

## **Arsenic and Fluoride in Groundwater of a Loessical Unconfined Aquifer, Cordoba, Argentina.**

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**Abstract:** *La Colacha basin (Córdoba province, Argentina) is a piedmont rural area where groundwater is used for different activities. The objective of this work is to assess the controls on geochemistry processes in the unconfined loessical aquifer, especially those related to arsenic and fluoride. Low groundwater velocities and bicarbonate sodium water types predominate. The results of the numerical models show that salt dissolution and cation exchange are the main geochemical processes in the aquifer. High values of As and F were identified and although they do not follow clear trends with major ions, the multivariate statistical analysis shows that there is affinity between As and F with pH and alkaline waters. Furthermore, As and F are positive correlated, which account for their similar origin (lithological control) and their entering in solution under similar geochemical aquifer conditions. It is assumed that the volcanic glass, in a moderate to high pH aquifer environment, may be altered, supplying As and F ions to the solution. Fluoride may be supplied also from other F bearing minerals identified in this geological setting (fluorite and fluoroapatite). In this oxidant aquifer environment, arsenates may also be desorbed from the surface of secondary amorphous Fe and Mn oxides.*

**Keywords:** *geochemistry, loess, water quality*

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### **I. Introduction and Objectives**

Arsenic and fluoride dissolved in groundwater is a global problem, affecting many countries worldwide. Arsenic enriched groundwater is found in many parts of the world, including Bangladesh, India, Korea, [1], Mexico [2], Argentina [3, 4], among others. Fluoride is also a global problem and a common natural element in groundwater supplies from industrialized and developing countries. East Africa, Inner Mongolia in China and India contain the most extensive areas of high fluoride groundwaters [5], but fluoride problems are reported in many other areas of the world including Korea, Indonesia and Argentina [6, 3, 7]. It seems that whilst arsenic is a problem particularly in sedimentary aquifers [8], fluoride problems occur frequently in both bedrock and sedimentary groundwaters [9, 4].

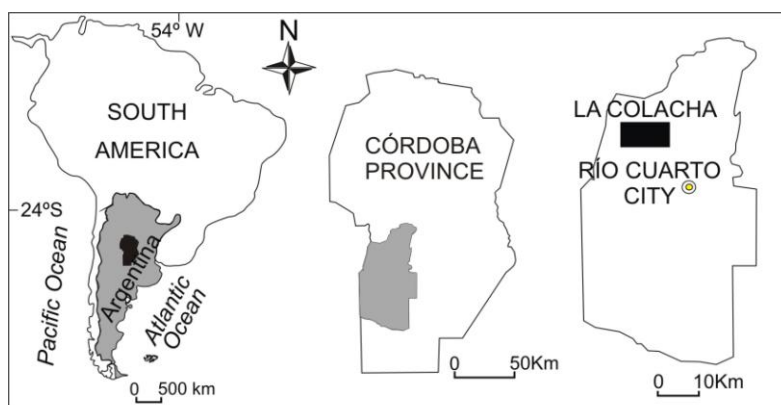
The occurrence of As and F is often natural and controlled by the geological environment. According to [10], arsenic mobility in groundwater is severely restricted by adsorption on Fe(OH)<sub>3</sub> and Al(OH)<sub>3</sub>. Under certain geological conditions, the most important natural sources of As are the sulphurous minerals (orpiment (As<sub>2</sub>S<sub>3</sub>), arsenopyrite (FeAsS), realgar (AsS) and enargite (Cu<sub>3</sub>AsS<sub>4</sub>). Arsenic can be minor constituent of sulfides (pyrite, chalcopyrite, galena, pyrrhotite) and some oxides (iron mainly). Relating to fluorides, there is no a single and simple reason to explain their presence and behavior in groundwater. From forming rock minerals, fluoride is an essential component only in fluorite (CaF<sub>2</sub>) and topaz (Al<sub>2</sub>SiO<sub>4</sub> (F, OH)<sub>2</sub>), but it is also found in accessory minerals such as cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and apatite (3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>Ca (F, Cl)<sub>2</sub>). Minerals like phlogopite, biotite, epidote and amphibole (tremolite and hornblende) also have F. Ultramafic rocks have less than 100 ppm of F while granitic rocks have F in the order of 800 ppm [11].

In Argentina more than 1.2 million people depend on groundwater whose arsenic concentration is greater than 0.05 mg/L predominantly in rural areas, especially in the Pampean Plain, a vast flat plain that has resulted primarily from aeolian (loess) deposition [4]. Different authors measured arsenic concentrations more than 3,000 µg/L and fluoride concentrations greater than 10 mg/L, [3] [4]. The problems are known to extend to the very north of the typical loess regions of Argentina, including Tucuman Province where high levels of As and F have also been found [12].

In Córdoba province, dental fluorosis in children, youngsters and adults have been identified [4] while arsenicism health problems have been described in the North East part of the province by physicians long time ago [13, 14]. Considering the three decades of geochemical water studies in this region [3, 4], and the diffusion of this problem in mass media, people is becoming conscious about the drinking water that must be used, but more studies are necessary.

In this framework, the overall aim of this work was to better understand the controls on geochemistry in part of the unconfined aquifer of the Pampean Plain, especially those related to arsenic and fluoride dissolved in groundwater to have basic information for the resource management. The selected area for this study is La

Colacha basin (Córdoba province, Argentina), a typical piedmont rural area (Figure 1), where groundwater studies were carried out due to the importance of the unconfined aquifer for human consumption and rural water supply (mainly cattle).



**Figure 1.** Location of study area

## **II. Materials and Methods**

The research was carried out at 1:50,000 scale, based on the analysis and compilation of satellite images (Google Earth, Landsat ETM) and topographic sheets from National Geographic Institute (NGI). Background information (geological, geomorphological, climatic, etc.) of the study area was collected and analyzed [15, 16]. The precipitation data was analyzed and interpreted using a local 30 years series (1985-2015). The regional geological and hydrogeological features were identified at field. The geological and geomorphological study was performed through the description of the relief and the outcropping lithological profiles. The hydrogeological data were obtained surveying 45 wells which penetrate the upper 15 m of the unconfined sedimentary aquifer. Thirty four groundwater samples were obtained and field parameters were measured in situ: pH, electrical conductivity (EC) and temperature (T) using a multiparametric portable probe with GPS, Hanna HI 9829. The samples were collected in 1 L plastic bottles and were analyzed within 24 h of collection, in the laboratory of the National University of Río Cuarto. The following parameters were analyzed:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , As and F [17]. The mean percentage error of the analysis was 2.1 % and did not exceed 7.7 %. Fluoride was measured using ion selective electrode and arsenic was determined in an external laboratory (*K-DIAL*, Río Cuarto, Córdoba, Arg.) by means of Atomic Absorption Spectroscopy (AAS). The major ions results were analyzed using PHREEQC software [18] to evaluate the main geochemical processes in selected groundwater flow lines using the geochemical inverse model concept. The whole analysis linking geochemical environment with As and F was made using descriptive statistical techniques (multivariate analysis) by means of specific software [19]. Accordingly, to explain relationships between all chemical variables, cluster analysis in R mode and factorial (main components) analysis were made. Taking into account the known relationship and dependence between pH and  $\text{CO}_3^{2-}$  the latter was not considered for the multivariate analysis. The chemical variables were standardized because of the very different scales of pH and EC to the meq/L used for the chemical concentrations in the cluster analysis.

## **III. Geology, Hydrogeology and Climate**

The regional climate is sub-humid dry, with an annual mean precipitation (P) of 780 mm. About 75-80% of precipitation is concentrated during the end of spring, summer and early autumn. In the average water balance, the annual mean potential evapotranspiration (PET) is 820 mm whereas the actual evapotranspiration (AET) is 780 mm. However, the water balance shows alternating water deficit and water excess periods, especially depending on the annual precipitation. When water excesses occur, they are distributed in surface runoff and groundwater recharge [20].

The Colacha stream basin is mostly located in the Comechingones Mountains piedmont area. The upper basin is developed in the mountain, where metamorphic rocks outcrop (Figure 2A). The rest of the area is covered by Holocene and Upper Pleistocene sediments. Most of the basin area is covered by silty-sandy eolian sediments of loessical type, while sandy-gravel fluvial deposits are restricted to the streams surroundings. Colluvial deposits may be found near the mountains. The abundance of calcrete layers and carbonate nodules across the basin should be noted, because of their role in groundwater geochemical features [4]. The basin has an undulating relief, with a regional slope in the order of 2%. Taking into account the geophysical data, the less permeable rock that outcrops in the mountain, forms the base of the sedimentary aquifer in the piedmont [14]. Therefore, the sedimentary aquifer has a variable thickness, between few meters and almost 80 m.

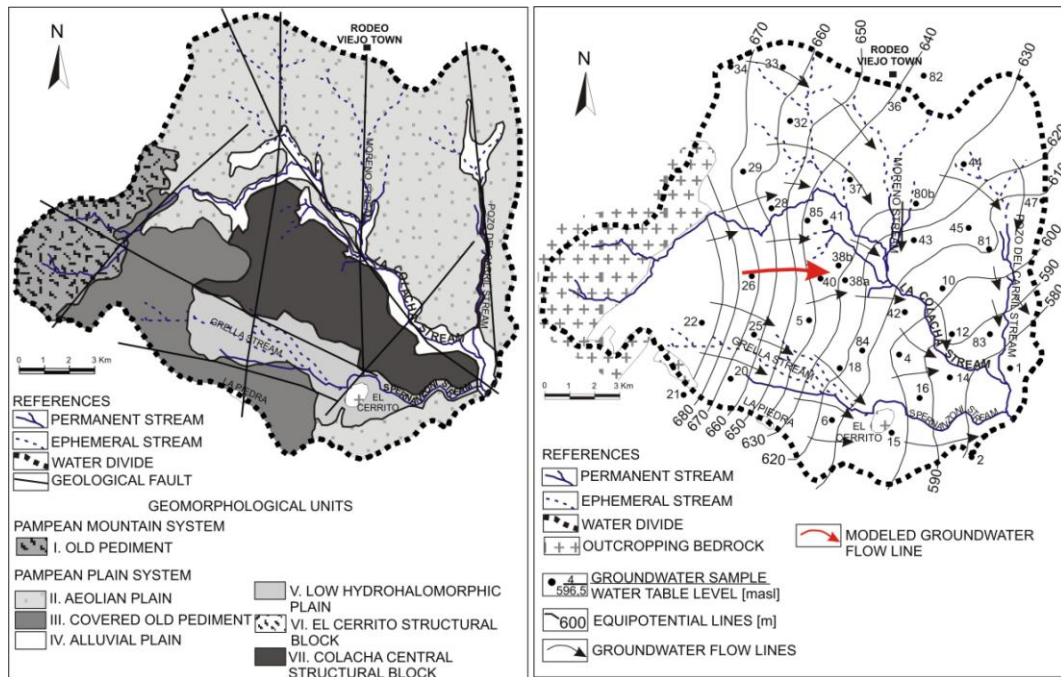


Figure 2. A)- Geological-geomorphological map of La Colacha basin. B)- Equipotential map of the unconfined aquifer.

The hydraulic parameters of the aquifer were defined according to the textural characteristics of the sediments and *in situ* aquifer tests [14]. In relation to the eolian environment, the average value of aquifer transmissivity (T) is 80-400 m<sup>2</sup>/day, the hydraulic conductivity (K) is 1-5 m/day and the average storage coefficient (S) is in the order of 0.15. The groundwater flow direction can be observed in figure 2B. Groundwater flows towards the main stream of La Colacha system in a NW-SE direction (Figure 2B) with low velocities in the order of 0.05 m/d. In relation to the mineralogy determined for the regional eolian sediments [4], the very fine sand and silty fractions present abundant volcanic glass, quartz, plagioclase, potassium feldspar, amphiboles, pyroxenes, biotites, apatites and Fe oxides. Fluorite appears in the mountains and may exist as an inclusion in biotite [4].

#### IV. Results and Discussion

##### Groundwater Geochemistry

The results (Table 1) show a large degree of spatial variation of total dissolved solids (TDS), between 623 mg/L and 3,484 mg/L (Figure 3), being the smallest values related to recharge areas, closer to the mountains. The pH values are generally slightly basic with a median value of 7.9 and the most basic at 8.4. It was observed that the dominant cation in all of the samples is sodium, which always represents 65.7 % or more of the cations. The major anions are split between being dominated by HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>=</sup> or both. This gives rise to water types ranging from sodium bicarbonate waters (61.7%) to sodium sulfate waters (17.6 %) and including mixed anion HCO<sub>3</sub>-SO<sub>4</sub> types in between (20.6%). The more salty and sodium sulfate waters prevail in the central part of the basin, where the most fine cemented sediments predominate.

Table 1 Statistical parameters from univariate descriptive analysis

	N	Minimum	Maximum	Average	Deviation
pH	34	7.29	8.40	7.85	.26
EC (μS/cm)	34	721.00	5260.00	1900.06	1250.14
TDS (mg/L)	34	622.99	3483.80	1366.25	681.98
CO <sub>5</sub> (mg/L)	34	0.00	2.40	0.11	.45
HCO <sub>3</sub> (mg/L)	34	372.50	687.50	544.96	89.44
SO <sub>4</sub> (mg/L)	34	21.60	1206.80	298.24	324.66
Cl (mg/L)	34	5.70	328.60	73.36	75.08
Na (mg/L)	34	156.50	967.60	357.96	200.75
K (mg/L)	34	3.70	40.40	17.19	9.79
Ca (mg/L)	34	4.80	82.40	25.74	17.33
Mg (mg/L)	34	2.400	65.400	15.59	13.30
As (mg/L)	34	.027	.239	0.10	.06
F (mg/L)	34	1.45	10.50	4.35	2.48

To evaluate general geochemical processes numerical inverse modeling along different flow lines were carried out considering the explained hydrogeological features, in order to evaluate the adjustment to the conceptual model. In this paper only one example is showed. Therefore, it was considered that the water sample 38a is the result of geochemical evolution along a groundwater flow line coming from the upper piedmont area, represented in the model by the water sample 26 (Table 2, Figure 2B).

**Table 2.** Chemical analysis of the initial (IS) and final (FS) solutions.

Case N° 1	N°	pH	Cond.	TDS	CO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> H	SO <sub>4</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>
	Sample		μS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
	M <sub>26</sub> (SI)	7.90	1031	1043	0.0	645.0	46.0	10.0	267.9	10.7	12.0	5.9
	M <sub>38</sub> (SF)	7.90	5260	3042	0.0	625.0	1206.8	228.6	768.5	40.4	82.4	65.4

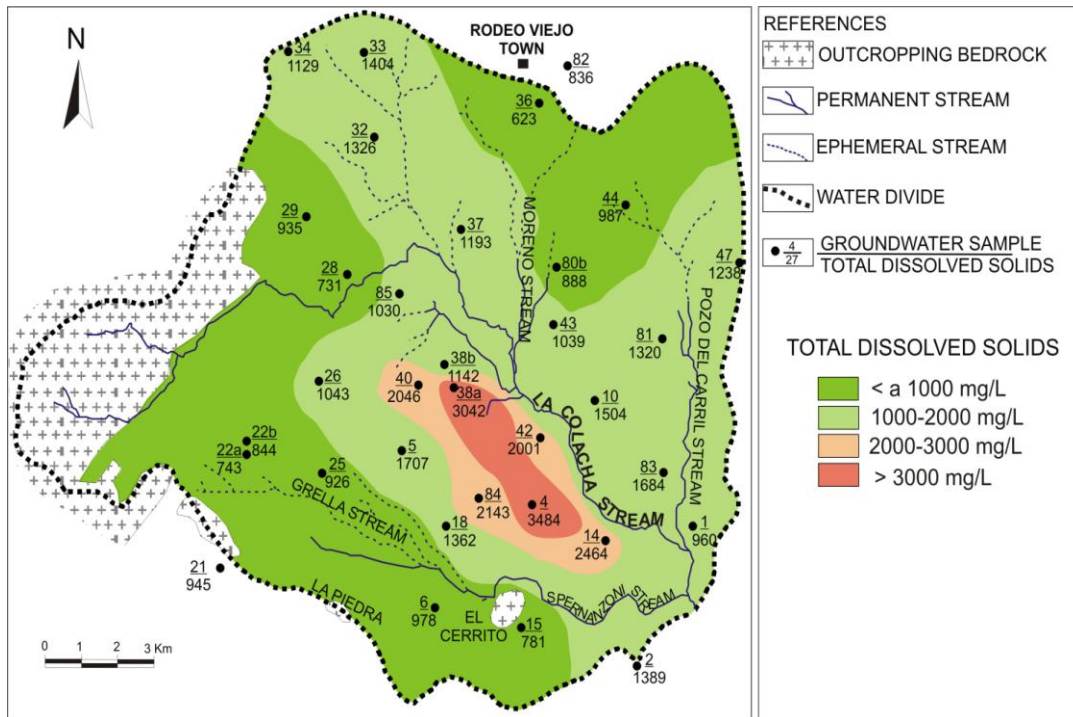
The results showed that to obtain the sodium sulphate water type of sample 38a (final solution), taking into consideration the saturation indexes (Table 3), the initial solution (sample 26) must evolve along the flow line and salt dissolution and cation exchange must occur (Table 4), being secondary silicate hydrolysis (Table 3 and Table 4). These geochemical processes are classical in the regional loessical or sandy aquifers [21].

**Table 3.** Saturation Index (SI) for the phases considered in the modeled samples

Contemplated Phases		Modeled samples	
		M26	M38
Calcite	CaCO <sub>3</sub>	0.30	0.45
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	-2.77	-0.95
Halite	NaCl	-7.17	-5.44
CO <sub>2</sub> (g)	CO <sub>2</sub>	-2.03	-1.68

**Table 4** Numerical modeling results (PHREEQC)

Obtained Models		Contemplated Phases [mmol/L]										
		Calcite	Halite	Gypsum	CO <sub>2</sub> (g)	NaX	CaX <sub>2</sub>	MgX <sub>2</sub>	KX	Illite	Feld.K	Albite
Case 1 M26-M38	N°13	0.2	6.2	12.1	0.1	20.6	-10.5	--	0.4	9.8	-5.5	-5.9
	N°15	0.6	6.2	12.1	-0.5	28.5	-11.0	-3.3	--	22.9	-13.0	-13.7
	N°27	0.2	6.2	12.1	--	19.4	-10.5	0.5	0.5	7.7	-4.3	-4.6
	N°29	0.2	6.2	12.1	--	20.8	-10.6	--	0.4	9.8	-5.5	-5.8
	N°31	1.1	6.2	12.2	--	29.9	-11.5	-3.4	--	23.5	-13.3	-14.1
	N°32	1.0	6.2	12.1	--	29.5	-11.5	-3.2	--	22.8	-12.9	-13.7



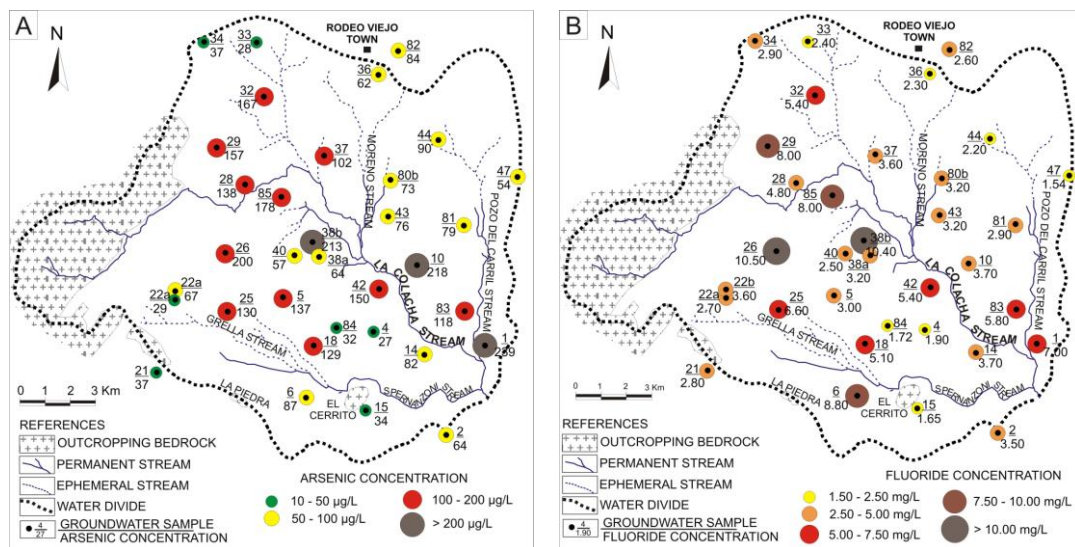
**Figure 3.** Map of the total dissolved solids in groundwater



**Geochemistry of Arsenic and Fluoride**

Arsenic concentrations range from 27 µg/L to 239 µg/L, with an average of 100 µg/L. All the samples exceed the World Health Organization (WHO) guideline for As of 10 µg/L and 76 % of the samples exceed the Cordoba province transitory standard of 50 µg/L. The spatial distribution of As is showed in figure 4A. In relation to As sources, some authors [22] [3] measured As and F values in volcanic glass and assumed that, in a moderate to high pH environment, the volcanic glass may be altered supplying ions to the solution. Also, the arsenates may be desorbed from the surface of secondary amorphous Fe and Mn oxides as was stated by [24] for a loess aquifer in La Pampa province (Arg.). They establish that Fe minerals that retain As (magnetite, ilmenite, biotite, goethite and hematite) may be an As source. In this situation, As suffers desorption from oxides under conditions of high pH and alkalinity in slow groundwater flows conditions. Indeed, and as was indicated by [24], the arsenate desorption from iron oxide surface is favored at high pH due to change in the net surface charge of the oxide from positive to negative with increasing pH above the zero point charge (7.7 to 8.0 for goethite or ferrihydrite). In the study made in La Pampa Province (Arg.) [23] estimated a value of  $K_d$  (partition coefficient) of 0.94 kg L<sup>-1</sup> for As in loess sediments. This low value indicates the weak binding of As to sediments, a central aspect in the presence of As dissolved in water.

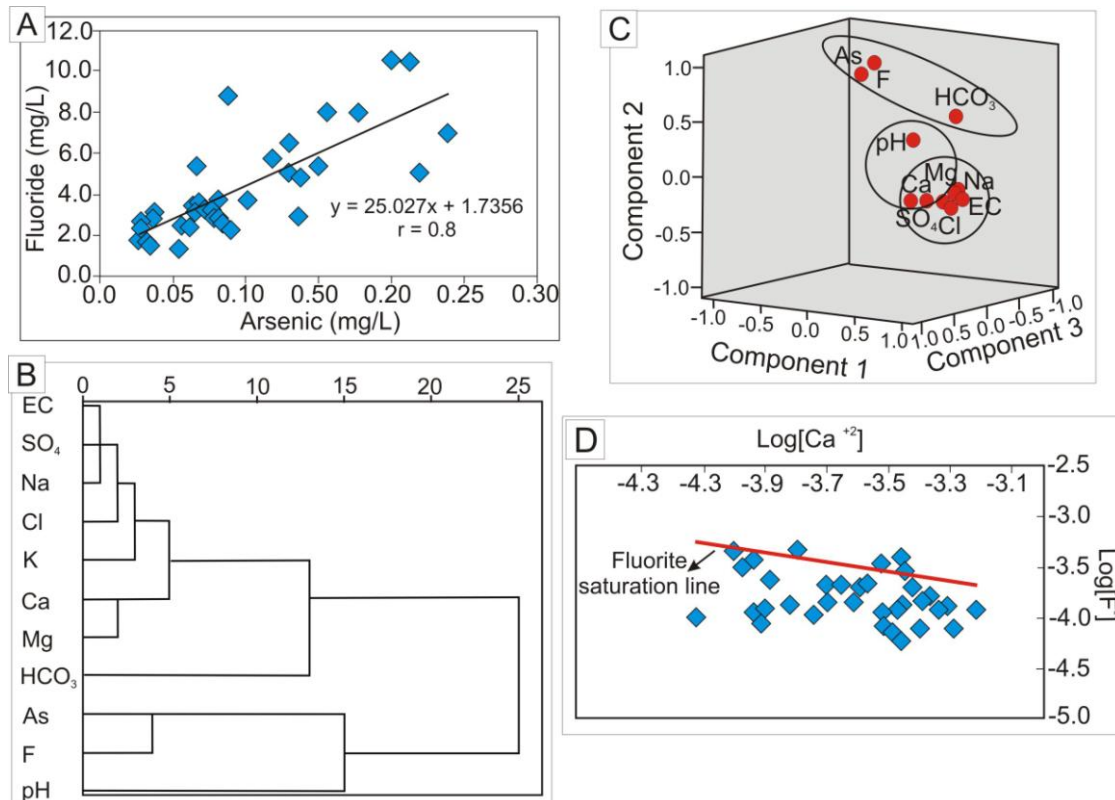
Relating to fluoride in the studied basin, the results show a concentration range from 1.45 to 10.5 mg/L with an average of 4.35 mg /L. Taking into account the WHO guideline for F (1.5 mg/L), 97% of the samples exceed that limit. The spatial distribution is showed in figure 4B. In groundwater of the Pampean Plain, probable sources of this element may be mainly fluorite and fluorapatite and, subordinately, amphiboles, biotite, micas and pyroxenes, very common minerals in the loess sediments and the mountain rocks [25, 26, 4]. Also, [27] indicate that alkaline conditions with pH between 7.6 and 8.6 are favorable for the dissolution of mineral fluorite. According to [22, 2, 28], the F<sup>-</sup> contained in the volcanic glass could enter in solution, taking into account that volcanic glass is a reactive substance at high pH. Using geochemical numerical modeling, [29] also proposed fluorapatite dissolution. On the other hand, it is interesting to note that dissolved Ca is common in the pampean aquifers given the CaCO<sub>3</sub> present in sediments (dispersed in the mass, as carbonate nodules or as calcretes layers). Calcium establishes a real barrier to mobility of F<sup>-</sup> because of their strong affinity. Then, precipitation of calcium fluoride in the aquifer itself would occur. For these reasons, it is expected that there is a positive F<sup>-</sup> correspondence with HCO<sub>3</sub><sup>-</sup> and Na<sup>+</sup> and good correlation but negative with Ca<sup>2+</sup> [7].



**Figure 4.** Spatial distribution in groundwater. A- Arsenic. B- Fluorides

In La Colacha basin, the variation in As and F do not follow clear trends with major ion chemistry but they are positive correlated each other (Figure 5A), a relationship that was found in other areas of the pampean plain [7]. This close relation may be showing that they have similar origin (lithological control) and enter in solution under similar geochemical aquifer conditions. The results of the multivariate statistical cluster analysis in the R mode show two groups, the major ions linked to EC (explaining water mineralization) and As and F associated, in a moderate degree, with pH (Figure 5B). The factorial analysis shows 3 main components (Figure 5C). The principal factor (explaining 53% of variance) is formed by EC and SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, expressing water mineralization. The second group (18 % of variance) is formed by As and F linking to HCO<sub>3</sub><sup>-</sup>, explaining the affinity of the ions with alkaline waters, and the third group (only 15 % of variance) is formed by pH (positive loading) opposite to Ca and Mg (with negative factor loadings), explaining the control of pH on calcite and dolomite equilibria.

It is worthy to highlight that almost all the samples resulted undersaturated in fluorite (Figure 5D), which explains the high amounts of F in these sodium waters, taking into account that if high quantities of Ca remained dissolved, fluorite could precipitate. In relation to As, the oxidant aquifer environment represented by dissolved oxygen (OD) in the order of 6 mg/l in this basin, as was stated by [16], would favor the predominance of  $As^{5+}$ , and the geochemical conditions previously described (high pH, alkaline waters) would collaborate in As desorption from the Fe oxide surfaces, as was described in pampean aquifers by [24, 4].



**Figure 5.** A)- Correlation between arsenic and fluoride in groundwater. B)- Factorial analysis (Principal components). C)- Cluster analysis in R mode (between chemical variables). D)- Location of groundwater samples in relation to fluorite saturation line.

### V. Conclusions

The studied basin shows geological, lithological and mineralogical characteristics that explain groundwater features. The unconfined aquifer is made up especially by loessical sediments where low groundwater velocities occur. Bicarbonate sodium groundwater predominates, with moderate to high pH. The more salty and sodium sulfate waters prevail in the central part of the basin where the most fine cemented sediments prevail. The results of the numerical models in selected groundwater flow lines show that the salt dissolution and cation exchange and, secondary, mineral hydrolysis, are the main geochemical processes that support the chemical water composition in this aquifer.

In this study, high values of As and F were identified. Although the variation in As and F concentrations do not follow clear trends with major ion chemistry, the multivariate statistical analysis show that there is an affinity between As and F with pH and alkaline waters. Furthermore, As and F are positive correlated, a close relation that would prove that they have similar origin (lithological control) and that they enter in solution under similar geochemical aquifer conditions.

It is assumed that the volcanic glass, in a moderate to high pH environment, may be altered supplying As and F ions to the solution. Fluoride may be supplied from other F bearing mineral identified in this geological setting like fluorite and fluoroapatite, among others. Almost all the samples resulted undersaturated in fluorite which explains the high amounts of F in these sodium waters. Although there is no speciation of the dissolved arsenic, it is assumed that, in this oxidant aquifer environment,  $As^{5+}$  may dominate. Thus, arsenates may also be desorbed from the surface of secondary amorphous Fe and Mn oxides under conditions of high pH and alkalinity in these slow groundwater flows conditions. The results obtained in this work and others mentioned for the regional aquifers, suggest the necessity to make As speciation and epidemiological and toxicological studies related to As and F, which are scarce in Cordoba province.

## Acknowledgements

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## References

- [1] V. K Saxena, and S. Ahmed. Dissolution of fluoride in groundwater: a water-rock interaction study. *Environmental Geology* 40, 2001, 1084–1087
- [2] M.A. Armienta. And N. Segovia, Arsenic and fluoride in the groundwater of Mexico, *Environmental. Geochem. Health.* 30(4), 2008, 345-353
- [3] H. Nicolli, J. Suriano, M. Gómez Peral, L. Ferpozzi and O. Balean, Groundwater contamination with Arsenic and other trace elements in an area of the province of Córdoba. Argentina. *Environmental Geology and Water Sciences.* 14 (1), 1989, 3-16
- [4] M. Blarasin, A. Cabrera, E. Matteoda, M. Aguirre, J. Giuliano Albo, F. Bécher Quinodóz, L. Maldonado and H. Frontera. *Recursos hídricos subterráneos Parte II: Aspectos geoquímicos, isotópicos, contaminación y aptitudes de uso.* En: Relatorio del XIX Congreso Geológico Argentino: Geología y Recursos Naturales de la Provincia de Córdoba. (Eds. Roberto D. Martino y Alina B. Guerreschi), Córdoba, 2014. Asociación Geológica Argentina.
- [5] G. Jacks, P. Bhattacharya, V. Chaudhary and K.P. Singh, Controls on the genesis of some high fluoride groundwaters in India. *Applied Geochemistry*, 20, 2004, 221-228.
- [6] H. Heikens, S. Sumarti, M., van Bergen, M. Widianarko, B. Fokkert, van Leeuwen K. and W. Seinen, The impact of the hyperacid Ljen crater lake: risks of the excess fluoride to human health, *Science of the Total Environment.* 346, 2005, 56-69.
- [7] M. Blarasin, A. Cabrera, F. Hildmann, E. Matteoda, F. Becher, J. Giuliano Albo and L. Maldonado, Fluorides in the phreatic aquifer of the loess plain. Cordoba province. Argentina. *Journal of Environmental Hydrology.* 19 (17), 2011, 1-10.
- [8] P. Bhattacharya, A. Welch, K.M. Ahmed, G. Jacks and R. Naidu, Arsenic in groundwater of sedimentary aquifers. *Ed. Appl. Geochem.*, 19, 2004, 163-167.
- [9] K. Kim, and Y. Jeong, Factors influencing natural occurrence of fluoride rich groundwaters: a case study in the southeastern part of the Korean peninsula. *Chemosphere*, 58, 2005, 1399-1408.
- [10] P. Smedley, Arsenic in rural groundwater in Ghana. *Journal of African Earth Sciences*, 22 (4), 1996, 459-470.
- [11] S. Koritnig, *Fluorine.* In Handbook of Geochemistry. 2 (1), 1972, 9E1–9D11, Springer-Verlag
- [12] H. B. Nicolli, A. Tineo, J.W. García and C.M. Falcon, *Presencia de As en las aguas subterráneas del sector Sur de la prov. de Tucumán. Argentina.* En Galindo. G. Fernandez Turiel. J. Parada. M. y Gimeno Torrente. D. (eds.) *Arsénico en aguas: origen. movilidad y tratamiento.* 2007, 107-114. Río Cuarto
- [13] A. Ayerza, Arsenicismo regional endémico (keratoderma y melanoderma combinadas). *Boletín de la Academia de Medicina*, 2(3), 1917, 11-24.
- [14] M. Goyenechea. Sobre la nueva enfermedad descubierta en Bell Ville, *Revista Médica de Rosario*, 7, 1917, 485
- [15] M. Blarasin, A. Cabrera, M. Paris, M. Cantú and J. Bellin, *Hidrogeoquímica y monitoreo de indicadores del acuífero freático en una cuenca rural pedemontana para evaluar cambios ambientales, Cba. Argentina.* En “Hidrología Subterránea y aspectos ambientales, 2005, 245-256.
- [16] F. Bécher Quinodóz, Relaciones entre Actividades agropecuarias y la presencia de metales pesados en suelos y aguas subterráneas. Tesis de Licenciatura UNRC. Inédito. 288 pp. 2010
- [17] APHA (American Public Health Association), AWWA (American Water Works Association), WPCF (Water pollution Control Federation). Standard methods for the examination of water and wastewater, 21th edn. Washington. 2005
- [18] D.L. Parkhurst, and C.A.J. Appelo, User’s Guide to PHREEQC (version 2). A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: *U.S. Geological Survey Water-Resources Investigations Report:* 99-4259, 312 p. 1999
- [19] SPSS, I. SPSS Statistics version 21. *Chicago, Illinois USA.* 2012
- [20] Blarasin, M., F. Bécher Quinodóz, A. Cabrera, E. Matteoda, N. Alincastro, J. Giuliano Albo. Weekly and monthly ground water recharge estimation in a rural piedmont environment using the water table fluctuation method. *International Journal of Environmental & Agriculture Research*, 2 (5), 2016, 104-113
- [21] F. Bécher Quinodóz, M. Blarasin, H. Panarello, and E. Ducos, Assessing interactions between groundwater and surface water in a Pampean stream, *Hydrology Research*, nh2016100, 2016 in press.
- [22] H. Nicolli, P.L. Smedley and J.O. Tullio, Aguas subterráneas con altos contenidos de F. As y otros oligoelementos en el Norte de La Pampa. *Congreso Internacional del Agua.* III (40), 1997
- [23] P. Smedley, D. Macdonald, H. Nicolli, A. Barros, J. Tullio and J. Pearce. *Arsenic and other quality problems in groundwater from Northern La Pampa province. Arg. Nottingham.* TR WC/99/36. British Geological Survey. 2000,
- [24] W. Stumm and J. J. Morgan, *Aquatic Chemistry.* Wiley, New York. 1996
- [25] G. Villalba, *Estudio geohidrológico con énfasis en la geoquímica del flúor de la cuenca del arroyo El Talita. Dpto. Río Cuarto. Córdoba.* Tesis de Licenciatura Universidad Nacional de Río Cuarto (inédita). 1999
- [26] J. Coniglio, L. Pinotti, F. D’Eramo, M. Demartis and H. Oddino, Fluorita accesoria en granitos de alto potasio: su aplicación en la prospección de mineralizaciones de W-Mo + Ag + Au magmáticas – hidrotermales. *IX Congreso de Mineralogía y Metalogenia*, 1, 2008, 113-120.
- [27] V. Saxena, and S. Ahmed, Dissolution of fluoride in groundwater: a water-rock interaction study, *Environmental geology*, 40(9), 2001, 1084-1087.
- [28] A.P. Viero, C. Roisenberg, A. Roisenberg and A. Vigo, The origin of fluoride in the granitic aquifer of Porto Alegre. Brazil, *Environmental Geology*, 56, 2009, 1707-1719.
- [29] R. Vivona, E. Preziosi, B. Madé and y G. Giuliano, Occurrence of minor toxic elements in volcanic sedimentary aquifers: a case study in central Italy, *Hydrogeology Journal*, 15(6), 2007, 1183-1196