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Lead, zinc, and antimony contamination of the Rio Chilco-Rio Tupiza drainage system, Southern Bolivia

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Abstract An intense, but localized rainfall event in February 2003, led to the severe erosion and failure of a tailings disposal impoundment at the Abaró Antimony Mine in southern Bolivia. The failure released approximately 5,500 m³ of contaminated tailings into the Rio Chilco-Rio Tupiza drainage system. The impacts of the event on sediment quality are examined and compared to contamination resulting from historic mining operations in the headwaters of the basin. Of primary concern are contaminated floodplain soils located along downstream reaches of the Rio Tupiza which were found to contain lead (Pb), zinc (Zn), and antimony (Sb) concentrations that locally exceed Canadian, German, and Dutch guidelines for agricultural use. Spatial patterns in sediment-borne trace metal concentrations, combined with Pb isotopic data, indicate that Pb, Zn, and Sb are derived from three tributary basins draining the Abaró, Chilcobija, and Tatasi-Portugalete mining dis-

tricts. Downstream of each tributary, geographical patterns in trace metal concentrations reflect local geomorphic changes throughout the drainage system. Trace metal concentrations within the Rio Chilco decrease rapidly downstream as a result of dilution by uncontaminated sediments and storage of metal enriched particles (e.g., sulfide minerals) in the channel bed as a result of ongoing aggradation. Storage in the floodplains is limited. These processes significantly reduced the dispersal and, thus, the relative environmental affects of tailings eroded from the Abaró Mine during the 2003 flood. In contrast, storage of Pb, Zn, and Sb in floodplains along the Rio Tupiza is significant, the majority of which is derived from historic mining operations, particularly mining within the Tatasi-Portugalete district.

Keywords Heavy metals · Tailings spill · Pb isotopes · Geomorphic response · Rio Tupiza · Bolivia

Introduction

Mine disposals including dumps and tailings piles are a ubiquitous feature of both surface and underground (hard-rock) mining operations. During approximately the past 35 years, 59 major metal-related tailings impoundments have failed worldwide, releasing contaminated water and sediment into riverine environ-

ments (Table 1) (WISE 2003). One such failure occurred at the Abaró Antimony Mine located approximately 70 km northwest of Tupiza on the eastern flank of the Andes in southern Bolivia (Fig. 1). At the mine site, liquid and solid wastes were disposed of in a small tributary valley (Fig. 2). During an intense, but localized rainfall-runoff event in February 2003, tailings materials from the tributary were eroded and transported 1.2 km

downstream through a narrow bedrock channel to the Rio Chilco (Fig. 1). In August 2003, officials from the Departments of Tarija, Chuquisaca, and Potosí declared the reach extending from Abaró to the lower Pilcomayo a “zone of hydrologic emergency”. The declaration was put forth on the assumption that the tailings dam failure, combined with the release of toxic metals from historic mining operations, had the potential to negatively affect both ecological and human health over distances of several hundred kilometers (La Mañana 2003). However, geochemical data defining the magnitude of contamination produced by the spill and historic mining operations were minimal. Thus, a geomorphological–geochemical study was initiated by the authors in November 2003 to assess the extent of lead (Pb), zinc (Zn), and antimony (Sb) contamination of the Rio Chilco–Rio Tupiza–Rio drainage system, including the area downstream of the Abaró Mine (Fig. 1). The initial results of the investigation included (1) an assessment of the potential environmental impact of the 2003 Abaró tailings spill, (2) an estimate of the magnitude of contamination resulting from historic mining operations in the headwaters of the Rio Tupiza, (3) the identification of the primary sources of metal contamination to the Rio Chilco–Rio Tupiza drainage system, and (4) the primary mechanisms leading to downstream declines in metal and Sb concentration.

Inherent in the analysis is the use of Pb isotopic fingerprinting methods to identify the source(s) of Pb and other trace metals to specific reaches of the Rio Chilco–Rio Tupiza drainage system. Pb isotopic data have been

widely used to delineate the primary sources of Pb in air and aerosols (Chow and Johnstone 1965; Ault et al. 1970; Chow and Earl 1972), ice (Rosman et al. 1993), soils (Gulson et al. 1981; Steinmann and Stille 1997; Hansmann and Köppel 2000), lacustrine sediments (Shirahaa et al. 1980; Petit et al. 1984; Moor et al. 1996), peat bogs (Shotyk et al. 1998; Weiss et al. 1999), and tree rings (Marcantonio et al. 1998; Watmough et al. 1999). However, relatively few studies have applied Pb isotopic techniques to the analysis of mining and milling wastes (see Hudson-Edwards et al. 1999; Steding et al. 2000; Miller et al. 2002 for exceptions). The results of this study show that in combination with total elemental concentration data, Pb isotopes may provide a particularly useful means of more accurately determining contaminant sources.

Geographic and geologic setting

The Rio Chilco heads within the southern segment of the Cordillera Oriental of southwestern Bolivia (Fig. 1). It then joins the Rio Tupiza, a large ephemeral river that flows in an easterly to southeasterly direction through the town of Tupiza before entering the Rio San Juan del Oro. Within and adjacent to the basin, mineralization is associated with two different types of ore deposits. The Tatasi-Portugalete mining district is centered around a polymetallic vein deposit that is located within the headwaters of the Rio Tatasi (Fig. 1). This deposit is part of the Bolivian Tin Belt and is associated with a Miocene (15.6 Ma) dacitic dome complex that intrudes the sedimentary basement rocks composed of Ordovician shales and slates. The Ordovician sequence is, in turn, unconformably overlain by Cretaceous conglomerates, limestones, and calcareous sandstones. Ore minerals include cassiterite, galena, and sphalerite which are accompanied by gangue minerals like pyrite, chalcopyrite, marcasite, quartz, and bournonite, among others. Upper levels of the veins are enriched in tin (Sn) and silver (Ag); with increasing depth the mineralogy of the veins shift to different paragenetic assemblages including Ag, Zn, and Pb sulfides (Gustavson 1991). Several large mine and mill tailings piles occur within the Tatasi-Portugalete district and serve as a source of trace metals to the Rio Tatasi.

The other major type of ore deposits in the Rio Tupiza basin are associated with the Bolivian antimony belt. At Chilcobija, the country's largest Sb mine, vein deposits are hosted in Ordovician rocks. Three main systems of veins have been exploited within the Ordovician sequence and the remaining Sb reserves are primarily contained within these mineralized structures. Ore minerals include stibnite, galena, and sphalerite, which are combined with gangue minerals including quartz, pyrite, and arsenopyrite. Gold (Au) was also extracted

Table 1 Selected Tailings Dam Failures (modified from WISE 2003)

Mine (location and year)	Volume of Material Released m ³
Aznalcóllar (Spain 1998)	1,300,000 ^a
Harmony, Merries (South Africa 1994)	600,000 ^b
Buffalo Creek (USA 1972)	500,000 ^b
Sgurigrad (Bulgaria 1996)	220,000 ^b
Aberfan (UK 1966)	162,000 ^b
Mike Horse (USA 1975)	150,000 ^b
Bilbao (Spain 1969)	115,000 ^b
Baia Mare (Romania 2000)	100,000 ^c
Ages (USA 1981)	96,000 ^d
Huelva (Spain 1998)	50,000 ^b
Stancil, Perryville (USA 1989)	39,000 ^b
Dean Mica (USA 1974)	38,000 ^b
Arcturus (Zimbabwe 1978)	30,000 ^b
Maggie Pie (UK 1970)	15,000 ^b
Borsa (Romania 2000)	8,000 ^c
Abaró (Bolivia 2003)	5,500 ^a

^aMetal enriched tailings

^bWaste

^cEffluent and tailings

^dCoal refuse

^eCyanide contaminated effluent & tailings

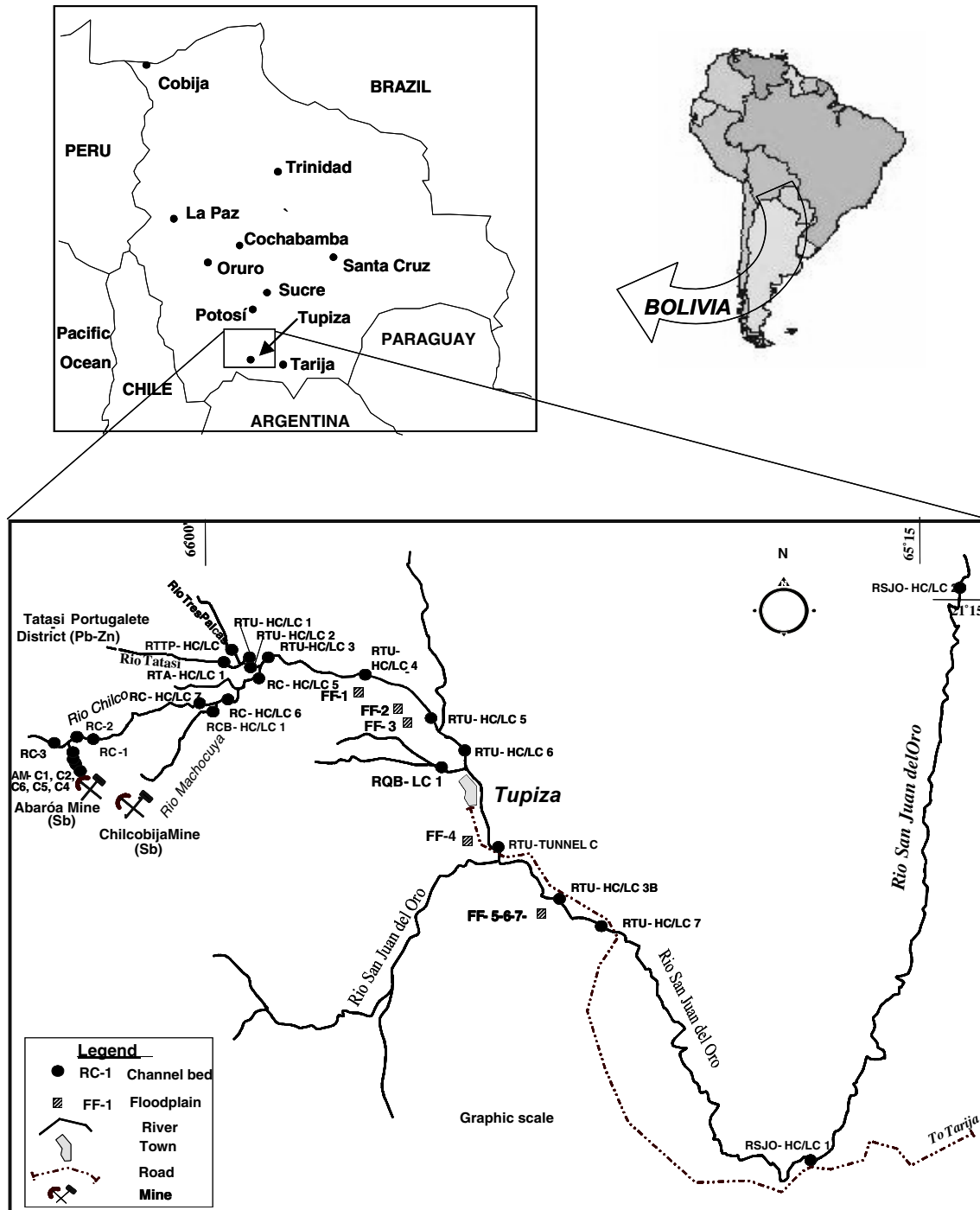


Fig. 1 Location map of the study area showing the distribution of sampling sites along the Rio Chilco-Rio Tupiza drainage system

as a by-product in the past. During peak production Chilcobija had a capacity of 12,000 tons per year of Sb concentrate, but during the past decade, annual production declined to 4,000–5,000 tons. The mine was closed in 1997 after Sb prices decreased, making oper-

ation uneconomical (Carlin 1998). However, some small mines in the area survived the continuous decline in prices, including Abaró, located approximately 4.5 km from Chilcobija.

The Abaró Mine is located along a tributary to the Rio Chilco, referred to here as the Rio Abaró. It is positioned along the western edge of the Altiplano. This area is composed of Paleozoic lithologies that have been

deformed into narrow north–south oriented anticlines and synclines. The landscape is dominated by a high altitude, low-relief plateau that is locally dissected by deep valleys that cut the country rock. The ore deposits at Abaróa were discovered in the 1950's, but unfortunately, neither the beneficiation methods nor production at the mine were recorded. However, at the time of sampling in 2003, 40–50 tons/day of ore containing 7% Sb were processed by crushing, milling and froth floatation (J. Arias, personal communication). The mill reportedly had the capacity to process 150 tons of ore per day.

In February 2003, an unusually high magnitude, low duration flood event eroded a dam composed of tailings that had been built across a sediment/contaminant filled valley (Fig. 2; Owens et al. 2001). The waste materials were subsequently transported downstream through a small tributary incised into bedrock before reaching the Rio Chilco approximately 1.2 km downstream from the mine site (Fig. 3). The Rio Chilco, a tributary to the Rio Tupiza, also receives waste materials from the Chilcobija Mine by way of the Rio Machocuya (Fig. 1).

With the exception of small developments in the vicinity of the mine sites, the population density in the headwaters is extremely low. Adjacent and downstream of Tupiza, however, floodplain deposits are extensively utilized for farming. Specific crops include fruits (apples, peaches), vegetables (onions, carrots, lettuce, beets), and other products (mainly cereals). Thus, contamination of agricultural soils and the products grown on them, is a major concern.

Methods

The investigation was based on a geomorphological–geochemical approach in which geomorphic principles



Fig. 2 Abaróa tailings impoundment. Photo was taken in November 2003, 8 months after the flood event. The dam (composed of the light colored sediments) was constructed after the event as part of the site remediation program. Eroded tailings were primarily derived from the region immediately behind the dam



Fig. 3 Bedrock channel between the Abaróa Mine and the Rio Chilco. Dashed white lines correspond to the high-water marks formed by deposition of silt during the 2003 flood. Note the limited space available for sediment storage

were used to gain a more in-depth understanding of the transport and fate of trace metal contaminants in the Rio Tupiza basin than could have been obtained by focusing solely on geochemical processes. The scientific basis for the geomorphological–geochemical approach is that trace metal contaminants are predominantly transported in the particulate form (Gibbs 1977), and therefore their spatial distribution within the river system can be related to the geomorphology and sedimentology of the alluvial deposits (Miller 1997; Hudson-Edwards et al. 2003). Thus, geochemical, geomorphic, and sedimentologic data were collected. Specific components of the utilized approach include (1) a geomorphic/sedimentologic analysis of the depositional features and processes downstream of the Abaróa Mine, (2) the documentation of trace metal concentrations and Pb isotopic abundances within modern and historic alluvial deposits, and (3) an assessment of the primary controls on both depositional patterns and metal concentrations.

The selection of sampling locations within the channel of the investigated rivers requires a brief description of the channel bed morphology. Some reaches (e.g., along the Rio Abaróa and the upper reaches of the Rio Chilco) were characterized by a low-relief channel bed which could not be easily differentiated into separate macroscale, depositional units. Further, downstream (such as along the Rio Tupiza and Rio San Juan del Oro), the channel bed could be differentiated into high- and low-channel deposits (using the nomenclature of Hudson-Edwards et al. 2001). High-channel deposits are inundated during floods that occur in the wet season; in contrast, the low-channel deposits are more frequently inundated, being affected by even minor runoff events. Hudson-Edwards et al. (2001) demonstrated that within

other parts of the Rio Pilcomayo basin, trace metal concentrations could differ between the two deposit types. In this investigation both types of deposits were sampled where they occurred. Samples were collected from multiple locations (~10) oriented perpendicular to flow and composited to form a single sample for that site.

Samples of agricultural soils were also collected from the surface (upper 5 cm) of floodplains positioned along the Rio Tupiza and Rio San Juan del Oro. In each case, multiple subsamples were taken along a transect oriented parallel to the river and composited. The process was generally repeated for different distances from the channel banks to assess changes in elemental concentrations with distance from the river. In addition, cores up to 1.2 m in depth were obtained using a soil probe and sub-sampled at selected intervals ranging from 10 to 15 cm. To determine local background concentrations of Pb, Zn, and Sb, sediment samples from alluvial fans located at the mouth of drainages, and which were thought to be devoid of anthropogenic contaminants, were also collected. Fan materials exhibiting elevated concentrations and which appeared as outliers on cumulative frequency plots were removed from the background data set. Finally, tailings materials were obtained upstream of current and historic tailings dams at both the Abaróa and Chilcobija Mines to characterize the trace metal content of waste materials at the mine sites.

All of the sediment samples were placed in polypropylene sampling containers and packaged in plastic bags before they were shipped to the Nevada Bureau of Mines and Geology for analysis. The samples were analyzed for Pb, Zn, and Sb as well as for ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb . Multielemental analyses involved the digestion of 200 mg of dried and homogenized sediment, <2 mm in size, in 125 ml polypropylene screw-top bottles containing 4 ml of aqua regia. These were sealed and held in a 100°C oven for 60 min. The leaches were then transferred to 200 ml volumetric flasks and brought up to volume with deionized water. Quantification of analytes was performed with a Micromass Platform ICP-HEX-MS. The Platform was calibrated with USGS standard reference materials GXR-1, GXR-2, and GXR-5 and NIST standard reference materials 2709 and 2711. A comparison of the measured Pb, Zn, and Sb concentrations with the certified concentrations for the five standards yielded an accuracy of $\pm 3\text{--}5\%$ of the amount present. Pb isotopic ratios were corrected to NIST 981, a common Pb isotope standard. Since the isotopic data are used in a comparative manner, precision is of most importance. Precision determined by comparing data from individual digestions was typically 0.2–0.3 % relative deviation (one sigma). Instrumental error was better.

In addition to the geochemical analyses, selected samples were analyzed to determine the percentage of particles <63 μm in size within the samples. Grain size distribution was determined using wet sieving techniques.

Results and discussion

The Abaróa tailings dam spill

Mill tailings at the Abaróa Mine are pumped into a small tributary where they have accumulated to considerable depth (>20 m) (Fig. 2). The quantity of materials eroded from the accumulated tailings was determined by surveying the dimensions of gullies and other eroded areas created during the February 2003 runoff event. The topographic data indicated that approximately 5,500 m^3 of contaminated sediments were eroded from the site. The estimate is likely to be slightly lower than the amount of tailings that were actually removed from the site as some gullies were too small to be measured and others were filled during the construction of a new dam across the mouth of the tributary following the event. Nonetheless, the tailings spill was relatively small, particularly in comparison to those listed in Table 1.

Somewhat surprisingly, the concentration of Pb, Zn, and Sb in the channel bed sediments collected between the Abaróa Mine and the Rio Chilco is higher than those in tailings from the disposal impoundment (Table 2). These differences in concentration can be attributed in part to an increase in the quantity of chemically reactive fine-grained sediment within the channel bed materials (Table 2). The fine-grained sediments accumulated, presumably during the waning stages of the event, as thin silt and clay layers draped within shallow depressions and cracks in the bedrock exposed in the channel floor. It is also possible, however, that changes in water chemistry downstream of the mine led to the sorption, co-precipitation, and/or complexing of metals on particle surfaces, increasing concentrations in the channel bed sediments within the Rio Abaróa.

The concentrations of Pb, Zn, and Sb within the channel bed materials between the Abaróa Mine and the Rio Machocuya are shown in Fig. 4. In many investigations, spatial trends in trace metal concentrations are interpreted by analyzing only the fine-grained sediments (e.g., <63 μm size fraction). The intent of analyzing the fine sediment is to remove the effects caused by varying grain size distributions on elemental concentrations (Ackermann 1980; Horowitz and Elrick 1988). In this case, however, the channel bed materials along Rio Chilco and Rio Tupiza were generally comprised of less

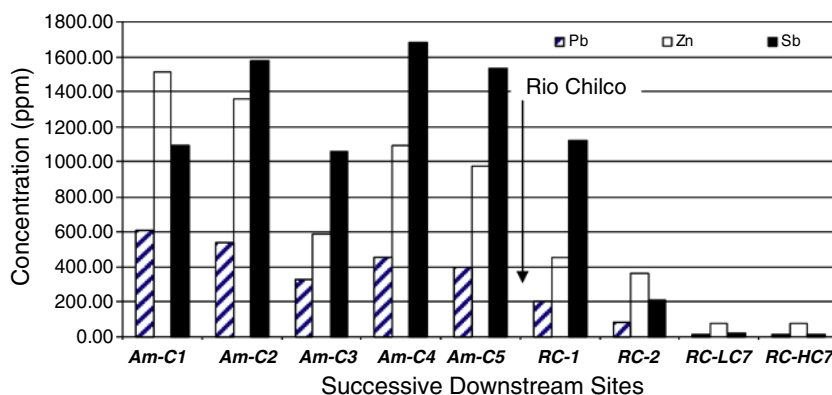
Table 2 Statistical summary of geochemical data for selected materials and river reaches; reach locations are shown on Fig. 1

Media/Reach	Pb (μg/g)	Zn (μg/g)	Sb (μg/g)	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁸ Pb	% < 63 μm
Background Materials (n = 4)						
Average	18.17	93.08	3.06	1.1851	0.4840	8
Maximum	24.61	139.3	3.77	1.1915	0.4885	10
Minimum	11.64	71.90	2.37	1.1777	0.4768	4
SD	5.51	31.32	0.57	0.0064	0.0053	2
Abaróa Tailings (n = 3)						
Average	85.04	216.7	1123	1.1552	0.4709	48
Maximum	114.5	279.3	1115	1.1625	0.4721	95
Minimum	63.41	131.5	1093	1.1507	0.4686	17
SD	26.26	76.46	28.69	0.0064	0.0019	41
Chilcobija Tailings (n = 2)						
Average	163.1	90.31	1846	1.1575	0.4649	85
Maximum	179.8	107.6	2503	1.1587	0.4652	95
Minimum	146.4	72.98	1189	1.1563	0.4646	74
SD	23.63	24.51	929.4	0.0017	0.0004	15
Rio Tatasi (mouth of basin) (n = 6)						
Average	77.06	382.4	16.60	1.1939	0.4794	13
Maximum	136.0	689.3	29.71	1.2156	0.4863	20
Minimum	40.24	188.9	7.45	1.1817	0.4726	6
SD	33.20	170.2	8.67	0.0129	0.0049	5
Abaróa Mine to Rio Chilco (n = 5)						
Average	466.1	1105	1388	1.1666	0.4731	38
Maximum	610.9	1515	1681	1.1718	0.4774	53
Minimum	330.5	587.4	1060	1.1619	0.4713	26
SD	111.1	360.2	290.7	0.0036	0.0025	13
Rio Abaróa to Rio Machocuya (n = 4)						
Average	80.03	245.4	341.9	1.1660	0.4739	14
Maximum	206.2	458.5	1118	1.1671	0.4828	43
Minimum	12.13	76.20	17.46	1.1638	0.4674	1
SD	90.80	197.2	525.7	0.0015	0.0065	19
Rio Machocuya to Rio Tatasi (n = 3)						
Average	18.23	91.47	27.42	1.1745	0.4725	7
Maximum	23.88	106.7	39.75	1.1856	0.4789	18
Minimum	11.69	82.08	16.03	1.1600	0.4671	1
SD	6.14	13.28	11.89	0.0131	0.0060	6
Rio Tupiza to Rio San Juan del Oro (n = 11)						
Average	41.62	242.3	16.08	1.1906	0.4784	13
Maximum	69.17	657.2	31.83	1.2141	0.4897	20
Minimum	11.69	51.11	4.06	1.1625	0.4637	7
SD	19.91	166.7	7.75	0.0138	0.0067	4
Rio San Juan del Oro (n = 4)						
Average	77	49.56	2.77	1.1829	0.4787	17
Maximum	17.45	70.88	7.24	1.1960	0.4872	42
Minimum	7.45	34.39	0.88	1.1660	0.4689	6
SD	4.58	15.32	3.03	0.0137	0.0079	11
Floodplain Soils (n = 14)						
Average	94.09	310.7	37.40	1.1880	0.4765	43
Maximum	241.2	643.4	111.3	1.2131	0.4908	68
Minimum	27.21	103.9	7.15	1.1665	0.4673	17
SD	74.07	215.3	35.47	0.0155	0.0073	14

than 15% by weight of silt and clay-sized particles. In addition, the size of the sulfide grains shown in Fig. 5 demonstrates that a significant dispersal pathway is through the physical movement of sand-sized, metal bearing particles (e.g., sphalerite and galena). Thus, the sand-sized sediment fraction can not be ignored as a media for the downstream transport of Zn, Pb, and Sb from the mine site. Similar conclusions have been reached by other investigators for mine impacted rivers (Moore et al. 1989; Horowitz 1991). The concentrations reported here, then, are for < 2 mm size fraction.

Figure 4 shows that the concentration of Pb and Zn decline semi-systematically downstream of the Abaróa Mine until reaching the confluence between the Rio Chilco and the Rio Machocuya. Such downstream decreases in contaminant concentrations are common below point sources of pollution and have generally be attributed to four factors. They include (1) hydraulic sorting of channel sediments on the basis of particle density, size and shape, (2) the dilution of contaminants by “clean” sediments, (3) losses through deposition and storage in alluvial deposits located along the river, and

Fig. 4 Downstream changes in Pb, Zn, and Sb concentration within channel bed sediments between the Abaró Mine and the mouth of the Rio Machocuya. Elemental concentrations decrease rapidly upon reaching the Rio Chilco as a result of both dilution and sediment storage. See Fig. 1 for sample site locations



(4) biological uptake or geochemical processes leading to chemical remobilization (Lewin and Macklin 1987; Macklin 1988; Wolfenden and Lewin 1978; Macklin 1996; Taylor and Kesterton 2002). Within the Rio Abaró, storage of the contaminated sediments was negligible as alluvial deposits are practically non-existent within the incised bedrock channel (Fig. 3). In addition, there are few tributaries to the Rio Abaró and, thus, dilution is not a significant process. Hydraulic sorting, however, appears to have led to both a change in the size and composition of the sediments along the Rio Abaró. With respect to the latter, visual estimates of the sulfide mineral content of the tailings and channel bed sediments suggest that the percentage of sulfide minerals decreases in the alluvial materials away from the mine site (Fig. 5b, c). Presumably, the hydraulically heavier nature of the sulfides allowed them to remain closer to the mine than hydraulically lighter sediments because the sulfide particles settled more quickly, were transported less rapidly, or were entrained less frequently than hydraulically lighter grains of similar size, such as quartz (Slingerland and Smith 1986). Grain size of the sediment also changes downstream; the percentage of sediment < 63 μm in size changes from 53 to 25% between the Abaró Mine and the Rio Chilco. Although some of the sulfide minerals are sand sized, the majority fall in the silt-size range as a result of the milling operations. Thus, the downstream increase in grain size can be attributed to the preferential deposition of hydraulically heavier fine-grained particles (relative to fine sand-sized quartz grains) along the upstream reaches. An increase in the concentration of sulfide minerals by hydraulic sorting does not appear to have contributed to the increased metal concentrations in the channel bed sediment in comparison to the tailings. As mentioned earlier, qualitative observations showed that the tailings were enriched in comparison to the channel sediments in sulfide minerals (Fig. 5).

Upon entering the Rio Chilco, sediment-associated Pb and Zn concentrations are immediately reduced by at least 50%; Sb concentration also declines. The abrupt

change in concentration is presumably related to dilution as sediments from the Rio Abaró are mixed with substantially larger volumes (and larger particles) of sediment within the Rio Chilco; the width, for example, of the Rio Chilco exceeds that of the Rio Abaró by an order of magnitude (a change from approximately 3.5 to 50 m). In addition, the quasi-braided nature of the Rio Chilco is indicative of high bedload transport rates that greatly exceed that of the bedrock-lined channel of the Rio Abaró.

Further downstream of the Rio Abaró, Pb, Zn, and Sb concentrations rapidly decline to near background concentrations (determined from the analysis of alluvial fan deposits) before reaching the Rio Machocuya. Even if all of the anthropogenically derived trace metals measured within the channel were related to the spill (which is unlikely as described below), the impacts of the event on sediment quality within the channel bed appears to have been limited to 25 km from the mine site.

An argument can be made that once the fine-grained tailings were entrained, they were transported great distances downstream without being deposited within the channel bed. However, effluent released during the flood event is also likely to have been significantly diluted upon entering the Rio Chilco, thereby limiting its spatial impacts. Silt-lines on the bedrock walls of the Rio Abaró allowed the maximum flood stage, and thus the cross sectional area of the flow, to be accurately determined (Fig. 3). These data were combined with estimates of channel roughness and measured slope values at three locations to determine the maximum discharge associated with the tailings spill using the slope-area method of peak discharge estimation (Dalrymple and Benson 1967; O'Connor and Webb 1988). It was estimated from paleoflood data that peak flow within the channel was on the order of 13.5 cm. The flow stage within the Rio Chilco during the event could not be determined. However, examination of the floodplain located immediately downstream of the tributary's mouth in November 2003, revealed no evidence of recent

overbank flooding (e.g., flood debris), nor was there evidence of any recent overbank deposition. These observations suggest that deposition of contaminated debris from the Abaróa tailings spill were confined to the channel of the Rio Chilco-Rio Tupiza drainage system, and that the maximum flows within the channel were less than, but presumably close to, the bankfull discharge. The bankfull discharge was conservatively determined, again using the slope-area method, to be approximately 75 cm, almost six times higher than the discharge from the tributary. Thus, the flood flow emanating from the Rio Abaróa was presumably small in comparison to the flow within the Rio Chilco at the mouth of the tributary, even if flow within the Rio Chilco was below bankfull. Clearly, the differences in the flow magnitudes would have led to significant dilution of the constituents released from the impoundment.

Confinement of the flood flows to the axial channel, combined with dilution and the rapid downstream decline in Pb, Zn, and Sb concentrations in the channel bed sediments, all suggest that the spatial impacts of the 2003 event were limited. The potential environmental consequences of the event were also reduced by: (1) a low population density and a lack of agriculture along this reach, (2) ephemeral stream conditions which limit the diversity of the aquatic biota, and (3) metal transport in association with metal sulfides which restrict their bioavailability.

Other sources of contamination

Geographical patterns in elemental concentration

Geographical patterns in trace metal concentrations are commonly used to identify contaminant sources. In this case, “hotspots” are interpreted to represent points of trace metal influx to the axial drainage system. Figure 6 demonstrates that concentrations of Pb, Zn, or Sb increase immediately downstream of the mouth of all three tributaries possessing significant mining operations including the Rio Abaróa, the Rio Machocuya, and the Rio Tatasi. In the case of the Rio Abaróa, the largest increase in concentration is associated with Sb. In contrast, Zn and, to a lesser degree, Pb concentrations increase downstream of the Rio Tatasi, while changes in Sb are negligible. Increased concentrations downstream of the Rio Machocuya are most pronounced for Zn, although minor increases also occur for Pb and Sb.

The minimal input of Pb, Zn, and Sb from the Chilcobija Mine (via the Rio Machocuya) is surprising given the size of the operation and the known, historical releases of contaminated tailings to the headwaters of the Rio Machocuya. The contrasting impact on sediment quality between the Chilcobija and Abaróa Mines

is presumably related to the increased distance of the former from the Rio Chilco which allows for a greater opportunity for elemental dilution and storage to occur. Moreover, it once again demonstrates that Pb, Zn, and Sb concentrations in channel bed sediments decrease rapidly downstream; in this instance, background values of Pb and Sb are approached within approximately 15 km of the mine site.

Pb isotopic fingerprinting of tailings materials

The use of Pb isotopes to determine sources of trace metals in riverine environments is still in its infancy. Nonetheless, results from the few studies that have been conducted indicate that the technique holds considerable promise (see, for example, Miller et al. 2002). Here, three isotopes of Pb were used to geochemically fingerprint mining wastes from the Abaróa, Chilcobija and Tatasi-Portugalete mines. They include the radiogenic isotopes of ^{206}Pb , ^{207}Pb , and ^{208}Pb which represent the daughter products of ^{238}U , ^{235}U , and ^{232}Th , respectively. Unlike many of the lighter isotopes, fractionation of the Pb signature is thought to be negligible during industrial processing (milling) or biological uptake (Ault et al. 1970; Graney et al. 1995) allowing them to serve as excellent tracers of anthropogenic and natural Pb in the near surface environment.

Figure 7 plots the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios for a wide variety of sample types from the Rio Chilco-Rio Tupiza drainage system. Although there is considerable scatter in the data, two trends are apparent. The end members of the upper trend are formed by tailings samples from the Abaróa Mine and sediments collected from uncontaminated alluvial fan deposits. The fan deposits are assumed to possess the isotopic signatures of the naturally occurring Pb within the region's alluvial sediments (i.e., background). The end members of the lower trend are represented by tailings samples from the Chilcobija Mine and samples from the mouth of the Rio Tatasi. The latter materials are assumed to represent the general signature of Pb from the Tatasi-Portugalete mines (although the range of isotopic ratios has undoubtedly been modified during the downstream transport of the tailings materials). The use of the Pb isotopic signature of sediment from the mouth of the Rio Tatasi as a general descriptor of Pb from the Tatasi-Portugalete mining district is supported by Pb concentrations that exceed local background values by a factor of at least 3 (Table 2). Figure 7 demonstrates that the Pb isotopic signature of the tailings materials from the Abaróa and Chilcobija mines differ, in spite of the fact that both are associated with the Bolivian Antimony Belt. This is not altogether surprising in that the nature and age of the ore deposits vary between the two mine sites.

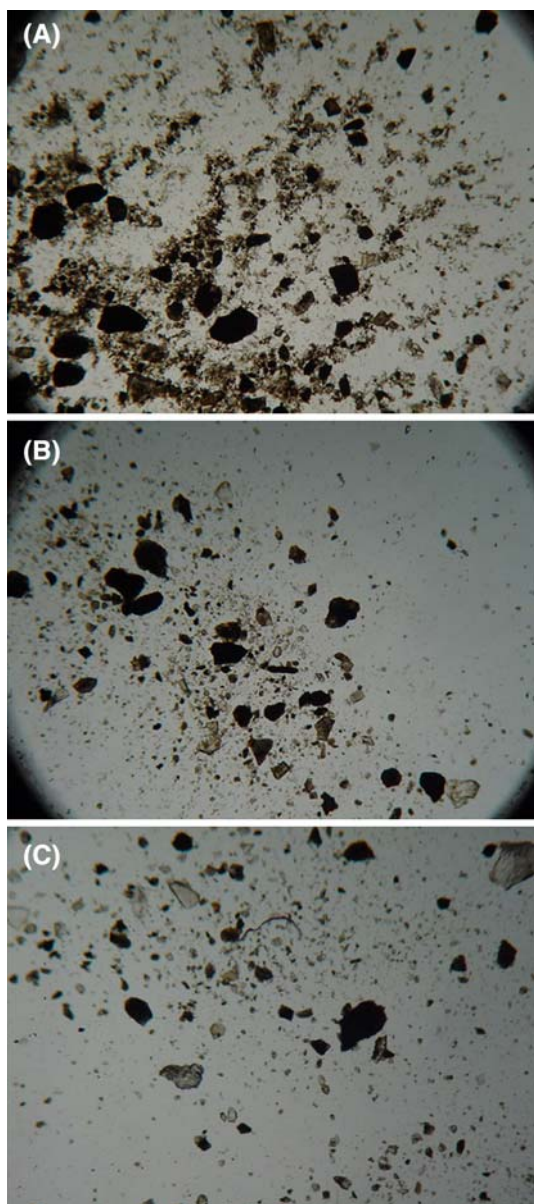


Fig. 5 Photomicrographs of **a** Abaróá tailings, **b** channel bed sediments immediately below the tailings impoundment, and **c** channel bed materials near the mouth of the Rio Abaróá. Opaque minerals (*black* in photomicrographs) represent sulfide minerals. Visual estimates suggest only limited differences in sulfide content between the tailings and upstream channel bed sediments, but a decrease in sulfide content further downstream

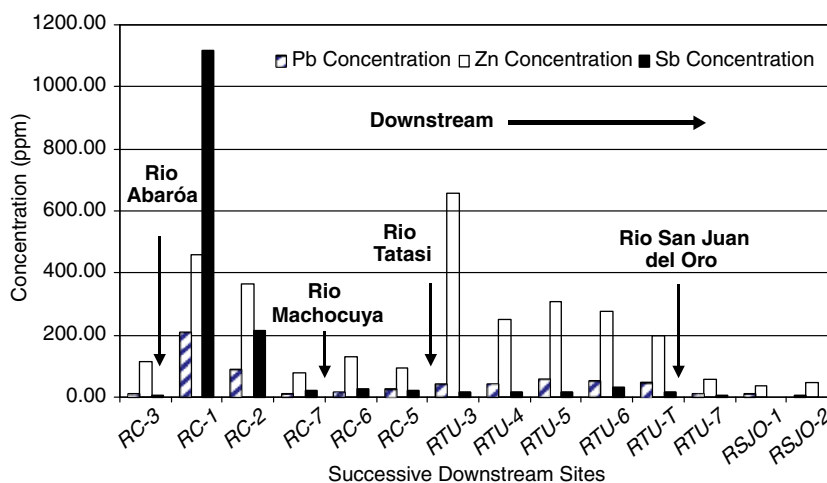
Linear trends within three component systems (in this case consisting of ^{206}Pb , ^{207}Pb , and ^{208}Pb) are interpreted as evidence that the samples are composed of a mixture of Pb from two distinct sources that possess isotopic compositions that plot at the opposing ends of the line (i.e., the end members). Thus, the two trends on Fig. 7 provide important insights into the predominant source of Pb to the axial drainage system.

For example, samples collected between the Abaróá Mine and the confluence of the Rio Chilco with the Rio Machocuya generally coincide with the upper trend, suggesting that Pb is predominantly derived from the Abaróá Mine and the local alluvial deposits (as expected). Variation in isotopic ratios around the trend presumably indicates that Pb is also derived from other sources such as the underlying bedrock. Miller et al. (in preparation), for instance, have shown that the isotopic signature of the Mesozoic strata along the Rio Pilcomayo (located north of the study area) is significantly different than that of the Ordovician rocks, and that the intermixing of sediments from the two lithologies can produce spatial variations in the isotopic composition of uncontaminated alluvial deposits. A sample collected immediately upstream of the Rio Machocuya clearly possesses a relatively low $^{206}\text{Pb}/^{208}\text{Pb}$ ratio, and therefore falls along the lower trend. It is possible that it was contaminated by particles from the Chilcobija Mine by tributary backwater effects during flooding, or by the deposition of locally derived, wind blown sediments.

Sediments collected at the mouth of the Rio Machocuya possess $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios similar to tailings from the Chilcobija Mine (Fig. 7). However, samples collected downstream of the Rio Machocuya, but upstream of the Rio Tatasi (Fig. 1) plot along both the upper and lower trends. In the former case, the data suggest that Pb in some channel sediments is primarily derived from the Rio Abaróá and the local geological substrates. The sample that plots along the lower trend exhibits a signature similar to that observed in channel bed sediments from the Rio Tatasi. The implication is that most of the Pb within the sample is from the Tatasi-Portulagete mines, rather than the Chilcobija. Given that the sample was collected immediately upstream of the Rio Tatasi, it is once again possible that local backwater effects or wind may have led to the local upstream deposition of material from the Rio Tatasi along the Rio Chilco. Moreover, it implies that backwater effects associated with differences in the timing of peak flow conditions between the major tributaries exceeds 100 m. Although possible based on depth-gradient relationships, it was more than anticipated in these high gradient rivers.

Downstream of the Rio Tatasi, all of the samples but one plotted along the lower trend. Moreover, the majority of the samples exhibit $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios similar to that observed in channel bed sediments from the Rio Tatasi. These data indicate that most of the Pb observed within channel bed materials between the Rio Tatasi and the Rio San Juan del Oro is derived from the Tatasi-Portulagete mines. The influx of metals from the Tatasi-Portulagete mines was expected as several large waste disposal piles are located

Fig. 6 Concentrations of Pb, Zn, and Sb along the Rio Chilco, Rio Tupiza, and Rio San Juan del Oro. Increases in concentration occur immediately downstream of the Rio Abaró, the Rio Tatasi, and to a much lesser degree, the Rio Machocuya. See Fig. 1 for location of sample sites



within the mining district in the headwaters of the Rio Tatasi. Moreover, the erosion and influx of these tailings, and their potential impacts on the riverine environment, have been recognized for some time. In fact, COMIBOL (the former state company which owns the mines) is currently attempting to remediate the impacts associated with the tailings piles. Nonetheless, the degree to which alluvial sediments along the Rio Tatasi are contaminated has yet to be quantified. The elevated concentrations of Pb, Zn, and Sb observed here in channel bed sediments near the mouth of the Rio Tatasi (Table 2), clearly demonstrates that metal enriched sediments have been transported to the Rio Tupiza located more than 25 km downstream of the mines. It is also worth noting that in contrast to the rapid downstream declines in Pb, Zn, and Sb concentration observed along the Rio Chilco, the concentrations along the Rio Tupiza downstream of RTU-4 remain nearly constant at values well above background (Figs. 1,6). As suggested by the isotopic data, the lack of a significant downstream decrease in concentration along this reach of the Rio Tupiza could be attributed to the input of substantial quantities of tailings from the Tatasi-Portulagete mines which override the effects of dilution caused by the input of sediment from the Rio Chilco and other tributaries to the Rio Tupiza. Other factors, however, could also play a role, including (1) the input of metal enriched sediment from contaminated floodplain deposits, and/or (2) a change in geomorphic processes affecting storage above and below the mouth of the Rio Tatasi.

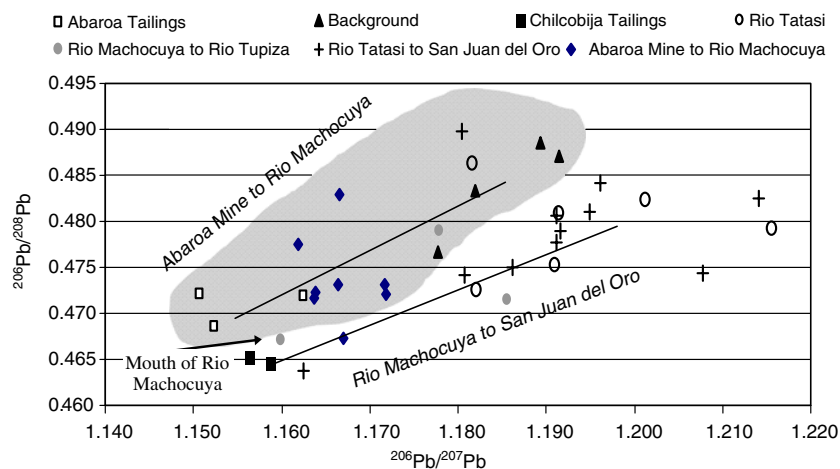
Channel storage

Previous studies have shown that spatial trends in trace metal concentrations are closely linked to the deposition and storage of contaminated particles along a river

system (Owens et al. 2001; Walling et al. 2003). In most cases, the storage of sediment within the channel, as opposed to the floodplain, is minimal. For example, the storage of fine-grained sediments to which trace metals are most likely to be attached was found to be less than about 10% of total suspended sediment load exported from the rivers Ouse, Wharfe, and Tweed in the UK (Owens et al. 1999; Walling et al. 1998). Similar values were found for metals along the Rivers Aire and Swale, where the storage of Pb and Zn was less than about 3% of the total annual sediment load (Walling et al. 2003). These calculations prompted Walling et al. (2003) to suggest that channel storage is of limited importance in regulating the downstream transport of contaminants through many river systems. In marked contrast to channel storage, floodplains are perceived as significant storage sites. Previous studies, for example, have shown that 10–50% or more of the total annual load may be either temporarily or semi-permanently stored in floodplain deposits (Macklin 1996; Marron 1992; Walling et al. 2003). Moreover, the residence time of the contaminants also differs substantially between channel and floodplain deposits. Although poorly constrained, residence times for fine-grained channel sediments is generally less than 5 years as a result for frequent sediment reworking during flood events (Walling et al. 2003), whereas contaminants may be stored for decades, centuries, or even millennia in floodplain environments (Macklin 1996; Miller 1997; Coulthard and Macklin 2003).

It should be recognized, however, that the above data are for relatively stable rivers which are not undergoing significant aggradation. Changes in river form and process, such as associated with aggradation, can significantly affect both floodplain and channel storage processes (Lewin and Macklin 1987; Macklin 1996; Miller 1997). Field observations made in November 2003, indicate that the Rio Chilco and Rio Tupiza are

Fig. 7 Three-component diagram showing differences in Pb isotopic abundances of selected sediment types within the Rio Chilco-Rio Tupiza drainage system. Trend lines are drawn between sample means for end member media types



undergoing significant changes in channel form which may influence both the longitudinal patterns in Pb, Zn, and Sb concentrations and their storage along the drainage system.

Downstream of the Rio Abaróá, channel bed sediments in the Rio Chilco span the width of the valley and significant floodplain deposits are absent. Those that exist generally occur in protected areas behind prograding tributary fan deposits or in bedrock alcoves. Accumulations of sediment along the base of the hillslopes are rare and where they occur, they are typically associated with mass wasting deposits. Perhaps the most significant accumulations of sediment along the Rio Chilco are associated with large alluvial fans associated with relatively steep tributaries. The distal fan deposits are typically truncated, indicating that at least some of the fan deposits have been redistributed within the channel. The upper reach of the Rio Tupiza is characterized by a similar morphology to the Rio Chilco. However, a few kilometers downstream of the Rio Tupiza's confluence with the Rio Chilco, floodplain deposits begin to occur along the channel. The extent and continuity of the floodplain increases downstream. Floodplains by RTU-FF1 are on the order of 10's to 100's of meters in width and are used for agriculture (Fig. 1).

The observed distribution of landforms is thought to be primarily related to adjustments in channel gradient caused by a significant episode of aggradation that is more pronounced along the Rio Chilco and the upstream most reaches of the Rio Tupiza. Aggradation has presumably led to the reworking and burial of older alluvial floodplain deposits within the upstream reaches of the drainage network. This interpretation is supported by the more frequent inundation and damage to a railroad that lies adjacent to the Rio Tupiza. In fact, a local resident stated that in the past, large trucks which utilized the dry, axial stream bed as a

road during the dry season could access many upstream tributaries by driving under the railroad bridges. Now, however, upstream tributary channels are less than 1–2 m below the bridge, or have aggraded to such an extent that the channel beneath the bridge must be maintained by local dredging (Fig. 8). Detailed engineering documents to quantify the degree of aggradation that has occurred have yet to be found. Nonetheless, these consistent anecdotal reports by several local residences suggest that at least 2–3 m of aggradation has occurred along the Rio Chilco and upper Rio Tupiza during the past decade.

The primary cause of aggradation is currently under investigation. However, it is clear that the sediment is derived in large part from the gullying and erosion of upland valleys and the influx of large amounts of sediment by mass wasting processes. Following a mass wasting event, sediment which reaches tributary channels is transported to the axial drainage system where it may be temporarily stored in the large, tributary fans.

Channel bed aggradation has three important influences on the rate and dispersal of Pb, Zn, and Sb from the mine sites. First, larger quantities of trace elements are likely to be stored in the channel bed during aggradation than would otherwise be the case. For example, if it is assumed that 2 m of aggradation occurred along the Rio Chilco between the Rio Abaróá and the Rio Machocuya, approximately 237,700 kg of Pb, 728,800 kg of Zn, and 1,015,400 kg of Sb could be stored in the channel bed if concentrations were equal to the average concentrations currently observed along the reach. Put differently, these rough calculations suggest that between 1×10^6 and 3×10^6 metric tons of tailings could be stored in the channel bed (depending on the metal used to make the calculation) if it is assumed that the tailings exhibited a uniform concentration equivalent to the averages determined herein. This is on par with



Fig. 8 Railroad bridge crossing a tributary to the Rio Tupiza immediately downstream of the Rio Tatasi. A local resident stated that in the recent past, large trucks could pass beneath the bridge. Currently, maximum depth below the bridge is approximately 1.5 m

the total quantity of mill tailings produced at the Abaróa Mine during its history of operation. The second affect of channel aggradation is that the excessive amount of tributary sediment that enters the channel will enhance the magnitude of dilution that can occur, thereby reducing trace element concentrations associated with contaminated particles. Third, channel bed aggradation has presumably led to the reworking and burial of upstream floodplain deposits, limiting their effectiveness as both a source and sink for Pb, Zn, and Sb.

Floodplain contamination and storage

The potential for contaminated particles to be remobilized from floodplain deposits raises the possibility that where they exist, they could serve as an important source of Pb, Zn, and Sb to the modern river system (Macklin 1996; Miller et al. 1998). Moreover, downstream changes in their extent and distribution could potentially lead to differences in the geographical patterns of elemental concentration observed along the drainage system. To determine the degree to which Pb, Zn, and Sb are currently stored within the floodplain of the Rio Tupiza, and the likelihood that the floodplain deposits serve as a current source of contaminants, spatial variations in metal concentrations were determined at five sites along the channel (Fig. 1). At each site samples were collected at 10, 35, and 50 m from the channel margins and from cores that extracted sediments to depth of up to 1.2 m.

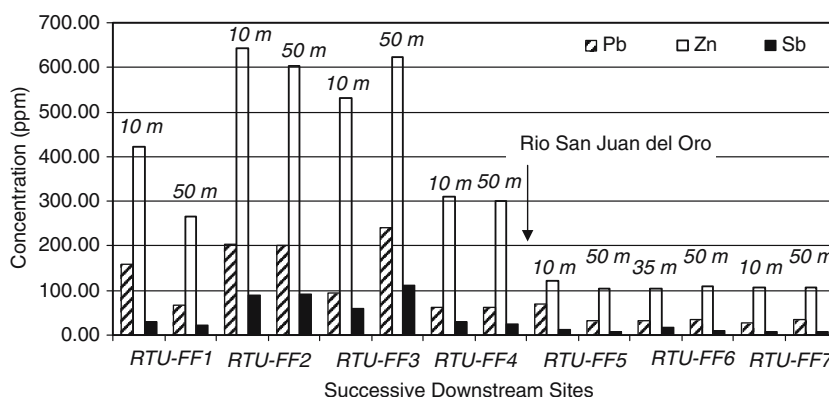
With the exception of Sb, trace metal concentrations were higher in the floodplain deposits than in the channel bed materials (Table 2). For example, the mean concentration for Pb and Zn within the floodplain deposits is higher than for any channel bed sample if samples from the Rio Abaróa are excluded (based on *t*-test; $P < 0.05$). Differences in Sb concentration between the channel and the floodplain are not statistically significant.

It is probable that the elevated levels of Pb and Zn within the floodplains are a consequence of the preferential deposition of fine-grained sediments within the floodplains during overbank flooding. For example, the silt and clay grain size fraction (composed of particles $< 63 \mu\text{m}$ in size) ranges from 41 to 62% in floodplain sediments. In contrast, the low- and high-channel deposits adjacent to the sampled fields contain between 12 and 16% silt-clay.

The concentrations of Pb, Zn, and Sb in surface sediments of the floodplains are shown in Fig. 9. Spatial trends in elemental concentration as a function of distance from the channel vary between sites and tend to be rather minor ($< 10\%$). Similarly, systematic downstream trends in concentration between sampling sites RTU-FF1 and RTU-FF4 (Fig. 1) are lacking (Fig. 9). However, the elevated concentrations of Pb, Zn, and Sb within these floodplain deposits suggest that they could represent a current source of trace metals to the channel. At sites downstream of RTU-FF4, concentrations of Pb and Sb are lower than the other upstream floodplains and are similar to, or slightly above, the range of local background values (Fig. 9, Table 2). The observed decrease in concentration between site RTU-FF4 and RTU-FF5 is presumably related to dilution associated with the influx of sediment from the Rio San Juan del Oro, one of the largest rivers in the area.

Pb, Zn, and Sb concentrations vary significantly as a function of depth in the upstream sampling sites (i.e., RTU-FF1–RTU-FF4). Nonetheless, concentrations are generally well above background values. As was the case for the surface sediments, concentrations are elevated above those found in the adjacent channel bed materials. In addition, while the exact contribution from the mines cannot be determined, it appears likely that relatively high $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, when coupled with high Pb concentrations, indicate that Pb is primarily derived from the mines within the Rio Tatasi. In contrast, relatively low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios imply an influx of sediment from the Sb mines within the Rio Chilco basin. Figure 10 demonstrates that sediment-borne trace metals from the Abaróa and/or Chilcobija mines were being transported further downstream in the past than they currently are. The cause(s) for the recent reduction in transport from the mines cannot be determined with the existing data, but most likely depends on both the history of mining activity and variations in contaminated

Fig. 9 Pb, Zn, and Sb concentrations at the surface (upper 5 cm) of floodplain soils located along the Rio Tupiza. See Fig. 1 for sampling locations



sediment transport rates and dispersal processes. The onset of aggradation, which is thought to have begun within approximately the past decade, could dramatically increase the storage of sediment-associated trace metals within the channel bed, thereby decreasing downstream transport.

Potential environmental impacts to agricultural activities

Floodplains located along the Rio Tupiza are used extensively for agricultural purposes. The primary crops include a host of vegetables (e.g., corn and potatoes) which are consumed locally and sold in small communities within the region. Metal concentrations measured within the soils developed on floodplains at sites RTU-FF2 and RTU-FF3 possess values that exceed international guidelines for agricultural use. For example, Pb in the upper layers of the floodplain at RTU-FF2 exceeds the Canadian guideline of 200 ppm, while Zn is above Canadian, German, and Dutch guideline values (Table 3). Sb is three times higher than the Canadian guideline value of 20 ppm. Similarly, floodplain deposits at RTU-FF3 exhibited Pb concentrations of 326 ppm at the ground surface, which exceed the Canadian guideline. Zn concentrations again exceed all three guideline values. In contrast, concentrations of Pb, Zn, and Sb in the farthest downstream floodplain samples (RTU-FF5, 6, 7; Fig. 1) are below all three guidelines (Table 3).

The locally elevated levels of Pb, Zn, and Sb in agricultural soils indicate that the potential exists for the degradation of human health through the consumption of contaminated produce. Metal uptake by plants grown in polluted soils is related to numerous factors in addition to metal concentrations within the soil, including its speciation, soil pH, temperature, cation exchange capacity of the soil, organic matter content, plant species, and the means through which metals are distributed

to plant parts during growth (Haghiri 1973, 1974; Abdel-Sabour et al. 1988; Ward and Savage 1994; Voutsas et al. 1996; Albering et al. 1999). Thus, metal concentrations that exceed guideline values in soils do not necessarily lead to elevated concentrations in agricultural food stocks. For example, Miller et al. (2004) found that concentrations of trace metals in vegetables grown on highly contaminated farm fields along the Rio Pilcomayo contained metal concentrations that were generally below existing guidelines for metal content in commercially-sold vegetables. Thus, the consumption of contaminated produce did not appear to represent a significant exposure pathway in the four communities that were studied (although a possible exception existed for Pb in carrots, lettuce, and beetroots from Sotomayor and Tuero Chico, where 37 and 55% of the samples, respectively exceeded recommended guidelines). Limited accumulation of the examined metals may have been related to their bioavailability in the soils, particularly the occurrence of metals in sulfide minerals. Similar results have been presented for other sites as well. Albering et al. (1999), for example, found that Zn and Cd concentrations in the crops of the River Meuse were within the range of background values in spite of the fact that they were grown on severely polluted floodplain soils. They suggested that the lack of Cd and Zn accumulation in the crops was due to the relatively high pH of the floodplain soil (6.9 ± 0.6) that reduced the availability of the metals for plant uptake. The point to be made, then, is that additional studies are warranted to determine if crops grown on severely contaminated soils possess a local risk to human health, but high concentrations in soils do not necessarily indicate an immediate health risk.

Conclusions

Spatial trends in Pb, Zn, and Sb concentrations, combined with Pb isotopic data, indicate the sediment-

borne trace metals are entering the Rio Chilco-Rio Tupiza drainage system from three tributaries, each of which possess significant mining operations. The tributaries include the Rio Abaró, the Rio Machocuya and the Rio Tatasi. Although production at the Abaró Mine is limited, it appears to be the primary source of Sb to the modern channel bed of the Rio Chilco. Antimony from the Chilcobija Mine is currently limited, in spite of the fact that it was the largest Sb mine in Bolivia and tailings materials remain in the basin. Concentrations of Pb, Zn, and Sb downstream of both mines decrease rapidly as a result of dilution by

uncontaminated sediments and the storage of metal enriched particles (e.g., sulfide minerals) in the channel bed during aggradation.

In contrast to geographical patterns of Pb observed within the modern channel bed, Pb isotopic ratios measured within older floodplain deposits located further downstream (and adjacent to Tupiza) suggest that contaminated sediments from the Abaró and/or Chilcobija mines were distributed over a greater distance in historic times. The recent decrease in metal transport may be related to (1) larger releases of contaminated sediment during periods of peak production

Fig. 10 **a** relationship between total Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for selected sediment types; **b** variations in Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in floodplain deposits as a function of depth

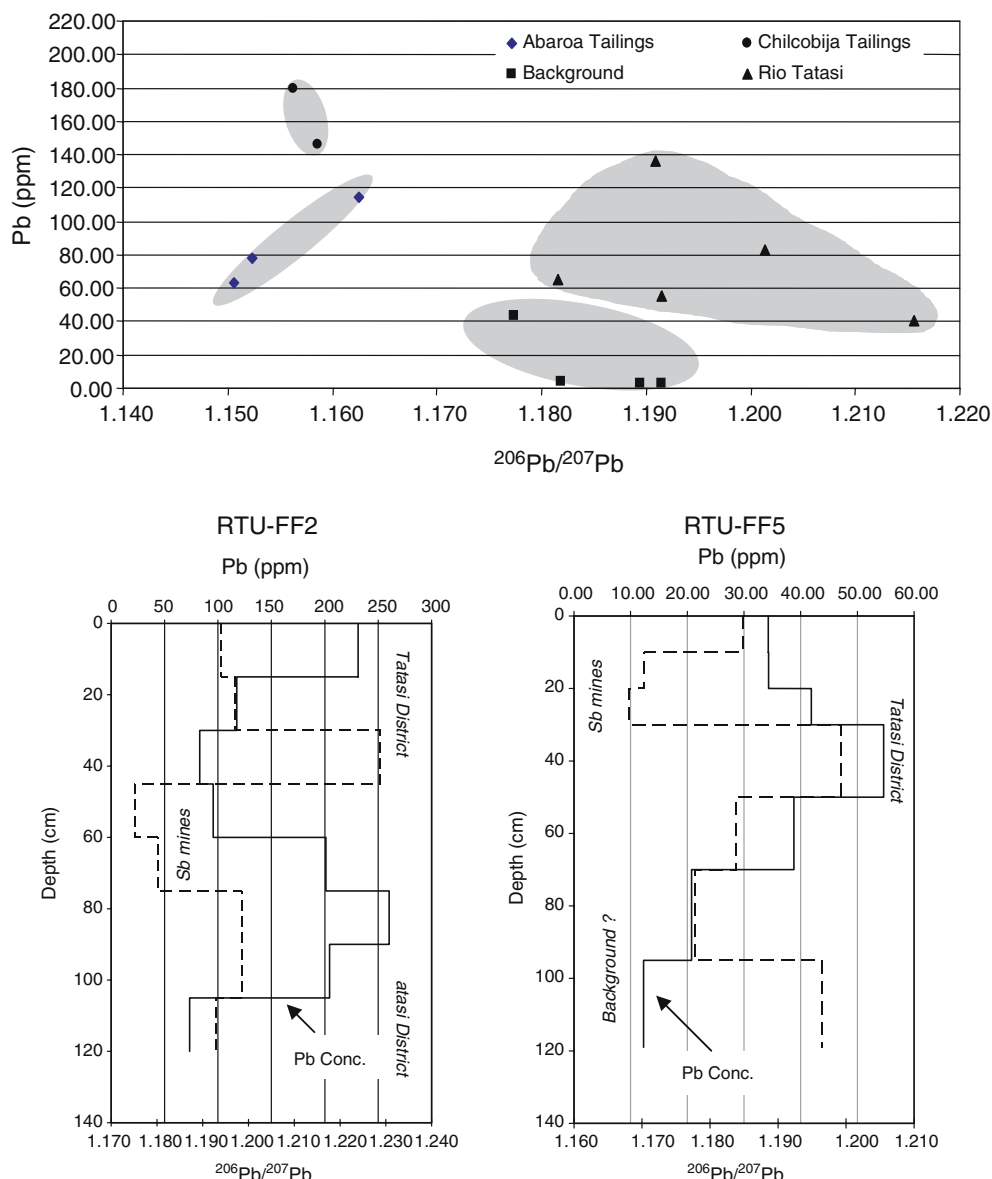


Table 3 Comparison of floodplain soils data with selected guidelines for agricultural use

		Pb	Zn	Sb
Typical conc. (rocks) ^a				
Granite		17	50	0.2
Sandstone		7	16	0.4
Shales		20	95	1
Río Pilcomayo Basin		18	66	
Regional background		(6–34)	(17–132)	
Health guidelines				
Dutch		530	720	–
Action levels ^b				
Canada guidelines		200	400	20
Maximum limits ^c				
Germany		500	300	–
Maximum limits ^c				
RTUFF 1–35	35 m Adjacent to river	158.7	421.9	30.7
RTUFF 1–50	50 m Adjacent to river	65.9	266.6	22.4
RTU-FF 2–10	10 m Adjacent to river	202.8	643.4	88.5
RTU-FF 2–50	50 m adjacent to river	199.8	602.5	92.2
RTU-FF2-C A	0–15 cm	231.2	750.7	94.3
RTU-FF2-C B	15–30 cm	117.6	380.9	46.2
RTU-FF2-C C	30–45 cm	83.0	288.0	30.3
RTU-FF2-C D	45–60 cm	95.5	264.4	19.2
RTU-FF2-C E	60–75 cm	201.1	247.8	20.2
RTU-FF2-C F	75–90 cm	260.2	264.1	23.3
RTU-FF2-C G	90–105 cm	204.5	193.3	17.3
RTU-FF2-C H	105–120 cm	73.5	93.4	7.2
RTU-FF3–10	10 m adjacent to river	93.8	532.4	59.1
RTU-FF3–50	50 m adjacent to river	241.1	623.1	111.3
RTU-FF3-C A	0–15 cm	326.2	785.4	103.0
RTU-FF3-C B	15–30 cm	122.2	365.7	44.0
RTU-FF3-C C	30–45 cm	184.4	466.2	61.4
RTU-FF4-C 10	10 m adjacent to river	61.4	309.3	29.5
RTU-FF4-C 50	50 m adjacent to river	61.1	299.4	25.8
RTU-FF5-C 10	10 m adjacent to river	69.7	120.6	13.4
RTU-FF5-C 50	50 m adjacent to river	33.1	105.1	7.2
RTU-FF5-C A	0–10 cm	34.3	99.1	6.3
RTU-FF5-C B	10–20 cm	34.3	92.3	8.2
RTU-FF5-C C	20–30 cm	41.9	105.3	8.8
RTU-FF5-C D	30–50 cm	54.6	109.3	10.4
RTU-FF5-C E	50–70 cm	38.8	94.2	11.0
RTU-FF5-C F	70–95 cm	20.7	62.2	9.4
RTU-FF5-C G	95–124 cm	12.3	52.6	8.0
RTU-FF6–10	10 m adjacent to river	32.9	103.9	16.6
RTU-FF6–50	50 m adjacent to river	34.8	108.4	11.1
RTU-FF7–10	10 m adjacent to river	27.2	106.7	8.5
RTU-FF7–50	50 m adjacent to river	34.8	105.8	7.4

^aFrom Turekian (1971) and Martinand Meybeck (1979)^bKabata-Pedias (1995)^cMHSPE (2000)

at the Sb mines, (2) a change in sediment storage processes associated, for example, with the onset of channel bed aggradation during approximately the past decade, and/or (3) a combination of the previous two factors. The floodplains now serve as an additional source of contaminated sediment to the downstream reaches of the Río Tupiza.

Tailings eroded and transported downstream during the February 2003, flood were confined to the axial channel of the Río Chilco and the environmental impacts of the event appear to have been minor. Pb, Zn, and Sb concentrations decrease to background values within 25 km of the mine site, and the contaminated reach is devoid of significant populations and agriculture. In addition, the quantity of Pb, Zn, and Sb introduced to the drainage system by the event was limited in comparison to releases associated with historic mining operations in the Río Tatasi basin. Most of the Pb and Zn found within channel and floodplain deposits of the Río Tupiza were derived from Tatasi-Portugalete mining district via the Río Tatasi. Locally, concentrations within the surface soils of the floodplains exceed Canadian, German, and/or Dutch guidelines for agricultural use. The potential uptake of metals and Sb by crops grown on the contaminated soils near Tupiza requires additional study given its potential to affect human health. However, concentrations measured downstream of the confluence between the Río Tupiza and the Río San Juan del Oro suggests that regional impacts of mining operations within the upper reaches of the basin are minimal and are unlikely to significantly affect the aquatic systems located along the Río Pilaya or Río Pilcomayo under the current physio-chemical conditions.

As legal issues surrounding riverine contamination become more complex, and the levels of contamination of concern lower, the difficulty of assessing contaminant sources will increase. This has prompted a call for more forensic and quantitative approaches to source determination. The results from this study clearly demonstrate that Pb isotopes can be used to track the movement of sediment-borne trace metals from mining operations through river systems. Moreover, Pb fingerprinting methods can be applied even when multiple sources of Pb exist and for riverine environments where Pb levels are near the concentrations observed in natural geologic materials (i.e., close to background).

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