Hydrochemical investigation and vulnerability assessment of the Los Bambinos aquifer in Costa Rica

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Abstract

In this study, a hydrochemical and biological investigation, and a vulnerability assessment were conducted on the Los Bambinos aquifer during the spring of 2020. A literature study on previous studies conducted in the area was also made. This aquifer is located on the southwestern slope of the Barva volcano, northeast of Alajuela, Costa Rica.

The hydrochemical investigation found the groundwater to be of bicarbonate-mixed type, which is consistent with previous research in nearby areas. The validity of the chemical analyses was evaluated and a number of discrepancies were found. Due to this fact, the results could not be used to draw general conclusions of the aquifer conditions. The results from the biological analyses from one of the test sites exceeded the recommended limit for coliform bacteria, while the other sites were within the limits.

A groundwater vulnerability assessment was made using the GOD method, which is a GIS-based qualitative method. The study area was divided in smaller areas depending on their hydrogeological character. The three parameters Groundwater confinement (G), Overlaying strata (O) and Depth to groundwater table or top aquifer if confined (D), were decided for each area. A GOD vulnerability index were calculated for each area based on their G, O and D values. According to the assessment, the vulnerability ranged between low and high and was generally low. In areas with higher permeability and in rivers and river gorges it was higher. The results of the vulnerability assessment confirmed the findings of previous studies made in the area.

Keywords: Hydrochemistry, Aquifer pollution vulnerability assessment, Los Bambinos aquifer, Barva aquifer, Alajuela, GOD, DRASTIC, Groundwater quality

Resumen

En este estudio, se realizó una investigación hidroquímica y biológica, así como una evaluación de vulnerabilidad en el acuífero Los Bambinos durante la primavera de 2020. También se realizó un estudio de literatura sobre estudios previos realizados en el área. Este acuífero está ubicado en la ladera suroeste de la montaña Guararí, al noreste de Alajuela, Costa Rica.

La investigación hidroquímica encontró que el agua subterránea es de tipo bicarbonato mixto, lo que es consistente con investigaciones previas en áreas cercanas. Se evaluó la validez de los análisis químicos y se encontraron varias discrepancias. Debido a este hecho, los resultados no pudieron usarse para sacar conclusiones generales de las condiciones del acuífero. Los resultados de los análisis biológicos de uno de los sitios de prueba excedieron el límite recomendado para bacterias coliformes, mientras que los otros sitios estaban dentro de los límites.

Se realizó una evaluación de vulnerabilidad del agua subterránea utilizando el método GOD, que es un método cualitativo basado en GIS. El área de estudio se dividió en diferentes áreas según su carácter hidrogeológico. En cada área se decidieron los tres parámetros: Grado de confinamiento hidráulico (G), Ocurrencia del sustrato suprayacente (O) y Distancia al nivel del agua subterránea o al techo del acuífero (D). Se calculó un índice de vulnerabilidad de GOD para cada área en función de sus valores de G, O y D. Según la evaluación, la vulnerabilidad oscilaba entre baja y alta, y en general era baja. En áreas con mayor permeabilidad y en ríos y gargantas del río era mayor. Los resultados de la evaluación de vulnerabilidad confirmaron los hallazgos de estudios previos realizados en el área.

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Chapter 1

Introduction

The United Nations lists Clean Water and Sanitation as the sixth Sustainable Development Goal (SDG) that are intended to be reached by 2030. The official goal is formulated as *Ensure availability and sustainable management of water and sanitation for all*. Listed as targets within this goal are: a sustainable supply of drinking water, a sustainable withdrawal of freshwater, and an established protection of aquifers (United Nations Sustainable Development, n.d.). One way of achieving these targets lies in understanding the capacities of available water resources and their vulnerabilities.

In Costa Rica, groundwater is the main drinking water source (Ruepert et al., 2005); approximately 88 percent of the all consumptive* use of water in the country comes from groundwater (Ballestero et al., 2007).

1.1 Purpose and objectives

The purpose of this study is to evaluate the hydrochemical quality conditions and pollution vulnerability of part of the Los Bambinos aquifer, on the southwestern slope of the Barva volcano, northeast of Alajuela, Costa Rica. Through these evaluations, a greater knowledge of the groundwater resources in the area is being achieved, which can be of use to policy makers and the Asociación Administradora de Sistemas de Acueductos y Alcantarillados de Carrizal (ASADA de Carrizal), the organisation that supplies the municipality of Carrizal with drinking water from Los Bambinos.

The objectives of this project are to:

- Conduct a hydrochemical investigation of the groundwater throughout the aquifer.

- Evaluate the groundwater vulnerability to pollution through the GOD system (Foster et al., 2007).

1.2 Methodology

The vulnerability evaluation is conducted through GIS analyses, along with desk studies of the geological composition in the area. The method of groundwater pollution vulnerability assessment used is the GOD method. Specifically the GOD method was chosen due to the available data type in the study area.

*Hydroelectric generation is not included in the term consumptive use, but all other uses are included.

1.3 Limitations

The main limitations of this thesis are related to the lack of time, since the field work was abruptly terminated due to external factors (COVID-19 pandemic). This prevented completing the hydrochemical survey and collecting more field data.

Chapter 2

Background

ASADA Carrizal is one of over 2000 non-profit organizations, administrating communal aqueducts and one of several institutions providing communities with clean drinking water (Dirección De Agua, 2020).

ASADA Carrizal manages four spring sites, from where the water is collected and transported for domestic use. The four sites include several smaller springs. As of the 1st of May 2020, the water is distributed to 1521 subscribers according to ASADA Carrizal.

Through a cooperation with the Universidad Técnica Nacional (UTN) in Alajuela, the ASADA Carrizal has an ongoing investigation of the aquifer conditions, to determine recharge sites, capacity, water quality etc. This thesis contributes to this work, which is part of the Costa Rica's sustainable development within the water sector.

2.1 Sustainable Development

In September 2016, the Government of Costa Rica signed a National Pact for the Sustainable Development Goals (SDGs) together with the head of the three branches of the Republic, the civil society, religious organisations, businesses and citizens (United Nations in Costa Rica, 2017).

Costa Rica identified three SDGs as their entry points to work with (United Nations in Costa Rica, 2017):

- Goal 1: End poverty in all its forms everywhere.
- Goal 9: Build resilient infrastructure, promote inclusive and sustainable industrialization, and foster innovation.
- Goal 12: Ensure sustainable consumption and production patterns.

Costa Rica does not list *Goal 6: Clean water and sanitation* as one of the entry points. The country is distinguished for having a high standard of drinking water and sanitation services (Organización Panamericana de la Salud, Ministerio de Salud, 2003), having one of the highest coverage ratios* in rural areas in Latin America. However, tap water is only considered potable in 60 percent of the area, according to the national standards (Madrigal-Ballestero et al., 2013).

The abundance of water in the country has been crucial for economical, social and cultural development. However, the resource has been treated as an unlimited

*How many households that are connected to the water system.

natural resource, which has led to environmental and social conflicts. The high availability of water has contributed to an inadequate legal and institutional framework in the country (Guzman-Arias et al., 2013).

The biggest problems have been considered to be associated with the lack of one institution having full responsibility for the planning and management of water resources, together with an old-fashioned water law from 1942 (Guzman-Arias et al., 2013). The law does not take groundwater into account, but focuses on surface water. This is an issue as 70 percent of the water supply in Costa Rica comes from groundwater (Global Water Partnership, 2020).

In 2017, a new water law based on the principles of Dublin and Integrated Management of Water Resources (IWRM) was approved in a first debate. For the law to come into force it however needs to be approved in the congress twice. The purpose of the proposed law is stated as (La Gaceta, 2017):

> The purpose of this law is to regulate and protect the development and sustainable use of continental, insular and marine water resources, considering it a fundamental resource for life, limited and vulnerable.
>
> The management of the water resource will be comprehensive in order to guarantee its universal, solidary, balanced and equitable access, in adequate quantity and quality, to satisfy the social, environmental and economic needs of present and future generations, and the sustainable development of the nation.
>
> Said management must be applied taking into consideration the vulnerability, adaptation and mitigation of climate change that affects, directly or indirectly, the water resource and associated ecosystems.

It should be pointed out that the purpose and content of the law can be changed before it is approved the second time.

The Costa Rican Institute of Water and Sanitation (ICAA) was founded in 1961 to oversee the supply and quality of drinking water and to be responsible for the design, construction and management of the infrastructure providing drinking water to urban and rural communities (Madrigal-Ballestero et al., 2013).

Community-based drinking water organizations (CBDWO) are important for decentralized water management and thus they are important in rural Costa Rica. The sustainablity of CBDWO in Costa Rica has shown to be highly variable due to differences in water infrastructure, governance structure and socio-economic conditions in different areas. The result is that many inhabitants in the rural areas suffer from water shortage and poor water quality (Madrigal-Ballestero et al., 2013).

ICAA has promoted the implementation of a voluntary certification program as a tool of overcoming bad water quality. It awards organisations that adopt and meet technical standards for good water quality. A periodical monitoring must be made of the standards and the organisations meeting the standards receive a "Water Quality Seal" and a white flag which they can display in a public spot. If they fail to keep to the standards, the flag is revoked. The National Laboratory for Water Quality Analysis (LNA), a branch of ICAA, is administrating the "Water Quality Seal", and thus it is an indirect mechanism of upward accountability (Madrigal-Ballestero et al., 2013).

Concerning the aquifers, there are two main factors threatening the aquifers: the change in land use and the change in consumption patterns and groundwater extraction rates. The current knowledge about aquifer hydrology and recharge zones in the area are however insufficient (Organización Panamericana de la Salud, Ministerio de Salud, 2003).

A number of communities get their water from the Los Bambinos aquifer and with an increasing population, the water demand increases. It is therefore relevant to discuss the sustainability of the water supply coming from the Los Bambinos aquifer.

2.2 Site description

2.2.1 Climate

The climate in Costa Rica is tropical, with large variability over the country. The mountain chain extending from northwest to southeast divides the country in two slopes: the Pacific and the Caribbean. Each side of these slopes have very different regimes when it comes to precipitation and temperature patterns (Instituto Meteorológico Nacional, n.d.).

The study area of this thesis is located on the southwestern slope of the Barva volcano, situated in the Central Valley of Costa Rica, on the Pacific slope. In Figure 2.1, the study area is shown in the map of Costa Rica. The study area extends northeast to southwest and crosses the borders of the three cantons (municipalities) Alajuela, Santa Barbara and Barva. The study area also crosses the border between the two provinces Alajuela and Heredia (where Santa Barbara and Barva are located).

The Pacific slope is characterised with having a well-defined dry and rain season. December to March is normally dry season and in April there is a transition to rain period. The rain season spans from May to October, with November being a transition month to dry season again. The two slopes are furthermore divided into seven different climatic zones, depending on the altitude and orientation of the mountains, among other parameters. The study area is situated in the Central Pacific climate zone, close to Carrizal (Instituto Meteorológico Nacional, n.d.).

The temperature and precipitation distribution in Carrizal throughout the year is presented in Figure 2.2 as a mean between the years 1901 and 2016. The average monthly temperature varies between 22 °C in December and 24 °C in April. The average monthly precipitation varies between 105 mm in March and 467 mm in October (World Bank Group, n.d.).

The topography of the study area is shown in Figure 2.3, where the Barva volcano is shown in the top right corner, as well as the peak Cerro Guararí, at the north section of the study area. The overall slope of the area is from northeast to southwest, and it is assumed that the groundwater flows in this direction, as the surface water does (Centro de Investigaciones en Ciencias Geológicas, 2015a).

2.2.2 Geology and hydrogeology

The northern slope of the Central Valley consists of a number of hydrogeological formations: Barva, Tiribí and Colima. The aquifers Colima and Barva supply 65

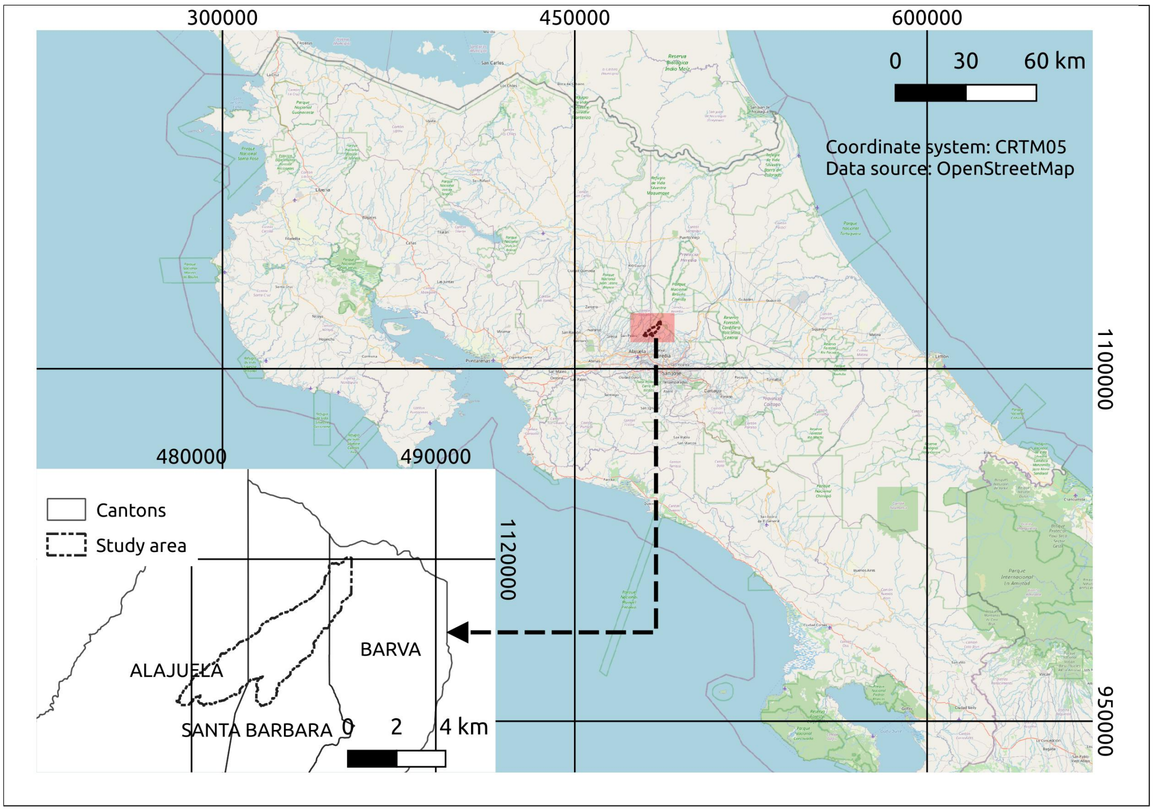

Figure 2.1: Map showing the study area and the three cantons (municipalities) that it spans.

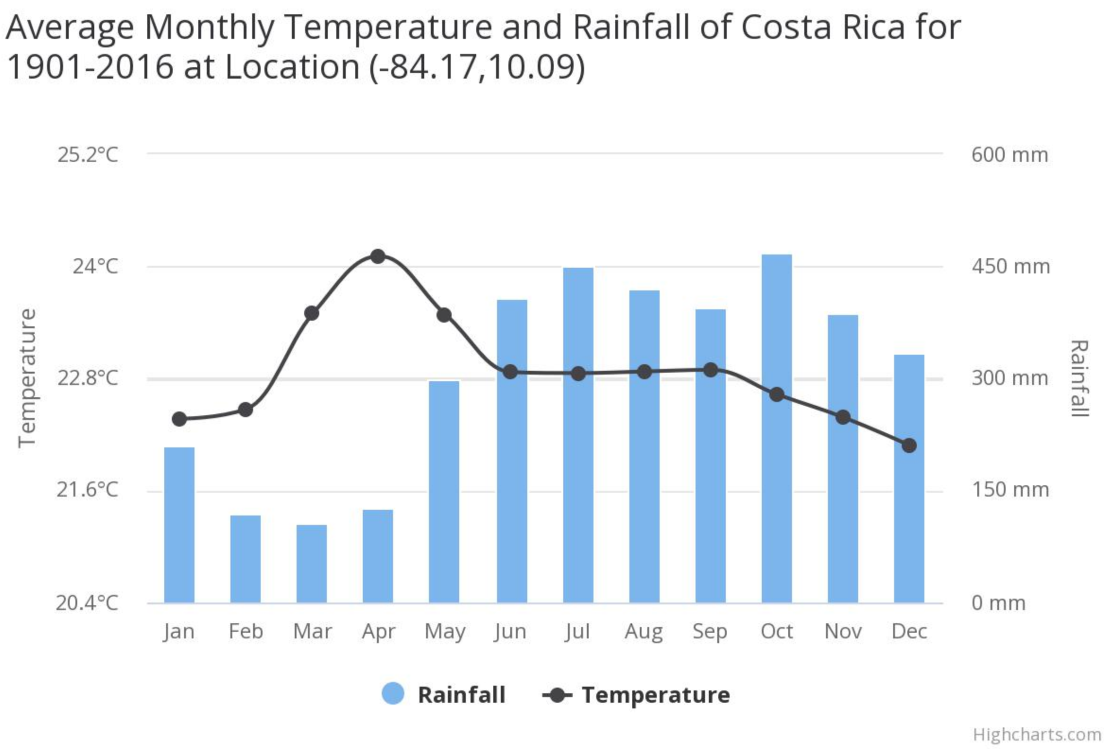

Figure 2.2: Graph of average monthly temperature and precipitation in Carrizal, Costa Rica. At -84.17,10.09 (UTM) (World Bank Group, n.d.).

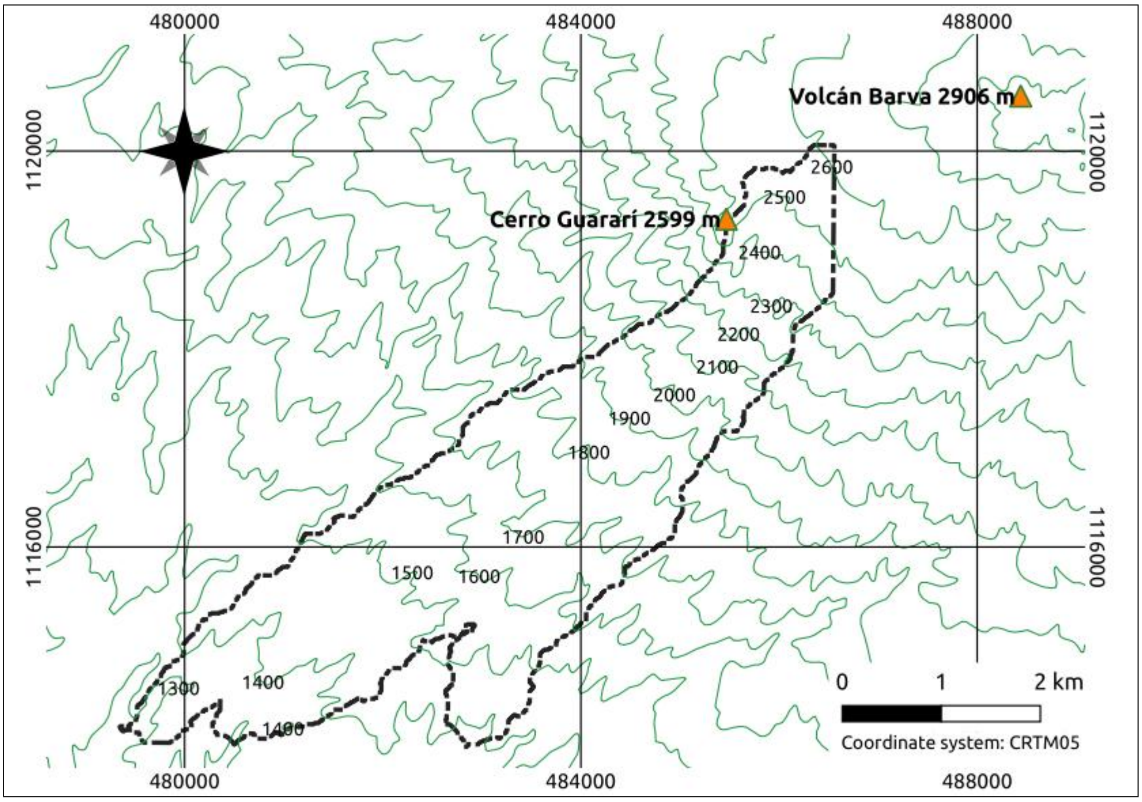

Figure 2.3: Map showing the topography of the study area, as well as the location of Cerro Guararí and Volcán Barva.

percent of the population in the Great Metropolitan Area with drinking water and are among the most exploited aquifers in the country (Ramírez Chavarría, 2014).

The hydrogeological formations include different subdivisions called members, and these are shown in Figure 2.4. As the Barva formation is the uppermost formation and the one of interest for this thesis, the order of its members are presented in the figure. However, the extensions of the members are not uniform throughout the formation, i.e. at parts of the Barva formation Crater is the uppermost member, while at other parts Porrosatí or Carbonal are the uppermost members. The members of Tiribí and Colima are shown in the figure, but not their internal layering. The thickness of the formations are presented. However there is no scale in the figure.

Barva has a thickness of up to 100 meters, with an average thickness of 50 meters, and it consists of six members: Bermúdez, Porrosatí, Carbonal, Los Angeles, Bambinos and Crater. Bermúdez, in which the Barva Inferior aquifer lies, consists of fractured, andesitic lavas and has a high permeability and is therefore considered an aquifer. Bermúdez has a variable thickness of 29 to 41 meters. Los Angeles and Bambinos, also called Barva Superior aquifer, consists of brecciated lava forming small, perched aquifers. The secondary permeability is high due to fissures (Ramírez Chavarría, 2014).

Porrosatí and Carbonal consists of coarse, volcanic sand and clay tuffs, forming large aquitards overlaying the local aquifers Barva Superior and at some locations are found outcropping and overlaying only the Barva Inferior aquifer. The thickness varies largely due to the material, which is a product of volcanic eruptions filling

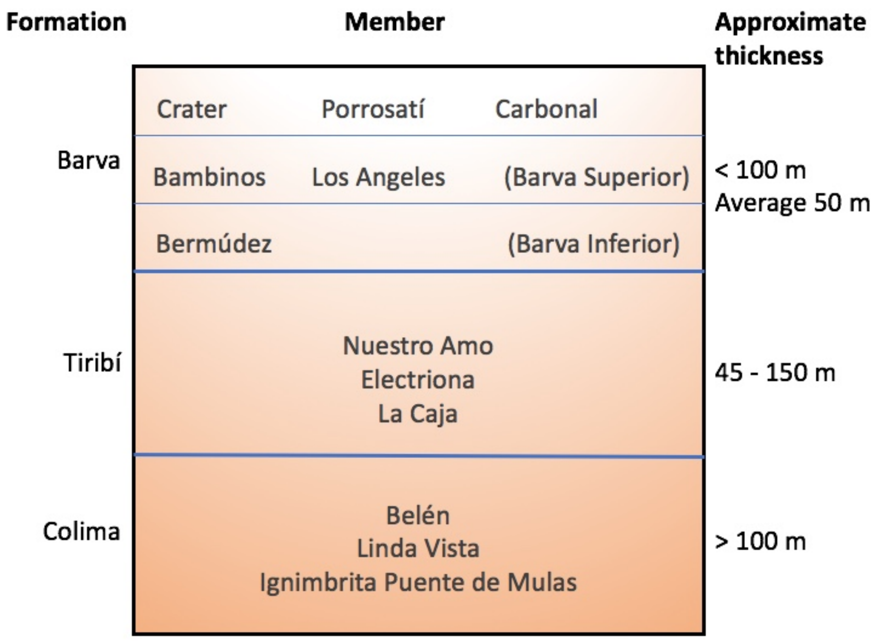

Figure 2.4: Geological table with the formations and their approximate thickness as well as their respective members, in the study area. With data from Ramírez Chavarría (2014)

the existing paleotopographies[*]. Crater consists of recent pyroclasts which partially cover the Barva Superior aquifer. The thickness of Crater is less than 10 m and the permeability is moderate (Ramírez Chavarría, 2014).

Tiribí has a thickness varying between 45 and 150 meters and consists of the members: Nuestro Amo, Electriona and La Caja. The formation consists of pyroclasts and is considered an aquitard with a hydraulic conductivity of $1.16–2.27 \cdot 10^{-4}$ m/d (Ramírez Chavarría, 2014).

Colima consists of the three members: Belén, Linda Vista and Ignimbrita Puente de Mulas. Its thickness is over 100 m. Belén consists of several andesite lava flows, seperated by lithic tuffs that act as aquitards separating the aquifers. The permeability of the member differs and depends on the fractures or the brecciated characteristics. It is only the two upper lava flows that are known and the aquifer Colima Inferior lies here (Ramírez Chavarría, 2014).

2.2.3 Sample locations

Seven springs are investigated during this work. They are located in the catchment areas of the rivers Quizarraces, Ahogado and Guararí along the slope of Cerro Guararí.

Five of the springs are maintained by ASADA, while the other two (Diogenes and Lomas de Guararí) are in private use. The sample locations are shown in Figure 2.5. At all of the springs operated by ASADA, constructions had been made to avoid contamination of the water.

[*] Prehistoric topography/topography that was present at the time of eruption.

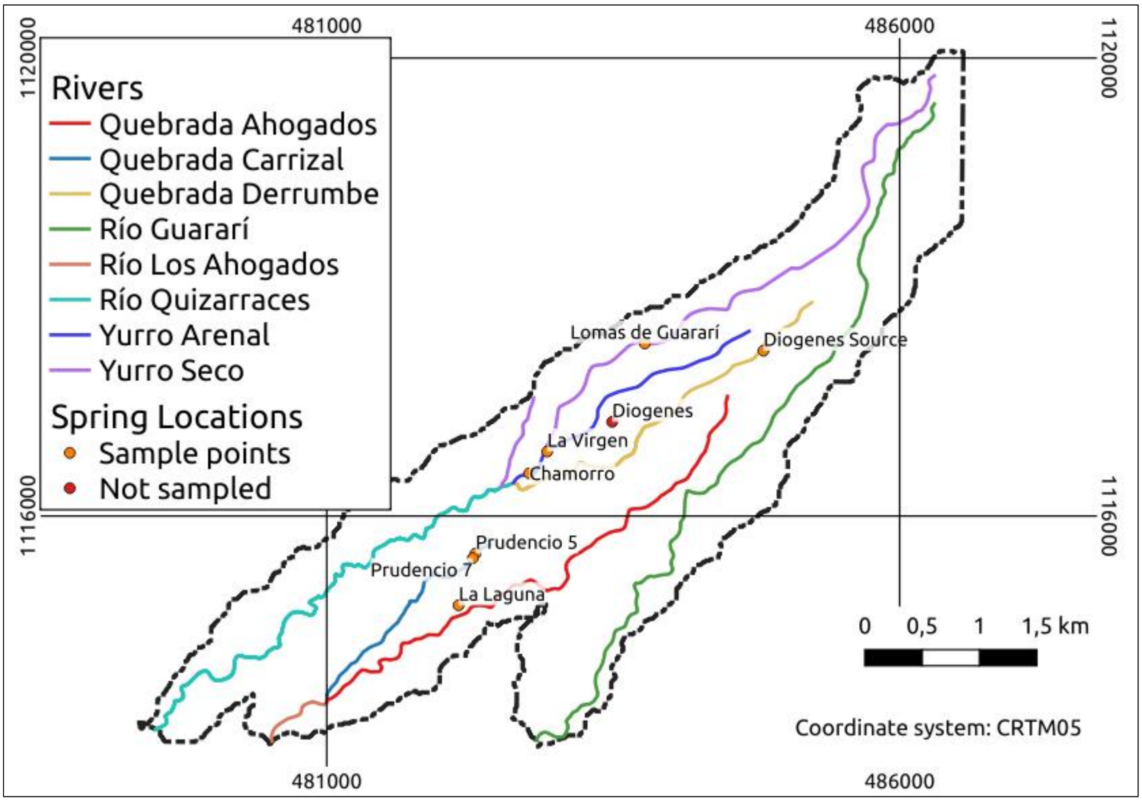

Figure 2.5: Map showing study area as well as major rivers and sample locations.

Diogenes

The spring Diogenes is located on private land, at a shelter for homeless dogs. Within the shelter there are two springs situated at a distance of 1.5 km from each other.

The downstream spring, which is named Diogenes, consists of a number of smaller springs scattered along a section at 1755 masl, according to elevation data. The water from the smaller springs is collected in a concrete well, along with water from the upstream spring.

The upstream spring, labelled *Diogenes Source* in this thesis, is situated at the end of a gorge, surrounded by dense forest at 1986 masl. Water is being discharged from the end wall of the gorge, from an approximately 5 meters high and 5 to 10 meters wide section. The wall seems to mainly consist of clayey soil, with some coarser material higher up on the wall, above the area where the water is flowing.

In front of the spring, constructions are erected to gather and transport a majority of the flowing water. Several pipes direct the water away from the spring, and presumably downstream to the collecting well. The water that is not collected by the constructions is discharged into the river Quebrada Derrumbe. The capacity of the spring is unknown.

Lomas de Guararí

The spring Lomas de Guararí is located on private land, along the river Yurro Seco, 1 km due west from the Diogenes Source. The spring is located on the northern slope of the river gorge, some distance above the river bed, at an altitude of 1840 masl. A concrete housing surrounds the spring, from which water is transported in pipes. The river gorge is covered in dense forest, while the surrounding area consists of pastures. The capacity of the spring is unknown.

La Virgen de Lourdes

La Virgen de Lourdes is the main spring of ASADA de Carrizal. Situated at 1640 masl on the eastern slope of the river gorge of Río Quizarraces, the spring is surrounded by a protective area of 7 hectares. La Virgen is located 2.1 km from Diogenes Source, and 1.3 km from Lomas de Guararí. ASADA maintains four springs in the area (numbered from 1 to 4) but they only use the water from the main spring, number 1. The capacity from spring number 1 varies from 15 L/s to 45 L/s throughout the year. During February and March 2020 at the time Virgen was visited, the capacity was at 45 L/s (Mejias Alvarez, 2020).

The protected area used to consist of coffee plantations, but since 2000 ASADA has been conducting a reforestation project in the area.

Chamorro

Around 250 meters south from La Virgen lies the spring Chamorro, ASADA spring number 12, also known as El Gringo. Located at 1580 masl on the southern slope of the Yurro Arenal river gorge. The spring has a constant capacity of 3 L/s. ASADA manages the spring, but the water is discharged to the river (Mejias Alvarez, 2020).

Prudencio

Around 900 meters southwest from Chamorro lies Prudencio, ASADA spring numbers 5 to 10, at an altitude of 1510 masl. Prudencio consists of six springs situated along a stretch of 100 meters in a canyon previously consisting of a coffee plantation. Roughly 5000 m^2 surrounding the springs are protected by the ASADA and consists of dense forest. Surrounding the protected area are plantations as well as roads and houses.

The water from springs 5, 7 and 8 is collected, filtrated and chlorinated in a tank before distribution, while the water from springs 6, 9 and 10 is diverted out to the river Quebrada Carrizal due to the low flow from these springs. The total capacity from Prudencio is in the range of 25 L/s. A previous analysis of the water from Prudencio indicated the presence of coliform bacteria in spring number 7 (Mejias Alvarez, 2020).

La Laguna

ASADA spring number 11. Located 450 meters south of Prudencio at 1460 masl. La Laguna is situated at the high end of a river gorge surrounded by coffee plantations. The springs capacity is roughly 1.5 L/s and some of the water is used for irrigation, while the rest is discharged to the river Quebrada Ahogados (Mejias Alvarez, 2020).

Chapter 3

Theory and previous studies

In this chapter, theory on water sampling, chemical data evaluation, hydrogeology, water quality and vulnerability assessment are presented, together with previous studies in the area, both on water chemistry and vulnerability assessments.

3.1 Water sampling

The way that groundwater samples are collected will affect the validity of any conclusions that are drawn from the analysis results. It is therefore important to follow standard procedures when samples are collected. The theory presented is taken from Brassington (2017).

The sampling procedure is designed so that the water chemistry will not be changed by the process, and this will lead to a higher level of confidence when comparing the results from one site to another. The procedure should consequently be the same for all samples and it includes all steps of the sampling: preparation, in field, sample storage and transportation. Sampling procedure lists both for prior field and in field are presented here.

Prior field

Prepare for groundwater sampling:

- Prepare a list of springs (and wells) that are going to be sampled, including map references. Plan for a number of sample points, with alternative to stop earlier if needed.
- Make sure that there are no physical obstacles in the way for the sampling, such as fences.
- Prepare a list of determinants, including on-site measurements and laboratory analyzes.
- Prepare sample bottles with correct labelling. Do not forget to take spare bottles in case something goes wrong.
- Arrange for temporary sample storage if necessary.
- Place the empty bottles in cold boxes with ice packs and some sort of packing such as bubble-wrap.
- Prepare field sheets (preferably computer-made) with details of each sample site.

- Assemble the needed equipment.
- Make sure you have the necessary safety equipment and communicate with the supervisors where you will go and when you plan to be back.
- Calibrate instruments, such as pH and conductivity meter

In field

If sampling from a spring with catch pit:

- Use appropriate safety equipment
- Remove cover from catch pit, make sure no debris falls in.
- Lay out sampling equipment on ground or plastic sheet if dirty.
- Measure and record conductivity and temperature at in-flow point.
- Fill sample bottles as required. Label bottles and place in cold boxes, without direct contact with ice packs.
- Clean equipment and rinse with de-ionized water.

Field measurements should be taken of parameters that are likely to change before the samples are being tested in the laboratory, such as pH that can be affected by the atmospheric CO_2. The parameters should however be measured in the laboratory as well.

The accuracy of the laboratory results should be checked by including a duplicate of at least one of the samples. These two samples should have different identifications. If there are any discrepancies outside the error, this should be discussed with the staff and, if possible, more analyses should be made on the water.

3.2 Chemical data evaluation

3.2.1 Charge balance error

A clear indicator of the validity of laboratory results is the electrical balance. As no water sample can be electrically charged, there should always be a balance between the sum of cations and the sum of anions. There are a number of definitions of the *Charge balance error* (CBE), but the one used in this study, as well as in software based on PHREEQC[*], is shown in Equation 3.1 (Parkhurst et al., 2013):

$$Charge\ balance\ error = \frac{Sum\ cations - Sum\ anions}{Sum\ cations + Sum\ anions} \times 100 \qquad (3.1)$$

Due to statistical and analytical errors, it is not possible to expect a CBE of 0 %, but if the error is higher than 5 %, it is recommended to examine the analytical and sampling procedures (Appelo et al., 2005).

[*]A geochemical modeling software used for aqueous geochemical calculations. See www.usgs.gov/software/phreeqc-version-3

3.2.2 Water hardness and cationic content

The total hardness of a water sample is defined as the total concentration of the multivalent cations present in the sample. In the case of this study, the total hardness can be calculated as the sum of the magnesium and calcium ions, the two most prevalent multivalent cations in groundwater samples (Appelo et al., 2005). As the laboratory presented the hardness in mg/L of $CaCO_3$, the hardness of the samples can be calculated from Equation 3.2, which is derived from the molecular weights of the three compounds.

$$[CaCO_3] = 2.5[Ca^{2+}] + 4.1[Mg^{2+}] \tag{3.2}$$

By using the relation between the cationic concentration and the total hardness of the samples, the accuracy of the laboratory results can be evaluated.

3.2.3 Electrical conductivity

As the electrical conductivity of a sample is related to the ionic composition of the sample, it can be calculated from the concentration of the species of the sample and the temperature. Shown in Equation 3.3 is the relation used by PHREEQC to calculate the electrical conductivity of a solution. The equation shows the electrical conductivity (EC, unit S/m), the Faraday constant (F = 96485 C/mol), the gas constant (R = 8.31446 J/(K mol)), absolute temperature (T, unit K), the diffusive coefficient of ion i (D_i, unit m^2/s), the charge number (z_i, no unit), the activity constant (γ_i, no unit) and the molar concentration (c_i, mol/L). Finally, the exponent α, as determined from Equation 3.4, is used to correct for ion-ion interactions. The parameter I is the ionic strength (mol/L) (aqion, 2020).

$$EC = \left(\frac{F^2}{RT}\right) \sum_i D_i z_i^2 \left(\gamma_i\right)^{\alpha} c_i \tag{3.3}$$

$$\alpha = \begin{cases} 0.6/\mid z_i \mid^{0.5} = const, & \text{if } I \leq 0.36 \mid z_i \mid \\ \sqrt{I}/\mid z_i \mid, & \text{otherwise} \end{cases} \tag{3.4}$$

From Equation 3.3, the temperature dependence of the electric conductivity can be derived. By combining equations for conductivity, diffusion and viscosity, the resulting Equation 3.5 can be used to determine the conductivity at 25 °C. The parameters A and B are found in the parametrisation of the viscosity of water and are both temperature dependent. This non-linear temperature compensation is used by the PHREEQC software (aqion, 2020).

$$EC_{25} = 1.125 \cdot 10^{-A/B} \cdot EC \tag{3.5}$$

The electrical conductivity at 25 °C (in µS/cm) of a sample can be used to give an estimate of the sum of anions through Equation 3.6. The relationship is valid for an electrical conductivity of up to 1500 µS/cm and can be used to validate the laboratory results (Appelo et al., 2005).

$$\Sigma\ anions = \Sigma\ cations \approx EC_{25}/100 \tag{3.6}$$

3.2.4 Chemical presentation of major ions

The hydrochemical data can be presented through a number of diagrams that are used to indicate the type of groundwater in the samples. By presenting both the absolute and the relative concentrations of the major ions of a sample, it can be shown what geological setting the sample is collected from.

In this report, the major ions are presented through Stiff diagrams, Piper diagrams and X-Y diagrams.

Stiff diagrams

A Stiff diagram generally consists of three or four horizontal axes with the concentration (in meq/L) of one or two cations displayed to the left, and one or two anions to the right. The compounds shown in the three first axes is generally consistent over different studies, while the fourth axis is optional and its parameters differ depending on the study. In Figure 3.1, six samples are represented using Stiff diagrams. The example uses four horizontal axis, with the first showing K^+ and Na^+ to Cl^-, the second Ca^{2+} to HCO_3^-, the third Mg^{2+} to SO_4^{2-}, and the fourth Fe (total) to NO_3^-. Sample 4 in the figure show a high concentration of calcium and bicarbonate, indicating water with a limestone origin, while Sample 1 show very dilute concentrations of all species, indicating rainwater origin. Sample 3 is similar to Sample 4, with a high bicarbonate concentration, but also a higher magnesium concentration, indicating Dolomite ($CaMg(CO_3)_2$) origin (Appelo et al., 2005).

By representing chemical data with Stiff diagrams, the dominant species of the samples is easy to determine, as well as the concentrations. When presenting data from a series of samples collected from e.g. a catchment area, it is common to use Stiff diagrams as map markers. This gives a quick overview of the hydrochemical evolution of the groundwater in an area (Fetter, 2014).

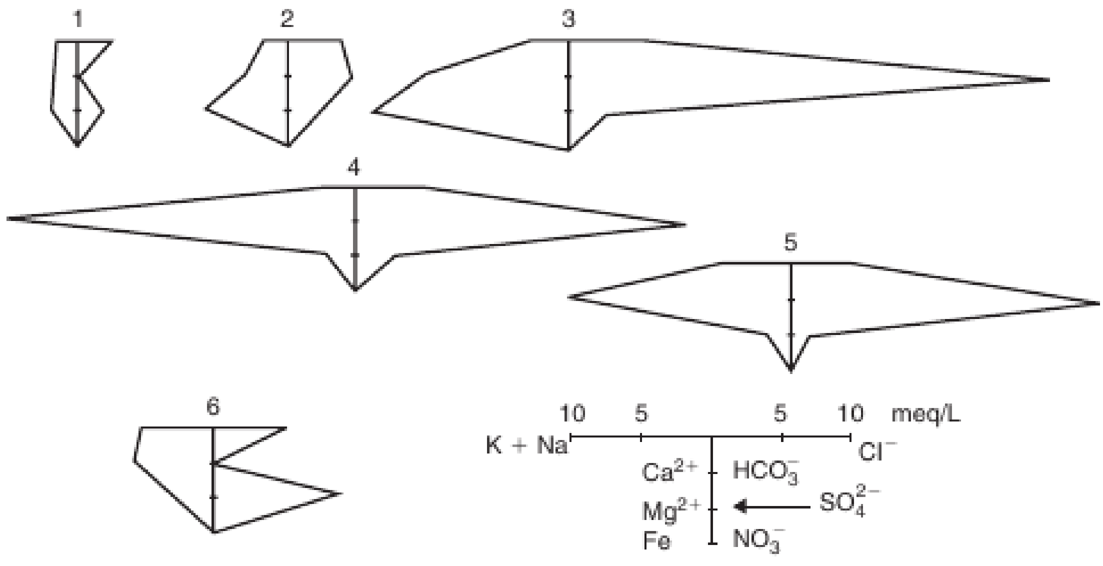

Figure 3.1: Stiff diagrams examples showing distinct patterns for differing types of water (Appelo et al., 2005).

Piper diagrams

Piper diagrams consists of two trilinear plots, one showing the percentage of the major cations, and the other showing the percentage of the major anions (e.g. meq/L Mg^{2+}/total cations (meq/L)), as well as a diamond shaped field between the two plots (see Figure 3.2). The cation axes groups Na^{+} and K^{+} on one axis, and shows Mg^{2+} and Ca^{2+} on the other two. The anion axes groups CO_3^{2-} and HCO_3^{-} on one axis, and shows Cl^{-} and SO_4^{2-} on the other two. Each vertex of the trilinear plots indicate 100 % concentration of one ion or ion group.

The diamond shaped field shows all eight major ions, in four groups: Mg^{2+} and Ca^{2+}, Na^{+} and K^{+}, CO_3^{2-} and HCO_3^{-}, Cl^{-} and SO_4^{2-}.

As shown in Figure 3.2, the Piper diagram can be used to classify the type of water. A water sample with calcite origin is expected to be located in the Calcium and Bicarbonate areas, while a marine water sample is likely to be located in the Sodium/Potassium and Chloride areas.

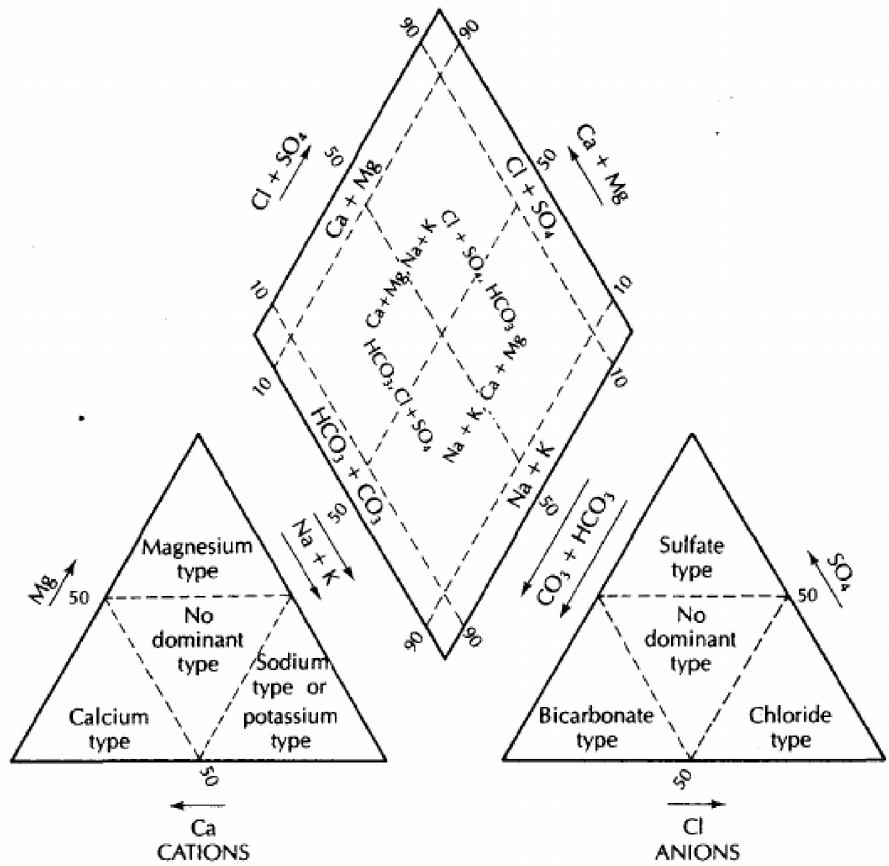

Figure 3.2: Piper diagram showing water classification system for natural waters (Fetter, 2014).

X-Y diagrams

One final visual representation of ionic content used in this study is X-Y diagrams, or scatterplots. For hydrochemical data, there are three major types of X-Y diagrams that can be constructed. The first is to plot an ion (or a group of ions such as sodium and potassium, or total cations) against another ion (or group of ions). From this it is possible to determine if there is a visible trend in the ratio of certain constituents in the data. The second type of X-Y diagram is to plot a constituent (ion/ions) against a chemical attribute of the water (such as pH, electric conductance, temperature etc). And finally it is possible to plot two chemical attributes against each other (Briel, 1993).

The advantages of X-Y diagrams over Piper diagrams is that they are easier to read and that they show the absolute concentrations of the samples (in meq/L), and not the percentage (as the Piper plot does). One downside is that the amount of data shown in each plot is lower, and several graphs are needed to show all available data. An example is shown in Figure 3.3, where six diagrams are required to show the ratios of the major ions in the gathered samples. As plot *a* and *b* in Figure 3.3 shows, there is likely a linear relation between the ratio of calcium and magnesium to sodium and potassium (that is, the samples would be shown in a distinct cluster in a Piper plot), but the total concentration ranges from a few meq/L to 30 meq/L, a fact that would not be shown in a Piper plot.

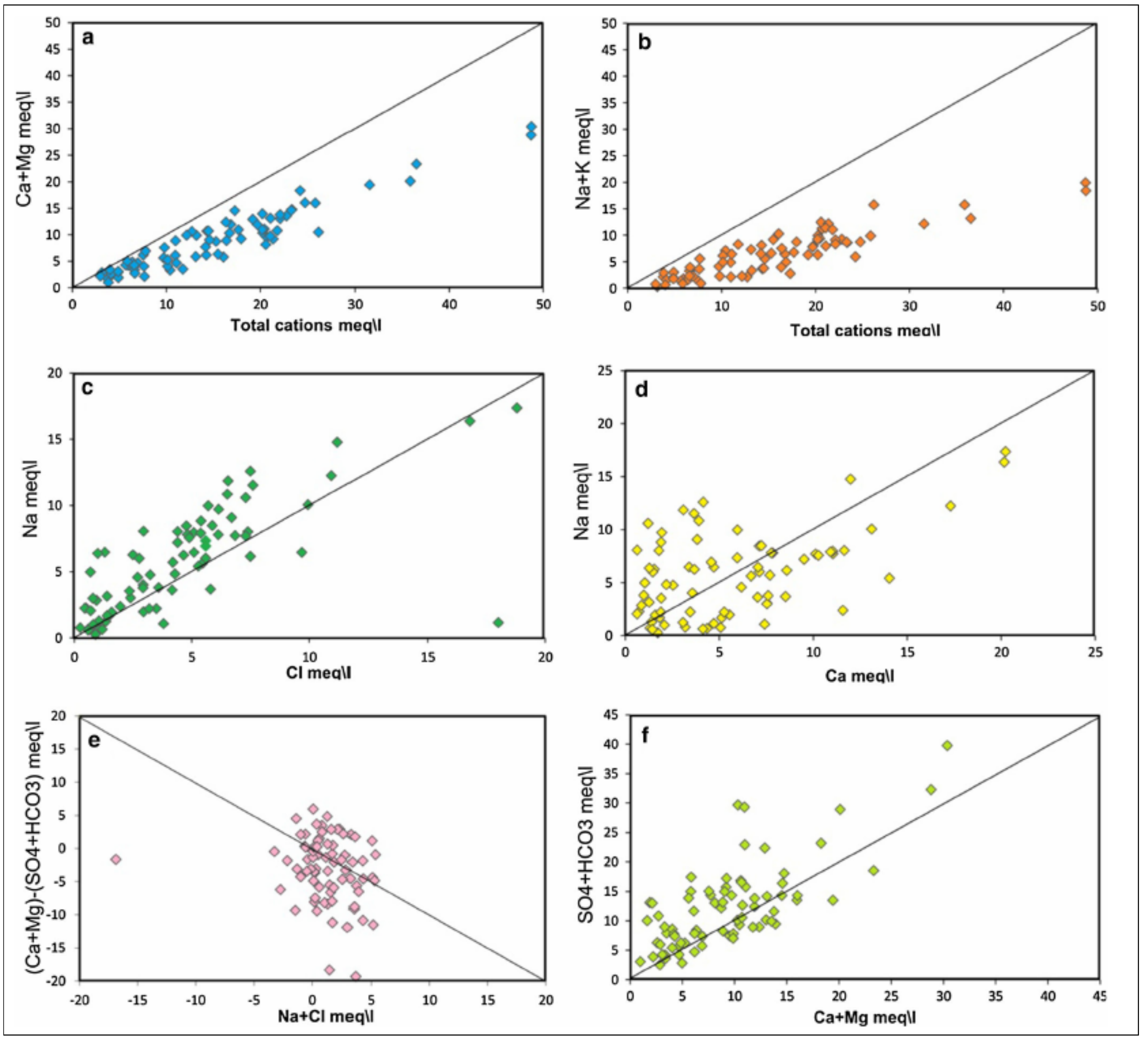

Figure 3.3: Example X-Y diagrams from a hydrochemical survey conducted in the Ardabil area, Iran (Aghazadeh et al., 2017).

3.3 Water quality

For drinking water in Costa Rica, there exist four levels of water quality control, named N1 to N4. The four control levels are described in Table 3.1. As shown, not all water supplies need to conduct all four controls, in fact N4 is only used in special situations, such as when an inspection has found reason to believe that the risk of contamination is high. As the ASADA of Carrizal supplies water to 1521 households, the only control necessary for the drinking water from their wells is level N1 (La Gaceta, 2005).

Table 3.1: Water quality control levels N1 to N4 (La Gaceta, 2005).

Control level	Parameters	Reason for investigation
N1	Coliformic bacteria Physiochemical parameters	All aqueducts
N2	Hydrochemical parameters Major ions	All aqueducts with a supplied population greater than 10 000
N3	Nitrite, ammonium Heavy metals Pesticide residues	All aqueducts with a supplied population greater than 50 000
N4	Situational dependent.	Occasional program only executed when imminent risk of contamination is identified.

The parameters listed in N1 are shown in Table 3.2, along with the recommended and maximum admissible values. The recommended value is defined as that substance concentration or density of bacteria that involves minimal or acceptable risk to the health of consumers of drinking water. The maximum admissible value is that concentration of substance or density of bacteria from which there is rejection of water by consumers or an unacceptable risk to health. As shown in Table 3.2, any presence of coliform bacteria exceeds both the recommended and maximum admissible value. Water that exceeds the maximum admissible value requires immediate corrective actions (La Gaceta, 2005).

The parameters of control level N2 are presented in Section 5.1.7, along with the chemical data from the collected samples of this study.

Table 3.2: Water quality parameters of level N1 (La Gaceta, 2005).

Parameter	Recommended value	Maximum admissible value
Fecal coliform (NMP/100 mL)	Absent	Absent
Escherichia Coli (NMP/100 mL)	Absent	Absent
Apparent colour (mg/L U Pt-Co)	5	15
Turbidity (UNT)	<1	5
Odor	Acceptable	Acceptable
Temperature (°C)	18	30
pH	6.5	8.5
Conductivity (µS/cm)	400	–
Free residual chlorine (mg/L)	0.3	0.6
Combined residual chlorine (mg/L)	1	1.8

3.4 Vulnerability assessment

The increasing groundwater contamination has induced the concept of aquifer vulnerability, which has been used by policy makers and researchers globally for the past three to four decades (Machiwal et al., 2018). The concept is used to measure the susceptibility of an aquifer to being adversely affected by an imposed contaminant load from the land surface (Foster et al., 2013).

The term and concept of 'aquifer pollution vulnerability' should not be regarded as a truth, because (Foster et al., 2013):

- All aquifers are vulnerable to pollution to some extent, by persistent and highly mobile contaminants.
- In reality, vulnerability depends on contaminant type and scenario.

However, the concept is used interdisciplinary between hydrogeologists, planners and decision-makers, and it acts as a support in environmental, land use and water management sectors (Machiwal et al., 2018).

The concept of aquifer vulnerability can be divided in two types: a) intrinsic vulnerability and b) specific vulnerability. The first mentioned is defined as the vulnerability of groundwater to be be contaminated by anthropogenic activities, without taken into consideration the nature of the contaminants. Specific vulnerability is, on the other hand, defined as the vulnerability of groundwater to particular contaminants or a group of contaminants. This type of vulnerability takes physical and biogeochemical attenuation processes in consideration (Machiwal et al., 2018).

There exists a number of different methods for vulnerability assessment, which can be divided mainly in three different categories: a) GIS-based qualitative methods, b) process-based qualitative methods, and c) statistical methods (Machiwal et al., 2018). Two commonly used methods are GOD and DRASTIC, both being GIS-based qualitative methods (Chamanehpour et al., 2020) and both also being used for porous-media aquifers (Machiwal et al., 2018). The GIS-based qualitative methods are economic, less time consuming and they are the most common qualitative methods to assess intrinsic vulnerability of an aquifer (Machiwal et al., 2018).

3.4.1 Limitations with vulnerability mapping

There are a number of limitations and procedural issues when working with vulnerability mapping.

Aquifer pollution vulnerability assessments are meant to provide a general framework as a base to groundwater protection policies. The resulting maps should only be used as giving a first, general indication in the potential pollution risk. Many simplifications are being made in the assessment process (Foster et al., 2007).

The accuracy of GIS-based qualitative methods has been debated due to the uncertainty in the assumptions involved. Three major limitations with qualitative methods have been listed by Machiwal et al. (2018): a) aquifer vulnerability may be opposed by quantitative terms, b) difficulty in quantifying uncertainty associated with vulnerability assessments in order to handle inaccuracies, and c) homogeneous results observed over certain spatial scales in many parts of the world, which restrict discrimination and delimitation of areas of different vulnerability to pollution.

3.4.2 GOD method

The GOD method is an aquifer pollution vulnerability assessment commonly used in Latin America and the Caribbean since the 1990s (Foster et al., 2007). It is categorised as a GIS-based qualitative method (Machiwal et al., 2018).

The so-called GOD vulnerability index is based on the following three parameters (Foster et al., 2007):

- **G**roundwater confinement.
- **O**verlying strata, lithological character.
- **D**epth to groundwater table or top aquifer if confined.

The value for the three parameters can be 0-1.0, 0.4-1.0 and 0.6-1.0 respectively. A higher value indicates a higher vulnerability for pollution. The workflow of how to determine the values for the three parameters are shown in Figure 3.4. Firstly, the G parameter is decided depending on the confinement of the aquifer. If there is no aquifer present (none), the value will be 0. A confined aquifer gives a lower value and an unconfined gives a value of 1. The next step is to decide what overlying strata there is on top of the aquifer in question. This gives an O value between 0.4 and 1.0; a higher value having higher permeability. If the O value is between 0.4 and 0.8, the groundwater depth is used to find the D value. A lower groundwater depth gives a higher D value. If the O value is between 0.8 and 1.0, the D value will be 1.0. The vulnerability index is the product of the values for the parameters, resulting in a final value between 0 and 1.0. (Foster et al., 2007)

The vulnerability index translates to five different vulnerability classes: negligible, low, moderate, high or extreme. The definition of the five vulnerability classes are shown in Table 3.3 (Foster et al., 2007).

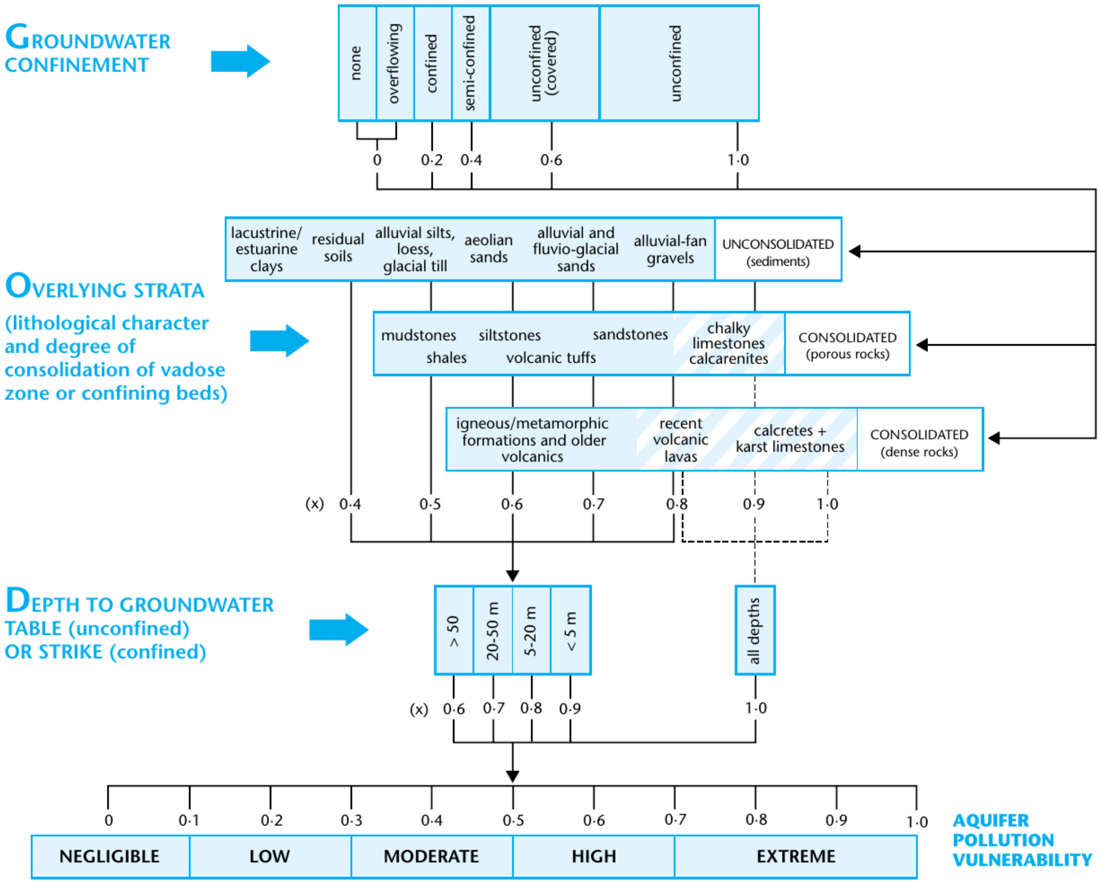

Figure 3.4: Workflow to determine groundwater vulnerability (Foster et al., 2007).

Table 3.3: Vulnerability classes with definitions (Foster et al., 2007).

VULNERABILITY CLASS	CORRESPONDING DEFINITION
Extreme	vulnerable to most water pollutants with rapid impact in many pollution scenarios
High	vulnerable to many pollutants (except those strongly absorbed or readily transformed) in many pollution scenarios
Moderate	vulnerable to some pollutants but only when continuously discharged or leached
Low	only vulnerable to conservative pollutants in the long term when continuously and widely discharged or leached
Negligible	confining beds present with no significant vertical groundwater flow (leakage)

3.4.3 DRASTIC method

The DRASTIC method for vulnerability assessment is the most common and world-wide used method and it has been used since the late 1980's (Chamanehpour et al., 2020).

The assessment is based on seven factors (Machiwal et al., 2018):

- **D**epth to groundwater
- **R**echarge (net)
- **A**quifer media
- **S**oil media
- **T**opography (slope)
- **I**mpact of vadose zone
- **C**onductivity (hydraulic) of aquifer

In each cell or point in a study area, the D, R, A, S, T, I and C is evaluated.

A vulnerability index (DI) for each cell or point is calculated with the linear relationship in Equation 3.7 (Chamanehpour et al., 2020):

$$DI = D_r D_w + R_r R_w + A_r A_w + S_r S_w + T_r T_w + I_r I_w + C_r C_w \tag{3.7}$$

Where r represents the rate and w the weighting of each parameter.

The rating value (r) ranges from 1 to 10, 1 representing the lowest vulnerability and 10 the highest. The weighting (w) of the parameters range between 1 and 5. A high DI implies a high vulnerability (Chamanehpour et al., 2020).

In the DRASTIC method, a classification of the vulnerability with a set range is not included. A commonly used classification is: very high vulnerability (>199), high vulnerability (160–199), moderate vulnerability (120–159), low vulnerability (80–119), and very low vulnerability (<79) (Mendoza et al., 2006).

3.5 Previous Research

3.5.1 Hydrochemical surveys

Two hydrochemical studies conducted within the Central Valley of Costa Rica are examined as part of this thesis. One study conducted from 2002 to 2004 in the Barva aquifer, and the other conducted in 1999 on the south side of the valley. The results from these studies are compared with the chemical data collected for this thesis. The comparison is used both to draw conclusions of the hydrogeological conditions of the aquifer, as well as to assess the validity of the chemical analyses.

Barva aquifer

An extensive hydrogeochemical survey of the Barva aquifer was conducted from September 2002 to May 2004 by Madrigal-Solís et al. (2017). Water samples were collected from 51 springs and wells throughout the aquifer. From 23 of these sites, additional sampling was conducted every third month, resulting in 5 to 9 samples from each site. The data delivered from these samples resulted in an in depth description of the hydrogeochemical conditions in the Barva aquifer (Madrigal-Solís et al., 2017).

The samples were collected at altitudes ranging from 487 to 2 396 meters above sea level and a geographical range of around 20 km. A majority of the groundwater samples were collected from the different Barva aquifer members (Bambinos, Los Ángeles and Barva interior), and some samples were collected from deeper wells that are in contact with the Colima aquifer. The geology of the Barva members are generally lavas and pyroclastics, while the Colima aquifer consists of andesite (Madrigal-Solís et al., 2017).

The study area is situated directly south of the area chosen for this study. In Figure 3.5 the sample sites are shown, as well as the river Itiquís in the upper centre of the map. The river Quizarraces (shown in Figure 2.5) connects to Itiquís just north of the area shown in this map (Madrigal-Solís et al., 2017).

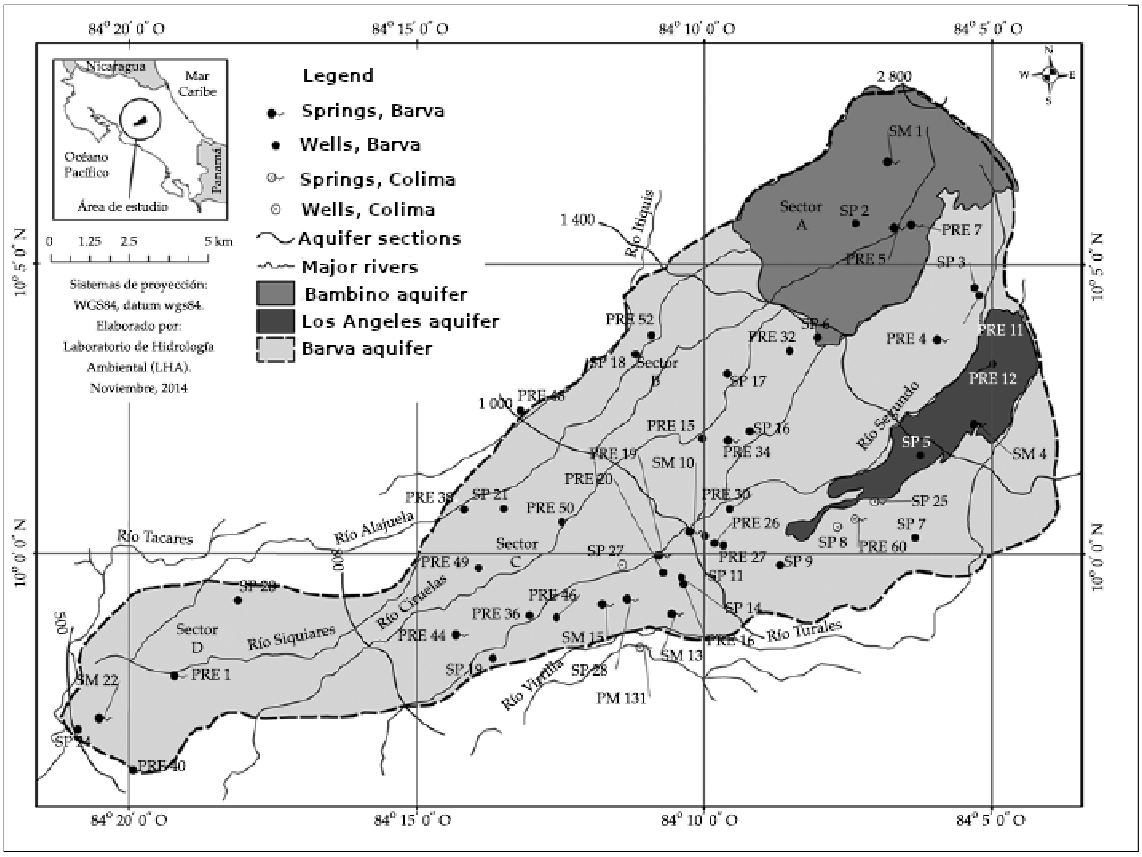

Figure 3.5: Map showing the study area and sample locations of the 2017 Barva aquifer study (Madrigal-Solís et al., 2017).

The physicochemical parameters determined for the samples collected from the Barva aquifer and the ranges of concentrations are shown in Table 3.4. The study found that there was no significant difference in chemical composition between the rainy and the dry seasons of the year (Madrigal-Solís et al., 2017).

Table 3.4: Chemical data from the Barva aquifer (Madrigal-Solís et al., 2017).

Parameter	Min	Max	Average	s
EC (uS/cm)	23	417	167.7	79.7
pH	5.7	7.5	6.6	–
HCO_3^- (mg/L)	16.8	258.5	77.1	39.4
SO_4^{2-} (mg/L)	0.6	24.2	4.3	4.7
Cl^-(mg/L)	0.7	21.3	5.4	4.5
Ca^{2+} (mg/L)	2.7	60.0	16.5	10.0
Mg^{2+} (mg/L)	1.4	14.3	7.4	3.3
Na^+ (mg/L)	0.8	22.5	7.3	3.8
K^+ (mg/L)	1.0	5.1	3.0	1.0
NO_3^- (mg/L)	0.06	10.61	3.65	3.16
Total hardness (mg/L $CaCO_3$)	12.5	199.6	71.5	36.4

Due to discrepancies in the chemical analyses of the magnesium and calcium concentrations conducted for this thesis (See Section 5.1.2), the concentration of these ions are compared with the ones determined by Madrigal-Solís et al. (2017). The distribution of these major cations are shown in Figure 3.6. Note that while calcium has a wide spread of concentrations (up to 60 mg/L for one sample), magnesium is distinctly clustered in the range 2 to 14 mg/L.

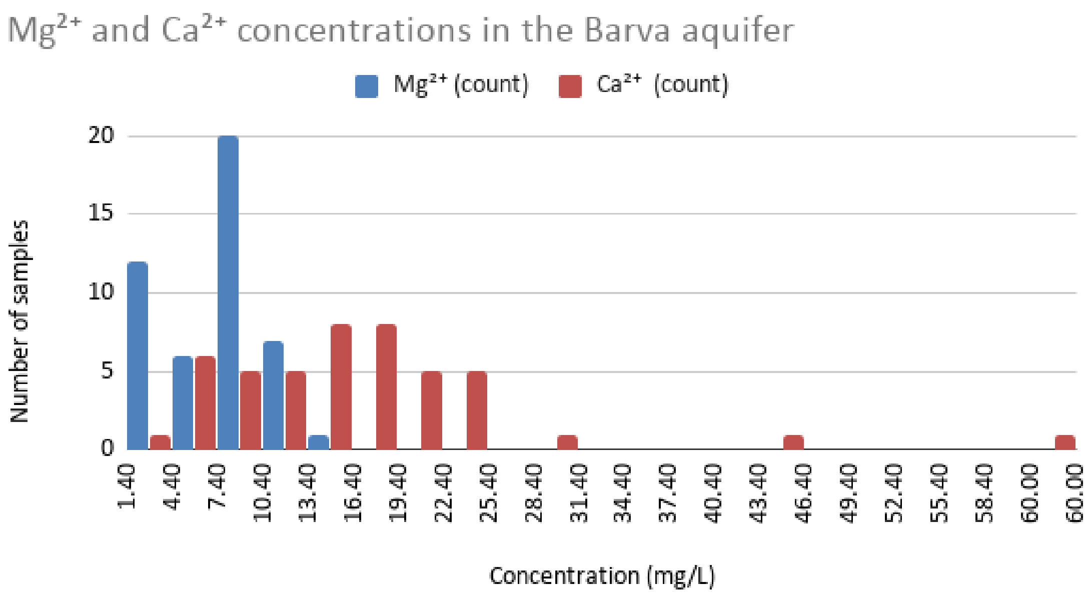

Figure 3.6: Histogram showing the concentration distribution of Mg^{2+} and Ca^{2+} ions throughout the Barva aquifer with data from Madrigal-Solís et al. (2017).

The distribution of the calculated total hardness is shown in Figure 3.7. The majority of the samples are in the range of 20 to 110 mg/L $CaCO_3$, with some outliers.

A piper diagram with all the collected samples from Madrigal-Solís et al. (2017) is shown in Figure 3.8. The left trilinear plot shows that there is no single dominant cation, though calcium and magnesium are more dominant than potassium

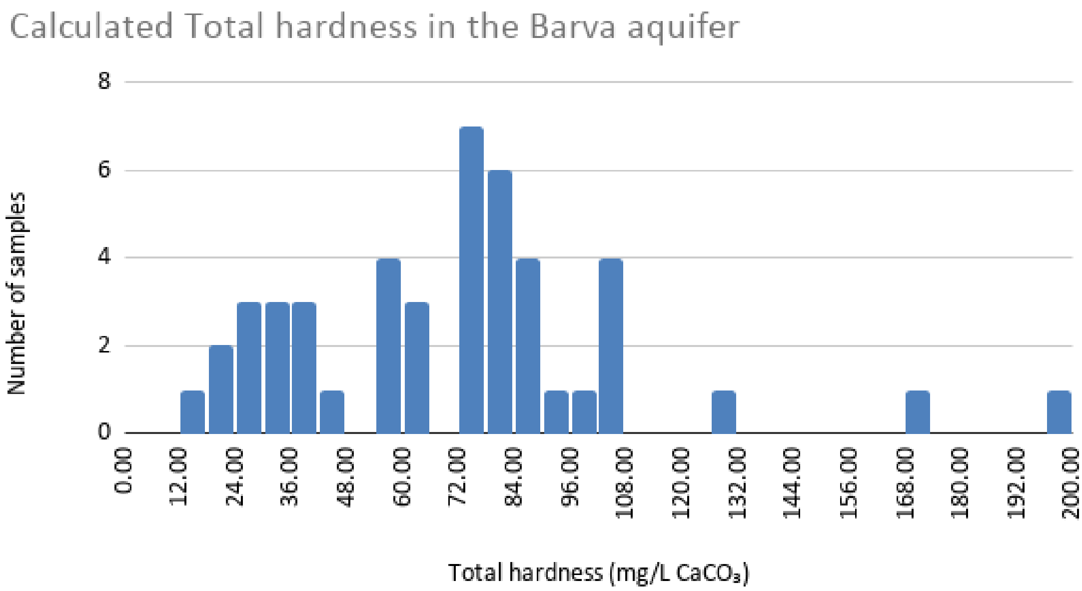

Figure 3.7: Histogram showing the total hardness distribution throughout the Barva aquifer with data from Madrigal-Solís et al. (2017).

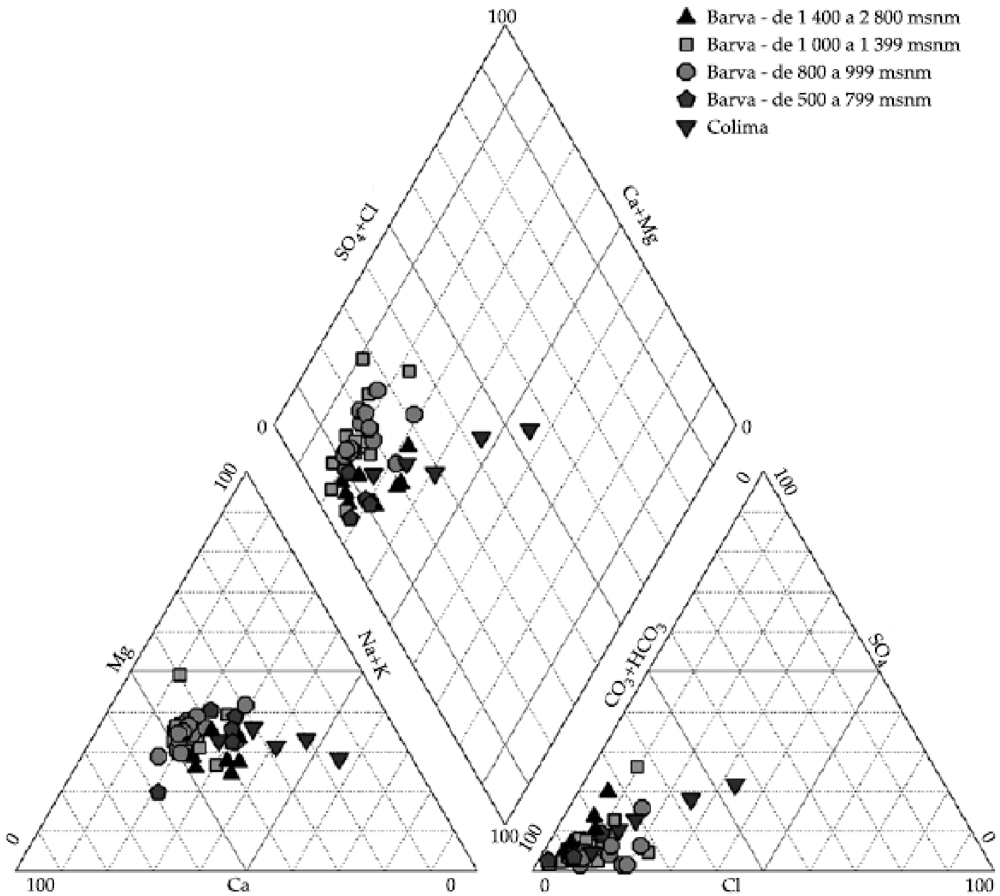

Figure 3.8: Piper diagram showing the ionic composition distribution throughout the Barva aquifer (Madrigal-Solís et al., 2017).

and sodium. The right trilinear plot shows a clear dominance of bicarbonate over chloride and sulfate. The diamond plot confirms this relation. Some of the samples are collected from the underlying aquifer *Colima*, and these samples are slightly seperated from the clusters originating in the Barva aquifer.

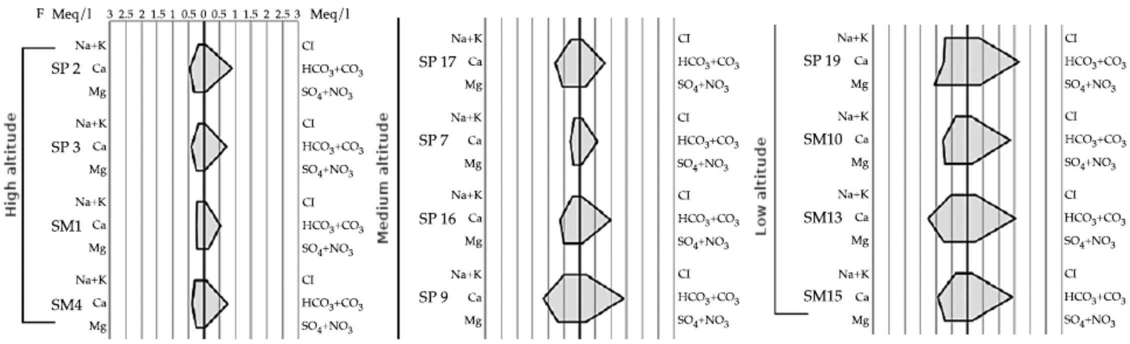

Figure 3.9: Stiff diagrams showing the chemical composition of twelve samples collected from the Barva aquifer. The x-axes shows the concentrations in meq/L, with a max value of 3 (Madrigal-Solís et al., 2017).

In Figure 3.9, Stiff patterns of the chemical composition of twelve samples are shown. The leftmost samples are all collected at a high altitude (1400 – 2800 masl), the middle at a medium altitude (1000 – 1400 masl), and the rightmost at a low altitude (800 – 1000 masl). While there is some variation, the diagrams show that as the water travels farther through the aquifer the Stiff patterns become wider due to the dissolution of minerals. The major ions in most of the samples are bicarbonate and calcium.

What is clear from the conducted investigation, is that in order to show a pattern of how the water chemistry evolves along the flow paths of an aquifer, a great number of samples are required. As there is always variations in both the samples collected, and the laboratory results, only collecting a few samples can result in showing patterns or discrepancies that do not exist.

Pacacua and Peña Negra

A study conducted by Vargas et al. (1999) on the southern side of the central valley south of San José investigated the physicochemical conditions of the two areas Pacacua and Peña Negra (Location of the sample sites and its relation to the study area of this thesis is shown in Figure 3.10). The geological conditions at Peña Negra is described as sandstones with vulcanic influences, as well as some limestone stratas. The Pacacua formation consists of sandstone, tuffs and shales with volcanic influences. As the geological composition at these sites differ from the volcanic rock at the Barva aquifer, the chemical composition of the groundwater is expected to reflect this difference.

Seven samples were collected from four springs in Pacacua, and eight were collected from four springs in Peña Negra. The physicochemical parameters determined and the ranges of concentrations are shown for Pacacua in Table 3.5 and for Peña Negra in Table 3.6 (Vargas et al., 1999).

The distribution of the concentrations of magnesium and calcium from both sites are shown in Figure 3.11. Note that while calcium has a wide spread of con-

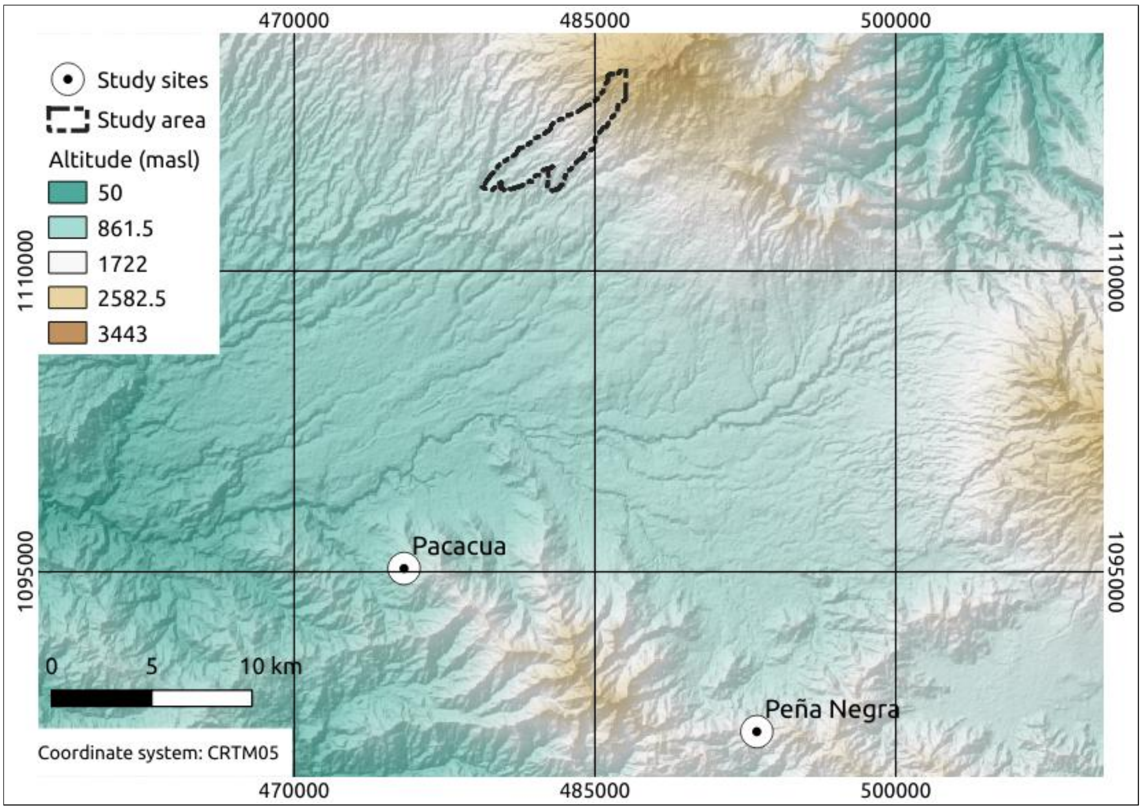

Figure 3.10: Map showing the Costa Rican central valley and the study locations of the hydrogeochemical surveys conducted at Pacacua and Peña Negra. San José is located at the center of the map.

Table 3.5: Chemical data from Pacacua (Vargas et al., 1999).

Parameter	Min	Max	Average	s
pH	5.6	7.1	6.2	–
Ca^{2+} (mg/L)	3.0	20.3	10.3	6.6
Mg^{2+} (mg/L)	2.7	7.7	5.9	1.7
Cl^- (mg/L)	4.0	8.0	5.7	2.1
SO_4^{2-} (mg/L)	5.8	13.8	9.2	2.6
SiO_2 (mg/L)	29.8	39.2	35.2	3.0
NH_4^+ (mg/L)	0.1	0.4	0.3	0.1
Fe Total (mg/L)	0.02	0.2	0.09	0.1
NO_3^- (mg/L)	0.4	18.8	8.3	7.8
Na^+ (mg/L)	5.8	7.3	6.5	0.7
K^+ (mg/L)	0.8	2.3	1.7	0.6
PO_4^{3-} (mg/L)	0.1	0.5	0.2	0.1
HCO_3^- (mg/L)	13.2	48.4	27.0	14.2
Total alkalinity (mg/L)	21.6	79.4	44.3	23.4
CE (µS/cm)	88	152	111	26.2
Total hardness (mg/L $CaCO_3$)	22.3	80.3	49.8	20.9

Table 3.6: Chemical data from Peña Negra (Vargas et al., 1999).

Parameter	Min	Max	Average	s
pH	6.3	6.7	6.4	–
Ca^{2+} (mg/L)	3.0	25.6	12.5	9.8
Mg^{2+} (mg/L)	3.6	6.8	5.0	1.3
Cl^- (mg/L)	6.0	11.9	8.2	1.5
SO_4^{2-} (mg/L)	2.3	9.9	5.9	2.4
SiO_2 (mg/L)	34.5	93.9	76.9	19.6
NH_4^+ (mg/L)	0.1	0.6	0.4	0.2
Fe Total (mg/L)	0.1	1.1	0.5	0.3
NO_3^- (mg/L)	0.4	49.20	8.5	15.8
Na^+ (mg/L)	5.7	9.3	8.0	1.4
K^+ (mg/L)	0.6	2.5	1.7	0.6
PO_4^{3-} (mg/L)	0.04	0.2	0.1	0.1
HCO_3^- (mg/L)	8.8	57.2	29.2	13.2
Total alkalinity (mg/L)	14.4	93.8	47.8	21.6
CE (µS/cm)	60	160	109	33.7
Total hardness (mg/L $CaCO_3$)	26.0	88.2	51.7	24.6

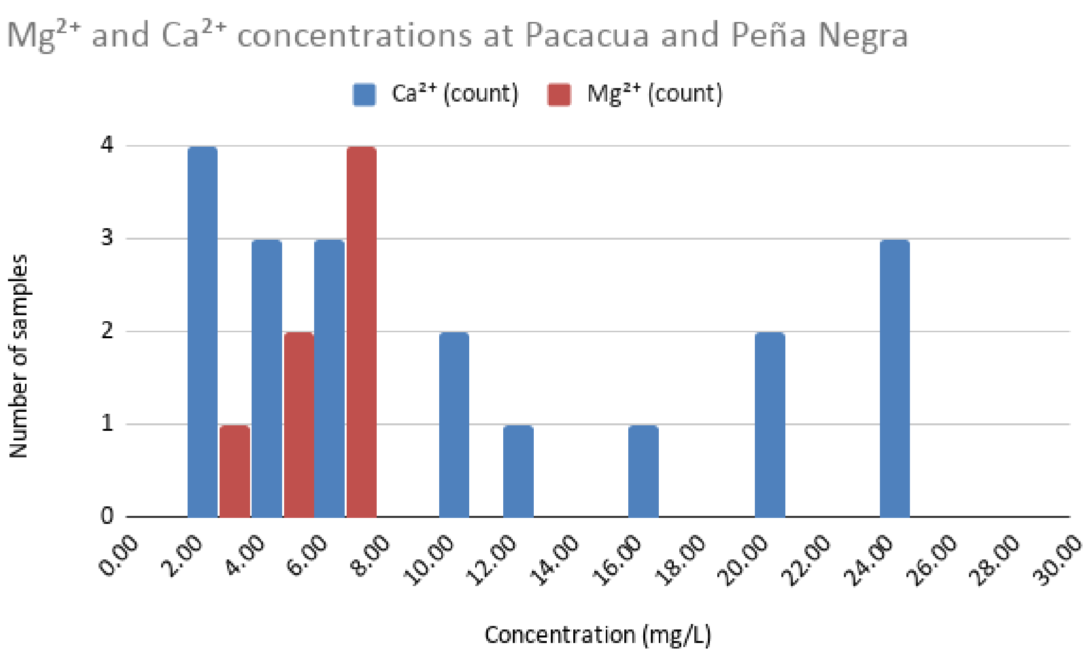

Figure 3.11: Histogram showing the concentration distribution of Mg^{2+} and Ca^{2+} ions at the Pacacua and Peña Negra sites with data from Vargas et al. (1999).

centrations (up to 24 mg/L), magnesium is distinctly clustered in the range 4 to 8 mg/L.

The total hardness of the samples from Pacacua and Peña Negra is shown in Figure 3.12. The range of values is lower and smaller than the concentrations in Madrigal-Solís et al. (2017), with values ranging from 22 to 88 mg/L $CaCO_3$, with a high and a low cluster of concentrations.

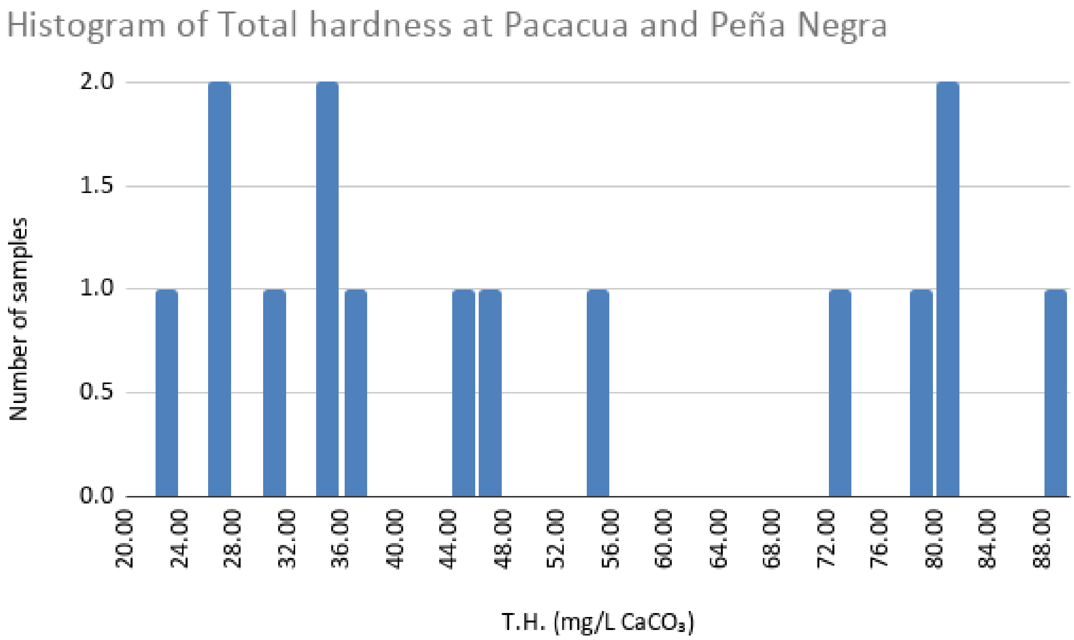

Figure 3.12: Histogram showing the total hardness distribution at the Pacacua and Peña Negra sites with data from Vargas et al. (1999).

The samples from Pacacua and Peña Negra are illustrated in a Piper diagram in Figure 3.13. The samples from both sites show a bicarbonate dominance, with two samples showing no significant anionic dominance. Three of the four sites sampled in Pacacua show calcium as the major cation, while three of the four sites in Peña Negra show magnesium, sodium and potassium as the major cations. Note the difference from Figure 3.8.

From the chemical data collected at Pacacua and Peña Negra, eight Stiff patterns have been generated, shown in Figure 3.14. At Pacacua, samples P1, P2 and P4 are all located within a few hundred meters, while P5 is situated roughly one kilometre downstream from this cluster. Even though the three sample sites are so closely situated, there is no clear similarity between the Stiff patterns of these sites. An explanation could be that the study collected three samples at P1, two samples at P2 (the averages of these samples are presented in the figure) but only one sample each from P4 and P5.

Similarly, at Peña Negra, three samples were collected from both PN-1 and PN-2, but only one sample each from PN-3 and PN-4. The geographical distribution of the sample sites at Peña Negra is even less than at Pacacua. All four sites are located within a stretch of a few hundred meters, but the Stiff pattern from PN-2 still differs heavily from the other three.

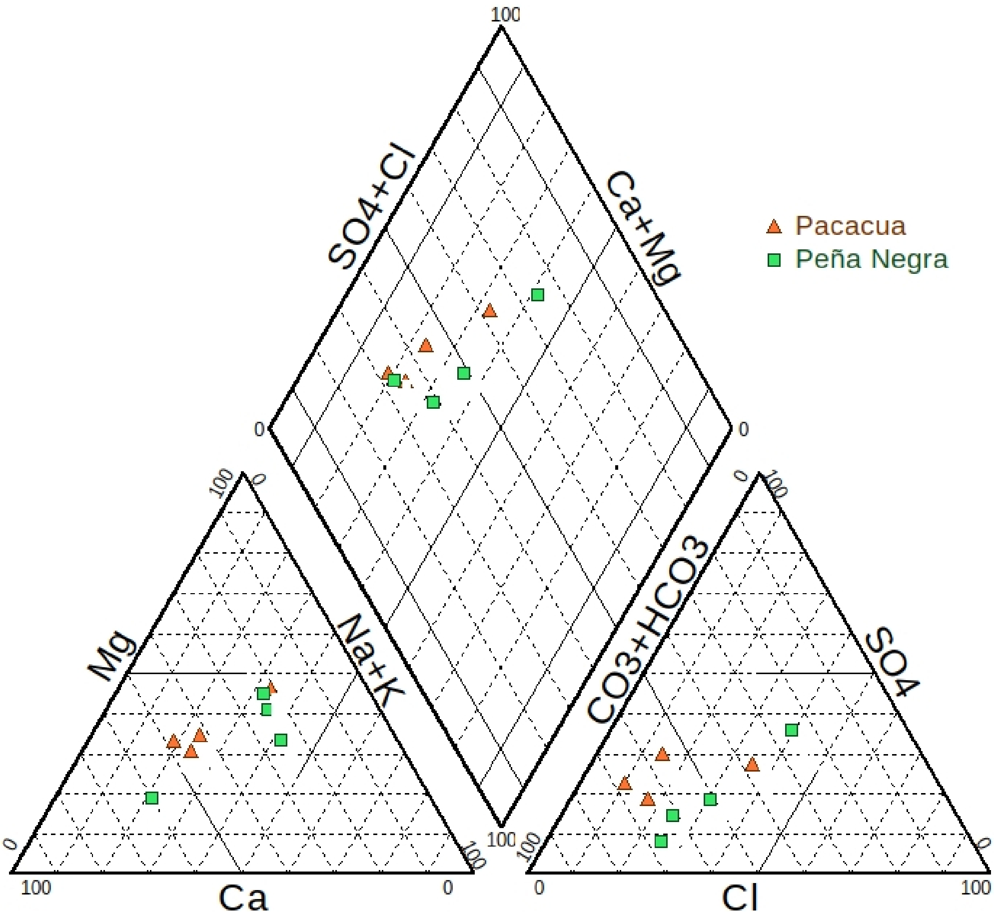

Figure 3.13: Piper diagram showing the analyses from Pacacua and Peña Negra with data from Vargas et al. (1999).

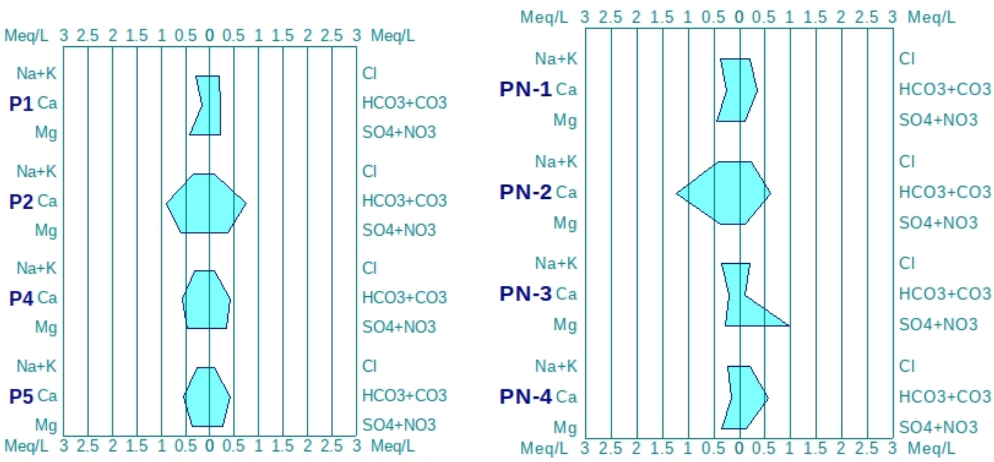

Figure 3.14: Stiff patterns from Pacacua (P1-5) and Peña Negra (PN1-4) with data from Vargas et al. (1999).

3.5.2 Vulnerability assessments

Three previous GOD vulnerability assessment studies, and one DRASTIC vulnerability assessment study, conducted in the area have been examined as part of this thesis. Two of the GOD assessments were made in the Alajuela canton; one from 2010 and one from 2015, and one in the Santa Barbara canton conducted in 2015. The DRASTIC assessment was conducted in 2020.

The locations of the four studies are shown in Figure 3.15, along with the study area of this thesis. *Alajuela* is the location of Centro de Investigaciones en Ciencias Geológicas (2015b), *ProDUS* is the location of Programa de Investigación y Desarrollo Urbano Sostenible (ProDUS) Universidad de Costa Rica (2010), *Santa Barbara* is the location of Centro de Investigaciones en Ciencias Geológicas (2015a) and *DRASTIC* is the location of Quirós Alemán et al. (2020).

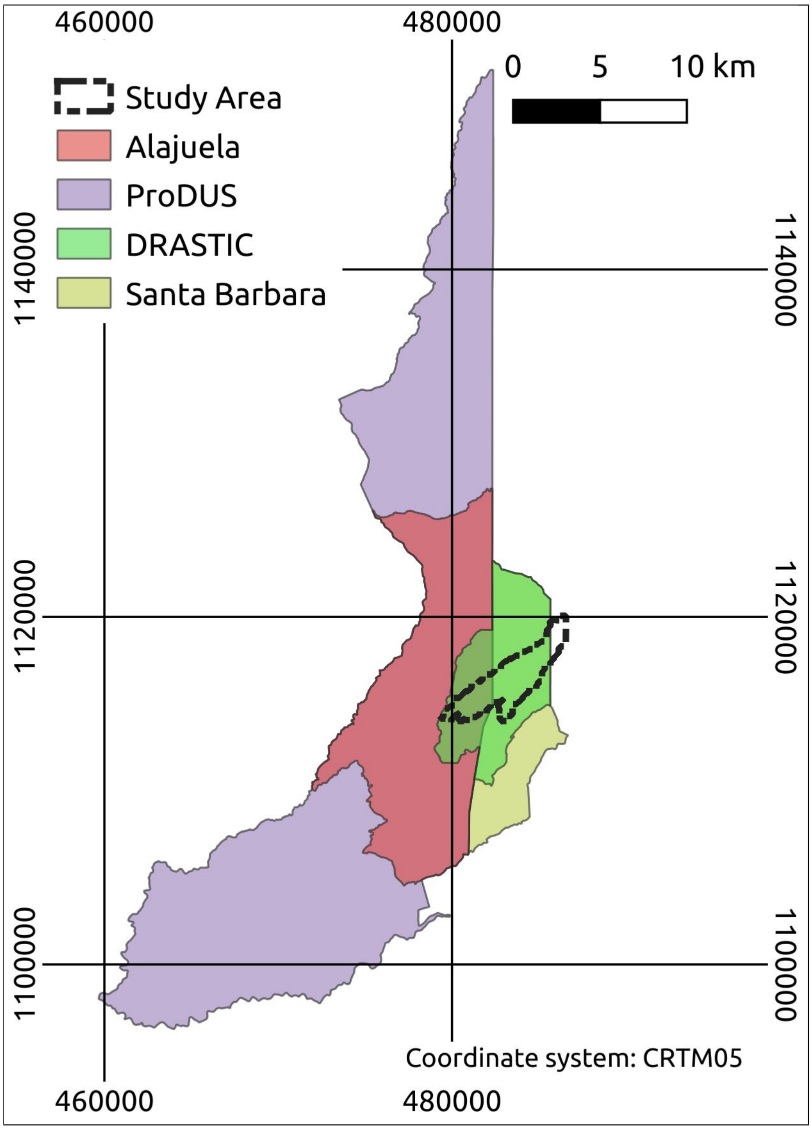

Figure 3.15: Map showing the locations of previous studies.

GOD

In Nevermann (2005), the vulnerability of the canton Alajuela was assessed by first dividing the canton in two sectors: the Pacific slope and the North slope. In the Pacific slope there exists hydrogeological data in the form of well lithology and water levels. The Pacific slope sector is of relevance for this thesis (Programa de Investigación y Desarrollo Urbano Sostenible (ProDUS) Universidad de Costa Rica, 2010).

In the study ten cross-section profiles were constructed, whereof one goes through the study area of this thesis. This profile goes through the three borehole wells BA-838, BA-786 and BA-854 and is shown in Figure 3.16.

In the assessment, the area was divided in three sectors, whereof two of them were treated the same way and the third was treated differently. The groundwater in the third sector was assessed to be less vulnerable to pollution than the other two. This assessment was motivated with the lack of an upper layer of lava in this section leading to the assumption that the aquifer is situated in lower lava formations which are more protected from the soil surface, thus leading to a lower vulnerability.

Buffers were made around the river beds, constituting the river gorges. The buffers were 100 m in the first two sectors and 25 m in the third.

The vulnerability was finally assessed to be high in the river beds, medium in the river gorges and low outside of the river areas. In the third sector it was assessed to be medium in the river beds and low in the river gorges and outside of the river beds. The resulting vulnerability map can be seen in Figure 3.17.

Each step in the assessment is not clearly stated and therefore it is unclear if the methodology/workflow for the GOD assessment was followed properly.

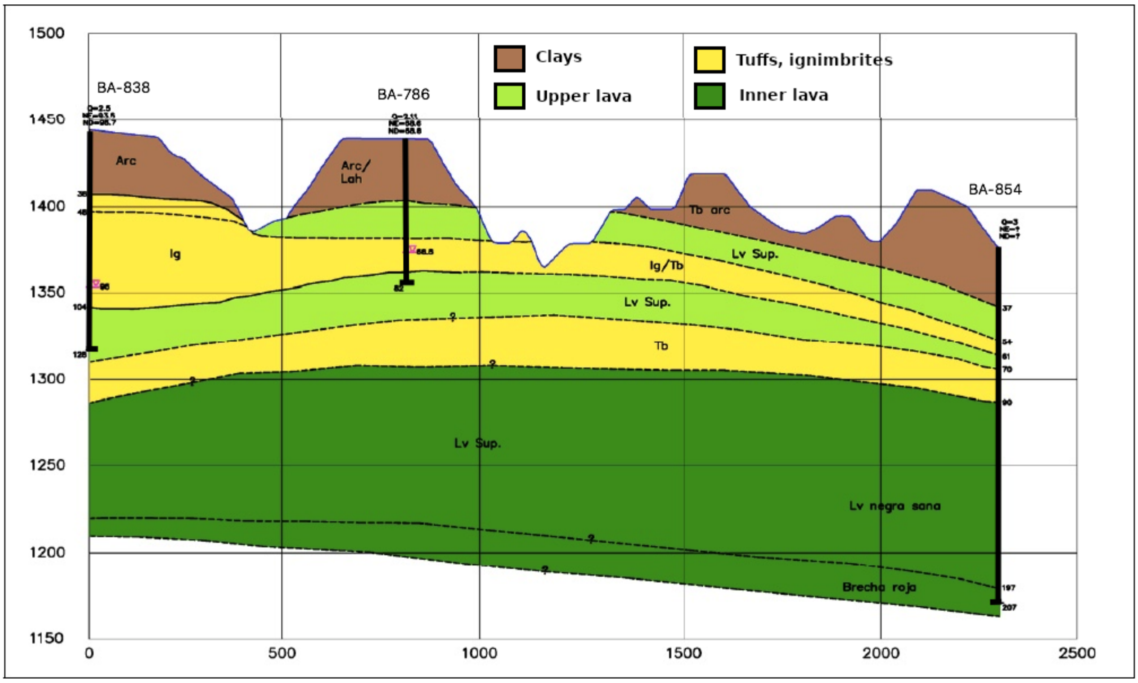

Figure 3.16: Cross-section profile going through BA-838, BA-786 and BA-854 (Programa de Investigación y Desarrollo Urbano Sostenible (ProDUS) Universidad de Costa Rica, 2010). See Profile C-C' in Figure 4.1 for its location.

In Centro de Investigaciones en Ciencias Geológicas (2015b) the canton was divided in five sectors: Poasito, La Paz, Colima, Achiote, Bambinos and Bermúdez,

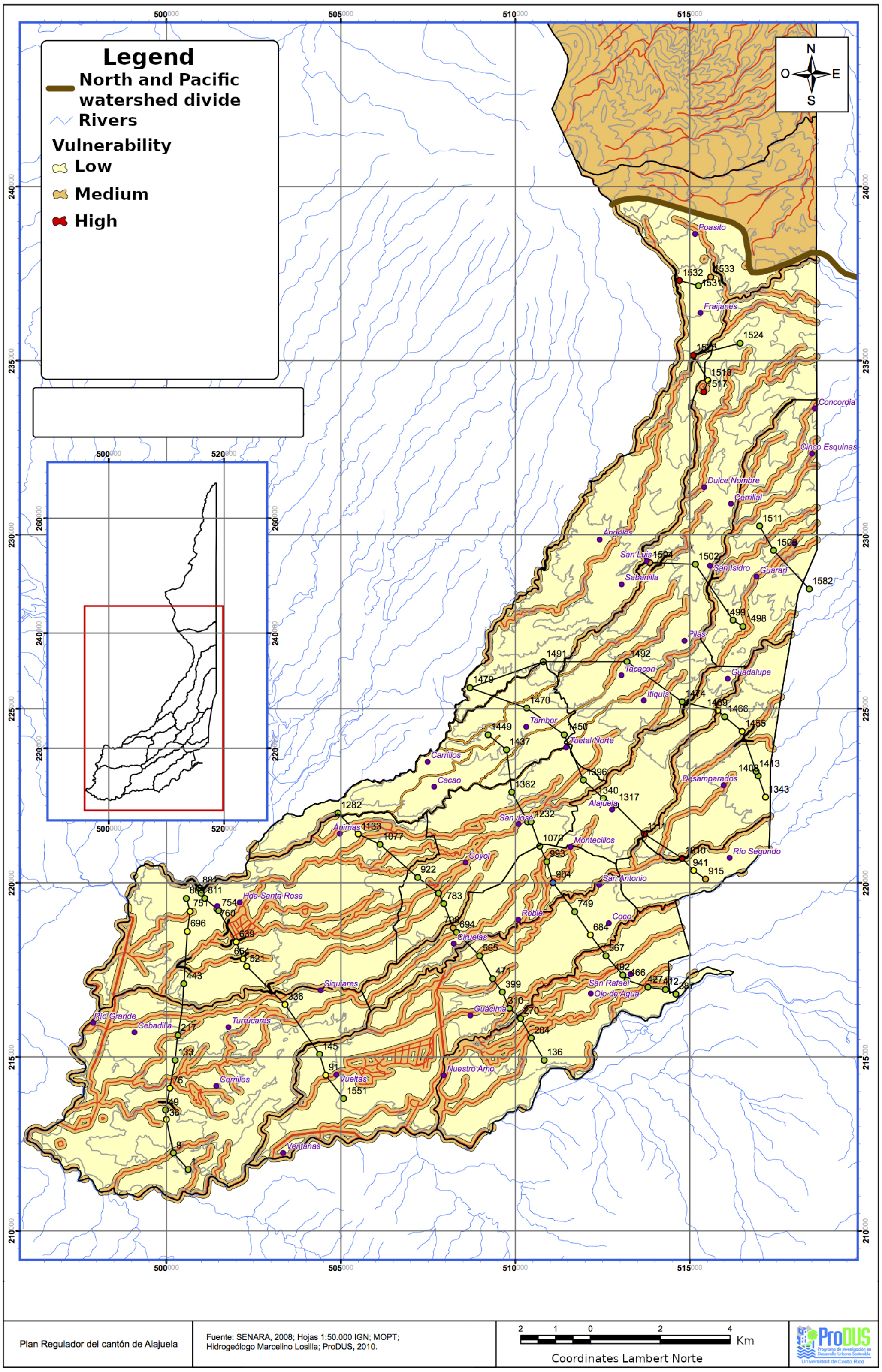

Figure 3.17: GOD vulnerability map from Programa de Investigación y Desarrollo Urbano Sostenible (ProDUS) Universidad de Costa Rica (2010)

based on the hydrogeology. Furthermore, the sectors were divided in "zonas rocosas" and "zonas fallada", where zonas fallada are zones with faults and zonas rocosas are the rest of the areas, where no faults are present.

Buffers of 200 m on each side was made around the faults due to the increased risk of pollution.

The resulting vulnerability assessment map is shown in Figure 3.18 (Centro de Investigaciones en Ciencias Geológicas, 2015b).

In Centro de Investigaciones en Ciencias Geológicas (2015a) the province was first divided in the three cantons: Santa Barbara, Santa San Rafael and San Isidro, whereof the first mentioned is of interest in this thesis.

The vulnerability in Santa Barbara was assessed differently depending on the hydrogeology. The uppermost geological formation in the canton are the Los Bambinos formation and the Bermúdez formation respectively.

In the areas for the respective formation, subdivisions were made depending on the distance to the groundwater. Where Los Bambinos is the uppermost layer, the depth to the groundwater was stated as 20-100 m and the D value was set to be 0.5. This value does not exist in the methodology of the GOD assessment. Greater than 50 m yields a value of 0.6 and that is the lowest value to choose from, which can be seen in Figure 3.4 (Centro de Investigaciones en Ciencias Geológicas, 2015a).

The methodology for the GOD assessment have been followed, however several of the parameter values are decided wrongly. The result of the assessment is shown in Figure 3.19.

DRASTIC

A vulnerability assessment using the DRASTIC method was conducted in the spring of 2020 by students at the Universidad Técnica Nacional de Alajuela as a final project (Quirós Alemán et al., 2020). The study has not been published or reviewed and its results are not discussed in depth in this thesis.

The area of study contains the districts of Carrizal de Alajuela, Santo Domingo and Puraba de Heredia, which coincides partly with the study area of this thesis.

It is presented that all factors except the T-factor (topography) is the same throughout the study area. The final result of the vulnerability assessment is shown in Figure 3.20 together with the shape of the study area for this thesis. The vulnerability ranges from Low to Very High (Quirós Alemán et al., 2020).

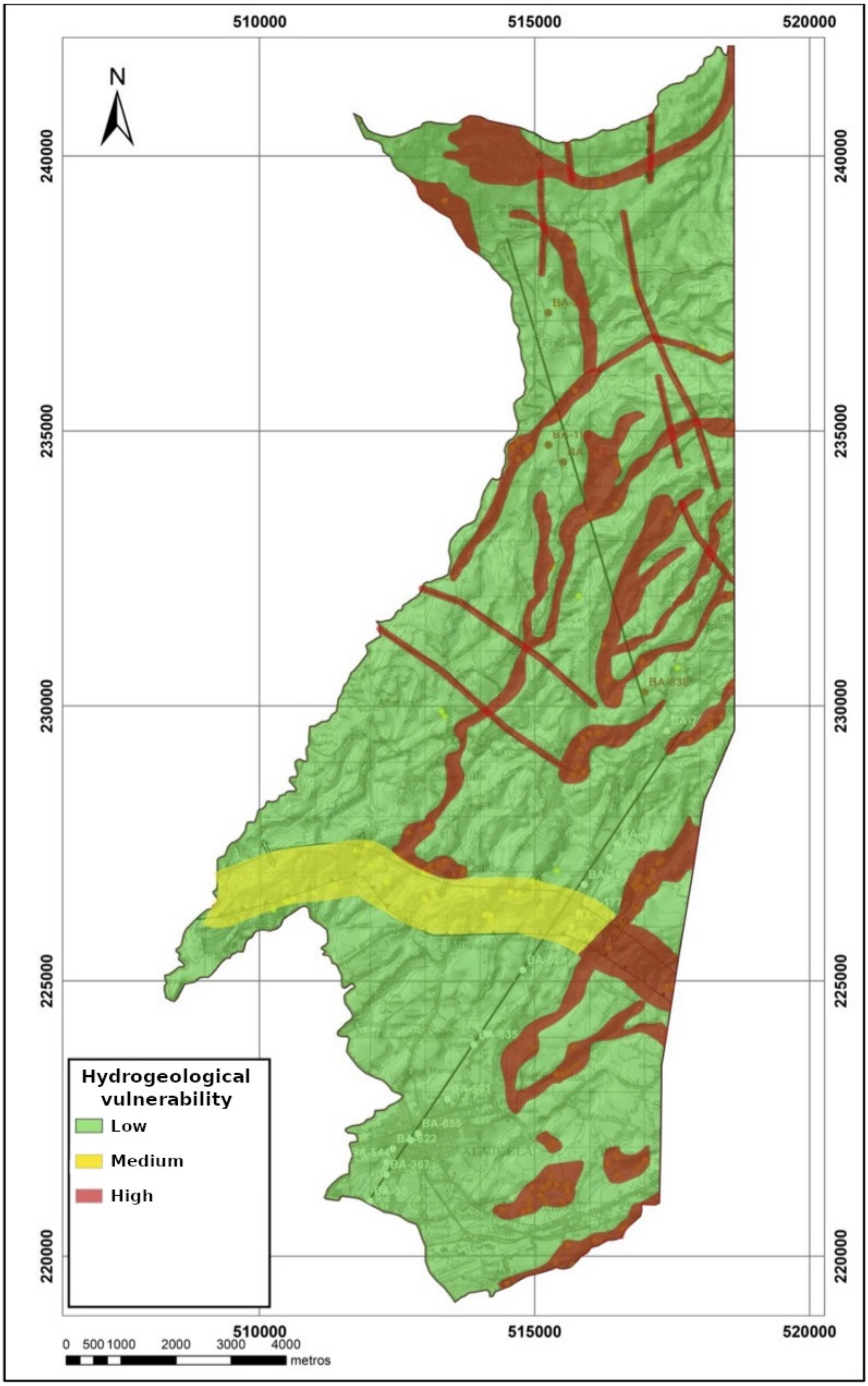

Figure 3.18: GOD vulnerability assessment map from Centro de Investigaciones en Ciencias Geológicas (2015b).

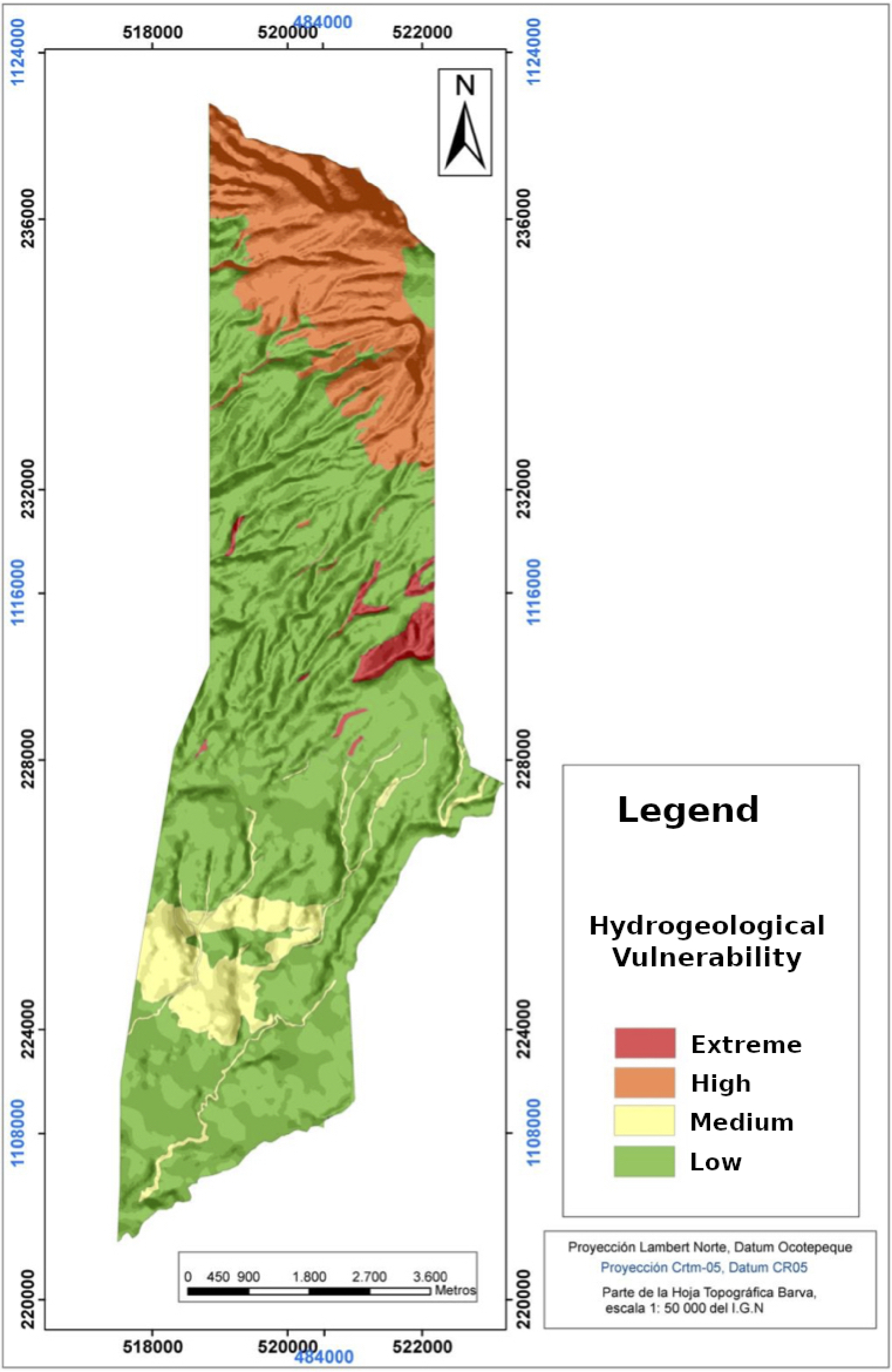

Figure 3.19: GOD vulnerability assessment map for Santa Barbara from Centro de Investigaciones en Ciencias Geológicas (2015a).

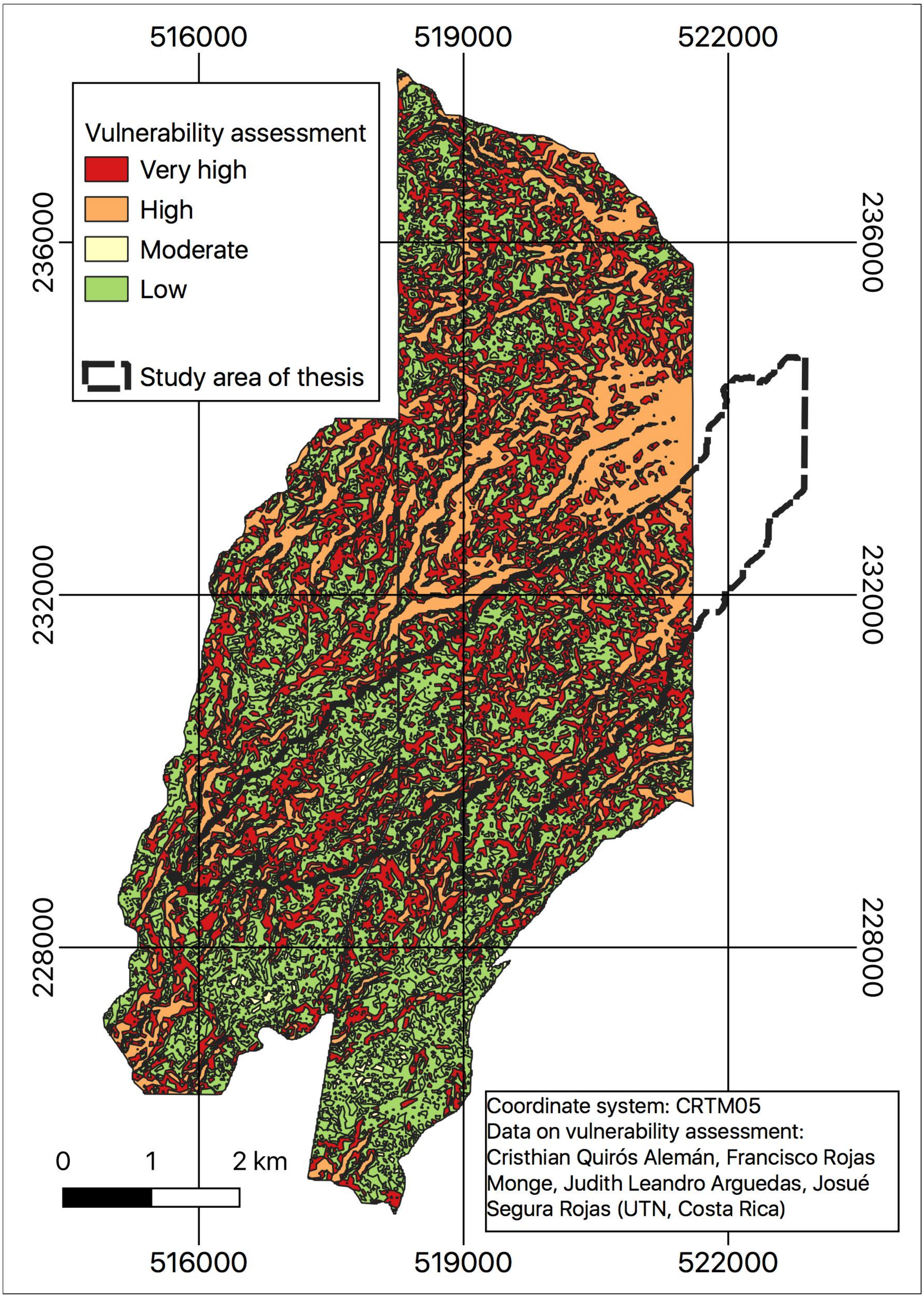

Figure 3.20: DRASTIC vulnerability assessment map (data from Quirós Alemán et al. (2020), by permission) with contours of study area of this thesis.

Chapter 4

Methods

In this chapter, the methods used are presented in four sections: sampling procedures, validity of laboratory results, water composition evaluation and vulnerability assessment.

4.1 Sampling procedures

The sampling methodology follows the procedures shown in Section 3.1. In the field, the following parameters were measured:

- Location
- Altitude
- Temperature
- pH
- Electrical conductivity
- Reduction potential

Locations were determined using *Garmin GPSMAP 78s*, which used GPS data to determine the altitude as well. The other parameters were all determined using the multiparameter meter *Orion star A329*. A beaker of 1 L was rinsed three times using spring water before measuring the parameters in it.

Biological samples were collected in sterilised, transparent containers measuring 120 mL (except for the first collected sample, where a similar container only measuring 50 mL was used). The biological containers were stored in an ice box, with paper isolation from the ice. The physicochemical samples were collected in gallon cans that were rinsed three times using spring water before collecting the samples.

The samples were delivered the same day to *Laboratorio de Análisis Químicos y Ambientales Gaia* (`https://www.labgaia.com/`) in San Rafael, Alajuela. Gaia is accredited by the Costa Rican accreditaion body ECA (*Ente Costarricense de Acreditación* `https://www.eca.or.cr/`). Two analyses were ordered per sample, one biological and one physicochemical.

4.1.1 Sample points

Groundwater samples were collected from eight springs (described in Section 2.2.3) located along the catchment areas of the rivers Quizarraces, Ahogado and Guararí along the slope of Cerro Guararí northeast of Carrizal. The eight sample sites are

Table 4.1: List of sample sites number, name and date of collection.

Sample number	Sample site	Date
1	Diogenes	04/03/20
2	Prudencio #7	05/03/20
3	Prudencio #5	05/03/20
4	La Laguna	05/03/20
5	Chamorro	05/03/20
6	Lomas de Guarari	12/03/20
7	La Virgen (1)	12/03/20
8	La Virgen (2)	12/03/20

listed in Table 4.1, along with their sample number and date of collection, and shown in Figure 2.5.

Sample sites 1 and 6 are under private use, while the other sites are maintained by ASADA. At Diogenes, the sample was collected at the upper spring. This location was also the only one where the water was not collected from any man made construction (i.e. pipes) but from the wall where the water was flowing. At Prudencio and La Virgen de Lourdes, a number of springs were present at each site. At Prudencio, samples were collected from the two major springs, number 5 and 7, and at La Virgen de Lourdes, two duplicate samples were collected from spring number 1.

4.2 Validity of laboratory results

In order to determine the validity of the laboratory analyses, a number of parameters were evaluated. Parameters determined both at sample sites and in the laboratory (pH, temperature and electrical conductivity) could be compared without processing. The chemical concentrations determined by the laboratory required processing before they could be evaluated.

4.2.1 Water hardness and cationic content

By comparing the ionic concentrations with chemical analyses of water samples collected some kilometres south of this study area (Madrigal-Solís et al., 2017), a systematic discrepancy in the magnesium concentration was discovered. As the magnesium, calcium, and water hardness of the samples did not follow the relation of Equation 3.2, the magnesium concentration was instead calculated from the calcium content and the total hardness determined by the laboratory. The reasoning for this procedure is shown in Section 5.1.2.

4.2.2 Data validation

In order to validate the chemical data supplied by the lab, a numerical solver was used to determine the charge balance error, alkalinity, water hardness, and electrical conductivity. The software used was *aqion*, which uses PHREEQC as its internal numerical solver (aqion, 2020). In order to determine the alkalinity, the carbonic concentrations in the water samples were set to 1 mg/L, and adjusted so that a charge balance was reached by the software.

4.3 Water composition evaluation

The validated chemical data is presented as discussed in Section 3.2.4.

Python scripts (created by Montoya (2019), with some modifications) were used to create georeferenced Stiff diagrams that were imported into QGIS.

Piper diagrams were generated using the software Diagrammes, created by Simler (2020) of the Laboratoire d'Hydrogéologie d'Avignon.

X-Y diagrams were generated by converting the concentrations to meq/L and plotting relevant constituents using a spreadsheet software such as Microsoft Excel.

4.4 Vulnerability assessment

The area of study for the vulnerability assessment was decided based on the catchment areas of the rivers Quizarraces, Ahogado and Guararí. The software used to define the catchment areas and furthermore conduct the vulnerability assessment was the open-source geographical information system QGIS (QGIS, 2020). The catchment areas were defined from a digital elevation map of the area. The three catchment areas were merged into one large catchment area for the three rivers, shown in Figure 4.1.

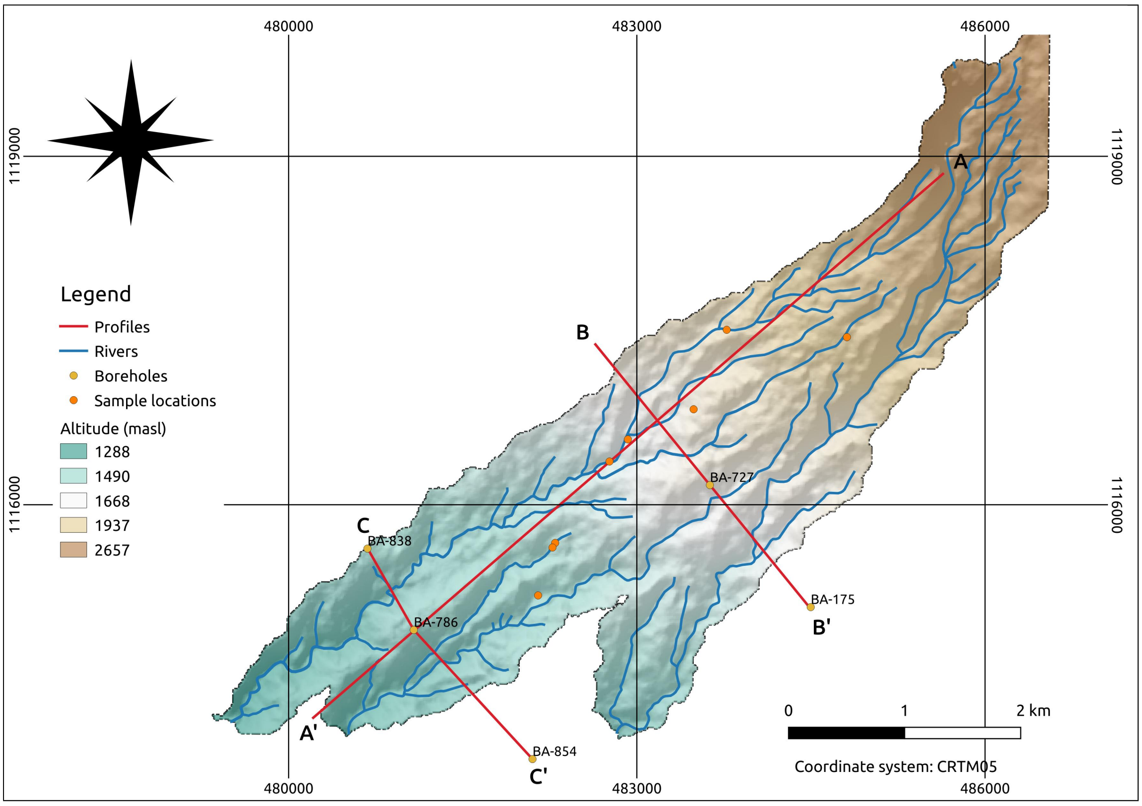

Figure 4.1: Map showing the catchment areas of the rivers Quizarraces, Ahogado and Guararí, and the three profiles A, B and C.

In order to assess the vulnerability of the area, firstly a conceptual model of the area was made. Lithology from a number of boreholes and the previous studies, presented in Section 3.5.2, was also examined to get knowledge on the geology and hydrogeology. With information from the lithologies and the previous studies, a number of geological units were found.

Three profiles; one along the flow direction and two perpendicular to the first; were made in QGIS. The profiles were chosen so that they would go through at least one borehole in order to get known lithographic data to insert in a sketch of the profile. The respective situations of the profiles are shown in Figure 4.1. A manual interpolation of the geology was made in between the boreholes. The profiles are shown in Figures 4.2, 4.3 and 4.4.

Due to a lack of data, the most upstream, northeastern, part of the catchment area was clipped and discarded. The remaining area was decided as the study area for the vulnerability assessment.

The study area was first divided in two categories depending on the uppermost geological unit: Bambinos and Porrosatí. A third category was added to represent the bordering area between the two units: Bambino buffers.

Data of the uppermost geological unit was clipped together with the study area in QGIS, creating a layer showing the two units Bambinos and Porrosatí in the area of interest. Buffers of 100 m were created around Bambinos.

On top of these three categories, buffers were also made on and around the rivers as following:

- River beds of 25 m
- River gorges
  - 100 m on big rivers
  - 25 m on small rivers

When the width of the buffers around the rivers were decided, it was matched with an ortophoto so that it would cover the rivers in the majority of the study area. This is the reason of choosing buffers of 100 and 25 meters respectively for the rivers and small rivers.

With this, nine different scenarios were established. The G, O and D values, as well as the final aquifer pollution vulnerability value- and assessment were decided for each scenario according to the methodology presented in Figure 3.4. The values for each parameter are shown in nine respective tables in Appendix C.

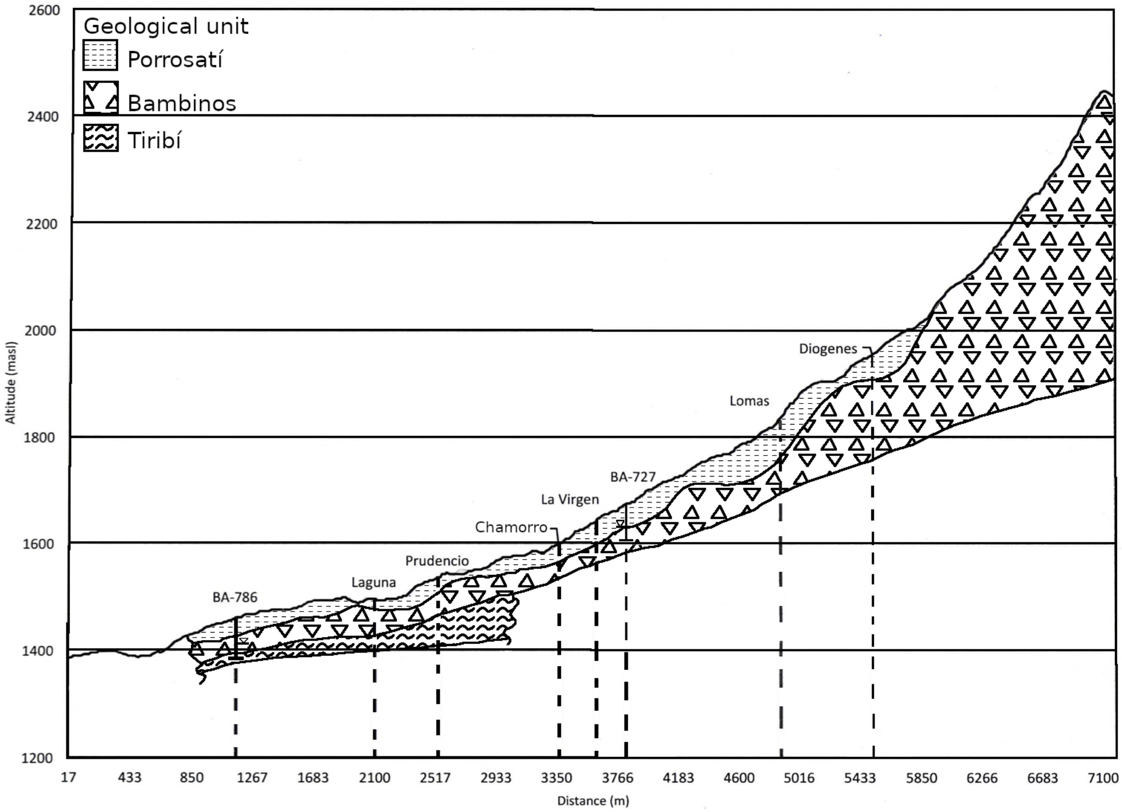

Figure 4.2: Cross-section of the profile A-A'. Note that not all of the springs and boreholes are located at the cross-section. See Figure 4.1.

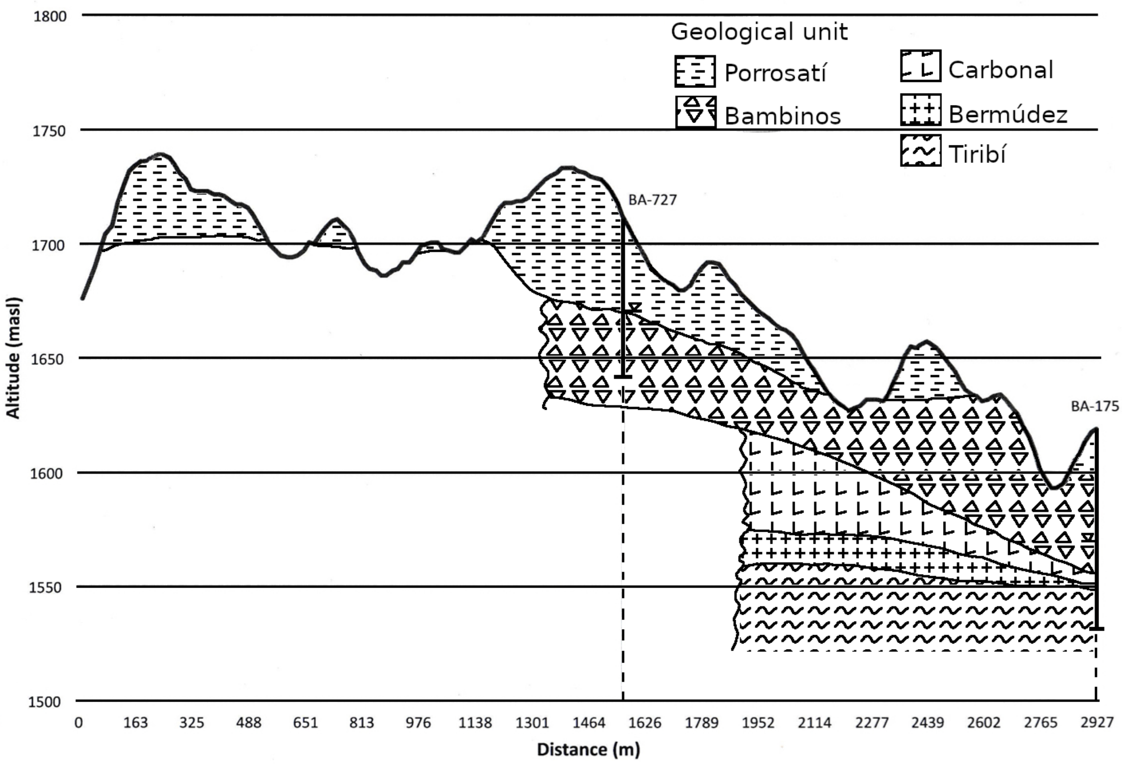

Figure 4.3: Cross-section of the profile B-B'.

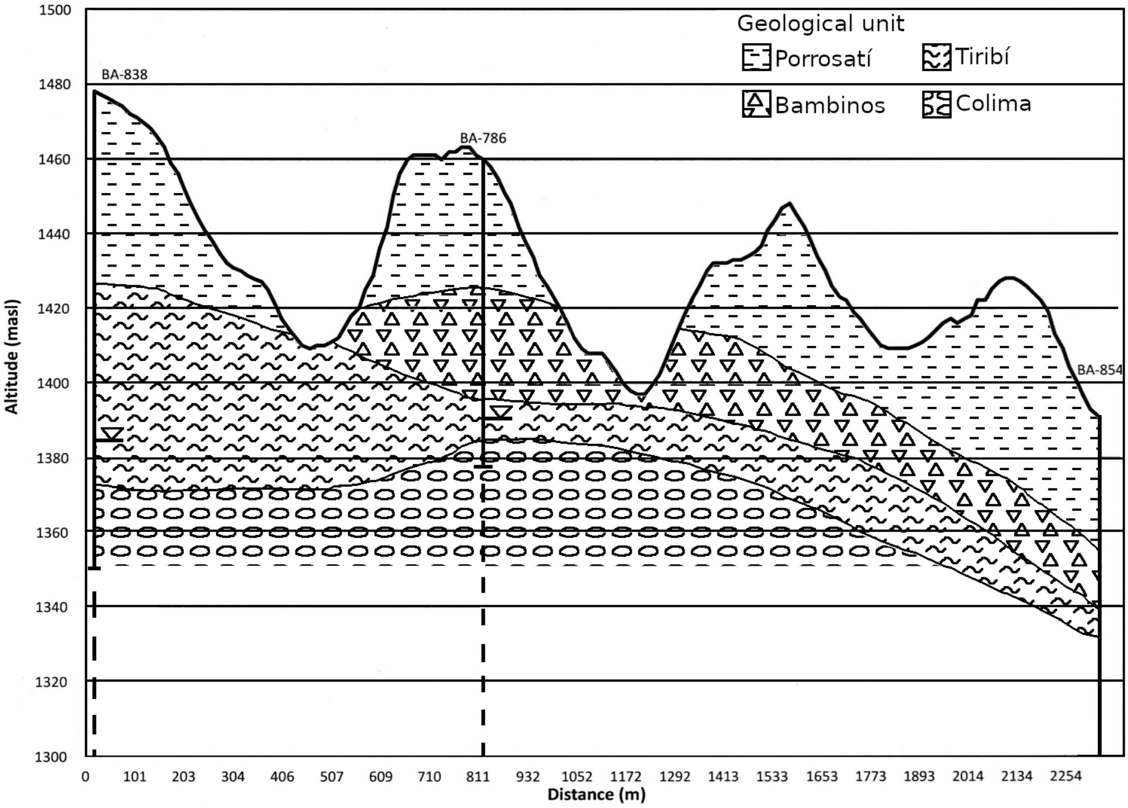

Figure 4.4: Cross-section of the profile C-C'. The depth of the rightmost borehole, BA-854, is 207 meters.

Chapter 5

Results

The results of the study are presented in this chapter. The chapter is divided in two sections: hydrochemical results and vulnerability assessment.

5.1 Hydrochemical results

The physicochemical and the biological laboratory results were delivered three weeks from the sample date, after the abrupt interruption of the field work and return from Costa Rica. The complete data from the laboratory analyses is presented in Appendix A. The data collected from in field measurements is presented in Appendix B.

5.1.1 Duplicate samples

The chemical results from the two duplicate samples collected at La Virgen de Lourdes are shown in Table 5.1. The results show one major discrepancy in the amount of calcium in the samples, and one minor in the amount of iron. Sample 1 contains 12 ± 1 mg/L calcium ions while Sample 2 contains 26 ± 1 mg/L. The amount of iron in Sample 1 is 0.23 ± 0.01 mg/L while Sample 2 contains 0.19 ± 0.01 mg/L. The difference in calcium and iron is higher than the stated error margin.

Table 5.1: Laboratory results from the duplicate samples collected from Virgen de Lourdes. Note the differences in Ca-concentration.

Parameter	La Virgen (1)	La Virgen (2)
pH	8.1 ± 0.1	8.1 ± 0.1
Temperature (°C)	20 ± 2	20 ± 2
Total hardness (mg/L $CaCO_3$)	59 ± 4	55 ± 2
EC (µS/cm)	101 ± 6	101 ± 7
Cl (mg/L)	0.0055 ± 0.0006	0.0052 ± 0.0004
Ca (mg/L)	12 ± 1	26 ± 1
Fe (mg/L)	0.23 ± 0.01	0.19 ± 0.01
Mg (mg/L)	18 ± 1	20 ± 1
K (mg/L)	5.5 ± 0.2	5.3 ± 0.2
Na (mg/L)	11 ± 1	12 ± 1

Also note that even though Sample 2 has more than double the amount of calcium than Sample 1, and magnesium at the same magnitude, the total hardness of the sample is lower than for Sample 1 (55 to 59 mg/L $CaCO_3$). The laboratory failed to deliver an explanation to these inconsistencies in the analyses.

5.1.2 Total hardness and cation concentration

Using Equation 3.2, it is clear that the laboratory results are inconsistent, which is shown in Figure 5.1, where the water hardness determined by the laboratory is compared to the water hardness calculated from the ionic content presented by the laboratory. The average titrated hardness of the samples is 50.1 mg/L, while the average calculated hardness is 111.5 mg/L. The error between the calculated and the titrated value ranges from a factor of 1.7 to 2.7, with an average of 2.2.

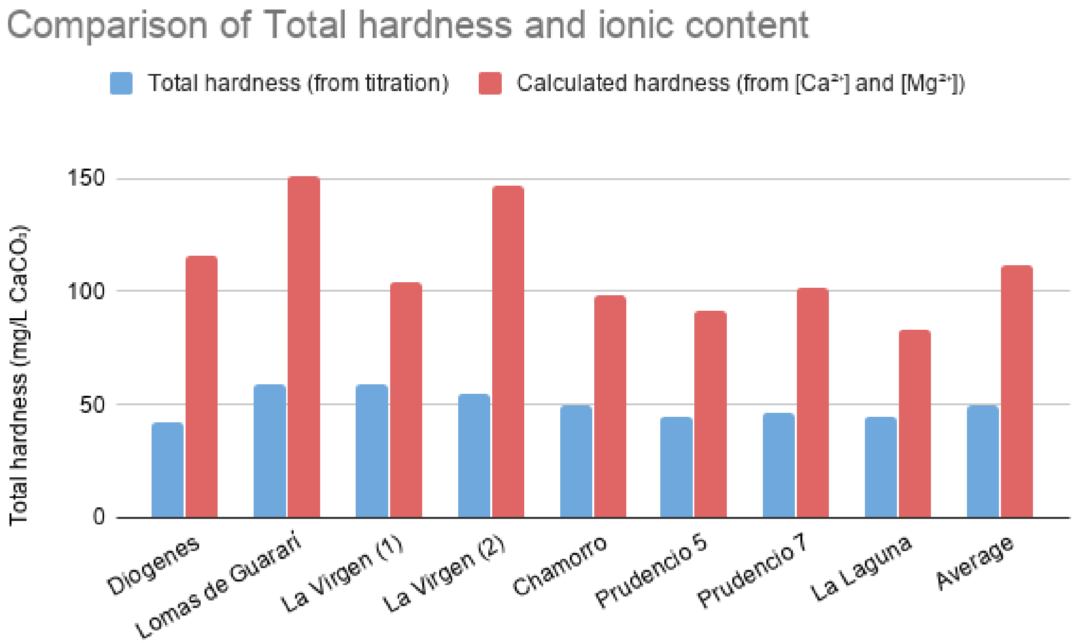

Figure 5.1: Total hardness determined by the laboratory compared with total hardness calculated from the ionic concentrations in the samples.

The concentrations of the magnesium ions found in this study were much higher than those in the two studies presented in Section 3.5.1. The survey conducted of the Barva aquifer just south of this study area found magnesium concentrations mainly in the range of 2 to 10 mg/L, with some samples having a higher concentration of 12 to 14 mg/L. Similar ranges for calcium concentrations were presented as 10 to 20 mg/L (Madrigal-Solís et al., 2017).

The results of this study showed magnesium concentrations in the range of 13 to 21 mg/L, and calcium concentrations in the range of 11 to 13 mg/L, with two samples having a calcium concentration of 26 mg/L. As the water samples collected for Madrigal-Solís et al. (2017) were collected further downstream within the same aquifer as the ones collected for this study, it seems unreasonable that the cationic concentrations are higher in the upstream springs.

As the calcium concentration and the titrated hardness values presented by the laboratory were within the ranges found in previous studies, Equation 3.2 was used to calculate magnesium concentrations. Table 5.2 shows the two different values of magnesium concentrations. Note that for the samples collected from Lomas de Guararí and La Virgen (2) a negative concentration of magnesium is required for the given hardness and calcium concentration to match. It is also these two samples that showed a two times higher concentration of calcium (26 mg/L) than the other samples.

Table 5.2: Magnesium concentrations determined by laboratory as well as from hardness–cation relationship.

Sample location	Mg from laboratory (mg/L)	Mg from hardness and Ca (mg/L)	Relative error
Diogenes	21 ± 2	2.93	0.86
Lomas de Guararí	21 ± 2	-1.46	1.07
La Virgen (1)	18 ± 1	7.07	0.61
La Virgen (2)	20 ± 1	-2.44	1.12
Chamorro	16 ± 1	4.27	0.73
Prudencio 5	15 ± 1	3.66	0.76
Prudencio 7	18 ± 1	4.51	0.75
La Laguna	13 ± 1	3.66	0.72

If Equation 3.2 is used with magnesium and hardness as inputs to determine the calcium concentrations, the result is a negative concentration of calcium ions for all samples.

5.1.3 Validation through aqion

The samples were validated through the PHREEQC-based software aqion (aqion, 2020). Two validations were conducted for each sample, one with the original magnesium concentrations, and one with the calculated concentration shown in Table 5.2 (except for those with negative concentrations where only the first validation was conducted).

Alkalinity

As alkalinity was not supplied in the laboratory results, it had to be calculated using aqion. The calculated alkalinity as well as the bicarbonate concentrations are shown in Table 5.3. The table shows that a clear majority of the alkalinity of the samples are of bicarbonate type.

The second column of bicarbonate concentrations are within the range of concentrations shown in Table 3.4 ($\overline{x}$=77.1 mg/L, s=39.4), while the first column is somewhat higher. Both bicarbonate concentrations are significantly higher than the results from Pacacua (Table 3.5, $\overline{x}$=27.0 mg/L, s=14.2) and Peña Negra (Table 3.6, $\overline{x}$=29.2 mg/L, s=13.2). Note especially the high concentrations determined for Lomas de Guararí and Virgen (2) in Table 5.3.

Electrical conductivity

As the electrical conductivity was measured both at site and at the laboratory, as well as calculated through aqion, four different values were determined for each sample. The averages of the four values are 59 µS/cm (field data), 97 µS/cm (laboratory data), 257 µS/cm (calculated using laboratory concentrations), and 144 µS/cm (calculated using calculated magnesium concentrations).

Table 5.3: Table showing the determined alkalinity and bicarbonate concentrations using both laboratory determined and calculated magnesium concentrations.

	Alkalinity (mg/L HCO_3^-)		$[HCO_3^-]$ (mg/L)	
Sample site	Lab. $[Mg^{2+}]$	Calc. $[Mg^{2+}]$	Lab. $[Mg^{2+}]$	Calc. $[Mg^{2+}]$
Diogenes	180.06	89.30	177.08	88.46
Lomas de Guararí	227.68	–	216.93	–
Virgen (1)	165.15	110.35	160.01	107.57
Virgen (2)	220.20	–	211.88	–
Chamorro	140.81	81.91	136.33	79.84
Prudencio 5	137.69	78.78	134.74	77.51
Prudencio 7	158.48	90.73	154.57	88.91
La Laguna	117.44	70.53	115.37	69.55

The four values were compared with the cationic content of the samples as per Equation 3.6 (which states that $\frac{100 \cdot \Sigma\ cations}{EC_{25}} \approx 1$) and are shown in Table 5.4. The calculated conductivity show a high correlation with the cationic content (close to unity), which is expected from the relation between conductivity and ionic content which the software utilises. Using the laboratory determined magnesium concentrations results in an average ratio of 4.97 (for field EC) and 2.86 (for laboratory EC). The calculated magnesium concentrations results in an average ratio of 2.57 (field EC) and 1.54 (laboratory EC). The error is significantly lower when using the calculated magnesium concentrations.

The reason for the low electrical conductivity measured in the field could be the lack of available calibration equipment. The conductivity/pH-meter was calibrated once by personnel at UTN before the samples were collected.

Table 5.4: Ratios of cationic content and electrical conductivity using Equation 3.6. At the range of electrical conductivity the value should be close to unity.

Magnesium concentration	Laboratory			Calculated		
Electrical conductivity	Field	Lab.	aqion	Field	Lab.	aqion
Diogenes	2.89	3.20	1.07	1.50	1.66	1.03
Lomas	7.77	3.92	1.11	–	–	–
Virgen1	5.15	2.67	1.09	3.45	1.79	1.06
Virgen2	6.86	3.56	1.11	–	–	–
Chamorro	4.36	2.42	1.08	2.60	1.45	1.03
Prudencio7	4.91	2.74	1.03	3.05	1.70	1.04
Prudencio5	4.27	2.34	1.06	2.58	1.41	1.03
Laguna	3.58	2.02	1.05	2.22	1.25	1.02
Average	4.97	2.86	1.08	2.57	1.54	1.03

From these validations, the magnesium concentrations determined by the laboratory were discarded, and the calculated concentrations were used instead. The samples collected from Lomas de Guararí and Virgen (2) are not used in any of the following validations.

Charge balance error and anionic content

The charge balance errors of the samples (using the calculated magnesium concentrations) were calculated through aqion and are shown in Table 5.5. The charge balance error of the data from the laboratory is actually somewhat higher, as the software required the input of 1 mg/L of total carbonic content in the water. The actual anionic content determined by the laboratory consisted only of chloride (ranging from $8.46 \cdot 10^{-5}$ to $1.97 \cdot 10^{-4}$ meq/L) and nitrate (ranging from $<8 \cdot 10^{-4}$ to $9.52 \cdot 10^{-2}$ meq/L).

Table 5.5: Cationic and anionic concentrations as well as charge balance error for six of the collected samples.

	Total cations (meq/L)	Total anions (meq/L)	CBE (%)
Diogenes	1.54	0.16	81.5
Virgen1	1.81	0.083	91.3
Chamorro	1.42	0.16	80.0
Prudencio5	1.37	0.16	79.2
Prudencio7	1.58	0.18	80.1
Laguna	1.22	0.14	79.3
Average	1.49	0.15	81.9

The low concentrations of anions is noteworthy, especially the low concentrations of chloride and sulfate (which was below the lab's detectable level of 2 mg/L). The concentrations of chloride in Madrigal-Solís et al. (2017) is about a 1000 times higher ($\overline{x}$=5.4 mg/L, s=4.5) than what is determined for the samples of this study ($\overline{x}$=0.0056 mg/L, s=0.0015), while the sulfate concentrations were often below 2 mg/L. The concentrations of chloride and sulfate in Pacacua and Peña Negra are also significantly higher than what was determined in this study.

However, the average concentration of chloride in the Barva aquifer (from Madrigal-Solís et al. (2017)) is only 0.15 meq/L, and the average sulfate concentration only 0.045 meq/L. With the average concentration of bicarbonate being 1.26 meq/L, it is likely that the high charge balance error is due to the lack of bicarbonates in the analyses (See Table 3.4).

5.1.4 X-Y diagrams

Using the calculated magnesium concentrations above, the following X-Y diagrams were created. In Figure 5.2, the ratios between the two major cationic groups (Ca+Mg, and Na+K) are shown. The graphs show the spread of concentrations in the samples, and that the dominant cations in all the samples are calcium and magnesium.

In Figure 5.3, the ratios of sodium to chloride and sodium to calcium are shown. That only trace amounts of chloride is found in the samples is clear from the graph, as the 1:1 line in the graph is indistinguishable from the horizontal axis at this scale. Calcium is shown to be in a clear abundance over sodium, with concentrations around 0.6 meq/L, and sodium in the range of 0.2 to 0.5 meq/L.

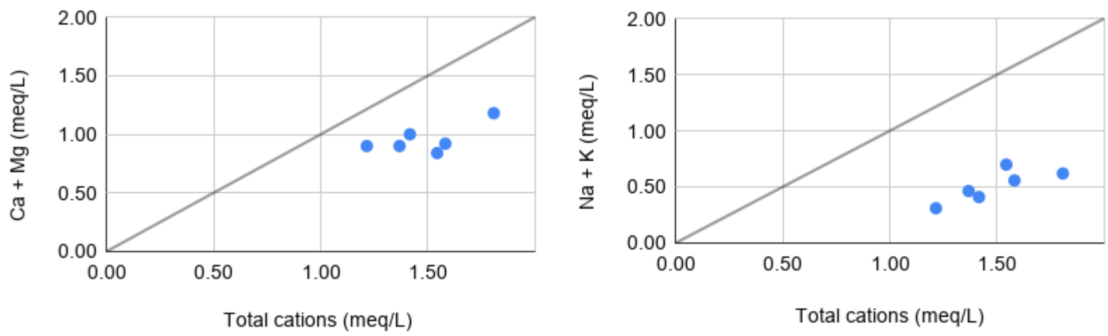

Figure 5.2: X-Y diagrams showing Ca + Mg (left) and Na + K (right) to total cationic concentration of the samples. The solid lines denote 1:1 ratio.

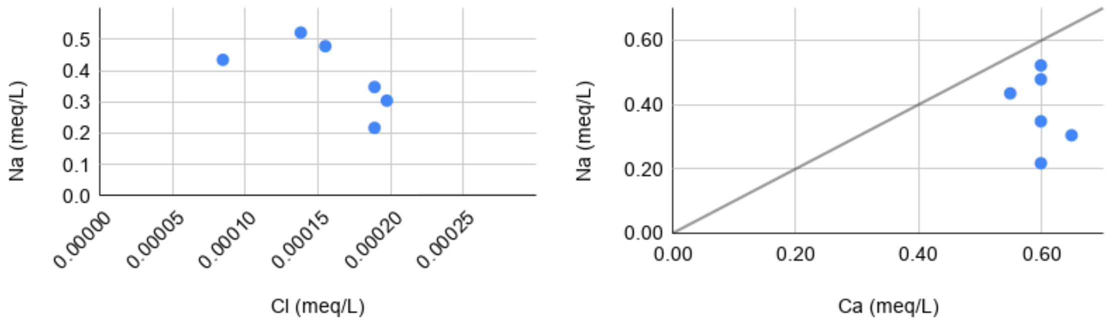

Figure 5.3: X-Y diagrams showing sodium to chloride (left) and sodium to calcium (right). The solid lines denote 1:1 ratio.

In Figure 5.4, the ratio of calcium to magnesium is shown, with calcium being dominant in all samples except one. The sample collected at La Virgen (1) showed concentrations of 0.60 and 0.58 meq/L of calcium and magnesium respectively.

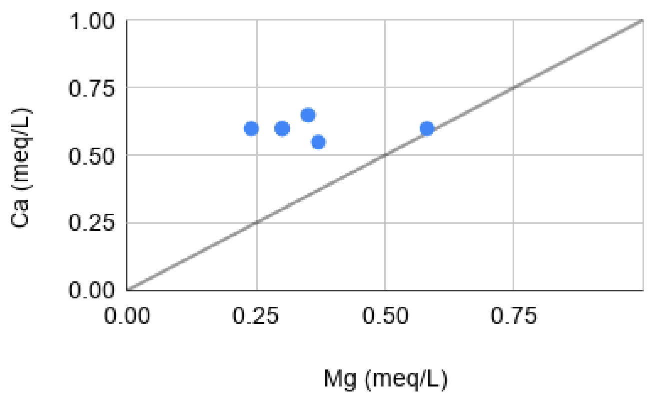

Figure 5.4: X-Y diagrams showing calcium to magnesium. The solid lines denote 1:1 ratio.

In Figure 5.5, the differences between field and laboratory measurements of pH and electrical conductivity are shown. Only in the sample collected at Diogenes is there a difference in pH (8.52 in field and 7.35 in lab). This could be partially explained by the long transport time for this sample, as the temperature when collected was 17.3°C while at the laboratory it was reported as 29°C. Another part of the explanation could be the exposure to atmospheric CO_2. The electrical conductivity

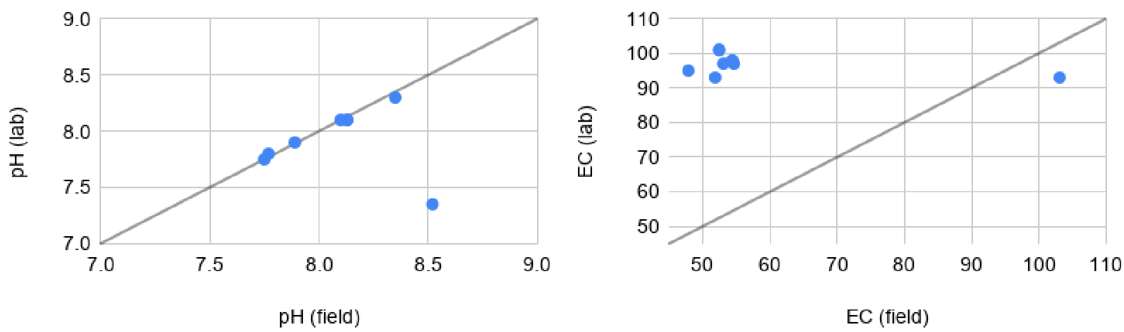

Figure 5.5: X-Y diagrams showing pH (left) and electrical conductivity (right) as measured in field and in the laboratory. The solid lines denote 1:1 ratio.

measured in the laboratory is generally twice as large as the conductivity measured in the field. The only discrepancy in this case is again the sample collected at Diogenes, which showed a higher value in the field (103 µS/cm) than in the laboratory (93 µS/cm).

5.1.5 Stiff diagrams

Stiff diagrams showing the chemical composition from six of the samples are shown at their respective locations in Figure 5.6. Due to the scale of the map, the concentrations of the diagrams is not shown. The Stiff diagrams are therefore also presented side by side in Figure 5.7. The scale of the plots is the same as in Figures 3.9 and 3.14 (max values of 3 meq/L on each axis).

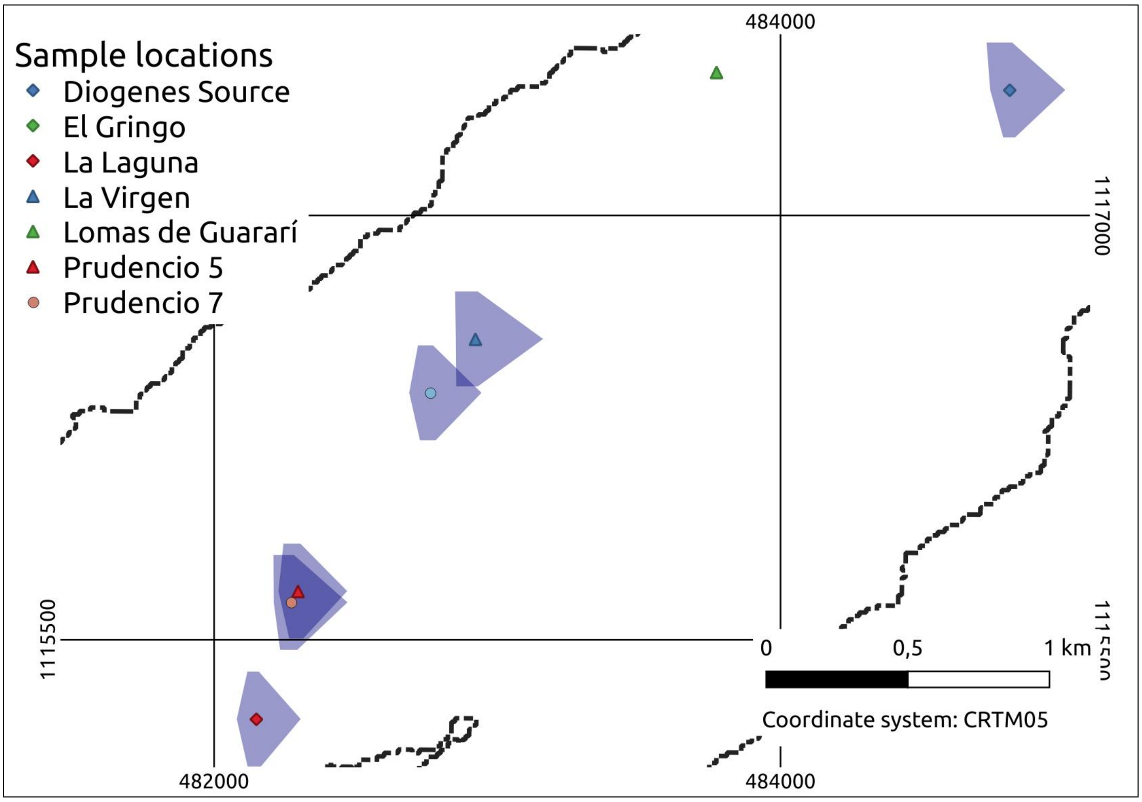

Figure 5.6: Map showing stiff diagrams at sample locations.

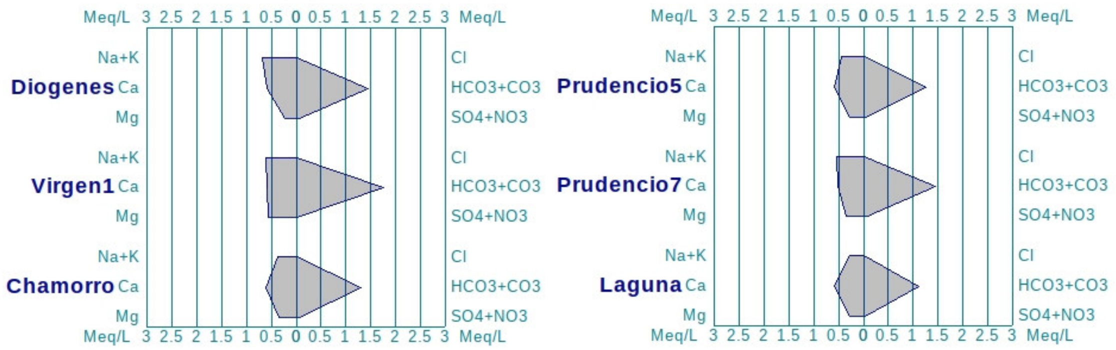

Figure 5.7: Stiff plots generated from the collected samples.

5.1.6 Piper diagrams

Two piper diagrams are shown. One in Figure 5.8 showing the same constituents as the Piper diagrams shown in Section 3.2.4 and 3.5.1 and another one in Figure 5.9 that includes NO_3^- among the anions. The reason for this is the high dominance of bicarbonates in the water, that compared to sulfate and chlorine constitutes approximately 100 % of the anionic content of the samples.

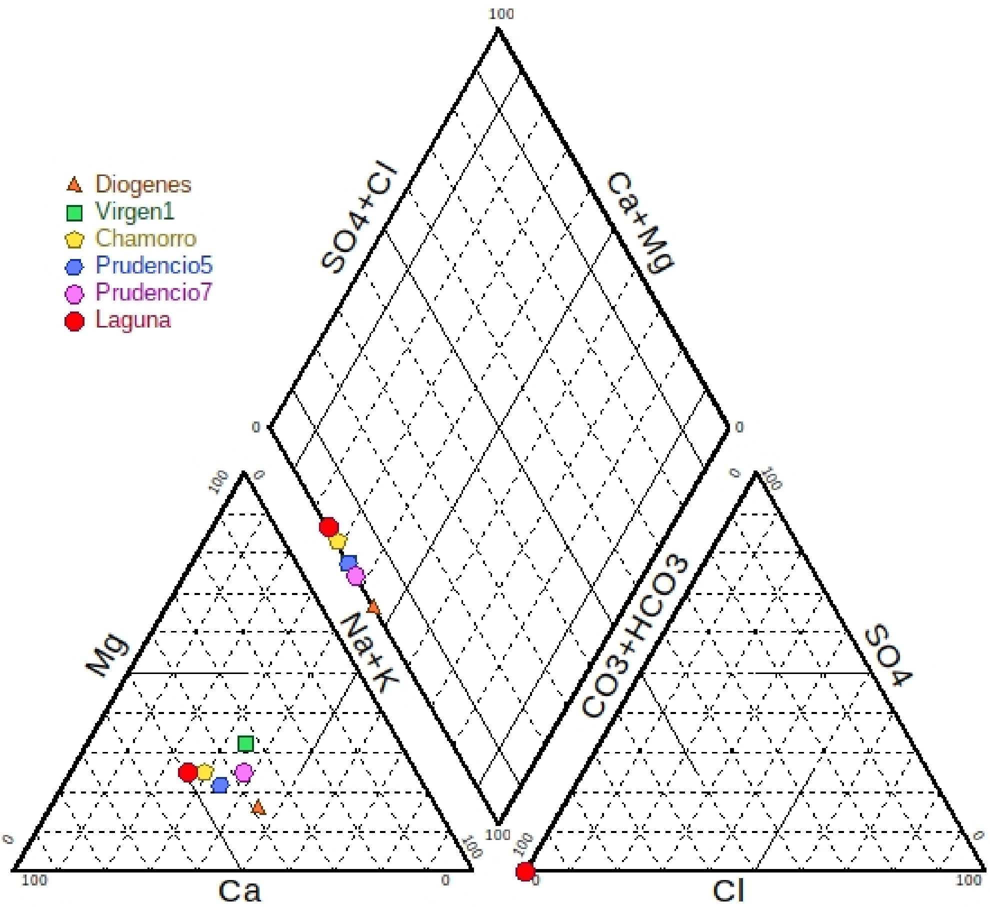

Figure 5.8: Piper diagram showing the collected samples.

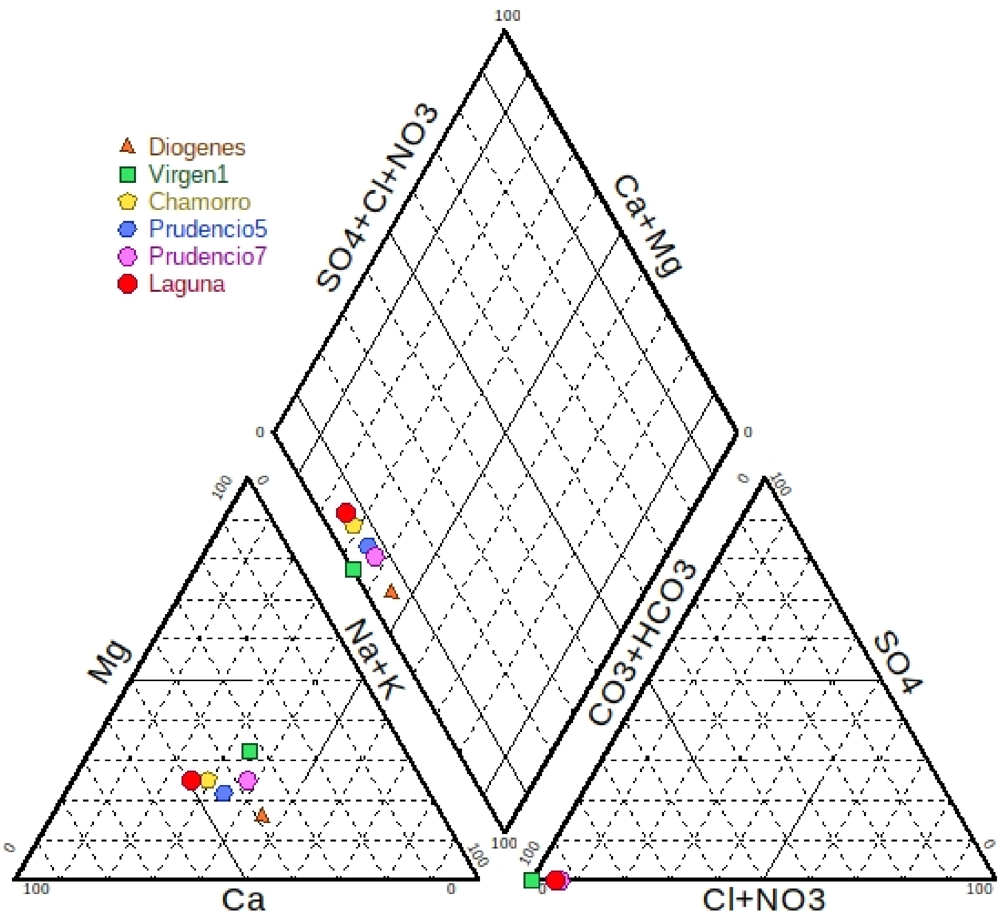

Figure 5.9: Piper diagram of the collected samples, including nitrate concentrations.

5.1.7 Drinking levels

As discussed in Section 3.3, the drinking water regulation of Costa Rica consists of four levels of control. From the laboratory results presented by laboratory Gaia, it is possible to determine the water quality according to levels N1 and N2.

For N1, it is only the sample collected from Diogenes that exceeds one of the maximum admissible values, namely the presence of coliform bacteria (E. Coli). The sample showed 240 MPN/100mL of E. Coli. The results from the biological analyses are shown in Appendix A. Aerobic heterotrophs are found in small numbers (2–9 CFU/mL) at the springs Chamorro, Prudencio and La Laguna, and in higher numbers at Diogenes ($>$ 250 CFU/mL). The samples collected at Lomas de Guararí and La Virgen showed no aerobic heterotrophs. All samples except Diogenes showed less than 1.8 MPN/100 mL of coliform bacteria.

For N2, the results are presented in Table 5.6. The table shows the lowest, highest and average concentration of the ions from the eight samples. As the magnesium concentrations from the laboratory are higher than the ones calculated in Section 5.1.2, the laboratory determined concentrations are shown for all species. Only the iron content exceeds the maximum admissible value, and only in the sample collected at Prudencio 7, where the iron content was 2.9 mg/L. Without this sample, the highest iron content is 0.23 mg/L (in La Virgen (1)) and the average 0.18 mg/L, well below the maximum admissible value of 0.3 mg/L.

Table 5.6: Chemical composition of samples and guideline values of ion concentrations (La Gaceta, 2005).

Parameter	Min	Max	Average	Recommended value	Maximum admissible value
Total hardness	42	59	50.1	400	500
Chloride	0.003	0.007	0.0053	25	250
Calcium	11	26	15.5	100	–
Nitrate	3.7	5.9	4.8	25	50
Iron	0.14	2.9	0.52	–	0.3
Sulfate	–	–	<2	25	250
Magnesium	13	21	17.8	30	50
Potassium	3.6	6.9	4.99	–	10
Sodium	5	13	9.75	25	200
Fluoride	–	–	<0.03	–	0.7 – 1.5
Manganese	–	–	<0.02	0.1	0.5
Aluminum	–	–	<0.02	0.2	–
Zinc	–	–	<0.02	–	3
Copper	–	–	<0.01	1.0	2.0
Lead	–	–	<0.0005	–	0.01

5.2 Vulnerability assessment

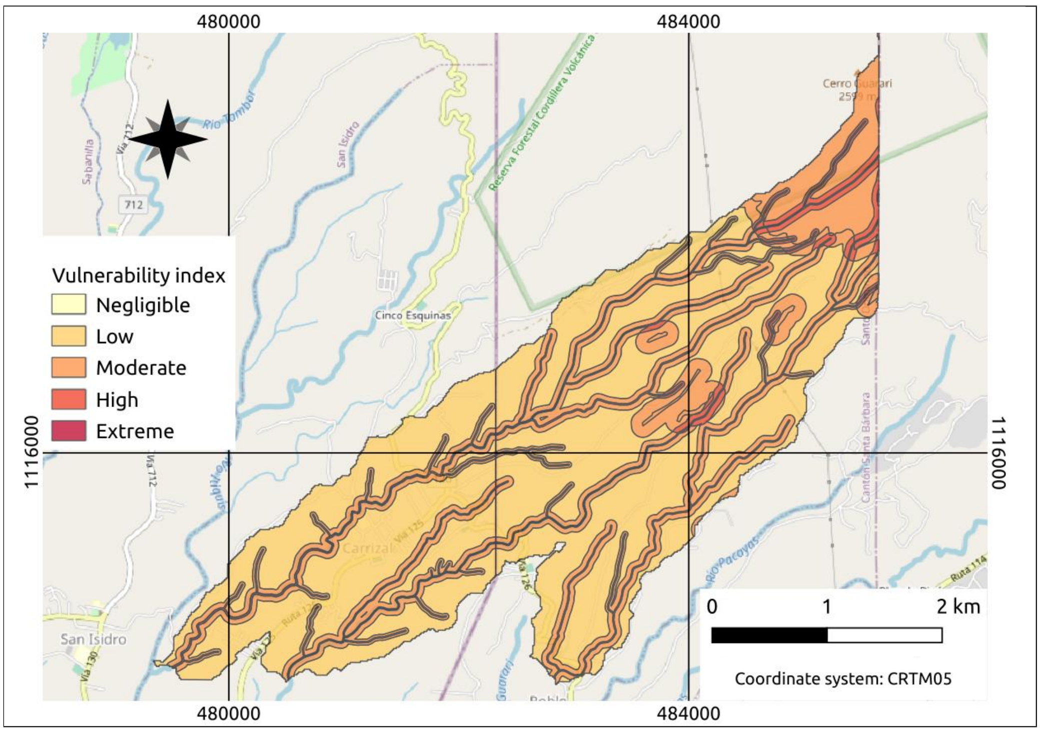

Figure 5.10: Vulnerability assessment map of the chosen study area.

The vulnerability in the study area ranges between low and high, as can be seen in Figure 5.10. All river beds are estimated to have a high vulnerability. All river gorges in the Porrosatí category are estimated to have a moderate vulnerability and the river gorges in Bambino and Bambino buffers are estimated to have a high vulnerability. In the northeast, where Bambino is the uppermost unit, the index is estimated to be moderate. In the rest of the study area (Porrosatí) it is assumed to be low, except for the Bambino buffers that are moderate.

The aquifer pollution vulnerability value and the corresponding vulnerability assessment is presented in Appendix C.

Chapter 6

Discussion

In the following chapter, a discussion on the results and findings is made. The chapter includes the sections chemical results, including the subsections validity of laboratory analyses, hydrochemical evaluation and drinking levels; vulnerability assessment and sustainable development.

6.1 Chemical results

6.1.1 Validity of laboratory analyses

The results from the laboratory analyses showed a number of inconsistencies, the two major ones being the lack of relationship between cationic content and the hardness values of the samples, and the differences between the duplicate samples collected from La Virgen.

As shown in Section 5.1.2, the hardness values determined through titration at the laboratory do not match the cationic concentrations. The cationic concentrations are much higher than the hardness values for all samples (Figure 5.1). One explanation for this is the lack of filtering equipment when the samples were collected. If there were solids, such as e.g. dolomite, present in the samples when the calcium and magnesium concentrations were determined, it is possible that the compounds were dissolved during the analysis procedure, thus resulting in higher concentrations.

Through the comparison with previous studies, it is reasonable that it is only the magnesium concentrations that are dubious, as all other concentrations are within the ranges of the previous studies. However, the duplicate samples show a major difference in the calcium concentration (12 ± 1 and 26 ± 1 mg/L respectively), while the magnesium concentrations are similar (18 ± 1 and 20 ± 1 mg/L respectively). If traces of particles in the samples is the cause of the high concentrations of magnesium, it seems unlikely that the duplicate samples would be so similar.

The high charge balance errors of the samples are clear indicators that the anionic content of the samples has not been properly determined. It is unfortunate that the laboratory did not include an alkalinity determination in its analyses, as bicarbonate is likely to be the major anion of the samples. Of the other anions in the samples, the concentrations of chloride and sulfate are also dubious. All these discrepancies make it hard to draw conclusions from the chemical compositions of the samples.

Communication with the laboratory that conducted the analyses were severely hampered by the COVID-19 pandemic as activities in Costa Rica were closed down. It is therefore not clear why the laboratory did not include alkalinity in the results. However, as the physicochemical analyses conducted match the N2 control level for drinking water quality, it is likely that there was a mistake in communication when the analyses were ordered. Instead of a thorough physicochemical analysis of the chemical species of the samples, a thorough analysis for drinking water seems to have been ordered.

6.1.2 Hydrochemical evaluation

Due to the many inconsistencies shown in the laboratory data, it is not reasonable to use only the data from this thesis to draw conclusions of the geological conditions in the Bambino aquifer. Instead, the data can be compared with the previous studies shown in Section 3.5.1, and mainly with the study conducted in the southern section of the Barva aquifer by Madrigal-Solís et al. (2017).

The main difference between the waters collected from the Barva aquifer and the waters collected from Pacacua and Peña Negra is in the dominance of bicarbonate in the samples. At the Barva Aquifer, bicarbonates constitute 70–90 % of the anionic content (Figure 3.8), while at Pacacua and Peña Negra bicarbonates are mainly in the range of 50–70 %, showing a clear influence of sulphate and chloride (Figure 3.13). This is most likely a result of the different lithologies of the sites: volcanic (Barva) and sandstone with volcanic influences and some limestone stratas (Pacacua and Peña Negra).

By comparing the cations in the Stiff patterns in Figure 5.7 with Figure 3.9, the patterns are similar to the ones collected from a medium altitude (1000 − 1400 masl), with cationic concentrations of around 0.5 meq/L. This would indicate that the water paths in Los Bambinos are longer than the ones in Barva, as the samples in this thesis are all collected at a high altitude (above 1400 masl).

Similarly, the Piper diagrams (Figure 5.8 and 5.9), show bicarbonate-mixed waters, similar to what was found in the southern parts of the Barva aquifer (Figure 3.8).

These results do not indicate that the hydrogeological conditions of the Bambinos member of the Barva aquifer differ drastically from the southern parts of the Barva aquifer.

6.1.3 Drinking levels

The results of this thesis showed that the water collected was generally within the drinking water quality regulations of Costa Rica, with two exceptions: Diogenes contained E. Coli, and Prudencio 7 had an iron concentration of almost 10 times the maximum admissible value (2.9 mg/L, with the maximum admissible value being 0.3 mg/L).

As described in Section 4.1, the water for the biological analysis at Diogenes was collected in the wrong type of container that was only 50 mL instead of the 100 mL, which the laboratory required. The container was of course sterilized and can not account for the presence of fecal coliform bacteria, but it could impact the determined concentration of bacteria. It has not been possible to determine any clear reason for the presence of the E. Coli in the sample. The closest construction to the spring site is over 200 meters away, and the forest surrounding the site would seem too dense for accidental human contamination. However, Diogenes is the only spring that does not have a protective construction surrounding the spring, and the water ran across the soil wall for a few meters before collection. Finally, the presence of ten or so dogs at the time of sampling can not be disregarded as a possible contamination source.

A new biological analysis is recommended for Diogenes, with water sampled from the collecting pipes instead of the soil wall, and using the correct containers.

The high iron concentration at Prudencio 7 can most likely not be given a geological explanation. As the iron content in Prudencio 5, less than 100 meters upstream from Prudencio 7, was only 0.14 mg/L (20 times less than that at Prudencio 7), the iron is most likely not present in the groundwater. It is more likely that the high iron content is the result of either iron leaching at the man made construction that collects the spring water, or from faulty laboratory procedures. Either way, it is recommended that the construction at Prudencio 7 is inspected for any possible iron source, and a new chemical analysis be conducted.

6.2 Vulnerability assessment

The GOD vulnerability assessment showed results of low vulnerability in the area where Porrosatí is the uppermost unit and where there is no influences of river beds or river gorges. Porrosatí is considered an aquitard with low permeability and a geology consisting of coarse, volcanic sand and clay tuffs, which supports this result.

In the area where Bambino is the uppermost layer, the vulnerability is moderate. Bambinos characteristics with brecciated lava forming perched aquifers would generally imply a good permeability and this supports a higher vulnerability compared with the area where there is an overlaying layer of Porrosatí. The river gorges in Bambino and in Bambino buffers have a high vulnerability. The depth to the groundwater is assumed to be fairly low (5-20 m). This combined with the good permeability of the unit and that the aquifer is unconfined supports the result.

The vulnerability in all river beds are high as a result of the assumption that the groundwater is very close to or at the bottom of the river beds. This results in an interaction between river water and groundwater, with a possibility of the river water infiltrating to and affecting the groundwater. The river beds can consequently act as recharge areas for the groundwater. Furthermore, rivers can transport contaminants to sections of the river where infiltration to the groundwater takes place. The assumption furthermore affects both the G and D value directly and it is therefore the same in all river beds. The overlaying strata is not the same in all river beds, but the resulting O value is the same.

The method on deciding the width of the buffers is fast but not exact. Some of the small rivers were hard to see on the ortophoto. It could be explained with a presence of water in the rain season giving support for the rivers in the GIS data. The ortophoto can have been taken when it was dry season, and therefore the creeks are not visible. Other inconsistencies can be that there actually are no creeks in some areas. The procedure of choosing width of the buffers could have been done more carefully by having different widths in different rivers or at different places along the rivers. More research could have been done on the rivers to try to find information about the widths of the rivers and river gorges. Different options on how to include the rivers were regarded. The option that was chosen is considered reasonable in the context.

In Programa de Investigación y Desarrollo Urbano Sostenible (ProDUS) Universidad de Costa Rica (2010), the buffers were chosen as 100 m everywhere except in the area where the vulnerability was generally considered to be lower. Neither in Centro de Investigaciones en Ciencias Geológicas (2015b) nor in Centro de Investigaciones en Ciencias Geológicas (2015a) were rivers included in a systematic way.

Vulnerability assessments, including the GOD method, have advantages due to the possibility to compare results. Taking decisions, such as how to include rivers in the assessment, however makes it clear that it is in fact hard to know in what extent a comparison is fair. In the four different GOD assessments, the decision on whether to include rivers, and if so how, were most probably made differently. It is important to consider this when comparing results. Even if the same method was used, different steps along the way can have been made differently and the result can therefore differ.

The previously conducted GOD assessments in the area supports the results found in this study: the vulnerability is overall low. In the river beds and river gorges, which were explicitly included in Nevermann (2005), the vulnerability was higher. In Centro de Investigaciones en Ciencias Geológicas (2015b), faults were included and in these areas the vulnerability was higher.

Due to the fact that the DRASTIC study has not been reviewed, in-depth discussions on the result is not made. It was however clear that this study gave a more detailed impression than all of the GOD assessments and that the reason for the degree of detail was the inclusion of the factor of the topography. For the other six parameters, there were no variation in the area. Looking at the vulnerability map, it was also seen that the rivers in the area were not visible and were most likely not included in the assessment.

As said, the degree of detail was generally bigger in the DRASTIC study. It did however not show any difference in vulnerability in the rivers and river gorges, which the GOD assessments conducted by the authors and Nevermann (2005) did. The DRASTIC method does not have a fixed classification, which makes it less easily comparable with other studies from the same method if compared to GOD assessments. Two DRASTIC studies can have different ranges for their classification which could furthermore yield completely different results. The GOD method has an advantage in this; there is set ranges for every parameter and for the final vulnerability classification.

As has been said in previous publications, there are limitations with vulnerability assessments. It should only be used as a first, general indication and the result should not be regarded as the sole truth. This applies to all vulnerability assessment methods.

It would be of great interest to include more parameters and extend the assessment to a risk assessment, which includes hazards that are human induced. Parameters that could be included in such assessment are, for example, land use and the use of chemicals. This would give a better estimation of how high the risk is for an aquifer to be contaminated. The time and resources were not sufficient to include this in the thesis.

6.3 Sustainable Development

Even though Costa Rica is generally known for having a high drinking water standard, the water is only potable in approximately 60 percent of the country's area.

The economical, social and cultural development that has taken place had probably not been possible without the abundance of relatively good water. However, the development has not been sustainable which has led to conflicts. With an increasing population, the demand of water will increase and the importance of a sustainable development with it.

The sustainability of the crucial Community-based drinking water organizations (CBDWOs) in the rural communities of the country have shown to differ largely. The voluntary certification program *Water Quality Seal* is an initiative that could promote a higher water quality. The problem with voluntary initiatives is that the engagement and socio-economic conditions and consequently, the result, can vary largely in different CBDWOs. A voluntary program will most likely be adopted by communities that already have better overall living conditions. There is a great risk that the inequality in the communities therefore continues to be present and it could even increase. The Water Quality Seal and similar projects can result in an increase in the number of persons having access to clean water. It is however not likely a tool that is sufficient to ensure clean drinking water to everyone, which is stated by UN as a goal to be reached by 2030.

The new law proposal that could come into force after the next debate would favour a continuing, more sustainable development. This law change would include groundwater as a fundamental resource that requires a sustainable consumption, and resolves the issue of groundwater not being included in the country's water law.

There remains the more complex issue of no one sole institution being responsible for the country's water resources. As there are many different organisations and institutions involved today, it can be difficult to change the infrastructure management. It will be interesting to see if the new law is going to have any impact on this matter.

The knowledge produced through this thesis on the vulnerability and chemical composition of the Bambino aquifer will hopefully be useful for a continued sustainable withdrawal of groundwater by the ASADA of Carrizal.

Chapter 7

Conclusions

The hydrochemical investigation of the groundwater showed that six of the eight collected samples were determined to be of bicarbonate-mixed type. The two other samples were deemed too inconsistent to classify. As the laboratory analyses conducted failed a number of validation procedures, their use in determining the aquifer conditions are limited. However, as they do not contradict the other research conducted at the Barva aquifer, it is reasonable to assume uniform hydrochemical conditions throughout the Bambinos member of the Barva aquifer.

The evaluation of the groundwater vulnerability through the GOD system conducted in the study area showed that the vulnerability is generally low. In the areas with a more permeable uppermost layer, the vulnerability was assessed as moderate. All river beds were assessed as having a high vulnerability, while the river gorges were assessed as having moderate or high vulnerability, depending on the uppermost layer. These results show the importance of protecting the rivers and river gorges in the area from contamination.

7.1 Recommendations

- In order to conduct a more rigorous investigation of the hydrogeological conditions, it is recommended to collect several samples from each site, preferably over a longer time period, and use more rigorous sampling protocols. The collected water needs to be filtered, and it has to be ensured that the laboratory follows established standards for water chemical analyses.

- For the vulnerability assessment of the area to be more useful, it is recommended to extend the assessment from vulnerability to a risk assessment, including human induced hazards. It is suggested to include the land use in the area and the use of chemicals, their quantity and toxicity.

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Appendix A

Laboratory results

Table A.1: Chemical data delivered from the laboratory. All units mg/L unless otherwise stated.

	Cl	Ca	NO3	Fe
Diogenes Source	0.0049 ± 0.0003	12 ± 1	5 ± 1	0.15 ± 0.01
Lomas de Guarari	0.0037 ± 0.0005	26 ± 1	<0.05	0.17 ± 0.01
La Virgen (1)	0.0055 ± 0.0006	12 ± 1	<0.05	0.23 ± 0.01
La Virgen (2)	0.0052 ± 0.0004	26 ± 1	<0.05	0.19 ± 0.01
Chamorro	0.0070 ± 0.0003	13 ± 1	4.6 ± 0.9	0.19 ± 0.01
Prudencio 5	0.0067 ± 0.0004	12 ± 1	4.8 ± 0.9	0.14 ± 0.01
Prudencio 7	0.003 ± 0.0003	11 ± 1	5.9 ± 0.1	2.9 ± 0.1
La Laguna	0.0067 ± 0.0005	12 ± 2	3.7 ± 0.9	0.16 ± 0.01

Table A.2: Chemical data delivered from the laboratory. All units mg/L unless otherwise stated.

	Mg	K	Na	SO4
Diogenes Source	21 ± 2	6.9 ± 0.2	12 ± 1	<2
Lomas de Guarari	21 ± 2	5.2 ± 0.2	13 ± 1	<2
La Virgen (1)	18 ± 1	5.5 ± 0.2	11 ± 1	<2
La Virgen (2)	20 ± 1	5.3 ± 0.2	12 ± 1	<2
Chamorro	16 ± 1	4.1 ± 0.2	7 ± 2	<2
Prudencio 5	15 ± 1	4.5 ± 0.2	8 ± 2	<2
Prudencio 7	18 ± 1	4.8 ± 0.2	10 ± 1	<2
La Laguna	13 ± 1	3.6 ± 0.2	5 ± 1	<2

Table A.3: Chemical data delivered from the laboratory. All units mg/L unless otherwise stated.

	F	Mn	Al	Zn	Cu	Pb
Diogenes Source	<0.03	<0.02	<0.02	<0.02	<0.01	<0.0005
Lomas de Guarari	<0.03	<0.02	<0.02	<0.02	<0.01	<0.0005
La Virgen (1)	<0.03	<0.02	<0.02	<0.02	<0.01	<0.0005
La Virgen (2)	<0.03	<0.02	<0.02	<0.02	<0.01	<0.0005
Chamorro	<0.03	<0.02	<0.02	<0.02	<0.01	<0.0005
Prudencio 5	<0.03	<0.02	<0.02	<0.02	<0.01	<0.0005
Prudencio 7	<0.03	<0.02	<0.02	<0.02	<0.01	<0.0005
La Laguna	<0.03	<0.02	<0.02	<0.02	<0.01	<0.0005

Table A.4: Chemical data delivered from the laboratory. All units mg/L unless otherwise stated.

	pH (no unit)	Temperature (°C)	Odor (no unit)	Turbidity (UNT)
Diogenes Source	7.35	29	Aceptable	0.55
Lomas de Guararí	8.2	16	Aceptable	0.2
La Virgen (1)	8.1	20	Aceptable	0.1
La Virgen (2)	8.1	20	Aceptable	0.1
Chamorro	8.1	22	Aceptable	0.1
Prudencio 5	7.9	19	Aceptable	0.1
Prudencio 7	7.75	19	Aceptable	0.1
La Laguna	7.8	19	Aceptable	0.1

Table A.5: Chemical data delivered from the laboratory. All units mg/L unless otherwise stated.

	Color (U Pt-Co)	Free residual chlorine	Combined residual Chlorine	Total hardness
Diogenes Source	<2	<0.01	<0.01	42
Lomas de Guararí	4.5	<0.01	<0.01	59
La Virgen (1)	<2	<0.01	<0.01	59
La Virgen (2)	<2	<0.01	<0.01	55
Chamorro	<2	<0.01	<0.01	50
Prudencio 5	<2	<0.01	<0.01	45
Prudencio 7	<2	<0.01	<0.01	46
La Laguna	<2	<0.01	<0.01	45

Table A.6: Biological results delivered from the laboratory

	Aerobic heterotrophs (CFU/mL)	Fecal coliform (MPN/100 mL)	Escherichia Coli (MPN/100 mL)
Diogenes Source	≥250	240	240
Lomas de Guararí	0	<1.8	<1.8
La Virgen (1)	0	<1.8	<1.8
La Virgen (2)	0	<1.8	<1.8
Chamorro	9	<1.8	<1.8
Prudencio 5	6	<1.8	<1.8
Prudencio 7	3	<1.8	<1.8
La Laguna	2	<1.8	<1.8

Appendix B

Field data

Table B.1: Location data of the seven sample sites. Altitudes with asterisk are determined from digital elevation data in QGIS.

	X	Y	Accuracy (m)	Altitude (masl)
Diogenes	-84.1386	10.10575	3	1986
Prudencio 7	-84.16174	10.08936	10	1497
Prudencio 5	-84.16153	10.08972	2	1508
La Laguna	-84.16287	10.08563	–	1460*
Chamorro	-84.15726	10.09606	–	1580*
Lomas de Guararí	-84°08.883	10°06.379	30	1840*
La Virgen de Lourdes	-84°09.349	10°05.867	7	1647

Table B.2: Physicochemical data collected from the seven sample sites.

	T (°C)	Eh (mV)	pH	EC (µS/cm)
Diogenes	17.3	-30.3	8.52	103.1
Prudencio 7	18.8	13.1	7.75	51.87
Prudencio 5	18.6	0.5	7.89	53.09
La Laguna	19.4	12.4	7.77	54.65
Chamorro	17.8	-6.5	8.1	54.4
Lomas de Guararí	16.5	-20.1	8.35	47.89
La Virgen de Lourdes	19.9	-7.9	8.13	52.45

Appendix C

GOD tables

Table C.1: GOD evaluation table for river beds in the Bambino formation.

Bambino: river beds	
Groundwater confinement	Unconfined
Value	1.00
Overlying strata	Brecciated lava
Value	0.70
Depth to groundwater level	< 5 m
Value	0.90
Aquifer pollution vulnerability value	0.63
Aquifer pollution vulnerability assessment	High

Table C.2: GOD evaluation table for river gorges in the Bambino formation.

Bambino: river gorges	
Groundwater confinement	Unconfined
Value	1,00
Overlying strata	Brecciated lava
Value	0,70
Depth to groundwater level	5–20 m
Value	0,80
Aquifer pollution vulnerability value	0,56
Aquifer pollution vulnerability assessment	High

Table C.3: GOD evaluation table the Bambino formation

Bambino	
Groundwater confinement	Unconfined
Value	1,00
Overlying strata	Brecciated lava
Value	0,70
Depth to groundwater level	20–50 m
Value	0,70
Aquifer pollution vulnerability value	0,49
Aquifer pollution vulnerability assessment	Moderate

Table C.4: GOD evaluation table for river beds in the Porrosatí formation

Porrosatí: river beds	
Groundwater confinement	Unconfined (thin covering layer)
Value	0,90
Overlying strata	Tuffs
Value	0,70
Depth to groundwater level	< 5 m
Value	0,90
Aquifer pollution vulnerability value	0,57
Aquifer pollution vulnerability assessment	High

Table C.5: GOD evaluation table for river gorges in the Porrosatí formation

Porrosatí: river gorges	
Groundwater confinement	Unconfined (thin covering layer)
Value	0,90
Overlying strata	Tuffs
Value	0,65
Depth to groundwater level	5–20 m
Value	0,80
Aquifer pollution vulnerability value	0,47
Aquifer pollution vulnerability assessment	Moderate

Table C.6: GOD evaluation table for the Porrosatí formation

Porrosatí	
Groundwater confinement	Unconfined (covered)
Value	0,60
Overlying strata	Clayey tuffs
Value	0,55
Depth to groundwater level	20–50 m
Value	0,70
Aquifer pollution vulnerability value	0,23
Aquifer pollution vulnerability assessment	Low

Table C.7: GOD evaluation table for river beds in the Bambino buffers

Bambino buffer: river beds	
Groundwater confinement	Unconfined
Value	1,00
Overlying strata	Brecciated lava
Value	0,70
Depth to groundwater level	$<$ 5 m
Value	0,90
Aquifer pollution vulnerability value	0,63
Aquifer pollution vulnerability assessment	High

Table C.8: GOD evaluation table for river gorges in the Bambino buffers

Bambino buffer: river gorges	
Groundwater confinement	Unconfined
Value	1,00
Overlying strata	Brecciated lava
Value	0,7
Depth to groundwater level	5–20 m
Value	0,8
Aquifer pollution vulnerability value	0,56
Aquifer pollution vulnerability assessment	High

Table C.9: GOD evaluation table for the Bambino buffers

Bambino buffer	
Groundwater confinement	Unconfined (semi-covered)
Value	0,80
Overlying strata	Clayey tuffs
Value	0,55
Depth to groundwater level	20–50 m
Value	0,70
Aquifer pollution vulnerability value	0,31
Aquifer pollution vulnerability assessment	Moderate