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Anthropogenic Influence on the Water Quality in the Lake Poopó Area, Bolivia

A Minor Field Study

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Abstract

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Problem Definition: For several hundreds of years, mining in Bolivia has been an important part of the economy. The mining activity has a negative effect on both the environment and the health of the people. Previous studies conducted in the Lake Poopó area show elevated concentrations of heavy metals and ions harmful to people and nature. Also, previous studies indicate that the contamination from mining activities is significant for the water quality. Four larger rivers flow through the studied area; the Poopó, Pazña, Urmiri and Antequera Rivers. A large quantity of mines but also farms and villages are situated in the basins of some of these rivers. This, together with the geological composition of the bedrock, highly pollutes the water that in turn is used by the people in these villages.

Objectives: The main objective of this thesis is to gather knowledge of the present environmental condition of the Poopó, Pazña, Urmiri, and Antequera River basins, with focus on heavy metal concentrations in superficial waters. Also, to increase the understanding of how the heavy metal concentrations have changed during the years of studies conducted in the area.

The questions to answer include:

- What are the concentrations of the heavy metals cadmium, copper, zinc, manganese, iron, arsenic, and lead in the Poopó, Pazña, Urmiri, and Antequera River basins?
- Do the heavy metal concentrations change over time?
- How much of the heavy metal concentrations are caused by anthropogenic and natural contamination, respectively?
- How is the water quality compared to the health-based WHO guidelines for drinking-water?

Our hope with this study is that the gained knowledge will help in the effort of developing long-term sustainable plans for remediation and water resource management that will benefit the people living in the Poopó, Pazña, Urmiri, and Antequera River basins.

Method: This thesis summarizes information from previous studies as well as analyzes data values from a field trip conducted in June 2013. During the field trip samples of surface water were collected and analyzed. In the field, the parameters pH, Eh, temperature, conductivity, TDS, and alkalinity were measured and the water samples were divided into two bottles for further analysis in laboratory. At the San Andrés University in La Paz the water was analyzed regarding concentrations of the ions nitrate, sulfate, chloride, sodium, potassium, calcium, and magnesium and the concentrations of the heavy metals lead,

manganese, arsenic, iron, copper, zinc, and cadmium. Data from previous studies were collected, organized and compared in order to see if and how the heavy metal concentrations change over time.

Results and Conclusion:
Current Situation
The samples collected during the field trip in June 2013 make up the current situation analysis. The concentrations for nitrate, cadmium and arsenic all exceed the WHO health-based guideline values for drinking-water in the Antequera River. A thermal spring that leaks into the Urmiri River, together with the natural bedrock weathering, affects the water and elevates temperature, chloride, sodium, and cadmium concentrations. Since there is no larger mine activity contaminating the water in the Urmiri River, a comparison between the Antequera and Urmiri River gives an approximate indication of how much the mines affect the water quality. This comparison indicates that the Antequera River is highly polluted due to contamination from mines, especially regarding cadmium. The results also indicate that the characteristics of Pazña River are a mixture of those of Urmiri and Antequera River. Furthermore, it seems as though the mine-influenced sampling site MAD1, a tributary of the Poopó River, impairs the water quality of the main river to a great extent.

Historical Situation
The data from previous studies have been divided into dry and rainy period, respectively, where an analysis of heavy metal contamination has been made only of the dry season data values. This study, similar to the study of the current situation, indicates that the area north east of the Lake Poopó is polluted and that Antequera River is the river most affected by mining activity. In that particular river, the concentrations for cadmium, iron, zinc and manganese exceed the WHO guideline values at almost every sampling site and date. Especially cadmium vastly exceeds the WHO limit. Meanwhile, the values for the Urmiri River rarely exceed the WHO guideline values. The heavy metal values for Pazña River are also often above the WHO guideline values, probably due to the inflow from Antequera River. The sampling site MAD1 greatly affects the Poopó River and elevates the heavy metal concentrations. A clear trend for all four rivers is the constantly elevated concentrations of cadmium that is neither increasing nor decreasing up to June 2013. For sampling sites PAZR1 and POR3, where the data sampling starts as early as 2001, the arsenic and lead concentrations are high above the WHO guideline values until June 2007. After this, the levels seem to have stabilized close to or below the WHO guideline values. Sampling site MAD1 does not, however, follow this pattern but instead has extremely elevated arsenic and lead concentration up to June 2013. The sampling site AVR1 has only been studied since 2007. There, the levels of arsenic and lead have historically had one peak each but otherwise stay around the WHO guideline values for drinking-water.

Keywords: Mining, Water quality, Heavy metals, Ions, Superficial waters, Antequera, Pazña, Urmiri, Poopó
Number of words: 9

Sammanfattning

Titel: Antropologisk påverkan på vattenkvalitén i området kring sjön Poopó, Bolivia

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Problemställning: Bolivias gruvdrift går tillbaka flera hundra år i tiden och är av stor vikt för landets ekonomi. Tyvärr har gruvdriften en negativ inverkan på miljön och människors hälsa. Tidigare studier gjorda i området kring sjön Poopó visar på förhöjda värden av tungmetaller och joner som är skadliga för människa och natur. Dessa studier visar även att kontaminationen från gruvdriften signifikant påverkar vattenkvalitén. Genom det undersökta området rinner fyra större floder: Poopó, Pazña, Urmiri och Antequera. Flertalet gruvor men även byar och jordbruk finns inom dessa floders avrinningsområden. Detta, tillsammans med den geologiska kompositionen av berggrunden, gör att vattnet som människorna i området använder blir kraftigt nedsmutsat av tungmetaller och joner.

Målsättning: Huvudmålet med denna rapport är att öka förståelsen för vattenkvalitén i avrinningsområdena till floderna Poopó, Pazña, Urmiri och Antequera, med fokus på tungmetaller i ytvatten. Målet är även att öka förståelsen för hur koncentrationerna av tungmetaller har ändrats under de år som området har studerats.

De frågor som besvaras är:

- Vad är koncentrationen av tungmetallerna kadmium, koppar, zink, mangan, järn, arsenik och bly i avrinningsområdena till floderna Poopó, Pazña, Urmiri och Antequera?
- Ändras tungmetallernas koncentration över tiden?
- Till vilken grad påverkas tungmetallernas koncentrationer av antropogen respektive naturlig förorening?
- Hur står sig vattenkvalitén i jämförelse med WHO hälsobaserade riktlinjer för dricksvatten?

Den yttersta ambitionen med denna studie är att den ska hjälpa i framtagandet av långsiktigt hållbara saneringsplaner samt planer för vattenresurshantering, vilket skulle säkra tillgången till rent vatten för de som lever i avrinningsområdena till floderna Poopó, Pazña, Urmiri och Antequera.

Metod: Denna rapport är baserad på information från tidigare studier samt en fältstudie utförd i juni 2013. Under fältstudien togs och analyserades prover från ytvatten. I fält togs mätvärden för parametrarna pH, Eh, temperatur, konduktivitet, TDS och alkalinitet. Proverna delades även upp i två flaskor för vidare analys i laboratorium. I laboratoriet på San Andrés Universitet i La Paz analyserades jonerna nitrat, sulfat, klor, natrium, kalium, kalcium och magnesium samt tungmetallerna bly, mangan, arsenik, järn, zink och kadmium.

Datavärden från tidigare studier sammanställdes och jämfördes för att visa om de olika tungmetallernas koncentrationer ändras över tiden och i sådana fall undersöka hur.

Resultat och slutsats:

Nuvarande situation

Analysen av den nuvarande situationen baseras på proverna som tog under juni 2013. I floden Antequera överskrids WHOs hälsobaserade riktlinjer för kadmium, nitrat och arsenik. En varm källa, tillsammans med läckage från berggrunden, påverkar floden Urmiris vatten och höjer värdena för temperatur, natrium, klor och kadmium. Däremot finns det inte någon större gruvaktivitet som påverkar Urmiris vatten, varav en approximativ jämförelse kan göras mellan Antequera och Urmiri för att visa ungefär till vilken grad gruvdriften påverkar vattenkvalitén. Denna jämförelse indikerar att floden Antequera är kontaminerad på grund av gruvorna, speciellt vad det gäller kadmium. Övriga resultat visar att floden Pazñas egenskaper är en blandning av egenskaperna hos floderna Urmiri och Antequera. Dessutom verkar det som om att den starkt gruvpåverkade mätpunkten MAD1, en biflod till floden Poopó, till stor grad försämrar vattenkvalitén i denna flod.

Historisk situation

Datavärdena från tidigare studier har delats upp i våt-och torrperiod men en analys av tungmetallkontaminationen har endast gjort över datavärden från torrperioden. Denna studie indikerar, precis som studien för den nuvarande situationen, att området nordost om sjön Poopó är förorenat samt att floden Antequera är den flod som är mest påverkad av gruvdriften. I den floden överstiger koncentrationerna för kadmium, zink, järn och mangan WHOs riktvärden för dricksvatten vid nästan varje provpunkt och provtillfälle. Särskilt kadmium överstiger kraftigt WHOs riktvärden. Å andra sidan överstiger värdena för floden Urmiri sällan WHOs riktvärden. Tungmetallvärdena för floden Pazña överstiger ofta WHOs riktvärden, förmodligen på grund av tillflödet från floden Antequera. Provpunkten MAD1, positionerad vid ett utflöde från en gruva, påverkar i hög grad floden Poopó och höjer dess tungmetallkoncentrationer. En tydlig trend för alla fyra floder är de konstant förhöjda koncentrationerna av kadmium som varken visar en minskande eller en ökande trend sett under hela studieperioden. För provpunkterna PAZR1 och POR3, där insamlandet av data började redan 2001, är halterna för arsenik och bly högt över WHOs riktvärden fram till och med juni 2007. Efter det verkar det som om värdena stabiliseras runt WHOs riktvärden. Provpunkt MAD1 följer inte detta mönster utan har extremt förhöjda värden av arsenik och bly ända fram till juni 2013. Provpunkt AVR1 har bara studerats sedan 2007. Där har värdena för arsenik och bly haft varsitt extremvärde, i övrigt ligger de runt WHOs riktvärden.

Nyckelord: Gruvdrift, Vattenkvalitet, Tungmetaller, Joner, Ytvatten, Antequera, Pazña, Urmiri, Poopó
Antal ord: 9

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Contents

1 Introduction

In the year 2000 the so-called Cochabamba Water War took place in Bolivia due to a privatization of the city's water supply, after which the following was written:

> "As the April blockades were winding down, one family stopped me on their way home. 'Compañero, now the water is going to be ours, what have we really gained?' a woman asked me. 'My husband will still have to look for work. As a mother and a wife, I will still have to go out into the street to sell things, and my children will have to drop out of school because there's just not enough money. Even if they give us the water for free, our situation still won't have gotten any better. We want (then-president) Banzer to leave, his ministers to go with him and all the corrupt politicians to leave. We want social justice. We want our lives to change." (24)

Bolivia has 10,496 million inhabitants (9). The official languages are Spanish and more than 36 indigenous languages, where Quechua and Aymara are the main ones. In Bolivia 88 % have access to clean water. However, 67 % of the population live in rural areas where the access to clean water is much more scarce. For example, in the rural areas 72 % have sustainable access to drinking water but only 24% have access to sanitation facilities (9).

Figure 1.1 The Pazña River flowing through the studied area in the Bolivian Altiplano

This study was performed in the region northeast of Lake Poopó, at an average altitude of 3 800 meters above sea level at the Bolivian Altiplano. The area is part of the large basin called Titicaca-Desaguadero-Poopó-Salares hydrological system, TDPS. Approximately two thirds of

the basin is located in Bolivia and one third in Peru and Chile. The Poopó basin consists of two lakes, Lake Poopó and Lake Uru-Uru. Lake Uru-Uru is located upstream of Lake Poopó and only receives water from the Desaguadero River, while Lake Poopó receives water both from Lake Uru-Uru as well as from many smaller inflowing rivers. A great number of these rivers are rich in dissolved solids due to the mining activity as well as weathering processes (4).

Conclusions from previous studies conducted in this area conclude that a considerable quantity of the water has high concentrations of both salinity and heavy metals. As an effect of the bad water quality the people living in the region suffer from scarcity of water and reliable access to clean water, which further influence the health as well as the economic situation (4). To be able to defeat poverty, sustainable and efficient management of water resources is one of the most important challenges. Secure access to clean water leads to improved human health, food security, education, and economy (8).

1.1 Background

Bolivia is a financially weak country rich in natural resources and biological diversity, situated in the middle of South America. The country is located in the tropical zone, with the Andes in the west and the lowland in the east. Due to the structure of the landscape Bolivia does not have a uniform climate. The studied area lies in the Altiplano, in the mountains of Bolivia. There, the seasons are clearly separated by a rainy season, from November to March, and a rainy season from April to October (3). The Altiplano is characterized by a semi-arid climate with extreme temperature variations, from -10°C to 14°C in the winter and from -2°C to 18°C in the summer (4).

Bolivia has a long-standing mining tradition dating back as far as 2000 BC, when first the Tiwanaku and then the Inca civilizations started extracting minerals. As part of the Andean cultures, indigenous people have always respected the nature. When the Spaniards conquered the Inca Empire the extraction grew to new proportions. From then on large amounts of different minerals have been extracted with a great negative environmental impact as a result. For example, high concentrations of heavy metals have been found in crops and marine life. These metals may accumulate and negatively affect the population and animals. The harsh climate that characterizes the Altiplano also has a negative effect on the environment (4).

The rivers in this area receive natural contamination from the Andean Cordillera in the west. This is due to the geological composition of the bedrock and soils. Thermal springs, high in alkalinity, also affect the chemical composition of the waters (4). Several villages and farms are situated in the basins of the rivers. They also affect the water quality since many lack proper waste water treatment. Some villages lead their drinking water in pipes from high upstream in the river, before any mining activity has affected the water (11).

Bolivia has a turbulent political history with over 200 different governments since the liberation from Spain in 1825. Attempts are being made to improve the country’s welfare

through social reforms and transfer of natural resource ownership to the public sector, but the country is still suffering from widespread poverty and social distress (7).

The area northeast of Lake Poopó has been studied for many years and much of the mining activities are situated there. In this thesis the occurrence of heavy metals in four river basins is studied. Data from previous studies are also compared and a historical comparison and evaluation of the changes in heavy metal concentration is made in this thesis. During a two-month visit to Bolivia the samples were gathered, analyzed and evaluated.

1.2 Objectives

The main objective of this thesis is to gather knowledge of the present environmental condition of the Poopó, Pazña, Urmiri, and Antequera River basins, with focus on heavy metal concentrations in superficial waters. Also, to increase the understanding of how the heavy metal concentrations have changed during the years of studies conducted in the area.

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Figure 1.2 The surroundings of sampling site AVR1

2 Theoretical Background

2.1 Previous Studies

The first environmental evaluation project in the Lake Poopó region was the *Oruro Pilot Project*. It started in 1993 and was funded by the World Bank and the Swedish International Development Agency, SIDA (28). The Swedish Geological AB was also involved in the project and helped in the investigations. The project focused on the mining and industrial sectors and the aim was to generate an *Environmental Master Plan*. The publications from this project inform about mining activities, the socio-economic situation, hydrology, flora and fauna of the region (26).

In 1996 Troëng and Riviera performed geological mapping of the entire area around Lake Poopó. Their work gave information about the general geological structures, where the mineral deposits are situated and how they were formed (25).

Since 2001 research in the Lake Poopó region has been carried out at the Higher University of San Andrés, La Paz, Bolivia. This research is financed by SAREC (the research department within SIDA). One important part of this research is the exchanging of doctoral, master, and bachelor students between Bolivia and Sweden. María Eugenia García, who is supervising this Bachelor´s thesis, is one of many who have taken part in this research.

Several Master´s theses have been conducted in the region of Lake Poopó. Amongst them; Lilja & Linde (2006) who analyzed the concentration of heavy metals in the sub basins in the Poopó region, Mikaelsson & Ny (2009) who investigated the ground- and surface water quality in the same sub basins, and Rosenberg & Stålhammar (2010) who, also in the same sub basins, evaluated heavy metals in water influenced by mining activities.

Between 2007 and 2011, a cooperative project funded by the European Commission took place in the Lake Poopó sub-catchment area; CAMINAR (Catchment Management and Mining Impacts in Arid and Semi-Arid South America) (2). The purpose of CAMINAR was to develop strategies, policies and technology in order to sustainably manage the arid and semi-arid catchment areas affected by mining in Peru, Chile and Bolivia (1). The objective of the project in Bolivia was to evaluate the water resources in areas influenced by mining in the Lake Poopó catchment area as well as to present a plan for sustainable management in the area. Studies including analysis of heavy metal concentrations were performed on a regular basis in the study area throughout the period of the project, during dry as well as rainy season (2).

2.2 Mining

2.2.1 History

Bolivia has a long history of mining, dating back as far as the Tiwanaku civilization (2000 B.C-1200 A.D.). The extensive mining industry began in the 16th Century when the Spanish conquistadores arrived. At that time silver and gold were the two most important metals produced. For several hundreds of years Bolivia was one of the major mining countries in the world. But in the 18th Century Bolivian mining was almost in ruins due to low mineral concentrations and the indigenous people's struggle for independence. During the 19th Century mining in Bolivia started to grow again and by the beginning of the 20th Century, Bolivia was a major tin producer. After the global crisis in 1929 investments reduced and mining declined. During World War II the demand for minerals was high but Bolivia did not take advantage of the situation. Bolivia exported tin to USA for $0.41 per pound while the international market prices were as high as $4.50 per pound (4).

In 1952 the Corporacion Minera de Bolivia, COMIBOL, was formed. The objective with COMIBOL was to organize the national mines and employ laid-off miners from private mines. The production was low due to high inflation, low tin price and low tin concentrations. In the 70´s COMIBOL saw a slight increase thanks to political stability and higher international prices. In 1985 the tin world market collapsed. The Bolivian government decided to implement a new economic policy that reduced the role of the state in the mining sector. This forced COMIBOL to close many of its mining operations and 75 % of the employees were fired, only the most economically viable mining operations continued. As an effect many laid off miners formed mining cooperatives and continued the mining activities in COMIBOL´s closed mines. They also started to extract other metals, such as zinc, lead, and tungsten. The establishment of a free market has helped the mining industry grow through foreign investment and during the 90´s the mining cooperative sector was the main producer of gold and tin in Bolivia (4).

Especially in the northern parts of the Lake Poopó intensive mining and metallurgic activity dates back several centuries. In 1810 an ore deposit was discovered in the studied area and today there are six mines affecting the examined water; Bolívar, Totoral, Avicaya, Machacamarca, Tihuanacu, and Poopó, as well as some small-scale mines. A Swiss company called Sinchi Wayra owns the Bolívar mine. The mine goes deep below the water table and the company pump up and discharges 95 to 115 l/s of water to the Antequera River (29).

2.2.2 Current Situation

The people of the Poopó region are underprivileged and live a meager life in terms of monetary wealth. In the lower parts of the studied area the inhabitants mainly live off livestock and agriculture. Higher up in the mountains these sources of income are coupled with mining. The most common mined minerals are lead, tin, gold, silver, zinc, and copper (30). The mining activities have a great negative effect on the surrounding environment

since waste water from the mines sometimes is dumped directly into the rivers without treatment. Waste from humans and agriculture also enters the rivers without treatment. Together with the natural contamination this results in high concentrations of different pollutants in the water. Though it is known that the river water is high in salinity and contains pollutants; it is used for irrigation, as drinking water for animals and humans, as well as for cooking (30). Two major mine-related issues currently affecting the area is the leakage from old and new tailings as well as the Acid Rock Drainage.

Tailings
The waste from the mines is stored as tailings. If the drainage from the tailings and the mines is not treated it may contain high concentrations of heavy metals and sulphur. Therefore the drainage from mines and tailings is the greatest environmental hazard of the mining industry (27). However, the tailings from the Bolívar mine are confined with clay and geotextile linings and they have monitoring wells in order to detect leakage into underground waters (4).

Acid Rock Drainage
The process where sulphur in minerals is oxidized to sulphate is called Acid Rock Drainage, ARD. If this process occurs in water the pH is reduced to extremely low values. To a certain point this takes place naturally but is often related to human activity, such as mining. The anthropogenic activities expose the rock to air and the rock may therefore be oxidized to a larger extent (31). The main constituent connected to ARD is pyrite, FeS_2. The reaction when pyrite oxidizes releases sulphuric acid that lowers the pH and drastically increases the leaching ability of heavy metals (26).

2.3 Heavy metals

2.3.1 Toxicology

Heavy metals can be found in the earth's crust. Some of them are vital to humans, plants, and animals, meaning that they function as trace elements (32). By definition, heavy metals are non-degradable and therefore they may accumulate if the intake is higher than the excretion. When plants and animals absorb water and soil rich in heavy metals these enter the biological system. The heavy metals may then accumulate and move up the food chain. However, it is not only the concentration that makes heavy metals poisonous. The toxicity also depends on the form and state of the metal. Freely dissolved ions are often more toxic than complex molecules. When short organic molecules bind to metals they become more soluble and the bioavailability increases. This leads to easier transport of metals to and within an organism (33). The major reason for the toxicity of heavy metals is due to their high affinity for sulphur. Some heavy metals bind easily to amino acids containing sulphur, which may lead to enzyme or cell interference. Therefore specific heavy metals affect a specific enzyme in an organ in the body (34).

All heavy metals are not poisonous, including manganese, zinc, copper, and iron. However, if exposed to these for a sufficient period of time and/or in sufficient concentrations the heavy metal is directly toxic to aquatic organisms and humans. Some heavy metals, such as arsenic, lead, and cadmium are not trace elements and therefore not essential to life and may thus present an immediate risk to living organisms (32).

2.3.2 Mobility in Surface Waters

Heavy metals are introduced to the environment in different ways. For example weathering processes, volcanic eruptions or anthropogenic activities, like mining or construction (32). The final sinks for non-volatile metals are sediments and soils. The primary source of heavy metals for natural waters is normally atmospheric deposition (35).

The mobility of heavy metals in the environment is dependent on the speciation of the metal, meaning its form. The speciation is controlled by redox and pH, and determines the rate of absorption and the affinity for binding to particles. This in turn controls the evaporation, volatility and sedimentation of a metal (33).

Most heavy metals are insoluble in alkaline to neutral conditions. Organisms may at those conditions assimilate the metals. Also, the metals may be absorbed by particulate matter, forming precipitates that sink down to the sediments. This may entail a measured concentration of heavy metals in water that is lower than the actual total concentration. It has been found that the concentration of heavy metals is higher in sediments than in the water (32).

2.3.3 Properties of Heavy Metals

Arsenic
Arsenic differs from most others metals since it tends to increase in both solubility and concentration in water with higher pH (34). It is primarily present as an anion in natural systems, and not as a cation. Also, arsenic undergoes many oxidation steps itself. The most common form in natural waters is arsenate (AsO_4^{3-}), which acts as an acid and may protonate in three steps (36). However, under anaerobic conditions arsenite (AsO_3^{3-}) is the most common form. The levels of arsenic depend mostly on the local geology since the solubility and concentration increases with higher pH. The major contribution of arsenic to the environment is as a by-product when melting ores of copper and iron (37). Under anaerobic conditions reductive dissolution of iron results in release of arsenic bound to iron oxides. Arsenic can be absorbed by different minerals, such as iron oxides, aluminum, manganese, and clay particles (38).

The toxicity of arsenic is not entirely understood but after being absorbed, the metabolism is characterized by the reduction from the form +V to +III (39). It is believed that arsenic binds to enzymes, thus inhibiting them. Symptoms of arsenic poisoning are; vomiting, bloody diarrhea, oesophageal, and abdominal pain. If exposed to arsenic via drinking water for a longer time, the symptoms are cancer of the urinary bladder, kidney, and skin (40).

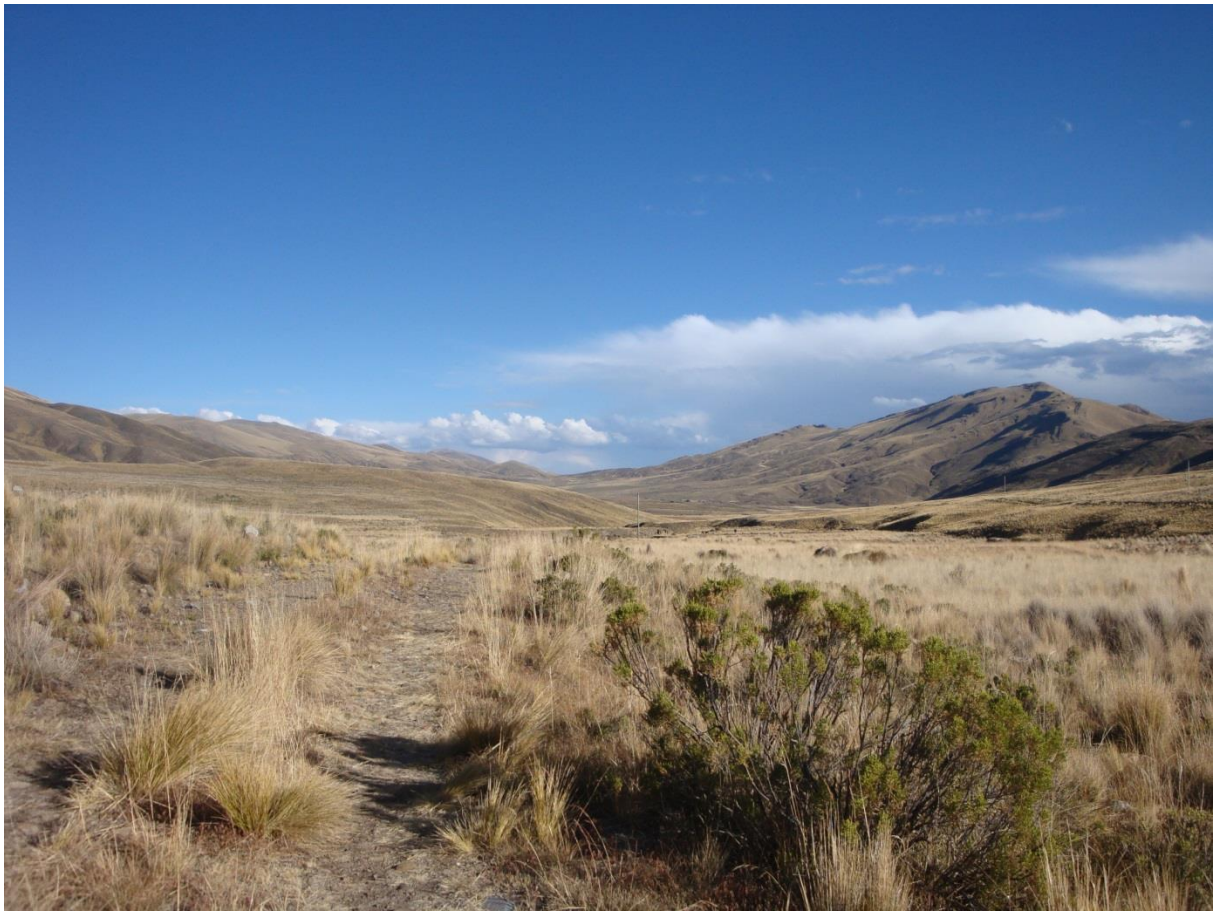

Figure 2.2 Part of the Urmiri River basin

Lead

Lead is a common metal found in soils and rocks all over the world, albeit in low concentrations. The average concentration in the earth's crust is 16 ppm (34). Lead is primarily mined from the mineral galena (PbS), and it only requires low temperatures to be extracted. Studies indicate that civilizations extracted lead from galena by burning wood 3500 years ago. Today lead is mostly used in batteries but earlier it was used as pigment in paints, as drying agent in oil paints, and as an agent in gasoline and ammunition. Other environmental concerns are the emissions to the atmosphere due to ore smelting, which is responsible for 80 % of the anthropogenic emissions. Natural sources of lead to the atmosphere are forest fires, volcanic eruptions and soil particles carried by the wind (32). In natural waters lead is mostly found as carbonate or chloride complexes. Lead may also bind to organic compounds, clay minerals or suspended compounds. Especially in very acidic soils, lead binds hard to organic compounds. Due to the formation of low soluble compounds such as lead carbonate, lead phosphate, and lead sulphate; the mobility of lead is very restricted in soils (34).

Lead is a general metabolic poison that when absorbed by the body is transported to all organs. It interacts with proteins and inhibits enzymes. Anemia and damage to the central nervous system and kidneys are some of the syndromes of lead poisoning (32).

Cadmium

Cadmium is found in very low concentrations in soils and rocks. Therefore cadmium is not mined in and of itself but obtained as a by-product when extracting other minerals, mainly zinc and sulphide, but also lead and copper (32). In natural waters cadmium normally is found as suspended complexes with iron and manganese or bound to organic compounds. There is a strong connection between pH and cadmium concentrations. If the pH is low the concentration of cadmium is high. The mobility is determined by pH and redox potential. These variables determine if cadmium is absorbed by clay minerals, iron oxides or sulphate oxides, which greatly reduces the mobility in soils. The ion Cd^{2+} is the dominant form of cadmium in surface waters with pH below 8 (34). Weathering and erosion are natural sources of cadmium. However, the anthropogenic emissions are in general 2,6 times larger. The major source is the manufacturing of end products, mainly NiCd batteries. To the atmosphere the mining activities are responsible for more than 50 % of the emissions (32).

It is believed that it is only the ion Cd^{2+} that is toxic. When cadmium is ingested it is transported to all organs but most of it accumulates in the kidney and liver. Due to the fact that cadmium has a half-life of 16 to 33 years in the human body, the long term and low level exposure may lead to accumulation and eventually reach toxic levels in the body. One historic example of cadmium exposure is the Itai-itai disease in Japan during the 1950s. There, mining activities polluted the river with cadmium that ended up on the rice paddies (32).

Zinc

Zinc is a common mineral in soils and rocks. It mostly forms hydroxy or carbonate complexes or is found as free zinc ions. In natural waters zinc is often bound to organic complexes and found in low concentrations. The solubility is closely connected to pH. At a pH below 5 the concentration of zinc increases (34). Zinc is widely used. For example, it is used to galvanize iron and steel, as the negative electrode in electric dry cells and as a part of brass alloys (37).

Zinc is an essential nutrient and deficiency may lead to inhibition of growth, decreased appetite, abnormalities in fetal development and weakened immune system (41). Zinc is also important for the reactions of the carbon dioxide metabolism and for the storage of insulin in the pancreas (37). Elevated levels of zinc may lead to copper deficiency (42). In natural waters high levels of zinc may be harmful to fish and other aquatic organisms (43).

Copper

Copper is a very common substance that has been used by humans for a long time. Today copper is widely used in both industry and agriculture. Therefore increasing amounts of copper end up in the environment. Copper can be released to the environment both by natural and anthropogenic sources. For example, copper may be released by forest fires, sea spray, decaying vegetation, mining activities, and combustion of fossil fuels. Copper often binds hard to organic matter or minerals in the sediment or soil. Therefore copper seldom reaches the groundwater. However it can travel far in surface waters, as free ions or suspended on sludge particles (13).

Copper does not break down in nature and may therefore accumulate in an organism (13). It is the soluble copper that threatens human health the most. Though copper is an essential

nutrient (deficiency may lead to anemia and inhibition of certain enzymes), a higher concentration of copper is toxic, especially to bacteria. Therefore, the major symptom of copper poisoning is inhibition of the intestinal flora (44).

Manganese
Though manganese is the twelfth most abundant element in the earth's crust it is seldom found in concentrations high enough to form an ore. Therefore the reserve of manganese mainly originates from other mined minerals containing manganese. Today manganese is very important in the steel industry. Almost 90 % of all consumed manganese goes into steel as an alloying element. Manganese dioxide is used as a depolarizer in dry-cell batteries. Manganese in an essential trace element for all living organisms, for example, plants need manganese to photosynthesize and for their reproduction. The content of manganese in the earth's crust varies widely. In some places it is only around 50 ppm and in other places it can be up to 10 000 ppm. It is only the divalent cation, Mn^{2+} that is soluble and mobile in the soil and which plants may absorb (14).

In acid soil manganese may increase in concentration and become toxic to certain species. If humans are exposed to toxic doses of manganese it may affect the pulmonary system or the central nervous system (14).

Iron
Iron is the most utilized metal in the world and by mass the most abundant element on earth. Iron is very common and easy to mine and therefore it is rather inexpensive. It also has a high durability and is thus widely used all over the world. The best known alloy of iron is steel. In acidic to neutral oxygen rich water, iron is mainly present as $Fe(OH)_2^+$. In oxygen poor conditions iron is mainly present as binary iron, Fe^{2+}. Most iron compounds are water soluble. A natural source of iron is the weathering of the minerals magnetite, hematite, goethite, and siderite. Every year 500 million tons of iron are produced and 300 million tons are recycled. Iron is used in everyday life with applications ranging from food containers to fertilizers (13).

Iron is an essential nutrient to all organisms. In humans it is a central component in haemoglobin and in several essential enzymes, and it plays an important role in the DNA synthesis. Iron deficiency may lead to anemia and affect the immune system negatively. Iron overdose is rare; however, iron compounds may have a negative effect on human health. Water soluble iron compounds such as $FeCl_2$ and $FeSO_4$ are lethal for adults in doses of 10-50 g. Iron dust is known to cause lung disease and different iron chelates may be toxic (13).

2.4 Ions

Sulfate
Early on in the earth´s development, sulfates mostly originated from igneous rocks and volcanic eruptions. In the present era, sulfates are mostly recycled from the atmosphere and from sedimentary rocks. The chemical behavior of sulfur is strongly related to the redox properties of aqueous systems. Sulfur exists in the oxidation states from S^{2-} to S^{6+}. The anion

sulfate, SO_4^{2-}, which is the highest oxidized form of sulfur, forms a very stable structure with oxygen. In reduced form sulfur, S^{2-}, form sulfides of low solubility with most metals. Iron sulfides have an important impact on sulfur geochemistry because iron is a common and widely spread metal in nature. In waters with pH of 3 or less significant amounts of partially dissociated sulfuric acid in the form of HSO_4^- may be present. Therefore, it is possible that the sulfate concentration in water decreases when the pH is around 3 (45).

Nitrate

On earth, nitrogen exists in oxidation states from N^{3-} to N^{3+}. In the atmosphere the most common form is nitrogen gas, N_2. Due to the strong bonds between the nitrogen atoms, nitrogen gas is very stable. However, there are some bacteria and algae that can bind nitrogen gas from the atmosphere and transform the gas into organic nitrogen (46). Normally, the concentrations of nitrate in groundwater are low but the concentrations may increase due to anthropogenic activities. Such activities are burning of fossil fuels and leakage of fertilizers, dunghills, and sewage pipes (47). If children are exposed to excessive amounts of nitrate it may lead to serious illness like shortness of breath and blue baby syndrome (15).

Chloride

Even though chloride is a minor constituent in the earth's crust, it is a major dissolved element of most natural waters. Sea water has high concentrations of chloride. This is probably due to accumulation of chloride from volcanic gases. Many minerals have chloride as their essential constituent. Locally, volcanic water in thermal spring systems may be an important source of chloride. Chloride salts are highly soluble and therefore chloride is rarely removed from water by precipitation except under the influence of evaporation or freezing. Also, chloride seldom participates in chemical exchange, biological activity or adsorption (45). There are no observed toxic effects of chloride on human health, except congestive heart failure due to excessive intake of sodium chloride. However, that seems to be more related to the sodium ion than the chloride ion (16).

Other Ions in Water - Na, K, Ca, Mg

Sodium, potassium, calcium and magnesium are four common ions in natural waters. Usually they exist as simple ions (Na^+, K^+, Ca^{2+}, Mg^{2+}) but can also form complexes. Calcium takes part in the carbonate equilibrium and its concentration is regulated by the solubility of $CaCO_3$/$CaSO_4$. All four ions are essential to life. For example, Na^+ and K^+ are a part of cell membranes and therefore help transport and keep balance of substances while magnesium is an important compound in chlorophyll. Calcium is used for generating endo- or exoskeletons. In water chemistry the term *hardness* is the unit of measure for the number of multivalent cations, out of which the most abundant are the cations of magnesium and calcium. Water containing large amounts of magnesium and calcium is therefore called hard water (37).

2.5 Field Parameters

2.5.1 Conductivity & TDS

The amount of dissolved ions in water is measured as electrical conductivity. The definition of electrical conductivity is the ability for one cubic meter of water to carry an electrical current. It is measured in Siemens per unit length. The conductivity depends on the ions present as well as on the nature of the dissolved ions (43). High concentration of ions in the water increases the conductivity. Conductivity cannot be converted directly into ion content since the conductivity depends on the mobility of the ions and their valance (48). The conductivity is an approximate measurement of mineral electrolytes for water containing inorganic compounds. For wastewater containing salts and organic acids the conductivity is an approximate measurement of minerals and organic electrolytes. When taking the temperature into consideration the specific conductivity is obtained (43).

Total Dissolved Solids (TDS) is correlated to the conductivity and is defined as the total amount of inorganic salts and organic matter dissolved in the water. A TDS compound must be able to pass through a two micrometer filter (49). Suspended sediment, colloids or dissolved gases are excluded from TDS. High TDS often means high concentration of salts, which could give bad taste to the water (50).

2.5.2 Salinity

The definition of salinity is the sum of all ionic compounds dissolved in the water. It can be determined by measuring the electrical conductivity or estimated from the TDS content. The salinity is determined by the geology of the catchment area and by the dissolution and precipitation of minerals. Therefore a larger catchment area indicates higher values of salinity. Also, younger geological material often gives higher values of salinity than older geological material (51). The definitions of the different water types are presented in Table 2.1.

Table 2.1 Different water types and their salt content

Water Type	**Salt Content (mg/l)**
Fresh Water	< 1000
Brackish Water	1000 – 20 000
Saline Water	Around 35 000
Brine Water	Significantly higher than 35 000

Salt lakes can be found in semi-arid and arid areas. If the evaporation is high the ion concentration increases. This effect can accelerate if the lake is endorheic (51).

2.5.3 pH & the Carbonate/Bicarbonate Buffer System

In addition to water molecules pure water contains dissociated H^+ and OH^- ions in very low concentrations. The pH value is a measurement of the concentration of H^+ in a liquid and is defined as the negative logarithm of the hydrogen-ion concentration. Water with pH below 7 is considered acidic, water with pH over 7 is considered alkaline and water with pH 7 is considered neutral. The carbonate equilibrium system is a buffer system that has great impact on the pH. This buffer system determines the pH to 5,6 for pure water (with no other ions) in a closed system. The carbonate equilibrium system is dependent on the solubility of carbon dioxide in water, which in turn is determined by the atmospheric pressure of carbon dioxide (43). When carbon dioxide (CO_2) comes in contact with water it dissolves and the aqueous CO_2 will, to some extent, associate with water molecules to form carbonic acid, bicarbonate ions and finally carbonate ions (52). Equation A describes the process:

$$H_2O + CO_2(g) \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \qquad \text{(A)}$$

The dissolution of CO_2 continues until equilibrium state is reached or, in other words, when the concentration of dissolved CO_2 is proportional to the partial pressure of CO_2 in the gas phase, according to Henry´s Law (52). This correlation is shown in equation B:

$$[H_2CO_3] = K_H * P_{CO_2} \qquad \text{(B)}$$

In water with pH below 4,5 bicarbonate (HCO_3^-) and carbonate (CO_2^{2-}) exist in insignificant concentrations and hence the equilibrium is strongly shifted to the left. In other words, there is a high concentration of carbonic acid. The concentration of HCO_3^- increases with increasing pH until it reaches a maximum at pH 8,3. If pH continues to increase, the concentration of HCO_3^- decreases and instead CO_3^{2-} starts to increase and has its maximum at pH 10,5. In natural surface waters the pH levels are usually 6,5 to 8,5 (43).

2.5.4 Oxygen Redox Potential (ORP)

In a redox reaction one element is reduced and gains electrons while the other element is oxidized and donates electrons. The process is defined as a reaction where electrons are transferred from one element to another (53). The process may also be thought of as a reaction involving transfer of oxygen. However, most redox reactions in natural environments do not use molecular oxygen directly. A redox reaction may be divided into two half-cell reactions, one for each reactant. Each half-cell reaction has a so called standard reduction potential, ORP, which is the standard measure of the redox state of natural water (35). The standard reduction potential is defined as the electric potential relative to a specific half-cell reaction. It is measured in Volts (52). To simplify, one may describe the redox potential as a measurement of how many ¨free¨ electrons there are in a system, in other words, how many electrons that can be transferred within the system. A positive value of the redox potential indicates oxidizing conditions and a negative value indicates reducing. It is assumed that all redox reactions are in equilibrium when discussing ORP of a solution.

However, this is not the ¨normal¨ case in nature since natural water contains several redox pairs, each with individual values of ORP (35).

2.5.5 Dissolved Oxygen

Water both produces and consumes oxygen. Oxygen from the atmosphere is dissolved in water and is also produced by plants during photosynthesis. Respiration by aquatic organisms, decomposition and different chemical reactions consume oxygen. Dissolved oxygen, measured as DO, is essential for aquatic life and is one of the most important oxidants in redox reactions (43). The level of DO varies during a 24-hour period, with altitude and with temperature (19). Normally the saturation level of oxygen lies between 85-95 % in unpolluted surface water (43).

2.5.6 Alkalinity

Alkalinity is a measure of the buffer capacity of a specific water body and can be expressed as the concentration of calcium carbonate or analogously as the total concentration of carbonate and bicarbonate (eq. C):

$$Alk = [HCO_3] + 2[CO_3^{2-}] = [CaCO_3] \quad \text{(C)}$$

Alkalinity can be calculated through the stoichiometric correlation between carbonate and hydrogen forming carbonic acid (eq. D), resulting in an estimation of alkalinity according to equation E:

$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3 \quad \text{(D)}$$

$$Alk = 2 * \frac{V_{HCl} * [HCl] * M_{CaCO_3}}{V_s} \quad \text{(E)}$$

where V_{HCl} is the added volume of acid, $[HCl]$ is the concentration of acid, M_{CaCO_3} is the molar mass of calcium carbonate and V_s is the volume of sample.

3 Methodology

3.1 Data Sampling

The sites for data sampling were selected from a number of standardized sampling sites with predefined GPS-coordinates (see table 3.1). An overview of the study area can be seen in figure 3.1. In figure 3.2, the north part of the study area is shown while the south part is visualized in figure 3.3. Geographical information, pictures and measurements are made with Google Earth.

In this chapter, specific information is also presented about the sampling sites studied more in chapter 4.2; POR3, MAD1, PAZR1, AVR1 and CABT1.

Four different rivers are studied that are all different in length from first to last sampling site at each river; Antequera River (16635m), Urmiri River (13995m), Pazña River (5215m), and Poopó River (5233m). The first three are seen in figure 3.2 while Poopó River is seen in figure 3.3.

Table 3.1 UTM coordinates for the sampling sites

UTM coordinates - zone 19K		
Sampling site	**Easting**	**Northing**
BODI1	0725275	7956447
TOTV2	0725130	7954922
TOTR1	0724722	7954208
TOTR2	0723994	7953177
AVR2	0723257	7950256
AVR1	0721868	7948248
CUCC1	0720880	7952031
AVR3	0720873	7945302
URR2	0729626	7948149
URR1	0727604	7944725
URC1	0724127	7944804
URV1	0724168	7944495
URR3	0721998	7943603
PAZR1	0720514	7941971
PALR2	0718183	7942031
CABT1	0717889	7965957
MAD1	0715384	7966183
POR3	0713497	7965977

Figure 3.1 Overview of the study area, with villages Poopó & Pazña as well as Lake Poopó marked with yellow pins

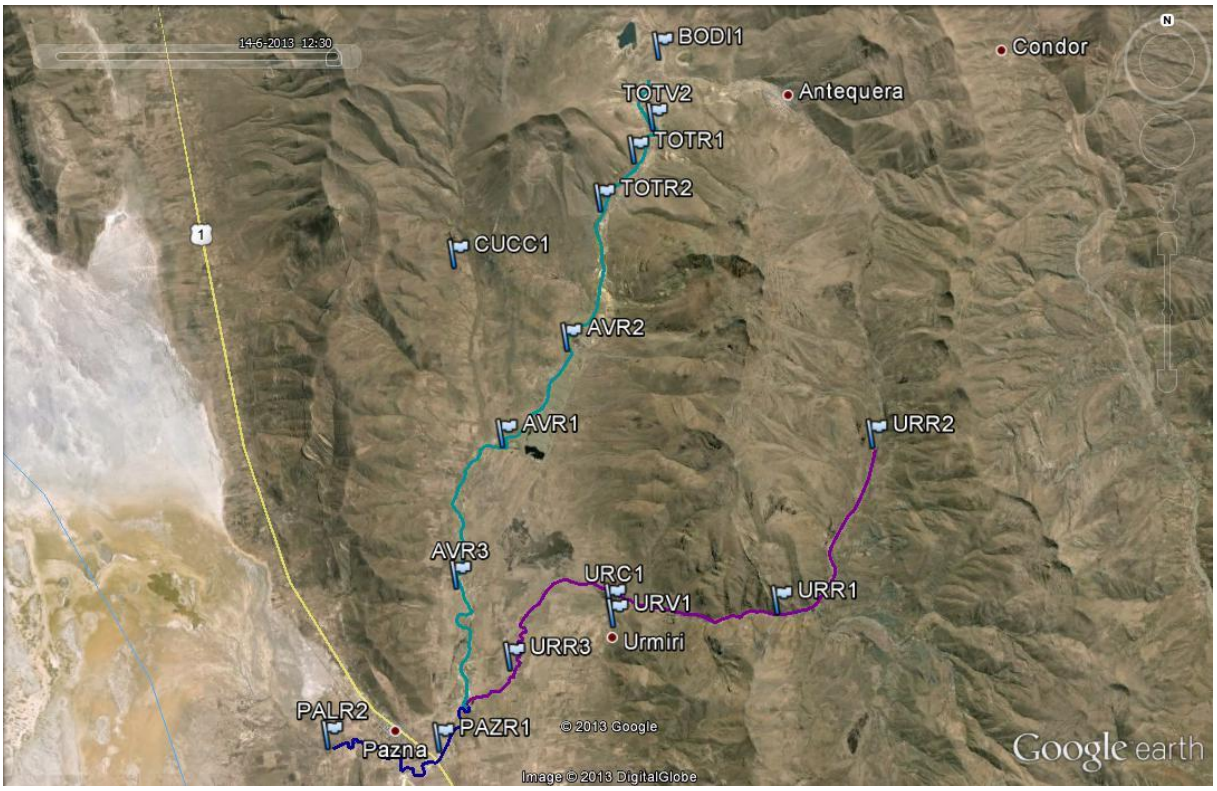

Figure 3.2 South part of the study area with Urmiri River in purple, Antequera River in teal and Pazña River in blue. Pazña village is seen at the bottom left in the picture.

Figure 3.3 North part of the study area with Poopó River marked with teal. Poopó village is seen to the left in the picture.

CABT1
At the start of the Poopó River, sampling site CABT1 is located right at the outflow of a natural underground spring (fig. 4.1).

MAD1
Sampling site MAD1 (fig. 3.4) is situated at a minor outflow from a mountain in which extensive mining takes place. The small stream is a tributary to Poopó River. Sara Eklund and Efraín Blanco are seen in the picture.

Figure 3.4 Sampling site MAD1

POR3
Sampling site POR3 (fig. 3.5) lies downstream of both a major mining area northeast of Poopó (fig. 3.3) as well as a mining discharge flow from MAD1. Also the discharge from the Poopó village joins with the Poopó River in which POR3 is situated. The Poopó River starts at the underground spring leaking out at sampling site CABT1.

Figure 3.5 Sampling site POR3, facing upstream Poopó River

PAZR1
At a picturesque location shortly after the joining of Urmiri River and Antequera River into Pazña River (see fig. 3.2), sampling site PAZR1 is located. Characterized by the mixture of a relatively unaffected river (Urmiri) with one surrounded by major mining activities (Antequera), PAZR1 is an interesting site to study.

Figure 3.6 Sampling site PAZR1, facing upstream Pazña River

AVR1
Compared to the sampling sites upstream Antequera River, the surroundings of AVR1 shows no signs of obvious contamination. The sampling site is situated right before the inflow of the tributary coming from sampling site CUCC1.

Figure 3.7 Sampling site AVR1, facing downstream Antequera River

3.2 Water Analysis

3.2.1 Heavy Metals

The laboratory analysis of the water included concentrations of copper (Cu), cadmium (Cd), manganese (Mn), zinc (Zn), iron (Fe), lead (Pb) and arsenic (As). An AAnalyst 200 atomic absorption spectrometer (fig. 3.8) was used to quantify the concentrations of Cu, Cd, Mn, Zn, Fe. For Pb and As, generally present in lower concentrations, the analysis was made using equipment with a lower detection limit, namely an Aanalyst 100 atomic absorption spectrometer with a HGA850 graphite furnace.

Figure 3.8 AAnalyst 200 atomic absorption spectrometer

3.2.2 Field Parameters

Measurements of temperature, pH, conductivity, specific conductivity, TDS, salinity, ORP, and DO were made in the field using a HI 9828 Multiparameter meter. The value of ORP was recorded as the first value attained by the meter. The rest of the values were obtained as the stabilized values provided. Alkalinity was measured in the field through titrating pre-filtered samples with HCl until the added indicator solution precipitated. Alkalinity was only estimated for samples with a higher pH-value than 5,4.

3.2.3 Bicarbonate and Carbonate

During the field study, alkalinity was measured by titration of the samples with hydrochloric acid using an indicator to determine the point where all the content of bicarbonate and carbonate had combined with the acid. The ions bicarbonate and carbonate were assumed to account for all of the alkalinity. The pK_a-value of HCO_3^- was estimated as a constant 10,32. By combining the definition of alkalinity (eq. C) with the dissociation formula of bicarbonate into carbonate (eq. F), the concentration of bicarbonate (eq. G) was estimated whereafter the concentration of carbonate was estimated with equation F:

$$Alk = [HCO_3] + 2[CO_3^{2-}] = [CaCO_3] \quad \text{(C)}$$

$$[CO_3^{2-}] = \frac{[HCO_3^-]}{10^{pK_a - pH}} \quad \text{(F)}$$

$$[HCO_3^-] = \frac{0.5 * Alk * 10^{pK_a - pH}}{1 + 0.5 * 10^{pK_a - pH}} \quad \text{(G)}$$

where pK_a is the dissociation constant of bicarbonate into carbonate (assumed at standard conditions) and pH the pH of the specific sample.

3.2.4 Anions

The concentrations of sulfate and nitrate were estimated using a Hach DR 2800 portable spectrophotometer using specific *permachem* reagents for sulfate and nitrate, respectively. The technical supervisor estimated the concentration of chloride independently.

Figure 3.9 The portable spectrophotometer used for measuring sulfate and nitrate concentrations

3.2.5 Cations

The analyses of potassium (K), sodium (Na), calcium (Ca), and magnesium (Mg) were made with an AAnalyst 200 atomic absorption spectrometer independently by the technical supervisor.

3.3 Compiling Data

For the comparison of how heavy metal and ion concentrations have changed during the years, data was collected from the CAMINAR project (17, 18, 20), from studies made by Maria Eugenia Garcia (4), as well as from previous MFS-studies (12, 5, 6). For the purpose of a good overview in the tables, the data values provided were adjusted after the number of decimals, so that each value would get a maximum specific number of significant figures for each parameter (normally three). Parameters with a non-decimal value higher than three significant figures, as well as data given with less than three significant figures, were left unchanged. Parameters with a value of zero and no decimals are assumed not to have been quantified in the other studies. A division between wet and dry period was made according to the CAMINAR standards (17).

3.4 Sources of Error

3.4.1 Sampling

Regarding the field parameters, a number of uncertainties exist regarding the attained values. First of all, the weather changed from sunny to cloudy during the time the samples were being taken. This has a slight impact on the temperature of the water and thus also indirectly on the rest of the field parameter values, especially the specific conductivity, ORP and DO. Another source of error is the difficulty of determining the point of time at which the meter can be considered to supply stabilized values. This was especially difficult regarding ORP where the value never stabilized. To mitigate the error, Efraín Blanco (11) assumed that the primary value of the meter was the most accurate. Therefore the values of ORP for each sampling point were obtained as the first value that the meter supplied. Additionally, the sampled water might not be fully homogenous in terms of TDS, salinity and conductivity. Due to the low water turbulence at some sampling sites, caused by a lack of current, there might have been minor differences in field parameter values at different locations within the sampling sites. Finally the low flow of water at some sampling sites made both measuring of field parameters and sampling difficult.

Errors might also have been introduced during the sampling as some bottles, though not previously used, were not sufficiently pre-washed before being filled with water samples.

3.4.2 Laboratory Procedures

A small error is introduced via the estimation of carbonate and bicarbonate concentrations, as the temperature of the water at a specific sampling site is not taken into account for the temperature-dependent dissociation constant of bicarbonate into carbonate. The assumption that this constant is not temperature-dependent is made due to simplification of calculations. Also, some values of bicarbonate and carbonate could not be calculated as values of alkalinity and/or pH were missing. These values were therefore taken directly from the data of ions. This might introduce a minor error when comparing these data to data where the values have been estimated from pH and alkalinity according to equations F and G.

A larger source of error is the dilution that had to be made. As the samples had very high concentrations of heavy metals and ions, they had to be diluted up to 10 000 times in order to lower the concentrations below the maximum detection limit of the specific analysis equipment. The final dilution factor is dependent on the preciseness of the adjustable pipettes used for measuring volumes, which is why the calculated dilution factor might differ from the actual dilution factor. The larger the dilution factor, the larger the error becomes for the final estimated concentration.

The ion analysis in the laboratory took place during the months of July and August. This may lead to ion concentrations that differ somewhat from the concentrations at the time of sampling (14-15 June). The change in concentration is explained by chemical reactions that may take place between the different chemical species in the samples.

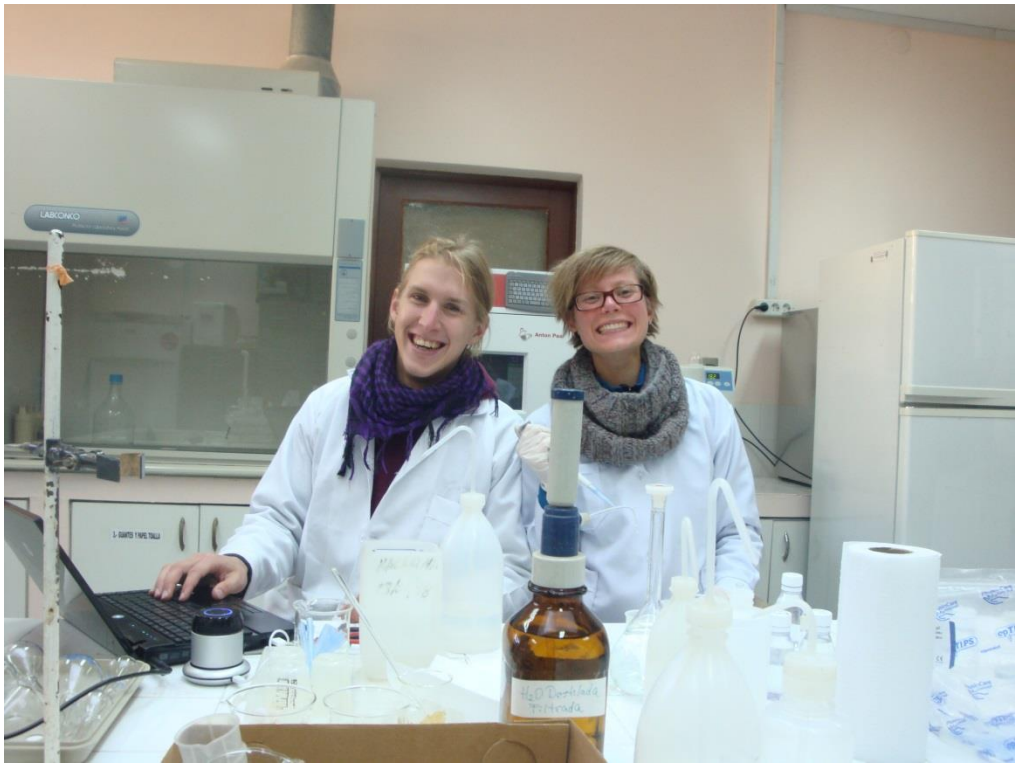

Figure 3.10 Johan Lundström and Sara Eklund performing the analysis in the laboratory

4 Results

All results from the study in Bolivia are presented in this chapter. The chapter is divided into two parts; the first part shows the results from the study performed during the summer of 2013 and the second part presents a comparison between heavy metal data from previous studies. In all the tables, the results are divided into Poopó River, Antequera River, Urmiri River and Pazña River, respectively. Also, the sampling sites are organized starting with the furthest upstream sampling site to the left (figures) or at the top (tables). Some of the analyzed concentrations are below the detection limit, for which the detection limit values 'x' are put in the table cells as '<x'. This means that the concentration is unknown between zero and the detection limit. In the graphs, concentrations below the detection limit are interpreted and plotted as being zero. For the graphs, the concentration value seen when marking a specific data point is not accurate. The accurate values are found in the data tables.

All concentration and ion values are compared to guideline values for drinking-water established by the World Health Organization (WHO) in 2011 (21). These are found in Appendix table A.1. Some of the values are not health-based due to the normally low concentrations found in drinking-water. However, as stated in the heavy metal and ion theory section, all heavy metals and most ions can be toxic in high enough concentrations. Values exceeding the WHO guidelines for drinking-water are marked with a light red color.

4.1 Current Situation

4.1.1 Field Parameters

In this section the field parameters such as pH, temperature, conductivity and salinity are presented for all sampling sites from the four studied rivers (see table 4.1). As evident from the table the field parameter values of the tributaries have a large effect on the subsequent sampling sites. For pH-values below 5,4, alkalinity has not been calculated, hence marked with a zero in table 4.1.

Figure 4.1 Efraín Blanco, Johan Lundström and Sara Eklund (from the left), measuring the field parameters at sampling site CABT1

Table 4.1 Field parameters from the four studied rivers

River	Sampling site	Date	TDS (mg/l)	Conductivity (mS/cm)	Spec. conductivity (ms/cm^2)	Temperature (°C)	pH	ORP (mV)	DO (mg/l)	Alkalinity (mg/l)
Antequera	BODI1*	2013-05-14	1934	3,87	2741	9,66	8,22	70	1,18	80,1
	TOTV2	2013-05-15	224	0,447	344	12,9	6,92	84	1,13	260
	TOTR1	2013-05-15	1698	3,40	2454	10,4	4,91	86	1,78	0
	TOTR2	2013-05-15	1733	3,47	2482	10,1	4,52	240	1,74	0
	AVR2	2013-05-15	1741	3,48	2491	10,0	4,27	436	1,73	0
	AVR1	2013-05-15	1360	2,72	1996	11,0	3,56	498	1,73	0
	CUCC1*	2013-05-15	110	0,219	167	12,4	7,78	45	2,38	200
	AVR3	2013-05-15	1092	2,18	1773	15,1	3,79	382	2,00	0
Urmiri	URR2	2013-05-14	131	0,263	183	9,02	8,66	150	1,21	400
	URR1	2013-05-14	148	0,296	207	9,25	9,06	170	1,34	460
	URC1	2013-05-14	931	1,86	1669	19,5	8,14	20	1,56	761
	URV1*	2013-05-14	672	1,34	1132	16,7	7,82	-50	0,00	1361
	URR3	2013-05-14	612	1,22	1018	16,2	8,35	75	1,94	681
Pazña	PAZR1	2013-05-14	929	1,86	1455	13,6	5,07	227	1,29	0
	PALR2	2013-05-14	964	1,93	1208	5,37	5,49	140	1,81	40,0
Poopó	CABT1	2013-05-14	135	0,270	180	7,48	8,18	178	0,81	280
	MAD1*	2013-05-14	6637	13,3	12440	21,7	2,53	386	0,17	0
	POR3	2013-05-14	3039	6,08	4885	14,7	8,43	106	0,92	440

*Tributary

4.1.2 Heavy metal and ion concentrations

In the tables below, all analyzed values for the heavy metals (table 4.2) and ions (table 4.3) are shown to give an overview of how the heavy metal concentrations vary along the four different rivers and how these values correspond to WHO guideline values for drinking water.

The Antequera River is to a great extent influenced by mining activities while the Urmiri River is mainly polluted by natural weathering. Comparing these rivers, a large difference between the concentrations of cadmium, iron, zinc and manganese can be seen (table 4.2).

Table 4.2 Heavy metal concentrations for the four rivers studied

		Unit:	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
		WHO guideline:	10	10	3	2000	2000	3000	400
River	**Sampling site**	**Date**	**As**	**Pb**	**Cd**	**Cu**	**Fe**	**Zn**	**Mn**
Antequera	BODI1*	2013-05-14	<5	<5	980	<100	23494	81500	4745
	TOTV2	2013-05-15	<5	<5	59	<100	127	423	<70
	TOTR1	2013-05-15	<5	<5	932	111	2174	122400	6880
	TOTR2	2013-05-15	9,29	9,01	936	494	8660	126761	6680
	AVR2	2013-05-15	929	9,43	791	1860	51130	119219	7614
	AVR1	2013-05-15	<5	<5	433	484	1051	55263	14250
	CUCC1*	2013-05-15	<5	<5	59	<100	143	57	<70
	AVR3	2013-05-15	<5	<5	381	423	444	95000	11832
Urmiri	URR2	2013-05-14	<5	<5	62	<100	131	45	<70
	URR1	2013-05-14	<5	<5	67	<100	132	46	107
	URC1	2013-05-14	<5	<5	57	<100	188	50	101
	URV1*	2013-05-14	<5	<5	56	<100	128	47	72
	URR3	2013-05-14	<5	<5	54	<100	127	47	<70
Pazña	PAZR1	2013-05-14	<5	6,04	305	302	277	29500	8100
	PALR2	2013-05-14	<5	<5	301	300	207	66897	8275
Poopó	CABT1	2013-05-14	<5	<5	<30	<100	173	79	<70
	MAD1*	2013-05-14	2458	618	10310	1790	3296000	1274000	17477
	POR3	2013-05-14	<5	<5	95	<100	179	2128	407

*Tributary

Table 4.3 Ion concentrations for the four rivers studied

		Unit:	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
		WHO guideline:	-	-	50	250	250	500 (hardness)		200	-
River	**Sampling site**	**Date**	**CO3**	**HCO3**	**NO3**	**SO4**	**Cl**	**Ca**	**Mg**	**Na**	**K**
Antequera	BODI1*	2013-05-14	0,626	78,8	384	2600	159	982	22,8	94,6	14,8
	TOTV2	2013-05-15	0,104	260	6,7**	160	56,0	42,6	13,3	33,6	4,52
	TOTR1	2013-05-15	0	0	182	2310	134	753	26,8	78,6	13,6
	TOTR2	2013-05-15	0	0	154	2380	135	741	28,4	81,4	10,5
	AVR2	2013-05-15	0	0	210	2520	135	689	30,0	80,6	11,1
	AVR1	2013-05-15	0	0	1054	1666	111	458	31,2	65,6	10,1
	CUCC1*	2013-05-15	0,574	199	-	58	17,8	17,9	7,40	9,70	3,11
	AVR3	2013-05-15	0	0	165	1386	98,6	369	16,2	59,0	8,32
Urmiri	URR2	2013-05-14	8,39	384	0,0**	47,0	16,8	23,9	11,3	9,10	2,92
	URR1	2013-05-14	22,8	415	0,1**	54,0	46,7	28,0	10,7	27,8	4,11
	URC1	2013-05-14	4,96	751	12,4	48,0	512	48,4	11,4	314	29,5
	URV1*	2013-05-14	4,28	1353	3,8	80,0	469	34,6	19,0	297	11,4
	URR3	2013-05-14	7,14	666	8,2	47,0	335	42,2	10,0	204	20,9
Pazña	PAZR1	2013-05-14	0	0	91,2	969	200	259	30,0	122	13,2
	PALR2	2013-05-14	0	40,0	14,6	972	268	258	28,0	165	13,5
Poopó	CABT1	2013-05-14	2,00	276	1,08	49,0	51,5	21,3	8,00	31,1	4,10
	MAD1*	2013-05-14	0	0	1066	9100	3222	261	185	2030	96,0
	POR3	2013-05-14	5,53	429	4,2	342	6107	122	20,7	3920	59,2

** Analyzed through ion chromatography

* Tributary stream

The heavy metal that most often exceeds the WHO guideline values for drinking-water is cadmium (table 4.2). The WHO value for cadmium is health-based. The sampling site with the highest heavy metal concentrations is MAD1 which also reflects on the subsequent sampling point POR3. Iron, zinc and manganese vary greatly from one sampling point to the next. Similar patterns are seen for ions in table 4.3. Sulfate is the ion that most often exceeds WHO guideline values. However, nitrate is the only ion that has health-based guideline values. Nitrate also exceeds these guideline values at many sampling sites.

In the following two sections, graphs with the analyzed values from Antequera River and Urmiri River are presented, starting with ion concentrations. The heavy metals are plotted and commented after the ion concentrations. Due to the few sampling sites, values from Poopó River and Pazña River are not included. Only ion and heavy metal concentrations exceeding the health-based WHO guideline values for drinking-water are presented (for the others, see Appendix B). These guideline values are denoted by a light green dashed line in the figures, called 'WHO limit'. Nitrate is the only ion that has a WHO health-based guideline value. The heavy metals that have health-based guideline values are copper, arsenic, lead and cadmium. The other ions and heavy metals are normally not of health concern at levels found in drinking-water but may however according to WHO "affect acceptability of drinking-water" (21). See Appendix A.1 for more information.

Antequera River

In the following figures, the ion and heavy metal concentrations of Antequera River are shown. Graphs for nitrate (figure 4.3), cadmium (figure 4.4), and arsenic (figure 4.5) are presented. While the nitrate concentration is just above WHO guideline values with the exception of the peak at AVR1, the arsenic concentration is constantly below the WHO guideline values except for the sampling site right before AVR1, namely AVR2. The cadmium content rises dramatically from TOTV2 to TOTR1 to peak at TOTR2 (fig. 4.4).

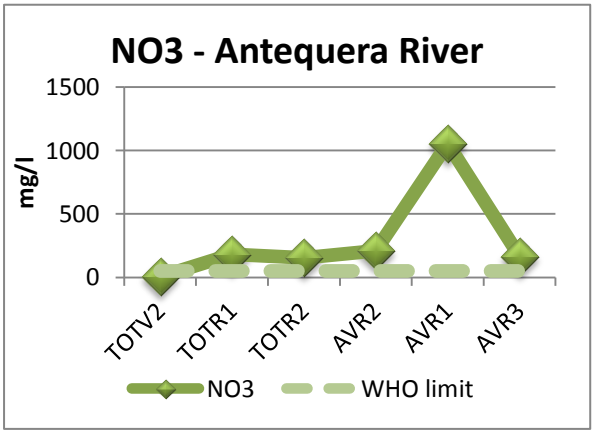

Figure 4.3 NO3 concentration along Antequera River

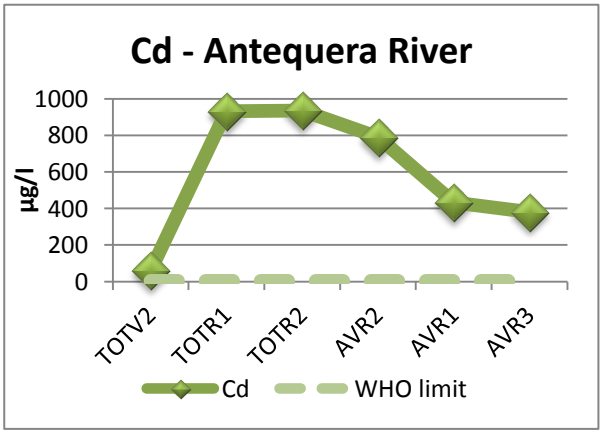

Figure 4.4 Cd concentration along Antequera River

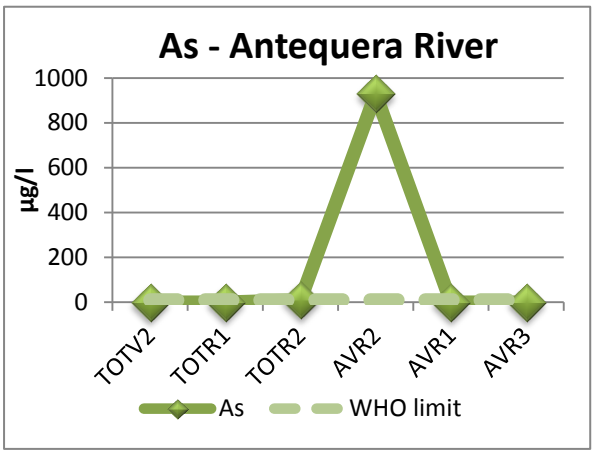

Figure 4.5 As concentration along Antequera River

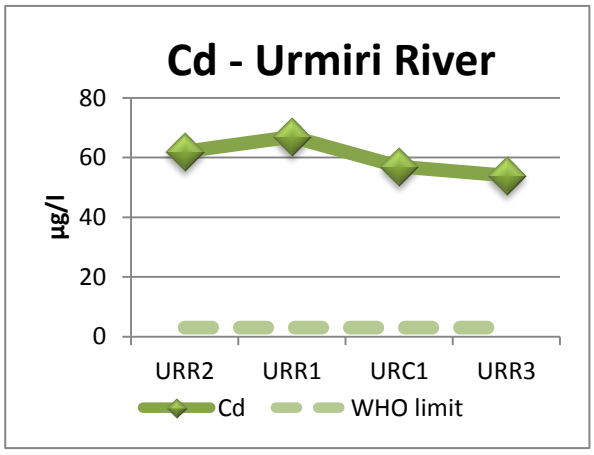

Figure 4.6 Cd concentration along Urmiri River

Urmiri River

Regarding the heavy metals and ions in Urmiri River, only cadmium (figure 4.6) exceeds the WHO health-based guideline values. In figure 4.7, a comparison has been made between Urmiri River and Antequera River regarding the cadmium concentration. The cadmium content of Urmiri River is relatively unchanged (it varies between around 67 to 54 µg/l of cadmium). For the Antequera River the concentration varies approximately from a starting value of 59 µg/ via a maximum value of 936 µg/l to a final value of 433 µg/l.

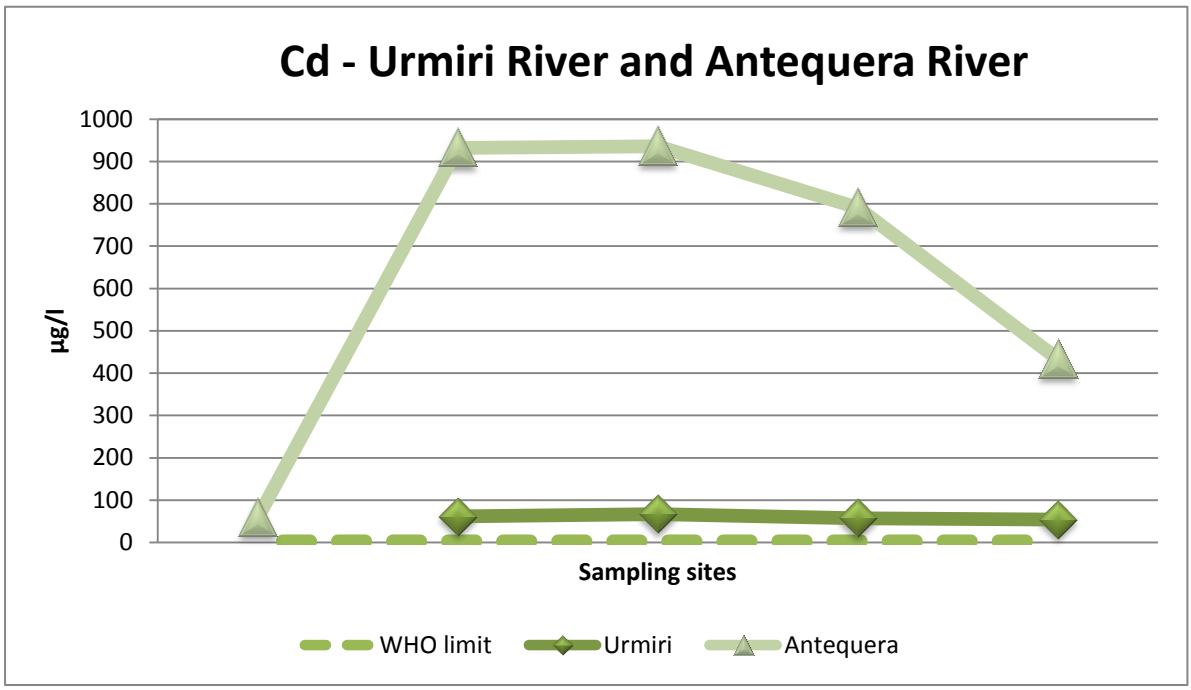

Figure 4.7 Cd concentration along Urmiri River (dark green, squares) and Antequera River (light green, triangles)

4.2 Historical Situation

In the following section, data of heavy metals from previous studies for dry period are presented in graphs. However, similar to the analysis of current situation, only heavy metals of concentrations exceeding the health-based WHO guideline values are presented in graphs. Analyzed values from the same sampling site are shown together in order to compare data over time. The five sampling sites with the largest amount of previous data are shown and compared in graphs following the tables. In some graphs, the extreme values of arsenic concentration for study 19 had to be excluded so as to provide a good overview in the graphs. All heavy metal concentrations for dry period are shown in one table. In Appendix C, values for heavy metals and ion concentrations as well as parameter values from all the compared studies for all the sampling sites are shown (including data for wet period).

In table 4.4 below, the historic concentrations of heavy metals for the four studied rivers are presented together with the data from the current study. The pink filled values exceed the WHO guideline values for drinking-water.

Table 4.4 Historic heavy metal concentrations for the four rivers studied

			Unit:	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
		WHO guideline value:		10	10	3	2000	2000	3000	400
River	**Sampling site**	**Study**	**Date**	**As**	**Pb**	**Cd**	**Cu**	**Fe**	**Zn**	**Mn**
Antequera	BODI1*	17	Jun. 2007	<5	<5	53	<0,2	<100	2195	-
		19	Sep. 2007	17510	432	492	28	36020	103800	-
		10	Aug. 2008	<5	<5	-	-	131	73	<100
		13	May. 2009	<5	24,9	1 082 000	142	176000	187500	11700
		16	Jun. 2013	<5	<5	980	58	23494	81500	4745
	TOTV2	10	Aug. 2008	9,2	<5	-	-	122	295	<100
		13	May. 2009	<5	<5	-	-	<100	869	<100
		16	Jun. 2013	<5	<5	59	29	127	423	59
	TOTR1	17	Jun. 2007	8,96	9,38	398	52	1881	84200	-
		19	Sep. 2007	5866	442	1123	247	46720	237000	-
		10	Aug. 2008	<5	<5	627	100	170	114800	4550
		13	May. 2009	<5	7,67	1662	399	610	319000	16325
		16	Jun. 2013	<5	<5	932	111	2174	122400	6880
	TOTR2	10	Aug. 2008	<5	<5	616	121	240	125400	5400
		13	May. 2009	<5	6,52	1560	374	2030	273000	15425
		16	Jun. 2013	9,29	9,01	936	494	8660	126761	6680
	AVR2	19	Sep. 2007	6591	36,1	822	761	71950	198000	-
		10	Aug. 2008	655	5,9	547	906	67250	160000	8900
		13	May. 2009	351	8,60	1003	1512	126400	118750	13625
		16	Jun. 2013	929	9,43	791	1860	51130	119219	7614

			Unit:	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
			WHO guideline:	10	10	3	2000	2000	3000	400
	Sampling site	Study	Date	As	Pb	Cd	Cu	Fe	Zn	Mn
	AVR1	17	Jun. 2007	<5	<5	499	1365	3829	129000	-
		19	Sep. 2007	18100	503	524	781	3290	139200	-
		10	Aug. 2008	<5	<5	554	550	8975	179000	13950
		13	May. 2009	<5	<5	622	622	3675	145000	19600
		7	Jul. 2009	19,7	<2,30	477	614	4202	284325	-
		7	Sep. 2009	14,5	<2,30	604	701	4333	122691	-
		7	Oct. 2009	6,57	16,4	476	680	5461	120860	-
		16	Jun. 2013	<5	<5	433	484	1051	55263	14250
	CUCC1*	10	Aug. 2008	5,3	<5	-	-	167	<30	<100
		13	May. 2009	12,2	<5	-	-	<100	105	<100
		7	Jul. 2009	23,9	<2,30	0,979	1,79	1,79	21,6	-
		16	Jun. 2013	<5	<5	59	38	143	57	64
	AVR3	17	Jun. 2007	78,6	<5	648	1011	114750	172000	-
		10	Aug. 2008	<5	<5	478	490	5550	155500	13800
		13	May. 2009	<5	<5	431	447	1285	194750	12500
		16	Jun. 2013	<5	<5	381	423	444	95000	11832
Urmiri	URR2	10	Aug. 2008	<5	<5	-	-	105	<30	<100
		13	May. 2009	<5	<5	-	-	<100	26,0	<100
		16	Jun. 2013	<5	<5	62	34	131	45	61
	URR1	17	Jun. 2007	<5	<5	<1,2	0,949	<100	<30	-
		19	Sep. 2007	7458	<5	<1,2	38	<100	<30	-
		10	Aug. 2008	5,40	<5	-	-	<100	<30	<100
		13	May. 2009	9,86	<5	-	-	<100	<30	<100
		16	Jun. 2013	<5	<5	67	27	132	46	107

	Sampling site	Study	Date	As	Pb	Cd	Cu	Fe	Zn	Mn
	URC1	19	Sep. 2007	10640	465	<1,2	27	<100	<30	-
		10	Aug. 2008	<5	<5	-	-	<100	<30	164
		13	May 2009	<5	<5	-	-	<100	<30	<100
		16	Jun. 2013	<5	<5	57	23	188	50	101
	URV1*	13	May. 2009	<5	<5	-	-	<100	<30	<100
		16	Jun. 2013	<5	<5	56	23	128	47	72
	URR3	17	Jun. 2007	<5	<5	<1,2	1,34	<100	<30	-
		10	Aug. 2008	<5	<5	-	-	<100	<30	<100
		13	May. 2009	<5	<5	-	-	<100	<30	<100
		16	Jun. 2013	<5	<5	54	24	127	47	66
Pazña	PAZR1	1	Jul. 2001	<10	<10	171	-	297	4173	-
		2	Oct. 2001	203	18,8	497	-	7	17,1	-
		5	Aug. 2003	171	154	192	-	1,9	282600	-
		17	Jun. 2007	<5	291	306	347	1337	80200	-
		19	Sep. 2007	17670	<5	348	405	677	92200	-
		10	Aug. 2008	<5	<5	456	467	349	120600	11600
		15	Sep. 2008	<5	<5	478	535	1450	103200	19550
		13	May. 2009	5,75	<5	334	317	205	87400	10000
		7	Sep. 2009	20,5	13,8	486	532	1578	107738	-
		7	Oct. 2009	29,3	<2,30	457	435	809	101984	-
		16	Jun. 2013	<5	6,04	305	302	277	29500	8100
	PALR2	10	Aug. 2008	17,9	5,25	392	389	506	106000	10150
		13	May. 2009	16,7	<5	309	288	413	1412500	9200
		16	Jun. 2013	<5	<5	301	300	207	66897	8275

			Unit:	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
			WHO guideline:	10	10	3	2000	2000	3000	400
River	**Sampling site**	**Study**	**Date**	**As**	**Pb**	**Cd**	**Cu**	**Fe**	**Zn**	**Mn**
Poopó	CABT1	17	Jun. 2007	<5	308	<1,2	1,01	<100	<30	-
		7	Jul. 2009	6,19	<2,30	<0,459	1,29	9,56	52,8	-
		7	Sep. 2009	14,8	<2,30	1,13	4,93	276	11,7	-
		7	Oct. 2009	5,6	19,9	1,62	5,14	4,68	47,9	-
		16	Jun. 2013	<5	<5	4,1	31	173	79	59
	MAD1*	17	Jun. 2007	6,80	355	34	15,0	67050	2020	-
		7	Jul. 2009	27,6	<2,30	10,7	6,89	5045	929	-
		7	Sep. 2009	16,9	2,93	11,8	10,6	35389	843	-
		7	Oct. 2009	43,3	23,5	7,27	10,2	27684	777	-
		16	Jun. 2013	2458	618	10310	1790	3296000	1274000	17477
	POR3	1	Jul. 2001	2074	<10	-	-	-	109	-
		2	Oct. 2001	4667	10,0	<10	-	957	133	-
		5	Aug. 2003	11140	157	78,4	-	19,6	43,8	-
		6	Oct. 2006	5508	177	39	-	145	-	-
		17	Jun. 2007	<5	307	22	10,0	333	207	-
		10	Aug. 2008	20	5,7	-	-	196	80	<100
		7	Jul. 2009	34,9	<2,30	4,38	4,98	143	168	-
		7	Sep. 2009	17,0	11,9	8,79	11,5	561	195	-
		7	Oct. 2009	33,5	15,6	2,96	10,4	11,8	55,5	-
		16	Jun. 2013	<5	<5	95	29	179	2128	407

4.2.1 POR3

In figure 4.8 (cadmium), 4.9 (arsenic), and 4.10 (lead), heavy metal concentrations exceeding the health-based WHO guideline values for drinking water are shown. For cadmium, there is a peak concentration of cadmium in August 2003, where after the concentration drops to finally have an ultimate peak in June 2013 (fig. 4.8). Arsenic increases up until August 2003 where a peak is seen (fig. 4.9). After this point, the arsenic concentration decreases to finally stay around the WHO guideline value. The lead concentration shows a peak in June 2007 where after it decreases to concentrations close to WHO guideline values (fig. 4.10).

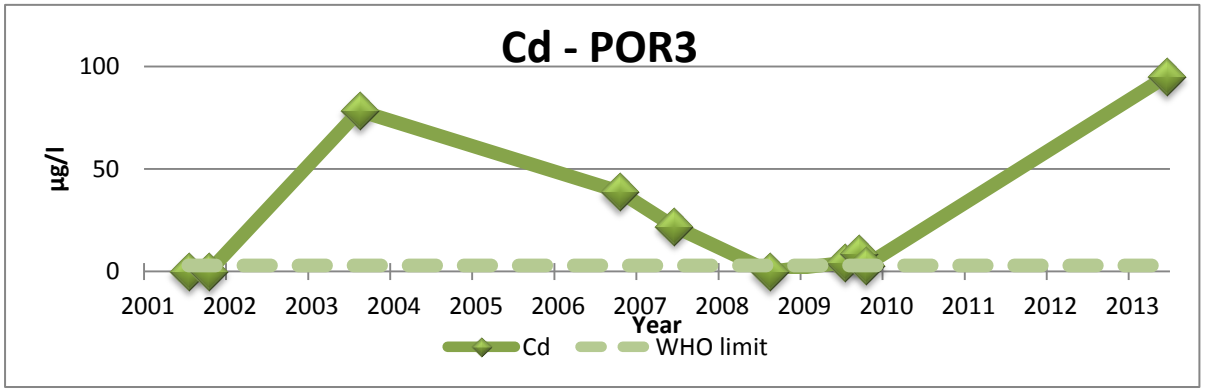

Figure 4.8 Historic Cd concentrations at sampling site POR3

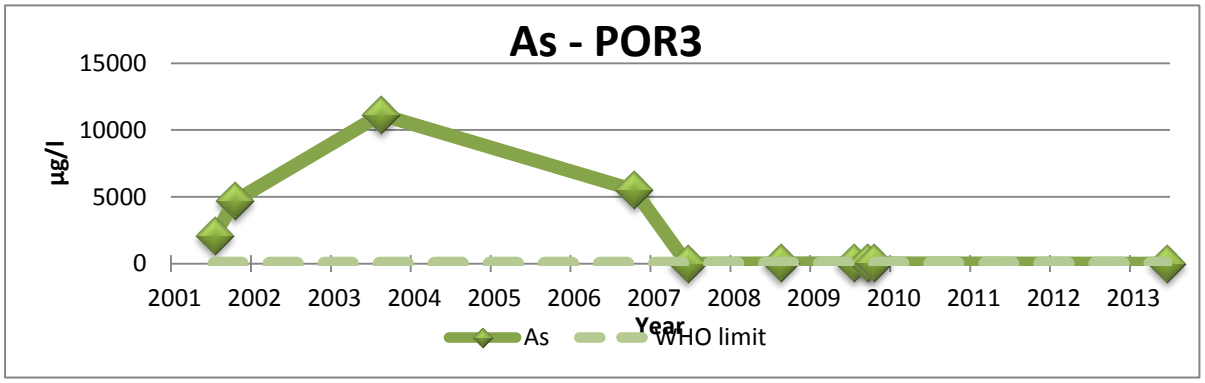

Figure 4.9 Historic As concentrations at sampling site POR3

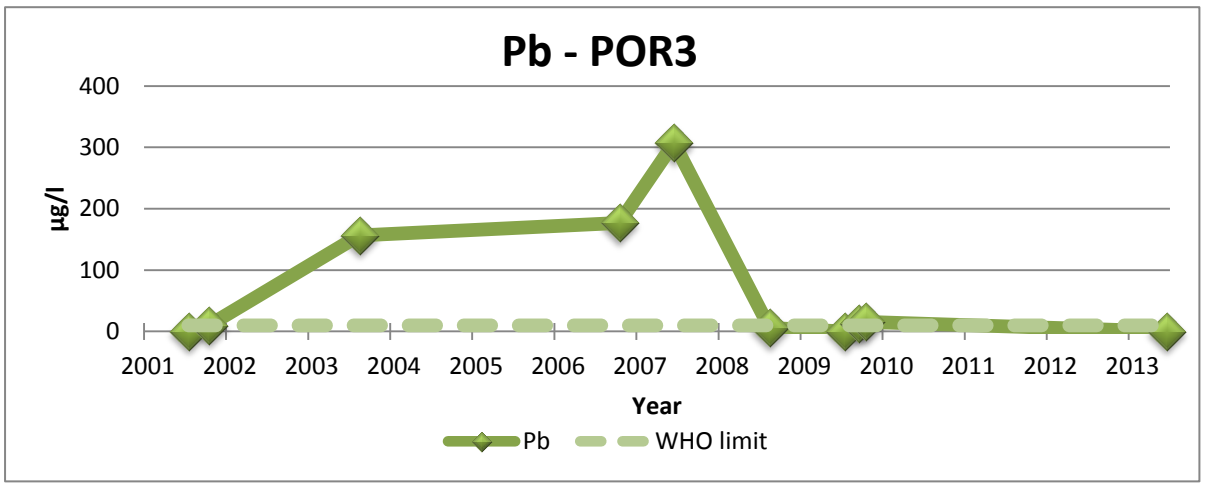

Figure 4.10 Historic Pb concentrations at sampling site POR3

4.2.2 PAZR1

Graphs showing heavy metal concentrations for PAZR1 are shown below. Concentrations for lead are found in figure 4.11, for cadmium in figure 4.12, and for arsenic in figure 4.13. For lead, the concentration rises up to a peak in June 2007 whereafter it decreases to levels close to WHO guidelines values (fig. 4.11). The cadmium concentration varies greatly, in an interval of around 170 to 500 µg/l, but is constantly more than 55 times greater than the WHO guideline values (fig. 4.12). The arsenic concentration peaks in October 2001 at approximately 200 µg/l, whereafter it decreases to levels around WHO guideline values (fig. 4.13).

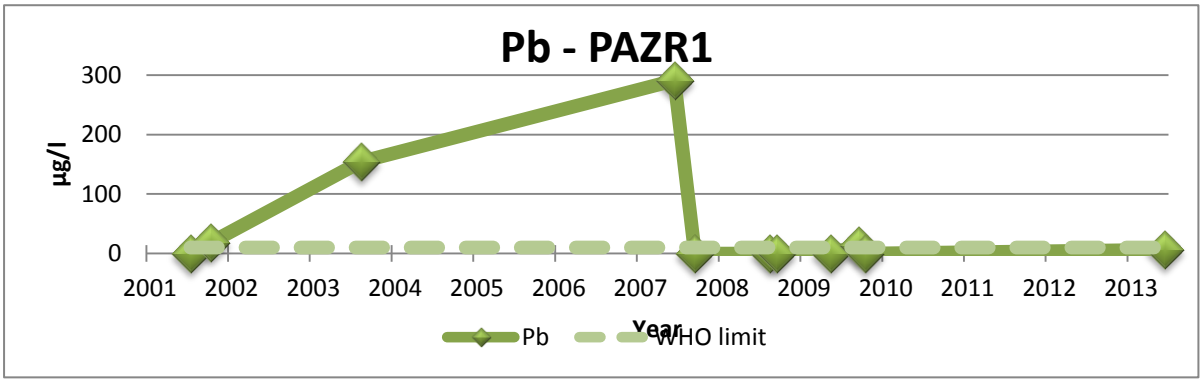

Figure 4.11 Historic Pb concentrations at sampling site PAZR1

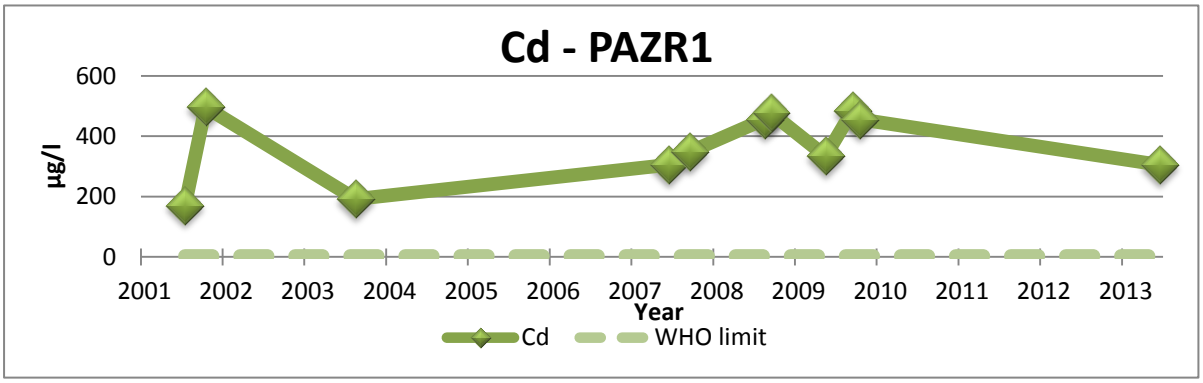

Figure 4.12 Historic Cd concentrations at sampling site PAZR1

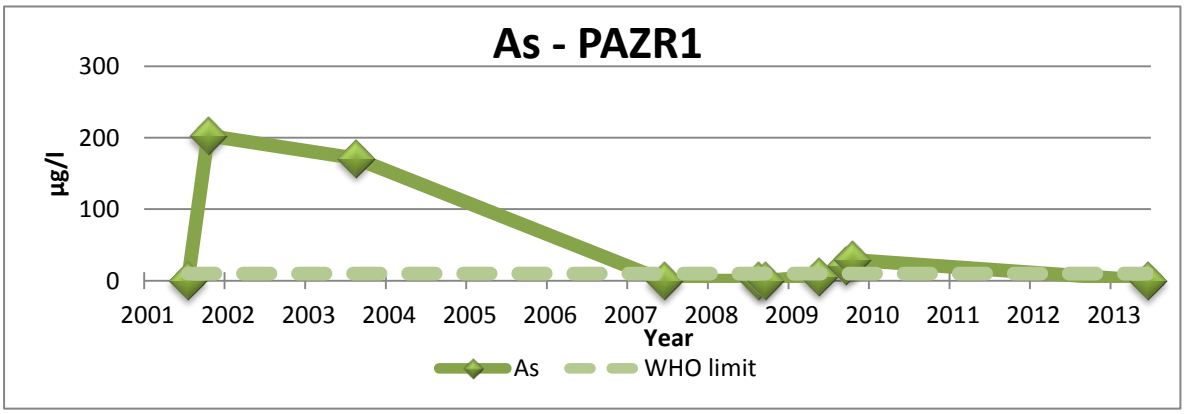

Figure 4.13 Historic As concentrations at sampling site PAZR1, excluding extreme value from study 19

4.2.3 AVR1

In figure 4.14, 4.15, and 4.16, graphs for heavy metals lead, arsenic and cadmium are shown for sampling site AVR1. The lead concentration (fig. 4.14) is constantly close to WHO guideline values except from in September 2007. The arsenic levels (fig. 4.15) peak in 2009 with values above WHO guideline values, but is in June 2013 below the detection limit of 10 µg/l. Cadmium concentrations (fig. 4.16) is constantly more than 140 times above the WHO guideline values for drinking water and varies within an interval of around 620 to 430 µg/l.

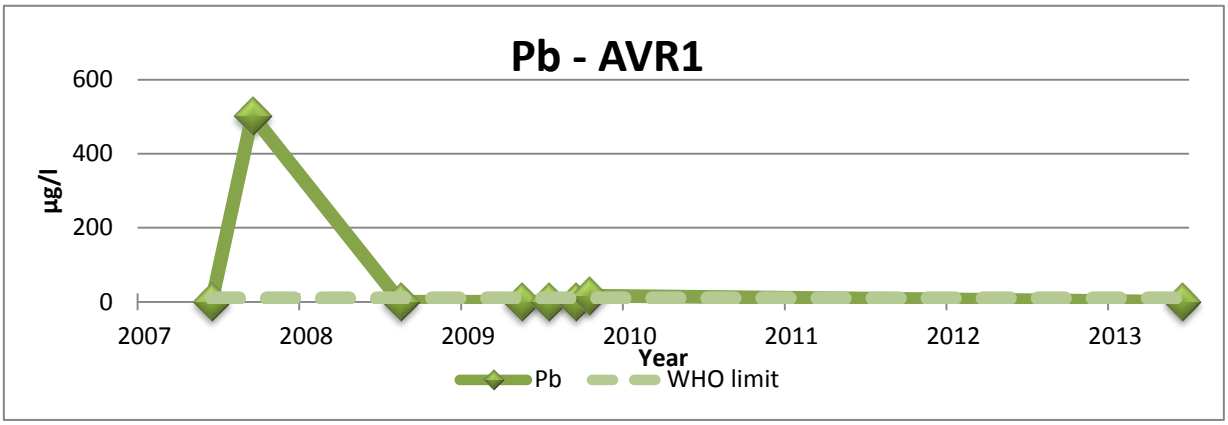

Figure 4.14 Historic Pb concentrations at sampling site AVR1

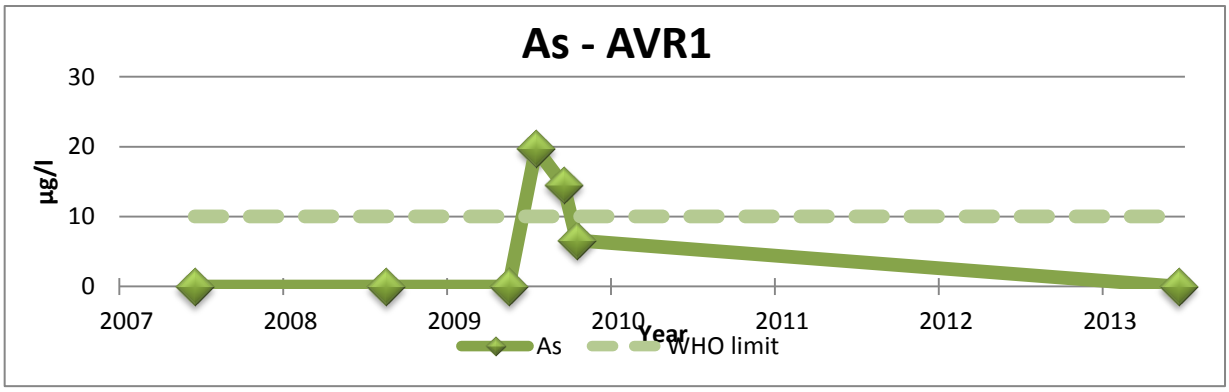

Figure 4.15 Historic As concentrations at sampling site AVR1

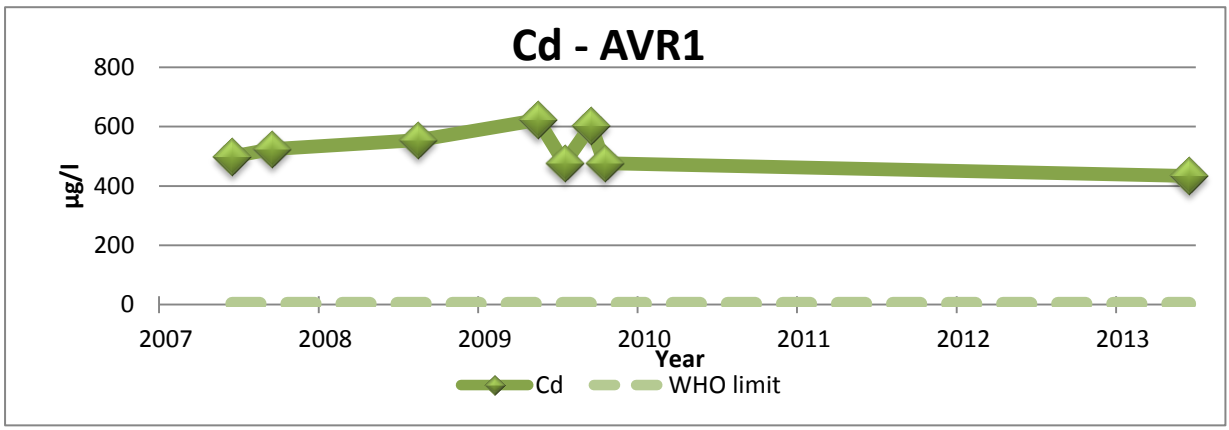

Figure 4.16 Historic Cd concentrations at sampling site AVR1

4.2.4 CABT1 & MAD1

In this chapter, graphs comparing historical data from sampling site CABT1 and MAD1 are presented. Graph lines ending without reaching a specific point data value (such as in figure 4.17 and 4.19) means that the next value is many times higher and does not fit in the graph. In figure 4.17 the arsenic concentrations are plotted, in figure 4.18 the lead concentrations, and in 4.19 the cadmium concentrations. The arsenic concentrations of CABT1 and MAD1 follow a similar pattern up to September 2009 where the arsenic concentration of MAD1 increases dramatically to 2458 µg/l in June 2013 (not seen in graph). The lead concentrations in CABT1 and MAD1 are similar until June 2013 where the concentration at MAD1 peaks around 620 µg/l while for CABT1 the concentration is below detection limit. For cadmium (fig. 4.19), the concentrations at the two sampling sites are almost the same in 2009 but higher for MAD1 in June 2007. After 2009, the cadmium concentration at MAD1 increases to 10310 µg/l in June 2013, over 3400 times above the WHO guideline value for drinking water, while the concentration at CABT1 at the same time is just above the WHO guideline value.

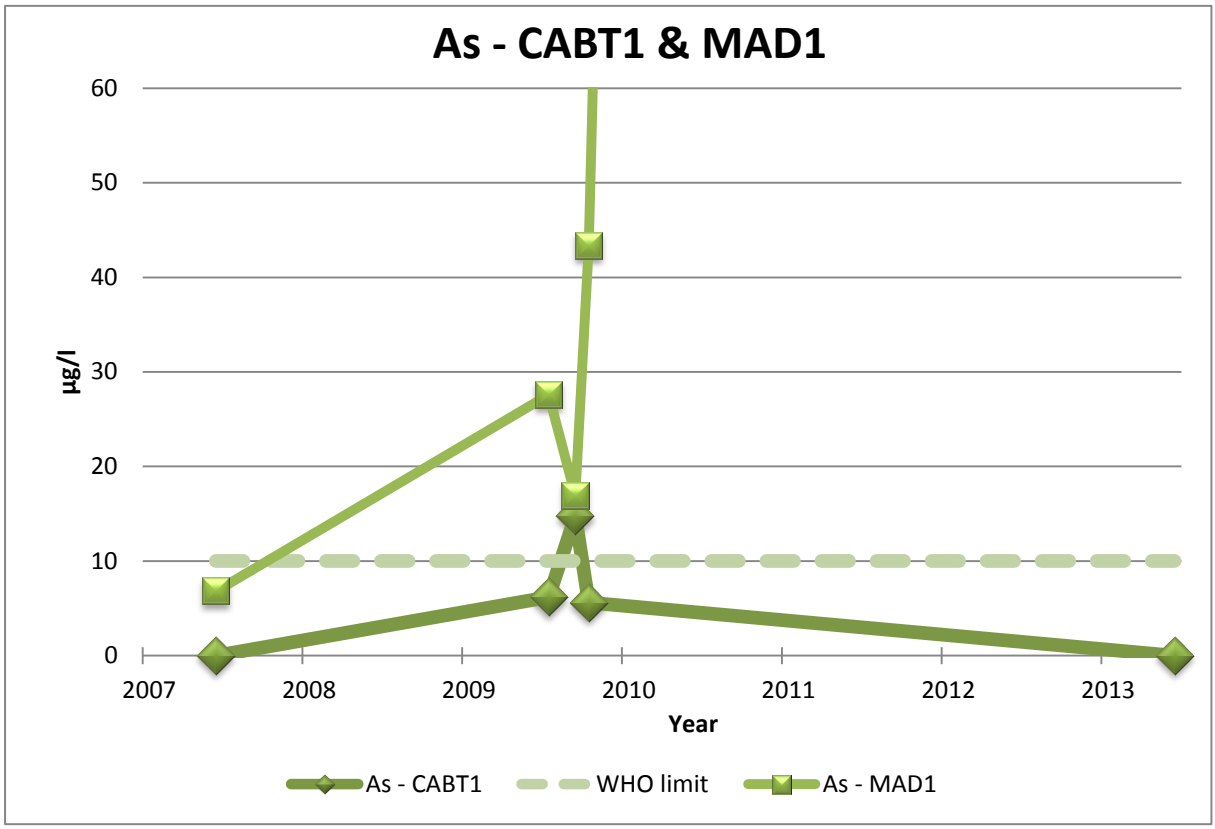

Figure 4.17 Historic As concentrations at sampling sites CABT1 & MAD1

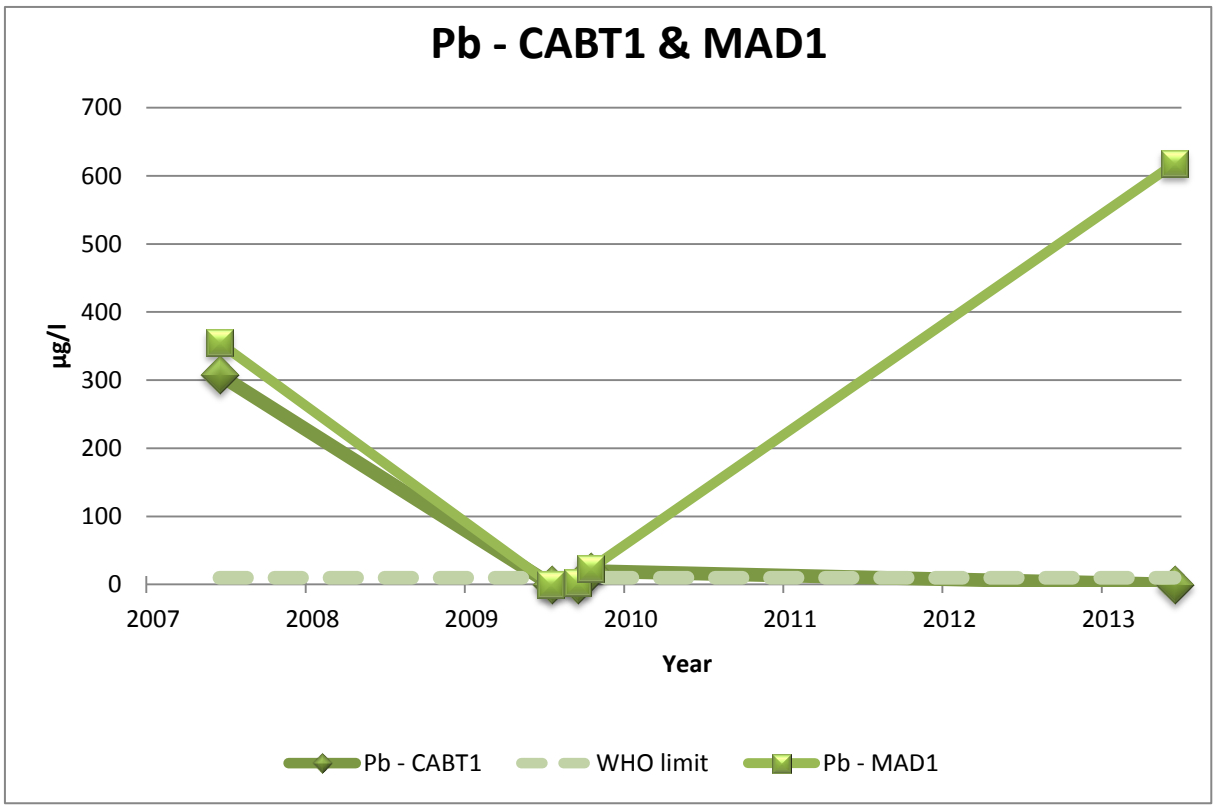

Figure 4.18 Historic Pb concentrations at sampling sites CABT1 & MAD1

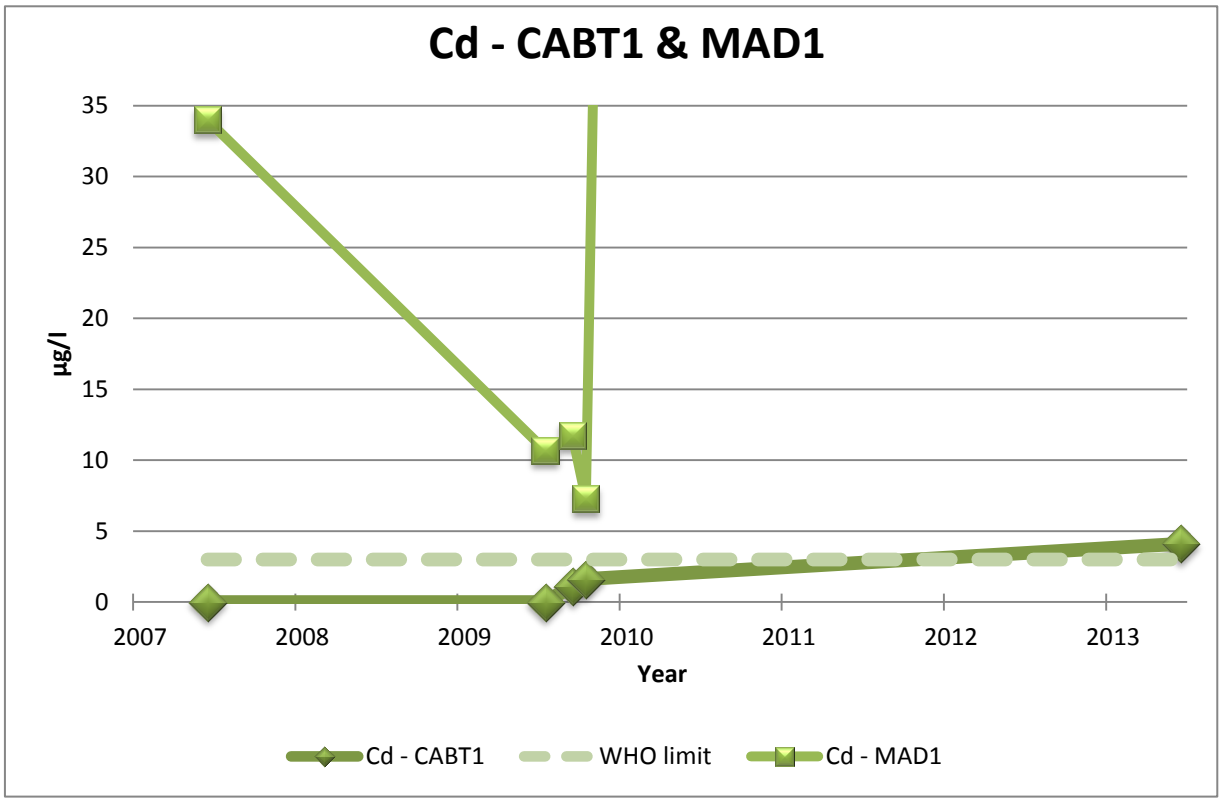

Figure 4.19 Historic Cd concentrations at sampling sites CABT1 & MAD1

5 Discussion

5.1 Current Situation

5.1.1 Antequera River

The water quality of the Antequera River is poor. Nitrate, cadmium and arsenic exceed WHO health-based guideline values for drinking-water. Comparing the graphs for nitrate and arsenic, a particularly interesting sampling site is AVR2. As described, AVR2 is situated downstream the highly contaminated TOTR2, which is surrounded by tailings. The drainage from tailings and mines is the greatest environmental hazard of mining. This might explain the concentration peak of arsenic at AVR2. Interestingly, the arsenic concentration at the next sampling site, AVR1, is significantly lower despite the vast input of arsenic to the Antequera River at AVR2. The decrease of arsenic concentration may be explained by the drop in pH (by 0,71) taking place between the sampling sites. The arsenic concentration determination is also highly dependent on the oxygen reduction potential (ORP) of the water. In the Antequera River the ORP is increasing downstream, potentially leading to a decrease of measured arsenic concentrations as the heavy metal binds to iron and precipitates, ending up as part of the sediment. The hypothesis that the drop in arsenic concentration after AVR2 is explained by pH is strengthened by the fact that the iron concentration at AVR1 also has decreased severely. This would suggest that an arsenic-iron precipitation and sedimentation has taken place.

Meanwhile, nitrate seems to have its peak at AVR1. This could be due to a delay in the system. Normally concentrations of nitrate are low but may increase due to anthropogenic activities. There are several villages in the basin of the Antequera River from which waste water and use of fertilizers may pollute the Antequera River.

Cadmium most probably originates from the mine waste water influenced BODI1, where cadmium concentrations are over 320 times higher than the WHO guideline value. The anthropogenic sources of cadmium are in general 2,6 times greater than the natural. The reason why cadmium peaks at TOTR1 and not at TOTV2, the sampling site right after BODI1, might be because of a decrease in pH that increases solubility of cadmium. The pH decreases from pH 6,92 at TOTV2 to 4,91 at TOTR1. The severe drop of pH from sampling site TOTV2 to TOTR1 might also explain the low concentrations of zinc, manganese, iron and cadmium at TOTV2. A high pH decreases solubility of these heavy metals. Meanwhile, BODI1 has an even higher pH than TOTV2 but still shows high concentrations of heavy metals. This is probably explained by the extreme amount of heavy metals leaking from the mine at that sampling site. Cadmium shows a constant decrease downstream in the river, implying that no large sources leak cadmium into the river. Tributary CUCC1, not influenced by any major mining activities and characterized by low ion and heavy metal concentrations, seem to dilute the contaminants after its inflow right after AVR1.

5.1.2 Urmiri River

Urmiri River undergoes a rapid change of conductivity after sampling point URR1. This is probably due to underground thermal water that blends with the river once the river starts to flow underground (after URR1). Accordingly, the temperature of URC1, the following sample point, is about 10°C higher than at URR1. Chloride and sodium concentrations also peak at URC1, further strengthening the hypothesis of thermal water leaking into the river. Thermal springs may, accordingly, be an important source of chloride. Regarding cadmium, the concentrations are above the WHO guideline values but are at the same time relatively constant throughout the river. This fact, added to the knowledge that no major mining activity is taking place in the area, to a large degree proves that is can be assumed that this cadmium mostly originates from natural leakage from the surrounding bedrock.

5.1.3 Pazña and Poopó Rivers

Pazña River has two sampling sites and Poopó River has three sampling sites, where one is from a tributary stream. Therefore no graphs were made for these rivers. Instead all results are shown in the tables 4.1, 4.2, 4.3 and in Appendix B. The tributary stream with the sampling point MAD1 has great influence on the water in Poopó River. The tributary stream enters between the points CABT1 and POR3 and when comparing the analyzed values for both heavy metals and ions in these points, it is clear that MAD1 is the main reason for the increased values in POR3. The concentration values for MAD1 are extremely high and all the heavy metals except for copper vastly exceed the WHO guideline values for drinking-water. Especially the concentration for lead is very high at sampling site MAD1.

The Pazña River is a junction river of the Urmiri and Antequera rivers. This can be seen when comparing the results. The concentrations of heavy metals and ions in Pazña River are almost the average values between Urmiri and Antequera River. Urmiri River has high pH and is a relatively non-contaminated river whilst Antequera River has low pH with both ions and heavy metals exceeding the WHO guideline values. Pazña River has a higher pH than Antequera River but also a significantly lower pH than Urmiri River. Pazña River has higher values for ions and heavy metals than Urmiri, but not as high as the values for Antequera.

5.1.4 Summary

Assuming that the bedrock in Urmiri River basin is similar to the bedrock of Antequera River basin, characteristics of Urmiri River can in general be used as a measure of the natural contamination of heavy metals in the area. This comparison, seen in figure 4.7, strengthens the hypothesis of a major anthropological contamination of Antequera River basin due to mining activities. This is especially clear regarding cadmium, where Antequera River is characterized by concentrations more than 300 times above the WHO guideline values for

drinking-water, while the more natural levels (seen in Urmiri River) are 20 times above WHO guidelines. Accordingly, cadmium is found in low concentrations in soils and rocks and even though weathering and erosion increase the levels of cadmium, the anthropogenic sources are generally 2,6 times greater.

Meanwhile, the arsenic contamination is probably underestimated for the area since the solubility of arsenic decreases with lower pH, which is especially clear for Antequera River and Pazña River with pH levels as low as 3,65. The arsenic and lead concentrations are especially elevated in Antequera River and at sampling site MAD1. However the cadmium concentration exceed the WHO guideline values at all but one sampling site and is vastly elevated in the mine influenced rivers Antequera and Pazña.

The same pattern can be seen for the heavy metals iron, zinc and manganese. Manganese and zinc both exceed the WHO guideline values at most sampling sites in the rivers Antequera and Pazña as well as at the sampling site MAD1. Iron concentrations do not exceed WHO guideline values in Pazña River, but they do in both Antequera River and at sampling site MAD1. The solubility of zinc is closely connected to pH, just as for arsenic. In Antequera River, the pH drops under 5 downstream from the sampling site TOTR1, whereby the solubility of zinc increases and starts to leach from the bedrock. This could explain the extremely high zinc concentrations in Antequera River. Regarding the ions, nitrate and sulfate seems to be the most important contaminants that the anthropological activities contribute with.

Figure 5.1 Urmiri village in the Urmiri River basin

5.2 Historical Situation

Many historical concentration values exceed the WHO guideline values for drinking-water, especially the values for Antequera River. There, cadmium, iron, zinc and manganese exceed the WHO guideline values almost in every study for every sampling site. The opposite can be seen for the values from the Urmiri River. There, the values almost never exceed the WHO guideline values except for a few times for cadmium and arsenic as well as for one time for lead. This corresponds to the conclusion regarding the current situation, namely that no large mines pollute the Urmiri River, as is the case for the Antequera River. As a result, the drainage from the tailings and mines lead to constantly elevated concentrations of heavy metals especially in the Antequera River. Not only do the mining activities contribute to drainage high in heavy metals, they also contribute to ARD. This further elevates the concentrations of ions and heavy metals by exposing rock to oxidization. The Pazña River is a mixture of water from the Urmiri and Antequera Rivers. Accordingly, many values in the Pazña River exceed the WHO guideline values but not near as much as the values in the Antequera River. Many values from the Poopó River also exceed the WHO guideline values, especially for arsenic, lead and cadmium. However, when studying table 4.4 the highest values can be found from sampling sites POR3 and especially MAD1, downstream the less polluted CABT1. This indicates that the tributary MAD1 pollutes the Poopó River. The same indication was given by the current situation analysis. A clear trend is the constantly high

concentrations of cadmium vastly exceeding the WHO guideline value in all four rivers. The cadmium concentrations seem to be neither increasing nor decreasing up to present date, which is true for almost all sampling sites and rivers. Sampling site MAD1 does not follow this pattern but instead has extremely elevated arsenic and lead concentrations up to present date. This could be explained by the fact that MAD1 is situated directly at a mine waste outlet from which the contamination has not been decreased. Cadmium is very toxic to humans and has a half-life of 16-33 years and may therefore accumulate in the organs during a long time. It may also cause the Itai-itai disease which weakens the bones and causes great pain to the victim. Eventually it can cause death due to kidney failure.

From section 4.2.1 to section 4.2.4, graphs further show how the heavy metal concentrations vary over time in the sampling sites POR3, PAZR1, AVR1 and well as CABT1 and MAD1. For sampling sites PAZR1 and POR3, where the data sampling starts as early as 2001, the arsenic and lead concentrations are high above the WHO guideline values until June 2007. Thereafter the levels seem to have stabilized close to or under the WHO guideline values. The sampling point AVR1 has not been studied as long as POR3 or PAZR1 and only has data values from 2007 and onward. At AVR1 the concentrations for lead and arsenic stay below or near the WHO guideline values except for one peak for each heavy metal. There is a strong connection between pH, ORP and the arsenic and lead concentrations. Even though no clear trends can be seen regarding the pH, the ORP in for example POR3 show an increasing trend. Since arsenic binds to iron and precipitates to the sediment under aerobic conditions (high ORP), this indicates that the measured arsenic concentrations in POR3 would show a decreasing trend. Even though the correlation is not entirely accurate, figure 4.9 indicates that it might be of importance since arsenic levels are truly decreasing. Meanwhile, lead is a common heavy metal found in low concentrations in soils and rocks. Lead often forms carbonate or chloride complexes but also binds to organic compounds, especially in acidic soils. The reason why the lead concentrations decrease in AVR1 and PAZR1 could theoretically be a pH decrease which would make the lead bind to organic compounds in the sediment. However, no clear pH decrease can be seen during the studied time period; in fact, the pH for AVR1 and PAZR1 is actually higher in the data from June 2013 than in any other data sets. An increase in pH normally means an increase of arsenic concentration due to increased mobility. Yet the arsenic concentration decreases almost in the same way as the concentration of lead decreases. It is clear that pH is not the only factor affecting the heavy metal concentrations. For example, different minerals such as manganese and clay particles can absorb arsenic. The extremely high values of manganese in sampling sites AVR1, PAZR1 and MAD1, combined with relatively low concentration of arsenic, indicate that manganese absorption of arsenic may have occurred.

No graphs have been made for zinc, iron and manganese. Table 4.4 clearly shows that these concentrations greatly exceed the WHO guidelines, especially in rivers influenced by mining such as the Antequera and Pazña River. The concentrations in these rivers constitute an environmental as well as a health-threat due to the extremely high levels.

5.3 Review of Results

Estimation of anion concentrations (sulfate, nitrate, chloride) was first analyzed with chromatography at first without dilution of the samples. Thereafter dilutions were made to a different extent depending on how much the specific anion concentration exceeded the maximum quantification limit. However, as the samples were severely contaminated it was discovered that cross-contamination took place between different analyses. This led to the need for alternative quantification methods for the anions for the majority of samples. Had the anion concentrations in the samples been approximated through previous sampling data, the dilutions could have been made accordingly and most importantly dilution would commence before the analysis. Together with the analysis of a blank between each real sample, this would significantly have decreased the cross-contamination and thus the reliability of the chromatography method. Having disregarded most of the data from the chromatography analyzer, a HI 98185 pH/ORP/ISE portable meter was instead used to analyze chloride using ion selective electrodes. However, when analyzing duplicates, a RAD of up to 19,4 % was attained, which is well above the maximum acceptable RAD of 10 % that UMSA has set as standard. Therefore all of the performed analyses with this method were disregarded. Nitrate and sulfate concentrations were next estimated using UV-equipment. Lack of reagent solutions to add to the samples led to the analysis of only 14 out of the total 18 samples for nitrate concentration and the analysis of only 5 duplicates for sulfate concentration (where the mean value was utilized as raw data for the current study). As chloride concentrations could not be analyzed with the UV-method and the reagents needed for the quantification through titration were missing, no reliable results for chloride concentrations were attained. Problems of similar nature regarding use of the equipment for analysis of cation together with lack of supervision and time for the analysis also meant that no reliable results were gathered on our part regarding cation concentrations. The analysis of cation as well as chloride concentrations was therefore made retrospectively on commission by our technical supervisor at UMSA, Efraín Blanco.

No RAD-values were estimated for our results due to lack of laboratory time and equipment/material (such as reagents). Therefore no control of the deviation of the results has been made which might have an effect on the precision of the results. However, we believe that the other sources of error (such as having to dilute up to 10 000 times) are such great sources of error that our laboratory results can only be seen as approximations. On the other hand, it is clear that these approximations often are well above the WHO guideline values, which is perhaps the most important fact to prove.

Figure 5.2 Downstream sampling site PAZR1, with Sara Eklund collecting water sample

6 Conclusions

The studied area northeast of Lake Poopó is polluted, both because of the mines and tailings and also because of the villages and farms. The villages and farms most likely lack adequate treatment facilities both for outgoing wastewater and incoming drinking-water. The mining activities contribute to increased concentrations of heavy metals, which is especially clear regarding cadmium. Zink and manganese concentrations are also extremely high in the mining areas. The waste water from villages and farms probably mainly increase the nitrate concentrations. The concentrations of ions and heavy metals are close to or above WHO guideline values during the entire study period, except for copper that never has exceeded the guideline values from WHO. For arsenic and lead, the concentrations seem to have decreased with time, which might be explained by a change in pH. The Antequera River is the most polluted River of the four studied rivers. This is due to the many tailings and mines in the basin of the Antequera River, but also the numerous villages. Urmiri River is the least polluted river. There are neither mining activities with significant impact nor any considerable impact from villages and farms on the water in the river. A thermal spring that enters the river has some impact regarding the temperature and the weathering of the bedrock contributes to an increased concentration of cadmium. Disregarding these natural effects, it can be concluded that the Urmiri River suffers from no major anthropogenic contamination. The Pazña River is more contaminated than Urmiri River, but not as much as Antequera River. The Poopó River runs through the Poopó village. The water quality is fairly good upstream of the tributary MAD1. However, downstream of MAD1 the values for both ions and heavy metals increase. MAD1 is a sampling site situated directly at a mine outlet stream. Probably because the waste water from the mine is not treated correctly, the result is high concentrations of ions and heavy metals in the Poopó River. The Poopó village is situated further downstream of MAD1. Fortunately, the people of the village lead water in pipes taken upstream of MAD1. The waste water from the village may also have a negative effect on the water quality since it probably is not treated in any way.

7 Recommendations

7.1 Improvement Plans

The mining activities are without a doubt the most important source of contamination in the rivers of the Lake Poopó area. The major sources of heavy metals and ions are the large-scale mining, the small-scale mining and mining waste placed along the rivers. Therefore, the most efficient way of improving the water quality would be to implement cleaner and more environmentally friendly operational procedures in the mines. However, changes are hard to implement due to the poor economic situation, the political situation and the social situation. Since many of the workers in the mines also live in the surrounding villages, it is very important to inform about the risks and what measures that can be taken to improve the water quality and thus the living standard of the people. For example, sedimentation dams could be built and the tailings could be properly closed. One change that would have great effect is to relocate the small-scale mining workers to the large-scale mines. This change is probably hard to implement but would minimize the untreated waste. Especially since larger mines are easier to monitor by the government to ensure compliance with the environmental regulations. Also, installing reservoir tanks in the populated areas could solve the problem of uneven water distribution during the year due to the dry and wet period. Another negative influence on the water quality is the human waste due to farming. One change that would have a great positive effect would be the building of sanitary facilities. A biological treatment would also improve the water quality and decrease the high nitrate concentrations. The waste-water treatment plants should be examined and improved.

Sufficient amounts of data and information have been acquired to implement these measures as soon as possible.

7.2 Further Studies

A comparison between values from the dry and wet periods would be of great help for understanding the different influences of the water chemistry. It would also indicate how changes in climate (droughts, rainy periods, etc.) affect the water chemistry. Such a study could include how future climate change might affect the Altiplano area and the leakage of heavy metals. The properties of heavy metals should then also be studied to draw conclusions on whether an increasing drought, which is the most probable scenario for the Altiplano in the future, decreases leakage of heavy metals from the bedrock or not. Further studies of the wells and the groundwater should be carried out, whereby clearer conclusions about the ground and surface water interactions could be drawn. Another interesting factor to study is the amount of organic material in water and sediment, especially since organic

material absorbs heavy metals. This absorption may cause the measured concentration of heavy metals in the water to be lower than the actual concentration. By studying the organic material content, the reliability of the results from the heavy metal analysis could be estimated. This study also lacks statistical tests of the historical changes in important field parameters such as pH, ORP and DO. In future studies, an incorporation of these tests would make conclusions regarding historical trends more accurate. Also, a study of facilities for cleaning wastewater and incoming drinking-water should be made. Where exactly are the drinking-water wells and the wastewater treatment plants (if any) located, how well do they function and how could one improve the water treatment? An exact definition of the location of the mines should also be made, including how much waste is produced, what type of environmental regulations are implemented, etc. An anthropological study should address the issue of how to deal with the problem of the possibly short lifespan for workers in cooperative mining. This problem is related to the hypothesis that workers might, because of their possibly shorter lifespan, start to care even less for the environment and their own health. The same workers also live in the villages that are polluted by the mining activities. Finally, and perhaps most importantly, a toxicology study should be performed to evaluate how the heavy metals accumulate in different organisms of different food chains. This study should include humans and those current health-issues in the area's population that can be related to exposure to the high levels of heavy metals. Coupled with scientific data from reports such as this one, the anthropological and mining studies would examine the *cause* of the contamination while an in-depth toxicology study would give a clear answer as to what is the *effect* of the contamination on the organisms living in the ecosystems of the Poopó area.

Figure 7.1 Despite the dark clouds gathering over the Lake Poopó area; Eklund and Lundström remain optimistic

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9 Appendix

Appendix A – Bolivian law and WHO guidelines
Appendix B – Additional data, current situation
Appendix C – Additional data, historical situation

Table A.1 WHO and Bolivian law guideline values for drinking-water regarding studied heavy metals and ions (21, 22, 23)

Type	Parameter	WHO guideline value	Bolivian law guideline value	Comments
Heavy metals	Arsenic (As)	10 µg/l	50 µg/l	Apart from occupational exposure, the most important routes of exposure are through food and drinking-water, including beverages that are made from drinking-water. In circumstances where soups or similar dishes are a staple part of the diet, the drinking water contribution through preparation of food will be even greater.
	Cadmium (Cd)	3 µg/l	2 µg/l	Cadmium is released to the environment in wastewater, and diffuse pollution is caused by contamination from fertilizers and local air pollution.
	Copper (Cu)	2000 µg/l	1000 µg/l	Copper concentrations in treated water often increase during distribution, especially in systems with an acid pH or high-carbonate waters with an alkaline pH. Copper is not removed by conventional treatment processes. However, copper is not normally a raw water contaminant.
	Iron (Fe)	2000 µg/l*	300 µg/l	Not of health concern at levels found in drinking-water but may affect acceptability of drinking-water
	Lead (Pb)	10 µg/l	50 µg/l	Infants and children are considered to be the most sensitive subgroups of the population.
	Manganese (Mn)	400 µg/l*	100 µg/l	Not of health concern at levels found in drinking-water but may affect acceptability of drinking-water
	Zinc (Zn)	3000 µg/l*	5000 µg/l	Not of health concern at levels found in drinking-water but may affect acceptability of drinking-water

Type	Parameter	WHO guideline value	Bolivian law guideline value	Comments
Ions	Chloride (Cl)	250 mg/l*	250 mg/l	Not of health concern at levels found in drinking-water but may affect acceptability of drinking-water
	Hardness (Mg, Ca)	500 mg/l*	None	Not of health concern at levels found in drinking-water but may affect acceptability of drinking-water
	Nitrate (NO3)	50 mg/l	None	All water systems that practice chloramination should closely and regularly monitor their systems to verify disinfectant levels, microbiological quality and nitrite levels.
	Potassium (K)	None*	None	Occurs in drinking-water at concentrations well below those of health concern
	Sodium (Na)	200 mg/l*	200 mg/l	No health-based guideline value has been derived as the contribution from drinking-water to daily intake is small.
	Sulfate (SO4)	250 mg/l*	250 mg/l	The presence of sulfate in drinking-water can cause noticeable taste, and very high levels might cause a laxative effect in unaccustomed consumers. It is generally considered that taste impairment is minimal at levels below 250 mg/l.
	HCO3 and CO3	-	-	-
	PO4	-	-	-

* No health-based guideline value has been established

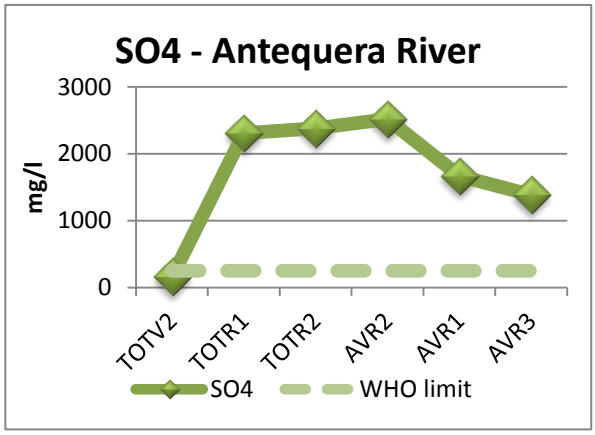

Figure B.1 SO4 concentration along Antequera River

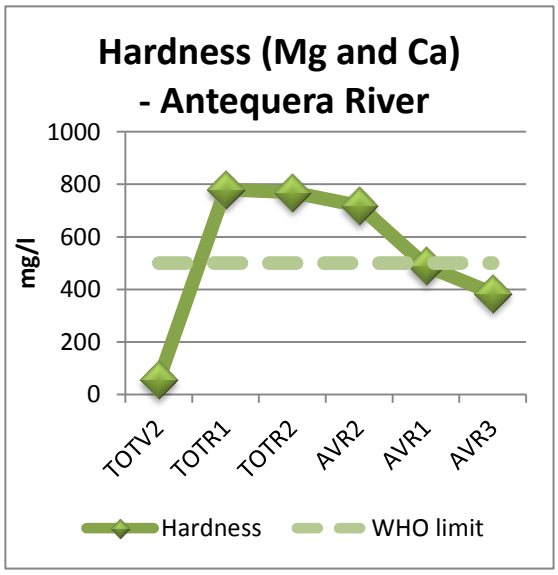

Figure B.2 Mg and Ca concentration (hardness) along Antequera River

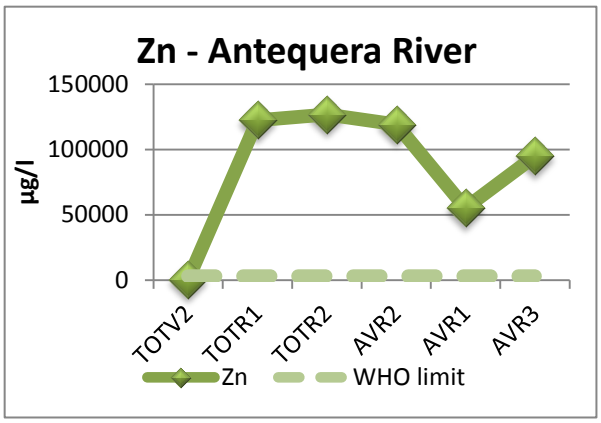

Figure B.3 Zn concentration along Antequera River

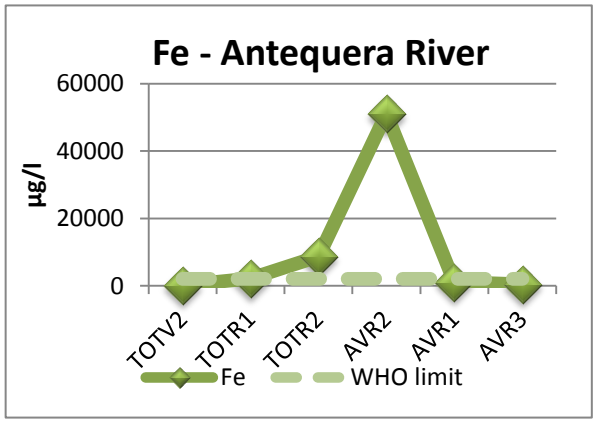

Figure B.4 Fe concentration along Antequera River

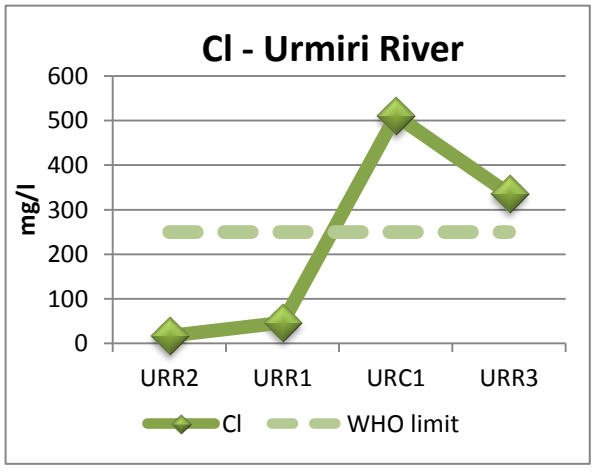

Figure B.5 Cl concentration along Urmiri River

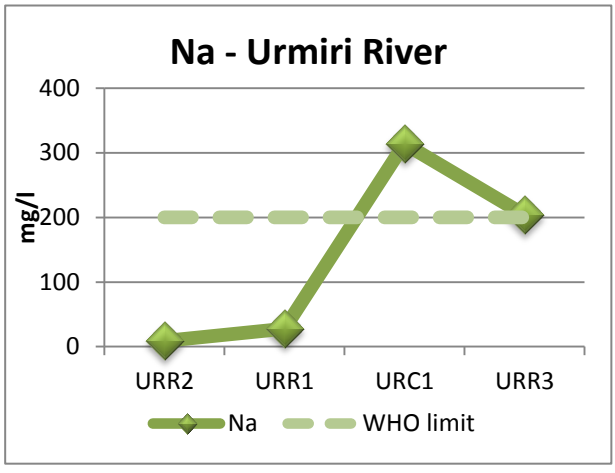

Figure B.6 Na concentration along Urmiri River

Table C.1 Historical ion concentrations for dry period

			Unit:	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
		WHO guideline:		-	-	250	500 (hardness)		200	-	50	-	250
River	**Sampling site**	**Study**	**Date**	**CO3**	**HCO3**	**Cl**	**Ca**	**Mg**	**Na**	**K**	**NO3**	**PO4**	**SO4**
Antequera	BODI1*	17	Jun. 2007	21,6	0	62,5	645	13,8	30,6	7,56	3,53	0,03	1711
		19	Sep. 2007	0	14,6	119	460	38,5	25,3	9,33	0,838	1,50	1329
		10	Aug. 2008	0,0**	256**	438	678	0,30	41,2	9,62	2,05	-	1060
		13	May 2009	0	0	-	406	46,8	58,3	29,2	-	-	-
		16	Jun. 2013	0,626	78,8	159	982	22,8	94,6	14,8	384	-	2600
	TOTV2	10	Aug. 2008	0,456	72,3	35,0	39,4	12,0	31,0	3,90	1,28	-	106
		13	May 2009	0,0118	85,4	-	39,0	12,8	29,6	4,11	-	-	-
		16	Jun. 2013	0,104	260	56,0	42,6	13,3	33,6	4,52	6,75	-	160
	TOTR1	17	Jun. 2007	0	0	35,3	402	28,0	26,4	10,9	2,65	0,10	1356
		19	Sep. 2007	0	0	104	334	40,4	28,2	9,15	3,53	0,10	1547
		10	Aug. 2008	0	0	24,0	518	29,8	698	9,23	1,14	-	1769
		13	May 2009	0	0	-	216	54,8	26,3	10,8	-	-	-
		16	Jun. 2013	0	0	134	753	26,8	78,6	13,6	182	-	2310
	TOTR2	10	Aug. 2008	0	0	190	502	31,8	24,4	9,20	1,29	-	214
		13	May 2009	0	0	-	223	52,8	28,9	11,7	-	-	-
		16	Jun. 2013	0	0	135	741	28,4	81,4	10,5	154	-	2380
	AVR2	19	Sep. 2007	0	0	144	354	46,8	54,9	11,1	3,53	0,11	1585
		10	Aug. 2008	0	0	225	340	36,9	59,2	7,12	0,817	-	2030
		13	May 2009	0	0	-	232	49,4	68,4	10,1	-	-	-
		16	Jun. 2013	0	0	135	689	30,0	80,6	11,1	210	-	2520

	Sampling site	Study	Date	CO3	HCO3	Cl	Ca	Mg	Na	K	NO3	PO4	SO4
	AVR1	19	Sep. 2007	0	0	107	255	36,8	56,7	6,60	3,09	0,09	1261
		10	Aug. 2008	0	0	87,5	236	48,1	47,4	6,03	0,734	-	1694
		13	May 2009	0	0	-	229	45,2	50,8	7,65	-	-	-
		7	Jul. 2009	0	0	-	1492	62,4	127	9,61	-	-	-
		7	Sep. 2009	0	0	-	399	48,5	66,2	8,37	-	-	-
		7	Oct. 2009	0	0	-	354	47,2	67,9	7,05	-	-	-
		16	Jun. 2013	0	0	111	458	31,2	65,6	10,1	1054	-	1666
	CUCC1*	7	Jul. 2009	2,00	34,0	-	19,4	11,0	16,2	271	-	-	-
		10	Aug. 2008	30,0	26,6	11,0	22,0	8,15	12,4	3,82	0,160	-	52,8
		13	May 2009	48,0	46,9	-	19,4	7,03	12,6	3,71	-	-	-
		16	Jun. 2013	0,574	199	17,8	17,9	7,40	9,70	3,11	-	-	58,0
	AVR3	17	Jun. 2007	0	0	76,2	286	35,1	66,2	7,79	2,65	0,47	1680
		10	Aug. 2008	0	0	48,0	200	48,2	38,5	5,00	0,854	-	1097
		13	May 2009	0	0	-	161	36,4	50,3	7,80	-	-	-
		16	Jun. 2013	0	0	98,6	369	16,2	59,0	8,32	165	-	1386
Urmiri	URR2	10	Aug. 2008	0,238	97,2	8,0	22,7	10,3	15,5	2,02	0,0854	-	70,3
		13	May 2009	0,0826	134	-	25,6	11,8	16,4	2,15	-	-	-
		16	Jun. 2013	8,39	384	16,8	23,9	11,3	9,10	2,92	0,0216	-	47,0
	URR1	17	Jun. 2007	97,2	0	275	39,1	9,53	147	19,4	0,882	0,17	35,2
		19	Sep. 2007	50,4	0	10,4	23,3	8,98	17,8	3,05	1,32	0,18	43,6
		10	Aug. 2008	0,651	96,3	11,0	23,7	11,0	13,8	2,91	0,0779	-	102
		13	May 2009	0,555	133	-	23,8	9,93	17,4	3,22	-	-	-
		16	Jun. 2013	22,8	415	46,7	28,0	10,7	27,8	4,11	0,103	-	54,0

	Sampling site	Study	Date	CO3	HCO3	Cl	Ca	Mg	Na	K	NO3	PO4	SO4
	URC1	19	Sep. 2007	0	271	776	59,3	11,6	513	43,5	0,926	0,22	35,8
		10	Aug. 2008	0,300	280	291	64,1	12,8	487	44,9	0,363	-	57,0
		13	May 2009	0,806	267	-	44,4	10,8	264	42,0	-	-	-
		16	Jun. 2013	4,96	751	512	48,4	11,4	314	29,5	12,4	-	48,0
	URV1*	13	May 2009	0,0427	427	-	32,6	18,5	213	11,6	-	-	-
		16	Jun. 2013	4,28	1353	469	34,6	19,0	297	11,4	3,80	-	80,0
	URR3	17	Jun. 2007	0	117	6,53	23,68	8,53	17,5	3,12	1,76	0,30	38,6
		10	Aug. 2008	6,67	305	650	59,1	14,8	317	22,2	0,0592	-	42,1
		13	May 2009	0,240	219	-	47,7	13,6	244	25,6	-	-	-
		16	Jun. 2013	7,14	666	335	42,2	10,0	204	20,9	8,20	-	47,0
Pazña	PAZR1	1	Jul. 2001	0,00000838	8,00	148	140	101	62,9	16,5	2,64	0,45	637
		2	Oct. 2001	0	0	161	140	30,2	151	25,9	3,52	0,11	545
		5	Aug. 2003	0,00000820	13,0	178	155	42,2	106	4,75	0,880	0,07	1014
		17	Jun. 2007	0	0	89,7	153	29,1	78,9	11,3	3,09	0,18	1678
		19	Sep. 2007	0	14,6	152	191	36,2	129	12,0	2,21	0,11	875
		10	Aug. 2008	0	0	225	189	41,5	166	13,2	0,434	-	500
		15	Sep. 2008	0	0	101	198	32,4	211	10,7	0,336	-	889
		7	Sep. 2009	0	0	-	315	49,5	89,4	13,2	-	-	-
		7	Oct. 2009	0	0	-	260	48,0	92,3	13,9	-	-	-
		13	May 2009	0	0	-	147	34,0	109	13,9	-	-	-
		16	Jun. 2013	0	0	200	259	30,0	122	13,2	91,2	-	969
	PALR2	10	Aug. 2008	0	0	708	183	42,6	281	16,2	0,348	-	2675
		13	May 2009	0	0	-	153	34,2	144	12,4	-	-	-
		16	Jun. 2013	0,000592	40,0	268	258	28,0	165	13,5	14,6	-	972

River	Sampling site	Study	Date	CO3	HCO3	Cl	Ca	Mg	Na	K	NO3	PO4	SO4
Poopó	CABT1	17	Jun. 2007	0	417	3669	119	26,4	3835	180	0,882	0,26	173
		7	Jul. 2009	0,0932	69,1	-	23,9	13,6	46,5	274	-	-	-
		7	Sep. 2009	0,700	140	-	27,9	9,90	33,7	2,93	-	-	-
		7	Oct. 2009	5,86	52,3	-	27,8	9,69	35,2	2,98	-	-	-
		16	Jun. 2013	2,00	276	51,5	21,3	8,00	31,1	4,10	1,08	-	49,0
	MAD1*	17	Jun. 2007	0	39,1	3474	125	70,8	2880	113	0,882	0,09	438
		10	Aug. 2008	0	0	850	113	84,6	2850	77,6	0,172	-	370
		7	Jul. 2009	0,00133	16,0	-	264	125	> 1000	392	-	-	-
		7	Sep. 2009	2,95	417	-	127	74,7	5689	69,8	-	-	-
		7	Oct. 2009	0,0411	31,9	-	100	61,8	4565	58,8	-	-	-
		16	Jun. 2013	0	0	3222	261	185	2030	96,0	1066	-	9100
	POR3	1	Jul. 2001	11,7	107	2228	34,6	6,00	1716	65,9	3,52	0,10	260
		2	Oct. 2001	4,33	137	1881	90,1	23,6	1195	126	3,52	0,25	130
		5	Aug. 2003	17,7	132	3722	110	37,2	2075	128	1,76	0,015	171
		6	Oct. 2006	0,2**	1,1**	3217	187	27,0	2000	106	4,10	0,20	265
		17	Jun. 2007	90,0	0	2904	106	27,6	2048	116	3,97	0,12	229
		10	Aug. 2008	0**	0**	750	103	33,2	2470	131	1,54	-	250
		7	Jul. 2009	8,69	135	-	261	39,5	>1000	510	-	-	-
		7	Sep. 2009	0,803	422	-	129	28,6	5551	103	-	-	-
		7	Oct. 2009	5,71	117	-	95,5	27,4	5794	105	-	-	-
		16	Jun. 2013	5,53	429	6107	122	20,7	3920	59,2	4,20	-	342

*Tributary

Table C.2 Historical field parameter values for dry period

River	Sampling site	Study	Date	TDS (mg/l)	Conductivity (mS/cm)	Spec. conductivity (mS/cm2)	Temperature (°C)	pH	ORP (mV)	DO (mg/l)	Alkalinity (mg/l)	TSS (mg/l)
Antequera	BODI1*	17	Jun. 2007	1340	2,67	-	9,35	8,53	-97	5,88	-	-
		19	Sep. 2007	1240	2,47	-	17,5	6,3	28	4,35	-	-
		10	Aug. 2008	-	-	-	-	-	-	-	256	7,5
		13	May 2009	2070	3,99	-	11,1	2,78	-7,6	-	0	-
		16	Jun. 2013	1934	3,87	2741	9,7	8,22	70	1,18	80,1	-
	TOTV2	10	Aug. 2008	212	8,12	-	11,4	8,12	-153	-	73,2	5,7
		13	May 2009	245	0,506	-	14,5	6,46	-205	-	85,4	-
		16	Jun. 2013	224	0,447	344	12,9	6,92	84	1,13	260	-
	TOTR1	17	Jun. 2007	1050	2,09	-	17,0	4,69	111	5,00	-	-
		19	Sep. 2007	1290	2,58	-	12,4	3,88	159	5,85	-	-
		10	Aug. 2008	1341	4,59	-	10,7	4,59	31	-	0	945
		13	May 2009	1251	2,47	-	14,8	2,95	-14	-	0	-
		16	Jun. 2013	1698	3,40	2454	10,4	4,91	86	1,78	0	-
	TOTR2	10	Aug. 2008	131	2,57	-		5,88	84	-	0	755
		13	May 2009	1269	2,50	-	13,9	2,87	-14	-	0	-
		16	Jun. 2013	1733	3,47	2482	10,1	4,52	240	1,74	0	-
	AVR2	19	Sep. 2007	14400	2,87	-	19,8	3,18	206	5,68	-	-
		10	Aug. 2008	1413	2,77	-	13,4	2,68	132	-	0	581
		13	May 2009	1535	3,00	-	12,9	2,54	6,7	-	0	-
		16	Jun. 2013	1741	3,48	2491	10,0	4,27	436	1,73	0	-

	Sampling site	Study	Date	TDS (mg/l)	Conductivity (mS/cm)	Spec. conductivity (ms/cm2)	Temperature (°C)	pH	ORP (mV)	DO (mg/l)	Alkalinity (mg/l)	TSS (mg/l)
	AVR1	17	Jun. 2007	1210	2,40	-	11,7	2,91	204	4,43	-	-
		19	Sep. 2007	1270	2,53	-	13,1	3,10	207	3,37	-	-
		10	Aug. 2008	1349	2,64	-	13,1	2,41	7147	-	0	1,8
		13	May 2009	1327	2,81	-	14,6	2,07	34	-	0	-
		7	Jul. 2009	1888	1,95	2,91	7,67	2,83	785	13,9	-	-
		7	Sep. 2009	1830	1,93	2,83	8,5	3,15	731	8,95	-	-
		7	Oct. 2009	1890	2,00	2,91	8,6	1,85	779	6,00	-	-
		16	Jun. 2013	1360	2,72	1996	11,0	3,56	498	1,73	0	-
	CUCC1*	10	Aug. 2008	127	0,265	-	19,6	9,13	-208	-	30,0	3,3
		13	May 2009	115	0,241	-	15,6	8,39	-310	-	48,0	-
		7	Jul. 2009	158	0,190	0,245	14,1	9,09	346	13,9	38,0	-
		16	Jun. 2013	110	0,219	167	12,4	7,78	45	2,38	200	-
	AVR3	17	Jun. 2007	1390	2,76	-	13,7	3,06	197	4,67	-	-
		10	Aug. 2008	1056	2,10	-	15,5	2,64	137	-	0	1219
		13	May 2009	881	1,76	-	19,4	2,22	30	-	0	-
		16	Jun. 2013	1092	2,18	1773	15,1	3,79	382	2,00	0	-
Urmiri	URR2	10	Aug. 2008	133	0,275	-	11,5	7,71	-127	-	97,6	1,2
		13	May 2009	1465	0,305	-	11,5	7,11	-241	-	134	-
		16	Jun. 2013	131	0,263	183	9,02	8,66	150	1,21	400	-
	URR1	17	Jun. 2007	700	1,41	-	14,2	8,65	-105	6,17	-	-
		19	Sep. 2007	150	0,29	-	18,3	8,25	-96	5,85	-	-
		10	Aug. 2008	146	0,304	-	13,8	8,15	-151	-	97,6	14,4
		13	May 2009	140	0,291	-	10,9	7,94	-285	-	134	-
		16	Jun. 2013	148	0,296	207	9,25	9,06	170	1,34	460	-

	Sampling site	Study	Date	TDS (mg/l)	Conductivity (mS/cm)	Spec. conductivity (ms/cm2)	Temperature (°C)	pH	ORP (mV)	DO (mg/l)	Alkalinity (mg/l)	TSS (mg/l)
	URC1	19	Sep. 2007	1560	3,11	-	26,1	7,95	75	-	-	-
		10	Aug. 2008	1816	3,52	-	26,0	7,35	-115	-	281	6,9
		13	May 2009	1209	2,39	-	24,1	7,80	-244	-	268	-
		16	Jun. 2013	931	1,86	1669	19,5	8,14	20	1,56	761	-
	URV1*	13	May 2009	697	1,41	-	17,7	6,32	-196	-	427	-
		16	Jun. 2013	672	1,34	1132	16,7	7,82	-50	0,00	1361	-
	URR3	17	Jun. 2007	141	0,281	-	13,3	7,69	-52	5,45	-	-
		10	Aug. 2008	883	1,76	-	-	8,66	-182	-	318	2,7
		13	May 2009	848	1,67	-	16,9	7,36	-254	-	220	-
		16	Jun. 2013	612	1,22	1018	16,2	8,35	75	1,94	681	-
Pazña	PAZR1	1	Jul. 2001	-	1,65	-	10,5	4,34	168	-	8	-
		2	Oct. 2001	1090	2,16	-	14,0	3,05	207	-	0	-
		5	Aug. 2003	946	1,89	-	12,5	4,12	-	-	13	-
		17	Jun. 2007	824	1,64	-	12,1	4,81	103	5,83	-	-
		19	Sep. 2007	90	1,96	-	11,2	4,71	11,3	6,51	-	-
		10	Aug. 2008	9790	1,95	-	18,0	3,61	87	-	0	1,1
		15	Sep. 2008	1081	2,15	-	18,5	3,12	113	-	0	-
		13	May 2009	911	1,82	-	9,00	4,55	-104	-	0	-
		7	Sep. 2009	1470	1,93	2,26	17,6	3,65	611	8,79	0	-
		7	Oct. 2009	1460	2,10	2,24	21,6	2,03	556	5,19	0	-
		16	Jun. 2013	929	1,86	1455	13,6	5,07	227	1,29	0	-
	PALR2	10	Aug. 2008	1071	2,13	-	16,9	4,13	58	-	0	13,7
		13	May 2009	997	1,99	-	14,5	3,78	-60	-	0	-
		16	Jun. 2013	964	1,93	1208	5,37	5,49	140	1,81	40,0	-

RIver	Sampling site	Study	Date	TDS (mg/l)	Conductivity (mS/cm)	Spec. conductivity (ms/cm2)	Temperature (°C)	pH	ORP (mV)	DO (mg/l)	Alkalinity (mg/l)	TSS (mg/l)
Poopó	CABT1	17	Jun. 2007	158	0,315	-	12,6	7,41	-38	7,53	-	-
		7	Jul. 2009	234	0,25	0,359	9,52	7,45	410,5**	10,5	69,3	-
		7	Sep. 2009	50	0,06	0,11	11,6	8,02	-12,8**	-	141	-
		7	Oct. 2009	290	0,35	0,45	13,8	9,37	434	4,46	64,0	-
		16	Jun. 2013	135	0,270	180	7,48	8,18	178	0,81	280	-
	MAD1*	17	Jun. 2007	7060	14,1	-	21,3	6,51	11	6,20	-	-
		10	Aug. 2008	8490	15,1	-	20,9	5,72	-26,1	-	0	-
		7	Jul. 2009	9423	11,9	13,2	20,2	6,24	249**	4,78	16,0	-
		7	Sep. 2009	80	0,09	0,18	19,5	8,17	-21,1**	-	423	-
		7	Oct. 2009	9600	14,0	14,8	22,3	7,43	190	4,66	32,0	-
		16	Jun. 2013	6637	13,3	12440	21,7	2,53	386	0,17	0	-
	POR3	1	Jul. 2001	-	7,98	-	15,3	9,36	-	-	130	-
		2	Oct. 2001	5450	1,09	-	14,8	8,82	-108	-	146	-
		5	Aug. 2003	6430	12,8	-	14,0	9,45	-	-	167	-
		6	Oct. 2006	5590	0,112	-	20,5	9,65	-134	-	-	-
		17	Jun. 2007	5270	10,5	-	19,2	8,74	-115	7,80	-	-
		10	Aug. 2008	7640	13,7	-	21,5	8,56	-178	-	-	-
		7	Jul. 2009	8345	10,5	11,6	20,0	9,13	368**	13,0	152	-
		7	Sep. 2009	6870	6,48	12,4	16,2	7,60	9,9**	-	423	-
		7	Oct. 2009	9700	14,3	14,9	23,1	9,01	358	11,7	128	-
		16	Jun. 2013	3039	6,08	4885	14,7	8,43	106	0,92	440	-

* Tributary

** The two different measurements (Jul. / Sep.) are made with two different meters

Table C.3 Historical heavy metal concentrations for wet period

			Unit:	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
			WHO guideline:	10	10	3	2000	2000	3000	400
River	**Sampling site**	**Study**	**Date**	**As**	**Pb**	**Cd**	**Cu**	**Fe**	**Zn**	**Mn**
Antequera	BODI1*	18	Nov. 2007	31,6	483	437	37	41650	85000	-
		14	Nov. 2008	13,8	<5	1165	<0,2	40300	149000	5320
		11	Dec. 2008	<5	<5	-	-	<100	881	631
		12	Feb. 2009	<5	<5	-	-	351	23475	1683
	TOTV2	14	Nov. 2008	<5	<5	-	-	107	493	<100
		11	Dec. 2008	<5	<5	-	-	<100	422	<100
		12	Feb. 2009	<5	<5	-	-	<100	1056	<100
	TOTR1	18	Nov. 2007	14,3	658	921	184	44725	195000	-
		14	Nov. 2008	5,81	15,5	1266	92,0	30300	182500	11700
		11	Dec. 2008	<5	<5	1288	39,0	21000	152000	9250
		12	Feb. 2009	<5	<5	845	151	25300	121500	6700
	TOTR2	14	Nov. 2008	12,0	27,7	1350	102	34650	201200	9100
		11	Dec. 2008	8,11	6,73	1042	50,0	7700	122200	8850
		12	Feb. 2009	10,1	<5	875	167	33000	121400	6900
	AVR2	18	Nov. 2007	3176	437	372	187	112000	188000	-
		14	Nov. 2008	47,3	<5	969	512	58500	181000	13700
		11	Dec. 2008	763	19,2	1291	1299	82200	187500	12150
		12	Feb. 2009	709	<5	998	742	60000	161500	9900
	AVR1	18	Nov. 2007	<5	439	587	683	3087	194000	-
		14	Nov. 2008	7,31	<5	681	533	5750	167750	26400
		11	Dec. 2008	19,8	<5	638	579	5510	158750	28900
		12	Feb. 2009	13,5	<5	835	694	4885	642	20925

			Unit:	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
			WHO guideline:	10	10	3	2000	2000	3000	400
	Sampling site	Study	Date	As	Pb	Cd	Cu	Fe	Zn	Mn
	CUCC1*	14	Nov. 2008	19,1	<5	-	-	<100	<30	<100
		11	Dec. 2008	19,2	<5	-	-	<100	66,0	<100
		12	Feb. 2009	<5	<5	-	-	<100	<30	<100
	AVR3	14	Nov. 2008	19,8	<5	633	532	2915	148750	21800
		11	Dec. 2008	13,4	<5	627	634	2844	148750	24800
		12	Feb. 2009	16,6	<5	761	656	3205	154500	19800
Urmiri	URR2	14	Nov. 2008	5,53	<5	-	-	<100	<30	<100
		11	Dec. 2008	5,70	<5	-	-	<100	49,0	<100
		12	Feb. 2009	5,61	<5	-	-	<100	<30	<100
	URR1	18	Nov. 2007	7,57	6,42	<1,2	11	154	<30	-
		14	Nov. 2008	14,3	<5	<1,2	0,256	<100	83,0	<100
		11	Dec. 2008	9,36	<5	-	-	<100	38,0	<100
		12	Feb. 2009	11,8	<5	-	-	<100	<30	<100
	URC1	18	Nov. 2007	6,99	6,17	1,44	16	169	<30	-
		14	Nov. 2008	<5	<5	-	-	139	<30	252
		11	Dec. 2008	13,7	<5	-	-	156	43,0	235
		12	Feb. 2009	<5	<5	-	-	<100	<30	<100
	URV1*	18	Nov. 2007	<5	5,51	<1,2	17	345	<30	-
		14	Nov. 2008	12,1	<5	-	-	320	<30	<100
		11	Dec. 2008	8,66	<5	-	-	160	33,0	<100
		12	Feb. 2009	<5	<5	-	-	<100	<30	<100

			Unit:	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
		WHO guideline:		10	10	3	2000	2000	3000	400
	Sampling site	**Study**	**Date**	**As**	**Pb**	**Cd**	**Cu**	**Fe**	**Zn**	**Mn**
	URR3	14	Nov. 2008	16,7	<5	-	-	<100	<30	<100
		11	Dec. 2008	11,0	<5	-	-	<100	30,0	<100
		12	Feb. 2009	13,9	<5	-	-	<100	278	<100
Pazña	PAZR1	3	Mar. 2002	50,9	61,1	236	-	4800	34800	-
		4	Dec. 2002	212	19,2	267	-	8550	78889	-
		18	Nov. 2007	<5	10,4	446	644	2336	130000	-
		14	Nov. 2008	11,5	1,10	553	548	1073	140750	19400
		11	Dec. 2008	25,9	<5	576	552	1367	117000	18600
		12	Feb. 2009	18,7	<5	698	620	2950	149000	19900
	PALR2	14	Nov. 2008	15,4	<5	470	367	353	109250	16800
		11	Dec. 2008	7,31	<5	505	449	487	116750	19300
		12	Feb. 2009	11,4	<5	656	565	1895	129500	17875
Poopó	CABT1	18	Nov. 2007	<5	<5	<1,2	21	190	77	-
		14	Nov. 2008	5,80	<5	-	-	185	<30	<100
		11	Dec. 2008	<5	<5	-	-	<100	<30	<100
		12	Feb. 2009	<5	<5	-	-	<100	<30	<100
	MAD1*	18	Nov. 2007	19,7	<5	3,33	25	75000	1395	-
		14	Nov. 2008	<5	<5	4,70	0,643	40550	1330	6915
		11	Dec. 2008	<5	<5	4,65	1,16	28000	1270	6230
		12	Feb. 2009	<5	17,2	13,0	19,0	45950	1440	6515

			Unit:	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
		WHO guideline:		10	10	3	2000	2000	3000	400
	Sampling site	**Study**	**Date**	**As**	**Pb**	**Cd**	**Cu**	**Fe**	**Zn**	**Mn**
	POR3	3	Mar. 2002	834	49,9	<10	-	122	383	-
		4	Dec. 2002	726	17,0	<10	-	27,9	535	-
		6	Dec. 2006	12050	385	4,39	-	234	-	-
		18	Nov. 2007	5,32	<5	16,2	25	253	1630	-
		14	Nov. 2008	18,8	<5	-	-	153	288	<100
		11	Dec. 2008	11,7	5,72	-	-	113	163	338
		12	Feb. 2009	5,83	15,4	-	-	<100	71,0	<100

* Tributary

Table C.4 Historical ion concentrations for wet period

			Unit:	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
			WHO guideline:	-	-	250	500 (hardness)		200	-	50	-	250
River	**Sampling site**	**Study**	**Date**	**CO3**	**HCO3**	**Cl**	**Ca**	**Mg**	**Na**	**K**	**NO3**	**PO4**	**SO4**
Antequera	BODI1*	14	Nov. 2008	0,000	0,000	125	378	36,7	46,9	11,0	14,3	-	1563
		11	Dec. 2008	0,0612	58,5	179	1210	11,6	50,1	14,7	-	-	3626
		12	Feb. 2009	0,0345	48,7	256	1349	15,7	45,8	11,0	1,52	0,0615	2162
	TOTV2	14	Nov. 2008	0,000	0,000	23,0	33,4	11,4	27,5	3,54	5,98	-	136
		11	Dec. 2008	0,133	124	27,6	43,9	11,8	34,6	4,68	-	-	188
		12	Feb. 2009	0,0878	73,0	30,2	71,8	12,0	31,2	3,53	1,52	0,0926	112
	TOTR1	14	Nov. 2008	0,000	0,000	300	429	40,0	39,6	10,4	7,96	-	2300
		11	Dec. 2008	0,000	0,000	126	902	32,4	51,5	12,1	-	-	2232
		12	Feb. 2009	0,000	0,000	151	914	25,7	37,4	10,0	1,52	0,0696	1720
	TOTR2	14	Nov. 2008	0,000	0,000	430	329	59,5	200	11,6	7,82	-	2350
		11	Dec. 2008	0,000	0,000	130	937	30,3	55,7	13,3	-	-	2789
		12	Feb. 2009	0,000	0,000	186	914	26,7	39,6	10,6	2,03	0,0654	1860
	AVR2	14	Nov. 2008	0,000	0,000	430	310	41,7	56,3	9,15	12,1	-	1080
		11	Dec. 2008	0,000	0,000	139	482	44,8	67,9	10,7	-	-	2929
		12	Feb. 2009	0,000	0,000	213	789	35,1	57,7	9,23	7,88	0,0668	2092
	AVR1	18	Nov. 2007	-	139	74,2	256	42,5	50,6	6,79	-	0,10	1262
		14	Nov. 2008	0,000	0,000	120	226	45,6	52,9	5,49	2,68	-	2100
		11	Dec. 2008	0,000	0,000	663	258	48,6	71,2	6,08	-	-	2232
		12	Feb. 2009	0,000	0,000	67,7	483	46,2	58,4	7,30	1,91	0,0755	1674
	CUCC1*	14	Nov. 2008	0,318	131	21,0	20,7	8,11	15,8	2,44	0,180	-	188
		11	Dec. 2008	3,19	65,6	13,8	26,6	8,60	53,4	3,50	-	-	102
		12	Feb. 2009	20,9	0,245	13,1	34,8	6,20	13,5	3,46	-	0,0755	53,0

	Sampling site	Study	Date	CO3	HCO3	Cl	Ca	Mg	Na	K	NO3	PO4	SO4
	AVR3	14	Nov. 2008	0,000	0,000	57,0	214	44,0	55,9	7,32	3,18	-	1400
		11	Dec. 2008	0,000	0,000	89,2	236	45,0	77,0	8,30	-	-	1981
		12	Feb. 2009	0,000	0,000	168	457	45,2	73,5	10,5	2,29	0,0740	1627
Urmiri	URR2	14	Nov. 2008	0,000	0,000	1,00	28,3	13,4	40,8	1,95	0,0500	-	165
		11	Dec. 2008	0,185	219	13,4	29,6	13,6	18,4	2,70	-	-	97,6
		12	Feb. 2009	4,12	63,8	17,4	54,4	12,8	17,9	3,24	0,127	0,0945	126
	URR1	18	Nov. 2007	-	373	10,1	9,17	4,43	14,3	3,02	0,88	0,16	43,2
		14	Nov. 2008	0,491	197	31,0	26,0	10,9	74,3	13,7	0,0500	-	195
		11	Dec. 2008	1,67	202	12,8	29,7	10,9	18,3	3,29	-	-	79,5
		12	Feb. 2009	29,2	1,53	16,8	48,8	10,2	18,1	3,33	0,381	0,0696	342
	URC1	18	Nov. 2007	-	271	1029	37,8	6,50	752	70,8	1,76	0,17	32,6
		14	Nov. 2008	0,220	629	2150	12,1	4,99	59,7	2,54	1,11	-	40,0
		11	Dec. 2008	4,10	305	552	82,6	12,4	984	65,9	-	-	62,8
		12	Feb. 2009	1,24	136	291	86,4	10,3	349	61,2	0,508	0,0984	64,2
	URV1*	18	Nov. 2007	50,4	-	196	32,5	17,6	213	8,15	0,44	0,06	67,8
		14	Nov. 2008	0,197	622	475	26,8	28,2	218	7,52	1,68	-	60,0
		11	Dec. 2008	2,64	297	208	52,8	19,6	549	10,7	-	-	105
		12	Feb. 2009	3,08	445	452	62,6	17,5	422	9525	0,889	0,0628	90,7
	URR 3	14	Nov. 2008	2,03	75,2	650	28,4	12,9	203	20,9	0,0500	-	93,8
		11	Dec. 2008	22,7	44,5	580	59,2	19,2	410	29,5	-	-	65,6
		12	Feb. 2009	6,13	65,7	894	119	20,0	359	28,8	0,508	0,0641	46,0

River	Sampling site	Study	Date	CO3	HCO3	Cl	Ca	Mg	Na	K	NO3	PO4	SO4
Pazña	PAZR1	3	Mar. 2002	0,000	0,000	188	95,2	35,3	152	43,8	-	0,0900	587
		4	Dec. 2002	0,000	0,000	86,2	144	-	111	8,68	2,64	0,218	656
		18	Nov. 2007	-	110	135	218	41,3	91,8	12,15	3,09	0,04	1009
		14	Nov. 2008	0,000	0,000	270	216	45,6	86,5	12,0	2,07	-	1750
		11	Dec. 2008	0,000	0,000	129	387	25,4	91,6	10,0	-	-	1581
		12	Feb. 2009	0,000	0,000	135	400	48,0	82,2	10,7	1,78	0,0641	1813
	PALR2	9	Mar. 2008	-	-	23,0	190	14,0	79,0	7,60	5,30	-	750
		14	Nov. 2008	0,000	0,000	820	188	42,4	369	14,0	2,39	-	2250
		11	Dec. 2008	0,000	0,000	219	226	45,6	191	16,6	-	-	1702
		12	Feb. 2009	0,000	0,000	278	448	52,3	129	11,8	3,30	0,0682	2232
Poopó	CABT1	18	Nov. 2007	-	132	66,0	31,7	8,73	34,5	5,09	-	0,22	40,5
		14	Nov. 2008	0,190	153	155	25,7	10,2	41,0	3,54	0,110	-	125
		11	Dec. 2008	0,221	175	79,3	50,0	11,0	42,1	3,98	-	-	71,1
		12	Feb. 2009	0,771	46,5	66,6	38,3	7,73	31,7	3,26	0,381	0,121	272
	MAD1*	18	Nov. 2007	-	-	4273	128	81,0	267	106	-	-	335
		14	Nov. 2008	0,000	0,000	1583	113	108	2613	93,5	0,430	-	538
		11	Dec. 2008	0,002	29,3	877	131	69,6	2910	95,4	-	-	586
		12	Feb. 2009	0,008	73,2	2182	234	76,6	2690	98,0	0,254	0,0682	530
	POR3	3	Mar. 2002	0,511	93,0	497	26,6	5,9	345	23,4	-	0,360	59,4
		4	Dec. 2002	0,142	118	1095	40,3	15,5	844	50,5	3,52	1,33	138
		6	Dec. 2006	0,130	1,40	5500	153	25,0	1007	101	3,00	-	3800
		18	Nov. 2007	112	-	4771	132	35,2	2770	152	3,97	0,11	295
		14	Nov. 2008	0,586	424	1035	112	33,5	2410	8,94	4,59	-	363
		11	Dec. 2008	4,28	200	4313	241	33,7	2615	113	-	-	391
		12	Feb. 2009	1,48	110	3069	107	15,9	1070	71,5	0,254	0,0591	251

* Tributary

Table C.5 Historical field parameters for wet period

River	Sampling site	Study	Date	TDS (mg/l)	Conductivity (mS/cm)	Temperature (°C)	pH	ORP (mV)	Alkalinity (mg/l)	TSS (mg/l)	DO (mg/l)
Antequera	BODI1*	18	Nov. 2007	1436	2,89	12,8	6,49	10	4,35	-	-
		14	Nov. 2008	1535	3,00	18,9	4,88	19,4	-	-	4,35
		11	Dec. 2008	1766	3,43	21,6	7,34	-49,0	58,6	54	-
		12	Feb. 2009	1666	3,24	12,4	7,17	-93,0	48,8	-	-
	TOTV2	14	Nov. 2008	226	0,467	15,2	6,15	-49,2	0	3,6	-
		11	Dec. 2008	235	0,486	21,0	7,35	-49,5	124	0,60	-
		12	Feb. 2009	238	0,493	14,3	7,4	-106	73,2	-	-
	TOTR1	18	Nov. 2007	1370	2,73	13,1	4,50	116	-	-	5,28
		14	Nov. 2008	1513	2,96	22,3	2,66	140	0	350	-
		11	Dec. 2008	1628	3,17	15,3	4,74	131	0	730	-
		12	Feb. 2009	1426	2,80	20,5	4,95	39,3	0	-	-
	TOTR2	14	Nov. 2008	1551	3,03	23,1	2,54	148	0	270	-
		11	Dec. 2008	1638	3,19	17,9	3,94	176	0	230	-
		12	Feb. 2009	147,1	2,88	16,8	4,09	74,9	0	-	-
	AVR2	18	Nov. 2007	1310	2,60	10,1	3,49	168	-	-	1,73
		14	Nov. 2008	1630	3,16	19,1	1,96	176	0	640	-
		11	Dec. 2008	1868	3,62	21,1	3,15	223	0	170	-
		12	Feb. 2009	1624	3,17	13,3	3,48	160	0	-	-
	AVR1	18	Nov. 2007	1320	2,63	12,2	2,87	-202	-	-	2,62
		14	Nov. 2008	1478	2,89	16,0	1,84	180	0	3,2	-
		11	Dec. 2008	1495	2,93	17,4	2,97	229	0	270	-
		12	Feb. 2009	1488	2,91	13,8	5,24	11,3	0	-	-

	Sampling site	Study	Date	TDS (mg/l)	Conductivity (mS/cm)	Temperature (°C)	pH	ORP (mV)	Alkalinity (mg/l)	TSS (mg/l)	DO (mg/l)
	CUCC1*	14	Nov. 2008	143	0,298	14,1	7,70	-31,2	132	3,0	-
		11	Dec. 2008	152	0,316	25,3	9,01	-109	72,0	7,8	-
		12	Feb. 2009	113	0,236	14,8	12,3	-370	42,0	-	-
	AVR3	14	Nov. 2008	1224	2,42	13,6	2,20	157	0	2,2	-
		11	Dec. 2008	1284	2,53	20,6	3,84	183	0	1,4	-
		12	Feb. 2009	1346	2,65	14,5	3,37	170	0	-	-
Urmiri	URR2	14	Nov. 2008	192	0,397	15,5	6,17	-50,6	0	1,0	-
		11	Dec. 2008	180	0,370	18,1	7,25	-7,8	220	1,0	-
		12	Feb. 2009	176	0,366	14,2	9,13	-200	72,0	-	-
	URR1	18	Nov. 2007	150	0,30	17,0	8,57	-10,4	-	-	6,56
		14	Nov. 2008	168	0,349	16,5	7,72	-132	198	22	-
		11	Dec. 2008	165	0,343	18,1	8,24	-63,0	205	2,0	-
		12	Feb. 2009	157	0,00327	14,2	11,6	-329	60,0	-	-
	URC1	18	Nov. 2007	2070	4,14	27,3	7,63	-54	-	-	3,71
		14	Nov. 2008	2490	4,77	26,1	6,86	-86,9	630	12	-
		11	Dec. 2008	2580	4,93	29,4	8,45	-77,8	313	6,6	-
		12	Feb. 2009	1201	2,37	21,7	8,28	-157	138	-	-
	URV1*	18	Nov. 2007	710	1,40	15,8	7,34	-34	-	-	2,81
		14	Nov. 2008	742	1,50	16,9	6,82	-84,7	622	14	-
		11	Dec. 2008	739	1,49	17,4	8,27	-64,7	302	4,0	-
		12	Feb. 2009	669	1,35	15,9	8,16	-148	451	-	-
	URR3	14	Nov. 2008	1860	3,60	17,6	8,75	-189	79,2	6,2	-
		11	Dec. 2008	1142	2,26	19,7	10,0	-163	90,0	2,6	-
		12	Feb. 2009	1223	2,42	16,0	9,29	-210	78,0	-	-

River	Sampling site	Study	Date	TDS (mg/l)	Conductivity (mS/cm)	Temperature (°C)	pH	ORP (mV)	Alkalinity (mg/l)	TSS (mg/l)	DO (mg/l)
Pazña	PAZR1	3	Mar. 2002	607	1,21	19,4	3,71	-	0	16	-
		4	Dec. 2002	0,899	1,79	8,5	1,94	259	0	-	-
		18	Nov. 2007	1070	2,13	14,4	3,64	164	-	-	4,94
		14	Nov. 2008	1172	2,32	19,7	2,63	140	0	2,2	-
		11	Dec. 2008	1243	2,45	15,1	4,25	157	0	2,8	-
		12	Feb. 2009	1345	2,64	16,3	4,33	116	0	-	-
	PALR2	14	Nov. 2008	1215	2,40	20,3	3,62	86,8	0	14	-
		11	Dec. 2008	1334	2,62	14,1	5,51	-87,7	0	9,4	-
		12	Feb. 2009	1315	2,59	11,9	3,46	107	0	-	-
Poopó	CABT1	18	Nov. 2007	228	0,454	15,8	7,42	-39	-	-	3,94
		14	Nov. 2008	242	0,501	18,6	7,41	-116	154	22	-
		11	Dec. 2008	259	0,535	20,1	7,42	-53,3	176	8,8	-
		12	Feb. 2009	158	0,329	15,4	8,54	-114	48,0	-	-
	MAD1*	18	Nov. 2007	7190	14,4	19,1	6,50	11	-	-	3,64
		14	Nov. 2008	9090	16,1	21,1	5,27	-1,3	0	77	-
		11	Dec. 2008	9130	16,2	22,6	6,25	11,9	29,3	61	-
		12	Feb. 2009	9000	16,0	23,1	6,36	-50,0	73,2	-	-
	POR3	3	Mar. 2002	973	1,94	19,1	8,06	-	94,0	53	-
		4	Dec. 2002	2,64	5,26	22,0	7,40	-25,9	118	-	-
		6	Dec. 2006	5070	0,101	22,2	9,35	-	-	-	-
		18	Nov. 2007	7350	14,7	14,5	7,97	-69	-	-	9,06
		14	Nov. 2008	9420	16,7	13,6	7,46	-124	425	83	-
		12	Feb. 2009	3880	26,5	27,7	8,45	-108	113	-	-

* Tributary