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Groundwater Quality Assessment in Central Argentine Provinces

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Abstract: In order to assess groundwater quality in the Northeast of Córdoba and Northwest of Santa Fe, both of them Argentine provinces, representative samples of groundwater used for animal consumption, irrigation and, to a lesser extent, human consumption were taken at various locations and depths, and identified with their GPS coordinates. The knowledge of the groundwater quality is of vital importance for the people who use it. In all, 50 samples were analyzed in duplicate for color, turbidity, hydrogen potential, conductivity, hardness, total alkalinity, chloride, sulfate and total dissolved solids. Nitrates, nitrites, ammonium, arsenic, iron and fluoride concentrations were also determined according standard references. The chemical oxygen demand assay was performed on 50% of the samples. The results were subjected to a statistical analysis in order to establish the concentration of certain components in water and the influence of the geographic location. A strong positive relationship was found between hardness, chloride and sulfate, and no dependence was found between the total alkalinity and the remaining parameters. Different kind of positive relationship has been found between the research parameters: strong, between nitrites, fluoride and ammonium; moderately between arsenic and COD; and finally soft for nitrates with nitrites. In addition, no relationship nitrates and iron has been found. It was determined that none of the samples, taken between May and November 2013, complied with the Argentine Food Code requirements for drinking water and therefore, to animal and human feed consumption, their acceptability is excluded.

Keywords: Groundwater, Potability, Argentine Food Code

1. Introduction

Presently, in some areas of the Argentinian provinces of Córdoba and Santa Fe, residents drill boreholes in order to obtain groundwater, which they use for animal consumption, irrigation and, to a lesser extent, human consumption. There are also locations where there is no tap water and residents use groundwater for all household needs. The area under study is representative of the Northeast (NE) of the province of Córdoba and Northwest (NW) of the province of Santa Fe, a dairy region with numerous milking yard farms and intense agricultural and livestock activity due to the favorable local soil and climate conditions. Critical groundwater components include nitrites, nitrates, ammonium, arsenic, iron and fluoride. A short review of these parameters as obtained from Di.P.A.S. [1] can be found below.

In natural waters, nitrogen is present in different forms, including organic nitrogen (vegetable and animal protein and manure), ammoniacal nitrogen (metabolic, agriculture and industrial processes), and nitrate and nitrite compounds. Decomposition by microorganisms transforms the organic nitrogen material into ammoniacal nitrogen. In nature, in the presence of oxygen, ammoniacal nitrogen turns into nitrites, and then nitrates. Ammonia in water indicates possible contamination with bacteria, sewage, or animal manure. The natural nitrate and nitrite concentrations have been gradually increasing due to fertilizers, sewage, and industrial liquid waste produced by livestock activities, combustion and aerosols. The most important effects of nitrates on the environment are the pollution of water bodies with nitrogen compounds (and microorganisms), leading to eutrophication and urban air pollution. The presence of ammonia in drinking water does not have an immediate effect on health; however, ammonia can reduce disinfection efficiency, cause the formation of nitrites in distribution systems, obstruct manganese elimination by filtration, and cause organoleptic problems [2].

Arsenic can be found in water naturally, and sometimes in very high concentrations, since it is present in the crust of the earth. It is formed by erosion or volcanic processes, but it can also be caused by industrial discharges. In the environment, inorganic arsenic is found as metallic arsenic, trivalent arsenic (III) like arsenic trioxide (As_3O_5), and pentavalent arsenic (V) like arsenic pentoxide (As_2O_5). It appears in high concentrations in soft waters rich in sodium bicarbonate (alkaline). On the other hand, in waters rich in calcium and magnesium salts, arsenic either does not appear or is present in low concentrations. Due to the accumulation of arsenic in the human body and its toxicity and carcinogenic action, this parameter must be monitored in the supply of water.

Fluoride, as an element, can be found in volcanic gases and in sedimentary or igneous rocks. Fluoride compounds are found in groundwater in larger quantities than in surface water. Intake of certain concentrations of fluoride ions in drinking water prevents tooth decay. It is also known that fluoride causes dental fluorosis, which causes white spots to appear on teeth when the fluoride content of consumption water exceeds an acceptable proportion.

Iron in high concentrations can cause stains in fabrics and sanitary devices, impart color and turbidity to water, and confer a characteristic metallic taste on it. In water deposits or in areas with low water circulation, ferruginous and manganous waters can promote the development of iron and manganese bacteria, with the development of color and fetid odor.

In Argentine, previous studies have been performed on the quality of groundwater and surface water. For example, nitrate pollution of aquifers in rural areas was investigated in the area near Balcarce city, in the province of Buenos Aires [3]. Galindo *et al.* [4], analyzed the quality of surface water and groundwater in the Northeast of the province of Buenos Aires. In addition, Nicolli *el at.* [5], and Raychowdhury, *et al.* [6] analyzed the arsenic content and trace elements in groundwater in the Chaco Pampeana region. The researches of Smedley *et al.* [7]; Borzi *et al.* [8] and Zabala *et al.* [9] in La Pampa province; Pampean region and Pampeano aquifer in the Del Azul Creek basin respectively, focused on the hydrogeochemistry of arsenic, fluoride, nitrates and other inorganic components in groundwater.

The parameters herein investigated were separated into characterization parameters, including color, turbidity, hydrogen potential, conductivity, hardness, total alkalinity, chloride, sulfate, total dissolved solids (TDS), and research parameters, including nitrates, nitrites, ammonium, arsenic, iron and fluoride, and chemistry oxygen demand (COD). With this aim, 50 groundwater samples were analyzed in duplicate for all the aforementioned parameters and the chemical oxygen demand assay was performed on 50% of the samples. Table 1 shows the maximum allowable values for water potability according to the Argentine Food Code (AFC) [10] relevant to the characterization and research parameters studied in this work.

Table 1. *Maximum values allowed for the characterization and research parameters for potable water, according to the AFC.*

	Parameter (unit of measurement)	Maximum value allowed
Characterization	Color	3 NTU
	Turbidity	5, Pt-Co scale
	pH (upH)	6.5-8.5
	Conductivity (dS/m)	Not mentioned
	Hardness (mg/L)	400
	Total alkalinity (mg/L)	Not mentioned
	Chloride (mg/L)	350
	Sulfate (mg/L)	400
	TDS (mg/L)	1500
Research	Arsenic (mg/L)	< 0.05
	Nitrites (mg/L)	0.1
	Nitrates (mg/L)	45
	Ammonium (mg/L)	0.20
	Iron (mg/L)	0.30
	Fluoride (mg/L)	0.7 to 1.2 at T* = 17.7°C
	COD (mg/L)	Not mentioned

*Annual temperature average

2. Materials and Methods

Samples of groundwater were taken in clean 1-L bottles, after allowing for a 3-min recirculation of water. Color, turbidity, hydrogen potential, conductivity, hardness, total alkalinity, chloride, sulfate and TDS were determined as characterization parameters, and nitrates, nitrites, ammonium, arsenic, iron and fluoride and COD were determined as research parameters.

Table 2 presents the analytical method, the standard reference, the reagents and the equipments used in the different analytical techniques, according to Clesceri (1992) [11].

Table 2. *Analytical method, standard reference, reagent and equipment according to [11].*

Analysis	Analytical method	Standard Reference	Reagents	Equipment
Color	Visual	2120 B	-	Glassware
Turbidity	Nephelometric	2130 B	-	Spectrophotometer
Alkalinity	Titration	2320 B	HCl 0.1N, Phenolphthalein 0.1%, Helianthine 0.1%	Glassware
Hardness	Titration	2140 C	EDTA 0.1 M, Eriochrome Black T	Glassware
Conductivity	Conductimetric	2510 B	KCl 0.1 N	Conductivity meter
Chloride	Argentometric	$Cl^{(-)}$ B	$AgNO_3$ 0.1 N, K_2CrO_4 5%	Glassware
pH	Electrometric	4500 $H^{(+)}$ B	Buffer pH 7, Buffer pH 4	pH meter
TDS	Gravimetric	2540 C	-	Drying oven
Ammonium	Nesslerization	4500 NH_3C	Nessler reagent, HACH no. 21194-49. HACH no. 23766-26 reagent. HACH no. 23765-26 APV	Spectrophotometer
Nitrates	Cadmiun reduction	4500 $NO_3^{(-)}$ F	NitraVer5 reagent, HACH no. 14034-99	Spectrophotometer
Nitrites	Colorimetric	4500$NO_2^{(-)}$ B	NitriVer3 reagent, HACH no. 21071-69	Spectrophotometer
Sulfate	Turbidimetric	4500$SO_4^{(2-)}$ E	SulfaVer4 reagent, HACH no. 12065-99	Spectrophotometer
COD	Colorimetric	5220 D	COD reagent at 150 mg/L, HACH no. 212580-25	Thermoreactor
Arsenic	Colorimetric	3500 AsC	Arsen 50 Quantofix reagent, no. 332706, Macherey-Nagel	Kit of materials
Iron	Colorimetric	3500 Fe D	FerroVer Reagent, HACH no. 21057-69	Spectrophotometer
Fluoride	Colorimetric	4500 F D	Spadns reagent, HACH no. 444-49	Spectrophotometer

The following are the equipments with their models: Comboi HI 98130 conductivity meter, Hach DR2800 spectrophotometer, Altronix TPX-I pH meter, VelpScientífica ECO25 thermoreactor. Also, a drying oven model Dalvo SB464, a METTLER gravimetric scale model P1000N (0.001 g), and a Denver analytical scale model APX-200 (0.0001 g) were used.

Standard deviation (SD) and standard error (SE) were used to evaluate the differences between the samples as per the following equations:

$$SD_i = \sqrt{\sum_i^N \left(Q_i^{\text{average}} - Q_i^{\exp}\right)^2 / (N-1)} \quad (1)$$

$$SE_i = \frac{SD_i}{\sqrt{N}} \quad (2)$$

where Q_i are the different parameters studied, N is the number of experimental data, *exp* indicates experimental data, and *average* is the mean value obtained from the data.

3. Results and Discussion

Tables A1-A2, and Table A3 available in Appendix A and B respectively, summarizes all the information on the 50 groundwater samples with their decimal GPS (geographic positioning system) coordinates, sexagesimal GPS coordinates, vector GPS coordinates, water well depth, stratified depth criterion, presence of sediments, presence of odor, color, turbidity, hydrogen potential, conductivity, hardness, total alkalinity, chloride, sulfate, TDS, nitrates, nitrites, ammonium, arsenic, iron and fluoride, and COD. The samples were obtained in the Northeast (NE) of the province of Córdoba, and Northwest (NW) of the province of Santa Fe.

From this study, it can be deduced that 26% of the samples present sediments, while only one sample presents odor; 20% of the analyzed samples exceed the maximum allowed value for color, while 14% exceed the turbidity allowed value for potable water according to the AFC. The samples tested can be classified depending on the depth at which they were obtained: 10 m (2%), 12 m (2%), 15 m (6%), 18 m (8%), 20 m (34%), 25 m (12%), 50 m (18%), 80 m (12%), 110 m (4%), and 130 m (2%). The depths were stratified using the following criterion: shallow depths (10 m, 12 m, and 15 m), corresponding to 10% of the samples; medium depths (18 m, 20 m, 25 m, and 50 m) with 72% of the samples; and great depths (80 m, 110 m, and 130 m) with 18% of the samples.

Figures 1-2 show the influence of well depth on the characterization parameters (hardness, total alkalinity, chloride, sulfate, TDS) and on the research parameters (nitrates, nitrites, ammonium, arsenic, fluoride, iron and COD), respectively. The segment of each bar is the standard deviation obtained from the different samples at each well depth. The horizontal lines represent the applicable maximum allowable values for the range [10] showed in Table 1. The sample taken at a 12 m well depth was not included in Figure 2, due to its low representativeness.

As can be seen in Figure 1(A), the hardness content for the samples of 12, 18, 80, 110 and 130 m are within the maximum allowable values as per AFC. The remaining parameters, chloride, Fig. 1(C); sulfate, Fig. 1(D); and TDS, Fig. 1(E) exceed the allowed values for most of the samples. From Table A2, available in the Appendix A section, it can be seen that 32% of the samples exceed the maximum allowable values for hardness, 62% for chloride and sulfate, and 82% for TDS according to the AFC.

In Figure 1(B), total alkalinity is shown to decrease with well depth, while the content of fluoride, sulfate and TDS do not depend on this parameter. As shown in Figure 1(C-E), the dependence of fluoride, sulfate and TDS concentrations with well depth can be observed to be similar between each other.

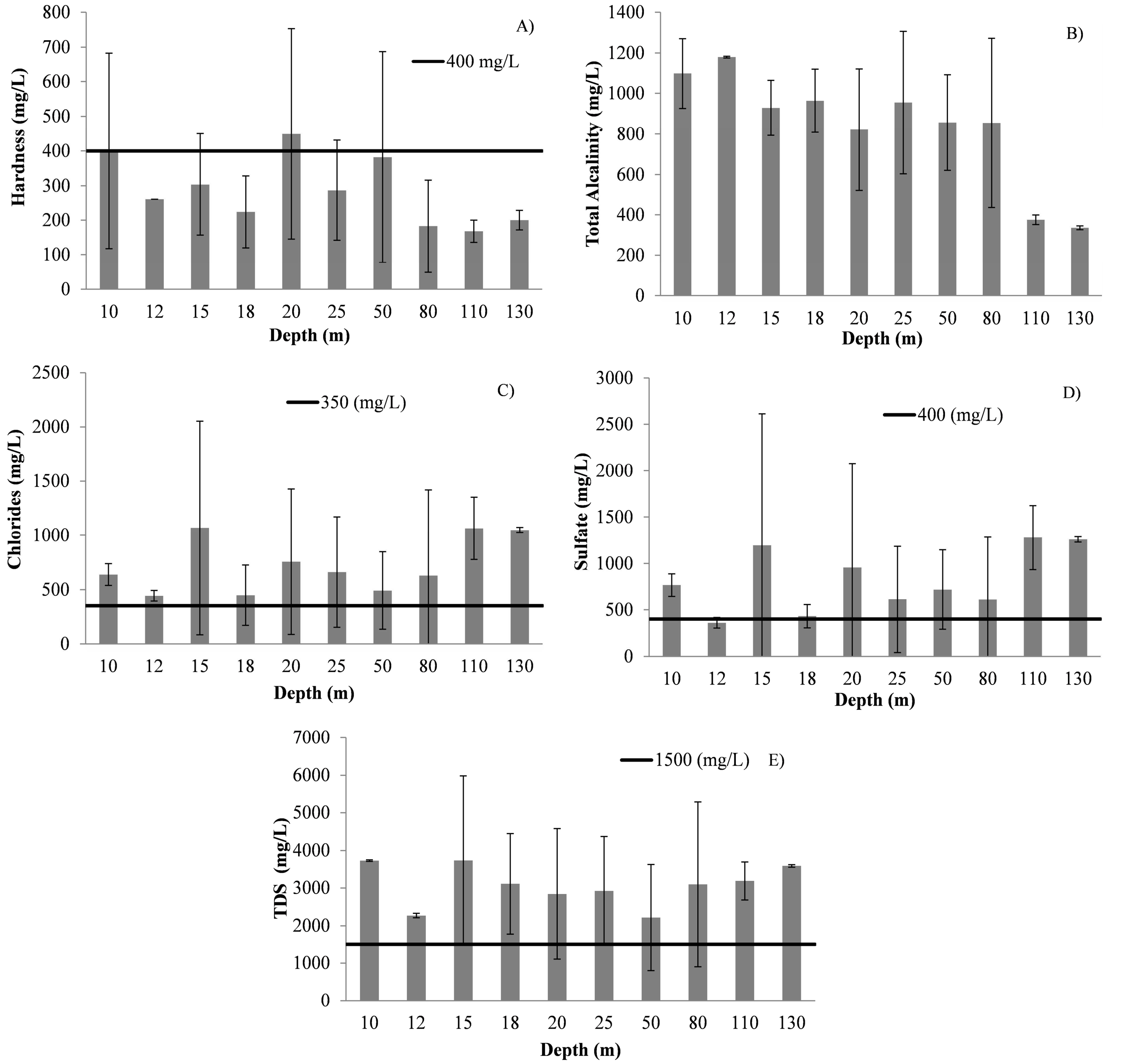

Figure 1. *Concentrations representing (A) hardness, (B) total alkalinity, (C) chloride, (D) sulfate and (E) TDS parameters for different depths. The horizontal lines represent the allowable limit according to the AFC as shown in Table 1.*

Figure 2(A) shows a logarithmic trend in nitrate concentration versus well depth; that means that lower concentrations of nitrates can be found for greater well depths. Nitrite concentration shows a lower dependence on well depth, while ammonium, arsenic, iron and fluoride concentrations do not show dependence with this parameter, as per Figure 2(B-E). The geological origin of arsenic, iron and fluoride explains the different concentration values for the different depths.

Of the total of samples, 52% exceeded the maximum allowable values according to the AFC in nitrates, 46% in nitrites, 86% in ammonium, 68% in arsenic, 60% in fluoride and 38% in iron. These values, which can be obtained from Table A3, are available in the Appendix B section and can be observed in Figure 2.

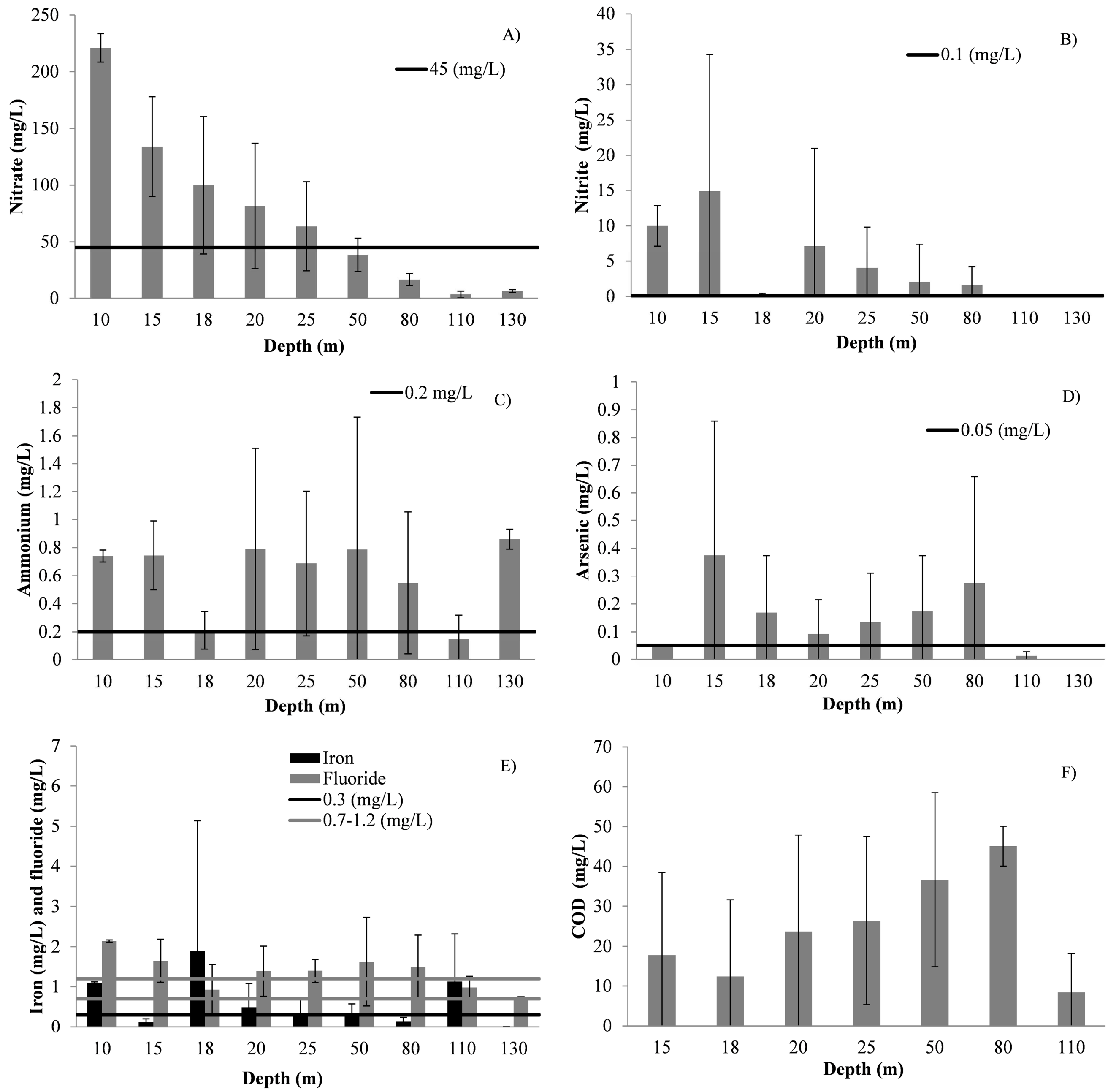

Figure 2. *Concentration representing (A) nitrates, (B) nitrites, (C) ammonium, (D) arsenic, (E) iron and fluoride, (F) COD (mg/L) according to the depth of the groundwater analyzed. The horizontal lines represent the allowable limit according to the AFC as shown in Table 1.*

Table 3 shows the average, SD, maximum value (max), and median values for the research and characterization parameters obtained for the groundwater samples analyzed at all the different well depths. Furthermore, Table 4 shows the statistical analysis in average, SD, SE, minimum (min) and maximum for the characterization and research parameters according to the stratified depth criterion. From Table 4, it can be deduced that there is no dependence of chloride, sulfate, TDS, iron and COD with well depth, while it the concentration of nitrates, nitrites, ammonium, arsenic and fluoride can be found to decrease with well depth. Table 4 also includes the ANOVA letters for the different parameters investigated, following the stratified depth criterion. From this analysis, of the characterization parameters, total alkalinity and hardness present a strong and moderate dependence with the stratified depth respectively. However, chloride, sulfate and TDS do not present dependence with well depth. Regarding the research parameters ammonium, arsenic, fluoride, iron and COD, there is no significant dependence with well depth, while nitrate and nitrite variables vary significantly with this parameter. Nitrate and nitrite concentrations decrease as depth increases, with greater influence for nitrates than for nitrites. This is consistent, since nitrites are derived from the biological reduction of nitrates.

Table 3. *Statistical values obtained for the characterization and research parameters measured on the water samples.*

Parameter (unit)	***Average***	***SD***	***Max***	***Median***
Characterization				
pH (upH)	7.5716	0.5223	9.280	7.435
Conductivity (dS/m)	4.3928	2.3171	10.38	4.120
Hardness (mg/L)	337.72	253.88	1600	260.0
Total Alkalinity (mg/L)	850.42	310.29	1708	876.5
Chloride (mg/L)	686.06	598.82	2592	488.0
Sulfate (mg/L)	805.85	837.18	4814	539.5
TDS (mg/L)	2881.0	1635.6	7058	2737
Research				
Nitrates (mg/L)	66.374	56.610	230	45.84
Nitrites (mg/L)	4.6069	10.332	60.0	0.081
Ammonium (mg/L)	0.6615	0.6573	3.86	0.480
Arsenic (mg/L)	0.1495	0.2336	1.00	0.050
Fluoride (mg/L)	1.3911	0.7353	4.56	1.250
Iron (mg/L)	0.5081	1.0722	7.56	0.160
COD (mg/L)	23.550	22.123	69.5	25.60

Table 4. *Statistical analysis of the parameters according to the stratified depth criterion. Letters for the ANOVA analysis based on a Fisher's LSD (least significant difference) of (p< 0.05) for the parameters*.*

Variable	**Stratified depth**	**n**	**Average (mg/L)**	**ANOVA letters**	**SD (mg/L)**	**SE (mg/L)**	**Min (mg/L)**	**Max (mg/L)**
	Characterization parameters							
Hardness	Low	10	314	AB	152.26	48.148	200.0	600.0
	Medium	72	380.17	A	275.64	32.485	60.00	1600
	High	18	181.11	B	108.89	25.667	70.00	440.0
Total alkalinity	Low	10	1012.8	A	161.42	51.045	755.0	1220
	Medium	72	867.93	A	282.17	33.254	244.0	1708
	High	18	690.17	B	412.72	97.280	220.0	1446
Chloride	Low	10	857.60	A	786.54	248.73	266.0	2343
	Medium	72	640.51	A	550.51	64.879	73.00	2592
	High	18	773.00	A	678.89	160.02	71.00	2236
Sulfate	Low	10	941.20	A	1115.6	352.80	38.00	3100
	Medium	72	781.08	A	846.25	99.732	74.00	4814
	High	18	829.78	A	646.26	152.32	85.00	2100
TDS	Low	10	3445.9	A	1783.9	564.11	1863	6610
	Medium	72	2730.1	A	1574.1	185.51	33.00	7058
	High	18	3171.0	A	1781.1	419.81	258.0	6059
	Research parameters							
Nitrates	Low	10	139.79	A	59.037	18.669	71.76	230.0
	Medium	72	69.679	B	50.040	5.8973	7.970	201.0
	High	18	12.368	C	7.4039	1.7451	0.880	22.15
Nitrites	Low	10	10.944	A	15.707	4.9671	0.040	42.90
	Medium	72	4.6091	AB	10.371	1.2223	0.017	60.00
	High	18	1.0780	B	2.2241	0.5242	0	7.000
Ammonium	Low	10	0.6331	A	0.2952	0.0934	0.169	1.080
	Medium	72	0.7075	A	0.7281	0.0858	0	3.860
	High	18	0.4933	A	0.4655	0.1097	0	1.430
Arsenic	Low	10	0.2360	A	0.4035	0.1276	0.005	1.000
	Medium	72	0.1283	A	0.1637	0.0193	0	0.500
	High	18	0.1861	A	0.3346	0.0789	0	1.000
Fluoride	Low	10	1.5110	A	0.7087	0.2241	0.4600	2.160
	Medium	72	1.3981	A	0.7509	0.0885	0	4.560
	High	18	1.2967	A	0.7144	0.1684	0.7	3.200
Iron	Low	10	0.3070	A	0.4179	0.1321	0.040	1.110
	Medium	72	0.5779	A	1.2066	0.1422	0.030	7.560
	High	18	0.3406	A	0.6685	0.1576	0.010	2.180
COD	Low	6	11.850	A	18.453	5.8352	0	38.50
	Medium	38	25.861	A	22.721	2.6777	0	69.50
	High	6	20.617	A	20.508	4.8338	0	48.60

*For a given parameter, averages with the same letter do not present significant differences ($p < 0.05$)

In order to assess the variability of the characterization and research parameters with the geographical positions, a multivariate analysis was used on the principal components (PC) using Infostat, a statistical software [12].

Gabriel, K.R. [13-14] proposed scatter diagrams, called biplots, where the observations and variables are on the same plane in order to obtain joint relations between the different parameters. In this case, these biplots were used to show the geographic coordinates and the different values for the characterization and research parameters.

GPS coordinates for each sample, given in the sexagesimal system, were converted into a single vector (GPS vector coordinates) obtained as the square root of the sum of the squares of the West longitude and South latitude coordinates, respectively. This vector was also multiplied by a factor of 10 for a better identification of the different samples on the biplot. The GPS vector coordinates for each groundwater sample is available in Table A1 of the Appendix A section.

Figure 3 represents the biplot of the geographic locations identified with points, using hardness, total alkalinity, chloride, sulfate and TDS as characterization variables. Two reduced dimensions were used, representing 74.5% of the samples. The cophenetic correlation coefficient was 0.956, an acceptable value for the reduction degree achieved. The PC1 and PC2 described are 56.2% and 18.3%, respectively; 56.2% of the variability of the samples (PC1) was defined for hardness, chloride and sulfate, with a high projection on the positive PC1 semiaxis. The weights of these variables were similar, suggesting similar contribution of each variable to sample variability. On the other hand, 18.3% of sample variability was represented by total alkalinity and TDS variables, with a greater influence for total alkalinity than for TDS on the positive PC2 semiaxis.

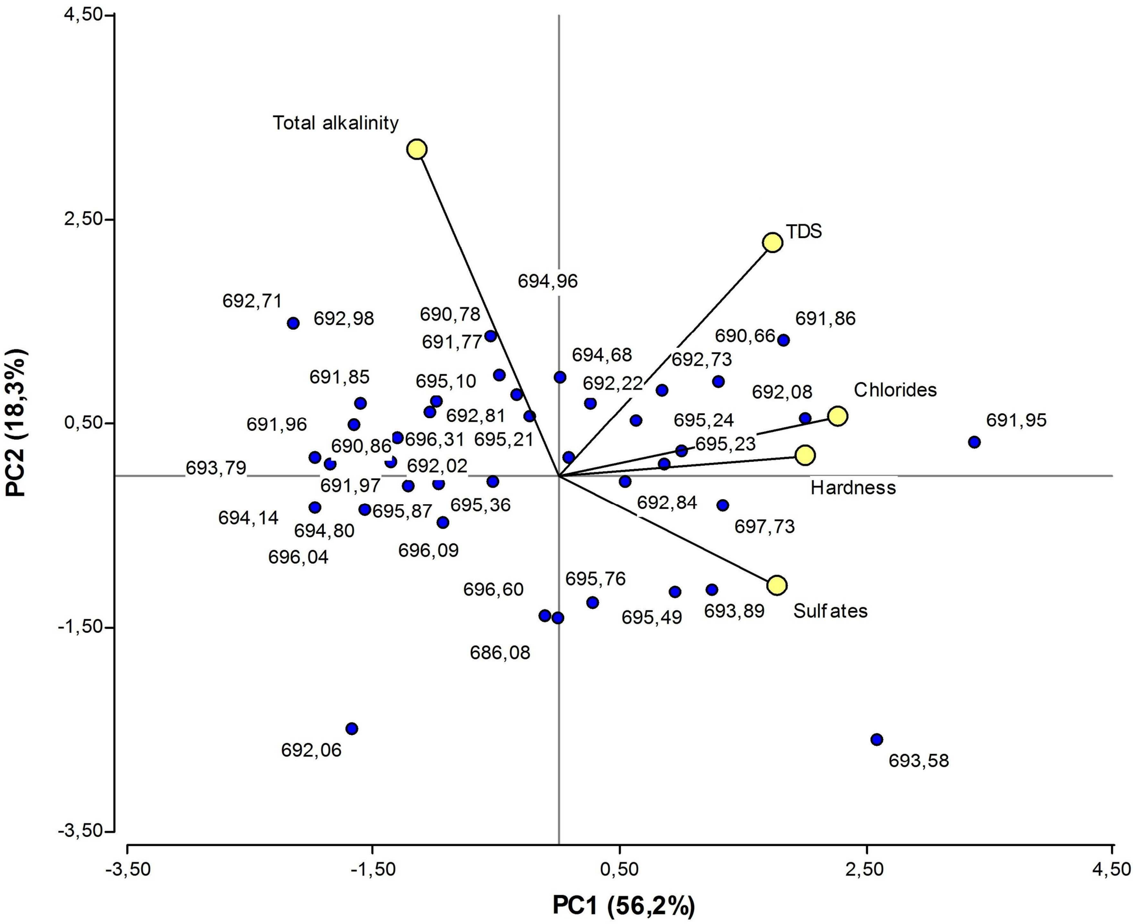

Figure 3. *Multivariate analysis of characterization parameters and GPS vector coordinates.*

For PC1, the following sites were located: 691.86, 690.66, 692.73, 694.68, 692.22, 692.08, 695.24, 691.95, 695.23, 692.84, 697.73, 695.76, 695.49, 693.89, and 693.58. The negative PC1 semiaxis was not been defined for the mayority proyection of any parameteres. From the data dispersion, it can be seen that the composition of all the samples located on the positive PC1 semiaxis is similar, but different from the composition of those located on the PC1 negative semiaxis. However, it is not possible to infer which samples cause this difference.

On the other hand, the following sites were located on the positive PC2 semiaxis: 691.95, 691.86, 692.08, 690.66, 659.23, 692.73, 694.68, 692.22, 694.96, 695.21, 692.81, 690.78, 691.77, 695.10, 696.31, 692.02, 690.86, 692.98, 691.85, 691.86, 692.71, and 693.79. On the other hand, the negative PC2 semiaxis contains only sulfate with a low contribution. From Figure 3, it can be deduced there is a strong positive relationship between hardness, chloride and sulfate, and no dependence at all between total alkalinity and the remaining parameters.

Figure 4 represents the biplot of the geographic locations, identified with points, and nitrates, nitrites, ammonium, arsenic, fluoride, iron and COD as research parameters. The PC1 and PC2 allow for an explanation of 60% of the total variability. The cophenetic correlation coefficient, as a measurement of the degree of dimensional reduction achieved, was 0.915. PC1 and PC2 were 40.3% and 19.4%, respectively: 40.3% of sample variability was explained by nitrites, ammonium, arsenic, fluoride and COD, because they were the variables with greatest projection on the positive PC1 semiaxis. The weights of the variables were similar, suggesting similar contributions of each variable to sample variability. On the other hand, 19.4% of their variability was explained by nitrates and iron, with more weight on the PC2 axis and more contribution of nitrates than iron.

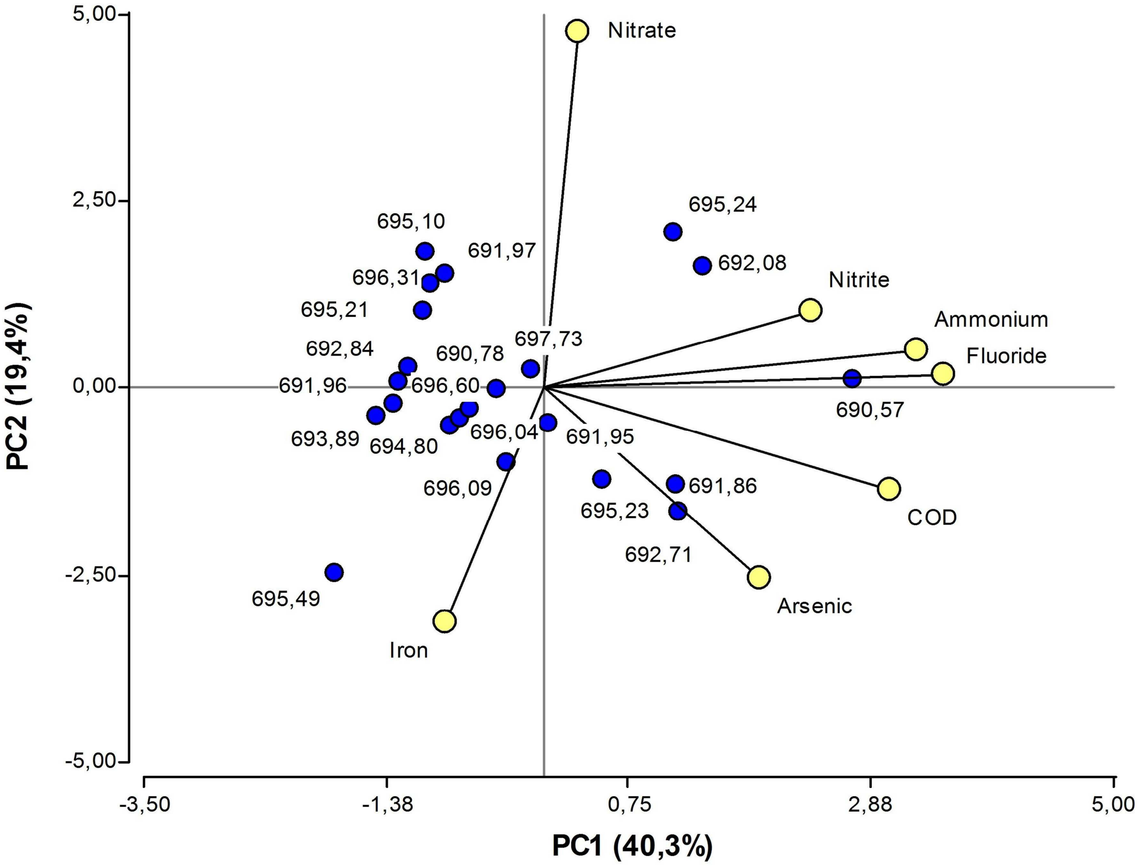

Figure 4. *Multivariate analysis of research parameters and GPS vector coordinates.*

The following geographic coordinates were located on the positive PC1 region: 695.24, 692.08, 690.57, 691.95, 691.86, 695.23, and 692.71. The negative PC1 axis was described for iron with a low vector weight, including the following sites: 695.59, 696.09, 696.04, 694.80, 693.89, 696.60, 691.96, 690.78, 692.84, 697.73, 695.21, 696.31, 691.97, and 695.10. The same as in Figure 3, the composition of all the samples located on the positive PC1 semiaxis is similar, but different from the composition of those located on the PC1 negative semiaxis. However, it is not possible to infer which samples cause this difference.

The PC2 was defined by nitrates along the positive PC2 semiaxis. In this region, the following geographic vector coordinates were located: 695.24, 695.08, 697.73, 691.97, 690.78, 695.10, 696.60, 696.31, 695.21, 692.84, and 691.96. On the other hand, in the negative PC2 semiaxis, only iron was found for the coordinates 691.86, 691.95, 695.23, 692.71, 696.04, 696.09, 694.80, 693.89, and 695.49.

Strong positive relationships between nitrites, fluoride and ammonium were found, as well as moderately positive relationships between arsenic and COD, and slightly positive relationships between nitrates and nitrites. In addition, no relationship was found between nitrates and iron. Besides, no relationship between iron and the remaining parameters was found, and its presence does not seem to be related to the geographical position: it is dispersed in the areas analyzed. Furthermore, the geographical positions 691.86 and 672.81 are similar in terms of COD and arsenic.

4. Conclusion

A total of 50 groundwater samples, taken between May and November 2013, were analyzed for color, turbidity, hydrogen potential, conductivity, hardness, total alkalinity, chloride, sulfate, TDS, nitrates, nitrites, ammonium, arsenic, iron and fluoride, and COD. The groundwater samples, identified with their GPS coordinates, are representative of the Northeast (NE) and Northwest (NW) of the Argentinian provinces of Córdoba and Santa Fe, respectively. The results were statistically analyzed in order to determine the influence of the geographic location on the different parameters.

The presence of arsenic, iron and fluoride is due to a geological process, and their values are different. From the ANOVA study, a strong dependence can be deduced between groundwater depth and the total alkalinity and nitrate concentrations, while the relationship with the hardness and nitrite concentrations is only moderate.

The multivariate analysis performed on the principal components has made it possible to discriminate the dependence of the different parameters with their corresponding geographical positions. A strong positive relationship was found between hardness, chloride and sulfate, and no dependence was found between the total alkalinity and the remaining parameters. Different kind of positive relationship has been found between the research parameters: strong, between nitrites, fluoride and ammonium; moderately between arsenic and COD; and finally soft for nitrates with nitrites. In addition, no relationship nitrates and iron has been found. Finally, from the 50 samples analyzed of groundwater, none of them is included in the potable water term, according to the AFC for drinking water. Therefore, to animal and human feed consumption, their acceptability is excluded, while is necessary to investigate other parameters before watering.

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Appendix A

Characterization of 50 groundwater samples from Northeast (NE) of Córdoba, and northwest (NW) of Santa Fe provinces, Argentine.

Table A1. *Characterization Parameters: Date sample, town, decimal GPS, depth, stratified depth and sediment of the groundwater samples analyzed*

Sample	Data Sample	Town	Decimal GPS	Depth (m)	Stratified depth	Sediment
1	07-Apr-13	Colonia Tacurales, Santa Fe	-30.80283	20	Medium	no
1			-61.78967	20	Medium	no
2	07-Apr-13	Colonia Tacurales, Santa Fe	-30.80909	20	Medium	no
2			-61.80388	20	Medium	no
3	07-Apr-13	Morteros, Córdoba	-30.56867	18	Medium	yes
3			-61.08200	18	Medium	yes
4	14-Apr-13	Morteros, Córdoba	-30.74131	15	Low	yes
4			-62.00596	15	Low	yes
5	14-Apr-13	Morteros, Córdoba	-30.72799	20	Medium	no
5			-62.08520	20	Medium	no
6	19-Apr-13	Brinkmann, Córdoba	-30.86910	20	Medium	no
6			-62.02750	20	Medium	no
7	19-Apr-13	Colonia Vignaud, Córdoba	-30.83160	20	Medium	no
7			-61.95430	20	Medium	no
8	19-Apr-13	Brinkmann, Córdoba	-30.86910	20	Medium	no
8			-62.02700	20	Medium	no
9	08-May-13	San Francisco, Córdoba	-31.42943	20	Medium	no
9			-62.08498	20	Medium	no
10	14-May-13	Sastre, Santa Fe	-31.77221	12	Low	no
10			-61.82398	12	Low	no
11	17-May-13	Morteros, Córdoba	-30.71373	15	Low	no
11			-61.88282	15	Low	no
12	17-May-13	Morteros, Córdoba	-30.72362	18	Medium	no
12			-61.86919	18	Medium	no
13	17-May-13	Morteros, Córdoba	-30.70257	20	Medium	yes
13			-61.86673	20	Medium	yes
14	17-May-13	Morteros, Córdoba	-30.70623	50	Medium	yes
14			-62.01003	50	Medium	yes
15	17-May-13	Brinkman, Córdoba	-30.86938	25	Medium	no
15			-62.04218	25	Medium	no
16	07-Jun-13	Morteros, Córdoba	-30.61788	80	High	yes
16			-62.05190	80	High	yes
17	07-Jun-13	Brinkmann, Córdoba	-30.85731	80	High	yes

Sample	Data Sample	Town	Decimal GPS	Depth (m)	Stratified depth	Sediment
17			-62.02967	80	High	yes
18	25-Jun-13	Morteros, Córdoba	-30.71437	15	Low	no
18			-62.00696	15	Low	no
19	28-Jun-13	Morteros, Córdoba	-30.68093	80	High	yes
19			-62.00968	80	High	yes
20	28-Jun-13	Colonia 10 de Julio, Córdoba	-30.51911	20	Medium	no
20			-62.18560	20	Medium	no
21	29-Jun-13	Freyre, Córdoba	-31.18889	20	Medium	no
21			-62.10472	20	Medium	no
22	17-Jul-13	Freyre, Córdoba	-31.20806	18	Medium	no
22			-62.11028	18	Medium	no
23	17-Jul-13	Freyre, Córdoba	-31.22667	50	Medium	no
23			-62.11306	50	Medium	no
24	26-Jul-13	Freyre, Córdoba	-31.21472	25	Medium	no
24			-62.12278	25	Medium	no
25	29-Jul-13	Altos de Chipión, Córdoba	-31.00000	80	High	no
25			-62.32500	80	High	no
26	12-ag-13	Freyre, Córdoba	-31.26111	110	High	no
26			-62.12750	110	High	no
27	13-Aug-13	Morteros, Córdoba	-30.63528	80	High	no
27			-62.05833	80	High	no
28	13-Aug-13	Morteros, Córdoba	-30.66083	25	Medium	no
28			-62.02056	25	Medium	no
29	13-Aug-13	Colonia 10 de Julio, Córdoba	-30.58056	50	Medium	yes
29			-62.05111	50	Medium	yes
30	16-Aug-13	Porteña, Córdoba	-30.99417	50	Medium	no
30			-62.11000	50	Medium	no
31	16-Aug-13	Porteña, Córdoba	-31.07444	20	Medium	yes
31			-62.00694	20	Medium	yes
32	21-Aug-13	Altos de Chipión, Córdoba	-30.99222	50	Medium	no
32			-62.32389	50	Medium	no
33	21-Aug-13	Altos de Chipión, Córdoba	-30.99972	50	Medium	no
33			-62.32556	50	Medium	no
34	13-Set-13	Freyre, Córdoba	-31.23528	50	Medium	no
34			-62.11139	50	Medium	no
35	23-Set-13	Colonia Vignaud, Córdoba	-30.84325	80	High	no
35			-61.95335	80	High	no
36	02-Nov-13	Colonia Valtelina, Córdoba	-31.06861	25	Medium	no
36			-62.19200	25	Medium	no
37	02-Nov-13	Colonia Vignaud, Córdoba	-30.81250	20	Medium	no
37			-61.98611	20	Medium	no
38	19-Nov-13	Colonia Castelar, Santa Fe	-31.60588	20	Medium	no
38			-62.04460	20	Medium	no
39	19-Nov-13	Frontera, Santa Fe	-31.43917	130	High	no
39			-62.06752	130	High	no
40	20-Nov-13	Zenon Pereyra, Santa Fe	-31.56192	18	Medium	no
40			-61.89731	18	Medium	no
41	19-Nov-13	Esmeralda, Santa Fe	-31.61645	20	Medium	no
41			-61.93303	20	Medium	no
42	23-Nov-13	Freyre, Córdoba	-31.14930	50	Medium	yes
42			-62.43370	50	Medium	yes
43	24-Nov-13	Freyre, Córdoba	-31.10450	20	Medium	yes
43			-62.13810	20	Medium	yes
44	24-Nov-13	Freyre, Córdoba	-31.18470	20	Medium	yes
44			-62.28970	20	Medium	yes
45	24-Nov-13	Sarmiento, Santa Fe	-31.11640	25	Medium	yes
45			-61.14540	25	Medium	yes
46	25-Nov-13	Porteña, Córdoba	-62.06194	25	Medium	no
46			-31.01167	25	Medium	no
47	04-Dec-13	Altos de Chipión, Córdoba	-30.95000	50	Medium	no
47			-62.35000	50	Medium	no
48	04-Dec-13	Altos de Chipión, Córdoba	-30.95000	20	Medium	no
48			-62.35000	20	Medium	no
49	04-Dec-13	La Paquita, Córdoba	-30.90772	10	Low	no
49			-62.21396	10	Low	no
50	18-Dec-13	Porteña, Córdoba	-31.07274	110	High	no
50			-62.04333	110	High	no

Table A2. *Characterization Parameters: Olor, color, turbidity, pH, conductivity, hardness, Total alkalinity, chloride, sulfate and TDS of the groundwater samples analyzed*

Sample	Olor	Color	Turbidity	pH (upH)	Conductivity (dS/m)	Hardness (mg/L)	Total alkalinity (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	TDS (mg/L)
1	no	5	3	7.25	4.75	560	805	993	700	3230
1	no	5	3	7.21	4.68	562	781	995	900	3182
2	no	5	3	7.44	10.21	1340	475	2556	2500	6963
2	no	5	3	7.46	10.38	1600	477	2592	2700	7058
3	no	> 5	> 3	7.38	4.84	280	817	886	600	3291
3	no	> 5	> 3	7.38	4.88	320	781	889	400	3318
4	no	> 5	> 3	8.79	9.72	560	780	2308	2900	6610
4	no	> 5	> 3	8.76	9.68	400	755	2343	3100	6582
5	no	> 5	3	9.22	5.64	400	1045	1491	500	3849
5	no	> 5	3	9.19	5.68	320	826	1420	700	3849
6	no	5	3	7.15	7.66	440	634	1917	1000	5209
6	no	5	3	7.18	7.64	440	878	1882	980	5195
7	no	5	3	7.94	2.85	200	1000	230	340	1938
7	no	5	3	7.8	2.74	240	1049	284	360	1863
8	no	>5	>3	7.26	1.58	480	634	74	74	1074
8	no	>5	>3	7.27	1.56	460	708	73	75	1061
9	no	5	3	7.43	3.01	190	976	355	800	2047
9	no	5	3	7.48	2.96	200	970	373	860	2013
10	no	5	3	7.19	3.40	260	1177	479	320	2312
10	no	5	3	7.2	3.28	260	1183	408	400	2230
11	no	5	3	7.87	4.1	200	1098	604	38	2788
11	no	5	3	7.9	3.96	240	1025	606	40	2693
12	no	5	3	7.45	7.4	120	1098	320	520	5032
12	no	5	3	7.5	7.42	200	1074	322	524	5046
13	no	> 5	>3	7.12	7.58	600	903	817	920	5154
13	no	> 5	>3	7.13	7.24	640	903	817	1090	4858
14	no	> 5	> 3	7.66	2.2	200	1025	107	260	1496
14	no	> 5	> 3	7.74	2.2	120	1135	81	300	1496
15	no	5	3	7.53	2.8	220	1196	213	260	1904
15	no	5	3	7.56	2.82	160	1267	391	280	1917
16	yes	> 5	> 3	8.86	8.73	440	517	2236	1600	5936
16	yes	> 5	> 3	8.98	8.91	440	523	2201	2100	6059
17	no	> 5	3	8.28	8.4	120	828	142	118	5712
17	no	> 5	3	8.35	8.39	200	804	177	118	5705
18	no	5	3	7.25	2.89	210	957	284	520	1911
18	no	5	3	7.23	2.74	210	957	266	560	1863
19	no	> 5	3	7.88	2.97	80	1147	355	340	2079
19	no	> 5	3	7.99	2.99	100	1147	284	320	1972
20	no	5	3	7.72	2.33	150	1464	213	255	1584
20	no	5	3	7.62	2.4	170	1708	284	268	1632
21	no	5	3	7.8	4.85	570	1098	568	680	3395
21	no	5	3	7.88	4.78	540	976	710	781	3250
22	no	5	3	7.83	3.5	300	976	284	340	2380
22	no	5	3	7.87	3.56	360	1220	426	511	2420
23	no	5	3	7.03	3.64	820	830	462	554	2475
23	no	5	3	7.09	3.68	860	854	604	725	2502
24	no	5	3	7.05	6.15	410	610	1207	380	4182
24	no	5	3	7.04	6.1	390	604	1047	340	4148
25	no	5	3	7.26	2.5	80	1446	178	250	1700
25	no	5	3	7.34	2.59	120	1446	142	250	1761
26	no	5	3	7.07	4.34	190	396	816	980	2591
26	no	5	3	7.01	4.33	200	396	816	980	2944
27	no	5	3	7.43	4.14	230	970	852	1022	2815
27	no	5	3	7.38	4.22	230	976	852	1022	2869
28	no	5	3	7.19	7.74	410	1067	1544	1852	5263
28	no	5	3	7.3	7.78	370	1073	1437	1724	5290
29	no	5	3	7.45	4.42	170	1213	781	937	3005
29	no	5	3	7.47	4.23	340	1098	745	894	2876
30	no	> 5	> 3	9.24	1.71	70	943	177	213	1163
30	no	> 5	> 3	9.28	1.81	60	949	142	170	1231
31	no	5	3	7.38	6.96	710	647	1065	4733	177
31	no	5	3	7.35	7.08	680	634	1065	4814	188
32	no	5	3	7.26	1.8	120	1183	213	1224	40
32	no	5	3	7.24	1.8	110	1104	178	1224	33

Sample	Olor	Color	Turbidity	pH (upH)	Conductivity (dS/m)	Hardness (mg/L)	Total alkalinity (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	TDS (mg/L)
33	no	5	3	7.4	0.77	170	573	107	128	523
33	no	5	3	7.41	0.73	150	567	107	128	523
34	no	5	3	7.33	6.05	340	787	1136	1363	4114
34	no	5	3	7.34	6.03	330	793	1029	1235	4100
35	no	5	3	6.63	0.39	80	220	71	85	265
35	no	5	3	6.6	0.38	70	226	71	85	258
36	no	5	3	7.37	4.09	150	1342	532.5	639	2781.2
36	no	5	3	7.39	4.29	140	1281	532.5	639	2917.2
37	no	5	3	7.46	6.06	370	890.6	852	1022.4	4120.8
37	no	5	3	7.51	6.11	360	890.6	887.5	1065	4154.8
38	no	5	3	7.65	3.11	220	1068	284	340	2170
38	no	5	3	7.65	3.11	220	1068	284	340	2170
39	no	5	3	7.45	5.32	220	342	1065	1278	3618
39	no	5	3	7.51	5.25	180	329	1030	1236	3570
40	no	5	3	7.9	2.46	110	864	248	297	1722
40	no	5	3	7.87	2.43	100	875	213	255	1700
41	no	5	3	7.59	3.99	370	830	426	511	2793
41	no	5	3	7.57	4.15	210	811	426	525	2900
42	no	5	3	7.2	5.1	700	580	710	852	3570
42	no	5	3	7.3	5.16	760	640	852	1022	3612
43	no	5	3	7.41	2.25	280	305	355	420	1570
43	no	5	3	7.47	2.35	380	366	213	256	1650
44	no	5	3	7.44	2.5	380	244	355	426	1750
44	no	5	3	7.48	3.5	420	610	497	1108	2450
45	no	5	3	7.28	2.9	440	366	284	340	2030
45	no	5	3	7.32	2.92	500	427	426	510	2040
46	no	5	3	7.31	1.95	110	1128	178	213	1326
46	no	5	3	7.28	1.9	140	1098	142	170	1292
47	no	5	3	7.33	5	760	555	639	767	3500
47	no	5	3	7.37	5.2	800	580	781	937	3640
48	no	5	3	7.64	1.58	260	610	142	170	1068
48	no	5	3	7.68	1.62	300	634	248	297	1102
49	no	5	3	7.67	5.47	200	976	568	682	3720
49	no	5	3	7.71	5.52	600	1220	710	852	3750
50	no	5	3	7.38	5.14	138	353	1311	1574	3610
50	no	5	3	7.42	5.18	142	357	1315	1578	3614

Appendix B

Research parameters of 50 groundwater samples from Northeast (NE) of Córdoba, and northwest (NW) of Santa Fe provinces, Argentine.

Table A3. *Research Parameters: Nitrate, Nitrite, ammonium, arsenic, fluoride, iron and COD of the groundwater samples analyzed*

Sample	Nitrate (mg/L)	Nitrite (mg/L)	Ammonium (mg/L)	Arsenic (mg/L)	Fluoride (mg/L)	Iron (mg/L)	COD (mgO_2/L)
1	94.80	0.080	0.273	0.025	1.54	0.40	
1	137.30	0.050	0.286	0.025	1.61	0.30	
2	80.60	0.050	3.146	0.050	3.00	0.35	69.5
2	38.10	0.030	2.639	0.050	2.88	0.35	46.9
3	63.80	0.165	0.312	0.050	0.00	7.56	
3	54.50	0.162	0.324	0.100	0.00	6.68	
4	202.40	42.900	0.793	0.050	2.05	0.05	38.5
4	177.20	36.300	0.858	0.100	1.93	0.08	32.6
5	18.60	6.000	1.360	0.300	0.67	0.10	
5	17.27	10.000	1.380	0.300	1.11	0.09	
6	63.35	0.043	0.350	0.050	0.70	0.05	0
6	57.15	0.026	0.290	0.050	0.70	0.08	0
7	49.00	4.000	0.350	0.050	0.75	0.19	
7	39.00	7.000	0.350	0.050	0.75	0.14	
8	82.00	7.000	0.820	0.025	0.80	2.09	0
8	93.00	11.000	0.820	0.025	0.84	1.94	0
9	8.86	0.020	0.390	0.050	0.81	0.03	
9	7.97	0.017	0.260	0.050	0.87	0.03	
10	71.76	0.040	0.169	0.005	0.46	0.08	0

Sample	Nitrate (mg/L)	Nitrite (mg/L)	Ammonium (mg/L)	Arsenic (mg/L)	Fluoride (mg/L)	Iron (mg/L)	COD (mgO_2/L)
10	81.50	0.053	0.221	0.005	0.48	0.11	0
11	110.80	6.000	0.440	1.000	1.98	0.24	
11	103.20	4.000	0.470	1.000	1.96	0.21	
12	100.60	0.069	0.220	0.050	1.34	0.35	0
12	96.70	0.033	0.240	0.050	1.68	0.42	0
13	129.80	6.000	0.650	0.050	1.89	1.37	
13	139.10	8.000	0.620	0.050	1.92	1.62	
14	34.60	0.056	0.650	0.050	0.98	0.44	0
14	27.00	0.066	0.600	0.050	0.78	0.46	0
15	33.70	0.060	0.260	0.100	1.40	0.06	
15	35.20	0.036	0.140	0.100	1.43	0.04	
16	13.10	0.050	1.430	0.000	0.70	0.12	41.5
16	9.10	0.040	1.430	0.000	0.76	0.13	48.6
17	22.15	0.043	0.260	0.100	1.70	0.11	
17	19.50	0.041	0.470	0.100	1.80	0.13	
18	105.00	0.056	0.820	0.050	0.74	0.08	0
18	104.00	0.086	1.080	0.050	1.23	0.04	0
19	21.30	4.000	0.890	1.000	3.20	0.18	
19	20.80	6.000	0.920	1.000	2.60	0.12	
20	30.50	0.030	0.700	0.500	1.98	0.68	48.0
20	31.90	0.040	0.730	0.500	2.04	0.45	52.0
21	158.00	0.082	0.400	0.050	1.35	0.16	
21	150.00	0.092	0.320	0.050	1.45	0.18	
22	184.00	0.530	0.000	0.050	1.30	0.03	39.4
22	201.00	0.640	0.000	0.050	1.36	0.07	34.8
23	26.60	1.000	0.012	0.000	1.40	0.12	
23	27.50	2.300	0.017	0.000	1.46	0.16	
24	138.00	2.000	1.404	0.000	1.80	0.09	32.5
24	151.00	2.200	1.989	0.000	2.01	0.07	45.6
25	19.00	0.036	0.200	0.500	0.85	0.04	
25	18.00	0.049	0.170	0.500	0.95	0.06	
26	6.20	0.023	0.290	0.000	0.70	2.18	15.3
26	5.30	0.013	0.300	0.000	0.78	2.14	18.3
27	19.00	7.000	0.390	0.050	1.00	0.27	
27	18.60	2.000	0.410	0.050	0.90	0.38	
28	62.90	7.000	0.730	0.500	1.35	0.97	43.5
28	66.40	9.000	0.690	0.500	1.30	0.98	55.2
29	21.30	0.040	0.520	0.100	1.39	0.56	
29	19.90	0.060	0.600	0.100	1.45	0.53	
30	51.00	11.000	2.560	0.500	4.44	0.18	55.8
30	51.00	21.000	3.860	0.500	4.56	0.17	64.3
31	177.00	50.000	2.180	0.050	2.33	0.50	
31	188.00	60.000	2.200	0.050	2.11	0.64	
32	39.90	0.116	0.220	0.100	0.89	0.21	29.8
32	32.80	0.073	0.290	0.100	1.10	0.17	32.7
33	31.00	0.040	0.440	0.300	0.90	0.20	
33	30.00	0.043	0.580	0.300	1.10	0.15	
34	34.00	0.106	0.260	0.500	1.20	0.10	43.5
34	31.00	0.129	0.280	0.500	1.32	0.10	52.8
35	8.86	0.020	0.000	0.000	1.77	0.02	
35	7.53	0.023	0.000	0.000	1.75	0.03	
36	51.39	0.059	0.420	0.100	1.05	0.04	0
36	45.19	0.049	0.420	0.100	1.09	0.07	0
37	140.00	21.000	0.810	0.100	0.80	0.09	
37	153.00	24.000	0.770	0.100	0.90	0.08	
38	132.00	0.040	0.400	0.100	1.10	0.48	0
38	132.00	0.040	0.400	0.100	1.60	0.54	0
39	7.09	0.031	0.810	0.000	0.70	0.01	
39	5.32	0.035	0.910	0.000	0.74	0.01	
40	55.00	0.040	0.310	0.500	0.84	0.04	0
40	42.90	0.059	0.270	0.500	0.88	0.03	0
41	106.70	16.500	0.680	0.100	1.00	0.06	
41	121.80	13.200	0.770	0.100	0.96	0.07	
42	68.20	0.320	0.820	0.010	1.06	0.38	43.8
42	71.70	0.300	0.820	0.010	1.10	0.38	43.4
43	35.00	0.040	0.470	0.025	1.20	0.09	

Sample	Nitrate (mg/L)	Nitrite (mg/L)	Ammonium (mg/L)	Arsenic (mg/L)	Fluoride (mg/L)	Iron (mg/L)	COD (mgO_2/L)
43	38.00	0.060	0.500	0.025	1.26	0.13	
44	31.00	0.050	0.520	0.025	1.23	0.16	32.0
44	49.00	0.070	0.550	0.025	1.27	0.20	32.0
45	53.00	10.000	0.580	0.010	1.54	0.15	
45	49.00	18.000	0.640	0.010	1.50	0.15	
46	43.00	0.110	0.490	0.100	1.20	0.70	15.5
46	33.00	0.120	0.490	0.100	1.10	0.50	18.5
47	44.70	0.090	0.790	0.000	2.02	0.82	
47	46.50	0.110	0.840	0.000	2.06	0.86	
48	18.20	0.049	0.210	0.025	1.91	1.47	23.4
48	19.90	0.063	0.260	0.025	1.95	1.51	27.8
49	212.00	8.000	0.710	0.050	2.12	1.07	
49	230.00	12.000	0.770	0.050	2.16	1.11	
50	0.88	0.000	0.000	0.023	1.20	0.08	0
50	0.90	0.000	0.000	0.027	1.24	0.12	0

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