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Ground Water and Surface Water Influence on the Water Quality in the Antequera River basin, Bolivia

A Minor Field Study

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Abstract

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Problem Definition: The Antequera Basin of 150 km² is a sub-basin to Lake Poopó, located at an altitude of 3800 meters above sea level on the Bolivian high plateau. Lake Poopó is a terminal lake with high salinity and heavy pollution from centuries of extensive mining activity. The climate is semiarid-cold with an average precipitation of 450 mm/year and potential evaporation of 1700 mm/year. Almost all rain falls during December to March and the temperature varies from -2 to 18°C during the summer and from -10 to 14°C during the winter. Antequera River is seasonal, only carrying water during the rainy season.

The social situation is marked by poverty and scarcity of water. The sub-basin Antequera has a population of about 4300 inhabitants. The inhabitants of lower part of the basin mainly earn their living from agriculture and livestock and in the upper part mining activity is important. The water quality is fairly good in the uppermost part of the basin while there are problems with pollution due to mining activity further down.

Objectives: This study aims to investigate the ground water and surface water system in River Antequera and how the water quality changes along the river. Also to find out if anthropogenic and natural influences affect the surface water quality.

Method: A field study was done at the end of the rainy season, in the beginning of March 2008, to collect water samples and measure river flow, pH and TDS. The samples were analyzed regarding concentrations of Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, NO₃⁻, Cl⁻ and alkalinity. The water quality and flow was compared along the river to find out if anthropogenic influence and ground water affect the surface water quality.

Conclusions: In the uppermost part of Antequera basin the river water quality is of fairly good quality except in regards of nitrate. A bit further downstream the area is full of old mine residue and active and deserted mines surround the river. pH in the river drops to around 2-3 here and remains low throughout its course. All concentrations of analyzed ions increase significantly in the reach through the mine district due to extensive weathering. Further south a tributary is connecting and this result in dilution. As the river approaches the low land all ion concentrations increase

which indicates intrusion of shallow ground water. Sodium and chloride keeps increasing toward the saline Lake Poopó. Measurements of total dissolved solids (TDS) in wells show ground water becoming more saline close to the lake.

Key words: Water quality, river flow, surface water, ground water, cations, anions, pH, TDS, Antequera, Lake Poopó, mining activity.

Sammanfattning

Titel: Grundvatten och ytvattens påverkan på vattenkvalitén i avrinningsområdet Antequera i Bolivia.

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Problem definition: Avrinningsområdet Antequera med en area av 150 km² är en del av avrinningsområdet Poopó, beläget 3800 meter över havet i de bolivianska Anderna. Sjön Poopó är en terminal sjö som har hög salthalt och är sen årtionden kraftigt förorenad av gruvverksamhet. Klimatet klassificeras som kall halvöken med en årlig nederbörd på 450 mm och en årlig avdunstning på 1700 mm. Det mesta av regnet faller under december till mars och temperaturen varierar mellan -2 och 18 °C sommartid och mellan -10 och 14 °C vintertid. Floden Antequera är säsongsberoende och är endast vattenfylld under regnperioden.

I avrinningsområdet Antequera bor ca 4300 personer och fattigdom och bristen på vatten i området är utpräglad. Invånarna i den nedre delen av området försörjer sig till stor del på jordbruk och boskapsskötsel medan gruvdriften är en viktig sysselsättning i den övre delen av området. Vattenkvalitén är relativt god i den översta delen av området, innan gruvorna, medan vattenkvalitén i den nedre delen är kraftigt påverkad av gruvdriften.

Målsättning: Syftet med detta examensarbete är att beskriva grundvatten och ytvattensystemet i floden Antequera och undersöka hur vattenkvalitén förändras utmed floden samt undersöka om mänsklig påverkan och grundvatten har någon effekt på ytvattenkvalitén.

Metod: En fältstudie utfördes i slutet av regnperioden, i början av mars 2009, då vattenprover samlades in för analys och i fält mättes flöde, pH och TDS. Vattenproverna analyserades med avseende på Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, NO₃⁻, Cl⁻ och alkalinitet. Vattenkvalitén och flödet utmed floden jämfördes för att dra slutsatser om mänsklig påverkan och grundvatten har någon effekt på ytvattenkvalitén..

Slutsats: I den övre delen av avrinningsområdet Antequera är vattenkvalitén av relativt god kvalitet med undantag för nitrat. En bit längre nerströms är området i anslutning till floden fullt av gamla gruvrester samt ett flertal aktiva och stängda gruvor. pH i floden sjunker kraftigt i detta område, till omkring 2-3, och fortsätter att vara lågt utmed resten av floden. Alla analyserade joner ökar avsevärt i vattnet från

detta område på grund av ökad vittring. Längre nedströms ansluter ett tillflöde till floden vilket resulterar i utspädning. I och med att floden passerar de nedre delarna ökar alla joners koncentrationer ytterligare vilket indikerar tillförsel av ytligt grundvatten. Natrium och klorid fortsätter öka hela vägen ner till den salta sjön Poopó. Uppmätt TDS i brunnar visar på att grundvattnet är saltare nära Poopó sjön.

Nyckelord: Vattenkvalité, flöde, ytvatten, grundvatten, katjoner, anjoner, pH, TDS, Antequera, Poopó, gruvaktivitet

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1 Introduction

One of the most important challenges of defeating poverty is to have sustainable and efficient management of water resources. Human health, a secured food supply and agriculture are directly connected to access and quality of water. An important condition to economical growth is to assure reliable water resources (SIDA 2007).

The Bolivian high plateau, the Altiplano, is a poor and under developed region and has for centuries been contaminated by heavy metals, of both natural and anthropogenic sources. Most of the anthropogenic contamination is a result of mining activities and these activities has with time caused severe damage to the water resources and disturbances in the ecological system (García et al 2003).

The River Antequera, located in this region, has been investigated in previous studies. It was found that the water in the very upstream parts of the basin is of fairly good quality but further downstream active and deserted mines have affected the water quality, and may also have affected the ground water (García 2006).

To be able to take action and use proper means to improve the environmental conditions and secure a water supply of decent quality it is necessary to understand how and why the water quality changes along the river and in wells close to the river.

This study aims to investigate the ground water and surface water system in River Antequera and how the chemical composition changes along the river.

2 Background

Bolivia is located in the center of the continent of South America. The nation is landlocked and surrounded by Argentina, Brazil, Chile, Paraguay and Peru. It is rich in natural resources such as natural gas, oil and minerals such as tin, silver, gold, copper, lead and zinc (Nationalencyklopedin 2008). Despite of the richness in natural resources, Bolivia is the poorest country in South America with major economic and social inequalities that are clearly linked to ethnic discrimination. It is also one of the most unequal countries in the world in terms of how resources are distributed (SIDA 2008).

Bolivia has a population of about 9.4 million inhabitants and more than 30 languages are spoken of between 30 to 40 different ethnical groups. The two major groups are Aymara and Quechua who live on the Altiplano. Depending on definition 60-80 % of the population is of indigenous origin. The large economical inequalities; an unfair distribution of resources and the problems with racism are major issues for the country and the situation has for long time been marked by social instability. Bolivia has for a long time been one of the poorest and least developed countries in Latin America. The year 2005 GNP per capita was 2 700 dollar (Latinamerika.nu 2006; internet reference). According to WHO and UNICEF (2004) 36 % of the population

in Bolivia lives in rural areas. 68 % of them have sustainable access to drinking water supply, 44% have piped water that is distributed to their house for private use. The sanitation systems are badly developed in rural areas of Bolivia; only 22 % of the rural population has access to private or public sanitation facilities (UNICEF & WHO 2008).

The southwestern part of Bolivia is a high plateau called Altiplano situated in the Andean mountain range which runs through the entire South American continent. The mountain range divides into two main chains called the Occidental and the Oriental chain and between the two chains is the Bolivian high located. It is an arid wide plain, stretching from Peru in the north to Chile in the south. There are two major lakes in the high plateau, the Lake Titicaca, partly situated in Peru, and the smaller Lake Poopó.

This study is performed in the Lake Poopó region, at an average altitude of 3 800 meters above sea level. Lake Poopó is a very shallow lake which can cover an area up to 3000 km² during the rainy season. During dry season, the surface area decreases to less than half of the wet-season area and it has even dried out on several occasions (Pillco and Bengtsson 2006). The study is concentrated to the Antequera River basin.

The climate in the region is strongly marked by its geographical setting. Being located at a high altitude the temperature is low considering the proximity to the equator. The close distance to the equator as well as the high altitude results in a strong solar radiation and an intensive evaporation (PPO 1996).

The inhabitants in this area have poor living standards due to poverty and the scarcity of water. On top of the scarcity, the water has high salinity and heavy pollution of both heavy metals and domestic waste water in the Antequera river basin (García 2006). There are locations with lack of drinking water along the rivers, which is partly because almost all the rain falls during December to March (Pillco and Bengtsson 2006).

2.1 Previous studies

Anna Ekdahl (2007) has investigated how to improve the water management in the Antequera River basin in the Lake Poopó region and how that would lead to improved living conditions. In her doctoral dissertation Maria García (2006) made a synthesis of the heavy metal conditions in the entire Poopó basin including the Antequera River basin. Lilja & Linde (2006) found TDS and heavy metal concentrations to be lower and pH to be higher in the upper parts of the rivers Poopó, Huani and Marques, before the rivers pass by mining industries. The three rivers are like Antequera tributaries in the Poopó basin.

There are only few measurements of groundwater quality, but the metal concentrations are higher than in the upstream surface waters (García 2006). Further

downstream in the basin there are mines or deserted mines, which influence the surface water and maybe also the groundwater. Near the lake the river forms a delta. The surface water disperses at not very high flows, the water seems to infiltrate before reaching the lake (Pillco and Bengtsson 2006). To be able to take action and use proper means to improve the environmental conditions and secure water supply of decent quality it is necessary to understand how the water quality changes along the river and in wells close to the river. It is also important to investigate what the external additions are; if they are from anthropogenic or natural origin. Not until then can it be determined where water supply can be secured, and not until then means of remediation can be suggested.

Due to extended dry periods, lack of water is a large problem and it causes many conflicts. The mining industry extracts a lot of water which can cause lack of groundwater for irrigation and human consumption in some villages. The use of bad quality water is a health issue for human, livestock and wildlife around the Lake Poopó. Anna Ekdahl (2007) interviewed stock-farmers in the study area and according to them it is common that livestock suffers from diarrhea, inflamed livers and lungs when they drink water from the river. There are no water regulations and therefore the conflicts will get more serious as the demand and water use increases (Ekdahl 2007).

2.2 Objective

The first objective is to follow the Antequera River downstream and investigate how and why the chemical composition changes along the path. In order to distinguish if the surface water and ground water are connected, sampled water from the river will be compared with sampled water from wells situated close to the river.

The second objective is to compare water in wells according to the topography; to compare wells close to Lake Poopó with wells higher up in the mountains; also compare water in wells situated close to each other to see if the ground water originates from the same aquifer.

Focus questions

- How does the flow change along the river and why? Discharge or recharge from the surroundings?
- If the chemical composition changes along the river; why does it change?
- Are there any anthropogenic or natural influences affecting the water quality? In that case; which type of influence and how does it affect the water quality?
- Is it possible to see a significant difference in water chemistry in the wells according to topography?
- If the chemistry differs in wells located close to each other, is it possible that the ground water originates from different aquifers?

3 Description of Study Area

In this chapter the study area is described. Hydrology of Altiplano, Antequera and Urmiri basin, hydrogeology properties, geology, climate and vegetation, population, current situation, mining activity and thermal springs in the area are described.

3.1 Hydrology

The Andean zone makes up for about two thirds of the country and is located above an altitude of 3000 meter above sea level, with several peaks of more than 6000 meters above sea level. The Andean mountain range divides Bolivia in two parts. The western one is called Cordillera Occidental and goes towards the coast of the Pacific Ocean. The east one, Cordillera Real, spans toward southeast to south and converges with the west mountain range again in what is called Cordillera Central. Between the east and west offshoot is the Bolivian high plateau formed, the Altiplano (Troëng & Riera 1996).

3.1.1 Altiplano

In the Andean highlands there is one large basin called the TDPS; Titicaca-Desaguadero-Poopó-Salares hydrological system and it covers an area of approximately 191 000 km² (see Figure 3.1). About two thirds of the basin is located in Bolivia and the rest is located in Peru and Chile. The two main lakes in the Altiplano; Lake Titicaca and Lake Poopó, have very different characteristics. The depth of Lake Titicaca is 200-300 meters, while the maximum depth of Lake Poopó is only a few meters. The two lakes are linked together by the Desaguadero River and the river contributes with a large part of the inflow to Lake Poopó (Pillco & Bengtsson 2007).

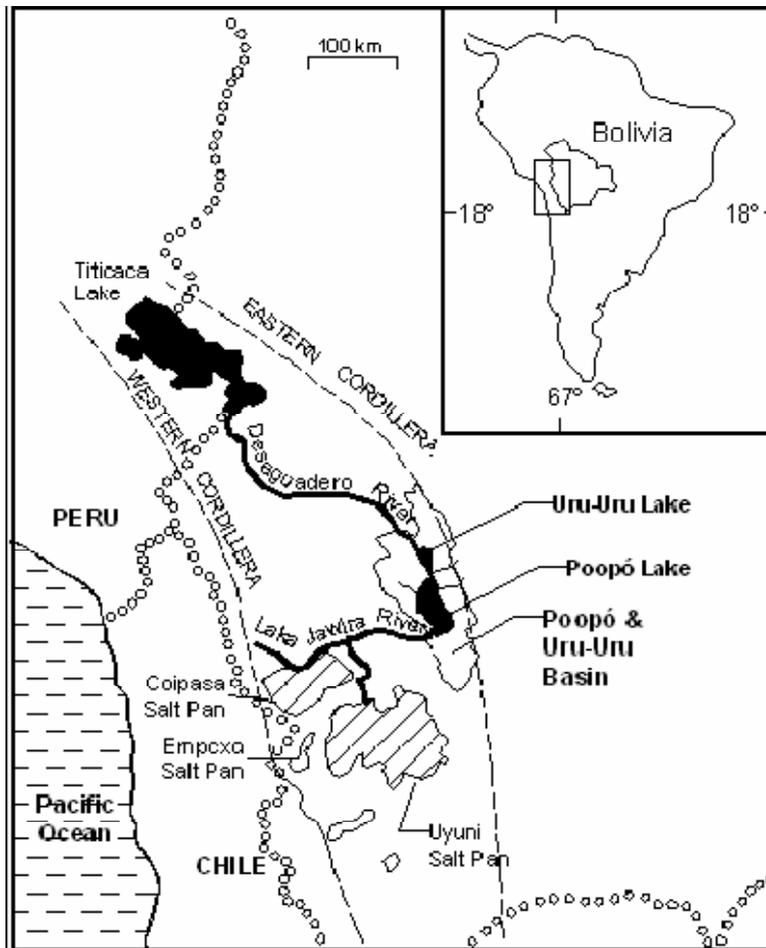


Figure 3.1 The TPDS (Titicaca-Desaguadero-Poopó-Salares) system. The Altiplano is situated in between Eastern and Western Cordillera (Pillco & Bengtsson 2006).

Lake Poopó is a saline lake. A saline lake is caused either by evaporation exceeding inflow or by the inflow being saline or both. Lake Poopó is a terminal lake most years and the evaporation is high. On top of this many of the inflowing rivers are rich in dissolved solids as a result of the extensive mining activity that has been going on for centuries (García 2006).

Poopó basin consists of the two lakes; Lake Poopó and Lake Uru-Uru. The smaller Lake Uru-Uru is located upstream Lake Poopó and it receives water only from Desaguadero River when the river flow is very high. Due to the high evaporation and the shallow maximum depth, less than one meter, Lake Uru-Uru dries up every year. In the wet season (December-March) the surface area of the two lakes Lake Poopó and Lake Uru-Uru can cover up two 15 % of the total area of the basin (Pillco 2007).

3.1.2 Antequera and Urmiri basin

The region from the Eastern Cordillera to Lake Poopó consists of many small rivers and streams. Several of them are seasonal, which means that they have water during the rainy season, while during the rest of the year many of the rivers dry out (Pillco & Bengtsson 2006).

The study area is situated north-east of Lake Poopó (see Figure 3.2) and consists of two river basins; the upper basin of Antequera with an area of 150 km² and the basin of Urmiri, an eastern branch, with an area of 76 km² (Ekdahl 2007). The rivers are formed in the mountainous parts of the basins and reach the plain areas where they join together and form River Pazña. As many of the other rivers in the area, River Antequera has a strong seasonal hydrological pattern. Due to the flat landscape and highly permeable soil in the lower part of the basin, the river terminates in a delta, where much water infiltrates rather than having a surface discharge into Lake Poopó (Pillco & Bengtsson 2006).

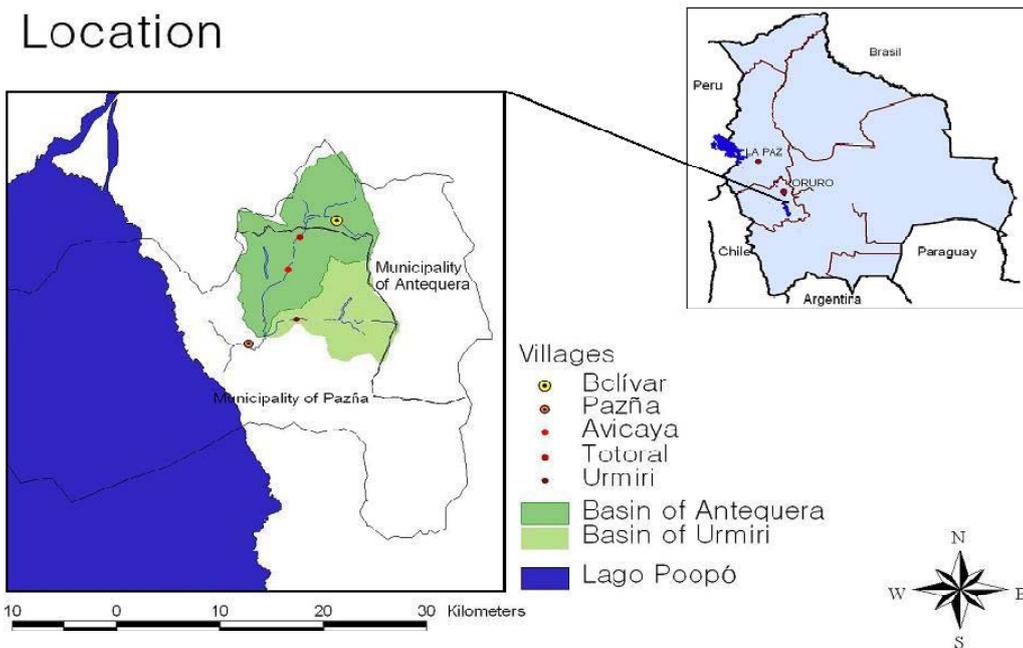


Figure 3.2. The studied catchments; Antequera and Urmiri (Ekdahl 2007).

Due to the high evaporation in the region, the rivers dry out in the dry period every year (Pillco & Bengtsson 2006), while they can contain a lot of water during the rainy season. The maximum average flow in January measured during the years 1960-2002 is 2.5 m³/s (Pillco Zolá 2002 cited in Ekdahl 2007).

3.2 Hydrogeology

In the Altiplano hydro-geological province, fresh water is scarce or lacking and the quality and availability vary from north to south. The best quality of ground water can be found in the northern region between Lake Titicaca and La Paz, while the southern part of the Altiplano has low precipitation and high salinity which contribute to poor ground water quality. The aquifers are from Quaternary age and are of unconfined to semi-confined type, consisting of unconsolidated to semi-consolidated gravel, sand silt and clay interbedded with layers of salt. In these aquifers, brackish to saline water is available in meager to small quantities (Water Resources Assessment of Bolivia 2004).

3.3 Geology

The Poopó basin can be divided into two physiographic units; the Eastern Cordillera and the Altiplano (see Figure 3.1). Eastern Cordillera consists of mountain ranges up to 4000-4500 m in altitude, separated by deep valleys. To the west, the Central Altiplano Plateau is situated with an altitude of approximately 3700 m and in this area Lake Poopó is situated (Troëng & Riera 1996).

3.3.1 Altiplano

The two physiological units (the Eastern Cordillera and the Altiplano) have distinct morphological, structural and geological habits (Troëng & Riera 1996). Eastern Cordillera and the Altiplano are separated by the Poopó-Uyuni fault system (García 2006). The major processes of mountain formation in the Bolivian Andes took place during the late Devonian, late Triassic, and throughout the late Tertiary and Quaternary (Bates & Sweet 1965). Andean tectonism is the reason of most of the tectonic features in the area, and is mainly of post-Oligocene age. The bedrock in the area is dominated of folded Lower Palaeozoic marine clastic sediments. The Altiplano, to the west of the fault, is covered by extensive Quaternary deposits. The Eastern Cordillera is a series of Paleozoic sediments from the Ordovician to the Devonian, a Mesozoic sequence from the Jurassic to the Cretaceous and some Tertiary sediment. Above the rocks Tertiary volcanics have been deposited in different effusive volcanic fields (Troëng & Riera 1996).

The main metallic deposits are located within the tin belt, which extends for more than 800 km from north-western Argentina to south-eastern Peru, following the Paleozoic block of Bolivia's Eastern Cordillera. This poly-metallic belt has both longitudinal and lateral variations concerning age, type and mineral contents of the deposits. The Lake Poopó is located in the middle part of this belt; characterized by an intrusive, essentially sub volcanic Miocene magmatism, with a large number of hydrothermal deposits of tin, silver, zinc, lead, gold, wolfram and other accessory metals (Troëng & Riera 1996).

Gravel and sand deposits are to a great extent associated with the rivers in the area. Limestone originates from the Quaternary era and has a wide distribution. The limestone in the northern part of the Poopó basin is covered by recent sediments. The limestone layers are generally orientated horizontal and are compositionally homogeneous with an average content of 87% CaCO₃. Igneous and sedimentary rocks can be found of smaller dimensions in Poopó and Antequera basins (Troëng & Riera 1996).

3.3.2 Antequera and Urmiri basin

A detailed description and a geological map of the study basin can be seen in Appendix 1. Below a more brief description of the geology in the study basins are presented.

The mountains consist predominantly of thick layers of grey-white quartzite deposited in a marine proximal environment and pelitic rocks (Troëng & Riera 1996). Pelitic rocks are formed from aluminum sedimentary rocks, commonly shales and mudstones (Australian Museum 2007).

The Altiplano is made up of glacial sediments deposited in a continental glacial environment. It includes glacial, fluvio-glacial, and colluvioglacial deposits. The deposits are products of the erosion during the latest glacial period. This unit consists of boulders, pebbles, gravel, sand, silt and clay forming moraines and other deposits (Troëng & Riera 1996).

The area around River Antequera consists of sands, silts, clays limestone and evaporates. The lower part of the basin consist of eolian deposits (wind deposits) made up of fine to medium grained sand. The upper part consists of alluvial and colluvial sediments. It was deposited in a continental environment and includes alluvial fans, colluvial, fluvial and terrace deposits made up principally of gravel, sand, silt and clay. These deposits are found in the valleys and slopes of the hills and have a high content of tin (Troëng & Riera 1996).

3.4 Climate and vegetation

The Altiplano has a harsh climate, classified as semiarid-cold for the northern and middle parts. The area is characterized by two seasons; the summer, November to March, is the wet season and the winter, April to October, is the dry season. The mean annual rainfall in the Altiplano Basin varies between 800 and 200 mm in the north-south direction. (Pillco and Bengtsson 2006) Based on measurements made by PPO, 2006 during the period 1975-1995 the average annual rainfall in the town of Pazña is measured to 450 mm and the annual potential evaporation is calculated to be 1700 mm. The average temperature in the area during the summer is approximately 12-14 °C, while the average during the winter is 6-7 °C (PPO 1996). Temperature varying from -10°C to 14°C in the winter and from -2°C to 18°C in the summer.

The precipitation over Altiplano is sensitive to variations in the large-scale circulation patterns. The effects of ENSO, El Niño-Southern Oscillation, on the atmospheric circulation are observed as variations in the amount of precipitation in the Altiplano-area so that El Niño years are related to below-normal precipitation and La Niña years to the opposite (Pillco & Bengtsson 2006). In the region also frequent hail storms and frosts occur. Directly related to the natural rain and flooding systems it is also common with droughts and floods, which in turn cause environmental, economic and social impacts (García 2006).

The vegetation in the area is typical for the arid to semiarid climate and does not allow for much agriculture. The flora in the area consists of perennial grasses, interspersed with scrubs of thola (see Figure 3.3) and dispersed bushes. There are some trees in the area, most in protected areas such as in the village squares. Also some small species of cactus is growing in the area. The grass is used as forage for livestock such as llamas, sheep and donkeys. Many of the plants in the area are so called halófitas, which can manage in environments with high contents of salts (Ekdahl 2007). To a lesser degree the soils are used for cultivation of potato, barley, quinoa, cañahua etc (Montes de Oca 1989 cited in Troëng & Riera 1996).



Figure 3.3. The vegetation in the Altiplano consists mainly of Thola.

3.5 Population

The life expectancy is 72 years in urban areas in Bolivia, but much lower in the Altiplano; about 50 years in some villages and 45 years in the mining towns (INE 1999 cited in García 2006). The largest town and the economic centre of the region is Oruro with approximately 200 000 residents (PPO 9603 1996 cited in García 2006). In 2001 the municipalities of Antequera and Pazña had 3352 and 5469 inhabitants respectively and both municipalities had a negative growth rate. Migration is a problem in the small villages due to the decreasing mining activities and the lack of alternative income sources, also many young people leave for studies in larger cities and many never return (Ekdahl 2007).

3.6 Current situation

There are many small communities in the rural area around Lake Poopó inhabited by poor villagers. Inhabitants in the lower parts of the study area mainly earn their livings by breeding livestock, primarily cattle and sheep, and agriculture where the agriculture is sustained by irrigation and seasonal rain. In the mountains the main activity, apart from livestock and agriculture, is mining which contribute to high pollution of minerals in lakes, rivers and soil. The most mined minerals are tin, lead, silver, zinc, gold and copper (Capriles 1997 cited in Pillco 2007). Wastewater from the mining activities is sometimes dumped into rivers without proper treatment, mainly from small-scale mining. This in addition to natural contamination and pollution from human activity and agriculture will result in high concentrations of pollutants in the water. Despite the pollutants and the high salinity, river water is used for irrigation and the groundwater is used for household needs such as cooking and drinking water for humans and animals (Pillco 2007).

3.7 Mining

The polymetallic Bolívar vein deposit in the Antequera basin was discovered in 1810 and the exploitation started out as superficial silver extraction (García 2006). There are three mines in the Antequera basin; Bolívar, Totoral and Avicaya and the location of the mines can be seen in Figure 3.2 in Chapter 3.3.1. The Bolívar mine is owned by a multinational Swiss company called Sinchi Wayra. It is a deep underground mine working far below the water table and they pump up and discharge about 95 to 115 l/s of water to the tributary to Antequera (Ekdahl 2007). The mine at Marta is also owned by Sinchi Wayra but not currently active and the Bolívar mine has been runed by a cooperative. Apart from these there are also several small-scale miners in the area (Ekdahl 2007). Miners use sulfuric acid in the pretreatment of ores and the acid effluents are often released into the river without neutralizing treatment (García 2006).

3.8 Thermal springs

There are two larger well known thermal springs in the area of Antequera and Urmiri basins where two thermal baths are located as can be seen in the map in Figure 3.4. Apart from this there may exist other small thermal springs since the geology in the area shows plenty of faulting and faulting may favor structural springs.

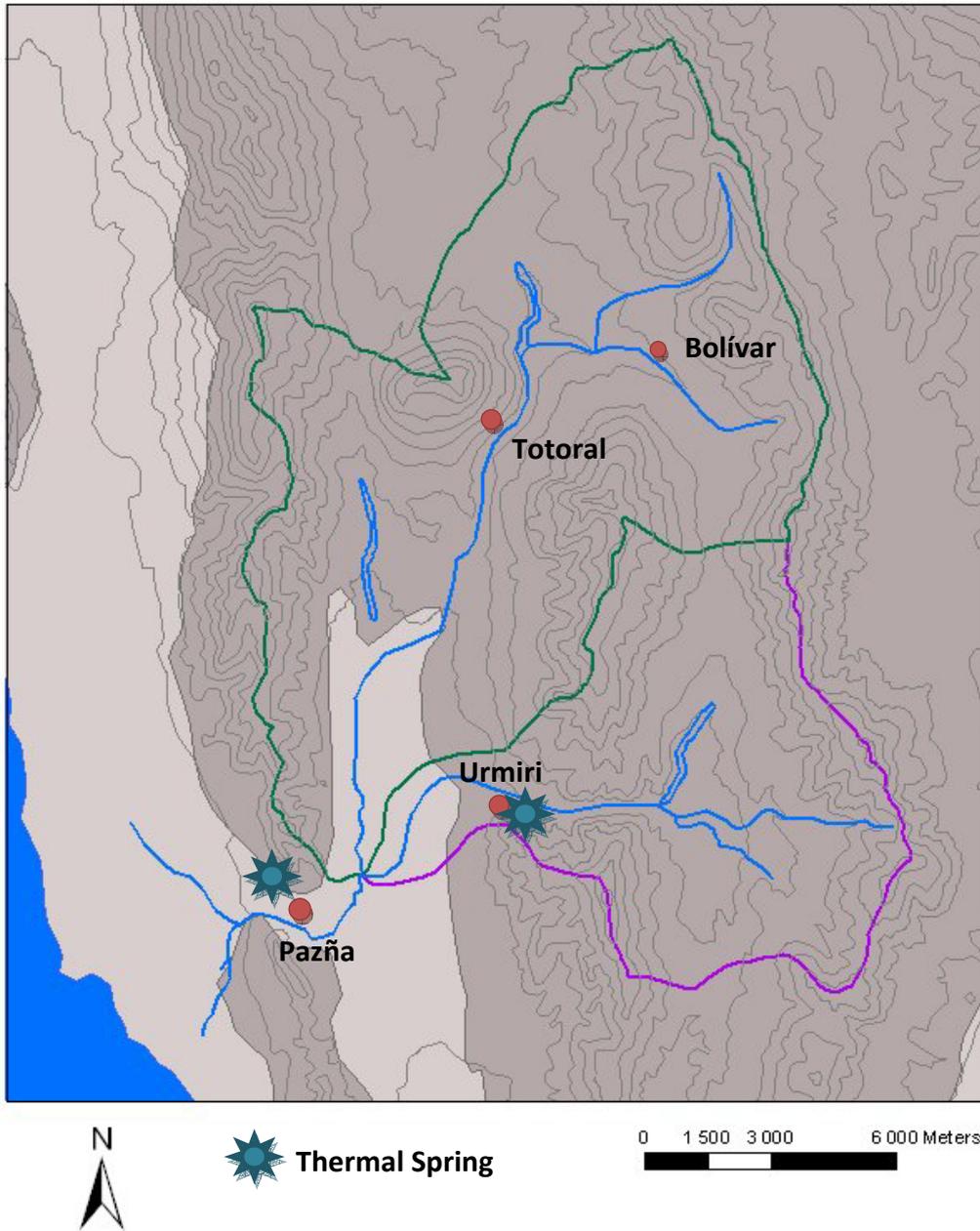


Figure 3.4 Position of thermal springs in Antequera and Urmiri basins.

The thermal water at Pazña and Urmiri has a meteoric origin as they only contain minerals present in the rock in the area and the springs are located in geological faults (Ekdahl 2007).

4 Methodology

The water sampling was carried out during a field trip in the beginning of March 2008. Basic physical properties of the water was analyzed in the field and chemical properties were analyzed in the laboratory at the University of San Andrés, La Paz.

4.1 Field study

Two field trips were carried out in Antequera and Urmiri basins. The first trip was performed in the middle of February (14th to 16th of February) 2008. The purpose of the trip was to inspect the area in order to decide where to collect the samples. The sampling locations were located using a GPS-instrument (Garmin GPS12XL, 12 channels). During this trip also the local inhabitants were asked for permission to collect samples from their wells. No samples were collected during the first trip.

The second trip was performed at the end of February and the beginning of March 2008 (28th February to 2nd of March) and during this trip all the samples were collected and the flow in the river was measured at a number of sites.

4.2 Flow measurement

The river flow was measured in a cross section at each location of chemical sampling. By measuring the velocity at several points and at different depth within the river cross section, the total flow could be computed.

The velocity was measured with a mini-flow meter; OTT hydrometrie, Contador Z30, having a propeller diameter of 4 cm. In each point the velocity was measured at approximately 20%, 60% and 80% of the total water depth. In shallow parts, one or two different depths were sufficient. The velocity was measured during 30 seconds. The coordinates of each point were recorded in terms of depth and length from shore.

4.3 Water sampling

During the second field trip, water samples were collected from nine river locations, thirteen wells, a mine outlet, a pipeline and discharge from a thermal spring in the study area. Hence water samples were collected at total 25 locations (see Figure 4.2), all with duplicates, for analyze in the laboratory. The water from the river was sampled using a bucket. The wells were sampled and the sample water was taken from half of the water depth, using a water collector tube; Nansen Wildco, model 1930-D65 0797 (see Figure 4.1).



Figure 4.1. A Nansen Wildco water collecting tube was used for ground water sampling.

4.4 Physical analysis

In the field the coordinates and the altitude of the sampling points was measured with two different GPS meters (Garmin GPS map 765 and Garmin GPS12XL, 12 channels). The water depths in the wells were measured with a measuring tape. In the field pH; electrical conductivity; temperature; total dissolved solids (TDS); and redox potential were measured using a Hach pH-meter.

4.5 Chemical analysis

In the field the collected water was filtered through a 45 μm filter before it was poured into polyethylene bottles, two large bottles (volume 150 ml) and two small ones (volume 75 ml) for each sampling location. The further chemical analyses were done in the laboratory at the Chemistry Research Institute, University of San Andres in La Paz, Bolivia. Most of the analyses were done during four weeks in the middle of March to the middle of April 2008. The samples were stored in a refrigerator before the chemical analyzing started.

4.5.1 Calcium, Magnesium, Sodium and Potassium

The cations calcium, magnesium, sodium and potassium were measured with flame atomic absorption spectrometry, FAAS. The analyses were done using a Perkin Elmer AAnalyst 100 Atomic Absorption Spectrometer and the system consists of a high efficiency burner system. The burning system provides the thermal energy necessary to dissociate the chemical compounds, providing free analyte atoms so that atomic absorption occurs. The amount electromagnetic waves absorbed at a specific wavelength is measured by the spectrometer using a hollow cathode lamp as the primary light source, a monochromator and a detector. Background absorbance caused by non-atomic species in the atom cloud is corrected by a deuterium arc lamp (PerkinElmer Instruments, 2000). It was necessary to repeat some samples because wrong dilution factor was used, and therefore also the standard curve was repeated during these occasions, resulting in different correlation coefficients, r , for different standard curves. The r^2 -value for the calibration curve for calcium was 0.9967. The r^2 -

value for magnesium ranged from 0.9985 to 0.9991, the r^2 -value for potassium ranged from 0.9951 to 0.9988 and the r^2 -value for sodium ranged from 0.9796 to 0.9988.

4.5.2 Sulfate (SO_4^{2-})

In the laboratory the samples were prepared by adding buffer solution (5 ml per 25 ml total volume) and distilled water to the water sample. The chemical composition of the buffer solution can be seen in Appendix 2.

BaCl_2 was added to the sample to form BaSO_4 crystals of uniform size (5 ml per 50 ml total solution) and the solution was mixed with a magnetic stirrer for one minute. After stirring the sample was left to rest for four minutes, to give crystals time to form, and then the turbidity was measured in a spectrophotometer (Thermo Spectronic-vision32 Software V1.24) at a wavelength of 420 nm. Wave length absorption was measured and the concentration of sulfate was obtained from a standard curve. The standard curve had been created as a linear relationship formed by the concentrations 0, 4, 8, 12, 16 and 20 mg/l SO_4^{2-} . Some samples needed to be repeated with corrected dilution factor and therefore also the standard curve was repeated during these occasions resulting in different correlation coefficients, r , for different standard curves. The r^2 -value ranged from 0.9857 to 0.9999. Preparation of the standards can be seen in Appendix 3.

4.5.3 Nitrate (NO_3^-)

The samples were prepared by adding 1 ml 0.1 M HCl to 5 ml water sample to prevent hydroxide and carbonate interference. 220 nm and 275 nm wave length absorbance was measured to correct for organic content. The calibration curve was made by plotting the concentration of standards (10, 20, 30 and 40 mg/l NO_3^-) against their absorbance at 220 nm minus two times their absorbance at 275 nm, forming a linear relationship. It was necessary to repeat some samples because wrong dilution factor was used, and therefore also the standard curve was repeated during these occasions, resulting in different correlation coefficients, r , for different standard curves. The r^2 -value for the calibration curves ranged from 0.9787 to 0.9948. The absorbance was measured with a spectrophotometer (Thermo Spectronic-vision32 Software V1.24).

4.5.4 Chloride (Cl^-)

In the laboratory the samples were prepared by mixing 1 ml $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$, 2.5 ml 10 % HNO_3 and 1 ml $\text{Hg}(\text{SCN})_2$ and then filled up with water sample in 25 ml volumetric flask. The chloride form a compound with the Hg^{2+} -ion and SCN^- form a compound with Fe^{3+} , which absorbs UV-light at 480 nm. A calibration curve was made by plotting standard concentrations (0, 10, 20, 30, 40 and 50 mg/l Cl^-) against their absorbance, resulting in a linear relationship. It was necessary to repeat some samples with a corrected dilution factor and therefore also the standard curve was repeated during these occasions resulting in different correlation coefficients, r , for different standard curves. The r^2 -value for the calibration curves ranged from 0.9909

to 0.9975. Preparation of the standards can be seen in Appendix 3. The turbidity was measured as absorbance of 480 nm wavelength in a spectrophotometer (Thermo Spectronic-vision32 Software V1.24)

4.5.5 Alkalinity

The alkalinity was determined in the field by titrating 5 ml sample with 0.01 M HCl to pH 4.5. The water samples consist of natural water, therefore it was assumed that bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) account for all alkalinity.

If the pH is less than 8.2 it is assumed that all the alkalinity is produced by bicarbonate (HCO_3^-) and the carbonate (CO_3^{2-}) assumed to be zero. While as if pH reaches above 8.2 the alkalinity instead is assumed to be from carbonate (CO_3^{2-}) and the bicarbonate (HCO_3^-) is assumed to be zero (Davis & DeWiest 1966).

4.6 Description of sampling locations

Water was sampled in the river from upstream to downstream at nine river locations, one sample from a mine outlet, one from a thermal spring and one from a pipeline. In connection to the river points, also water was sampling from thirteen wells close to the river. In this chapter the locations are described from upstream to downstream. How the sampling points are situated along the rivers can be seen in Figure 4.2 and in a geological map in Appendix 1.

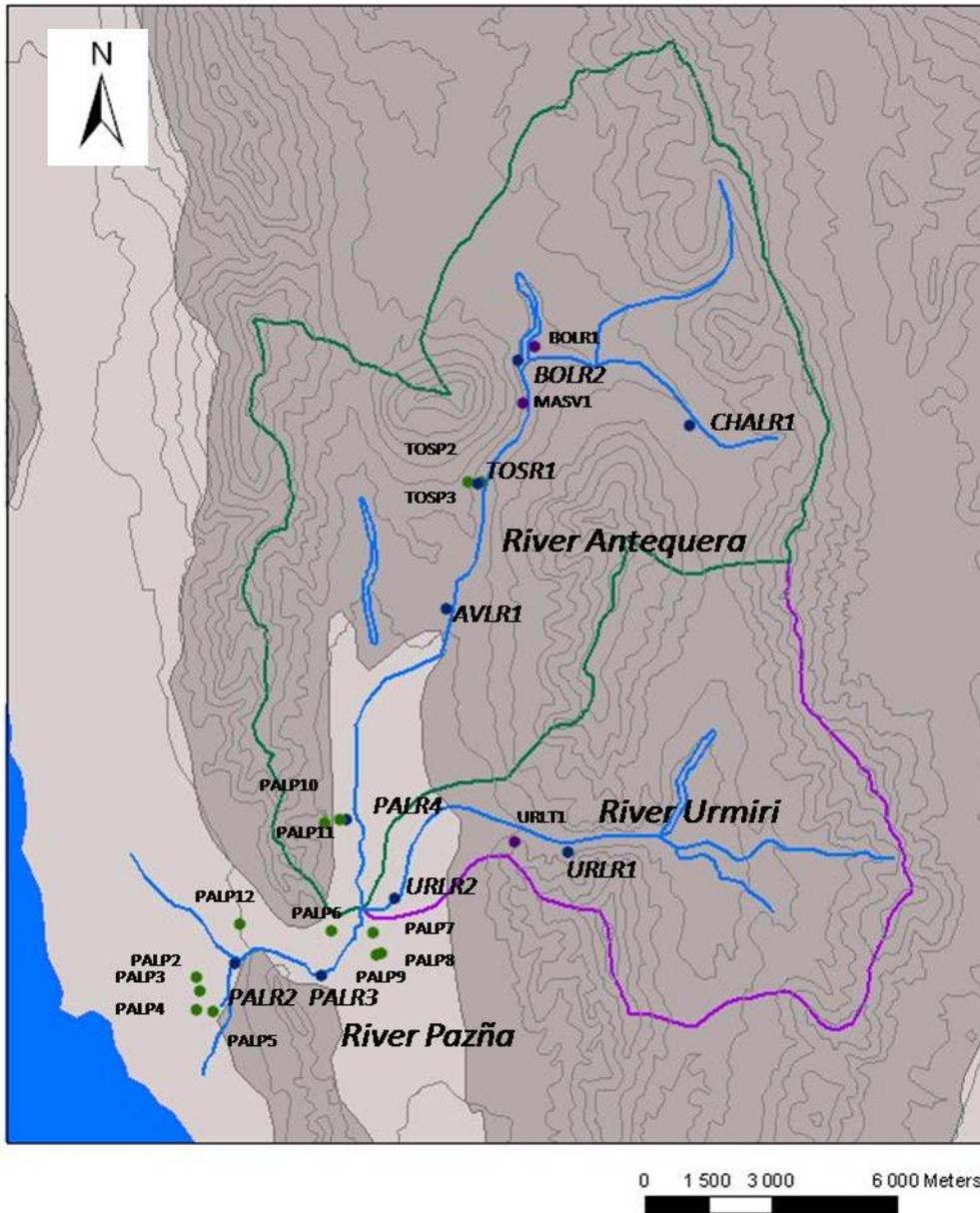


Figure 4.2. Position of the sampling points in river Antequera, Urmiri and Pazña and wells close to the rivers. Sampling points situated in the river are marked with larger font.

CHALR1 is the most upstream sampling point in River Antequera, situated upstream the mine Bolívar. The water originates from the mountains meandering through a river valley with steep mountain sides. The river bed consists of coarse material as stones of different sizes and the shore is dominated by sand (see Figure 4.3).



Figure 4.3. The most upstream sampling point, CHALR1.



Figure 4.4. Flow measurements at the second sampling point BOLR1, an outlet from the mine Bolívar.

The measuring point BOLR1 is not situated in River Antequera; instead it is an outlet from the mine Bolívar, which discharges water into River Antequera. The river bed of the stream from the Bolívar mine consists of coarse material such as stones, but also more impermeable material such as fine sand (see Figure 4.4).

BOLR2 is the second sampling point in the river and is located downstream the Bolivar mine outlet. It was hard to overview the area since it consist of several river branches. A possible misinterpretation cannot be ruled out and this should be kept in mind while interpreting the collected data. The river divides into several smaller parts which made it hard to decide where to collect the chemical sample and it was impossible to measure the flow. The river bed and the surrounding area consist of soft impermeable material such as clay; the water was very turbid and the vegetation in the surroundings was almost non-existent.

MASV1 is a sampling point of water discharged from a pipeline into the river as can be seen in Figure 4.5. The origin of the pipelined water is probably from further uphill the mountains. Women and children in the village were laundering cloth in the water. Also at this site the river bed consists of compact fine sediments and different sized stones.



Figure 4.5. The sampling point MASV1 where the water was sampled from a pipeline.



Figure 4.6. The sampling point TOSR1, located close to the mine Totoral.

TOSR1 is the next sampling point from the river. It is situated close to the Totoral mine. The valley opens up a little and the river divides into several branches as it meanders. The surrounding mountain sides are steep, which can be seen in Figure 4.6. The river bed at this location consists of coarse material such as stones of different size and also compact fine sand. Close to TOSR1 sampling was done from two wells, TOSP2 and TOSP3 (see Figure 4.2).

AVLR1 is a sampling point close to the mine Avicaya, situated downstream from Totoral in river Antequera and can be seen in Figure 4.7. The water at this location differed a lot from the other sampling points with respect to the turbidity. At this location the water was very turbid, while the water at the other sampling sites had been fairly clear. The river bed consist of till.



Figure 4.7. The sampling point AVLR1 situated close to the mine Avicaya.



Figure 4.8. The sampling point PALR4, the last sampling point in River Antequera.

PALR4 is the last sampling point in river Antequera before it merges with River Urmiri and becomes River Pazña (see Figure 4.8). At this point the river is fairly wide and shallow and the water is clear. As can be seen in Figure 4.8, the bottom of river valley is flat and vegetation is sparse. The river bed is hard and compact; consist

of both fine and coarse material. Close to PALR4, water was sampled from two wells, PALP10 and PALP11 (see Figure 4.2).

PALR3 is the first sampling point after the two rivers, Antequera and Urmiri, have merged together; thus in the River Pazña. At this location the river is divided into two branches. As can be seen in Figure 4.9, the topographic settings are similar to PALR4. However, the river bed mainly consists of compact fine sediments; the size of the stones is considerably smaller than at PALR4. Water was also sampled from wells in the same area as PALR3. As can be seen in Figure 4.2, PALP 7, PALP8 and PALP9 are close to both URLR2 and PALR3, situated in between the two river sampling points, south of the river. PALP6 is situated north of the river, close to PALR3.



Figure 4.9. The sampling point PALR3, which is the first measuring point in River Pazña.



Figure 4.10. The most downstream sampling point in River Pazña, PALR2, closest to Lake Poopó.

PALR2 is the most downstream measuring point in the river and also closest to Lake Poopó. As can be seen in Figure 4.10, the landscape surrounding the river is quite different from upstream. It is flat and the surroundings are richer in vegetation. The sediments are very fine and sandy and have a whiter color, which may indicate on precipitated salts. The river bed consists of fine sediments such as sand. North of the river, sampling from a well; PALP12, was done. Downstream PALR2, between the river and Lake Poopó, water was sampled at different wells situated relatively close to each other; PALP2, PALP3, PALP4 and PALP5. Locations of the wells in relation to the river can be seen in Figure 4.2.

URLR1 is the most upstream sampling point in River Urmiri, situated upstream the thermal spring seen in Figure 3.4. The stream water at this point originates from the mountains and, as can be seen in Figure 4.11, the vegetation is abundant around the river. The river bed consists of stones and a concrete construction.



Figure 4.11. The most upstream sample point in River Urmiri, URLR1.



Figure 4.12. Sampling point URLT1, which is a thermal spring close to River Urmiri.

URLT1 is water sample from the thermal spring close to Urmiri (see Figure 4.2). The sample was taken from the spring (see Figure 4.12) situated in the hillside. The temperature of this water was significantly higher than the other water samples. The vegetation around the spring is abundant and consists mainly of different grass.

URLR2 is the sampling point in River Urmiri located downstream the thermal spring (see Figure 4.2). The river crosses through a road made of concrete where the river is very wide (see Figure 4.13). The sample is taken out downstream the road, where the river comes together and becomes narrower. The river bed consists of fine sand and stones with different sizes.



Figure 4.13. The sampling point URLR2, after the thermal spring in River Urmiri.

4.7 Control of Results

To be able to quantify the accuracy of the chemical analyzes an ion balance was interpreted and duplicate samples were analyzed for each sampling point. The methodology for the calculations is presented in this chapter.

4.7.1 Ion Balance

All natural waters should be electrically neutral with regard to dissolved ions which means that the number of moles negative charges should be equal to the number of moles positive charges in the water. Comparison of anions and cations gives an evaluation of the quality of the analyses. The concentration of the ions (mg/l) is converted into the unit milliequivalents per liter, which means that also the charges of the ions in water solution are taken into consideration. According to Fetter (2001) the charge balance error (CBE) can then be calculated from equation (1).

$$CBE = \frac{\sum cations - \sum anions}{\sum cations + \sum anions} \quad (1)$$

4.7.2 Accuracy of Analyzes

To be sure of the analyze accuracy the samples were analyzed with duplicates for all parameters and the percentage of the relative average deviation (RAD) was calculated as in equation (2). The RAD is recommended to be less than 10% according to the standards at University of San Andres, La Paz, this means that the maximum dispersion for the two duplicates of the same sample should not exceed 10%. The equation for the calculations can be seen in equation (2).

$$RAD = \frac{\sqrt{\sum(x - \bar{x})^2}}{\bar{x}} \quad (2)$$

5 Literature Survey

In this chapter some background information about the measured parameters and ions are presented. Also a brief introduction of chemical concepts such as chemical weathering, ion exchange, redox processes and a short description of the influence of thermal springs on the water quality is presented.

5.1 pH

Pure water contains, in addition to water molecules, also dissociated H^+ and OH^- ions in very low concentrations (Davis & DeWiest 1966). The expression of pH is defined as the negative logarithm of the hydrogen-ion concentration.

In most natural waters the pH is controlled by the carbon dioxide-bicarbonate-carbonate system. Because the solubility of carbon dioxide in water changes with pressure and temperature, also pH is depending on these parameters (Davis & DeWiest 1966).

In general very high pH values, above 8.5, are usually associated with sodium-carbonate-bicarbonate waters. While very low pH values, below 4.0, are associated with waters containing free acids derived from oxidizing sulfide minerals, usually pyrite, or from waters in contact with volcanic gases containing hydrogen sulfides (H_2S) and hydrochloric acid (HCl). In general also water from limestone has a higher pH than water from clay-rich sediments (Davis & DeWiest 1966).

5.2 Electrical Conductivity

The electrical conductivity of a solution is defined as the ability of a cubic centimeter to conduct an electrical current (Davis & DeWiest 1966). The electrical conductivity depends on the amount of ions in the solution; more ions lead to higher conductivity. However, conductivity cannot be converted directly into ion content because it also depends on the temperature of the solution, and the mobility and the number and type of chemical bonds within the ion.

5.3 Total Dissolved Solids (TDS)

In a water sample, Total Dissolved Solids includes all solid material in solution, whether ionized or not. TDS does not include suspended sediment, colloids or dissolved gases (Davis & DeWiest 1966).

5.4 Redox Potential (Eh)

Redox reaction is a process in which one constituent is being oxidized and the other reduced. The oxidant is the electron acceptor and the reductant is the donor, therefore a redox reaction can be described as a transfer of electrons. A redox reaction can be

split up into two half-reactions, one describing each reactant and redox potential (Eh) is the standard measure of the redox state of natural water. It is defined as the electric potential, measured in volts, relative a specific half cell reaction. Positive values indicate oxidizing conditions and negative values indicate reducing (Appelo & Postma 1996 cited in Selander & Svan 2007).

Because Eh is defined for a specific half-cell reaction, problems occur when discussing the redox condition of a natural environment. Natural waters contain several redox pairs, each with individual values of Eh. When discussing Eh of a solution, the assumption has been made that all redox reactions in the system are in equilibrium, but this is not common in nature (Drever 1997 cited in Selander & Svan 2007).

5.5 Ions in Water

In this chapter some background information of the analyzed ions are presented.

5.5.1 Calcium (Ca²⁺)

Calcium is a major constituent of many common rock minerals and a major component of the solutes in most natural waters. The ion is an essential element for plants and animals. Calcium has only one oxidation state, Ca²⁺, and it is an important component in many igneous-rock minerals, especially in chain silicates pyroxene, amphibole and feldspars. The group of plagioclase feldspar minerals contains various proportions of albite (NaAlSi₃O₈) and anorthite (CaAl₂Si₂O₈). Calcium also occurs in other silicate minerals produced in metamorphism. Water that has been in contact with igneous and metamorphic rocks expects to contain some calcium but the concentration is generally low, mainly because the decomposition of most igneous-rock minerals is slow (Hem 1985).

In sedimentary rocks, the most common forms of calcium are carbonates, such as calcite, aragonite and dolomite. Calcite and aragonite are two crystalline forms with different crystal shape but the same formula CaCO₃ and the mineral dolomite can be represented as CaMg(CO₃)₂ (Hem 1985).

In sandstone and other detrital rocks, calcium carbonates often occur as cement between particles or as partial filling of interstices. Calcium also takes place as adsorbed ions on negatively charged mineral surfaces in soils and rocks. Calcium is generally the most common divalent ion in solution and divalent ions are more strongly bound to particles than monovalent ions at surface charge sites. Most such charge sites are therefore occupied by calcium ions in river or ground-water systems. In solution the most important ion pair is CaSO₄(aq) (Hem 1985).

5.5.2 Magnesium (Mg²⁺)

Magnesium and calcium may be considered to have similar effects in some aspects of water chemistry due to their contribution to hardness in water. Magnesium has, like

calcium, only one oxidation state of significant in water chemistry, Mg^{2+} , and it is also essential in plant and animal nutrition. On the other hand, magnesium ions are smaller than calcium and have therefore tendency to attach small spaces in water molecules (Hem 1985).

Magnesium is a major component in dark-colored ferromagnesian minerals in igneous rocks. In altered rocks, magnesium occurs as magnesian mineral species such as chlorites and serpentine. Sedimentary forms of magnesium include carbonates such as magnesite ($MgCO_3$) and hydromagnesit ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$). Magnesium also occurs as dolomite ($CaMg(CO_3)_2$) which is a sedimentary carbonate rock and a mineral composed by same amount magnesium and calcium formed as crystals (Hem 1985).

The predominant form of magnesium in solution in natural water is the magnesium ion Mg^{2+} , and the ion pair $MgSO_4(aq)$ has about the same stability as the ion pair $CaSO_4(aq)$. Magnesium complexes with carbonate and bicarbonate, and they have similar stability as the same species of calcium (Hem 1985).

5.5.3 Sodium (Na^+)

Sodium is an alkali-metal which means that the oxidation state is 1+ and it is, like calcium and magnesium, also essential for animal and plant nutrition. Sodium ions, Na^+ , do not participate in redox processes and they are not strongly hydrated. Sodium occurs in higher amount than potassium in igneous rocks but is much less abundant in sediments (Hem 1985).

When sodium has been brought into solution, it tends to remain in that position and there are no important precipitation reactions that can maintain low sodium concentrations in water. Sodium ions are retained by adsorption on mineral surfaces, particularly by minerals having high cation-exchange capacities such as clays. The interactions between surfaces and monovalent ions, such as sodium, are however much lower than the interactions between surfaces and divalent ions, such as Mg^{2+} and Ca^{2+} . In fresh water systems, cation-exchange processes tend to extract divalent ions from solution and replace them with monovalent ions (Hem 1985). If, for example, water rich in Ca^{2+} infiltrates through a soil horizon or through an aquifer, ion exchange might occur. By adsorption the Ca^{2+} -ions are fixed in the ion exchange medium while Na^+ -ions are released. The concentration of Ca^{2+} in the water will decrease while the Na^+ -concentration will increase. However, the total amount of dissolved ions will remain the same (Svensson 2005).

Sodium exists in igneous rocks as feldspar minerals such as plagioclase series ranging in composition from albite, $NaAlSi_3O_8$, to anorthite, $CaAl_2Si_2O_8$. Species containing sodium and calcium are vulnerable to weathering because they yield the metal cation and silica to solution and it is common that clay mineral is formed with aluminum and part of the original silica (Hem 1985).

5.5.4 Potassium (K⁺)

Potassium, K, is more common in sedimentary rocks than in igneous rocks. The behavior of potassium is slightly different than sodium in natural systems. Sodium tends to remain in solution once it has been liberated from silicate-minerals while potassium has more difficult to be released from silicate minerals and tends to reincorporate into solid weathering products, especially clay minerals. Therefore the concentration of potassium is general much lower than the concentration of sodium in natural waters (Hem 1985).

Potassium is involved in the biosphere, especially in vegetation and soil and, like calcium, magnesium and sodium; potassium is an essential element for both plants and animals (Hem 1985).

The minerals containing potassium in silicate rocks are the feldspars orthoclase and microcline (KAlSi₃O₈) and the feldspathoid leucite (KAlSi₂O₆). Potassium feldspars are resistant to attack by water. Normally potassium would be expected to be adsorbed less strongly in ion-exchange reactions than sodium due to the potassium ion being larger than the sodium ion. However that is not the case because potassium is incorporated in a special way into some clay-mineral structures. For example in illite, a clay-sized mica mineral, potassium is incorporated in spaces between crystal layers, and can therefore not be removed by further ion-exchange reactions (Hem 1985).

5.5.5 Sulfate (SO₄²⁻)

Sulfur occurs in oxidation states ranging from S²⁻ to S⁶⁺ and the chemical behavior of sulfur is strongly related to redox properties of aqueous systems. The anion Sulfate, SO₄²⁻, is the highest oxidized form of sulfur which forms a stable, four-coordinated structure with oxygen. Sulfur in reduced form, S²⁻, forms sulfides of low solubility with most metals. Iron is common and widely distributed and therefore iron sulfides have an important influence on sulfur geochemistry. Sulfur is essential for plants and animals (Hem 1985).

In early history of the hydrosphere, most sulfates originated from igneous rocks and volcanic sources. In the present, sulfates are mainly recycled from the atmosphere and from the solution of sulfate minerals in sedimentary rocks. Atmospheric precipitation contains sulfate. Sulfate in the atmosphere is derived from dust particles containing sulfate minerals, from oxidation of sulfur dioxide gas, SO₂, and from oxidation of hydrogen sulfide gas, H₂S. Sources of hydrogen sulfide gas in the atmosphere are decomposition of organic material and locally from volcanic emanations, while sulfur dioxide is discharge to the atmosphere from volcanic sources and from burning of fossil fuels. In a chemical oxidized environment, sulfur exists as sulfate ions, SO₄²⁻, and in a reduced chemical environment, sulfur occur as H₂S (Davis & DeWiest 1966).

One of the most effective natural processes for removal of sulfate from water is sulfate reduction by bacteria, since sulfate bacteria use sulfides and sulfate in their life

cycles. The bacteria obtain energy from oxidation of organic compounds and in the process they receive oxygen from sulfate ions in subsurface water. The bi-product during the process is hydrogen sulfide gas due to reduction of sulfate ions (Davis & DeWiest 1966).

If iron is present under moderately reducing conditions in the water, iron sulfide, FeS, may be precipitated, and then both iron and sulfide will be removed from the water (Davis & DeWiest 1966).

If water has a pH of 3 or less it may contain significant amounts of partially dissociated sulfuric acid in the form of HSO_4^- . Therefore it is possible that the sulfate concentration in water decreases when the pH is around 3 (Hem 1985).

5.5.6 Nitrate (NO_3^-)

Nitrogen is an important element in plant and animal nutrition. In the atmosphere, hydrosphere and biosphere nitrogen occurs at oxidation states ranging from N^{3-} to N^{5+} . In the Earth's atmosphere, most of the nitrogen occurs as nitrogen gas, N_2 (Hem 1985).

Nitrogen gas in the atmosphere is very stable due to strong bonds between the nitrogen atoms. However, N_2 can be fixed from the atmosphere by some bacteria and blue-green algae, which incorporate it into organic nitrogen (Stumm & Morgan 1996).

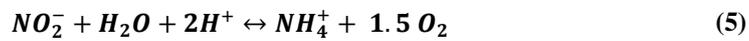
The concentration of nitrate in groundwater is low during normal conditions because nitrogen minerals are very rare in the Earth crust. On the other hand, the concentration can be high due to external additions such as nitrogen rich atmospheric precipitation due to mans use of fossil fuel, plant nutrient leakage from farming and use of fertilizer, point sources as dunghills and sewage pipes and mineralization of organic nitrogen (Svensson 2005).

The external additions contribute with ammonia, NH_4^+ , to the soils. Under aerobic conditions, microorganisms mediate the nitrification of NH_4^+ to NO_2^- and NO_3^- . The relationship can be seen in equation (3).



Oxidation of NH_4^+ is mediated by the bacterium *Nitrosomanas*, and the oxidation of NO_2^- by the bacterium *Nitrobacter*. Nitrate, NO_3^- , does not participate in ion exchange in the soil and is therefore readily eluted into the groundwater (Stumm & Morgan 1996).

Low pH will cause low concentration of NO_3^- , as it turns into NH_4^+ which can be explained from equations (4) and (5).



The equations are dependent of $[H^+]$, which means that low pH (high concentration of H^+) will force the nitrification towards the right, and there will be more ammonia (Stumm & Morgan 1996).

5.5.7 Chloride (Cl⁻)

Chloride is a major dissolved element of most natural waters even though it is a minor constituent of the earth's crust. Minerals that contain chloride as an essential constituent are sodalite and apatite in igneous and metamorphic rocks. Micas, hornblende and natural glass also contain significant amounts of chloride. The high amount of chloride in sea water is probably a result of continuous contribution of chloride from volcanic gases which has accumulated in sea water (Davis & DeWiest 1966).

According to Davis and DeWiest (1966) most of the chloride in ground water derives from four different sources:

1. Chloride from old sea water entrapped in sediments
2. Solution of halite and related minerals in evaporate deposits
3. Chloride contributed by rain or snow and concentration by evaporation
4. Solution of dry fallout from the atmosphere, particularly in arid regions

Locally, also volcanic water in thermal spring systems may be an important source of chloride. The most important source of chloride in near-surface water seems to be chloride transported in the atmosphere and carried to the earth by rain and snow. Chloride is rarely removed from water by precipitation except under the influence of evaporation or freezing. The reason for this is that chloride salts are highly soluble. It is also rare that chloride participates in exchange, adsorption or biological activity (Davis & DeWiest 1966).

5.6 Alkalinity

Alkalinity is the ability of a solution to neutralize acid. It can be measured by the amount of a standard concentration sulfuric acid required to titrate a water sample to pH 4.5. If the water has a pH below 9.0, the alkalinity is almost entirely produced by bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. In natural waters it is very rare with a pH above 9.0, and the alkalinity can be used to determine the concentrations of bicarbonate and carbonate ions in the water (Davis & DeWiest 1966).

Below pH 8.2 most of the carbonate ions add hydrogen and become bicarbonate ions therefore the alkalinity titration below pH 8.2 is a measure of bicarbonate ions.

However above pH 8.2 the dissociation of bicarbonate to carbonate ions is effective and the alkalinity here is then a measure of carbonate ions (Davis & DeWiest 1966).

If the pH is high, the concentration of H⁺-ions is low, which will drive equation (6) towards the left. Below pH 8.2 most carbonate ions will add hydrogen to become bicarbonate ions and equation (6) will move towards the right (Davis & DeWiest 1966).



When the pH is below 4.5 most of the bicarbonate ions are converted to carbonic acid molecules (Davis & DeWiest 1966) according to equation (7).



In ground water, most of the carbonate and bicarbonate derive from carbon dioxide (CO₂) in the atmosphere and the soil, and solution of carbonate rocks. Bicarbonate can also be obtained from carbon dioxide generated by diagenesis of organic compounds (Davis & DeWiest 1966).

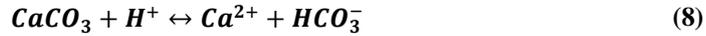
5.7 Chemical Weathering

Weathering is a process by which parent rocks are broken down mechanically or are chemically dissolved. Water occupies a central role in these processes and acts both as a reactant and as a transporting agent of suspended and dissolved material. During chemical weathering, rocks and primary minerals undergo chemical reactions with water, thereby being transformed first to solutes and soils and later on to sediments and sedimentary rocks. Evaporite minerals are very soluble and dissolve rapidly (Stumm & Morgan 1996). Due to the acid mine water leaching into the ground and River Antequera, and the coarse material, there are high weathering potential.

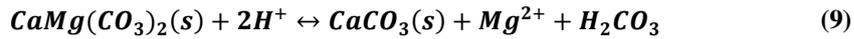
Generally groundwater has higher concentration of ions than surface water. This is because groundwater often is older than surface water and weathering has taken place during a long time (Stumm & Morgan 1996).

Mining activity and old deposits cause acid rock drainage which is one of the major anthropogenic hazards in the Antequera basin. The contaminated mine water originates from working drainage, waste rock dumps and mill tailings. Mining waste is often crushed which gives it a large surface area exposed to oxidizing conditions (García 2006). The oxidation of sulfuric rock like pyrite, which is a common mineral in the polymetallic vein, produces sulfuric acid and result in a highly acid drainage (Fetter 2001). The low-pH drainage increases the weathering and cause extensive leakage of heavy metals and salinity (Stumm & Morgan 1996).

Materials rich in calcium carbonate raise the Ca^{2+} concentration if weathering takes place, weathering of CaCO_3 is dependent on pH (equation (8)).



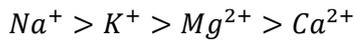
The weathering of dolomite is pH-dependent which can be seen in equation (9).



Lower pH gives rise to more weathering of dolomite (Stumm & Morgan 1996).

5.8 Ion Exchange

Ion exchange is a process when ions attracted to a solid surface may be exchanged for other ions in solution. In natural soils the most common is cation exchange, however also anion exchange can occur. A general ordering of cation exchangeability for the most common ions in groundwater is

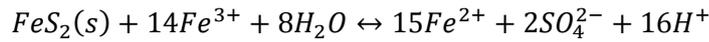
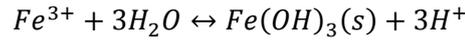
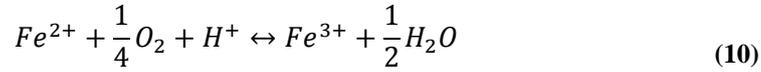
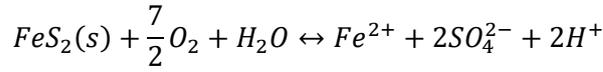


The divalent ions are more strongly bonded and tend to replace monovalent ions (Fetter 2001).

5.9 Redox processes

A redox reaction is a chemical reaction where a reductant donor electrons and an oxidant accept electrons. Because there are no free electrons, every oxidation is accompanied by a reduction, in other words; an oxidant is a substance that causes oxidation to occur while being reduced itself (Stumm & Morgan 1996).

There are a lot of mine tailings along the River Antequera were significant oxidation of pyrite results in high load of sulfate (García 2006). The reaction can be seen in equation (10) (Stumm & Morgan 1996).



The oxidation of pyrite (FeS_2) releases dissolved ferrous iron (Fe^{2+}) and acidity (H^+) to the water. The ferrous iron is then oxidized to ferric iron (Fe^{3+}). Ferric iron is then hydrolyzed to form insoluble $Fe(OH)_3$ and more acidity is produced. Ferric iron can also be reduced by pyrite, which results in ferrous iron, sulfate and acidity (Stumm & Morgan 1996).

5.10 Thermal Springs

The geology in the area shows plenty of faulting and faulting may favor structural springs. If an impermeable faulted rock unit is bordering an aquifer this can form a regional ground-water boundary and force water from the aquifer to discharge as a fault spring (Fetter 2001). Rock temperature increases with depth and if ground water is circulated to a significantly depth it can gain high temperature. The increased water temperature raises solubility and dissolution rate of most minerals. The solute concentration of thermal water is therefore in general much higher than for regular ground water (Hem 1985).

6 Results

The results from the flow measurements, measurements of physical parameters and results from the chemical analyses are presented in this chapter.

6.1 Flow measurement

Data from the flow measurements in River Antequera and River Urmiri are presented in Table 6.1 and locations can be seen in Figure 6.1. The results are presented with two significant figures. The measurements were accomplished with help from Ramiro Pillco Zolá at the Institute of Hydraulics and Hydrology at the University of San Andrés, La Paz. The flow increases along River Antequera. However at some sampling points the flow was measured to decrease from one point to another located further down; between TOSR1 and AVL1, and between PALR3 and PALR2. In River Urmiri the flow at two measuring points were measured and the result shows a decrease in flow at URLR2 located downstream URLR1.

Table 6.1. The measured flow at each sampling site presented from upstream to downstream.

Sampling point	Flow (l/s)	Date
<i>Antequera</i>		
CHAR1	14	29-Feb-08
TOSR1	120	29-Feb-08
AVLR1	110	29-Feb-08
PALR4	250	2-Mar-08
PALR3	340	1-Mar-08
PALR2	310	1-Mar-08
<i>Urmiri</i>		
URLR1	88	29-Feb-08
URLR2	34	1-Mar-08

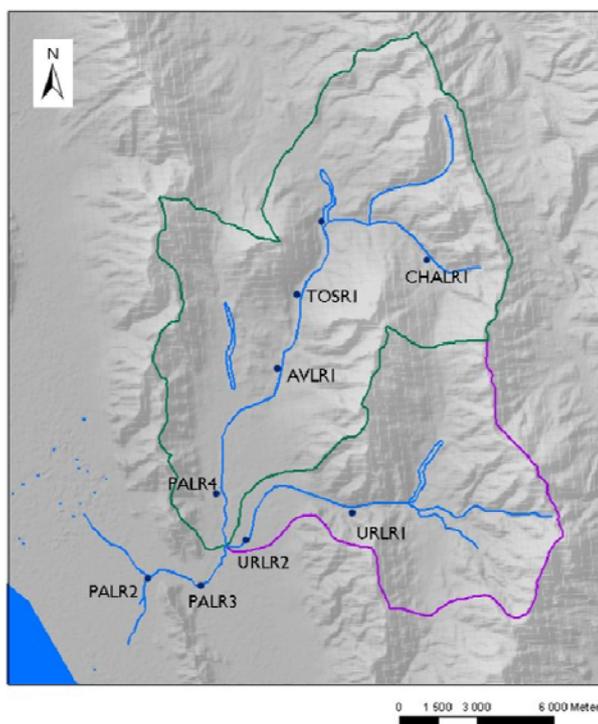


Figure 6.1. Locations of measured flow.

6.2 Physical analysis

The physical parameters; temperature, pH, electrical conductivity, total dissolved solids and redox potential were measured in field and the results can be seen in Table 6.2. The temperature ranges between 12.4 and 20.5 °C for the ground water. The temperature in the thermal spring (URLT1) is high, 55.5 °C. In the surface water the temperature ranges between 16.3 and 22.8 °C. The pH in the ground water is more alkaline than the surface water. The highest pH in surface water is at CHALR1; pH 7.6, located before the mines. In River Urmiri the surface water is alkaline with a pH of 8.1-8.9. The pH of ground water ranges from 5.9 to 8.9. The high electrical conductivity and total dissolved solids indicate high salinity. Redox potential of all ground water samples indicates reduced environment (except in TOSP3) and the majority of the surface waters indicate oxidized environment.

Table 6.2 Physical data measured in field divided in ground water and surface water arranged from upstream to downstream.

Sampling point	T (°C)	pH	C (µS/cm)	TDS (mg/l)	Eh (mV)	Flow (l/s)	Date
<i>Ground Water</i>							
TOSP2	17.5	6.7	1118	614	-22		29-Feb-08
TOSP3	20.5	5.9	98	52	20		29-Feb-08
PALP10	13.8	7.4	657	356	-55		2-Mar-08
PALP11	13.0	8.9	680	368	-127		2-Mar-08
PALP6	17.0	7.3	704	383	-54		1-Mar-08
PALP7	15.1	7.4	3130	1788	-55		1-Mar-08
PALP9	15.2	7.2	3360	1937	-49		1-Mar-08
PALP8	16.6	7.4	3060	1750	-55		1-Mar-08
PALP12	15.5	7.4	11620	7150	-56		1-Mar-08
PALP2	14.6	7.2	3210	1843	-48		1-Mar-08
PALP3	12.4	7.5	2520	1427	-61		1-Mar-08
PALP4	14.3	7.6	2520	1168	-68		1-Mar-08
PALP5	15.1	7.5	3890	2260	-63		1-Mar-08
URLT1	55.5	6.7	5400	3160	-23		29-Feb-08
<i>Surface Water</i>							
CHALR1	16.3	7.6	212	113	-69	14	29-Feb-08
BOLR1	16.6	4.3	2880	1642	100	64	29-Feb-08
BOLR2	19	2.2	1773	988	208		29-Feb-08
MASV1	18.7	6.9	363	194.8	-31		29-Feb-08
TOSR1	22.5	3.2	2400	1359	161	120	29-Feb-08
AVLR1	21.2	2.7	2430	1376	186	110	29-Feb-08
PALR4	19.5	3.0	1643	913	168	250	2-Mar-08
PALR3	22.1	3.1	1661	924	164	340	1-Mar-08
PALR2	17.3	3.0	1653	920	164	310	1-Mar-08
URLR1	16.6	7.0	238	126.5	-93	88	29-Feb-08
URLR2	22.8	8.9	1473	815	-132	34	1-Mar-08

6.3 Chemical analysis

The chemical analyses were performed in the chemical laboratory at the University of San Andrés in La Paz; the results can be seen in Table 6.3 (details in Appendix 4). The analyses were accomplished with guidance from the employees at the university. The results are presented with two significant figures. Calcium content of the groundwater is in the range 5.9-220 mg/l, and in the surface water 16-600 mg/l. Magnesium is in the range 0.9-44 mg/l for the ground water and the surface water in the range 3.1-16 mg/l. Sodium is in the range 7.4-3300 mg/l for ground water and 13-290 mg/l for surface water. Potassium is in range 2.3-150 mg/l for ground water and 2.4-9.9 mg/l for surface water. Sulfate occurs in higher concentrations in the surface water, 23-2500 mg/l, to compare with ground water, 27-630 mg/l. The concentrations of nitrate vary significantly in the water samples, especially in the surface water, however all the ground water samples contain nitrate; 72-1300 mg/l. In the surface water nitrate concentrations are in the range 0-1300 mg/l. Chloride concentrations are in the range 0-2500 mg/l for ground water and 0.8-670 mg/l for surface water. All the ground water samples contain alkalinity in form of bicarbonate except PALP11 were

the alkalinity is in form of carbonate. According to the surface water only CHALR1, MASV1, URLR1 and URLR2 contain bicarbonate or carbonate.

Table 6.3. Results from the chemical analyses performed in the chemical laboratory at University of San Andrés, La Paz. The results are divided into ground water and surface water from upstream to downstream.

Sampling point	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	SO42- (mg/l)	NO3 (mg/l)	Cl (mg/l)	HCO3 (mg/l)	CO3 (mg/l)	Sampled
<i>Ground Water</i>										
TOSP2	28	1.4	210	24	270	72	42	120	0	29-Feb-08
TOSP3	5.9	0.9	7.4	2.3	27	1300	0	*	*	29-Feb-08
PALP10	83	7.3	46	10	130	840	48	250	0	2-Mar-08
PALP11	91	6.2	50	6.2	130	710	15	0	120	2-Mar-08
PALP6	77	7.6	53	11	180	1100	31	210	0	1-Mar-08
PALP7	200	40	590	46	140	1200	14	560	0	1-Mar-08
PALP9	210	44	650	48	160	1100	1600	540	0	1-Mar-08
PALP8	160	35	640	45	200	1100	1300	550	0	1-Mar-08
PALP12	190	28	3300	150	78	760	17	790	0	1-Mar-08
PALP2	220	18	640	33	630	620	1000	220	0	1-Mar-08
PALP3	180	11	480	34	440	1100	690	370	0	1-Mar-08
PALP4	190	10	390	24	480	720	38	230	0	1-Mar-08
PALP5	310	14	770	38	400	1100	1800	510	0	1-Mar-08
URLT1	110	5.8	1400	85	31	870	2500	620	0	29-Feb-08
<i>Surface Water</i>										
CHALR1	16	3.1	13	3.7	43	700	0.8	120	0	29-Feb-08
BOLR1	600	14	60	18	2500	16	44	0	0	29-Feb-08
BOLR2	29	8.5	13	2.4	1400	33	22	0	0	29-Feb-08
MASV1	36	3.8	32	3.5	76	980	29	110	0	29-Feb-08
TOSR1	400	16	32	14	2100	12	20	0	0	29-Feb-08
AVLR1	270	15	38	9.9	1600	16	4.1	0	0	29-Feb-08
PALR4	150	9.9	47	5.3	230	0	30	0	0	2-Mar-08
PALR3	190	15	60	7.4	490	1100	46	0	0	1-Mar-08
PALR2	190	14	79	7.6	750	5.3	23	0	0	1-Mar-08
URLR1	19	3.2	15	3.1	44	1300	15	130	0	29-Feb-08
URLR2	70	5.6	290	22	23	320	670	0	130	1-Mar-08

* No titration performed

6.4 Ion balance

The charge balance error (CBE) was calculated and the results can be seen Table 6.4 (the calculation performed can be found in Appendix 5). The charge balance error varies at the different sample points. Surface water ranges from -85% to -7%, hence there is an excess of anions in the water. In the ground water CBE ranges from -93% to 71%; there are an excess of cations in PALP12, PALP4 and TOSP2 and an excess of anions in the other ground water samples.

Table 6.4. Calculated Charge Balance Error (CBE) in the surface water and ground water samples.

Sampling point	sum anions (meq/l)	sum cations (meq/l)	CBE	Sampling point	sum anions (meq/l)	sum cations (meq/l)	CBE
<i>Ground Water</i>				<i>Surface Water</i>			
TOSP2	11	-10	6%	CHALR1	2	-14	-78%
TOSP3	1	-22	-93%	BOLR1	34	-54	-22%
PALP10	7	-22	-51%	BOLR2	3	-30	-83%
PALP11	7	-19	-43%	MASV1	4	-20	-70%
PALP6	7	-26	-57%	TOSR1	23	-44	-32%
PALP7	40	-32	11%	AVLR1	17	-34	-34%
PALP9	44	-75	-27%	PALR4	10	-18	-26%
PALP8	40	-68	-26%	PALR3	14	-29	-37%
PALP12	159	-27	71%	PALR2	14	-16	-7%
PALP2	41	-55	-14%	URLR1	2	-24	-85%
PALP3	32	-52	-25%	URLR2	17	-29	-26%
PALP4	28	-26	3%				
PALP5	51	-85	-25%				
URLT1	69	-95	-16%				

6.5 Accuracy of data

The accuracy of data in this study is uncertain due to different aspects. Only one sampling was done during one field trip, it is therefore not possible to compare the ion concentrations with other analysis. The field study was done at the end of February, but the chemical analyses were not performed until the end of March due to problems with the laboratory equipment. The plastic bottles with water samples were supposed to be stored dark in the refrigerator while they were waiting for analysis, but they did not. The water samples were stored in the refrigerator the first week after the field trip, but the rest of the time they were stored in room temperature in the laboratory. This may influence the results because the higher temperature may promote bacterial growth and chemical processes to occur in the bottles.

Due to high ion concentrations some of the water samples had to be diluted to be able to analyze. The dilution factors were guessed according to the value of conductivity, and if a dilution was wrong it had to be re-analyzed. The analyze equipment was available during a limited time at each occasion because many students at San Andres University used the equipment. Therefore it happened several times that samples from the different locations were not analyzed the same day for the same parameter and this may influence the results.

The laboratory at San Andres University did not have a dishwasher and therefore all the glass equipment, used for mixing the samples, was washed-up by hand. The analysis of sulfate, nitrate and chloride are sensitive processes and requires

uncontaminated equipment, otherwise the results may be affected. It is possible that the human factor influenced this aspect.

It was not the same person that analyzed all the samples in the laboratory and different persons with their different routines may also have affected the results. When the water was filtered in field, some filters were cleaned and used more than once which can contaminate the water sample.

The method for measuring the flow seems to be reliable. However sometimes it was difficult to measure due to uneven river bed and stones, but at each measuring location the flow was measured in several points in the cross section. It was not possible to measure the flow in the sampling point BOLR2 since the river divides into several smaller parts.

The physical parameters such as pH, Eh, electrical conductivity, temperature and alkalinity were measured in field and are considered being close to the correct value since the Hach pH-meter was calibrated before the field trip.

7 Discussion

In this chapter measured flows and the chemical analyses are discussed and compared with the results of other studies. The changes of pH in River Antequera and the analyzed ions are discussed and the variations along the river. Also anthropogenic influence and ground water affect the water quality in Antequera and the ion balance of the analyzed cations and anions are discussed.

7.1 Measured Flow

The flow conditions are discussed in two chapters, the first contains an analysis of the measured flow in River Antequera and the second contains a comparison of the flow during the year.

7.1.1 Measured River Flow

The measured flow data is presented In Table 6.1. The flow increases much from CHALR1 to TOSR1. Between TOSR1 and AVL R the flow is practically constant and then increases significantly before reaching PALR4. This large increase is most likely due to a tributary from the north-northwest, south of the small town Avicaya.

PALR3 is the first measuring point after the two rivers, Antequera and Urmiri, have merged and the flow here is 340 l/s which is 56 l /s more than sum of PALR4 and URLR2. This could have several reasons. First of all the flow generally increases downstream due to increased catchment area and there could also be a measuring error in either one of these three points.

It is interesting though, that the flow in PALR3 (340 l/s) is approximately the same as the sum of PALR4 and URLR1 (338 l/s) this may indicate that the water takes another way around URLR2, reaching the river further downstream either by another tributary or via groundwater. The idea of water from Urmiri passing through a shallow ground water aquifer prior reaching River Pazña can be given some support by the increase of Ca and Mg ions at PALR3 compared to PALR4. The amount of the increase corresponds quite well to the imagined case if ground water of the same quality as in nearby wells were introduced at 60 l/s into the river. A calculated mass balance can be seen in Appendix 6.

7.1.2 River Flow over the Year

The upper Antequera river basin is mountainous, sometimes with steep slopes and exposed bedrock and the vegetation is sparse. During the wet season the flow in the rather mountainous catchment is characterized by many short but high peaks. However, the flow does not change much during the dry season because it then mainly consists of base flow from the deeper groundwater (PPO 1996).

The water samples were collected between the 29th February and the 2nd March which is the end of the wet season. The last rainfall had occurred three days before, on the 26th February, with a total precipitation of 2 mm. There had also been three days with small precipitations on the 21st to the 23rd and before then, no rain for about two and a half weeks. The rain gauge data can be seen in Figure 7.1.

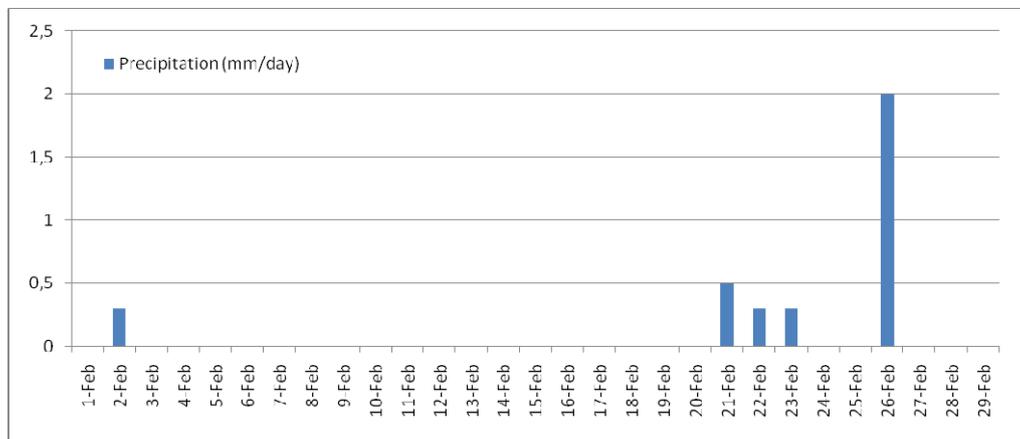


Figure 7.1. Daily precipitation data from weather station in Pazña for February 2008.

The potential evaporation calculated with the Penman formula is in Pazña 148 mm for March (4.9 mm/day) and 128 mm for April (4.1 mm/day) according to PPO 1996. A mean monthly evaporation based on A-pan measurements during 1990-1995 presented in PPO 1996 was 192 and 187 mm/month for March and April respectively, which gives a daily evaporation of about 6.2 mm/day. Although the measurements generally are of poor quality it is clear that the precipitation is small compared to the

expected evaporation for the time of the field trip and hence it is reasonable to assume that the river mainly consist of base flow.

Figure 7.2 shows the average monthly flow between 1960 and 2002 in River Pazña and the distribution over the year. March and April is at the end of the high flow. There is almost no flow at all during the dry period, this indicates no base flow and very spars, if any, contact with a deeper aquifer (at least not with a recharge exceeding the daily evaporation).

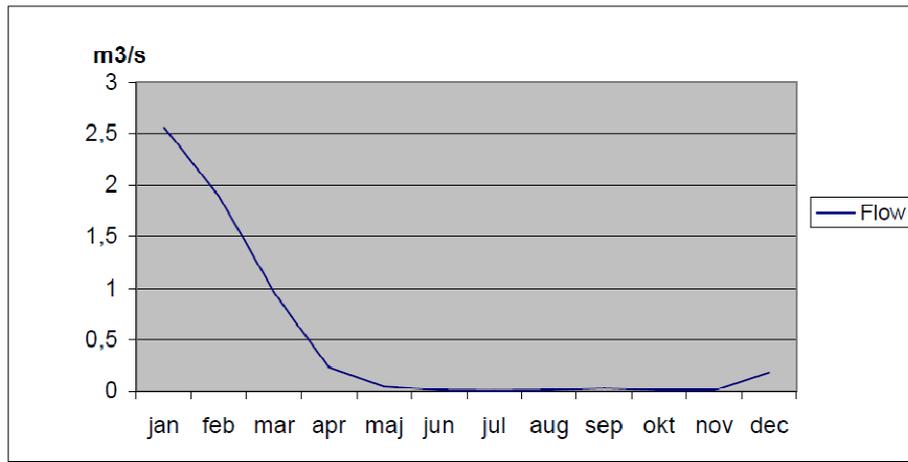


Figure 7.2. The average flow between 1960 and 2002 in the River Pazña and its yearly distribution (Pillco Zolá 2002 cited in Ekdahl 2007).

7.2 pH

The change in pH along the River Antequera can be seen in Figure 7.3. The pH in CHALR1 is neutral, around 7. BOLR2 is situated after the mine Bolívar and the pH in this point decreases significantly, the pH is around 2, which is an effect of the mining activity. Deposits from mines are rich in minerals containing sulfur and iron. One common mineral is pyrite (FeS_2) and when water and air react with the material the sulfide mineral is oxidized and hydrogen ions are released and the pH will drop. There are also a lot of mine tailings along the river where significant oxidation of these type of minerals results in low pH.

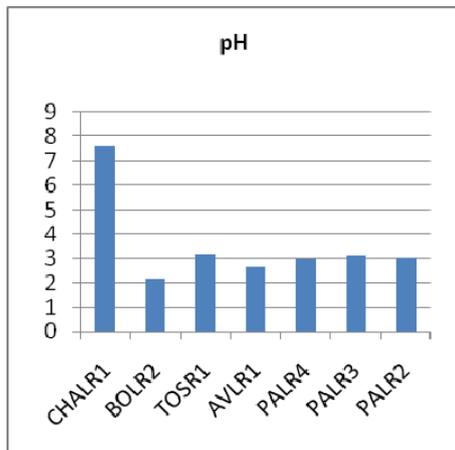


Figure 7.3. pH along the River Antequera.

At the sampling point further down in River Antequera the pH remains low along the river. There is a lot of mining activity along the river and this will affect the pH in all sampling points. Water having a pH of 3 or less may contain significant amounts of partially dissociated sulfuric acid in the form of HSO_4^- (Hem 1985). HSO_4^- has not been evaluated and this may be one reason of the unbalanced ion balance.

7.3 Chemical Analyses

The change in concentration of the analyzed ions along River Antequera and possible explanations of the change is discussed in this chapter.

7.3.1 Calcium (Ca^{2+})

The Ca^{2+} concentration increases and decreases along the river (see Figure 7.4). Calcium concentration in the first measuring point CHALR1 is low. At BOLR2 the concentration is still relatively low but slightly increased. The effluent water from the Bolívar mine measured in BOLR1 had a high Ca^{2+} content of 600 mg/l and this will most likely have an effect on quality in the river. At the next sampling point, TOSR1, the concentration have had a significant increase. The concentration then decreases further downstream through AVL1 and PALR4. At the two sampling points closest to Lake Poopó, PALR3 and PALR2, the Ca^{2+} concentration is constant, however higher than in PALR4.

The increase of calcium concentration in the upstream part of the river can be explained in different ways. One explanation can be the effluent water from the Bolivar mine and a second one is the surrounding materials in the river bed. pH is low in the river and the shores in the upstream part of the valley are surrounded by coarse material and old mine residues. Materials rich in calcium carbonate will raise the Ca^{2+} concentration if weathering takes place and weathering of CaCO_3 is dependent of pH.

The decrease of calcium concentration that takes place between TOSR1 and PALR4 can also have different explanations. One explanation can be dilution with surface water with lower ion content. The flow does not increase from TOSR1 to AVLR1, but between AVLR1 and PALR4 there is a tributary and the flow is doubled. However, the water quality of this contributing stream is unknown. Ion exchange can also be one explanation of the decrease in Ca^{2+} concentration, as sodium may replace the calcium ions in water.

The rise between PALR4 and PALR3 may be due to recharge from shallow ground water. Generally groundwater has higher concentration of ions than surface water therefore a reason for the increase can be the result of groundwater intrusion.

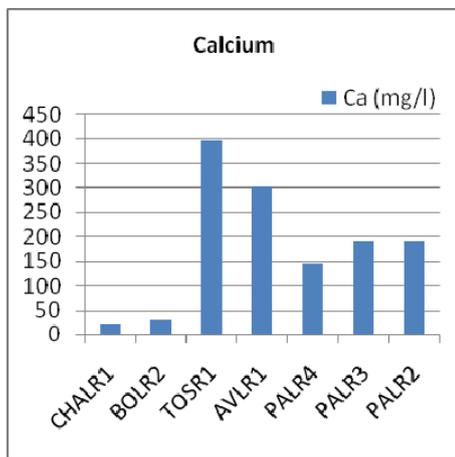


Figure 7.4. Calcium-concentration along the River Antequera in mg/l.

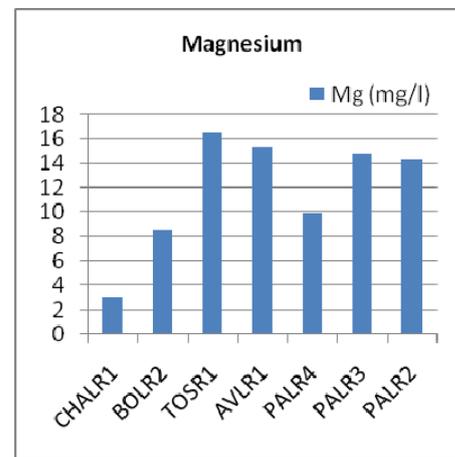


Figure 7.5. Magnesium-concentration along the River Antequera in mg/l.

7.3.2 Magnesium (Mg^{2+})

The Mg^{2+} concentration increases and decreases along the river (see Figure 7.5). Magnesium concentration at the first measuring point CHALR1 is low. The concentration then increases through BOLR2 and TOSR1. There is no significant change at AVLR1 only a slight decrease. At PALR4, the concentration has decreased. At the sampling point PALR3 the Mg^{2+} concentration increase again and reaches similar values as in AVLR1 and it is then more or less constant at PALR2.

The increase of magnesium is probably due to weathering of dolomite or another magnesium rich mineral. Lower pH will give rise to more weathering of dolomite (Stumm & Morgan 1996).

Magnesium decreases slightly between TOSR1 and AVLR1, and PALR3 and one explanation can be dilution of surface water with less ion content. After AVLR1 and before the sampling point PALR4 there is at least one unknown inflow of surface water to River Antequera which can explain the decrease of magnesium.

7.3.3 Sodium (Na^+)

Na^+ increases all the way downstream along the river (Figure 7.6). The first measuring point, CHALR1, has the lowest concentration and the concentration increases from BOLR2 and downstream along the river and reaches the highest concentration in PALR2, which is the measuring point closest to Lake Poopó. When sodium has been brought into solution, it tends to remain in that position and there are no important precipitation reactions or redox processes that can maintain low sodium concentrations in water (Hem 1985).

The rising content of sodium can be the result of weathering, ion exchange and saline groundwater intrusion.

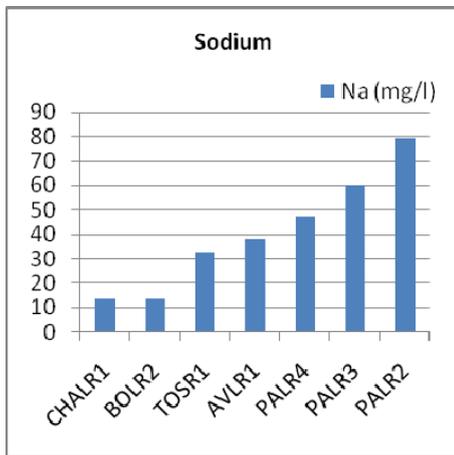


Figure 7.6. Sodium-concentration along the River Antequera in mg/l.

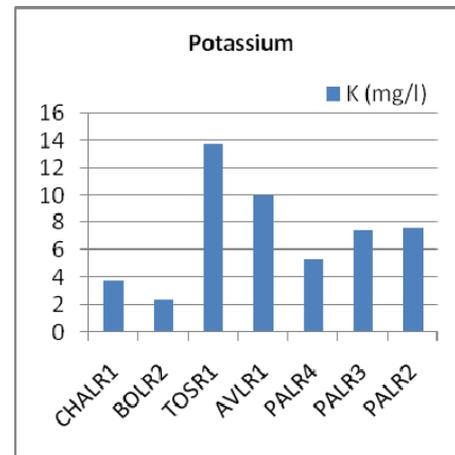


Figure 7.7. Potassium-concentration along the River Antequera in mg/l.

7.3.4 Potassium (K^+)

The K^+ concentration increases and decreases along the river (see Figure 7.7). Concentration of potassium at the first measuring point CHALR1 is relative low. At the second measuring point BOLR2 the concentration decreases. At next sampling point, TOSR1, the concentration increases and further downstream, AVL1, K^+ slightly decreases. At PALR4 the concentration decreases. At the sampling point PALR3 the K^+ concentration increase again and reaches similar values as at AVL1 and is then more or less constant at PALR2.

The increase of potassium concentration at TOSR1 is probably due to the mining activity close to the river. The mine deposits are rich in potassium which is released by weathering.

7.3.5 Sulfate (SO₄²⁻)

The SO₄²⁻ concentration increases and decreases along the river (see Figure 7.8). Sulfate concentration at the first measuring point CHALR1 is low. At the second measuring point BOLR2 the concentration increases significant and continues to increases at TOSR1. The reasons are the mining activity and mine deposits contributing with high amounts of sulfate in the soil and water. There are also a lot of mine tailings along the river were significant oxidation of pyrite results in high load of sulfate.

Further downstream, at sampling point AVLR1, SO₄²⁻ decreases. At the next location, PALR4, the concentration decreases significantly. The reason for the decrease can be dilution by water from the tributary connecting to Antequera north of the sampling point.

If the water has a pH of 3 or less it may contain significant amounts of partially dissociated sulfuric acid in the form of HSO₄⁻. This can explain why the sulfate concentration decreases when the pH is around 3 (Hem 1985).

Iron sulfide may be precipitated in the river giving it a red color. If the water is turbulent, the particles can be kept in suspension. From PALR4 until the Lake Poopó, sulfate concentration increases.

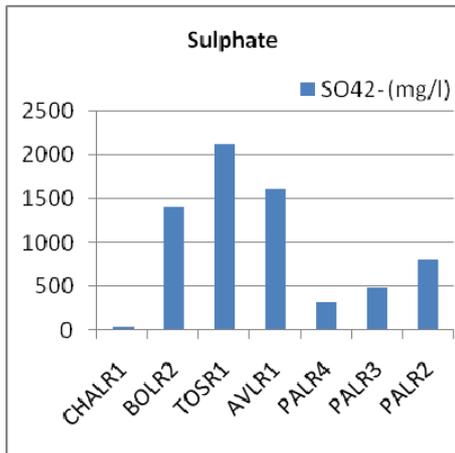


Figure 7.8. Sulfate-concentration along the River Antequera in mg/l.

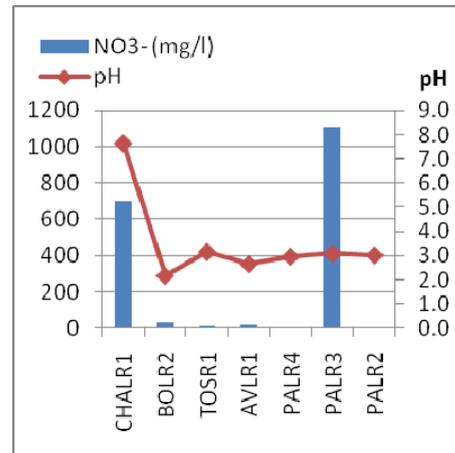


Figure 7.9. Nitrate-concentration in mg/l and pH along the River Antequera.

7.3.6 Nitrate (NO₃⁻)

The nitrate fluctuates significantly along the river (see Figure 7.9). The additions of nitrate are probably due to farming and livestock in the surrounding area. Low pH will cause low concentration of nitrate as it turns into NH₄⁺ and this can explain why the nitrogen-concentration decreases when the pH is low.

PALR3 is an exception; at this location nitrogen-concentration is high even though the pH is low. The explanation of this is probably because the sampling point is situated close to the town of Pazña and polluted by human waste.

7.3.7 Chloride (Cl⁻)

Cl⁻ increases all the way downstream along the river (see Figure 7.10). The last measuring point PALR2 shows a deviant trend which is a suspected analyze error. The chloride contents increases significantly at TOSR1 and PALR3.

There can be different explanations of the significant change in chloride concentration at TOSR1. Extended weathering or intrusions of saline groundwater are two possible reasons for the change of chloride content in the water. The most possible reason for the high concentration of chloride in PALR3 is saline groundwater intrusion.

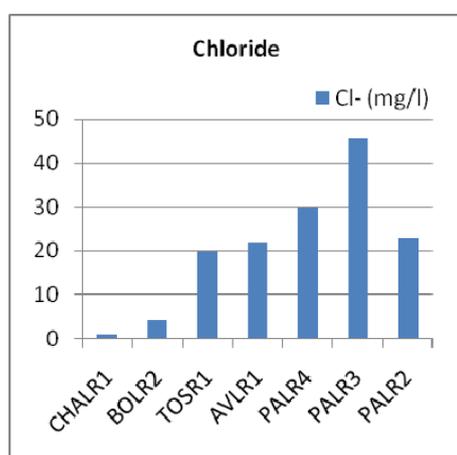


Figure 7.10. Chloride-concentration along the River Antequera in mg/l.

7.3.8 Summary Chemical Analyzes

At CHALR1, in the most upstream part of Antequera basin, the river water quality is of fairly good quality except with regards of nitrate. The area from Bolívar down to Avicaya is full of old mine residues and active and deserted mines surround the river. pH drops rapidly to around 2-3 and remain low throughout course of the river. All the ion concentrations increase significantly in the reach from Bolívar to Avicaya due to extensive weathering. Deposits from mines are especially rich in sulfur and iron and sulfur oxidation lowers pH. The weathering is a result of low pH water percolating mine tailings.

South of Avicaya is a tributary connecting to River Antequera. The contribution of water from this stream results in dilution which can be seen in concentrations of calcium, magnesium, potassium and sulfate. Sodium and chloride increases. There is

no change in nitrate, and neither a change in pH. pH in Antequera is already very low and an addition of alkaline water would have no effect on the pH of the river water.

As the river approaches the town Pazña all ion concentrations increase. The increase of calcium, magnesium and potassium may indicate intrusion of shallow ground water. Sodium and chloride keeps increasing toward the saline Lake Poopó.

7.4 Water Quality

To distinguish the quality of the sampled water the concentration of the analyzed ions, pH and total dissolved solids are compared with the drinking water guidelines of World Health Organization (WHO). According to WHO there are no health-based guidelines values proposed for calcium, hardness, sodium, sulfate, chloride, total dissolved solids and pH, however they advise taste thresholds (Appendix 7). Nitrate though has a limit value of 50 mg/l in drinking water.

The measured ion concentrations are compared to the guidelines of WHO in Table 7.1. Calcium concentration and hardness in almost all samples; ground water and surface water, are not in the range of the recommended value. Sodium concentration excess the recommended value in almost all the ground water samples while the surface water samples are in the range, except from the sampling point downstream the thermal spring (URLR2). The high concentration is probably due to the thermal spring contributing with high sodium concentration. Sulfate concentration exceeds the recommended concentration in some of the ground water samples and the high concentrations are probably due to mining activity in the area. In the surface water in the upstream part of River Antequera the sulfate concentration is in the range of the recommended value from WHO, while in the middle and downstream part the sulfate is far beyond (490-2500 mg/l) the recommended value. Nitrate concentration exceed the limited value in all the ground water samples, while in the river there are some sampling points which are in the range of the guidelines of WHO, however the most upstream water sample has high load of nitrate. Chloride concentration exceed the recommended value in the ground water from the downstream part of the basin, while it is of fairly good quality in the upstream part according to chloride. All the samples of the surface water are in the range of the recommended value except the sample from the point located after the thermal spring (URLR2).

The water quality in the most upstream sampling point (CHALR1) is comparatively good due to the guidelines of WHO except for nitrate which exceeds the guideline value significantly (700 mg/l compared to the guideline value of 50 mg/l).

Table 7.1. Measured ion concentrations compared to drinking water guidelines of World Health Organization (WHO). Marked values differ from recommendations.

Sampling point	Ca (mg/l)	Mg + Ca (mg/l)	Na (mg/l)	SO42- (mg/l)	NO3 (mg/l)	Cl (mg/l)	TDS (mg/l)	pH
WHO guidelines	100-300	< 200	< 200	< 250	< 50	< 250	< 600	6.5-9.5
<i>Ground Water</i>								
PALP10	83	90.3	46	130	840	48	356	7.4
PALP11	91	97.2	50	130	710	15	368	8.9
PALP12	190	218	3300	78	760	17	7150	7.4
PALP2	220	238	640	630	620	1000	1843	7.2
PALP3	180	191	480	440	1100	690	1427	7.5
PALP4	190	200	390	480	720	38	1168	7.6
PALP5	310	324	770	400	1100	1800	2260	7.5
PALP6	77	84.6	53	180	1100	31	383	7.3
PALP7	200	240	590	140	1200	14	1788	7.4
PALP8	160	195	640	200	1100	1300	1750	7.4
PALP9	210	254	650	160	1100	1600	1937	7.2
TOSP2	28	29.4	210	270	72	42	614	6.7
TOSP3	5.9	6.8	7.4	27	1300	0	52	5.9
URLT1	110	115.8	1400	31	870	2500	3160	6.7
<i>Surface Water</i>								
AVLR1	270	285	38	1600	16	4.1	1376	2.7
BOLR1	600	614	60	2500	16	44	1642	4.3
BOLR2	29	37.5	13	1400	33	22	988	2.2
CHALR1	16	19.1	13	43	700	0.8	113	7.6
MASV1	36	39.8	32	76	980	29	195	6.9
PALR2	190	204	79	750	5.3	23	920	3.0
PALR3	190	205	60	490	1100	46	924	3.1
PALR4	150	159.9	47	810	0	30	913	3.0
TOSR1	400	416	32	2100	12	20	1359	3.2
URLR1	19	22.2	15	44	1300	15	127	8.1
URLR2	70	75.6	290	23	320	670	815	8.9

7.5 Anthropogenic and Natural Influence

The most important anthropogenic influences affecting the water quality in River Antequera are mining activities, livestock and human waste. The most important influences of natural origin are thermal springs and, to some extent, ground water intrusion.

7.5.1 Mining activities

The towns of the upstream part of Antequera basin have developed together with the mining industries. There are both active and deserted mines in the area and the river is surrounded by piles of mining residue. Bolívar is a large company and large companies in general have more sufficient waste water treatment than small

companies. However the smaller mining industries and the residues have large impact on the water quality. All the measured ions increase downstream the mines, especially sulfate, and the water quality is therefore poor (see Table 6.3). The mining activities along River Antequera are an important anthropogenic influence which affects the water quality along the whole river.

7.5.2 Livestock and Human wastes

Livestock and farming is present in the downstream part of Antequera basin. Animal farming and human waste often give rise to nitrate in water. The uppermost part of the river is rich in nitrate and so is also the river stretch passing Pazña. However, the effect of livestock on the water quality is small due to insignificant activity of livestock and farming. Further investigations have to be done to assure the effect of livestock and human waste on the water quality.

7.5.3 Thermal springs

There is a thermal spring in Urmiri basin located close to the river. The water chemistry shows overall a high ion content, especially for sodium and chloride (1400 mg/l and 2500 mg/l respectively). North-west of Pazña there is another thermal spring situated which seems to affect one of the analyzed wells (PALP12). The well has a high sodium concentration; 3300 mg/l, however the chloride concentration is low, only 20 mg/l. The low chloride concentration is probably due to an analyze error.

7.5.4 Groundwater intrusion

There are indications of ground water intrusion into River Antequera in the lower parts of the basin. The flow increase as well as magnesium and calcium concentrations, this is discussed in Chapter 7.1.

7.6 Chemistry in ground water

The TDS analyses shows lower concentrations of total dissolved solids in wells located in the upstream part of the basin compared to most of the wells in the downstream part (Table 7.2 and Figure 7.11). PALP6 is an exception which indicates that there is more than one aquifer.

Table 7.2. Total dissolved solids (TDS) in ground water sorted by increasing concentrations. The wells located in the uppstream part of the basin are lower in TDS than the wells in the downstream part.

Sampling point	TDS (mg/l)
TOSP3	52
PALP10	360
PALP11	370
PALP6	380
TOSP2	610
PALP4	1200
PALP3	1400
PALP8	1800
PALP7	1800
PALP2	1800
PALP9	1900
PALP5	2300
URLT1	3200
PALP12	7200

Wells located in the upstream part of Antequera River

Wells located in the downstream part of Antequera River.

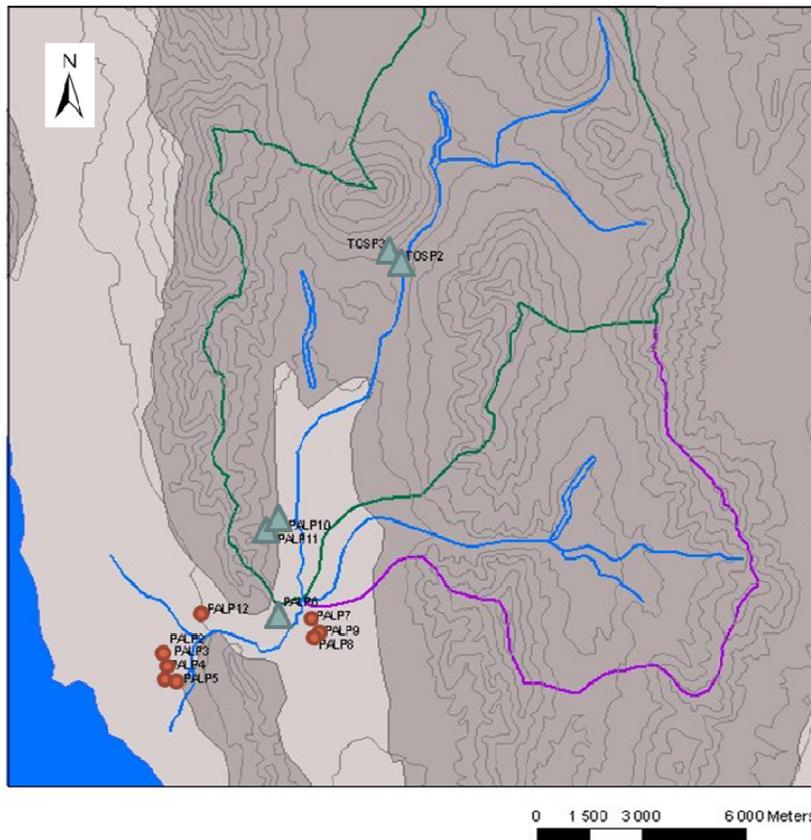


Figure 7.11 Locations of wells. Wells marked with a triangular shape have lower TDS value, ranging from 52 to 600 mg/l. Wells marked with a circle have higher TDS value, from 1200 to 7200 mg/l.

The water samples were classified into different water types due to the most abundant cation and anion (Appendix 8). Some of the ground waters were of the same type according to ion composition and were organized into three different groups with same composition, see Table 7.3. However the locations of the waters samples in the first group PALP6, PALP10 and PALP 11; classified as Ca/NO₃-type, are widely spread and it is not possible to draw any conclusions of the geological influence on the water quality. Also the second group PALP2, PALP5, PALP 8 and PALP9; classified as Na/Cl-type, and the third group PALP4, PALP7 and PALP12; classified as Na/NO₃-type, are wide spread on the geographical map. It is not possible to draw any conclusions if the water origin from the same or different aquifers due to the lack of data and the few measuring points in this study. Further investigations and sampling from more wells is necessary.

Table 7.3. Classification of ground water with similar water composition.

Sampling point	Classification (cation/anion)
PALP6	Ca/NO ₃
PALP10	Ca/NO ₃
PALP11	Ca/NO ₃
PALP2	Na/Cl
PALP5	Na/Cl
PALP8	Na/Cl
PALP9	Na/Cl
PALP4	Na/NO ₃
PALP7	Na/NO ₃
PALP12	Na/NO ₃

7.6.1 Sulfate in ground water

As River Pazña approaches Lake Poopó the river disappears in a delta and the surface water seems to infiltrate. This hypothesis about infiltration to the ground water can be further supported by the result of the sulfate ion analyzes. The sulfate concentration is high in the wells located in the area closest to Lake Poopó at the low reach of the river. The geomorphology where the wells PALP2, PALP3, PALP4 and PALP5 are located is similar to the one where the wells PALP7, PALP8 and PALP9 are situated (Appendix 1). Even though the wells are situated in the same type of geology, there is a distinct difference in sulfate concentrations (Table 7.4). The higher sulfate concentration in the ground water where River Pazña ends could likely be an effect of the polluted stream water infiltrating to the ground water.

Table 7.4. Sulfate concentrations found in wells.

Sampling point	SO4 (mg/l)
<i>Ground Water</i>	
PALP10	130
PALP11	130
PALP12	78
PALP2	630
PALP3	440
PALP4	480
PALP5	400
PALP6	180
PALP7	140
PALP8	200
PALP9	160
TOSP2	270
TOSP3	27
URLT1	31

Wells located in the downstream part of Antequera River

Wells located in area with similar geomorphology as the group above.

7.7 Ion balance

The ion balance shows a large charge balance error (CBE) for most of the evaluated water samples (see Appendix 5). The ion analyses are of poor quality. Only three of the water samples show to be of descent quality according to the ion balance: PALP4, TOSP2 and PALR2. However, the chloride concentration in PALR2 is suspect to be a measuring error (to low concentration) and therefore the CBE-value in this water is probably larger than the estimated value. The problem is for the main part of the analyses are an abundance of negative charged ions. This is either due to a lack in the selection of analyzed cations or due to analytic errors. Zinc, iron and silicate were not analyzed in this study and these ions may occur in significant amounts and could therefore be of importance in the ion balance.

The well PALP12 has a high sodium concentration; 3300 mg/l, however the chloride concentration is low, only 20 mg/l. The low chloride concentration is probably an analytic error considering the ion balance; a large amount of negatively charged ions are missing, CBE 71%. Most of the water samples have a negative CBE-value indicating a structural error.

The missing cations in the ion balance are probably due to a systematic measuring error. There was calibration problem with the spectrophotometer which analyzed the cations calcium, magnesium, sodium and potassium in the laboratory at San Andrés University where the analysis were performed.

8 Conclusions

Naturally the flow increases as the runoff area increases and this is true for the upstream part of the basin. There is a significant increase south of the small town Avicaya most likely due to a tributary from the north-northwest. Urmiri connects to Antequera north-east of Pazña and the flow increases. However, it is likely that some of the river water passes sub-surface, outside the river bed. The flow decreases in the lower part either due to withdrawals for irrigation or infiltration.

In the most upper part of Antequera basin the river water quality is of fairly good quality except with regards to nitrate. The area from Bolívar down to Avicaya is full of old mine residues. Active and deserted mines surround the river. pH drops rapidly to around 2-3 and remains low throughout course of the river. All concentrations of ions increase significantly in the reach from Bolívar to Avicaya due to extensive weathering. Deposits from mines are especially rich in sulfur and iron and sulfur oxidation lowers pH. The weathering is a result of low pH water percolating mine tailings.

South of Avicaya is a tributary connecting to River Antequera. The contribution of water from this stream results in dilution and can be seen in concentrations of calcium, magnesium, potassium and sulfate. Sodium and chloride increases. There is no change in nitrate, but neither is there a change in pH. pH in Antequera is already low and an addition of alkaline water would have no effect.

As the river approaches the town Pazña all ion concentrations increase. The increase of calcium, magnesium and potassium may indicate intrusion of shallow ground water. Sodium and chloride keeps increasing toward the saline Lake Poopó.

Mining activities are the most important anthropogenic influence affecting the water quality in River Antequera. The most important natural disturbances affecting the water quality are attributed to thermal springs and to some extent ground water intrusion.

The lack of data and the few measuring points does not make it not possible to draw any conclusions of whether or not the water origins from same or different aquifers. However, there is a difference in total dissolved solids showing ground water close to the lake being more saline.

The accuracy about data in this study is uncertain due to different aspects. Only one sampling was done during one field trip, it is therefore not possible to compare the ion concentrations with other analysis. The ion analyzes are of poor quality. The ion balance shows a large charge balance error (CBE) for most of the evaluated water samples.

9 Recommendations

The surface water in the most upper part of River Antequera is of fairly good quality except with regards of nitrate. Maybe it is possible to install biologic treatment which can remove nitrate and then distribute the treated water to the inhabitants via pipelines. However it is required to make a water balance in order to decide if there is enough water to supply the villages in the area. The problem with an uneven distribution over the year has to be solved; perhaps some sort of reservoir or tank can be installed.

It can be interesting to investigate the water quality of the tributary stream of River Antequera south of Avicaya. If the quality is good enough it may be possible to use the water for irrigation and domestic water supply. However it is necessary to quantify the amount of water available.

Almost all the ground water has an excess of nitrate according to the guideline value recommended by WHO. Some of the waters are of fairly good quality according to the other parameters. Also here one proposal can be to install a small scale biological treatment in connection to the wells in order to remove nitrate. Today, households use the ground water without any treatment and with pre-treatment the water will be more suitable for irrigation and drinking water. It is of course also necessary to analyze the ground water due to heavy metals.

To be able to draw conclusions of the aquifers in the area more investigations have to be done. It is necessary to analyze waters in a large number of wells and it is also important to get an idea of how the water is moving in the ground. The hydraulic conductivity can be determined from pumping tests.

According to the investigations in this study it is not possible to draw sufficient conclusions about the ground water and surface water interactions. It is necessary to do further investigations to get a better idea of how the ground water and surface water system works. Further investigations can be hydraulic and isotopic measurements and determination of the ground water age. Hydrogeochemical modeling can be a useful tool. It is of importance to investigate ground water and surface water both during the dry and wet season, and compare the results. In this study the investigations was carried out only during the end of the wet reason.

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Appendix 1; Geology in Antequera and Urmiri basin

The geological properties of the study basin and the sampling points can be seen in Figure App.0.1 and descriptions of the different geological units are described below.

The Mountains are of Upper and Lower Silurian sedimentary rocks. The Lower Silurian sedimentary rocks (Ss1) consist predominantly of thick layers of grey-white quartzite deposited in a marine proximal environment. It may have a thickness of up to 250 m and thins out towards east. The Upper Silurian sedimentary rock (Ss2) includes what is called the Unica formation and the Catavi Formation. The Unica Formation is pelitic rocks with a thickness of around 1000 m (Troëng & Riera 1996). Pelitic rocks are formed from aluminum sedimentary rocks, commonly shales and mudstones (Australian Museum 2007).

The Unica Formation becomes more sandy as it passes into the Catavi formation and the Catavi Formation includes proximal, micaceous sandstones, intercalated with shale's and siltstones. The metamorphic grade of the Paleozoic is low with crystallization of mica and chlorite principally. Different sub-volcanic stocks and volcanic fields exist in the Eastern Cordillera. The intrusive bodies, Miocene sub-volcanic rocks (Msv), are peraluminous and dacitic to rhyodacitic and intrude into Paleozoic sediments (Troëng & Riera 1996).

The Altiplano dries out and the Pleistocene to Holocene glacial sediments (PHsg) are made up of sediments deposited in a continental glacial environment and includes glacial, fluvioglacial, and colluvioglacial deposits. The deposits are products of the erosion during the latest glacial period. This unit consists of boulders, pebbles, gravel, sand silt and clay forming moraines and other deposits (Troëng & Riera 1996).

The Pleistocene to Holocene lacustrine and fluvial deposits (PHsL) were deposited in a lacustrine to fluvial and evaporitic continental setting. It formed sands, silts, clays limestone and evaporates. The Holocene eolian sediments (Hse) are eolian deposits (wind deposits) made up of fine to medium grained sand. The Holocene alluvial and colluvial sediments (Hsa) consists of material deposited in a continental environment and includes alluvial fans, colluvial, fluvial and terrace deposits made up principally of gravel, sand, silt and clay. These deposits are found in the valleys and slopes of the hills and mountains of Paleozoic blocks and they have a high content of tin (Troëng & Riera 1996).

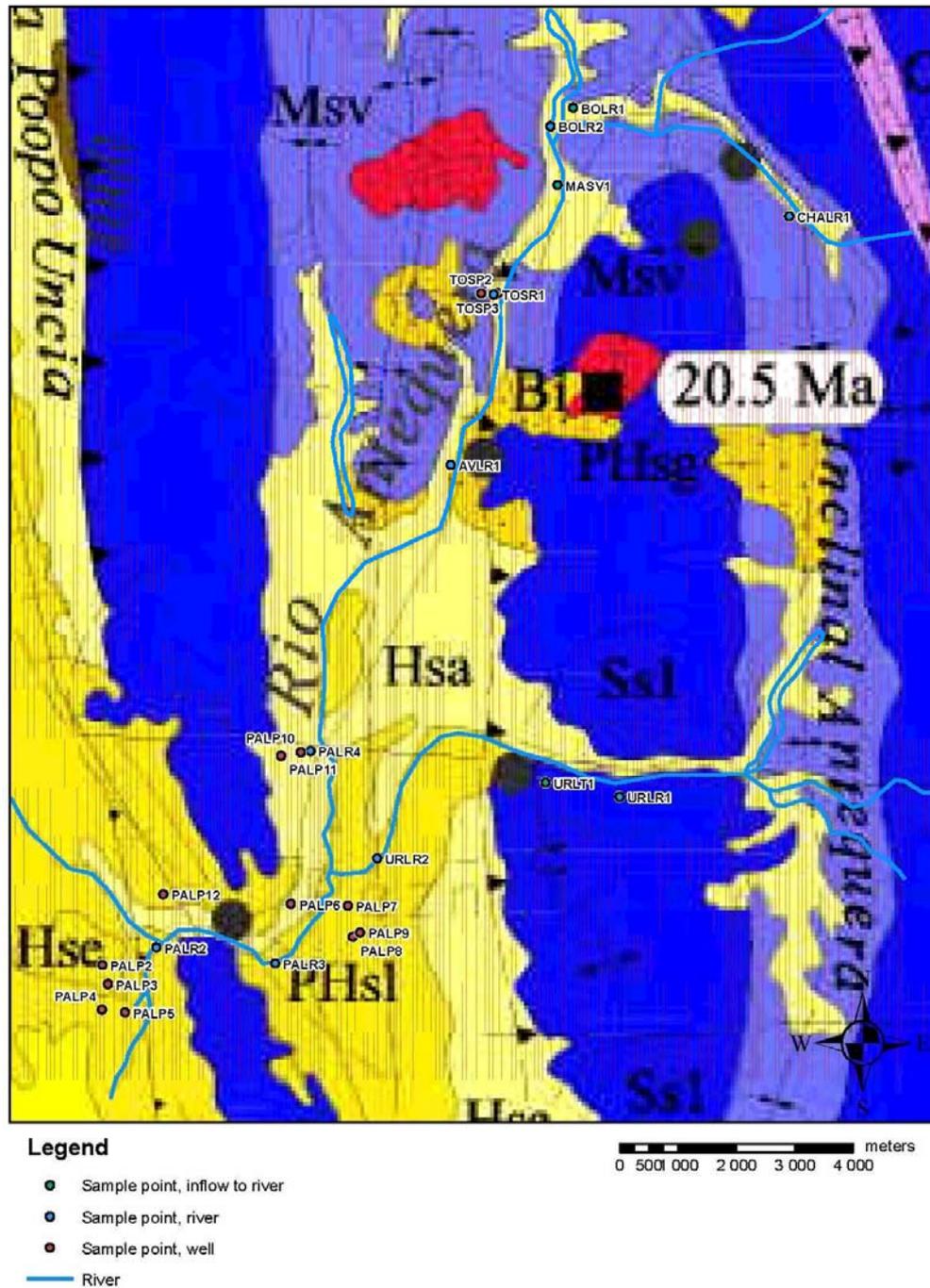


Figure App.0.1. In this figure the geological properties in the basins of Antequera and Urmiri and the sampling locations can be seen (geological information from Claire & Riera 1999).

Appendix 2; Chemical composition of buffer solution

500 ml buffer solution contains:

15, 1100 g $MgCl_2 \cdot 6H_2O$

2, 5168 g CH_3COON_9

0, 5192 g KNO_3

10, 00 ml CH_3COOH 98%

Appendix 3; Preparing of standards

The standards for Chloride were prepared as follow:

Conc. (mg/l)	Cl- (500 mg/l) (ml)	Hg(SCN)2 (ml)	Fe(NH4)(SO4)2 (ml)	HNO3 (ml)	Distilled water (ml)
0	0	0	1	2,5	21,5
10	0,5	1	1	2,5	21
20	1	1	1	2,5	20,5
30	1,5	1	1	2,5	20
40	2	1	1	2,5	19,5
50	2,5	1	1	2,5	19

The standards for Sulfate were prepared as follow:

Conc. (mg/l)	SO4 (100 mg/l) (ml)	Buffer solution (ml)	BaCl2 (10%) (ml)	Distilled water (ml)
0	0	5	2,5	20
4	1	5	2,5	19
8	2	5	2,5	18
12	3	5	2,5	17
16	4	5	2,5	16
20	5	5	2,5	15

Appendix 4; Chemical data

Calcium

Sampling point	Conc. (mg/l)	RAD	Sampled	Analysed
<i>Ground Water</i>				
TOSP2	28	2.1%	29-Feb-08	21-Mar-08
TOSP3	5.9	0.8%	29-Feb-08	21-Mar-08
PALP10	83	0.0%	2-Mar-08	21-Mar-08
PALP11	91	1.0%	2-Mar-08	21-Mar-08
PALP6	77	0.7%	1-Mar-08	21-Mar-08
PALP7	200	1.1%	1-Mar-08	21-Mar-08
PALP9	210	0.3%	1-Mar-08	21-Mar-08
PALP8	160	0.0%	1-Mar-08	21-Mar-08
PALP12	190	0.3%	1-Mar-08	3-Apr-08
PALP2	220	2.3%	1-Mar-08	21-Mar-08
PALP3	180	0.2%	1-Mar-08	21-Mar-08
PALP4	190	1.0%	1-Mar-08	21-Mar-08
PALP5	310	1.8%	1-Mar-08	21-Mar-08
URLT1	110	0.3%	29-Feb-08	21-Mar-08
<i>Surface Water</i>				
CHALR1	16	1.0%	29-Feb-08	3-Apr-08
BOLR1	600	0.2%	29-Feb-08	3-Apr-08
BOLR2	29	0.2%	29-Feb-08	3-Apr-08
MASV1	36	0.7%	29-Feb-08	21-Mar-08
TOSR1	400	1.6%	29-Feb-08	21-Mar-08
AVLR1	270	1.6%	29-Feb-08	3-Apr-08
PALR4	150	0.0%	2-Mar-08	21-Mar-08
PALR3	190	0.1%	1-Mar-08	21-Mar-08
PALR2	190	0.4%	1-Mar-08	21-Mar-08
URLR1	19	0.4%	29-Feb-08	3-Apr-08
URLR2	70	2.2%	1-Mar-08	21-Mar-08

Magnesium

Sampling point	Conc. (mg/l)	RAD	Sampled	Analysed
<i>Ground Water</i>				
TOSP2	1.4	1.7%	29-Feb-08	3-Apr-08
TOSP3	0.9	6.0%	29-Feb-08	3-Apr-08
PALP10	7.3	0.5%	2-Mar-08	19-Mar-08
PALP11	6.2	1.1%	2-Mar-08	19-Mar-08
PALP6	7.6	0.5%	1-Mar-08	3-Apr-08
PALP7	40	0.4%	1-Mar-08	19-Mar-08
PALP9	44	3.2%	1-Mar-08	3-Apr-08
PALP8	35	1.0%	1-Mar-08	19-Mar-08
PALP12	28	0.6%	1-Mar-08	19-Mar-08
PALP2	18	1.6%	1-Mar-08	3-Apr-08
PALP3	11	1.0%	1-Mar-08	19-Mar-08
PALP4	10	0.7%	1-Mar-08	3-Apr-08
PALP5	14	0.2%	1-Mar-08	23-Jun-08
URLT1	5.8	1.8%	29-Feb-08	3-Apr-08
<i>Surface Water</i>				
CHALR1	3.1	0.6%	29-Feb-08	19-Mar-08
BOLR1	14	0.3%	29-Feb-08	19-Mar-08
BOLR2	8.5	1.0%	29-Feb-08	3-Apr-08
MASV1	3.8	0.5%	29-Feb-08	19-Mar-08
TOSR1	16	3.0%	29-Feb-08	19-Mar-08
AVLR1	15	2.8%	29-Feb-08	19-Mar-08
PALR4	9.9	1.1%	2-Mar-08	19-Mar-08
PALR3	15	1.0%	1-Mar-08	3-Apr-08
PALR2	14	0.2%	1-Mar-08	3-Apr-08
URLR1	3.2	0.6%	29-Feb-08	19-Mar-08
URLR2	5.6	0.0%	1-Mar-08	19-Mar-08

Sodium

Sampling point	Conc. (mg/l)	RAD	Sampled	Analysed
<i>Ground Water</i>				
TOSP2	210	3.1%	29-Feb-08	3-Apr-08
TOSP3	7.4	0.0%	29-Feb-08	20-Mar-08
PALP10	46	1.8%	2-Mar-08	20-Mar-08
PALP11	50	0.5%	2-Mar-08	20-Mar-08
PALP6	53	0.8%	1-Mar-08	3-Apr-08
PALP7	590	1.3%	1-Mar-08	20-Mar-08
PALP9	650	1.8%	1-Mar-08	20-Mar-08
PALP8	640	1.8%	1-Mar-08	20-Mar-08
PALP12	3300	0.4%	1-Mar-08	20-Mar-08
PALP2	640	1.4%	1-Mar-08	20-Mar-08
PALP3	480	2.8%	1-Mar-08	20-Mar-08
PALP4	390	0.7%	1-Mar-08	20-Mar-08
PALP5	770	4.6%	1-Mar-08	20-Mar-08
URLT1	1400	6.8%	29-Feb-08	20-Mar-08
<i>Surface Water</i>				
CHALR1	13	3.2%	29-Feb-08	20-Mar-08
BOLR1	60	1.1%	29-Feb-08	3-Apr-08
BOLR2	13	0.5%	29-Feb-08	20-Mar-08
MASV1	32	0.9%	29-Feb-08	3-Apr-08
TOSR1	32	7.9%	29-Feb-08	3-Apr-08
AVLR1	38	1.3%	29-Feb-08	3-Apr-08
PALR4	47	0.8%	2-Mar-08	20-Mar-08
PALR3	60	1.2%	1-Mar-08	3-Apr-08
PALR2	79	1.1%	1-Mar-08	3-Apr-08
URLR1	15	0.5%	29-Feb-08	20-Mar-08
URLR2	290	0.0%	1-Mar-08	20-Mar-08

Potassium

Sampling point	Conc. (mg/l)	RAD	Sampled	Analysed
<i>Ground Water</i>				
TOSP2	24	0.9%	29-Feb-08	20-Mar-08
TOSP3	2.3	1.5%	29-Feb-08	20-Mar-08
PALP10	10	1.1%	2-Mar-08	3-Apr-08
PALP11	6.2	0.3%	2-Mar-08	3-Apr-08
PALP6	11	1.7%	1-Mar-08	20-Mar-08
PALP7	46	0.5%	1-Mar-08	3-Apr-08
PALP9	48	3.2%	1-Mar-08	3-Apr-08
PALP8	45	3.1%	1-Mar-08	3-Apr-08
PALP12	150	0.9%	1-Mar-08	3-Apr-08
PALP2	33	1.5%	1-Mar-08	3-Apr-08
PALP3	34	1.1%	1-Mar-08	3-Apr-08
PALP4	24	0.6%	1-Mar-08	20-Mar-08
PALP5	38	1.3%	1-Mar-08	3-Apr-08
URLT1	85	0.3%	29-Feb-08	3-Apr-08
<i>Surface Water</i>				
CHALR1	3.7	5.0%	29-Feb-08	20-Mar-08
BOLR1	18	3.4%	29-Feb-08	20-Mar-08
BOLR2	2.4	2.4%	29-Feb-08	20-Mar-08
MASV1	3.5	1.8%	29-Feb-08	3-Apr-08
TOSR1	14	5.7%	29-Feb-08	20-Mar-08
AVLR1	9.9	2.0%	29-Feb-08	20-Mar-08
PALR4	5.3	1.3%	2-Mar-08	20-Mar-08
PALR3	7.4	0.0%	1-Mar-08	20-Mar-08
PALR2	7.6	1.9%	1-Mar-08	20-Mar-08
URLR1	3.1	3.1%	29-Feb-08	20-Mar-08
URLR2	22	0.9%	1-Mar-08	20-Mar-08

Ground Water and Surface Water Influence on the Water Quality in the Antequera River basin, Bolivia

Sulfate

Sampling point	Conc. (mg/l)	RAD	Sampled	Analyzed
<i>Ground Water</i>				
TOSP2	270	3.6%	29-Feb-08	25-Mar-08
TOSP3	27	3.3%	29-Feb-08	4-Apr-08
PALP10	130	0.9%	2-Mar-08	25-Mar-08
PALP11	130	1.1%	2-Mar-08	25-Mar-08
PALP6	180	3.8%	1-Mar-08	25-Mar-08
PALP7	140	1.0%	1-Mar-08	9-Apr-08
PALP9	160	2.3%	1-Mar-08	9-Apr-08
PALP8	200	2.1%	1-Mar-08	25-Mar-08
PALP12	78	5.9%	1-Mar-08	9-Apr-08
PALP2	630	7.6%	1-Mar-08	25-Mar-08
PALP3	440	0.3%	1-Mar-08	25-Mar-08
PALP4	480	8.5%	1-Mar-08	25-Mar-08
PALP5	400	6.1%	1-Mar-08	25-Mar-08
URLT1	31	0.1%	29-Feb-08	9-Apr-08
<i>Surface Water</i>				
CHALR1	43	9.9%	29-Feb-08	25-Mar-08
BOLR1	2500	0.6%	29-Feb-08	9-Apr-08
BOLR2	1400	1.0%	29-Feb-08	9-Apr-08
MASV1	76	3.5%	29-Feb-08	25-Mar-08
TOSR1	2100	7.2%	29-Feb-08	9-Apr-08
AVLR1	1600	*	29-Feb-08	
PALR4	230	*	2-Mar-08	
PALR3	490	6.8%	1-Mar-08	25-Mar-08
PALR2	750	6.8%	1-Mar-08	16-Apr-08
URLR1	44	4.1%	29-Feb-08	25-Mar-08
URLR2	23	*	1-Mar-08	

* No RAD-value calculated, analyze preformed by Boris Javier Valdivia

Chloride

Sampling point	Conc. (mg/l)	RAD	Sampled	Analyzed
<i>Ground Water</i>				
TOSP2	42	2.0%	29-Feb-08	15-Apr-08
TOSP3	0	*	29-Feb-08	11-Apr-08
PALP10	48	0.6%	2-Mar-08	2-Apr-08
PALP11	15	0.8%	2-Mar-08	15-Apr-08
PALP6	31	4.1%	1-Mar-08	15-Apr-08
PALP7	14	5.2%	1-Mar-08	15-Apr-08
PALP9	1600	0.9%	1-Mar-08	2-Apr-08
PALP8	1300	2.8%	1-Mar-08	2-Apr-08
PALP12	17	0.5%	1-Mar-08	15-Apr-08
PALP2	1000	1.6%	1-Mar-08	2-Apr-08
PALP3	690	2.6%	1-Mar-08	2-Apr-08
PALP4	38	0.4%	1-Mar-08	15-Apr-08
PALP5	1800	3.6%	1-Mar-08	2-Apr-08
URLT1	2500	2.9%	29-Feb-08	2-Apr-08
<i>Surface Water</i>				
CHALR1	0.8	7.3%	29-Feb-08	11-Apr-08
BOLR1	44	4.1%	29-Feb-08	15-Apr-08
BOLR2	22	4.8%	29-Feb-08	16-Apr-08
MASV1	29	2.4%	29-Feb-08	2-Apr-08
TOSR1	20	9.6%	29-Feb-08	15-Apr-08
AVLR1	4.1	5.7%	29-Feb-08	16-Apr-08
PALR4	30	6.3%	2-Mar-08	11-Apr-08
PALR3	46	5.5%	1-Mar-08	11-Apr-08
PALR2	23	7.0%	1-Mar-08	16-Apr-08
URLR1	15	1.9%	29-Feb-08	2-Apr-08
URLR2	670	3.6%	1-Mar-08	2-Apr-08

* No concentration detected

Nitrate

Sampling point	Conc. (mg/l)	RAD	Sampled	Analyzed
<i>Ground Water</i>				
TOSP2	72	0.7%	29-Feb-08	18-Apr-08
TOSP3	1300	8.3%	29-Feb-08	17-Apr-08
PALP10	840	3.4%	2-Mar-08	18-Apr-08
PALP11	710	3.1%	2-Mar-08	18-Apr-08
PALP6	1100	4.4%	1-Mar-08	17-Apr-08
PALP7	1200	3.4%	1-Mar-08	17-Apr-08
PALP9	1100	0.2%	1-Mar-08	21-Apr-08
PALP8	1100	1.3%	1-Mar-08	17-Apr-08
PALP12	760	0.9%	1-Mar-08	18-Apr-08
PALP2	620	0.4%	1-Mar-08	18-Apr-08
PALP3	1100	0.6%	1-Mar-08	17-Apr-08
PALP4	720	5.2%	1-Mar-08	18-Apr-08
PALP5	1100	3.2%	1-Mar-08	17-Apr-08
URLT1	870	9.9%	29-Feb-08	18-Apr-08
<i>Surface Water</i>				
CHALR1	700	1.8%	29-Feb-08	18-Apr-08
BOLR1	16	2.5%	29-Feb-08	18-Apr-08
BOLR2	33	2.1%	29-Feb-08	21-Apr-08
MASV1	980	1.6%	29-Feb-08	21-Apr-08
TOSR1	12	2.3%	29-Feb-08	21-Apr-08
AVLR1	16	4.3%	29-Feb-08	21-Apr-08
PALR4	0	*	2-Mar-08	18-Apr-08
PALR3	1100	4.8%	1-Mar-08	17-Apr-08
PALR2	5.3	8.4%	1-Mar-08	31-Mar-08
URLR1	1300	4.6%	29-Feb-08	21-Apr-08
URLR2	320	0.1%	1-Mar-08	21-Apr-08

* No concentration detected

Appendix 5; Ion Balance

Calculation of Ion Balance

Sampling point	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	SO42- (mg/l)	NO3 (mg/l)	Cl (mg/l)	HCO3 (mg/l)	CO3 (mg/l)
Ground Water									
PALP10	83	7.3	46	10	130	840	48	250	0
PALP11	91	6.2	50	6.2	130	710	15	0	120
PALP12	190	28	3300	150	78	760	17	790	0
PALP2	220	18	640	33	630	620	1000	220	0
PALP3	180	11	480	34	440	1100	690	370	0
PALP4	190	10	390	24	480	720	38	230	0
PALP5	310	14	770	38	400	1100	1800	510	0
PALP6	77	7.6	53	11	180	1100	31	210	0
PALP7	200	40	590	46	140	1200	14	560	0
PALP8	160	35	640	45	200	1100	1300	550	0
PALP9	210	44	650	48	160	1100	1600	540	0
TOSP2	28	1.4	210	24	270	72	42	120	0
TOSP3	5.9	0.9	7.4	2.3	27	1300	0	***	***
URLT1	110	5.8	1400	85	31	870	2500	620	0

Sampling point	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	SO42- (mg/l)	NO3 (mg/l)	Cl (mg/l)	HCO3 (mg/l)	CO3 (mg/l)
Surface Water									
AVLR1	270	15	38	9.9	1600	16	4.1	0	0
BOLR1	600	14	60	18	2500	16	44	0	0
BOLR2	29	8.5	13	2.4	1400	33	22	0	0
CHALR1	16	3.1	13	3.7	43	700	0.8	120	0
MASV1	36	3.8	32	3.5	76	980	29	110	0
PALR2	190	14	79	7.6	750	5.3	23	0	0
PALR3	190	15	60	7.4	490	1100	46	0	0
PALR4	150	9.9	47	5.3	810	0	30	0	0
TOSR1	400	16	32	14	2100	12	20	0	0
URLR1	19	3.2	15	3.1	44	1300	15	130	0
URLR2	70	5.6	290	22	23	320	670	0	130

Codex	charge	mole weight
Ca(2+)	(mg)	2 40.08
Mg(2+)	(mg)	2 24.31
Na(+)	(mg/)	1 22.99
K(+)	(mg/l)	1 39.1
SO4(2-)	(ppf)	-2 96.07
NO3(-)	(ppi)	-1 62.01
Cl(-)	(ppm)	-1 35.45
HCO3	(mg/)	-1 61.01
CO3	(mg/l)	-2 60.01

* No RAD-value calculated, analyze performed by Boris Javier Valdivia

** No concentration detected

*** No titration performed

[meq/l]=[mg/l]*charge/molarweight

Sampling point	Ca (meq/l)	Mg (meq/l)	Na (meq/l)	K (meq/l)	SO42- (meq/l)	NO3 (meq/l)	Cl (meq/l)	HCO3 (meq/l)	CO3 (meq/l)	sum anion	sum cation	CBE
Ground Water												
PALP10	4.141717	0.600576	2.00087	0.255754	-2.70636	-13.5462	-1.35402	-4.09769	0	6.998917	-21.7043	-51%
PALP11	4.540918	0.510078	2.174859	0.158568	-2.70636	-11.4498	-0.42313	0	-3.99933	7.384423	-18.5786	-43%
PALP12	9.481038	2.303579	143.5407	3.836317	-1.62382	-12.2561	-0.47955	-12.9487	0	159.1616	-27.3081	71%
PALP2	10.97804	1.480872	27.83819	0.84399	-13.1154	-9.99839	-28.2087	-3.60597	0	41.1411	-54.9285	-14%
PALP3	8.982036	0.904977	20.87864	0.869565	-9.15999	-17.7391	-19.464	-6.06458	0	31.63522	-52.4277	-25%
PALP4	9.481038	0.822707	16.9639	0.613811	-9.99271	-11.611	-1.07193	-3.76987	0	27.88145	-26.4456	3%
PALP5	15.46906	1.151789	33.49282	0.971867	-8.32726	-17.7391	-50.7757	-8.35929	0	51.08554	-85.2014	-25%
PALP6	3.842315	0.625257	2.30535	0.28133	-3.74727	-17.7391	-0.87447	-3.44206	0	7.054253	-25.8029	-57%
PALP7	9.98004	3.290827	25.66333	1.176471	-2.91454	-19.3517	-0.39492	-9.17882	0	40.11067	-31.84	11%
PALP8	7.984032	2.879473	27.83819	1.150895	-4.16363	-17.7391	-36.6714	-9.01492	0	39.85259	-67.589	-26%
PALP9	10.47904	3.61991	28.27316	1.227621	-3.3309	-17.7391	-45.134	-8.85101	0	43.59974	-75.055	-27%
TOSP2	1.397206	0.115179	9.134406	0.613811	-5.6209	-1.1611	-1.18477	-1.96689	0	11.2606	-9.93366	6%
TOSP3	0.294411	0.074044	0.321879	0.058824	-0.56209	-20.9644	0	#VALUE!	#VALUE!	0.749157	#VALUE!	#VALUE!
URLT1	5.489022	0.47717	60.89604	2.173913	-0.64536	-14.03	-70.5219	-10.1623	0	69.03615	-95.3595	-16%
Surface Water												
AVLR1	13.47305	1.23406	1.652893	0.253197	-33.309	-0.25802	-0.11566	0	0	16.6132	-33.6827	-34%
BOLR1	29.94012	1.151789	2.60983	0.460358	-52.0454	-0.25802	-1.24118	0	0	34.1621	-53.5446	-22%
BOLR2	1.447106	0.699301	0.565463	0.061381	-29.1454	-0.53217	-0.62059	0	0	2.773251	-30.2982	-83%
CHALR1	0.798403	0.255039	0.565463	0.094629	-0.89518	-11.2885	-0.02257	-1.96689	0	1.713535	-14.1731	-78%
MASV1	1.796407	0.312629	1.39191	0.089514	-1.58218	-15.8039	-0.81805	-1.80298	0	3.590459	-20.0071	-70%
PALR2	9.481038	1.151789	3.436277	0.194373	-15.6136	-0.08547	-0.6488	0	0	14.26348	-16.3479	-7%
PALR3	9.481038	1.23406	2.60983	0.189258	-10.2009	-17.7391	-1.2976	0	0	13.51419	-29.2376	-37%
PALR4	7.48503	0.81448	2.044367	0.13555	-16.8627	0	-0.84626	0	0	10.47943	-17.709	-26%
TOSR1	19.96008	1.316331	1.39191	0.358056	-43.7181	-0.19352	-0.56417	0	0	23.02638	-44.4758	-32%
URLR1	0.948104	0.263266	0.652458	0.079284	-0.916	-20.9644	-0.42313	-2.1308	0	1.943111	-24.4343	-85%
URLR2	3.493014	0.460716	12.61418	0.56266	-0.47882	-5.16046	-18.8999	0	-4.33261	17.13057	-28.8717	-26%

Charge balance error:

CBE = (abs(sum(cation))-abs(sum(anion)))/(abs(sum(cation))+abs(sum(anion)))

Appendix 6; Mass Balance

Mass Balance to Support Theory of Groundwater Intrusion

Sampling point	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	SO42- (mg/l)	NO3 (mg/l)	Cl (mg/l)	HCO3 (mg/l)	CO3 (mg/l)	Sampling point	Flow (l/s)
<i>Ground Water</i>										<i>Antequera</i>	
PALP6	77	7.6	53	11	180	1100	31	210	0	CHAR1	14.4
PALP7	200	40	590	46	140	1200	14	560	0	BOLR1	64.2
PALP8	160	35	640	45	200	1100	1300	550	0	TOSR1	115.3
PALP9	210	44	650	48	160	1100	1600	540	0	AVLR1	114.9
<i>Surface Water</i>										PALR4	250.2
PALR3	190	15	60	7.4	490	1100	46	0	0	PALR3	344.9
PALR4	150	9.9	47	5.3	810	0	30	0	0	PALR2	305
URLR2	70	5.6	290	22	23	320	670	0	130	<i>Urmir</i>	
Mass flow (mg/s)										URLR1	87.6
<i>Ground Water</i>										URLR2	33.7
PALP6	4150.3	409.64	2856.7	592.9	9702	59290	1670.9	11319	0		53.9
PALP7	10780	2156	31801	2479.4	7546	64680	754.6	30184	0		
PALP8	8624	1886.5	34496	2425.5	10780	59290	70070	29645	0		
PALP9	11319	2371.6	35035	2587.2	8624	59290	86240	29106	0		
<i>Surface Water</i>											
PALR4	37530	2476.98	11759.4	1326.06	202662	0	7506	0	0		
URLR2	2359	188.72	9773	741.4	775.1	10784	22579	0	4381		
PALR4 + UI	39889	2665.7	21532.4	2067.46	203437.1	10784	30085	0	4381		
Sum of PALR4, URLR2 and presented well											
PALP6	44039.3	3075.34	24389.1	2660.36	213139.1	70074	31755.9	11319	4381		
PALP7	50669	4821.7	53333.4	4546.86	210983.1	75464	30839.6	30184	4381		
PALP8	48513	4552.2	56028.4	4492.96	214217.1	70074	100155	29645	4381		
PALP9	51208	5037.3	56567.4	4654.66	212061.1	70074	116325	29106	4381		
Mass flow at											
PALR3	65531	5173.5	20694	2552.26	169001	379390	15865.4	0	0		
PALP6	-20%	-25%	8%	2%	12%	-69%	33%	1			
PALP7	-13%	-4%	44%	28%	11%	-67%	32%				
PALP8	-15%	-6%	46%	28%	12%	-69%	73%				
PALP9	-12%	-1%	46%	29%	11%	-69%	76%				

Appendix 7; Drinking water guidelines of World Health Organization (WHO 2009)

Parameter	Guideline value according to WHO	
Calcium (Ca)	100-300* mg/l	Depending on associated anion
Hardness (Ca and Mg)	< 200* mg/l	Excess can result in scale deposition and bad taste
Sodium (Na)	< 200* mg/l	Excess may give rise to unacceptable taste
Sulfate (SO ₄)	< 250* mg/l	Excess can cause noticeable taste, very high levels might cause laxative effect
Nitrate (NO ₃)	< 50 mg/l	Can affect the blood's ability to transport oxygen, specially in infants
Chloride (Cl)	< 250* mg/l	Excess can give rise to detectable taste in water
Total Dissolved Solids (TDS)	< 600* mg/l	No data on possible health effect in drinking-water available
pH	6.5-9.5*	No direct impact on consumers, although an important water quality parameter

* no health-based guideline value is proposed

Appendix 8; Classification of Ground Water

Classification of groundwater

Sampling point	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	SO42- (mg/l)	NO3 (mg/l)	Cl (mg/l)	HCO3 (mg/l)	CO3 (mg/l)	
PALP10	83	7.3	46	10	130	840	48	250	0	
PALP11	91	6.2	50	6.2	130	710	15	0	120	
PALP12	190	28	3300	150	78	760	17	790	0	
PALP2	220	18	640	33	630	620	1000	220	0	
PALP3	180	11	480	34	440	1100	690	370	0	
PALP4	190	10	390	24	480	720	38	230	0	
PALP5	310	14	770	38	400	1100	1800	510	0	
PALP6	77	7.6	53	11	180	1100	31	210	0	
PALP7	200	40	590	46	140	1200	14	560	0	
PALP8	160	35	640	45	200	1100	1300	550	0	
PALP9	210	44	650	48	160	1100	1600	540	0	
TOSP2	28	1.4	210	24	270	72	42	120	0	
TOSP3	5.9	0.9	7.4	2.3	27	1300	0	***	***	
URLT1	110	5.8	1400	85	31	870	2500	620	0	

[meq/l]=[mg/l]*charge/molarweight

Codex	charge	mole weight
Ca(2+)	(mg)	2 40.08
Mg(2+)	(mg)	2 24.31
Na(+)	(mg/)	1 22.99
K(+)	(mg/l)	1 39.1
SO4(2-)	(ppm)	-2 96.07
NO3(-)	(ppm)	-1 62.01
Cl(-)	(ppm)	-1 35.45
HCO3	(mg/)	-1 61.01
CO3	(mg/l)	-2 60.01

*** No titration performed

Sampling point	Ca (meq/l)	Mg (meq/l)	Na (meq/l)	K (meq/l)	SO42- (meq/l)	NO3 (meq/l)	Cl (meq/l)	HCO3 (meq/l)	CO3 (meq/l)	sum + (meq/l)	sum - (meq/l)
PALP10	4.141717	0.600576	2.00087	0.255754	-2.70636	-13.5462	-1.35402	-4.09769	0	6.998917	-21.7043
PALP11	4.540918	0.510078	2.174859	0.158568	-2.70636	-11.4498	-0.42313	0	-3.99933	7.384423	-18.5786
PALP12	9.481038	2.303579	143.5407	3.836317	-1.62382	-12.2561	-0.47955	0	0	159.1616	-14.3595
PALP2	10.97804	1.480872	27.83819	0.84399	-13.1154	-9.99839	-28.2087	0	0	41.1411	-51.3226
PALP3	8.982036	0.904977	20.87864	0.869565	-9.15999	-17.7391	-19.464	0	0	31.63522	-46.3631
PALP4	9.481038	0.822707	16.9639	0.613811	-9.99271	-11.611	-1.07193	0	0	27.88145	-22.6757
PALP5	15.46906	1.151789	33.49282	0.971867	-8.32726	-17.7391	-50.7757	0	0	51.08554	-76.8421
PALP6	3.842315	0.625257	2.30535	0.28133	-3.74727	-17.7391	-0.87447	0	0	7.054253	-22.3608
PALP7	9.98004	3.290827	25.66333	1.176471	-2.91454	-19.3517	-0.39492	0	0	40.11067	-22.6612
PALP8	7.984032	2.879473	27.83819	1.150895	-4.16363	-17.7391	-36.6714	0	0	39.85259	-58.5741
PALP9	10.47904	3.61991	28.27316	1.227621	-3.3309	-17.7391	-45.134	0	0	43.59974	-66.204
TOSP2	1.397206	0.115179	9.134406	0.613811	-5.6209	-1.1611	-1.18477	0	0	11.2606	-7.96677
TOSP3	0.294411	0.074044	0.321879	0.058824	-0.56209	-20.9644	0	#VALUE!	#VALUE!	0.749157	#VALUE!
URLT1	5.489022	0.47717	60.89604	2.173913	-0.64536	-14.03	-70.5219	0	0	69.03615	-85.1972

Sampling point	Ca (%)	Mg (%)	Na (%)	K (%)	SO42- (%)	NO3 (%)	Cl (%)	HCO3 (%)	CO3 (%)	dominant cation	anion
PALP10	59%	9%	29%	4%	12%	62%	6%	19%	0%	Ca	NO3
PALP11	61%	7%	29%	2%	15%	62%	2%	0%	22%	Ca	NO4
PALP12	6%	1%	90%	2%	11%	85%	3%	0%	0%	Na	NO5
PALP2	27%	4%	68%	2%	26%	19%	55%	0%	0%	Na	Cl
PALP3	28%	3%	66%	3%	20%	38%	42%	0%	0%	Na	Cl-NO3
PALP4	34%	3%	61%	2%	44%	51%	5%	0%	0%	Na	NO3
PALP5	30%	2%	66%	2%	11%	23%	66%	0%	0%	Na	Cl
PALP6	54%	9%	33%	4%	17%	79%	4%	0%	0%	Ca	NO3
PALP7	25%	8%	64%	3%	13%	85%	2%	0%	0%	Na	NO4
PALP8	20%	7%	70%	3%	7%	30%	63%	0%	0%	Na	Cl
PALP9	24%	8%	65%	3%	5%	27%	68%	0%	0%	Na	Cl
TOSP2	12%	1%	81%	5%	71%	15%	15%	0%	0%	Na	SO4
TOSP3	39%	10%	43%	8%	#VALUE!	#VALUE!	#VALUE!	#VALUE!	#VALUE!	Na-Ca	NO3
URLT1	8%	1%	88%	3%	1%	16%	83%	0%	0%	Na	Cl

Sampling point	dominant cation	anion
TOSP3	Na-Ca	NO3
PALP2	Na	Cl
PALP5	Na	Cl
PALP8	Na	Cl
PALP9	Na	Cl
URLT1	Na	Cl
PALP3	Na	Cl-NO3
PALP12	Na	NO3
PALP4	Na	NO3
PALP7	Na	NO3
TOSP2	Na	SO4
PALP10	Ca	NO3
PALP11	Ca	NO3
PALP6	Ca	NO3