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The Paraná Aquifer in the border region of the departments Buenos Aires, Entre Ríos and Santa Fe (Argentina)

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Contents

Abstract

Water is an essential resource for human kind, especially as indispensable nutrient. Due to climate change and pollution the resource is an endangered one. New ways and sources need to be explored to secure the water supply. Therefore the suitability of the "Paraná Aquifer" for drinking water supply is verified. Eight chemical parameters are compared to the World Health Organization standards. In additon, the elevation of the "Paraná Formation" is modeled to test the availability of the water from the "Paraná Aquifer" by three different interpolation method. Because of the importance of groundwater management, the groundwater flow direction and the location of the recharge zone is also modeled by three different approaches and two different interpolation method. Comparing the chemical properties of the groundwater from the "Paraná Aquifer" to the World Health Organization standards, the groundwater shows a poor quality and therefore it is not suitable for drinking water supply purposes. The interpolated elevation of the "Paraná Fromation" is between 60 ma.s.l. and −120 ma.s.l.. Because the elevation and the depth are in the same range, the groundwater is considered to be mineable. The interpolated groundwater direction can be divided in five different sections, however, a predominant southward groundwater flow direction can be detected. The groundwater recharge zone is located in the department of "Entre Ríos" at the same location where the outcrops of the "Paraná Fromation"are also located. The final assessment of the suitability of the Parana Aquifer for drinking water supply can not be made. Because important data such as the reload amount is missing.

Zusammenfassung:

Wasser ist eine essentielle Ressource für die Menschenheit, insbesondere als unverzichtbarer Nährstoff. Aufgrund des Klimawandels und der Umweltverschmutzung ist die Ressource gefährdet. Neue Wege und Quellen müssen gefunden werden, um die Wasserversorgung zu sichern. Daher wird die Eignung des "Paraná Aquifers" für die Trinkwasserversorgung überprüft. Acht chemische Parameter werden mit den Standards der Weltgesundheitsorganisation verglichen. Darüber hinaus wird die Höhe über dem Meeresspiegel der "Paraná Formation" durch drei verschiedene Interpolationsmethoden modelliert, so dass die Verfügbarkeit des Wassers aus dem "Paraná Aquifer" verifiziert werden kann. Aufgrund der Bedeutung für die Grundwasserbewirtschaftung werden auch die Grundwasserströmungsrichtung und der Ort der Grundwasserneubildung modelliert, dies wird durch drei verschiedene Ansätze und zwei unterschiedliche Interpolationsmethoden gemacht. Werden die chemischen Eigenschaften des Grundwassers mit denen der Weltgesundheitsorganisation verglichen, so weist das Grundwasser eine schlechte und für die Trinkwasserversorgung ungeeignete Wasserqualität auf. Die interpolierte Höhe über dem Meeresspiegel der "Paraná Fromation" liegt zwischen 60 mü.NHN und −120 mü.NHN. Da die Elevation und die Tiefe im selben Bereich liegen, wird das Grundwasser als abbaubar angesehen. Die interpolierte Grundwasserrichtung kann in fünf verschiedene Abschnitte unterteilt werden, wobei eine vorherrschende Grundwasserströmungsrichtung nach Süden ausgemacht werden kann. Die Zone der Grundwasseranreicherung befindet sich im Regierungsbezirk "Entre Ríos", wo sich auch die Aufschlüsse der "Paraná Formation" befinden. Eine abschließende Beurteilung der Eignung des "Paraná Aquifer" für die Trinkwasserversorgung ist nicht möglich, weil wichtige Daten, wie zum Beispiel der Nachladebetrag, fehlen.

Resumen:
El agua es un recurso esencial para la humanidad, especialmente como nutriente indispensable. Debido al cambio climático y la contaminación, este recurso está en peligro. Se deben encontrar nuevas formas y fuentes para asegurar el suministro de agua. Por lo tanto en este trabajo, se verifica la idoneidad del "Paraná Acuífero" para el suministro de agua potable. Se comparan ocho parámetros químicos con los estándares de la Organización Mundial de la Salud. Además, la elevación de la "Paraná Formacíon" se modela para probar la disponibilidad del agua del "Paraná Aquifer " mediante tres métodos diferentes de interpolación. Debido a la importancia de la gestión del agua subterránea, también se modela la dirección del flujo del agua subterránea y la ubicación de la zona de recarga mediante tres enfoques diferentes y dos métodos de interpolación diferentes. Comparando las propiedades químicas de las aguas subterráneas del "Paraná Acuífero" con las normas de la Organización Mundial de la Salud, el agua subterránea muestra una mala calidad y y no es adecuada para el suministro de agua potable. La elevación interpolada de "Paraná Fromation" está entre 60 msnm Y −120 msnm. Debido a que la elevación y la profundidad están en el mismo rango, las aguas subterráneas se consideran explotables. La dirección del agua subterránea interpolada se puede dividir en cinco secciones diferentes, sin embargo, se puede detectar una dirección de flujo de agua subterránea predominante hacia el sur. La zona de recarga de aguas subterráneas está ubicada en el departamento de "Entre Ríos " donde también se encuentran los afloramientos del "Paraná Fromation". No se puede hacer una evaluación final de la idoneidad del "Paraná Acuífero " para el suministro de agua potable. Debido a que faltan datos importantes, por ejemplo la cantidad de recarga.

1 Introduction

1.1 Significance of Water

Water is one of the most important resources for human kind. This is due to the variable use of water for example in technical processes and recreation, but especially because water is an essential nutrient for all living organisms. A lack of drinking water whether caused by insufficient water availability or non sufficient quality of the water can cause major diseases. A relative common example for that is the black foot disease which occurs in India and Bangladesh due to arsenic polluted water [26].
Also in Argentina, there are many challenges in terms of water supply, for example the fair distribution of the resource. Two-thirds of Argentina suffers from acute water scarcity[30]. In addition, ground and surface waters are often polluted and overburdened, particularly in the vicinity of large urban and industrial centers[30], like in the surroundings of the capital „Ciudad Autónoma de Buenos Aires“, the so called „Gran Buenos Aires“ [25]. Other problems in this area include drinking and sewage supplies [30][25], for example currently only 5.3 % of wastewater is treated [23]. Also in contrast to the capital, where almost all households benefit from a functioning drinking water supply, in the metropolitan region only 68.1 % of households have access to drinking water[25]. Due to this lack of water supply in this region additional possibilities to provide water has to be found. Therefore this study tries to determine the suitability of the “Paraná Aquifer“ for drinking water supply purposes.

1.2 Objectives of the study

This study has four major objectives. First, it should be verified whether the groundwater of the “Paraná Aquifer“ is suitable for drinking water supply. For this purpose, eight chemical water properties are compared with the threshold limits set by the World Health Organization (WHO).
The second objective is to determine the availability of groundwater. With sustainable management of the resource groundwater, the extraction of groundwater should not exceed the natural recharge of groundwater[32]. Therefore, the availability of groundwater is highly dependent on natural groundwater recharge, but there are other factors that limit the availability of groundwater. For example the availability of groundwater also depends on a proper well design [11]. A proper well design depends on the hydraulic characteristics of the aquifer, the quality of the groundwater and the depth of the aquifer [11]. The depth of the aquifer also affects the cost of the produced water due to the higher energy demand for deeper water resources[31]. Therefore the elevation of the top of the “Paraná Formation“ will be modeled.Different modeling approaches will be used and compared to develope a reasonable subsurface map.
Furthermore the direction of groundwater flow and the location of the recharge zone of the “Paraná Aquifer“ should be identified. This is to be achieved by the modeling of the hydraulic heads and typical chemical patterns. For the modeling, different modeling methods will be used and compared. Afterwards the results are used to develope a realistic groundwater flow direction map.

2 Study area and available data

2.1 Geological site and geographical location of the Paraná Formation

The "Paraná Formation" is one of the most extensive geological units of the "Chacoparanense Basin" in the Argentine Republic. However, the lack of information on the hydrogeological properties of this formation is large, because of the expected low usability for drinking water supply purposes. The quality of water is low due to the high salinity for drinking water supply purpose[3]. For example, the salinity of the area of the „Ciudad Paraná" is between 420 mg/L and 2597 mg/L, which is a moderate salinity [4]. The high salinity samples ($2000 - 2600$ mg/L) in the area of the city of Paraná were found where the samples exclusively consist of the water of the Paraná Aquifer [4]. The age of the Paraná Aquifer is considered to correspond to the medium-upper Miocene (Serravaliano) due to the antiquity of the abundant palaeontological material that it contains [15]. The Paraná Aquifer is defined as a succesion of sands, silts and greenish-gray clay which are superimposed by argillaceous sands and organogenic limestones. This unit is characterized by abundant marine fossils, accumulating in some zones to constitute banks of great lateral continuity and of a remarkable thickness [16]. The location of the "Paraná Formation" (as outcrop and in the subsoil) is shown in figure 1. The locations are described more in detail in the following.

The type section is located in the „Ciudad Paraná" in the area of Puerto Nuevo (Quebrada La Santiagueña), nevertheless the outcrop continues from Puerto Nuevo til Bajada Grande [15]. In the south of Paraná the outcrops have superficial expression in several sectors of the departments Diamante and Victoria [15]. But there are also other notable outcrops in the north of the area located in the region of Villa Urquiza, El Cerro, Brugo until near Hernandarias[15].

In the western center of Entre Rios, west of Corrientes, Chaco-Formosa, Santa Fe, in the east of Córdoba and in the north of Buenos Aires lies the geological structure subterranean. The thickness of the Paraná Aquifer varies between 100 to 200 m [15].

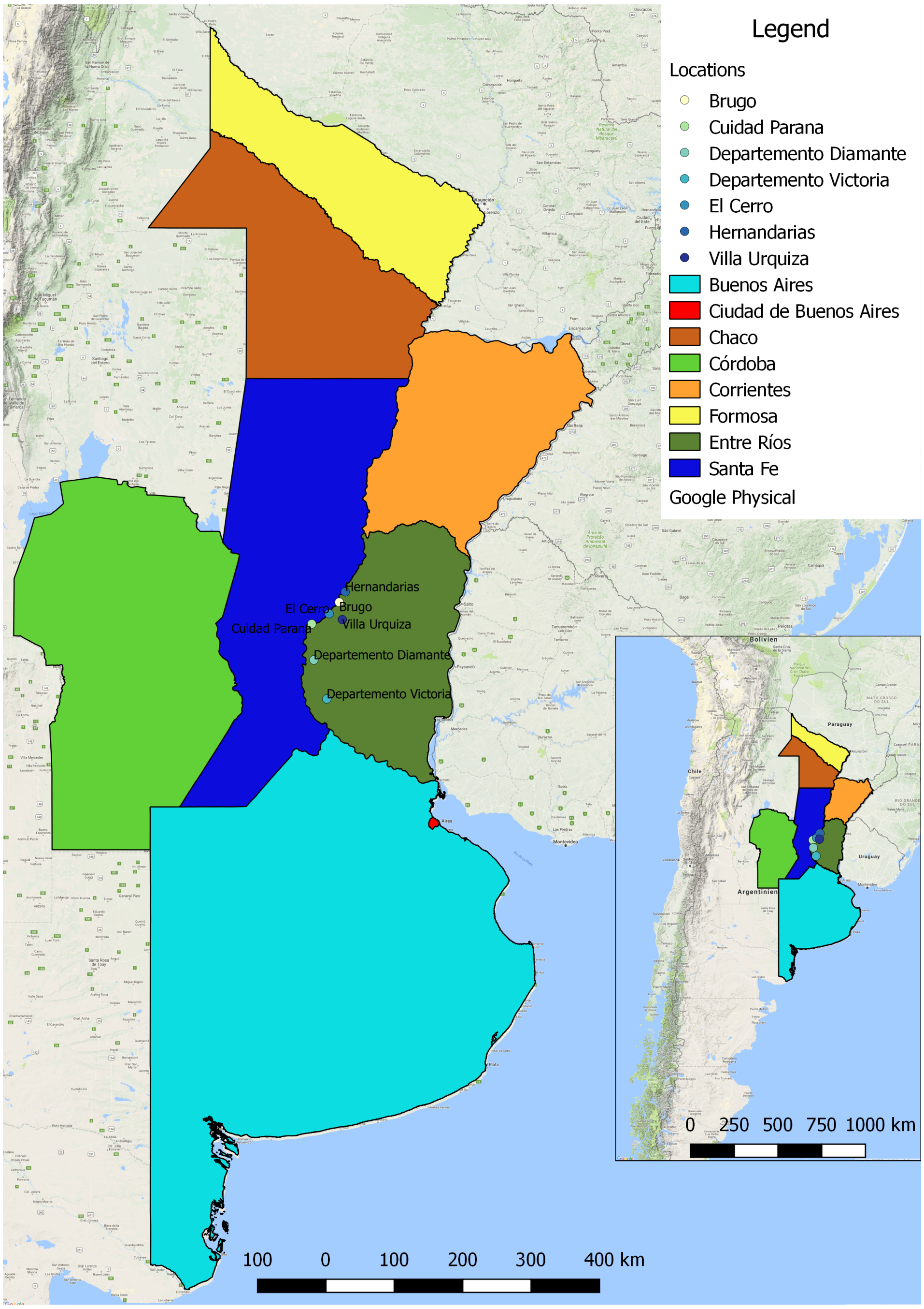

Figure 1: Overview of the distribution of the “Paraná Formation“ as outcrops and in the subsurface.

The drillings made in the area of the type section indicate a concordance stratification, the lithology of the type area is shown in figure 2. Below the “Paraná Formation“ is a layer of brown and reddish-brown clays probably equivalent to the so called “Fray Formation Bentos“[15].
The base of the “Paraná Formation“ is formed by about 65 m of green, plastic clay. Followed by two banks of fine white sands of about $8 - 10$ m, each one interbedded by green clays. These clayey grayish green sand is covered by limes and organogenic limes. The limes and organogenic limes have a maximum thickness of about 6 m. The limestones and organic limestones form the end of the “Paraná Formation“ and are followed by the “Pampa Silts“. In this area the thickness of the “Paraná Formation“ is about $100 - 110$ m [15].

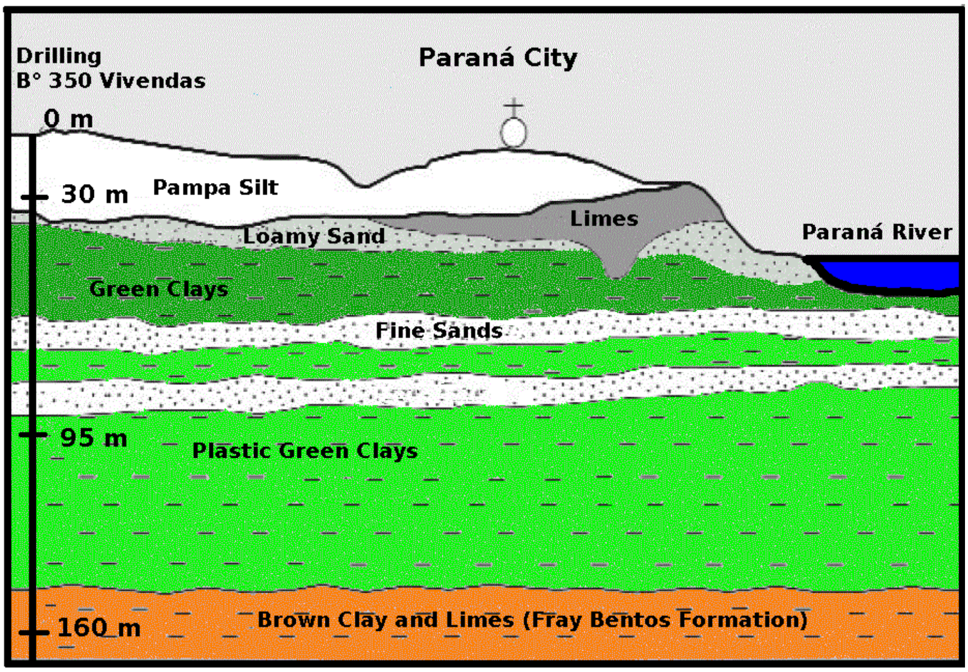

Figure 2: The lithological cross section of the Paraná Aquifer (adapted from [16] and [18]).

Until now the geological profile of several outcrops in the region of Entre Rios were described by other authors such as D'Orbigny, Aceñolaza and Silva Busso. A few examples of outcrops and their exact location are listed in table 1. The geological profile of the outcrop of the quarry "Laguna El Pescado" is shown in figure 3 and described in the following.

Table 1: Outcrops of the "Paraná Formation" in the region Entre Rios, exact coordinates and elevation in meter above sea level [4].

Outcrop	**North**	**East**	**Elevation (m.a.s.l.)**
Canyon $A°$ Ensenada	-31.129611	-60.434361	39
Canyon $A°$ Doll	-32.306944	-60.426389	32
Stone pit $C°$ Matanza	-32.593611	-60.187500	29
Canyon de $C°$ La Cueva	-32.597694	-60.189583	43
Stone pit Los Ramblones	-32.505556	-60.208333	35
Stone pit Laguna El Pescado	-32.723056	-59.981667	34

A typical geological profile of an outcrop is shown in figure 3 and a typical geological profile of a drilling core in the department of Buenos Aires is shown in figure 4.

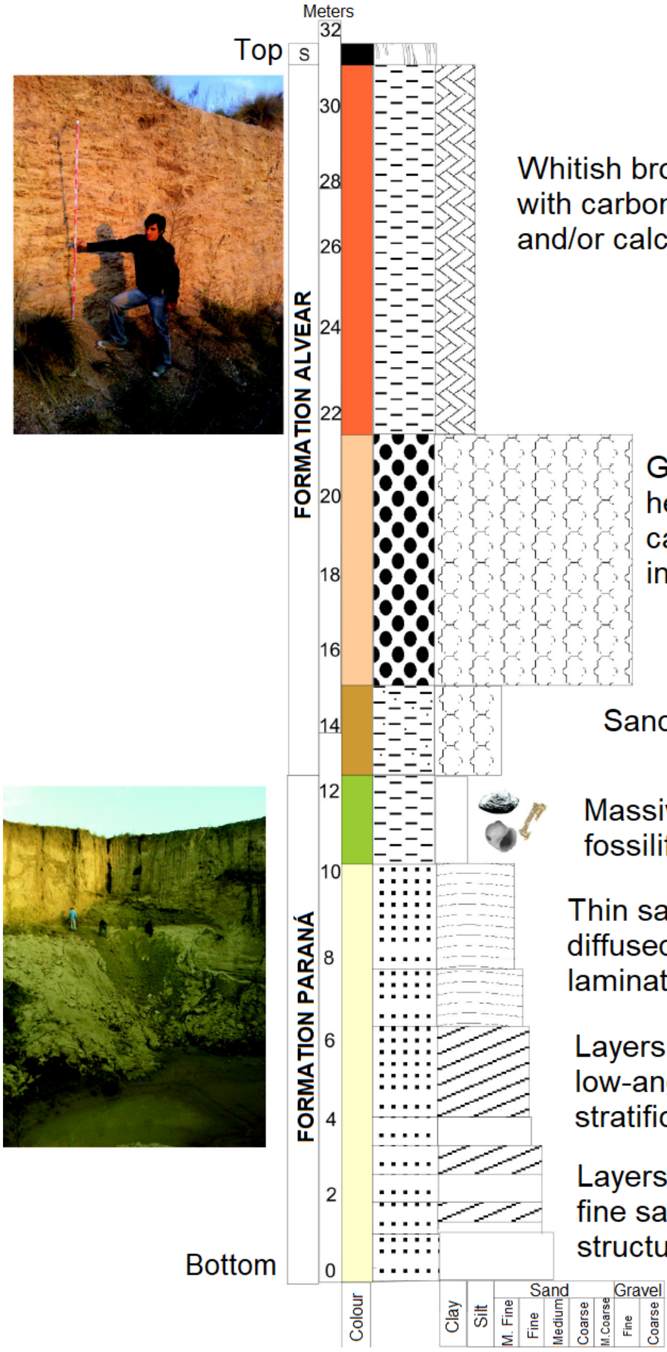

Figure 3: Geological profile of the outcrop of the quarry Laguna El Pescado in the department Victoria in the province Entre Ríos [4]. With the geographical location at −32.723056 °N −59.981667 °E

In the quarry Laguna El Pescado the "Paraná Formation" is covered by the "Alvear Formation". The "Alvear Formation" is about 20 m thick and has three different layers with different thicknesses. The top layer is a layer of brown clayey silt with carbonated nodules and or calcretes. The middle layer is a layer of heavily cemented and calcified pelitic intraclast and the lowest layer of this formation is a layer of loamy sand. The top of the "Paraná Formation" forms a layer of massive silty clay in part fossiliferous. Then follows a layer of sand with different stratification. The entire sand layer of the "Paraná Formation" is about 10 m and therefore five times as large as the layer of silty clay.

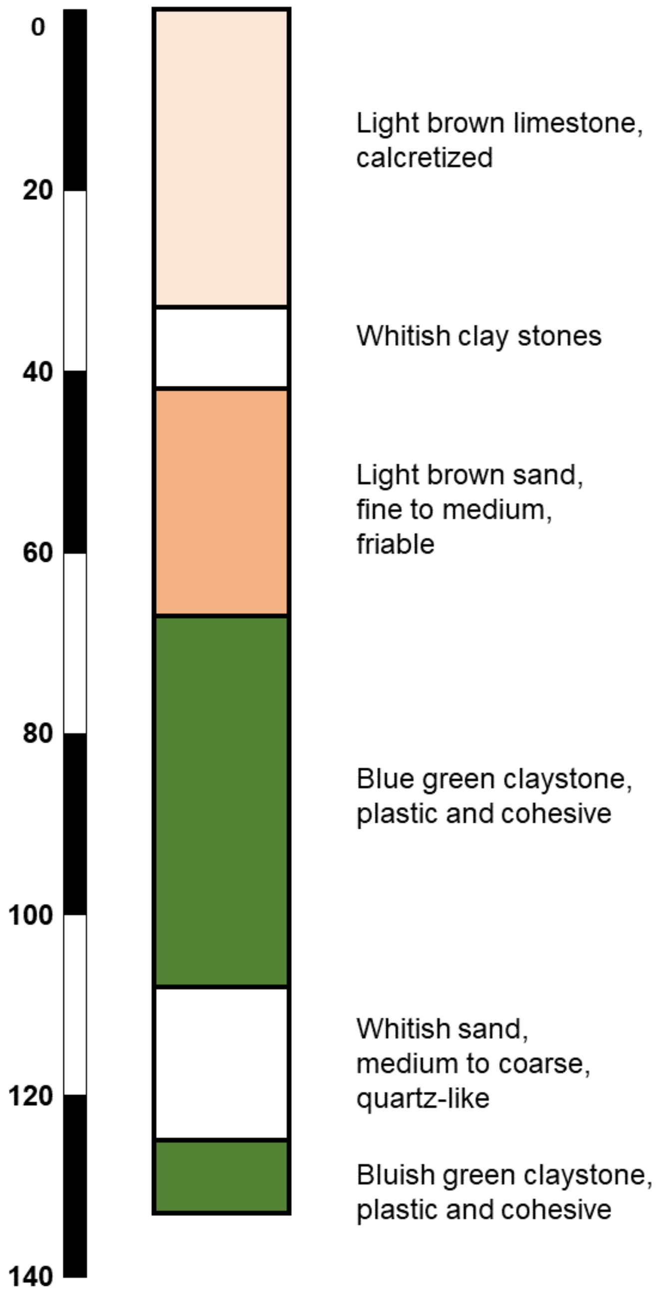

Figure 4: Drilling core of the well in the department of Buenos Aires located at “Cooperativa de Obras y servicios Publicos, Viviendas y Servicios Asistenciales de Martin Coronado COMACO“ with the geographical location $-34.585836\,°N$ $-58.591475\,°E$.

The top of the drilling core in the department of Buenos Aires located at “Cooperativa de Obras y servicios Publicos, Viviendas y Servicios Asistenciales de Martin Coronado COMACO“ is formed by a layer of light brown calcretized limestones. Then is followed by a layer of whitish clay which is followed by light brown fine to medium sand. Then follow a layer of blue green claystones and a whitish medium to coarse sand which is interbedded with another layer of blue green claystones.

2.2 Geographical location

The study area is located in the east and northeast of Argentina in the departments “Ciudad Autónoma de Buenos Aires“ (CABA), “Buenos Aires“, “Entre Ríos“ and “Santa Fe“. The study area has a size about $120,000\,\mathrm{km}^2$. The biggest part with approximately $87,800\,\mathrm{km}^2$ is located in the department of “Buenos Aires“. The part of the study area located in the department “Entre Ríos“ has the size of about $22,000\,\mathrm{km}^2$ and the part located in the department “Santa Fe“ has an area of approximately $10,000\,\mathrm{km}^2$. With about $200\,\mathrm{km}^2$ the smallest part is located in the department “CABA“ and covers the hole area of the department.
Figure 5 shows an overview map of the study area. In addition to the above mentioned departments, figure 5 shows the so called are “Gran Buenos Aires“, which has an area of about $3,880\,\mathrm{km}^2$ and 150 locations were the “Paraná Formation“ does not occur neither in the subsoil nor as outcrop. Therefore this location were assumed to respresent the natural border of the “Paraná Formation“ in the east of the departments “Entre Ríos“ and “Buenos Aires“. Twelve of the 150 wells are located in the study area.
The northern border is the shortest border with about 66 km and reaches from $-31.7\,°\mathrm{N}$ $-60.4\,°\mathrm{E}$ to $-31.7\,°\mathrm{N}$ $-61.1\,°\mathrm{E}$ (World Geodetic System 1984). The western border reaches from $-31.7\,°\mathrm{N}$ $-61.1\,°\mathrm{E}$ to $-36.3\,°\mathrm{N}$ $-61.1\,°\mathrm{E}$ and is therefore about 512 km long. The southern border is about 364 km long and reaches from $-36.3\,°\mathrm{N}$ $-61.1\,°\mathrm{E}$ to $-36.3\,°\mathrm{N}$ $57.1\,°\mathrm{E}$. The eastern border in the department of “Buenos Aires“ is the Atlantic coast. In “Entre Ríos“ the eastern border of the study area starts at the coordinates $-33.4\,°\mathrm{N}$ $58.4\,°\mathrm{E}$ and ends at $-31.7\,°\mathrm{N}$ $-60.4\,°\mathrm{E}$.
For the different parts of this study (hydrochemial properties, the elevation of the “Paraná Formation“ and the groundwater flow dircetion) different wells and amount of wells are used. Therefore, the different conditions for each part are explained more in detail below.

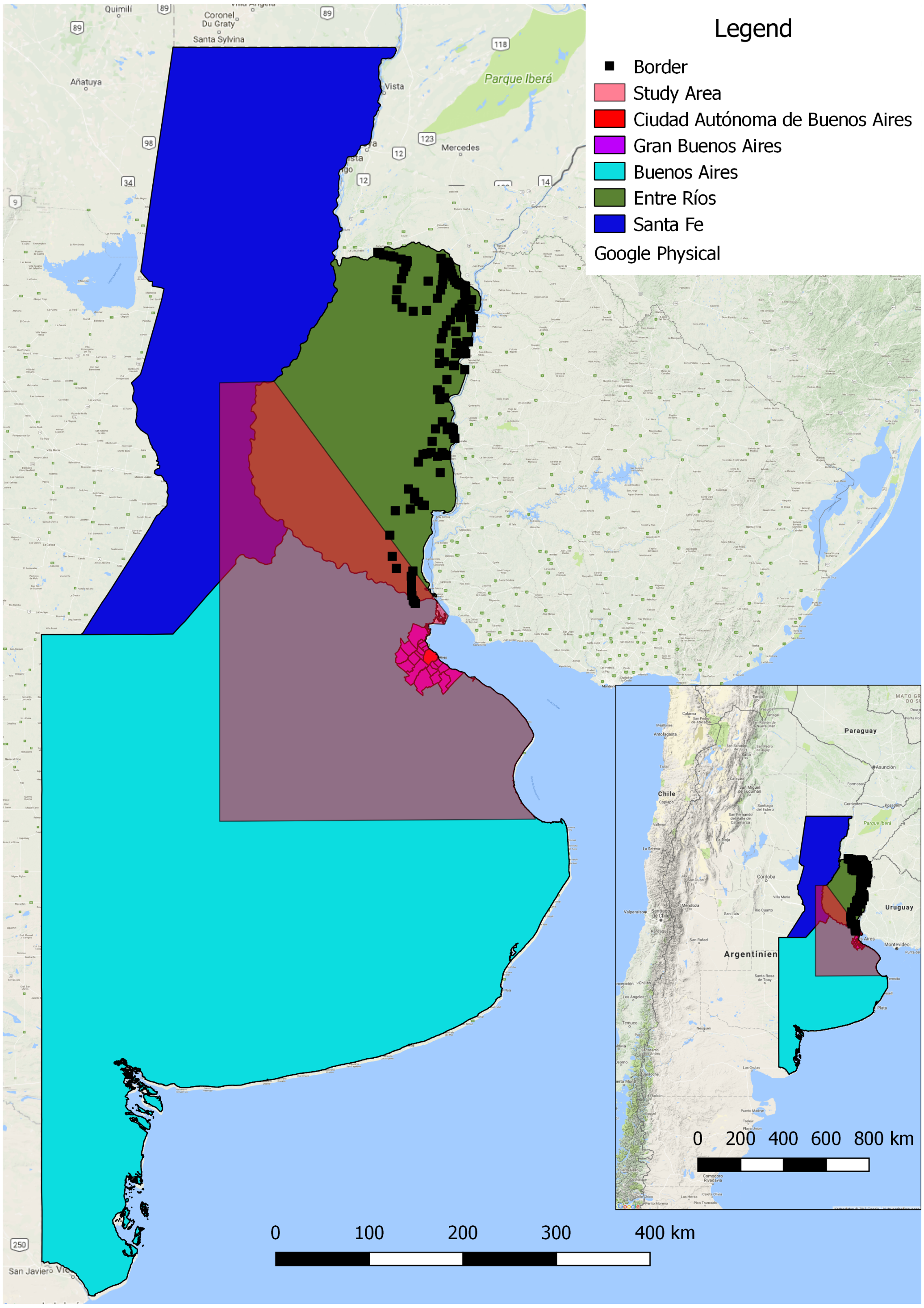

Figure 5: Overview map of the study area with the natural east border of the "Paraná Formation". The dark red highlighted department is "CABA", the cyan highlighted department is "Buenos Aires", the green highlighted department is "Entre Ríos" and the blue one is "Santa Fe". The purple highlighted area is the so called "Gran Buenos Aires". And the light red higlighted area is the study area. The black squares, mark 150 locations were the "Paraná Formation" does not occur neither in the subsoil nor as outcrop.

2.3 Land use and topography of the study area

Figure 6 shows the land cover map of continental South America. The location of the study area is marked with a red rectangle. The main land use in the study area is the the cultivation of crops. Especially in the south of the study area almost all the land is used as cropland only a small part of this area is used as shrubland or is a semiarid environment. In the north of the study area, land use is changing and agriculture is declining and the land is used more as shrubland. In addition, a part of the land in the north is present as a savanna and a semiarid environment.

Figure 6: Land cover map of continental South America based on Collection 5 MODIS Land Cover Type product for year 2012 (adapted from [2]).

Figure 7 shows the topographic map of the study area. The maximum altitude that can be seen in this figure is 331 m.a.s.l. and the minimum altitude is 0 m.a.s.l. The resolution of the altitude is not uniform. The maximum altitude of 331 m.a.s.l. is outside the study area in Uruguay. The maximum altitude in the study area is between 147 m.a.s.l. and 164 m.a.s.l. in the north of the study area near the “Ciudad de Paraná“. The minimum altitude of 0 m.a.s.l. can be found at several locations in the study area for example in the west of the study area in the region of the river delta of the “Río de la Plata “ or near the capital “Ciudad Autónoma de Buenos Aires“.

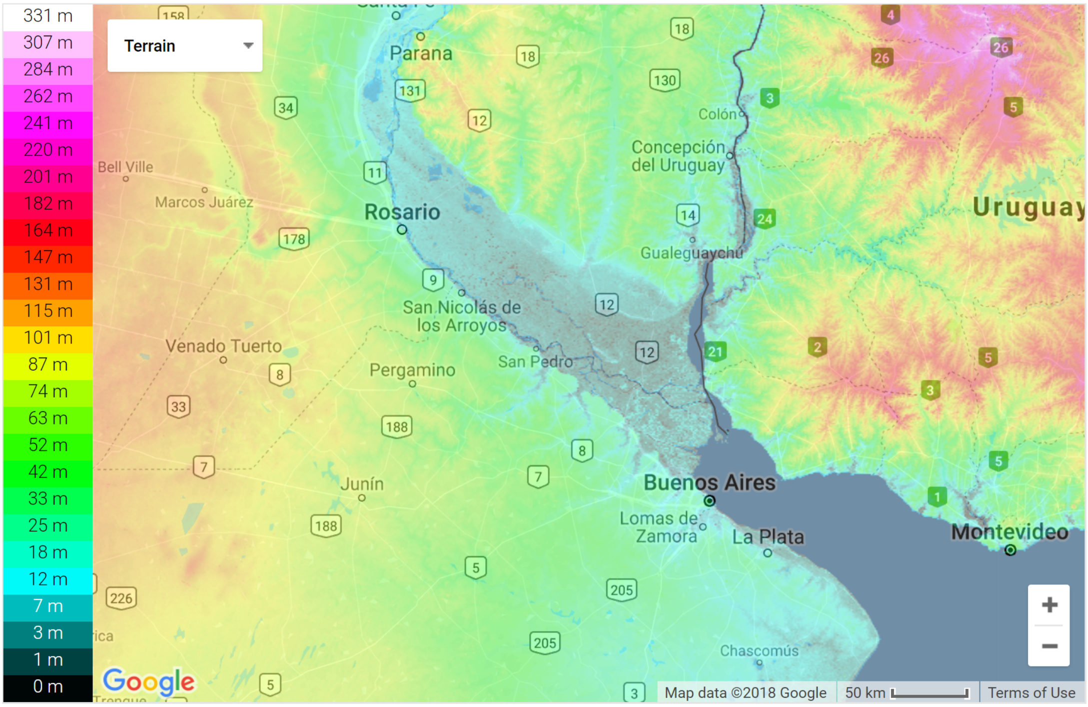

Figure 7: Topographic map of the study area `www.topographic-map.com`.

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2.4 Available hydrochemical data

For this study the hydrochemical properties of the groundwater of 27 wells are investigated. Their locations are shown in figure 8. The size of the study area is $120,000\,km^2$. It has to be noted that the wells are unequally distributed, thus in large area no information on the hydrogeochemical status can be gained. The lack of information in some areas make a reliable statement about the hydrogeochemical situation of the “Paraná Aquifer“ difficult. This is mainly due to the fact that the hydrogeochemical heterogeneity of the “Paraná Aquifer“ is unknown.

The majority of the 27 wells are located in the department “Buenos Aires“, only seven of them are located in the department “Entre Ríos“ and none of the wells is located in the department “Santa Fe“. Only six of the 20 wells in the department “Buenos Aires‘, are outside of the capital and its surroundings, the so called “Gran Buenos Aires“. Three of the 14 wells in “Gran Buenos Aires“ are in the “Ciudad Autónoma de Buenos Aires“. The areas of “Gran Buenos Aires“ and “Ciudad Autónoma de Buenos Aires“ are $3,880\,km^2$ and $203\,km^2$,respectively. Also the different wells do not provide the same level of information, because in some wells more hydrochemical parameters were measured than in others. The maximum number of chemical properties which were determined are nine. The collected data are the concentration of bicarbonate, calcium, chloride, magnesium, potassium, sodium, and sulfate and the conductivity. The total dissolved solids concentration is calculated from the conductivity.

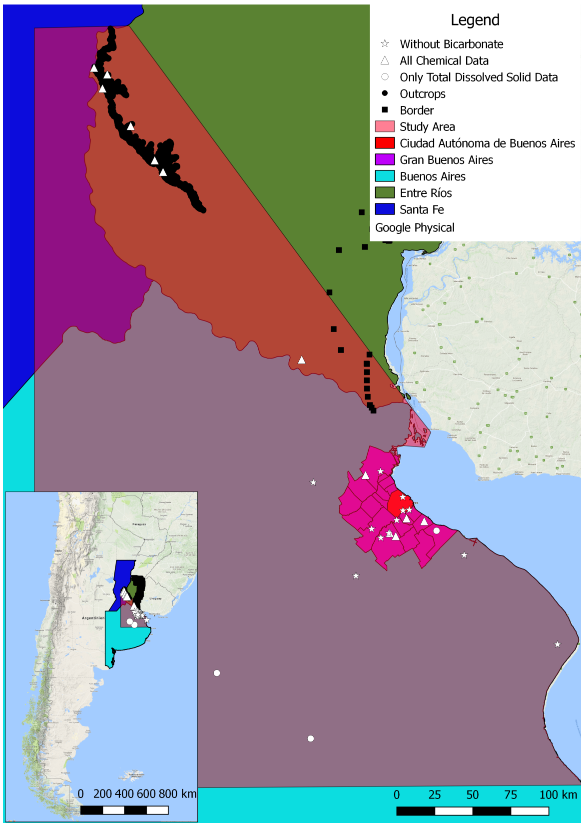

Figure 8: The study area including the 27 wells and measured properties at each well location used for the hydrochemical investigation of the “Parana Formation“.

2.5 Elevation of the top of the “Paraná Formation“.

Figure 9 shows the 378 wells and 6018 outcrops which were used to model the elevation of top of the “Paraná Formation“. In total there were 6396 data points used for the modeling of the elevation of the “Paraná Formation“. Figure 10 shows a detail view to the 6018 outcrops.

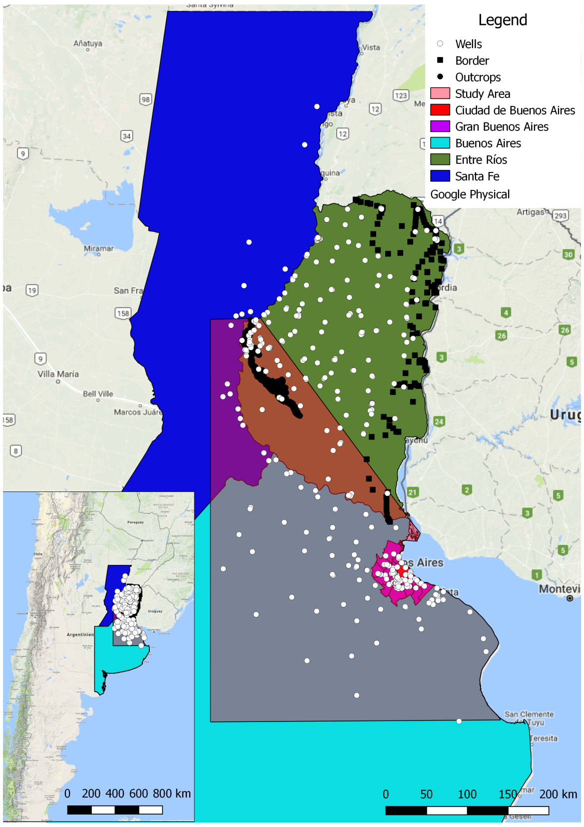

Figure 9: Overview map of the 378 wells and 6018 outcrops that were used to model the elevation of the “Paraná Formation“.

In the department of “Entre Ríos“ there are 204 wells, in the department of “Buenos Aires“ 158 wells are located and in the department of “Santa Fe“ 16. Not all of the 378 wells are located in the study area, in total 226 wells are located in the study area. Nevertheless, for the interpolation of the elevation of the “Paraná Formation“, the wells outside the study area are also used to get a better information of the border region of the study area. Only one of the wells located in the department of “Buenos Aires“ is not located in the study area. 61 of the 204 wells located in the department “Entre Ríos“ are also located in the study area. Half of the 16 wells in the state “Santa Fe“ are also located in the study area.
For 253 of the 378 coordinates were available. The others were located using coordinates derived from “Google Maps“. Most of the wells were built near a train station. Therefore, the wells with no location were located at the train station in the different cities or districts. Due to the size of the study area, the way to locate the well is fair enough. An absolute error of 1 km of the location would mean a maximal relative error of about 2 % in east-west direction and in north-south direction about 0.2 % .
The wells that were located with “Google Maps“ are the well from 1 to 25, 33, 50 and 72 to 168.
Also it has to be mentioned that the descriptions of the wells did not have a uniform altitude unit due to the fact that the wells were constructed in different decades. Therefore the altitude was determinate via `https://www.daftlogic.com/sandbox-google-maps-find-altitude.htm`.

The area where all data points are present is about $300,000\,\text{km}^2$. But it has to be noted, that the data are not equally distributed. For example in “Gran Buenos Aires“ are 90 wells. The area of this region is $3,880\,\text{km}^2$ which represents about 3 % of the total study area. In comparison the 6018 outcrops are located in the west or south-west of the department of “Entre Ríos“. The size of the area, where all the outcrops appears is about $1900\,\text{km}^2$ which represents only about 1 %. The size of the area was approximated by “QGIS 2.18.14 Las Palmas“.

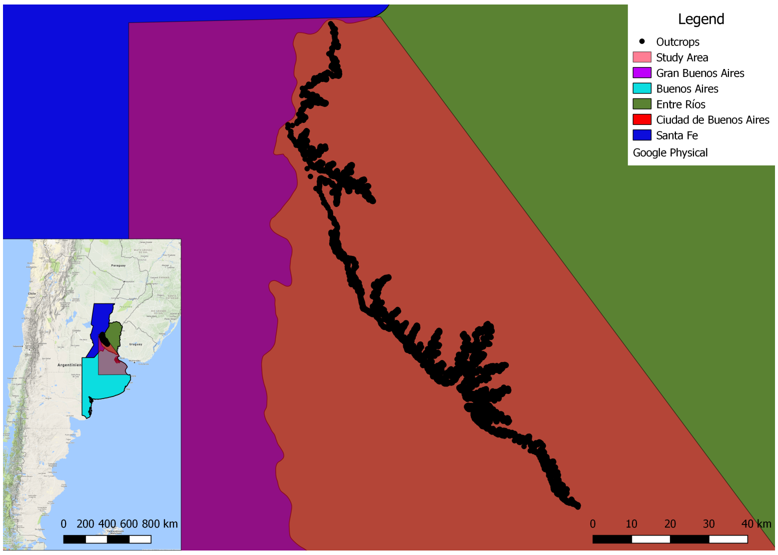

Figure 10: Detail view of the outcrops of the “Paraná Formation“ in the northeast of the study area. The white circles represents the wells that penetrate the “Paraná Formation“ and the black circles represents the outcrops of the “Paraná Formation“.

2.6 Groundwater levels of the “Paraná Aquifer“

The hydrualic head of 18 different wells are used in this study and their locations are shown in figure 11. The size of the study area is $120,000\,\text{km}^2$. It has to be noted that the wells are unequally distributed. Almost two-third, 11 of the 18 wells are located in the departement of “Buenos Aires“, seven of them are located in the department “Entre Ríos“ and none of the well is located in the department “Santa Fe“. Only four of the 11 wells in the department “Buenos Aires‘ are outside of “Gran Buenos Aires“ and three of the 11 are in the “Ciudad Autónoma de Buenos Aires“. That means in “Gran Buenos Aires“ a well represents an average area of $431\,\text{km}^2$ that is about half of the size of Berlin. In the “Ciudad Autónoma de Buenos Aires“ a well represents an area of about $68\,\text{km}^2$ which is 0.1 times the size of Berlin. In the center, the west and the south-west of the study area, there are no hydraulic head data available.

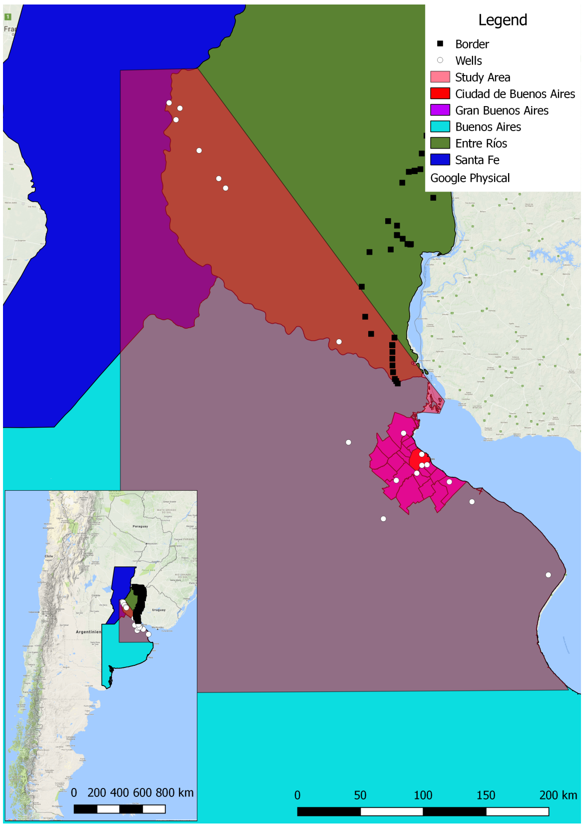

Figure 11: The study area with the 18 wells for determination of the groundwater flow direction of the “Paraná Aquifer“. The white circle are the wells with the hydraulic head data and the black square are locations where the “Paraná Formation“does not occur neither as outcrop nor in the subsoil.

3 Material & Methods

3.1 Hydrochemical analyzes of the groundwater of the "Parana Aquifer"

The hydrochemical analysis is used for two different reasons. The first reason is to determine if the water of the "Paraná Aquifer" is suitable for drinking water supply purposes. The other reason is to predict a groundwater flow direction due to the evolution of chemical properties of the groundwater. Due to the high number of determined parameters, the individual determination methods are not explained in detail. Instead, table 2 shows the methods used for the determination. The used methods are standard methods of the Environmental Protection Agency (EPA).

Table 2: Chemical parameter, shortcut of the chemical parameter, methods of analysis and unit of the determined chemical property of the water of the "Paraná Aquifer".

Parameter	**Shortcut**	**EPA-Reference**	**Analytical method**	**Unit**
Bicarbonate	HCO_3^-	SM 4500	Titration	mg/L
Calcium	Ca^{2+}	EPA 3005 A/7000	Flame atomic absorption spectroscopy	mg/L
Chloride	Cl^-	SM 4500	Titration	mg/L
Conductivity	ρ	SM 2510	Conductivity meter	µS/cm
Magnesium	Mg^{2+}	EPA 3005 A/7000	Flame atomic absorption spectroscopy	mg/L
Potassium	K^+	EPA 3005 A/7000	Flame atomic absorption spectroscopy	mg/L
Sodium	Na^+	EPA 3005 A/7000	Flame atomic absorption spectroscopy	mg/L
Sulfate	SO_4^{2-}	SM 4500	Titration	mg/L
Total dissolved solids	TDS	$0.69\ \mathrm{(cm \cdot mg)/(L \cdot \mu S)} \cdot \rho$	Calculation	mg/L

Conductivity is not treated as a stand-alone parameter in the results, as no limit of the World Health Organization was found for the conductivity. However, the parameter total dissolved solids is directly derivable from the conductivity and a comparison for this parameter to the limits of the World Health Organization was performed.

3.2 Elevation of the “Paraná Formation“.

The interpolation were done in the “Transverse Mercator projection“ in the sixth meridian strip of Argentina. The elevation of the top of the “Paraná Formation“ is predicted by three different interpolation methods using the “Golden Software Surfer 9“. The methods are “Kriging“, “Natural Neighbor“ and “Local Polynomial“.

3.2.1 Universal kriging

Kriging is a statistical tool developed by G. Matheron[17] and was originally developed particularly for ore reserve estimation, but nowadays it is also used for other spatial estimation applications in other fields like hydrology and soil science. For example, the U.S. EPA used kriging to develop maps to qualify the risk of sites for toxic contamination[1].
The kriging method is a linear interpolation and it is often associated with the acronym B.L.U.E. for “best linear unbiased estimator“[20] [7]. To compute a model, the kriging method uses the available data for weighted linear combinations[20]. The aims of kriging are to minimize the variance of erros σ_R^2 and to equal the mean residual or error m_R to 0 [20]. Based on the principle of spatial autocorrelation, that means observations close to each other are more alike than those that are far apart [35]. Also kriging assumes that a value of an attribute at an unsampled location is a weighted average of known data points that are within a local neighborhood surrounding the unsampled point[35].
There are several types of kriging like ordinary and universal kriging[8].
“Golden Software Surfer 9“ uses the following equation to compute the model by kriging [44]:

$$Z_A = \sum_{i=1}^{n} W_i \cdot Z_i \tag{1}$$

Here Z_A is the estimated grid value of node A, n is the number of neighboring data values used for estimation, Z_i is the value at location i with weight W_i [44]. To ensure that there is no bias towards clustered data points the value of weights will sum up to 1 [44].
The software “Golden Software Surfer 9“ has six different settings to improve the kriging interpolation. These settings can change the “Variogram Model“, “Output Grid of Kriging Standard Deviations“, “Kriging Type“, “Drift Type“, “Search options“ and “Search ellipse“.
The “Variogram Model“ influences the quantitative and statistical description of the surfaces roughness [44]. The variogram is the degree of variance between data at two locations, x and y [44]. The components of the variogram that can be changed are the type of the variogram, meaning whether it is linear, expentionial etc., the slope and the anisotropy ratio and angle. The variogram type which was used is linear, the slope is 1, the anisotropy ratio is 1 and the angle 0.
The “Output Grid of Kriging Standard Deviations“ influences the standard deviation of the interpolation and therefore the value of the interpolated grid node [44]. No “Output Grid of Kriging Standard Deviations“ was used for the interpolations.
“Golden Software Surfer 9“ provides “point kriging“ and “block kriging“[44]. Point kriging estimates the value of a point from a set of nearby values, block kriging on the other hand estimates the average value of the rectangular blocks centered on the grid nodes [44]. The used kriging type was point kriging.
The “Drift Type“ determines whether ordinary kriging or universal kriging is used [44]. No “Drift Type“ was used, therefore the interpolation is done by ordinary kriging. The “Search options“ define which points are used for the interpolation of the surface [44]. There are six different options that can be used, those are “no search“, “number of sectors to search“, “maximum number of data to use for all sectors“, “maximum number of data to use from each sector“, “minium number of data

in all sectors“ and “assign NoData to node if more than this many sector are empty“. If the “no search“ option is selected, surfer will use all data points to interpolate the grid file[44]. This option is appropriate if the data are evenly distrubted or the data sets are smaller than 250 data points [44]. Applying the option “number of sectors to search“ divides the area in fractions and is useful for clustered data [44]. The option “maximum number of data to use for all sectors“ limits the number of points which are used for the overall interpolation [44]. The option “maximum number of data to use from each sector“ specifies the number of points used from each sector [44]. The option “minimum number of data in all sectors“ will assign a “NoData“ value if there are not enough points found for the interpolation of a grid node [44]. “NoData“ value imply insufficient data and trim the contour lines in the map [44]. The option “assign NoData to node if more than this many sector are empty“ assign a grid node to a “NoData“ value if there are not enough sectors for the grid node [44].
The “search ellipse“ defines the extent of the local neighborhood which is used to interpolate and can be influenced by the “search option“[44]. The “search ellipse“ is modified by radius 1, radius 2 and the angle. The distance in positive data units are represented by radius 1 and radius 2, the radii values set the length of search which is indicated in direction of an angle [44]. The orientation of the angle is between the positive x axis and the radius 1 of the ellipse axis [44]. If no points exist in the “search ellipse“the grid node will be assigned the “NoData“ value [44]. If radius 1 and radius 2 are both equal, the x and the y-direction contributes equal weight to the interpolation [44].The following table shows the interpolation used search options.

Table 3: The used “search options“ for kriging and local polynomial for the interpolation of availability and access of groundwater via “Golden Software Surfer 9“.

Search options	**Value**
Number of sector to search	4
Maximum number of data to use from all sectors	64
Maximum number of data to use from each sectors	16
Minimum number of data in all sectors	8
Blank node if more than this sector are empty	3

3.2.2 Local Polynomial

The interpolation method local polynomial, is a generalization of the kernel regression and can be applied to a wide range of problems[21]. Local polynomial uses the mapped data to approximate the geographic coordinates of the sampling points due to polynomial expansion[48]. The data are divided in localized “windows“, the “windows“ can be moved around and the surface value at the centre of the “window“, the so called “node“, is estimated [48]. The best results for the interpolation with local polynomial are achieved with data sets that are relatively smooth within the “windows“[44]. The local polynomial uses a weighted least squares fit to compute the value of the node in the “windows“[12], this means that the data which are closer to the interpolated node have a higher influence [44]. The method ensures that the trend surface has a minimized sum of squared deviations [48]. Local polynomial is a moderately quick deterministic interpolation method that is smooth[48].
The order of the polynomial that is use to interpolate the data can be ajusted by “Golden Software Surfer 9“. The polynomial can be of the first, second or third order [44].
In this study a polynomial of the first order was used, this means a plane is fitted through the data [44]. The following equation was used to compute the interpolation [44]:

$$F(X, Y) = a + bX + cY \tag{2}$$

Here $F(X, Y)$ is the interpolated value, X and Y are geographical coordinates and a, b and c are polynomial coefficients.
For local polynomial four different settings can be adjusted. The four settings are “Power“, “Polynomial Order “, “Search options“ and “Search ellipse“. The “Power“ is used to minimize the sum of the squared residual and is applied to the weight calculation [44]. The “Power“ can be set to a value between 0 and 20 [44], the “Power“ was set to a value of 2. As already mentioned “Golden Software Surfer 9“ can be used first, second or third polynomial order and for the interpolation first order was applied. The “Search options“ and “Search ellipse“ are explained in section 3.2.1. The “search options“ which were applied are equal to those applied for the kriging method and listed in table 3.

3.2.3 Natural Neighbor

Natural neighbor is an interpolation method that was first introducted by Sibson [40] [41]. Natural neighbor coordinates, also called Sibson coordinates, is an interpolation scheme for multivariate data fitting and smoothing[33]. Voronoi diagrams of a set of sites are used for the interpolation by a weighted average method [38]. The weights are generated by geometrical constructions for each datum in the natural neighbor subset [13]. Therefore first the Voronoi diagrams of the original data are constructed. Then a Voronoi diagram of the interpolated value is imposed. The weights correspond to the proportion of the original Voronoi diagram in the impossed Voronoi diagram. The weights are between 0 and 1 [13]. To provide the interpolation value, the individual weights are applied to the affiliated original data, and these values are summed up [13]. Instead of other interpolation method, natural neighbor is not distance based but it is area or volume based.

Natural neighbor is a common interpolation method for data sets with dense data in some areas and sparse data in others [44]. Typical for natural neighbor is that the interpolation does not extrapolate the Z data of the original data set and also that no data are generate in areas without data [44]. The natural neighbor approach is a conservative and robust interpretation of the data [13]. The mathematical expression for the natural neighbor concept is the following [38]:

$$F(X,Y) \hat{=} \sum w_i(X,Y) \cdot f(s_i) \tag{3}$$

Here $F(X,Y)$ is the interpolated value at point (X,Y), $w_i(X,Y)$ is the weight of the original data s_i from a set of sites $S = s_1...s_n$ and $f(s_i)$ is the value of the original data at the point s_i. The weight w_i is determined by the following equation [38]:

$$w_i = \frac{Area(V_{S\cup\{q\}}(q)) \cap V_S(s_i)}{Area(V_{S\cup\{q\}}(q))} \tag{4}$$

Here $V_S(s_i)$ is the Voronoi cell of s_i in Voronoi diagram of S $Vor(S)$ and $V_{S\cup\{q\}}(q))$ is the Vornonoi cell of q in $Vor(S \cup \{q\})$.

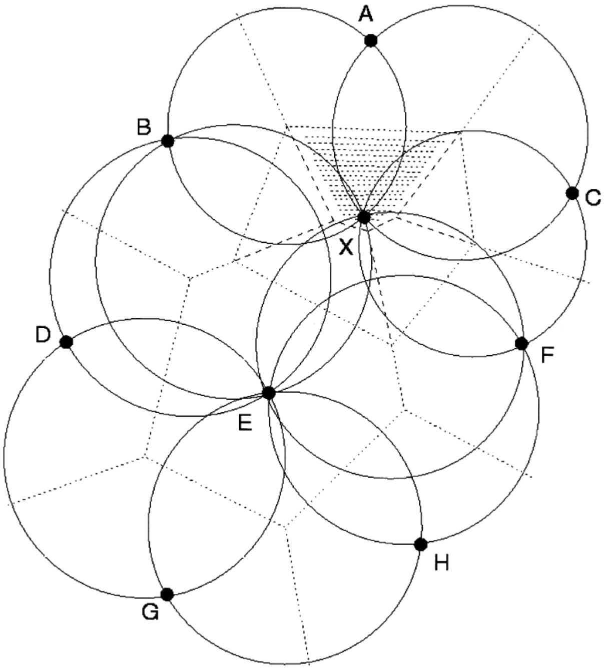

Figure 12: Example for a natural neighbor interpolation including all Voronoi polygon of data and the Voronoi polygon of interpolation point[13].

Figure 12 shows an example of the functioning of the natural neighbor interpolation. For the interpolation of X the weight in respect of the value of A is the shaded region, the so called fractional area [13]. The fractional area is the area of overlap between the Voronoi polygon associated with A and the imposed Voronoi polygon associated with X [13].
"Golden Software Surfer 9" allows for the natural neighbor interpolation to define aniostrophy ratio and aniostrophy angle in order to increase the weight of one direction [44]. In this study the aniostrophy ratio was set to 1 and the aniostrophy angle to 0, that means that all direction are equaly weighted [44].

3.3 Groundwater flow direction

The interpolations of the groundwater flow direction were done in the “Transverse Mercator projection“ in the sixth meridian strip of Argentina. The suggested groundwater flow direction is also modeled to determine, if the recharge area of the “Paraná Aquifer“ is located in the deparment of “Entre Ríos“. The groundwater flow direction and the location of the recharge zone were modeled by two different interpolation methods and three different approaches.
The used modeling methods are as follows: Kriging and Natural Neighbor.
The first approach is the interpolation of the hydraulic head. The second and third approach to interpolated the groundwater flow direction use the evolution of hydrochemical properties and it is often used for deep aquifer where only scarce hydrogeological data exist [29]. The groundwater flow influence hydrochemical patterns for example by leaching of the aquifer system[24] There are several typical hydrochemical evolutions in groundwater flow direction of an aquifer system [24].
For the second approach the typical hydrochemical evolution which was taken advantage of in this study is that the groundwater developes from polluted with, for instance, sulfate, nitrate, potassium, and persistent xenobiotics to unpolluted [36] [49]. This evolution has two reason elimination processes like filtration and the increasing age of the water[24]. The increased age results in a lower pollution because the load before the onset of industrialization was lower[36][49]. The for the modeling used chemical property of the groundwater with this typical flow pattern was the potassium concentration.
The for the third approach used typical pattern is that the water developes from fresh to brackish or saline water[36]. The for the modeling used chemical property of the groundwater with this typical flow pattern is the total dissolved solid concentration.
Also due to the comparing of the different approaches and the modeled groundwater flow direction it should be proved if the groundwater recharge zone is in Entre Ríos.
For the modeling the contouring and $3D$ surface mapping software “Golden Software Surfer 9“ was used.

3.3.1 Universal Kriging

The interpolation method kriging is explained in detail in section 3.2.1. In contrast to the modeling of the elevation of the “Paraná Formation“ for the modeling of the groundwater flow direction “no search options“ were used. This is because in the study area are less than 250 data points (only 19 for hydraulic head and 24, respectively 27 for the hydrochemical evolution approaches). That “no search options“ were used means that every interpolated value has been interpolated with all existing data.

3.3.2 Natural Neighbor

The interpolation method natural neighbor is explained in detail in section 3.2.3. Like for the modeling of the elevation of the “Paraná Formation“ the aniostrophy ratio was set to 1 and the aniostrophy angle to 0.

4 Results

4.1 Hydrochemical analyzes of the groundwater of the “Parana Aquifer“

For each hydrochemical properties, there are different number of measurements available. For bicarbonate are 12, for calcium, chloride, magnesium, potassium, sodium and sulfate are 24 measurements and for total dissolved solids are 27 measurments available. Figure 13 shows box-and-whisker diagrams for the eight investigated hydrochemical parameters and table 4 shows the associated statistical values.

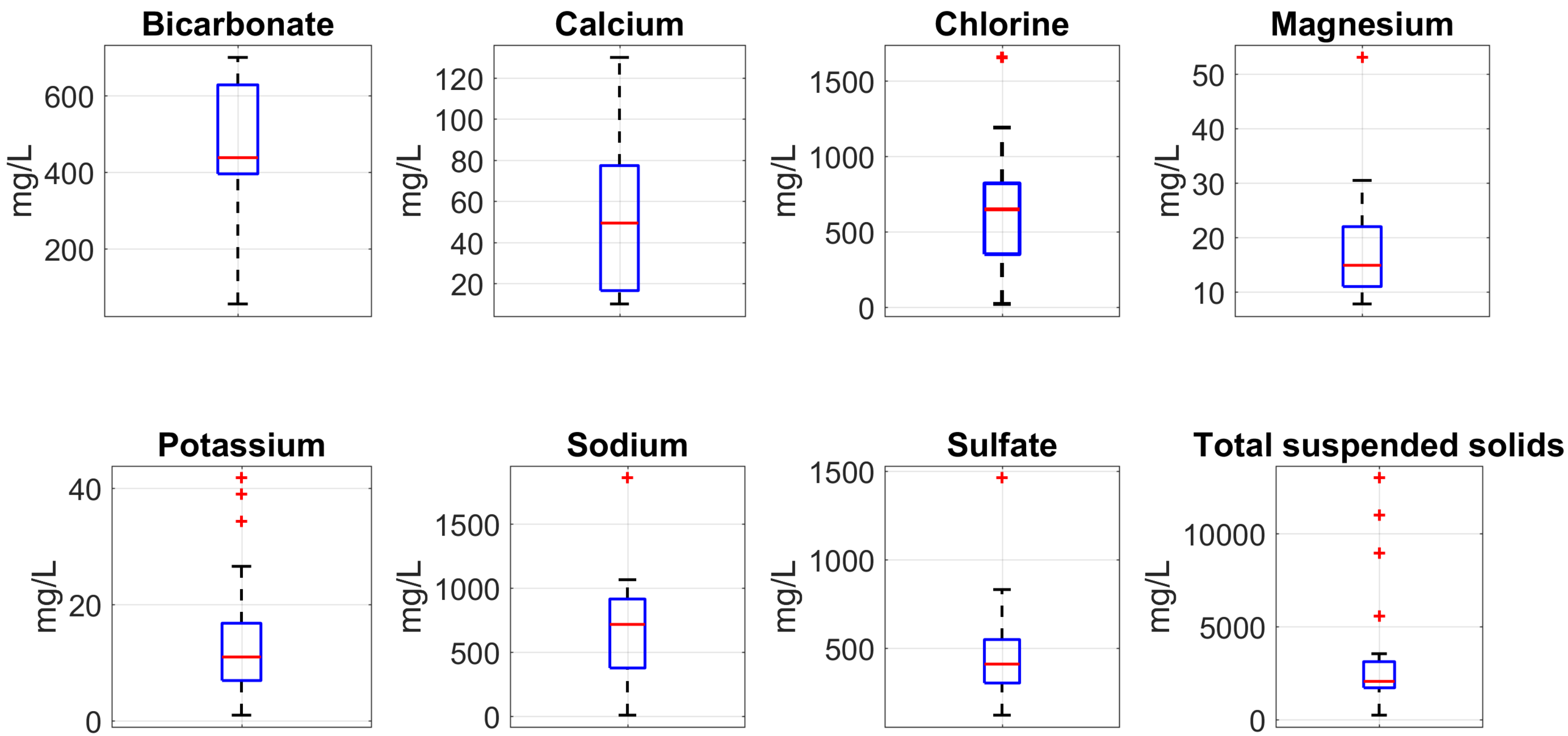

Figure 13: Box-and-whisker diagrams for the investigated hydrochemical parameters.

Table 4: Summary of the static values of the investigated hydrochemical parameters.

Parameter	**Unit**	**Calcium**	**Magnesium**	**Potassium**	**Sodium**	**Bicarbonate**	**Chloride**	**Sulfate**	**Total dissolved solids**
Average	mg/L	52.2	18.3	14.2	697.9	465.6	641.9	464.6	3218
Standard Devation	mg/L	38.5	10.3	11.0	372.6	189.7	380.2	289.7	3017
Relativ Standard Devation	%	73.8	56.6	77.9	53.4	40.8	59.2	62.4	94
Median	mg/L	49.3	15.0	11.0	716.0	438.0	647.5	409.0	2050
Lower quartile	mg/L	16.5	11.0	7.0	375.0	395.5	350.0	301.6	1710
Upper quartile	mg/L	77.4	22.0	16.8	914.0	628.5	820.0	547.7	3112
Interquartile range	mg/L	60.9	11.0	9.8	539	233.0	470.0	246.1	1402
Quartile deviation	mg/L	30.5	5.5	4.9	269.5	116.5	235.0	123.1	701
Maximal value	mg/L	130.0	53.1	41.8	1860.0	700.3	1655.0	1463.0	13000
Minimal value	mg/L	10.0	7.8	1.0	7.0	55.0	20.0	120.0	237

All investigated hydrochemical properties of the groundwater of the "Paraná Aquifer" show a wide range of concentrations. The values of the individual parameters mostly spread over a range of one order of magnitude. Only the minimal and maxium value of magnesium got a differnce that is lower than one magnitude (sevenfold). The highest relative differnce between minimun and maximum value got sodium, the minimal value is about 266 times smaller than the maxium value. The highest absolut difference in concentration between different sampling points got total dissolved solids with 12763 mg/L. The wide range of the concentration can be seen also by the high relative standard devation, the lowest relative standard devation is 40.8 % for bicarbonate. Also the interquartile range, the difference between the upper and the lower quartile, implies the high variability of the concentration of the different sampling sites. The data sets of chloride, magnesium, sodium and sulfate each have one outlier, potassium three and total suspended solids four. The data quality seems to be low, but it has to be mentioned that the study area is very large and therefore the hydrochemical properties may change due to solving and dissolving interactions while flowing. Also, the sampling time of each groundwater sample is not known, but sampling at different times may lead to reduced data quality due to seasonal variations in hydrochemical properties. Because groundwater quality may undergo seasonal change[42]. Especially due to the very high standard deviation, also measurement or sampling errors can not be excluded.

Because of the wide range of the data is not meaningful only compare the mean value with the limits of the WHO, therefore also the median, maximal value, minimal value, the upper and the lower quartile will be take into account. Table 5 shows the limit for the investigated hydrochemical parameter as proposed by the World Health Organization.

Table 5: Investigated hydrochemical parameter, limits as proposed by the World Health Organization [14] [34] Guidelines from 2004 marked with *.

Parameter	**WHO Limit 2004/2011**
Bicarbonate*	200 mg/L
Calcium	75 mg/L
Chloride	250 mg/L
Magnesium	50 mg/L
Potassium*	100 mg/L
Sodium	200 mg/L
Sulfate	250 mg/L
Total dissolved solids	1200 mg/L

For bicarbonate only the minimum value with 55.0 mg/L is lower than the proposed limit value of 200 mg/L. Even the lower quartile is with 395.5 mg/L almost twice as much as the proposed limit. That means that at best 25 % of the samples fulfill the WHO standards. Therefore, water treatment is recommended for bicarbonate before the water can be used for drinking water supply.
Only the maximum 130.0 mg/L and the upper quartile 77.4 mg/L of the calcium concentrations exceed the limit of 75 mg/L. That means that about 75 % of the measured data fulfill the regulations, therefore for calcium the need of water treatment depends on the location of the drinking water supply well.
The threshold limit for chloride of 250 mg/L is only met by the minimum value of 20 mg/L. For example the average value of chlorine of 641.9 mg/L exceed the threshold limit about three times and the value of the lower quartile of 350 mg/L exceed the limit one point four times. This means that 75 % of the sampled data exceeded the limit of at least one point four times, therefore water treatment is recommended for chloride.
The maximum concentration value of magnesium 53.1 mg/L is the only value that exceed the WHO limit of 50 mg/L. Therefore, for magnesium water treatment is not necessarily recommended and it depends on the location of groundwater extraction.
Not even the maximum level of potassium exceeds the WHO limit. The maximum value of 41.8 mg/L is not even half of the suggested limit of 100 mg/L. Therefore, for potassium no water treatment is necessary and also it does not depend on the location of the drinking water supply well.
The minimal sodium concentration of 7.0 mg/L is the only concentration value that does not exceed the limit of 200 mg/L. The other values do exceed the limits for example the median value of 716.0 mg/L does exceed the limit about three point six times. That means that 50 % of the measured samples to exceed the limit at least about three point six times, therefore water treatment for sodium is strongly recommended before using the water for drinking water supply.
The limit for sulfate is 250 mg/L, only the minimum value of 120 mg/L does not exceed the limit. The mean value of 464.6 mg/L exceed the limit about two point three times and the lower quartile 301.6 mg/L about one point five times. That means that 75 % of the sample data exceed the limit at least for one point five times therefore water treament for sulfate is recommended.
For total dissolved solid only the minimum value of 237 mg/L does not exceed the limit of the WHO of 1200 mg/L. The second lowest total dissolved solids concentration is 1242 mg/L, see electronic appendix, 42 mg/L higher than the WHO limit. Since the minimum is almost one magnitude smaller than the subsequent value, the minimum may be an outlier. The maximum value of 13000 mg/L for the total dissolved solid concentration exceed the limit more than one magnitude. However it has to be mentioned that the maximum value seems to be an outlier. Nevertheless the lower quartile of the total dissolved solid concentration of 1710 mg/L exceed the limit of the WHO about one point four times. That means that at least 75 % of the measured data do not fulfill the regulations. Therefore for TDS water treatment is recommended before using the water for drinking water supply purpose.

In summary, comparing the the groundwater of the “Paraná Aquifer“ to the WHO-limits, the groundwater is not suitable for drinking water supply purposes without treatment. Only all statistical values of potassium and magnesium with deficiencies can be reconciled with the limits proposed by the WHO. On the other hand, it should be mentioned that there is no limit for the calcium concentration in the “German Drinking Water Ordinance“, as a high calcium concentration is not dangerous for humans [19]. However, a high calcium concentration affects the demands on the drinking water supply system[19]. Also it should also be mentioned that many chemicals that potentially endanger the quality of the groundwater are not included in this work. As well the potential hazard of microorganism is not considered. Because of these reasons water treatment is highly recommended even if the data is subject to a high degree of statistical uncertainty, for example the huge distance between the different wells, the unknown sampling times etc. However, water scarcity is being recognised as a present or future threat to human kind. Therefore, also alternatives such as desalination must be considered to ensure the drinking water supply [10].

4.2 Elevation of the “Paraná Formation“.

The results of the interpolation of the elevation of the top of the “Paraná Formation“ are important for different reasons. First it is important for the availability of groundwater, because the smaller the distance between ground and “Paraná Formation“ the more cost-efficient water can be taken from the “Paraná Formation“. This is because the pumping costs are lower due to the fact of less energy demand. It is assumed that the “Paraná Aquifer“ is also closer to the ground where the “Paraná Formation“ is also closer to the ground. Also the elevation of the “Paraná Formation“ is important for the results of the groundwater flow direction. Like shown in formula **??**, the inclination of the aquifer influence the groundwater flow direction.
The interpolation was done in the “Transverse Mercator projection“ in the sixth meridian strip of Argentina. The interpolation limits in x-direction are $6,129,026$ and $6,472,792$ and in y-direction $5,981,244$ and $6,772,615$, for more detail information see the grid report in the electronic appendix. A total of 6396 data were used for the interpolation, the data includes 378 wells and $6,018$ outcrops. The maximum height and depth of the interpolation, the resolution as well as the interpolated area are varying form the different interpolation methods and are described more in detail in the following. The quality of the different interpolation will be compared by the sum of squared residuals (SSR) and the coefficient of determination (R^2). The sum of squared residuals are determinted by the following equation:

$$SSR = \sum_{i=1}^{n}(Z_i - H_i)^2 \tag{5}$$

Here Z_i is the elevation at location i and H_i is the interpolated value at location i. The smaller the sum of the squared residuals, the better the interpolation is considered.
The coefficient of determination is determinted by the following equation:

$$R^2 = 1 - \frac{SSR}{SSD} \tag{6}$$

Here SSR is the sum of squared residuals and SSD is the sum of squares of the differences from the mean, which is calculated by the following equation:

$$SSD = \sum_{i=1}^{n}(Z_i - \bar{Z})^2 \tag{7}$$

Here Z_i is the elevation at location i and $\bar{Z}$ is the mean value of all elevations. $\bar{Z}$ the mean value of all elevations is $1,9343,29$, see electronic appendix.
Table 6 shows the relationship between the quality of interpolation and the coefficient of determination.

Table 6: Relationship between the quality of interpolation and the coefficient of determination [27].

Quality of Interpolation	**Coefficient of determination**
Excellent	$R^2 < 0.9$
Very good	$R^2 < 0.8$
Good	$R^2 < 0.7$
Poor	$R^2 < 0.5$

4.2.1 Universal Kriging

Figure 14 shows the results of the interpolation of the elevation of the top of the "Paraná Formation" in meter above sea level, done by the kriging interpolation method. The resolution of figure 14 is 20 m, the maxium depth that can be seen is between −100 m and −120 m above sea level and the maximal height is between 60 m and 80 m above sea level.

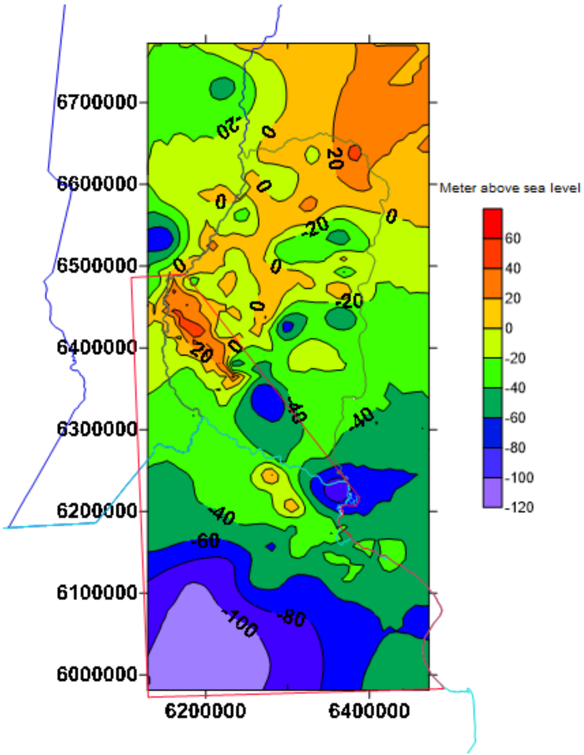

Figure 14: Interpolation of the elevation of the top of the "Paraná Formation" in meter above sea level done by the kriging interpolation method.

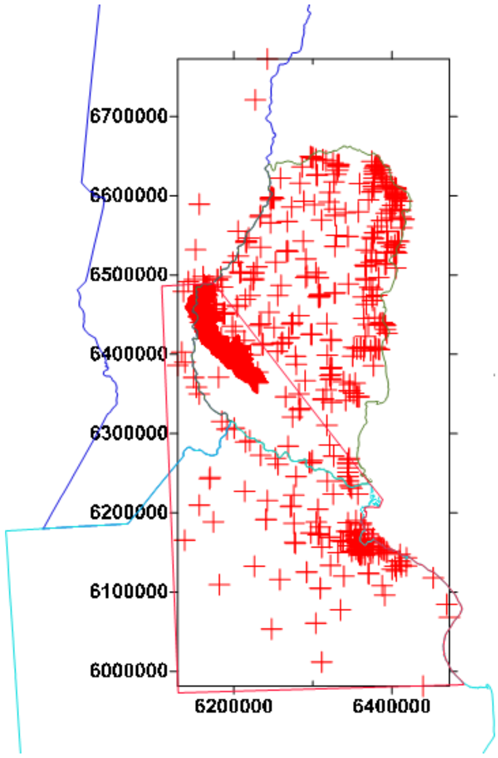

Figure 15: The vertices used for the interpolation of the top of the "Paraná Formation", including the 6018 outcrops and the 378 wells.

The interpolated area measured by "QGIS 2.18.14 Las Palmas" is about 273, 000 km^2 and so approximately 2.3 as big as the study area. For this reason, the interpolation exceeded the study area, but not only the study area was exceeded. As well the natural boundary of the "Paraná Formation" in the east of "Entre Ríos" was not considered by the interpolation. Also it has to be mentioned that not everywhere in the study area interpolation values exist, an area of about 6, 200 km^2 (about 5 % of the study area) was not considered by the interpolation. In the west, the south and the southeast are areas where no elevation of the "Paraná Formation" was interpolated.
The interpolated maximum elevation of the top of the "Paraná Formation" is about 55 m above sea level and the minimum value is about −110 m above sea level , see figure 14. The maximum value marked by the dark red color can be found outside and inside of the study area. Outside the study area is near or beyond the border of the "Paraná Formation" at location x about 6, 400, 000 and y about 6, 650, 000. Inside the study area the maximum value is located in the northwest of the study area nearby or equal to the location of the outcrops of the "Paraná Formation" at location x about 6, 200, 000 and y about 6, 420, 000. The absolut minimum of the "Paraná Formation" of −110 m is located in the southwest of the study area between x 6, 129, 026 and 6, 270, 000 and y 5, 981, 244 and 6, 100, 000.

There are serveral local minima and maxima inside and outside the study area. The local maxima which are inside the study area are two local maxima with a value between 0 m to 20 m marked by the yellow color, three local maxima with a value between −20 m to −40 m marked by the ligth green color and one a value between −40 m to −60 m marked by the dark green color. The two local maxima with the yellow color are located close to each other at x about 6, 280, 000 and y about 6, 270, 000, respectively at x about 6, 320, 000 and y about 6, 200, 000. These two maxima start as one maxima with a value between −20 m and 0 m and then culminate in the two individual maxima. The local maxima with the value between −20 m to −40 m are located at x about 6, 375, 000 and y about 6, 150, 000, x about 6, 400, 000 and y about 6, 170, 000 and x about 6, 425, 000 and y about 6, 150, 000. The local maxima with a value between −20 m to −40 m, which are located more eastern, are only partially inside the study area. The local maxima with a value between −40 m to −60 m in located in the southeast of the study area between x 6, 400, 000 and 6, 472, 792 and y 5, 981, 244 and 6, 050, 000.
There are four local minima in the study area, two of them are near the eastern border of the study area, one is in the center and one in the north. One local minima is between −40 m to −80 m shown by the dark green and blue color and one of the local minima is between −60 m to −100 m shown by the dark color and dark purple color, one is between −60 m to −80 m shown by the blue color and the other is between −40 m to −60 m shown by the dark green color. The local minimum with a value between −40 m to −80 m is located at x about 6, 275, 000 and y about 6, 325, 000. This local minima is only partially inside the study area. Nevertheless it has to mentioned that the bigger part of the local minima is inside the study area. The local area with a value between −60 m to −100 m is also only partially located in the study area and located at x about 6, 360, 000 and y about 6, 225, 000. The local minima with a value between −60 m to −80 m is located at x about 6, 280, 000 and y about 6, 160, 000. The local minima with a value between −40 m to −60 m is located at about 6, 240, 000 and y about 6, 380, 000
The difference of the interpolated elevation between the maxima of the study area and northwest border is between 60 m and 100 m. The by “QGIS 2.18.14 Las Palmas“ approximated distance between the center of the maxima and the northwest intersection of the study area and the interpolation is about 77 km. That means that the average inclination in the northwest direciton of the top the “Paraná Formation“ is between 0.08 % and 0.13 %. The difference of the interpolated elevation between the maxima of the study area and minima of the elevation in the southwest of the studyarea is between 140 m and 180 m. The by “QGIS 2.18.14 Las Palmas“ approximated distance between the center of the maxima and the southwest intersection of the study area and the interpolation is about 456 km. That means that the average inclination in the southwest direction of the top the “Paraná Formation“ is between 0.03 % and 0.04 %.
The sum of squares of the differences from the mean is 1, 934, 329 and the sum of squared residual for the kriging interpolation method is 647, 693, therefore the coefficient of determination is 0.888, see electronic appendix. If the coefficient of determination is compared to table 6, it indicates a very good interpolation.

4.2.2 Local Polynomial

Figure 16 shows the results of the interpolation of the elevation of the top of the "Paraná Formation" in meter above sea level, done by the local polynomial interpolation method. The resolution of figure 16 is 25 m, the maxium depth that can be seen is −170 m above sea level and the maximal height is 95 m above sea level.

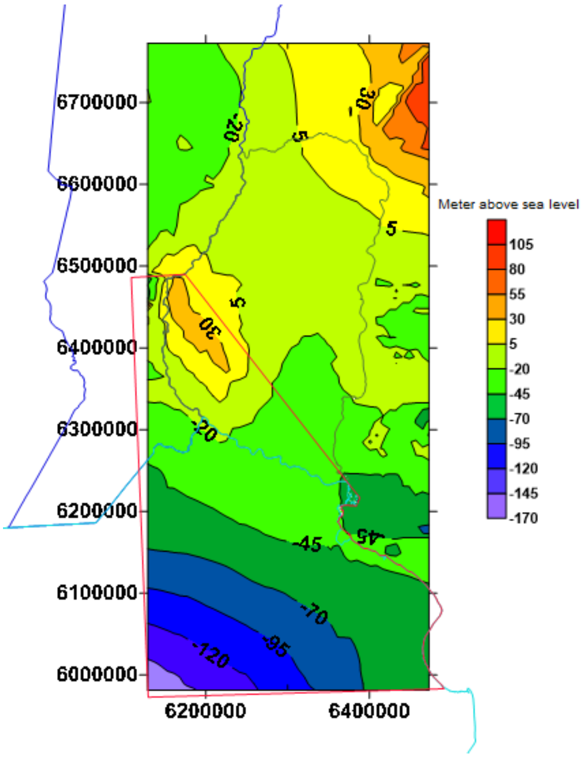

Figure 16: Interpolation of the elevation of the top of the "Paraná Formation" in meter above sea level done by the local polynomial interpolation method.

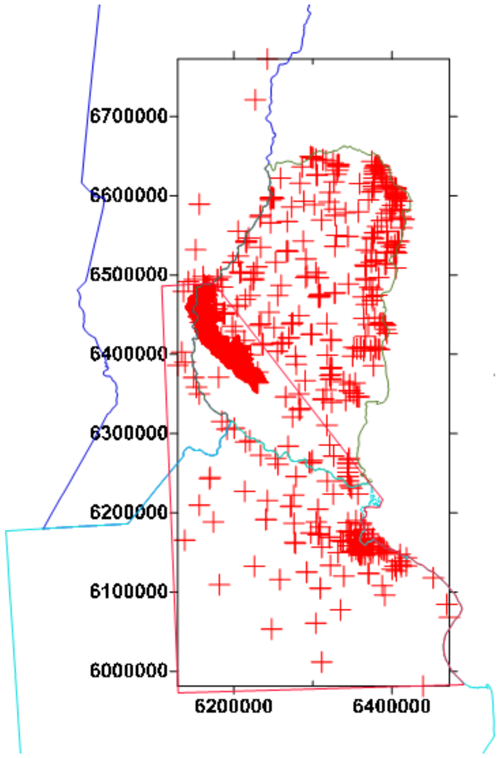

Figure 17: The vertices used for the interpolation of the top of the "Paraná Formation", including the 6018 outcrops and the 378 wells.

Like for the kriging method, the interpolated area measured by "QGIS 2.18.14 Las Palmas" is about 273, 000 km^2 and so approximately two point three as big as the study area. For this reason, the interpolation exceeded the study area, but not only the study area was exceeded. As well the natural boundary of the "Paraná Formation" in the east of "Entre Ríos" was not considered by the interpolation. Also it has to be mentioned that not everywhere in the study area interpolation values exist, an area of about 6, 200 km^2 (about 5 % of the study area) was not considered by the interpolation. In the west, the south and the southeast are areas where no elevation of the "Paraná Formation" was interpolated.
The maximum interpolation value of the top of the "Paraná Formation" is about 103 m above sea level and the minimum is about −161 m above sea level, see electronic appendix. The maximum value which is marked by the dark red color, can only be found outside the study area. The maximum value is not only outside the study area is also beyond the east border of the "Paraná Formation" in the department of "Entre Ríos". The coordinates of the loaction of the maximum are approximately x 6, 400, 000 and y 6, 700, 000. Outside the study area, there can be found several local maxima and minima respectively.

In the study area the maximum value is between 30 m and 55 m marked with the light orange color. The maximum value is located in the north of the study area, where the outcrops are located, the coordinates are x 6, 175, 000 and y 6, 450, 000. In the study area no local maxima exist and only one local minima. The local minima is located in the east of the study area at x 6, 375, 000 about and y about 6, 250, 000. The larger part of the local minima is outside the study area and it is between −45 m and −70 m above sea level.
In the northwest of the study area are two minima with a value between −45 m and −70 m highlighted with the light green color. The loaction of these minima are x 6, 129, 026 and y 6, 375, 000 an then x 6, 129, 026 and 6, 475, 000 respectively . Due to the proximity of these minima it could be that they are actually only one, but because of the limit of the interpolation they appeared as two. The absolute minimum value is located in the southwest of the study area and is between −145 m and −170 m above sea level. The location of the absolute minima is approximately at x between 6, 129, 026 and 6, 200, 000 and y between 5, 981, 244 and 6, 030, 000.
The distance between the center of the maxima in the study area and the intersection between the border of the study area and the interpolation is about 75 km. The height difference of the maximun and the lowest value in the northwest of the study area is between 75 m and 125 m, therefore the average inclination of the "Paraná Formation" in northwest direction is between 0.10 % and 0.17 %.
The distance between the maxima of the study area and the minimum in the southwest is approximately 308 km. The height difference between the maxima and the minima in the southwest is between 175 m and 225 m. Therefore, the average inclination of the "Paraná Formation"is between 0.06 % and 0.07 %.
The sum of squares of the differences from the mean is 1, 934, 329, the sum of squared residual for the local polynomial interpolation method is 486, 533 therefore the coefficient of determination is 0.937, see electronic appendix. If the coefficient of determination is compared to table 6, it indicates an excellent interpolation.

4.2.3 Natural neighbor

Figure 18 shows the results of the interpolation of the elevation of the top of the "Paraná Formation" in meter above sea level, done by the natural neighbor interpolation method. The resolution of figure 18 is 20 m, the maxium depth that can be seen is −120 m above sea level and the maximal height is 80 m above sea level.

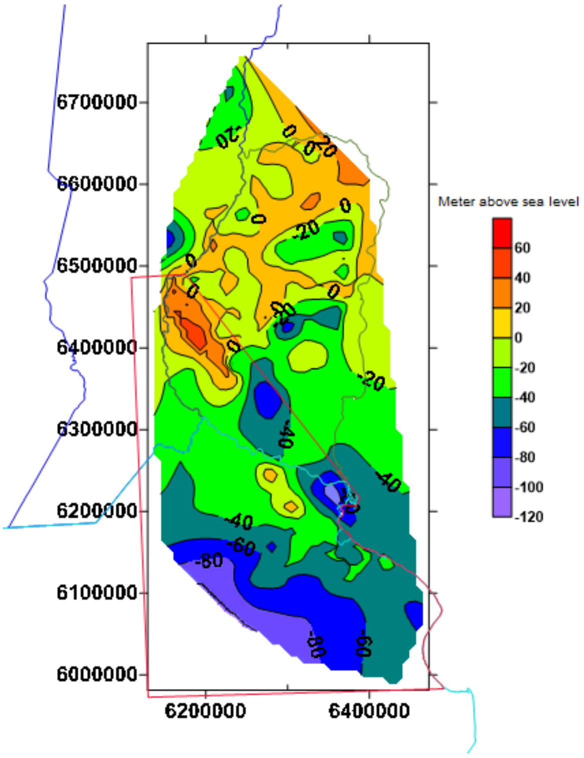

Figure 18: Interpolation of the elevation of the top of the "Paraná Formation" in meter above sea level done by the natural neighbor interpolation method.

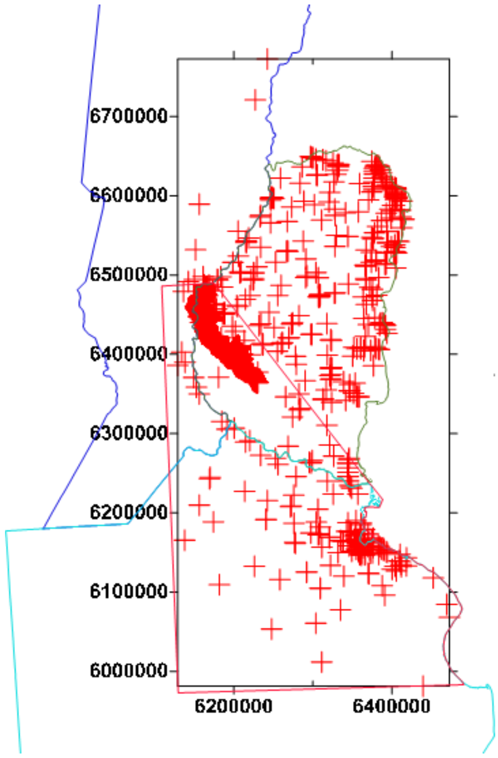

Figure 19: The vertices used for the interpolation of the top of the "Paraná Formation", including the 6018 outcrops and the 378 wells.

Unlike the other interpolations, the result of "natural neighbor" is not rectangular shaped and also the interpolated area of interpolation is smaller. The interpolated area is about 183, 000 km^2 and therefore one point five times as big as the study area. Because the interpolation area is bigger than the study area, the interpolation exceeds the limits of the study area. But not only the limit of the study area was exceeded also the border of the "Paraná Formation" was exceeded. However it has to be menitoned that over 25 % (about 33, 000 km^2) of the study area has no interpolation values. The areas were no interpolation value exist are in the west, south and east.
The interpolated maximum altitude of the top of the "Paraná Formation" is about 55 m above sea level and the minimum altitude is about −102 m above sea level, see electronic appendix. The maximum value between 40 m and 60 m is located in the study area. It is marked with the dark red color that can be found at the location x about 6, 175, 000 and y about 6, 425, 000. The minimum value between −100 m and −120 m can be found at the southwest of the interpolation and is marked with the light purple color. The minimum is located at x about 6, 225, 000 and y about 6, 075, 000.
There are several local maxima and minima inside and outside the of the study area. There are three local maxima in the study area, two with a value between 0 m and 20 m, marked with the yellow color

and one with a value between −40 m and −20 m marked with the light green color. The two local maxima with a value between 0 m and 20 m are located close to each other at x about 6, 290, 000 and y about 6, 250, 000 and at x about 6, 310, 000 and y about 6, 200, 000 respectively. These two maxima start as one maxima with a value between −20 m and then culminate in the two individual maxima. The other maximum with a value between −40 m and −20 m is located at x about 6, 420, 000 and y about 6, 140, 000 and is close to the eastern border of the study area.
The local minimum with a value between −40 m and −80 m is located at x about 6, 280, 000 and y about 6, 350, 000. The minimum at this location is only partially in the study area. The two local minima with a value between −60 m and −80 m are located at x about 6, 280, 000 and y about 6, 160, 000 and then 6, 270, 000 and y about 6, 450, 000 respectively. The local maximum with a value between −60 m and −100 m at x about 6, 360, 000 and y about 6, 230, 000 the local minima is only partially in the study area.
The distance between the center of the maximum in the north of the study area and the intersection of the interpolation and the study area is about 78 km. The height difference between the maximum and this location is between 40 m and 80 m. Therefore, the average inclination of the “Paraná Formation“ in northwest direction is between 0.05 % and 0.10 %.
The distance between the maxima and the absolute minima in the study area is about 329 km and the height difference is between 140 m and 180 m. Therefore, the average inclination of the “Paraná Formation“ in southwest direction is between 0.04 % and 0.05 %.
The sum of squares of the differences from the mean is 1, 934, 329 the sum of squared residual is 535, 550 therefore the coefficient of determination is 0.923, see electronic appendix. If the coefficient of determination is compared to table 6, it indicates an excellent interpolation.

4.2.4 Conclusion

If the sum of the residuals and the coefficient of determination of the different interpolation methods (kriging, local polynominal and natural neighbor) are compared, the different methods can be considered as almost equally good. The coefficients of determination are between 0.888 and 0.937 which indicates very good to excellent interpolations. However, it has to mentioned that due to fact of the unevenly distribution, the interpolation of some areas are more reliable. That can be seen by a comparsion between the average area for different parts of the study area. For example, if the average area in square kilometer represented by a data point in the area of the outcrops and in the southwest of the study area are compared, it is noticeable that a data point in the area of the outcrops represents 87, 000 times smaller area.

If the results of the different interpolation methods are compared, several differences can be noticed. Especially the result of the interpolation method local polynomial differs from the other interpolation methods. For example, the result of the local polynomial interpolation has only one local minima and no local maxima in the study area. The other interpolation have both, more local minima and also local maxima. Also the absolute maxima of the local polynomial interpolation are much higher and the absolute minima value are much lower than for the other interpolation methods. The absolute maxima value of the local polynomial with about 103 m above sea level is about two times higher than the absolute maxima of the other interpolations with about 55 m above sea level. The maximum measured elevation of the "Paraná Formation" is 67 m above sea level and thus approximately 22 % higher than the maximum interpolation values of the methods kriging and natural neighbor. The maximum value of local polynomial is about 54 % higher than the maximum measured elevation. Also the location of the absolute maximum value of the local polynomial interpolation is different than the other interpolation methods. Nevertheless is has to be mentioned as well the location as the range of the maximum value inside the study area is for all interpolation methods similar or equal. The location of the maximum value is equal to the location of the outcrops.

Also the absolute minimum value differs form the different interpolation methods. For kriging the absolute minimum value is −110 m above sea level, for local polynomial is −161 m above sea level and for natural neighbor is −102 m above sea level. The difference between kriging and natural neighbor can be neglected because the difference is only about 10 % which is fair enough for an interpolation. The difference between local polynomial and the other is much higher. Also the diffence between the minimal measured elevation and the local polynomial interpolation is higher than the other interpolations. The minimum measured elevation of the "Paraná Formation" is −117 m above sea level. Therefore, the absolute minima of the kriging interpolation is about 5 % lower than the measured minimum elevation, the absolute minima of the natural neighbor interpolation is about 13 % lower than the measured minimum elevation and the absolute minima of the local polynomial interpolation is about 38 % higher than the measured minimum elevation. However, it has to be mentioned that the location of the absolute minima is the same. The location of the absolute minimum value is in the southwest of the study area.

The most obvious difference betweeen the natural neighbor and the other interpolation is that the interpolated area is smaller than the interpolated areas of kriging and local polynomial respectively. The interpolated area of the natural neighbor interpolation is about 183, 000 km^2 and the area of the interpolation methods kriging and local polynomial are 273, 000 km^2. The interpolated areas of kriging and local polynomial is about 49 % bigger than the interpolated area of natural neighbor.

However, there are also properties of the interpolations which are similar or equal, especially when comparing the results of kriging and natural neighbor interpolation. Like mentioned before, the location of the maximum and the minium in the study area are equal. Comparing the interpolation methods kriging and natural neighbor, the location and elevation of some local maxima and local minima are also similar. Good examples for this is the local minima with a value between −60 m

and -80 m above sea level located at x about 6, 280, 000 and y about 6, 160, 000 or the two local maxima which start as one maxima with a value between -20 m and 0 m and then culminate in the two individual maxima with a value between 0 m and 20 m. These maximas are located at x about 6, 300, 000 and y about 6, 250, 000.
Also the average inclinations in the directions northwest and southwest are similar. The estimated average inclination in northwest direction is between 0.05 % and 0.17 %. The estimated average inclination in southwest direction is between 0.03 % and 0.07 %. Both of the average inclination towards northwest and southwest are very small. Both average inclinations are much less than one percent.
Because of these similarities the in figure 20 elevation of the “Paraná Formation“ is suggested. The resolution of figure 18 is 20 m, the maxium depth that can be seen is -120 m above sea level and the maximal height is 60 m above sea level.

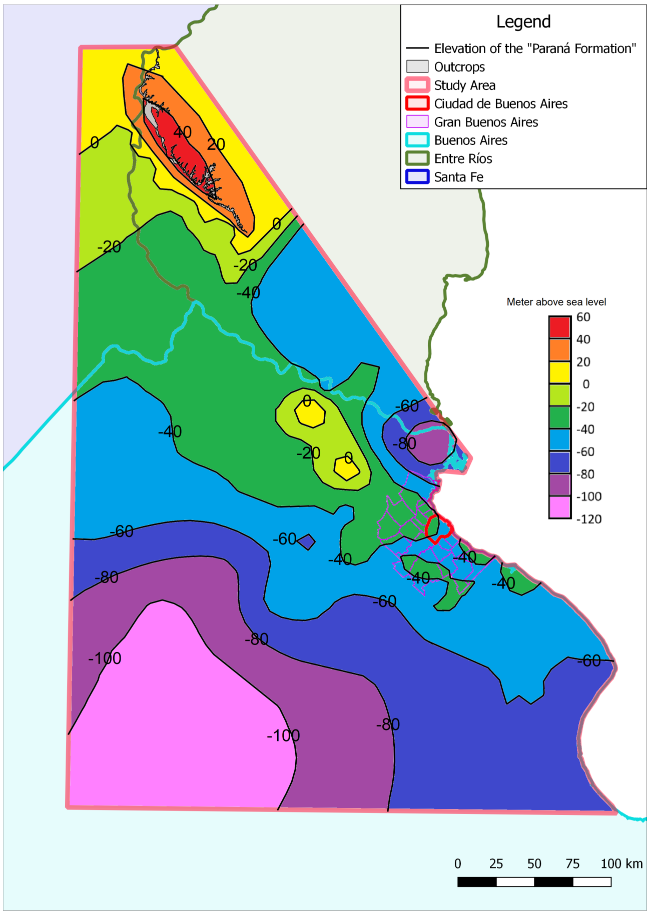

Figure 20: Supposed elevation of the top of the “Paraná Formation“ in meter above sea level.

The outcrops in “Entre Ríos“ are the highest elevation of the “Paraná Formation“ in the study area. The maximum elevation is between 40 m and 60 m and marked with the red color. A part of the outcrops are between 20 m and 40 m marked with the orange color. In the north of the study area, there are even some outcrops that are between 0 m and 20 m. Also at the northern border of the study area the elevation of the “Paraná Formation“ is between 0 m and 20 m.
The minimum elevation of the “Paraná Formation“ is in the southwest of the study area and has a value between -100 m and -120 m and is marked with the light purple color.
There are several local maxima and local minima in the study area. Three local maxima with a value

between −20 m and −40 m are located in the area of “Gran Buenos Aires“ and marked with the dark green color. The two local maxima which starts as one maxima with a value between −20 m and 0 m and then culminate in the two individual maxima with a value between 0 m and 20 m are in the northeast of the department of “Buenos Aires“.
There are two local minima in the study area, one with an elevation between −60 m and −100 m is located in the east of the study area in the border region between “Buenos Aires“ and “Entre Ríos“. The other is roughly in the center of the study area with an elevation between −60 m and −80 m.
The distance between the center of the maxima and the northwest conor of the study area is about 100 km and the difference of the elevation is between 20 m and 60 m. Therefore, the average inclination in northwest direction is between 0.02 % and 0.06 %. The distance between the absolute maxima in the north and the absolute minima in the southwest is about 310 km and the difference of the elevation is between 140 m and 180 m. Therefore, the average inclination in southwest direction is between 0.05 % and 0.06 %.
In addition it has to be mentioned that an interpolation of the top of the “Paraná Formation“ only allows limited conclusions to the “Paraná Aquifer“. This is because sometimes the formation occurs incomplete and the sand layer of the “Paraná Formation“ do not appear in the subsurface, where the green clay layer occurs. Also the thickness of the individual layers of the “Paraná Formation“ varies at different locations and therefore the conclusions from the elevation of “Paraná Formation“ to the elevation of the “Paraná Aquifer“ are even more difficult and uncertain. As well the depth of the “Paraná Formation“ could be due to the topograpy of the overlaying land higher than the elevation.
Nevertheless, groundwater that is even located at a depth of several hundreds of meters is used for drinking water supply purposes [22]. Therefore, it is likely that the water from the “Paraná Aquifer“ can be exploited.

4.3 Groundwater flow direction

The results for the groundwater flow direction is important to determine the recharge zone of the “Paraná Aquifer“. The recharge zone of an aquifer is the starting point of the groundwater flow and is important for the management of groundwater. The location of this point is modeled by two different interpolation methods and two different approaches. The interpolation methods are kriging and natural neighbor.
The first approach is the interpolation of the hydraulic head and the second is the evolution of hydrochemical properties in an aquifer. For the first appraoch, the modeling of the hydraulic head of 18 wells was performed. For the second approach, two different hydrochemical pattern were used. First the distribution of the concentration of potassium in the study area was modeled, therefore 24 wells were used. If there is no pollution, the potassium concentration developes from a high to a low concentration in the direction of the groundwater flow [24]. Than the distribution of the total dissolved solid concentration in the study area was modeled, therefore 27 wells were used. The total dissolved solid concentration developes from a low to a high concentration in the direction of groundwater flow[24].
The interpolation was done in the “Transverse Mercator projection“ in the sixth meridian strip of Argentina. The interpolation limits and the interpolated area are varying for the different interpolation approaches and are described more in detail in the following.
The quality of the different interpolation will be compared by the sum of squared residuals (SSR) and the coefficient of determination (R^2) which are explained in section 4.2.

4.3.1 Universal Kriging

4.3.1.1 Modelling of the groundwater flow direction by hydraulic head.

Figure 21 shows the kriging method interpolated hydraluic head in 0 m and the deriven groundwater flow direction. The maximum hydraulic head that can be seen in this figure is 47.5 m, the minimum hydraulic head is 0 m and the resolution is 2.5 m.

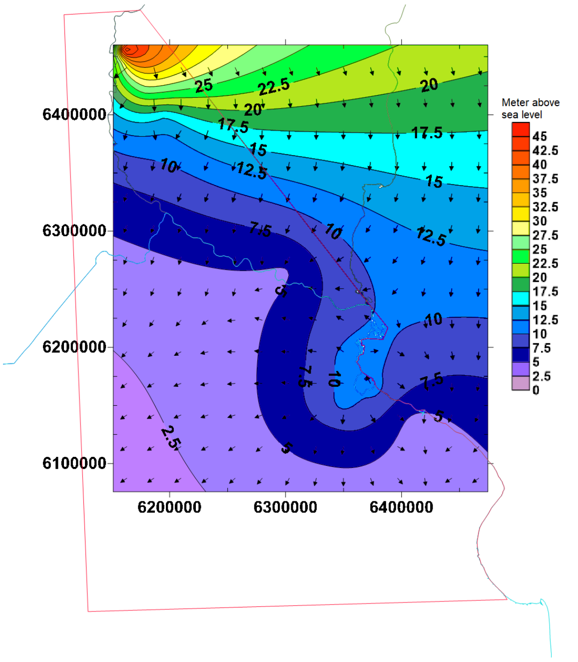

Figure 21: The contour map and proposed groundwater flow direction modeled by the kriging method from the hydraulic head data.

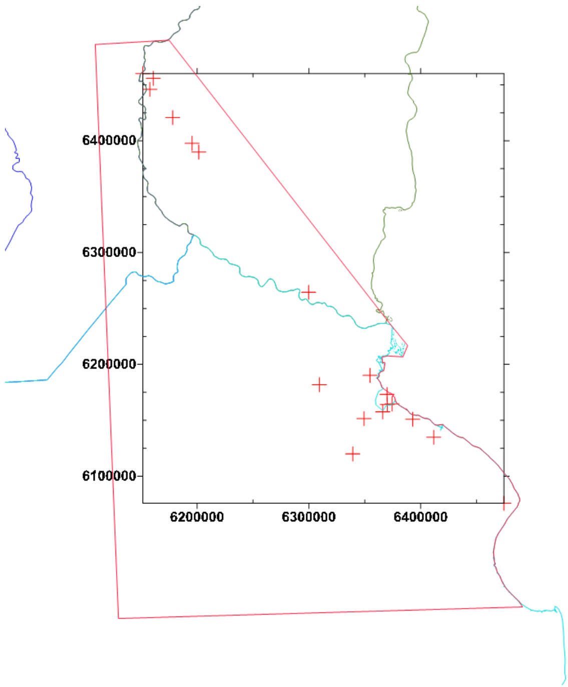

Figure 22: The vertices used for the interpolation of the hydraulic head contour map and the dirven groundwater flow direction.

The interpolation was done with 18 wells in the limits of x between 6, 151, 407 and 6, 474, 439 and y between 6, 075, 817 and 6, 460, 052. The interpolation is rectangular shaped and has an area of 125, 000 km^2. Therefore the interpolated area is 5, 000 km^2 bigger than the study area. However in the study area about 54, 000 km^2 (45 %) has no interpolation values. Also it has to be mentioned that in the east, the interpolation values not only exceeded the study area but also the border of the "Paraná Formation".

The interpolated maximum value of the hydraulic head is 46.5 m and the interpolated minimum value is 1.3 m, see electronic appendix. The interpolated maximum hydraulic head can be found in the north of the study area at x about 6, 175, 000 and y about 6, 460, 000 at the same location like the outcrops. The interpolated minimum hydraulic head can be found in the southwest of the study area at a location x between 6, 151, 407 and 6, 225, 000 and y between 6, 075, 817 and 6, 200, 000. The maximum and the minimum of the hydraulic head are more or less perpendicular to each other.

The distance measured by "QGIS 2.18.14 Las Palmas" between the maximum hydraulic head isoline of 45 m to the the minimum hydraulic head isoline of 2.5 m is about 325 km and therefore the average hydraulic gradient in southern direction is $-0.13\,{}^{\text{m}}/_{\text{km}}$. But it has to be mentioned that the hydraulic gradient in the north is much higher than in the south. The by "QGIS 2.18.14 Las Palmas" measured

distance between the maximum hydraulic head isoline and the perpendicular point on the hydraulic head isoline of 10 m is about 91 km. The derived hydraulic gradient in southern direction is $-0.38\,\mathrm{m/km}$ and therefore two point nine times as high as the average hydraulic gradient. The perpendicular distance from the same point on the hydraulic head isoline of 10 m to the the hydraulic head isoline of 2.5 m is about 234 km. Therefore, the hydraulic gradient is $-0.03\,\mathrm{m/km}$ and therefore four times smaller than the average hydraulic gradient. In the east of the study area at x between about 6,350,000 and 6,450,000 and y between about 6,150,000 and 6,240,000 is a local maxima which influence also the interpolated groundwater flow direction. The distance between the hydraulic head isoline of the local maxima with a value of 10 m and the minimum hydraulic head isoline with a value of 2.5 m is approximately 167 km. The derived hydraulic gradient is $-0.04\,\mathrm{m/km}$ to the southwest. Therefore, in this region the interpolation suggests a southwest groundwater flow direction. However, the interpolation suggests a predominantly south-facing groundwater flow direction. Additionally, if the results of the elevation of the "Paraná Formation" is considered then it has to be noted that the inclination of the "Paraná Formation" and the groundwater flow direction are similar. Even if the groundwater flow direction and the inclination of an aquifer does not have to match, as equation **??** shows, this match can be used as an indication of the correctness of the interpolation of the groundwater flow direction. If the highest hydraulic head is considered as recharge zone of the "Paraná Aquifer" the interpolation suggested that the recharge area is located at the location of the outcrops.
The sum of squares of the differences from the mean is 1,974 and the sum of squared residual for the kriging interpolation method is 21 therefore the coefficient of determination is 0.989, see electronic appendix. If the coefficient of determination is compared to table 6, it indicates an excellent interpolation.

4.3.1.2 Modelling of the groundwater flow direction by evolution of potassium concentration.

Figure 23 shows the kriging method interpolated, potassium concentration in mg/L and the deriven groundwater flow direction. The maximum potassium concentration that can be seen in this figure is 38 mg/L, the minimum potassium concentration is 0 mg/L and the resolution is 4 mg/L.

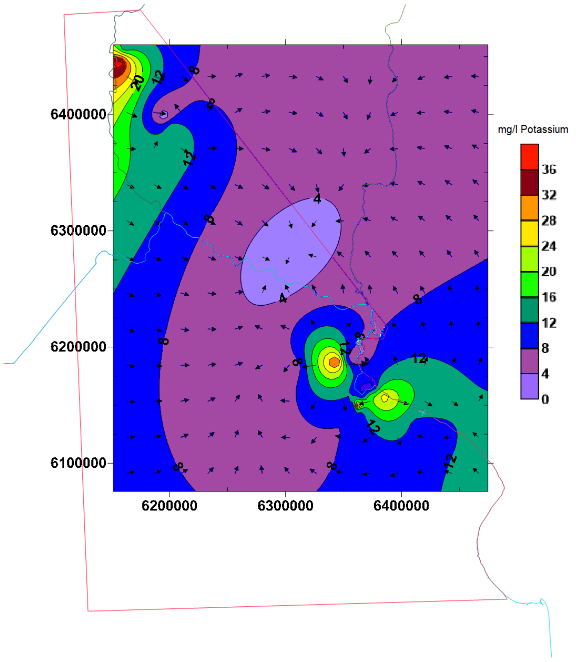

Figure 23: The interpolated distrubtion of the potassium concentration and the therefore dirven groundwater flow direction.

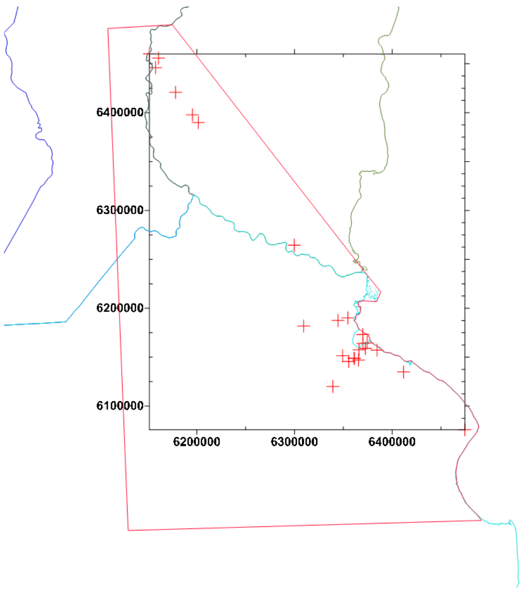

Figure 24: The vertices used for the interpolation of the distrubtion of the potassium concentration and the dirven groundwater flow direction.

Like for the interpolation of the groundwater flow direction by hydraulic head the interpolation was done in the limits of x between 6,151,407 and 6,474,439 and y between 6,075,817 and 6,460,052, but there were 24 wells used for the interpolation. The interpolation is rectangular shaped and has an area of 125,000 km². Therefore the interpolated area is 5,000 km² bigger than the study area. However in the study area about 54,000 km² (45 %) has no interpolation values and the interpolation exceed the eastern border of the "Paraná Formation". If the interpolated area was considered, a well represents an average area of about 5,210 km² that is about two times the Saarland. If only the interpolated area in the study area was considered, a well resprents an average area of about 2,750 km² that is about one point one times the Saarland.
The interpolated maximum potassium concentration is 37.4 mg/L and the interpolated minimum potassium concentration is 1.1 mg/L. The interpolated maximum potassium concentration can be found at x about 6,160,000 and y about 6,440,000. The interpolated minimum potassium concentration could be found in two locations, at x about 6,200,000 and y about 6,400,000, and x between 6,260,000 and 6,350,000 y between 6,235,000 and 6,325,000. Whether both or only one of these sites actually contains the minimum interpolated potassium concentration it can not be precisely determined due to the resolution in figure 23. Also it has to be mentioned that a part of the area at x betwenn 6,260,000 and 6,350,000 y between 6,235,000 and 6,325,000 with a potassium concentration between 0 mg/L and 4 mg/L is outside the study area. Also there are three local maxima near by the "Ciudad Autónoma

de Buenos Aires". The first local maxima with a potassium concentration between 32 mg/L and 36 mg/L is located at x about 6, 360, 000 and y about 6, 150, 000, the second local maxima with a potassium concentration between 28 mg/L and 32 mg/L is located at x about 6, 340, 000 and y about 6, 190, 000 and the last local maxima with a potassium concentration between 24 mg/L and 28 mg/L is located at x about 6, 385, 000 and y about 6, 160, 000.
The interpolation done by the kriging method of the potassium concentration indicates two different groundwater flow direction from individual starting points and therefore recharge zones. The first recharge zone is the absolute maxima located at the outcrops and ends in the two individual minima. Since the two minima are closed area, they represent a sink or a storage of groundwater because from them no further groundwater flow occurs. However, the indicated groundwater flow from the outcrops is directed predominantly southeast. The other recharge zone is located near the "Ciudad Autónoma de Buenos Aires" and indicated by the local maxima. The indicated groundwater flow from the local maxima is directed predominantly nortwest and therefore in the opposite direction as the indicated groundwater flow from the outcrops.
Nevertheless, it has to be mentioned that the "Paraná Formation" at this location does not have contact to the surface. Therefore, no simple explanation for the recharge mechanism in this area can be found. Additionally, potassium is one of the major ions and a widespread fertilizer [39] and a common indicator for pollution due to human activity like intensive agriculture[37]. Due to this fact, pollution could influence the potassium concentration and therefore the result of the interpolation.
The sum of squares of the differences from the mean is 2, 810 and the sum of squared residual for the kriging interpolation method is 571, therefore the coefficient of determination is 0.797, see electronic appendix. If the coefficient of determination is compared to table 6, it indicates a good interpolation.

4.3.1.3 Modelling of the groundwater flow direction by evolution of total solved solids.

Figure 25 shows the kriging method interpolated total solved solids concentration in mg/L and the deriven groundwater flow direction. The maximum total solved solids that can be seen in this figure is 14000 mg/L, the minimum total solved solids is 0 mg/L and the resolution is 1000 mg/L.

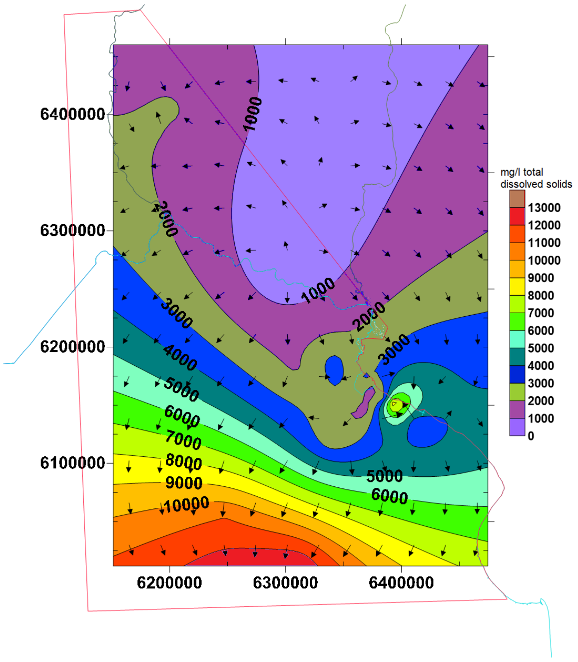

Figure 25: The interpolated distrubtion of the total dissolved solids concentration and the therefore dirven groundwater flow direction.

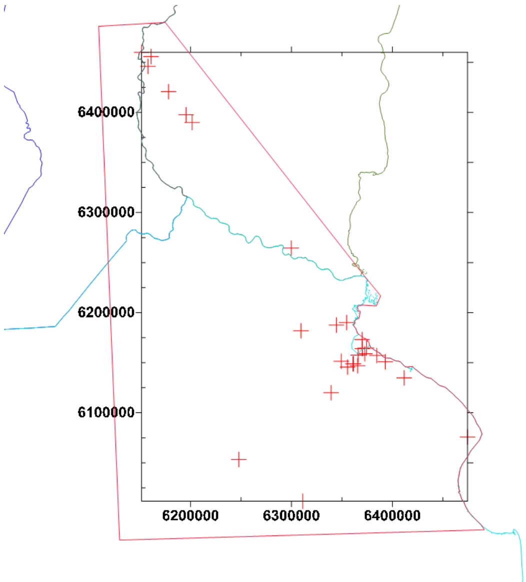

Figure 26: The vertices used for the interpolation of the distrubtion of the total dissolved solids and the dirven groundwater flow direction.

The interpolation was done with 27 wells in the limits of x between 6, 151, 407 and 6, 474, 439 and y between 6, 011, 640 and 6, 460, 052. The interpolation is rectangular shaped and has an area of about 145, 500 km^2. Therefore, the interpolated area is about 25, 500 km^2 bigger than the study area. However, in the study area about 28, 000 km^2 (23 %) has no interpolation values. Also it has to be mentioned that in the east the interpolation values does not only exceed the study area but also the border of the “Paraná Formation“.

The maximal interpolated total dissolved solid concentration is 12992 mg/L and the minimum interpolated total dissolved solid concentration is 257 mg/L. The interpolated maximum total dissolved solids concentration is located at x between 6, 215, 000 and 6, 330, 000 and y between 6, 011, 640 and 6, 015, 000. The minimum of the interpolated total dissolved solids is only partially in the study area. It exceeded as well the limit of the study area as the limit of the “Paraná Formation“. In the study area it is located at x between 6, 250, 000 and 6, 350, 000 and y between 6, 240, 000 and 6, 375, 000. In the study area, there are also three local maxima and two local minima located. All the local maxima and local minima are located in the east of the study area near the “Ciudad Autónoma de Buenos Aires“. The exact locations of the local maxima with a total dissolved solid concentration between 3000 mg/L and 4000 mg/L are x about 6, 370, 000 and y about 6, 175, 000 and x about 6, 345, 000 and y about 6, 180, 000 respectively. The local maxima starting with a value of 5000 mg/L and increasing to a value between 8000 mg/L and 9000 mg/L is located at x about 6, 390, 000 and y about 6, 150, 000. The local minima with a total dissolved solids concentration between 1000 mg/L and 2000 mg/L is located at

x about 6, 150, 000 and y about 6, 370, 000 and the other minima with a total dissolved solids concentration between 3000 mg/L and 4000 mg/L is located at x about 6, 420, 000 and y about 6, 130, 000.
In contrast to the potassium concentration, the total suspended solids concentration increases in the flow direction. Therefore, the interpolated groundwater recharge zone is located where the lowest total dissolved solids concentration is located. The predominant groundwater flow direction is therefore south facing from the absolute minimum to the absolute maximum. On the other hand, the local maxima near the “Cuidad Autónoma de Buenos Aires“ are supposed to be sink or storage of the groundwater, because from there no further groundwater flow occurs. The local minima can be considered as additional sources of water for the Paraná Aquifer. Nevertheless, it seems that the local minima do not influence the groundwater flow directon.
Also it has to be mentioned that unlike the other interpolation approaches, the location of the groundwater recharge zone does not overlap with the outcrops of the “Paraná Formation“ in the department of “Entre Ríos“. The location of the minimum total dissolved solids concentration is located in the middle east of the study area. Therefore, this interpolation suggests that the groundwater recharge zone is located there. Also it has to be mentioned, that it seems that the minimum total dissolved solids concentration between 0 mg/L and 1000 mg/L exceeds the limit of the interpolation. Therefore it could be that the recharge zone is located outside the interpolated area.
Like for the potassium concentration, the concentration of total dissolved solids can be influenced by fertilizer [39]. Total dissolved solids is a sum parameter for cations and anions[28] and some of this ions are used for fertilization. If the total dissolved solids concentration is influenced by pollution then the interpolated groundwater flow direction is influenced as well.
However if the results of the elevation of the “Paraná Formation“ is considered and the the inclination of the “Paraná Formation“ is compared to the predominat groundwater flow direction both are southfacing. Even if the groundwater flow direction and the inclination of an aquifer does not have to match, as equation **??** shows, this match can be used as an indication of the correctness of the interpolation of the groundwater flow direction.
The sum of squares of the differences from the mean is 236, 591, 461 and the sum of squared residual for the kriging interpolation method is 1, 643, 225, therefore the coefficient of determination is 0.993, see electronic appendix. If the coefficient of determination is compared to table 6, it indicates an excellent interpolation.

4.3.2 Natural neighbor

4.3.2.1 Modelling of the groundwater flow direction by hydraulic head.

Figure 27 shows the natural neighbor method interpolated hydraluic head in 0 m and the deriven groundwater flow direction. The maximum hydraulic head that can be seen in this figure is 45 m, the minimum hydraulic head is 2.5 m and the resolution is 2.5 m.

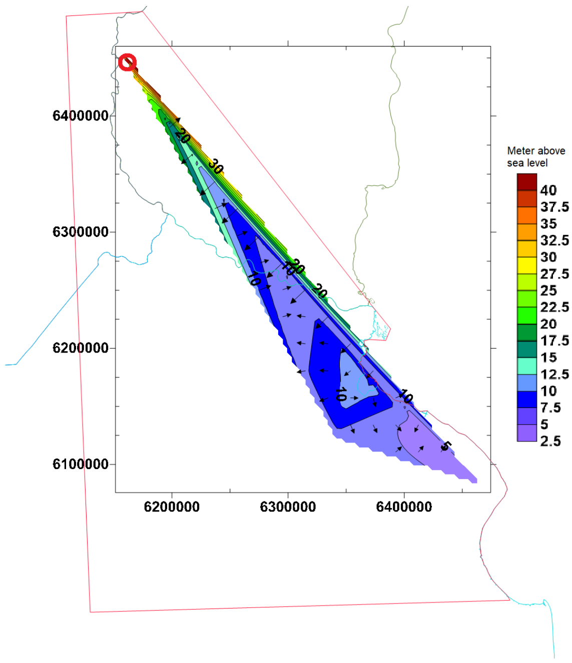

Figure 27: The contour map and proposed groundwater flow direction modeled by the natural neighbor method from the hydraulic head data.

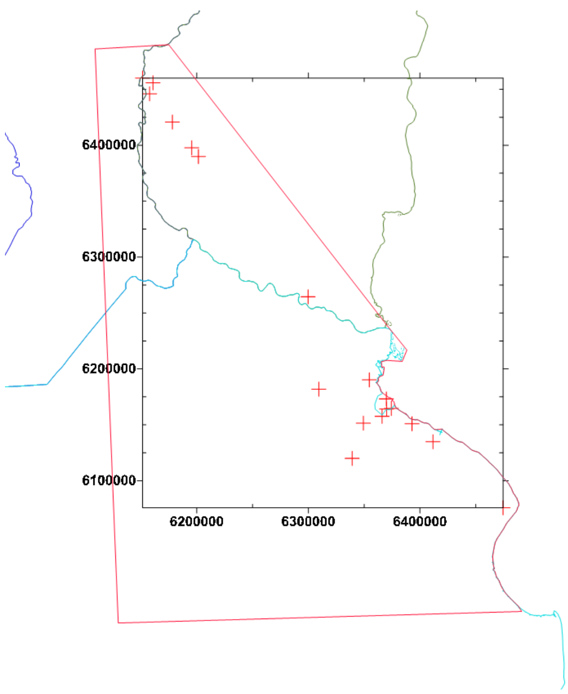

Figure 28: The vertices used for the interpolation of the hydraulic head contour map and the dirven groundwater flow direction.

The interpolation was done with 18 wells in the limits of x between 6, 151, 407 and 6, 474, 439 and y between 6, 075, 817 and 6, 460, 052. The interpolation has an area of about 17.000 km^2 but it has to be mentioned that about 600 km^2 of the interpolated area are outside the study area. Therefore only 16.400 km^2 (about 14 %) of the study area is represented by the interpolation.
The natural neighbor interpolated maximum hydraulic head is 42.2 m and the interpolated minimum hydraulic head is 4.0 m. The interpolated maximum hydraulic head(highlighted with the red circle) is located at x about 6, 160, 000 and y 6, 440, 000 at the location of the outcrops of the "Paraná Formation". The absolute minimum is located between x 6, 390, 000 and 6, 460, 000 and y between 6, 075, 817 and 6, 145, 000 in the southeast of the study area. There are several local minima and maxima of the interpolated hydraulic head but the local extreme value with the highest area is located between x 6, 320, 000 and 6, 390, 000 and y between 6, 120, 000 and 6, 230, 000 near the capital and its surrounding the so called „Gran Buenos Aires". The local maximum at this location starts with a hydraulic head of 7.5 m and increases up to a hydraulic head between 10 m and 12.5 m. With "QGIS 2.18.14 Las Palmas" the estimated distance between the highest hydraulic head isoline of 40 m and the lowest hydraulic isoline of 5 m is 388 km. Therefore, the deriven hydraulic gradient in southeast direction is $-0.9\,\mathrm{m/km}$. However, it has to be mentioned that the groundwater flow direction vector do not

indicate any predominant groundwater flow direction. In the northern part of the interpolation, the groundwater flow direction was indicated as well in the east as in the west. Til the southern part of the local maxima located between x $6,320,000$ and $6,390,000$ and y between $6,120,000$ and $6,230,000$ there is no predominat groundwater flow direction visible. When the y-coordinate reach a value below $6,150,000$ the groundwater flow direction adjust to southeast.
However it has to be mentioned that the highest hydraulic head is located where the outcrops of the “Paraná Formation“ are located. Therefore, the interpolation suggested that the recharge zone of the “Paraná Aquifer“ is located at the outcrops.
The sum of squares of the differences from the mean is $1,974$ and the sum of squared residual for the kriging interpolation method is 21, therefore the coefficient of determination is 0.989, see electronic appendix. If the coefficient of determination is compared to table 6, it indicates an excellent interpolation.

4.3.2.2 Modelling of the groundwater flow direction by evolution of potassium concentration.

Figure 29 shows the natural neighbor method interpolated potassium concentration in mg/L and the deriven groundwater flow direction. The maximum potassium concentration that can be seen in this figure is 32 mg/L, the minimum potassium concentration is 0 mg/L and the resolution is 4 mg/L.

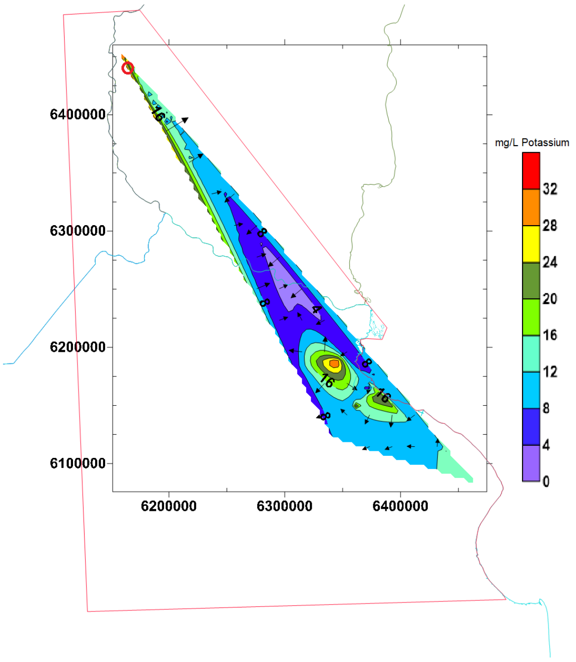

Figure 29: The interpolated distrubtion of the potassium concentration and the therefore dirven groundwater flow direction.

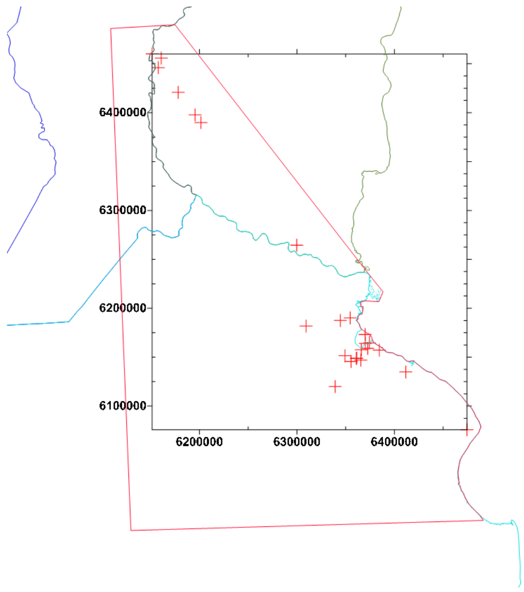

Figure 30: The vertices used for the interpolation of the distrubtion of the potassium concentration and the dirven groundwater flow direction.

The interpolation was done with 24 wells in the limits of x between 6, 151, 407 and 6, 474, 439 and y between 6, 075, 817 and 6, 460, 052. The interpolation has an area of about 17.000 km^2 but it has to be mentioned that about 600 km^2 of the interpolated area are outside the study area. Therefore, only 16.400 km^2 (about 14 %) of the study area is represented by the interpolation. If the interpolated area inside the study area is considered, a well represents an average of about 680 km^2 zero point three times the sizes of the Saarland.
The natural neighbor method interpolated maximum potassium concentartion is 31.7 mg/L and the interpolated minimum potassium concentration is 1.4 mg/L, see electronic appendix. The abolute maximum concentration is located at x about 6, 170, 000 and y about 6, 440, 000 and highlighted with the red circle. The absoulte minimum is located at x between x 6, 285, 000 and 6, 340, 000 and y between 6, 220, 000 and 6, 290, 000 at the border of the departments "Buenos Aires" and "Entre Ríos". There are several local maxima and minima of the interpolated potassium concentration. However, two are particularly noticeable due to their large area. This two are located near the capital and its surroundings the so called "Gran Buenos Aires". The local maxima that starts with a potassium concentration of 12 mg/L and increases to a potassium concentration between 28 mg/L and 30 mg/L is located at x 6, 320, 000 and 6, 370, 000 and y between 6, 155, 000 and 6, 200, 000. The other local maxima that is located at x 6, 285, 000 and 6, 340, 000 and y between 6, 220, 000 and 6, 290, 000 begins with a potassium concentration of 12 mg/L. Actually, this maxima culminates in two different local maximas, one

with a potassium concentration between 20 mg/L and 24 mg/L the other with a potassium concentration between 24 mg/L and 28 mg/L.
The groundwater flow interpolated by the potassium concentration can be divided into four different areas of different groundwater flow directions. In the north to a y-coordinate of about 6, 330, 000, the interpolated groundwater flow direction is directed east. From y 6, 330, 000 to 6, 170, 000, no predominantly groundwater flow direction can be determined. However, all the water from this area flows in the direction of the absolute minimum potassium concentration between 0 mg/L and 4 mg/L. From y 6, 170, 000 to 6, 100, 000, the interpolated predominant groundwaterflow direction is westfacing. In the sotheast corner there is a local maxima which indicates a groundwaterflow direction northfacing.
The natural neighbor interpolation of the potassium concentration suggested several recharge areas. The first suggestion for a recharge zone is the absolute maxima located by the outcrops in the department of "Entre Ríos". The other are the local maxima near the "Ciudad Autónoma de Buenos Aires", but like for the kriging interpolation method, it has to be menitoned that the "Paraná Formation" at this location does not have contact to the surface. Therefore, no simple explanation for the recharge mechanism in this area can be found. Also like formerly mentioned, potassium is one of the major ions and a widespread fertilizer [39] and a common indicator for pollution due to human activity like intensive agriculture[37]. Due to this fact, pollution could influence the potassium concentration and therefore the result of the interpolation.
The sum of squares of the differences from the mean is 2, 810 and the sum of squared residual for the kriging interpolation method is 718, therefore the coefficient of determination is 0.744, see electronic appendix. If the coefficient of determination is compared to table 6, it indicates a good interpolation.

4.3.2.3 Modelling of the groundwater flow direction by evolution of total solved solids.

Figure 31 shows the natural neighbor method interpolated total solved solids concentration in mg/L and the deriven groundwater flow direction. The maximum total solved solids that can be seen in this figure is 14000 mg/L, the minimum total solved solids is 0 mg/L and the resolution is 1000 mg/L.

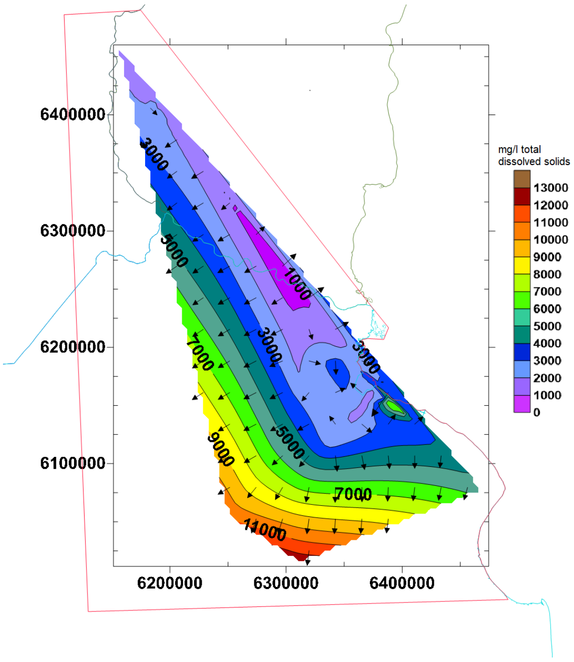

Figure 31: The interpolated distrubtion of the total dissolved solids concentration and the therefore dirven groundwater flow direction.

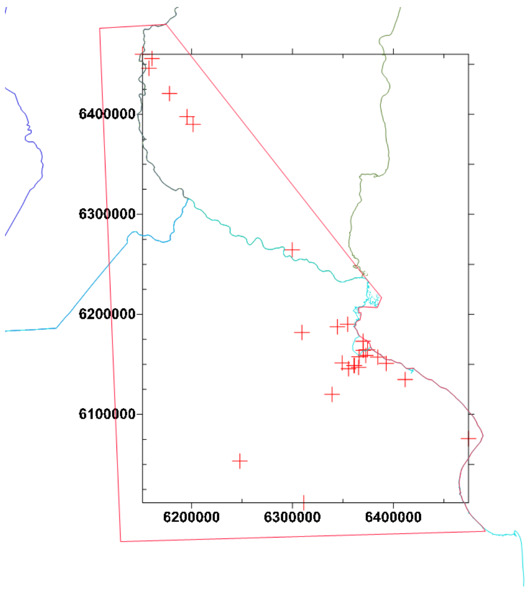

Figure 32: The vertices used for the interpolation of the distrubtion of the total dissolved solids and the dirven groundwater flow direction.

The interpolation was done with 27 wells in the limits of x between 6, 151, 407 and 6, 474, 439 and y between 6, 011, 640 and 6, 460, 052. The interpolation has an area of about 51, 000 km^2. A small part of the interpolatied area about 600 km^2 is outside the study area. Therefore, about 69, 400 km^2 (57.5 %) has no interpolated value. If only the interpolated are inside the study area is considered a well represents an average area of 2570 km^2, that is about the size of the Saarland.
The by the natural neighbor method interpolated maximum total dissolved solids concentration is 12607 mg/L and the interpolated minimum total dissolved solids concentration is 328 mg/L, see electronic appendix. The interpolated maximum potassium concentration between 12, 000 mg/L and 13000 mg/L is located in the southwest of the interpolation between x 6, 290, 000 and 6, 330, 000 and y between 6, 011, 640 and 6, 030, 000. The interpolated minimum potassium concentration between 0 mg/L and 1, 000 mg/L is located in middle east of the study area between x 6, 255, 000 and 6, 325, 000 and y between 6, 235, 000 and 6, 320, 000. In total there are six local extreme values two of them are local maxima and four of them are local minima. The two local maxima are located near the "Ciudad Autónoma de Buenos Aires". The local maxima located at x between 6, 335, 000 and 6, 360, 000 and y between 6, 165, 000 and 6, 190, 000 has a total dissolved solid concentration between 3000 mg/L and 4000 mg/L. The other local maxima begins with a total dissolved solid concentration of 4000 mg/L and culminate in a total dissolved solid concentration between 6000 mg/L and 7000 mg/L and is located at x between 6, 380, 000 and 6, 410, 000 and y between 6, 140, 000 and 6, 165, 000. Three of the four local minima is located close to the absolute minima at x between 6, 250, 000 and 6, 260, 000 and y between

$6,320,000$ and $6,340,000$ and have a value between 0 mg/L and 1000 mg/L. The other local minima is located near the "Ciudad Autónoma de Buenos Aires" like the local maxima. This local minima has a total dissolved solid concentration between 1000 mg/L and 2000 mg/L and is located at x between $6,360,000$ and $6,750,000$ and y between $6,130,000$ and $6,160,000$. The two local maxima near the "Ciudad Autónoma de Buenos Aires" can be considered as sink or storage of groundwater and the local minima as an additionally source of groundwater.

The total dissolved solid concentration interpolated groundwater flow direction has a clearly predominant direction. The predominat groundwater flow direction is southwest facing. Additionally if the results of the elevation of the "Paraná Formation" are considered, it has to be notice that the inclination of the "Paraná Formation" and the groundwater flow direction are similar. Even if the groundwater flow direction and the inclination of an aquifer does not have to match, as equation **??** shows, this match can be used as an indication of the correctness of the interpolation of the groundwater flow direction.

The sum of squares of the differences from the mean is $236,591,461$ and the sum of squared residual for the kriging interpolation method is $10,681,052$ therefore the coefficient of determination is 0.955, see electronic appendix. If the coefficient of determination is compared to table 6, it indicates an excellent interpolation.

4.3.3 Conclusion

The different interpolation methods (kriging and natural neighbor), shows no significant quality differences. However, the different approaches of the interpolations (hydraulic head, potassium concentration and total dissolved solids) shows them. While the interpolations of the hydraulic head and the total dissolved solids concentration have comparable coefficient of determination and therefore comparable qualities of interpolation, the coefficients of determination of the interpolation of the potassium concentration are much lower. For the evaluation of the interpolations, the coffecients of determinations alone are not sufficient.
In addition, the size of the interpolated area and is important. Since for the kriging mehtod these are of the same order of magnitude for the individual approaches, these can be considered equivalent. For the natural neighbor interpolation the approach to model the groundwater flow direction by the distribution of the total dissolved solids concentration has an area about 3 times bigger as the other approaches. Therefore, this approach is considered to be less precise then the other two approaches of the natural neighbor interpolation. In general the interpolated areas of the natural neighbor method are smaller. Due to this fact, the results of the natural neighbor can be considered as more precise as the result of the kriging method.
However, it should be noted, that the amount of available data is small for the size of the interpolated data. Therefore, in general the results are imprecise. Due to this impreciseness of the interpolation, the results may not provide important informations of the aquifer like the location of storage and watersheds. This inaccuracy also influences the interpolated groundwater flow direction. For this reason, the individual results are compared with each other and from that a groundwater flow direction and a hydraulic head contour map was derived. In addition, it must be mentioned that the interpolation of the hydraulic head is considered to be more robust. In contrast to the potassium and total dissolved solids concentration, the hydraulic head can not be affected by pollution or interactions with the aquifer. Figure 6 shows a land cover map of continental South America. If the location of the study area(marked with red rectangle) is compared with the land use of this area, it has to be noted that this area is mainly used as cropland. Due to land use, pollution of groundwater with potassium and therefore an influence on the interpolation results can not be excluded. Additionally the potassium and total dissolved solids concentrations could be influenced by solving and dissolving interactions with the aquifer.
If the results of the interpolation of the hydraulic head for the different method are compared, several properties have to be noted. Not only typical properties of the individual methods like the interpolated area are different. The location of the absolute minima differs form the different interpolation method. The absolute interpolated minima of the kriging method is in the southwest of the study area, whereas the absolute interpolated minima of the natural neighbor method is in the southeast. In east-west direction, the two interpolated minimum hydraulic heads are more than 230 km apart. But it has to be mentioned, that the interpolated hydraulic head value in the southeast is the same (between 2.5 m and 5 m). Also it has to be mentioned that where the interpolated absolute minima interpolated by the kriging method is located, the natural neighbor method has no interpolation values. Furthermore, in contrast to the result of the kriging interpolation, the natural neighbor interpolation shows local minima and local maxima. However, the by the different method interpolated maxima are at the same location, in the north of the study area where the outcrops are located. Since only the location of the maxima of the different methods match, the groundwater flow direction also does not match. While the interpolation of the hydraulic head of the natural neighbor method does not reveal any predominat groundwater flow direction, the kriging method shows a clearly predominat south-facing groundwater flow.
Comparing the results of the interpolation of the potassium concentration for the different method, no major difference can be noted. Of course, the size of the interpolated area is different, but the

locations of different properties are similar. For example, the interpolated area and the shape of the area of absolute maxima and absolute minima are differnt respectively, but the location overlaps. The absolute maxima of the different interpolation are both in the north of the study area equal the location of the outcrops. Also for both interpolation the absolut minima is located near the border of the departments “Buenos Aires“ and “Entre Ríos“. Even the location and the potassium concentration of the two local maxima near the “Ciudad Autónoma de Buenos Aires“ are almost equal. But it has to be mentioned, that the natural neighbor method shows several small local minima and maxima respectively that do not occur in the kriging interpolation. Also the different results have in common that the groundwater flow direction can be divided in several areas. Nevertheless, it has to be mention that the interpolated groundwater flow direction of the kriging mehtod has two predominat groundwater flow directions. On the other hand the interpolated groundwater flow direction of the natural neighbor has four directions.
Similar to the two interpolation results of the potassium concentration, the results of the interpolations of the total dissolved solids concentration hardly differ. For example, the location of the absolute minima and absolute maxima are simliar. Only the shape and the area of the extreme values are different. The location as well as the interpolated total dissolved solids concentration of some local extrem values near the „Ciudad Autónoma de Buenos Aires“ are similar. Only one local minima with a total dissolved solids concentration between 3000 mg/L and 4000 mg/L appears in the result interpolated via the kriging method. Both methods show a clear predominat southwest directe groundwater flow.
If the different approaches in general are compared, it has to be noted that the amount and location of the wells are different. This fact could influence the interpolation results a lot, especially if the location of minima and maxima are changing. For both methods, the interpolated minima of the potassium concentration and the total dissolved solid concentration are located in the same region between the department of “Buenos Aires“ and “Entre Ríos“. However, this implies contradictory groundwater flow direction for the different approaches as the potassium concentration decreases and total dissolved solids increase in the direction of groundwater flow. Also it has to be mentioned that the measured total dissolved solids concentration at this location is about one order of magnitude lower than the other measured total dissolved solids concentrations. And therefore like mentioned in section 4.1 it may be that the minimum of the total dissolved solids concentration is an outlier.
By the kriging method interpolated minima of the hydraulic head and also by the kriging method interpolated maxima of the total dissolved solids concentration are both located in the south west of the study area. Also the second lowest potassium concentration interpolated by the kriging method can be found in the southwest. The natural neighbor interpolations do not have interpolation values in this region. The only approach that has interpolation values near this area is the total dissolved solids concentration. And like the kriging method, the maximal total dissolved solids concentration is located there. Due to the fact, that in this area the hydraulic head and the potassium concentration for the kriging method are low and the total dissolved solids concentration for both interpolation methods are high, allows the conclusion that the groundwater flow is directed to this area.
The maxima for both interpolation method of the hydraulic head and the potassium concentration are located in the north of the study area at the location of the outcrops. For both interpolation methods, the minima for of the total dissolved solids concentration is not located at the same location as the outcrops. Nevertheless, it has to be mentioned that the second lowest total dissolved solids concentration can be found at the same location as the outcrops. Due the fact, that for both interpolation method two out of three approaches suggests that the groundwater flow emanates from the region where the outcrops are located, this region is considered to be the groundwater recharge zone. Also the elevation of the “Paraná Formation“ indicates in the study area a groundwater flow direction from the outcrops towards south. The hydraulic head contour map of the “Paraná Aquifer“ is in meter and explained more in detail below.

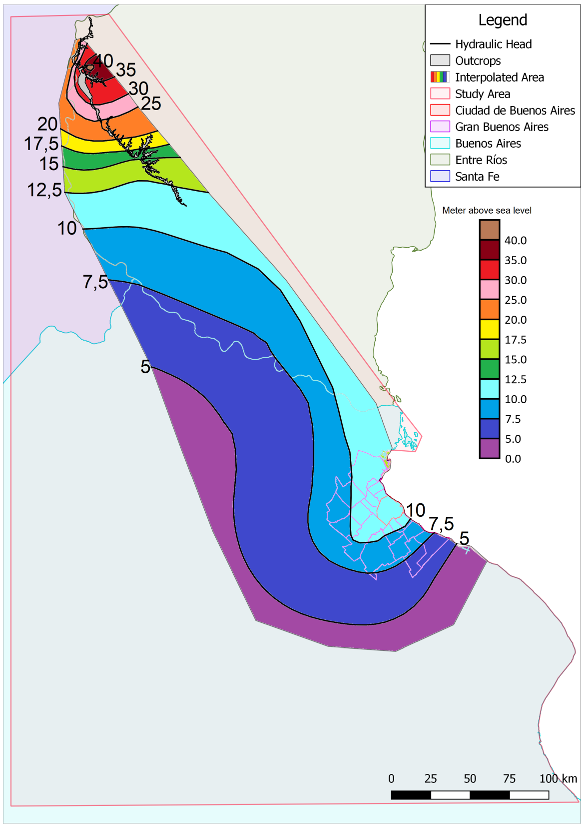

Figure 33: Supposed hydraulic head contour map of the "Paraná Aquifer" in meter.

Figure 33 shows the hydraulic head contour map derived from the two interpolation methods and three interpolation approaches. An area about $44,000\,\text{km}^2$ are represented by a hydraulic head value. That is about $27,000\,\text{km}^2$ bigger than the interpolated area of the natural neighbor method and about $10,000\,\text{km}^2$ smaller than the interpolated area inside the study area of the kriging method. If this area is compared to the total study area about 37 % of the study area have an interpolated hydraulic head value. For example, in the south and the southwest are no prediction about the hydraulic head and the groundwater flow direction was done. This is justified by the fact that there are no wells, see figure 11.

The highest hydraulic head has a value of 40 m and is located in the north of the study area by the outcrops. Because in this area the outcrops are the only connection with subsurface, it seems to be logical that the outcrops are responsible for the recharge of the aquifer. The lowest hydraulic head is 5 m, the resoultion of the hydraulic head is not uniform. From a hydraulic head between 5 m and 20 m the hydraulic head has a resolution of 2.5 m, thenceforth the resolution is 5 m.

It is assumed that the groundwater spreads from the groundwater recharge zone in the different geographic direction. Therefore, the outcrops are not only the groundwater recharge zone of the "Paraná Aquifer", but also a watershed. When the hydraulic head reaches a value of 20 m, the groundwater flow in the study area has a predominant flow direction. The predominant groundwater flow direction is first southfacing until the hydraulic head reach a value of 10 m and then it is changing. Following the 10 m contour line, a shift in the groundwater flow direction is visible. The groundwater flow emanating from the 10 m contour line can be divided in five different sectors with different groundwaterflow direction. In the north, the predominat groundwater flow direction is south, then it changes to southwest, then to west and then again to southwest and then again to the south. If the various hydraulic gradients are estimated using "QGIS 2.18.14 Las Palmas", the results are as follows.

For the first section from the Outcrops exact location −32.02 °N −60.56 °E (World Geodetic System 1984) with a hydraulic head value of 40 m.a.s.l. to the almost perpendicular point at the hydraulic head contour line of 10 m with the exact location −33.14 °N −60.20 °E the distance is about 139 km. Therefore, the derived hydraulic gradient is −0.22 m/km. For the second section in the South of the department of “Entre Ríos“ exact location −33.14 °N −59.16 °E with a hydraulic head value of 10 m to the the point at the hydraulic head contour line of 5 m with the exact location −33.82 °N 59.69 °E the distance is about 89 km. Therefore the derived hydraulic gradient is −0.06 m/km. For the third section in the north of „Gran Buenos Aires“ exact location −34.08 °N −58.80 °E with a hydraulic head value of 10 m to the almost horizontal point with the exact location −34.18 °N −59.96 °E at the hydraulic head contour line of 5 m the distance is about 71 km. Therefore the derived hydraulic gradient is −0.07 m/km. For the fourth section in the “Ciudad Autónoma de Buenos Aires“ exact location −34.75 °N −58.67 °E with a hydraulic head value of 10 m to the point with the exact location −33.14 °N −60.20 °E at the hydraulic head contour line of 5 m the distance is about 57 km. Therefore, the derived hydraulic gradient is −0.09 m/km. For the last section from in the south of the “Ciudad Autónoma de Buenos Aires“ exact location −34.79 °N −58.51 °E with a hydraulic head value of 10 m to the almost perpendicular point with the exact used location −35.28 °N −58.48 °E on the hydraulic head contour line of 5 m the distance is about 54 km. Therefore, the derived hydraulic gradient is −0.09 m/km. Natural groundwater surfaces typically have a hydraulic gradient within the range of 1 m/km and 10 m/km [5]. Therefore the estimated hydraulic gradient would be very small even under the usual occurring hydraulic gradients. Also compared to the “Guarani Aquifer System“ one of the biggest aquifers in the world, the hydraulic gradient is small. The hydraulic gradient of the “Guarani Aquifer System“ is between 1 m/km and 5 m/km [43]. The changes of the groundwater flow direction could be influenced by the border of the “Paraná Formation“ or by another source of groundwater. The “Paraná Formation“ also have outcrops in Uruguay and it is not clear whether or not they have an influence on the “Paraná Formation“ in the department of “Buenos Aires“. Due to this fact, it can not be clearly clarified what causes the changes of the groundwater flow direction.

When the supposed groundwater flow direction in figure 33 is subjected to a plausibility check, several things are noticeable. The groundwater flow direction is often correlated with topography [45]. Assuming that the groundwater flow direction of the “Paraná Aquifer“ is also correlated with the topography, the following can be ascertained. The location of the outcrops is the location with the highest altitude, see figure 7. Therefore, it seems to be reasonable that the groundwater flow emanates from their. Because the outcrops are a local elevation it also seems to be reasonable that the groundwater spreads in every direction. Nevertheless, in the south of the study area in the department of “Buenos Aires“ the inclination of the topography is contrary to the groundwater flow direction. Under the the assumption that the groundwater flow direction is correlated with topography, this seems unrealistic. However, it should be noted that the slope of the topography in “Buenos Aires“ is not strongly pronounced. In addition it should be noted that the groundwater flow direction in the east of the study area is contrary towards the location of the sea. This would contradict the natural water cycle and is therefore considered unrealistic. Due to the result of this plausibility check small-scale investigations of the flow direction of the “Paraná Aquifer“ are recommended.

5 Discussion

The objective of this study was to verify the suitability of the “Paraná Aquifer“ for drinking water supply purposes. The concentration of eight hydrochemical properties of the groundwater were determined by Environmental Protection Agency standard methods and then compared to the limits of the World Health Organization. In addition the aviability of the groundwater of the “Paraná Aquifer“ was investigated. Therefore, the top of the elevation of the “Paraná Formation“ was interpolated by the three method kriging, local polynominal and natural neighbor. Also the groundwater flow direction and the location of the groundwater recharge zone were interpolated, because they are important data for groundwater management. For these interpolation two different interpolation methods and three different approaches were used. The used interpolation method were kriging and natural neighbor. The used approaches were the interpolation of hydraulic head data and the typical the evolution of potassium concentration and the total dissolved solids concentration in a hydrosome, respectively.
The results of the hydrochemical properties are highly variable. This can easily be explained by the size of the study area and the distance of the individual sampling points. Due to the typical hydrochemical evolutions in an aquifer system [36] and the long distance between the individual sampling points, the variablity seems to be logical. Also it has to be mentioned that the sampling time for the several groundwater samples are not known. Chemical properties can also undergo seasonal changes [42], due to the sampling at differnt times the variabilty could be increased. Almost all investigated hydrochemical properties exceeded the limits of the World Health Organisation at least at one location. Therefore, the groundwater of the “Paraná Aquifer“ can be considered as not suitable for drinking water supply purposes without treatment. This result coincides with scientific findings from other studies [3]. Furthermore many chemicals that potentially endanger the quality of the groundwater like arsenic are not included in this work. As well as the potential hazard of microorganism is not considered. Because of these reasons further investigation of the quality of the groundwater for drinkingwater supply purposes have to be done.
The interpoaltion of the elevation of the “Paraná Formation“ are subjected to uncertainties. For example, some of the wells were located via “Google Maps“ because no information of the exact location was available. This uncertainty factor can be neglected due to the size of the study area and the chosen method to locate the wells can be considered as accurate enough. Another uncertainty were the geological descriptions of the different wells. These geological descriptions must be interpreted, but with these interpretations errors can occur and these can affect the interpolations. Also it has to be mentioned that an interpolation of the top of the “Paraná Formation“ only allow limited conculusions to the “Paraná Aquifer“. This is because sometimes the formation occurs incomplete and the sand layer of the “Paraná Formation“ do not appear, where the green clay layer occurs. Also it has to be mentioned that the distribution of the well in the study area is unequally. The interpolated minimum elevation of the different interpolation is -170 m.a.s.l. Therefore, exploiting the water of the “Paraná Aquifer“ seems to be possible. Because groundwater that is even located at a depth of several hundreds of meters is used for drinking water supply purposes [22]. However, due to the evaluation of the different interpolation methods by the coefficient of determination they can be considered as good. The evaluation of the different methods show that the quality of the interpolations are almost equal. An additional comparison of the different interpolation results shows many similarities, especially comparing the results of the kriging and natural neighbor interpolation. Not only the range of the interpolated elevation of the “Paraná Formation“ as well as some specific properties of the interpolations are equal, like local extreme values.
The interpolation of the groundwater flow direction is associated with some uncertainties. The huge distance between the individual wells abd the huge areas without wells makes the interpolations questionable. Important information of the aquifer, such as watersheds may not be provided due to the inaccuracy of the interpolation. However, no more data was available, therefore, the groundwater

flow direction and the location of the groundwater recharge zone were modeled by two different interpolation methods as well as three different interpolation approaches. If the different interpolation methods are compared with each other by the coefficient of determination, no significant difference can be determinted. But when comparing the different interpolation approaches, it can be seen that the hydraulic head and total dissolved solids concentrations are equally good, but the potassium concentration approach is inferior. The comparatively poorer quality of the interpolation of the potassium concentration could be caused by pollution. Also for the interpolation of the total dissolved solids concentration, contamination can not be completely ruled out. However, a comparison of the interpolations was made. Due to the similarities, a distribution of the hydraulic head and the groundwater flow direction has been proposed. However, due to a plausibility check, which considered the result questionable, small-scale investigations of the flow direction of the "Paraná Aquifer" should still be done.

In conclusion, based on available data, no conclusive assesment can be done on the suitability of the "Paraná Aquifer" for drinking water supply. For this assessment, important data are missing, such as further information on water quality or detailed information on groundwater recharge. However, for using the water of the "Paraná Aquifer" for drinking water supply purposes water treatment is essential.

6 Outlook

For the final assesment of the suitability of the “Paraná Aquifer“ more information has to be collected and evaluated. Further analysis to determine the suitability of groundwater for drinking water should be realised. Not only further chemical parameters but also microbiological parameters should be investigated. If the water of the “Paraná Aquifer“ is used for drinking water supply purposes, water treatment is unavoidable, but only with a comprehensive knowledge of the water quality an adequate water treatment can be carried out. Only with this comprehensive knowledge the effort and the cost of a water treatment can be estimated. If these costs can be estimated, a comparison with seawater desalination should also be made. Since, in contrast to the water from the “Paraná Aquifer“, probably lower additional pumping costs incurred, seawater desalination could represent a more economic alternative.

In order to better estimate the pumping costs associated with the use of the “Paraná Aquifer“ for drinking water supply, further investigations should be carried out to verify and improve the interpolation results of the elevation of the “Paraná Formation“. First, it should be tried to provide the information about the elevations not only for the top of the “Parana Formation“, but also for the “Paraná Aquifer“. Because many drilling cores do not provide any information of the “Paraná Aquifer“, this is difficult. But for example, geophysical method can be a comparatively inexpensive alternative for drilling with the same depth of investigation [9]. However, it has to be mentioned that the size of the study area is huge and to generate and process the necessary data a huge effort is needed. Perhaps it would therefore make more sense to do several small-scale studies for a closer look at elevation of the “Parana Formation“.

The same applies to the investigation of the groundwater flow direction and the necessary more detailed investigation of the groundwater recharge zone. The more detailed investigation of the groundwater recharge zone is necessary, for proper management of groundwater systems, because accurate estimation of groundwater recharge is extremely important[47]. For example, investigation of stable isotope combined with groundwater level data have proven to be effective in helping to understand the recharge in a bedrock aquifer [46] [6]. There are also a number of ways to improve the results interpolation of the groundwater flow direction. The simplest and probably most effective option would be to increase the quantity of wells used for interpolation. Wells in the department of “Santa Fe“ also should be considered. This would have the advantage that the outcrops could be clearly identified as a watershed and thus as a groundwater recharge zone.

In conclusion, due to the large size of the “Paraná Formation“ and the low exploration, especially with respect to the “Paraná Aquifer“, it offers a multitude of possibilities to extend the knowledge of this geological formation.

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