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ORIGINAL ARTICLE

Designing and validating a groundwater sampling campaign in an unmonitored aquifer: Patiño aquifer case

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Abstract
Groundwater quality sampling campaigns are crucial for the characterization and monitoring of aquifers, especially in urban settings where contamination have an anthropogenic origin due to common practices developed in urban areas. In Paraguay, the Patiño aquifer is located below the largest and most densely populated urban area, and supplies water to 31% of the country's population (approximately 2.1 million people), it has more than 8,000 potential pollution sources and over 2800 deep wells. Water quality campaigns are performed irregularly, and there is no characterization of water type or water quality for the aquifer. This study presents a novel well selection protocol for the purposes of a water quality campaign and the results of its application. This protocol is based on a multi-objective evolutionary algorithm that uses known risk of contamination data, well location, and accessibility to wells (i.e. public vs. privately owned wells) to maximize the chances of finding groundwater contamination. In total, twenty-one water quality parameters were evaluated in 66 wells that were selected based on our sampling protocol. Of these wells, 83% were found to have values outside the permissible limit, according to the regulations considered. In addition, the presence of nitrate concentrations was found to be above the permissible limits in 42% of the wells. Our well selection protocol had a 50% success rate at finding samples outside the permissible limits, while two previous campaigns with no optimized selection protocol showed a 21 and 37% success rate.

Keywords Sampling campaign · Well selection protocol · Multi-objective problem · NSGA-II · Water type · Water quality index (WQI) · Groundwater contamination

Introduction

Urban groundwater as a resource faces a number of threats due to population growth, increasing urbanization and climate change (Flörke et al. 2018; Gohar et al. 2019; Kløve et al. 2014; Newcomer et al. 2014; Zendehbad et al. 2019). Among these threats are, overexploitation, contamination by natural or anthropogenic sources, and loss of recharge capacity. These threats are even more exacerbated in areas with poor sewage collection systems, lack of a proper monitoring plan, and a poor characterization of the subsurface.

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Due to the lack of a management plan, water quality of urban aquifers have been contaminated with a series of pollutants that include heavy metals, n-species, chlorinated hydrocarbons, phenols, cyanide, pesticides, major inorganic species and bacteria (Grischek et al. 1996; Gulgundi and Shetty 2018; Ikem et al. 2002; Nas and Berktay 2010; Robinson and Gronow 1992; Rothwell et al. 2005; Zendehbad et al. 2019). Generally, the major sources of these contaminants are sewage systems, household waste pits, poor disposal of chemical and industrial waste, and leakage of underground storage tanks or accidental spills (Sagar et al. 2015).

Water supply and water quality problems have constituted one of the most critical problems in many large cities. Urban sprawl, which in addition to the polluting effects, also affects the recharge capacity of aquifers and reduces the dilution processes. Moreover, defective urban sewage networks allow around 50% of transported water to be leaked into the aquifer, causing additional contamination problems (Bertrand et al. 2016; Nobre et al. 2007; Zendehbad et al. 2019). All these processes are present in the Patiño Aquifer, which sits below the capital city of Paraguay, Asuncion.

Asuncion's metropolitan area (AMA) has experienced exponential urban growth in the last decades, producing a profound impact on the recharge and the water quality of the Patiño Aquifer. The Patiño aquifer (1173 km^2) is the main source of water for the AMA, providing drinking water to about 2.1 million inhabitants which are agglomerated in the urban area that extends for 567 km^2 over the aquifer. Within this area, there are more than 2800 known extraction wells. Moreover, it is estimated that there are more than 8000 potential sources of contamination (DGEEC 2013) and 79% of houses in the AMA have septic tanks or a permeable pit as means of wastewater disposal (DGEEC 2013).

Therefore, urban discharges and overexploitation of the Patiño aquifer are a constant threat to its water quality. In addition, the absence of information on its quality, given that there is no constant monitoring makes any type of proactive management difficult. The few studies that exist provide a limited understanding of the water quality and quantity of the aquifer. These studies have in general focused on hunting down contamination pockets with no clear protocol other than sampling wells that are available.

For instance, Facetti et al. (2019) sampled 90 existing wells, covering the entire area of the aquifer in areas near gas stations, to analyze the levels of methyl tert-Butyl ether (MTBE) and related products. They detected MTBE in 44% of the wells, tert-Butyl alcohol (TBA) in 21% of the wells and tert-Butyl formate (TBF) in 13% of the wells. Another study, done by the consulting firm INCLAM-HQA (2017) sampled 36 existing piezometers, covering the entire area of the aquifer, the parameters evaluated were static level, and 19 physicochemical and bacteriological parameters. The measured nitrate values exceeded the maximum limit in 25% of the samples collected. In addition, they observed an increase in salinity at some control points. The objective of these sampling campaigns was to categorize the water quality in the aquifer. Houben et al. (2012), sampled 65 existing wells, covering 79 km^2, in the San Lorenzo stream water basin, where they searched for the presence of physico-chemical, bacteriological parameters and heavy metals. They detected total coliforms in 38% of the samples, E. Coli in 9% of the samples and nitrates in 17% of the samples, which evidenced practices of inadequate sanitation. These three studies focused on characterizing the area but with no clear protocol on how wells were selected besides general heuristics of where there might be a well with easy access. The question that arises from these studies is if the optimal well locations were chosen to fulfill the proposed objectives or if a more efficient use of resources could have been done to carry out the sampling campaign.

The focus of this study is to present a systematic protocol to designing a water quality sampling campaign based on a multi-objective approach, followed by the results of the application of the protocol, an analysis of the sampling results and a comparison of the success rates of this study with other studies done in the same area. The multi-objective selection of sampling wells is based on the fitness of four objective functions that are evaluated through the NSGA-II algorithm (Deb et al. 2002) with preference ordering. It is worth mentioning that the NSGA-II algorithm has been widely used and validated for designing sampling and monitoring networks (Alzraiee et al. 2013; Bashi-Azghadi and Kerachian 2010; Dhar 2013; Dhar and Patil 2012; Kollat and Reed 2006; Yeh 2015). The Preference Ordering (PO), which allows for more specificity in selecting possible solutions has not been used in these types of applications before. One of our contributions is the addition of this process to help deal with the issue of having multiple conflicting objectives, where improvement in one objective decreases performance in some other objectives (Deb 2011). The results presented are based on the sampling of 66 wells during a sampling campaign of the urbanized area of the Patiño Aquifer.

The paper is separated into three parts which entail the materials and methods used to carry out the sampling campaign, the analysis of the sampling results, and finally, the conclusions obtained.

Materials and methods

Study area and objective functions

The Patiño aquifer is located in the Eastern Region of Paraguay, it is an unconfined aquifer with a total extension of 1173 km^2 (TNO 2001). The aquifer has a triangular shape and is bordered in the northwest and west by the Paraguay River; to the east and south it is defined by a Paleozoic fault related to volcanic manifestations. The northern border of the aquifer is not well defined, but it coincides with the Paraguay River. The main formation of the aquifer consists of a fine-grained to very fine-grained sandstone, in lower proportion medium-grained with occasional clay levels (CKC-JNS 2007).

This study focuses on the northern portion of the aquifer where the Asuncion Metropolitan Area (AMA) sits on an area of 567 km^2. Figure 1 shows the study area, which is composed of Asunción and 10 other surrounding cities, as well as the location of the more than 8000 potential sources of contamination. Over the AMA there are 2819 extraction wells where 1059 correspond to communal water distribution wells (sanitation boards as they are known), 1745 are private wells and 15 piezometers.

The well selection protocol was based on the fitness of four objectives functions. Two of the objective functions

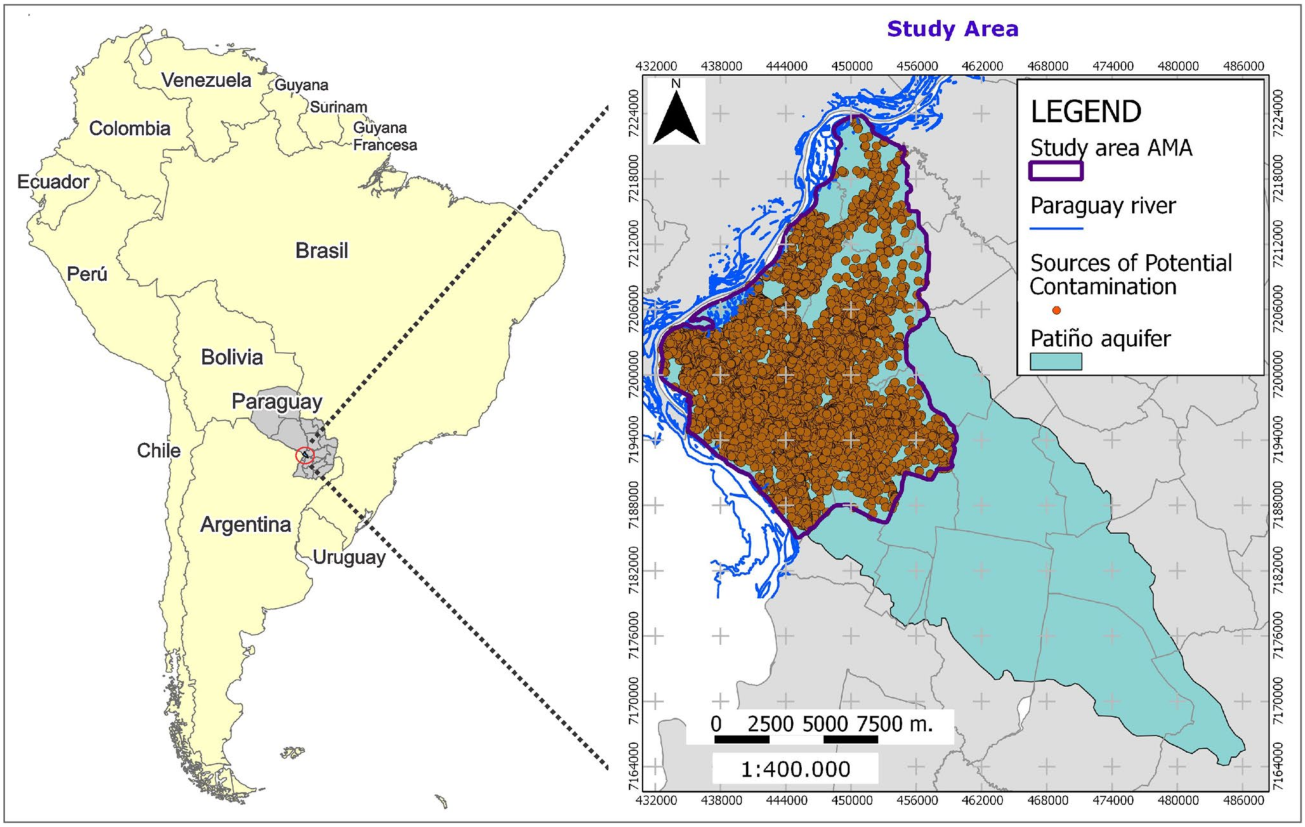

Fig. 1 Map of the AMA study area, the Patiño aquifer and the distribution of the more than 8,000 potential sources of contamination

proposed are based on information developed in a previous study by Baez et al. (2019) where two risk of contamination maps over the Patiño aquifer were developed. The Baez et al. (2019) study used a modification of the well-known DRASTIC (Aller et al. 1987) vulnerability model, in which anthropogenic parameters were added to the model and the resulting risk indices were then calibrated with measured values of total nitrogen (TN) and total coliforms (TC). The maps have a normalized risk index (I) with values between 0 and 100, with a value of 100 representing the highest risk. The aforementioned study went further and did a geostatistical comparison of the two risk maps showing that on average only 16% of the area have similar risk indices, which implied that one risk map cannot suffice when describing the risk of contamination of the aquifer. The study also showed that 42% of the aquifer has a medium to high risk of contamination, where AMA is the most affected area. The risk indices for TN and TC are shown in Fig. 2 together with the distribution of the existing wells.

The other two objective functions respond to financial constraints and well accessibility. Given that the resources available only permitted the sampling of 66 wells, the third objective was set to spread the wells as far apart as possible. The fourth objective focused on selecting wells that were easier to access than others: public wells, owned by sanitation boards or government institutions, were selected over private wells, that were inside private lots or were otherwise inaccessible.

Multi-objective algorithm

The optimization algorithm used for the selection of sampling wells is based on the Non-dominated Sorting Genetic Algorithm II (NSGA-II) proposed by Deb et al. (2002), which is a multi-objective evolutionary algorithm (MOEA). This algorithm assigns fitness values to each possible solution of a given population of solutions and also has a preservation of diversity functionality by calculating the crowding distance between solutions. The advantage of the NSGA-II model is that multiple conflicting objectives can be considered simultaneously and a very large decision space (Dhar and Patil 2012; Kollat and Reed 2006). Thus, in these types of problems a set of optimal solutions are defined, whose values are known as the Pareto Optimal Front.

However, the problem with the NSGA-II classification procedure is that when more than three objectives are considered, the number of solutions being classified in the optimal front only depends on the crowding distance (i.e.

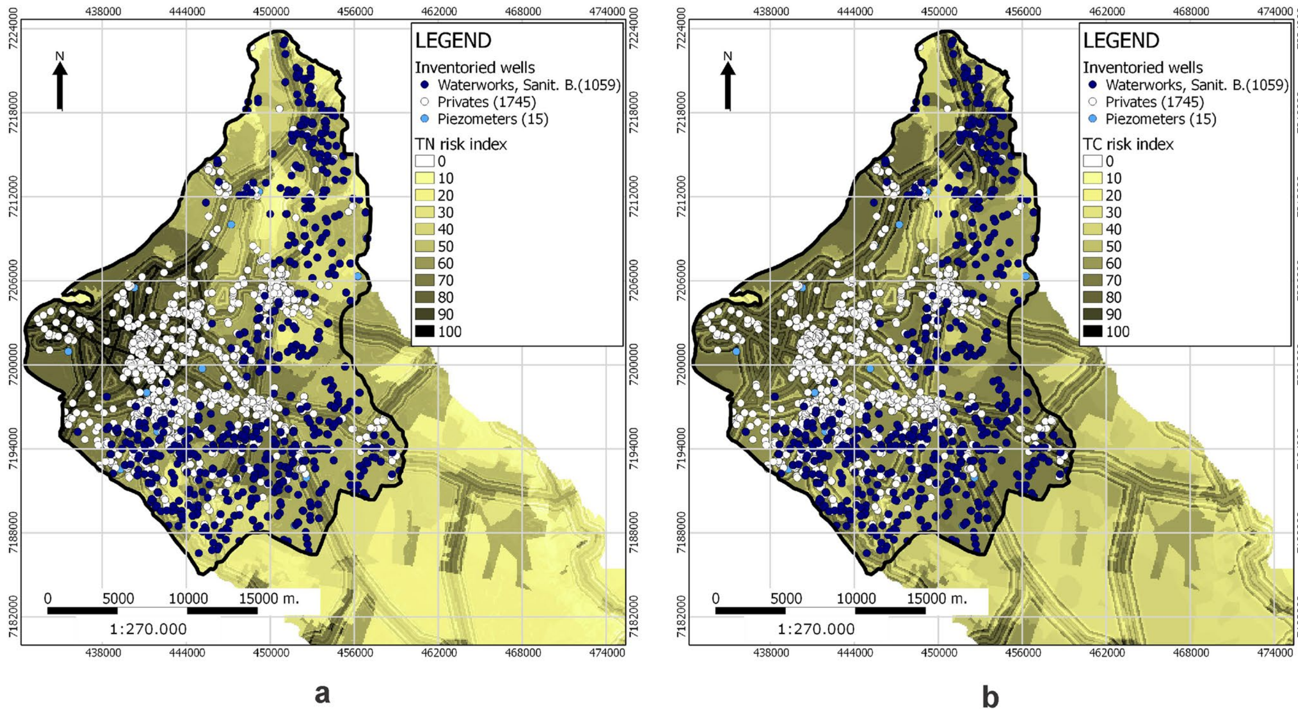

Fig. 2 Distribution of the 2819 wells with the contamination risk maps created in Baez et al. (2019) as base maps. (a) Contamination risk for TN concentrations. (b) Contamination risk for TC concentrations

diversity). The crowding distance loses its efficiency when increasing the dimensions of the problem since it is based on measuring cuboids with respect to the closest individuals, which only works well with two objectives (Santiago et al. 2016). To avoid this problem, in this study a modification of the NSGA-II, based on the Di Pierro (2006) method, called Preference Ordering (PO) was implemented. With the implementation of the PO method two solutions are compared to establish how many objectives is one solution better than the other. For instance, solution A is ranked over solution B if it performs better in more objectives than solution B, and vice versa. The general scheme of the algorithm implemented is shown in Fig. 3.

For our implementation, the input data was stored in a PostgreSQL database (PostgreSQL 1996) and its spatial extension PostGIS (PostGIS 2015), which is dedicated to the manipulation of georeferenced data. The input data consisted of information from 2819 well records, that contain the following values: risk index for nitrogen contamination (ITN), risk index for total coliform contamination (ITC), type of well (waterworks, sanitation boards, piezometers or private well) and the well coordinates (X, Y).

The NSGA-II was implemented following the proposal of Deb et al. (2002). It starts with an initial population of N possible solutions—each solution holds 66 well locations randomly selected with their respective ITN, ITC, type of well and coverage area data. These solutions are evaluated for their fitness, ranked in order and used to create a new child population of solutions through mutation and crossing operators. The parent and child population come together and the N fittest solutions are passed onto the next generation. To select the fittest solutions, the non-dominance ordering and a PO ranking is assigned to each solution, following the proposal of Di Pierro (2006).

Definition of objective functions

The multi-objective problem of sampling wells for groundwater quality sampling campaign in the Patiño aquifer was defined as follows:

$$F(x) = (f_1(x), f_2(x), f_3(x), f_4(x))$$

where,

i. $f_1(x)$: Maximize the wells near high risk of contamination by Total Nitrogen.
ii. $f_2(x)$: Maximize the wells near high risk of contamination by Total Coliform.
iii. $f_3(x)$: Maximize the coverage area of the 66 wells selected.
iv. $f_4(x)$: Maximize wells of public access.

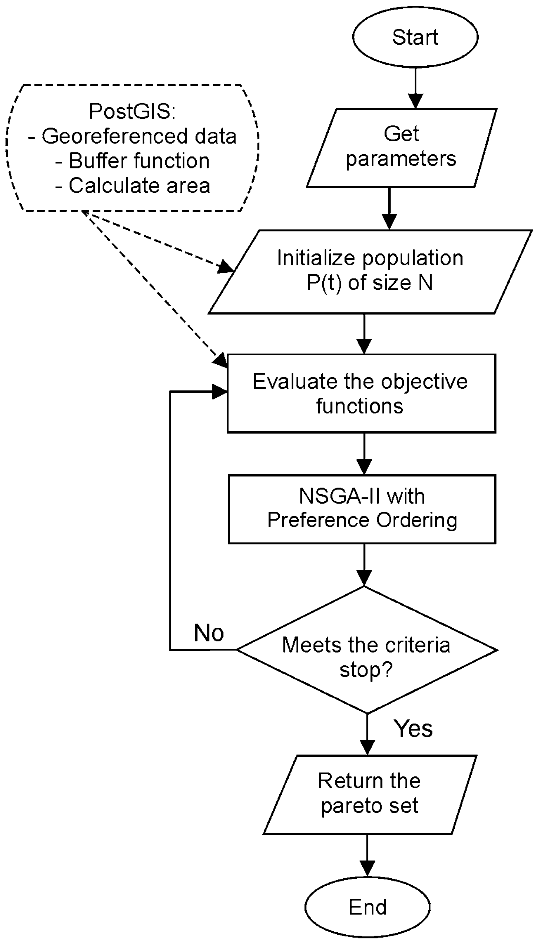

Fig. 3 Flowchart of the computational resolution method implemented for optimal well selection. The flowchart shows the process of evaluation of each solution based on the NSGA-II algorithm

where x is a vector of n possible well locations that were considered. In this study n is 66. The different objective functions were defined as follows:

i. Maximize the contamination risk index by Total Nitrogen concentration: This objective maximizes the accumulated total of the contamination risk indices by the TN concentration as follows:

$$f_1(x) = \sum_{i=1}^{n} ITN_i \tag{1}$$

where ITN_i is the TN risk index value located at well i and n is the total number of wells to be selected as a possible solution.

ii. Maximize the contamination risk index by Total Coliform concentration: This objective maximizes the accumulated total of the contamination risk indices by the TC concentration as follows:

$$f_2(x) = \sum_{i=1}^{n} ITC_i \tag{2}$$

where ITC_i is the TC risk index value located at well i and n is the total number of wells to be selected as a possible solution.

iii. Maximize the coverage area: This objective maximizes the total coverage area, assuming each well has a radius of influence of 1600 m—derived by dividing the total area (i.e. 567 km^2) by the number of wells that can be sampled (i.e. 66 wells). The calculation involved in this function adjusts for coverage areas that might overlap to avoid double counting. The optimization function is defined as:

$$f_3(x) = \sum_{i=1}^{n} A_i \tag{3}$$

where A_i is the adjusted area for well i and n is the total number of wells to be selected as a possible solution.

iv. Maximize public access wells: This objective considers maximizing the selection of wells that are easier to access than others. That is, the wells that fall under the public domain, such as waterworks, sanitation boards, piezometers or research projects, are ranked higher over those wells that are privately owned. The model considers maximizing the priority of the wells to be selected, as follows:

$$f_4(x) = \sum_{i=1}^{n} Ip_i \tag{4}$$

$$Ip_i = \begin{cases} 1 \\ 0 \end{cases}$$

where Ip_i is the level of priority of the well. The Priority is 1 for wells of public access and 0 for those that are privately owned.

Selection of monitoring parameters

The parameters analyzed in this study consisted in 6 parameters measured in situ: pH, electrical conductivity (EC), dissolved oxygen (OD), salinity, temperature (T) and turbidity, and 21 parameters measured in the laboratory: N-ammonia, N-nitrites, nitrates, total alkalinity, organic matter, conductivity, pH, bicarbonate, carbonate, sulfate, magnesium, calcium, sodium, potassium, chloride, arsenic, mercury, manganese, copper, total chromium and fecal coliforms. These parameters were selected considering the World Health Organization (WHO) regulations (WHO 2017), where they recommend certain parameters for the operational monitoring/sampling of water quality. These parameters were selected from the point of view of their importance at the time of assessing the overall quality of the water for public supply purposes.

Obtaining samples and parameters analyzed

The main objective of the sampling campaign was to evaluate the quality of the groundwater of the Patiño aquifer in the AMA and to characterize the types of water found under the AMA. Samples were taken during the months of June to December 2018. For each of the selected wells, both in-situ and laboratory measurements were performed.

The parameters evaluated in-situ were measured using a portable multiparameter probe that measured temperature, dissolved oxygen, pH, conductivity, turbidity, and salinity. The data obtained were recorded in sampling sheets containing: name of the station, identifier code of the point, location of the station, geographical coordinates of the point, sampling date, type of sample (effluent, well water, treated water, surface water, others), and the values of the measured parameters.

The data collection supplies consisted of two 1-L plastic containers for physicochemical analysis, one 200 mL sterile plastic bottle for bacteriological analysis, adhesive labels, brushes, pens, buckets, disposable gloves and a cooler containing ice. To extract samples, a submersible pump with a 100-m long hose, alongside a groundwater level measurement probe with the same length, a 30-m long extension cable and a handheld GPS were used. Before each field visit, the multiparameter probe was calibrated with traceable calibration solutions.

The on-site procedure to get a sample of water consisted of sampling raw groundwater through a tap if available or directly pumping a sample from the well. To prevent sampling stagnant/standing water, a 15-min water purge was performed for all wells.

The parameters analyzed in the laboratory and their respective techniques are indicated in Table 1. The general method corresponds to the Standard Methods 22nd Edition (SM, Standard Methods for the Examination of Water and Wastewater), Water Technical Manual (MTA)—Calais 312, Plate count method.

Data analysis

For all the sampled wells an exploratory analysis was carried out that consisted in calculating the average, the standard deviation, the coefficient of variation and the minimum and maximum concentration values. The classification was done in two different formats, one that looked at the drinking water standards and the other that looked at a water quality index.

First, the analyzed parameters were compared with three regulations to have a broader perspective on the suitability of the groundwater: The standards for drinking purposes

Table 1 Parameters measured with their respective analytical technique and unit of measurement

Parameter	Unit	Analytical technique
pH	pH unit	Standard Methods 4500-H^+ B—pH Value in Water by Potentiometry Using a Standard Hydrogen Electrode—22th. Ed
Conductivity	µS/cm	Standard Methods 2510 B—Conductivity Value in Water by Laboratory's Method—17th. Ed
Total alkalinity	mg $CaCO_3$/L	Standard Methods 2320 B. Titration Method—22th. Ed
Ammoniacal Nitrogen	mg/L	Standard Methods 4500 NH_3 D. Phenol salt Method—17th. Ed
Nitrite Nitrogen	mg/L	Standard Methods 4500-NO_2 $^-$B. Colorimetric Method—17th. Ed
Nitrates	mg/L	Standard Methods 4500 NO_3^- B—Ultraviolet Spectrophotometric Screening Method—22 th. Ed
Organic matter	mg O_2/L	Determination of permanganate oxidability Method. MTA N° 312
Calcium	mg Ca/L	Standard Methods 3500-Ca-B. EDTA Titrimetric Method- 22 th. Ed
Magnesium	mg Mg/L	Standard Methods 3500-Mg B Calculation Method—22 th. Ed
Chloride	mg Cl/L	Standard Methods 4500-Cl^- B. Argentometric Method—22 th. Ed
Sulfates	mg/L	Standard Methods 4500-SO_4^{-2} E. Turbidimetric method—17th. Ed
Sodium	mg/L	Standard Methods 3111 B Flame atomic Absorption Spectrometry—22th. Ed
Potassium	mg/L	Standard Methods 3111 B Flame atomic Absorption Spectrometry—22th. Ed
Mercury	mg Hg/L	Standard Methods 3112-Hg—Cold Vapor Atomic Absorption Spectrometry—22th. Ed
Total chromium	mg Cr/L	Standard Methods 3111 B—Flame atomic Absorption Spectrometry – 22th. Ed
Arsenic	mg As/L	Standard Methods 3500-As C—Silver Diethyldithiocarbamate Method
Manganese	mg Mn/L	Standard Methods 3111 B Flame atomic Absorption Spectrometry—22th. Ed
Copper	mg Cu/L	Standard Methods 3111 B Flame atomic Absorption Spectrometry—22th. Ed
Bicarbonate	mg $CaCo_3$/L	Standard Methods 2320 B
Carbonate	mg $CaCo_3$/L	Standard Methods 2320 B
Fecal coliforms	UFC/100 mL	Standard Methods 9221E Fecal coliform procedure. 9221 C Estimation of Bacterial Density

as recommended by WHO (2017), the European Directive 98/83 (EU 1998) on drinking water quality, and the allowed maximum levels set by the local Sanitary Services Regulatory Entity (ERSSAN) in Law No. 1614 (2000). This analysis was done to classify how many samples were above recommended drinking water standards.

According to the WHO (2017), drinking water standards are guidelines that describe reasonable minimum requirements (permissible limits) and are defined by numerical values of water components, that must be met to protect the health of consumers. When defining mandatory standards, the local environmental, economic and cultural conditions are considered. That is to say that each local jurisdiction can have different permissible levels depending on socioeconomical and environmental constraints. Therefore, what can be suitable in one region might not be suitable for another.

In contrast, water quality refers to an overarching concept that allows for a standardized format to compare different regions. In this context, the Water Quality Index (WQI), proposed by Brown et al. (1972), responds to the general suitability of the water for drinking purposes, independent of regulations. The WQI also offers an indication of the level of treatment that might be needed or how fragile the water might be. In contrast, water quality standards are binary and only offer a suitable or unsuitable label.

Therefore, to understand the impact of all the parameters as a whole, a water quality index (WQI) was also calculated using the methodology proposed by Sadat-Noori et al. (2014), who define WQI as a rating that provides the composite influence of all water quality parameters as it compares to certain standards. For this study the standards for drinking purposes as recommended by EU (1998) and the Paraguayan Law No. 1614 (2000), were considered for the WQI calculation, selecting the most restrictive permissible limit.

The parameters considered for the WQI calculation were pH, total dissolved solids (TDS), chloride, sulfate, sodium, potassium, calcium, magnesium, total hardness and nitrates.

Though TDS was not measured directly, the methodology proposed by Rusydi (2018) was used to derive it by Electrical Conductivity value. Similarly, total hardness was derived from the measured concentrations of calcium and magnesium.

First, a unit weight was assigned to each of the parameters under consideration (w_i) according to its health effects when present in drinking water (Table 2). Then, the relative weight for each parameter is computed using Eq. (5):

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \tag{5}$$

where W_i is the relative weight, w_i is the weight of each parameter and n is the number of parameters. The weight (w_i), the calculated relative weight (W_i) values, and the standards for each parameter are given in Table 2.

Table 2 Weight and relative weight for each parameter

Chemical parameter	Standard	Weight (wi)	Relative weight (Wi)
pH	6.5–8.5*	4	0.105
TDS (mg/L)	1000*	5	0.132
Chloride (mg/L)	250	5	0.132
Sulfate (mg/L)	250	5	0.132
Sodium (mg/L)	200	4	0.105
Potassium (mg/L)	12*	2	0.053
Calcium (mg/L)	100*	3	0.079
Magnesium (mg/L)	50*	3	0.079
Total hardness (mg/L)	400*	2	0.053
Nitrates (mg/L)	45*	5	0.132
		$\Sigma wi = 38$	$\Sigma Wi = 1$

Weight values according to the methodology proposed by Sadat-Noori et al. (2014) and supplemented with Varol and Davraz (2015)

*Values established in the Law No. 1614 (2000). General regulatory and tariff framework of the public service for the provision of drinking water and sanitary sewerage for the Republic of Paraguay. National Paraguayan Congress and Sanitary Services Regulatory Entity (ERSSAN). 2000

The next step was to calculate the quality rating scale for each parameter (q_i) using Eq. (6):

$$q_i = \frac{|C_i - I_i|}{S_i - I_i} \text{x} 100 \tag{6}$$

where q_i is the quality rating, C_i is the concentration corresponding to i^{th} parameter at a given sampling location, I_i is the ideal value of i^{th} parameter in pure water, and S_i is the drinking water standard for i^{th} parameter. It is worth noting that pH is the only parameter that has an ideal value and for the other parameters the ideal value is set to zero (i.e., I_{pH}= 7, and $I_i = 0$ for all other parameters).

For computing the WQI, the sub-index (SI) is determined for each chemical parameter using Eq. (7), which is then used to determine the WQI according to Eq. (8):

$$SI_i = W_i \text{x} q_i \tag{7}$$

$$WQI = \sum_{i=1}^{n} SI_i \tag{8}$$

where SI_i is the sub-index of i^{th} parameter, W_i is the relative weight of each parameter, q_i is the quality rating, and n is the number of parameters.

The WQI was classified by the following ranges: between 0–50 (Excellent water), 50–100 (Good water), 100–200 (Poor water), 200–300 (Very Poor water) and > 300 (Water unsuitable for drinking purpose).

Furthermore, to understand the type of geochemical process that is present in the aquifer holds, a Piper diagram (Piper 1944) was calculated. This is a widely used graph that shows the general chemical character of water, where anions and cations are included simultaneously and plotted in two equilateral triangles. The vertexes of the cation triangle are Ca^{2+}, Mg^{2+} and $Na^{+}+K^{+}$. The vertexes of the anion triangle are SO_4^{2-}, Cl^{-} and $CO_3^{2-}+HCO_3^{-}$. The data of the triangular diagrams are then projected in a central rhombus in which the composition of the water is deduced from anions and cations represented (Güler et al. 2002).

Additionally, the risk maps by Baez et al. (2019) that were used as input data were plotted against the actual measurements of the field sampling campaign as validation of the previous work. This comparison allowed us to discern if high values of Total Nitrogen were found where high values of risk indices were independently calculated.

Finally, to evaluate the presented protocol, the results obtained in this study were compared with those obtained in Houben et al. (2012) and INCLAM-HQA (2017), both of them carried out in the Patiño aquifer area. These studies did not implement a specific protocol for the selection of wells for their sampling campaign. To compare the effectiveness of their selection to our well selection protocol, we ran their selection through our algorithm and calculated the score for each objective function. Similarly, we calculated the effectiveness of each study, ours included, by considering how many of the sampled wells showed parameters outside the permissible limits. Protocol efficiency was defined as the ratio of the number of wells with parameters outside permissible range to the number of wells sampled.

Results and discussions

This section presents the results obtained from the application of the algorithm, the sampling campaign and the subsequent data analysis performed.

Selected wells

The algorithm was implemented to select 66 sampling wells out of the 2819 possible wells. Multiple runs of the algorithm were performed, presenting an improvement in the front as the number of generations increased. A total of 1000 generations were generated and a pareto front with 61 solutions was obtained.

The last generation of solutions is seen in Fig. 4 where the selected solution is highlighted. Figure 4 presents solutions after a min–max normalization. The selected solution was the one who had the highest sum of the four normalized objectives. The map in Fig. 5 shows the spatial location of the 66 selected wells, and where the sampling was performed.

Analysis of water quality results

There were 66 samples that went through analysis, and whose results are presented in Table 3. The table presents the 21 analyzed parameters in the sampling campaign, together with the statistical summary and the permissible limits according to national or regional regulations (WHO, EU and ERSSAN). For some of the parameters analyzed, such as organic matter and carbonate, the regulations used do not have reference values.

Of the 21 parameters analyzed, nine (43%) were found to be outside the standards for drinking purposes, of these, two parameters (nitrates and fecal coliforms) have direct adverse effects on consumer health (WHO 2017). The parameters found outside the limits according to regulations and their possible causes are described subsequently.

The pH values ranged between 5.12 and 8.14, with an average of 6.26 and a standard deviation of 0.79. In total, 65% of the samples presented pH values outside the limit. The pH indicates the degree of acidity or basicity of the water, and although it does not usually directly affect

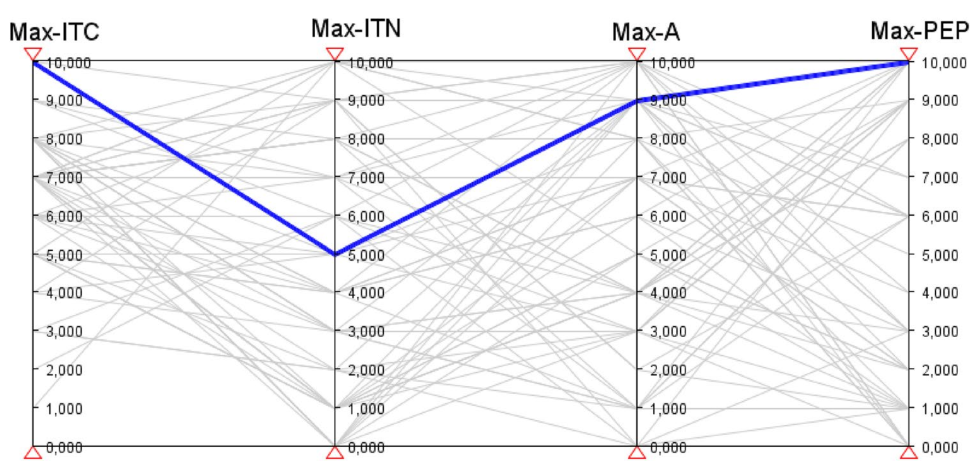

Fig. 4 Graph of parallel coordinates of the Pareto front with 61 optimal solutions. The selected solution is highlighted. Each axis represents the normalized value of the four different objectives

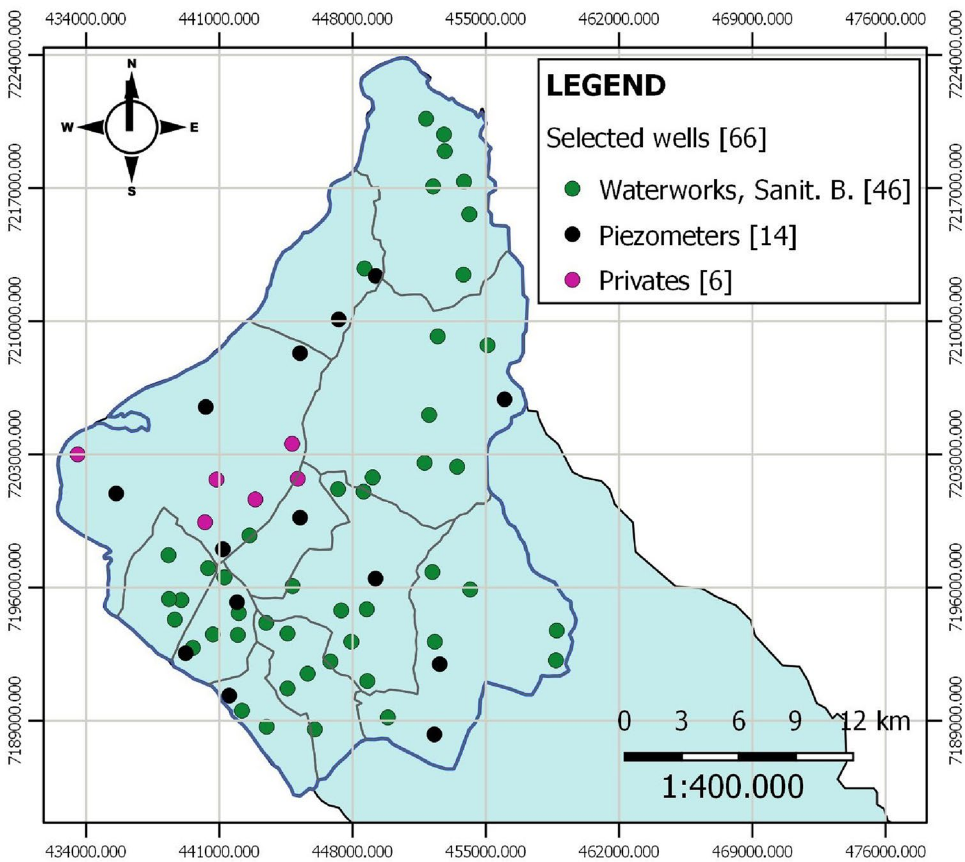

Fig. 5 Distribution of the 66 wells selected using the NSGA-II with Preference Ordering. The wells are separated by the ownership and type, water works (or sanitation boards) that are of public access, piezometers and private wells

consumers, it is one of the most important operational parameters of water quality (WHO 2017).

The nitrate (NO_3) analysis showed an average value of 47.83 mg/L, exceeding the strictest permitted limit (45 mg/L), with a range between 0.014 and 234 mg/L, and a standard deviation of 49.37 mg/L. Water intake with high concentrations of nitrate is reduced to nitrite in the stomach and can oxidize hemoglobin to methemoglobin, blocking the transport of oxygen through the body, causing cyanosis and asphyxiation (WHO 2017). The presence of nitrate in water is associated with agricultural practices, fertilizers, wastewater and on-site sanitation (WHO 2008)—in the case of the Patiño aquifer we hypothesize the latter being the principal cause.

Figure 6 shows the wells with nitrate concentrations that exceeded the permitted limits, corresponding to 42% of the samples. A general hypothesis for the presence of nitrates is that they originate from the high population density (Fig. 6a), added to the high density of cesspools (Fig. 6b).

Ammoniacal nitrogen (NH3-N) values ranged between 0.012 and 12.02 mg/L, with the highest values corresponding to the wells located in the center of the study area, with 9% of the samples exceeding the permitted limits (0.5 mg/L). The presence of Ammoniacal nitrogen is associated with domestic or industrial sewage, animal waste and recent drainage discharges; its intake has no immediate impact on health (WHO 2008). A similar hypothesis as before still holds given the presence of cesspools and added to this some potential industrial sites might be the sources of these contaminants.

The electrical conductivity values fluctuated between a range of 73.2 and 2410 µS/cm, with an average of 335.82 µS/cm and standard deviation of 341.58 µS/cm. Considering Law No. 1614 (2000), 20% of the samples exceed the recommended limit (<400 µS/cm). The variation reflected the existence of different types of water in the study area, considering the content of dissolved salts. All the samples that were out of the permissible range are found in the northeast section of the aquifer which is heavily exploited and has a large history of industrial processes such as bottling companies and tanneries. A hypothesis is that this overexploitation is drawing deeper water that due to the natural dissolution of naturally occurring soluble minerals present a higher presence of salts. With that said, at this moment the hypothesis that the presence of salts is due to anthropogenic sources cannot be discarded.

The analyzed magnesium (Mg) values ranged between 0.96 and 52.25 mg/L, with an average of 8.85 mg/L. Law No. 1614 (2000) recommends a magnesium concentration of <50 mg/L. Generally, water hardness is derived from the

Table 3 Descriptive statistics of the physicochemical and metal characteristics of the samples analyzed in the laboratory, and the limit values established by WHO, EU and ERSSAN

Parameters	Minimum	Maximum	Average	Stand. Dev	Permissible limit according to regulations				Out of the permissible limit
					WHO (1)	EU (2)	Law No. 1,614/2000 ERSSAN		
							Permissible	Recommended	
N-Ammo-niacal (mg/L)	0.012	12.02	0.39	1.67	–	0.50	–	–	6
N-Nitrites (mg/L)	0.0025	0.083	0.004	0.0099	3	0.50	–	–	0
Nitrates (mg/L)	0.014	234.0	47.83	49.37	50	50	45	0	28
Total Alkalinity (mg/L)	1.50	201.00	35.17	40.10	–	–	250	≤ 120	–
Organic matter (mg/L)	0.008	5.64	0.76	0.99	–	–	–	–	–
Conductivity (uS/cm)	73.2	2410.0	335.82	341.58	–	2500	1250	≤ 400	1
pH	5.12	8.14	6.26	0.79	–	6.5–9.5	6.5–8.5	6.5–8.5	43
Bicarbonate (mg/L)**	1.5	201.0	35.21	40.36	–	–	–	–	–
Carbonate (mg/L)	0.0	5.69	0.0862	0.70	–	–	–	–	–
Sulfate (mg/L)	0.0	239.45	14.89	35.09	–	250	–	–	0
Magnesium (mg/L)	0.96	52.25	8.85	7.73	–	–	50	≤ 30	1
Calcium (mg/L)	0.33	36.79	13.88	8.09	–	–	100	≤ 100	-
Sodium (mg/L)	1.99	388.0	27.39	53.54	–	200	–	–	1
Potassium (mg/L)	0.99	19.2	6.66	4.39	–	–	12	≤ 10	10
Chloride (mg/L)	1.48	453.3	38.88	69.05	–	250	–	–	2
Arsenic (mg/L)	< 0.03*	< 0.03*	< 0.03*	0.0	0.01	0.01	0.5	0	0
Mercury (mg/L)	< 0.0005*	< 0.0005*	< 0.0005*	0.0	0.001	0.001	–	–	0
Manganese (mg/L)	< 0.05*	< 0.05*	< 0.05*	0.0	0.4	0.05	–	–	0
Copper (mg/L)	< 0.05*	< 0.05*	< 0.05*	0.0	2.0	2.0	–	–	0
Total chromium (mg/L)	< 0.1*	< 0.1*	< 0.1*	0.0	0.05	0.05	–	–	–
Fecal Coliforms (UFC/100 mL)	0	18,900	292.42	2325.99	0.0	0.0	0.0	0.0	3

*Constant values due to the precision of laboratory equipment

**Not used for WQI calculation

(1) Values taken from "Guidelines for drinking−water quality: fourth edition incorporating first addendum". Geneva: World Health Organization (WHO). 2017

(2) Values taken from the Directive related with quality of water intended for human consumption. European Directive 98/83/EC. 1998

(3) Values established in the Law No. 1614 (2000) "General regulatory and tariff framework of the public service for the provision of drinking water and sanitary sewerage for the Republic of Paraguay". Congress of the Paraguayan Nation and Sanitary Services Regulatory Entity (ERSSAN). 2000

presence of calcium and magnesium. Taste acceptability, on the part of the population, of the degree of water hardness may vary (WHO 2017). The concentrations of magnesium found outside the permissible limits could be related to low pH values since under these conditions the dissolution of minerals and rocks that contain these ions is facilitated.

Sodium (Na) values were presented in a range of 1.99 to 388 mg/L, with an average of 27.39 mg/L, and a standard deviation of 53.54 mg/L. In one well the value exceeded the permissible limit (> 200) with a concentration of 388. The presence of sodium in water is associated with the intrusion of sewage, industrial landfills and seawater (Wright 2004); and of natural origin due to the presence of sedimentary rocks, the exchange of calcium and magnesium for sodium (WHO 2008).

The chloride (Cl) values were present in a range of 1.48–453.3 mg/L, with an average of 38.88 mg/L, and a standard deviation of 69.05 mg/L. In two wells, the presence of chloride above the permissible limit (> 250 mg/L) was identified. The presence of chloride in water could be associated with the intrusion of sewage, industrial landfills and/or other anthropogenic sources (Wright 2004).

Fecal coliform (FC) concentrations (> 0) were present in three wells. Its intake produces infectious and parasitic diseases of the digestive system, such as diarrhea, cholera, dysentery; and its presence is associated with contaminated or abandoned wells, septic tanks, latrines and fecal matter derived from intensive livestock farming (WHO 2008).

The 66 samples were taken at different depths, between 20 to 180 m, so to understand if there was a trend related

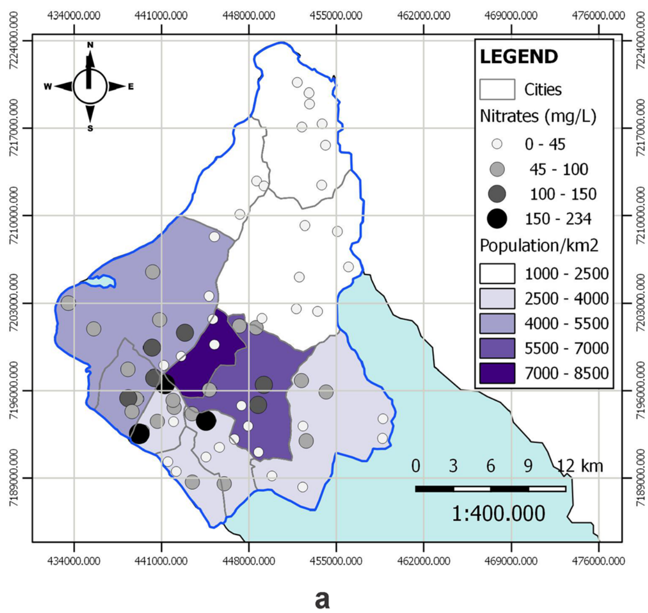

Fig. 6 Distribution of Nitrate (mg/L) concentration values sampled with the base map. **a** The population density per km^2 by city. **b** The density of cesspools per hectare. For reference permissible limit value 45 (mg/L). The highest concentrations of nitrates are related to the areas of high population density and the presence of cesspools

to depth, Fig. 7 was produced. Results show that there is no correlation between concentration values and depths, that is, there is a presence of high and low concentrations at different depths.

In summary, there were a total of 55 wells that had at least one value outside the permissible limit—corresponding to 83% of the samples. The southwestern part of the study area is the one of greatest concern, identifying up to three parameters outside the limit per well, mainly with parameters such as N-ammonia and nitrates, or nitrates and fecal coliforms. This area corresponds with the highest industrial presence and high density of cesspools.

Water type characterization

For the characterization of the type of water, the Piper diagram was used because it allows for the identification of the dominant geochemical components. Figure 8a shows the Piper diagram, which was elaborated from the analysis of the 66 samples. The different shapes displayed in the Piper

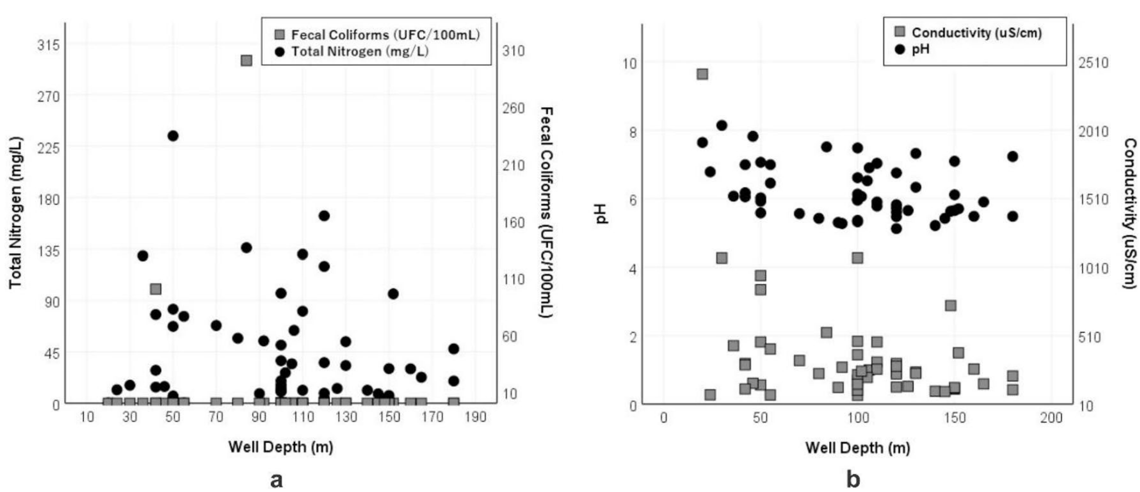

Fig. 7 Dual-axis graphs. **a** Total Nitrogen and Conductivity vs Well depth. **b** pH and fecal coliforms concentrations vs. well depth. There is no clear correlation between depth and water physicochemical parameters

diagram correspond to the samples collected in the cities that compromise the study area.

The concentrations of predominant ions in groundwater (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, CO_3^{2-}, SO_4^{2-} and Cl^{-}), are used to calculate the position of the different shapes in the Piper Diagrams. The calculation is based on the principle that the concentration of positive ions should be equal to the concentration of negative ions in a complete hydrochemical analysis (Feitosa et al. 2008).

The predominant type of water was the mixed calcium-magnesium-chloride (mixed Ca–Mg–Cl), with 47% of the total samples, characteristic of areas consisting mainly of limestones. In a smaller percentage, we identified sulfated calcium type (Ca-SO_4) with 17% of the wells in the high internal areas typical of soils, where evaporitic materials prevail with a predominance of gypsum; the sodium-chloride type (Na-Cl) with 17% of the wells in the northern areas of the aquifer where the influence of salty waters is important; 14% of the calcium-bicarbonate type (Ca-HCO_3) is presented in areas with limestone rocks; 5% of samples of mixed calcium- sodium-bicarbonate type (Ca-Na-HCO_3); and 2% of samples of the bicarbonate sodium type (Na-HCO_3). Figure 8b shows the aquifer map with the spatial distribution of water types, based on the results obtained in the Piper diagram.

According to the results, calcium chloride type waters predominate, present in almost the entire aquifer, and on the other hand, sodium chloride, in the northern part of the aquifer. The origin of this chemistry could be related to the strong anthropic pressures, in highly urbanized areas, with a very varied typology of potential sources of contamination and the lack of wastewater treatment. The absence of land-use plans makes it difficult to understand and control these pressures.

There are different hypotheses on the origin of the sodium chloride type waters. There is a strong hypothesis that there is a hydraulic connection with the northern Chaco (across the river) which has known chlorinated formations (Gadea 2019). Also, salinized waters could be naturogenic to the Patiño aquifer; chlorinated water could be found at depth, and outcropping in the aquifer's edge zones, specifically in the north of the aquifer, where it discharges to the Paraguay River (INCLAM-HQA 2017).

Water quality index

The water quality index indicated that 75% of sampled wells have a water categorized as "excellent", 23% of sampled wells have water categorized as "good" and 2% of the wells are shown to have a water quality index categorized as "poor". This calculation is the result of the combination of 10 environmental parameters (pH, TDS, chloride, sulfate, sodium, potassium, calcium, magnesium, total hardness and nitrates) and provides integrated information regarding the overall water quality.

Figure 9 illustrates the spatial distribution WQI map. The WQI map indicates that samples with good to poor waters are in the region of the aquifer, where there are

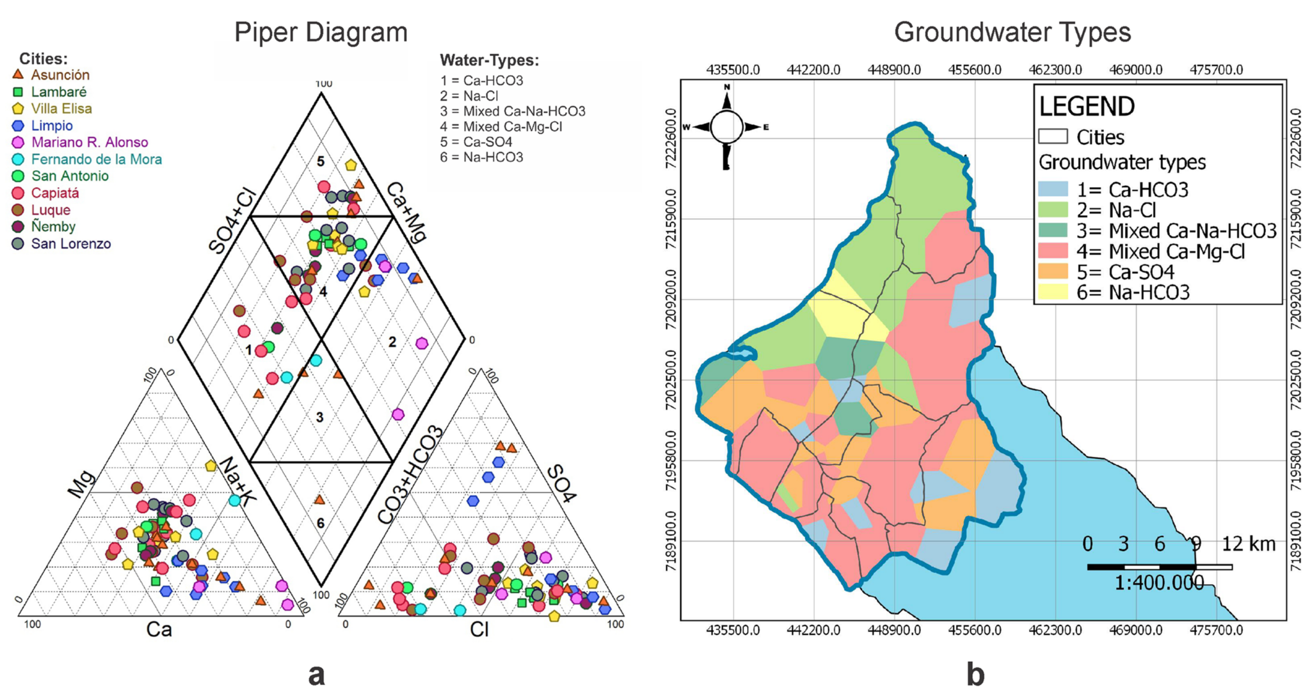

Fig. 8 **a** Piper diagram of the analysis results of 66 sampled points. **b** Water types identified from the Piper diagram

high concentrations of nitrates (93 mg/L on average), in addition there is a high population density average of 4134 inhabitants per km^2, with an average density of 6.29 cesspools per hectare; and in the northern region where the influence of salty waters is important, with high sodium values (up to 284 mg/L).

The results obtained with WQI indicate that most samples were "excellent" or "good", but when evaluating specific parameters, 9 parameters (Table 3) were identified as being above the permissible and acceptable values. In that sense, WQI depicts a general grade for the water suitability for drinking purposes which is useful only for comparing different sampling campaigns. In this context, the WQI method should be re-evaluated as a proxy for water suitability and whether it would be worthwhile to consider parameters that do not directly affect consumer health.

Validation of the input data used

Applying the validation between the measured values of total nitrogen and the independently developed risk map a correlation $\rho = 0.74$ was obtained, which for one validates the previous work by Baez et al. (2019) and also supplies confirmation for the robustness of the selection protocol presented in this study. Figure 10 presents the values of the Risk Index developed in the aforementioned study against sample values from a 2006, 2010 and this study's 2018 water quality campaign.

Evaluation of the protocol through a comparison with other sampling campaigns

Finally, to evaluate the effectiveness of the protocol implemented in the present study, we have compared our selection protocol and results with two other campaigns carried out by Houben et al. (2012) and INCLAM-HQA (2017) in the Patiño aquifer area. As mentioned in the methodology, the objective of each comparative study was to characterize potential contamination.

In the INCLAM-HQA (2017) study they sampled 19 wells in 567 km^2, prioritized sampling in 11 piezometers already built and designed for monitoring and another 8 deep wells, currently in use and aimed at large water consumers such as public institutions, petrol stations, car washes, waterworks and sanitation boards. The selected wells were considered important because they were distributed in areas related to nitrate contamination and the presence of high salinity—identified through a previous sampling campaign.

In the Houben et al. (2012) study they sampled 65 wells over a 79 km^2 area within the Patiño aquifer, specifically in the water basin of the San Lorenzo stream, within an urban area with different types of industries, businesses and few installed sanitary services. The aim was to immediately assess the state of the aquifer, focusing on a smaller area with great anthropic pressure with a very varied typology of potential sources of contamination.

In comparison, in the present study we developed a systematic way to carry out a sampling campaign considering the four objectives, as shown in Sect. 2.2.1. As an indicator of effectiveness, the wells selected in the other studies were evaluated using the four objectives that were developed in

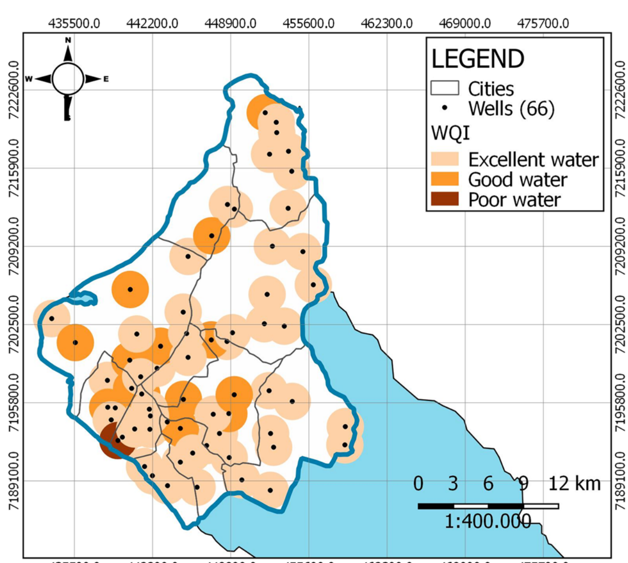

Fig. 9 Spatial distribution map of the water quality

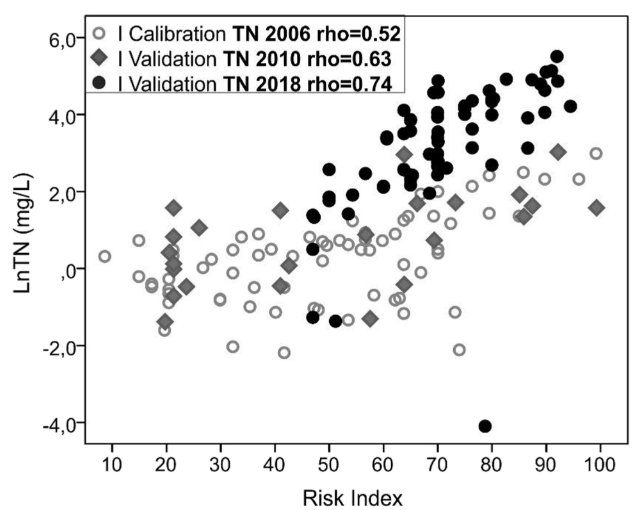

Fig. 10 Dispersion diagram of the natural log of total nitrogen concentrations of 2006, 2010 and this study's 2018 sampling campaign against the contamination risk index model calibrated with the total nitrogen of 2006 (Baez et al. 2019)

Table 4 Comparison of sampling campaigns over the Patiño aquifer. Only the wells sampled in the AMA are considered

Study	Study area (km^2)	Monit param	Sampled wells	Objectives				Flagged wells	Protocol efficiency
				1. ITC Sum	2. ITN Sum	3. Covered Area	4. Priority wells		
Present study	567	21	66	10	5.2	9.0	10.0	33	0.50
INCLAM-HQA (2017)	567	19	19	1.6	0.0	9.7	10.0	7	0.37
Houben et al. (2012)	79	31	63	5.5	0.0	10.0	0.0	13	0.21

this protocol to understand how they stacked up with our selection. As a second measure of effectiveness, the number of wells which were found to have parameters outside the allowed ranges (flagged wells) were compared to the total number of wells that were sampled.

According to Table 4, the present study has a better performance in the four objectives evaluated: greater ITN sum, greater ITC sum, greater covered area and a greater number of wells with priority. Also, evaluating the protocol efficiency as wells outside the limits over total sampled wells, the present study has a better performance over the other two campaigns.

The chemical or bacteriological parameters outside the limit in Houben et al. (2012) were sodium, nitrates and fecal coliforms; in INCLAM-HQA (2017) the parameters outside the range were sodium, nitrate, chloride, potassium and E. coli; while in the present study we found sodium, nitrates, N-ammonia, chloride and fecal coliforms. In that sense, this study has performed better or in equal manner when categorizing the number of parameters identified outside the acceptable limits.

Conclusions

We have presented and evaluated a systematic approach to carry out a groundwater sampling campaign in an urban aquifer. Previous studies done in the Patiño Aquifer (Baez et al. 2019; Facetti et al. 2019; Houben et al. 2012; INCLAM-HQA 2017) have warned about the risk of prevailing aquifer contamination, and some of these studies performed a groundwater sampling campaign but did so without a consistent objective-based approach. These studies selected wells using field information, and general accessibility of wells.

In this study, we have presented a well selection protocol based on the NSGA-II algorithm with preference ordering using four objective functions. We further showed its application by selecting 66 wells to sample out of a total population of more than 2800. The subsequent sampling that was carried out included the chemical and biological analysis of 21 parameters. The pH values were found out range in 65% of the wells, followed by nitrate concentrations where 42% of the wells sampled had values outside the permissible range.

By performing a Piper Graph analysis, the predominant water was found to be mixed calcium-magnesium-chloride type with 47% of the total samples falling under this category. This type of water is characteristic of areas consisting mainly of limestones.

The water quality index (WQI) indicated that 75% of sampled wells have the type of water categorized as "excellent", 23% of sampled wells have the type of water categorized "good" and 2% of the wells have water categorized as "poor". Though this rating might indicate a positive evaluation of the water in reality it reduces the effect of certain parameters that might be out of range. This is to prove that WQI serves as a general indicator of how much treatment a water might need but not of its potability.

As a validation of the proposed protocol a comparison with two other sampling campaigns conducted in the Patiño aquifer was done. The validation consisted of comparing the efficiency of the number of wells sampled to the number of well found to have parameters outside regulated limits. The comparison showed that 50% of the wells selected under this study found parameters outside the limit, while the other two sampling campaigns, which did not follow our selection protocol, showed a 21 and 37% efficiency rate.

We believe that our study makes a strong case for incorporating previous in-depth analysis of contamination risks of the sampling area, as well location information to determine the wells to be sampled. It is understandable that time constraints sometimes dictate well selection but we have shown that a simple set of four linear objective functions can provide insights and better results when characterizing urban aquifer contamination.

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References

Alzraiee AH, Bau DA, Garcia LA (2013) Multiobjective design of aquifer monitoring networks for optimal spatial prediction and geostatistical parameter estimation. Water Resour Res 49(6):3670–3684. https://doi.org/10.1002/wrcr.20300

Aller L, Bennett T, Lehr JH, Petty RJ, Hackett G (1987) DRASTIC: A standardized system for evaluating ground water pollution potential using hydrogeologic settings. US Environmental Protection Agency, Washington, DC, p 455

Baez L, Villalba C, Nogues JP (2019) Comparison of contaminant-specific risk maps for an urban aquifer: Patiño aquifer case. Environ Earth Sci 78(5):137. https://doi.org/10.1007/s12665-019-8141-3

Bashi-Azghadi SN, Kerachian R (2010) Locating monitoring wells in groundwater systems using embedded optimization and simulation models. Sci Total Environ 408(10):2189–2198. https://doi.org/10.1016/j.scitotenv.2010.02.004

Bertrand G, Hirata R, Pauwels H, Cary L, Petelet-Giraud E, Chatton E, Batista J (2016) Groundwater contamination in coastal urban areas: anthropogenic pressure and natural attenuation processes. Example of Recife (PE State, NE Brazil). J Contam Hydrol 192:165–180. https://doi.org/10.1016/j.jconhyd.2016.07.008

Brown RM, McClelland NI, Deininger RA, O'Connor MF (1972) A water quality index—crashing the psychological barrier. In Indicators of environmental quality Springer, Boston

CKC-JNS (2007) Estudio de Políticas y Manejo Ambiental de Aguas Subterráneas en el Área Metropolitana de Asunción—Acuífero Patiño. Asunción, Paraguay

Deb K (2011) Multi-objective optimisation using evolutionary algorithms: an introduction. In: Multi-objective evolutionary optimisation for product design and manufacturing. Springer, London, pp 3–34

Deb K, Pratap A, Agarwal S, Meyarivan TAMT (2002) A fast and elitist multiobjective genetic algorithm: NSGA-II. IEEE Trans Evol Comput 6(2):182–197. https://doi.org/10.1109/4235.996017

DGEEC (2013) Compendio Estadístico Año 2012. https://www.dgeec.gov.py/Publicaciones/Biblioteca/compendio2012/Compendio%20Estadistico%202012.pdf. Accessed 27 Mar 2020

Dhar A (2013) Geostatistics-based design of regional groundwater monitoring framework ISH. J Hydraul Eng 19(2):80–87. https://doi.org/10.1080/09715010.2013.787713

Dhar A, Patil RS (2012) Multiobjective design of groundwater monitoring network under epistemic uncertainty. Water Resources Manag 26(7):1809–1825. https://doi.org/10.1007/s11269-012-9988-1

Di Pierro F (2006) Many-objective evolutionary algorithms and applications to water resources engineering. Doctoral dissertation University of Exeter

EU (1998) Directive related with quality of water intended for human consumption. 98/83/EC Official Journal of the European Communities L330: 32–54

Facetti JF, Nunez R, Gomez C, Ojeda J, Bernal C, Leon-Ovelar R, Carvallo F (2019) Methyl tert-butyl ether (MtBE) in deepwells of the Patiño Aquifer, Paraguay: a preliminary characterization. Sci Total Environ 647:1640–1650. https://doi.org/10.1016/j.scitotenv.2018.08.062

Feitosa FAC, Manoel Filho J, Feitosa EC, Demetrio JGAC (2008) Hidrogeología: conceptos y aplicaciones. 3.ed. Fortaleza:Asociación Española para la Inteligencia Artificial CPRM, 812 p

Flörke M, Schneider C, McDonald RI (2018) Water Competition between Cities and Agriculture Driven by Climate Change and Urban Growth. Nat Sustain 1(1):5. https://doi.org/10.1038/s41893-017-0006-8

Gadea M (2019) Determinación de los Niveles de Salinidad del Acuífero Patiño Reportes científicos de la FACEN 10(2). https://doi.org/10.18004/rcfacen.2019.10.2.77

Gohar AA, Cashman A, Ward FA (2019) Managing food and water security in small island states: new evidence from economic modelling of climate stressed groundwater resources. J Hydrol 569:239–251. https://doi.org/10.1016/j.jhydrol.2018.12.008

Grischek T, Nestler W, Piechniczek D, Fischer T (1996) Urban groundwater in Dresden. Germany Hydrogeol Journal 4(1):48–63. https://doi.org/10.1007/s100400050088

Güler C, Thyne GD, McCray JE, Turner KA (2002) Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. Hydrogeol J 10:455–474. https://doi.org/10.1007/s10040-002-0196-6

Gulgundi MS, Shetty A (2018) Groundwater quality assessment of urban bengaluru using multivariate statistical techniques. Appl Water Sci 8(1):43. https://doi.org/10.1007/s13201-018-0684-z

Houben G, Rojas C, Romero A, Cabral N, Olavarrieta A, Enciso C, Brunelli ML, Colmán F, Silvero J, Almada M, Cruzans G (2012) Informe técnico: Investigación de la calidad del agua. Cuenca hídrica del arroyo San Lorenzo, Departamento Central. Proyecto "Manejo sostenible y protección de las aguas subterráneas en Paraguay"(PAS-PY). In: Secretaría del Ambiente. http://www.mades.gov.py/wp-content/uploads/2018/06/Informe-Final-San-Lorenzo.pdf. Accessed 22 Feb 2020

Ikem A, Osibanjo O, Sridhar MKC, Sobande A (2002) Evaluation of groundwater quality characteristics near two waste sites in Ibadan and Lagos. Nigeria Water, Air, and Soil Pollution 140(1–4):307–333. https://doi.org/10.1023/A:1020165403531

INCLAM-HQA (2017) Diagnóstico del Acuífero Patiño, en Proyecto BID PR-T 1207 "Estudio de Recursos Hídricos y Vulnerabilidad Climática del Acuífero Patiño". http://www.mades.gov.py/wp-content/uploads/2019/09/PR-T1207-Diagnostico.pdf. Accessed 10 Mar 2021

Kløve B et al (2014) Climate change impacts on groundwater and dependent ecosystems. J Hydrol 518:250–266. https://doi.org/10.1016/j.jhydrol.2013.06.037

Kollat JB, Reed PM (2006) Comparing state-of-the-art evolutionary multi-objective algorithms for long-term groundwater monitoring design. Adv Water Resour 29(6):792–807. https://doi.org/10.1016/j.advwatres.2005.07.010

Law No. 1614 (2000) General regulatory and tariff framework of the public service for the provision of drinking water and sanitary sewerage for the Republic of Paraguay, Congress of the Paraguayan Nation and Sanitary Services Regulatory Entity (ERSSAN). Asuncion, Paraguay, November, 2000. https://www.bacn.gov.py/leyes-paraguayas/1694/ley-n-1614-general-del-marco-regulatorio-y-tarifario-del-servicio-publico-de-provision-de-agua-potable-y-alcantarillado-sanitario-para-la-republica-del-paraguay. Accessed 08 Mar 2021

Nas B, Berktay A (2010) Groundwater quality mapping in urban groundwater using GIS. Environ Monit Assess 160(1–4):215–227. https://doi.org/10.1007/s10661-008-0689-4

Newcomer ME, Gurdak JJ, Sklar LS, Nanus L (2014) Urban recharge beneath low impact development and effects of climate variability and change. Water Resour Res 50(2):1716–1734. https://doi.org/10.1002/2013WR014282

Nobre RCM, Rotunno OC, Mansur WJ, Nobre MMM, Cosenza CAN (2007) Groundwater vulnerability and risk mapping using GIS, modeling and a fuzzy logic tool. J Contaminant Hyrol 94(3–4):277–292. https://doi.org/10.1016/j.jconhyd.2007.07.008

Piper AM (1944) A Graphic Procedure in the Geochemical Interpretation of Water-Analyses. Trans Am Geophys Union 25:914–923. https://doi.org/10.1029/TR025i006p00914

PostGIS (2015) Spatial and Geographic objects for PostgreSQL. Open source geospatial foundation project.https://www.postgis.net/. Accessed 24 Mar 2020

PostgreSQL B (1996) PostgreSQL: The world's most advanced open source ralational database. Web resource. https://www.postgresql.org/about/. Accessed 24 Mar 2020

Robinson H, Gronow J (1992) Groundwater protection in the UK: assessment of the landfill leachate source-term. JIWMEZ 6(2):229–236

Rothwell JJ, Robinson SG, Evans MG, Yang J, Allott TEH (2005) Heavy metal release by peat erosion in the Peak District, southern Pennines. UK Hydrol Processes 19(15):2973–2989. https://doi.org/10.1002/hyp.5811

Rusydi AF (2018) Correlation between conductivity and total dissolved solid in various type of water: a review. In: Paper presented at the Global Colloquium on GeoSciences and Engineering

Sadat-Noori SM, Ebrahimi K, Liaghat AM (2014) Groundwater quality assessment using the water quality index and GIS in Saveh-Nobaran aquifer. Iran Environ Earth Sci 71(9):3827–3843. https://doi.org/10.1007/s12665-013-2770-8

Sagar SS, Chavan RP, Patil CL, Shinde DN, Kekane SS (2015) Physico-chemical parameters for testing of water-A review. Int J Chem Stud 3(4):24–28

Santiago A, Dorronsoro B, Nebro AJ, Fraire H (2016) Un nuevo método de estimación de densidad para problemas de optimización con tres objetivos usando metaheurısticas. In: XVII Conferencia de la Asociación Española para la Inteligencia Artificial, 2016. pp 345–354

TNO (2001) Informe técnico: Estudio del Acuífero Patiño. Fortalecimiento de los Estudios Hidrogeológicos del SENASA (FEHS). Asunción, Paraguay

Varol S, Davraz A (2015) Evaluation of the groundwater quality with WQI (Water Quality Index) and multivariate analysis: a case study of the Tefenni plain (Burdur/Turkey). Environ Earth Sci 73(4):1725–1744. https://doi.org/10.1007/s12665-014-3531-z

WHO (2008) Guidelines for drinking-water quality, 3rd edition: Volume 1 - Recommendations. Geneva

WHO (2017) Guidelines for drinking-water quality: 4th edition incorporating first addendum. Geneva

Wright J (2004) Environmental chemistry. Routledge

Yeh WW (2015) Optimization methods for groundwater modeling and management. Hydrogeol J 23(6):1051–1065. https://doi.org/10.1007/s10040-015-1260-3

Zendehbad M, Cepuder P, Loiskandl W, Stumpp C (2019) Source identification of nitrate contamination in the urban aquifer of Mashhad. Iran J Hydrol 25:100618. https://doi.org/10.1016/j.ejrh.2019.100618

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