19°32'50.55" W 65°38'17.46". This community is comprised of approximately 120 people. The principal economic activity of this community is the exploitation of the Keguayuní mine. Local agricultural production is used for residents' own consumption. AMD from the Keguayuní mine flows during the wet season to the Huari-Huari River which converges 100 km downstream with the Pilcomayo River.

Results and Discussion

Irrigation water

Irrigation water, agricultural soil, and potato metal concentrations were evaluated with health guidelines from different countries due to the lack of these criteria in Bolivia. Physical parameter data for sampled waters are summarized in Table 1.

Table 1. Physical parameters measured in irrigation water.

Site	pH	Alkalinity (mg/L as $CaCO_3$)	Dissolved Oxygen (mg/L)	Specific Conductance (µS/cm)	Temperature (°C)
Reference	8.55	35	9.6	151	11.3
Mondragón	8.01	104	9.29	1175	13.9
Villacollu	7.33	10	8.80	1400	4.2
La Lava	2.75	0	11.22	1530	12.0
Keguayuní	4.36	0	6.70	2900	11.9

The reference water had the highest pH and lowest specific conductivity, which is characteristic of fresh waters unaffected by AMD. Mondragón's specific conductivity was high compared with the reference site, and its elevated pH and alkalinity are likely due to municipal wastewater and ore processing plant effluent influences. Irrigation water in Villacollu had a circumneutral pH and an elevated specific conductivity. The irrigation water from the La Lava River had a low pH, and high specific conductivity compared with the reference site. Keguayuní′s waters had low pH and the highest specific conductivity. Anion concentrations found in the irrigation water applied on the potato crops are presented in Table 2.

Table 2. Anion results from irrigation water. All values are in mg/L.

	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Reference	4.1	<0.5	<0.5	<0.5	<0.5	32
Mondragón	99	5.6	1.5	0.6	<0.5	370
Villacollu	9.6	6.1	1.6	1.9	<0.5	560
La Lava	1.8	5.9	2.5	1.2	<0.5	844
Keguayuní	4.0	17.9	<0.5	2.7	<0.5	1990

The anion results indicated the lowest sulfate, nitrite and nitrate concentrations for the reference site. Mondragón had the highest chloride concentration. Elevated chloride is indicative of municipal wastewater contamination (Metcalf and Eddy, 1991). Irrigation waters at Villacollu, La Lava, Keguayuní and to a lesser extent Mondragón all exhibited characteristics of mine drainage impacts. The elevated sulfate in these waters is likely a result of metal sulfide weathering, the cause of AMD (Watzlaf et al. 2004). Blasting agents likely contribute considerable concentrations of ammonium, nitrate and nitrite to mine waters (Sanmugasunderam et al. 1987; Häyrynen et al. 2009). It is likely that elevated concentrations of ammonium were also present in the mining-influenced waters because municipal wastewaters commonly contain 12-50 mg/L of NH_4^+ as N (Metcalf and Eddy, 1991) and active mine waters often contain 20-75 mg/L of NH_4^+ (Sanmugasunderam et al. 1987). Interestingly, the presence of reactive nitrogen compounds in these waters may help mitigate the multiple negative stresses on agricultural productivity from AMD exposure. Villacollu, La Lava and Keguayuní had the highest sulfate, nitrite and nitrate concentrations because mine water was the primary contamination source entering these waters. The Keguayuní irrigation water had the highest sulfate, nitrite and nitrate concentrations because it was essentially undiluted mine drainage from an active mine.

By comparing the mean of the total metal results with the different health guidelines (Table 3), the reference site irrigation water is observably less affected by AMD in comparison with the other four sites. La Lava exceeded UNFAO guidelines for Al, Cd, Cu, Fe, Mn, and Zn. Canadian and Australian guidelines were exceeded for As, Cd, Pb, and Zn in this location. La Lava had the highest total Al and Fe concentrations. Keguayuní exceeded UNFAO, Canadian, and Australian guidelines for Cd and Zn and it presented higher concentration compared with the values from La Lava, Villacollu, and Mondragón, except for Fe, As, and Al.

Villacollu waters contained lower concentrations of Fe and other metals (Table 3). However, AMD with elevated concentrations of metals have been reported by Strosnider (2007) (e.g., 2450 mg/L +/- 100 of Fe) to be discharged to the stream before it reaches the dam. Increased residence time caused by the dam over the Villacollu River could decrease metal concentrations by precipitation. However, substantial biologically mediated removal of metals in these conditions is not expected due to low ambient temperatures (Watzlaf et al., 2004).

Miller et al., (2004) reported total concentrations of 2.5 mg/L Zn, 0.005 mg/L As, 0.002 mg/L Cd, 0.002 mg/L Cu, and <0.002 mg/L Pb at the Northern end of Mondragón for irrigation water that was derived from local springs and applied to different fields. Indicating that elevated metals concentrations are not unusual in the Tarapaya River, Smolders et al. (2003) reported total concentrations of 2.3 mg/L Pb, 0.3 mg/L Cd, 1.7 mg/L Cu, 12.4 mg/L Zn along the Tarapaya River closer to the city of Potosí. Approximately 14 km upstream, Strosnider et al. (2008) documented total concentrations of 1.2 mg/L Pb, 0.11 mg/L Cd, 0.93 mg/L Cu and 30 mg/L Zn.

Table 3. Mean total metals in irrigation waters with respect to health guidelines (mg/L). Italicized, underlined, and bolded values exceed Canadian, Australian long term, and Australian short term irrigation water guidelines, respectively.

	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
__Canadian__[1]		_0.1_		_0.01_			_0.2_							_0.01_	_2.0_
__Australia L.T__[2]		0.1		0.01			0.2							2.0	2.0
__Australia S.T__[2]		__2.0__		__0.05__			__5.0__							__5.0__	__5.0__
__UNFAO*__	20	2.0		0.05	5.0	1.0	5.0	20			10		2.0	10	10
__UNFAO**__	5.0	0.1		0.01	0.05	0.1	0.2	5.0			0.2		0.2	5.0	2.0
__UNFAO***__	5.0	0.2		0.05	1.0	1.0	0.5	2.0			0.2		0.2	5.0	2.0
__Reference__	0.4	BDL	17.3	BDL	ND	BDL	0.00	0.43	3.6	2.7	0.05	6.0	0.03	BDL	0.09
__Mondragón__	2.3	_0.3_***	135	_0.02_**	0.00	0.00	__0.14__	17.5**	17.9	12.2	1.2**	69.7	0.04	_0.33_	___5.8**___
__Villacollu__	1.0	ND	130	___0.11*___	0.02	BDL	0.01	1.0	9.8	32.5	9.0**	21.3	0.06	BDL	___48.9*___
__La Lava__	39*	_0.1_**	59.3	___0.21*___	0.4**	0.01	___9.1*___	110*	4.3	27.1	13.1*	7.0	0.19	_0.26_	___60.6*___
__Keguayuní__	4.8	ND	51.2	___11.3*___	0.7**	0.00	___35.1*___	45.1*	7.9	64.6	54.4*	10.8	0.5**	0.13	___1180*___

[1] From Water Research Crop and Agriculture and Agri-food Canada (1999), (Miller et al., 2004).

[2] From ANZECC (1992), (Miller et al., 2004)

Values over the UNFAO irrigation and livestock water guidelines (Strosnider, 2008).
*Short term (<20 years) of continuous irrigation usage
**Long term (>20 years) of continuous irrigation usage
***livestock drinking water usage
BDL = below detection limit
ND = not determined

Dissolved metals (Table 4) at the reference site did not exceed any guidelines. Mondragón exceeded the UNFAO long term (>20 years) standards for continuous irrigation usage for Mn. Villacollu exceeded UNFAO, Canadian, and Australian guidelines for Cd and Zn. UNFAO long term standards were exceeded at this site for Mn. La Lava dissolved metals exceeded all guidelines for Cd, Cu, and Zn. UNFAO guidelines were exceeded for Al, Co, Fe, and Mn at La

Lava as well. Cd, Cu, Mn, Fe, and Zn exceeded all UNFAO guidelines in Keguayuní, and Co and Ni only exceeded the long term standards in the UNFAO irrigation and livestock watering guidelines.

Similar concentrations of dissolved metals were reported by Smolders et al. (2003) for Cd, Cu, Pb, and Zn along the Tarapaya River close to the city of Potosí. The low concentrations reported in Table 4 were apparently due to the adsorption of metals to the suspended sediment and decreased solubility of metals due to the high pH of the water.

Table 4. Irrigation water dissolved metals with respect to health guidelines. Italicized, underlined, and bolded values exceed Canadian, Australian long term, and Australian short term irrigation water guidelines, respectively.

	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
Canadian		*0.1*		*0.01*			*0.2*							*0.01*	*2.0*
Australia L.T^1		0.1		0.01			0.2							2.0	2.0
Australia S.T^2		**2.0**		**0.05**			**5.0**							**5.0**	**5.0**
UNFAO*	20	2.0		0.05	5.0	1.0	5.0	20			10		2.0	10	10
UNFAO**	5.0	0.1		0.01	0.05	0.1	0.2	5.0			0.2		0.2	5.0	2.0
UNFAO***	5.0	0.2		0.05	1.0	1.0	0.5	2.0			0.2		0.2	5.0	2.0
Reference	0.03	ND	17	BDL	ND	ND	BDL	0.09	3.4	2.5	0.03	5.9	0.03	ND	0.08
Mondragón	0.07	0.04	131	0.00	0.01	0.00	0.02	0.1	17.2	11.3	1.0**	68.4	0.03	BDL	0.9
Villacollu	0.09	ND	130	***0.1****	0.02	BDL	0.01	0.3	9.5	32.5	9.04**	20.9	0.06	BDL	***48****
La Lava	37.1*	BDL	59	***0.2****	0.4**	0.01	***8.9****	95*	3.8	26.7	13*	7.0	0.2**	*0.2*	***60****
Keguayuní	4.2	ND	51	***11.4****	0.7**	0.00	***34.7****	42*	7.7	63.4	53*	10.7	0.5**	*0.1*	***1190****

[1] From Water Research Crop and Agriculture and Agri-food Canada (1999), (Miller et al., 2004).

[2] From ANZECC (1992), (Miller et al., 2004)

Values over the UNFAO irrigation and livestock water guidelines (Strosnider, 2008).

*Short term (<20 years) of continuous irrigation usage

**Long term (>20 years) of continuous irrigation usage

***livestock drinking water usage

BDL = below detection limit

ND = not determined

Irrigated Soils

Soils at all sites contained metal concentrations that were greater than various health guidelines. Metals concentrations in agricultural soils were compared to Dutch, Canadian, and German health guidelines for Cd, Cu, Pb, and Zn (Table 5). Generally, the CIMA (Centro de Investigacion Minero Ambiental) and CREW (Center for Restoration of Ecosystems and

Table 5. Mean soil results (mg/kg) with respect to agricultural soil guidelines. Italicized, underlined and bolded values exceed Dutch, Canadian, and German guidelines, respectively.

	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
Dutch				*12*			*190*							*530*	*720*
Canadian				8			100							200	400
German				**2**			**500**							**500**	**300**
Reference 1															
CREW results	15600	30	4300	**3.3**	12	22	9.4	29300	6400	1400	418	373	24	97	125
Reference 2															
CREW results	13100	23	3800	**2.9**	11	16	9.1	25900	5000	9000	496	383	16	70	150
Reference 3															
CREW results	13300	18	4200	**3.0**	11	16	8.6	26400	5200	8300	536	417	16	52	180
CIMA results							5	24000			530			38	
Mondragón 1															
CREW results	11500	536	16000	***17.4***	15.3	12.3	***526***	41200	5000	7600	1200	568	19.2	***570***	***3500***
CIMA results				***17.3***			*445*	32700			1100			***656***	***3100***
Mondragón 2															
CREW results	9800	489	10500	***16.7***	14.8	9.8	***583***	37400	3900	5800	1200	451	16.6	416	***3000***
CIMA results				***11.0***			***500***	30700			1200			472	***2700***
Mondragón 3															
CREW results	9000	327	11900	***12.2***	2.5	9.1	*384*	28200	3900	5700	718	558	17.2	355	***1700***
Villacollu 1															
Crew results	11400	13.7	2900	**2.3**	5.3	6.1	10.5	12400	3500	2900	262	353	6.7	54.7	204
Cima Results							6.8	12300			266			32.7	206
Villacollu 2															
Crew results	12800	13.0	4800	**2.7**	5.9	7.3	8.1	17400	3600	3900	312	439	7.1	33.5	196
Cima Results							6.0	14900			318			16.7	192
Villacollu 3															
Crew results	16400	13.9	4000	**2.8**	7.3	10.2	9.2	20400	4000	4000	406	422	9.0	37.3	133
Cima Results							6	16900			396			22	114
La lava 1															
CREW results	11300	72.8	2900	**3.8**	1.7	9.0	93.5	23800	3700	3800	476	376	9.7	130	**675**
CIMA results				1.8			53.8	19000			410			79.5	**603**
La lava 2															
CREW results	10500	70.4	2700	**3.7**	1.7	9.3	92.7	24400	3400	3600	451	354	8.5	127	**564**
CIMA results				1.5			83.5	17400			371			122	289
La lava 3															
CREW results	10600	60.9	2700	**3.8**	1.6	8.8	79.7	23800	3500	3800	461	339	9.5	126	**651**
CIMA results							90.3	19600			479			154	**661**
Keguayuní 1															
CREW results	15500	16.5	1400	**7.8**	4.9	11.7	32.8	30600	3300	2600	890	202	11.3	54.1	**399**
CIMA results				**4.5**			29.5	27100			871			57.5	**392**
Keguayuní 2															
CREW results	13400	14.0	1600	**6.6**	3.2	10.2	30.9	38300	3200	2200	4800	222	13.0	77.8	**619**
CIMA results				**3**			28	31000			3900			82.7	**647**

Watersheds) analyzed results compared well. Despite the relatively un-impacted irrigation water applied at the reference site, it exceeded the stringent German health guideline for Cd. Villacollu soils also exceeded the German Cd guideline. Interestingly, Villacollu also presented the lowest values of As and Pb, despite its proximity to Cerro Rico. However, the other exposed sites exceeded multiple guidelines for multiple ecotoxic metals. As, Ca, Cd, Cu, Fe, Pb and Zn concentrations in the Mondragón soil contained the highest values compared with the other sampled sites. Dutch, Canadian, and German health guidelines for Cd, Cu, and Zn concentrations were exceeded. For all Mondragón sites, Pb concentrations exceeded the Canadian guidelines, but the Mondragón 1 site exceeded all guidelines for each metal. Canadian and German guidelines were exceeded at La Lava for Zn concentrations. La Lava also exceeded the German Cd guideline. Keguayuní exceeded the German guidelines for Cd, and Zn, and the Canadian guideline for Zn. Overall, results indicate that contaminated irrigation waters are degrading farmland because exposed soils generally have concentrations of metals orders of magnitude greater than the reference.

Miller et al., (2004) reported soil concentrations for Pb, Zn, Cu, Cd, and As at the northern end of Mondragón. Concentrations of these soils sampled adjacent to the Tarapaya River were similar to those concentrations found in this research. Miller et al., (2004) stated that soils sampled from lower terraces (close to the impacted stream) are more contaminated than those soils located in upper fields. This indicates that a factor affecting soil metal concentration furthermore than irrigation water could be the deposition of these elements by flooding. Keguayuní is located on 5 to 10 percent sloped terraces a few meters above the AMD stream. There is no flooding condition in this site, and it is irrigated with water containing the highest concentration of metals in this study. Soil samples from Mondragón on other hand, were taken from the low adjacent terraces of the stream which may be flooded during the wet season. Flooding in the sampled Mondragón sites could be an important cause of the metal deposition and accumulation.

Potatoes sampled in exposed sites exceeded metals concentrations according to the health guideline summary complied by Miller et al. (2004). This guideline is applicable to commercially sold vegetables (Table 6). Potato Cd guidelines were exceeded by Mondragón, Villacollu, La Lava, and Keguayuní, but not for the reference site. Guidelines for Zn were exceeded by all the sampled sites including the reference site. Pb guidelines were exceeded by

Mondragón, Villacollu 2, La Lava, and Keguayuní potatoes. The Cu guideline was not exceeded. Mondragón potatoes contained the highest concentrations of Cd, Cu, Mn, and Zn, followed by La Lava, and Keguayuní. Generally, the magnitude of soil metal contamination was proportional to potato metal concentrations.

Oporto et al. (2007) stated that elevated soil Cd bioavailability might explain elevated Cd potato concentrations. Cl^- forms complexes with Cd^{2+}, increasing Cd bioavailability (Oporto et al. 2007). Soils sampled from Mondragón have the highest Cd concentrations and they were irrigated with waters containing the highest Cl^- concentrations yet Cd, Pb and Zn concentrations were lower than other sites, excluding the reference. Mondragón potatoes contained the highest Cd concentration, providing support for Oporto et al.'s (2007) hypothesis.

Table 6. Health guidelines and mean potato metal concentration in mg/kg (Miller et al. 2004). Underlined values exceed the food health guideline.

	Al	**As**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Zn**
Guideline[C]				0.1[A]			20[B]							0.25[A]	50[B]
Reference	10.2	2.5	841	0.04	0.00	0.30	5.9	45.8	16600	1000	6.6	236	0.00	0.22	81.0
Mondragón	14.6	1.7	1700	1.31	0	0.34	14.1	48.0	22200	1200	13.0	322	BDL	2.59	202
Villacollu 1	11.1	5.1	822	0.19	0.12	0.53	6.5	23.2	16600	1100	4.4	173	0.19	0.00	96
Villacollu 2	11.8	3.5	911	0.23	0.00	0.27	5.0	25.9	18400	1200	5.7	327	0.15	3.60	93.2
Villacollu 3	36.2	6.4	2200	0.12	0	0.27	4.7	35.8	14400	1000	4.2	171	0	0	88.4
La lava	11.4	2.5	507	0.29	0.07	0.28	12.3	151	20700	1100	7.6	455	0.56	0.86	167
Keguayuní 1	21.9	9.0	429	1.02	0.00	0.45	10.2	53.3	19100	1300	5.6	143	0.54	1.64	102
Keguayuní 2	11.9	2.8	523	0.10	0.00	0.22	6.9	29.0	16700	1000	5.3	150	0.51	3.5	77.8

[A] EC regulation 466/2001

[B] Food standards committee guideline 1950

Guideline summary taken from Pless-Mulloi et al. (2001)

Irrigation water, agricultural soil, and potato tuber metal concentrations in the reference site did not exceed health guidelines except for Zn in the potatoes and Cd in the soils. Elevated reference site potato Zn concentrations could be attributed to the naturally elevated background concentrations of trace metals in this metal-rich province. The most contaminated potato tubers were found at Mondragón. Mondragón irrigation water did not contain the highest concentrations of total and dissolved trace metals. However, the Mondragón soils had the highest concentrations of As, Cd, Fe, Pb, and Zn, likely because of long term application of these waters.

Potato Cd, Pb, and Zn exceeded the commercially sold vegetable guideline for Mondragón, Villacollu, La Lava, and Keguayuní. However, Zn concentrations in reference site potatoes also exceeded this guideline, likely due to naturally elevated background concentrations. Zn, Pb, and Cd are ecotoxic metals that represent a risk due to human and animal consumption of potatoes in these communities.

Conclusions

Irrigation waters affected by AMD in the Mondragón, Villacollu, La Lava, and Keguayuní communities have contaminated soils and potatoes with high concentrations of ecotoxic metals. Potosí lacks adequate water and food sources which is a detriment to economic and agricultural livelihood in the region. Surface water resources are crucial for domestic and wild animals, as well as for irrigation. High concentrations of Cd, Pb, and Zn found in potatoes in the sampled sites may potentially risk the health of the local communities. New reliable and cost-effective technologies should be applied to improve the water quality in this region.

Literature Cited

Häyrynen, K., E. Pongrácz, V. Väisänen, N. Pap, M. Mänttäri, J. Langwaldt and R.L. Keiski. 2009. Concentration of ammonium and nitrate from mine water by reverse osmosis and nanofiltration. Desalination 240: 280-289. http://dx.doi.org/10.1016/j.desal.2008.02.027.

Hudson-Edwards, K.A., J.R. Miller, D. Preston, P.J. Lechler, M.G. Macklin, J.S. Miners and J.N. Turner. 2003. Effects of heavy metal pollution in the Pilcomayo river system, Bolivia, on resident human populations. Journal De Physique IV. 107: 637-640. http://dx.doi.org/10.1051/jp4:20030384.

Instituto Nacional de Estadística (INE). 2002. Censo Nacional de Población y vivienda 2001. http://www.ine.gov.bo/default.aspx

Metcalf and Eddy. 1991. Wastewater Engineering: Treatment, Disposal and Reuse. 3rd Ed. McGraw Hill. pp. 1334

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 Picomayo 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.

Choque, C.P. 2007. Evaluación del grado de contaminación minera en las aguas de la microcuenca Villacollu Mayu. Tesis Magistral, Universidad Autónoma Tomás Frías. Potosí, Bolivia. pp. 93?

Sanmugasunderam, V., V.I. Lakshmanan, J. Christison and M. McKim. 1987. Can microorganisms be used to control nitrate levels in mining process effluents? Hydrometallurgy 18: 383-395.

https://doi.org/10.1016/0304-386X(87)90077-6

Smolder, A.J.P., Lock, R.A.C., Van der Velde, G., Medina H.R.I., Roelofs J.G.M. 2003. Effects of mining activities on heavy metal concentrations in water, sediments, and macroinvertebrates in different reaches in the Pilcomayo River, South America. Arch. Environ. Contam. Toxicol. 44, 314–323. http://dx.doi.org/10.1007/s00244-002-2042-1.

Smolders, A.J.P., K.A. Hudson-Edwards, G. Van der Velde and J.G.M. Roelofs. 2004. Controls on water chemistry of the Pilcomayo river (Bolivia, South-America). Applied Geochemistry. 19: 1745-1758. http://dx.doi.org/10.1016/j.apgeochem.2004.05.0018.

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, 2007 National Meeting of the American Society of Mining and Reclamation, Gillette, WY. pp. 788-803 http://dx.doi.org/10.21000/jasmr07010788

Strosnider, W.H., F. Llanos and R.W. Nairn. 2008. A legacy of nearly 500 years of mining in Potosí, Bolivia: stream water quality. Proceedings, 2008 National Meeting of the American Society of Mining and Reclamation, Richmond, VA. pp. 19

https://doi.org/10.21000/JASMR08011232

Watzlaf, G.R., K.T. Schroeder, R.L.P. Kleinmann, C.L. Kairies, and R.W. Nairn. 2004. The passive treatment of coal mine drainage. NETL, US Department of Energy, Pittsburg, PA. pp. 73