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Evaluation of the Hydrochemical and Water Quality Characteristics of an Aquifer Located in an Urbanized Area

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Abstract: Groundwater is an important source of fresh water in the world. However, the excessive extraction and increasing pollution represent a major challenge for water sustainability in Mexico. Nowadays, since water quality changes in aquifers are not noticeable, aquifer monitoring and assessment are imperious. In this study, the water quality of the Cuernavaca aquifer was evaluated using a database of 23 parameters in 4 sampling points from 2012 to 2019. The spatial behavior of water quality variables was described by using interpolation. The temporal evaluation of groundwater quality was carried out through time series. Water quality indices (WQI) were obtained in this aquifer and the WQI values suggest that the groundwater could be considered as good quality for potable use and of medium-high quality for irrigation. The chemical characteristics of the groundwater were also evaluated using Gibb, Piper, and Schoeller diagrams. Finally, with a total of 34 samples of each parameter in each sampling site, a multivariate statistical analysis was performed using a Pearson correlation and hierarchical cluster analysis. This analysis showed a correlation between hydrochemical features and groundwater quality parameters, where nitrates presented the highest number of significant correlations with other parameters. These results may be useful for the authorities to adopt planning methods to improve the sustainable development of the aquifer.

Keywords: Cuernavaca aquifer; hydrochemistry; water quality index; time series analysis; spatial analysis

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1. Introduction

Groundwater is one of the most important natural resources and plays an important role in ecosystems [1]. It is widely used for domestic, industrial, and agricultural activities; hence, its demand is constantly increasing [2–5]. Population growth, accidental spills, surface leaching, runoff, and the extensive use of fertilizers in irrigated areas are considered the main causes of groundwater alteration [6,7]. Furthermore, agricultural activities modify groundwater conditions with nutrients and pesticides coming from leachate infiltration into the soil. Therefore, the use of fertilizers, pesticides, and herbicides in agriculture are major threats to aquifers [8–10]. In addition, the deterioration of an aquifer can be also related to natural causes such as floods, droughts, and salinization [11–13]. Once the aquifer is altered, it is complex and expensive to reverse the damage [12,14]. Therefore, groundwater quality must be monitored regularly to prevent aquifer alterations.

Many studies have been proposed for the assessment of aquifer vulnerability. Bannenberg et al. [6] evaluated the hydrological regime and hydrochemical features of the Flamouria aquifer in Edessa, Greece. They found that groundwater quality was not suitable for irrigation use since the high alkalinity and total dissolved solids found in groundwater could generate excessive salinization of the soil. Kumar et al. [8] conducted a hydrochemical study to assess the water quality suitability for drinking and irrigation purposes. As a result, they found a high concentration of some ions, such as As, Fe, and Mn, in an aquifer located in the Central Ganga Basin. Loh et al. [15] evaluated the suitability of an aquifer in Ghana for domestic and irrigation purposes. They used conventional hydrochemical and mass balance models to reveal relationships between water parameters and the main influence on the chemistry of the aquifer under study. As a result, they found that the groundwater in the area is permissible for agricultural irrigation.

Zakaria et al. [16] evaluated the hydrochemistry of groundwater in the Anayari catchment to identify the hydrogeochemical processes that are responsible for the main ions in groundwater. Their results showed good quality for irrigation without prior treatment. Wisitthammasri et al. [17] studied the water quality and hydrochemical characteristics of an aquifer in Thailand using multivariate statistical analysis to identify preliminary ion sources. This multivariate analysis evidenced the ion exchange between Ca^{2+} and Na^{+} from the weathering of silicates and calcite. Some commonly used multivariate statistical techniques, such as Pearson correlations and Hierarchical Cluster Analysis (HCA), have been used to illustrate the relationship between many groundwater variables and describe the relationship between them [18]. These studies have been carried out to develop appropriate groundwater management strategies and policies to protect aquifers. According to Elumalai et al. [4], multivariate statistical analyses are important because they provide essential information on groundwater quality and the processes responsible for its alteration.

Another tool for groundwater water quality assessment is the water quality index (WQI). This tool has been widely used by several researchers [8,14,19] since it simplifies the interpretation of water quality behavior. El Osta et al. [19] used this technique to classify the suitability of groundwater. As a result, they found that only a low percentage of the samples were classified as good to excellent to be used, while the rest of the samples were inadequate and required treatment to be used as drinking water. Another effective tool for assessing groundwater quality and its variability is that recommended by Kumar et al. [8] who evaluated the groundwater quality based on the Geographic Information System (GIS) through the Groundwater Quality Index (GQI) in an aquifer in southern India. They mention that this method is reliable for groundwater quality assessment and serves as a useful tool for decision-makers for efficient groundwater quality monitoring and management mainly in agricultural areas which have a great influence on groundwater recharge and quality.

In recent years, population growth and the increase of agricultural areas and indus-trial activities have intensified water demand, threatening the sustainable use of ground-water in the Cuernavaca aquifer. Despite this situation has been locally evidenced, no formal studies have been carried out to demonstrate the effect of these activities on groundwater resources. The novelty of this study lies in describing the hydrological and hydrochemical conditions of this aquifer to identify its vulnerability. The geohydrological features of the Cuernavaca aquifer are described using Gibb, Piper, and Schoeller diagrams. Groundwater quality evaluation is carried out based on time series analysis, water quality distribution maps, and water quality indices. This study performs a multivariate and correlation analysis to identify possible pollution sources and proposes better water management strategies for this aquifer.

2. Materials and Methods

2.1. Study Area

The study area is in the state of Morelos, Mexico with an approximate area of 820 km^2 (Figure 1). Mean annual precipitation, evapotranspiration, and air temperature are 1278 mm, 874.7 mm, and 19.4 °C, respectively. The highest rainfall values are observed from July to September, which corresponds to the summer season, and less significant precipitations are registered in winter from October to January mainly caused by cold fronts. The Cuernavaca aquifer is a free, heterogeneous, and anisotropic aquifer with surface geology that is represented by lithological units mainly of sedimentary and volcanic origin [20] and does not show any significant structural complications. The static water level of this aquifer varies from 20 to 100 m.

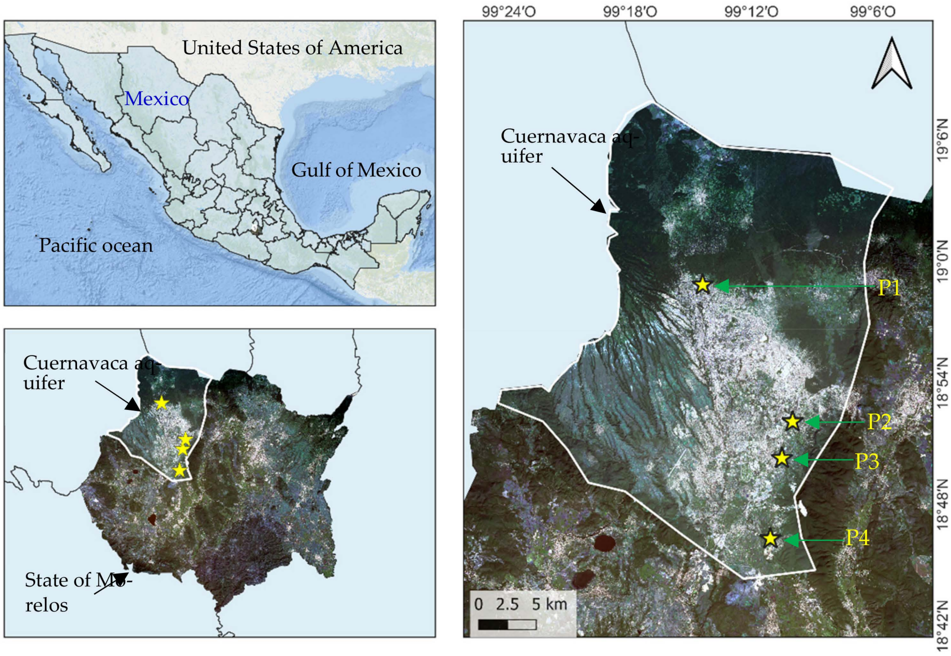


Figure 1. Location of the Cuernavaca aquifer and location of sampling wells.

2.2. Data Collection

In Mexico, the National Water Commission (CONAGUA) is a federal agency responsible for monitoring, surveillance, and management of aquifers [21]. The analysis of the groundwater samples was carried out by an accredited laboratory [22] which applied a methodology based on the standard methods (APHA) [23]. The data used in this study were obtained by this federal agency. For economic and strategic reasons, four sampling wells were monitored, which were in sites with intense anthropogenic activity. These wells are used for water consumption. The extraction of groundwater for consumption purposes is carried out using pumping systems.

The hydrochemical and water quality parameters considered in this study were: bicarbonates (HCO^{3-}), fecal coliforms (FC), total organic carbon (TOC), ammonium (NH_3), nitrites (NO^{2-}), nitrates (NO^{3-}), organic nitrogen (ON), total nitrogen (TN), total phosphorus (TP), total dissolved solids (TDS), electrical conductivity (EC), pH, chlorides (Cl^-), fluorides (F), silicon oxides (SiO_2), potassium (K^+), manganese (Mn), sodium (Na^+), sulfates ($SO_4{}^{2-}$), calcium (Ca^{2+}), magnesium (Mg^{2+}), total hardness (TH), water temperature (WT).

Quality control (QC) and quality assurance (QA). The sampling wells were monitored by CONAGUA. An accredited laboratory carried out the analysis of 23 parameters sampled every six months in the 2012–2019 period. The water sampling was carried out according to Mexican regulations. Based on these regulations, chemical products of analytical grade were required for the preparation of the standard solutions and reagents. In addition, replicates were performed to ensure the reliability of the results and comply with quality control required by the General Directorate of Standards and the Federal Law on Metrology and Normalization.

2.3. Spatial and Temporal Assessment of Groundwater Quality

The spatial evaluation of the groundwater quality of the Cuernavaca aquifer was carried out through interpolation of the measured parameters as suggested by other studies [24,25]. The inverse distance weighting (IDW) interpolation method was used to describe the spatial distribution of the groundwater quality values through the study area by using the QGIS 3.18 software. The weights used in the IDW method were calculated according to the weighting strategy proposed by Bartier [25]. These weight values are determined based on the distance between the sampling points according to Equation (1).

$$z_{x,y} = \frac{\sum_{i=1}^{n} z_i d_{x,y,i}^{-\beta}}{\sum_{i=1}^{n} d_{x,y,i}^{-\beta}} \tag{1}$$

where $z_{x,\,y}$ is the water quality parameter to be estimated; z_i represent the measured value for the sampling point; $d_{x,\,y,\,i}$ is the distance between $z_{x,\,y}$ and z_i; and β is a user-defined coefficient (the software default value of 2 was used for the β coefficient).

Temporal evaluation of groundwater quality was performed using time series analysis to determine possible groundwater quality temporal trends using biannual sampling data from 2012 to 2019. A temporal analysis was carried out by describing the groundwater quality variations over time. Finally, groundwater quality data were compared to World Health Organization (WHO) and local guidelines.

2.4. Water Quality Assessment

2.4.1. Drinking Water Quality Index

The drinking water quality index (DWQI) is frequently used to determine the suitability of groundwaters. In this study, the determination of DWQI was performed according to Equations (2)–(5) [14,26,27].

$$W_i = \frac{w_i}{\sum_i^n w_i} \tag{2}$$

$$Q_i = \frac{e_i - v_i}{b_i - v_i} * 100 \tag{3}$$

$$SI = W_i * Q_i \tag{4}$$

$$DWQI = \sum_{i=1}^{n} SI \tag{5}$$

where W_i is the relative weight; w_i is the weight assigned to each parameter according to its relative importance for drinking water (the maximum weight of "5" has been assigned for the highest importance and the minimum weight of "2" for the lowest importance); "n" is the number of groundwater parameters; Q_i: is the rating according to the distribution of the "ith" parameter. e_i: is the concentration of each parameter; v_i: is the optimum value of the parameter ("0" is considered as optimum value for all parameters, except pH which is "7"); b_i is the guideline value [28] for each parameter; SI: is the sub-index of "ith" parameter. According to some researchers [14,29,30], the optimum values and weights for the parameters of the DWQI are: pH (b_i = 8.5, w_i = 4, W_i = 0.13), TDS (mg/L, b_i = 500, w_i = 4, W_i = 0.13), total hardness (mg/L, b_i = 300, w_i = 3, W_i = 0.10), calcium (mg/L, b_i = 75, w_i = 3, W_i = 0.10), magnesium (mg/L, b_i = 30, w_i = 3, W_i = 0.10), nitrates (mg/L, b_i = 45, w_i = 4, W_i = 0.13), chlorides (mg/L, b_i = 250, w_i = 2, W_i = 0.06), sulfates (mg/L, b_i = 200, w_i = 2, W_i = 0.06), fluorides (mg/L, b_i = 1, w_i = 4, W_i = 0.13), and total alkalinity (mg/L, b_i = 200, w_i = 2, W_i = 0.06). Based on the results of Equation (4), the aquifer water was then classified into different categories: DWQI < 50 (excellent), DWQI = 50–100 (good), DWQI = 100–150 (moderate), DWQI = 150–200 (poor) and DWQI $\geq$ 200 (extremely poor).

2.4.2. Hydrochemical Characteristics

The chemical composition of groundwater is highly variable. Hence, the hydrochemical classification and groundwater chemical composition evolution were determined by using the Gibb, Piper, and Schoeller plots [15,31]. Then, the suitability of the groundwater for irrigation was evaluated by using the groundwater indices shown in Table 1.

2.4.3. Multivariate Statistical Analysis

Multivariate statistical techniques such as Pearson correlation and hierarchical cluster analysis (HCA) were used to figure out the relationship between the water quality variables. This multivariate statistical analysis was used to identify the factors and possible sources that could explain the behavior of the groundwater quality of the aquifer [32–35]. In addition, a dendrogram was performed using the ward conglomeration method with a Euclidean distance metric [7,15].

Table 1. Groundwater indices based on hydrochemical features.

Indices	Acronym	Equation	References
Sodium adsorption ratio	SAR	$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}}$	Abdelaziz et al. [34]
Soluble sodium percentage	SSP	$SSP = \frac{Na^{+}}{Ca^{2+}+Mg^{2+}+K^{+}} * 100$	Tefera et al. [31]
Sodium percentage	%Na	$\%Na = \frac{(Na^{+}+K)}{(Ca^{2+}+Mg^{2+}Na^{+}+K^{+})} * 100$	Abbasnia et al. [36]
Residual Sodium Carbonate	RSC	$RSC = (HCO_3^{-}) - \left(Ca^{2+} + Mg^{2+}\right)$	Zakaria et al. [16]
Magnesium Hazard	MH	$MH = \frac{Mg^{2+}}{Mg^{2+}+Ca^{2+}} * 100$	Hossain et al. [37]
Permeability index	PI	$PI = \frac{Na^{+}+K^{+}+\sqrt{HCO_3^{-}}}{Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}} * 100$	Kumar et al. [8]
Kelly Ratio	KR	$KR = \frac{Na^{+}}{Mg^{2+}+Ca^{2+}}$	Acharia et al. [27]
Total Hardness	TH	$TH = (Ca + Mg) * 50$	Tefera et al. [31]

3. Results and Discussion

3.1. Descriptive Analysis of Groundwater Quality Parameters

The total dissolved solids reflect the behavior of the salt concentration of the aquifer. These solids were found in a range of 75–688 mg/L and a mean value of 316 mg/L was registered. This value is low compared to that reported by Tefera et al. [31], who found concentrations up to 2777.6 mg/L. According to WHO [28], groundwaters with TDS values higher than 500 mg/L could be considered unsuitable for drinking water supply. The total hardness was found in a range of 24.6–456.8 mg/L. However, the mean value (179.2 mg/L) is below the concentration of 300 mg/L suggested by WHO [28] for drinking water. This value is also below the total hardness found by Kumar et al. [8], who presented concentrations greater than 292 mg/L in an unconfined aquifer located in the Central Ganga Basin, India.

The electrical conductivity of the Cuernavaca aquifer was between 90 and 991 µS/cm with a mean conductivity of 409.8 µS/cm. A high variation of electrical conductivity was observed in this aquifer, where the lowest conductivity values were found in sampling well one. Anthropogenic activities, such as agriculture, and rainwater filtration could be the reason for this variation. Jama et al. [38] presented concentrations up to 11,950 µS/cm in the unconfined Doukkala Aquifer located in a large agricultural region in Morocco. The groundwater of the Cuernavaca aquifer is slightly alkaline since its pH is in the range of 6.2–8.4 (the water is considered alkaline when pH > 8 and acidic when pH < 6). This pH range is within the drinking water standards of the WHO (6.5–8.5).

Nitrogen and phosphorus were below the permissible limits proposed by local standards. The TN and TP concentrations found were between 0.012–7.02 and 0.001–0.39 mg/L, respectively. Nitrogen concentrations are not usually frequent in natural soils, they occur due to the contact of the soil cover with nitrated fertilizers, animal waste, domestic effluents, and septic tanks [14]. The total organic carbon was found in a range of 0.07–2.57 mg/L. The presence of organic matter in the Cuernavaca aquifer could be related to the infiltration of the organic matter produced naturally by plants and animals due to excretion and decomposition. This situation is corroborated since fecal coliforms were found in the aquifer, with a mean value of 276.6 CFU/100 mL. The presence of fecal coliforms in groundwater could indicate pollution from anthropogenic sources since the sampling wells are in an urban area with a large population. Table 2 presents the mean values of the water quality parameters measured in the Cuernavaca aquifer from 2012 to 2019.

Table 2. Range, standard deviation and mean values for water quality parameters in the Cuernavaca aquifer from 2012 to 2019.

Parameters	Abbreviation	Minimum	Maximum	Mean	Standard Deviation
Bicarbonates (mg/L)	HCO^{3-}	48.40	294.90	145.12	79.75
Fecal coliforms (MPN/100 mL)	FC	1.00	2909.00	276.62	719.15
Total organic carbon (mg/L)	TOC	0.08	2.87	0.92	0.72
Ammonium (mg/L)	NH_3	0.00	0.61	0.07	0.12
Nitrites (mg/L)	NO^{2-}	0.00	0.04	0.01	0.01
Nitrates (mg/L)	NO^{3-}	0.00	6.87	3.24	2.13
Organic Nitrogen (mg/L)	ON	0.00	1.55	0.24	0.29
Total nitrogen (mg/L)	TN	0.01	7.03	3.56	2.20
Total phosphorus (mg/L)	TP	0.00	0.40	0.15	0.09
Total dissolved solids (mg/L)	TDS	64.64	688.00	316.01	195.16
Electrical conductivity (μS/cm)	EC	90.00	991.00	409.79	266.25
pH	PH	6.20	8.40	7.29	0.45
Chlorides (mg/L)	Cl^{-}	8.44	78.25	23.89	20.62
Fluorides (mg/L)	F	0.04	0.97	0.32	0.19
Silicon oxides (mg/L)	SiO_2	30.42	91.29	67.10	13.56
Potassium (mg/L)	K^{+}	1.32	7.72	3.68	1.60
Manganese (mg/L)	Mn	0.00	0.48	0.01	0.08
Sodium (mg/L)	Na^{+}	1.92	40.01	18.59	9.43
Sulfates (mg/L)	$SO_4{}^{2-}$	0.82	226.38	48.41	49.98
Calcium (mg/L)	Ca^{2+}	3.87	121.10	41.93	37.57
Magnesium (mg/L)	Mg^{2+}	3.82	50.47	19.25	13.07
Total hardness (mg/L)	TH	24.60	456.80	184.46	141.14
Water temperature (°C)	WT	17.25	22.49	20.24	21.68

The concentrations of some mineral compounds such as calcium and magnesium cause the precipitation of these salts. In the Cuernavaca aquifer, calcium was found in concentrations from 3.88 to 121.1 mg/L and a mean value of 41.9 mg/L, while magnesium was found from 3.8 to 50.5 mg/L with a mean value of 19.2 mg/L. The presence of concentrations of these salts (Mg^{2+} and Ca^{2+}) is due to the geological features of the aquifer. Sodium and potassium were found in a range of 1.92–37.5 and 1.3–6.6 respectively. The mean values for all major cations were within the maximum permissible limit [28].

Bicarbonates were within a range of 48.4–295 mg/L and a mean value of 145.1 mg/L was calculated. It is noteworthy that carbonates were not found in the samples. Sulfates in the Cuernavaca aquifer are between 0.8 and 136 mg/L, which are below the $SO_4{}^{2-}$ concentrations reported in other studies [39] and the guidelines recommended by the WHO [28]. Moreover, the chlorides presented a concentration between 8.4 and 78.2 mg/L, while nitrates showed a maximum concentration up to 6.2 mg/L, with a mean value of 3.2 mg/L. Both anions' mean values were also below the WHO maximum allowable values. Adimalla and Qian [14] suggest that nitrates could be found in groundwaters due to anthropogenic activity. They reported NO_3 concentrations up to 198.17 mg/L in groundwater under the influence of agriculture activities in Nanganur, India. In this study, a high variation in NO_3 concentrations was found between sampling sites, where the highest concentration was found in sampling site 2. Cadmium, chromium, mercury, lead, zinc, and arsenic were also analyzed in this study; however, the concentrations found could be negligible because low concentrations were observed (cadmium < 0.0002 mg/L; chromium < 0.00088 mg/L; mercury < 0.00009 mg/L, lead < 0.00154 mg/L, zinc < 0.002 mg/L and arsenic < 0.00139 mg/L). According to these results, the influence of geogenic sources was evidenced, where leaching and weathering of rocks and the use of pesticides and fertilizers could be recognized as the main driving factors for the hydrochemical and water quality of the aquifer.

3.2. Spatial and Temporal Variations of Measuring Indicators

A total of 23 water quality parameters were analyzed at four sampling wells. These sampling wells are located within the urban area of the city of Cuernavaca, which has different elevations as shown in Figure 2.

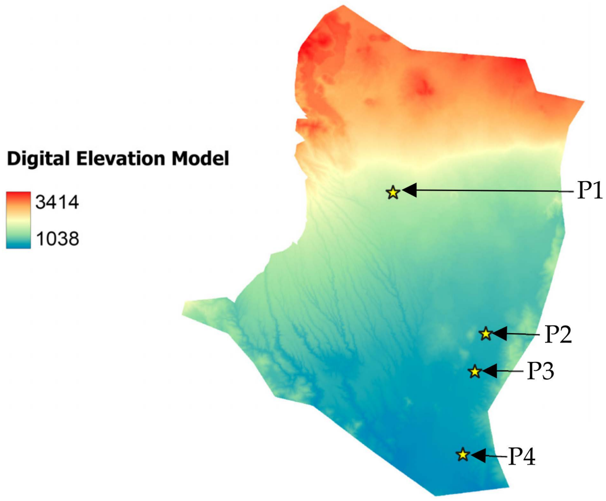


Figure 2. Elevations of the Cuernavaca aquifer.

The land use and soil classifications in the study area are shown in Figures 3 and 4, respectively. These figures demonstrate that P1 is in a wooded area with little human settlement, close to the annual rainfed agricultural area. The dominant soil type in this area is Luvic phaeozem which is characterized by organic matter and scarce carbonates. This sample site is next to an oak-pine forest land-use zone. Sample sites P2, P3, and P4 have similar characteristics because they are in irrigated agricultural areas close to the urban area. These sites are in a Pelic vertisol soil characterized by high mineral content.

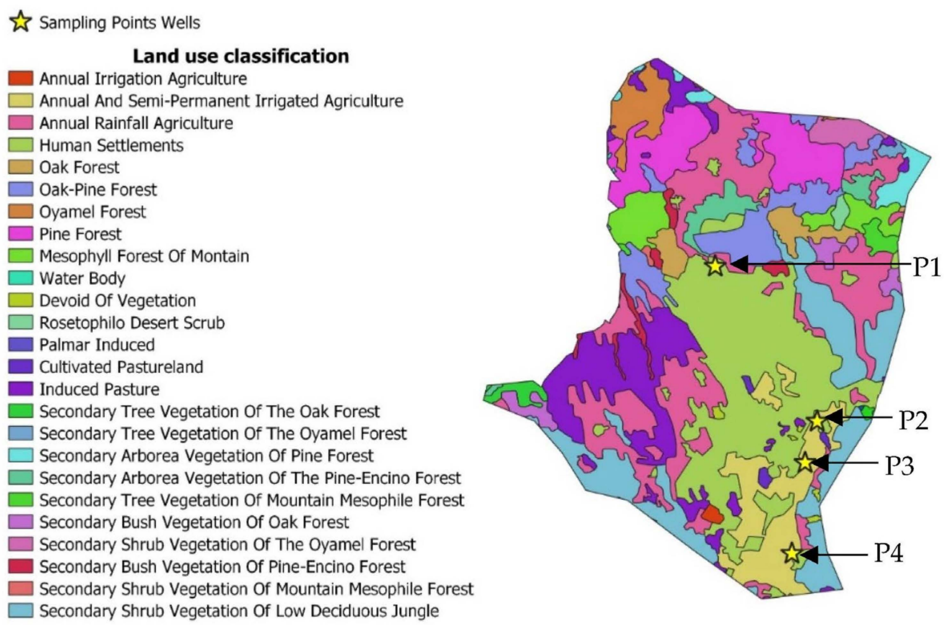


Figure 3. Land use classification of the Cuernavaca aquifer.

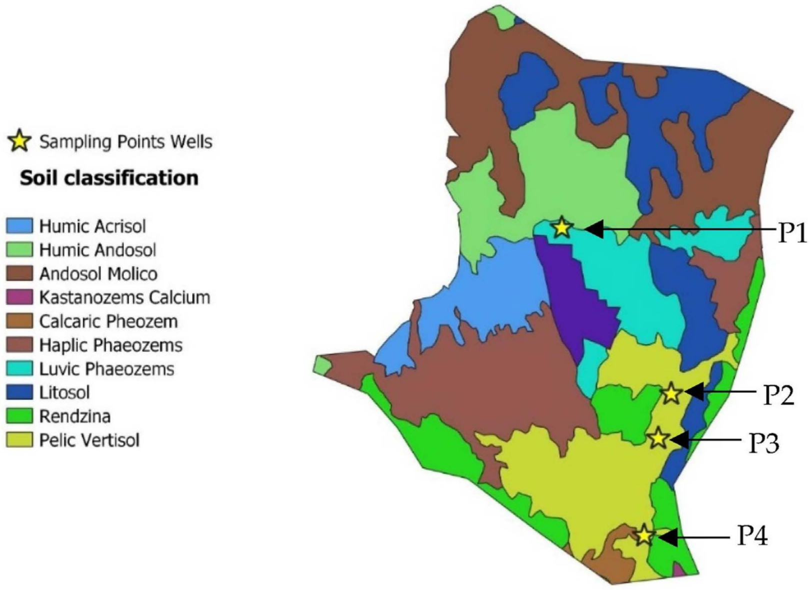


Figure 4. Soil classification of the Cuernavaca aquifer.

Figure 5 presents the spatial interpolation of the water quality parameters in the Cuernavaca aquifer. The highest values for all the parameters analyzed were observed in sampling point two (P2), while sampling point one (P1) presented the lowest values. This situation could be related to the soil type in the area. Since the highest elevation is observed in P1, the rest of the sample points located in lower elevation areas could be influenced by the erosion, transport, and deposition of contaminants.

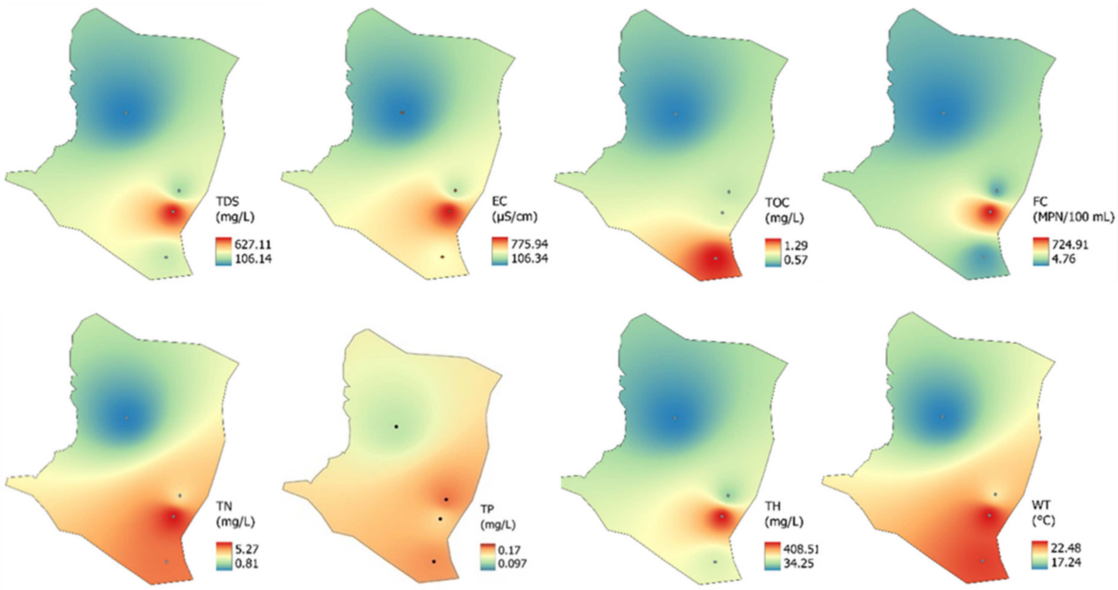


Figure 5. Spatial behavior of physicochemical parameters in the Cuernavaca aquifer.

Figure 6 presents the spatial behavior of the major ions. The presence of ions in the sampling wells is due to interactions with the geological material of the aquifer, natural processes of rock dissolution, and ion leaching. This figure shows that higher concentrations of ions were found at the P2. At this site, groundwater is not suitable for domestic use according to WHO [28] guidelines. The spatial distribution of these chemical elements highlights the vulnerability of the aquifer, especially at P2. Since the concentrations of ions at P1, P3, and P4 sites are similar, they could be considered reference values for the major ions in the Cuernavaca aquifer. It is noteworthy that the concentration of ions in all the groundwater samples was found to be within the WHO desirable limits for agricultural irrigation [6,28].

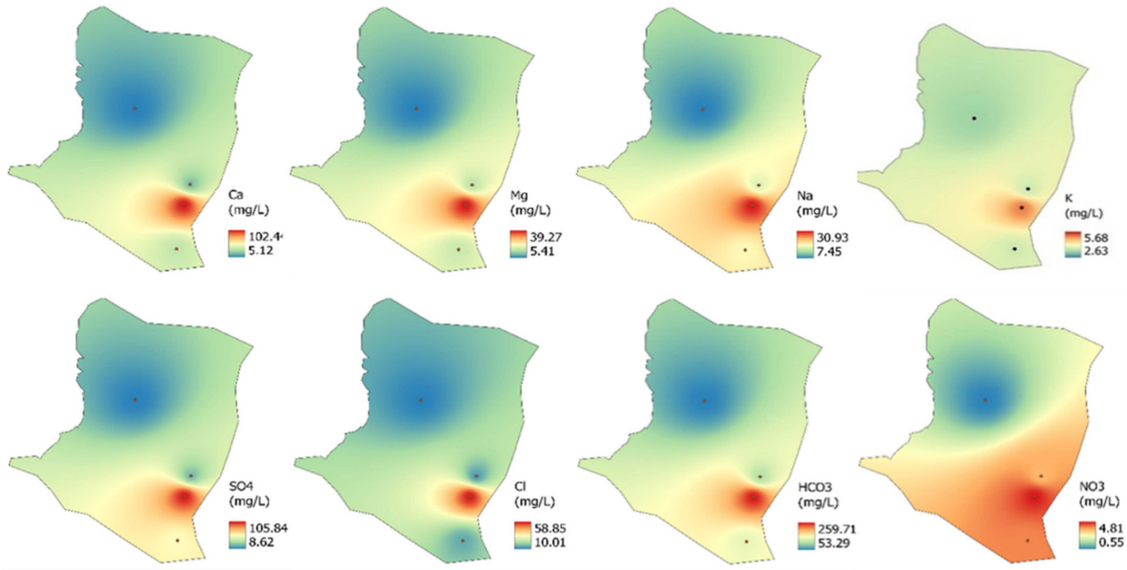


Figure 6. Spatial behavior of major ions in the Cuernavaca aquifer.

Figure 7 presents the temporal variation of the water quality parameters from 2012 to 2019. No trends, seasonal or cyclic patterns were found in the groundwater quality data. The time series also demonstrated that P2 showed higher values in almost all parameters. Lower concentrations of the physicochemical and major ions are observed at P1 since this site is at a higher elevation where the runoff of anthropogenic contaminants is significantly low. Similar values are presented by Adimalla et al. [14], who evaluated the groundwater of Nanganur county in India. Based on these results, they consider that groundwater quality does not represent health risks for drinking water use and only recommend groundwater defluoridation.

Table 3 presents the ANOVA statistical analysis of the groundwater quality parameters. This table showed that 15 parameters had a statistically significant variation from a spatial point of view. However, only 4 groundwater quality parameters showed a temporal significant variation.

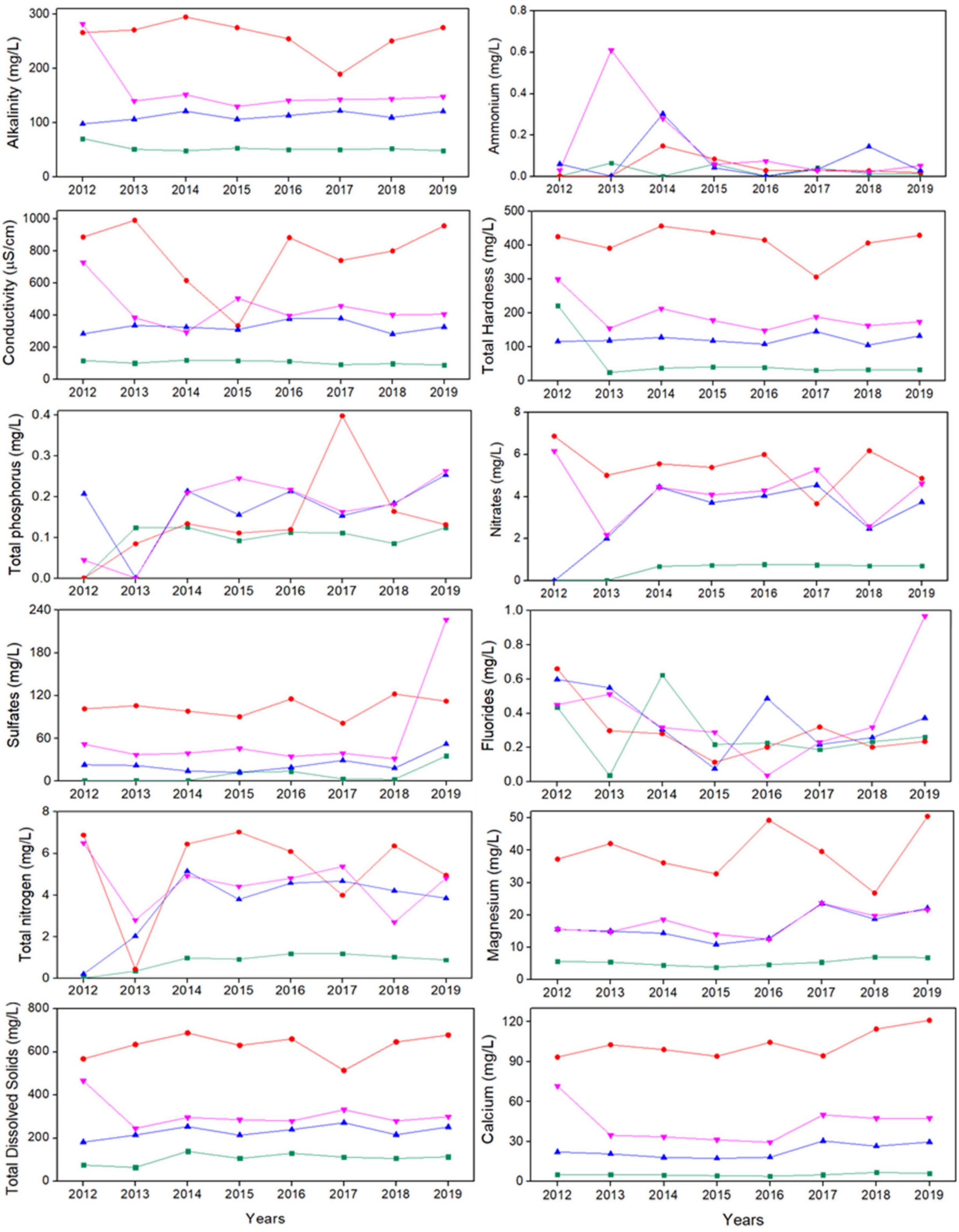


Figure 7. Variation of water quality parameters over time (2012–2019) at P1 (-■-), P2 (-●-), P3 (-▲-) y P4 (-▼-).

Table 3. Spatial and temporal statistical analysis (ANOVA) of the water quality parameters measured in the Cuernavaca aquifer.

Parameter	Site (Spatial)	Year (Temporal)
	p-Value	*p*-Value
Bicarbonates (mg/L)	0.0000 *	0.7058
Fecal coliforms NMP/100 mL	0.2229	0.8342
Total organic carbon (mg/L)	0.3044	0.1937
Ammonium (mg/L)	0.3219	0.4469
Nitrites (mg/L)	0.7001	0.4622
Nitrates (mg/L)	0.0000 *	0.0911
Organic Nitrogen (mg/L)	0.1192	0.1272
Total nitrogen (mg/L)	0.0000 *	0.1061
Total phosphorus (mg/L)	0.2540	0.0283
Total dissolved solids (mg/L)	0.0000 *	0.5686
Electrical conductivity µS/cm	0.0000 *	0.4360
pH	0.0002 *	0.0034
Chlorides (mg/L)	0.0000 *	0.4176
Fluorides (mg/L)	0.3992	0.0844
Silicon oxides (mg/L)	0.0315 *	0.0001 *
Potassium (mg/L)	0.0001 *	0.2912
Manganese (mg/L)	0.5720	0.8024
Sodium (mg/L)	0.0000 *	0.0143 *
Sulfates (mg/L)	0.0000 *	0.0134 *
Calcium (mg/L)	0.0000 *	0.2466
Magnesium (mg/L)	0.0000 *	0.0058 *
Total hardness (mg/L)	0.0000 *	0.3337
Water temperature °C	0.0000 *	0.8973

* *p*-value $\leq$ 0.05) is statistically significant.

3.3. Multivariate Statistical Analysis

Figure 8 shows the Pearson correlations between the groundwater quality parameters. Pearson correlation coefficient (*r*) ranges from −1 to +1 and measures the strength of the linear relationship between parameters [9]. A high negative correlation is found when *r* is close to −1 but *r* values close to +1 indicate a high positive correlation. A Pearson correlation (*r*) close to 0 indicates that there is no linear relationship between the two variables.

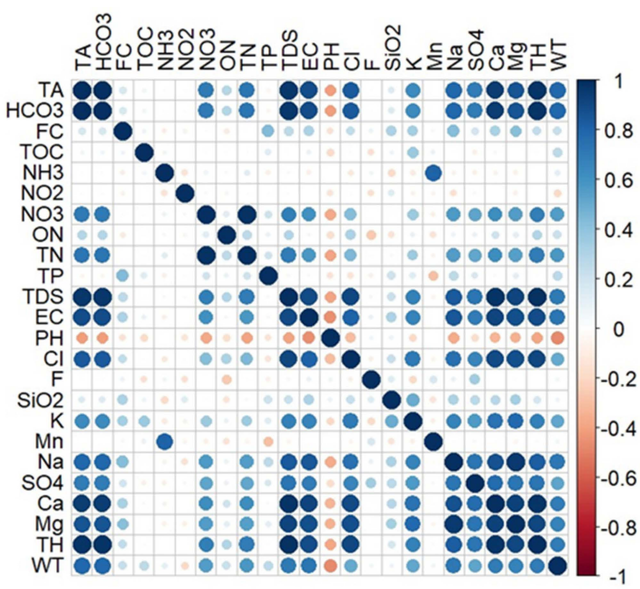


Figure 8. Pearson correlation coefficients of the water quality parameters of the Cuernavaca aquifer.

Nitrates presented the highest number of correlations with other parameters. This parameter is correlated with TN, TDS, EC, PH, Cl^-, K^+, Na^+, SO_4, Ca^{2+}, Mg^{2+}, TH, and WT. TA is related to HCO_3^-, NO_3^-, TN, TDS, EC, Cl^-, Na^+, Ca^{2+}, Mg^{2+}, TH, and WT. Bicarbonates showed a high correlation with NO_3^-, TN, TDS, EC, Cl^-, Na^+, Ca^{2+}, Mg^{2+}, TH, and WT. Total nitrogen is associated with TDS, EC, Na^+, SO_4^{2-}, Ca^{2+}, Mg^{2+}, TH, and WT. Total dissolved solids are highly related to ions, TH, EC, and WT. The electrical conductivity attributes a higher correlation with Cl^-, K^+, Na^+, SO_4^{2-}, Ca^{2+}, Mg^{2+}, TH, and WT. Chlorides are significantly related to K^+, Na^+, SO_4^{2-}, Ca^{2+}, Mg^{2+}, and TH. Potassium is related to other ions such as Na^+, SO_4, Ca^{2+}, Mg^{2+}, and TH. In turn, sodium is related to SO_4^{2-}, Ca^{2+}, Mg^{2+}, and TH). Sulfates are related to Ca^{2+}, Mg^{2+}, and TH, and calcium shows a correlation with Mg and TH. This method has been used for the evaluation of groundwater quality. Strong correlations between major ions are also reported by Miao et al. [40]. This situation evidenced that the groundwater quality of a coastal city in China was affected by various factors, such as dissolution and water evaporation.

Since a high amount of groundwater quality parameters were correlated with each other, a hierarchical cluster analysis was carried out (Figure 9). Hierarchical cluster analysis was used to further unearth the main chemical processes controlling groundwater chemistry in the aquifer [15,34]. This analysis included the 23 analyzed parameters and 34 water samples at different times of the year. The dendrogram formed the main cluster which in turn formed two groups. The first group includes only fluorides and sulfates. The second main group is composed of the rest of the water quality analyzed parameters. Several subgroups are evidenced, such as those formed by TDS, EC, and TH, TA, and HCO_3^-, and SiO_2, K, Ca^{2+}, and Mg^{2+}. These results corroborated the relationship between the observed parameters in the Pearson correlations. The relationship between the groundwater parameters indicated a common source. Due to the nature of these subgroups, groundwater quality is derived from geogenic sources, mainly carbonate mineral solutions [32]. Abdelaziz et al. [34] also noted that the dendrogram can be used to classify the groundwater quality parameters and found great similarities with the grouping carried out by the principal components analysis.

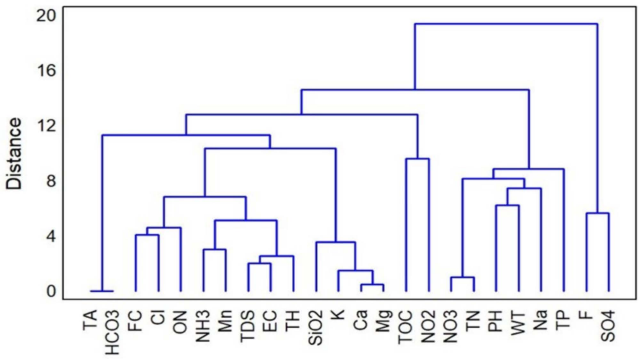


Figure 9. Hierarchical cluster analysis for groundwater quality parameters monitored in the Cuernavaca aquifer from 2012 to 2019.

3.4. Drinking Water Quality Index

Table 4 shows the DWQI obtained in the four sampling sites of the Cuernavaca aquifer. DWQI range from 11.2 to 78.2 were obtained from 2012 to 2019, where 70% of the samples showed an excellent groundwater quality, mainly in the P1, P3, and P4 sampling sites, as shown in Figure 10. P1 showed the best water quality, possibly because this sampling site is at the highest elevation and close to a protected green area. In contrast, P2 showed a high variation of groundwater quality because it is in a highly-populated area. Similar DWQI results are reported by Ahmed et al. [41], who mentioned that the DWQI ranged from 1.86 to 82.25 for water samples from different sampling sites of an aquifer in India.

Table 4. Classification of the water quality index and percentage of the values of the Cuernavaca aquifer samples.

DWQI	Classification of Water	Samples	% of Samples
<50	Excellent water	24	70.5
50–100	Good water	10	29.5
100–200	Poor water	0	0
200–300	Very poor water	0	0
>300	Unsuitable for drinking	0	0

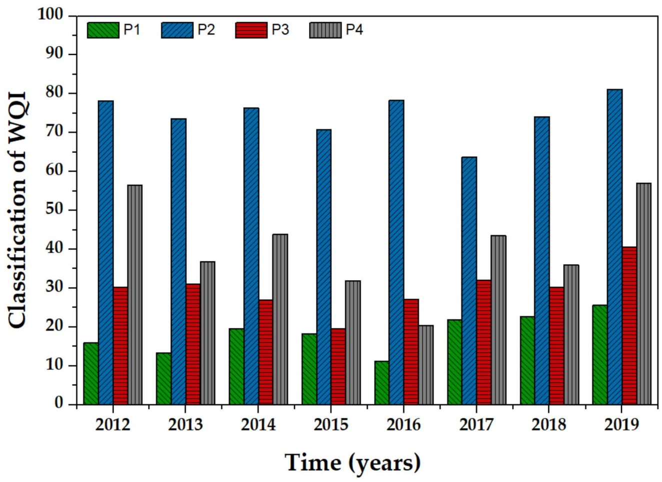


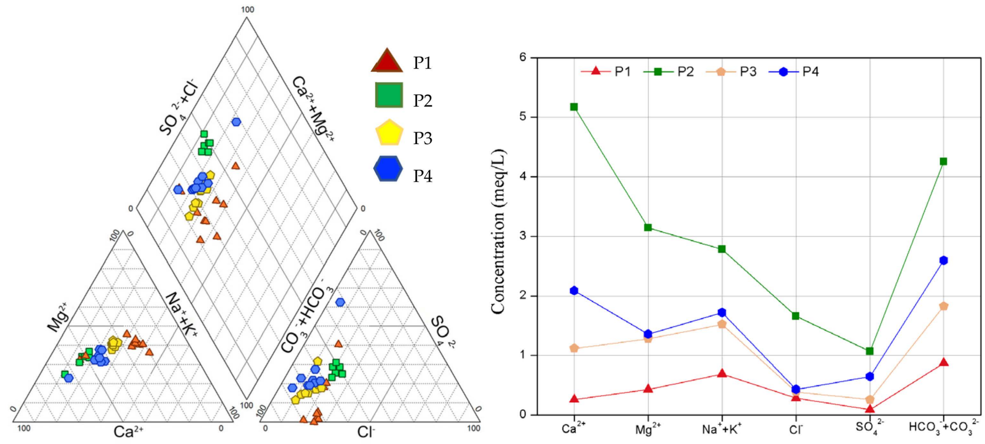
Figure 10. Variation of the water quality index in the sampling wells of the Cuernavaca aquifer.

3.5. Hydrochemical Characteristics

Hydrochemical analysis was carried out to characterize the Cuernavaca aquifer's groundwater. A high content of salts in groundwater could lead to the salinization of the soils and crop yield losses due to dehydration of plants [38,42]. The concentrations of salts in the Cuernavaca aquifer showed the following behavior:

$$HCO_3^- > Ca^{2+} > Na^+ > Mg^{2+} > Cl^- > SO_4^{2-} > K^+ > NO_3^-$$

Figure 11a shows the Piper triangular diagram. In this figure, the mean values of 34 samples at each sampling point were used. This diagram is a graphical representation of groundwater chemistry, where the relative concentrations of cations and anions are shown by separate ternary plots. In the lower-left ternary plot (cation diagram), a dominance of Mg^{2+} and Na^+ + K^+ is observed. This dominance could be related to progressive evaporation and ion exchange processes [43]. The lower-right ternary plot (anion diagram) indicated that the groundwater chemistry of the Cuernavaca aquifer is highly influenced by Calcium-bicarbonate type and Bicarbonate type [44]. These results are consistent with the results suggested by other researchers [45]. Figure 11b shows the Schoeller diagram which exhibits a similar behavior of cations and anions in the multiple samples from different wells. This diagram demonstrated that the highest equivalent concentrations of the ions were present in sampling site P2, where Ca^{2+} and HCO_3^- showed the highest equivalent concentrations of cations and anions, respectively. Similar results were presented by Tefera et al. [31] in Tana basin in Ethiopia. However, Abotalib et al. [46] obtained opposite results to those presented in this study for an aquifer located in hyperarid deserts in central Egypt.



(**a**) (**b**)

Figure 11. Piper (**a**), and Schoeller (**b**) diagrams for groundwater chemistry composition at P1 (-▲-), P2 (-■-), P3 (-⬠-) y P4 (-⬢-).

El Osta et al. [19] suggest that the groundwater chemistry of an aquifer is the result of evaporation, weathering, and rock-water interaction. In this study, the Gibbs diagram (Figure 12) showed that the cations and anions in the aquifer are primarily controlled by rock–water interaction. The dissolution of the rock in the aquifer is evidenced since a high content of chlorides and sulfates is observed. Therefore, this process regulates groundwater chemistry and quality. Likewise, this diagram suggests that the P2 site could be controlled by evaporation. This process produces dissolved solutes in groundwater and soil in areas with little depth [15,19,47,48].

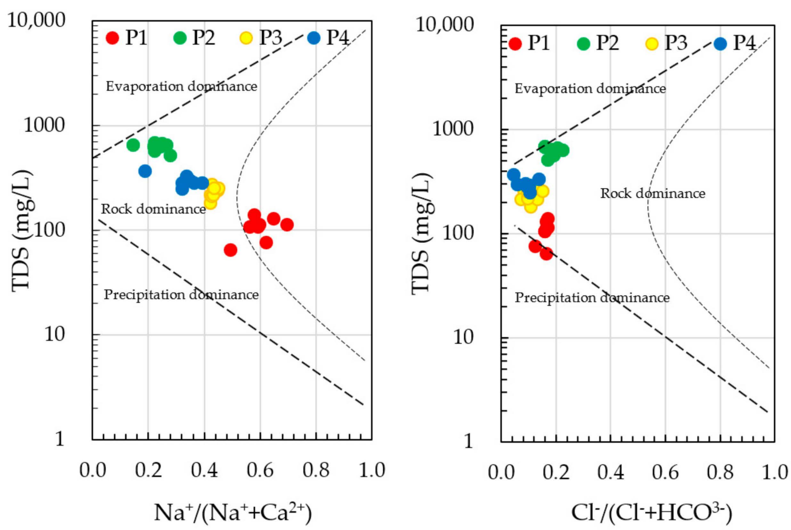


Figure 12. Gibbs diagram showing the source of cations and anions in the Cuernavaca aquifer at P1 (-●-), P2 (-●-), P3 (-●-) y P4 (-●-) sites.

3.6. Groundwater Indices Based on Hydrochemical Features

Figure 13 presents the classification of water quality for irrigation purposes. Some groundwater indices obtained in this study suggest that the Cuernavaca aquifer has a good quality for irrigation purposes. For example, the SAR index classified the groundwater as excellent, which indicates that there is no risk of sodium for irrigation. The RSC index also showed that all samples presented a good quality of water for irrigation. Based on the KR index, the groundwater of the Cuernavaca aquifer was adequate in most of the samples (84%).

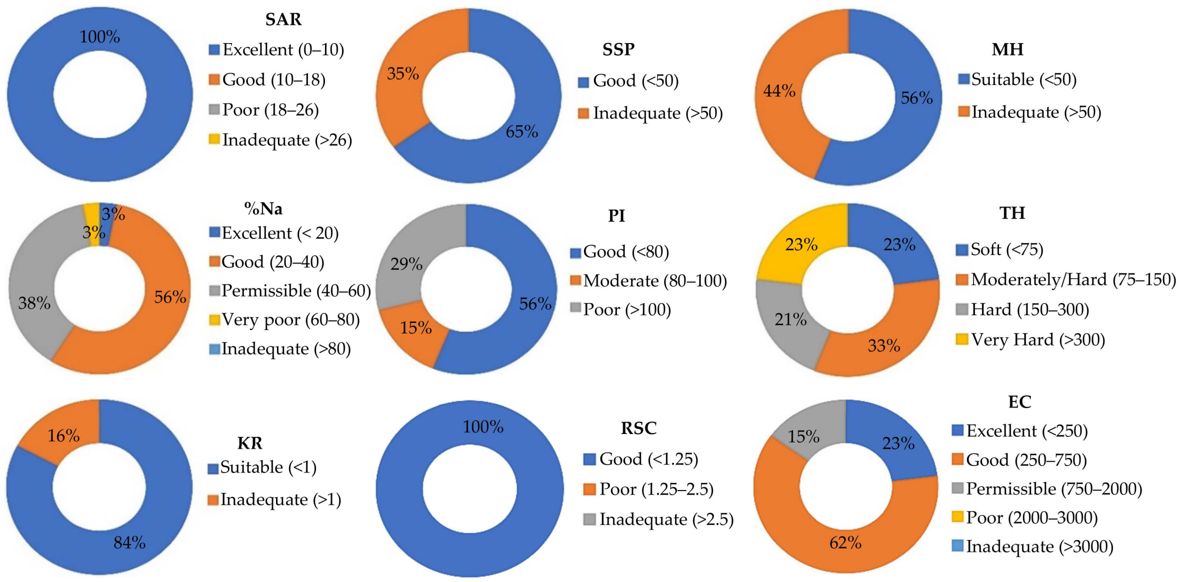


Figure 13. Classification of water samples for irrigation purposes in the Cuernavaca aquifer.

However, other groundwater indices suggest that groundwater quality is inadequate for irrigation. The SSP index showed that 65% of the samples have good water quality, mainly at P2 and P4. However, most of the samples at P1 and P3 showed an inadequate quality. Tefera et al. [31] reported that 53.3% of samples analyzed in alluvial aquifers in the Upper Blue Nile Basin, Ethiopia, could be considered good quality but 46.7% of the samples could be considered unsuitable. The MH index demonstrated that 56% of the samples have adequate quality at P2 and P4, but inadequate at P1 and P3. The high sodium levels found at these sampling sites could be related to weathering of Na-containing basaltic rocks. However, the content of calcium (41.93 mg/L) and magnesium (19.25 mg/L) in the groundwater of the aquifer maintains an equilibrium state. The groundwater of the Cuernavaca aquifer could be considered good quality according to the %Na. Most of the samples (56%) are within 20–40% Na. However, high sodium percentages were recorded in 38% of the samples, mainly at P1. The presence of high levels of sodium could reduce soil permeability. Similar results were obtained when using the PI index. Good water quality was observed in 56% of the samples, but it is noteworthy that 29% of the samples were within the poor-quality range (PI > 100). This groundwater quality index is related to the texture and structure of the soil. Since a high content of ions such as sodium, magnesium, calcium, and bicarbonates were found in the aquifer, the PI index also suggests that the use of groundwater for irrigation could affect the soil permeability [19]. Moreover, the high levels of bicarbonates over calcium and magnesium make groundwater unsuitable for irrigation uses.

The hardness of groundwater varied from soft to very hard. This variation is related to urbanization since soft groundwater was found at P1, characterized by the presence of agricultural areas, with low population density and small settlements, while very hard groundwater was located at P2 which is characterized by a mineralized subsoil. Hardness levels found in this study could be considered normal according to that suggested by Udeshani [49], who reports similar TH values in the groundwater of Sri Lanka.

The electrical conductivity in the Cuernavaca aquifer was found between 90 and 991 μS/cm. Despite this high variation, most of the samples were in a good quality range according to Tutmez's [50] classification (EC level between 0 and 750 mS/cm). The levels of electrical conductivity have been increasing during the last years. This increase could be also related to the loss of vegetation cover due to urbanization [51]. However, electrical conductivity in groundwater showed a satisfactory quality classification because the presence of ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, HCO^{3-}, $SO4^{2+}$, and NO^{3-}) is within the permissible limits according to the standards of the World Health Organization

(WHO). Determining groundwater suitability is important to understand the potential negative impacts of the high content of ions on crop production and mitigate groundwater contamination problems to improve healthy crop production [31].

4. Conclusions

- The hydrological and hydrochemical conditions of the Cuernavaca aquifer were evaluated through the application of water quality indices and statistical techniques. This study provides an approach to the spatial and temporal behavior of an urbanized aquifer and assesses its vulnerability due to population growth.
- This study identified spatial variations between the sampling sites and evidenced the influence of urbanization on groundwater chemistry and quality in the Cuernavaca aquifer. The spatial variation of the chemical elements highlights the vulnerability of the aquifer, especially at P2.
- The time series analysis demonstrated no trend, seasonal, or cyclic patterns in the groundwater quality data. The multivariate statistical analysis showed a high number of correlations between the groundwater parameters. These parameters were grouped based on hierarchical cluster analysis which revealed the main chemical processes controlling groundwater chemistry in the aquifer.
- Most of the parameters (physicochemical and ions) measured in the Cuernavaca aquifer were within the standards allowed by the WHO for irrigation purposes. This situation was confirmed by the water quality indexes since the groundwater of the aquifer was classified as good quality. However, the presence of fecal coliforms, organic matter, and the high content of ions such as Ca^{2+}, Mg^{2+}, and HCO_3^- is an important situation that must be addressed to reduce the vulnerability of the aquifer.
- This study provides an approach to describe the behavior of the hydrochemical features and water quality of the Cuernavaca aquifer and points out the main driving factors for the deterioration of groundwater quality in an aquifer located in an urban area.

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