ASSESSMENT OF HEAVY METALS CONTAMINATION FROM POINT SOURCES IN THE ABARÓA – TUPIZA BASIN, BOLIVIAN SOUTHERN REGION

A thesis presented to the faculty of the Graduate School of Western Carolina University in partial fulfillment of the requirements for the degree of Master of Science.

By

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Abstract

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Heavy metal contamination in rivers downstream from mining operations is an important environmental concern due to the potential release of metals that affect water quality. The downstream transport of particulate bound metals and their subsequent storage in alluvial deposits is of particular concern because they may pose a significant threat to the quality of agricultural crops grown on floodplains. This study examines the downstream transport and storage of contaminated sediment derived from three mining centers in southern Bolivia: the Abaróa, the Chilcobija, and the Tatasi – Portugalete District. It also examines the consequences of erosion of mine tailings impounded within a small river valley at the Abaróa Mine site.

Trace metal concentrations (including lead, zinc, and antimony) within the bed sediments of a bedrock constrained channel located immediately downstream of the Abaróa Mine gradually decrease downstream until reaching the Rio Chilco, where concentrations abruptly decrease. Metal concentrations within the bed sediments are similar to background concentrations within approximately 30 km of the Abaróa Mine. However, Pb and Zn concentrations locally increase farther downstream along the Rio

Tupiza – San Juan del Oro as a result of the influx of mining debris from polymetallic mining operations within the Rio Tatasi basin and, to a lesser degree, the Rio Chilcobija. Downstream of the tributaries Rio Abaróa, and Rio Tatasi, Pb, Zn, and Sb concentrations decrease gradually until reaching concentrations similar to local background.

The spatial distribution of metals in floodplain deposits differs from site to site. In floodplains closest to the mines such as FF-1 and FF-2, relatively elevated metal concentrations were found at sites located near the channel separated 10 and 35 m, whereas lower concentrations occurred at distances greater than 50 m from the channel. The opposite trend was observed in floodplain FF-3, and in the floodplain farthest downstream the difference in metal content was negligible. However, it is difficult to define a particular trend due to the small variations among and within the sites.

Vertically, most of the floodplains exhibit the highest concentrations at the surface. Highly variable concentrations exist at greater depths, although the lowest metal concentrations were often at the base of the core. This spatial pattern suggests that sediments contaminated by Pb, Zn, and Sb have been deposited on the floodplain over the past several decades.

Concentrations of heavy metals in floodplain deposits are higher than in channel bed sediments. Grain size data demonstrate that silt and clay is more abundant in floodplain deposits (~50%) than in channel sediments (~15%). These differences imply that differences in heavy metal concentrations are due to variations in the abundance of chemically reactive, fine sediments within the deposits.

Locally, soil concentrations in floodplain soils exceed Dutch, Canadian, and German guideline values for agricultural use. In fact, the German guidelines are locally exceeded by two orders of magnitude. These data indicate that additional studies related to the accumulation of heavy metals within agricultural products should be conducted to more fully assess the potential impacts of metal contamination on human health.

Impacts on human health and the environment caused by the Abaróa dam failure were apparently limited, as indicated by rapid downstream reduction in metal concentrations. The continuous inputs of sediments stored within the floodplain deposits during bank erosion may be a more important source of metals for the rivers.

Introduction

Fluvial processes are the principal mechanisms responsible for the transportation and redistribution of trace metals in riverine environments; for this reason it is important to understand the short- and long-term processes of sediment transport and storage. Moreover, these processes are critical to the development of environmental remediation strategies in basins affected by metal pollution (Macklin, 1996). The study of sediment routing systems must consider both natural and anthropogenic contaminant sources, metal dispersal mechanisms in channel and overbank environments, and the spatial-temporal patterns of metal storage in floodplains as secondary sources of metal contamination.

Among the various fluvial deposits, the most relevant to metal contamination are floodplain and channel bed sediments. This is due to their high potential to be remobilized, thereby becoming a source of pollution. The likelihood of the remobilization of contaminated sediments depends on (1) the location of the sediments in the valley with respect to the active channel, and (2) the intensity of geomorphic processes along the river. When channel banks or low elevation surfaces have high metal concentrations, or the river is geomorphically active, the storage of metalliferous sediments may be short, posing a later threat of metal pollution that can affect different media downstream (James, 1989; Marcus, 1989; Leece and Pavlowsky, 1997; Hudson-Edwards et al., 1999; Zhao et al., 1999). In contrast, if metal concentrations are spread more widely and evenly across the floodplain, or are present on higher topographic positions that are geomorphically less active, sediment bound-metals may remain stored for decades or centuries (Foster and Charlesworth, 1996; Miller, 1997; Hudson-Edwards et al., 1999; Zhao et al., 1999; Coulthard and Macklin, 2003). Metal concentrations are often higher in floodplains with lower relief where the sedimentation rate is rapid and continuous. Hence, metals associated with sediments may remain in the sediment routing system long after the sources of metal releases have slowed or ceased.

The release of minerals and other chemical compounds (e.g. xantates, cyanide, etc.) included in mining wastes can also affect water quality, and if they become bioavailable, they can impact microorganisms, plants, and animals as well as human health. As a consequence of bioaccumulation, the most affected areas are where farm lands are located in polluted fluvial deposits, and contaminated waters are used for irrigation and drinking purposes.

Previous analyses have demonstrated that trace metal concentration in suspended sediments (as well as those within the channel bed and banks) is significantly higher than that of metals dissolved within the water column (Gibbs, 1977). Thus, for a majority of trace metals, more than 90% of the load is associated with the physical movement of particulate matter (Gibbs, 1977; Meybeck and Helmer, 1989; Horowitz, 1991). Consequently, any attempt to quantitatively determine the dispersal of heavy metals within river systems must consider the geomorphic/hydrologic processes involved in particle transport and deposition.

Transport rates and dispersal patterns of sediment-associated metals are controlled by four factors: (1) hydraulic sorting of channel sediments on the basis of particle density, size, and shape; (2) mixing processes with resultant addition or dilution of trace metals; (3) losses through deposition and storage in lateral and vertical accretion deposits; and (4) geochemical processes such as chemical sorption/desorption, solution, and co-precipitation (Lewin and Macklin, 1987; Macklin, 1988; Wolfenden and Lewin, 1978; Macklin, 1996; Taylor and Kesterton, 2002).

Fluctuating inputs of heavy metals to river systems controlled by changes in inundation frequency and deposition rate are commonly reflected in floodplain sequences by variable amounts of trace metals in vertical sediment profiles (Rang and Schouten, 1989; Macklin et al., 1992). Therefore, floodplains and overbank sediments constitute a record of the timing and rates of contaminant loadings. Peak concentrations of Pb and Zn from mining records have been associated with peaks in metal concentrations observed in vertical profiles from alluvial deposits. Hence, the layers of materials containing heavy metals correlate with the production or sudden increase in the load of metals from upstream mining operations (Macklin, 1985; Knox, 1987; Rowan et al., 1995). While metal concentrations have been used as stratigraphic markers with satisfactory results, heavy metals are expected to migrate downward in vertical profiles. Lowering of the water table, for example, can lead to the oxidative remobilization of heavy metals previously stored in anoxic conditions. Mobilization can also be initiated by acidification through weathering, pedogenic processes, and or by intensive use of fertilizers; another factor is atmospheric deposition especially in industrial areas where gas emissions and precipitation occur (Salomons and Forstner, 1984; Hudson-Edwards et al., 1998; Van den Berg et al., 1998).

Waste mine disposals including dumps and tailings are one of the most ubiquitous features of both surface and underground hardrock mining operations. Tailing piles are commonly located within small tributary channels along the base of hillslopes and in natural depressions. Tailings disposed in tributaries may form a dam that can block the flow of water along the channel. In other locations, tailings are intentionally used to create impoundments in which effluents are stored as a part of the beneficiation process or for pollution control. Regardless of the nature of these tailings dams, they are prone to failure, and during the past 40 years, more than 75 major failures have released heavy metals and other contaminants into riverine environments (Table 1). This equates to nearly two major tailings dam failures per year, not including those in secluded regions, which are seldom reported.

There are several important differences between transport and storage of contaminated sediment following a dam failure and those occurring during "normal" hydrologic/sedimentologic conditions. First, a large number of dam failures are initiated by low frequency-high magnitude rainfall-runoff events. Second, there is an abundance of easily eroded sediment (tailings materials) available at the site of the dam break. The instantaneous movement of these materials may create abnormally high sediment concentrations and the rheology of the flows may vary considerably over relatively short distances, changing regimes, for example, from a debris flow to a hyperconcentrated flow to a water flood. The resulting flood within the channel may be exacerbated by the

Table 1: Tailings dam failures resulting from heavy rains associated with high magnitude rainfall – runoff events (MRF 2002).

Mine (location - year)	Volume of material released - m3
Harmony, Merriespruit (South Africa - 1994)	600,000 a
Buffalo Creek (W. Virginia, USA - 1972)	500,000 a
Porco (Bolivia - 1996)	235,000 b
Sgurigrad (Bulgaria - 1996)	220,000 a
Aberfan (Wales, UK - 1966)	162,000 a
Mike Horse (Montana, USA - 1975)	150,000 a
Bilbao (Spain - 1969)	115,000 a
Baia Mare (Romania - 2000)	100,000 c
Ages (Kentucky, USA - 1981)	96,000 d
Huelva (Spain - 1998)	50,000 b
Stancil, Perryville (Maryland, USA - 1989)	39,000 a
Dean Mica (N. Carolina, USA - 1974)	38,000 a
Arcturus (Zimbabwe - 1978)	30,000 a
Maggie Pie (UK - 1970)	15,000 a
Borsa (Romania - 2000)	8,000 e

a) Waste
b) Effluent and tailings
c) Metal enriched tailings
d) Coal refuse
e) Cyanide contaminated effluent and tailings

sudden release of effluent stored behind the dam. Thus, the downstream transport and deposition of contaminated particles derived from breached tailings dams commonly occur under extreme flood conditions (Miller et al., 2003) and are typically characterized by high (anomalous) concentrations of metals downstream

The primary objective of this investigation is to determine how metal-enriched sediments are distributed and stored along the Chilco and Tupiza – San Juan del Oro rivers. Secondary objectives of this research are to determine: (1) historical loading rates of heavy metals to the river by examining metal concentrations in floodplain and terrace deposits of varying age, and (2) the primary sources of metals to the river system.

As described above, alluvial deposits are natural receptors of sediment-bound metals; thus, deposit sampling and analysis may identify the relative chronology of heavy metal deposition along the river. Metal concentrations determined in soils developed on terraces and floodplain deposits will also be compared with previously established guidelines for cultivated fields. This comparison will allow definition of the degree of contamination of the soils and estimation of the potential effects on human health and the environment.

Study Area

Geographical and Geological Setting

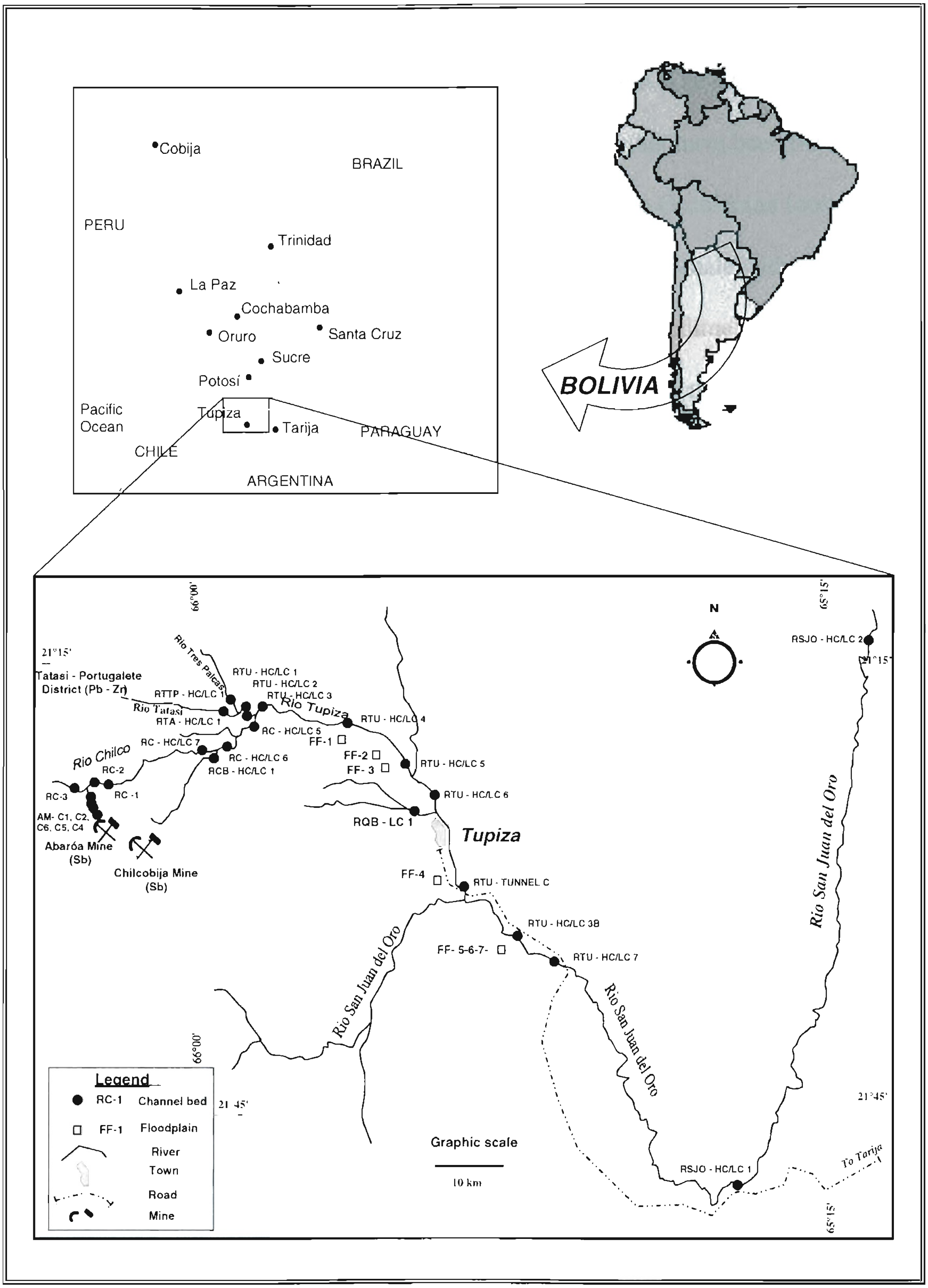
The Abaróa – Tupiza Basin has been selected for study for two major reasons. First, it is part of the Pilaya Basin, which in turn is a major tributary of the Rio Pilcomayo, a highly important river system for water supply and economic reasons in southern Bolivia. Second, a tailings dam failure occurred at the Abaróa Mine in 2003, causing the movement of mineralized materials downstream, thereby becoming a significant environmental concern with the three Bolivian states, which border the drainage system.

In February 2003 an unusually high magnitude, low duration flood event eroded a tailings dam built across a contaminated sediment filled valley. The waste materials were subsequently transported downstream through a small tributary that traverses a bedrock canyon for approximately 1.2 km before reaching the Rio Chilco. The Rio Chilco is partially filled with alluvial and reworked colluvial sediments from the uplands and is a tributary to the Tupiza - San Juan del Oro river system.

The Rio Tupiza - San Juan del Oro is a braided river exhibiting a parabolic planform in which one limb flows in a southeasterly direction and passes near the city of Tupiza and the second flows north – northeast. This latter section of river is located approximately halfway between Tupiza and Tarija and ultimately joins the Rio Pilaya (Fig. 1).

The intersection of two drainages, the Rio Tres Palcas and Rio Tatasi, becomes the headwaters of Rio Tupiza. The name of the river is changed to Rio Tupiza immediately downstream from the junction of those streams at 65° 58' W, 21°18' S. Approximately 47 km downstream, the Rio Tupiza joins with the Rio San Juan del Oro. Rio Chilco is a tributary to the Rio Tupiza 3.5 km downstream of the intersection between the Rio Tres Palcas and Rio Tatasi. It is approximately 28 km from the mouth of the Abaróa Valley to the confluence with Rio Tupiza (Fig. 1).

Figure 1. Geographic map of the study area showing the location of sampling sites.



Geology of the Basin

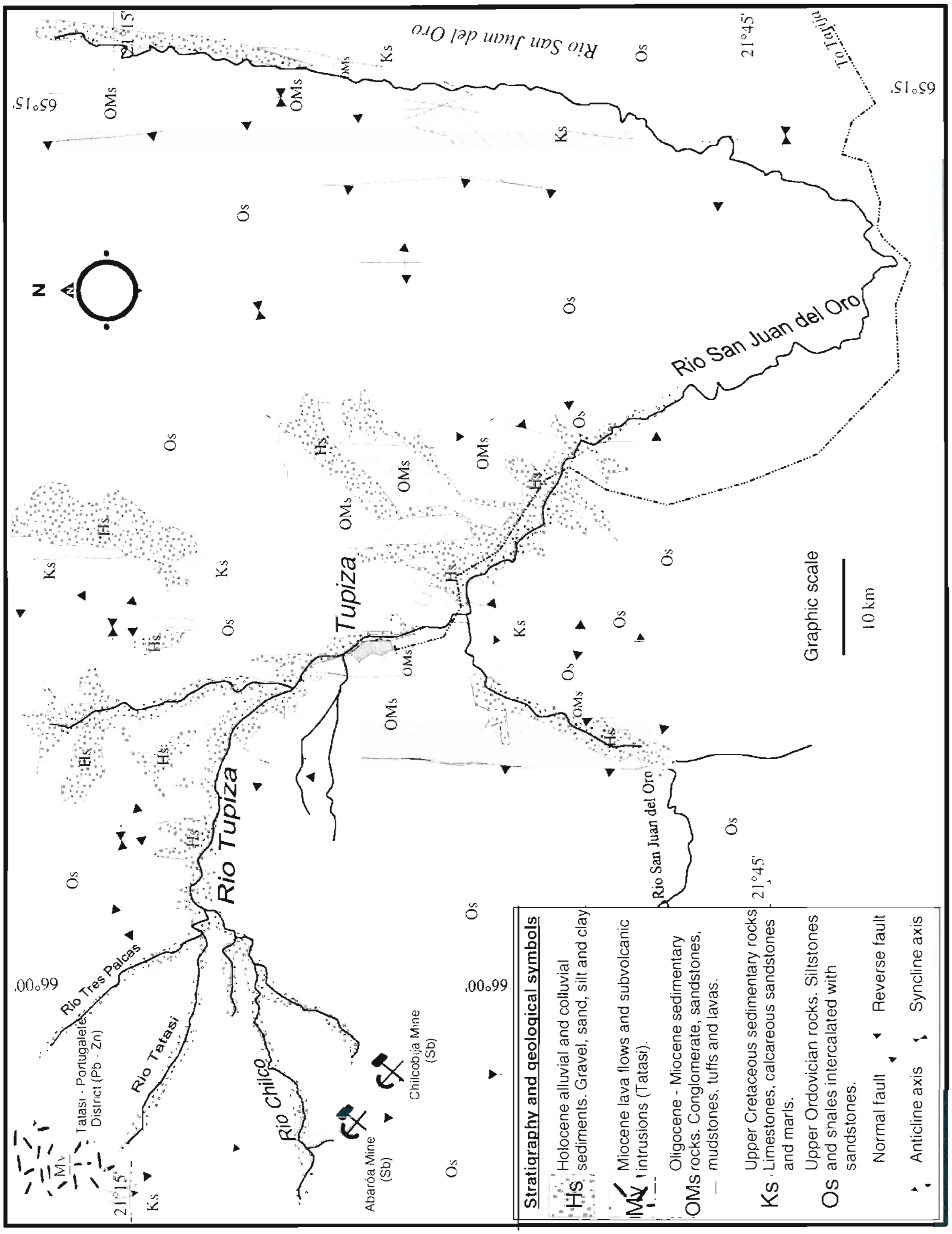
The Abaróa–Tupiza basin is located in the southern segment of the Cordillera Oriental, and lies adjacent to the western edge of the Altiplano. The basin is underlain by Paleozoic formations as well as Mesozoic – Cenozoic rocks that have been modified by tectonic events. The oldest rocks exposed in the area belong to Ordovician formations (Os) lithologically consisting of continuous beds of siltstone and shale with local horizons of sandstone (ca. 3200 m thick). Oligocene -Miocene sedimentary rocks (OMs) unconformably overlie the Ordovician sequence and are represented by reddish polymictic conglomerates with clasts of shale, sandstone, limestone, and quartz at the base. At the top of the sequence are unconsolidated sediments with pink clayey sandstones, mudstones, and tuffs and juxtaposed conglomerates with clasts of sandstones, shales, and andesites. Likewise, a Miocene intrusive dome complex (Mv) is emplaced in Ordovician rocks. Locally, Cretaceous rocks (Ks) are exposed. They are characterized by conglomerates at the base and interbedded siltstones, sandstones and basalts farther up-section. The Ordovician rocks have also been affected by low-grade, regional metamorphism and are intensely deformed into narrow synclines and anticlines (Fig. 2).

The Abaróa, Chilco and Tupiza-San Juan del Oro valleys traverse this complicated sequence of sedimentary deposits. The Chilco and Abaróa valleys are incised entirely into Ordovician rocks; the lithologic contact with Miocene rocks is positioned approximately 20 km downstream from the confluence of the Tatasi and Tres Palcas Rivers. The Oligocene-Miocene sequence extends for 15 km until Cretaceous rocks are exposed in a narrow elongated syncline that occurs approximately 3 km along the valley. Underlying this fold are Ordovician rocks that extend for 180 km. The drainage system cuts the stratigraphy nearly perpendicularly (NW- SE) in the first segment and in the second it is sub-parallel to the regional trend (N-S).

Holocene-age sediments (Hs) fill the valleys. The Abaróa valley, minor in size and extension, is filled with intermittent and thin alluvial and colluvial sediments. Rio Chilco and Rio Tupiza – San Juan del Oro valleys are filled primarily with alluvial sediments contained within terrace and floodplain deposits. The terrace deposits are composed of semi-consolidated gravel, sand, and clay with tuffaceous horizons (Geobol, 1991a, 1991b). Floodplain alluvial deposits include unconsolidated pebbles, gravel, sand, silt and clay; colluvial deposits locally occur along the valleys and consist of unconsolidated boulders and gravels (Geobol, 1991a, 1991b).

Within and adjacent to the basin, mineralization is associated with two different types of ore deposits. The Tatasi –Portugalete mining district is a polymetallic vein deposit, the other deposit type includes antimony vein deposits of the Bolivian antimony belt in which the Chilcobija and Abaróa mines are located. Chilcobija is the country's largest antimony deposit; this deposit is owned by Empresa Minera Unificada Sociedad Anónima (EMUSA) and had a capacity of 12,000 tons per year of antimony concentrate. During the past decade it produced 4,000 to 5,000 tons of antimony per year. The closure of the mine occurred after antimony prices decreased making operation costs uneconomical (Carlin, 1998). However, some small mines survived the continuous decline in prices, including the Abaróa Mine that is owned and operated by Compañia

Figure 2. Geological map of the basin showing major stratigraphic units and faults. (Geobol, 1991; Servicio Nacional de Geologia y Mineria, 1999).



Minera Salinas. There are no available historical mine production records; however, the discovery of these deposits occurred in the 1950s.

Currently, materials extracted from the Abaróa Mine are processed by crushing, milling, and froth floatation. The capacity of the plant is 150 tons/day, but in November 2003 only 40 to 50 tons/day containing 7% antimony were processed (J. Arias personal communication, Nov. 2003). The actual production is probably less than in the 1970s when antimony production was stimulated by an increasing demand for metals.

The Chilcobija antimony mine is a vein deposit hosted in Ordovician rocks; three main systems of veins have been exploited within the Ordovician sequence and the remaining antimony reserves are primarily associated with these mineralized structures. Hydrothermal fluids filled the fractures and bedding planes with ore minerals such as stibnite, galena, and sphalerite, which are combined with gangue minerals including quartz, pyrite, and arsenopyrite. Gold was extracted as a by-product in the past.

Within the Abaróa Valley, a small tributary was dammed and filled with tailings generated from the processing of antimony ore from the Abaróa Mine. A second old tailings dam is filled by water and sediment downstream (Fig. 3).

The Tatasi- Portugalete mining district is located within the headwaters of Rio Tatasi. 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. These Ordovician rocks are unconformably overlain by Cretaceous conglomerates, limestones, and calcareous sandstones. Mineralized

Figure 3. Panoramic view of the Abaróa Valley. A concrete tailings dam traverses the valley in the foreground; dumps and the beneficiation plant are in the background.

structures are related to two vein systems, trending N60°W and N50°E, within a shear zone dissecting Miocene tuffs, breccia-tuffs, and the dacitic intrusive. Ore minerals include cassiterite, galena, electrum, and sphalerite and are accompanied by gangue minerals including pyrite, chalcopyrite, marcasite, quartz, and bournonite, among others. Upper levels of the veins are enriched in tin and silver; with increasing depth the mineralogy of the veins shifts to different paragenetic assemblages including Ag – Zn – Pb sulfides and sulfosalts. The edges of the veins show marked zonation by silicic, argillic, and propilitic alterations. Hence, the primary commodities are Pb, Zn, Ag, although Sn is also mined (Gustavson Associates, 1991).

Several mining waste disposal sites are located in the Tatasi –Portugalete district. The Corporación Minera de Bolivia (COMIBOL), the former state mining company that owns the mine, is carrying out a remediation program with economic support from the Government of Denmark.

Methods

The study objectives were accomplished by manipulating and interpreting a combination of field and laboratory data. Fieldwork involved geomorphological differentiation of alluvial deposits along the Rio Chilco – Rio Tupiza drainage as well as the collection of geochemical samples. Laboratory analysis included the geochemical and physical analysis of the collected samples.

Identifying Metal Sources

The Abaróa Mine is not the only mining operation within the Rio Tupiza basin. Other mining operations include Chilcobija, the largest antimony mine in Bolivia, and several polymetallic mines within the headwaters of the Rio Tatasi. Given that each of these mines is known to have released significant quantities of contaminated materials into tributaries of the Chilco-Tupiza- San Juan del Oro river system, the alluvial deposits within the drainage are contaminated by multiple sources.

The relative importance of these deposits as metal sources was determined by examining spatial patterns of trace metals in channel bed and floodplain deposits. Similarly, background values were obtained by analyzing non-contaminated (pre-mining) alluvial deposits. Metal concentrations defined as background were used to identify metal anomalies, and thus, potential zones of metal influx.

Field Investigations

Assessing Downstream Trends in Metal Concentrations

Inherent in this aspect of the investigation is a geomorphic/sedimentologic analysis of the depositional processes that occurred downstream of the breach, the three-dimensional (downstream, vertical, and cross-valley) variations in trace metal concentrations within newly formed alluvial deposits, and an assessment of the controls on both depositional patterns and metal concentrations.

Samples were collected for physical and chemical analyses from tailings materials, channel sediments, soils developed in floodplain and terrace deposits, alluvial fan sediments, and other alluvial materials such as point bar and slackwater deposits. The number of samples collected from each deposit type is presented in Table 2.

A short description of the channel bed morphology is required to understand the sampling protocols used to collect the channel sediments. Some reaches were characterized by either ephemeral flow conditions (e.g. Abaróa Valley) or perennial flow conditions (such as the Rio Chilco), but exhibited a channel bed that could not be differentiated into separate units. Sediment samples from these locations were collected from the upper 5 cm of the channel bed along transects oriented perpendicular to flow. Farther downstream (such as along the Rio Tupiza – San Juan del Oro), reaches characterized by perennial flow could be differentiated into high- and low-channel bed deposits. High channel deposits are inundated only during high flow conditions for the period of the wet season, whereas the low-channel deposits are inundated during the entire year (Fig. 4). Both of these deposit types were sampled. The high-channel samples were collected from multiple locations perpendicular to the valley and mixed to form one sample. In contrast, low-channel samples represented fresh sediments collected from the edge of the actual active channel or thalweg.

Soil samples were taken from the surface (upper 5 cm) of terraces and floodplains down the Rio Chilco and Rio Tupiza, along transects located at varying distances from the channel banks. In most of the floodplains cores up to one-meter depth were obtained. In order to determine the local background concentrations of trace elements, alluvial fans

Figure 4. Schematic cross section of high-channel, low–channel, and floodplain deposits.

Floodplain

Wet and dry season

Channel bed sediments

Floodplain

Wet season

High channel sediments

Dry season

Low channel sediments

were sampled along transects located at the mouth of drainages presumed not to possess mining or other point sources of contamination. Tailings samples were collected upstream of current and historic tailings dams at the Abaróa Mine site as well as from tailings piles at the Chilcobija antimony mine (Table 2). All of the samples were analyzed for a suite of seventeen elements.

Samples were collected from the upper 5 cm of both the high- and low channel systems following procedures outlined in Miller et al. (2003). In addition, samples were collected from historical and recent floodplain deposits. The floodplain deposits were primarily obtained using an auger sampler, and reached core depths of approximately 1.20 m. The sediment samples were placed in polypropylene sampling containers, packaged in plastic bags and shipped to the Nevada Bureau of Mines and Geology, where they were analyzed for chromium, cobalt, nickel, copper, zinc, molybdenum, silver, cadmium, tin, tungsten, gold, lead, antimony, arsenic, mercury, thallium, and manganese concentrations using the analytical methods presented below. In this study, however, we will focus only on lead, zinc, and antimony.

The volume of tailings materials eroded from the mine site was determined by surveying the width, depth, and length of the dam breach and other gullies that existed within the tailings piles at the Abaróa Mine. Surveying was conducted using tape and stadia rod methods. Conversion of data from units of volume to weight was based on estimates of bulk density.

Determination of flood discharges relied on slope-area paleoflow calculations. More specifically, flow depth and width were determined from silt lines along bedrock reaches located downstream from the mine. Estimates of flow velocity were determined by applying Manning's equation to measured channel dimensions, slope, and estimated roughness values (Watson and Burnet, 1995).

Analytical Procedures

Multielemental analyses involve 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 leachates were transferred to 200 ml volumetric flasks, diluted to the mark with deionized water, and were analyzed by Inductively Coupled Plasma – Mass Spectrometry (Miller et al., 2003).

Organic matter content was analyzed via loss on ignition (LOI). Each sample was dried for 24 hours at room temperature, disaggregated with a mortar and pestle and heated in a muffle furnace at 550° C for four hours. The sample was cooled in a desiccator for at least two hours before determining weight loss. These samples were also analyzed for grain size using 230 mesh sieve which allowed for the determination of the silt – clay (= fines, <63 μm) fraction and sand fraction (> 63 μm). The analysis relied on wet sieving techniques.

The total organic content (TOC) and grain size data were used to mathematically normalize the metal concentrations measured in the bulk samples. Normalization was conducted in order to enhance the interpretation and correlation of metallic concentrations with contrasting sediment textures and compositions. Grain size and organic contents were also utilized to compare heavy metal concentrations between depositional sites such as the channel bed and floodplain. Normalization relied on the following formulas:

Organic Matter

Normalized Concentration = (DF *Bulk Metal Concentration)
where DF = Dilution Factor = 100/ (% organic matter)

Silt clay fraction

Normalized Concentration = (DF *Bulk Metal Concentration)
where DF = 100/ (100 - % of sediment greater than size range of interest), or
DF = 100/ (100 - % >63 μm).

In order to gain a first approximation of the potential environmental impacts on human and ecosystem health, the trace metal concentrations observed in the channel bed and floodplain/terrace deposits were compared to Dutch, Canadian, and German guidelines as well as background values. Comparisons to background were conducted using both bulk and grain-size normalized data to remove the effects of grain size variations on elemental concentrations.

Table 2: Statistical summary of Pb, Zn, and Sb concentrations (ppm), silt-clay fraction (%) and total organic content (TOC) in %. Data based on reaches, alluvial deposits, and mine sites.

	Pb	Zn	Sb	Silt-clay	TOC
Abaroa Mine to Rio Chilco (n=9)					
Average	294.49	723.28	922.84	27.68	4.28
Maximum	610.87	1515.43	1681.06	52.80	7.00
Minimum	12.13	76.20	17.46	1.20	1.71
St. dev.	225.06	533.86	670.55	19.62	1.68
Rio Tatasi to Rio Tupiza (n=6)					
Average	77.06	382.41	16.60	13.44	2.31
Maximum	135.96	689.30	29.71	20.47	2.67
Minimum	40.24	188.94	7.45	6.20	1.68
St. dev.	33.20	170.20	8.67	5.20	0.40
Chilcobija to Tatasi (n= 4)					
Average	16.09	86.99	21.13	11.27	1.69
Maximum	23.88	106.66	39.75	18.10	2.26
Minimum	9.70	73.58	2.28	6.32	1.29
St. dev.	6.58	14.06	15.88	5.06	0.43
Río Tres Palcas (n=2)					
Average	21.12	115.35	9.42	13.11	2.89
Maximum	29.64	155.04	14.40	15.30	3.01
Minimum	12.61	75.66	4.45	10.92	2.77
St. dev.	12.04	56.13	7.04	3.09	0.17
Rio Tupiza to End of Sampling. High-Channel (n=6)					
Average	37.78	159.41	11.95	19.29	2.00
Maximum	69.17	286.28	22.99	42.15	2.59
Minimum	13.45	46.68	0.88	9.48	1.37
St. dev.	25.29	114.07	8.98	13.14	0.49
Rio Tupiza to End of Sampling. Low-channel (n=8)					
Average	33.21	227.88	12.43	10.63	2.38
Maximum	56.47	657.21	31.83	16.96	3.63
Minimum	7.45	34.39	0.88	5.50	1.28
St. dev.	20.33	205.02	10.16	3.91	0.76
Rio Chilco-Rio Tupiza-Rio San Juan del Oro (n=14)					
Average	44.40	218.80	107.08	10.18	2.46
Maximum	206.15	657.21	1118.24	42.53	3.63
Minimum	7.45	34.39	0.88	0.42	1.28
St. dev.	52.04	181.72	295.99	10.50	0.64
Alluvial Fans - Background (n=4)					
Average	18.17	93.08	3.06	4.15	2.55
Maximum	24.61	139.26	3.77	5.69	3.43
Minimum	11.64	71.90	2.37	2.25	1.39
St. dev.	5.51	31.32	0.57	1.43	0.90

	Pb	Zn	Sb	Silt-clay	TOC
Terraces (n=3)					
Average	14.18	78.71	3.79	31.98	5.08
Maximum	17.11	91.06	4.26	33.95	6.05
Minimum	11.27	60.72	3.27	28.99	3.44
St. dev.	2.92	15.94	0.50	2.63	1.42
Abaroa Tailings -fresh (n=3)					
Average	85.04	216.69	1122.80	47.98	4.52
Maximum	114.25	279.33	1150.02	94.52	5.07
Minimum	63.41	131.49	1092.84	16.68	3.52
St. dev.	26.26	76.46	28.69	41.09	0.87
Abaroa Tailings -old (n=4)					
Average	46.36	78.52	1539.49	39.54	4.53
Maximum	118.35	103.17	2821.03	80.96	5.73
Minimum	13.23	66.58	15.48	11.15	3.61
St. dev.	48.68	16.81	1179.71	31.26	1.00
Chilcobija Tailings (n=2)					
Average	163.13	90.31	1846.25	84.58	20.77
Maximum	179.84	107.64	2503.41	95.39	22.52
Minimum	146.42	72.98	1189.09	73.78	19.01
St. dev.	23.63	24.51	929.36	15.28	2.48
Soil Surface/Distance (n=14)					
Average	94.09	310.65	37.40	42.97	7.40
Maximum	241.15	643.39	111.29	67.91	13.97
Minimum	27.21	103.86	7.15	16.71	3.26
St. dev.	74.07	215.31	35.47	14.36	3.35
Core FF-5 (n=7)					
Average	33.85	87.88	8.87	53.57	7.17
Maximum	54.63	109.33	10.97	62.35	14.43
Minimum	12.27	52.64	6.33	39.08	2.90
St. dev.	13.89	21.80	1.56	10.25	3.96
Core FF-3 (n=3)					
Average	210.90	539.12	69.45	41.83	11.86
Maximum	326.15	785.38	102.97	55.69	13.77
Minimum	122.15	365.74	44.02	26.15	8.83
St. dev.	104.55	219.11	30.30	14.85	2.65
Core FF-2 (n=8)					
Average	158.32	310.33	32.25	62.51	6.85
Maximum	260.25	750.72	94.32	73.31	8.00
Minimum	73.48	93.41	7.18	42.57	5.52
St. dev.	73.81	195.79	27.51	10.25	0.82
Rio Chilco (n=8)					
Average	48.06	166.18	181.52	12.79	2.62
Maximum	206.15	458.51	1118.24	42.53	7.00
Minimum	9.70	73.58	2.28	1.20	1.29
St. dev.	68.70	154.63	384.65	13.00	1.86

Results

Metal Concentrations within Mine Tailings

Tailings are accumulations of mining and milling waste. Materials extracted during the mining process include the ore deposits and the surrounding host rock. Thus, mineral extraction involves the mixing of rock and ore deposits and, by applying metallurgical methods, the subsequent separation of the minerals of interest from the rest of the debris. Tailings usually exhibit elevated metal concentrations and have been ground to a relatively uniform size. Tailing piles are frequently disposed in either natural depressions or valleys. At the Abaróa Mine tailing piles are disposed of on the side slope of the valley across from the beneficiation plant (Fig. 5), while at the Chilcobija Mine new and old tailings are located in several shallow natural depressions because the area is characterized by a smoothly undulated topography.

Pb, Zn, and Sb concentrations do not differ significantly in tailings from the two antimony mines. The highest value of Pb corresponds to new tailings materials from Chilcobija and the lowest concentrations were found at the Abaróa Mine. The highest concentration of Zn was found in Abaróa tailings whereas the lowest concentration was found in the new Chilcobija tailings. The highest concentration of Sb was found in the old tailings from the Abaróa Mine and the lowest in the old tailings from the Chilcobija Mine. Statistical tests were not applied because of the small number of samples.

Figure 5. Eroded tailings dam at Abaróa Mine. Pre-erosion level is marked by white colored materials. Earthen dam in foreground was built as part of a mitigation plan.

Pb, Zn, and Sb concentrations in tailings materials are lower than concentrations in sediments collected immediately downstream within the Abaróa Valley. Sb concentrations in tailings materials as well as in channel sediments vary within a small range, while Pb and Zn concentrations are considerably higher in channel sediments than in tailings materials. Pb and Zn concentrations are five times higher in channel sediments. Considering the nature of tailings materials, intended as homogenous sediments conformed by ore sulfides, gangue minerals, and host rock, higher metal contents were expected in those samples (Table 3 and Appendix A).

Table 3. Heavy metal concentrations in tailings from the Abaróa and Chilcobija mines. Including samples from channel adjacent to the Abaróa tailings. Units in ppm.

	Pb	Zn	Sb
Abaroa tailings			
Average	71.22	149.59	1585.15
Max	118.35	279.33	2821.03
Min	20.89	69.25	1092.84
Chilcobija tailings			
Average	93.09	102.71	1098.01
Max	179.84	131.03	2503.41
Min	20.88	72.98	310.85
Adjacent channel samples			
Average	466.06	1105.60	1387.59
Max	610.87	1515.43	1681.06
Min	330.53	587.35	1060.08

The tailings materials from the two mines differ with respect to the total organic matter and silt-clay contents (Table 2 and Appendix B). The lower values for both parameters are associated with the Abaróa tailings. The mean of total organic contents are 4.5% for Abaróa and 14% for Chilcobija. The amount of silt-clay sized particles is 43% and 56% for Abaróa and Chilcobija tailings, respectively. Two samples of tailings were predominantly fine grained; one was from the middle of the failed tailing impoundment at Abaróa. It contained 94.5% silt and clay. The other was from the new Chilcobija tailings pile and contained 95% of silt-clay.

Alluvial Fan and Terrace Deposits

Numerous tributaries along the axial drainage systems within the study area have created alluvial fans at their mouth. These fan deposits are continually reworked and are assumed to be uncontaminated by anthropogenic sources of trace metals. Moreover, the deposits are located above the general level of flooding, and, therefore, cannot be contaminated by polluted floodwaters (Fig. 6). It is presumed, then, that the concentrations of metals measured within these sediments represent local background values (Table 4 and Appendix A).

Figure 6. Alluvial fan deposits intersecting Rio Tupiza. Presumed unrelated to any source of contamination.

Similarly, a number of small terrace deposits located along the Rio Chilco constitute a natural record of sedimentation. Based on their height about the channel, and the degree of soil development, their age is thought to be beyond that of anthropogenic activity in the area. As a result, trace metal concentrations determined in those deposits are believed to correspond to regional background values for alluvial materials. Two samples from alluvial fans showed higher metal concentrations than any of the other samples. The elevated concentrations were likely produced by localized occurrences of natural mineralization. In fact, subsequent investigations reveal small mine workings within their basins. Thus, these samples were considered outliers and were not included in the calculations used to determine local background values summarized in Table 4.

Table 4: Local background concentrations based on alluvial fan and terrace deposits (n=7).

	Pb	Zn	Sb
Background values (alluvial fan plus terraces)			
Mean	16.46	86.93	3.37
St. dev.	4.75	25.18	0.63
Min	11.27	60.72	2.37
Max	24.61	139.26	4.26
Regional background[1]	(6-34)	(17-132)	---
Rio Pilcomayo Basin[1]	18.00	66.00	---
Sandstones	7.00	16.00	0.40

Concentration units given in parts per million

[1] Data from Miller et al. (2003)

( ) Range

Local background values are higher in comparison to the average crustal values for sandstones, but they are consistent with the regional background and the mean background concentrations for the Pilcomayo Basin.

River Bed Sediments

Spatial Trends in Trace Metal Concentrations

The Abaróa – Tupiza – San Juan del Oro Basin is one of the largest systems in Bolivia. This river system extends for approximately 300 km and constitutes the second largest tributary to the Pilaya River, which in turn is a tributary to the Rio Pilcomayo. Water from the Rio Tupiza is used for irrigation, and its discharge constitutes the main water resource in the Tupiza region.

Heavy metal concentrations were examined from the Abaróa Valley, located just downstream from the tailings dam, and at multiple locations downstream along the Rio Chilco to the Tupiza- San Juan del Oro Rivers. The last sample site is located 229 km away from the Abaróa Mine.

In general, trace element concentrations follow a decreasing downstream trend. However, there are local disruptions in this pattern that are of significance to understanding elemental sources and sinks. In order to facilitate the following description of the spatial distribution of metals in the channel bed, the discussion considers three river reaches that include a longitudinal section through the Abaróa Valley, a reach of the Rio Chilco, and a reach of the Rio Tupiza – San Juan del Oro (Fig.1 and Appendix C).

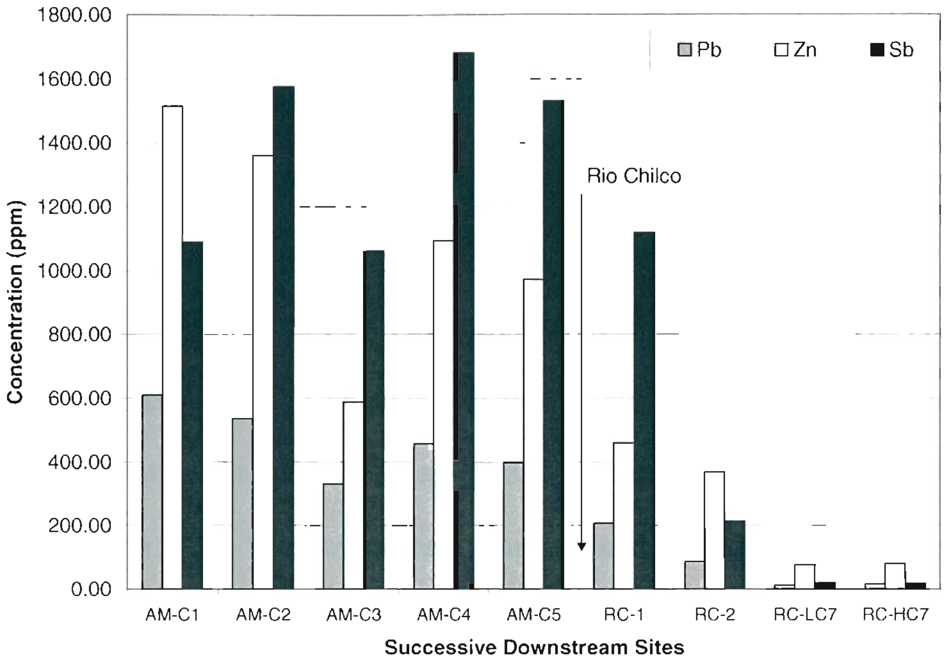
Abaróa Valley:

The Abaróa Valley contains a narrow ephemeral channel that heads upstream from the Abaróa Mine and extends approximately 1.2 km downstream of the mine until it reaches the Rio Chilco. Stratified Paleozoic rocks strike semi-perpendicular to the stream and outcrop in the wall as well as along the channel bed. Small accumulations of sediment locally cover the bedrock in the channel. Water within the channel is released by the mill processing plant rather than being from groundwater discharge.

Five channel samples were taken (AM- C1, C2, C4, C5, and C6) in that section of the river. Heavy metal concentrations were the highest found in the study area and exhibited a fairly consistent decreasing downstream trend. Lead concentrations ranged from 610 to 330 ppm, zinc from 1515 to 587 ppm and antimony from 1681 to 1060 ppm (Fig. 7 and Appendix A).

The percentage of silt - clay determined for all five samples follows a decreasing downstream trend. The estimated average for the fine grained fraction is 38% by weight. The highest measured by weight corresponds to the first upstream sample (50%), while the lowest corresponds to the last downstream sample (25%) silt-clay. The amount of total organic matter was consistent and averaged approximately 5%. (Table 2 and Appendix B).

Figure 7. Heavy metal concentrations in channel bed samples along Abaróa Valley and Rio Chilco reach.



<u>Rio Chilco:</u>

The Rio Chilco is the longest drainage basin, receiving water and sediments from the antimony mines in the area. It is a perennial river possessing an average width of 50 m along the 30-km reach located between the mouth of the Abaróa Valley and its confluence with the Rio Tupiza. Sediments are lithologically and texturally diverse. Some small, discontinuous floodplain and terrace deposits are located on both sides of the channel. Alternating sequences of Paleozoic shales and siltstones underlie the channel.

Ten samples were taken at six sites, eight of which correspond to paired samples of low and high-channel deposits and two correspond to the channel bed. Lead, zinc, and antimony concentrations follow a decreasing downstream trend. The two channel samples (RC-C2 and RC-C1) taken immediately downstream from the intersection of the Abaróa Valley and the Rio Chilco, exhibit concentrations well above local background (Fig. 7). Concentrations subsequently decline downstream, reaching concentrations comparable to locally defined background values at RC-C7 . The downstream gradient between these samples is significant, considering that these two sites are separated only by approximately 1 km. Pb, and Zn concentrations decrease by several fold. The decreasing trend is still more evident taking into account the difference between the highest concentrations in the first two samples and the remaining samples collected downstream from them. The downstream samples exhibit concentrations comparable to local background levels. The sample (RC-HC3/LC3) located upstream from the confluence of the Rio Chilco and the Abaróa Valley also exhibits concentrations within the range of local background values (Figure 7.).

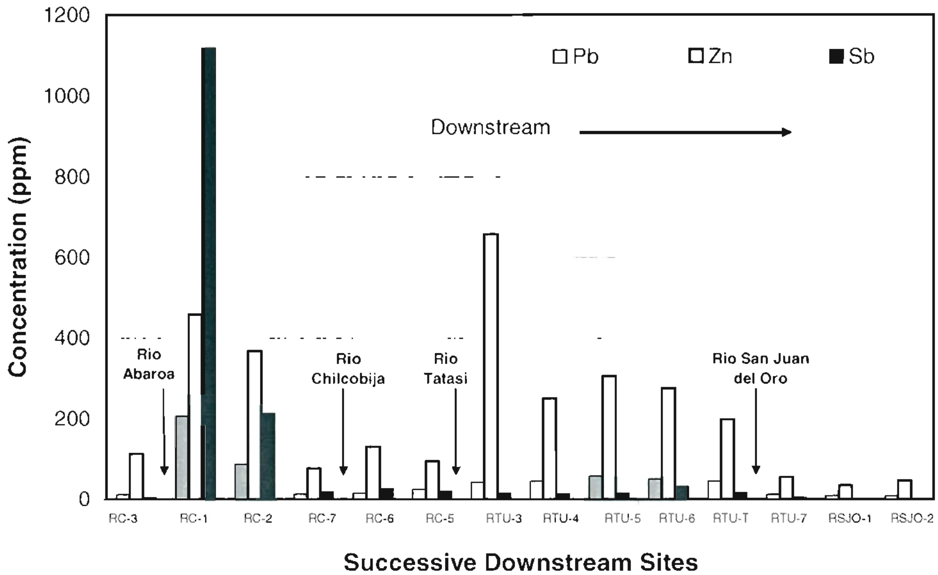
High and low-channel sediments are predominantly composed of sand-sized sediment. However, significant textural differences exist between them. In high-channel sediments, the fine fraction (<63 μm) ranges from 8 to 42% by weight, but for low-channel sediments the range is from 0.4% by weight to approximately 4.0%. The average amounts of silt - clay better illustrate these differences; the average for low-channel sediment is 2.5% and for high-channel sediments is approximately 15.0%. The quantity of fine-grained sediments does not follow a specific pattern downstream. In addition, total organic content is more uniform; the average for high-channel samples is 2.8%, whereas for low-channel sediments it is 2.5% (Table 2 and Appendix B).

Rio Tupiza – San Juan del Oro

The Rio Tupiza – San Juan del Oro system constitutes the main regional drainage basin in the area, receiving flow from the Rio Chilco, Tatasi, Chilcobija, and Tres Palcas, among others. It is a perennial, braided river extending for up to 300 km downstream with an average width of 100 m, although local lithological and structural differences cause it to vary from narrow and steep to wide and flat. Stream sediments vary from clay to boulders up to 50 cm in diameter, the latter consisting of lithologies from the underlying bedrock, including Paleozoic, Mesozoic, and Cenozoic formations.

Twenty-one samples were taken at 10 sites along an approximately 200 km reach. At most locations, a pair of samples were collected, one representing the high and the other the low-channel deposits. Concentration ranges for Pb, Zn, and Sb are summarized in Table 2. Along the Rio Tupiza (from 35 km to 76 km), trace metal concentrations are slightly elevated above the background levels. Lead concentrations are variable, ranging from 69.17 to 44.50 ppm. Zinc exhibits a similar behavior, varying from 286.0 to 199.0 ppm. In contrast, antimony exhibits a semi-systematic decreasing trend until the last sampling site where concentrations reach 7.2 ppm, one of the lowest values of antimony determined in this study. In a section of the river between 76 km and the last downstream sampling site (229 km from Abaróa), Pb and Zn concentrations decrease substantially reaching concentrations analogous to the minimum of the background levels. Therefore, Pb and Zn concentrations in the Tupiza-San Juan del Oro reach can be grouped in two sections one with high and the second essentially with low –background - concentrations. (Fig. 8 and Appendix A).

Figure 8. Downstream distribution trend of heavy metals along the Rios Tupiza – San Juan del Oro. Graph includes Rio Chilco reach and intersections of tributaries.



As was the case for the Rio Chilco, the amounts of fine-grained sediments in high and low-channel sediments differ. The average of the percent by weight for the silt-clay fraction is approximately 20% for high-channel sediments, and for low-channel sediments it was estimated at 12%. Only one high-channel sample contained a large amount of fine sediment (42%). The averages of organic matter content are similar for high and low-channel sediments and they are in the order of 2% (Table 2 and Appendix B).

Concentrations Associated with Tributary Channels

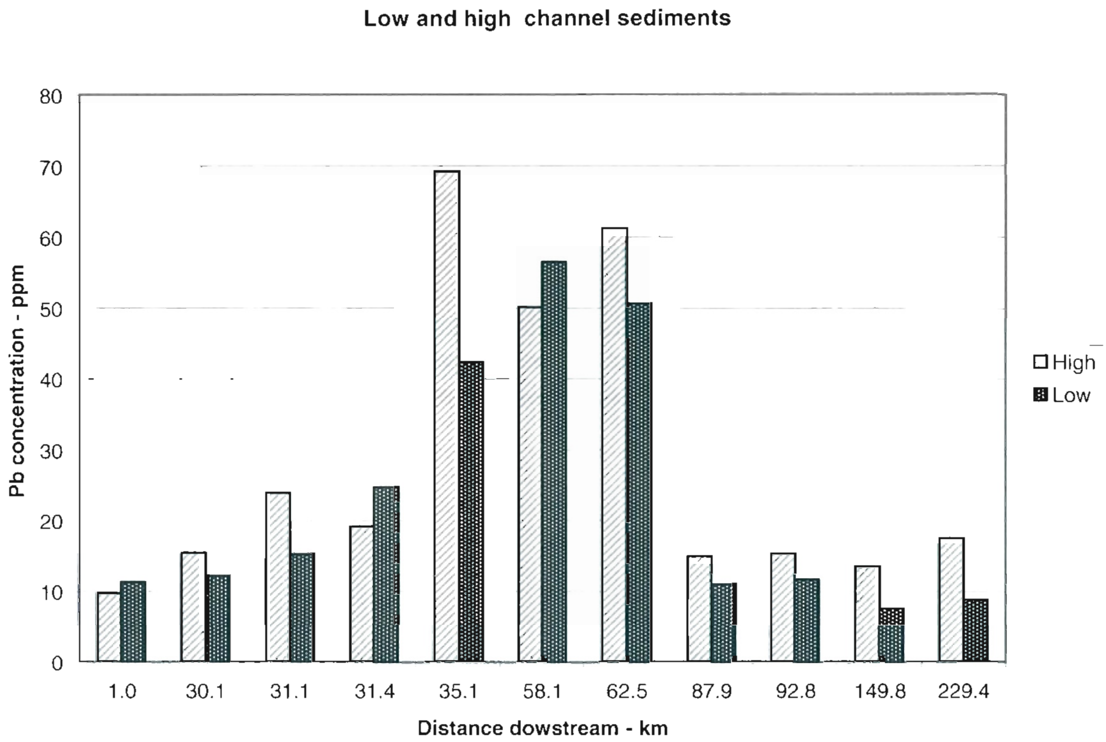
Within low-channel deposits, the highest concentrations of trace elements were commonly found in sediments located downstream of major tributaries known to possess active or historic mining operations. For example, zinc reached its highest concentrations along the Rio Tupiza downstream of the confluence with the Rio Tatasi, whereas antimony exhibited its highest concentration along the Rio Chilco immediately downstream of the drainage from the Abaróa mine site. In contrast, relatively low concentrations of lead and zinc were observed along the Rio Chilco and the Rio Tupiza – San Juan del Oro at sites well removed from tributary drainages with known mining activity (Fig. 8 and Appendix A and C).

Figure 9 compares metal concentrations in high and low-channel sediments. It illustrates that the downstream trends in trace element concentrations within low and high-channel deposits are not identical (also Appendix A). Trends upstream of the Rio Tatasi for both deposit types show minor variations in Pb and Zn; they are almost indistinguishable. In contrast, downstream from the Rio Tatasi, Pb concentrations tend to be higher in high water channel samples than within low-channel samples. Locally, Zn differences exceed twofold. Sb concentrations typically follow the same trend as Pb and Zn, except immediately downstream of the Chilcobija and Tatasi confluences.

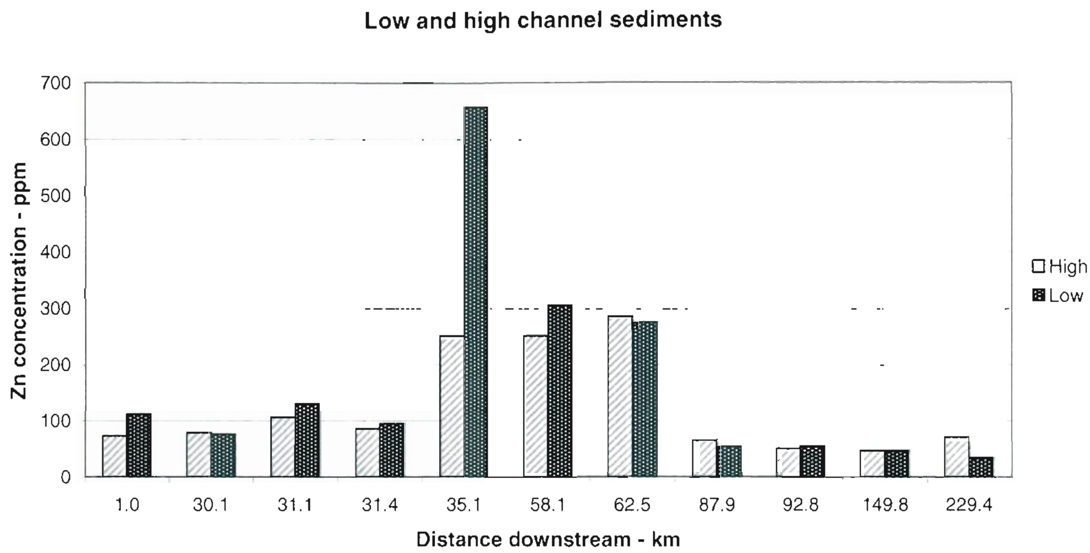
As noted earlier, Pb, Zn, and Sb concentrations from distal reaches of the Rio Chilco and Tupiza-San Juan del Oro and also from the tributary Rio Tres Palcas are similar to or close to the mean background values for those metals. Differences in the concentrations between the two deposit types are minor.

Figure 9. Heavy metal concentrations in high and low-channel sediments. Each pair of samples taken at the same sampling site. A) Pb, B) Zn, and C) Sb

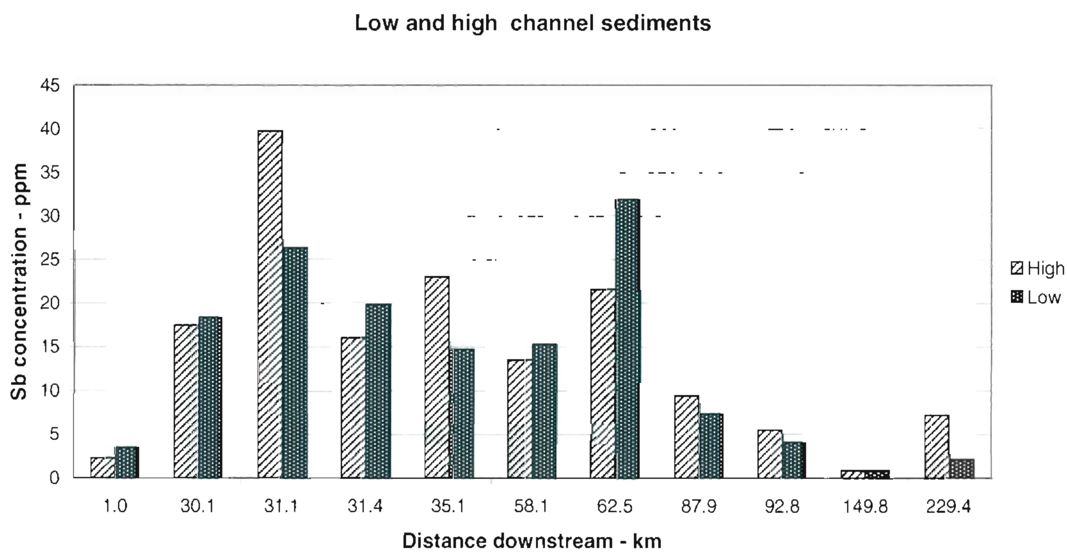
A)



B)


Low and high channel sediments
Zn concentration - ppm
700
600
500
400
300
200
100
0
1.0
30.1
31.1
31.4
35.1
58.1
62.5
87.9
92.8
149.8
229.4
Distance downstream - km
High
Low

C)


Low and high channel sediments
Sb concentration - ppm
45
40
35
30
25
20
15
10
5
0
1.0
30.1
31.1
31.4
35.1
58.1
62.5
87.9
92.8
149.8
229.4
Distance downstream - km
High
Low

Floodplain Deposits

Floodplain deposits are located intermittently along both sides of the Rio Tupiza – San Juan del Oro. Soils developed on these features are utilized for farming to grow host vegetables (e.g., corn and potatoes) and various fruits, both of which are sold in local communities (Fig. 10).

Figure 10. Farm fields developed on floodplain deposits. Rio San Juan del Oro is on the left; notice that floodplain surface is less than a meter above the channel bed.

In order to determine changes in metal concentrations as a function of depth within these fields, soil profiles were cored and subsampled over a depth of up to 1 m. Surface samples were also collected at 10, 35, and 50 m from the channel margins. For the purpose of understanding differences between metal concentrations in the channel and floodplain deposits, the surface and subsurface (core) samples were grouped together. With the exception of Sb, trace metal concentrations were higher in the floodplain deposits than in the channel bed materials (Table 6 and Appendix A). For example, the mean concentration of zinc within the floodplain deposits is higher than for any channel bed sample if the stream samples from the Abaróa valley are excluded ($p<0.05$). Similarly, Pb concentrations in the floodplain deposits are higher than within the channel bed deposits and the mine tailings at Abaróa and Chilcobija ($p<0.05$) summarized in Table 6. In contrast, the mean Sb concentration is threefold lower in the floodplain than in the channel and high-channel sediments (but higher than in the low-channel sediments). However, these contrasting results are not statistically significant.

Metal concentrations in soils developed on floodplains (FF-2 and FF-3) closest to the mines possessed values that exceed international guidelines. For example, Pb in the upper layers of the floodplain exceeds the Canadian guideline (200 ppm), while Zn is above all three guidelines values (Table 7). Sb is three times higher than the Canadian guideline value of 20 ppm. Floodplain deposits at FF-3 exhibited Pb concentrations of 326 ppm immediately below the ground surface, which exceed the Canadian guidelines (200 ppm). Zinc concentrations again exceed all three guideline values. In contrast,

Table 5. Summary of metal concentrations in floodplains and channel bed sediments. Units given in ppm.

	Pb	Zn	Sb
Floodplain deposits including vertical profile and surficial samples n=32			
Minimum	326.15	785.38	111.29
Minimum	12.27	52.64	4.62
Average	104.57	277.67	31.22
St. dev.	84.19	215.94	31.24
Normalized mean	230.3	654.9	76.4
Low water channel sediments n=18 Rio Chilco and Rio Tupiza - San Juan del Oro			
Minimum	135.96	689.30	31.83
Minimum	7.45	34.39	0.88
Average	31.57	211.35	12.71
St. dev.	31.42	204.75	9.67
Normalized mean	524.0	4142.5	572.6
Channel and high water channel sediments n=19 Rio Chilco and Rio Tupiza - San Juan del Oro without Abaroa Valley samples			
Minimum	206.15	458.51	1118.24
Minimum	9.70	46.68	0.88
Average	48.36	182.24	84.15
St. dev.	46.99	124.94	254.65
Normalized mean	264.0	1131.7	79.5
Terraces and alluvial fan sediments (background) n=7			
Minimum	11.27	60.72	2.37
Minimum	24.61	139.26	4.26
Average	16.46	86.93	3.37
St. dev.	4.75	25.18	0.63

concentrations of Pb, Zn, and Sb in the farthest downstream floodplain sampled are below the Canadian, German, and Dutch guidelines (Table 7).

Spatial Trends in Metal Concentrations within Floodplain Deposits

Floodplain sediments exhibited different spatial patterns in elemental concentrations between the sampled sites. The floodplain sampling site closest to the Abaróa mine is FF-1. Here the highest concentration of Zn (422 ppm) was found to be immediately adjacent to the channel; at 50 m from the channel the concentration had decreased to 266 ppm. Similar changes in Pb and Sb concentrations occur, decreasing with distance from the channel from 158 ppm to 65.9 ppm for Pb and 30.6 to 22.4 ppm for Sb. At site FF-2, spatial differences in Zn, Pb, and Sb concentrations observed between 10 and 50 m from the channel were negligible. At site FF-3, the highest concentrations in Zn, Pb, and Sb occurred at the sites farthest from the channel. Thus, on the sites separated 10 and 50 m from the channel, concentrations vary from 523 to 623 ppm for Zn, 93.8 to 241 ppm for Pb, and from 59.1 to 111 ppm for Sb (Fig. 11 and Appendix A).

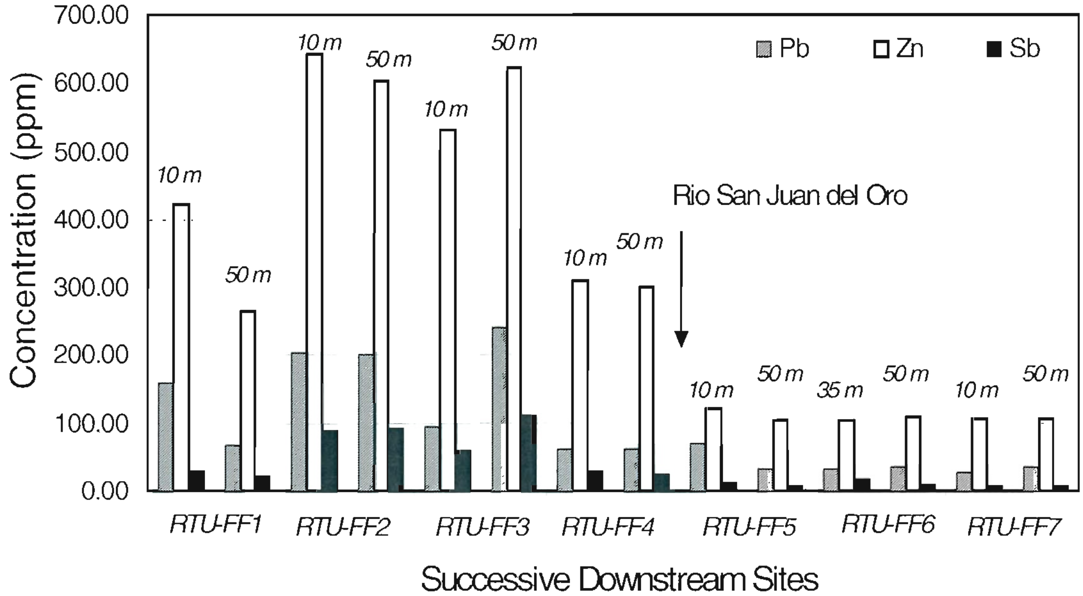
Floodplains located farther downstream exhibit similar and less variable concentrations across their surfaces. At sites downstream of FF-4, the difference in concentrations at 10 and 50 m from the channel for all the three elements is small, and there is no a systematic pattern. In addition, concentrations of Pb and Sb are lower than the other upstream floodplains and are similar to the range of local background values; only Zn concentrations are above background.

Table 6. Heavy metal concentrations in floodplain deposits. International guidelines for the same metals used to determine the degree of soil contamination. Units in parts per million (ppm). Bolded concentrations above the guidelines.

		Pb	Zn	Sb
Typical conc. (rocks)1				
1. Granite		17	50	0.2
2. Sandstone		7	16	0.4
3. Shales		20	95	1
Río Pilcomayo Basin		18	66	
Regional background		(6-34)	(17-132)	
Health guidelines				
Dutch		530	720	-
Action levels (2)				
Canada guidelines		200	400	20
Maximum limits (3)				
Germany		500	300	-
Maximum limits (3)				
RTUFF1-35	35 m adjacent to river	158.7	421.9	30.7
RTUFF1-50	50 m adjacent to river	65.9	266.6	22.4
RTU-FF2-10	10 m adjacent to river	202.8	643.4	88.5
RTU-FF2-50	50 m adjacent to river	199.8	602.5	92.2
RTU-FF2-CA	0 - 15 cm	231.2	750.7	94.3
RTU-FF2-CB	15 - 30 cm	117.6	380.9	46.2
RTU-FF2-CC	30 - 45 cm	83.0	288.0	30.3
RTU-FF2-CD	45 - 60 cm	95.5	264.4	19.2
RTU-FF2-CE	60 - 75 cm	201.1	247.8	20.2
RTU-FF2-CF	75 - 90 cm	260.2	264.1	23.3
RTU-FF2-CG	90 - 105 cm	204.5	193.3	17.3
RTU-FF2-CH	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-CA	0 - 15 cm	326.2	785.4	103.0
RTU-FF3-CB	15 - 30 cm	122.2	365.7	44.0
RTU-FF3-CC	30 - 45 cm	184.4	466.2	61.4
RTU-FF4-10	10 m adjacent to river	61.4	309.3	29.5
RTU-FF4-50	50 m adjacent to river	61.1	299.4	25.8
RTUFF5-10	10 m adjacent to river	69.7	120.6	13.4
RTUFF5-50	50 m adjacent to river	33.1	105.1	7.2
RTUFF5 - CA	0 - 10 cm	34.3	99.1	6.3
RTUFF5 - CB	10 - 20 cm	34.3	92.3	8.2
RTUFF5 - CC	20 - 30 cm	41.9	105.3	8.8
RTUFF5 - CD	30 - 50 cm	54.6	109.3	10.4
RTUFF5 - CE	50 - 70 cm	38.8	94.2	11.0
RTUFF5 - CF	70 - 95 cm	20.7	62.2	9.4
RTUFF5 - CG	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
RTUFF7-10	10 m adjacent to river	27.2	106.7	8.5
RTUFF7-50	50 m adjacent to river	34.8	105.8	7.4

(1) = From Turekian (1971) and Martin and Meybeck (1979)
(2) = From Kabata - Pendias (1995)
(3) = From MHSPE (2000)

Figure 11. Concentrations of heavy metals on floodplains. Surficial samples separated from the active channel.

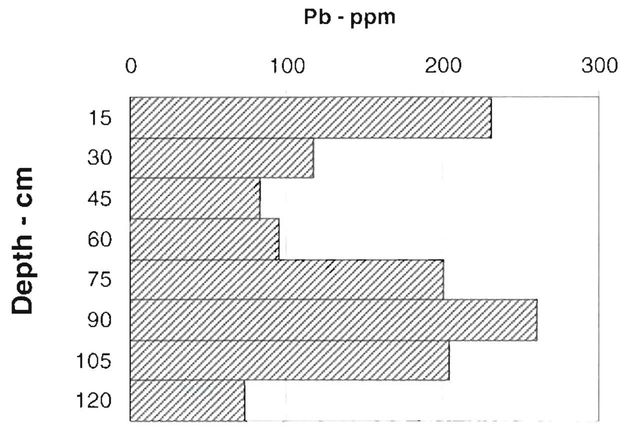


Vertical Profile Distribution of Heavy Metals in Floodplain Deposits

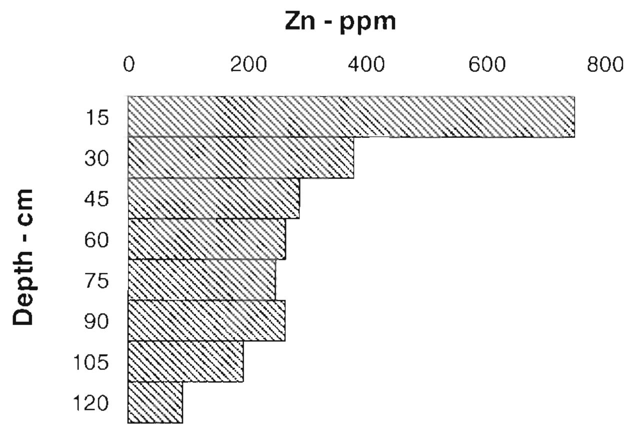
Data from the core at FF-2 illustrate that Pb exhibits a different vertical concentration pattern than Zn or Sb. In the case of Pb, the highest values are found at the surface and between 60 and 75 cm from the surface. Concentrations are the lowest at the base of the core. In terms of Zn and Sb, the highest concentrations are found at the surface, decrease to about one-half of the surface values between 15 and 30 cm, and then decrease again at the base of the core (Figs. 12 A, B, and C).

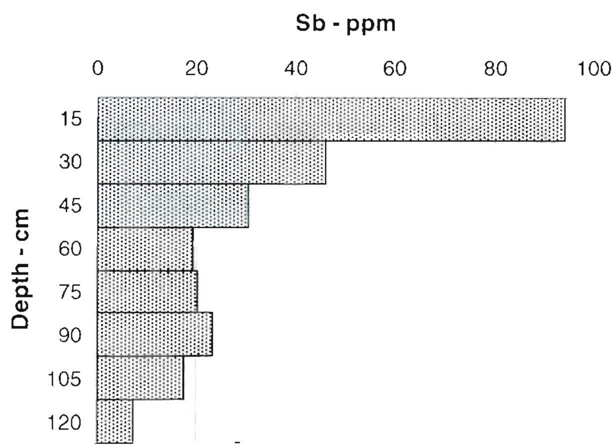
Figure 12. Heavy metal distribution for profile FF-2; total depth is 124 cm, the sampling interval is 15 cm. A) Pb, B) Zn, and C) Sb.

A)



B)





Pb concentrations are higher by more than ten times that of local background values. For instance, the first or surficial interval and three deep intervals from 60 to 105 cm exhibit Pb concentrations up to 200 ppm. Surficial Zn concentrations are eight times higher than the background value. The interval immediately below the surface is approximately four times higher, and the rest of core samples are at least double the background parameters. The lowest interval is comparable with the mean local background concentration. Sb concentrations in the surficial interval exceed background concentrations by approximately ten times; the interval below is four times higher and the other intervals are two times above the mean (except the last interval that is similar to the mean background value).

The sand and the fine-grained fraction are similar throughout the profile, although minor variations ranging from 52 to 70% do occur. Total organic matter contents are less variable; most intervals contain up to 5% (Appendix B).

At FF-3, Zn, Pb, and Sb show similar patterns to FF-2. The highest concentrations for all of these three elements were found at the surface, then decrease by approximately 50% (Figs. 13 A, B, and C). However, Pb, Zn, and Sb alongside the profile FF-3 exceed the background values. Pb concentration at the surficial interval (0-15 cm) is significantly higher than background concentrations. The second interval is also above the background parameter by fivefold and the deepest interval is seven times higher. Zn concentrations in the surficial interval exceed the background values by eightfold, whereas the intermediate interval is four times greater than background.

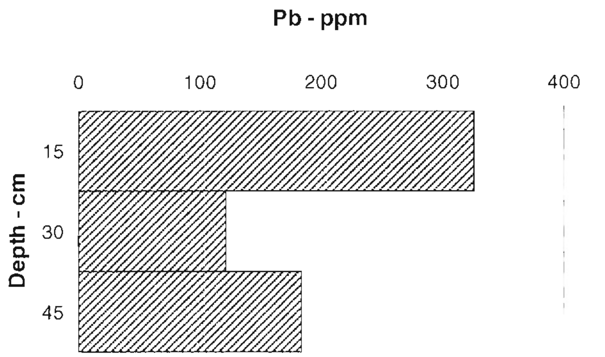
The core is composed of silt-clay and sand fractions in relatively similar amounts. The estimated average of the silt-clay fraction was 47%. Toward the bottom the coarse fraction percentage decreases to 26%. Organic matter contents are consistent in all of the intervals and the average is around 13% (Appendix B).

At FF-5, the most downstream site, the vertical distributions of Pb, Zn, and Sb follow a similar pattern, with slightly elevated concentrations at deep intervals. The highest concentrations of Pb and Zn were found between 20 and 50 cm depth, while the highest concentrations of Sb are in the interval from 30 to 70 cm. The lowest concentrations of Pb and Zn were found between 50 cm and the base of the core; in contrast, the lowest Sb concentrations are between the surface and 30 cm depth. However, the difference in concentrations in the whole core for all the three metals is small (Figs. 14 A, B, and C and Appendix A).

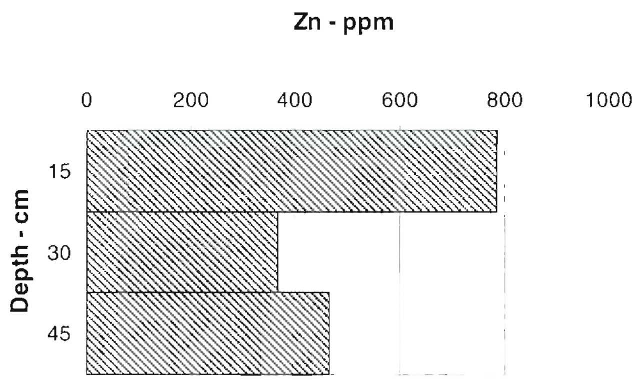
As was mentioned earlier, the farthest floodplains from the mines contain metals in lower concentrations and comparable to background values. The highest concentrations of Pb exceed the maximum concentrations measured in background deposits. The rest of the samples exhibit concentrations close to the mean background value (16.06 ppm). Zn does not show a clear difference among depth intervals; from the surface to 70 cm the contents are similar to the mean background (84.38 ppm). Only between 70 and 124 cm (the bottom of the profile) are concentrations lower than the mean value. The lowest concentration at the surface is lower than the mean background value; contents in the other intervals toward the base of the core are quite similar to the

Figure 13. Metal concentrations along the vertical profile at FF-3. Total depth is 45 cm, sampling interval is 15 cm; A) Pb, B) Zn, and C) Sb.

A)



B)



C)

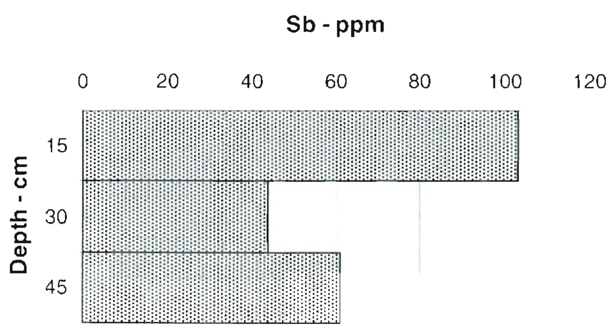
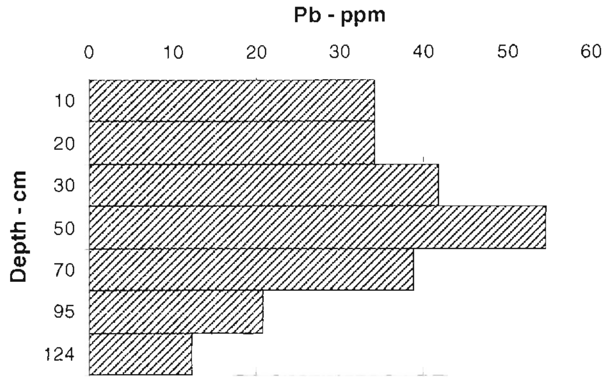
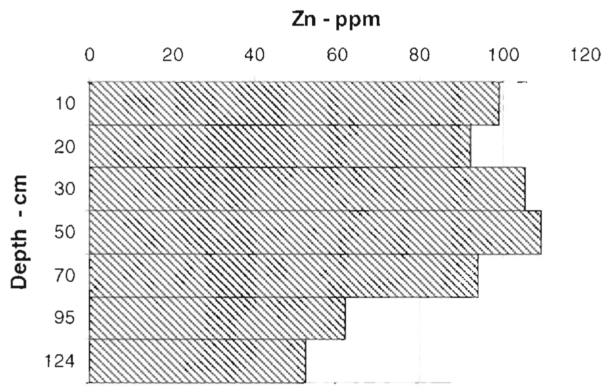


Figure 14. Heavy metal concentrations in floodplain sediments at site FF-5. Total depth is 124 cm, sampling interval is 10 cm; A) Pb, B) Zn, and C) Sb.

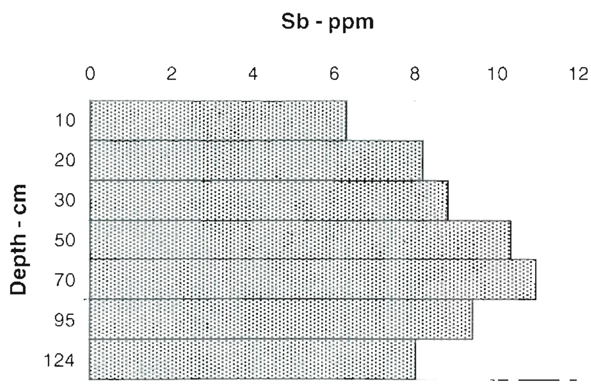
A)



B)



C)



mean background concentration. Therefore, metal concentrations in the farthest floodplains are the lowest and comparable to local background parameters.

For most intervals, the obtained percentage of the silt-clay fraction is above 50% and the maximum is 62%. The mean total organic matter content is approximately 8%. The first two intervals below the ground surface, however, contain 10% and 14% of organic matter, respectively (Appendix B).

Discussion

Downstream Trends in Elemental Concentrations

The accumulation of trace metals bound to particulate matter within the Rio Tupiza drainage system is related to two different process: (1) the slow continuous accumulation of contaminated sediments from mining operations over periods of years to decades, and (2) the rapid erosion, transport, and deposition of tailings materials during dam failures or intense rainfall-runoff events, such as that which occurred in February 2003.

A common approach to deciphering the sources of trace elements in alluvial deposits is through an examination of the spatial variations in their concentrations. Within the Rio Tupiza-San Juan del Oro basin, Sb, Pb, and Zn concentrations follow a general downstream decreasing trend. Regardless of whether the sediment was derived from a tailings dam failure or through accumulation of material over long periods of time, there is a general downstream decrease in metal concentrations. However, along this river, there are reaches that exhibit systematic variations in metal values, which are superimposed on the overall trend. These localized trends provide important clues to the primary sources of the trace metals.

Downstream increases occur in Sb concentrations along the Rio Chilco at its confluence with both the Abaróa Valley and the Rio Chilcobija (Fig. 7) suggesting that Sb is entering the river from the two Sb mines. This is supported by Sb concentrations that are well above background values. The elevated concentrations of Pb and Zn and their geographical pattern within the Abaróa Valley illustrate that the Abaróa Mine contributes other metals to the Rio Chilco as well (Fig. 7). However, the minimal changes in their concentrations from up- to downstream along the Rio Abaróa-Rio Chilco system that the impacts of the Abaróa Mine upon modern channel bed sediment quality is spatially limited to <30 km. The same is true for the Chilcobija Mine.

The minimal change in Pb and Zn concentrations within the Rio Chilco is presumably related to the size of the Rio Chilco. The Rio Chilco transports significantly larger volumes of clean sediments downstream due to its much larger size in comparison to the Abaróa drainage system. Thus, the mixing of clean sediments with contaminated sediments from the Abaróa Valley results in the dilution of metal concentrations, unless there is a significant influx of contaminated materials (as is apparently the case for Sb).

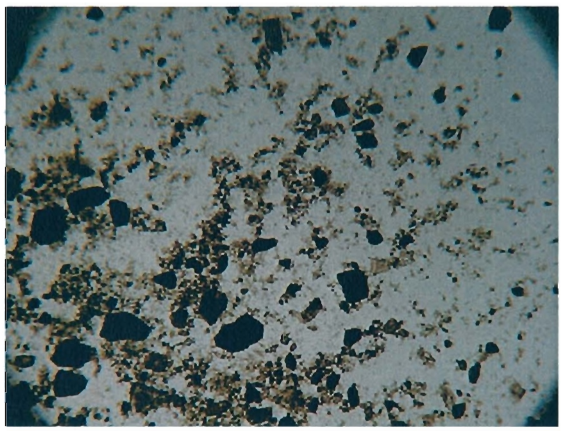
All three trace elements (Zn, Pb, and Sb) increase downstream of the Rio Tatasi. Given the relatively high concentrations of the elements measured in the bed sediments of the Rio Tatasi, the old polymetallic mines containing minerals of lead, zinc, silver, and tin appear to be a major source of trace metals in the Rio Tupiza valley. It is important to note, however, that the Rio Tatasi is a much more important source for Pb and Zn than Sb; changes in Sb concentration in channel bed sediments from up - to downstream of the Tatasi confluence are minimal.

Downstream of the major trace element sources, concentrations of the metals tend to decrease. For example, concentrations along the river within the Abaróa Valley decrease rapidly downstream along with the abundance of sulfide minerals (Fig. 15 A, B, C). These decreases in concentration are generally attributed to four factors: hydraulic sorting, chemical sorption-desorption processes, mixing processes and floodplain deposition, and storage. The particularly narrow geometry and length of the valley combined with the scarce development of floodplain and channel bed deposits suggest that the decreasing concentrations of the heavy metals are likely to be controlled by hydraulic sorting. This is supported by the percent of sulfides microscopically identified within the alluvial sediments and by a significant reduction in the silt and clay fraction from 52 to 26%. Organic matter contents are similar for this reach and vary from 4 to 5 % and are unlikely to influence metal concentrations. Therefore, the reduction in concentration is apparently related to a reduction in the quantities of silt and clay and to the concentration of heavy minerals close to the mine site.

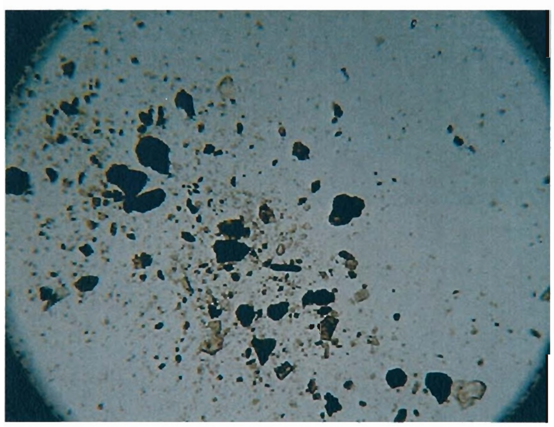
Pb, Zn, and Sb concentrations decrease downstream from major sources of metal inputs (i.e., the Abaróa, Chilcobija, and Tatasi basins) along the Rio Chilco-Rio Tupiza-San Juan del Oro system. In fact, along the Rio Tupiza – San Juan del Oro, trace metal concentrations decreased to the range of background levels (Fig. 8, Table 4). This behavior is due to the increasing volumes of clean sediments supplied to the river, which allows dilution to occur. The variations in trace element concentrations may result from the remobilization of sediments by erosion of contaminated floodplain sediments. Another factor that might be controlling the decline of metal concentrations is that

Figure 15 . Microphotographs of the Abaróa tailings and adjacent sediments. Note the difference in abundance and size of sulfides. Opaque minerals (black in the pictures) correspond to sulfide minerals: A) from eroded tailing; B) upstream channel sediments close to the tailings piles, and C) downstream channel sediments located close to the mouth of the Abaróa Valley.

A)



B)



C)

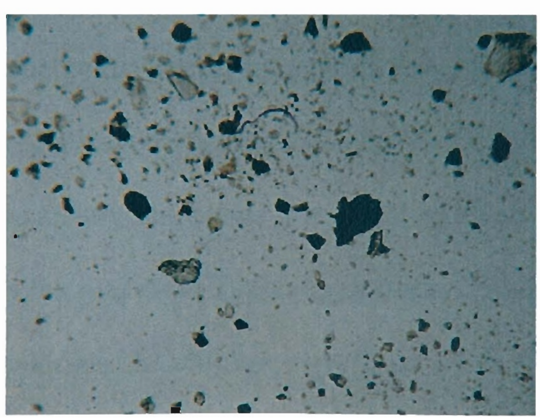


Figure 16. Bridge in the head waters of Rio Tupiza. In the past a road passed beneath the bridge, but due to channel bed aggradation, the bridge is only about 1.5 m above the river.

channels are currently undergoing significant aggradational processes. This is illustrated by the increased amount of sediments accumulated below the railroad bridge at the headwaters of Rio Tupiza and by statements from local residents. The local residents noted that in recent years the road from Tupiza to upstream villages was frequently buried by bed channel materials. In addition, significant effort is now required to remove sediments from beneath the railroad bridges to prevent their burial (Fig. 16).

Grain size analysis suggests that there is a relationship between metal concentration and silt-clay contents. The highest concentration in Pb, Zn, and Sb for the sample immediately downstream of the intersection between Rio Chilco and Abaróa Valley exhibits 42% fine grain sediment, while the lower concentrations downstream contain less than 10% fine sediment. Apparently the active phase is the silt-clay fraction and as such the metal contents are associated with it. The total organic matter contents are similar and appear to have little influence on metal concentrations; thus the concentrations appear to be more directly related to sediment size than to the total organic contents, correlation coefficients are more highly related to the grain size and lesser to total organic content.

The amount of fine sediment in high and low-channel deposits are similar downstream of the Rio Tupiza – San Juan del Oro. Therefore, the influence or control in metal concentrations in sediments does not adequately explain the variability in downstream metal concentrations in channel bed sediments. The minimal influence of grain size suggests that other factors control the downstream metal distribution.

Correlation coefficients corroborate the relationship and distribution of metals. Pearson product momentum coefficients were calculated between metals and the percent of fine grain size sediment and total organic content for the gathered channel and high-channel sediments of Rios Chilco and Tupiza – San Juan del Oro. The higher correlations are for Zn, Pb, Sb, and weak correlations are recognized for the group Pb, Sb, and silt-clay fraction. Organic matter and Pb, Zn, Sb are not correlated (Table 7).

The strong correlations between the specified trace metals suggest that: (1) metals were released from common sources and may originate from mineralized structures, and (2) their spatial and temporal distribution within fluvial sediments is a consequence of similar mechanisms associated with geomorphic events or the history of the fluvial system.

Table 7: Pearson product-moment correlation coefficients between heavy metals, including for silt-clay fraction and total organic content (TOC) in channel and high-channel sediments from Rio Chilco and Rio Tupiza – San Juan del Oro (n=19).

	Zn	*Pb*	*Sb*	*TOC*	*Silt-clay*
Zn	1				
Pb	0.91*	1			
Sb	0.61*	0.85*	1		
TOC	0.11	0.07	0.04	1	
Silt-clay	0.27*	0.49*	0.58*	-0.09	1

* Significant correlations ($p<0.05$)

Downstream Variations within Floodplain Deposits

The concentrations of trace metals within floodplain deposits decrease. The highest concentrations for Pb, Zn, and Sb were measured in the upper 15 cm of cores from the sites located closest to the mines along the upstream drainages. In addition, the floodplains sampled farthest downstream contained ten times lower metal concentrations than those upstream. It is likely that these differences in concentration are related to the influx of metals from mining operations (Fig. 11).

At most floodplain sampling locations, including FF-2, FF-3, and FF-5, the highest concentrations of Pb, Zn, and Sb were found within the first 15 cm of the ground surface. Concentrations below the surface were highly variable, though for sites FF-2 and FF-5, concentrations generally reached their lowest values at the base of the cores. This spatial pattern suggests that sediments contaminated by Pb, Zn, and Sb have been deposited on the floodplain surface through time. Unfortunately, the precise age of the deposits could not be determined. Nonetheless, farming on the fields is known to have occurred during the past several decades without significant aggradation on them. Thus, the accumulation of the contaminated sediments is thought to have occurred over periods of decades. Given the relatively high concentrations found in the deposits in comparison to background values, the metals are probably associated with early periods of mining, particularly periods when mining operations were more significant than at present. The high concentrations of Pb and Zn within the floodplain deposits suggest that the influx of metals from the polymetallic Tatasi – Portugalete mining district is particularly important during the past decade.

The metal concentrations within floodplains are significantly higher than those observed within the adjacent low- and high-channel deposits. For example, trace metal concentrations within channel sediments adjacent to floodplain sampling sites RTU-FF-1, RTU-FF-2, and RTU-FF-3 are significantly lower than within the floodplain. Thus, it seems likely that the elevated levels of the metals on the floodplains are a consequence of the deposition of fine-grained suspended sediments during overbank flooding in the wet season. This is supported by significant differences in the percentage of fine-grained sediment between these two deposit types. The fine fraction 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, respectively. In addition, organic matter contents in floodplains are significantly higher than in channel sediments. In the latter, the average organic carbon content is about 2% and for floodplains it ranges from 7 to 12%.

In most of the floodplains where farm fields are located the upper soil horizon is removed and influences the metal concentrations in that layer. As part of agricultural labors, the soil horizon from surface to twenty centimeters depth is mixed in order to break the dried clumps of sediments. Fertilizers, either chemical or natural, are also added at the time of planting. Therefore, it is possible that increases in metal concentrations are also associated with these agricultural activities.

Impact of the February 2003 Dam Failure on Trace Element Concentrations

The primary effect of the sudden dam failure of the Abaróa tailings pile was the transport and deposition of sediment-bound metals along the Abaróa Valley and subsequently to the Rio Chilco. The highest concentrations of Pb, Zn, and Sb in channel sediments correspond to sediments deposited along the Abaróa Valley and hundreds of meters downstream of the junction with Rio Chilco. Upon entering the Rio Chilco concentrations of heavy metals were diluted and decreased downstream until reaching background concentrations. Only the Abaróa channel contains small volumes of sediments with significant metal contents. This localized storage of metals results in reduced potential risks to exposure by living organisms.

The remobilization of sediment-bound metals from the tailings dam may have increased the concentrations of heavy metals in channel sediments. That is, the metal concentrations in sediments of Abaróa Valley and part of the Rio Chilco may have been lower before the dam failure.

The morphology of the valley and other features, including the old tailings, was not changed as a consequence of the dam failure. It is evident that the channel was not modified from its original configuration, probably because the channel was developed in bedrock. Other structures such as the old tailings and small terraces immediately downstream remain along the Abaróa Valley. The estimated volume of contaminated mill tailings removed is approximately 8,870 metric tons.

Potential Health Effects of Trace Metal Contamination

In riverine communities, the primary pathways of metal accumulation in humans is through the ingestion of contaminated drinking water, vegetables, fruits, fish, and soil both from hand-to-mouth contact and through the ingestion of soil particles clinging to unwashed food (Miller et al., 2003). The obtained metal concentrations in soils are slightly above the international guidelines. Based on this first approach, it is possible to assume that the soils are polluted (i.e., they pose a threat to human health). But in order to know in more detail the potential risks for human health and environment, it is necessary carrying out further investigation considering the other components mentioned.

Moreover, it is important to recognize that crops grown on contaminated soils may not necessarily accumulate toxic metals. For example, Miller et al. (2003) determined that metal concentrations for crops grown on contaminated soils within the upper reaches of the Rio Pilcomayo are low. They also pointed out that most vegetables did not contain significant quantities of heavy metals. The authors expected enrichment in Zn and Cd in vegetables due to the soils contaminated with these metals. Pb is considered to pose the most risk to consumers because it exceeds the minimum recommended guideline in commercially grown vegetables including lettuce, onions, and carrots.

Studies of heavy metal contamination in vegetables must consider numerous factors that affect metal uptake from polluted soils. These parameters include total amount of metal in the soil, the source and speciation of the soil metals, 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 (translocated) during growth (Haghiri, 1973, 1974; Abdel-Sabour et al., 1988; Ward and Savage, 1994; Vousta et al., 1996; Albering et al., 1999; Miller et al., 2003)

By analogy the polluted soils along the Rio Tupiza- San Juan del Oro have the following characteristics: (1) the highest concentrations of metals are in non-bioavailable forms within the soils, (2) metal concentrations are slightly above the guidelines for cultivated soils, (3) a complete assessment must consider the physical-chemical characteristics of the soils, (4) in the case of the Rio Pilcomayo, some crops were irrigated with contaminated waters, and (5) the most significant exposure pathway might be the ingestion of contaminated soil particles clinging to the surface or in leaves of the produce. A reduction in risk is possible through washing or peeling the vegetables prior to consumption (Miller et al., 2003).

Conclusions

The Abaróa -Tupiza basin located in southern Bolivia is surrounded by antimony and polymetallic deposits associated with the antimony and tin belts. These belts contain ores that differ genetically as well as in mineralogy and age. Each of these deposits has a different history with respect to the size, beneficiation techniques, minerals extracted, and the quantities of mine waste produced. It is known that the Tatasi – Portugalete mining district has been mined extensively and this is reflected in the amount of tailings produced, which are distributed nearby or in the headwaters of the Tatasi Basin. Similarly, Chilcobija is the largest antimony mine in Bolivia and tailings were disposed of in natural depressions around the mine area. In contrast, the Abaróa Mine is a small current operation for extraction of antimony; its tailings are disposed of with a small tributary to the Abaróa Valley.

Heavy metals released within the Abaróa Mine tailings are highly concentrated downstream from the source; however, they decrease rapidly in concentration downstream. High concentrations of Sb are the most persistent along the channel, while the reduction in Zn and Pb concentrations is by at least 50% by the time that the sediments reach the Rio Chilco. Downstream a decrease in metal concentrations occurs presumably as a result of the mixing with clean sediments and storage within the channel bed. Metal concentrations ultimately reach levels comparable to the local background. This effect is noticeable even between samples separated by less than a kilometer. The trend of gradually decreasing metal concentration within channel sediments is disrupted by the addition of sediments with high Pb and Zn concentrations from tributaries. Starting at the confluence between the drainage from a polymetallic Tatasi – Portugalete district and Rio Chilco, metal contents are greater than the previous section of the river and again the gradual drop of contents is observed downstream at least 150 km away from the last sampling site. The highest concentrations were found in high-channel deposits and appear to be influenced by the amount of silt-clay in these sediments.

Farm fields on the floodplain of the Rio Tupiza show different vertical and horizontal patterns in metal concentrations. Deposits close to the metal sources exhibit greater metal concentrations and accumulate more sediment-bound metals than fields farther downstream. Metals accumulated in the surface or upper soil horizons exhibit higher metal values. Nevertheless, a second zone of high Pb, Zn, and Sb concentrations exists at depth. These spatial trends have been interpreted to indicate that the region has a long history of metal influx to the rivers, and that the introduction of metals to the river has varied through time. In addition, the erosion of floodplain and terrace deposits may reintroduce metals to the river during future floods.

Comparison of metal concentrations between the channel bed sediments and the floodplain deposits illustrates that the floodplains exhibit higher metal values. These differences in concentration and metal storage appear to be related to the grain size characteristics of the deposits. The floodplains possess greater quantities of chemically reactive, fine-grained sediment than the channel bed materials (approximately 50% as compared to 15%). In addition, the difference in total organic contents might enhance the metal contents in floodplains; this is supported by the low percentage in channel sediments (2%) as opposed to approximately 10% in floodplain deposits.

Metal concentrations in soils developed on floodplains closest to the mines (FF-2 and FF-3) possessed values that exceed international guidelines. In contrast, concentrations of Pb, Zn, and Sb in the farthest downstream floodplain sampled are below the Canadian, German, and Dutch guidelines. These data suggest that additional work is needed to determine if the contaminated floodplains soils pose a local health threat.

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Appendices

Appendix A.

Analytical results for all collected sediments

Sample	Type	Pb (ppm)	Zn (ppm)	Sb (ppm)
Abaróa Valley				
AM-C1	Channel	610.87	1515.43	1089.83
AM-C2	Channel	536.91	1359.79	1575.86
AM-C4	Channel	330.53	587.35	1060.08
AM-C5	Channel	455.69	1092.77	1681.06
AM-C6	Channel	396.30	972.65	1531.10
Rio Chilco				
RC-C1	Channel	86.44	367.62	213.60
RC-C2	Channel	206.15	458.51	1118.24
RC-HC3	High channel	9.70	73.58	2.28
RC-HC5	High channel	19.11	85.65	16.03
RC-HC6	High channel	23.88	106.66	39.75
RC-HC7	High channel	15.41	79.17	17.46
RC-LC3	Low channel	11.25	112.34	3.45
RC-LC5	Low channel	24.69	95.06	19.78
RC-LC6	Low channel	15.21	130.46	26.28
RC-LC7	Low channel	12.13	76.20	18.34
RCT-1A	Terrace	17.11	91.06	4.26
RCT-1B	Terrace	14.16	84.36	3.82
RCT-1C	Terrace	11.27	60.72	3.27
RC-PB1	Point bar	43.21	193.18	93.28
RC-PB2	Point bar	27.83	113.95	83.31
RC-SL1A	Slack water	11.28	63.62	6.00
RC-SL1B	Slack water	9.69	55.57	1.71
RC-SLIC	Slack water	11.19	56.60	4.04

Appendix A Continued

Sample	Type	Pb (ppm)	Zn (ppm)	Sb (ppm)
Chilcobija tributary				
RCB-HC1	High channel	11.69	82.08	26.46
RCB-LC1	Low channel	12.52	84.11	16.94
Rio Tatasi				
RTA-HC1	High channel	83.25	343.56	23.44
RTA-LC1	Low channel	135.96	335.96	29.71
Rio Tres Palcas				
RTTP-HC1	High channel	29.64	155.04	14.40
RTTP-LC1	Low channel	12.61	75.66	4.45
Rio Tupiza - San Juan del Oro				
RTU-HC1	High channel	64.90	188.94	11.16
RTU-HC2	High channel	82.60	300.67	17.76
RTU-HC3	High channel	69.17	250.64	22.99
RTU-HC3B	High channel	14.86	66.01	9.42
RTU-HC5	High channel	50.13	250.86	13.49
RTU-HC6	High channel	61.20	286.28	21.58
RTU-HC7	High channel	15.30	51.11	5.51
RTU-TunnelC	Channel	44.48	198.68	17.21
RSJO-HC1	High channel	13.45	46.68	0.88
RSJO-HC2	High channel	17.45	70.88	7.24
Rio Tupiza – San Juan del Oro				
RTU-LC1	Low channel	55.40	436.02	10.08
RTU-LC2	Low channel	40.24	689.30	7.45

Appendix A Continued

Sample	Type	Pb (ppm)	Zn (ppm)	Sb (ppm)
RTU-LC3	Low channel	42.36	657.21	14.67
RTU-LC3B	Low channel	10.93	54.09	7.30
RTU-LC4	Low channel	43.90	250.81	13.37
RTU-LC5	Low channel	56.47	305.78	15.27
RTU-LC6	Low channel	50.59	274.79	31.83
RTU-LC7	Low channel	11.69	55.11	4.06
RSJO-LC1	Low channel	7.45	46.28	0.88
RSJO-LC2	Low channel	8.72	34.39	2.10
RTU-QF1	All. Fan	11.64	71.90	2.97
RTU-QF2	All. Fan	16.34	75.65	3.77
RTU-QF3	All. Fan	24.61	139.26	3.11
RTU-QF4	All. Fan	48.67	173.38	43.09
RTU-QF5	All. Fan	41.23	145.64	232.55
RTU-QF-6	All. Fan	20.08	85.52	2.37
RTUFF1-35	Floodplain	158.73	421.94	30.67
RTUFF1-50	Floodplain	65.93	266.59	22.43
RTU-FF2-10	Floodplain	202.83	643.39	88.50
RTU-FF2-50	Floodplain	199.83	602.46	92.15
RTU-FF2-CA	Floodplain	231.23	750.72	94.32
RTU-FF2-CB	Floodplain	117.59	380.94	46.16
RTU-FF2-CC	Floodplain	83.02	288.05	30.33
RTU-FF2-CD	Floodplain	95.46	264.37	19.18
RTU-FF2-CE	Floodplain	201.08	247.81	20.20
RTU-FF2-CF	Floodplain	260.25	264.05	23.34
RTU-FF2-CG	Floodplain	204.47	193.26	17.33
RTU-FF2-CH	Floodplain	73.48	93.41	7.18
RTU-FF3-10	Floodplain	93.80	532.38	59.08
RTU-FF3-50	Floodplain	241.15	623.07	111.29

Appendix A Continued

Sample	Type	Pb (ppm)	Zn (ppm)	Sb (ppm)
RTU-FF3-CA	Floodplain	326.15	785.38	102.97
RTU-FF3-CB	Floodplain	122.15	365.74	44.02
RTU-FF3-CC	Floodplain	184.40	466.24	61.36
RTU-FF4-10	Floodplain	61.39	309.35	29.51
RTU-FF4-50	Floodplain	61.07	299.39	25.79
RTUFF5-10	Floodplain	69.72	120.58	13.36
RTUFF5-50	Floodplain	33.07	105.14	7.15
Rio Tupiza – San Juan del Oro				
RTUFF5 – CA	Floodplain	34.29	99.13	6.33
RTUFF5 – CB	Floodplain	34.32	92.26	8.19
RTUFF5 – CC	Floodplain	41.87	105.33	8.81
RTUFF5 – CD	Floodplain	54.63	109.33	10.35
RTUFF5 – CE	Floodplain	38.80	94.25	10.97
RTUFF5 – CF	Floodplain	20.75	62.24	9.40
RTUFF5 – CG	Floodplain	12.27	52.64	8.03
RTU-FF6-10	Floodplain	32.93	103.86	16.57
RTU-FF6-50	Floodplain	34.76	108.41	11.09
RTUFF7-10	Floodplain	27.21	106.69	8.50
RTUFF7-50	Floodplain	34.82	105.80	7.45
RC-FP5	Floodplain	34.75	84.37	7.93
RTU-FP4	Floodplain	154.02	505.18	28.05
RSJO-FP2	Floodplain	17.57	64.67	4.62
Abaróa Mine fresh tailings				
AC-T1	Tailing	77.46	131.49	1092.84
AC-T2	Tailing	114.25	279.33	1150.02
AC-T3	Tailing	63.41	239.25	1125.56
Abaróa Mine old tailings				
AM-T1	Tailing	13.23	66.58	15.48
AM-TO1	Tailing	32.96	103.17	1961.39

Appendix A Continued

Sample	Type	Pb (ppm)	Zn (ppm)	Sb (ppm)
AM-TO2	Tailing	118.35	69.25	1360.08
AM-TO3	Tailing	20.89	75.09	2821.03
Chilcobija Mine new tailings				
CM-T1	Tailing	179.84	72.98	2503.41
CM-T1B	Tailing	146.42	107.64	1189.09
Chilcobija Mine old tailings				
CM-T2A	Tailing	25.22	131.03	388.66
CM-T2B	Tailing	20.88	99.19	310.85

Appendix B.

Loss on Ignition and wet sieving results for all collected samples

Sample	Type	Silt- clay %	Total Organic Content (%)
Abaróa Valley			
AM-C1	Channel	52.80	4.14
AM-C2	Channel	51.82	4.38
AM-C4	Channel	35.34	5.33
AM-C5	Channel	25.73	5.83
AM-C6	Channel	26.21	4.67
Rio Chilco			
RC-C1	Channel	5.25	2.96
RC-C2	Channel	42.53	2.53
RC-HC3	High channel	8.97	1.44
RC-HC5	High channel	6.32	1.29
RC-HC6	High channel	18.10	1.78
RC-HC7	High channel	8.25	7.00
RC-LC3	Low channel	3.55	2.62
RC-LC5	Low channel	4.45	2.44
RC-LC6	Low channel	0.42	3.06
RC-LC7	Low channel	1.20	1.71
RCT-1A	Terrace	33.01	6.05
RCT-1B	Terrace	28.99	5.74
RCT-1C	Terrace	33.95	3.44
RC-PB1	Point bar	5.81	2.50
RC-PB2	Point bar	23.27	2.69
RC-SL1A	Slack water	6.07	2.10
RC-SL1B	Slack water	25.34	2.58
RC-SLIC	Slack water	9.83	2.98
Chilcobija tributary			
RCB-HC1	High channel	11.68	2.26
RCB-LC1	Low channel	5.87	1.35
Rio Tatasi			
RTA-HC1	High channel	12.33	2.48
RTA-LC1	Low channel	6.20	1.68
Rio Tres Palcas			
RTTP-HC1	High channel	15.30	3.01
RTTP-LC1	Low channel	10.92	2.77

Appendix B Continued

Sample	Type	Silt- clay %	Total Organic Content (%)
Rio Tupiza - San Juan del Oro			
RTU-HC1	High channel	N/A	N/A
RTU-HC2	High channel	20.47	2.67
RTU-HC3	High channel	N/A	N/A
RTU-HC3B	High channel	16.76	0.72
RTU-HC5	High channel	13.19	2.38
RTU-HC6	High channel	18.10	1.78
RTU-HC7	High channel	13.55	1.86
RTU-TunnelC	Channel	7.19	3.63
RSJO-HC1	High channel	9.48	1.37
RSJO-HC2	High channel	42.15	2.59
Rio Tupiza - San Juan del Oro			
RTU-LC1	Low channel	15.54	2.56
RTU-LC2	Low channel	12.66	2.17
RTU-LC3	Low channel	10.26	2.19
RTU-LC3B	Low channel	13.46	1.44
RTU-LC4	Low channel	10.34	2.22
RTU-LC5	Low channel	11.10	2.71
RTU-LC6	Low channel	8.32	2.49
RTU-LC7	Low channel	16.96	1.55
RSJO-LC1	Low channel	5.50	1.28
RSJO-LC2	Low channel	15.41	3.00
RTU-QF1	All. Fan	2.25	1.39
RTU-QF2	All. Fan	4.47	2.30
RTU-QF3	All. Fan	4.20	3.08
RTU-QF4	All. Fan	13.39	2.36
RTU-QF5	All. Fan	10.57	2.97
RTU-QF-6	All. Fan	5.69	3.43
RTUFF1-35	Floodplain	6.15	59.26
RTUFF1-50	Floodplain	4.71	49.72
RTU-FF2-10	Floodplain	9.03	44.61
RTU-FF2-50	Floodplain	8.68	26.73
RTU-FF2-CA	Floodplain	8.00	59.71
RTU-FF2-CB	Floodplain	7.18	57.67
RTU-FF2-CC	Floodplain	6.91	71.29
RTU-FF2-CD	Floodplain	7.78	72.91
RTU-FF2-CE	Floodplain	6.77	60.20
RTU-FF2-CF	Floodplain	6.49	73.31
RTU-FF2-CG	Floodplain	6.16	62.46

Appendix B Continued

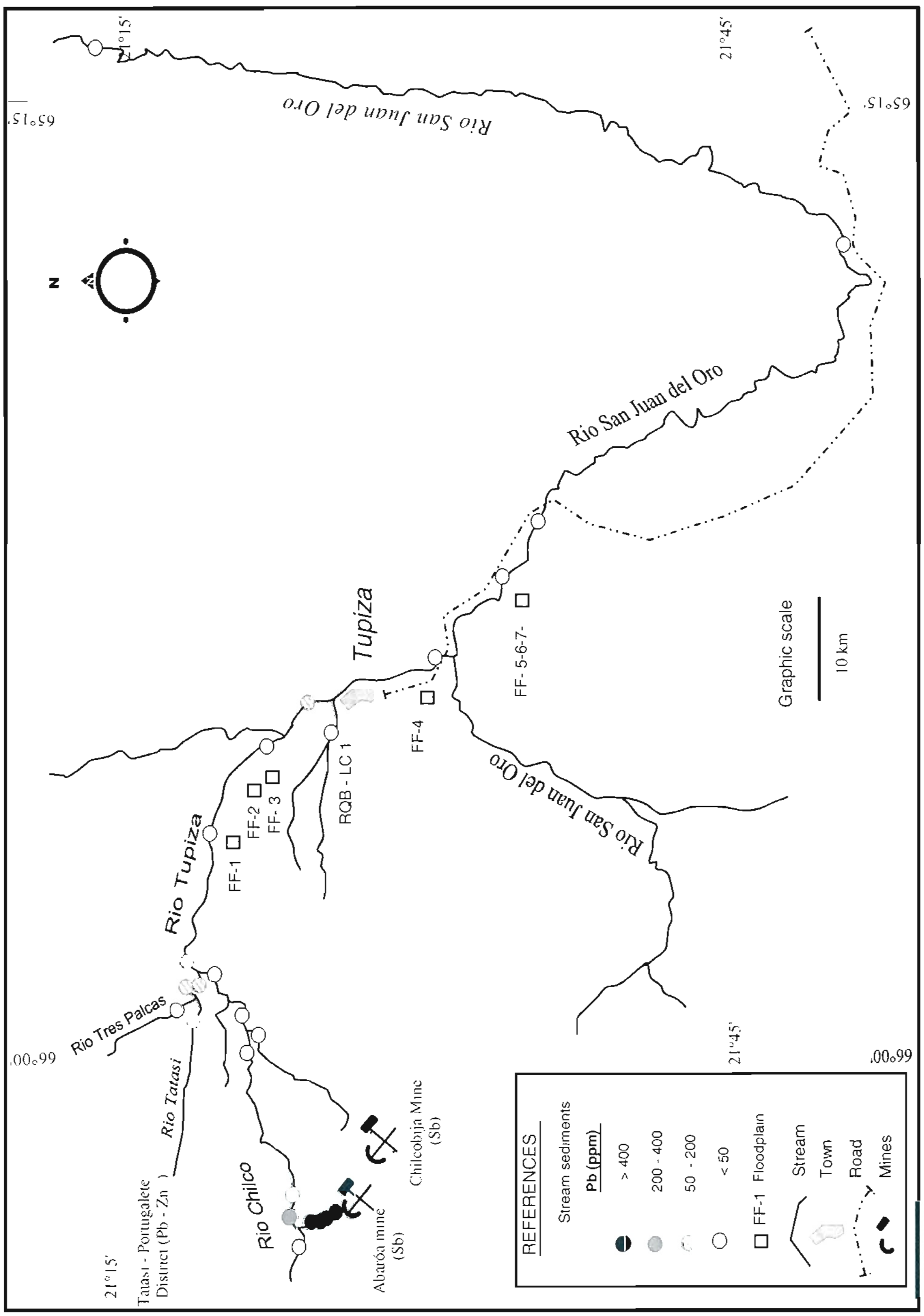
Sample	Type	Silt- clay %	Total Organic Content (%)
RTU-FF2-CH	Floodplain	5.52	42.57
RTU-FF3-10	Floodplain	13.76	43.35
RTU-FF3-50	Floodplain	13.97	67.91
RTU-FF3-CA	Floodplain	12.97	55.69
RTU-FF3-CB	Floodplain	13.77	43.65
RTU-FF3-CC	Floodplain	8.83	26.15
RTU-FF4-10	Floodplain	3.88	16.71
RTU-FF4-50	Floodplain	3.26	21.61
RTUFF5-10	Floodplain	6.10	54.33
RTUFF5-50	Floodplain	10.14	45.08
Rio Tupiza - San Juan del Oro			
RTUFF5 - CA	Floodplain	10.16	59.80
RTUFF5 - CB	Floodplain	14.43	62.35
RTUFF5 - CC	Floodplain	7.11	62.07
RTUFF5 - CD	Floodplain	6.11	62.08
RTUFF5 - CE	Floodplain	5.52	43.16
RTUFF5 - CF	Floodplain	3.95	46.43
RTUFF5 - CG	Floodplain	2.90	39.08
RTU-FF6-10	Floodplain	6.01	34.28
RTU-FF6-50	Floodplain	5.79	37.97
RTUFF7-10	Floodplain	5.02	48.96
RTUFF7-50	Floodplain	7.12	51.12
RC-FP5	flood plain	28.91	2.37
RTU-FP4	flood plain	24.28	3.06
RSJO-FP2	flood plain	38.14	2.09
Abaróa Mine fresh tailings			
AC-T1	Tailing	16.68	3.52
AC-T2	Tailing	94.52	5.07
AC-T3	Tailing	32.76	4.98
Abaróa Mine old tailings			
AM-T1	Tailing	11.15	3.81
AM-TO1	Tailing	45.75	4.98

Appendix B Continued

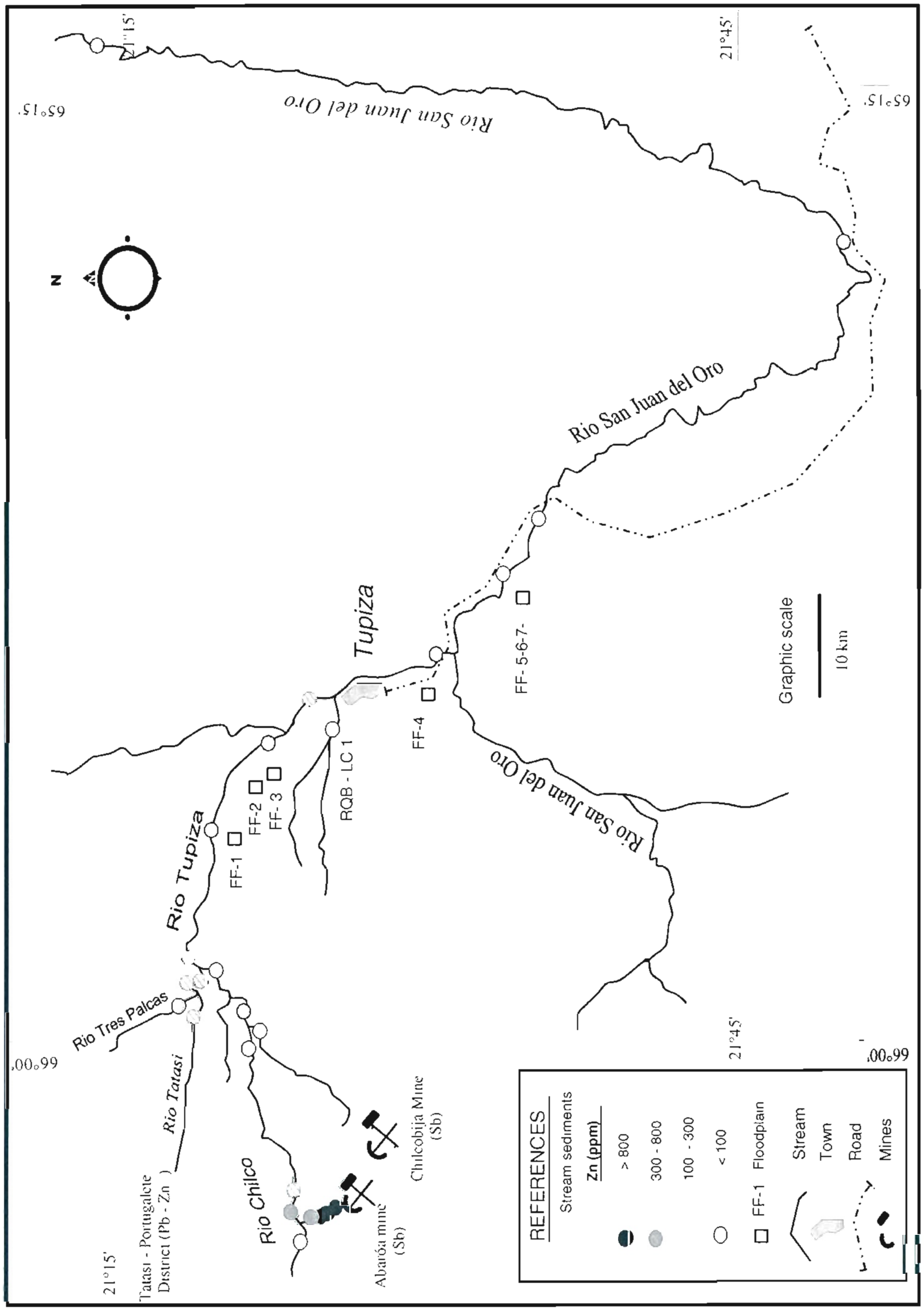
Sample	Type	Silt- clay %	Total Organic Content (%)
AM-TO2	Tailing	80.96	5.73
AM-TO3	Tailing	20.28	3.61
Chilcobija Mine new tailings			
CM-T1	Tailing	73.78	22.52
CM-T1B	Tailing	95.39	19.01
Chilcobija Mine old tailings			
CM-T2A	Tailing	19.18	9.69
CM-T2B	Tailing	35.03	6.85

Appendix C.

Lead concentrations for channel and high-channel along the Abaróa Valley, Rio Chilco and RioTupiza-San Juan del Oro



Appendix C Continued
Zinc concentrations for channel and high-channel along the Abaróa Valley, Rio Chilco and RioTupiza-San Juan del Oro



Appendix C Continued

Antimony concentrations for channel and high-channel along the Abaróa Valley, Rio Chilco and RioTupiza-San Juan del Oro