Geoscience Frontiers 11 (2020) 2197–2205

HOSTED BY

ELSEVIER

Contents lists available at ScienceDirect

Geoscience Frontiers

journal homepage: www.elsevier.com/locate/gsf

Research Paper

Statistical evaluation of fluoride contamination in groundwater resources of Santiago del Estero Province, Argentina

K. Rondano Gómez [a,b], C.E. López Pasquali [c], G. Paniagua González [b,*], P. Fernández Hernando [b], R.M. Garcinuño Martínez [b]

[a] *Departamento de Ciencias Básicas, Facultad de Ciencias Forestales, Universidad Nacional de Santiago Del Estero, Argentina*
[b] *Departamento de Ciencias Analíticas, Facultad de Ciencias, Universidad Nacional de Educación a Distancia, Spain*
[c] *Departamento de Química Analítica, Facultad de Agronomía y Agroindustrias, Universidad Nacional de Santiago Del Estero, Argentina*

ARTICLE INFO

Handling Editor: E. Shaji

Keywords:
Source water protection
Santiago del Estero
Multivariate statistical analysis
Fluoride
Spectrophotometry

ABSTRACT

This study investigates the suitability of statistical techniques for evaluating the fluoride content and the groundwater quality from Robles Department (RD) and Banda Department (BD) in Santiago del Estero (Argentina). For the original statistical study, evaluation of nine parameters (fluoride, pH, conductivity, atmospheric and water temperature, total dissolved solids, chloride, hardness, and alkalinity) of 110 collected underground water samples from 23 dispersed rural areas was proposed. Groundwater samples were obtained by sampling taken from wells at different depths. Fluoride levels were determined by a standard colorimetric method in two seasonal periods, the dry (from April to September) and rainy (from October to March) period. The analytical results obtained for physicochemical parameters such as pH, total dissolved solids (TDS), and temperature does not reveal any notable difference between the rainy and dry seasons studied. In both seasons, the atmospheric temperature average was 22 °C. With respect to fluoride content, approximately 50% of the analysed groundwater samples exceeded the limit established by current legislation (1.0 mg/L), obtaining concentration levels in the range of 0.01–2.80 mg/L. This study demonstrates the usefulness of the univariate statistical method (quartiles calculation, interquartile range IQR), multivariate principal component analysis (PCA), and cluster analysis to establish a better understanding of the state of the contamination of the waters in the region studied.

1. Introduction

Groundwater is the main fresh water renewable resource for humans. Wells and shallow aquifers constitute the most accessible and exploited reservoirs for drinking purposes; however, they are also susceptible to pollution by natural sources and anthropogenic activities (WHO, 2011; Machiwal et al., 2018). Water–rock interaction, mineral dissolution, groundwater residence time, flow paths, and human exploitation are the main factors deteriorating groundwater quality (Kumar et al., 2016). Many scientific articles concerning the contaminant elements contents such as volcanic ash coming from natural processes in groundwater in Argentina and the rest of Latin America have been widely reported (Esposito et al., 2011; Kim et al., 2012; Borgnino et al., 2013; García-Sánchez et al., 2013; Bustingorri and Lavado, 2014). Different scientific studies have provided information about the main components of these sediments being responsible for the most prevalent forms of arsenic and fluoride (Alarcón-Herrera et al., 2013; Martín et al., 2016; Zabala et al., 2016; Navarro et al., 2017).

Inorganic and organic fluorides (calcium fluoride, sodium fluoride, fluorapatite, and cryolite) present in igneous and sedimentary rocks, as well as in volcanic ashes, coal, and clays constitute the main source of fluoride in groundwater (Rao, 2003; Ozsvath, 2009; Rondano et al., 2010; Jagtap et al., 2012; Narsimha and Sudarshan, 2017). The concentration of fluoride in this type of water will depend on mineral solubility, characteristics, and chemical water composition (pH, alkalinity, salinity, redox reactions, chloride levels, total hardness, total dissolved solids, porosity, soil acidity, and temperature, among others), as well as the ability to generate an ion exchange with other substances present (Viswanathan et al., 2009; Banerjee, 2015; Sracek et al., 2015; Li et al., 2018). This phenomenon has become an environmental and health problem for water consumers. Groundwater with high fluoride concentration (>1.5 mg/L), according to World Health Organization (WHO,

* Corresponding author. C/ Senda del Rey No. 9, 28040, Madrid, Spain.
E-mail address: gpaniagua@ccia.uned.es (G. Paniagua González).
Peer-review under responsibility of China University of Geosciences (Beijing).

https://doi.org/10.1016/j.gsf.2020.02.018
Received 17 July 2019; Received in revised form 24 December 2019; Accepted 22 February 2020
Available online 26 March 2020

2011), affects more than 260 million people worldwide (Mondal et al., 2014). Fluoride is an essential micronutrient, which plays a fundamental role in bone formation, proper conservation of dental enamel, and the prevention of teeth from caries (Pollick, 2018). However, continued consumption of water with small amounts of fluoride could cause fluorosis (Viswanathan et al., 2009) producing dental problems, stains or cavities (Guissouma et al., 2017), and bone malformations (atrophy of growth and loss of mobility) (Kravchenko et al., 2014; Gupta et al., 2017).

The province of Santiago del Estero is located between 25°33'03"S and 30°41'20"S, 61°32'24"W and 65°10'46"W. The province is located in the Chaco Pampeana Plain, and is crossed by the Dulce River. The province is a large sedimentary loess plain that is limited to the south, west, and northwest by the mountains of Sumampa–Ambargasta (maximum elevation of 600 m), Guasayán (730 m), and Cerro del Remate (650 m), respectively.

The canyons of the Dulce River include reddish brown limolithic and silt-like conglomerates. In addition, a crystalline basement and acid volcanic rocks are distinguished, which usually contain high concentrations of fluoride, arsenic, and sulphates, among other components, producing natural fluoride and arsenic contamination (Martín and Palazzo, 2009).

The channel of the Dulce River is related to large mega fractures (meridian faults), which have led to major modifications along the river course generating deep tectonics that has affected the aquifers throughout the province.

Mechanically extracted groundwater in Santiago del Estero is the main water source of human consumption for people living in rural areas that belong to this region. This water is treated according to potable standards for the water supply to the cities and urbanized areas, but not in rural areas (Peralta and López Sardi, 2012). Most of the studies reported on water quality in the region of Santiago del Estero have focused on the problem of arsenic (Herrera et al., 2000; Nicolli et al., 2012; Pereyra et al., 2014; Litter et al., 2015). Currently, there is only a preliminary study conducted by the authors that evidenced the presence of high fluoride content in the water of rural areas in Robles Department (RD) and Banda Department (BD) (Rondano et al., 2008). Taking into account the problematic situation in a wide area of RD and BD in Santiago del Estero Province, the goals of the present study were to (1) evaluate the potential pollution situation of this region; (2) investigate the temporal evolution of groundwater quality in RD and BD during the dry (from April to September) and rainy seasons (from October to March) to determine the fluoride concentration variability; and (3) demonstrate the usefulness of univariate methods such as interquartile and interquartile range (IQR) calculation, and multivariate statistical methods such as principal component (PCA) and cluster analyses to identify the factors that influence the analysed system. The obtained results could provide a valuable tool for implementation of corrective measures to possible contamination situations.

2. Materials and methods

2.1. Reagents and materials

Zirconium oxychloride, sodium alizarin sulfonate (S-alizarin), black eriochrome T (BET), sodium ethylenediaminetetraacetate (EDTA-Na_2), hydroxylamine hydrochloride, and methyl orange were supplied by Merck (Germany). Sodium fluoride, sodium carbonate, potassium chromate, and calcium chloride were obtained from Biopack (Argentina). Hydrochloric acid, sulphuric acid, silver nitrate, sodium chloride, ammonium chloride, and ammonia were purchased from Cicarelli (Argentina). All reagents used were of analytical grade. Deionized water used for all aqueous solutions was obtained using a Milli-Q water system (Millipore, Germany). Calibrated plastic material was used for fluoride determination. For the rest of chemical parameter determination, calibrated glass material was utilized.

2.2. Study area

RD is located at the centre of Santiago del Estero Province, in north central Argentina. It is limited to the south by San Martin, to the east by Sarmiento, and to the west and north by two of the most populated and urbanized areas, Capital and Banda departments, respectively (Fig. 1). RD has an area of 1424 km^2 with a population of 44,415 and a population density of 30.8 people/km; 50% of its inhabitants live in rural areas (INDEC, 2010).

BD is located at the centre-west of Santiago del Estero Province. It is limited to the Capital, Rio Hondo, Robles, Jimenez, and Figueroa departments (Fig. 1). The Banda is the most important city in BD and is separated from the provincial capital by the Dulce River. BD has an area of approximately 3597 km^2, which represents 2.6% of the total provincial area. According to INDEC, 144,136 people live in this department. BD has a population density of 39.6 people/km^2, with an increase of 1.16% per year, from 2001 to the present. Approximately 15% of inhabitants live in rural areas.

RD and BD, as well as the rest of the province, are flat, extensive and extremely saline, founded on a crystalline base with fine-textured sediments (loess) such as volcanic ashes, sands, loams, and clays formed during the Pleistocene (Castro de Esparza, 2004; Mon and Gutiérrez, 2007; Nicolli et al., 2012).

This province belongs to the semi-arid Chaco region. Its climate varies from arid and semi-arid to continental-warm sub-humid, with average annual temperatures of 20−22 °C, and maximum temperatures of 45 °C in summer and minimums of −5 °C in winter. Two quite different seasons are found: the dry season, with average temperature of 12 °C, and the rainy season with average temperature of 30 °C and rainfall up to 900 mm (Lorenz et al., 2000; Gaillard de Benítez et al., 2014). The study area covers approximately 1000 km^2 and is shown in Fig. 1, and comprises 23 zones. In RD, the following zones are monitored: Los Romanos, La Florida, Los Arias, Los Pereyra, La Rivera, Higuera Chacra, Taco Pujio, Tala Pozo, San Marcos, Fernández, Pozo Suni, El Mistol, Colonia Jaime, Villa Hipólita, and Tramo 20. In BD, the following zones are monitored: El Puestito, Cara Pujio, San Juan, San Lorenzo, Victoria, 4 Horcones, Los Álamos, and Colonia Argentina.

2.3. Sampling techniques

A total of 110 groundwater samples were collected from different scattered rural dwellings located in RD and BD (Santiago del Estero, Argentina). The study area is shown in Fig. 1. The number of samples from each zone was as follows: Los Romanos (2), La Florida (8), Los Arias (9), Los Pereyra (6), La Rivera (4), Higuera Chacra (1), Taco Pujio (2), Tala Pozo (3), San Marcos (1), Fernández (4), Pozo Suni (10), El Mistol (5), Colonia Jaime (9), Villa Hipólita (4), Tramo 20 (3), El Puestito (4), Cara Pujio (9), San Juan (7), San Lorenzo (3), Victoria (1), 4 Horcones (2), Los Álamos (6), and Colonia Argentina (7). Most of the groundwater samples were extracted from aquifers or groundwater wells (not exceeding 30 m) by rudimentary drilling performed by rural inhabitants. These perforations consist of holes in the ground with very small diameters made by the introduction of metal tubes, which, with the help of the manual force and rudimentary tools turn in depth until reaching the underground aquifer. Once the drilling has been conducted, pumps that act as taps are placed for water extraction. The deepest perforations (up to 120 m) were performed by government entities with specialized tools. The well depth for sampling water goes from the soil to the surface of the water. Two samplings per year were taken, corresponding to the dry (April–September) and rainy season (October–March), respectively, during 2008–2013.

Sampling was performed in accordance with IRAM Norm 29012-2 (IRAM, Institute Argentine of Normalization and Certification of Materials). All samples were collected for laboratory analysis using 1 L polyethylene sterilized bottles and stored at 4 °C until analysis.

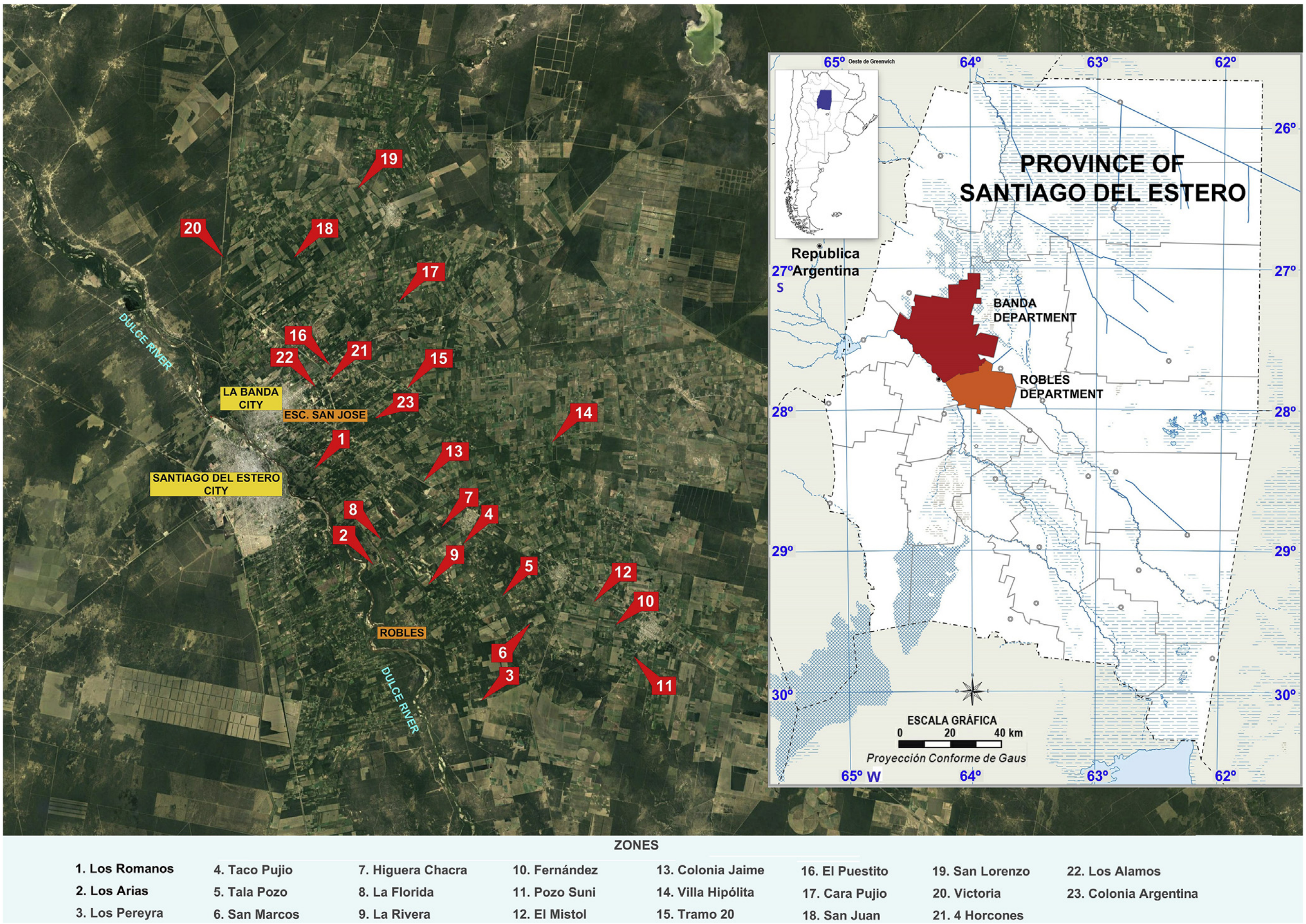

Fig. 1. Geographic location of the study area of Robles and Banda departments in Santiago del Estero Province (Argentina). Geographic distribution of sampling locations in both departments.

2.4. Water parameters determination

The environmental and water sample temperatures were determined in situ using a thermometer (Franklin RA, Argentina). Electrical conductivity (EC) and pH values were measured in the analytical laboratory of the National University of Santiago del Estero by a multiparameter 850081 (Sper Scientific LTD, USA) equipped with a combined glass electrode PY41 (Alpha, USA) and a conductivity cell 850084 (Sper Scientific LTD, USA). Total dissolved solids (TDS) were determined using the values obtained from electrical conductivity, applying a mathematical equation and dividing the conductivity values by a factor of two (Fuentes et al., 2002). Chloride concentration was analysed by the precipitation method. A 10 mL aliquot of each sample was placed in a flask and 1 mL of indicator solution (potassium chromate 5% w/v) was added. The mixture was titrated with 0.1 N silver nitrate until the indicator colour turned red. Total hardness was determined by complexometric titration. A volume of 5 mL of sample was placed in a flask and 1 mL of buffer (pH 10) plus 3 drops of the BET (indicator) solution were added. The mixture was titrated with 0.01 N EDTA-Na2. Total alkalinity was determined by acid–base titration. A 10 mL aliquot of sample with methyl orange indicator was titrated with certified 0.1 N HCl.

Fluoride content was determined by the standard colorimetric method using as a colour reagent a solution of zirconium oxychloride and sodium alizarin-sulfonate (S-alizarin) in acid medium (Bumsted and Wells, 1952; Crosby et al., 1968; Cardwell et al., 1988; Kundu et al., 2009).

2.5. Statistical analysis

In the present study, univariate and multivariate statistical methods were used to simplify and organize large data sets to provide meaningful insight into groundwater contamination in the Robles and Banda departments. More specifically, the statistical techniques examined the relationships among variables determined in several samples and returned a list of significant factors that control the related variables. All data sets of the studied parameters (fluoride content, pH, conductivity, environmental and water temperatures, TDS, chloride concentration, hardness, and alkalinity) during the dry and rainy seasons, were analysed by applying the univariate statistical method, which includes the lower, median, and upper quartiles (Q_1, Q_2, and Q_3) and the inter-quartile range (IQR). In addition, for the analysis of fluoride variability in both stations, the linear regression method was applied.

Principal components analysis (PCA) was chosen as the multivariate method to determine the variation in the parameter values between zones and sampling periods. Furthermore, the variation in fluoride level in the water samples collected depending on the well depth was studied by the cluster multivariate method (Salifu et al., 2012; Brahman et al., 2013). Microsoft Excel and Infostat softwares were used to perform univariate and multivariate statistical analysis of all data, respectively.

3. Results and discussion

3.1. Seasonal variation of groundwater quality: univariate study

The hydrochemical analysis (ambient and water temperatures, pH, conductivity, alkalinity, hardness, TDS, chloride, and fluoride concentrations) data of 110 groundwater samples collected from Robles and Banda departments during both dry and rainy seasons are presented in Supplementary Table 1. A univariate statistical analysis including the lower, median, and upper quartiles (Q1, Q2, and Q3) was performed, and the interquartile range (IQR) was calculated to provide meaningful insights about the deterioration in the groundwater quality (Table 1). The electrical conductivity (EC) data were in the range of 228–6770 μS/cm and 202–7320 μS/cm for dry and rainy seasons, respectively, which indicates the level of mineralization. In the dry season water sample temperature, T^a, was between 10 °C and 24 °C and pH was between 6.79 and 9.23. For the rainy season, water sample T^a was in the range of 19–36 °C and pH varied from 6.85 to 9.18. These results assume that 95% of the analysed samples were within the pH range (6.50–8.50) established by the World Health Organization (WHO) and the Argentine Food Code (2012) for human water consumption. The average environmental temperature of the workday in the dry season was 20 °C with a maximum value of 24 °C. Water and environment temperatures were higher for the rainy than the dry season. These values are logical since the rainy season coincides with summer. Alkalinity due to the presence of CO_3^{2-} and HCO_3^- is not harmful to human health; however, values higher than 500 mg/L cause an unpleasant taste. According to the results obtained for the dry season 35% of the analysed samples exceeded this value, which is reflected in the third quartile Q3 (590 mg/L) and the average obtained (484 mg/L). In the rainy season, alkalinity was in the range between 141 mg/L and 843 mg/L with an average of 417 mg/L, and only 29% of the samples exceeded the permissible limit of 500 mg/L. In both seasonal periods studied 4% the groundwater samples exceeded the TDS limit (1500 mg/L $CaCO_3$) established by the Argentine Food Code (2012). Nevertheless, 16% of samples showed a concentration above 1000 mg/L, which would be indicative of an important amount of ions in solution (Salifu et al., 2012) and could be explained by the presence of high concentrations of HCO_3^- salts. These results were according to the high alkalinity and pH of the samples tested. With respect to water total hardness, 5% and 14% of groundwater samples exceeded the limit of 400 mg/L during the rainy and dry seasons, respectively. Therefore, 10% of samples exceeded the chloride limit established by legislation (350 mg/L).

According to World Health Organization (WHO, 2008) and the Argentine Food Code (2012), the minimum and maximum fluoride concentration limits in water for human consumption must be established taking into account the air temperature average of the area under study (Sujana and Anand, 2011). During both seasons, the environmental temperature average was 22 °C, and the corresponding established limits were fixed at 0.70 mg/L and 1.00 mg/L as low and high values, respectively (Fig. 2). In this study, the fluoride content for groundwater samples ranged between 0.01 mg/L and 2.80 mg/L in the dry season and 0.01–2.35 in the rainy season. These high concentrations are included in the value of the third quartile (Q_3) of the distribution. Approximately 50% of the samples exceed the maximum limit of 1.00 mg/L F^- (Supplementary Table 1).

Fig. 2 shows the fluoride concentrations, in both the dry and rainy seasons. The horizontal lines indicate the minimum and maximum limits established by legislation. During the rainy season, a decrease in the fluoride concentration in 38% of samples can be observed, representing 47% of total samples. This might be explained by the excessive dilution of the groundwater because of rainfall. In the dry season, a wide concentration range was found (0.07–2.80 mg/L). Out of the 110 samples analysed, 51 samples showed values higher than the maximum (1.0 mg/L). In the rainy season, 42 samples, which represent 38% of the total samples, exceeded this limit. It was also observed that approximately the 50% of samples showed fluoride concentrations above the maximum limit for the two seasons studied. This fact might be indicative of considerable water pollution by fluoride.

In the dry season, 43.6% of the samples had fluoride content below 0.7 mg/L, which is the minimum amount in water recommended by current legislation, and 46.4% of the samples exceeded the maximum limit allowed (1.0 mg/L). Only 10% of the samples were in the range recommended by legislation (0.7–1.0 mg/L) as appropriate for human consumption.

In the rainy season, 39.1% of the samples have fluoride content below 0.7 mg/L and 37.3% of the samples exceeded the maximum limit. Therefore, 23.6% of the samples are in the range recommended.

3.2. Principal components analysis

Principal component analysis (PCA) is a multivariate statistical technique used to reduce the dimensionality of a data set (Terrádez Gurrea, 2010a,b), determine the causes of the variability that occur, and sort the data according to importance (Ramirez et al., 2005; Chávez et al., 2015). This technique transforms a number of variables with a certain degree of correlation, into another smaller number of uncorrelated variables called principal components, which result from linear combinations of the original variables. This technique is based on the decomposition of the original data matrix in three matrices: A, B, and C. Matrix A contains the coordinates of the samples in all the principal components established, matrix B (eigenvalues) contains the variances explained by the principal components, and matrix C or the load matrix (eigenvectors) contains the contribution coefficients of the original variables in the principal components (Davis, 1986; Ramírez et al., 2005; Chávez et al., 2015). The variation in parameters studied (alkalinity, TDS, pH, chloride, hardness, and fluoride concentration) in the groundwater samples of the research area vary differently and PCA is therefore

Table 1
Statistical results of the parameters measured in groundwater samples during the dry and rainy seasons indicating average, standard deviation, quartiles, and the interquartile range (n = 110).

Parameters	Dry season								Rainy season							
	Min	Max	Average	S_D	Q1	Q2	Q3	IQR	Min	Max	Average	S_D	Q1	Q2	Q3	IQR
pH	6.79	9.23	7.70	0.49	7.36	7.64	7.97	0.60	6.85	9.18	7.73	0.48	7.41	7.71	7.95	0.54
Temperature (°C)	10	24	20	3	20	21	22	2	19	36	24	3	22	23	26	4
EC (μS/cm)	228	6770	1459	845	875	1280	1748	873	202	7320	1455	894	850	1303	1858	1008
TDS (mg/L)	114	3385	729	423	437	640	874	437	101	3660	728	447	425	651	929	504
Alkalinity (mg/L)	157	1325	484	185	345	451	590	245	141	843	417	152	285	392	524	239
Cl^- (mg/L)	45	792	178	132	92	138	218	126	36	657	174	120	94	128	220	126
Hardness (mg/L)	30	906	236	167	132	197	290	158	20	1039	185	134	116	158	233	116
F^- (mg/L)	0.01	2.80	1.01	0.66	0.44	0.93	1.47	1.02	0.01	2.35	0.78	0.58	0.30	0.60	1.32	1.02

TDS: Alkalinity and hardness are expressed in mg/L $CaCO_3$; S_D: standard deviation.

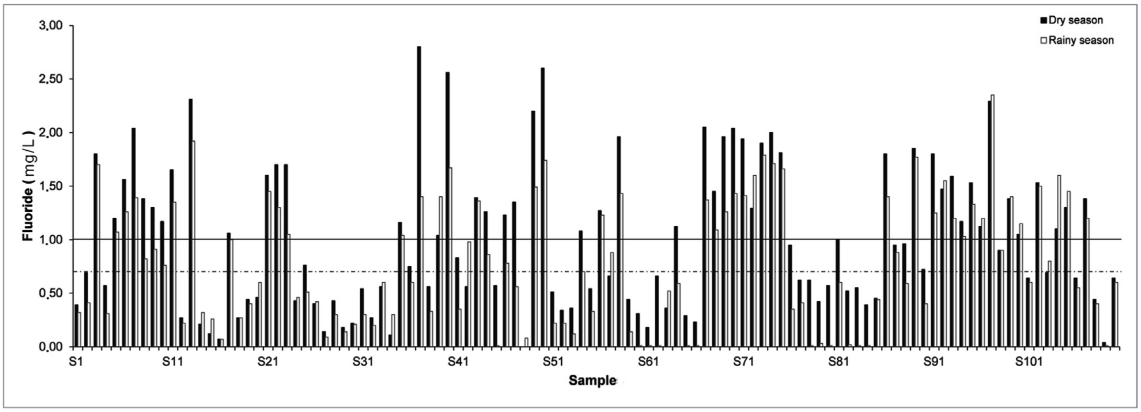

Fig. 2. Evaluation of the fluoride concentration (mg/L) in the samples collected during both dry and rainy seasons. (—) High and (---) low values established by legislation.

Table 2
Principal component loadings of variables, and percentage of partial and cumulative variances in dry and rainy seasons.

Variables	Dry season			Rainy season		
	PC1	PC2	PC3	PC1	PC2	PC3
Alkalinity	0.45	*0.32*	*−0.34*	0.48	0.43	*−0.09*
Fluoride	0.46	*0.08*	0.50	0.53	*0.15*	*−0.27*
pH	0.54	*−0.09*	*0.11*	0.54	*−0.26*	*0.29*
TDS	*0.20*	0.68	*−0.36*	*−0.04*	*0.27*	0.90
Chloride	*−0.20*	0.56	0.68	*0.10*	0.67	*−0.02*
Hardness	−0.46	*0.34*	*−0.16*	−0.43	0.46	*−0.16*
Partial Variance (%)	**46.5**	**23.2**	**13.9**	**39.3**	**27.9**	**17.2**
Cumulative Variance (%)	**46.5**	**69.7**	**83.6**	**39.3**	**67.2**	**84.4**

applied to the correlation matrix for the present study. When the correlation matrix is used, each variable is normalized to unit variance and contributes equally. The PCA results of six parameters evaluated from 110 groundwater samples, collected from the 23 zones under study, in both seasons, are shown in Table 2. To avoid the numerical range problems of the original variables, the PCA analysis was performed by diagonalization of the correlation matrix, so all variables contributed equally since they have been scaled with respect to the variance unit. The variables were grouped into three principal components (PC1, PC2, and PC3), which explain 83.6% and 84.4% of the cumulative variances for dry and rainy seasons, respectively. PC values (load) higher than 0.40 indicate a high association between the variables considered. Table 2 summarizes the PCA results including the contribution of each variable, the loading of each principal component and the explained and cumulative variances.

For the dry season, PC1 was responsible for 46.5% of the total variance. Absolute values higher than 0.40 correspond to alkalinity, fluoride content, pH, and hardness, and were highly correlated with PC1. PC2 explained 23.2% of the total variance and was mainly contributed by the variables of TDS and chloride concentration. Additionally, 13.9% of the total variance was explained in PC3 and fluoride and chloride concentrations gave the most contribution. For the rainy season, the variables of alkalinity, fluoride level, pH, and hardness were highly correlated with PC1 (with a partial variance of 39.3%); variables such as alkalinity, chloride concentration, and hardness were highly correlated with PC2 (partial variance: 27.9%); PC3 explained the 17.2% of the total variance, and TDS provided the most contribution.

The 23 zones studied were projected onto factorial axis representing the percentage variation in each principal component. Figs. 3 and 4 show the PCA plots for the variables studied in the dry and rainy seasons, respectively.

Fig. 3a shows the score plot for the first two PCs in the dry season, explaining 69.8% of the total variance. PC1 presents high loads in the variables of pH, alkalinity, hardness, and fluoride content. The corresponding areas to Fernández, Tala Pozo, Tramo 20, Los Arias, Pozo Suni, and San Marcos are associated with the high fluoride content. In addition, in the areas of the Fernández, Tala Pozo, and Tramo 20, the highest values of pH and alkalinity were found. Hardness has a strong association with Cara Pujio. PC2 explains the TDS and chloride variables. El Puestito and Colonia Argentina present a strong association to these variables.

Fig. 3b explains the 60.4% of cumulative variance, reflected in the PC1–PC3 components. This confirms the behaviour of PC1 observed previously and shows that PC3 confirms the strong association of fluoride with the zones Fernández, El Puestito, and Victoria, and chloride with El Puestito.

Fig. 3c explains the 37.1% of the cumulative variance, reflected in the PC2–PC3 components (Table 2). The figure shows the strong association that TDS has with Colonia Argentina.

Fig. 4a explains 67.2% of total variance reflected in components PC1–PC2, while Fig. 4b explains 56.5%, expressed in components PC1–PC3 (Table 2).

From the analysis of PC1 in Fig. 4a, it can be observed that the variable pH presents a strong association with the zones of Tramo 20 and San Marcos, while in Fig. 4b, it is also associated with Fernández and Tala Pozo.

It is also observed that the variable fluoride presents high loads in PC1, which are associated with the Fernández and Victoria areas, while in Fig. 4b this association is manifested with El Puestito, Victoria, and 4 Horcones. Both PC1 and PC2 show a strong association in Cara Pujio with hardness. PC2 indicates a strong relationship between chloride and El Puestito.

Fig. 4c represents 45.1% of the cumulative variance, manifested by the PC2–PC3 components. These components present loads greater than 0.40 with the variables alkalinity, chloride, hardness, and TDS (Table 2). Fig. 4c shows a high chloride association with the zones El Puestito, hardness with Cara Pujio, and TDS with Fernández.

3.3. Cluster analysis

The cluster analysis implements different processes to group objects described by a set of data from several variables (Li et al., 2012). In this work, the simple linkage method (Terrádez Gurrea, 2010a,b) was applied to determine the variation in fluoride concentration in groundwater samples depending on the well depth from which samples were collected. Supplementary Table 1 summarized the groundwater samples and the well depths. The results of the hierarchical cluster analysis were given as a dendrogram (Fig. 5). As can be seen from the figure, the samples collected from the different zones in the Robles and Banda departments

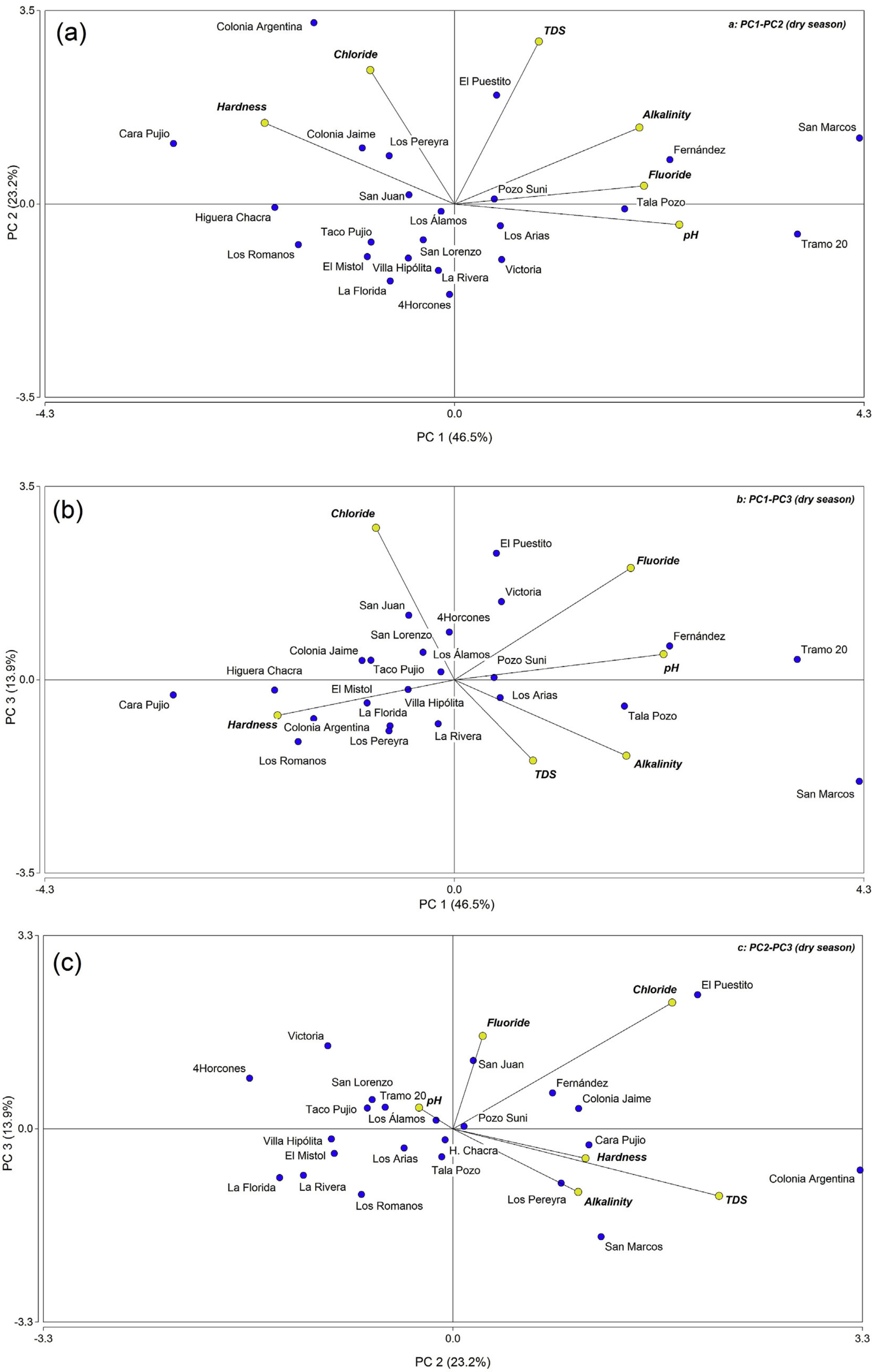

Fig. 3. Bivariate plots of the different PCs during the dry season: (a) PC1 *vs.* PC2, (b) PC1 *vs.* PC3 and (c) PC2 *vs.* PC3.

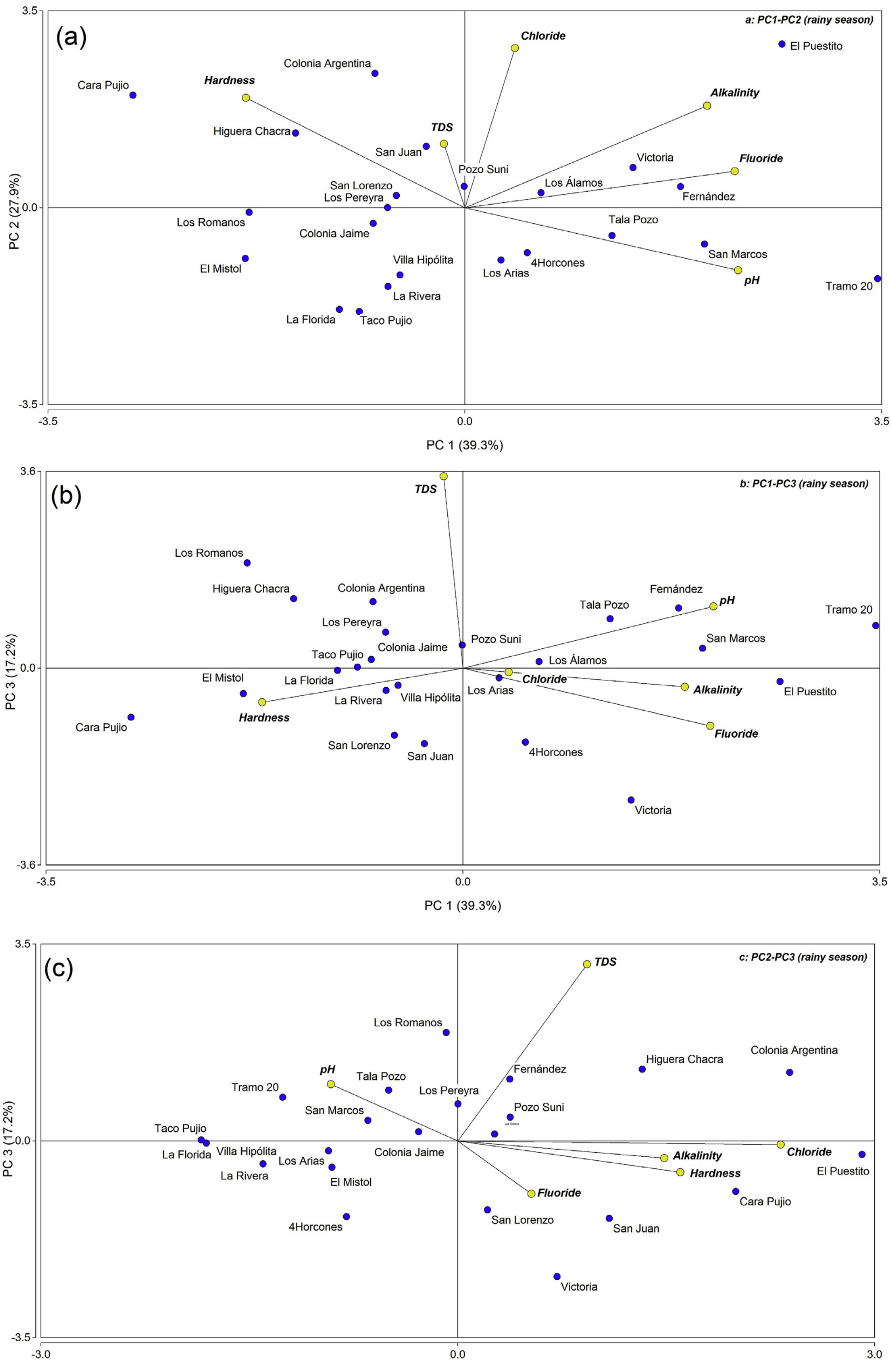

Fig. 4. Bivariate plots of the different PCs during the rainy season: (a) PC1 *vs.* PC2, (b) PC1 *vs.* PC3 and (c) PC2 *vs.* PC3.

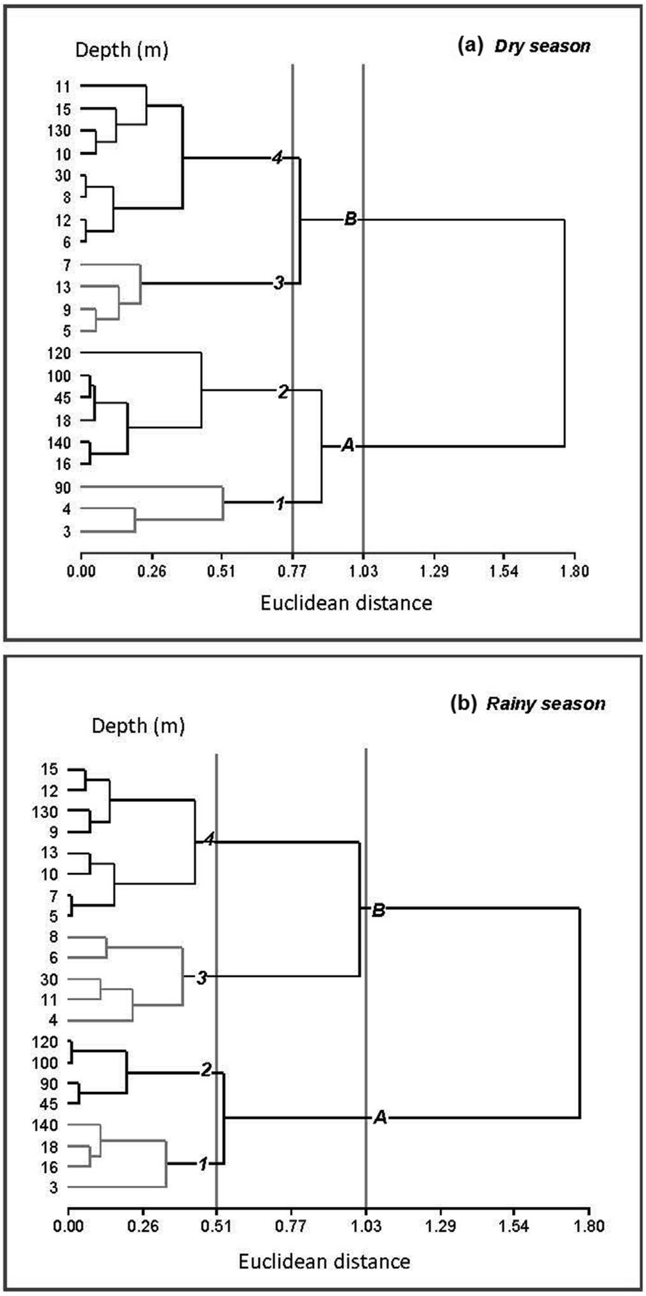

Fig. 5. Hierarchical cluster for the analysed groundwater samples depending on the wells depth in the (a) dry season and (b) rainy season.

during different seasons were clustered together. Fig. 5 shows the dry and rainy season dendograms, respectively. The horizontal axis indicates the Euclidean distances or the correlations between the well depths and the fluoride concentrations of the samples, and the vertical axis indicates the nominal variable (depth).

Two principal clusters (A and B) are observed when a Euclidean distance of 1.03 is considered (Fig. 5a). Cluster A groups include groundwater wells with lower fluoride levels, cluster B those with higher levels. When a Euclidean distance of 0.77 is applied, four clusters were obtained (1 and 2 corresponding to low fluoride values, 3 and 4 with high ones). Cluster 1 presents the lowest fluoride concentrations while cluster 4 includes those wells with higher fluoride content. In Fig. 5b (rainy season), two clusters (A and B) were observed at a distance of 1.03. Both included the same depth wells as in the dry season with exception of the 4 m depth well, which appears in cluster A instead of cluster B. When a distance of 0.51 was considered, 4 groups were obtained (1, 2, 3, and 4); in clusters 1 and 2 the fluoride contents were lower than in clusters 3 and 4. A similar behaviour was observed in both the rainy and dry seasons. In general, from the obtained results it could be concluded that fluoride concentration in the different studied wells is related to the well depth. In general, it is observed that the concentration of fluoride decreases when the depth of the well increases.

4. Conclusions

Groundwater extracted through the pumping wells is the main source of drinking water for the rural population of the region of Robles and Banda departments, located in Santiago del Estero Province, in north central Argentina. The hydrochemical analysis using univariate and multivariate statistical techniques such as quartiles and inter-quartile range calculation, linear regression method, principal components analysis, and cluster analysis have provided information about the environmental status and the groundwater quality of this region. According to results, the pH range and the TDS values were higher in the rainy season than in the dry season, while the values of alkalinity, chloride concentration, and hardness were higher in the dry season. Approximately, 50% of the total analysed samples showed high fluoride content during both dry and rainy seasons tested (up to 2.80 mg/L and 2.35 mg/L, respectively) and high chloride concentration (792 mg/L and 657 mg/L), higher than the values established by current legislation. The results of PCA allowed reduction of the original data matrix to three important PCs explaining 83.6% (dry season) and 84.4% (rainy season) of the total variance, and the PCA analysis determined that the groundwater samples from Fernández, El Puestito, 4 Horcones, and Victoria contained the highest fluoride contents in both seasons. Cluster analyses investigated the variation in fluoride level in the groundwater according to well depth. In general, it was observed that at depths under 13 m the fluoride concentrations increased considerably (1.05–2.80 mg/L) with respect to the limits allowed by legislation. These statistical studies can help to indicate the water quality of the wells.

The results obtained have shown that the groundwater in the study areas has a significant level of fluoride contamination. This fact could negatively affect the health of the rural population in these zones where they do not have access to another type of properly treated water. With the results obtained in this work, it is expected that the government becomes aware of the worrying pollution situation of the groundwater for the population living in Robles and Banda departments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was partially supported by the research project "Water and Environment", by the Secretary of Science and Technology of the University National of Santiago del Estero, Argentina (UNSE), National University of Distance Education (UNED) (project reference: 2017/CTINV-0024), and by the Comunidad of Madrid and European funding from FSE and FEDER programs (project S2018/BAA-4393, AVANSECAL-II-CM).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gsf.2020.02.018.

References

Alarcón-Herrera, M.T., Bundschuh, J., Nath, B., Nicolli, H., Gutiérrez, M., Reyes-Gómez, V., Nuñez, D., Martín Dominguez, I., Sracek, O., 2013. Co-occurrence of arsenic and fluoride in groundwater of semi-arid regions in Latin America: genesis, mobility and remediation. J. Hazard Mater. 262 (11), 960–969.

Argentine Food Code, 2012. Chapter XII: Water Beverages, Waters and Aerated Waters. National Administration of Medicines, Food and Medical Technology (ANMAT) (in Spanish).

Banerjee, A., 2015. Groundwater fluoride contamination: a reappraisal. Geosci. Front. 6 (2), 277–284.

Borgnino, L., Garcia, M.G., Bia, G., Stupar, Y.V., Le Coustumer, Ph, Depetris, P.J., 2013. Mechanisms of fluoride release in sediments of Argentina's central region. Sci. Total Environ. 443 (1), 245–255.

Brahman, K.D., Kazi, T.G., Afridi, H.I., Naseem, S., Arain, S.S., Ullah, N., 2013. Evaluation of high levels of fluoride, arsenic species and other physicochemical parameters in underground water of two sub-districts of Tharparkar, Pakistan: a multivariate study. Water Res. 47 (3), 1005–1020.

Bumsted, H.E., Wells, J.C., 1952. Spectrophotometric method for determination of fluoride ion. Anal. Chem. 24 (10), 1595–1597.

Bustingorri, C., Lavado, R.S., 2014. Soybean as affected by high concentrations of arsenic and fluoride in irrigation water in controlled conditions. Agric. Water Manag. 144 (10), 134–139.

Cardwell, T.J., Cattrall, R.W., Mitri, M., Hamilton, I.C., 1988. Flow-injection spectrophotometric determination of fluoride by using the zirconium/alizarin red S complex. Anal. Chim. Acta 214, 433–438.

Castro de Esparza, M., 2004. Arsénico en el agua de bebida de América Latina y su efecto en la salud pública. CEPIS/OPS 95, 1–12 (in Spanish).

Chávez, C.O., Sánchez, J.E., DelaCerda, J., 2015. Analysis of principal functional components in economic time series. GECONTEC: Int. J. Knowl.Technol.Manag 3 (2) (in Spanish).

Crosby, N.T., Dennis, A.L., Stevens, J.G., 1968. An evaluation of some methods for the determination of fluoride in potable waters and other aqueous solutions. Analyst 93 (1111), 643–652.

Davis, J.C., 1986. Statistics and Data Analysis in Geology, second ed. John Wiley and Sons, New York and London, pp. 563–565.

Esposito, M.E., Paoloni, J.D., Sequeira, M.E., Amiotti, N.M., Blanco, M.C., 2011. Natural contaminants in drinking waters (arsenic, boron, fluorine and vanadium) in the Southern Pampean Plain, Argentina. J. Environ. Protect. 2 (1), 97–108.

Fuentes, F. y, Massol, A., 2002. Physico-chemical parameters: total dissolved solids. Second part. In: Laboratory Manual. Ecology of Microorganisms, vol. 1. Puerto Rico University, pp. 1–245 (in Spanish).

Gaillard de Benítez, C., Pece, M., Juárez de Galíndez, M., Acosta, M., 2014. Modelaje de la biomasa aérea individual y otras relaciones dendrométricas de Prosopis nigra Gris en la provincia de Santiago del Estero, Argentina. Quebracho 22 (1–2), 17–29 (in Spanish).

García-Sánchez, J.J., Solache-Ríos, M., Martínez-Miranda, V., Solís Morelos, C., 2013. Removal of fluoride ions from drinking water and fluoride solutions. J. Colloid Interface Sci. 407 (10), 410–415.

Guissouma, W., Hakami, O., Al-Rajab, A.J. y Tarhouni J., 2017. Risk assessment of fluoride exposure in drinking water of Tunisia. Chemosphere 177 (6), 102–108.

Gupta, L., Zanwar, A., Agarwal, V., 2017. Skeletal fluorosis mimicking diffuse idiopathic skeletal hyperostosis. Indian J. Med. Specialities 8 (4), 213–214.

Herrera, H.B., Farías, B., Martín, R., Cortés, J., Storniolo, A., Thir, J.M., 2000. Origen y dinámica del Arsénico en el agua subterránea del Dpto. Robles-provincia de Santiago del Estero, Universidad Nacional de Santiago del Estero, Cofes. s.f (in Spanish with English abstract).

INDEC (National Institute of Statistics and Census of Argentina), 2010. Argentine National Census. Santiago del Estero (in Spanish).

IRAM (Argentine Institute for Standardization and Certification of Materials). Rules IRAM 29012-2. Quality of the Environment Water. Sampling. General Directives (in Spanish).

Jagtap, S., Yenkie, M.K., Labhsetwar, N., Rayalu, S., 2012. Fluoride in drinking water and defluoridation of water. Chem. Rev. 112 (4), 2454–2466.

Kim, S.H., Kim, K., Ko, K.S., Kim, Y., Lee, K.S., 2012. Co-contamination of arsenic and fluoride in the groundwater of unconsolidated aquifers under reducing environments. Chemosphere 87 (8), 851–856.

Kravchenko, J., Rango, T., Akushevich, I., Atlaw, B., McCornick, P.G., Merola, R.B., Paul, C., Weinthal, E., Harrison, C., Vengosh, A., Jeuland, M., 2014. The effect of non-fluoride factors on risk of dental fluorosis. Sci. Total Environ. 488–489 (8), 595–606.

Kumar, M., Das, A., Das, N., Goswami, R., Singh, U.K., 2016. Co-occurrence perspective of arsenic and fluoride in the groundwater of Diphu, Assam, Northeastern India. Chemosphere 150 (5), 227–238.

Kundu, M.C., Mandal, B., Chand, G., 2009. Nitrate and fluoride contamination in groundwater of an intensively managed agroecosystem: a functional relationship. Sci. Total Environ. 407 (8), 2771–2782.

Li, D., Gao, X., Wang, Y., Luo, W., 2018. Diverse mechanisms drive fluoride enrichment in groundwater in two neighboring sites in northern China. Environ. Pollut. 237 (6), 430–441.

Li, J., Wang, Y., Xie, X., Su, Ch, 2012. Hierarchical cluster analysis of arsenic and fluoride enrichments in groundwater from the Datong basin, Northern China. J. Geochem. Explor. 118 (7), 77–89.

Litter, M., Pereyra, S., López Pasquali, C.E., Iriel, A., Senn, A., García, F., Blanco Esmoris, M., Rondano, K., Pabón, D., Dicelio, L., Lagorio, M., Noel, G., 2015. Arsenic removal in localities of the province of Santiago del Estero, Argentina. Evaluation of access, use and quality of water in rural populations with arsenic problems. Ingeniería Sanitaria y Ambiental 125 (11), 13–25 (in Spanish with English asbtract).

Lorenz, G., Bonelli, C., Roldán, S., Araya, C., Rondano, K., 2000. Soil quality changes due to land use. In: A Kastanozem-Phaeozem soilscape of Semiarid Chaco. Mitteilungen der Deutsche Bodenkundliche Gesellschaft, vol. 93, pp. 169–172.

Machiwal, D., Jha, M.K., Singh, V.P., Mohan, Ch, 2018. Assessment and mapping of groundwater vulnerability to pollution: current status and challenges. Earth Sci. Rev. 185 (10), 901–927.

Martín, A.P., Palazzo, R., 2009. Contaminación natural por sulfatos en el sistema multiacuífero de la ciudad de Santiago del Estero, Argentina. Bol. Geol. Min. 120 (4), 563–582 (in Spanish with English abstract).

Martín, A., Paz, M.M., Palazzo, R., Lencina, S., 2016. Natural pollution by fluoride in the thermal complex emerging from the city of hot springs of Santiago del Estero. Trazos Journal. http://revistatrazos.ucse.edu.ar/index.php/2016/07/28/contaminacion-natural-fluor-complejo-termal-surgente-la-ciudad-termas-rio-hondo-santiago-del-estero/ (access 17 July 2019) (in Spanish).

Mon, R., Gutiérrez, A., 2007. Estructura del extremo sur del Sistema Subandino (provincias de Salta, Santiago del Estero y Tucumán). Rev. Asoc. Geol. Argent. 62 (1), 62–68 (in Spanish with English abstract).

Mondal, D., Gupta, S., Reddy, D.V., Nagabhushanam, P., 2014. Geochemical controls on fluoride concentrations in groundwater from alluvial aquifers of the Birbhum district, West Bengal, India. J. Geochem. Explor. 145 (10), 190–206.

Narsimha, A., Sudarshan, V., 2017. Contamination of fluoride in groundwater and its effect on human health: a case study in hard rock aquifers of Siddipet, Telangana State, India. Applied Water Science 7 (5), 2501–2512.

Navarro, O., González, J., Júnez-Ferreira, H.E., Bautista, C.F. y, Cardona, A., 2017. Correlation of arsenic and fluoride in the groundwater for human consumption in a semiarid region of Mexico. Procedia Engineering 186, 333–340.

Nicolli, H., Bundschuh, J., Blanco, M.C., Tujchneider, O.C., Panarello, H.O., Dapeña, C. y, Rusansky, J.E., 2012. Arsenic and associated trace-elements in groundwater from the Chaco-Pampean plain, Argentina: results from 100 years of research. Sci. Total Environ. 429 (7), 36–56.

Ozsvath, D.L., 2009. Fluoride and environmental health: a review. Rev. Environ. Sci. Biotechnol. 8 (1), 59–79.

Peralta, A., López Sardi, E.M., 2012. Los acuíferos de nuestro país: un tesoro para las generaciones venideras. Ciencia Tecnolog. 12, 73–82 (in Spanish with English abstract).

Pereyra, S., López Pasquali, C.E., Litter, M., 2014. Access, use and quality of water: water economy and policy in rural populations with arsenic problems in Santiago del Estero, Argentina. In: Litter, M., Nicolli, H.B., Meichtry, J.M., Quici, N., Bundschuh, J., Naidu, P. Bhattacharya y R. (Eds.), One Century of the Discovery of Arsenicosis in Latin America-As. CRC A.A. Balkema Publishers, Taylor and Francis Publishers, Buenos Aires, pp. 900–903.

Pollick, H., 2018. The role of fluoride in the prevention of tooth decay. Pediatr. Clin. 65 (5), 923–940.

Ramírez, A., Fernández, N., Solano, F., 2005. Dinámica fisicoquímica y calidad del agua en la microcuenca El Volcán, municipio de Pamplona, Colombia. Bistua 3 (1), 5–16 (in Spanish with English abstract).

Rao Nagendra, C.R., 2003. Fluoride and environment- a review. In: Bunch, M.J., Madha Suresh, V., Vasantha Kumaran, T. (Eds.), Proceedings of the Third International Conference on Environment and Health. Department of Geography, University of Madras and Faculty of Environmental Studies, York University, Chennai, India, pp. 386–399.

Rondano, K., Mellano, F., Rosas, D., García, P., López Pasquali, C.E., 2008. Arsénico y flúor en aguas de consumo de Robles, Santiago del Estero, Argentina. Revista Ciencia 3 (3), 69–78 (in Spanish with English abstract).

Rondano, K., Mellano, F., 2010. Los más tóxicos. En: Agua que has de Beber. Lucrecia. Santiago del Estero, Argentina, pp. 167–199 (in Spanish).

Salifu, A., Petrusevski, B., Ghebremichael, K., Buamah, R., Amy, G., 2012. Multivariate statistical analysis for fluoride occurrence in groundwater in the Northern region of Ghana. J. Contam. Hydrol. 140–141 (10), 34–44.

Sracek, O., Wanke, H., Ndakunda, N.N., Mihaljevič, M., Buzek, F., 2015. Geochemistry and fluoride levels of geothermal springs in Namibia. J. Geochem. Explor. 148, 96–104.

Sujana, M.G., Anand, S., 2011. Fluoride removal studies from contaminated ground water by using bauxite. Desalination 267 (2–3), 222–227.

Terrádez Gurrea, M., 2010a. Análisis de Componentes Principales, e-Math Project. Universidad Abierta de Cataluña. Funded by the Secretary of State for Education and Universities, p. 11 (in Spanish).

Terrádez Gurrea, M., 2010b. Análisis de Conglomerados, e-Math Project. Universidad Abierta de Cataluña. Funded by the Secretary of State for Education and Universities, p. 9 (in Spanish).

Viswanathan, G., Jaswanth, A., Gopalakrishnan, S., Sivailango, S., Aditya, G., 2009. Determining the optimal fluoride concentration in drinking water for fluoride endemic regions in South India. Sci. Total Environ. 407 (20), 5298–5307.

World Health Organization (WHO), 2011. Guidelines for drinking-water quality. World Health Organ 1 (4), 178.

Zabala, M.E., Manzano, M., Vives, L., 2016. Assessment of processes controlling the regional distribution of fluoride and arsenic in groundwater of the Pampeano Aquifer in the Del Azul Creek basin (Argentina). J. Hydrol. 541 (10), 1067–1087.