

Division of Water Resources Engineering
Lund Institute of Technology
Lund University
Master Thesis
Report TVRL 2006:12



LUND UNIVERSITY

Occurrence and distribution of heavy metals in three rivers on the Bolivian high plateau

A minor field study conducted in Bolivia
Master of Science Thesis in Environmental Engineering

Anders Lilja and Greger Linde
Lund 2006



Supervisors:

Adj. Prof. Kenneth M. Persson, Division of Water Resources Engineering, Lund Institute of Technology, Lund University, Sweden

M.Sc. Oswaldo Ramos and Maria E. García, Institute of Chemistry, University of San Andres, La Paz, Bolivia

Copyright © Anders Lilja & Greger Linde
Report TVRL 2006:12
Master of Science Thesis in Environmental Engineering
Minor Field Study

Division of Water Resources Engineering
Lund Institute of Technology, Lund University
Box 118
221 00 Lund
Sweden
Phone: +46 46 222 000

SUMMARY

Title: Occurrence and distribution of heavy metals in three rivers on the Bolivian high plateau

Authors: Anders Lilja and Greger Linde

Supervisors: Adj. Prof. Kenneth M. Persson, Division of Water Resources Engineering, Lund University, Sweden.
M. Sc. Oswaldo R. Ramos and Ph. D. student Maria E. García, Instituto de Investigaciones Químicas, San Andrés University, La Paz, Bolivia.

Problem Definition: Since ancient times, mining has been a central part of the Bolivian economy. However, the extraction of metals affects the environment negatively. Elevated levels of heavy metals and acidic pH-values in water courses close to mining activities are two well known problems. Earlier studies around the Poopó Lake have reported high levels of arsenic, lead and cadmium in rivers and their sediments, but knowledge about the interactions between heavy metals within the sediments and heavy metals in the waters are missing. Moreover, no studies of the spatial distribution along the rivers have been conducted. The Sora Sora River flows through the most important mining centre, Huanuni, and contains high levels of heavy metals and has a low pH. The Poopó River passes the mining community Poopó and contains high levels of arsenic. The pH of the river is alkaline and thermal waters enter the river, which may affect the water quality. The Marquez River is situated far from any mining communities, but the arsenic rich geology of the area causes high levels of arsenic within the river.

Objectives: The main objective of the present study is to gain knowledge of the environmental conditions, with focus on heavy metal concentrations in sediments and superficial waters, of the Sora Sora River, the Poopó River and the Marquez River. The main questions to answer are:

- What concentrations of the metals arsenic, lead, cadmium, and zinc are to be found in the sediments and superficial waters of the Poopó River, the Marquez River and the Sora Sora River?
- How much of the pollutants are due to natural conditions and anthropogenic sources, respectively?
- What can be said about the interactions between heavy metals in sediment and superficial waters?
- What are the factors controlling the heavy metal transport in the rivers?
- How high are the heavy metal concentrations compared with the permissible levels according to Bolivian law and WHO?
- How do the seasonal variations affect the rivers?

Method:

Water and sediment samples were taken along the chosen rivers during two field trips in October and December 2005. The water samples were analyzed for nitrate, phosphate and alkalinity in field. Also the parameters pH, Eh, temperature, conductivity, TDS and flow rate were measured in field. At the San Andrés University, La Paz, the water samples were analyzed for major ions and arsenic, cadmium, lead and iron. The sediment samples were analyzed for arsenic, cadmium, lead and zinc at the IBTEN laboratory, La Paz, and the grain size distribution of the sediment samples were determined at the San Andrés University, La Paz.

Results and Conclusions:

The rain period had not yet begun during the second sampling trip and all results thus represent the dry period. All rivers contain naturally high levels of dissolved arsenic and lead, exceeding the WHO-guideline values for drinking water. In the Poopó River, thermal waters cause very elevated levels of arsenic; as high levels as 12 mg/l were observed. Moreover, the thermal waters contribute with large amounts of TDS and change the river's water composition from a calcium-sulphate water to a sodium-chloride water. The processing plant pollutes the river with cadmium and levels of 0.04 mg/l were encountered. The processing plant may also be responsible for the higher pH-values encountered in the downstream parts. Elevated levels of arsenic, cadmium and zinc within the sediments were found at the most downstream part of the Poopó River, which is thought to be due to both sedimentation of suspended particles that have been adsorbing the metals and due to deposition of material from the mining activities. No acid rock drainage from the waste piles was observed, but is likely during the rain period. The sediments of the Marquez River contain low levels of arsenic, cadmium, lead and zinc, but the concentrations of arsenic and lead in solution were high. The Huanuni River is totally deteriorated because of the mining activities. The mining centre is the major pollution source causing elevated levels of arsenic, cadmium, iron and sulphate, and lowers the pH-value to about pH 3. However, the small scale mining along the river and leakage from the waste piles and the river's sediment also contributes with large amounts of arsenic and acidity. Arsenic, cadmium and iron levels of 12, 1.4 and 488 mg/l were observed and mass flows to the Poopó Lake as high as 300, 20 and 3000 kg/day were calculated. The mining activities also increase the concentrations of arsenic, cadmium and zinc in the sediments greatly. Deposition of mining material seems to be controlling the zinc and cadmium concentrations, whereas adsorption on suspended particles followed by sedimentation seems to control arsenic. Further studies measuring suspended particles and organic content are recommended for the understanding of the transport mechanisms and the interactions between sediment and water phase.

Key Words:

Heavy metals, superficial waters, sediments, ARD, Altiplano.

SAMMANFATTNING

Titel: Förekomst och spridning av tungmetaller i tre floder på den bolivianska högplatån

Författare: Anders Lilja och Greger Linde

Handledare: Adj. Prof. Kenneth M. Persson, Teknisk Vattenresurslära, Lunds Universitet, Sverige
M. Sc. Oswaldo R. Ramos och Ph. D. student María E. García, Instituto de Investigaciones Quimicas, Universidad Mayor de San Andrés, La Paz, Bolivia.

Problemställning: Brytning och bearbetning av mineraler har alltid utgjort en central del av Bolivias ekonomi, men har samtidigt kommit att påverka miljön negativt. Två välkända problem är förhöjda halter av tungmetaller och försurning av vattendrag i anknytning till gruvverksamheten. Tidigare studier av floder kring Poopó-sjön har visat höga halter av bl.a. arsenik, bly och kadmium, både löst i floderna och bundet i deras sediment. Det saknas dock kunskap om hur halterna i vatten och sediment påverkar varandra och om den spatiala spridningen längs med floderna. Sora Sora-floden flyter genom det stora gruvsamhället Huanuni och har höga koncentrationer av tungmetaller och lågt pH. Poopó-floden passerar gruvsamhället Poopó och har höga halter av arsenik och ett alkaliskt pH. I floden finns termala vattenkällor, vilka tros påverka vattenkvaliteten. Vid Marquez-floden finns ingen gruvverksamhet, men berggrunden är rik på arsenik, vilket orsakar höga halter i floden.

Målsättning: Den övergripande målsättningen med denna studie är att förstå de miljömässiga förhållandena i floderna Sora Sora, Poopó och Marquez, med fokus på tungmetaller i vatten- och sedimentfas. Mer specifikt vill vi besvara följande frågor:

- Hur höga är halterna av arsenik, bly, kadmium, zink och järn i floderna Poopó, Marquez and Sora Sora?
- Hur stor del av dessa härrör från antropogen påverkan och hur stor del är naturlig?
- Hur påverkar halterna i vatten- och sedimentfas varandra?
- Vilka faktorer bestämmer transporten av tungmetaller i floderna?
- Hur höga är halterna i jämförelse med WHO:s riktlinjer för dricksvatten och maximalt tillåtna värden enligt boliviansk lag?
- Hur stora är de säsongsmässiga variationerna?

Metod: Vatten- och sedimentprover togs längs med de utvalda floderna vid två tillfällen; det första i oktober och det andra i december 2005. I fält analyserades vattenproverna för nitrat, fosfat och alkalinitet, och

parametrarna pH, Eh, temperatur, konduktivitet, TDS och vattenföring mättes. Vid universitetet San Andrés, La Paz, analyserades vattenproverna för de vanligaste jonerna samt arsenik, kadmium, bly och järn. Sedimentproverna analyserades för arsenik, kadmium, bly och zink vid laboratoriet IBTEN, La Paz, och provernas kornstorleksfördelning bestämdes vid universitet San Andrés, La Paz.

Resultat och Slutsatser:

Regnperioden hade ännu inte börjat vid den andra fältresan, vilket innebär att samtliga värden representerar torrperioden och inga slutsatser om de säsongsmässiga variationerna har kunnat dras. Alla floder innehåller naturligt höga halter av löst arsenik och bly, vilka överstiger WHO:s riktlinjer för dricksvatten. I Poopó-floden orsakar termala vattenkällor mycket höga arsenikhalter och koncentrationer så höga som 12 mg/l påträffades. Dessutom bidrar de termala vattnen med stora mängder TDS och ändrar flodens vattensammansättning från ett kalcium-sulfat-vatten till ett natrium-klorid-vatten. Bearbetningsanläggningen vid Poopó-floden förorenar floden med kadmium och ett värde på 0.04 mg/l uppmättes. Sedimenten från flodens nedersta delar innehåller signifikant förhöjda halter av arsenik, kadmium och zink, vilket kan bero på både sedimentation av suspenderade partiklar som har adsorberat metallerna och på att gruvmaterial som innehåller dessa metaller hamnar i floden. Ingen sänkning av flodens pH-värde till följd av Acid Rock Drainage från de stora deponierna med restmaterial observerades. Deponierna tros emellertid läcka syra under regnperioden. Marquez-flodens sediment innehåller låga halter av kadmium, bly och zink, men vattenfasen innehåller höga halter av arsenik och bly. Huanuni-floden är totalt förstörd till följd av gruvverksamheten. Det stora gruvsamhället Huanuni är den största föroreningskällan och orsakar förhöjda halter av arsenik, kadmium, järn och sulfat samt sänker flodens pH-värde till omkring pH 3. Den småskaliga bearbetningen av mineral samt läckage från deponier längs med floden och flodens sediment tros emellertid också bidra med stora mängder arsenik och syra. Arsenik-, kadmium- och järnkoncentrationer på 12, 1.4 och 488 mg/l uppmättes och så höga massflöden som 300, 20 och 3000 kg/dag till Poopó sjön beräknades. Gruvverksamheten ger dessutom upphov till förhöjda halter av arsenik, kadmium och zink i flodens sediment. Kadmium- och zinkkoncentrationerna tycks vara orsakade av deponering av gruvmaterial i floden, medan arsenikkoncentrationerna tros vara orsakade av adsorption på suspenderade partiklar följt av sedimentation.

Ytterligare studier som bl.a. inkluderar suspenderade partiklar och halten av organiskt material rekommenderas för att förstå transportmekanismerna av tungmetaller samt utbytet mellan vatten- och sedimentfas bättre. Studier bör också genomföras under regnperioden för att kunna dra slutsatser om den säsongsmässiga variationen.

Nyckelord:

Tungmetaller, ytvatten, sediment, ARD, gruvverksamhet, Altiplano.

ACKNOWLEDGEMENTS

First we would like to thank the Division of Water Resources at Lund University and the Swedish International Development Cooperation Agency for the financial support to conduct this Master's Thesis.

We would also like to thank our supervisors: Adj. Prof. Kenneth M. Persson at the Division of Water Resources Engineering, Lund University, Ph. D. student María Eugenia García and M. Sc. Oswaldo Ramos Ramos, both at the Institute of Chemistry, San Andrés University, La Paz, Bolivia.

We are very thankful to all the people at the Institute of Chemistry, San Andrés, La Paz, Bolivia. Thank you Jorge Quintanilla, Mauricio, Elvira Guisbert, Israel and Gonzalo.

Special thanks to Annika Lindblad and Anna-Maria Kauffeld, our friends and our families.

CONTENTS

1. INTRODUCTION.....	1
1.1 BACKGROUND	1
1.2 OBJECTIVES.....	2
2. THEORETICAL BACKGROUND.....	3
2.1 MINING HISTORY	3
2.2 COOPERATIVE MINING.....	3
2.3 WASTE ROCK AND TAILING DEPOSITS	3
2.4 ACID ROCK DRAINAGE (ARD)	4
2.5 WATER SEDIMENT INTERACTIONS	4
2.5.1 SOLUBILITY EQUILIBRIUM	5
2.5.2 ADSORPTION	5
2.6 HEAVY METALS.....	7
2.6.1 ARSENIC	7
2.6.2 LEAD	8
2.6.3 CADMIUM.....	8
2.6.4 ZINC.....	9
3. METHODOLOGY.....	11
3.1 LITERATURE STUDY.....	11
3.2 SAMPLING PROCEDURES.....	11
3.3 WATER ANALYSIS	12
3.4 SEDIMENT ANALYSIS	14
3.5 ION BALANCE AND ELECTRICAL CONDUCTIVITY.....	15
3.6 SATURATION INDICES AND SPECIATION	15
3.7 MASS FLOW CALCULATIONS	15
3.8 RESIDENCE TIME.....	16
3.9 SOURCES OF ERROR	16
3.9.1 WATER ANALYSIS	16
3.9.2 SEDIMENT ANALYSIS	16
4. AREA DESCRIPTION	17
4.1 GENERAL AREA DESCRIPTION	17
4.1.1 DEMOGRAPHY	17
4.1.2 GEOLOGY	18
4.1.3 CLIMATE.....	19
4.1.4 HYDROLOGY.....	19
4.2 POOPÓ RIVER BASIN.....	20
4.3 MARQUEZ RIVER BASIN.....	21
4.4 SORA SORA RIVER BASIN	22
5. RESULTS.....	25
5.1 RESIDENCE TIME.....	26

5.2	GENERAL WATER CHEMISTRY	26
5.2.1	POOPÓ RIVER.....	27
5.2.2	MARQUEZ RIVER.....	28
5.2.3	HUANUNI RIVER.....	29
5.3	HEAVY METALS IN SOLUTION	30
5.3.1	POOPÓ RIVER.....	30
5.3.2	MARQUEZ RIVER.....	32
5.3.3	HUANUNI RIVER.....	34
5.4	SPECIATION	36
5.4.1	POOPÓ RIVER.....	36
5.4.2	MARQUEZ RIVER.....	36
5.4.3	HUANUNI RIVER.....	36
5.5	GRAIN SIZE DISTRIBUTION	37
5.6	HEAVY METALS IN SEDIMENTS	37
5.6.1	POOPÓ RIVER.....	37
5.6.2	MARQUEZ RIVER.....	39
5.6.3	HUANUNI RIVER.....	41
5.7	SATURATION INDICES FOR SELECTED MINERALS	44
5.7.1	POOPÓ RIVER.....	44
5.7.2	MARQUEZ RIVER.....	44
5.7.3	HUANUNI RIVER.....	44
5.8	MASS FLOWS	45
5.8.1	POOPÓ RIVER.....	45
5.8.2	MARQUEZ RIVER.....	45
5.8.3	HUANUNI RIVER.....	45
6.	DISCUSSION	47
6.1	POOPÓ RIVER	47
6.1.1	HEAVY METALS IN SOLUTION.....	47
6.1.2	HEAVY METALS IN SEDIMENTS.....	48
6.1.3	MASS FLOWS	49
6.2	MARQUEZ RIVER	50
6.2.1	HEAVY METALS IN SOLUTION.....	50
6.2.2	HEAVY METALS IN SEDIMENTS.....	51
6.2.3	MASS FLOWS	51
6.3	HUANUNI RIVER	51
6.3.1	HEAVY METALS IN SOLUTION.....	51
6.3.2	HEAVY METALS IN SEDIMENTS.....	52
6.3.3	MASS FLOWS	53
6.4	COMPARISON WITH EARLIER WORK	54
7.	CONCLUSIONS	55
7.1	POOPÓ RIVER	55
7.2	MARQUEZ RIVER	55
7.3	HUANUNI RIVER	56
8.	RECOMMENDATIONS	57
9.	REFERENCES	59

1. INTRODUCTION

1.1 Background

For hundreds of years mining and mineral processing have played a central role for the economics on the Bolivian Altiplano. Processing dates back as far as 2000 BC, when the Tiwanaku and later the Inca civilizations started the mineral extraction. As these civilizations were concurred by the Spanish colonizers, extraction and processing took different proportions. Since then large amounts of minerals have been extracted, often with a total lack of environmental control, and the impact has been both intensive and extensive (García et al., unpublished). The environmental degradation due to mining activities is worsened by the area's sensitivity to droughts. Together with the areas environmental condition, there is a long-lasting economic depression mainly due to the decline in mining and mineral processing (PPO 9701, 1997).

The mining industry has under gone quite a few changes over time, often connected to the ups and downs of market prices. Thus a wide variety of different techniques exist for extraction, where most of them have a negative impact on the environment. Old and closed mines, various mineral waste deposits and extraction sites often contribute with large amounts of acid drainage transporting large amounts of heavy metals directly in to the surrounding superficial waters. Around 120 mines are located in the Poopó basin, with its centre located in the north-eastern part. Leached heavy metals, either transported by superficial waters or sediments, end up in the ultimate recipient, Lake Poopó. Earlier studies (García et al., unpublished and PPO 9701, 1997) have shown that heavy metal concentrations in Lake Poopó are between 300 and 3500 times higher than values from world-wide lakes.

Beside the environmental degradation due to mining activities, high natural levels of metals in watercourses are also reported. Due to the widely varying geological composition of the bedrock and soils, natural background concentrations may some time exceed levels of "Predicted No-Effect Concentration" (PNEC), which are the highest concentrations at which aquatic life should be able to survive in balanced and sustainable communities. The highest naturally elevated concentrations have been found for arsenic, antimony and lead, all greatly exceeding world-wide background concentrations (PPO 9701, 1997). The distinction between anthropogenic and natural pollution has been possible by studying the rivers in the south, which are said to be affected only by natural weathering, and also by studying how the concentrations change along the rivers.

People living in the near vicinity of elevated heavy metal concentrations are likely to be affected. Not only the polluted waters possess a risk, but also airborne pollutions spread by refining in smelters and foundries. Elevated concentrations are found in crops and aquatic life, which may end up, and accumulate in the population. In general the surface waters are not good for human consumption. They also present a risk for animals and may not be suitable for irrigation (Quintanilla et al., 2001).

Since year 2000 there is an ongoing multidisciplinary investigation program, "*Interdisciplinary Study of the Altiplano region – Bolivia*". The project involves the University of San Andrés, La Paz and local institutes, e.g. the Binominal Authority of Lake Titicaca, and it is sponsored by the Swedish International Development Cooperation Agency. One subprogram of the project is "*Management of Water Resources – Hydrochemistry of the Poopó and Uru Uru basin*", involving the Chemistry Research

Institute, University of San Andrés, Bolivia, and the Institute of Technology, University of Lund, Sweden.

This thesis is a part of the project “*Management of Water Resources – Hydrochemistry of the Poopó and Uru Uru basin*” and contributes with knowledge of heavy metals in three specific rivers within the Poopó region.



Figure 1.1 Women and children washing clothes in Huanuni River

1.2 Objectives

The general objective of the present study is to gain knowledge of the environmental conditions, with focus on heavy metal concentrations in sediments and superficial waters, in three specific sub basins in the Poopó region; the sub basins of the rivers Sora Sora, Poopó and Marquez. Both Sora Sora and Poopó are greatly influenced by mining activities but differ in natural conditions. The water in Sora Sora is acid whereas the water in Poopó is alkaline. The third sub basin, Marquez, is not affected by mining but is exposed to high natural pollution of arsenic (García et al., unpublished and PPO 9612, 1996).

The specific objectives of the study are to:

- quantify the concentrations of the metals arsenic, lead, cadmium, and zinc in the sediments and superficial waters of the rivers Sora Sora, Poopó and Marquez,
- quantify the natural and anthropogenic pollution in these rivers,
- investigate the interactions between metal concentrations in sediments and in surface waters,
- asses the metal transport in the rivers,
- compare the water quality with maximum permissible levels for drinking water according to Bolivian law and WHO and to
- make a comparison between dry and wet periods.

2. THEORETICAL BACKGROUND

2.1 Mining History

During the 20th century the mining sector of Bolivia underwent quite some changes. From being dominated by private companies during the first half of the century, the three largest tin companies were nationalized in 1952. The Mining Corporation of Bolivia (COMIBOL) was created to run the now biggest tin producing enterprise in the world, with a workforce reaching 3600 men (Troëng & Riera, 1996). Great ups and downs followed due to inflation, low international demand and finally the collapse of the world tin market. During these hard times, the traditional underground mining of tin and silver vein deposits became less and less profitable which led to the growth of the new private sector, the medium mining sector (García, unpublished). In 1985 a new government came in to power and implemented a free market economy, reducing the state's role in the mining sector. Mines not profitable enough were closed and as many as 75 % of the COMIBOL workforce were dismissed. Many of the now unemployed miners formed cooperatives, and started running former COMIBOL operated mines (Troëng & Riera, 1996). In 1987, Bolivia's metal production declined drastically and almost came to an end. Recovery of the mining industry came from structural changes together with an increased international demand. The structural changes mainly consisted of the transformation from single-metal production (tin), to more diversified mining. The private medium-sized mining sector and cooperative sector became more important, and by 1992, the cooperative sector was the major producer of gold and tin in Bolivia together with a significant production of silver, antimony, lead and zinc (Redwood 1993 in Troëng & Riera, 1996).

2.2 Cooperative Mining

The work consists of small-scale mining of mines previously owned by companies or just re-working leftovers and tailings discharged by operating mills. These cooperatives are normally an informal type of companies owned by the miners themselves. Since the cut downs at COMIBOL, the number of people working in the cooperatives has increased a lot. The PPO investigation, Proyecto Piloto Oruru, estimated in 1996 that as many as 1200 workers were working with these kinds of activities, which exceeds the number of workers employed by COMIBOL. Cooperative mining is carried out in all mining districts on the Bolivian high plateau, with a concentration in the Huanuni mining centre.

Most of the mining consists of simple artesian work, mostly manual but sometimes using somewhat mechanized operations. Harmful chemicals like sulphuric acid, xanthate and kerosene are used to separate sulphides from the tin concentrates. Since simple ways of extracting minerals mostly are used by the cooperatives, the environmental impact is great (PPO 9611, 1996).

2.3 Waste Rock and Tailing Deposits

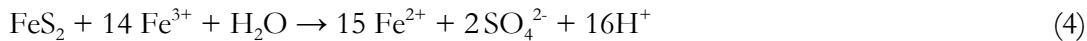
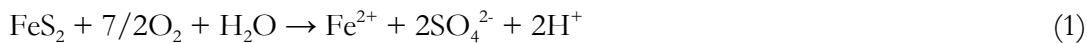
Of all the material excavated, only a very small percentage brings profit. The rest is considered waste, and is dumped close to the beneficial plants, often nearby or even into the rivers. During rainfall, water infiltrates the deposits causing leakage into the rivers. The unwanted rock materials normally do not contain any large amounts of heavy metals, but are still important to take into account due to their ability to produce acid rock drainage. The grain size of the waste plays an important role for the release of acid; the finer the waste material is, the more acid will be released. Tailings are fine-grained fractions of waste from the concentration process. The tailings

may enter the river and mix with the natural alluvial sediments and contaminate large stretches downstream the dumping sites (PPO 9611, 1996).

2.4 Acid Rock Drainage (ARD)

During the mining and processing of metal ores, it is not likely that all the wanted metals will be recovered. Hence, the waste produced will contain various amounts of heavy metals. Under normal conditions, these metals would not possess any great environmental threat due to their low mobility. For mining wastes it is a little bit different. All mineral deposits containing sulphides are a potential source of acid rock drainage. Some conditions are more prone than others to give rise to acid drainage. During the processing, the goal is to grind the original bedrock material to be able to separate the wanted minerals from the unwanted. This highly enlarges the area exposed to oxidising conditions. The coarseness of the material greatly affects both the oxidation processes and the leaching processes. After processing, the total surface exposed to oxidation may have been multiplied thousands of times compared to that of the original bedrock material. Once the sulphidic rocks are exposed to oxidizing conditions, the sulphides will be oxidised and sulphuric acid is released. With sulphuric acid present, the leachability of heavy metals may increase greatly (PPO 9611, 1996).

The most important mineral producing sulphuric acid is pyrite (FeS_2). The reactions for the breakdown of pyrite in the presence of water and oxygen to yield sulphuric acid are:



Which of the reactions that determines the rate is not fully understood. Some suggest that the oxidation of Fe^{2+} to Fe^{3+} , equation (2), is the rate-limiting step, while others claim it is the oxidation of FeS_2 with oxygen, equation (1). Whatever step considered being the rate limiting, the surface area available for oxidation is very important for the rate of releasing sulphuric acid (Kelly, M. 1988).

2.5 Water Sediment Interactions

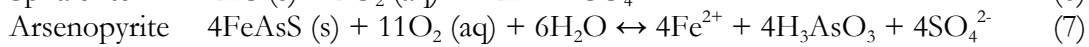
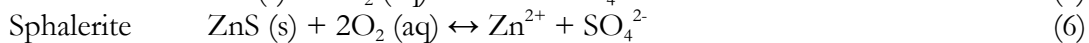
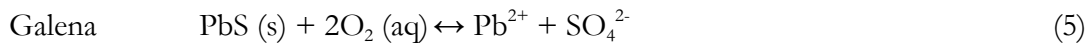
Sediments are not fixed arrangements, but ever changing. Sediment particles are transported and sedimentation/re-suspension takes place interchangeably. Volume and composition of sediments are depending on hydrological factors and dynamic processes at the river bottom, such as erosion, accumulation and transport. Higher velocity of the water results in that larger particles may be transported and a greater amount of sediments will be moved downstream.

Two major processes that may control the concentrations of dissolved heavy metals in the river are dissolution/precipitation of minerals and adsorption/desorption.

2.5.1 Solubility equilibrium

Concentration of a trace metal in solution may be determined by dissolution and precipitation of minerals. Knowing which minerals a water is or has been in contact with may thus explain the concentrations of dissolved trace metals. Drever (1982) gives some examples of investigations where the dissolution of surrounding minerals controls the concentration of trace minerals; kaolinite controlling aluminium, amorphous $\text{Fe}(\text{OH})_3$ controlling iron and vivianite controlling iron and phosphorous (Drever, 1982).

The dissolution of a mineral is determined by its solubility product. Sulphide minerals are easily dissolved in oxygenated waters (Drever, 1982) and the minerals galena (PbS), sphalerite (ZnS) and arsenopyrite (FeAsS) dissolves according to:



At equilibrium between a mineral and the solution the solubility constant, K_{sp} , equals the ion activity product, IAP . If the ion activity product is greater than the solubility constant of a specific mineral, i.e. observed concentrations are higher than equilibrium concentrations, the water is super-saturated with respect to that mineral. In natural waters the solubility of surrounding minerals may give the upper limits of trace element concentrations. Actual concentrations in a water are seldom more than 1000 times the equilibrium concentrations (Drever, 1982). If this is the case, other sources are contributing with the trace metal.

Many waters are sub-saturated with respect to surrounding minerals, i.e. the actual concentrations are lower than equilibrium concentrations. This could be due to that the mineral is not in good contact with the water. However, even if the contact between mineral and water is good, observed concentrations might still be lower than equilibrium concentrations. This indicates that it exists a sink for the trace element and in many cases adsorption onto particles is such a sink (Drever, 1982).

The saturation index, $S.I.$, is often used to determine whether a solution is sub-saturated, at equilibrium or super-saturated with respect to a mineral. The index is calculated as

$$S.I. = \log \frac{IAP}{K_{sp}} \quad (8)$$

A positive value of the saturation index means that the solution is super-saturated and a negative value that it is sub-saturated. At equilibrium the index should be zero.

2.5.2 Adsorption

Adsorption involves a variety of mechanisms resulting in that dissolved ions or molecules become attached onto the surface of a solid. The main mechanisms responsible for adsorption can be divided into ion exchange, specific adsorption, co-precipitation and organic complexation (Alloway, 1990). However, it is often very hard to distinguish between the different processes.

Sediment particles normally have a negatively charged surface and cations are attached by electrical forces to neutralize the surface charge. Some ions are more strongly attracted to the

particle surfaces than others, meaning that these can replace other ions from the particles. The ability to replace particles depends on the valency and the degree of hydration of the ions. The higher valency of an ion, the higher the replacing capacity, and the more hydrated an ion is the lower the replacing capacity. However, studies have shown that ions are adsorbed to a greater extent than would have been expected from the cation-exchange capacity. This is due to specific adsorption, which involves hydrolysis of metal ions (Alloway, 1990). Specific adsorption is very pH-dependent. At very low pH-values there is almost no adsorption at all and at high pH-values almost all cations are adsorbed. The transition from no adsorption to almost complete adsorption occurs over a narrow pH-range, different for different ions. Drever (1982) gives two explanation models, which both correspond well to observed data. The first explanation involves the hydrolysis of dissolved cations according to:



The hydration shell around the metal ion M^{2+} is stronger than around the hydrolysed $M(OH)^+$, preventing the metal ion from being adsorbed. Metal ions that are easily hydrolysed are therefore easily adsorbed. The equilibrium constant, pK, for the hydrolysis reaction (9) thus determines how easily a metal is adsorbed; the lower pK-value the more adsorption. The pK-values for the hydrolysis of cadmium, zinc and lead are 10.1, 9.0 and 7.7. Hence, lead is more easily adsorbed than zinc, which is more easily adsorbed than cadmium (Alloway 1990).

The other explanation model according to Drever involves complexation at the surface of the adsorbents (Drever 1982).

The best adsorbents are hydroxides and oxides of manganese, iron and aluminium, which can be very fine-grained with surface areas of the order $200 \text{ m}^2/\text{g}$. Due to their adsorbing properties they are often used as scavengers in wastewater treatment. Clay minerals and humic substances are also good adsorbents.

Co-precipitation occurs when a trace metal is incorporated in a solid phase that is being precipitated and involves clay minerals, hydrous iron and manganese oxides, and calcite. Furthermore, cadmium ions may replace calcium ions in calcite forming the CdCO_3 .

It is often complicated to determine which one of the mechanisms that is dominating, but different empirical formulas describe the equilibrium between adsorbed phase and solution phase well. Langmuir's adsorption isotherm has the following expression:

$$ads = ads_{\max} \cdot \frac{[C]}{K + [C]} \quad (10)$$

and the Freundlich adsorption isotherm

$$ads = ads_{\max} \cdot \frac{[C]^z}{K + [C]^z}, \quad (11)$$

where ads is the amount of the species adsorbed, ads_{\max} the maximum amount of the species that the adsorbent may adsorb and $[C]$ the concentration of the species in solution. K is a constant dependent on the organic content of the adsorbent and how the species distributes between organic phase and solid phase. A species that prefers the organic phase will be well adsorbed by

an adsorbent with high organic content. Furthermore, ads_{max} is also dependent of the organic content of the soil.

2.6 Heavy Metals

The poisonous effect that heavy metals possess on living organisms is a result of their ability to compete with trace elements used in enzymes. Due to the heavy metals possibility to be incorporated in the enzymes, their biological effects are of a wide variety. There is often an enzyme in a specific organ that is extra sensitive for heavy metal poisoning. This organ will be the first to be affected, and is called the critical organ. Many organs do not work at full capacity, but have a reserve capacity, and can work well in spite of a minor dysfunction. The brain is an organ that needs to be working without any drawbacks, and is often considered as a critical organ when exposed to small and medium amounts of heavy metals. The fact that heavy metals compete with trace elements needed to sustain life, puts people that have a lack of these trace elements, for example due to malnutrition, in an even more exposed situation and they are therefore more sensitive to heavy metal poisoning (Åslund, 1994).

2.6.1 Arsenic

The major arsenic minerals, according to the literature review of Smedley and Kinniburgh (2001), are arsenian pyrite ($Fe(S,As)_2$), arsenopyrite ($FeAsS$), realgar (AsS) and orpiment (As_2S_3), where the arsenic is present in the crystal structure as a substitute for sulphur. Pyrite is oxidized in aerobic environments, releasing sulphate and hydrogen ions and associated trace elements like arsenic. Other minerals that may contain high levels of arsenic are mainly iron oxides but also aluminium and manganese oxides, clay minerals and calcite (Smedley and Kinniburgh 2001). The arsenic content in soils and rocks vary in the range 1-40 ppm (Åslund, 1994). Smedley and Kinniburgh (2001) gives the following average values of arsenic in different types of rocks and soils; igneous rocks - 1.5 ppm, metamorphic rocks - 5 ppm, sedimentary rocks - 5-10 ppm, unconsolidated sediments - 3-10 ppm and soils - 5-10 ppm. Tailing piles and soils contaminated from mining activities often contain as high levels of arsenic as several thousands ppm.

The arsenic concentrations in rivers are normally low, 0.1-0.8 $\mu\text{g}/\text{l}$, and depend on the composition of the surface recharge, base flow and the bedrock lithology (Smedley and Kinniburgh 2001). However, the concentrations can be much higher in areas with inputs from geothermal waters and arsenic rich groundwater; values as high as 370 $\mu\text{g}/\text{l}$ have been reported from such areas (Nimick et al 1998. in Smedley and Kinniburgh 2001). High concentrations have also been reported for arid areas in northern Chile, which could be explained by evaporative concentration (Caceres et al. 1992 in Smedley and Kinniburgh 2001). Mining activities may also increase the arsenic concentrations drastically, mainly due to pyrite oxidation and release of associated arsenic. Average values of 200-300 $\mu\text{g}/\text{l}$ have been reported in rivers close to mining activity (Williams et al., 1996 and Smedley et al., 1996 in Smedley and Kinniburgh, 2001). However, oxide minerals, primarily iron oxide, adsorb arsenic strongly under oxidizing and neutral or slightly acidic conditions.

Arsenic can be present in nature in the oxidation states -3, 0, +3 and +5, but in natural waters it is normally present as the inorganic oxyanions of trivalent arsenite (H_3AsO_3) and pentavalent arsenate (H_3AsO_4). In oxidizing conditions at pH-values below 6.9, $H_2AsO_4^-$ is dominating and at higher pH-values $HAsO_4^{2-}$ is the more common species. In reducing conditions at pH-values below 9.2 the uncharged form of arsenite, H_3AsO_3 , dominates. In acidic and reducing conditions high concentrations of reduced sulphur can lead to the formation of sulphide minerals such as orpiment As_2S_3 and realgar AsS (Smedley and Kinniburgh 2001).

The most important minerals adsorbing arsenic are iron oxides, but also aluminium and manganese oxides, and clay minerals play an important role as absorbers (Smedley and Kinniburgh 2001). One important difference between arsenic and other heavy metals is that the adsorption for arsenate normally decreases with increasing pH-values (Dittmar, 2003). An important mechanism for arsenic release, not completely understood, is the reductive dissolution of iron (Smedley and Kinniburgh), which results in that arsenic bound to iron oxides is released in anaerobic conditions.

The toxicity of arsenic is not completely understood but is due to its similarity in biochemistry with phosphorous. It is thought that it binds to thiols in enzymes inhibiting them (Sterner 2003). Symptoms of acute poisoning are vomiting, oesophageal and abdominal pain and bloody diarrhoea. Long-term exposure of arsenic via drinking water may lead to cancer of skins, urinary bladder and kidney. Normally it takes more than ten years of exposure to develop the cancers. The first symptoms are pigmentation changes and thickening of the skin. It has been observed that concentrations as low as 0.05 mg/l in drinking water lead to an increased risk of lung and bladder cancer. In China arsenic in drinking water has been shown to cause severe diseases of blood vessels leading to gangrene (WHO, 2001). Furthermore, arsenic is bio-accumulated in aquatic ecosystems (Sterner 2003). This leads to high levels of organic arsenic in seafood. However, the organic forms are readily eliminated by the body making them much less toxic than arsenite and arsenate (WHO, 2001). The most toxic form of arsenic is arsine, but due to its instability it is seldom found in nature (Sterner, 2003).

2.6.2 Lead

Lead is widely distributed in the earth's crust, but often in low concentrations. The average content in soils and bedrock usually lies between 2 and 100 ppm and the earth's crust average amount of lead is 16 ppm (Åslund, 1994). Lead is mined primarily from deposits of the mineral galena (PbS).

The most important anthropogenic source of lead emissions to the atmosphere is the ore smelters. The amount emitted by smelters accounts for almost five times as much as do natural sources (Waldron, 1974 in Laws, 2000).

Lead is mainly found in natural waters as carbonate complexes and to a smaller extent as chloride complexes (Åsplund, 1979). Adsorption on particles plays an important role and lead often binds to organic compounds, humus particles or suspended compounds such as iron and manganese.

The ability of lead to move in soils is very much restricted, due to the formation of low soluble compounds such as lead sulphate, lead phosphate and lead carbonate. Lead may also be adsorbed to clay minerals. In the case of very acidic soils, lead binds tight to organic material (Åslund, 1994).

Lead is a general metabolic poison, which interacts with the proteins damaging tissue and interfering with the proper function of the enzymes (Waldron, 1974 in Laws 2000).

2.6.3 Cadmium

Normal concentrations found in soils and rocks are in the range 0.035-0.98 ppm and the average in earth's crust is 0.1-1 ppm. Cadmium is normally encountered together with zinc in sulphide minerals, but also with lead and copper. Zinc minerals may contain up to 1 weight percent of

cadmium (Åslund, 1994). Hence, there are no ore deposits sufficiently rich in cadmium to warrant the extraction of cadmium. Instead, cadmium is obtained as a byproduct of mining other metals (Waldron, 1974 in Laws 2000).

Cadmium in the form of sulphide has a very low solubility. In water, cadmium normally binds to particles and humus, and forms suspended complexes with for instance iron and manganese compounds. A strong connection between pH and cadmium concentrations has been shown. A lowering of pH normally gives rise to higher cadmium concentrations. In soils, pH and redox potential determine the mobility of cadmium. Adsorption by clay minerals, iron oxides and sulphide oxides greatly reduces the mobility (Åslund, 1994).

Only one single cadmium species is believed to be toxic, Cd^{2+} . Once ingested, cadmium will be transported to all organs, but the highest concentrations are to be found in the kidneys and the liver. Cadmium has a half-life of 16-33 years in the human body. Thus a long term, low level exposure may lead to the accumulation of toxic levels in the body. An example in history of chronic cadmium exposure is the Itai-Itai disease in Japan. Mining and smelter operations in the area were discharging wastewater to the nearby river, with high levels of cadmium finally accumulating in the humans living of the land. Most of the effluent waters from the mine were found to be weakly basic. Under such conditions, cadmium is highly insoluble and almost all of the emitted cadmium was transported downstream in particulate form. Filtered samples thus contained cadmium levels approved for drinking water. Analysis of suspended materials in the river showed an 80-fold increase in cadmium concentrations, in the end, ending up on the rice paddies. Once the problem was highlighted, a sedimentary pond was constructed to retain the wastewater. Since then there has been a sharp decline of Itai-Itai cases (Waldron, 1974 in Laws 2000).

2.6.4 Zinc

The average of zinc in earth's crust amounts to about 120 ppm and in soils and rocks its levels reach 10 - 300 ppm.

The amount of zinc in water is rarely governed by its solubility, but instead of the total amount of accessible zinc. In most cases natural waters contain low concentrations. Concentrations found are closely connected to pH. In waters with pH below 5, the highest concentrations are to be found (Åslund, 1994). Zinc is mainly found as hydroxy complexes, free zinc ions and as carbonate complexes. Zinc bound as hydroxy complexes are probably found in the colloidal form or adsorbed on solid particles. A significant amount of zinc in natural waters is bound in organic complexes, according to a number of earlier investigations (Asplund, 1979).

3. METHODOLOGY

3.1 Literature Study

One of the most thorough investigations done in the area is the Oruro Pilot Project (PPO), elaborated in 1993. The project was a collaboration between the Ministry for Sustainable Development and Environment (MDSMA), the National Secretariat of Mining (SNM) and the Swedish Geological AB (SGAB), assembled to address the serious environmental degradation of the Poopó basin. The main goal of the project was to contribute towards a better environmental management and sustainable development. Since the regions main source of income is closely related to the mining and metal-smelting industries, much work have been emphasizing on mineral resources. A lot of information regarding the hydrology, geology, climate, demography and various mining activities has been found in the results presented in the PPO reports.

More specific information about the geology of the area was found in Boletín del Servicio Geológico de Bolivia N°7, 1996 (Troëng & Riera, 1996), consisting of thematic maps of the mineral resources of Bolivia.

3.2 Sampling Procedures

The first field trip was conducted in September 2005 (23-25/9) with the ambition to locate appropriate sampling locations in the chosen rivers. Totally eleven sampling points were identified: four along the river Sora Sora, four at the river Poopó and three in the river Marquez. The points for sampling were chosen strategically in order to determine effects of known phenomena in the streams. The location of the sampling points was recorded with a Garmin GPS 12XL. Sampling and analyzing was carried out during the second and third field trip in early October (6-9/10) and early December (12-14/12), respectively.

Water was collected in one-litre polyethylene bottles and filtered through a 0.45- μ m filter for further analyze in the laboratory. For heavy metal analysis water was collected in 100-ml polyethylene bottles, and nitric acid was added. Approximately one kg of sediments was taken from the riverbed at each point in zip lock plastic bags.



Figure 3.1 Anders measuring the flow in Marquez River

3.3 Water Analysis

The water samples were analyzed for the physical parameters pH, Eh, temperature, conductivity and TDS; the major ions chloride, nitrate, sulphate, phosphate, carbonates, sodium, potassium, calcium and magnesium; and the trace metals arsenic, cadmium, lead, zinc and iron. The flow rates at each sampling point were estimated with the orange method.

TDS and conductivity were measured in field with a conductivity/TDS-meter (HACH Company model 44600) and temperature, pH and Eh, also in field, with a portable EC10 pH/mV/temperature-meter model 50058.

Major ions and trace metals were analyzed for at the laboratory of the San Andrés University, La Paz. The analyze methods used were based on the Standard Methods for the Examination of Water and Wastewater 20th ed. and chosen according to available equipment:

Nitrate – Direct spectrometry and Ultraviolet spectrofotometric method

Nitrate was analyzed for, both in field and in laboratory. In field a direct spectrometer (HACH DR/2000) with the detection limit 0.1 mg/l NO₃⁻ were used.

In laboratory an ultraviolet spectrofotometric method was used. Absorbance was measured at 220 nm and at 275 nm to correct for organic content. A calibration curve was made by plotting the concentration of standards (0, 1, 2, 4, 6 and 8 mg/l) against their absorbance at 220 nm minus two times their absorbance at 275 nm, resulting in a linear relationship. The samples were prepared by adding 10 ml of 0.1 M hydrogen acid to 25 ml of sample to prevent hydroxide and carbonate interference. The samples were then filled up to 50 ml with distilled water. The analyses were done two times independently of each other. The accuracy of the method was estimated by the difference of the two measurements. The r-values for the calibration curves were 0.999 both times. The absorbance was measured with a Hellos α instrument.

All values in the results are from the laboratory method, except from Huanuni River, sampling point H2, H3 and H4.

Chloride – Argentometric titration

The samples were titrated with 0.0141 M or 0.00141M silver nitrate depending on the chloride concentration. 1.0 ml of potassium chromate was added to the samples to indicate the endpoint. When adding silver nitrate, silver chloride is formed and when all chloride in the sample is consumed, orange colored silver chromate is formed. Two titrations were performed per sample and the accuracy of the method was estimated by the difference of them.

The samples from the Huanuni River, sampling points H2, H3 and H4 could not be analyzed with this method due to the low pH.

Chloride – Ultraviolet method spectrophotometric method

This method was used for the samples from the Huanuni River, point H2, H3 and H4. The samples were prepared with 2 ml of mercuric thiocyanate ($\text{Hg}(\text{SCN})_2$), 2 ml of $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$ and 5 ml of 10 % HNO_3 . The chloride complexes with the Hg^{2+} -ion and the thiocyanate form a complex with the Fe^{3+} -ion, which absorbs UV-light at 480 nm. A calibration curve was made by plotting standard concentrations (0, 10, 20, 30, 40 and 50 mg/l) against their absorbance, resulting in a linear relationship with $r = 0.927$. The absorbance was measured with a Hellölos α instrument.

Sulphate –Turbidimetric method

Acetic acid and barium chloride were added to the samples. The sulphate ions form barium sulphate crystals with uniform size. A calibration curve was made by plotting standard concentrations (0, 5, 10 and 15 mg/l SO_4^{2-}) against their absorbance at 420 nm, resulting in a linear relationship. The measurements were done with a Hellölos α instrument and the r-value were 0.999

Phosphate

Phosphate was analyzed for directly in field using the same direct spectrometer (HACH DR/2000) as for nitrate. Detection limit was 0.05 mg/l.

Bicarbonate and carbonate – Micro titration with hydrogen acid

In field, alkalinity was measured by titrating 0.5 ml of sample with 0.01 M HCl. Bicarbonate and carbonate were assumed to account for all alkalinity, Alk, which leads to the expression:

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (12)$$

The ratio between bicarbonate and carbonate is a function of the hydrogen concentration and the dissociation constant of bicarbonate into carbonate, pK_a , according to:

$$[\text{HCO}_3^-] = [\text{CO}_3^{2-}] \cdot 10^{\text{pK}_a - \text{pH}} \quad (13)$$

The concentrations of bicarbonate and carbonate were calculated by combining equations (12) and (13) to the following expression:

$$[\text{HCO}_3^-] = \frac{0.5 \cdot \text{Alk} \cdot 10^{\text{pK}_a - \text{pH}}}{1 + 0.5 \cdot 10^{\text{pK}_a - \text{pH}}} \quad (14)$$

Temperature dependent pK_a -values from Stumm and Morgan (1996) were used for the calculations.

Three titrations were done and the mean value of added HCl was used. The accuracy of the measurements was determined as the difference of the largest and smallest value.

Sodium, potassium, calcium and magnesium – Flame atomic absorption spectrometry, FAAS

The samples are aspirated into a flame where the metals are atomized. Light from a metal specific lamp is directed through the atomized sample and the amount of light absorbed is measured by a detector. Over a narrow range the concentration of the sample is directly proportional to the absorbance. Double analyses were done randomly and the accuracy was estimated by the difference between two measurements. The analyses were done with an AAAnalyst 100 instrument. The r-values for magnesium and calcium were 0.992 and 0.999 respectively. R-values for sodium and potassium are missing.

Arsenic, cadmium, lead, zinc – Graphite furnace atomic absorption spectrometry, GFAAS

The principle is the same as for FAAS but the elements are atomized in a graphite furnace. The analysis was done with an AAAnalyst 100 instrument. Detection limits are as follows: lead - 0.0015 mg/l, arsenic - 0.001 mg/l, cadmium - 0.005 mg/l, iron - 0.01 mg/l and zinc - 0.012 mg/l.

The water samples from the second trip were analyzed with the following methods:

Anions – Ion chromatography

The samples were injected into a carbonate-bicarbonate eluent stream and passed through a series of ion exchangers. First, the sample passes basic anion exchangers that separate the anions. Then, they pass a cation exchanger membrane that converts the anions into highly conductive forms. The anions in the sample are identified by comparing their retention time with standards and the concentrations are measured by the peak area or the peak height of the conductivity. Double analyses were done and the accuracy was estimated by the difference between two measurements.

Sodium, potassium, calcium and magnesium – Flame atomic absorption spectrometry, FAAS

Same as the analysis of the samples from the first trip.

Arsenic, cadmium, lead, zinc – Graphite furnace atomic absorption spectrometry, GFAAS

Same as the analysis of the samples from the first trip.

3.4 Sediment Analysis

The grain size distribution of the samples from the first trip were determined at the institute of Geology, San Andrés University, La Paz, by using shaking sieves with the diameters 5, 2.5, 1, 0.5 and 0.25 mm. Hence, the sediments were divided into six fractions: 0-0.25 mm, 0.25-0.5 mm, 0.5-1 mm, 1-2.5 mm, 2.5-5 mm and >5mm. As a measure of the coarseness of the sediments the grain size at 50 % of accumulated weight was used.

The sediment samples from both trips were analyzed for total heavy metal content at the laboratory of Centro de Investigaciones Nucleares Viacha, IBTEN, La Paz. Approximately 100 g of each sediment sample, representative for the 1 kg-sample, were analyzed. The samples were dried, digested with a mixture of hydrochloric acid and nitric acid and finally analyzed with

graphite furnace atomic absorption spectrometry. The detection limits were: lead - 0.0015 mg/l, arsenic - 0.001 mg/l, cadmium - 0.005 mg/l, iron - 0.01 mg/l and zinc - 0.012 mg/l.

3.5 Ion Balance and Electrical Conductivity

All natural waters are uncharged, meaning that the sum of positive charges equals the sum of negative charges. This relationship may be used when analyzing a water sample. The total activity of all cations multiplied with their charge should equal the total activity of all anions multiplied with their charge. Often the activity of an ion is approximated with its concentration. The difference between total cations and total anions expressed as percentage of total ion content could then be expressed as:

$$diff.(%) = 100 \cdot \frac{\Sigma \text{ cations} - \Sigma \text{ anions}}{\Sigma \text{ cations} + \Sigma \text{ anions}} \quad (15)$$

if all concentrations are given in meq/l. An unbalance between cations and anions indicates that not all major charged species has been analyzed or that errors exist at some analysis.

The electrical conductivity of a solution is a measure of its ability to carry an electrical current. The conductivity depends on the ions present in the solution. More ions in the solution lead to higher conductivity. However, conductivity cannot be converted directly to ion content. It depends on the mobility of the ions, their valency and on the temperature of the solution (Standard Methods for the Examination of Water and Wastewater 20th edition).

3.6 Saturation Indices and Speciation

To determine if the waters at the different sample points were at equilibrium with surrounding minerals, or if they were super-saturated or sub-saturated, the program Phreeqc Interactive 2.12.5 was used. For each sample an input file with major ion concentrations, pH, pe and temperature were created, yielding an output file with saturation indices for possible minerals present. The potential, Eh, which was measured in field, was converted into pe using the following relationship (Drever, 1982):

$$pe = \frac{F}{2.303 \cdot R \cdot T} \cdot E_h \quad (16)$$

where F is Faraday's constant: 23.06 kcal per volt gram equivalent,
R is the gas constant: $1.987 \cdot 10^{-3}$ kcal / (deg · mol)
T is the temperature in Kelvin

A speciation was also calculated by Phreeqc, suggesting the most abundant species in solution.

3.7 Mass Flow Calculations

The mass flows of the metals arsenic, cadmium, lead and iron at each sampling point were calculated as the concentration of the metal in solution times the flow.

3.8 Residence Time

To get an idea of what time span a particle spends in the rivers, the residence times within the rivers were estimated. The residence time within each river stretch was calculated by dividing the shortest distances between two adjacent points (known from the GPS measurements) by the average water velocity at the points. The total residence time within the rivers was calculated as the sum of the residence time for each river stretch.

3.9 Sources of Error

For many of the analyses it is difficult to determine the certainty. Errors may have been introduced both in field and in laboratory due to contamination, uncertainty of the methods and the human factor.

3.9.1 Water Analysis

During the second field trip, the direct spectrometer used for the nitrate and phosphate measurements broke down, which reduces the reliability for the measurements of these parameters, including the first trip. An other field parameter difficult to measure is the flow. Problems with determining the cross section area at the sampling points as well as preventing the orange from being interrupted in the shallow rivers make the measurements uncertain. The other parameters measured in field are thought to be fairly correct.

When filtering the water samples, the same filters were used more than once, which may contaminate the samples.

Problems at the University of San Andrés, e.g. strikes, made the time in between the sampling and the analysis at the laboratory unsatisfying long, which is thought to affect the analysis results.

3.9.2 Sediment Analysis

The sediment samples were collected over a stretch of about 30 m at each sampling point to represent that area. However, coarser material was not collected, due to the low ability to adsorb metals. Hence, the results of the grain size analysis may not reflect the reality of sampling points with a large fraction of coarse material. Moreover, the sediment samples were not taken at any specific depth, which also affects the results.

When drying the sediment samples, some extra heavy metals may have been added to the samples from the water phase. However, this part is thought to be low and can be neglected. Some uncertainties may also have been introduced to the heavy metal concentrations in the sediments when the 100 g were collected from the original samples of 1 kg.

4. AREA DESCRIPTION

4.1 General Area Description

Bolivia is situated in the central part of South America, bordering to Peru, Brazil, Paraguay, Argentina and Chile. The study area, which consists of the catchment areas of the rivers Sora, Poopó and Marquez, lies in the Oruro County and drains in the Lake Poopó. The area is situated on the Bolivian high plateau Altiplano, which stretches from Peru in the north, S 14° 30', to Chile in the South, S 21° 50', and is slightly declined with an altitude of 3805 m.a.s.l. in the north at Lake Titicaca and 3660 m.a.s.l. in the south at the Salar de Uyuni (PPOe-008, 1996).

The hydrology of Altiplano can be described by the endorheic TDPS-system; Titicaca-Desaguadero-Poopó-Salars, see figure 4.1. Endorheic means that the basin is closed with no outflow of water.

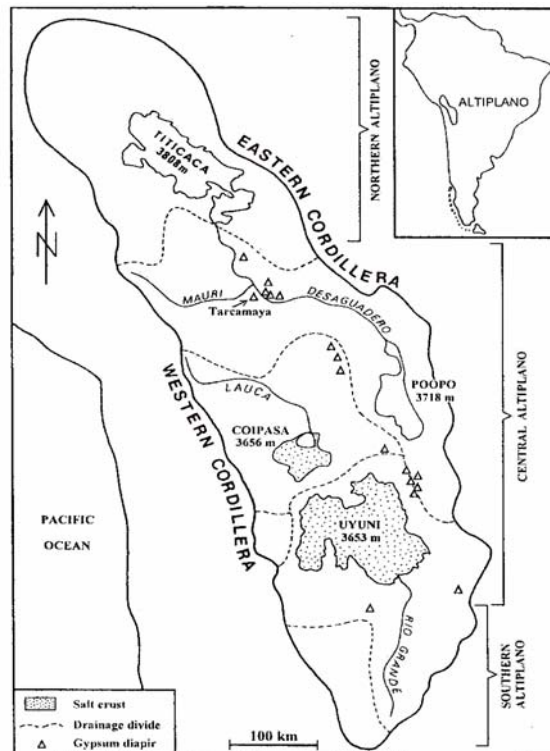


Figure 4.1. Location of the Altiplano and the TDPS system

4.1.1 Demography

The Lake Poopó lies in the Oruro County, which in 2001 had 392000 inhabitants out of which 60% lived in urban areas. 66% of the people in the area lived in poverty and 28% in extreme poverty. The biggest city is Oruro with 201500 inhabitants. Other smaller communities in the study area are Challapata, Huanuni, Huari and Poopó (Bolivia atlas estadístico de municipios, 2005).

The health of the people in the area is in general very poor. The infant mortality was in 2001 as high as 113 per 1000, the life expectancy less than 59 years and more than 50 % of the population were younger than 20 years. The most common causes of mortality in the area are respiratory and food related diseases. Most of the food related diseases are due to the lack of clean drinking water (PPO 9701).

Traditionally, the mineral sector has been the backbone of the Bolivian economy. Its importance has fluctuated over the years due to market prices, political instability and diverse structural changes of the mining sector. Recent changes in the government legislation and the adoption of a policy aimed at attracting foreign investors are beginning to change the decline of the mining sectors importance (Troëng & Riera, 1996). With today's mineral findings, the reserves are estimated to last for only 4-11 years more (based on data from 1997) with the current levels of extraction. Therefore, it is crucial to discover new findings. In the Poopó region no oil or gas has been found, and the potential for such discoveries seem limited (PPO 9701, 1997).

The soils in the area are in very poor conditions. Great areas are naked and exposed to wind and rain erosion, while others are too saline or contain too high concentrations of heavy metals, making them unfit for any economic use. Of the about 4.95 million hectares in the Oruro County, only about 30 % is covered with sufficient vegetation to support livestock ranching, and as little as 3 % of the area is considered being suited for agriculture. The fact that the area is often exposed to extreme variations of flooding and droughts makes the possibility for agriculture even more narrow (PPO 9701).

4.1.2 Geology

The Altiplano is separated from the Eastern Cordillera by the Uyuni-Uyuni fault system, see figure 4.2. Due to this division, two parts with distinct morphology, structural and geological habits are to be found. The central Altiplano, situated west of the fault, consists of a top layer of early Cenozoic lacustrine and fluvial sediments, resting on older Palaeozoic sedimentary rocks. The sediments consist of gravel, sand, silt, clay, limestone and evaporates, and are the most widespread on the Altiplano. East of the Uyuni-Uyuni fault, the Eastern Cordillera is located. It consists mainly of sedimentary rocks such as shales, siltstone, sandstone and quartzite. Beneath, older sedimentary rocks are situated, also from the Palaeozoic time period. Two major volcanic fields from the Cenozoic era are located in the north and south respectively.

Most metallic mineral deposits of the area are concentrated within the central part of the Eastern Cordillera Tin belt. The Tin belt extends from the south-eastern parts of Peru to the north-western part of Argentina and shows great variations in type, age and mineral contents. The mineralization is often related to intrusives emplaced during various magmatic episodes and related to tectonic events. These are of greisen and vein type and are found with in older sedimentary rocks and younger igneous rocks, characterized by quartz, sericite and tourmaline. The tin vein deposits in the area are of the richest in the world. Other important polymetallic veins are those of zinc, silver, lead and gold (Troëng & Riera, 1996).

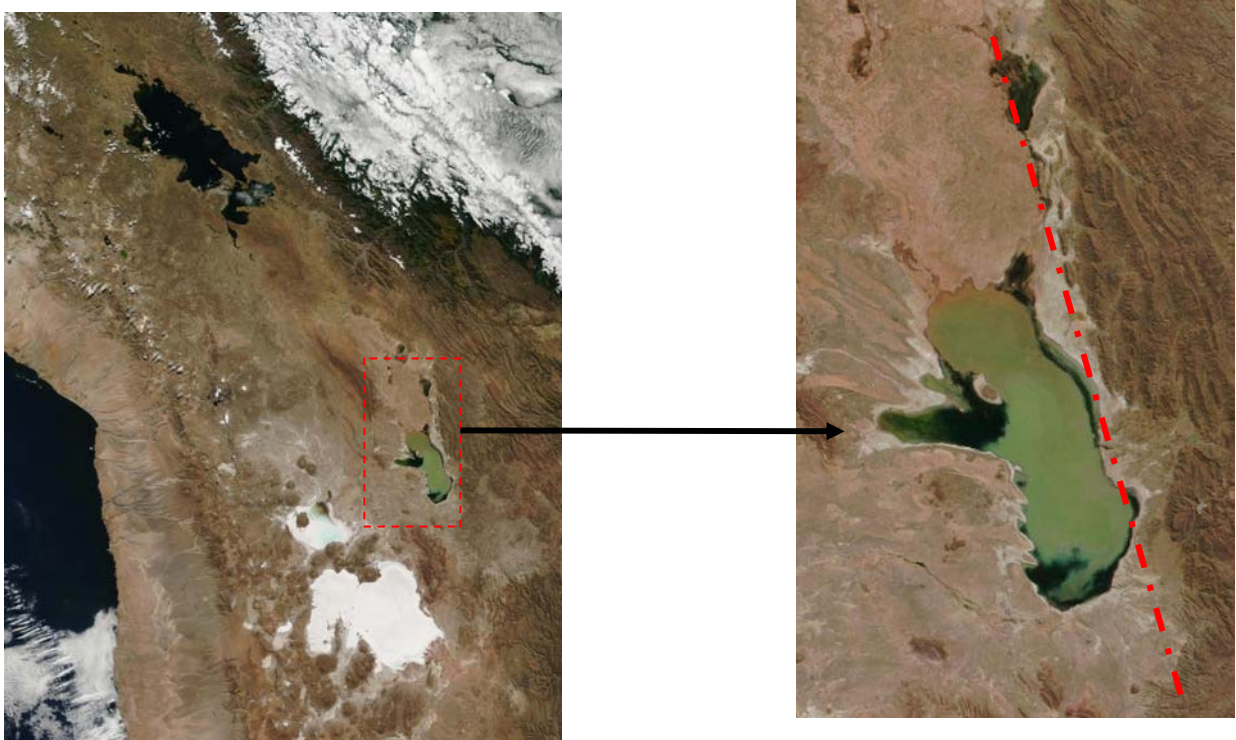


Figure 4.2 Satellite image showing Lake Poopó, and the fault, based on a image from NASA (2004)

4.1.3 Climate

The climate around Lake Poopó has been described by the UNEP (1996) as arid to semi-arid, that for most of the year have cold and dry conditions with almost all of the annual precipitation (300-400mm) falling between December and April (Troëng & Riera, 1996 and PPO 9606, 1996). The precipitation normally takes form in the east when humid air from the Amazons ascends over the eastern range of the Andes and is cooled down. Normally the precipitation falls in the form of rain as the rain period coincides with the summer months (PPO 9606).

The temperatures vary from +25 °C (mean 12-14 °C) during the summer months and drops down to -15 °C (mean 6-7 °C) in wintertime, May-August (Troëng & Riera, 1996). The differences between day and night are normally great (PPO 9606).

4.1.4 Hydrology

The main river flowing to the Lake Poopó is the 350 km long Desaguadero River, starting at the Lake Titicaca, and it accounts for the biggest water contribution to the Poopó Lake. However, the flow in the river varies both seasonally and annually. The mean flow during the years 1956 to 1983 was 16 m³/s and during the following years it was 110 m³/s, which was considered to be a very high value. Some kilometres north of Lake Poopó, at the mine La Joya, the river divides into two. The western river flows through the village Toledo and ends up in the north-eastern part of Lake Poopó and the eastern river flows to the lake Uru Uru situated north of Lake Poopó. A 20 kilometres long channel connects Lake Uru Uru and Lake Poopó. Other rivers contributing to Lake Poopó are the rivers Japo, Santa Fe, Huanuni, Sora Sora, Poopó and Antequera north-east of the lake and the rivers Marquez and Sevaruyo south of the lake. The flows in these rivers are however very small compared to the flow in Desaguadero. During periods with high water levels the river Laca Jahuira flows from Lake Poopó to the salt desert Salar de Coipasa. However, during dry periods the river barely exists (PPOe-008, 1996).



Figure 4.3 Satellite image based on an image from NASA (2004), showing the rivers of interest in the Poopó area.

The reports PPOe-008 and PPO 9606 emphasize the importance of the flow in Desaguadero for depth and extent of Lake Poopó. The flow in Desaguadero is very dependent on the water level in Lake Titicaca, making the water level high in Poopó when high in Titicaca. The maximum depth in Lake Poopó has varied between two and six meters and the extent of the lake between 2500 km² and 3500 km² due to variations in the flow of Desaguadero (PPOe-008, 1996). In 1994 Lake Poopó almost disappeared. PPO 9606 concluded that this was due to the low flow in the Desaguadero River during the earlier years.

4.2 Poopó River Basin

The basin of the Poopó River is situated on the eastern side of Lake Poopó in the south of the Sora Sora basin and comprises an area of 109 km². The river starts in the mountains in the east of the town Poopó and enters the Desaguadero close to the small community of Poopó. The substrate in the area consists mainly of Palaeozoic sediments (PPO 9612, 1996).

The pH in the river Poopó is alkaline and the river contains thermal waters (García et al., unpublished and PPO 9612, 1996).

The Poopó-Candelaria district has a long history of mining activity and has 200 adits and trenches with a total length of nearly 18 km today. The Poopó-Candelaria polymetallic belt is situated on the boarder of the Uyuni-Uyuni fault. West of the fault are great sedimentary deposits of gravel, sand and silt. East of the fault the Eastern Cordillera's Palaeozoic block is situated with its siltstone, quartzite and slate composition. Subvolcanic intrusions are also present in the area.

Major metals to be found in the polymetallic bearing belt of Poopó-Candeleria are silver (230-250 g/t), zinc (4-8 g/t) and tin (0.3-1.7 g/t).

The main mineral deposits in the Poopó district are sulfosalts-sphalerites-sulfostannates with galena (Ag, Sn, Zn, Pb), but deposits of cassiterites with sphalerites and sulfostannates (Sn, Zn, Ag) and stibnite with native gold and ferberite (Sb, Au, W) also exists.

The mineral wastes situated in the catchment of Poopó River are quite small in comparison to the deposits at Sora Sora. However, they still amount to 1 335 000 tons of material (PPO 9611).

The Poopó River starts in the mountains upstream the city of Poopó. The first sampling point, P1 is situated in the mountains approximately 40 km upstream the town Poopó. The ground seems to consist of sedimentary bedrock and the area around the river is pastureland. The second point, P2, is situated 20 km downstream the first point and the riverbed consists of coarser materials such as stones. The third point, P3, is situated downstream a spring of thermal waters, which most probably affects the water quality. The riverbed still consists of coarse material with stones covered of algae. The fourth point, P4, is situated downstream the city of Poopó and the mills, which may affect the water quality. The riverbed is wide and the sediment consists of finer materials. The river bottom is covered of red-brown fall out and the water contains algae.



Figure 4.4 Field work at the Poopó River, sampling point P1

4.3 Marquez River Basin

The basin of river Marquez is situated in the south of the Lake Poopó. The basin is characterized by the wide, open plateau of Los Frailes. The bedrock consists of volcanic rocks such as dacites and riolites from the late Mioceno-Plioceno with high concentrations of arsenic; up to 810 ppm (PPO 9612). This could be compared to the average arsenic content in igneous silica rocks, which is approximately 1 ppm (Wedephol 1991 in PPO 9612, 1996). Due to the high contents in the bedrock the Marquez River has natural high levels of arsenic, which exceeds the WHO guidelines (10 µg/l). PPO 9612 found levels between 68 and 150 µg/l during an eight months period, and García (García et al., unpublished) levels of 10 µg/l during the dry period and 140 µg/l during the rain period. The pH in the river is alkaline.

The Marquez River is the widest and it flows in a wide-open plateau. At the first sampling point, M1, the surrounding area is pastureland with a lot of lamas. The river sediment consists of fine materials with banks and deltas. The second sampling point, M2, is similar to the first one, but the surrounding land consists of quinoa cultivations.

4.4 Sora Sora River Basin

The basin of Sora Sora is situated north-east of Lake Poopó and covers an area of 591 km². The main rivers in the area are Huanuni, Ventaimedia, Japo, Santa Fé and Sora Sora. The river Huanuni starts in the mountains in the south-eastern part of the basin south-east of the small town Huanuni and flows in a north-western direction through the town towards the small village Sora Sora. Some kilometres downstream of the town Huanuni, at Playa Verde, the river Ventaimedia joins the Huanuni River. From here the river flows in a wide, open valley with sediments of gravel, sand and silt (PPO 9612).

The river Santa Fé starts in the north-eastern part of the basin in the mountains at the Morococala mine and flows in a western direction towards the village Sora Sora. The river Japo starts in the mountains in the northern part of the basin and joins Santa Fé after some kilometres. The river flows in a narrow canyon and contains small amounts of coarse sediments. Normally the rivers Santa Fé and Japo only contain water during the rain period. Before the village Sora Sora the river Santa Fé joins the Huanuni River and forms the river Sora Sora that flows through the small community of Machacamarca. Finally the river Sora Sora enters the river Desaguadero. (PPO 9612).

The pH in the rivers is in general acid due to the mining activity in the area (PPO 9612, 1996 and García et al, unpublished). However, the pH is alkaline in the river Huanuni upstream the mines and in the river Ventaimedia (PPO 9612).

The major principal mining districts located in the Sora Sora catchment area are Japo-Morococala and Huanuni. Since the late 1970's Huanuni has been Bolivia's main tin producer. The Huanuni mining district covers an area of 3.6 km by 2.8 km and reaches a vertical depth, underground workings and drillings, of more than 1000 m. The lithostratigraphic sequence where the mineralization is to be found is a lower Palaeozoic marine sedimentary series, which contains quartzite, slates and shales. The average tin composition is 3.6 % in actual reserves, but reaches up to 30 % in certain ore shoots. Other metallic contents are also present in the different deposits in the area (Ahlfeld et al. 1964 in Troëng & Riera, 1996): 100 to 5000 g/t of Ag, 4-38 % of Zn and 1-8 % of Pb (Troëng & Riera, 1996). The deposits in the Huanuni districts mainly consists of the minerals cassiterites with sphalerites and sulfostannates (Sn, Zn, Ag) but minor deposits of sulfosalts-sphalerites-sulfostannates with galena (Ag, Sn, Zn, Pb), wolframite-ferberite with stibnite (W, Sb) and sphalerite-argentiferous galena (Zn, Pb, Ag) also exists.

Accompanying the Huanuni tin mine, the Santa Elena Beneficiation plant is also situated in the area. In the Huanuni mining centre, a great deal of artesian mining is also taking place. The methods used are very simple, at times mechanized operations, and generally polluting the environment heavily (PPO 9611).

The Japo-Morococala district is located in the sub-basin of the Santa Fé River. However, the tin (in some extent Zn, Pb and Ag) deposits of Japo, Morococala and Santa Fé are now abandoned (PPO 9611). The main minerals in the district are cassiterites with sphalerites and sulfostannates (Sn, Zn, Ag).

All mining areas contain great loads of mining waste such as tailing and waste rock deposits, with various potential to produce acid rock drainage. The total sum of mineral wastes in the catchment area of Sora Sora according to the inventory made by PPO in 1996 amounts to 10 200 000 tons.

The first sampling point at the Sora Sora River, H1, is situated in a wide canyon upstream the city of Huanuni and is not affected by any mining activity. The riverbed is covered by grass and tufts, and surrounded by mountains. The second point, H2, is situated downstream the city of Huanuni at Playa Verde, which is a combined waste deposit of domestic and mining waste. The point is very affected by the town Huanuni and contains a lot of domestic wastes and coarse rock materials. At this point the river Ventaimedia joins the Sora Sora River. The third point, H3, is situated close to the church of Sora Sora and the surrounding area is steppe. The fourth point, H4, is situated at the closed mill Machacamarca. The point is surrounded by tailing deposits that may affect the water quality. At H2, H3 and H4 the river flows in a wide valley.

During sampling, the river Sora Sora mainly consisted of the Huanuni River, and the name Huanuni is often used to represent the Sora Sora River. In the following chapters Huanuni River is used and refers to the Sora Sora River.

5. RESULTS

In this chapter the results of the chemical analyses are presented. The location of the sampling points is presented in appendix A, table 1. First, in chapter 5.1, the calculated residence times within the rivers are presented.

This is followed by chapter 5.2, where the general water composition of the samples is presented. The samples are classified on the basis of the most abundant anions and cations, the amount of TDS and pH. If, for example, sulphate amounts to more than 50 % of the total anions, measured in meq/L, and calcium amounts to more than 50 % of the total cations, the sample is classified as a calcium-sulphate water. Focus is set on changes along the river and between the two sampling periods. Changes in flow rate and temperature are also presented.

In chapter 5.3 the results of the analyses for heavy metals in water are presented. Spatial trends and changes between the two sampling times are identified. The values are compared with the WHO guideline values for drinking water and the maximum permissible levels for drinking water according to Bolivian law. The values are also compared with previously reported values from dry and rain period in the years 2001 to 2003.

In chapter 5.4 the results of the speciation is presented.

Chapter 5.5 presents the grain size distribution of the sediments. The accumulated weight in percent is used for comparing sampling points.

In chapter 5.6 the heavy metal concentrations of the sediment samples are presented. The focus is set on changes along the rivers and changes between the two sampling trips. Also a comparison with values reported by García (unpublished) and a comparison with the global average content of the metals in the earth's crust is done.

Chapter 5.7 deals with saturation indices proposed by Phreeqc. Saturation indices presented are calculations based on water composition, suggesting minerals that may control the water composition.

In the last chapter, chapter 5.8, the mass flows of dissolved heavy metals are presented.

In the earlier study conducted by García, in total 5 sampling trips were conducted between the years 2001 and 2003 (García et al. unpublished). In that study one sampling point was chosen for each river, close to the outlet into Lake Poopó. These results were then divided into two major periods, one dry period and one rain period, May-September and December-March respectively. Our samples were taken in the beginning of October and in the middle of December. Since the characteristics of the rivers differ greatly depending on the season, the different dates of sampling between the studies should be kept in mind when comparing the results. In addition to the difference in date, the location of the sampling sites also differs. The sampling point representing Poopó in the study by García is located between our sampling points P3 and P4, very close to P4. In the river Marquez, Garcia's sampling point is situated about 20 km downstream our point M2 and in the river Huanuni, her sampling point lies in between our H3 and H4.

The results obtained for zinc concentrations in solution are thought to have been exposed to contamination during analysis, and are therefore left out in this report.

5.1 Residence Time

For the Poopó River an average residence time of 7 hours was calculated. For the Marquez River and the Huanuni River the times were 28 and 26 hours respectively. These values are average values for the two trips. For the Poopó River and the Huanuni River the last sampling points are located quite close to the Lake Poopó, while the last sampling point for the Marquez River is still far from the outlet.

5.2 General Water Chemistry

Physical parameters of the water samples, analysis results of major ions together with analysis accuracy, ion balances and a comparison between total anions, total cations and electrical conductivity are presented in appendix B.

The ion balances show great differences between total cation concentrations and total anion concentrations. In the samples P1, P2, M1, M2 and H1 the total cations are higher than total anions. The difference may be due to that there might have been some negatively charged species present in the samples that were not analyzed for. One such species is the weak silic acid, H_4SiO_4 , with $pK_{a1} = 9.9$ at $25\text{ }^\circ\text{C}$ (Drever 1982). Silic acid in natural waters is controlled by mineral dissolution. Some minerals releasing silic acid when being dissolved are quartz, amorphous silica, K-feldspar, kaolinite and muscovite. However, the equilibrium concentrations of these minerals are too low to explain the anion deficit. For example, the dissolution of amorphous silica yields a silic acid concentration of 2 mmol/l at equilibrium. The concentration of the deprotonated species $H_3SiO_3^-$ is a function of pH and H_4SiO_4 concentration according to:

$$[H_3SiO_3^-] = [H_4SiO_4]^{pH - pK_{a1}} \quad (17)$$

The dissolution of amorphous silica should thus give rise to $H_3SiO_3^-$ concentrations of 0.0025, 0.025 and 0.25 meq/l at pH-values of 7, 8 and 9 respectively, which is not enough to explain the anion deficit.

Other negatively charged species that may have been present in the samples, but not analyzed for are organic substances such as humic acids.

In the samples from P3 and P4 taken during the first trip the ion balance was good. This is due to the extremely high values of both chloride and sodium that balance each other. During the second trip the sodium concentrations at these sampling points was lower, which together with high chloride and sulphate concentrations resulted in a deficit of cations.

The samples H2, H3 and H4 contained higher levels of anions than cations, which is due to the extremely high values of sulphate and that the iron concentrations are not included in the balances. The iron concentrations are discussed in chapter 5.3 Heavy metals in solution.

5.2.1 Poopó River

The characteristics of the samples taken along the Poopó River are presented in table 5.1.

Table 5.1 Main characteristics of the samples from the Poopó River.

Sampling point	TDS (mg/l)	Water type	pH	Flow (l/s)	Temperature (°C)
P1	120 - 111	Calcium-sulphate	8.81 - 8.42	10 - 20	21 - 18
P2	140 - 154	Calcium-sulphate	8.70 - 7.96	70 - 110	19 - 17
P3	6110 - 5140	Sodium-chloride	8.75 - 8.43	70 - 220	32 - 26
P4	5590 - 5070	Sodium-chloride	9.65 - 9.35	80 - 120	21 - 22

Point 1 – P1

This first point is situated far from any anthropogenic influences, except those of smaller agricultural- and livestock activities.

The composition of the samples from P1 was found to be similar during both trips and the water is classified as a calcium-sulphate water. TDS was found to be moderate, 120 mg/l during the first trip and 111 mg/l during the second, and pH was alkaline during both trips, 8.81 during the first and 8.42 during the second. The major difference found between the two trips is the flow rate, being 10 l/s during the first visit and 20 l/s during the second.

Point 2 – P2

The second sampling point is located about 4.25 km as the crow flies downstream the first point. Not much differed between the two locations at the time of sampling. In times of higher water flows another river is connecting to the Poopó River just before the second point. However, this was not the case in either of the trips.

The water is classified as an alkaline calcium-sulphate water. The TDS concentration was found to be slightly higher than in the first point during both trips, 140 mg/l in the trip 1 sample and 154 in the trip 2 sample, which is due to an increase in chloride and sodium concentrations.

The flow rate was higher than in the first sampling point; 70 l/s during the first trip and 110 l/s during the second trip.

Point 3 – P3

This is the first point where great differences were found. Point three is situated about 2 km downstream point 2. In between these points a thermal spring is situated. Still no greater mining activities or waste heaps have been introduced in the path of the river.

Very elevated concentrations of all ions were found at P3 during both trips; TDS were found to be 6110 mg/l during the first trip and 5140 mg/l during the second. This increase is due to the thermal water. Sodium and chloride concentrations were found to be extremely high in the third point during both trips making the water a sodium-chloride water. During the first trip the sodium concentration were found to be 2280 mg/l (99 meq/l) and the chloride concentration 3690 mg/l (104 meq/l) making the ion balance good. During the second trip the sodium concentration was about half of the concentration found during the first trip whereas the chloride concentration was similar to the concentration during the first trip.

The fact that thermal water is mixed in between point 2 and 3 results in a great rise of temperature from around 19 to 31°C during the first trip and 17 to 26 °C during the second.

During the first trip the flow rate was 70 l/s in both point 2 and 3 whereas the flow increased from 110 l/s in point 2 to 220 l/s in point 3. However, the high value found in P3 during the second trip is thought to be an overestimation.

pH was still alkaline during both trips; 8.75 and 8.43.

Point 4 – P4

This point is situated about 3 km downstream point three. The major processing plant is situated between these two points, as well as the small village of Poopó. Quite big sedimentation dams and tailing deposits are also situated in the near vicinity of the riverbed. All water used in the plant is said to come from water pumped out from the mines, and then kept re-circulated without any discharge to the river.

Like the water from the third point, the water from the fourth had a very high TDS-level during both trips (5590 mg/l during the first trip and 5070 mg/l during the second) and could be classified as a sodium-chloride water. Both chloride and sodium concentrations were slightly lower than in the third point during the first trip. During the second trip the sodium concentration was similar to the concentration found in point 3, whereas a significant increase in chloride and sulphate concentrations was found. The very high levels of chloride and sodium may be due to an analyzing error as they exceed the TDS-value.

Point 4 had the highest pH-value during both trips; 9.65 during trip 1 and 9.35 during trip 2. The temperature had dropped to about 20 °C during both trips and the flow rate was estimated to 80 l/s during the first trip and 120 l/s during the second.

5.2.2 Marquez River

The characteristics of the samples taken along the Marquez River are presented in table 5.2.

Table 5.2 Main characteristics of the samples from the Poopó River.

Sampling point	TDS (mg/l)	Water type	pH	Flow (l/s)	Temperature (°C)
M1	350 - 441	Sodium-chloride	8.63 - 8.19	730 - 450	17 - 27
M2	690 - dry	Sodium-chloride	8.62 - dry	290 - dry	18 - dry
M3	dry	dry	dry	dry	dry

Point 1 – M1

Point 1 is the most southern point, situated in a very flat area. The only activity spotted in the area is that of llama livestock. The riverbed is wide, and consists of fine-grained material.

The TDS concentration was found to be moderate during both trips; 350 mg/l during the first trip and 441 mg/l during the second. During both trips the water could be classified as a slightly alkaline sodium-chloride water. The major differences found between the trips were lower TDS and higher flow during the first trip (730 and 450 l/s respectively). Furthermore, the temperature was higher during the second trip; 17 °C during the first trip and 27 °C during the second.

Point 2 – M2

The second point is situated 28 km downstream from point 1. The land use in this area is more concentrated to cultivation compared with M1. The riverbed is still wide and consists of fine-grained material. During the second trip the river was dry and no sampling was done.

The TDS was found to have increased from 350 mg/l in the first point to 690 mg/l in the second and the water could still be classified as slightly alkaline sodium-chloride water. Interesting is the decreasing flow along the river. In this point the flow was determined to 290 l/s compared to 730 l/s in the first point. During the second trip this point was dry and no samples were taken.

Point 3 – M3

During the very first field trip a third sampling point was chosen. However, this point turned out to be dry during the two following sampling trips.

5.2.3 Huanuni River

The characteristics of the samples taken along the river are presented in table 5.3.

Table 5.3 Main characteristics of the samples from the Huanuni River.

Sampling point	TDS (mg/l)	Water type	pH	Flow (l/s)	Temperature (°C)
H1	160 - 143	Ca-SO ₄ /Mg-SO ₄	7.32 - 7.23	10 - 20	13 - 13.5
H2	1470 - 1244	Sodium-sulphate	3.77 - 3.08	70 - 110	13.5 - 10.9
H3	1130 - 937	Calcium-Sulphate	2.56 - 3.32	70 - 220	14.6 - 12.9
H4	1090 - missing	Ca-SO ₄ /Na-SO ₄	2.95 - 2.83	80 - 120	16.3 - 11.6

Point 1 – H1

The sampling point is situated upstream the mining community Huanuni and is not affected by any mining activities. Hence, the surrounding bedrock should determine the water composition.

TDS was found to be low during both trips; 160 and 146 mg/l. The water from the first trip could be classified as a neutral calcium-sulphate water, whereas the water from the second trip could be classified as a neutral magnesium-sulphate water. The main difference between the first and the second trip is the high magnesium concentration in the water from the second trip. However, the electrical conductivity of the sample from the second trip indicates that the cation concentration should be lower, see appendix B table 7, and the high magnesium may be due to an analytical error.

The flow was higher during the second trip; 60 l/s compared to 20 l/s during the first trip.

Point 2 – H2

The sampling point is situated downstream the mining community Huanuni close to a domestic waste dump. Mining activities are supposed to have great impact on the water quality.

TDS was very high in the second point; 1470 mg/l during the first trip and 1244 mg/l during the second. The water from the first trip contained very high levels of sulphate and could be classified as a calcium-sulphate water. The sample from the second trip contained much lower levels of sulphate, but this is thought to be due to an analytical error. The water from the second trip is classified as a sodium-sulphate water. The pH was found to be acidic during both trips; 3.77 and 3.08.

The flow was measured to 40 l/s during the first trip and 200 l/s during the second. The flow during the first trip may have been underestimated.

Point 3 – H3

The third point is situated downstream the mining activities.

TDS was found to be high, 1130 mg/l during the first trip and 937 mg/l during the second, and the water from both trips could be classified as acidic calcium-sulphate water with pH-values of 2.56 and 3.32 during the first and second trip, respectively.

During the first trip a flow of 230 l/s was measured. For the second trip the flow was 180 l/s.

Point 4 – H4

This point is situated downstream of all mining activities, but huge tailing deposits from the former processing site Machacamarca are situated close to the sampling point.

The TDS concentration was still high, 1090 during the first trip; although a decrease from the second sampling point could be seen. During the first trip, the sulphate concentration was found to be similar to what was found at the third point, whereas an increase could be seen during the second trip between the third and the fourth sampling point. The water from the first trip could be classified as a calcium-sulphate water and the water from the second as a sodium-sulphate water. pH was found to be low during both trips; 2.95 during the first and 2.83 during the second.

The flow was measured to 190 l/s during the first trip and 300 l/s during the second.

5.3 Heavy Metals in Solution

5.3.1 Poopó River

Extremely high levels of arsenic were found in the samples from P3 and P4 exceeding both the WHO guideline value for drinking water (0.01 mg/l) and the maximum permissible level according to Bolivian law (0.05 mg/l), see figure 5.1. It should also be noticed that the samples from the upstream points P1 and P2 also contained levels above the WHO guideline values. During the first trip, the concentration increased from about 0.03 mg/l at the sampling points P1 and P2 to almost 5 mg/l at P3 and 5.5 mg/l at P4. The samples from the second trip contained even higher values at the two last points; 11 and 12 mg/l at P3 and P4 respectively. The levels at P3 and P4 exceed the previously reported values by García (unpublished), both for the dry and rain period; 2.1 and 0.8 mg/l respectively.

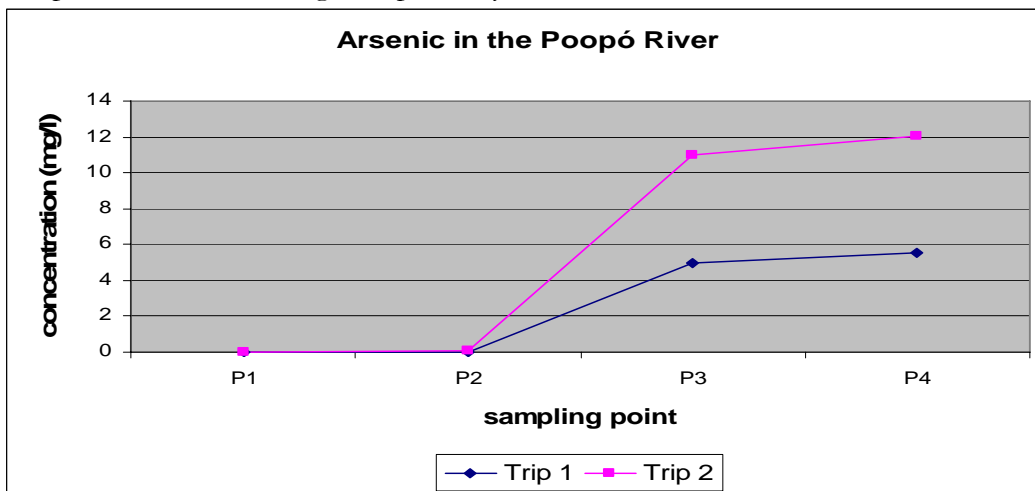


Figure 5.1 Arsenic concentrations along the Poopó River

The cadmium concentrations in the Poopó River were rather low at P1 and P2; less than 0.0001 mg/l during both trips. At P3, the concentrations were found to be 0.002 and 0.001 mg/l during the first and second trip, respectively. The increase between P2 and P3 may be due to the thermal water spring. However, the most significant change along the river was found at P4, especially during the first trip, see figure 5.2. At this sampling point, the concentration was 0.04 mg/l during the first trip and 0.0044 mg/l during the second trip. The high values are most probably due to the mining activities around the community Poopó. The lower value during the second trip could be due to a higher river flow. The concentration found at P4 during the first trip exceeds both the WHO and the Bolivian law values greatly (0.003 and 0.005 mg/l respectively), whereas the sample from the second trip only exceeds the WHO value. García also reported a very high value during the dry period, 0.3 mg/l, and a value of 0.01 mg/l during the rain period (García et al. unpublished).

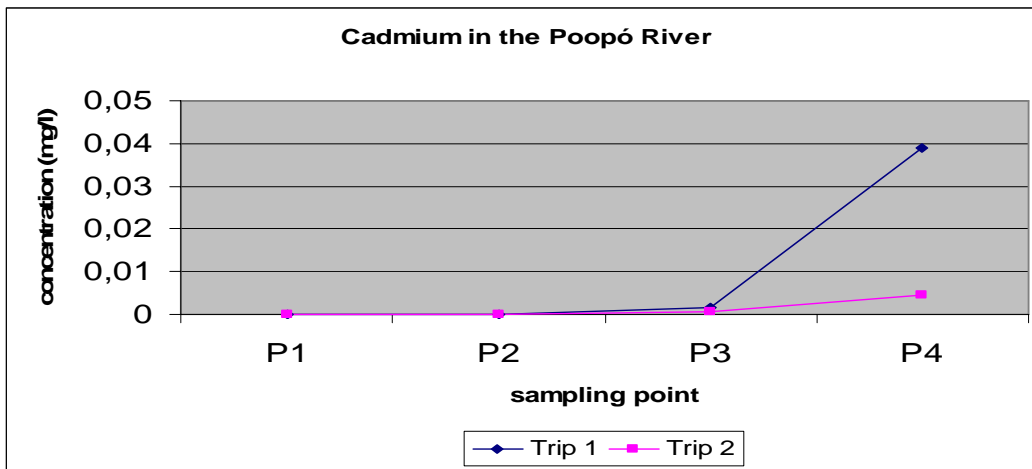


Figure 5.2 Cadmium concentrations along the Poopó River

Figure 5.3 illustrates the lead concentrations along the Poopó River. Slightly higher lead concentrations were found during the second trip than during the first trip. The lead concentrations in the samples from the first trip were in the range 0.18 to 0.27 mg/l, whereas the concentrations in the trip 2 samples were in the range 0.35 to 0.38 mg/l. All concentrations exceeded both the WHO and the Bolivian law values (0.01 and 0.05 mg/l respectively). The concentrations were also higher than the values reported by García who found levels below the detection limit during the dry period and 0.05 mg/l during the rain period (García unpublished).

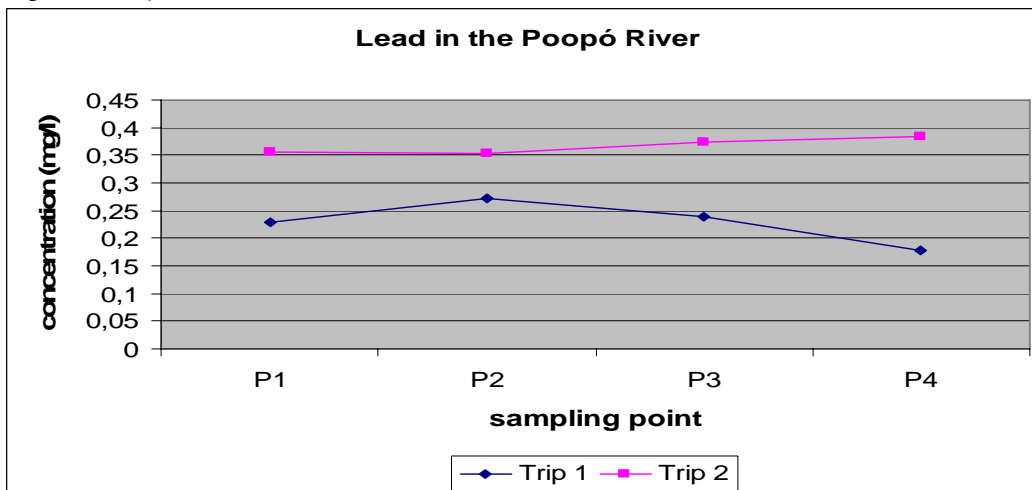


Figure 5.3 Lead concentrations along the Poopó River

In figure 5.4, the iron concentrations are presented. The concentrations increased continuously along the river. During the first trip the concentration increased from about 0.08 mg/l in the upstream parts to 0.15 mg/l in the downstream parts. During the second trip the concentrations were higher and increased from about 0.15 to 0.24 mg/l.

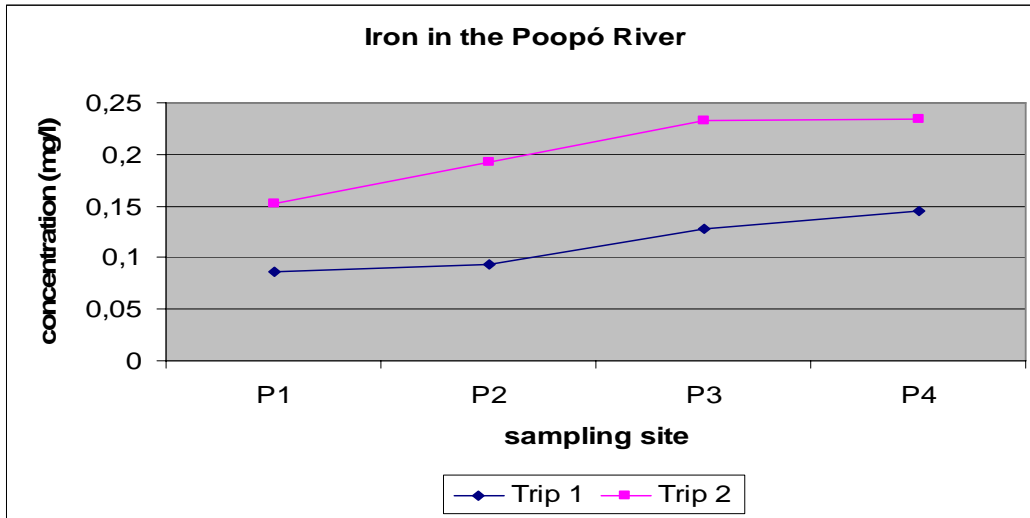


Figure 5.4 Iron concentrations along the Poopó River

5.3.2 Marquez River

The samples from the Marquez river contained arsenic levels between 0.14 and 0.17 mg/l (see figure 5.5), which exceed both the maximum permissible level for drinking water according to Bolivian law (0.05 mg/l) and the guide line value from WHO (0.01 mg/l). These concentrations are higher than the previously reported values by García from the dry period, 0.01 mg/l, and similar to values from the rain period, 0.14 mg/l (García et al. unpublished).

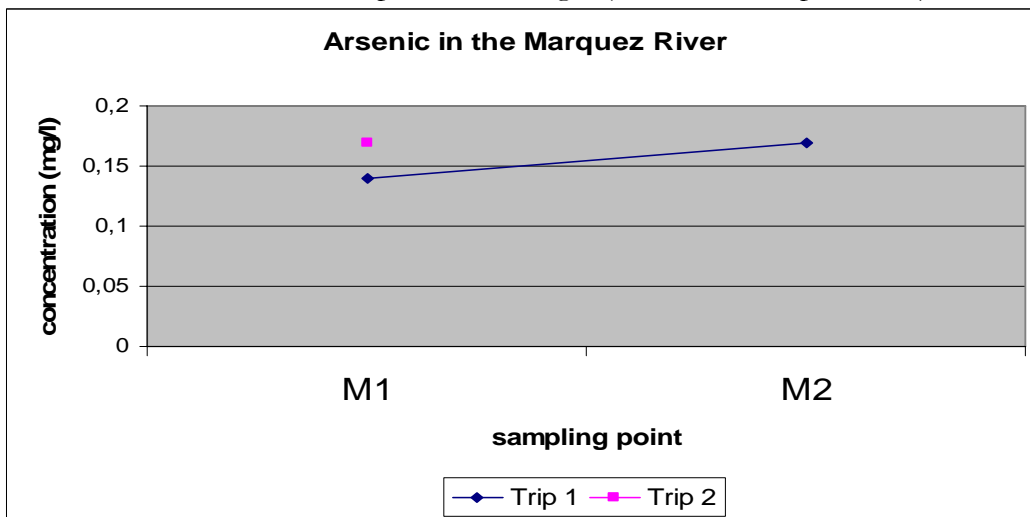


Figure 5.5 Arsenic concentrations along the Marquez River

The cadmium concentrations in the Marquez River were in the range 0.0004-0.002 mg/l (figure 5.6), which is below both the WHO and the Bolivian law values (0.003 and 0.005 mg/l respectively). García (unpublished) reported a very high cadmium concentration in Marquez during the dry period, 0.1 mg/l, whereas the concentration was below the detection limit during the rain period.

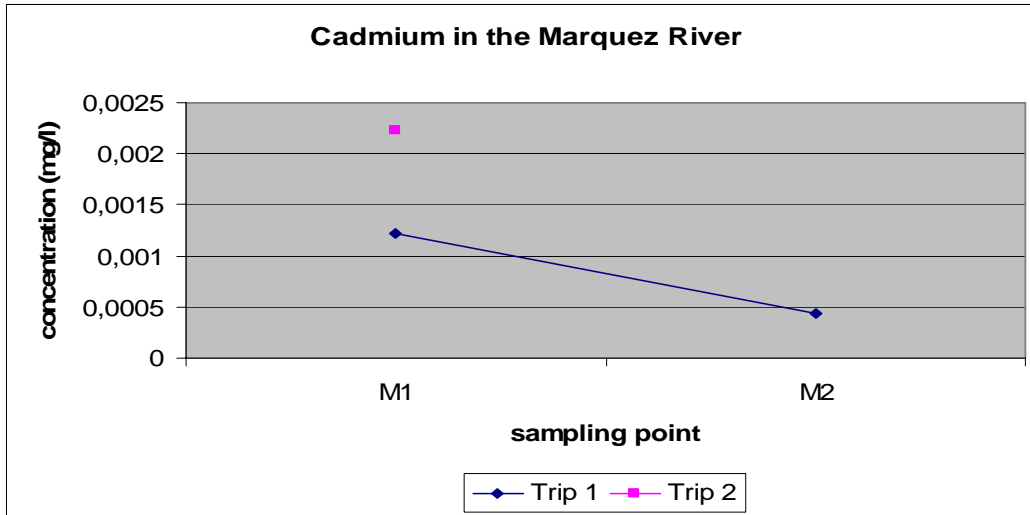


Figure 5.6 Cadmium concentrations along the Marquez River

The lead concentrations varied between 0.29 and 0.36 mg/l, with the highest value in the sample from the last point (M2), see figure 5.7. The concentrations exceed both the WHO and the Bolivian law values (0.01 and 0.05 mg/l). García (unpublished) reported lower concentrations during both dry and rain period (below detection limit and 0.07 mg/l respectively).

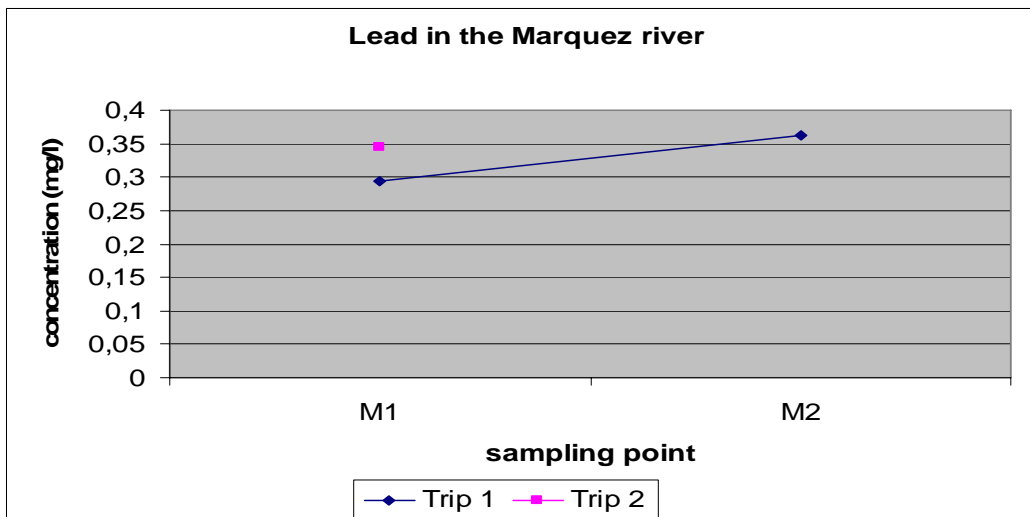


Figure 5.7 Lead concentrations along the Marquez River

The iron concentrations in the Marquez River were found to be about 0.05 mg/l during the first trip and about 0.25 mg/l during the second, see figure 5.8.

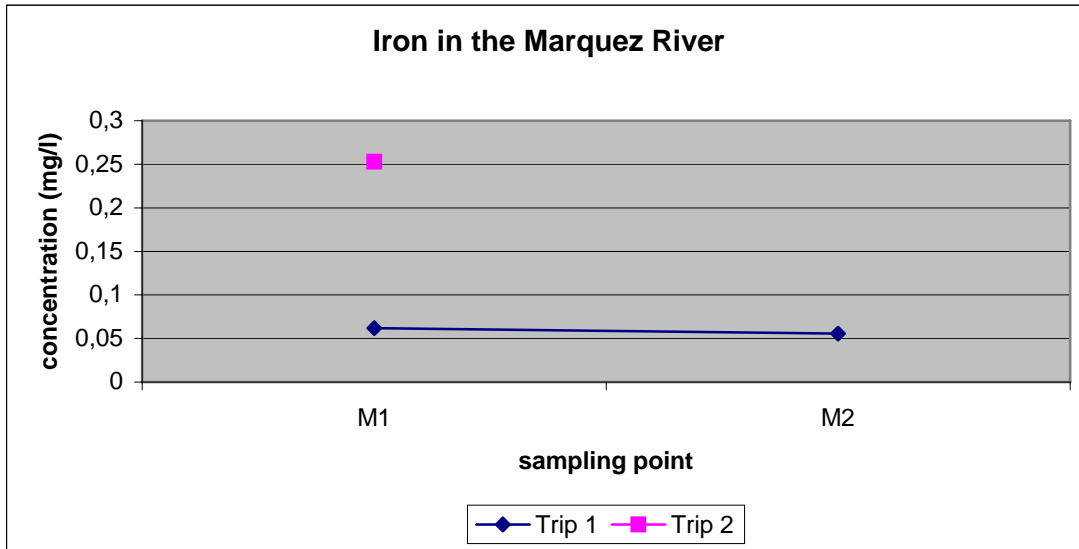


Figure 5.8 Iron concentrations along the Marquez River

5.3.3 Huanuni River

The arsenic concentrations found in the Huanuni River are presented in figure 5.9. The concentrations were very high in the samples from the points downstream the mining community Huanuni, i.e. H2, H3 and H4, exceeding both the WHO and the Bolivian law values greatly. During the first trip, the concentration was almost 6.4 mg/l in the first point downstream the mining community (H2) and increased to 8.4 mg/l in the last point (H4). During the second trip, the concentrations were even higher; between 10.5 and 11.7 mg/l. These values should be compared to the water upstream the mining community (H1), which contained concentrations just below 0.02 mg/l during both trips. The downstream values are also higher than the previously reported values by García during dry and rain period; 0.120 and 0.01 $\mu\text{g/l}$ respectively, (García et al. unpublished).

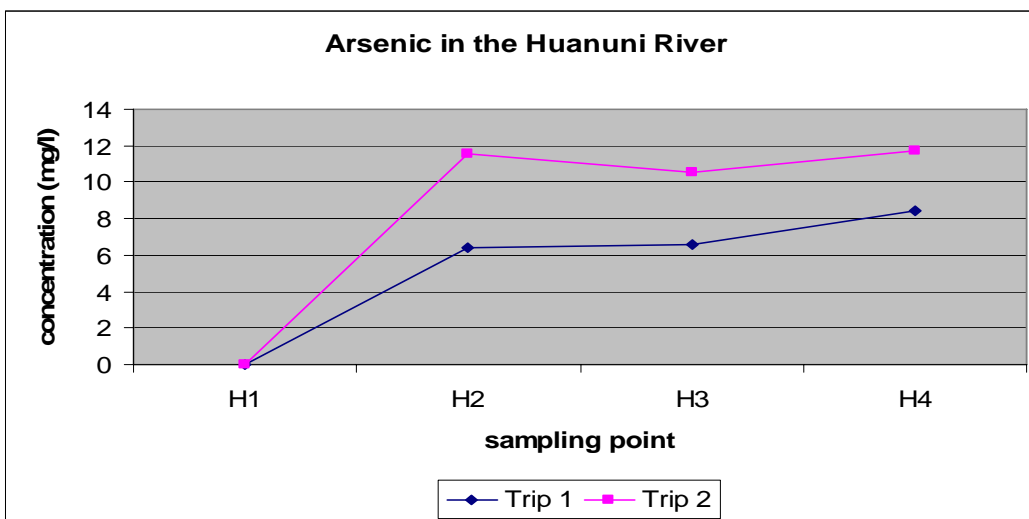


Figure 5.9 Arsenic concentrations along the Huanuni River

The cadmium concentrations in the Huanuni River are presented in figure 5.10. Very high cadmium levels were found downstream the mining community Huanuni exceeding both the WHO and the Bolivian law values greatly. During the first trip, the concentration was 1.38 mg/l at the second point and decreased along the river to 0.764 mg/l at the fourth point. During the

second trip the concentrations were lower at these points but still very high; 0.85 mg/l at H2 and 0.67 mg/l at H4. These values should be compared with the natural values upstream the mining community; 0.0025 and 0.005 mg/l during the first and the second trip, respectively.

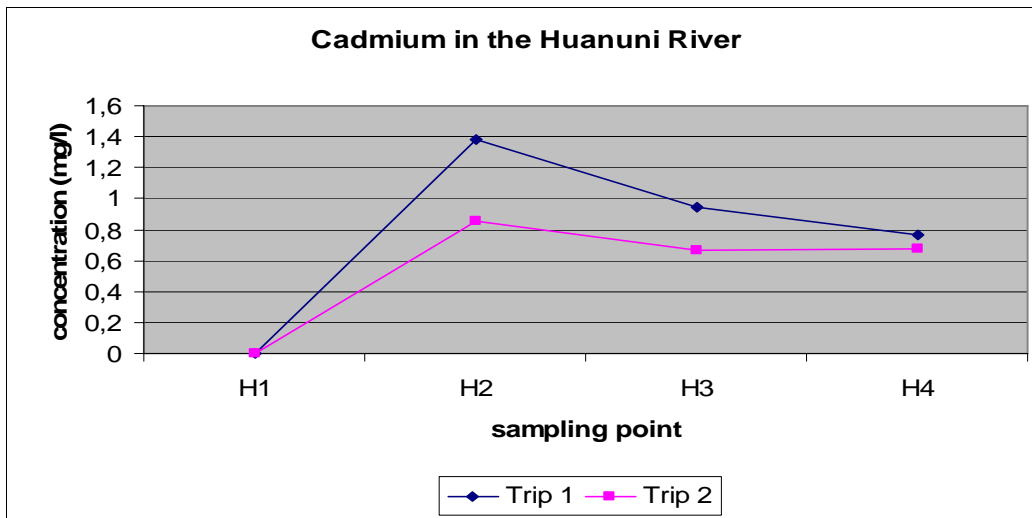


Figure 5.10 Cadmium concentrations along the Huanuni River

Figure 5.11 illustrates the lead concentrations along the Huanuni River. The concentrations were in the range 0.15-0.40 mg/l with lower concentrations in the trip 1 samples than in the trip 2 samples. No signs of a negative impact from the mining activities could be seen but all values exceeded both the WHO and the Bolivian law values.

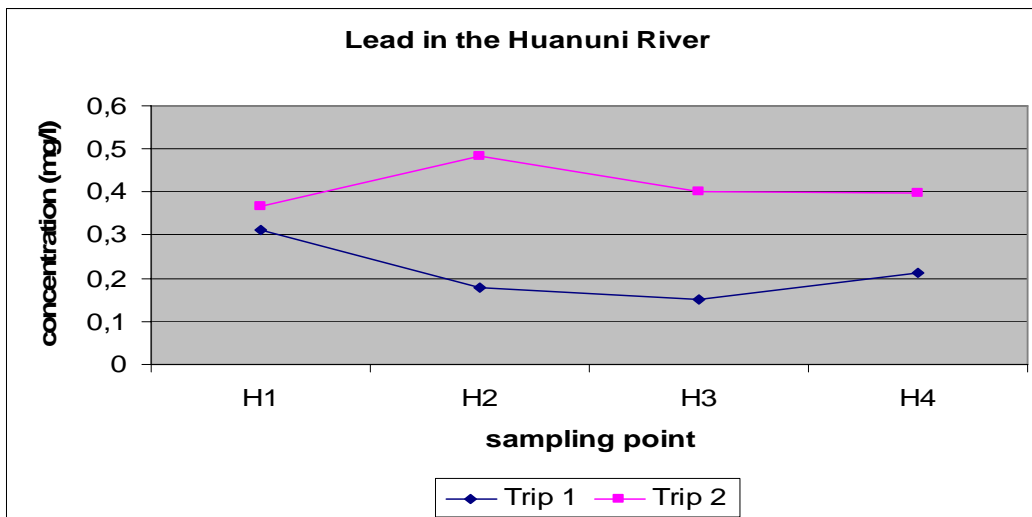


Figure 5.11 Lead concentrations along the Huanuni River

Very high iron concentrations were found in the Huanuni River downstream the mining community with a peak value at the second sampling point, H2, of 500 mg/l during the first trip and 400 mg/l during the second trip, see figure 5.12. This is clearly a result of acid rock drainage. Downstream H2 the concentration decreased along the river to about 120 mg/l at H4.

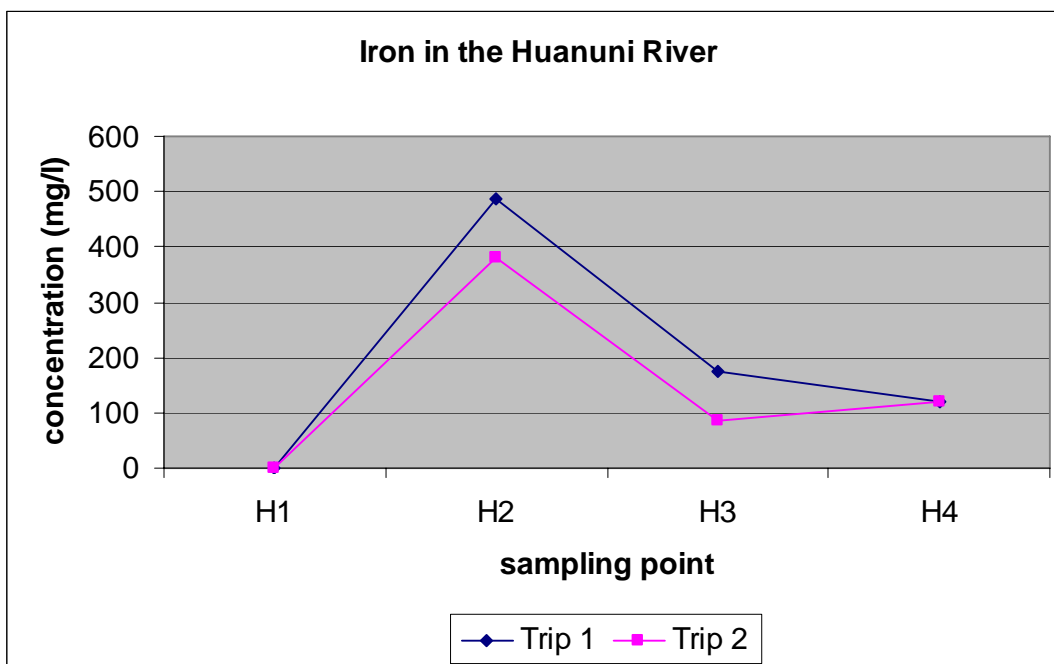


Figure 5.12 Iron concentrations along the Huanuni River

5.4 Speciation

The most common species of lead, iron and cadmium are presented in appendix E. In the Marquez River, the cadmium levels were so low that a speciation was found to be irrelevant. Hence, only lead and iron species are presented for the Marquez River. A speciation of arsenic was not done, as its behaviour is more complex.

5.4.1 Poopó River

According to Phreeqc the most abundant lead species in the samples from the Poopó River was PbOH^+ except for the last point where Pb(OH)_2 was the most common species.

At the two first points, the Fe^{2+} -ion was dominating among the iron. At the third point, P3, the conditions were different and the proportion of free iron(II)-ions was lower. In the last point, P4, three-valent iron dominates and the most abundant species is Fe(OH)_4^- . Hence, the river is changing character to more oxidized conditions downstream. The cadmium in the samples from P3 and P4 turned out to be dominated by CdCl^+ .

5.4.2 Marquez River

Two-valent free iron(II)-ions turned out to be the most abundant iron species in the samples from the river Marquez and Pb(OH)^+ was the most abundant lead species. However, the amount of PbCO_3 was significant in the last sampling point, M2.

5.4.3 Huanuni River

At all sampling points, all iron was of the oxidation state Fe^{2+} . The high levels of sulphate in the Huanuni River downstream the mining community, i.e. at H2, H3 and H4, results in that many of the waters' constituents form complexes with sulphate. At these points approximately one third of the iron was present as FeSO_4 and two-thirds as free iron(II)-ions and about 40 % of the

cadmium was present as CdSO_4 and 50 % as free cadmium-ions. The lead in these points was present as PbSO_4 (60 %), Pb^{2+} (35 %) and $\text{Pb}(\text{SO}_4)_2^{2-}$.

5.5 Grain Size Distribution

No significant differences in grain size of the sediment samples from the Poopó River could be seen. The size at 50 % of accumulated weight for the samples P1, P2, P3 and P4 was about 1.2, 1.15, 1.4 and 1.45 mm. The Marquez samples contained finer particles. The size at 50 % of accumulated weight was 0.15 and 0.42 mm for the samples from M1 and M2 respectively. Within the Huanuni River, the sample from H2 was the finest with 0.2 mm at 50 % of accumulated weight and the sample from H1 was the coarsest with 0.8 mm at 50 % of accumulated weight. Hence, the sediments of the Poopó River are coarser than the sediments of the Huanuni River and the Marquez River.

5.6 Heavy Metals in Sediments

Since no guideline concentrations have been found for metals in sediments, a comparison is made with mean values for the earth's crust found in literature.

5.6.1 Poopó River

The arsenic concentrations of the sediment samples from the Poopó River are presented in figure 5.13. The concentrations vary between 18.5 and 91.9 mg/kg with an average content of 42 mg/kg for the two trips. According to Smedley and Kinniburgh (2001) the global average of arsenic concentration in unconsolidated sediment lies in the range 3-10 mg/kg. None of the samples in the present study lies within that range. Values reported by García (unpublished) are even higher than the concentrations found in this study; 2400 mg/kg during the dry period (May-August) and 570 mg/kg during the wet period (December-March). The spatial development of arsenic in the river sediments is clearly visible in figure 5.12. The concentration was more or less constant at the first three sampling points, P1, P2 and P3, while a higher value was found at P4. During the second trip, the samples from the points P2, P3 and P4 contained less arsenic than during the first trip. The most significant difference was found at P4, where as much as 35 mg/kg have been mobilized and sent further downstream.

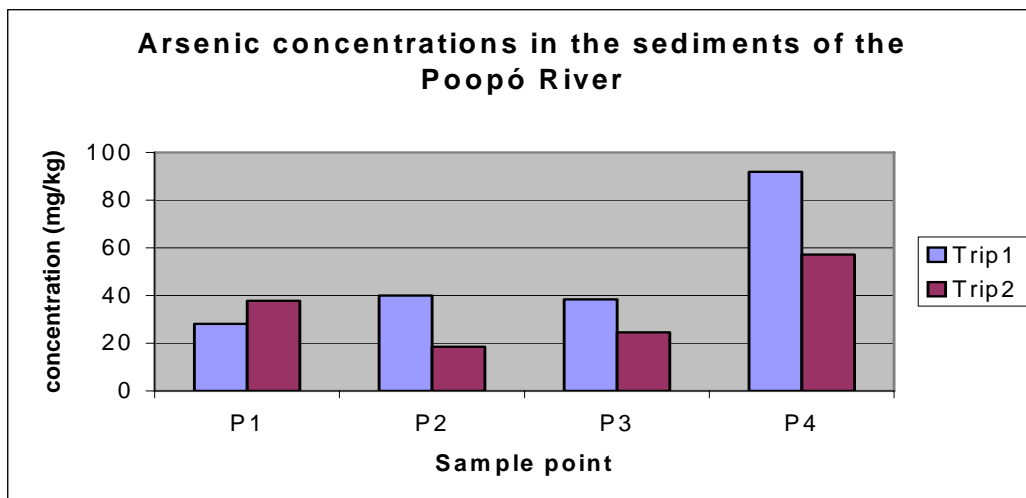


Figure 5.13 Arsenic in the river sediments of the Poopó River

The cadmium concentrations found in the sediment samples from the Poopó River are illustrated figure 5.14. The concentrations were between 0.45 and 11.1 mg/kg in the river sediment, with an average value of 3.1 mg/kg for the two trips. At the first three sampling points P1 to P3 almost all values are within the average cadmium concentration given by Åslund, 0.1-1 mg/kg (1994). At sampling point P4 highly elevated values were found during both trips. A similar trend to that of arsenic is clearly seen with highly elevated concentrations at P4. However, the values are much lower than the previously reported values by García; 120 mg/kg during the wet period and 30 mg/kg during the dry period.

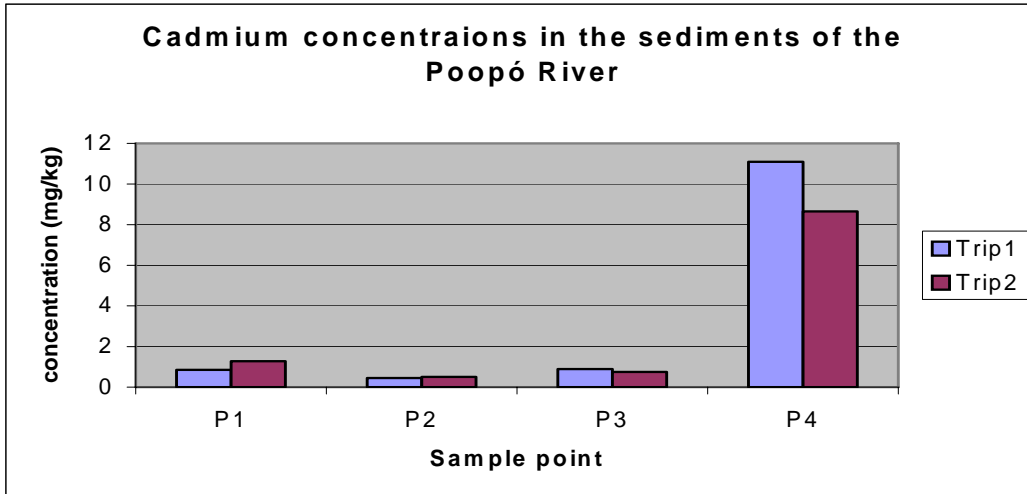


Figure 5.14 Cadmium in the river sediments of the Poopó River

Lead concentrations in sediments varied between 18.6 and 116.8 mg/kg and the average was 68 mg/kg, see figure 5.15. The lead concentrations at all the sampling points are higher than average values in the earth's crust, 16 mg/kg, given by Åslund (1994). Values obtained during the first and second trip differ. For both trips, low values were found at P3 and higher values were found at P4. Looking at P1, higher concentrations were found during the second trip, suggesting that the surroundings have contributed to higher lead concentrations between the two trips. At P2, a significant amount of the lead found during trip one, probably have been mobilized during the time between the two sampling trips. The amounts released at P2 are not found as increased levels in any of the sediment samples taken further downstream and may thus have been transported all the way to the Lake Poopó. As for arsenic and cadmium, the lead concentrations reported by García were higher; 8700 mg/kg during the dry period and 160 mg/kg during the rain period (García et al. unpublished).

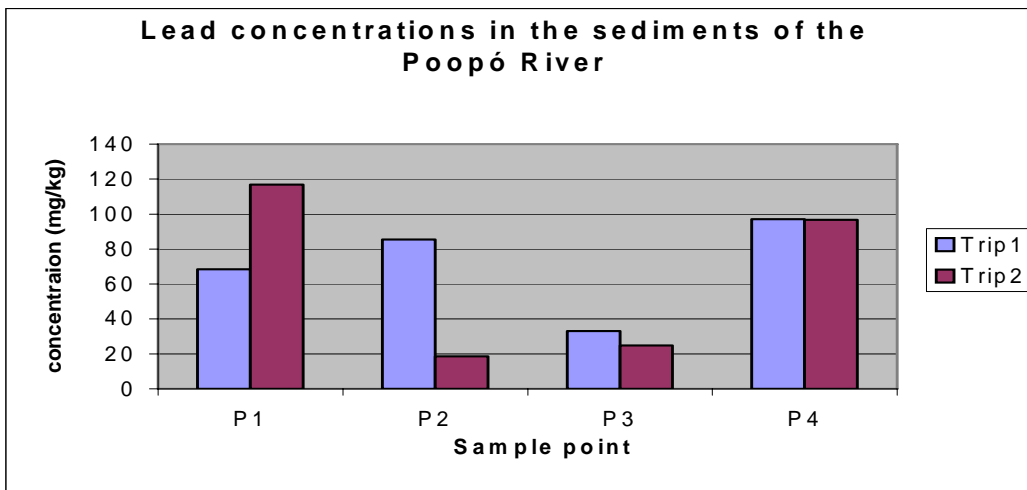


Figure 5.15 Lead in the river sediments of the Poopó River

The zinc concentrations are presented in figure 5.16. The concentrations varied between 94 mg/kg and 2084 mg/kg and the average zinc concentration in the sediments of the Poopó River was 619 mg/kg. The average concentration of zinc in earth's crust lies between 10-300 mg/kg. Hence, only concentrations in the last point, P4, clearly exceed these values. The spatial development of zinc in the sediments of the River Poopó is similar to the development of arsenic and cadmium; fairly low values at the first three sampling points and then a sharp increase at P4. García (unpublished) reported values of 1700 mg/kg and 1800 mg/kg for the dry period and wet period, respectively.

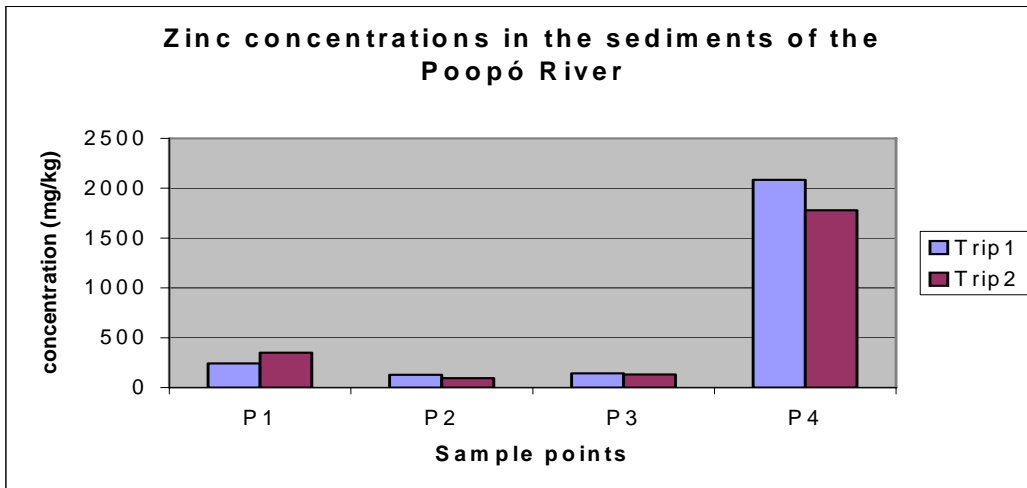


Figure 5.16 Zinc in the river sediments of the Poopó River

5.6.2 Marquez River

The arsenic concentration in the Marquez River increased downstream during the first trip, from 2 mg/kg at M1 to 3.4 mg/kg at M2, see figure 5.17. The concentration at M1 during the second trip was 0.2 mg/kg, which suggests that a large amount of the arsenic content, encountered during the first trip, had been transported downstream within the timeframe of the two samplings. The global average of arsenic concentration in unconsolidated sediment lies between 3-10 mg/kg according to Smedley and Kinniburgh (2001). Values reported by García are much higher; 30 mg/kg during the rain period and 400 mg/kg during the dry period (García et al. unpublished).

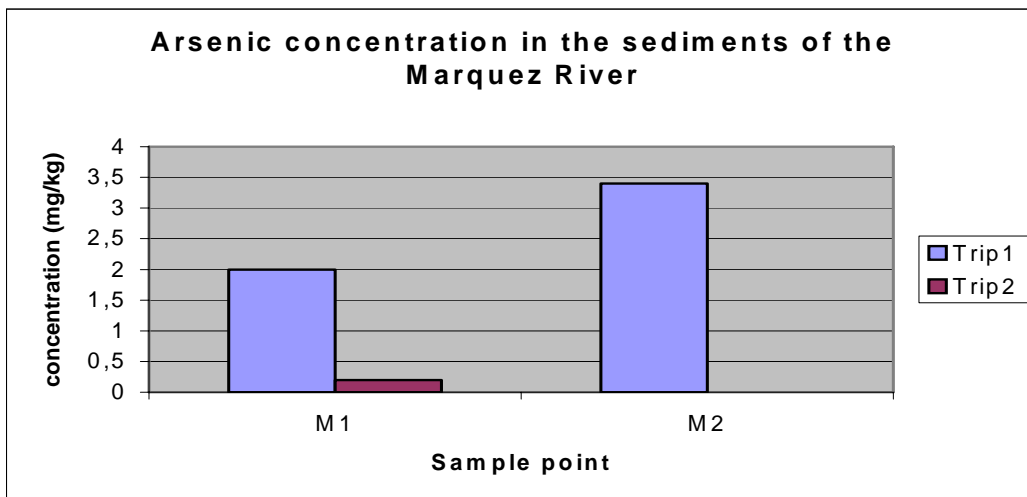


Figure 5.17 Arsenic in the river sediments of the Marquez River

The cadmium concentrations found in the Marquez River during the first trip for were 0.14 mg/kg at M1 and 0.25 mg/kg at M2, see figure 5.18. Hence, the cadmium content of the sediments increased downstream. The value found at M1 during the second trip was 0.3 mg/kg. The surroundings thus contributed with higher amounts of cadmium between the two periods. The average earth's crust value for cadmium is 0.1-1 mg/kg according to Åslund (1994). Our values are well within this span. Garcia's value for cadmium in the Marquez River was below the detection limit during both sampling periods (García unpublished).

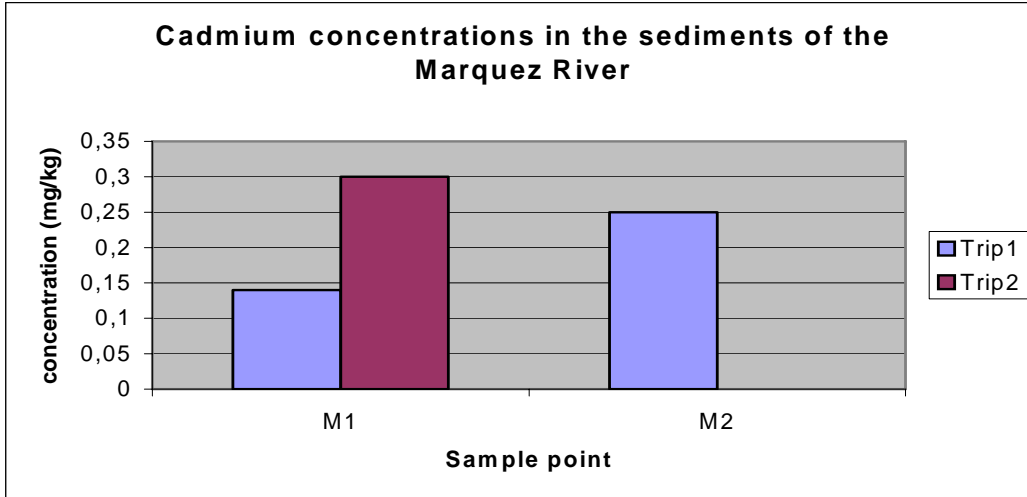


Figure 5.18 Cadmium in the river sediments of the Marquez River

Lead concentrations were determined to be 3.5 mg/kg at M1 and 2.1 mg/kg at M2 during the first trip, showing a decrease downstream the river, see figure 5.19. The concentration at M1 was 6.2 mg/kg during the second trip. Between the two trips, a significant increase of lead has taken place in the sediment at sampling point M1. Average lead concentration in earth's crust according to Åström (1994) is 16 mg/kg. Hence, the levels in the Marquez River are low. The values reported by García (unpublished) are several magnitudes greater; 60 mg/kg during the dry period and 30 mg/kg for rain period.

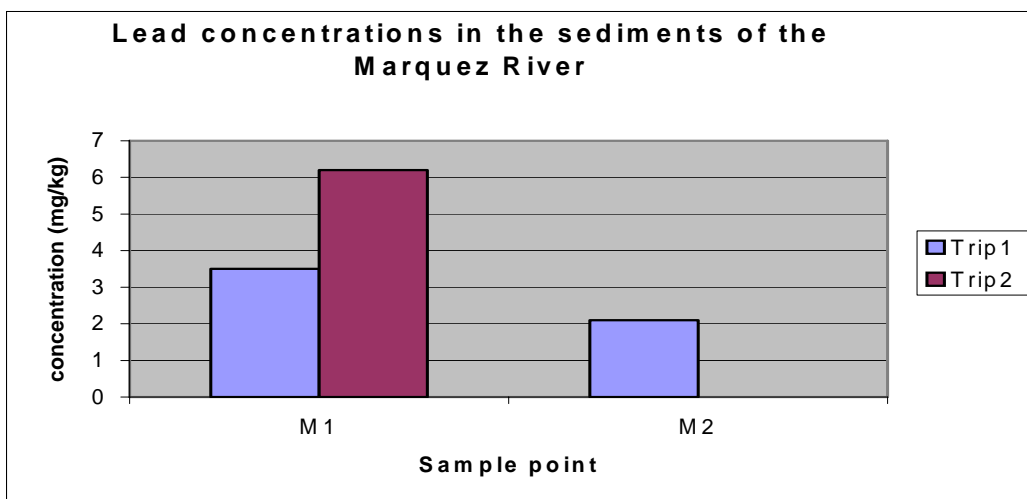


Figure 5.19 Lead in the river sediments of the Marquez River

The zinc concentrations of the Marquez River are presented in figure 5.20. During trip one a value of 29.8 mg/kg was found, while the zinc concentration found at the second trip was as

great as 1741 mg/kg. The other heavy metals also show an increase between trip one and two for the sampling point M1, with the exception of arsenic, but none of them are in the same magnitude as zinc. The extremely high value is thought to be due to an analyze error. Like arsenic and cadmium, zinc shows an increase in concentration downstream the river, from 29.8 mg/kg at M1 to 56.5 mg/kg in M2. Values from the first trip lie in the lower region of the earth's crust average for zinc, 10-300 mg/kg. The values reported by García are similar to the values found in this study; 60 mg/kg during the dry period and 120 mg/kg during the rain period (García et al. unpublished).

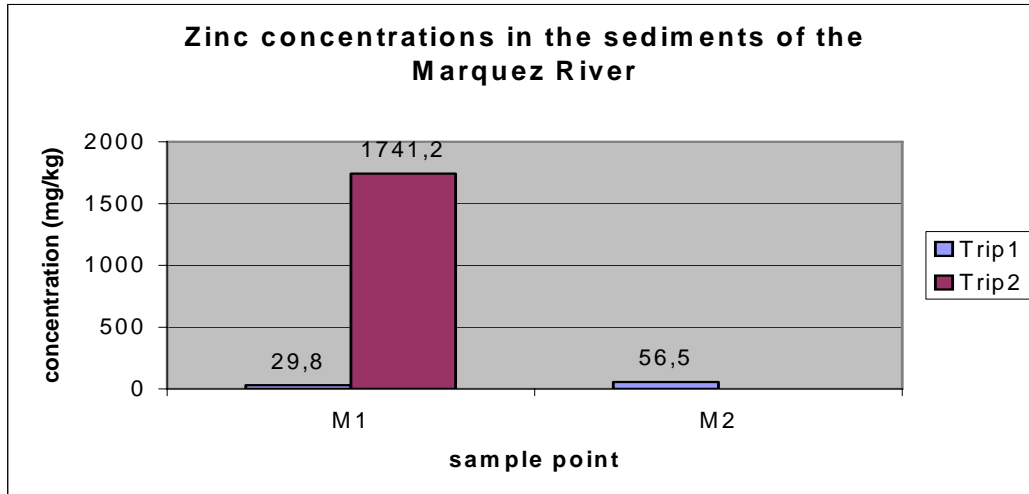


Figure 5.20 Zinc in the river sediments of the Marquez River

5.6.3 Huanuni River

The arsenic concentrations of the sediment samples from the Huanuni River are presented in figure 5.21. The levels varied between 10.9 mg/kg at sampling point H1 and 177 mg/kg at H3. The average arsenic concentration for the total stretch and for both trips is 77 mg/kg. Values for all samples are greater than the average value for unconsolidated sediments, 1-10 mg/kg (Smedley and Kinniburgh 2001). For trip one, a trend with increasing concentrations of arsenic in the sediments was found. Concentrations readily increased between H1 and H3. At H4 a drastic decrease was found. For trip two, a similar increase was found, but here the drastic decline at point H4 was missing. Sampling point H1 contained more arsenic during the second sampling trip, suggesting that the surroundings had contributed with arsenic during that time. At the sampling points H2 and H3, the arsenic concentrations were lower during the second trip. A part of the arsenic lost from the sediments of H2 and H3 during the period of sampling may be found in point H4, which clearly show an increase between trip one and two. The values reported by García once again were higher than those found in this study; 550 mg/kg during the dry period and 540 mg/kg during the rain period (García et al. unpublished).

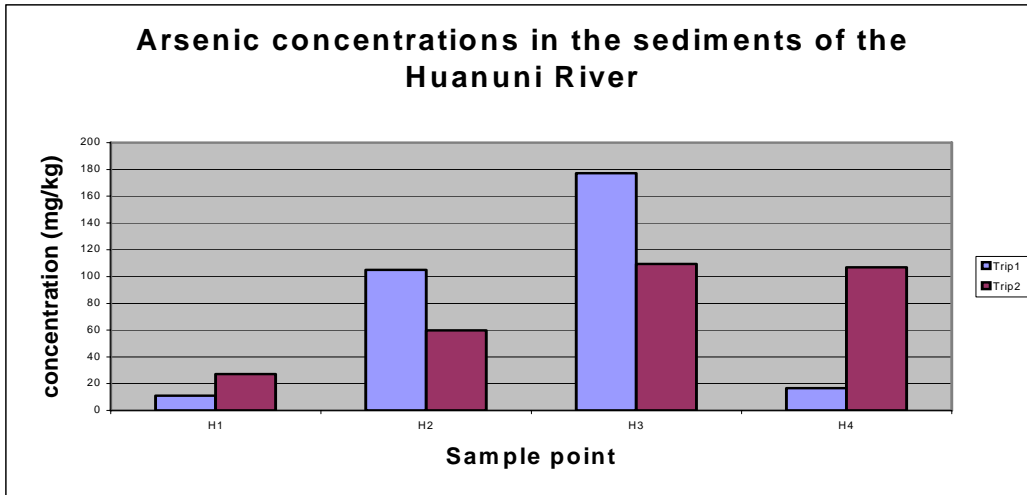


Figure 5.21 Arsenic in the river sediments of the Huanuni River

Cadmium values varied between 1.3 mg/kg and 11.4 mg/kg, with an average of 4.6 mg/kg. All values are greater than the average cadmium concentration 0.1-1 mg/kg in the earth's crust proposed by Åström (1994). As can be seen in figure 5.22, a high increase in cadmium concentration took place at sampling point H2, downstream the large mining district. Cadmium concentrations at H3 and H4 decreased compared with the very high values found at H2. They go back to concentrations similar as those found upstream the mining district. Samples taken during trip one and two, shows the same pattern, but differs in concentrations. At H1 a small increase of cadmium took place in between the two trips. The concentrations were lower at the points H2 and H4 during the second trip. Hence, cadmium is thought to have been transported further downstream in the system. The values reported by García for both dry and rain period are below the detection limit (García et al. unpublished).

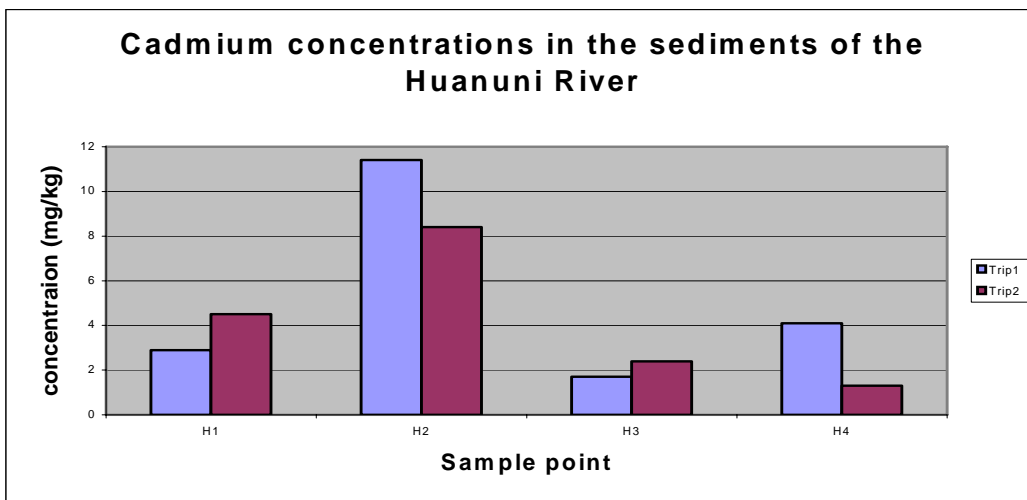


Figure 5.22 Cadmium in the river sediments of the Huanuni River

The lead concentrations of the sediment samples from the Huanuni River are presented in figure 5.23. The concentrations varied between 44 mg/kg and 146 mg/kg along the river with an average of 101 mg/kg. All values encountered were thus higher than the average lead concentration in earth's crust, 16 mg/kg stated by Åström (1994). The concentrations were more or less the same during both trips and they increased all along the river. No pronounced increase was found at sampling point H2, located just downstream the main mining activities. García

reported higher values; 280 mg/kg and 180 mg/kg for the dry period and rain period respectively (García et al. unpublished).

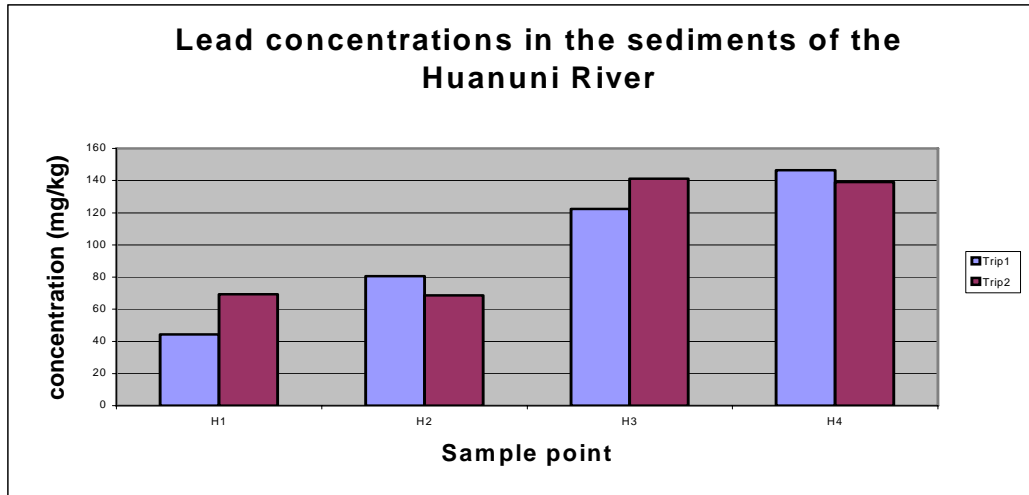


Figure 5.23 Cadmium in the river sediments of the Huanuni River

The zinc concentration of the sediment samples were found to vary between 2.1 mg/kg and 1131 mg/kg along the Huanuni River and the average zinc concentration was 454 mg/kg, see figure 5.24. Higher concentrations were found at H2, compared to the values found upstream the mining centre of Huanuni. Further downstream, at H3 and H4, lower zinc concentrations than those found at H1 were encountered. Higher values of zinc were found during the second trip at H1 than during the first trip. Lower zinc concentrations was found at sampling points H2 and H4 during the second trip, meaning that zinc had been transported from the sediments, further downstream, see figure 5.6. The values reported by García (unpublished) are roughly the same as our values in the last sampling point H4 for trip one: 120 mg/kg and 200 mg/kg during the dry and wet period respectively.

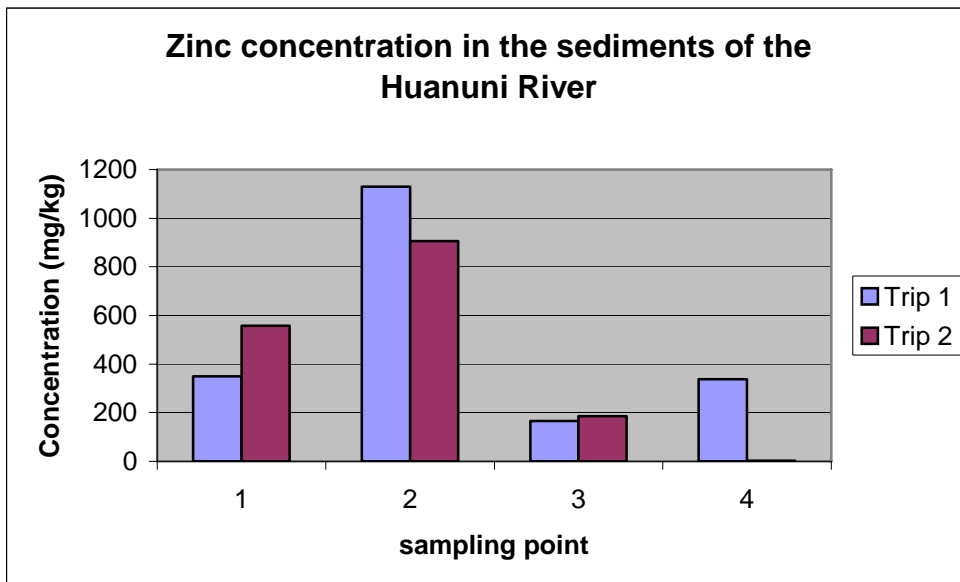


Figure 5.24 Zinc in the river sediments of the Huanuni River

5.7 Saturation Indices for Selected Minerals

The saturation indices for the selected lead, cadmium and iron minerals are presented in appendix F.

5.7.1 Poopó River

The lead concentrations of the samples from the Poopó River corresponded well to the dissolution of the mineral cerussite, PbCO_3 , indicating that the mineral may be present and controlling the lead concentration. The samples were super-saturated with respect to the mineral Pb(OH)_2 , meaning that lead may precipitate as this mineral.

All samples contained less cadmium than would be present due to the dissolution of the minerals CdSO_4 and Cd(OH)_2 . However, the sample from the last sampling point, P4, was just slightly sub-saturated with respect to Cd(OH)_2 . The cadmium in this sample could thus originate from the dissolution of Cd(OH)_2 .

All samples were very super-saturated with respect to the minerals goethite, FeOOH , and hematite, Fe_2O_3 , meaning that these may precipitate. The samples were very close to equilibrium with respect to amorphous Fe(OH)_3 , indicating that the dissolution of the mineral may control the iron concentration.

5.7.2 Marquez River

The lead concentrations of the Marquez samples were close to the equilibrium concentration of the dissolution of the mineral cerussite, PbCO_3 .

The samples were very sub-saturated with respect to the cadmium minerals Cd(OH)_2 and CdSO_4 meaning that if these were present the cadmium concentration would increase.

The iron concentrations turned out to correspond well with the dissolution of amorphous Fe(OH)_3 . The waters were very super-saturated with respect the minerals goethite, FeOOH , and hematite, Fe_2O_3 , suggesting that precipitation of these is likely.

5.7.3 Huanuni River

The samples from the Huanuni River were all slightly sub-saturated, but close to equilibrium, with respect to the lead mineral anglesite (PbSO_4). This suggests that the lead concentration may be controlled by dissolution of anglesite. The samples from the points H2, H3 and H4 are very sub-saturated and far from equilibrium with respect to the mineral Pb(OH)_2 .

All samples were very sub-saturated with respect to the cadmium minerals CdSO_4 and Cd(OH)_2 , meaning that the water would dissolve more of these if they were present.

The saturation index for goethite, FeOOH , was 3.16 at the first sampling point H1, meaning that the water is prone to precipitate that mineral. The water from the second sampling point, H2, was also super-saturated but closer to equilibrium. The samples from the two last points, H3 and H4, were both slightly sub-saturated with respect to goethite, suggesting that iron precipitates as goethite along the river to the third sampling point where equilibrium is achieved. The saturation index for the mineral hematite develops in a similar way along the river. The two first sampling

points, H1 and H2, are super-saturated with respect to the mineral, whereas the points H3 and H4 are slightly sub-saturated.

5.8 Mass Flows

The mass flows of dissolved arsenic, cadmium, lead and iron at all sampling points are presented in table 5.4. As the sampling points P4 and H4 are located close to the outlet into the Lake Poopó, the mass flows at these points are used as estimations of the transport of dissolved metals from the Poopó River and the Huanuni River.

Table 5.4 Mass flows of arsenic, cadmium, lead and iron in solution for the rivers Poopó, Marquez and Huanuni.

Sample	Arsenic (kg/day)		Cadmium (kg/day)		Lead (kg/day)		Iron (kg/day)	
	Trip 1	Trip 2	Trip 1	Trip 2	Trip 1	Trip 2	Trip 1	Trip2
P1	0.03	0.03	0	0	0.2	0.6	0.07	0.26
P2	0.16	0.4	0	0	1.7	3.4	0.57	1.8
P3	30	209 ¹	0.01	0.02 ¹	1.5	7.1 ¹	0.77	4.4 ¹
P4	38	125	0.27	0.05	1.2	4.0	1.0	2.4
M1	8.8	6.6	0.08	0.09	19	13	3.9	9.8
M2	4.2	Dry	0.01	Dry	9.1	Dry	1.4	Dry
H1	0.003	0.09	0.004	0.03	0.54	1.9	0.35	1.1
H2	22	199	4.8	15	0.62	8.4	1686	6592
H3	130	164	19	10	3.0	6.3	3500	1343
H4	138	304	13	17	3.5	10	1953	3082

¹The values are thought to be too high due to an over-estimation of the flow.

5.8.1 Poopó River

The mass flows at P3 during the second trip are thought to be too high due to an over-estimation of the flow. The highest mass flows within the Poopó River were found for arsenic; about 38 kg/day are thought to have been transported to the lake at the time for the first trip and about 125 kg/day at the second trip. The mass flow at the different sampling points shows clearly that the major part of arsenic is introduced at P3. However, significant amounts of arsenic have also been introduced into the river at the stretch between the sampling points P3 and P4.

The flows of lead and iron increase evenly along the river, indicating that no point sources for these metals exist.

5.8.2 Marquez River

The mass flows within the Marquez River were low for all metals. As the river dried out before entering the lake, no transport to it took place. It should however be noticed that the highest mass flow of lead of all sampling points were found at M1 and that the flows of arsenic and iron are much higher within the Marquez River than at the unpolluted parts of the rivers Poopó and Huanuni.

5.8.3 Huanuni River

Very large amounts of iron, arsenic and cadmium were found to be transported to the Poopó Lake from the Huanuni River; about 2000 kg/day of iron at the time for the first trip and 3000 kg/day at the second trip, about 140 kg/day of arsenic at the time for the first trip and 300 kg/day at the second and about 15 kg/day of cadmium at both trips.

6. DISCUSSION

6.1 Poopó River

In the Poopó River, water and sediment compositions are mainly effected by two factors. The thermal waters situated between sampling point P2 and P3, and the mining processing plant with its waste deposits located between P3 and P4.

6.1.1 Heavy metals in solution

Arsenic

When looking at the spatial distribution of arsenic in the Poopó River, low concentrations are found at the upstream sampling points P1 and P2. However, low concentrations are a matter of definition. The values found at P1 and P2 still exceed the WHO guidelines and are just below the limits set by the Bolivian law, but compared with downstream concentrations they are low. The extreme increase of arsenic concentration between P2 and P3 is clearly a result of the thermal waters entering the river. There is also a shift in water composition, from a calcium sulphate water to a sodium chloride water, due to the thermal water. It is more difficult to explain the higher values of arsenic found during the second trip in P3 and P4. Arsenic levels are double that of trip one, but this increase is not accompanied by an additional increase of sodium and chloride concentrations or by increased temperatures of the waters. This implies that the higher arsenic values found during the second trip could be due to that the thermal waters vary in composition, rather than that more thermal water entered the river during the second trip. Between sampling point P3 and P4, arsenic concentrations keep increasing, indicating that more arsenic is introduced into the river. This could be due to that the thermal waters also supply the river with particulate arsenic that dissolves further downstream, leakage from the sediments or due to some other pollution source, e.g. the mining processing plant or the waste deposits. Desorption of arsenic is known to be favoured by high pH-values (Smedley and Kinniburgh 2001). Hence, the high pH-value found in P4 would favour both desorption from particles originating from the thermal waters and leakage from the river's sediments.

Cadmium

The low cadmium levels found at the three first sampling points suggest that natural cadmium concentrations are low in the area. After the thermal water, a small increase may be noticed, but the levels are still very low. The significant higher levels found at P4, especially during the first trip, are thought to be due to the processing plant situated between P3 and P4. The plant mainly extracts zinc, and cadmium is often closely connected to zinc. The contribution to the river would thus depend on the activity at the plant, which would explain the lower concentration during the first trip. The plant and mines in the area are said to no longer be extracting any water from the Poopó River or discharging any waste in to it. Instead acid water from the mines is used and recycled. However, due to the short distances between the river and the plant, zero influence is not to be considered likely. The plant is using large amounts of quick lime, which may explain the extremely high pH values at P4.

Lead

The lead concentrations along the Poopó River do not show any greater spatial variations, and are therefore thought to be of natural origin. Levels are high, exceeding both WHO and Bolivian laws greatly. The surrounding geology thus contributes with large amounts of lead. According to calculations done for determining the saturation indices, the waters are super saturated, but quite

close to equilibrium with the mineral $\text{Pb}(\text{OH})_2$. For the mineral PbCO_3 , the saturation index is also close to equilibrium, but sub-saturated. PbOH^+ was found to be the most abundant species of lead for P1, P2 and P3 while $\text{Pb}(\text{OH})_2$ was the most dominant species at P4. The fact that $\text{Pb}(\text{OH})_2$ and PbOH^+ are the most abundant species is a consequence of the high pH contributing with large amount of hydroxide ions.

Iron

The iron levels are low and do not show any significant changes along the river. The iron concentration is therefore thought to be due to natural weathering. A small increase can be seen moving downstream, which is normal. The low values of iron, especially in P4 where a lot of mining waste is situated, indicates no acid rock drainage at the time of sampling, which is also strengthened by the low sulphate values and the high pH. This may be expected, since ARD in the surroundings is very dependent on precipitation, which there was none of during both sampling trips. However, ARD in the Poopó River should still be considered as a major pollution risk during the rain period.

6.1.2 Heavy metals in sediments

Arsenic

The uncertainty in sampling procedures of sediments complicates the analysis. One trend found for the arsenic concentrations in the sediments of the Poopó River is that there is a quite constant level at the first three sampling points, followed by higher values at P4. The similar values at P1, P2 and P3 are thought to represent natural concentrations of arsenic. Compared to global average values for unconsolidated sediments and the levels encountered in the Marquez River, these values are high, meaning that the area is naturally rich in arsenic. The fact that no increase was found at P3, even though the point is situated close to the thermal waters and contains high levels of arsenic in the water phase, indicates that even if the water composition favours precipitation the flow rate does not allow sedimentation. Instead sedimentation seems to occur further downstream at P4. The increase in pH at P4 may not favour the precipitation of arsenic, but the significant temperature decrease might. The lower water velocities are thought to be the main reason for the significant higher values of arsenic at this point. The particles in suspension this far downstream has been able to adsorb high concentrations of heavy metals, due to their long time in the system. So, even if the particles are of the same grain size upstream as downstream, downstream particles are thought to contain larger amounts of arsenic. During the rain period it is possible that the surrounding mining waste material may contribute with sediment particles high in heavy metals directly onto the riverbed.

Cadmium

For cadmium, a similar scenario as for arsenic was found, with low values at P1, P2 and P3, followed by an extreme increase at P4. The low levels at the upstream points, which are within the average concentration for the earth's crust, are thought to represent the natural conditions of the sediments and the higher values at P4 are, like for arsenic, mainly thought to be due to the lower water velocities allowing sedimentation of particles containing high levels of cadmium. Since the mining processing plant at P4 is thought to contribute with cadmium in the water phase, some particular cadmium may also be contributed, which would directly give rise to higher concentrations in the sediment. According to the theory, both the pH increase and the drop in temperature between P3 and P4, would favour adsorption of cadmium at P4.

Lead

The large variations of lead in the sediments are thought to be due to natural variations of lead along the river. The area is thus rich in lead compared to the average level of the earth's crust

Zinc

Zinc shows the same picture as arsenic and cadmium, with an extreme increase in levels at the last point. The natural levels of zinc in the area are lower than the average value for the earth's crust. As for cadmium, the same factors are thought to give rise to the increase in zinc concentrations at P4. Increased contribution from the mining processing plant, both in dissolved and particular phase, increase of pH favouring adsorption, and lower water velocities resulting in sedimentation, are thought to be the main reasons for the increase of zinc in the sediments at P4.

6.1.3 Mass flows

Arsenic

When looking at the mass flows along the Poopó River, a quite low amount of arsenic is transported from the two most upstream points. As the water passes the thermal springs between point P2 and P3, the amount of arsenic increases a lot. During the second trip, the thermal waters are thought to contribute with as much as 209 kg/day of dissolved arsenic, compared with the more moderate 30 kg/day during the first trip. The pronounced difference is due to the higher concentrations and higher flow during the second trip. The higher flow at P3 during the second trip is hard to explain. Either the flow at P3 has been overestimated during the sampling, and/or the flow at P4 for the second trip has been underestimated. If both the measured values were to represent prevailing conditions, a lot of water disappears during the short stretch down to P4. Most likely the flow in P3 is overestimated, and the extreme amounts of arsenic estimated for this point are too high. At the final point P4, some extra 8 kg/day are added in addition to the 30 kg/day from P3. This value of 38 kg/day would thus be a fairly good estimation of the amount of arsenic that ends up in the lake. For the second trip, 125 kg/day are being transported to the lake. The large difference found between the trips shows that the river's contribution of arsenic to the Poopó Lake varies, not just seasonally but also due to natural fluctuations of the thermal waters in the river.

Lower arsenic concentrations were found at the second trip than at first trip. This may suggest that during the time between the two trips, arsenic in the sediments have been mobilized and transported further downstream. At P2, the concentration seems to have been halved between the two trips, and at P3 decreased with roughly 40 %. A similar decrease is also found at P4. Looking at the differences at P4 from the two trips, the sediment has been leaching something like 35 mg/kg of arsenic, during the 2.5 months. However, it is hard to get an idea of what amount of particle arsenic that is transported to the lake from this figure.

Cadmium

The flow of cadmium in the Poopó River is rather small up till the fourth point. The amount, 0.27 and 0.05 kg/day for the first and second trip, respectively, seems small, but due to the toxic effects of cadmium even at small concentrations, they are of concern. In the sediments, the concentrations are so low at the first three sampling points that no conclusion can be made out of the changes between the trips. At the fourth point, cadmium follows the same development as arsenic, and the sediment seems to have released some cadmium in the time between the two trips.

Lead

The mass flows of lead for the two trips are increasing evenly downstream from P1 to P3. A decrease in mass flow takes place between P3 and P4. For the first trip, the decrease is rather small. It is hard to say of what magnitude the decrease is during the second trip, since the flow at P3 is thought to be lower than measured. The amounts of lead contributed by the Poopó River are quite small, 1.2 and 4.0 kg/day, and are thought to be due to only natural conditions.

Iron

The mass flow of iron increased continuously along the river. During the second trip, as discussed earlier, the high value at P3 is misleading. Hence, even trip two shows an evenly increase of iron. This points out that no unnatural contribution of iron takes place in the Poopó River.

6.2 Marquez River

The Marquez River was chosen for its natural and none anthropogenic influenced waters. The idea was to use the river for comparison with the other rivers, affected by anthropogenic sources. However, the natural conditions in the Marquez basin differ a bit too much to make any specific comparisons with the Poopó and Huanuni River.

6.2.1 Heavy metals in solution

Arsenic

The arsenic levels found in the Marquez River were high compared to the concentrations in the unpolluted parts of the Poopó River and the Huanuni River, and the concentrations exceed both WHO and Bolivian law values. This is thought to be due to the arsenic rich geology in the area, even though the concentrations within the sediments were found to be low. The slightly increase of the arsenic concentrations between the first and the second sampling point may be explained by the lower flow at M2. However, the mass flow decreased between the points, meaning that arsenic was removed from the water phase. This could be due to adsorption. An increase in the sediment content between the sampling points, even though small, was observed, which may be due to removal from the water phase. The water was super-saturated with respect to the iron minerals goethite and hematite, which indicates that these may precipitate and adsorb for instance arsenic. The arsenic concentrations found during the second trip was similar to the concentrations during the first trip. Based on this, the arsenic concentration is believed to be around 0.15 mg/l during the dry period.

Cadmium

The decrease of cadmium between the sampling points M1 and M2 indicates that cadmium was removed from the water phase. During the same stretch the level in the sediments increased. This indicates a transport from the water phase to the sediment phase along the river. However, it should be remembered that the levels in both water and sediments are low, in water less than 0.002 mg/l and in sediment less than 0.3 mg/kg, meaning that the changes may not be significant.

Lead

The lead concentration increased between the points M1 and M2, which could be due to the decreasing flow. However, the total mass flow decreases between the points indicating that lead is adsorbed or precipitated along the river. The significant increase in the sediment content between these points, from 3.5 mg/kg to 6.2 mg/kg, also indicates that lead is removed from the water phase to the sediment phase. It should also be mentioned that the levels are similar to the ones found in the other rivers.

Iron

The decreasing mass flow of iron between the two sampling points M1 and M2 indicates that iron is removed from the water phase. The iron level in the sediments was not measured, but the saturation indices for hematite and goethite makes clear that the river was super-saturated with respect to these.

6.2.2 Heavy metals in sediments

The higher levels of all metals (arsenic, cadmium, lead and zinc) at the second sampling point M2 is thought to be due to removal from the water phase as discussed in chapter 6.2.1. The alkaline pH, between 8.2 and 8.6, should favour adsorption. Moreover, the sediment particles were rather small and iron oxides and hydroxides are thought to be present, which also favours adsorption. As the flow decreased downstream, making the third sampling point dry during the first trip and the second dry during the second trip, the metals in solution will be deposited in the sediments and increase their content. The extremely high zinc value from the second sampling point from the first trip is thought to be due to an analytical error.

6.2.3 Mass flows

As the points downstream the river were dry during these sampling trips, no deposition in the lake took place. However, the mass flows clearly show that heavy metals, originating from the surrounding bedrock, are transported and deposited further downstream. The mass flows were rather small and the load to the lake during periods of higher flows is therefore also thought to be low.

6.3 Huanuni River

Large differences were found in water quality between the samples taken upstream the mining community Huanuni (H1) and the samples taken downstream (H2, H3, H4). The heavy metal content of the sediments also differed between the upper and the lower parts of the river.

6.3.1 Heavy metals in solution

Arsenic

The major increase of the arsenic concentration took place, as expected, between the first and the second sampling point. Many studies have shown high arsenic concentrations in rivers in mining areas (Smedley and Kinniburgh, 2001). It is also known that the mobility of arsenic is low in acidic environments and as the pH often is low due to acid mine drainage in mining areas the levels should be highest close to the mines (Smedley and Kinniburgh, 2001). However, this was not the case for the Huanuni River; the concentrations did not decrease after the sampling point P2 although the acidic pH. During the first trip the concentration continued to increase further downstream and during the second trip the concentration was more or less constant between P2 and P4. This means that significant amounts of arsenic were introduced all along the river. The possible sources for this are leakage from the tailings and piles along the river and leakage from the river sediments.

No clear explanation has been found for the higher arsenic concentrations during the second trip. The parameter that differed most between the trips is the flow, which was higher during the second trip in all points except from the third. The points H2, H3 and H4 were sampled during an intense rainfall at the second trip, which may have washed out arsenic from the surrounding mining waste.

Cadmium

The cadmium concentration along the river was similar during both trips. The peak-value in the second sampling point suggests that the mining community acts as a point source for cadmium. The mass flow indicates that cadmium was introduced to the river up to the third point, H3, during the first trip and up to the second point, H2, during the second trip. The major source of

cadmium thus seems to be the mining community. Cadmium may also have been removed from the river by sorption of iron oxides and hydroxides. The lower concentrations during the second trip may be due to dilution. García (unpublished) reported that cadmium concentrations in the area are lower during the rain period than during the dry period.

Lead

The lead concentration in the Huanuni River does not seem to be effected by the mining activities, but is naturally high. The saturation index for anglesite, PbSO_4 , along the river suggests that the concentration could be due to dissolution of that mineral.

Iron

The development of iron along the river makes clear that large amounts are introduced to the river by the mining community Huanuni. The high levels of iron and sulphate together with the acidic pH are typical for mining areas, where pyrite oxidation is enhanced. The decrease of the concentrations between H2 and H4 is explained by a higher river flow that dilutes the concentrations. However, the mass flows show that iron was introduced to the river up to the third point, H3, during the first trip and between the points H3 and H4 during the second trip. The increase during this part is thought to be due to acid rock drainage from the tailings and piles situated along the river, which is strengthened by the fact that the pH does not recover along the river. The Phreeqc calculations showed that the water was super-saturated with respect to the minerals hematite, Fe_2O_3 , and goethite, FeOOH , at the sampling points H1 and H2, and slightly sub-saturated at the sampling points H3 and H4. It is likely that iron precipitates between the points H1 and H3, which would lower the iron concentration and explain the decrease.

6.3.2 Heavy metals in sediments

The arsenic and lead concentrations in the sediment increased all along the river. For cadmium and lead elevated levels were found at the second sampling point.

Arsenic

The arsenic concentration of the sediments upstream the mining community was in the upper region or above the global average value for unconsolidated sediments. Hence, the area should be considered as rich in arsenic. The high arsenic levels of the sediment samples from H2 and H3 during the first trip could be due to solid waste material from the mining activities with high arsenic content or due to adsorption of dissolved arsenic followed by sedimentation. It is clear that mining waste are dumped along the river and maybe also in the river. The low pH and the presence of iron hydroxides and iron oxides, such as goethite and hematite, should favour adsorption. But, on the other hand similar conditions prevailed at the fourth point, H4, where the arsenic content in the sediment was very low. This suggests that adsorption may have occurred during the stretch H2 – H3, but not at H4. No difference in the size of the sediment particles in H3 and H4, that would have explained a lower adsorption at H4, were found.

During the second trip increased levels were found at the points H2, H3 and H4, which can be explained by adsorption and deposition of arsenic rich waste material. Even though it cannot be distinguished which factor that controls the high arsenic content in the sediments, it is obvious that the levels increase after the mining community.

Cadmium

The cadmium levels upstream the mining community were above the average content of the earth's crust, meaning that the area is rich in cadmium. The high cadmium levels at the second sampling point, H2, could be due to different processes. The mining community may deposit

cadmium rich material in the river, adsorption from the water phase could take place and cadmium may precipitate. The low pH should rather favour desorption than adsorption, but the presence of iron oxides and iron hydroxides favours adsorption. Furthermore, the sediment particles were finer at H2 than at H3 and H4, which may allow more adsorption at this point. The saturation index for the cadmium minerals makes it clear that the water is sub-saturated with respect to the minerals, meaning that precipitation of these should not occur. Based on these facts the levels are thought to be due to deposition of cadmium rich material and maybe also adsorption.

Lead

The lead concentration in the sediments was found to increase along the river and all values exceeded the global average value for the earth's crust. However, the low pH-values at the points H2, H3 and H4 should increase the mobility and favour desorption from the sediments. The reason for higher levels in the sediments downstream may be sedimentation of lead rich particles introduced by the mining activities.

Zinc

The high levels of zinc in the sediments from the second sampling point, H2, imply that the mining activities pollute the sediments with this metal. As for cadmium and lead, the low pH should favour desorption of zinc rather than adsorption. This may suggest that the metals are introduced as solid mining waste rather than dissolved ions that precipitate.

6.3.3 Mass flows

The estimated transport of the metals in water phase turned out to be huge. The load to the lake of all metals, especially of iron and arsenic, was higher during the second trip than during the first. As iron and arsenic are thought to be washed out from the tailings close to the river, the load of these to the lake should be higher during rain periods. The origin of cadmium is thought to be more dependent on the mining activities and should not be affected by rainfalls to the same degree as iron and arsenic.

Arsenic

The estimations indicate that the arsenic load to the lake was about 150 kg/day during the first trip and 300 kg/day during the second. During the first trip the main part of the arsenic seems to originate from secondary sources such as leakage from the sediments and waste material along the river, whereas the majority seems to originate directly from the mining community Huanuni during the second trip. Almost all arsenic seems to be introduced by mining activities and the natural part is very low.

Cadmium

About 15 kg/day of cadmium were transported to the river during both trips and a comparison of the mass flows upstream and downstream clearly indicates that almost all cadmium is of anthropogenic origin.

Lead

Between 4 and 10 kg/day of lead is thought to be transported to the lake. The lead seems not to originate from mining activities, but rather from natural weathering.

Iron

The iron load to the river seemed to be about 2000 kg/day during the first trip and about 3000 kg/day during the second trip. Upstream the mining community the mass flow is as low as 1 kg/day or less, which clearly shows that the high amounts are due to the mining activities.

6.4 Comparison with Earlier Work

The levels of heavy metal found in this study and previously reported levels (García et al unpublished), differ in most cases. The most striking difference between the studies is the very high iron concentration in Huanuni found in this study. The arsenic concentrations of the waters found in this study are generally higher than the previously reported values. This may indicate that the arsenic concentration actually has increased, but it should be remembered that the analyses were performed at different laboratories.

As the way of sampling sediments during this study may have differed from how the sampling was conducted by García, it is hard to compare the sediment concentrations. The samples could for instance have been taken at different depth, which may have effected the concentration greatly. Furthermore, only single samples were taken and the geographical variation, even within small areas, may be large. However, the values reported in this study are generally much lower than the values reported by García.

7. CONCLUSIONS

7.1 Poopó River

Overall, the Poopó River seems not to be heavily influenced by the mining activities in the area. The processing seems to have succeeded in reducing their influence on the Poopó River. However, waste material in the area and to some extent even the activities are still thought to affect the river, mainly the cadmium concentrations. Overall, the high heavy metal concentrations found in the Poopó River seem to be due to natural conditions.

The heavy metals found along the Poopó River can be said to be of three origins. Bedrock weathering, thermal spring discharge and those introduced by mining activity. All of them have shown to be of importance when discussing the high heavy metal concentrations. For arsenic, natural high levels are found. In the upstream areas of Poopó River, the weathering processes of surrounding bedrock contributes with high concentrations of arsenic, exceeding the WHO guidelines for drinking water. In addition to the weathering procedures, an extreme addition of arsenic takes place as the river passes the thermal waters, and arsenic concentrations in solution are as high as 12 mg/l.

The cadmium concentrations are low until the river water passes the mining processing plant at the end of the river. High cadmium concentrations together with an additional increase of pH are likely direct causes of the processing plant. The level is significantly increased and makes the water unsuitable for human consumption.

Lead concentrations are high in all parts of the river, with fairly constant levels. No changes are to be found either as the river passes the thermal waters or the processing plant. The surrounding bedrock seems to be rich in lead minerals and natural weathering procedures are thought to be the reason for high lead concentrations in the water. When comparing the limits for drinking water according to WHO, lead is the metal exceeding the guidelines the most.

The Poopó River contributes with large amounts of arsenic to the Poopó Lake. The load seems to be controlled by the composition of the thermal waters within the river. In this study arsenic mass flows of 38 kg/day and 125 kg/day to the lake were observed. The river's contribution of other metals to the lake is low.

The interactions between heavy metals in the aqueous phase and the metals found in the sediment are not clear. One conclusion to be made is that waters with high levels in solution show high levels in the sediments. Another conclusion is that higher metal concentrations are often found in the sediments further downstream the system.

7.2 Marquez River

The arsenic rich geology in the area around the Marquez River gives rise to high arsenic concentrations in the river that exceeds the WHO guideline values for drinking water. Also the lead concentrations in the river are high and exceed the WHO guideline value. The sediments of the river contain low levels of arsenic, cadmium, lead and zinc. During the dry period the river dries out before reaching the lake. Hence, no transport of metals to the lake occurs. The load to

the lake during periods of higher flow is thought to be low as the concentrations in the river are low.

7.3 Huanuni River

The natural levels of arsenic, cadmium, lead and iron in the Huanuni River, i.e. the concentrations in the unpolluted upper parts of the river, are all high exceeding or being close to the WHO guideline values for drinking water.

The mining community Huanuni deteriorates the water quality of the Huanuni River totally. The concentrations of arsenic, cadmium, iron and sulphate increases drastically downstream the mining community. Moreover, the pH drops from about 7 upstream the mining community to about 3 downstream, which is common for mining areas where pyrite oxidation is intense.

Iron and arsenic are thought to be introduced to the river mainly by direct discharge from the mining community, but significant amounts of arsenic are also introduced by leakage from the river sediments. Moreover, the tailings and piles are thought to leach iron and arsenic to the river during rainfalls. The arsenic concentration did not decrease along the river in spite of the acidic pH. The mining community seems to be the major source for cadmium and the sediments and mining waste along the river do not seem to be as important. Based on this the cadmium concentration is believed to be lower during the rain period due to dilution.

The river contains naturally high levels of lead, between 0.1 and 0.5 mg/l, exceeding the WHO guideline values for drinking water. The concentrations do not seem to be affected by the mining activities.

The mining community Huanuni most likely increases the levels of arsenic, cadmium and iron in the sediments of the Huanuni River. Regarding cadmium and zinc, the pollution is most obvious close to the mining community and the sediments seem to recover further downstream. Arsenic and lead, on the other hand, increases all the way along the river, which is thought to be due to sedimentation of particles containing these metals.

No clear relationship between the concentration in aqueous and sediment phase could be seen.

Huge amounts of arsenic, lead and cadmium are transported to the Poopó Lake due to the mining activities; about 200 kg/day of arsenic, about 15 kg/day of cadmium and about 2000 kg/day of iron. It should be remembered that these figures only represent the dry period. The load of arsenic and iron are thought to increase during the rain period.

8. RECOMMENDATIONS

The mining activities in the vicinity of the Huanuni River are without doubt the most important reason for deteriorating the river. The three major sources for heavy metals and acidity are the large scale mining, the small scale mining along the river, and finally the large amounts of waste located in the area. Measurements taken on the mining activities would of course be the most efficient way of reducing the heavy metal load into the river. Since there is a serious economic depression and living conditions are very harsh in the area, changes are probably hard to implement. However, sedimentation dams could be one measurement that might be implemented. Also, re-circulation measurements such as those introduced at the Poopó River could be taken. If possible, the small-scale artesian mining should be minimized. Relocating these workers, for instance to the large-scale mining, would probably improve the situation in the river greatly. Concerning the waste material in the area, one measurement would be to cover them with an impermeable layer to reduce the amounts of water percolating the waste.

To get a clearer view of the transport processes in the rivers, further studies should be done. Amounts of organic material in water and sediment, heavy metal concentrations in the suspended material and a better work-plan for sampling sediments would be of great interest. Organic material is known for adsorbing large amounts of heavy metals and is therefore a factor to be taken into consideration. By measuring the amounts of heavy metals on suspended particles, a better understanding of the transport processes would be gained. By determining at what depths the sediments should be taken and which fraction sizes that should be emphasized on, more could be said about the dynamics in the rivers.

9. References

BOOKS

- Alloway, B.J.** *Heavy metals in soils*, John Wiley and sons inc., Glasgow, 1990
- Asplund, J.** *Tungmetaller I naturliga vatten*, Statens naturvårdsverk, Stockholm, 1979.
- Drever, J.I.** *The geochemistry of natural waters*, Prentice-Hall inc., Englewood Cliffs, 1982.
- Kelly, M.** *Mining and the freshwater environment*, Elsevier science publishers ltd, Essex, 1988.
- Laws, E.A.** *Aquatic pollution – an introductory text*, John Wiley & Sons, 1993
- Sterner, O.** *Förgiftningar och miljöbot*, Lund Studentlitteratur, 2003
- Stumm, W and Morgan, J.J.** *Aquatic chemistry – Chemical equilibria and rates in natural waters*, John Wiley & Sons inc., New York, 1996.
- Troëng, B., Riera-Kilibarda C.** *Mapas temáticos de recursos minerales de Bolivia*, Boletín del Servicio geológico de Bolivia N°7, La Paz, 1996.
- Quintanilla, J. et al.** *Hidroquímica y contaminación de la cuenca endorreica del Altiplano*, Carlos Aguirre B., Carmen Miranda L. & Yola Verhasselt (edit.), Simposio internacional sobre el sistema del Lago Titicaca, 2001.
- Åslund, P.** *Metaller i vatten*, Hofors VA-hygien, 1994
- Instituto nacional de estadística Bolivia atlas estadístico de municipios**, 2005

ARTICLES

- Dittmar, T.** *Hydrochemical processes controlling arsenic and heavy metal contamination in the Elqui river system (Chile)*, Science of the total environment vol. 325, pp. 193-207, 2004
- García, M.E, Bengtsson, L., Berndtson, R. & Persson, K.M** *History of mining in the Lake Poopó region and environmental consequences*, unpublished
- García, M.E, Persson, K.M., Bengtsson, L. and Berndtson, R.** *Heavy metal distribution in a mining region, a case study of Lake Poopó, Bolivia*, unpublished
- Smedley, P.L., Kinniburgh, D.G.** *A review of the source, behaviour and distribution of arsenic in natural waters*, Applied Geochemistry vol. 17, pp. 517-568, 2001

LEGISLATION

Ley y reglamento del Medio Ambiente. Ley no 1333 de 27 de abril de 1992. pp. 300-303.

PPO-REPORTS

PPOe –008, 1996, Ministerio de Desarrollo Sostenible y Medio Ambiente & Swedish Geological AB, *Proyecto Piloto Oruro - Panorama de la fisiografía y geología del área del proyecto PPO.*

PPO 9606, 1996, Ministerio de Desarrollo Sostenible y Medio Ambiente & Swedish Geological AB, *Proyecto Piloto Oruro – Hidrología del área de PPO*

PPO 9607, 1996, Ministerio de Desarrollo Sostenible y Medio Ambiente & Swedish Geological AB, *Proyecto Piloto Oruro – Aspectos ambientales de los metales y metaloids en el sistema hidrológico del desaguadero*

PPO 9609, 1996, Ministerio de Desarrollo Sostenible y Medio Ambiente & Swedish Geological AB, *Proyecto Piloto Oruro – Depósitos de residuos minerales en el área del PPO. Caracterización de colas.*

PPO 9611, 1996, Ministerio de Desarrollo Sostenible y Medio Ambiente & Swedish Geological AB, *Proyecto Piloto Oruro – Mineral waste deposits in the PPO area*

PPO 9612, 1996, Ministerio de Desarrollo Sostenible y Medio Ambiente & Swedish Geological AB, *Proyecto Piloto Oruro – Impacto de la minería y el procesamiento de minerales en cursos de agua y lagos*

PPO 9701, 1997, Ministerio de Desarrollo Sostenible y Medio Ambiente & Swedish Geological AB, *Proyecto Piloto Oruro – Final report: Findings recommendations and the environmental management plan*

WEBPAGES

WHO, *Arsenic in drinking water 2001.* Retrieved 28 February from <http://www.who.int/mediacentre/factsheets/fs210/en/index.html>

WHO, *Guidelines for drinking-water quality, 3rd Ed 2004.* Retrieved 28 February from http://www.who.int/water_sanitation_health/dwq/en/gdwq3_ann4tab.pdf

APPENDICIES

Appendix A: Location of sampling points and physical parameters

Appendix B: Physical parameters and ion concentrations

Appendix C: Grain size distribution

Appendix D: Heavy metals in solution and sediment

Appendix E: Speciation

Appendix F: Saturation indices

Appendix A

Table 1 Location of sampling points

Sample point	Southern coordinate	Western coordinate	M.a.s.l.	Distance to adjacent point upstream (km)
P1	18° 24' 42"	66° 54' 10.6"	3912	0
P2	18° 23' 05.1"	66° 55' 53.4"	3824	4.25
P3	18° 22' 57.1"	66° 57' 05.1"	3783	2.12
P4	18° 23' 07.8"	66° 58' 45.4"	3748	2.96
M1	19° 35' 01"	66° 50' 09.1"	3769	0
M2	19° 22' 52.2"	67° 00' 08"	3752	28.2
M3	19° 12' 49.9"	67° 01' 29.7"	-	18.7
H1	18° 17' 18"	66° 48' 49"	3974	0
H2	18° 16' 16.1"	66° 52' 13.1"	3907	20.3
H3	18° 09' 57.7"	66° 57' 48.2"	3780	15.3
H4	18° 09' 24.8"	67° 00' 18.2"	3747	4.52

Appendix B

Table 1 Physical parameters

Sample	pH		Eh		Conductivity (μ S/cm)		TDS (mg/l)		Temperature ($^{\circ}$ C)		Flow (l/s)	
	Trip1	Trip2	Trip1	Trip2	Trip1	Trip2	Trip1	Trip2	Trip1	Trip2	Trip1	Trip2
P1	8.81	8.42	-98.7		2.4	2.2	120	111	21	18	10	20
P2	8.7	7.96	-84.6		3.7	3.1	140	154	19.3	16.9	70	110
P3	8.75	8.43	-91.7		122.2	102.7	6110	5140	31.6	26.2	70	220
P4	9.65	9.35	-133.6		111.6	101.3	5590	5070	20.5	22.2	80	120
M1	8.63	8.19	-80.6		6.8	8.8	350	441	16.5	27.3	730	450
M2	8.62	Dry	-79.9	Dry	13.8	Dry	690	Dry	17.7	Dry	290	Dry
H1	7.32	7.23	-13.4		3	2.9	160	146	13	13.5	20	60
H2	3.77	3.08	-167.2		29.3	25.0	1470	1244	13.5	10.9	40	200
H3	2.56	3.32	211.8		22.5	18.8	1130	937	14.6	12.9	230	180
H4	2.95	2.83	211.8		21.6	20.8	1090	missing	16.3	11.6	190	300

Table 2 Ion concentrations in mg/l. First trip.

Sample	Cl	NO3	SO4	PO4	HCO3	CO3	Na	K	Ca	Mg	H
P1	6	0	47	0.7	0.6	0.02	14	2	35	7	0
P2	30	0	47	0.3	0.8	0.02	26	3	47	9	0
P3	3692	2.5	194	1.1	2.2	0.06	2280	127	174	26	0
P4	3217	4.1	265	0.2	1.1	0.21	2000	106	187	27	0
M1	102	2.2	30	0.7	0.9	0.01	93	9	21	3	0
M2	246	1.7	85	0.8	1.9	0.03	199	16	75	10	0
H1	3	1.5	94	0.4	0.5	0	11	1	46	11	0
H2	63	0.9	2098	0.3	0	0	44	13	224	54	0.17
H3	34	0.9	1638	0.4	0	0	34	8	232	65	2.75
H4	2	0.4	1614	0.2	0	0	38	8	247	67	1.12

Table 3 Ion concentrations in mg/l. Second trip

Sample	Cl	NO3	SO4	PO4	HCO3	CO3	Na	K	Ca	Mg	H
P1	7	1.4	36	0.6	0.7	0	15	3	35.5	7	0
P2	23	0.9	40	0.4	0.9	0	25	3	39.7	8	0
P3	3100	0.1	130	0	2.1	0.03	1035	104	167.6	25	0
P4	5500	3.0	3800	0	1.4	0.13	1007	101	153	25	0
M1	158	0.3	25	1.3	1.6	0.01	152	12	29.6	2	0
M2											
H1	7	3.3	65	0	0.7	0	12	3	45.2	86	0
H2	36	5.3	80	0.2	0	0	381	10	192.3	28	0.83
H3	91	0.4	2300	0.1	0	0	35	6	237.3	62	0.48
H4	57	2.4	3500	0.2	0	0	333	6	233.7	71	1.48

Table 4 Analysis accuracy in mg/l

	Cl	NO3	SO4	PO4	HCO3	CO3	Na	K	Ca	Mg
First trip	+/- 0.5	+/- 0.2	---	---	+/- 0.08	+/- 0.001	+/- 0.6	+/- 0.5	+/- 2.3	+/- 0.4
Second trip	+/- 0.7	+/- 0.2	+/- 1.5 ¹	---	+/- 0.08	+/- 0.001	+/- 0.5	+/- 0.5	+/- 0.1	+/- 0.5

¹ The accuracy of the analysis for sulphate, second trip, was +/- 1.5 mg/l for the samples with low concentrations including Poopó point 3. Huanuni point 3 had an accuracy of +/- 40 mg/l. The samples Poopó point 4 and Huanuni point 4 are assumed to have an accuracy in the same order of magnitude as Huanuni point 3.

Table 5 Major ions and ion balances, first trip. All concentrations in meqv/L. The percentage difference is calculated as $(\Sigma \text{ Cations} - \Sigma \text{ Anions}) / (\Sigma \text{ Cations} + \Sigma \text{ Anions})$.

Sample	Cl	NO3	SO4	PO4	HCO3	CO3	Na	K	Ca	Mg	H	Σ Anions	Σ Cations	%-diff.
P1	0.16	0.00	0.99	0.02	0.01	0.00	0.59	0.05	1.75	0.55	0.00	1.19	2.94	42.47
P2	0.84	0.00	0.97	0.01	0.01	0.00	1.15	0.08	2.35	0.71	0.00	1.83	4.30	40.18
P3	104.15	0.04	4.04	0.03	0.04	0.00	99.17	3.24	8.70	2.13	0.00	108.30	113.24	2.23
P4	90.75	0.07	5.53	0.01	0.02	0.01	86.99	2.71	9.34	2.24	0.00	96.37	101.28	2.49
M1	2.88	0.03	0.63	0.02	0.02	0.00	4.06	0.24	1.04	0.26	0.00	3.58	5.59	21.91
M2	6.95	0.03	1.77	0.03	0.03	0.00	8.63	0.41	3.75	0.83	0.00	8.80	13.62	21.49
H1	0.10	0.03	1.97	0.01	0.01	0.00	0.46	0.02	2.30	0.90	0.00	2.11	3.68	27.13
H2	1.77	0.01	43.67	0.01	0.00	0.00	1.91	0.34	11.19	4.44	0.17	45.47	18.04	-43.18
H3	0.95	0.01	34.10	0.01	0.00	0.00	1.47	0.19	11.59	5.38	2.75	35.08	21.38	-24.25
H4	0.07	0.01	33.60	0.01	0.00	0.00	1.65	0.20	12.31	5.54	1.12	33.68	20.83	-23.58

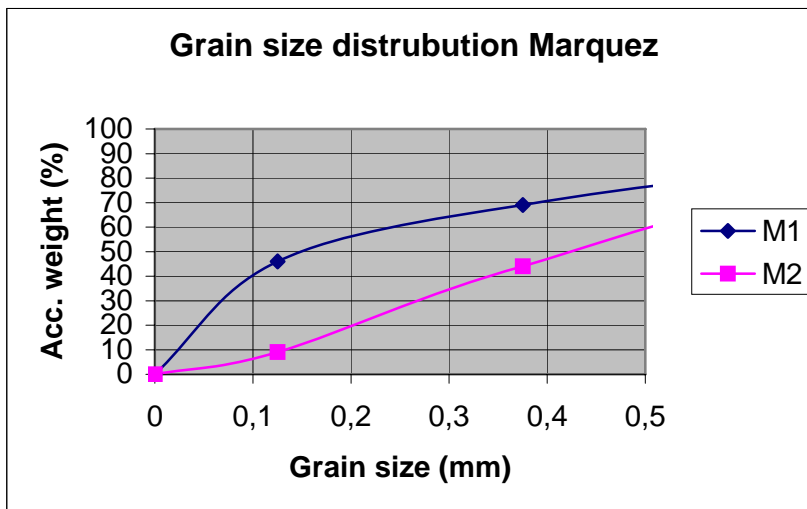
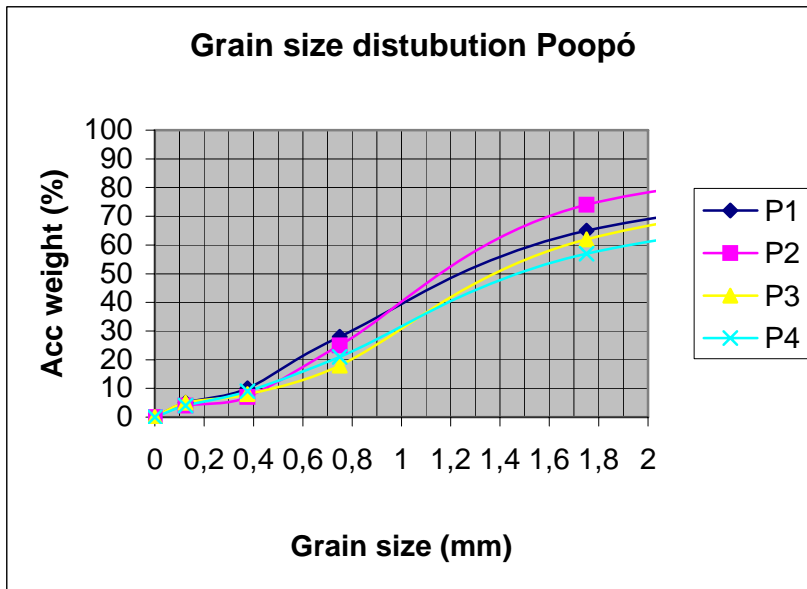
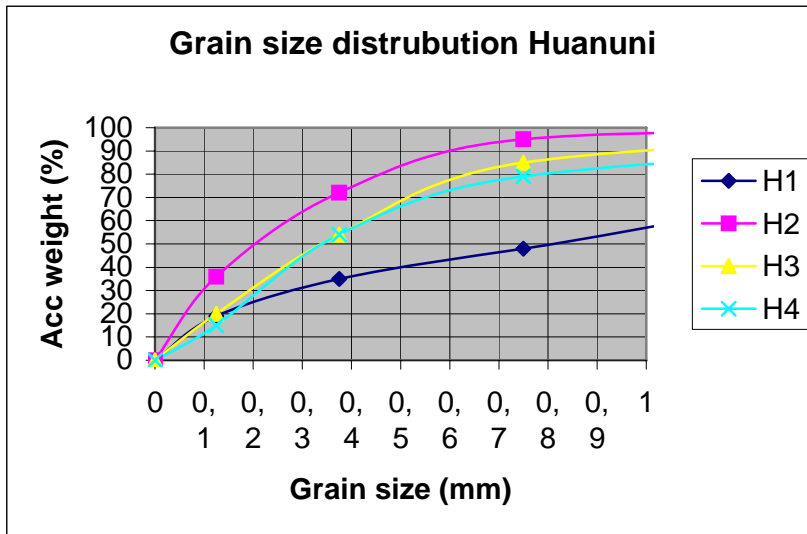
Table 6 Major ions and ion balances, second trip. All concentrations in meqv/L. The percentage difference is calculated as $(\Sigma \text{ Cations} - \Sigma \text{ Anions}) / (\Sigma \text{ Cations} + \Sigma \text{ Anions})$.

Sample	Cl	NO3	SO4	PO4	HCO3	CO3	Na	K	Ca	Mg	H	Σ Anions	Σ Cations	%-diff.
P1	0.21	0.02	0.76	0.02	0.01	0.00	0.64	0.06	1.77	0.58	0.00	1.02	3.05	49.76
P2	0.65	0.02	0.84	0.01	0.01	0.00	1.07	0.08	1.98	0.67	0.00	1.52	3.80	42.77
P3	87.48	0.00	2.79	0.00	0.03	0.00	45.02	2.65	8.36	2.02	0.00	90.31	58.05	-21.74
P4	155.18	0.05	78.25	0.00	0.02	0.00	43.80	2.58	7.64	2.02	0.00	233.50	56.04	-61.29
M1	4.46	0.01	0.53	0.04	0.03	0.00	6.61	0.30	1.48	0.20	0.00	5.06	8.59	25.87
M2														
H1	0.19	0.05	1.36	0.00	0.01	0.00	0.53	0.08	2.25	7.11	0.00	1.61	9.97	72.15
H2	1.00	0.08	1.67	0.01	0.00	0.00	16.57	0.26	9.60	2.27	0.83	2.76	28.70	82.43
H3	2.56	0.01	48.67	0.00	0.00	0.00	1.53	0.16	11.84	5.10	0.47	51.23	18.64	-46.65
H4	1.62	0.04	73.47	0.01	0.00	0.00	14.48	0.17	11.66	5.84	1.47	75.13	32.15	-40.06

Table 7 Total anion and cation concentrations together with conductivity

Sample	First trip			Second trip		
	Σ Anions (meq/l)	Σ Cations (meq/l)	Conductivity (μ S/cm)	Σ Anions (meq/l)	Σ Cations (meq/l)	Conductivity (μ S/cm)
P1	1.19	2.94	2.4	1.02	3.05	2.23
P2	1.83	4.30	3.7	1.52	3.80	3.07
P3	108.30	113.24	122.2	90.31	58.05	102.7
P4	96.37	101.28	111.6	233.50	56.04	101.3
M1	3.58	5.59	6.8	5.06	8.59	8.79
M2	8.80	13.62	13.8	Dry	Dry	Dry
H1	2.11	3.68	3	1.61	9.97	2.91
H2	45.47	18.04	29.3	2.76	28.70	25.0
H3	35.08	21.38	22.5	51.23	18.64	18.8
H4	33.68	20.83	21.6	75.13	32.15	20.8

Appendix C



Appendix D

Table 1 Heavy metal concentrations in solution

Sample	As ($\mu\text{g/l}$)		Cd ($\mu\text{g/l}$)		Pb (mg/l)		Fe (mg/l)	
	Trip 1	Trip 2	Trip 1	Trip 2	Trip 1	Trip 2	Trip 1	Trip 2
P1	34.97	20.22	0.0455	0.08	0.229	0.356	0.0855	0.153
P2	27.415	42.11	0.022	0.07	0.273	0.353	0.094	0.192
P3	4976	11000	1.771	0.796	0.240	0.375	0.128	0.233
P4	5508	12050	39	4.385	0.177	0.385	0.145	0.234
M1	139.3	169.1	1.2125	2.232	0.294	0.344	0.062	0.253
M2	169.05	Dry	0.4425	dry	0.363	dry	0.0555	dry
H1	17.3	18.29	2.476	4.88	0.313	0.366	0.2	0.216
H2	6392	11530	1384	852	0.179	0.485	487.8	381.5
H3	6538	10530	941	669	0.150	0.402	176.15	86.4
H4	8398	11730	764	674	0.213	0.398	118.95	118.9
WHO	10		3		0.01		---	
Bolivian law	50		5		0.05		0.2	

Table 2 Heavy metal concentrations in sediment

Sample	Arsenic (mg/kg)		Cadmium (mg/kg)		Lead (mg/kg)		Zinc (mg/kg)	
	Trip 1	Trip 2	Trip 1	Trip 2	Trip 1	Trip 2	Trip 1	Trip 2
P1	28.1	37.8	0.84	1.28	68.4	116.8	241.9	350
P2	40	18.5	0.45	0.5	85.4	18.6	129.6	94.4
P3	38.4	24.6	0.89	0.75	33	24.9	142	132.1
P4	91.9	57.2	11.1	8.65	97.1	96.8	2083.9	1778.5
M1	2	0.2	0.14	0.3	3.5	2.1	29.8	1741.2
M2	3.4	---	0.25	---	6.2	---	56.5	---
H1	10.9	27.1	2.9	4.5	44.4	69.4	349.9	557.2
H2	104.95	59.9	11.4	8.4	80.5	68.5	1130.7	905.5
H3	177.2	109.3	1.7	2.4	122.5	141.3	165.7	185.6
H4	16.6	106.9	4.1	1.3	146.5	139	338.1	2.1
D.L.	0.384		0.029		0.21		0.062	

Appendix E

Table 1 Speciation of lead in the Poopó River. The species are presented as percentage of total amount of lead.

Sample	Pb ²⁺	PbOH ⁺	Pb(OH) ₂	PbCO ₃	PbCl ⁺
P1	7 %	68 %	16 %	8 %	---
P2	8 %	64 %	12 %	15 %	---
P3	9 %	47 %	---	18 %	16 %
P4	---	40 %	53 %	2 %	---

Table 2 Speciation of iron and cadmium in the Poopó River. The species are presented as percentage of total amount of the metals.

Sample	Iron				Cadmium		
	Fe ²⁺	FeOH ⁺	Fe(OH) ₃	Fe(OH) ₄ ⁻	Cd ²⁺	CdCl ⁺	CdCl ₂
P1	82 %	11 %	2 %	---	---	---	---
P2	99 %	---	---	---	---	---	---
P3	53 %	7 %	19 %	16 %	18 %	63 %	16 %
P4	19 %	10 %	12 %	57 %	20 %	61 %	13 %

Table 3 Speciation of iron and lead in the Marquez River. The species are presented as percentage of total amount of the metals.

Sample	Iron		Lead			
	Fe ²⁺	FeSO ₄	Pb ²⁺	Pb(OH) ⁺	Pb(OH) ₂	PbCO ₃
M1	92 %	---	9 %	61 %	9 %	19 %
M2	89 %	---	9 %	49 %	7 %	32 %

Table 4 Speciation of iron, lead and cadmium in the Huanuni River.

Sample	Iron		Lead				Cadmium	
	Fe ²⁺	FeSO ₄	Pb ²⁺	PbOH ⁺	PbSO ₄	Pb(SO ₄) ₂ ²⁻	Cd ²⁺	CdSO ₄
H1	100 %	---	60 %	19 %	16 %	---	---	---
H2	68 %	32 %	60 %	---	35 %	5 %	49 %	40 %
H3	70 %	29 %	57 %	---	38 %	4 %	54 %	39 %
H4	69 %	31 %	59 %	---	37 %	4 %	53 %	41 %

Appendix F

Table 1 Saturation indices for some selected lead, cadmium and iron minerals in the Poopó River.

Sample	Cerrusite PbCO ₃	Pb(OH) ₂	Cd(OH) ₂	CdSO ₄	Fe(OH) ₃ (a)	Goethite FeOOH	Hematite Fe ₂ O ₃
P1	-1.12	2.08	---	---	0.43	6.17	14.34
P2	-0.76	1.96	---	---	0.25	5.93	13.84
P3	-0.85	2.15	-5.14	-11.93	0.92	7.04	16.12
P4	-1.93	2.48	-1.95	-10.77	1.48	7.21	16.40

Table 2 Saturation indices for some selected lead, cadmium and iron minerals in the Marquez River.

Sample	Cerrusite PbCO ₃	Pb(OH) ₂	Cd(OH) ₂	Fe(OH) ₃ (a)	Goethite FeOOH	Hematite Fe ₂ O ₃	Siderite FeCO ₃
M1	-0.56	1.79	-4.59	-0.40	5.18	12.32	-2.06
M2	-0.27	1.81	-5.24	-0.46	5.16	12.30	-1.86

Table 3 Saturation indices for some selected lead, cadmium and iron minerals in the Huanuni River.

Sample	Anglesite PbSO ₄	Pb(OH) ₂	CdSO ₄	Cd(OH) ₂	Goethite FeOOH	Hematite Fe ₂ O ₃	Fe(OH) ₃ (a)
H1	-1.51	-0.11	-11.38	-6.85	3.16	8.27	-2.29
H2	-1.18	-7.90	-8.06	-11.68	1.26	4.47	-4.20
H3	-1.28	-10.27	-8.21	-14.20	-1.80	-1.64	-7.31
H4	-1.12	-9.29	-8.21	-13.51	-1.35	-0.73	-6.92