Evaluation of Heavy Metals in Waters Influenced by Mining in the Poopó and Antequera River Basins, Oruro – Bolivia

A Minor Field Study

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ABSTRACT

Title
Evaluation of Heavy Metals in Waters Influenced by Mining in the Poopó and Antequera River basins, Oruro - Bolivia

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Problem definition
The Poopó and Antequera sub basins are part of the Lake Poopó basin, which is an enclosed basin in the Bolivian highlands. This basin has been studied for many years and it has been found that it is polluted, especially by heavy metals. The Lake Poopó is located on a high plateau at an altitude of 3700 meters in an arid/semi arid area, with one dry season and one rainy season per year. This high plateau is called the Altiplano and has for many hundreds of years been the centre of the Bolivian mining. For the people living in this area, scarcity of water is a major problem during the dry season. The poverty is widely spread in the area and the principal means of livelihood is agriculture. The mining activities are one other large economical income for the people, but the effects on the environment and water have been and are negative. Together with natural high levels of minerals in the bedrock and sediments there are problems with polluted waters together with the lack of water during the dry period.

Objectives
The overall goal of the thesis is to increase the understanding of the water quality in the Poopó and Antequera River basins. The following bullets are defined to concretise the purpose of the project:

- Assess the water quality and concentrations of heavy metals in the waters in Poopó and Antequera River basins.
- Investigate if the areas are affected by anthropogenic or natural means.
- Study if there is a difference of contamination between the surface waters and the groundwater.
- Examine if the pollutants are changing over time by comparing results from previous studies.
- Compare water quality with WHO guidelines for drinking water and the regulations in the Bolivian Law.

The ultimate ambition is that the increased understanding will lead to possible future remediation and secure the water resources for the people in the basins of Poopó River and Antequera River. This study is a small piece of this work.

Methods

This thesis is based on information from previous studies in the area and a visit in Bolivia from September to November 2009, including two field trips where water sampling of surface waters and groundwater was done. This period is the end of the dry season. The groundwater was retrieved through observation wells installed in the area. During the visits to the study areas field parameters were measured such as pH, temperature, alkalinity, redox potential and conductivity. Water samples were collected, which were sent to Sweden for analyses of heavy metals and cations, including As, Cd, Cu, Fe, Pb and Zn. The laboratory analyses were done by *Inductively Coupled Plasma Mass Spectrometry* at Stockholm University.

Results and Conclusions

In the Poopó River, the water is mainly affected by two factors; thermal waters and a mining processing plant with its waste deposits. The water quality upstream of these contributions is good regarding most elements. The levels of As, Cd, Pb and Fe are high in the Poopó River, where the arsenic concentrations are believed to be mostly of natural means. The high concentrations of As, Na, K, Ca, Mg and S are thought to originate naturally from the thermal spring. When it comes to Cd, Pb, Ni and Zn the major input to the Poopó River is acid rock drainage and the contribution from the mines close to the village.

The groundwater in Poopó River basin is of quite poor quality, especially near a pond close to a train station where one observation well is located. The situation in piezometer furthers to the north is different from the others which indicate that the direction of the groundwater is north to south, towards the river. Further out on the plains, there is no anthropogenic contamination in wells. In contrast, the levels of heavy metals in a piezometer close to the river are similar to the river water and are thought to be influenced by the river. More data about the groundwater should be collected.

In the Antequera River basin, the water quality in the river and groundwater upstream of a tailings dam is relatively good in comparison to WHO guidelines and could be used as drinking water, if it is treated for the high levels of arsenic and aluminium. Downstream of the large mine tailings the water quality in both the surface waters and groundwater is so poor, with high levels of all heavy metals. This water does not even approach to the standards in the worst “Class D” according to the Bolivian Law. This contamination seems to come from the tailings dam and there is also an influence on the groundwater.

Key words

Lake Poopó, Poopó River, Antequera River, heavy metals, mining, groundwater, surface water, thermal spring, arsenic, cadmium, iron, nickel, zinc

SAMMANFATTNING

Titel

Utvärdering av tungmetaller i vatten påverkat av gruvindustri i Poopó och Antequera avrinningsområden, Oruro - Bolivia

Författare

Malin Rosenberg
Kristofer Stålhammar

Handledare

Professor Lars Bengtsson

Problemställning

Floderna Poopó och Antequera är en del av avrinningsområdet till Poopósjön, som är ett slutet avringningsområde beläget på den bolivianska högplatån kallad Altiplano. Högplatån ligger på 3700 meters höjd och sträcker sig genom tre länder. Klimatet är torrt till delvis torrt, med en torrperiod och en regnperiod per år. Området kring Poopósjön har länge varit centrum för den bolivianska gruvindustrin. Sjön i sig är en naturligt salt sjö och den har under många år undersökts på grund av föroreningar. Under torrperioden torkar sjön nästan helt ut i och med att många bifloder torkar. Människorna i området lever i extrem fattigdom, med jordbruk som största sysselsättning men många jobbar även i gruvorna. Gruvdriften i området är en av de stora föroreningskällorna, då slaggprodukter oftast släpps ut i floderna utan rening. Till detta är de naturliga halterna av mineraler i berggrunden hög, vilket medför att vattnet i området är mycket förorenat. Under torrperioden är det dessutom vattenbrist i stora delar av områdena.

Målsättning

Det övergripande målet med denna studie är att öka förståelsen för vattenkvalitén i delavrinningsområdena Poopó och Antequera. För att definiera syftet med projektet har följande punkter tagits fram:

- Bedöma vattenkvalitén och koncentrationer av tungmetaller i yt- och grundvatten i avrinningsområdena Poopó och Antequera.
- Undersöka om ursprunget till föroreningarna är antropogent eller naturligt.
- Studera om det finns en skillnad i föroreningsgrad mellan yt- och grundvatten.
- Undersöka om föroreningarna förändras över tiden genom att jämföra resultat från tidigare studier.
- Jämföra vattenkvaliteten med WHO:s riktlinjer för dricksvatten och bestämmelser i den bolivianska lagen.

Den yttersta ambitionen är att ökad förståelse ska leda till eventuell framtida sanering och till säkra vattenresurser för människorna i delavrinningsområdena Poopó och Antequera. Denna uppsats är en liten del av detta arbete.

Metod

Denna rapport är baserad på information från tidigare studier och vattenprover tagna under ett besök i Bolivia hösten 2009. Under denna vistelse gjordes två fältresor under slutet av torrperioden, där vattenprover togs på ett antal utvalda platser i yt- och grundvatten. Grundvattnet pumpades ut från observationsbrunnar som är installerade i området. Fältparametrar som pH, temperatur, alkalinitet, redox potential och konduktivitet mättes i fält och vattenprover skickades till Sverige för att analyseras för bland annat As, Cd, Cu, Fe, Pb and Zn med *Inductively Coupled Plasma Mass Spectrometry*. Analyserna gjordes vid Stockholms Universitet.

Resultat och slutsatsar

I Poopófloden är vattnet i huvudsak påverkat av två faktorer; en varm källa, gruvdriften i området och dess avfallsdeponier. Vattenkvalitén uppströms dessa tillskott är bra med låga koncentrationer av de flesta ämnen. Nedströms är halterna av As, Cd, Pb och Fe höga i Poopófloden, där arsenikkoncentrationerna i vattnet tros ha främst naturliga orsaker. De höga halterna av As, Na, K, Ca, Mg och S tros ha sitt ursprung från den varma källan. När det gäller tillskottet till Poopófloden av Cd, Pb, Ni och Zn kommer det från utsläpp från gruvor och surt vatten som läcker från gruvrester.

Grundvattnet i Poopó avrinningsområde nedströms byn Poopó är av dålig kvalité, särskilt i närheten av en damm nära en järnvägsstation, där en av observationsbrunnarna 5 är placerad. Situationen i piezometern som ligger längst norrut skiljer sig från de andra, detta tyder på att riktningen av grundvattnenflödet är från nord till syd, mot floden. Ännu mer nedströms längre ut på slätten, finns det ingen mänsklig påverkan i brunnarna belägna där. Däremot är halterna av tungmetaller i piezometern närmast floden liknande de i flodvattnet och tros vara påverkad av floden. Mer värden om grundvattnet bör samlas in.

I avrinningsområdet Antequera är vattenkvalitén i floden och grundvattnet uppströms gruvresterna samt dess damm relativt bra och skulle kunna användas som dricksvatten, men endast om det behandlas för de höga nivåerna av arsenik och aluminium. Nedströms gruvresterna är vattenkvalitén i både yt- och grundvattnet så dåligt, med höga halter av de flesta tungmetaller. Detta vatten når inte ens upp till normerna ställda i den lägsta kategorin enligt den bolivianska lagen. Denna kontaminering verkar komma från gruvavfallet och det finns också en klar påverkan på grundvattnet.

Nyckelord

Poopósjön, Poopófloden, Antequerafloden, tungmetaller, gruvdrift, grundvatten, ytvatten, heta källor, arsenik, kadmium, järn, nickel, zink

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M.Sc. Mauricio Ormachea, at the San Andrés University for crucial help regarding our project during our initial time in La Paz. Also at the same institution Efrain Blanco and Maritza Mercado for their essential help during our first field trip and whose efficiency in the field is extraordinary. In the laboratories in La Paz, Macguiver Pillco who helped us prepare the samples before sending them to Sweden and our driver Victor Sotil for patience in the field while we were working and for the heavy metal from his radio. Ronald Zapata, at San Francisco Xavier de Chuquisaca University in Sucre, Bolivia for excellent teamwork in this project, both in the field and afterwards while analysing the results. Furthermore, we received good comments and ideas especially regarding the field parameters from Sylvia Kenny at Waterloo University, Canada.

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Malin Rosenberg and Kristofer Stålhammar
Lund, January 2010

Table of contents

1 Introduction

Bolivia is situated in the middle of South America with the Andes rising in the west of the country. It is a country with rich natural resources, where the major ones are mineral deposits and hydrocarbons, but also some renewable resources. The country is located in the tropical zone, but due to the mountains in the west and the lowland in the east Bolivia does not have a uniform climate. In the mountains the seasons are clearly separated by a dry season in the winters, June to August, and a rainy season in the summers, December to March (Encyclopaedia Britannica, 2009).

Bolivia declared independence from Spain in 1825 after several years of guerrilla war and uprisings. Before the Spaniards conquered the area it was part of the Inca Empire. After the independence the new nation did not get its economy going and Bolivia became the most backward of the new republics formed at that time. During the first 160 years the country had various political and economical agendas influenced by numerous wars and other instabilities. The mining of minerals has been the base of Bolivia’s economy for most of the time, but due to high production and low investments the development has been slow and the economical development has been absent. The outcome of this is that Bolivia is still one of the poorest countries of the continent. The last two decades the country's economy has improved but it is still receiving help from international organisations (Encyclopaedia Britannica, 2009).

This thesis is a part of a larger project at the University of San Andrés in La Paz, Bolivia, with economical support from the Swedish International Development Agency, SIDA. The project examines the waters and soils in the Lake Poopó basin in Bolivia. The area has been studied for many years and the lake has been found to be greatly polluted by heavy metals and is a natural saline lake (PPO 9701). In this thesis the occurrence of heavy metals in two river basins are studied, see Figure 1-1. These basins are located in the east part of the Lake Poopó basin, in the area where much of the mining activities are located. The samples for these analyses were gathered during a two month visit to Bolivia, where two field trips to the study area were carried out.

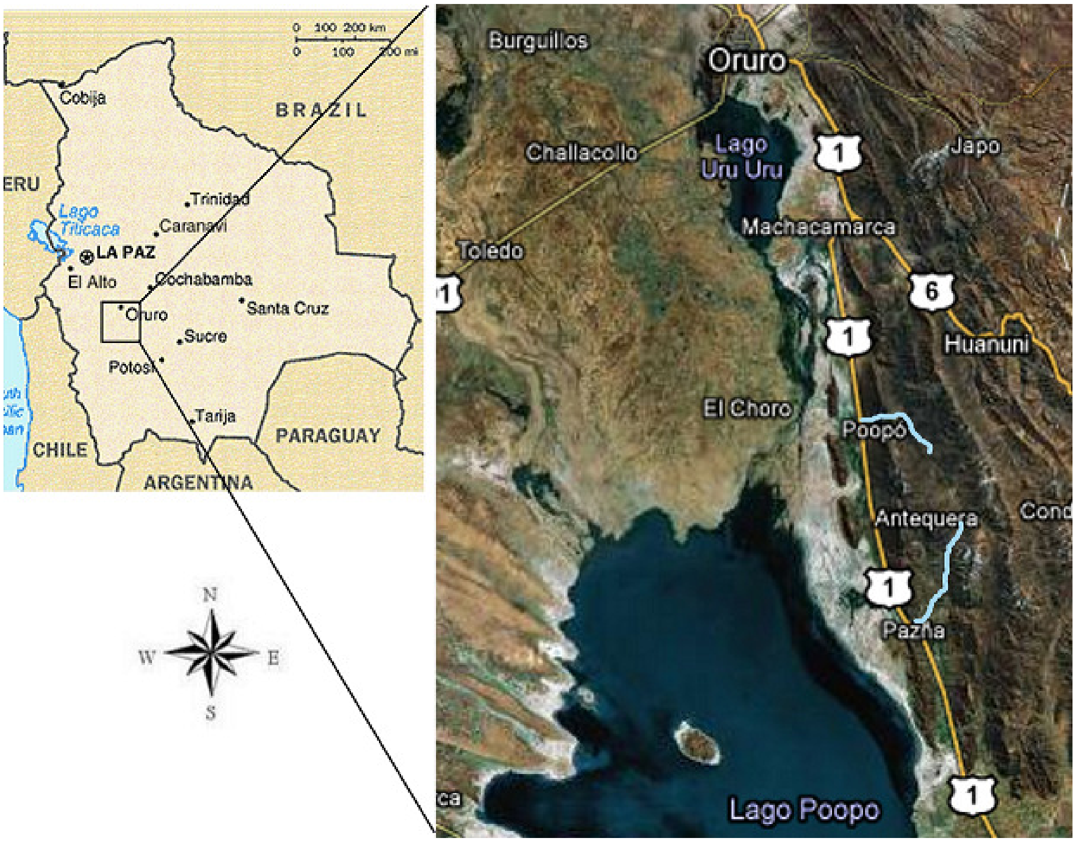


Figure 1-1. Map showing the study area and the investigated rivers of Poopó and Antequera sub basins, marked in light blue. Based on Bolivia map (2009) & Google Earth (2009).

1.1 Outline and objectives of the study

The overall goal of the thesis is to increase the understanding of the water quality in Poopó and Antequera River basins. The following points are defined to concretise this goal:

- Assess the water quality and concentrations of heavy metals in the waters in Poopó and Antequera River basins.
- Investigate if the areas are affected by anthropogenic or natural means.
- Study if there is a difference of contamination between the surface waters and the groundwater.
- Examine if the pollutants are changing over time by comparing results from previous studies.
- Compare water quality with WHO guidelines for drinking water and the regulations in the Bolivian Law.

The ultimate ambition is that the increased understanding will lead to possible future remediation and secure the water resources for the people in the basins of Poopó River and Antequera River. This thesis is a small piece of this work.

1.2 Previous studies and current work

The first major environmental evaluation in the region of Lake Poopó commenced in 1993 with the extensive work of the *Oruro Pilot Project.* The project was founded by the World Bank and the Swedish International Development Agency, SIDA (PPO 9701). The main purpose was to produce an *Environmental Master Plan* focusing on the mining and industrial sectors in the area. The company Swedish Geological AB was involved in the scheme and helped in the investigations. These publications include information about flora and fauna, geology, hydrology, mining activities and the socio-economic situation for the people living in the region (PPO 9401). During the 90's Troëng and Riera (1996) did geological mapping of the entire area around Lake Poopó. This work shows the general geological structures and mineral deposits, and also gives a description of how they were formed.

There is ongoing research of the region carried out at the University of San Andrés in La Paz, Bolivia. Some of the research is financed by the SAREC framework, which is the research department within SIDA. At the centre of this research is the interchanging of doctoral and master students between Bolivia and Sweden. PhD. Maria Eugenia García at the University of San Andrés, La Paz, Bolivia, is one of those who took part of this programme and studied the transport of heavy metals in Lake Poopó. Different professors have also been involved including Prof. Lars Bengtsson at the Department of Water Resources Engineering, Lund University, Sweden, who is also supervising this Master's thesis.

In 2006, Lilja & Linde investigated in their Master's thesis the occurrence of heavy metals in different rivers flowing into Lake Poopó. One of the examined rivers was Río Poopó which derives from the Poopó sub basin. In the adjacent sub basin to the South, Antequera, Ekdahl (2007) studied the abundance water and its utilization and how it affects the socio-economic situation amongst the population. Another thesis of Mikaelsson & Ny (2009), examined the surface- and groundwater quality in the same sub basin.

Today a group of doctoral and master students are working together to evaluate the Poopó and Antequera basins, within different fields, including the hydrogeology and isotope transport fields. The supervisor of this thesis, Oswaldo Ramos Ramos at the University of San Andrés, Bolivia and Kungliga Tekniska Högskolan, Sweden is doing research on the water resources in the area and the consequences of mining in the region. Ronald Zapata at San Francisco Xavier de Chuquisaca University, Bolivia, is measuring groundwater levels and studying how the groundwater is flowing in the sub basin of Poopó. Consequently, this thesis is a part of the collaboration of people and universities working within the same study area.

1.3 Delimitations of the project

This thesis covers the months of September and October in 2009, which is the dry season, including data that was collected earlier in the year from May to July. Because the seasons are very distinct over the year, and there are no samples collected during the rainy season, conclusions over the full situation can not be drawn for the whole year. Moreover, there is not much sampling done during earlier years which limits the statistical analyses when looking at changes over time. Furthermore, the study area is located very far away from civilisation in a remote area on the Altiplano where it would be difficult to conduct more than one field trip each month. In the area there is a limited number of sampling points which makes it difficult to fully understand the whole situation of the water resources in the area. Some of the sites are just simple surface water points where others have required more efforts in their preparations, for example by installation of piezometers. Because it is a costly and arduous process to put piezometers into the ground, this project is restricted to the wells that are already installed.

As with all investigations, this study is also just a model of the real world. By performing careful observations and measurements about the water system in the study area, better conclusions can be drawn. Another constraint is the number of times each sampling point has been sampled which is limited to the amount of field trips conducted.

2 Description of the Altiplano high plateau

The Altiplano is a 191 000 km² large high plateau situated in the Andes between the two mountain ranges Cordillera Oriental and Cordillera Occidental in western Bolivia, see figure 2-1. This high plateau is shared between three countries, Peru, Chile and Bolivia. The plateau is not completely flat but has mountains rising some hundred metres over the main elevation at 3700 metres; see Figure 2-1 (PPO 9603). The Altiplano is divided into four different eco-regions; semiarid/arid plateau, semiarid plateau, saline desert and dunes, with most of the lands belonging to the first two categories (PPO 9608).

Figure 2-1. Map showing the Bolivian Altiplano, with Lake Titicaca, River Desaquadero and Lake Poopó. Based on Graphic Maps (2010).

2.1 Climate and hydrology

Bolivia is situated in the tropical zone, but due to a variety of altitudes the climate differs a lot within the country. The climate in the Lake Poopó area has been described as semi-arid and cold (PPO 9608). The climate during a year is characterised by one rainy season during the summer month, December-March, and one dry season during winter June-August. The mean temperature is 10^{o}C, but it varies greatly during the day, with high temperatures in the days and very low temperatures during the nights (Rocha, 2002). The mean precipitation in the area is 364 mm, mostly falling in the summer months December-March. The climate variations often causes floods and droughts in the area and the region sometimes have extreme weather with hailstorms and frost (Rocha, 2002 and PP0 9606). The amount of rainfall in the area is affected by the El Niño and La Niña phenomena, with more rain during La Niña and less during El Niño (PPO 9612).

Lake Poopó is a part of Titicaca-Desaguadero-Poopó-Salar-system (TDPS-system), see figure 2-1, which is the major basin on the Altiplano and is an enclosed system. This basin originates in Lake Titicaca, which drains through the 300 km long Desaguadero River to Lake Poopó. The water level in the lake is totally dependent on the level in Titicaca. The Desaguadero River also provides Lake Uru Uru just north of

Lake Poopó with water, this lake later drains to Lake Poopó. In years with very high flows Lake Poopó drains through Lacajahuira River to the Coipasa salt plain in the south. These years it is possible for Lake Poopó and Lake Uru Uru to form one large lake. Lake Poopó and Lake Uru Uru are both shallow with depths between 0.5m and 2.5m. The average surface area of Lake Poopó between 1975 and 1995 was 1950 km², but the variations between two adjacent years can be large. Some years the lake is totally dry, while the following year the area can reach 3000 km² and spill over to the salt plains (Pillco, 2007). The average surface of Lake Uru Uru is 150 km² (UNEP, 1996 cited in García, 2007).

In addition to the Desaguadero River there are around 20 smaller rivers that originate on the east side of the lake, one on the west side and one in the south. The average flows in the regional rivers is in the range of 10-40 m³/s and in the Desaguadero the average flow is 66 m³/s (Pillco & Bengtsson, 2006 cited in Pillco, 2007). The most important rivers, beside Desaguadero, are Sora Sora, Pazña, Sevaruyo, Marquez and Lacajahuira (García, 2006).

2.2 Vegetation and animal life

The vegetation in the Poopó area is typical for the Altiplano and is called Puna Seca, dry Andean highland, where most of the land is covered by perennial grasses, like *Estepa ichu, Paja Brava* and the Thola bush, see Figure 2-2. The vegetation in the area of Lake Poopó is strongly influenced by earlier uses of trees as fuel and for construction purposes, which have resulted in an eradication of all trees (PPO 9608). On the hillsides in the Poopó basin the vegetation mostly consists of bushes and cactuses, adapted to high altitude and rocky ground (Rocha, 2002). The Altiplano wildlife is dominated by vicuñas, Andean fox, Southern viscacha, Molina's hog-nosed skunk and Andean hairy armadillo. Furthermore, some felines, like the puma and Andean mountain cat has been seen in the area (Rocha, 2002). Most of the land is used as pasture for sheep and llamas, but also alpacas and cattle. As most people in the area are dependent on the grazing of animals, the land is suffering from overgrazing (PPO 9608).

Figure 2-2. Photograph of parts of the Altiplano with Poopó Village in the centre.

2.3 Geology

The geological characteristics in the area around the Lake Poopó are separated by the Poopó-Uyuni fault. To the west of this fault the Altiplano spreads out on an elevation of 3700 m. This plateau consists of Cenozoic deposits. To the east the central part of the Eastern Cordillera rises. This mountain range consists of a series of sediments from different eras during Paleozoic, Mesozoic and Tertiary. These sediments have then been covered with volcanic deposits from Tertiary and then tilted. It is in the Eastern Cordillera that all of the different metal veins are found. This is where you find some of the World's richest tin veins and where important polymetallic veins are located. The metals found in these veins are zinc, silver, lead, tin, gold, wolfram and antimony and there are also findings of rare minerals (Troëng & Riera, 1996).

The soils in the mountain area are ephemeral and there is a continuous removal of mineral rich soils, due to the dry climate and the steep topography the area is not suitable for agriculture. Problems with the soils include vulnerability to erosion. Consisting of sand, silt and clay the soils move easily with water and wind. In the valleys the soils are sandy or sandy-clay and they are more suitable for agriculture, but with some limitation due to the climate and influences of salts (Ministerio de Desarollo Sostenible, 2005).

2.4 Socio-economic situation

The region around Lake Poopó, as the rest of the Altiplano, is an area with much poverty. It is estimated that 67% of the rural population are living under the limit for poverty and 33% under the limit for extreme poverty. The population growth is very low at a rate of 0.6 %, and this is partly due to the migration to other regions and cities. Another important factor is the high infant mortality at about 113/1000, which is the highest in South America. The most common reasons for mortality on the Altiplano are respiratory and gastro enteric diseases, where the latter is water related from not having safe drinking water and adequate sanitation. To further widen the picture of the difficult situation in the region, the life expectancy is 59 years (PPO 9701) and the rate of illiteracy in the area is 29 % (ALT, 1999 cited in Rocha, 2002). In the PPO-report 9401 it is stated that the problems of endemic poverty in the rural area are closely related to the environmental deterioration. In addition to this, the situation of indigenous people will need particular consideration given that this group is to the greatest extent affected by poverty. A lot of people are directly and indirectly affected by the mining industry. The people working in the mines are having problems with respiratory diseases in addition to the high risks of accidents. The general public health is poor because of the consequences of chronic metal intoxication (PPO 9701).

3 Mining and Legislation

This chapter includes a summary of the history of mining in Bolivia starting from the epoch of the Incas until today. There is also described how acid rock drainage is formed and its impact on the environment. Finally, the eligible concentrations are presented for various elements, for example heavy metals, together with a comparison of the drinking water guidelines from the World Health Organization and the Bolivian regulations.

3.1 History of mining in Bolivia

Mining in Bolivia goes back as far as the Incas, and the mining industry has for a long time been the most important sector for the Bolivian economy. The mining industry began with the Spanish colonisation in the 16th century and it was mostly silver and gold that was mined. In the beginning of the 19th century, wars and revolution weakened the industry. At the end of the same century the first mine started extracting tin in Bolivia, and the country has ever since been one of the world’s largest producers of the metal (Troëng & Riera, 1996).

The mines, mostly situated in the Altiplano area, were at the beginning and until the 20th century mostly owned by private companies. After the economic crisis in 1929 the mining declined and the investments reduced. Twenty years later, in 1952, the three largest tin companies was nationalised and the Mining Corporation of Bolivia, COMIBOL, was formed. The purpose of COMIBOL was to organise the national mines. At that time all mining operation was classified into three different categories; large-scale, medium-scale and small-scale. The large-scaled mining, governed by COMIBOL, re-employed many of the miners that earlier had been fired, due to financial problems in the private companies. The mining production of COMIBOL declined throughout the 1950's and it was not until the 70's that the company saw some improvements, due to increased tin prices in the world and some political stability in the country. In the 80's, COMIBOL suffered large financial losses, because they kept running the mines with too many workers. In 1985 the tin market collapsed, with the consequence that the mining operations were forced from tin-silver mining into other ore markets (Troëng & Riera, 1996).

In 1985, the new government decided to reduce the role of the state mining, the work force of COMIBOL was decreased and only the most economically viable mines were kept. Since then, the most important mining group in Bolivia is the medium-scale owned by private companies. One more sector, the cooperative-sector, was established due to the decreasing influence of COMIBOL. These cooperatives are formed by former COMIBOL workers that continued the mining activities in closed mines and deposits. Since the mid 80's the changes in the country's economic policy and the establishment of a free market, has given the mining industry an opportunity to develop with the help of foreign investments. There have also been explorations with new geological models and technology, leading to new ore findings (Troëng & Riera, 1996).

3.2 Mining and Acid Rock Drainage

Acid rock drainage, ARD, is a process where sulphur in minerals are oxidised to sulphate and in the contact with water it reduces the pH to extreme lows. This happens naturally to a certain degree, but is usually connected to human activities such as mining and construction. In these processes the rock is exposed to the atmosphere and may subsequently be oxidised in a larger extent than normal (Evangelou, 1998).

From mining processes the residues are stored as tailings. Drainage from these tailings and the mine itself can if not treated consist of numerous compounds of heavy metals and sulphur. The mineral strongly connected to acid drainage is pyrite, FeS_2, which is a common mineral that exists in and near almost all metal deposits in the crust of the Earth. Oxidation of pyrite is dependent on numerous parameters for example pH, air pressure, hydrology and other water characteristics. Another important factor is the bacteria group of *chemoautotrophs* which are using iron sulphide as an energy source (PPO 9401). Reaction (1) shown below is the overall process where pyrite gets oxidised. This reaction can result in a pH value below zero due to a high concentration of sulphuric acid (Appelo & Postma, 2005).

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + H^+ \qquad (1)$$

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (2)$$

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + ½H_2O \qquad (3)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3\mathrm{H}^+ \qquad (4)$$

$$FeS_2 + 7Fe_2(SO_4)_3 + 8\mathrm{H}_2O \rightarrow 15FeSO_4 + 8\mathrm{H}_2SO_4 \qquad (5)$$

Reaction (2)-(4) shows the steps in the oxidation of pyrite. As seen Fe^3+ and O_2 are the major oxidants of pyrite. When the pH value is lower than 4.5 the oxidation with Fe^3+ is much faster than the one with O_2. Reaction (2) becomes the limiting factor to the overall reaction rate. At very low pH, iron-oxidising bacteria can accelerate the Fe^2+ oxidation and may therefore be a major part in releasing acid to the environment (Evangelou, 1998).

3.3 The influence of mining on the environment in Bolivia

In Bolivia an environmental legislation have been absent until resent times and there are much work to be done before a good organisation is in place. The results is that most of the ore processing plants have disposed fine rock tailings into the streams, rivers and lakes and makes the problems of acid rock drainage are enormous. In fact, the ARD has been recognised as one of the main factors to the environmental degradation in the region. The affected water gets very acidic and usually contains heavy metals at extremely elevated concentrations. Some of the problems that have occurred are destruction of aquatic ecosystems and groundwater in the region. Issues from the acidification of waters also incorporate the masses of tailings which are being accumulated away from the streams, as well as the drainage from open and closed mines, called acid mine drainage (PPO 9401 & PPO 9701).

Some of the concerns include the lack of drinking water as well as metal contamination of water courses and soils which may affect the vegetation and agriculture (PPO 9701). One large contribution to ARD is the large mining companies dumping their waste on the riverbeds where cooperatives re-process the stones. Not only does the acid rock drainage increase this way, but also the working conditions for the labourers are very poor. It is believed that the only thing limiting a spread of illnesses is the low pH in the rivers (PPO 9611).

One concrete example of the environmental problems was during mid-1993, when the fisheries in the Poopó Lake collapsed since the fish populations nearly got eradicated. Investigations from the *Oruro Pilot Project* found high concentrations of heavy metals in the fish tissues and stated that the mining industry and the acid rock drainages was the major cause. Additionally, in other areas there has been a complete elimination of the invertebrate aquatic fauna in some of the rivers (PPO 9401). According to the final PPO-report 9701 there are no streams where the concentrations of metals match, or are lower than worldwide concentrations.

3.4 Water quality and legislation

The access to clean water in everyday life is not to be taken for granted. This is the case for many Bolivians living in the rural area of the Altiplano. According to Ekdahl (2007) the water quality in the Antequera basin has to improve otherwise the area will not sustain future growth and will probably depopulate. Similar conclusions can probably be drawn about the adjacent sub basin of Poopó. According to the World Health Organization, WHO, the access to water of good quality is crucial to the health of people. The quality of drinking water is controlled worldwide by different legislations. Most countries are following the directives from the WHO or at least to some extent a similarity to the recommendations. This is also the case with Bolivia who has put up its own environmental regulations and permissible contaminants levels. This section is thought to bring in the standards and differences set by the WHO and the Bolivian legislation for different specimens in water supplies.

The primary goal for the WHO guidelines is the protection of public health. The values are set to be suitable from large piped drinking-water systems in mega cities to non-piped systems in small individual communities. The WHO drinking water standards are divided into the microbial and chemical aspects. The latter one will be the only one in focus since this project and thesis is studying the affects of mining. In this field, the concerns about health seem to come from the effects after long exposure of chemicals. Nevertheless, there might also be a risk of acute poisoning if the contaminant comes in high concentrations. The guideline values are set at a level where there are no risks to health over a lifetime of consumption. Hence, the standards are health-based targets and are considered to be the core to achieve the main goal which is protecting the public health, see Table 1. Furthermore, it is important that the levels set are realistic and taking into account special circumstances in each situation of water distribution (WHO, 2008).

Table 1. WHO guideline values and corresponding regulations according to Bolivian Law for drinking water which is "Clase A".

Parameter	WHO (mg/l)	Bolivia (mg/l)
pH	6.5-9.5*	6-8.5
TDS	1000*	1000
DO	-	>80% ***
Aluminium	0.2*	-
Arsenic	0.01**	0.05
Cadmium	0.003	0.005
Calcium	200****	250
Chromium	0.05**	0.05
Copper	2	0.05
Fluoride	1.5	0.6-1.7
Lead	0.01	0.05
Iron	0.3	0.3
Magnesium	200****	100
Nickel	0.07	0.05
Sodium	200*	200
Sulphate	500*	300
Tin	-	2
Zinc	3*	0.2

* No health-based targets has been set
** Provisional value
*** Oxygen saturation level
****Measured as total hardness

The WHO guideline standards for the following specimens, shown in Table 1, are well-defined and may affect human health at elevated concentrations; cadmium, copper, fluoride, iron, lead and nickel. There are no standard values set for lithium or potassium. The rest of the elements and parameters have a further explanation in the WHO guidelines:

- There are no standards to *pH* but the operational levels for treatment usually have its optimum between 6.5 and 9.5.
- There is no maximum level of *TDS* according to health protection, but the water may become unpalatable at concentrations exceeding 1000 mg/l.
- For *DO* there is no recommended health-based value at all.
- The recommended value for *aluminium* is set based on coagulation optimisation basis in drinking-water plants.
- Values for a*rsenic* and *chromium* are set as provisional while waiting for more scientific research and certainties of how it affects the health.
- The recommendations for c*alcium* and m*agnesium* are derived from water hardness, where a total hardness of 200 mg/L may cause scale deposits.
- *Sodium* concentrations in drinking water are usually low and no health-based guideline has been set, but concentrations above 200 mg/L can cause bad taste.
- *Sulphate* has been found to be laxative in very high concentration; therefore the recommendation is that the value should not exceed 500 mg/L.

- The levels of t*in* in normal drinking-water are usually low and the toxicity levels for humans are several times higher. Therefore, no guideline value has been set.
- *Zinc* appears in waters at relatively low levels and does not affect humans. Already mentioned, zinc is also an essential trace element for living organisms. No standard value has been set concerning health but above 3 mg/l it may affect the colour to be opalescent.

The Bolivian Law (1992) has a set value to almost all specimens and water quality parameters. The levels of these parameters are controlled by different classifications of various waters, where the above standards are for drinking water and belong to Class A, see Table 1.The water in this category can be utilised for drinking after disinfection as the single treatment method. The regulations are similar to the WHO guidelines but differ sometimes, where some values are stricter and some not as stringent. According to the Bolivian Law (1992), there are other categories of water uses than the mentioned one. These classes, B, C and D, have lower requirements according to the water quality, but are used to regulate other applications such as waters used for industries, irrigation or recreation purposes, see Appendix B.

4 Study area - Poopó River basin

One of the studied areas is the Poopó River basin, see Figure 4-1, which is situated 56 kilometres south-east from the city of Oruro and a further 285 kilometres from La Paz, see Figure 2-2 for a typical sight of the Altiplano close to Poopó Village. The area of the sub basin is 109 km^2 and the Poopó River is flowing through the valley starting about 10 kilometres east of the village (PPO 9606). The population is about 3000 people excluding various settlements around the village which accounts for about 650 people. The ethnical groups are Quecha and Aymara (Ministerio de Desarollo Sostenible, 2005). The following sections include a description of the water resources, the mining activities, the sampling points and conclusions drawn in previous studies done in the basin.

Figure 4-1. Map showing the Poopó Village, with the river flowing from east to west, a large tailings dam marked in dark blue and the road and railroad at the west side of the village.

4.1 Superficial waters and groundwater

The Poopó River has its source about 10 kilometres upstream of the village and flow from south-east to west, towards Lake Poopó (PPO 9612 cited in Rocha, 2005). Most of the tributaries are seasonal, where one of the few permanent tributaries originates from a hot spring in the area, Cabreria, about 2.6 kilometres upstream from the village of Poopó (Ministerio de Desarollo Sostenible, 2005).

Potable water for the village is taken from a well, which is adjacent to the river approximately 3.6 kilometres upstream of the village. This is before there is an influence of water from the mine Machacamarquita and the thermal spring (Ministerio de Desarollo Sostenible, 2005). The water is then lead through a pipeline to the village which goes next to the river. The water is not being treated before it is distributed to the people in Poopó. After use, the wastewater is sent straight to the river without any treatment. Along the river where the village is situated the garbage is dumped on the river banks and in the river. Therefore, the water quality downstream the village is assumed to be very poor with a high pollution load. On top of this there is the impact of the mining in the area. The contaminants probably also affects the groundwater in the basin since a large tailings dam is located close to the river and the water from this dam travels downstream and towards the Poopó River. According to PPO 9701, the water quality in the Poopó River is worse than “Class D” which is a standard for industrial use, see Appendix B.

4.2 Mining and rock tailings

There are various mining companies in the district of Poopó, where the major one is Sinchi Wayra Company, which is owned by a Swiss company called Glencore (Glencore, 2009). Another important company is Compañia Minera Tiwanacu S.A. which was formed in 1981 after metal deposits were found in the area. During the following year the mining operations commenced. In the early 80's the extraction was made out of zinc, lead, silver and tin. A few years later the prices for silver and zinc went down and the company had to close down some of its operations. By 1995 the state-owned mining cooperation COMIBOL rented the mine and changed some of the extraction techniques, and later that year another company collaborated with them on the mining processing and the extraction rates were somewhere between 3000 and 4000 tonnes per month. A little later the mining group Ferrari started to rent different mine locations from the Tiwanacu Company in the sub basin of Poopó. The principal minerals extracted in the area today are still zinc, lead, copper and silver and two of the operating mines in the area are the San Francisco and Ferrari mines. But as mentioned before, it also exist other informal small-scale mining in the area (Ministerio de Desarollo Sostenible, 2005).

One of the bigger mines in the Poopó sub basin is Machacamarquita and it is located approximately 1 kilometre east, and upstream, of the Poopó village. It is owned by Tiwanacu but the operations have been closed for a few years since there have been some environmental irregularities (Ramos Ramos, 2009-10-09). Where the village is located, there is a drainage passage from the mine where all the drained water is being let out, see Figure 4-2. The water is collected in a small 10 m^2 sedimentation dam and then transported in a pipeline to the tailings dam, which is located just downstream of the village. There is water leaking from the in- and outlet of the small sedimentation pond straight to the river. This is the case when there are higher flows of water being drained from Machacamarquita. This water is not treated and is believed to contain high levels of contaminants. According to PPO 9401, it is important to do sampling over the different seasons since the drainage from inactive mines are directly related to the precipitation. There is also mine drainage from other mines going into the river without any treatment, for example the mine which is owned by Sinchi Wayra and other informal operations (Ramos Ramos, 2009-10-09).

Figure 4-2. Photograph of the mine drainage from the closed mine Machacamarquita, Poopó sub basin.

The mined rocks from Machacamarquita have during a 25 year period been transported to the tailing just west of the village for processing and extraction of metals. Even though Machacamarquita is closed today there are other mines providing rocks for processing. The rock tailings are then being put in piles where the tailings dam is situated, see Figure 4-1. The accumulated rock tailings from the Tiwanacu operations are more than 50 000 m^3 in total (Ministerio de Desarollo Sostenible, 2005).

The water in the dam derives from the mine drainage and is utilised for the processing operations. Before using the water, limestone is added, probably to make the pH higher. According to Hugo Miranda Lopez (2009-10-09), who works on the processing site, this water is mixed with recycled water from the tailings dam and used for the mineral processing. The surface of the rock tailings dam measures about 250 x 250 m^2 and is 9 metre higher than the surrounding landscape, the dam is shown in Figure 4-3 (Google Earth, 2009). The depth of the water is only about one metre. Some of the water is leaking through the dam and is collected in the north-west corner and pumped back to the dam (Lopez, 2009-10-09). In the case of a pump failure there is a risk that the water will continue in a canal out on the lower lying plains west and downstream of Poopó. Here the water may infiltrate to the groundwater and is thought to contaminate the area with heavy metals. A more severe damage is likely to be the cause by permeable layer underneath the tailings dam. It is believed that the water in the dam infiltrates through the soil layers and is transported with the groundwater out on the lower lying plains. There are also other smaller informal processing operations adjacent to the major tailings which also should contribute to a contamination.

Figure 4-3. The tailings dam in the Poopó River basin.

4.3 Sampling points

During a visit to Bolivia two field trips were conducted to the area and a number of sites were visited and water samples collected. This part includes a description of all the different sampling points along the Poopó River and the piezometers in the same basin. There are also observations about the nature and waters made during the field trips. The bolded letters down below are the names given to each site. For a full list of all the sampling points in the two sub basins including the UTM coordinates and altitudes, see Appendix A.

4.3.1 Surface water

There have been investigations of four sampling sites along the river. There were also samples taken from three additional waters in the area, including the potable water, the thermal spring and drainage water from a mine.

PO1 – *River water far up in the sub basin of Poopó*

The very first sampling point, *PO1*, is located about 7.7 kilometres upstream from the Poopó village at a small bridge called Puente Vilaque, see Figure 4-4. The area is dominated by low bushes and grasses, and there seems to be very little human activity in the area. The water at this site is thought to be free from major anthropogenic contributions such as mining operations, and there are no known thermal springs upstream from this place. Although it is important to remember that there are a few settlements upstream of this point which could give a small contribution of various contaminants to the river. These include irrigation- and drainage water from agriculture, water being used for domestic animals and human wastewater.

POP and **PO2** – *Potable water and t river water*
The second point along the river, *PO2*, is an area situated about 3.3 kilometres east of the Poopó village, see Figure 4-4. This is also the location where potable water is collected from a well, *POP*, and transported in a pipeline to the village for distribution. The origin of this water is not known. Possibly it could be infiltrated somewhere upstream and drained at this well or infiltrated from the river and collected at this point. The river water at this location is probably little affected by the mining in the area. However, the field trips revealed some mining activities upstream which might be able to impact the water at this point, both in the river and in the well.

Figure 4-4. Map over the sampling points along River Poopó including the position of POM 0-5 (Google Earth, 2009).

POTW and **PO3** – *Thermal spring and affected river water*
At about 2.6 kilometres upstream the village, in the middle of the river, there is a thermal spring contributing to the river, *POTW*, shown in Figure 4-4. The temperature from the upwelling is around 60°C and it smells strongly of sulphur. Everywhere there are crystallised salts in areas above the surface. The next point, *PO3*, is about 600 metres downstream from the hot spring and is a mixture of thermal water and river water, see Figure 4-4. At this site the temperature of the water is at about 30°C which is much higher than normal river water. Upstream of the sampling point there are trucks crossing in the river many times during the day, due to the mining operations, and the water looks very turbid.

PODW – *Drainage water from the Machacamarquita mine*
This sampling point is situated in the drainage from the Machacamarquita mine, which is located along the river at the height of the village, but on the other side, PODW in Figure 4-4. There is no influence from either the village or the thermal springs to this water. The sediments at the bottom of the little stream are red, see Figure 4-2. The presumptions are that the water contains a lot of iron and other metals. Around this site there are a lot of crystallised salts precipitated. Most of the drainage water is led in a pipeline to the tailings dam located across the river. But some of the water may surpass and go straight to the river.

PO4 – *River water downstream from the village*
The final site of surface water is located in the river a few hundred meters downstream from the village, named *PO4*, see Figure 4-4. At this point the water is influenced by the hot spring and the mining activities. Since this place is downstream from the village there is also a great impact from the wastewater and garbage dump. At the site there is garbage in the river.

4.3.2 Groundwater

There have been a number of sites investigated during the field trips for water sampling and data collection. All the groundwater investigated has been through different piezometers installed in the area. They are divided into two different groups depending on their positions in relation to the tailings dam.

POM 0-5 – *Piezometers just downstream from the tailings dam*
This set of piezometers was installed in April 2009 and are located about 400-600 metres west of the major tailings dam, see Figure 4-5. At each of the six sites, except POM 0, there exist two piezometers at different depths. The shallow ones are labelled *A* and extend about 5-6 metres down in the ground. The deeper piezometers are named *B* and have a depth of about 8-10 metres. The area is characterised by the typical Altiplano vegetation consisting of small bushes, grasses and mosses, all spread very sparsely around. There are no traces of precipitated salts on the ground.

Figure 4-5. Piezometers POM 0-5 downstream the tailings dam (dark blue in the center) just west of the village Poopó (Google Earth, 2009).

POM 6-8 and **POM R** – *Piezometers far from the tailings dam on the plains*
These piezometers were installed a little bit later in July 2009 and are located at the lower plains several hundred meters downstream of the tailings dam, see Figure 4-6. At the site of *POM 7* there are two piezometers located, *POM 7A* and *7B*, and they are positioned very close to the Poopó River about 2 kilometres from the major principal dam. The area is marked by higher vegetation just around the stream. There are also very low growing plants like grasses and mosses and huge scarce areas in between. This place has also a lot of crystallised salts on the ground. At another site, 2.6 kilometres west of the tailings dam, is the location of piezometer *POM 6A* and *6B*. At this point there is also another piezometer installed, *POM R*, which was found a couple of years ago but the origin is unknown. This piezometer has also a wider

diameter than the rest and the area lies far from any surface waters and is dominated by low growing mosses. Located in between *POM 0-5* and *POM 6/7* is another piezometer installed, named *POM 8*, at about 1.8 kilometres from the tailings. The surrounding area has low growing vegetation like mosses and grasses. This piezometer was installed during the first field trip. All of these piezometers, except from *POM R*, were drilled with a hand-powered auger.

Figure 4-6. Map showing the location of piezometers in the Poopó River basin and the tailings dam west of the village (Google Earth, 2009).

4.4 Conclusions drawn in previous studies

Earlier studies of the Poopó sub basin have found that the river is highly contaminated. In García (2006) it has been reported that the Poopó River had an alkaline pH. The Poopó River was rich in calcium, carbonates, chloride and the river had high sulphate concentrations. In the river the levels of arsenic and lead where found to be higher in the dry season, when most of the water originated from the thermal spring. This corresponded to a higher pH, which increases the mobility of arsenic. In the rainy season the concentrations of suspended solids increase. The Poopó River had the highest metal concentration of the rivers examined, most of it originated from natural sources. The concentration except from cadmium and arsenic increased in the rainy season.

In Lilja & Linde (2007) it has been found that the Poopó River to some extent is influenced by mining activities, but most of the elevated concentration of metals had natural origins as chemical weathering and thermal springs. It has been found that the levels of arsenic were extremely high towards the end of the river, ranging from 5 to 12 mg/L. In Lilja & Linde (2007) it was also reported that the cadmium levels were around 40-44 µg/L. According to García (2006) the values for cadmium in the rainy and dry season were 300 and 10 µg/L respectively. In Lilja & Linde (2007) the concentrations of lead were in the range of around 200-400 µg/L. The iron levels are reported to be in the range of 80-240 µg/L, increasing along the course of the river.

5 Study area - Antequera River basin

The Antequera River basin is located to the south of the Poopó River basin and has an area of 229 km^2, see Figure 5-1. In this basin there are two different municipalities: Antequera and Pazña. The sub basin is similar to Poopó, where people mostly live of farming or mining. The municipalities of Antequera and Pazña had in year 2001, 3352 and 5469 inhabitants respectively. The growth rate in the basin is negative due to migration to other regions in Bolivia (Ekdahl, 2007). The largest ethnical group is Quecha and most of the older population speaks Quecha, while the younger speaks Spanish (Rocha, 2008). One of the environmental problems includes the lack of treatment of solid waste in the river basin (Ekdahl, 2007). The following sections include a description of the water resources, the mining activities, the sampling points and previous studies done in the basin.

Figure 5-1. Figure showing the Antequera River, with a large tailing and dam in the down right corner and the village Pazña in the upper left corner. North in this picture is to the right.

5.1 Superficial waters and groundwater

The Antequera River originates on the hillsides about 13 km north-east of the village Pazña. The river then flow south-west, changes name to River Pazña and merges with the Urmiri River, continuing as River Pazña towards Lake Poopó (Google Earth, 2009). The area has a mean annual precipitation of 450 mm (PPO 9606). The drinking water in the basin is mainly taken from wells, but there are large problems with the water table and the wells in many villages are dried up during the dry season. Pazña Village gets its drinking water through a pipe from the river Urmiri, which is unaffected by the mining activities in the Antequera basin (Ekdahl, 2007). According to PPO 9701, the water quality in the Antequera River is worse than "Class D" which is a standard for industrial use, see Appendix B.

5.2 Mining and rock tailings

The main mine in the Antequera basin are the Bolivar mine, which was discovered in 1810 and during the first 80 years only silver was extracted (Ekdahl, 2007). In the Antequera basin, the company ESTALSA exploited the glacial-fluvial deposits during many years, but this activity stopped in 1996 (Ríos, 2002 cited in Ekdahl, 2007). Some of these mining operations included extraction of tin from the rocks in the river valley during the 1960's (Ramos Ramos, 2009-10-12). This activity resulted in a massive rock tailing, which parts of can be seen in Figure 5-2, and is about 2.5 kilometre long and 0.5 kilometre wide (Google Earth, 2009).

Figure 5-2. Photograph showing the massive tailings including its dam in the Antequera sub basin. The dam is holding a pH of 3.07 (Ekdahl, 2007).

Today there are three major mines in the Antequera basin. One of them is owned by Sinchi Wayra (Glencore, 2009) with 533 employees (Ekdahl, 2007). Another is owned by a small company called Minera Avicaya S.A. and the third is managed by a cooperative. Sinchi Wayra also owns another mine in the basin, but it is currently not running. The tailings from these mines are located near the mines. Only the tailings site for the Sinchi Wayra mine are built as a "no-discharge tailings" after international environmental standards (PPO 9604).

5.3 Sampling points

This part includes a description of all the different sampling points along the Antequera River and the piezometers in the same basin. There are also observations about the nature and waters made during the field trips. The bolded letters down below are the names given to each site. For a full list of all the sampling points in the two sub basins including the UTM coordinates and altitudes, see Appendix A.

AN1 and **AN2** – *River water*

At a location about 10 kilometres upstream in the river valley of Antequera the first sampling point is found, *AN1*, see Figure 5-3. The water sample is taken from a small stream. It is believed that this water is not likely to be affected by mining activities, although it would probably need some treatment like disinfection to be suitable for drinking. Another sampling point, *AN2*, is found just adjacent to the Pazña Village, Figure 5-3. The flow at this point is higher and likely to be very contaminated from the mine drainage, acid rock drainage and wastewater from upstream settlements. The surrounding area is very unclean and there is a lot of garbage.

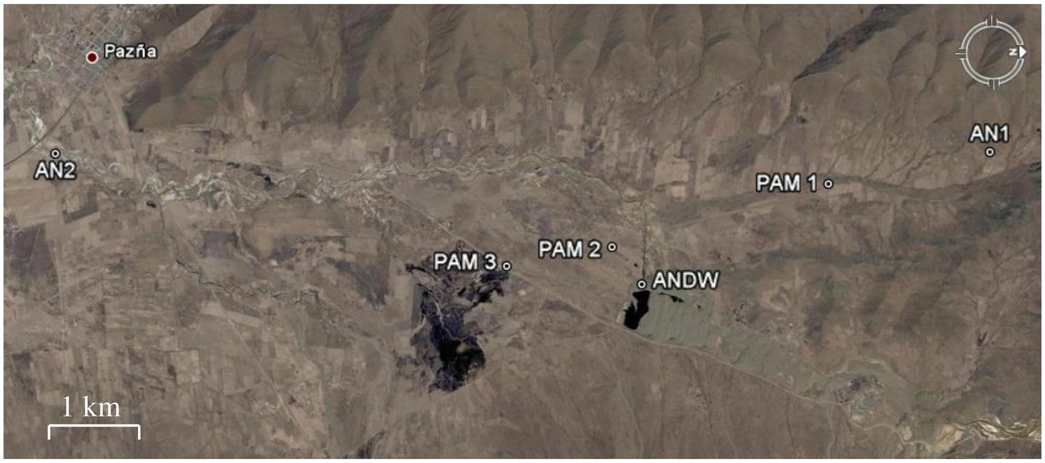


Figure 5-3. Sampling points in Antequera River basin (Google Earth, 2009).

ANDW – *Drainage water from a tailings dam*

At this site, *ANDW*, the water is drained from a large tailings dam and later mixed with the river. The tailing, which is located about 6 kilometres upstream, see Figure 5-3, is no longer in use for mining operations but still drains water at estimated rates of 30-50 litres per second. The quality of the water is likely to be very poor and toxic.

PAM 1-3 – *Piezometers installed in the area*

Three piezometers were installed in April 2009 and are spread out in the Antequera basin, see Figure 5-3. The first piezometer, *PAM 1,* is located about two kilometres upstream of the tailings dam and is not believed to be affected by the mine drainage. The second site, *PAM 2*, is situated 500 metres downstream from the dam and is probably affected by the mine drainage and its contamination. The final piezometer, *PAM 3*, is to be found 1.5 kilometres downstream of the tailings but away from the major river path.

5.4 Conclusions drawn in previous studies

Earlier studies of the Antequera River basin include the Master's thesis of Ekdahl (2007) who concluded that if the quality of the water and the access to it does not improve, the area will depopulate and become totally reliant on the mining, and disappear when the mineral deposits run out. There is also evidence of acid mine drainage in the valley since there are sites with elevated levels of iron, zinc and sulphate.

In this report there is also a compilation of the work made from others (López Cortés, 2006 cited in Ekdahl, 2007) where the pH values in the Antequera sub basin ranges from 7.3-7.9 in the groundwater and 2.8-7.3 in surface waters. For the heavy metals arsenic is 2 ppb in the groundwater and 13 ppb in the surface waters. Iron has values up to 0.6 mg/L in the groundwater and 300 mg/L in the surface waters and zinc is varying between 50-360 ppb in all of the waters in Antequera. The conclusion drawn is that the contamination gets heavier downstream.

Another study conducted in the area focuses on the water quality regarding ions (Mikaelsson & Ny, 2009). It was found that the pH in the groundwater is more alkaline than the surface waters. Before the influence from the mines the water has the highest pH value at 7.6. The pH in the groundwater ranges from 5.9 to 8.9. The redox potential is varying between -22 to -50 mV in the groundwater and this indicates reduced environments, where the majority of the surface waters indicate oxidised environments with values ranging from 100 to 200 mV.

The conclusions drawn in the report, by Mikaelsson & Ny, 2009, are that the water in the upstream parts of the basin is of relatively good quality, not counting on the elevated nitrate levels. Further downstream the groundwater is gets affected by mining and rock tailings. The level of pH is decreasing to about 2-3 and continues to be low for the rest of the river. The weathering processes increase the levels of ions along the river. The contribution from the Urmiri River dilutes the ions to some extent.

6 Water chemistry and heavy metals

In the evaluation of the quality of waters there are many different parameters and concentrations of various elements that could be measured. In this chapter the most common parameters used for water analyses are described and the properties of heavy metals and analysed ions are summarised.

6.1 Water chemistry

To analyse water quality the most commonly used parameters are pH, alkalinity, specific conductivity, redox potential, total dissolved solids and dissolved oxygen. These parameters are described in the following parts.

6.1.1 pH and alkalinity

The pH value is a measurement of the concentration of H^+ in a liquid. It is widely used in many different areas, in water quality it is used to determine if the water is acidic or alkaline. Water with pH below 7 is acidic and one with pH over 7 is alkaline, pH 7 is considered neutral. In a closed system with pure water the pH is only determined by the carbonate equilibrium system, which sets the pH at 5.6. Natural waters are influenced by other buffer systems and processes, but the carbonate system still has a large influence on pH. The carbonate system is based on the solubility of carbon dioxide in water, which is determined by the atmospheric pressure of CO_2. The air contains about 380 ppm CO_2. To calculate the concentration of carbonate acid in water Henry's law is used, shown below:
$[H_2CO_3] = K_H \cdot P_{CO_2}$, where K_H is the equilibrium constant and P_{CO2} is the partial pressure for carbon dioxide.

The dissolution of carbon dioxide follows the reactions (1)-(3).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad (1)$$
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad (2)$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \qquad (3)$$

The bicarbonate ion, HCO_3^-, does not exist in water with pH below 4.5 and the equilibrium is strongly shifted left. As the pH increases the concentration of bicarbonate ion rises and reaches a maximum pH of 8.3. When pH increases further the bicarbonate ion decreases in favour of the creation of the carbonate ion. At pH 10.5 the carbonate ion dominates the system. In natural surface waters the pH levels are usually 6.5 to 8.5, whereas in groundwater the range is 5.5-7.5 (Tölgyessy, 1993).

The buffering capacity of water is described by alkalinity and this is linked to the pH. It is defined as the sum of bases that can be titrated with a strong acid. The most important buffering system in natural waters is the carbonate equilibrium and other buffer systems usually are neglected. Alkalinity is then calculated as the sum of the concentrations of OH^-, CO^{2-} and HCO_3^-. As the pH generally is under 9 the CO^{2-} can be neglected together with OH^-. The alkalinity then becomes approximately equivalent to the concentration of bicarbonate. Alkalinity is measured by the titration of a strong acid, usually HCl or HSO_4, towards a pH value of 4.5 (Appelo & Postma, 2005).

6.1.2 Electrical conductivity and Total Dissolved Solids

Electrical conductivity is a measure of how much dissolved ions water contains. It is defined as the ability for one cubic meter to carry an electric current and is measured in Siemens per unit length. The conductivity is dependent on the temperature and the nature of the dissolved substances. Taking the temperature in consideration the specific conductivity is obtained. In natural waters containing inorganic compounds the conductivity is an approximate measurement of mineral electrolytes, while in wastewater containing salts and organic acids, it is the estimated quantity of the concentrations of minerals and organic electrolytes (Tölgyessy, 1993).

The total dissolved solids, TDS, are defined as the total amount of inorganic salts and organic matter dissolved in the water and is correlated to the conductivity. To be categorised as TDS the compounds should be able to pass through a two micrometer filter (Sawyer et al., 2003). A high TDS indicates high salt concentration and which could cause bad taste to the water (Weiner, 2008)

6.1.3 Dissolved Oxygen

The dissolved oxygen, DO, in waters is essential for life and it is also one of the most important oxidants in redox processes. In unpolluted surface waters the saturation level of oxygen is normally 85-95%, which varies during the day due to the photosynthesis (Tölgyessy, 1993). In water at normal atmospheric pressures and with a temperature of 5°C the saturation level is about 13 mg/L, while in groundwater the level of oxygen normally is lower (Appelo & Postma, 2005).

6.1.4 Redox Potential

Redox processes are described as reactions where electrons are transferred between elements. In the reaction one element is reduced and acts as an electron acceptor, where another one is oxidised and donates electrons. In order to derive expressions and standard potentials for these reactions they are usually divided into half cell reactions, one for each reactant. Each half cell reaction has a standard reduction potential, E°, which is relative to the standard reduction of H^+ to ½ H_2. For a half cell reaction, a high E° means that the process spontaneously goes from left to right, and vice versa for a low E° (Appelo & Postma, 2005). The redox potential, Eh, is a measurement of how many “free” electrons there are in a system. While electrons can not appear as “free”, it is the electrons that are transferable which are measured. These electrons determine which half reactions that will take place. In a system with low redox potential the supply of electrons is high and the environment is more reducing (Drever, 1997 cited in Selander & Svan, 2007). Measurements of the redox potential is uncertain but still gives a picture of what kind of chemical conditions are present (Appelo & Postma, 2005).

6.2 Heavy metals

Heavy metals occur widely in the crust of the Earth and some of them function as trace elements and are vital to plants and animals. However, in high concentrations many of them become poisonous. The heavy metals enter the biological systems when plants and animals absorb them from metal rich waters and soils. The metals then may bioaccumulate and move up the food chain. Although not all heavy metals are poisonous for humans and organisms, including Mn, Fe, Cu and Zn. Other heavy metals, like Pb, Cd and Hg, are not essential micronutrients and they present a risk for the organisms. It is important to remember that all heavy metals are toxic to aquatic organisms and humans if they come at sufficient levels of exposure. Heavy metals are being introduced to the environment and aquatic systems in many ways. They may be brought to the environment by weathering processes of soils and rocks, volcanic eruptions or by human activities like mining and processing. Almost all heavy metals have a high affinity for sulphur. For example, some metals like Pb, Cd and Hg, appear to be toxic largely because they bind into amino acids containing S. This might interfere with enzyme processes or interrupt other cell activities (Laws, 2000). Therefore, the heavy metals can have many different effects on biological systems. For humans there is often a particular enzyme in an organ in the body that is affected by a specific heavy metal (Åslund, 1994).

At normal or basic pH conditions most metals are highly insoluble in water. The metals are being taken up of particulate matters or assimilated by living organisms. Therefore, it is possible that the actual total metal concentration could be higher than the measured levels of the water. Some of the dissolved metals in waters might particulate and settle. It is found that the concentrations of heavy metals in sediment are many times higher than in the surrounding water phase. This is why benthic organisms are mostly affected by the metal concentrations in the sediments (Laws, 2000).

6.2.1 Arsenic

Arsenic, As, is found everywhere in the Earth's crust. The element is known since the times of Aristotle who described a sulphide of arsenic for the first time (Encyclopaedia Britannica, 2009). Arsenic is usually present in sulphides or metal arsenides and arsenates, and comes in the oxidation states of –III, 0, +III and +V. In natural waters there is typically arsenic in the form of arsenates (+V), but under anaerobic conditions there are arsenites (+III) being present instead (WHO, 2008). Arsenic differs from other heavy metals since it tends to increase the solubility and concentrations in water with higher pH. The levels of arsenic are therefore most affected by the local geology in the area (Åslund, 2009).

Most arsenic is a by-product when smelting ores of copper and lead. Metallic arsenic is retrieved when arsenopyrite, FeAsS, is heated to about $700^{o}C$. Other important forms of arsenic are the oxides, where the metal ores are roasted to form arsenious oxides, As_4O_6, which is the starting point of other arsenic compounds. The worldwide utilisation of arsenic is relatively low. There are only a few hundred tonnes a year produced and the main part comes from Sweden (Encyclopaedia Britannica, 2009).

Arsenic is not essential to humans, but after being absorbed, the metabolism is characterised by the reduction of arsenic in the oxidation state +V to +III. The latter one is combined in a series of reactions of oxidative methylation which is excreted by the urine. The most toxic variation of arsenic is arsine, which is a military gas. Other toxic forms consist of arsenites, arsenate and organic arsenic compounds. Organic As is normally more quickly discharged from the body than inorganic forms (WHO, 2008). Chronic arsenic poisoning has symptoms that are very severe as; gradual loss of strength, diarrhoea, anaemia and pigmentation of the skin which may lead to cancer (Encyclopaedia Britannica, 2009). There is also other evidence that arsenic poisoning may lead to cancer in the bladder, kidneys and in the lungs (WHO, 2008).

6.2.2 Cadmium

Cadmium, Cd, is commonly dispersed in the lithosphere but is typically found in very low concentrations in rocks and soils. Hence, there is no cadmium mining in itself, but it is usually obtained as a by-product when extracting other minerals, in sulphide ores containing zinc and sometimes lead and copper (Laws, 2000). Cadmium was discovered about 200 years ago together with minerals containing zinc complexes (Encyclopaedia Britannica, 2009). One of the main uses of cadmium is in NiCd batteries where it acts as the anode. Other common ways to utilise the element are as pigments in paints or in electroplating (Laws, 2000).

The emissions of cadmium to the atmosphere have both natural and anthropogenic causes. Some of the natural sources are from volcanic eruptions and forest fires where volatile metals are degassed and easily spread by the winds. Mining activities accounts for more than half of the major man-caused emissions of cadmium to the atmosphere, and the anthropogenic emissions to the air are 6-7 times higher than the natural reasons. Accounting for the natural fluxes of cadmium to aquatic systems is the weathering and erosion of soils and rocks. The anthropogenic emissions are a factor 2.6 larger than the natural causes and come mainly from manufacturing end-products, for example NiCd batteries (Laws, 2000). In the ground the pH and redox potential are the factors that influence the mobility of cadmium the most. In surface waters at pH levels below 8 the ion Cd^{2+} is the dominant form of cadmium (Åslund, 2009).

Cadmium is not essential for living organisms and it is supposed that the ion Cd^{2+} is the sole toxic form. The major reason for human intake of cadmium is by food, but this is very variable and depending to a great extent on the type of food. When cadmium is ingested it spreads everywhere in the body but mainly to the liver and kidneys. Working in an environment with cadmium vapour increases the risks of lung cancer. The infamous Itai-Itai disease in Japan shows how mining activities might be a risk to human health if not managed properly (Laws, 2000).

6.2.3 Lead

Lead, Pb, is found extensively in the soils and rocks over the whole Earth, usually in concentrations of a few parts per million. Lead is found in the mineral galena, PbS, which requires low temperatures to be extracted. This is the reason why ancient civilisations were able to achieve the lead from galena just by burning wood. There are indications that people used lead already 3500 years ago (Laws, 2000).

There are various uses of lead where the greatest application of lead today is in batteries. Other ways to utilise lead have been as pigments in paints, drying agents in oil paints or as a part in ammunition. All of which have been major environmental concerns, where the latter one creates problems for birds when they by mistake eat the ammunition left on the ground. A former main use of lead was in gasoline, where different lead compounds were mixed into the gasoline as an antiknocking agent. The emissions to the atmosphere is somewhat affected by natural causes like wind born soil particles, volcanoes and wild forest fires. About 12 times more comes from the anthropogenic, where the number one cause today is from ore smelting which accounts for 80% of the anthropogenic emissions (Laws, 2000).

The biggest source of lead for humans comes from food. Lead is used in some insecticides and residuals may be ingested this way. The tobacco plants are usually treated by this means and this becomes a major concern when smoking cigarettes. When lead is absorbed to the body and into the bloodstream and is transported to all organs. It interacts with proteins and interferes with proper functioning of enzymes. Anaemia is one of the syndromes of lead poisoning, where it disrupts enzymes involved in the production of haemoglobin and the iron uptake in the red blood cells. Other causes include damages of the central nervous system and kidneys (Laws, 2000). Children are especially vulnerable to the effects of lead poisoning, where it may harm their physical and mental development (WHO, 2008).

6.2.4 Nickel

Nickel, Ni, is abundant and found widely around the Earth's lithosphere especially in igneous rocks, as well as together with other elements such as arsenic and sulphur. Nickel was used industrially for almost two-thousand years as an alloying metal, but it was first isolated in 1751 and recognised as a new element (Encyclopaedia Britannica, 2009).

Nickel exists in a wide range of different oxidation states, but the Ni^{2+} ion is by far the most common type. This form exists in many complexes for example nickel chloride and nickel nitrate and is applied in electroplating baths, where the pure metal acts as a protecting coat on other metals. The majority of the produced nickel is used in different kinds of alloys for various purposes. The main alloys are together with iron and copper. Nickel was traditionally used widely in coinage, but nowadays the utilisation in batteries is very common. The element is resistant to alkaline elements and is used to a great extent for containers storing sodium hydroxide (Encyclopaedia Britannica, 2009).

Nickel is spread to the environment mainly from the mining and ore processing as well as from wastewaters discharged from industrial plants (Åslund, 1994 & Tölgyessy, 1993). According to Evangelou (1998) nickel in water causes reductions in the growth of aquatic plants where it might interfere with the photosynthesis reactions. For some species of fish it might be teratogenic as well. The exposure for humans usually comes from foods. Where nickel from waters usually constitutes a low risk since the levels are relatively low in normal drinking waters, but in cases where there is heavy contamination the input from waters might be large (WHO, 2008). Nickel in pure form is not as dangerous for human health as Ni-complexes which are poisonous and carcinogenic (Åslund, 1994).

6.2.5 Zinc

Zinc, Zn, is very commonly used in the Earth's soils and rocks and is usually found at levels of around 65 ppm. Zinc is typically found in the mineral ores of zincblende, which is a sulphide containing mineral. Metallic zinc came into use later than other common minerals. This is due to difficulties processing and extracting zinc from the metal ores. The Romans had the knowledge to produce brass, a zinc alloy, but not the element in a pure form (Encyclopaedia Britannica, 2009).

Zinc is very common to use and has great commercial importance. The number one utilisation of zinc is galvanising iron and steel. This means to put a layer of zinc above the metal to improve the protection against corrosion. Other uses of zinc are in brass alloys or in electric dry cells where zinc acts as the negative electrode. Various complexes of the element include zinc oxide, zinc sulphate, zinc chloride and zinc sulphide (Encyclopaedia Britannica, 2009).

Zinc is essential for the human body and the daily intake for an average man is 15-20 mg which comes mainly from food and water. There might be an elevated intake due to the dissolution of zinc from water pipes (WHO, 2008). The element is found in high concentrations in the red blood cells where it is critical for the enzyme carbonic anhydrase. This enzyme is important for the reactions of the CO_2 metabolism. Zn is also essential to assist in the storage of insulin in the pancreas (Encyclopaedia Britannica, 2009). The element zinc is not found to be mutagenic or carcinogenic to humans (Evangelou, 1998). In the case of zinc in natural water, high elevated levels of zinc can be detrimental for fish and other organisms living there and an acceptable level in rivers are therefore below 0.05 mg/L (Tölgyessy, 1993).

6.3 Ions

In water most elements are in the form of ions. There are negative cations or positive (anions) ions and they should balance each other. If not it is an indicator that there is something wrong in the system. It could just be a sign of missing data, but also a measurement of how good the water quality is. In this part the most common cations are briefly described, though they have a large impact on the quality and characteristics of water. Anions are not described, due to lack of results.

6.3.1 Potassium and Sodium

Sodium and potassium are two common ions in natural waters, usually in simple cation forms, Na^+ and K^+. In more mineralised waters they form ion complexes as $NaSO_4^-$, $NaCO_3^-$, $NaHCO_3^0$, KSO_4^-, KCO_3^- and $KHCO_3^0$ (Tölgyessy, 1993). In the crust of the Earth potassium is a one of the most common elements. It occurs in igneous rocks, shales and sediments in the forms of different minerals. In nature, potassium in the form of K^+ is needed in all biological life. For example in plants, potassium is needed in the regulation of osmosis and growth, in the photosynthesis and for the activation of enzymes. In animals the Na^+ and K^+ is used as cell membranes providing transport and balance of vital substances. Table salt is the most widespread compound which contains sodium. It frequently occurs in the crust of the Earth there are many other salts and minerals also containing the chemical constituent. In its elementary form, which is as a metal, it never exists naturally due to its high reactivity (Encyclopaedia Britannica, 2009). The concentrations of sodium and potassium are not significant from a health point of view, but studies have shown that high sodium concentrations can have a negative effect to people with heart diseases (Tölgyessy, 1993).

6.3.2 Calcium and Magnesium

In water, calcium and magnesium usually exist as simple ions, Ca^{2+} and Mg^{2+}, but they do also form different complexes. The level of calcium in water is regulated by the solubility of $CaCO_3/CaSO_4$ and will never exceed 1000 mg/L (Tölgyessy, 1993). Calcium occurs in nature in limestone, chalk, marble, dolomite, eggshells, pearls etc. The form of the element in these is calcite, also known as calcium carbonate. Calcium takes part in the carbonate equilibrium where calcite dissolves in water. While calcium is used in organisms to build shells and skeletons it is also essential to much animal and plant life. Magnesium also has an important role in life as a compound of chlorophyll in plants. In water chemistry, calcium and magnesium are often connected to the term water hardness, which is a measurement of dissolved minerals. Hard water, containing much calcium and magnesium, can cause deposits in water pipes (Encyclopaedia Britannica, 2009).

7 Methodology

This thesis is based on data that was gathered during a two month visit to Bolivia during September and October 2009 and some data collected earlier during the year from May to August. Furthermore, data and results from previous studies will be used and referred to, and put in comparison to the collected results from this project. With the assistance of the university in La Paz two field trips to the study area was carried out. During the field trips water samples from different locations where taken. While this is a part of a larger project most of the sampling points where already chosen and previous sampling had been done. All water samples were after preparation sent to Sweden to be analysed by *Inductively Coupled Plasma Mass Spectrometry* (ICP-MS) and *Ion Chromatography* (IC). Heavy metals and cations are measured in ICP-MS, while anions are analysed in IC. Due to problems with the IC the results from this part were unfortunately delayed and had to be excluded from this thesis.

To be able to study the groundwater in the area the university has installed piezometers. The piezometers consist of a plastic pipe put down in the ground and plugged at the end. At the bottom part, or at suitable depths, there are openings for water to enter from the surrounding ground and screened with a net to prevent soil and particles to enter. The pipes measure either 2 inches (5,08 cm) or 1 inch (2,54 cm) in diameters. Almost all of the piezometers were installed in April 2009 with a mechanical driller. Some of the piezometers have been installed in July 2009 and hand-drilled by an auger. All piezometers have a depth between five and eleven metres and are divided up in two groups, shallow ones which are five to six metres and deep ones around ten metres. One piezometer was installed during the first field trip, POM 8, where a full day was spent to drill six meters down in the ground to install the piezometer.

7.1 Literature study and sources of information

The literature study was carried out in La Paz using a variety of sources. For the theory about chemical parameters and heavy metals, mainly articles and books have been used as reference. Information about the Altiplano and study areas has mostly been supplied by material from the University of San Andrés in La Paz, although some information was described and collected during the two field trips. The reports from the *Oruro Pilot Project* have been studied at the *Servicio Nacional de Geología y Minería*, La Paz. Additional sources have been by word of mouth from university staff and mining personnel, and as far as possible referred to. On the internet, Google Earth was used to map the coordinates of the sampling sites and to present the study area.

7.2 Field trips

The first field trip was conducted from the 11th to 15th of September 2009. The University of San Andrés, La Paz, offered a jeep, staff and driver for all of the days. The base was at the city of Oruro from where daily trips to the study area were carried out. About a month later the second field trip was performed between the 9th to12th of October 2009.

At each of the 22 points the GPS-coordinates were taken with a GPS-navigator, model GPSmap 60CSx. This also registered altitude and relative distance to the village. The UTM-coordinates for each site are found in Appendix A.

The surface waters were collected straight from the river or the chosen sites. The total volume sampled at each site was 1-2 bottles containing 250 ml of water. The groundwater samples were taken from the different piezometers. Here the water levels and depths to the bottom of the piezometers were measured. Taking these two together with the diameter of the pipes the volume of water in the pipes was computed. It is necessary to pump at least three times the volume in the piezometers and measure the field data at each of the volumes. This was done to make sure that the parameters were stable, to get a representative value. Sometimes it was not possible to extract this much water due to dryer circumstances or lower flow rates caused by a low hydraulic conductivity. In these cases it was decided that the water volume pumped was enough, and that the subsequent measurements conducted as usual. The same amount of water was collected from the piezometers as from the surface water sites and brought back to the laboratories in La Paz for further analysis.

The field parameters measured on the sites were pH, conductivity, TDS and redox potential. Some locations also have got the data of dissolved oxygen, DO. This is because two different multi-meters were used at the different sites, model HACH EC10 Portable pH/mV/Temperature-meter (for the Redox potential there is an added value of +210mV) and YSI 556 (Multiprobe system). The latter one also includes the measurements of dissolved oxygen.

7.3 Water analyses

The analysis of ions was done in Sweden by *Inductively Coupled Plasma Mass Spectrometry*. To be able to send the samples to Sweden for analyses some preparations had to be done. Approximately 300 ml of all samples was filtered through a 0.45µm filter, using either an electrical or a manual pump. The samples from the first field trip were filtered in the laboratory, while most of the samples from the second trip were filtered directly. The filtered samples were then divided into two smaller bottles, approximately 30 ml, one for measuring heavy metals and cations and one for anions. In the samples for heavy metals 100 µL of HNO_3 were added to conserve them. At the second field trip samples for measurements of different ions of arsenic was taken. These samples were filtered through a 0.45µm filter and then filtered through a cartridge that absorbs arsenic (III). These samples were then treated in the same way as for the other heavy metals. All the prepared samples from September and October were sent to Sweden on the 15th of October and was analysed in the ICP in November and December 2009. Earlier sampling from May to July was analysed during the months of September and October.

The alkalinity of the samples from the first field trip was measured in the laboratory in La Paz a few days after the field trip. These samples were titrated to pH 4.5 with either HCl or H_2SO_4. The HCl concentration was 0.01 equivalents/L and the sample size 5 ml. The H_2SO_4 concentration was 0.16 equivalents/L and the sample volume 10 ml. At the second field trip the alkalinity was measured in the field. These samples were titrated with H_2SO_4, with a concentration of 0.16 equivalents/L and a sample volume of 10 ml. The indicators that were used in the process were Bromocresol Green–Methyl Red and Indigo-Carmine-Heliantina. These indicators are similar and changes colour at pH around 4.5.

7.4 Sources of error

The accuracy of the sampled data from the field trips is influenced by many factors such as equipment malfunction, contamination and human errors. These factors occur in both the field and the laboratory and will have an effect on the certainty of the data. There are also some uncertainties in the ICP-MS analysis.

There known sources of errors that occurred during the field trips and lab work in Bolivia. These include that during the first field trip in September the field measurements were conducted with two different “multimeters”. This may have resulted in differences due to calibration and different methods. For example there is a large difference in the values for the redox potential, which therefore has not been considered during the analyses. The samples from this trip were not filtered directly and the alkalinity was not measured until some days later in La Paz. During the time between the sampling and measuring, the samples were not stored in a refrigerator. This could result in some errors in the alkalinity measurements and therefore some of the alkalinity result is not presented, but can be found in Appendix C. During the second field trip in October problems with the calibration of the pH-meter occurred and this may result in pH values that strongly differ from previous values. These pH values is presented but is considered to be more uncertain than the others. There are also some errors in the measurements of dissolved oxygen due to aeration when pumping up water from the piezometers, so this data has not been considered reliable for the groundwater.

At both field trips the filtering was done with one filter at each new sampling site and it was washed with water or rinsed with paper if clogged. There were also some bottles that were not washed properly, and could result in contamination of the samples. During the field trips and consequent laboratory works there have been different people involved which could result in some errors due to different methods. An estimation of the total margin of error is 20 – 30 %, including both sampling and analysis. This error does affect the data, but it should not affect the overall picture too much, while it affects all samples to the same extent.

8 Results

All results from the field study in Bolivia are collected and analysed in this chapter. The results are divided in to Poopó River basin, with surface water and groundwater, and Antequera River basin, with all waters together. Some results are considered unreliable, see chapter 7.4 and is not presented here, see Appendix C and Appendix D for these results.

8.1 Poopó River basin – Surface water

In this part the results for the River Poopó are illustrated in Figure 8-2 to Figure 8-15. The elements are presented in an order based on similarities in how they act along the course of the river. The river with additional sampling points in drinking water, hot spring and mine drainage is schematically shown in Figure 8-1. In this figure the flow of the river is from left to right and the point PO1 is the one furthest upstream in the river.

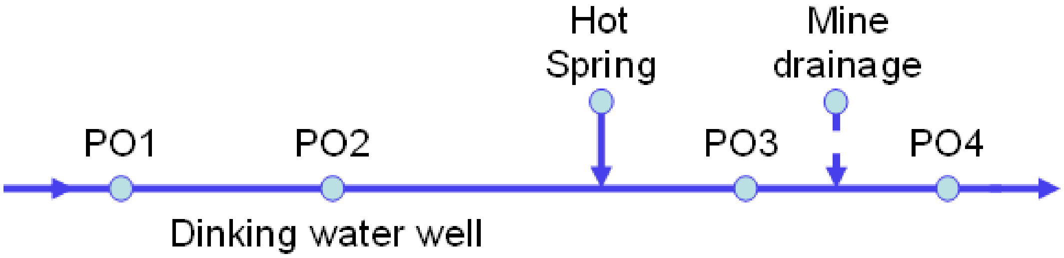


Figure 8-1. The picture is showing a schematic drawing of the Poopó River. PO1, PO2 and PO3 is situated upstream of the village Poopó and PO4 downstream of it. The "Mine drainage" is marking an uncertain number of drainages along this part of the river.

In some cases in the presentation of the results, the concentrations are very low, sometimes below the detection limits, DL. To make the diagrams and illustrations of the results easier to understand, and not having a blank spot, the DL values are put in and reflect the highest concentration an element is having at a site. This means that the concentration of an element is unknown between zero and the DL.

The pH values in the river, seen in Figure 8-2, are following the same pattern for both months, where the values are high upstream in the river at a level of 10. The values then drop around one to two units along the course of the river. Measurements from October show slightly higher levels. The alkalinity along the river, shown in Figure 8-3, is low in the upper parts. There is a peak just after the thermal spring, in which the value is 296 mg/L in October, followed by a decrease in the lower part of the river.

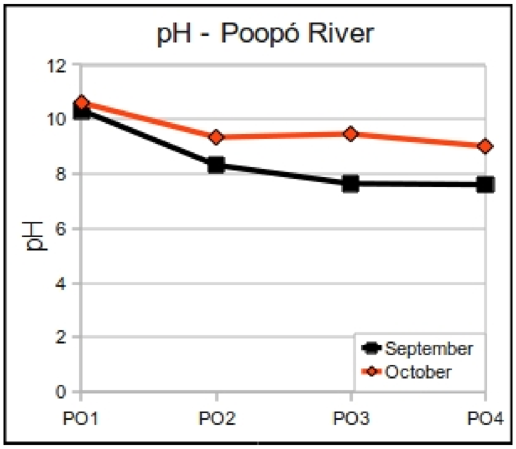


Figure 8-2. The graph shows how the pH changes along the course of the Poopó River. PO1 is the point furthest upstream in the river.

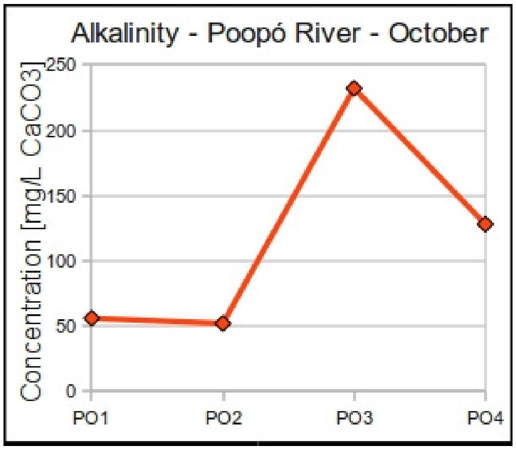


Figure 8-3. The diagram illustrates the alkalinity along the course of Poopó River in October. PO1 is the point furthest upstream in the river.

The specific conductivity, see Figure 8-4, at the two first sampling sites, PO1 and PO2, are really low, with levels close to zero. From the thermal spring there is a huge contribution at a level of 16 mS/cm in October. This makes the conductivity levels in the river at PO3 rise to just over 15 mS/cm for this month. The same pattern is seen for September but there is no record of the level for the thermal water. The specific conductivity rates keep holding high values just slightly declining to PO4. The same graph was retrieved for total dissolved solids due to the relation between the parameters.

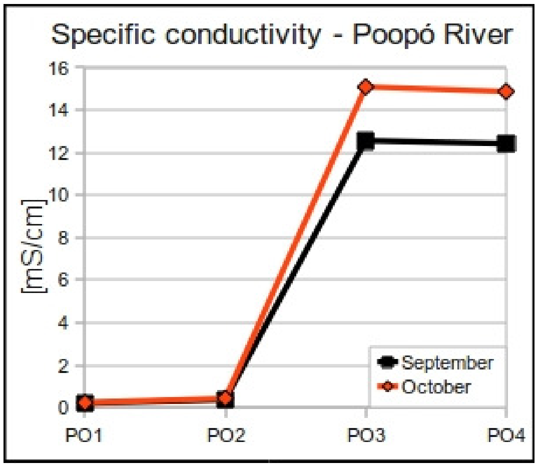


Figure 8-4. The diagram illustrates how the specific conductivity (25 ^{o}C) changes along the Poopó River. PO1 is the point furthest upstream in the river.

Continuing to the ICP results, arsenic has got very low values in the upper parts of the river, see Figure 8-5. The hot spring is contributing with high concentrations around 27 and 47 µg/L for September and October, respectively. This corresponds to the increase in PO3 just downstream of the spring. Looking at the levels downstream of PO3 there is a significant difference between September and October. In September the level decrease to 16 µg/L, while in October it continues to increase.

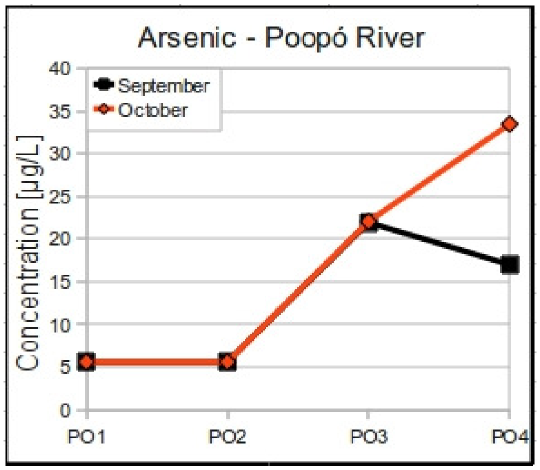


Figure 8-5. The diagram displays how the concentrations of arsenic are changing along course of the river. PO1 is the point furthest upstream in the river. The values of arsenic at PO1 and PO2 in both months are below the detection limit (5.6 µg/L).

The concentrations for cadmium and zinc follow the same model, see Figure 8-6 and Figure 8-7. The levels of each element are quite low in the upper parts of the river. The input from the thermal water is low. After the site of PO3, the values increase rapidly in September, but not in October. Overall, the levels of zinc are relatively low and do not extend above the water legislation, which is a maximum of 200 µg/L. In the case of cadmium the concentrations in PO4 hit above the permissible levels of drinking water in the Bolivian Law, 5 µg/L, and the WHO guideline value 3 µg/L.

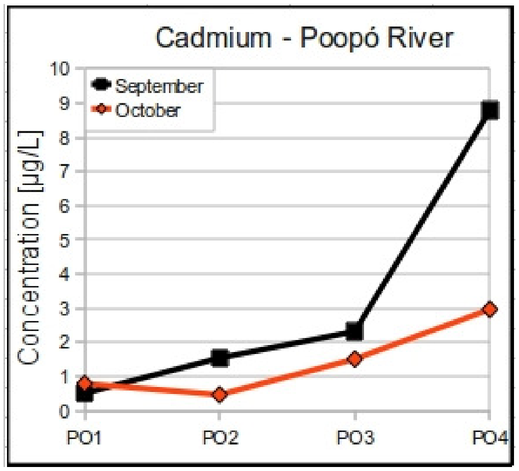


Figure 8-6. The concentrations of cadmium in the Poopó River. The value for cadmium at PO2 in October is below the DL (0.459 µg/L).

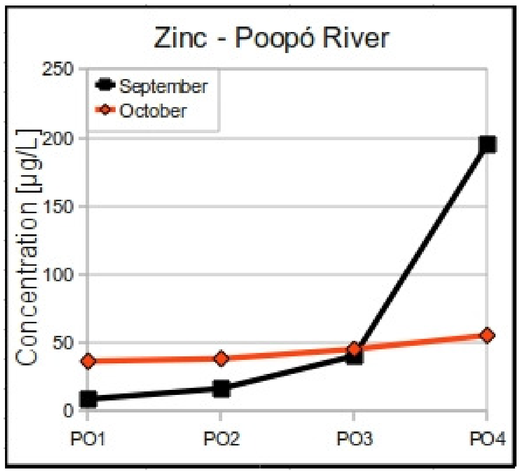


Figure 8-7. The concentrations of zinc in the Poopó River.

The levels of lead along the river, shown in Figure 8-8, are in the upper part relatively high and then decrease until PO2 and PO3. The contribution from the thermal water is low, followed by an increase further downstream at PO4. The concentrations in this point are above the WHO guideline values at 10 µg/L, but not the permissible level according to the Bolivian law.

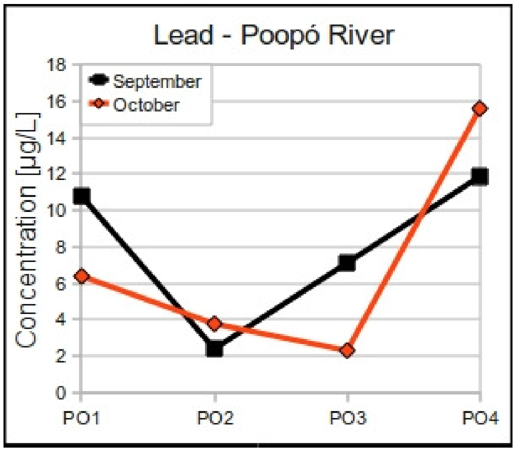


Figure 8-8. The figure is showing the concentrations of lead in the Poopó River. The value of lead at PO3 in October is below the detection limit (2.3 µg/L). PO1 is the point furthest upstream in the river.

A number of elements are showing the same pattern with a major increase in concentrations after the input from the thermal water; see
Figure 8-9 to Figure 8-13. When it comes to sodium and potassium the levels before the thermal spring is close to zero. The contribution from the hot spring is very high and reflects the values in PO3 and PO4. This model also includes copper and chromium, not displayed in this report, which reaches values in PO3 similar to the concentrations from the thermal waters. The concentrations of copper and chromium in the river are far below the permissible levels in the Bolivian legislation. Calcium, magnesium and sulphur are following a similar pattern as above where they are influenced by the thermal water, see Figure 8-11 to Figure 8-13. A difference is that these elements also increase in the upper part of the river and then continues to rise after the thermal spring as well.

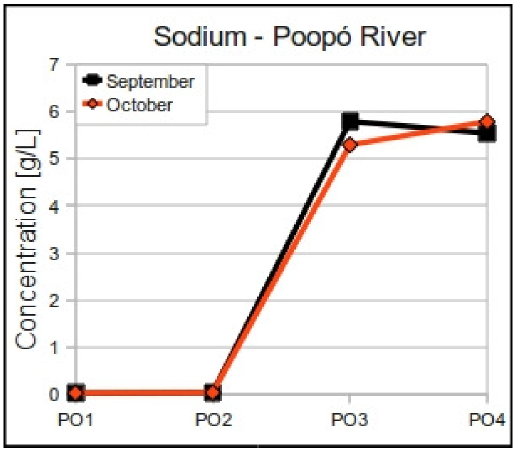


Figure 8-9. The graph is showing the levels of sodium along the course of Poopó River. PO1 is the point furthest upstream in the river.

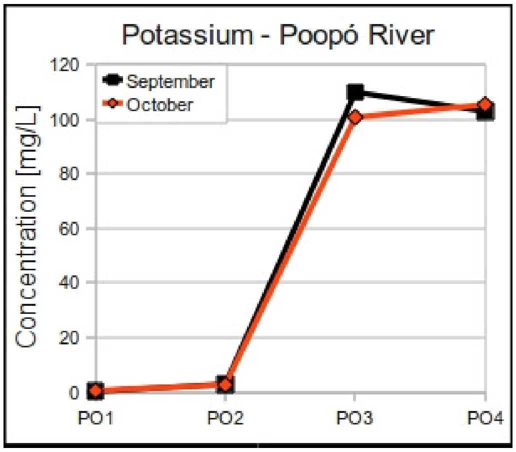


Figure 8-10. The diagram illustrates the concentration of potassium in the Poopó River. PO1 is the point furthest upstream in the river.

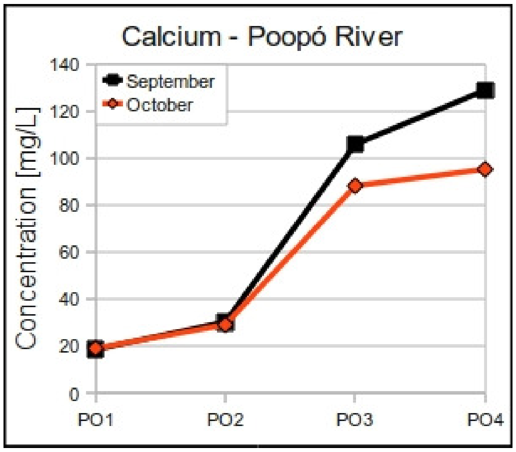


Figure 8-11. The figure is showing the concentrations of calcium along the course of Poopó River. PO1 is the point furthest upstream in the river.

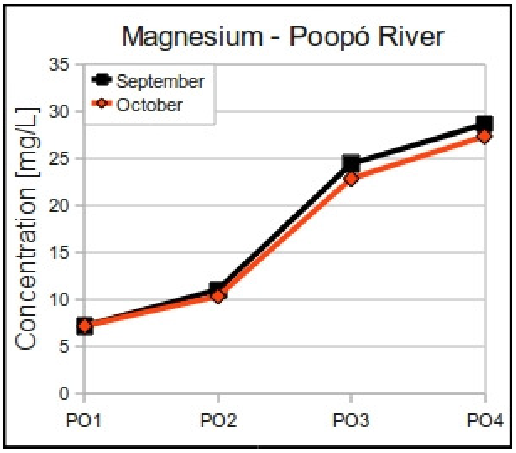


Figure 8-12. The graph is showing magnesium levels in the Poopó River. PO1 is the point furthest upstream in the river.

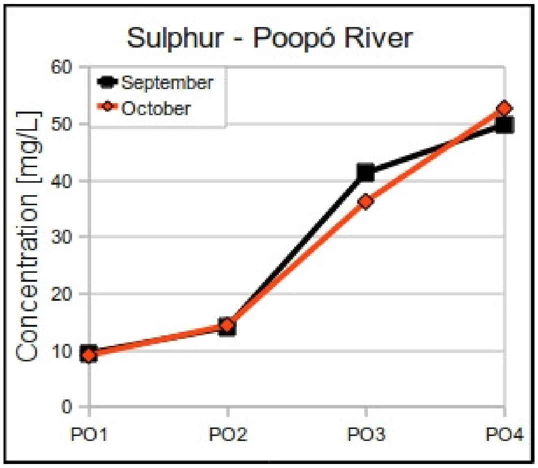


Figure 8-13. The concentrations of sulphur along the course of of the river

Compared to the previous elements a totally different result is displayed for iron and aluminium, see Figure 8-14 and Figure 8-15. These two elements follow the same pattern, where the levels in September are quite high in the upper parts of the river. After the thermal spring, the concentrations drop and then increase again further downstream. For iron, the value at PO4 is much higher than the permissible levels and for aluminium there are no health-based targets. In October, the pattern for iron and aluminium has changed along the river. Starting with very low values in the upper part of the river, a small increase is noted in PO3 corresponding to a high level in the thermal spring. After PO3 the concentrations drop to the same very low levels as before the influence of the thermal spring.

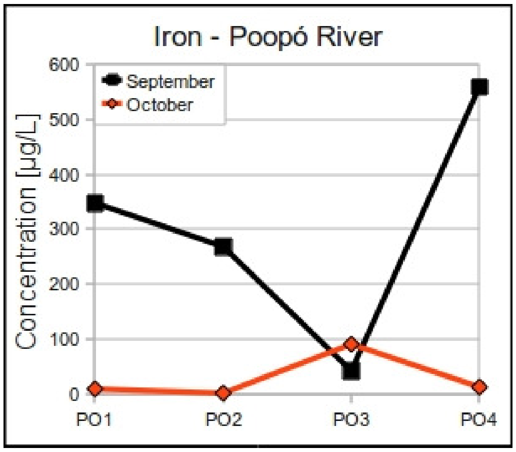


Figure 8-14. The chart is displaying the levels of iron in Poopó River. The value for iron at PO2 in October is below the DL (0.803 µg/L). PO1 is the point furthest upstream in the river.

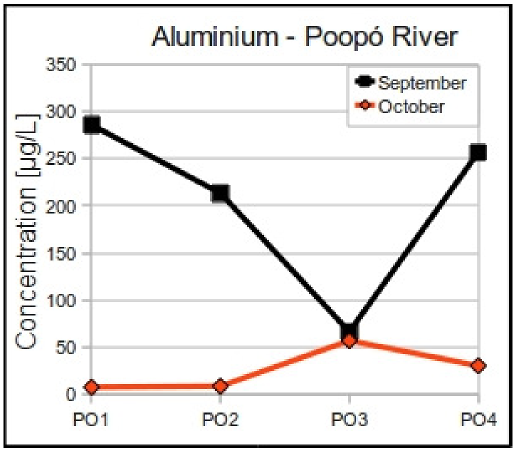


Figure 8-15. The graph is showing the concentrations of aluminium in Poopó River. PO1 is the point furthest upstream in the river.

The overall concentration of nickel in.the Poopó River is lower than the WHO guidelines and the Bolivian legislation. Unfortunately, there is no data for tin in the months of September and October. During an earlier sampling done in July, the concentrations of tin are very low compared to the permissible levels.

The drinking water for the Poopó Village is mostly of good drinking water quality, see Table 2. Although in some cases the concentrations exceed the WHO guidelines, none of the sampled months go above the levels in the Bolivian legislation for drinking water.

Table 2. The table demonstrates the concentrations (µg/L) of metals in the drinking water which was collected at sampling site *POP*. The highlighted fields are values that exceed the WHO guidelines. <DL indicates that the values are below the detection limit.

Parameter	July/August	September	October
Aluminium	28	230*	11
Arsenic	6.1	15**	<DL
Cadmium	0.46	1.1	1.6
Calcium	24000	28000	28000
Chromium	4.4	0.48	<DL
Copper	1.3	4.9	5.1
Lead	<DL	<DL	20***
Iron	9.6	280	4.7
Magnesium	14000	9900	9700
Nickel	2.5	5.0	<DL
Sodium	46000	34000	35000
Tin	39	n/a	n/a
Zinc	53	12	48

* Guideline value at 200 µg/L, but it is not a health-based target.
** Provisional guideline value at 10 µg/L.
*** Guideline value at 10 µg/L.

8.2 Poopó River basin – Groundwater

The following section presents the results for the groundwater in the Poopó River basin. The locations of the sampling wells are shown in Figure 8-16, together with the village and the tailings dam. At most of the wells there where samples taken from two depths, 5 and 10 metres, labelled A for the shallow one and B for the deep one.

Figure 8-16. Map showing the locations of the groundwater wells in the Poopó sub basin.

The pH values in the POM 1-5 at depth A, shown in Figure 8-17. The levels are quite stable in each well, but declining some over time. There are some dissimilarities, for example, for POM 2 in October where this measurement is higher than previous months. The difference between the wells is large and goes from 6 to 10. Well POM 2 and POM 5 have lower values than the rest, and it tend to be slightly lower in POM 2 and significantly lower in POM 5. It can also be seen that in POM 1 the pH is higher than the others. The same pattern of decreasing levels over time is seen for the pH values at depth B as well. The mean pH for the different depths of A and B, see Figure 8-18, does not vary that much between the depths, except for POM 1 where the mean pH in B is one unit lower than in A.

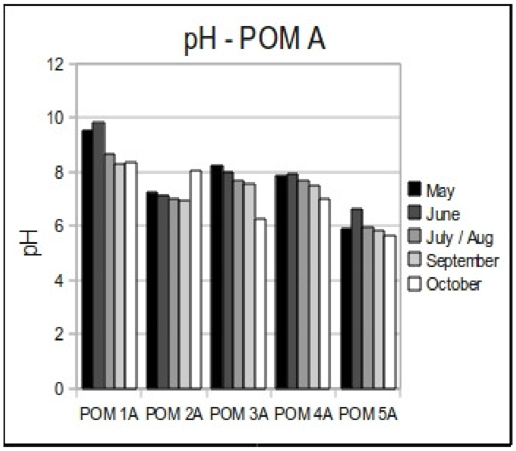


Figure 8-17. The graph presents how the pH levels vary spatially in the piezometers at depth A in the Poopó River basin.

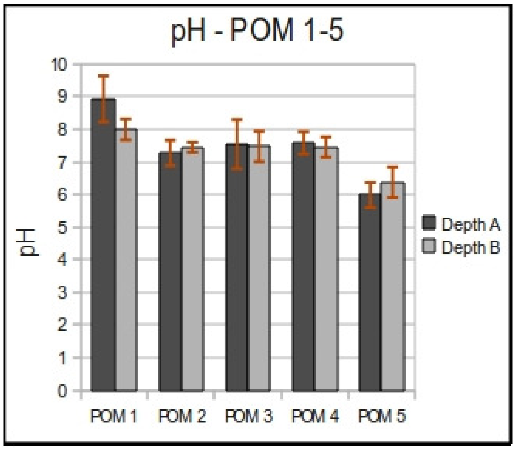


Figure 8-18. The figure illustrates the differences between the average pH over time in the shallow piezometers (A) and the deep ones (B). The data for October is not taken into account, due to uncertainties in the data, see chapter 7.4.

The alkalinity, shown in Figure 8-19, varies between the different sample points and also with the depth. At depth B the alkalinity seems to be lower in POM 2 and POM 5 compared to the others; this pattern is not seen in depth A due to a large difference between depth A and depth B in POM 1. The deeper wells, B, have an overall higher alkalinity compared to A. In well POM 5 the alkalinity is very low for both depths. Figure 8-20 demonstrates the alkalinity for all piezometers in the Poopó area. The graph for POM A and POM B are a calculated mean value for POM 1 to POM 5 per depth. It can be seen that wells further west, POM 6 and POM R, have higher alkalinity than the rest.

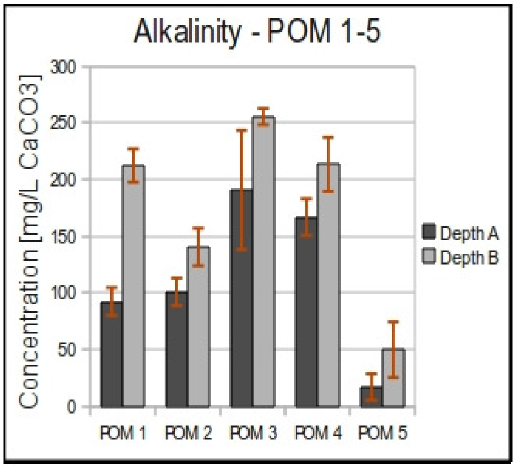


Figure 8-19. Graph showing the variations of the mean alkalinity over depth in the piezometers in the Poopó River basin. The mean value taken for all months at depth A and depth B.

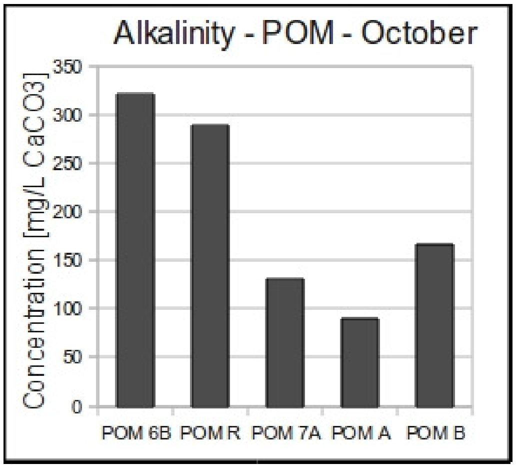


Figure 8-20. The graph is showing the alkalinity in the piezometers in the Poopó River basin for the month of October. The POM A and POM B values are a mean value of all well at each depth.

There is a clear trend that the conductivity levels are increasing over time in all the piezometers, see

Figure 8-21. In the wells, POM 2 and POM 5, the values are much higher than for the rest of the sites in the area. The levels in these two wells are higher than the other sampling points for all of the months. The same pattern of increasing levels over time is also seen for the specific conductivity for depth B. In Figure 8-22, the mean specific conductivity over each depth is shown. In the wells POM 2 and POM 5 the conductivity is constant over depth; while in the others it is lower at depth A. In POM 1 the conductivity for depth B is almost twice the magnitude as depth A.

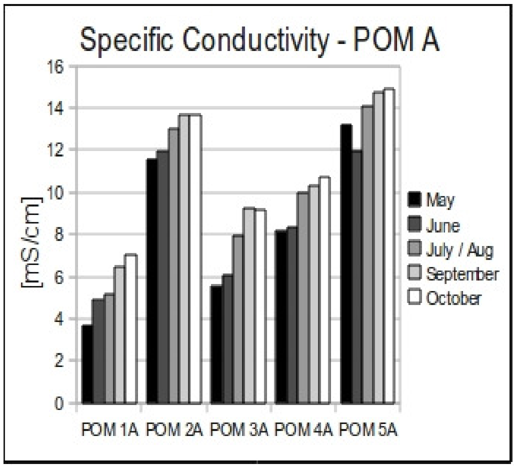


Figure 8-21 Chart showing how the specific conductivity varies over time in the piezometers with depth A in the Poopó River basin.

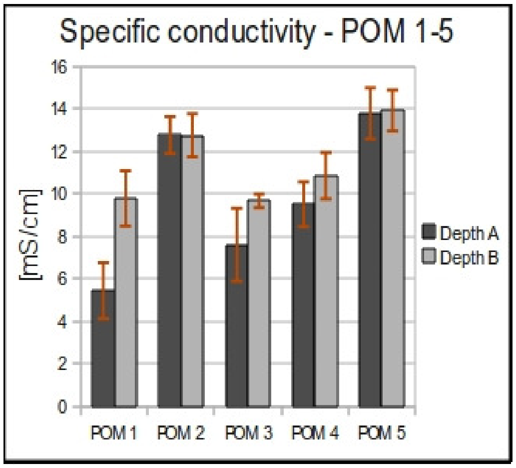


Figure 8-22. Graph illustrating the differences for mean conductivity between depth A and depth B. The mean value calculated from all months at depth A and depth B.

Continuing to the ICP result for the groundwater the levels of arsenic at depth A appear to be relatively steady at each piezometer location as well as over time, see Figure 8-23. The values at well POM 1 seem to be higher than the rest of the piezometers. A similar pattern is seen at depth B, which can be seen in Figure 8-24, where the calculated mean concentration over each depth is illustrated. This figure also shows that there are no distinct higher or lower levels at any depth. In all of the samples the concentrations are above the recommendations of WHO but below the Bolivian legislation, with one exception in POM 1A.

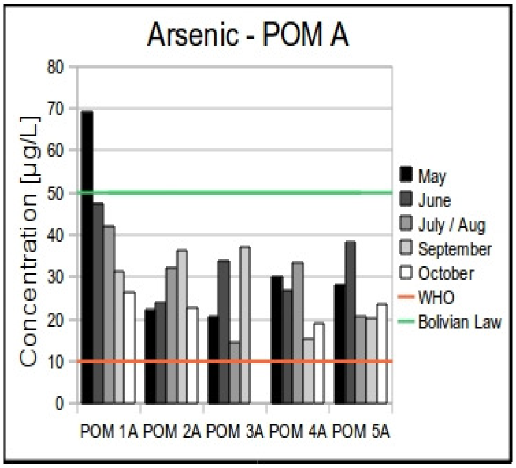


Figure 8-23. Graph showing the distribution of arsenic in the piezometers with depth A.

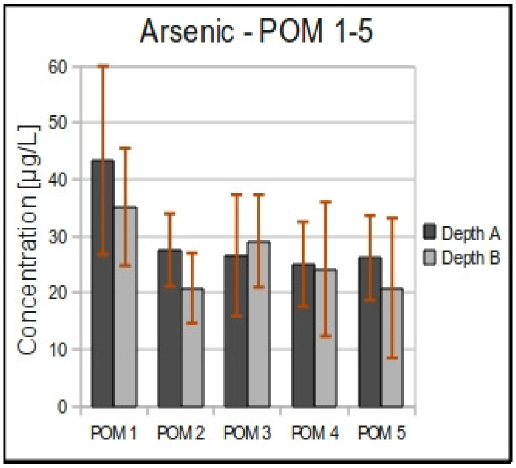


Figure 8-24. The diagram is illustrating the mean concentrations at the two different depths A and B. The mean value taken for all months at depth A and depth B.

Comparing all the piezometers in the sub basin, see Figure 8-25, the arsenic concentrations are higher further out on the plains, piezometer POM 6 and POM R. The levels are lower in POM 7 which is located close to the river. The concentrations in this piezometer are closer to the levels in POM A and POM B.

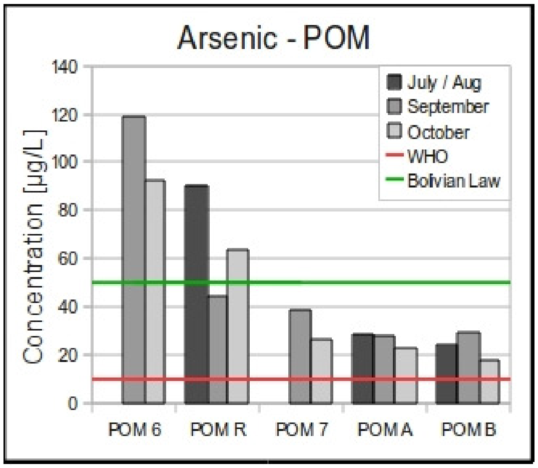


Figure 8-25. Graph illustrating the arsenic levels in the piezometers in the Poopó River basin. The levels for POM A and B is calculated mean values over each depth.

The concentrations of cadmium at depth A varies depending on sampling site seen in Figure 8-26. There are higher concentrations in POM 1, POM 2 and POM 5, where POM 5 has got a huge value at 1500-2000 µg/L in May to July. In POM 1 and POM 2 the values are in most cases above the drinking water recommendations from the WHO and the Bolivian Law. In POM 3 and POM 4 the values are in the lower ranges and below the Bolivian legislation and in most cases the WHO guidelines as well. The extreme levels in POM 5A also apply for depth B since the concentrations are within the same range. For both the depths in POM 5, the concentrations of cadmium in September and October are surprisingly below the detection limits.

In a comparison between the shallow piezometers at depth A with the deeper observation wells B, there are very little differences for POM 3 and POM 4, see Figure 8-27. For piezometers POM 1, POM 2 and POM 5 the concentrations in the shallower wells are having higher values. Looking at the levels of cadmium at the different piezometer sites in the sub basin shows that the levels are much lower far away from the tailings dam and river, see Figure 8-28. In contrast, the concentrations in POM 7, which is close to the river, have got a very high value. The concentrations of cadmium in observation well POM 0 seems to be at similar levels as the mean value at depth A, see Figure 8-28. This also complies with zinc.

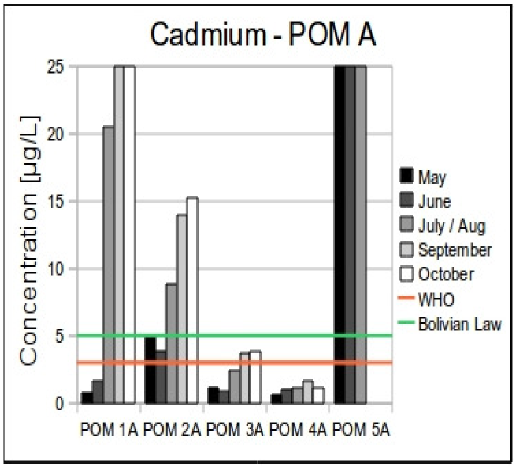


Figure 8-26. Graph showing the distribution of cadmium in the piezometers of POM A. The results for POM 5A reach values of about 1500-2000 µg/L.

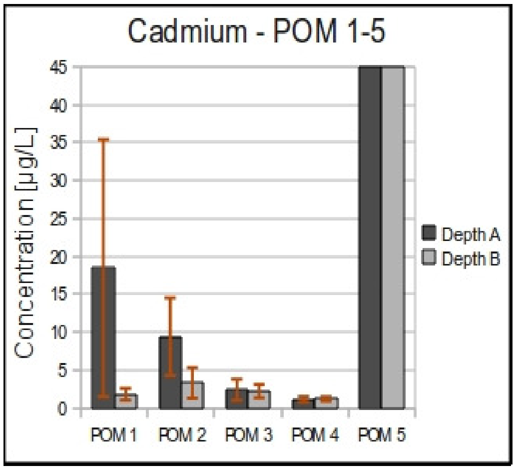


Figure 8-27. The diagram is illustrating the mean concentrations of cadmium and the differences between depth A and depth B. The mean value taken for all months at depth A and depth B.

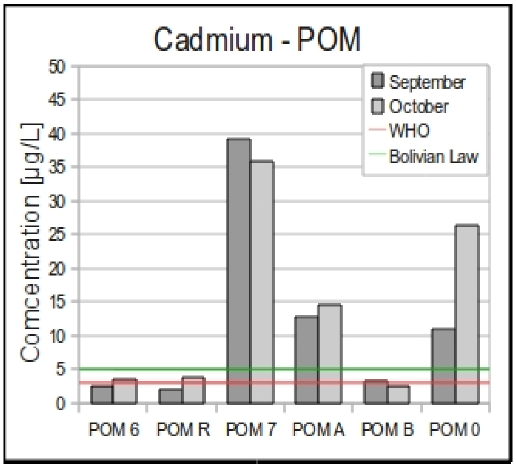
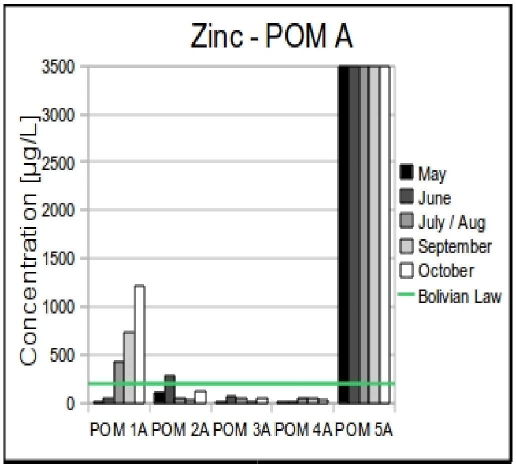


Figure 8-28. Graph illustrating the cadmium levels in the piezometers in the Poopó River basin. The levels for POM A and B is calculated mean values over each depth.

The concentrations of zinc at depth A are varying among the different wells seen in Figure 8-29. The values are low in the wells POM 2, POM 3 and POM 4, high in well POM 1 and extremely high in well POM 5. In POM 2, POM 3 and 4 the levels are in most cases below the Bolivian legislation. In POM 1, the concentrations for July-October are much higher than permitted for drinking water purposes. The zinc concentrations in POM 5 are all around 100 to 500 mg/L for all of the investigated months. The values at depth B, are lower than depth A at all sites, see Figure 8-30.

When it comes to the other piezometers in the Poopó sub basin, the concentrations of zinc further out on the plains, in POM 6 and POM R, are low and below the Bolivian legislation. Closer to the river in POM 7, the levels are above the law at around 300-400 µg/L but much lower than the guidelines of the WHO.



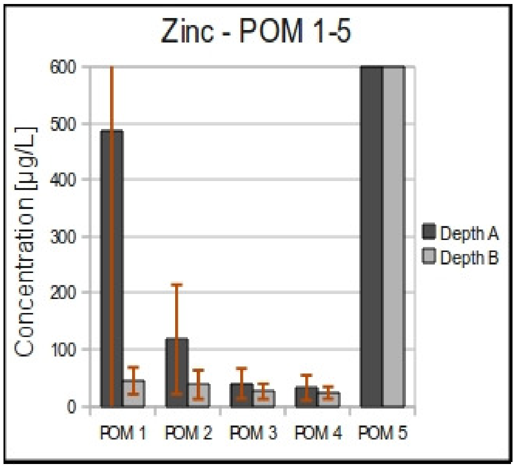
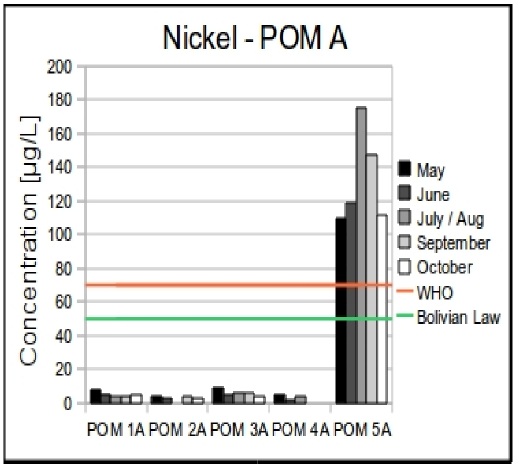


Figure 8-29. Graph showing the distribution of zinc in the piezometers with the depth A.

Figure 8-30. The diagram is illustrating the mean concentrations of zinc and the differences between depth A and depth B. The mean value taken for all months at depth A and depth B.

Levels of nickel and copper at depth A are shown in Figure 8-31 and Figure 8-32. There is a similar pattern for the two elements where the concentrations in POM 1 to POM 4 are very low and then the concentrations in POM 5 are high. The levels in the first four wells are under the standards set by the Bolivian legislation and the WHO guidelines for good drinking water, while for POM 5 the levels are above in most cases. The same pattern exists at depth B with low steady values in POM 1 to POM 4 and higher in POM 5. The concentrations at the other piezometers in the sub basin, POM 6, POM R and POM 7 are all very low.



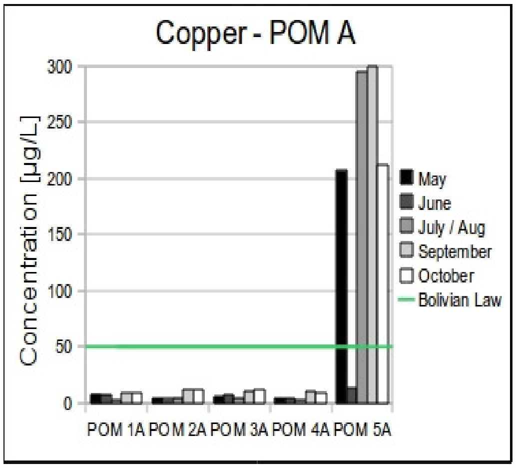


Figure 8-31. Graph showing the distribution of nickel in the piezometers with the depth A.

Figure 8-32. Graph showing the distribution of copper in the piezometers with the depth A.

The figures below show the concentrations of calcium, magnesium, sodium and sulphur at depth A. All four elements occur in the same pattern with higher levels in POM 2 and POM 5. There are lower values in the other observation wells, especially in POM 1. The concentrations of these four elements do not present any significant difference between depth A and depth B and the pattern between the sampling points is the same. The levels of calcium,

Figure 8-33, and magnesium, Figure 8-34, show that the hardness of the groundwater is quite high, given that the WHO guidelines in the graphs are set as a total hardness of the two elements. The concentration of these two elements in all the piezometers in the Poopó sub basin is quite the same, with a little elevation in the mean value for depth A and depth B compared to the rest.

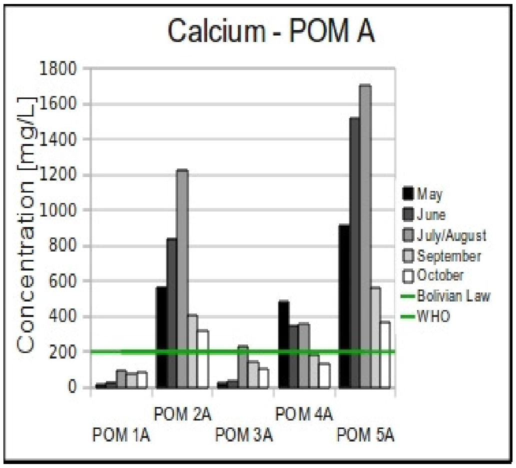


Figure 8-33. Graph showing the distribution of calcium in the piezometers with the depth A.

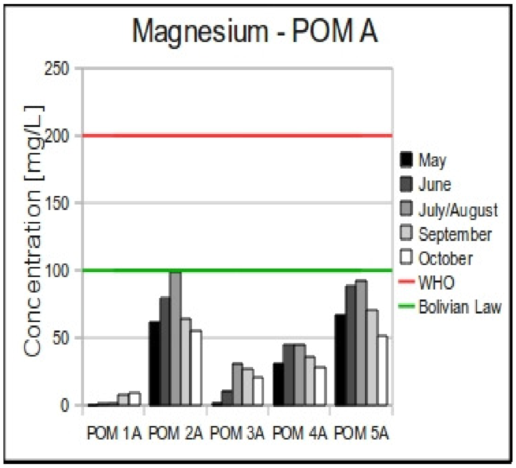


Figure 8-34. Graph showing the distribution of magnesium in the piezometers with the depth A.

In Figure 8-35 the results for sodium is seen. The levels are significantly higher than the WHO guidelines. The concentrations of sodium also seems to overall be lower in October, this also applies for the piezometers further out on the plains. While comparing the concentrations in POM 1 - POM 5 and the other wells they seem to be almost at the same level. The levels of sulphur, shown in Figure 8-36, in the wells are high, considering that the WHO guidelines in the graph is for sulphate, as there are none for sulphur. While sulphur in water appear mostly in oxidized form almost all samples show levels over the guidelines. Comparing to the other piezometers the concentrations of sulphur seems to be much higher than the mean values in depth A and depth B. In the rest of the piezometers, further away, the levels of magnesium and calcium are lower than in POM A and POM B, while sodium is in the same range. These elements exceed the Bolivian Law and the WHO guidelines mostly in POM 2 and POM 5, but also for POM 4 for calcium, all wells for sodium and none for magnesium, seen in Figure 8-33 to Figure 8-36.

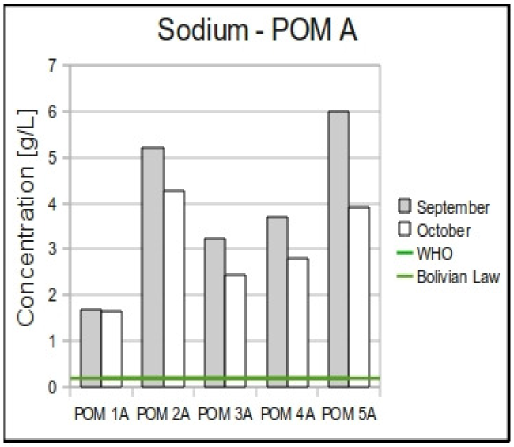


Figure 8-35. Graph showing the distribution of sodium in the piezometers with the depth A in September and October.

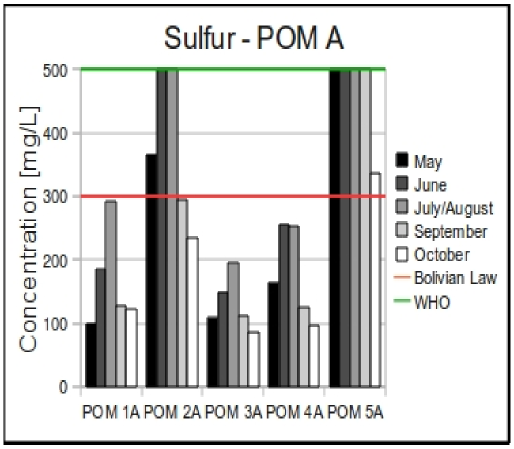


Figure 8-36. Graph showing the distribution of sulphur in the piezometers of POM A. The level for POM 5 in September is just over 500 mg/L. The other values in POM 2 and 5 not shown are over the range for the ICP in May to August, 500 mg/L.

The levels of aluminium, chromium, lead, lithium, tin and iron in the groundwater are relatively low and do not extort any potential risks. The concentrations of lead in the shallow piezometers at depth A, are so low that they at most sampling sites are below the limits of detection by the ICP. There is an exception where a value is above the WHO recommendations but it is still below the Bolivian Law. In comparison with the concentrations at depth B, the levels of lead seem to be a little bit higher but still with concentrations far below the Bolivian legislation for drinking water standards. In the other observation wells, POM 6, POM R and POM 7, the concentrations for these six elements are also low and below the WHO guidelines and Bolivian law in almost all cases. The only exceptions are aluminium and iron in POM 6 in October.

8.3 Antequera River basin

In this section the results for the Antequera basin are presented. In Figure 8-37, a schematic picture of the river and groundwater sampling points is shown. The surface water points are marked with light blue and the groundwater with gray. The flow of the river is from left to right in the picture.

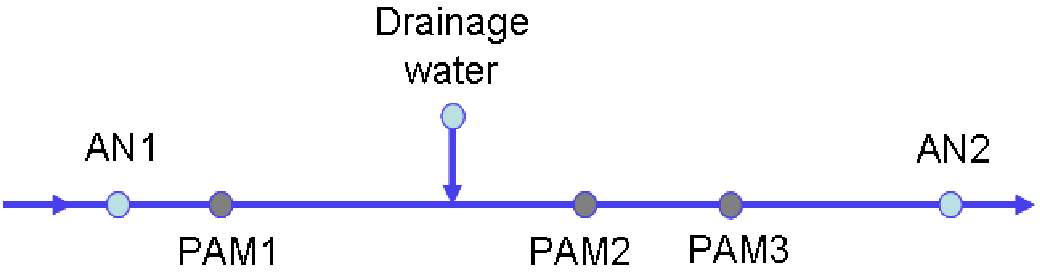


Figure 8-37. Schematic drawing over the Antequera River and the sampling points in the basin.

According to the graph in Figure 8-38, the pH levels in the Antequera River and the groundwater are all changing over time, but there is a larger difference depending on geographic positions. The values of the surface water at AN1 are much higher than at ANDW and AN2. The pH rates of the groundwater are highest at PAM 1 and than decreasing to PAM 2 and PAM 3. For both surface and groundwater there are lower values downstream of the contribution of the drainage water. For most of the sampling sites the values in October seems to be lower than the other months.

The levels of alkalinity in the river, seen in Figure 8-39, are higher in the upper part and are then decreasing along the river. The changes over time for most of the sampling points are relatively small. At the site of AN1 the alkalinity levels are about 40-60 mg/L and the nearby piezometer PAM 1 has much higher values around 140-160 mg/L. The contribution of the drainage water from the tailings dam affects the conditions. The water at this sampling point does not have any alkalinity at all. The same circumstance is found at the end of the river at site AN2. The alkalinity in the groundwater at PAM 2 and PAM 3B, downstream from the tailings dam, is noticeably lower than PAM 1. The results from the September field trip all show higher values than the other months. This data is left out as it is considered uncertain, see chapter 7.4, but can be found as reference in Appendix C, table 4.

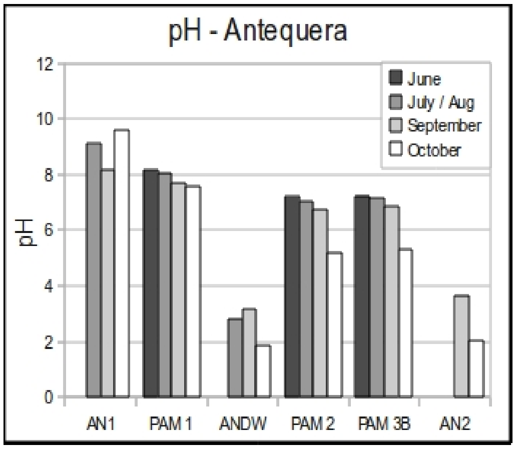


Figure 8-38. Graph showing the pH levels in the surface and groundwater in the Antequera River basin.

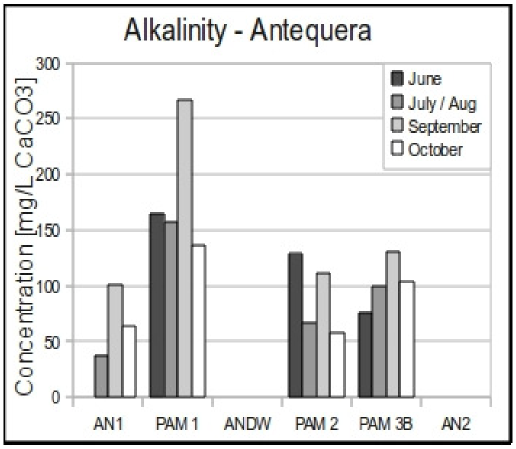


Figure 8-39. Figure showing the alkalinity concentrations in the Antequera River basin.

The specific conductivity at the sampling sites are relatively stable over time but are changing between the different places in the basin, see Figure 8-40. High up in the river valley of Antequera the sampling point AN1 has got a very low value including the nearby piezometer PAM 1. The contribution of drainage water at ANDW, which have high specific conductivity values, increases the levels at the end of the river at sampling point AN2. A difference for the groundwater is seen at sampling point PAM 2 and PAM 3B in comparison with PAM 1. These two sites are located downstream from the tailings dam, where PAM 2 is the closest, and the specific conductivity are increasing four to five times in contrast to PAM 1.

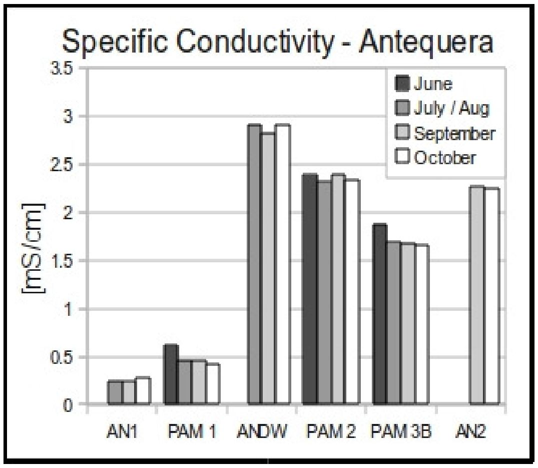


Figure 8-40. Graph showing the specific conductivity in the sub basin of Antequera.

Continuing to the ICP results, the most significant result is the one of ANDW. The levels of most heavy metals and salts reach very high levels at this point. This seems to have a significant impact on the river water in AN2 in all cases. The concentrations arsenic, shown in Figure 8-41, are quite similar in all sampling point and do not show any increase or decline at any point in the area. The levels are greater than the WHO guidelines at 10 µg/L, but not the Bolivian Law at 50 µg/L.

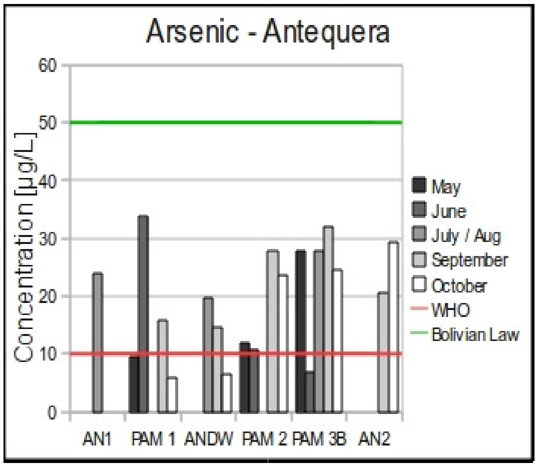
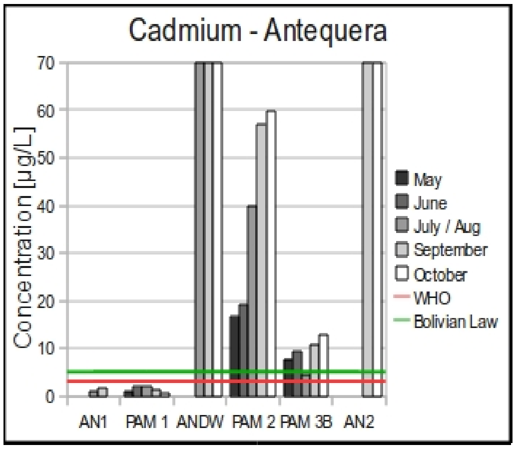


Figure 8-41. The graph shows the levels of arsenic in the Antequera basin. There are missing data in May, June and July/August, while no samples were taken in the river these months. Other missing data is levels under the detection limit.

Cadmium,
Figure 8-42, and zinc, Figure 8-43, show a pattern where there are low concentrations of all metals in both surface and groundwater upstream of the tailings dam. In drainage water and downstream the levels rise to high or extremely high values. The surface water show extremely high concentrations while the groundwater is not affected as much, but still has got high values. The same pattern is seen with nickel, but the difference between surface and groundwater is not as big as for the previous elements. Comparing the levels to the WHO guidelines and Bolivian Law all of the metals are below the set values before the tailings dam. Downstream of the tailings all elements in the surface water and the groundwater exceed the limits.



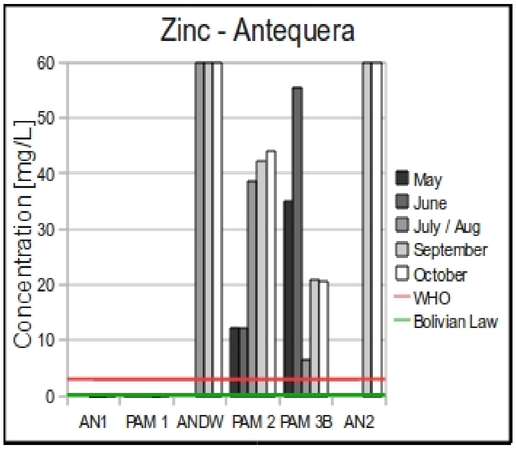
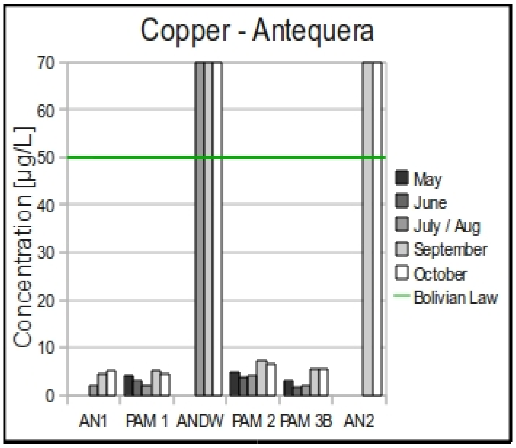


Figure 8-42. The figure demonstrates the concentrations of cadmium in the Antequera basin. The levels in ANDW and AN2 are approximately 500-600 and 480 µg/L respectively.

Figure 8-43. The diagram shows the concentrations of zinc in the Antequera River basin. The values in ANDW are for July/August approximately 250 mg/L and for September and October around 120 mg/L. In AN2 the levels are about 100 mg/L.

For copper shown in Figure 8-44 the concentrations in the surface water are high in the drainage water. The difference with this element is that the levels in the groundwater downstream of the tailings are not affected. In Figure 8-45, the concentrations of aluminium are displayed, which seems to be quite low in the surface water before the contribution at ANDW. The groundwater shows the opposite with quite high values before ANDW and then lower levels after. Comparing to the WHO guideline the levels in the groundwater lies below the recommended value, except some months in PAM 1. The surface water has low values before ANDW, while afterwards it exceeds the guidelines. This result is also observed with iron.



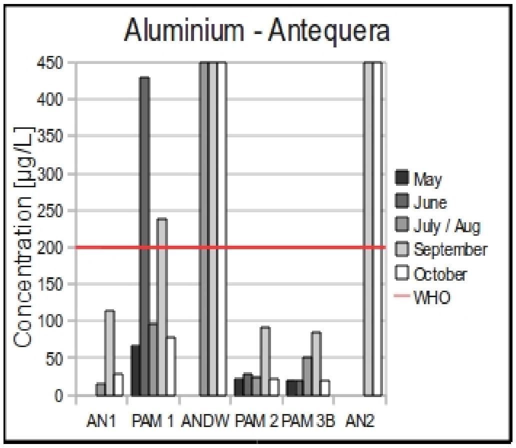


Figure 8-44. The graph illustrates the concentrations of copper in the Antequera basin. The values in ANDW are between 600 and 700 µg/L and in AN2 around 500 µg/L.

Figure 8-45. The graph shows the concentrations of aluminium in the Antequera basin. The values in ANDW and AN2 are around 35 and 20 mg/L respectively.

A second distinct pattern occurs with the elements calcium, sodium, lithium and magnesium, where the last one is seen in Figure 8-46. The concentrations of these elements upstream of the tailings dam are low. The drainage water has got relatively high concentration and the groundwater downstream has the same or a bit higher than in ANDW. In contrast to the previous elements the levels in the drainage water are relatively low and instead the groundwater is more affected. This pattern is almost seen with potassium as well, with the exception that there are very high values in AN1 and PAM1 in May to August, see Figure 8-47.

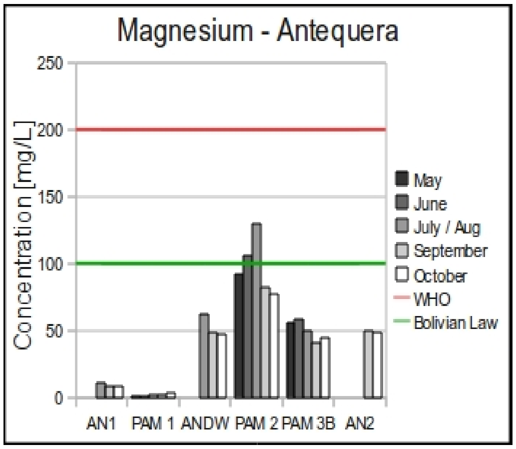


Figure 8-46. The diagram shows the concentrations of magnesium in the Antequera basin.

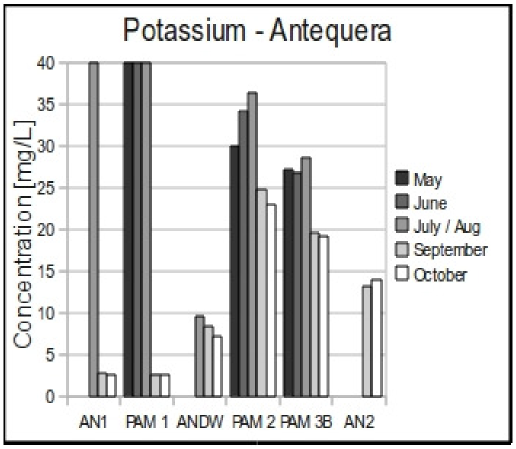


Figure 8-47. The diagram illustrates the concentrations of potassium in the Antequera basin. The values in May to July in PAM 1 are around 300 mg/L and for AN1 about 270 mg/L.

Other elements such as lead, tin and chromium was found to be at very low levels in most sampling points. Lead was most of the time below the detection limit, with a few exceptions.

9 Discussion

The overall situation in the study area seems to be quite poor concerning the environmental conditions and the water issues. There are management problems and poverty influencing the situation. Today there is no good management plan to work after to overcome the environmental problems. This has lead to issues between the local communities and the departmental government of Oruro of how to organise the administration. The affected communities in the region want to have more power over their own resources meanwhile the departmental authorities are talking about a general cooperation between different governmental agencies. These difficulties must be settled before actions can be defined and implemented. It is important to note that there is an environmental progress in the region, although slow it exists. There is also a motivation amongst the people around Lake Poopó to achieve successful outcomes (La Patria, 2009).

9.1 Poopó River basin – Surface water

Generally the river water in Poopó seems to be of good quality in the upper parts of the river, especially in sampling points PO1 and PO2, where the values of most elements are low, including arsenic, cadmium, sodium and magnesium.

Downstream of the sampling site PO2 the contribution from the thermal spring affects the overall trend in the river. The concentrations for a number of specimens increase a lot in PO3. This is to some extent explained by the much higher quantities of water that comes from the spring than from the river. Both the elements sodium and potassium are following this typical pattern, and increase many times due to the high concentrations in the thermal spring. After this point the levels are quite stable along the rest of the river. The field parameters of specific conductivity and total dissolved solids, TDS, also confirm this pattern where a lot of elements such as salts and ions are added from the thermal spring. Somewhat similar to this model is the cases for calcium, magnesium and sulphur. These specimens increase some before the influence of the thermal waters where the concentrations then increase a lot. After the hot spring the levels of the elements continue to increase between PO3 and PO4, but not as much. This continuous increase indicates that there might be weathering processes involved which add up the concentrations all along the Poopó River. There can also be an additional contamination at the village due to mine drainage and solid waste. Similar to the above elements is copper and chromium which exist, but at very low levels.

For some of the investigated elements, such as arsenic, cadmium and zinc, there is a significant difference between September and October. This could be due to the variations of how acidic or alkaline the water is and the different characteristics of the metals. The pH values found in this report are lower in September than October. In the upper part of the river arsenic comes at very low concentrations, below the detection limits and under any water legislation values, in both months. After the influence from the hot spring the levels raise to above the WHO guidelines in PO3. With a higher pH in October, arsenic increases its solubility and the concentrations become higher at PO4. At a lower pH, an opposite model occurs in September where the arsenic concentration drops to some extent. Arsenic is probably most influenced by the contribution of the thermal spring, which is much higher in October and not the pH levels in the river. Affected by the pH levels are cadmium and zinc and they follow a different pattern. Both elements come in very low concentrations upstream in the river in PO1 and PO2. The contribution from the thermal waters is very small in both months. In September there is a considerable increase in concentrations of cadmium and zinc between sampling point PO3 and PO4. This is probably due to acid mine drainage, with high levels of these elements, which influence the pH and is lower in September. In October, there is no such noticeable increase as in the previous month, instead the values rise just a little towards the end of the river. This could be due to less acid mine drainage to the river, which causes higher pH and lower levels of cadmium and zinc.

When it comes to the element lead a different model is shown. The values for both September and October start quite high in the upper parts of the river. In September, the concentrations in PO1 are just above the WHO guidelines. There is a direct decrease in concentrations to PO2. In October the level decreases slower and has its lowest value after the thermal spring. Then between PO3 and PO4 the values in both months increase to above the WHO standards, but they are still below the Bolivian legislation. The high value in the upper part of the river is hard to explain together with the decrease to the second sampling point. It could be due to the higher pH value, where lead dissolves more at a pH over 10 and under 9 (Qvarfort U. & Waleij A, 2004). The level of lead do not follow the pH totally and the increase further down in the river is probably due to the addition of acid mine drainage. Similar to the pattern of lead come iron and aluminium in September. The values are quite high in the upper parts of Poopó River, then the values drop until PO3. This could be an effect of precipitation of elements around the hot spring. It could also be some error in the data, as the values increase rapidly again. A totally different pattern is shown in October where the values are low in the upper parts of the river, peaks in PO3, and drop again until PO4. This could be explained by that the elements in the water from the thermal spring precipitates at the river beds downstream of the sampling point and do not reach PO4.

Taking the concentrations of the investigated elements in comparison with the health-based targets of WHO, it is shown that arsenic, cadmium, lead and iron are all exceeding the guideline values for drinking water in the Poopó River. This is especially the case in the lower parts of the river basin around PO4. For the first metal this can be explained by the contribution of arsenic from the thermal spring to the river. The other ones are probably affected by acid mine drainage and increases this way towards the end of the river. Elements that exist at low concentrations include nickel, copper, chromium, tin, aluminium and zinc. They do not pose any potential risk to human health. When it comes to the permissible levels for drinking water according to Bolivian Law, only cadmium and iron are exceeding the limits. The rest of the investigated elements are below national regulations. In the aspect of iron, the river at some points are so polluted that they would be considered to be categorised in “Class C”, see Table 1 in Appendix B. This means that the water could be used for recreation purposes and for watering of animals. After a full-scale treatment it could be used as drinking water. The levels of cadmium are high above the legislation and the river water is classified worse than “Class D”. This water cannot be used even for industrial purposes without treatment.

The drinking water for the village that is collected a few kilometres upstream and the measurements are done in a well, which is diverting water through a pipe to the village. Only arsenic and lead are above the health-based targets set by the WHO, but only during one sampling done for each month in September and October respectively. The concentrations for the other investigated metals do not pose any potential risk to human health. According to Bolivian Law, none of the investigations show any of the metals beyond the legislation levels for drinking water. This means that even though the water quality in the river is quite bad, there have been some installations done to improve the drinking water for the people.

Previous studies have demonstrated the increase of metals in the river to be caused both by natural and anthropogenic means. In García (2006) it has been found that the Poopó River had an alkaline pH where this study confirms this earlier conclusion. Furthermore, the high levels of calcium, carbonates, chloride and sulphate were reported in García (2006) which is confirmed in this thesis. There are some great differences in metal concentrations in this study compared with the work of Lilja & Linde (2007). Previously it has been found that the levels of arsenic were extremely high towards the end of the river, but this was not found in this study. Instead the maximum concentration in the lower parts of the Poopó River only reached 0.035 mg/L, although this is still above the WHO guidelines. Furthermore, the levels at PO1 and PO2 were higher in the previous study of Lilja & Linde (2007) in comparison with these investigations. This could be explained with natural variations or an occasional disturbance. Moreover, the concentrations of cadmium in the lower parts of the river basin seem to be much higher during earlier investigations. In Lilja & Linde (2007) it has been found that the cadmium levels were around 40-44 µg/L compared to a maximum of 3-9 µg/L in this study. Though, the same pattern is shown with lower values in PO1 and PO2 and higher values in PO3 and PO4. This is probably not affected by the thermal spring, but instead of acid mine drainage since the levels from the thermal spring is very low at 0.8-1 µg/L. According to García (2006) the values for cadmium in the rainy and dry seasons were 300 and 10 µg/L respectively. The dry season values correspond to the results in this study, as expected. When it comes to lead the values are much higher in Lilja & Linde (2007) in the range of around 200-400 µg/L compared to the levels retrieved in this thesis which reach a maximum of 16 µg/L. Instead the values in this study match better to the concentrations reported in García (2006). The iron values are different in this thesis, especially since they differ much along the course of the river for the two investigated months. In Lilja & Linde (2007) it has been found that the levels increase from 80 to 240 µg/L along the course of the river. In contrast, iron levels in this study instead range from 0 to 560 µg/L and do not follow the same pattern. All these differences could be due to variations in river flow or how much mining activities there are at time of sampling.

9.2 Poopó River basin – Groundwater

In the groundwater in the Poopó River basin there seem to be great spatial variations between the different piezometers, even in cases when they are very closely located. Since there are no previous studies done in the sub basin, the results in this study can not be compared to earlier results. When it comes to observation well POM 1-5 there are two major patterns described below, including the significant different levels in both POM 2 and 5 as well as another distinct example in POM 1. There are also some variations between the two depths A and B.

In piezometer POM 1-5 there appear to be lower pH in POM 2 and POM 5 compared to the other wells. At these two sites there are also significant lower levels of alkalinity but a higher specific conductivity than the other piezometers. This pattern is also seen for calcium, magnesium, sodium and sulphur where the levels in POM 2 and POM 5 are significantly higher than the rest. In POM 5 there are also extremely high values for cadmium, copper, nickel and zinc. Taking all these elements together at the sites of POM 2 and 5 it is given that these two wells are effected by something else than the others, especially POM 5. The two piezometers are positioned more close to one another compared to the rest. There is also located a pond close to POM 2 and POM 5 from where extra metal rich waters may infiltrate and be the reason for the elevated concentrations of heavy metals and lower levels of pH. The hydrogeology might also assist in this extra pollution if the two wells POM 2 and POM 5 are located in an area where the contribution from the pond is favoured and extra surface waters are infiltrated.

When looking at the difference between the two depths, depth A seems to have higher concentrations for cadmium and zinc, which could be explained by that the elements have not infiltrated to depth B to the same extent. As the soils in the area mostly contain silt, sand and clay, there is a possibility that at some sampling points there are layers of clay that prevent the contaminations to reach the deeper groundwater or at least confine the pollutants.

Looking at arsenic in observation wells POM 1-5, it is seen that the concentrations follow the levels of pH, with higher arsenic in POM 1 and lower in POM 2 and 5. POM 1A also has high levels of cadmium and zinc, while for calcium, magnesium and sodium the levels are lower compared to the other sites. Adding all this together there seems like POM 1 is influenced by something in the close surroundings, or perhaps the other way around, the other piezometers are influenced by something that does not reach POM 1. The last of these options seems to be the most accurate, due to the location of the wells. POM 1 is located furthest to the north and the closest other wells are POM 2 and 5, which are totally unlike POM 1. Continuing the differences due to location, POM 3 located furthest to the south seems to differ more from POM 2 and 5 comparing to POM 4, which is located a bit closer. Looking at POM 0 it seems to be more like POM 1, which could be a sign of some other influence for example from the large tailing or the smaller one close by. If assumed that there is an anthropogenic influence near to POM 5, supposedly the pond near to the train station, the contamination from this is most obvious in POM 5 and POM 2. It does not reach POM 1, but a small portion seems to reach POM 4. This could indicate that the groundwater flow is toward the river.

Looking at the additional piezometers further out on the plains, there is a significant difference from POM 1-5 to POM 6 and POM R. The levels in POM 7 are more close to POM 1-5. This indicates that the water in POM 6 and POM R is influence by some other sources, or the contaminations in the piezometers closer to the village has not been transported that far out. Assuming that the groundwater flows towards the river, in the direction north to south in this part, the water here should not get polluted by the water flowing in the river or closer to it. This seems to be the condition if you draw a conclusion from the results in this study.

To draw any conclusions of interactions between the groundwater and surface water in the Poopó sub basin is impossible, due to the lack of data. It is also difficult as there is no knowledge of the aquifers, and the only piezometer really close to the river is POM 7. When comparing the levels in the surface water at PO4 with the ones in POM 7 there is a great similarity for most elements. Elements that do not correspond are cadmium where the value in POM 7 is much higher than in any other sampling point and the levels of sodium and potassium is about twice as high in the surface water. The levels of aluminium and iron do also differ between the two points.

In observation well POM 1-5 there are many elements at lower concentrations including aluminium, chromium, lithium, tin and iron which all are relatively low and do not extort any potential harmful risks since they are below the WHO guidelines for drinking water. Lead also exists at low concentrations and in most of the months the levels are below the detection limit, with an exception for one month. All of these six metals are below the permissible levels set by the Bolivian Law. Not taking POM 5 into consideration for cadmium, zinc, copper and nickel, where all levels are extremely high, the levels in POM 1 and POM 2 exceed the WHO standards and the Bolivian Law in some samples. For the other classes in the Bolivian Law there are only some samples in POM 1 that exceed the "Class D" for zinc. For cadmium as it is the same limit for all classes POM 1 and POM 2 is over these too. The levels of sodium all exceed the WHO guidelines and all classes in the Bolivian Law. This result for sodium is not that surprising as the area and Lake Poopó in previous studies has been concluded to be saline. For magnesium none of the samples exceed any limit.

9.3 Antequera River basin

The water quality in the Antequera River basin appears to be good in the upper parts of the river basin, upstream of the large tailings dam at ANDW. In both surface and groundwater, most heavy metals and salts come at low concentrations, not exceeding the WHO guidelines. There are some exceptions from this in some of the investigated months, for example aluminium and arsenic that are above the health-based targets in some samples, but not all. This result, except for aluminium, was expected in this part of the basin which is fairly unaffected by mining. The high values of arsenic could be explained by the natural high arsenic levels in the ground. For aluminium, the concentration in the groundwater is higher before the tailings dam than after. Iron appears in the same pattern and this could be explained by the low pH in the drainage water. This can cause iron and aluminium to appear in reduced forms and dissolved in the water and are therefore transported downstream the river.

Downstream of the tailings the extreme concentrations in the surface water are explained by the drainage water ANDW from the tailings dam. This flow is large in comparison to the river flow. The water at this site is obviously to a large extent polluted by the rock tailings and mining activities. When it comes to the groundwater downstream the tailings the water quality is better than the river water. Although there is a significant raise in many elements such as cadmium, nickel and zinc. The pH is also a bit lower in PAM 2 and PAM 3 compared to PAM 1. This is likely to be the consequence of an influence on the groundwater by the surface water. The high values of metals in the groundwater after ANDW,but not as high as in the surface water, can be explained by the retardation of elements in the soils and the buffering capacity in the ground. For salts like calcium, magnesium, potassium the model is opposite. The concentrations in ANDW are lower compared to PAM 2 and PAM 3. This could be explained by dryer conditions and could correspond to the higher levels of cadmium and zinc in September and October, whereas it is the opposite for magnesium. A different pattern in the groundwater for copper can be explained by the fact that copper has less mobility in the ground compared to, for example, zinc (Sternbeck, 2000).

For the surface water downstream of the rock tailings the water quality is so bad that the levels exceed the Bolivian Law “Class D” in all cases for heavy metals, see Table 1 in Appendix B for water category B, C and D. The concentrations for calcium, magnesium and sodium are under the limits for “Class A”, which is the permissible levels for drinking water according to the Bolivian legislation, see Table 1. Upstream of the tailings only arsenic, tin and sodium have some values above the Bolivian law “Class A”, which means that this water almost is suitable for drinking purposes. Instead this water is classified in a lower category and could be used for irrigation if untreated. In the groundwater upstream of the tailings dam there is a similar situation as in the surface water except for aluminium and iron exceed the WHO guideline. As there are no limits in the Bolivian law for permissible levels of aluminium, this water is suitable for drinking purposes. The iron levels are only above the limit in September and are supposed to be lower most of the dry season. Downstream of the tailings the concentrations in the groundwater for calcium, cadmium, nickel, tin and zinc surpass the Bolivian law “Class D” which means that it is not suitable for any type of use if it is not treated before.

In comparison to previous studies the pH levels in the groundwater appear to be almost the same as in this study. Comparing to the master thesis by Mikaelsson and Ny (2009) the levels of calcium, magnesium, potassium and sodium are much higher in this thesis in most of the sampling points. The difference between the values in this study compared to Mikaelsson and Ny (2009) is large, where only the lowest values in September and October are close to the highest values in the previous study. This also means that there is an extreme change between July/August and September in this study. It should be noted that these higher values in May to July/August is in the sampling sites of ANDW and AN2, upstream the tailing the levels are similar to earlier studies. In these months the levels of sodium at these two points are ten times higher than earlier. Comparing to September and October the levels are slightly lower at about seven to eight times higher than before. It should also be considered that the study of Mikaelsson and Ny (2009) was preformed during the end of the rainy season, which could explain the lower values of salts in the water, caused by the higher water levels that wash out most of the salts. For arsenic, iron and zinc this thesis is compared to the values in López Cortés (2006) cited in Ekdahl (2007). Two of these elements, arsenic and zinc, are found to be much higher in both groundwater and surface water in this study compared to the previous one, and for iron the levels are lower instead. There is no information of when this study was conducted, which might influence the conclusions.

10 Conclusions

In the Poopó River, the water is mainly affected by two factors; the thermal waters situated between sampling point PO2 and PO3, and the mines and their waste deposits located between PO3 and PO4. The water quality upstream of the hot spring is good regarding most elements. The levels of As, Cd, Fe and Pb are high in Poopó River, where the arsenic concentrations are believed to be mostly of natural means. The high concentrations of As, Na, K, Ca, Mg and S are thought to originate naturally from the thermal spring. When it comes to Cd, Pb, Ni and Zn the major input to Poopó River is acid rock drainage and the contribution from the mines close to the village. Comparing to earlier studies the concentrations of the pollutants seem to have decreased some until today. But the levels of some heavy metals are still not fulfilling the Bolivian Law or the WHO guidelines. The drinking water to Poopó Village is of relatively good quality. It is only lead and arsenic that are above the WHO guidelines in some cases, but they are not exceeding the Bolivian legislation.

The groundwater downstream of Poopó Village is of quite poor quality, especially near the pond close to the train station where POM 5 is located. This contamination seems to spread to POM 2 and some to POM 4, while POM 3 does not appear to be affected that much yet. The situation in POM 1 is different from the others which indicate that the direction of the groundwater is towards the river. The situation is similar for observation well POM 0. This contamination is believed to be caused by human activities. Further out on the plains, there is no anthropogenic contamination in POM 6 and POM R. In contrast, the levels of heavy metals in POM 7 are similar to the river water in PO4 and are thought to be influenced by the river. More data about the groundwater should be collected.

In the Antequera River basin, the water quality in the river and groundwater upstream of the tailings dam is relatively good and could be used as drinking water, if it is treated for the high levels of arsenic and aluminium. Downstream of the large mine tailings the water quality in both the surface waters and groundwater is so poor, with high levels of all heavy metals. This water does not even approach the standards in the worst “Class D” according to the Bolivian Law. This contamination seems to come from the tailings dam and this also have an influence on the groundwater. In comparison to earlier studies the concentrations of Ca, Mg, K, Na, As and Zn are generally higher in this study, except from Fe which exist at lower levels.

11 Recommendations

Since the investigations in this thesis are made over a limited time period, more investigations should follow up this study. These examinations should be conducted especially during the rainy season to get a broader understanding of how the heavy metals act during this time of the year.

There should be carried out an assessment of the drinking water in Poopó Village, looking into how to protect the water and improve the quality further for the consumers. The thermal spring is responsible for huge amounts of natural contamination to Poopó River. Since it is not feasible to collect and treat all this water, because of the huge quantities, at least continuous monitoring of the elements should be done, especially of arsenic. The mine drainage should not be able to reach the Poopó River without treatment, which is the case in PODW where the water is leaking straight to the river at times. The waters from these mines, including both the operational and closed ones, should be identified, collected and then treated properly before discharged to the river. To further improve the state of the environment in Poopó River, the solid waste should be collected and deposited on another site separated from the waterways instead of being dumped straight into the river. As of now, the situation is very unhealthy for the people living in the village. An examination of the microbial hazards should be conducted. This should also be carried out as well for the drinking water in the Poopó Village.

There is a need of more data concerning the groundwater and further sampling should be done, especially during the rainy season. The groundwater flow in POM 0-5 should be determined and more observation wells should be installed. The small pond, which is situated close to and just west of POM 2 and 5, must be examined to see if it has got any links to the close by observation wells. A piezometer may be installed west of the railway station. To further understand the interactions between the Poopó River and the groundwater in the basin, extended measurements along the course of Poopó River should be conducted. One site may perhaps be close to POM 7.

Since the situation in the Antequera River basin is very severe due to the rock tailings, measures should be conducted to mitigate the problems of acid rock drainage. The drainage water ANDW should ideally be treated, but this can be difficult since there is a lack of funding for such treatment. Instead, some kind of re-circulation of the water where it is pumped back to the dam may be introduced. The quality of the water in the Antequera River will most likely improve significantly this way, although this will probably not help the contamination of the groundwater. There should also be an investigation of the water quality in the drinking water for Pazña Village. The study should look into how the levels of heavy metals are in this water, and if necessary, how to protect the consumers.

12 References

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13 Appendices

Appendix A	List of sampling points
Appendix B	Bolivian Law
Appendix C	Field parameters
Appendix D	Data from Inductively Coupled Plasma Mass Spectrometry

Appendix A - List of sampling points

Table 1. Coordinates and altitudes for each one of the sampling points.

Name*	Code**	Sub basin	Type	UTM Positions		Altitude [m]
PO1	VILR1	Poopó	River water	0721489	7962959	3897***
POP	CABT1	Poopó	Well	0717891	7965958	3812
PO2	KOVIR1	Poopó	River water	0717871	0765998	3808
POTW	CABTE	Poopó	Thermal spring	0717193	7966239	3794
PO3	CABR1	Poopó	River water	0716618	7966320	3783
PODW	MAD1	Poopó	Mine drainage	0715394	7966181	3760
PO4	POR3	Poopó	River water	0713496	7965978	3740
POM 0	POM 0	Poopó	Piezometer	0713533	7966428	3728
POM 1A	POM 1A	Poopó	Piezometer	0713345	7966591	3725
POM 1B	POM 1B					
POM 2A	POM 2A	Poopó	Piezometer	0713358	7966355	3726
POM 2B	POM 2B					
POM 3A	POM 3A	Poopó	Piezometer	0713388	7966209	3727
POM 3B	POM 3B					
POM 4A	POM 4A	Poopó	Piezometer	0713295	7966270	3725
POM 4B	POM 4B					
POM 5A	POM 5A	Poopó	Piezometer	0713279	7966416	3725
POM 5B	POM 5B					
POM 6A	POM 6A	Poopó	Piezometer	0711321	7966291	3726
POM 6B	POM 6B					
POM R	POM R	Poopó	Piezometer	0711318	7966296	3721
POM 7A	POM 7A	Poopó	Piezometer	0712236	7965570	3726
POM 7B	POM 7B					
POM 8	POM 8	Poopó	Piezometer	0712201	7966199	3727
PAM 1	PAM 1	Antequera	Piezometer	0721163	7950284	3814
PAM 2	PAM 2	Antequera	Piezometer	0721757	7947928	3785
PAM 3B	PAM 3B	Antequera	Piezometer	0721920	7946785	3781
AN1	CCO1	Antequera	Well / Surface water	0720884	7952036	3870
ANDW	AVR1	Antequera	Drainage water	0722174	7948233	3798***
AN2	PAZR1	Antequera	River water	0720513	7941972	3730

* This column refers to the name given to each sampling point in this report.

** Refers to the code given to the sampling sites during earlier studies.

*** These coordinates and altitudes are taken from Google Earth [2009-10-17].

Appendix B - Bolivian Law

Table 1. The Bolivian Law (1992) for other uses of water than for drinking purposes.

Parameter	"Clase B" [mg/l]	"Clase C" [mg/l]	"Clase D" [mg/l]
pH	6.0-9.0	6.0-8.5	6.0-9.0
TDS	1000	15000	15000
DO*	>70%	>60%	>50%
Aluminium	-	-	-
Arsenic	0.05	0.05	0.1
Cadmium	0.005	0.005	0.005
Calcium	300	300	400
Chloride	300	400	500
Chromium	0.6	0.6	0.6
Copper	1.0	1.0	1.0
Fluoride	0.6-1.7	0.6-1.7	0.6-1.7
Lead	0.05	0.05	0.1
Lithium	-	-	-
Iron	0.3	1.0	1.0
Magnesium	100	150	150
Nickel	0.5	0.5	0.5
Sodium	200	200	200
Sulphate	400	400	400
Tin	2.0	2.0	2.0
Zinc	0.2	0.5	0.5

* Oxygen saturation level

This information and above requirements in Table 1 is retrieved from the Bolivian Law (1992) which goes under the actual name of *Ley y Reglamento de Medio Ambiente*, Ley N^{o} 1333. The water in "Clase B" can function to irrigate fruits and vegetables. But it may not be used directly for drinking purposes, unless, it has been properly treated both physically and chemically; coagulation, flocculation, filtration and disinfection.

In the group of "Clase C" the water may be used for recreation purposes and for watering of animals. The water may be used for drinking purposes after proper physical-chemical treatments as in the case of "Clase B".

In this category, "Clase D", the waters can be used for industrial purposes without treatment. The water may also be utilized for drinking purposes, but only after prolonged pre-sedimentation and same treatment as for "Clase B".

Appendix C – Field parameters

Some of the sites were too dry to retrieve water from, hence no sampling was done. These cases are indicated by “–“in the following tables for May to October 2009.

Table 1. Field parameters collected in May 2009.

May									
Code	**Date**	**Temp.**	**Conductivity**	**Specific Conductivity**	**TDS**	**DO**	**pH**	**Redox potential***	**Alkalinity***
		[℃]	**[mS/cm]**	**[mS/cm, 25ºC]**	**[g/L]**	**[mg/L]**		**[mV]**	**[as mg/L CaCO3]**
POM 0	13/May	14,47	6,06	7,589	4,93	0,72	7,44	n/a	n/a
POM 1A	12/May	15,80	3,03	3,672	2,39	0,19	9,54	n/a	n/a
POM 1B	12/May	15,02	5,93	7,325	4,76	0,11	8,50	n/a	n/a
POM 2A	12/May	16,03	9,58	11,563	7,52	3,73	7,23	n/a	n/a
POM 2B	12/May	15,63	9,26	11,274	7,33	0,56	7,40	n/a	n/a
POM 3A	12/May	14,96	4,47	5,528	3,59	0,33	8,24	n/a	n/a
POM 3B	12/May	15,00	7,500	9,271	6,03	0,16	7,84	n/a	n/a
POM 4A	12/May	15,06	6,600	8,147	5,3	0,44	7,85	n/a	n/a
POM 4B	12/May	14,94	7,24	8,966	5,830	0,32	7,76	n/a	n/a
POM 5A	12/May	14,77	10,63	13,211	8,59	3,77	5,91	n/a	n/a
POM 5B	12/May	15,18	10,42	12,826	8,34	1,72	6,57	n/a	n/a

* The parameters were not measured and are not available.

Table 2. Field parameters collected in June 2009.

June									
Code	**Date**	**Temp.**	**Conductivity**	**Specific Conductivity**	**TDS**	**DO**	**pH**	**Redox potential**	**Alkalinity**
		[℃]	**[mS/cm]**	**[mS/cm, 25ºC]**	**[g/L]**	**[mg/L]**		**[mV]**	**[as mg/L CaCO3]**
POM 0	19/Jun	14,78	7,02	8,721	5,756	2,61	7,59	545,6	267
POM 1A	18/Jun	12,33	3,69	4,873	3,216	5,83	9,81	409,2	97,2
POM 1B	18/Jun	14,42	7,68	9,630	6,356	2,54	7,80	374,9	233
POM 2A	18/Jun	15,20	9,70	11,935	7,877	4,03	7,15	455,1	118
POM 2B	18/Jun	15,15	9,87	12,161	8,026	2,68	7,45	440,4	157
POM 3A	18/Jun	14,57	4,86	6,074	4,009	4,00	8,00	374,9	225
POM 3B	18/Jun	14,58	7,96	9,937	6,558	1,06	7,73	353,6	263
POM 4A	18/Jun	15,02	6,74	8,329	5,497	4,51	7,93	451,3	178,3
POM 4B	18/Jun	14,87	8,70	10,790	7,121	0,76	7,55	438,3	225
POM 5A	18/Jun	14,89	9,67	11,987	7,911	4,52	6,63	549,7	30
POM 5B	18/Jun	15,05	10,57	13,050	8,613	3,39	6,94	568,4	73
PAM 1	19/Jun	14,43	0,49	0,610	0,403	0,75	8,16	520,7	165,3
PAM 2	19/Jun	13,85	1,87	2,380	1,571	5,62	7,19	538,7	128,6
PAM 3B	19/Jun	13,45	1,46	1,877	1,239	2,67	7,24	518,5	76,4

Table 3. Field parameters collected in July/August 2009.

July / August									
Code	**Date**	**Temp.**	**Conductivity**	**Specific Conductivity**	**TDS**	**DO**	**pH**	**Redox potential**	**Alkalinity**
		[°C]	**[mS/cm]**	**[mS/cm, 25ºC]**	**[g/L]**	**[mg/L]**		**[mV]**	**[as mg/L CaCO3]**
POM 0	02/Aug	14,09	7,80	9,852	6,403	2,45	7,51	340,4	278
POM 1A	31/Jul	14,21	4,10	5,169	3,359	3,62	8,68	369,5	100,9
POM 1B	31/Jul	14,88	8,28	10,270	6,677	4,83	7,83	345,7	204
POM 2A	31/Jul	14,26	10,32	12,980	8,439	4,86	7,01	525,0	92,0
POM 2B	31/Jul	14,04	10,33	13,070	8,496	4,22	7,38	517,0	140
POM 3A	01/Aug	13,25	6,18	7,968	5,143	2,02	7,65	306,4	217,1
POM 3B	01/Aug	14,27	7,60	9,559	6,214	0,58	7,63	282,4	258
POM 4A	01/Aug	13,48	7,78	9,981	6,468	2,50	7,66	347,0	178
POM 4B	01/Aug	14,72	9,14	11,370	7,392	0,74	7,38	424,6	229,3
POM 5A	01/Aug	13,95	11,11	14,080	9,156	2,69	5,93	547,0	12,0
POM 5B	01/Aug	14,37	11,17	14,020	9,110	2,17	6,37	563,6	52
POM 6B	01/Aug	13,12	8,00	10,350	6,730	3,95	7,87	458,9	-
POM R	01/Aug	11,08	6,01	8,182	5,319	2,15	7,40	476,9	298
PAM 1	02/Aug	13,70	0,36	0,460	0,299	3,25	8,05	479,0	158
PAM 2	02/Aug	12,72	1,77	2,308	1,500	3,71	7,03	484,4	67
PAM 3B	02/Aug	13,27	1,31	1,682	1,093	2,16	7,14	532,1	100,0
CUCC1	28/Jul	14,10	0,19	0,245	0,158	13,90	9,09	346,3	38,0
AVR1	28/Jul	7,67	1,95	2,909	1,888	13,94	2,83	785,1	pH < 4,5
CABT1	28/Jul	9,52	0,25	0,359	0,234	10,46	7,45	410,5	69,3
CABTE	29/Jul	62,01	45,16	26,460	10,810	2,20	7,25	399,2	289,0
MAD1	29/Jul	20,16	11,94	13,160	9,423	4,78	6,24	249,6	16,0
POR3	29/Jul	20,04	10,52	11,620	8,345	12,95	9,13	368,0	151,9

Table 4. Field parameters collected in September 2009.

September									
Code	**Date**	**Temp.**	**Conductivity**	**Specific Conductivity**	**TDS**	**DO***	**pH**	**Redox potential**	**Alkalinity**
		[°C]	**[mS/cm]**	**[mS/cm, 25ºC]**	**[g/L]**	**[mg/L]**		**[mV]**	**[as mg/L CaCO3]**
POM 0	14/Sep	13,83	8,14	10,35	6,730	0,93	7,25	261,7	362,81
POM 1A	14/Sep	14,35	5,14	6,46	4,216	4,70	8,27	380,5	181,4
POM 1B	14/Sep	14,57	8,63	10,78	7,008	1,28	7,61	352,0	234
POM 2A	14/Sep	14,42	10,90	13,66	8,881	4,97	6,95	410,8	101
POM 2B	14/Sep	14,84	10,98	13,62	8,851	2,29	7,30	370,8	148
POM 3A	14/Sep	13,92	7,29	9,24	6,048	3,55	7,53	340,6	342,65
POM 3B	14/Sep	14,34	7,48	9,40	6,108	0,56	7,60	275,0	483,74
POM 4A	14/Sep	14,45	8,20	10,27	6,676	3,32	7,50	263,4	342,65
POM 4B	14/Sep	14,74	9,18	11,42	7,419	0,52	7,60	210,0	423,28
POM 5A	14/Sep	14,39	11,74	14,72	9,556	4,70	5,82	446,1	60,47
POM 5B	14/Sep	14,86	11,89	14,74	9,581	3,80	6,31	412,9	100,78
POM 6A	14/Sep	-	-	-	-	-	-	-	-
POM 6B	14/Sep	14,07	8,43	10,65	6,905	1,80	7,61	354,5	624,84
POM R	13/Sep	11,95	6,25	8,32	5,412	2,49	7,34	186,1	604,68
POM 7A	13/Sep	13,40	8,08	10,38	6,600	4,08	7,04	371,7	272,11
POM 7B	14/Sep	-	-	-	-	-	-	-	-
POM 8	14/Sep	14,45	6,80	8,52	5,537	4,90	7,40	275,9	503,9
PAM 1	13/Sep	13,25	0,35	0,45	0,292	1,89	7,69	613,8	267,07
PAM 2	13/Sep	12,48	1,82	2,39	1,555	3,06	6,73	541,0	110,86
PAM 3B	13/Sep	13,49	1,31	1,68	1,098	3,00	6,83	517,0	131,01
CCO1	13/Sep	12,8/12,6	0,12	0,23	0,12	n/a	8,18	-21,9***	100,78
AVR1	13/Sep	8,5	1,93	2,83	1,83	8,95	3,15	731,2	pH < 4,5
PAZR1	13/Sep	17,55	1,93	2,26	1,47	8,79	3,65	611,2	pH < 4,5
VILR1	11/Sep	19,5/16,1	0,10	0,2	0,1	n/a	10,33	-145,8***	120,94
CABT1	11/Sep	11,4/11,8	0,06	0,11	0,05	n/a	8,02	-12,8***	141,09
KOVIR1	11/Sep	11,3/11,7	0,20	0,38	0,18	n/a	8,32	-24,9***	125,98
CABTE	11/Sep	57,8	**	**	**	n/a	6,32	**	584,52
CABR1	14/Sep	29,5/29,1	6,56	12,55	6,95	n/a	7,64	6***	463,59
MAD1	12/Sep	19,1/19,8	0,09	0,18	0,08	n/a	8,17	-23,1***	60,47
POR3	12/Sep	15,7/16,6	6,48	12,41	6,87	n/a	7,6	9,9***	423,28

* Some of the samples were not measured for Dissolved Oxygen, and this data is not available.

** The samples were too warm for the multi-meter to measure.

*** Measured with another meter than the others (HACH EC10 Portable pH/mV/Temperature-meter).

Table 5. Field parameters collected in October 2009.

October									
Code	**Date**	**Temp.**	**Conductivity**	**Specific Conductivity**	**TDS**	**DO**	**pH**	**Redox potential**	**Alkalinity**
		[°C]	**[mS/cm]**	**[mS/cm, 25ºC]**	**[g/L]**	**[mg/L]**		**[mV]**	**[as mg/L CaCO3]**
POM 0	12/Oct	13,66	8,22	10,49	6,82	0,82	6,88	538	220
POM 1A	10/Oct	15,3	5,69	6,99	4,54	3,36	8,33	411,2	78
POM 1B	10/Oct	14,64	8,73	10,88	7,08	1,43	8,22	273,8	200
POM 2A	10/Oct	14,29	10,86	13,65	8,87	4,18	8,03	524,9	92
POM 2B	10/Oct	14,7	10,92	13,6	8,84	2,21	7,7	504,9	124
POM 3A	11/Oct	13,65	7,15	9,13	5,93	3,73	6,29	508,1	130
POM 3B	11/Oct	14,25	8,03	10,1	6,57	6,23	6,55	350,4	246
POM 4A	11/Oct	14,53	8,60	10,75	6,99	3,4	6,97	293,1	144
POM 4B	11/Oct	14,69	9,36	11,65	7,57	0,32	6,95	340,9	186
POM 5A	11/Oct	14,49	11,91	14,9	9,68	4,71	5,62	508,8	8
POM 5B	11/Oct	14,82	12,05	14,96	9,72	3,93	5,66	478,8	24
POM 6A	11/Oct	-	-	-	-	-	-	-	-
POM 6B	11/Oct	15,91	8,71	10,54	6,85	1,78	6,19	293	320
POM R	11/Oct	13,2	6,38	8,24	5,36	0,96	6,15	318,4	288
POM 7A	11/Oct	11,78	7,78	10,41	6,77	1,3	5,7	394,1	130
POM 7B	11/Oct	-	-	-	-	-	-	-	-
POM 8*	11/Oct	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
PAM 1	12/Oct	13,68	0,33	0,42	0,27	1,14	7,59	401	136
PAM 2	12/Oct	12,52	1,78	2,34	1,52	1,21	5,2	397,1	58
PAM 3B	12/Oct	13,47	1,29	1,65	1,07	0,82	5,31	417,1	104
CCO1	12/Oct	18	0,24	0,28	0,18	7,8	9,59	424,3	64
AVR1	12/Oct	8,6	2,00	2,91	1,89	6	1,85	778,7	pH < 4,5
PAZRI1	12/Oct	21,61	2,10	2,24	1,46	5,19	2,03	555,7	pH < 4,5
VILR1	10/Oct	16,1	0,19	0,23	0,15	6.58	10,61	485,7	56
CABT1	10/Oct	13,78	0,35	0,45	0,29	4,46	9,37	433,6	64
KOVIR1	10/Oct	18,66	0,38	0,44	0,28	7,4	9,34	435,3	52
CABTE	10/Oct	52,5	24,42	16,01	10,4	2,7	7,87	458,1	296
CABR1	10/Oct	30,75	16,74	15,08	9,81	8,1	9,46	448,4	232
MAD1	10/Oct	22,32	14,00	14,76	9,6	4,66	7,43	190,1	32
POR3	10/Oct	23,08	14,32	14,86	9,7	11,7	9,01	357,6	128

* The piezometer POM 8 was found broken as of 11/10, hence the sampling was not available.

Appendix D – Data from Inductively Coupled Plasma - MS

DL stands for Detection Limit and is the lowest concentration the ICP can measure
OR stands for Over Range and is the highest concentration the ICP can measure

Table 1. ICP data May 2009.

									May								
CODE	**Date**	**Al**	**As**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Li**	**Mg**	**Na**	**Ni**	**Pb**	**S**	**Sn**	**Zn**
DL:		0,679	5,6	0,161	0,459	0,481	0,341	0,803	0,84	1,776	0,06	0,214	1,24	2,301	15,2	7,072	1,116
OR >		5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	1*10^6	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5
Unit		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
POM 0	13-may	19,3326	30,53	40676,2	1,241	3,265	3,525	15,2889	79999,3	<DL	13472,8	OR	3,83822	<DL	106501	14,2539	41,04077
POM 1A	12-may	27,3696	69,07	15761,3	0,767	29,78	8,019	9,86937	30452	1129,11	869,467	OR	8,1183	<DL	99208,36	13,5632	10,18717
POM 2A	12-may	23,5896	22,15	567073	5,005	8,514	4,275	5,05844	309960	<DL	61932,6	OR	4,25234	<DL	365934,4	20,4047	110,7177
POM 1B	12-may	34,1414	42,31	24395,4	1,386	20,43	8,909	8,54758	90155,8	<DL	2329,93	OR	5,96636	<DL	103874,9	27,9978	16,57844
POM 2B	12-may	28,1526	19,47	540668	1,482	3,009	4,342	7,48266	296882	<DL	62179,2	OR	3,64143	<DL	350093,4	<DL	14,26691
POM 3A	12-may	38,4761	20,64	22134,4	1,178	8,904	5,975	12,103	52614,2	<DL	2342,92	OR	9,30772	<DL	108382	28,6046	8,757127
POM 3B	12-may	90,9238	28,23	114472	2,693	3,273	5,252	47,5193	409529	<DL	844,119	OR	4,12203	<DL	156904	9,7324	8,569242
POM 4A	12-may	35,3285	30,11	481699	0,615	6,15	4,241	11,19	61685,2	<DL	31419,4	OR	4,88506	<DL	163119,3	20,7553	6,184833
POM 4B	12-may	34,461	23,27	210634	1,322	8,54	5,335	15,3042	311871	<DL	29885,1	OR	6,66716	<DL	143948,5	20,6481	35,17625
POM 5A	12-may	28,0041	28,25	914643	1466	28,66	206,6	5,34524	339381	<DL	67317,9	OR	109,634	<DL	OR	10,9805	272910,6
POM 5B	12-may	19,8936	32,22	1143769	995	43,7	29,09	3,37452	299775	<DL	75252	OR	78,4958	<DL	OR	12,32	129386,4
PAM 1	13-may	65,8893	9,582	4770,39	0,923	23,81	4,083	18,9757	293366	384,383	999,483	194943	1,90705	<DL	21330,08	28,1905	91,83957
PAM 2	13-may	21,1222	11,93	725643	16,56	9,168	4,71	6,27147	29974,6	3702,98	92101,3	OR	62,2002	10,4434	OR	28,23	12291,28
PAM 3A	13-may	79,9329	20,08	445289	4,885	14,6	3,469	48,0063	24726,7	3161,27	64171,9	459990	62,0057	<DL	OR	33,0801	12059,57
PAM 3B	13-may	20,1106	27,84	369953	7,691	43,94	2,903	5,88914	27137,8	3273,35	55730,2	488944	130,117	<DL	OR	16,3631	34976,63
									June								
POM 0	19-jun	22,2993	31,18	111325	2,429	15,01	4,67	7,96877	348740	<DL	1689,46	OR	4,88967	<DL	154349,7	12,1172	57,58913
POM 1A	18-jun	25,0143	47,58	31153,3	1,617	30,69	7,425	7,02026	48729,2	2616,92	1481,28	OR	5,37796	<DL	183946,8	29,8327	42,54963
POM 1B	18-jun	16,8743	23,88	840639	3,861	65,93	3,563	3,0739	350128	<DL	79114,3	OR	2,75775	<DL	OR	<DL	276,3895
POM 2A	18-jun	39,028	38,61	48540,3	0,669	28,18	4,058	14,946	381646	<DL	2246,67	OR	2,79139	<DL	148453	17,341	69,7513
POM 2B	18-jun	20,1923	14,59	933740	1,774	10,12	4,251	3,20364	325123	<DL	78162,4	OR	5,6612	<DL	OR	<DL	42,47141
POM 3A	18-jun	110,53	33,93	35724	0,834	7,295	7,252	42,8549	75570,1	<DL	11315,7	OR	4,89187	<DL	149520,9	16,6061	72,65055
POM 3B	18-jun	17,6218	33,45	101334	1,603	14,94	4,909	5,54887	413491	<DL	1154,03	OR	1,9932	<DL	144164,8	35,8922	42,99832
POM 4A	18-jun	46,9986	26,93	348355	1,051	32,14	4,198	12,5639	324748	<DL	44908,9	OR	1,80561	<DL	255629,8	18,551	14,11292
POM 4B	18-jun	28,0816	27,89	278213	1,179	7,626	4,433	5,96601	371962	<DL	42985,1	OR	4,48481	<DL	187851,3	36,5173	13,06129
POM 5A	18-jun	33,0217	38,18	1515535	1711	5,909	13,37	53,735	330929	<DL	88348,6	OR	118,592	<DL	OR	28,1884	240168,2
POM 5B	18-jun	27,2007	35	1519729	1239	7,67	7,19	5,91785	299318	<DL	91423,7	OR	83,6996	6,30059	OR	17,1884	114310,9
PAM 1	19-jun	429,668	33,69	3805,77	1,819	10,9	2,842	136,145	310821	444,617	839,695	303691	4,96647	<DL	25140,04	32,176	63,21234
PAM 2	19-jun	28,6155	10,78	932506	19,03	12,86	3,717	12,4334	34082,9	4276,3	105999	777193	62,6598	<DL	OR	12,6386	12195,62
PAM 3B	19-jun	19,9819	6,908	363804	9,266	3,609	1,499	5,38884	26827,3	2957,5	58108,2	480626	157,653	<DL	OR	8,26193	55556,51

Table 2. ICP data July/August 2009.

									July/August								
CODE	**Date**	**Al**	**As**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Li**	**Mg**	**Na**	**Ni**	**Pb**	**S**	**Sn**	**Zn**
DL:		0,679	5,6	0,161	0,459	0,481	0,341	0,803	0,84	1,776	0,06	0,214	1,24	2,301	15,2	7,072	1,116
OR >		5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	1*10^6	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5
Unit		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
POM 0	02-Aug	25,8559	36,15	240863	3,539	6,012	3,677	7,76374	349547	<DL	34461,7	OR	5,68848	<DL	285863,6	10,6852	94,56741
POM 1A	31-Jul	34,792	42,12	96938,4	20,45	26,25	2,94	12,849	71283,6	<DL	2411,06	OR	3,73378	2,91358	291368,8	26,3208	434,9777
POM 1B	31-Jul	21,2441	37,5	99536,5	2,271	15,6	4,009	6,81845	364907	<DL	1714	OR	7,08088	<DL	160886,9	15,9163	31,0335
POM 2A	31-Jul	46,3156	32,39	1230433	8,884	12,96	5,035	19,401	354013	<DL	98870,1	OR	<DL	<DL	OR	34,0328	50,61208
POM 2B	31-Jul	25,5757	25,3	1132949	3,147	13,4	4,592	8,41506	341506	<DL	89827	OR	3,47527	<DL	OR	28,5584	25,97914
POM 3A	01-Aug	30,7384	14,49	234471	2,394	11,75	4,629	12,4816	81197,4	<DL	31646,6	OR	6,22751	<DL	194296	23,987	41,52432
POM 3B	01-Aug	23,0425	25,94	123940	1,374	5,855	3,627	6,57073	432583	<DL	376,829	OR	1,44146	<DL	150654,3	22,6864	17,10739
POM 4A	01-Aug	25,8227	33,27	354934	1,123	10,24	3,105	8,07712	327370	<DL	45476,7	OR	4,09025	<DL	251694,1	13,7388	57,64915
POM 4B	01-Aug	19,459	19,32	285943	0,973	39,58	3,18	10,5597	428736	<DL	44688,4	OR	3,78466	<DL	189947,2	<DL	12,47237
POM 5A	01-Aug	21,8782	20,53	1700621	2113	15,52	294,5	4,1927	326082	<DL	92902,6	OR	175,501	<DL	OR	29,7474	539615,5
POM 5B	01-Aug	31,0388	11,91	2237050	1948	14,5	44,7	10,2799	305884	<DL	107784	OR	145,532	<DL	OR	41,6797	337829
POM R	01-Aug	37,0649	90,58	373209	2,303	9,994	4,947	24,4115	338946	<DL	38078,1	OR	1,60527	<DL	112502,5	23,6919	116,6294
PAM 1	02-Aug	97,0536	<DL	7216,92	1,857	3,775	2,036	30,5313	288396	367,254	1312,62	181463	3,77151	2,82061	25399,71	25,9219	118,498
PAM 2	02-Aug	24,8056	<DL	1183772	39,87	9,602	3,933	5,19664	36355,6	4597,35	129413	715734	126,913	<DL	OR	18,1821	38592,75
PAM 3B	02-Aug	50,9814	27,81	374187	4,456	7,7	1,85	26,7037	28477,8	3253,67	49851,4	755430	37,3084	<DL	OR	23,5848	6529,929
CUCC1	28-Jul	14,0751	23,92	19355,7	0,979	5,194	1,786	15,5581	271491	282,304	11033,3	16240,2	4,88316	<DL	25868,3	29,4955	21,56207
AVR1	28-Jul	42616,1	19,73	1491561	476,9	27,88	614,1	4201,96	9605,34	1592,54	62353,1	126849	225,109	<DL	OR	22,3512	284324,8
CABT1	28-Jul	28,4283	6,186	23904,4	<DL	4,428	1,29	9,55847	274426	375,194	13639,4	46473,9	2,53042	<DL	21845,53	38,851	52,76909
CABTE	29-Jul	30,3726	36,48	251767	1,166	15,9	4,596	10,2556	595079	<DL	38531,8	OR	2,94221	<DL	99423,09	35,9296	39,25069
MAD1	29-Jul	390,854	27,59	263872	10,7	3,086	6,89	5044,58	391761	<DL	125386	OR	31,4097	<DL	208600,8	25,0852	928,9322
POR3	29-Jul	56,9769	34,88	261317	4,376	7,775	4,977	142,906	510048	<DL	39502,6	OR	1,46995	<DL	140471,5	32,7374	168,4928
VILR 1	29-Jul	50	31,06	<DL	15535	2,464	4,963	2,1291	9,72721	243,546	270,258	<DL	17063,6	86,6091	<DL	7896,41	2,15136

Table 3. ICP data September 2009.

									September								
CODE	**Date**	**Al**	**As**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Li**	**Mg**	**Na**	**Ni**	**Pb**	**S**	**Sn**	**Zn**
DL:		0,679	5,6	0,161	0,459	0,481	0,341	0,803	0,84	1,776	0,06	0,214	1,24	2,301	15,2	7,072	1,116
OR >		5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5		5*10^5	5*10^5	5*10^5	5*10^5	5*10^5
Unit		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
POM 0	14-Sep	39,011	<DL	81970,4	10,81	8,397	10,15	16,9746	93702,1	3,42761	15956,2	3492510	1,66778	11,0282	82041,37	*	351,9362
POM 1A	14-Sep	65,3275	31,18	80257	31,23	6,766	8,803	44,201	50734,9	2062,97	7537,72	1690040	4,26013	<DL	126403,8	*	722,5911
POM 1B	14-Sep	60,6847	40,23	66520,5	2,652	8,234	10,74	39,3088	52316,9	Check	14305	3868434	5,94071	9,95027	71210,05	*	35,04488
POM 2A	14-Sep	52,9196	36,29	402712	13,89	9,39	12,51	30,0193	98127,3	56,3982	64074,8	5183448	4,33906	5,57607	293641,3	*	30,49385
POM 2B	14-Sep	50,0871	28,85	364626	6,485	9,36	10,85	15,2793	93717,4	3166,19	59491,7	5231185	5,47114	9,573	254379,4	*	26,11926
POM 3A	14-Sep	43,2251	37,03	142009	3,696	8,607	11,08	18,1996	95645	3197,05	27309,4	3217607	5,94145	<DL	111673,4	*	18,09315
POM 3B	14-Sep	53,5123	18	85864,5	<DL	7,439	9,817	28,8613	73573,8	1633,84	19893,7	3708158	<DL	<DL	68535,8	*	32,5726
POM 4A	14-Sep	45,0904	15,52	187401	1,641	8,807	10,46	24,5409	65101,3	1545,5	36252,2	3711892	<DL	<DL	124085,4	*	49,58384
POM 4B	14-Sep	144,505	41,15	140786	0,878	9,037	11,18	95,8411	88528,6	2086,63	31199,7	4394945	<DL	11,0681	84376,45	*	31,99897
POM 5A	14-Sep	46,9564	20,24	559896	<DL	9,659	352,8	7,7258	95432,3	2305,06	70306,5	5997749	147,901	<DL	509482,1	*	187697,2
POM 5B	14-Sep	40,1198	17,81	511685	<DL	13,38	73,03	53,6522	84432,2	<DL	61525,2	4944134	113,146	<DL	422423,2	*	135824,8
POM 6B	14-Sep	65,3104	119,1	193621	2,475	9,187	13,51	37,9477	88792,6	1866,29	33519,9	3633374	4,54574	3,15166	61363,44	*	48,78265
POM R	13-Sep	74,0884	44,08	154956	1,921	7,932	9,046	57,4289	62179,3	1429,24	24618,8	2592987	<DL	4,07519	49551,32	*	51,96409
POM 7A	13-Sep	82,4797	38,92	116683	39,04	7,578	12,53	64,1843	66021,7	<DL	23858,1	3512498	3,35948	8,93211	49092,64	*	301,4656
POM 8	14-Sep	26,943	10,47	164873	3,639	12,07	13,61	33,3215	94537,5	<DL	32455,9	2426415	3,18915	6,75195	57322,16	*	105,275
PAM 1	13-Sep	237,874	15,74	7734,03	1,181	0,879	5,268	705,552	2587,53	125,263	2337,98	78107,7	<DL	4,80598	12090,48	*	3,116046
PAM 2	13-Sep	90,8748	27,74	373853	57,09	<DL	7,33	80,1412	24707	3783,69	82194,7	132762	129,881	6,74427	310837,8	*	42102,56
PAM 3B	13-Sep	84,338	31,95	185528	10,82	<DL	5,437	78,5469	19470,4	2502,87	40786,2	130830	65,1514	9,43203	175281,5	*	20768,62
CCO1	13-Sep	113,711	<DL	23730,3	1,575	<DL	4,431	165,533	2736,25	82,6687	8308,35	18643,7	<DL	<DL	15138,03	*	7,222538
AVR1	13-Sep	33382,3	14,49	399204	604,1	6,296	700,8	4332,86	8369,54	1205,8	48500,6	66160,3	179,646	<DL	368967,5	*	122691
PAZR1	13-Sep	22000,6	20,52	315450	485,9	3,535	532,3	1578,05	13166,2	1902,56	49532,1	89427,1	164,966	13,8223	295673,5	*	107738
VILR1	11-Sep	286,241	<DL	18744,5	0,503	0,552	5,532	347,792	237,125	77,2496	7191,95	17295,4	2,07519	10,7731	9484,504	*	8,972478
CABT1	11-Sep	229,326	14,75	27934,3	1,131	<DL	4,927	276,308	2926,64	148,245	9903,71	33672,1	4,9849	<DL	10807,51	*	11,66487
KOVIR1	11-Sep	213,564	<DL	30417,8	1,54	<DL	4,757	268,306	2887,13	126,528	11047,6	30507,4	5,33361	2,39761	14092,64	*	16,68642
CABTE	11-Sep	186,338	26,66	110537	1,033	9,191	11,43	275,873	114952	<DL	24305	6165172	<DL	2,38698	41036,6	*	11,81431
CABR1	14-Sep	66,0036	21,96	106144	2,31	9,048	11,83	41,2873	109835	2643,13	24442,3	5801770	<DL	7,10896	41334,86	*	40,42044
MAD1	12-Sep	282,038	16,9	127313	11,76	8,014	10,59	35388,9	69783,7	2085,16	74698,8	5689238	29,1423	2,93188	87589,38	*	842,5754
POR3	12-Sep	256,896	17,01	129144	8,787	9,082	11,47	560,559	102872	916,258	28639,2	5550806	1,47895	11,8644	49781,21	*	195,1649

* In September and October there were no analyses done of tin.

Table 4. ICP data October 2009

									October								
CODE	**Date**	**Al**	**As**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Li**	**Mg**	**Na**	**Ni**	**Pb**	**S**	**Sn**	**Zn**
DL:		0,679	5,6	0,161	0,459	0,481	0,341	0,803	0,84	1,776	0,06	0,214	1,24	2,301	15,2	7,072	1,116
OR >		5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5	5*10^5		5*10^5	5*10^5	5*10^5	5*10^5	5*10^5
Unit		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
POM 0	12-Oct	115,627	16,07	67706,5	26,33	7,141	11,84	115,177	79462,4	1416,29	14029,2	2818277	7,42433	<DL	69246,52	*	1268,489
POM 1A	10-Oct	77,871	26,61	87768,8	38,11	6,728	9,099	70,7116	49702,2	1277,14	9004,8	1638875	4,85639	<DL	122665	*	1224,087
POM 1B	10-Oct	78,4403	16,85	48320,1	1,98	7,384	8,503	51,7147	84823,4	1239,49	11862,4	2733863	<DL	<DL	51965,8	*	68,66413
POM 2A	10-Oct	75,7162	22,88	320834	15,25	8,701	11,82	62,2727	89352,4	Check	55206,6	4267984	3,32191	<DL	233541,7	*	119,9023
POM 2B	10-Oct	116,303	15,59	287621	3,553	9,347	12,2	122,118	83885,8	2787,17	50346,6	4251131	2,91806	4,62989	203239,6	*	79,41341
POM 3A	11-Oct	198,498	<DL	100637	3,81	6,457	11,36	184,525	84235,2	2803,43	21088,8	2454386	4,30736	<DL	85532,71	*	56,32243
POM 3B	11-Oct	53,5689	39,72	58511,6	3,204	7,491	8,004	39,9927	55361,9	1361,69	14991	2682639	1,38105	14,8691	46845,5	*	27,13569
POM 4A	11-Oct	86,5027	18,99	135887	1,162	7,377	9,04	71,9483	54438,6	50,6307	28473,2	2805959	<DL	<DL	95482,25	*	31,63062
POM 4B	11-Oct	35,3159	8,86	107067	1,558	7,729	8,876	8,33577	67224,8	1611,35	25495,8	3229220	2,47323	13,6496	62775,56	*	22,5519
POM 5A	11-Oct	187,633	23,37	365655	<DL	9,332	211,4	240,183	73249,4	1834,81	51763,9	3907154	111,946	10,8691	335676,5	*	141808
POM 5B	11-Oct	44,7127	7,001	465226	<DL	9,612	71,27	35,9984	77857,9	<DL	61581,8	4699696	119,112	7,50321	389412,6	*	149673,5
POM 6B	11-Oct	290,264	92,29	159000	3,471	7,934	11,3	433,256	82671,9	<DL	29283,1	3028520	3,7227	<DL	51735,93	*	149,6617
POM R	11-Oct	26,275	63,44	125512	3,695	7,385	8,65	7,22205	55910	1317,77	21161,8	2165916	3,54946	10,6202	40731,34	*	153,3528
POM 7A	11-Oct	84,0422	26,46	99405,5	35,88	7,302	12,46	93,5403	58320,8	2384,95	21532,1	2861112	<DL	10,0293	39643,35	*	404,2655
PAM 1	12-Oct	77,9185	5,96	11747,4	0,561	<DL	4,299	88,6055	2508,59	141,576	3459,42	3656,78	1,52777	<DL	11499,26	*	33,96473
PAM 2	12-Oct	22,6412	23,64	331536	59,77	0,824	6,589	6,86233	22965,6	3302,99	76553,5	135767	120,992	8,1784	288281,5	*	44129,45
PAM 3B	12-Oct	20,0671	24,55	200994	12,73	<DL	5,472	8,93073	19143	2540,67	44990,9	110818	64,2982	11,6645	173411,1	*	20516,17
CCO1	12-Oct	29,3695	<DL	25083,3	<DL	<DL	5,063	33,0899	2607,38	114,017	8213,99	19465	3,27639	<DL	15223,32	*	50,27414
AVR1	12-Oct	35557,8	6,574	354172	476,4	7,26	680,1	5460,74	7045,11	1476,21	47174,5	67867,7	187,704	16,3599	345081,5	*	120859,6
PAZRI1	12-Oct	17869,5	29,29	260352	456,6	1,424	434,8	809,437	13890,3	2017,54	48044,8	92322,7	147,259	<DL	254330,4	*	101983,6
VILR1	10-Oct	6,90626	<DL	19248,8	0,784	<DL	5,813	8,52592	487,879	106,46	7202,66	18182,3	1,42028	6,38232	9121,155	*	36,58749
CABT1	10-Oct	10,606	<DL	27777,4	1,622	<DL	5,143	4,67997	2979,17	186,764	9686,64	35223,1	<DL	19,8779	10022,1	*	47,88497
KOVIR1	10-Oct	7,89061	<DL	29260,6	<DL	<DL	4,197	<DL	2642,48	166,611	10347,5	28788,8	1,85949	3,76888	14396,98	*	38,39202
CABTE	10-Oct	25,0792	46,96	105694	0,795	9,38	8,237	166,92	113122	3,59629	24425,3	6151608	<DL	<DL	39880,43	*	58,60961
CABR1	10-Oct	56,4759	22,09	88460,9	1,506	9,33	8,89	90,1268	100681	3,31976	22861,1	5298417	<DL	<DL	36257,1	*	45,317
MAD1	10-Oct	99,7292	43,34	100306	7,273	7,987	10,16	27683,5	58839,2	3,29067	61757,3	4565099	20,204	23,5409	69321,99	*	777,1883
POR3	10-Oct	29,8361	33,52	95503,5	2,962	9,005	10,38	11,796	105315	3,57665	27371,5	5794370	<DL	15,594	52689,75	*	55,52306

* In September and October there were no analyses done of tin.