IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 12, Issue 4 Ver. I (April. 2018), PP 71-77
www.iosrjournals.org

Arsenic and Fluoride in Groundwater of the Sedimentary Aquifer in The Campus of The National University of Rio Cuarto, Córdoba, Argentina

Giacobone D.[1], M. Blarasin[2], E. Matteoda[3], A. Cabrera[4], V. Lutri[5]
And J. Felizzia[6]
[1,2,3,4,5,6]Department of Geology, FCEFQyN. National University of Río Cuarto. [5]CONICET
Corresponding Author: Giacobone D.[1]

Abstract : *Among the problems of groundwater in many countries worldwide, those related to high values of Arsenic and fluoride highlights. The objective of this work is to evaluate hydrogeological and geochemical aspects and the use aptitude of groundwater from the unconfined sedimentary aquifer of the UNRC Campus and its surroundings, with emphasis on the Arsenic and fluoride behavior. All the groundwater water samples are fresh and 64.28% are calcium bicarbonate type, aspect strongly related to the texture and mineralogy of the paleo-channels from which the groundwater is extracted. Arsenic and fluoride values (1 to 10 µg/L and 0.12 to 0.6 mg/L respectively) show a good correlation in the different hydrogeological units, which supports their similar behavior under given hydrogeological-geochemical conditions. The grouping and positive correlation between As and F with Na and HCO_3^- indicate that groundwater major ion chemistry plays a significant role in mobilizing these elements. In the studied zone the predominance of very low As and F values are related to the abundance of calcium groundwater whereas the little higher values appear in the eolian plain where sodium contents (as a result of cation exchange) and pH and HCO_3^- values (predominantly controlled by carbonate weathering reactions) are higher. The obtained results indicate a high aptitude of groundwater to be used for human consumption in the Campus.*

Keywords : *Arsenic, fluoride, hydrogeology, groundwater, geochemistry.*

Date of Submission: 09-04-2018 Date of acceptance: 23-04-2018

I. Introduction

Groundwater is an important geological modeling agent of the landscape and is part of numerous geological processes, as a result of the systematized and hierarchized spatial distribution of water flow and the ability to interact with the different environmental components [1]. Its importance not only lies in being a geological agent, but it is an indispensable natural resource for the development of societies and cultures. This situation exerts pressure on water resources, generating different impacts and the need to consider aspects to improve its governance [2]. Among the most relevant problems of groundwater in many countries worldwide, the poor natural features may be mentioned, especially those related to high values of Arsenic and fluoride. [3, 4, 5, 6]. It seems that whereas Arsenic is a problem that usually is found in sedimentary aquifers [7], fluoride problems occur frequently in both bedrock and sedimentary aquifers [8, 6].

In Argentina more than 1.2 million people depend on groundwater whith Arsenic concentration greater than 0.05 mg/L. This situation occurs especially in rural areas in the Pampean Plain, a vast flat plain that has resulted primarily from aeolian (loess) deposition [6]. Different authors measured very variable Arsenic concentrations up to 3,000 µg/L and fluoride concentrations up to 24 mg /L [5] [6]. In Córdoba province, dental fluorosis in children, youngsters and adults have been identified [6] while arsenicism health problems have been described in the North Eastern part of the province by physicians long time ago [9, 10]. Taking into account the geochemical water studies made in this large region [5, 6], and the diffusion of this problem in mass media, people is becoming conscious about the drinking water that must be used, but additional studies are necessary, especially in those areas with high quantity of inhabitants and relevant socioeconomic activities. In the case of the Campus of the National University of Rio Cuarto (UNRC), where approximately 10,000 people circulate daily, although it has distribution of potable water supplied by the Municipal Company (EMOS), there is a lack of detailed studies. The latter are related to the potential of own supply for different activities, both in relation to the available resources as well as to the quality and aptitude of groundwater use. The surface water of the Rio Cuarto River is discarded as the probable source of water, because the observed impact due to human activities and high load on suspended solids make the water use for various purposes less feasible. In this way, this study focused on groundwater, which at the moment is used on the campus for recreational, experimental and garden irrigation activities. Thus, the objective of this work is to evaluate hydrogeological and geochemical aspects and the use aptitude of groundwater from the unconfined aquifer of the Campus of the UNRC and its surroundings (Fig. 1), with emphasis on the Arsenic and fluoride behavior.

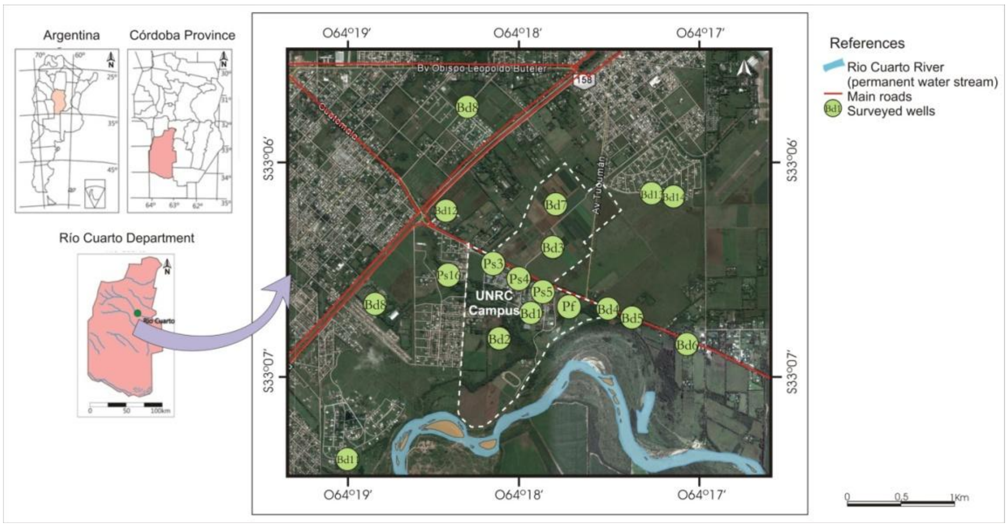

Fig. 1 Location of the study area and surveyed wells.

II. Methods

The research was carried out in an area of 17 km^2, based on the analysis and compilation of topographic sheets from National Geographic Institute (NGI) at 1:50,000 scale and satellite images (Google Earth, Landsat ETM). Background information (geological, geomorphological, climatic, etc.) of the study area was collected and analyzed [11, 6]. The precipitation data was analyzed and interpreted using a local 43 years series (1974-2017). The geological and geomorphological study was performed through the description of the relief and the outcropping lithological profiles. The hydrogeological data were obtained surveying 18 wells which penetrate the upper 15-50 m of the unconfined sedimentary aquifer. Fourteen 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 Rio Cuarto. The following parameters were analyzed: Na^+, K^+, HCO_3^-, Cl^-, Mg^{2+}, $Ca^{2+,}$ SO_4^{2-} ,NO_3^-, As and F^- [12]. The mean percentage error of the analysis did not exceed 8%. Fluoride was measured using an ORION ion selective electrode and total arsenic was determined releasing arsenic hydride later measuring in a HACH visible Spectrophotometer. The whole analysis linking geochemical environment with As and F was made using descriptive statistical techniques (multivariate analysis) by means of specific software (SSPS v.21). Accordingly, to explain relationships between all chemical variables, a cluster analysis in R mode was made. Taking into account the known relationship and dependence between pH and CO_3^- the latter was not considered for the multivariate analysis. The chemical variables were standardized because of the very different scales of pH and EC in relation to the other chemical variables which were expressed in mg/L.

III. Climatic And Geological Characterization

The regional climate is of mesothermal sub-humid-dry type with little to no water excess. The distribution of the precipitations exhibits a very marked seasonality, with a concentration of 74% from November to March (spring- summer), with an average precipitation of 799 mm.

The study of the regional and local geological framework, allows affirming that, although the igneous and metamorphic bedrock does not appear in the study area, it constitutes the base of the stratigraphic sequence [6]. The sedimentary formations recognized in the outcropping materials and up to 300 m deep in boreholes are of Cenozoic age [6]. Given the important structural control of the surrounding region, which influences the studied area, it can be affirmed that the stratigraphic sequence represents the climatic changes and the variations that occurred in the regional geological context, that is, pulses of uplift of the mountain ranges and periods of greater stability [13]. The climatic variations corresponding to the Quaternary period can be identified especially in the outcropping sequences and they extend in depth in the upper 150 m of the stratigraphic sequence. It is an alternation of sedimentary formations representative of a succession of wet and dry cycles. The first are related to interglacial periods during which the Rio Cuarto River deposited fluvial sediments [6, 13, 14]. The dry cycles are coincident with cold glacial epochs and were characterized by the deposition of important loesical sequences, being important the outcropping "Laguna Oscura" Formation from the Upper Holocene [15] that covers part of the study area and almost the whole South plain of Cordoba province. With the establishment of the current humid climate (1,100 BC), soil profiles were developed and, at the same time, the fluvial belt of the Rio Cuarto River was developed [13].

The geomorphological and lithological structural characteristics of the area allowed defining two large environments: fluvio-aeolian and fluvial. The first one presents a pattern whose most outstanding features are constituted by very fine silty sands dunes from the Upper Holocene (“Laguna Oscura” Formation) superimposed on fluvial deposits. The second is linked to the Quaternary activity of the Rio Cuarto River, determining fluvial geoforms associated with different hydrodynamic stages (different levels of terraces, meandering paleochannels of different size, meander migrations, channel bars, spills, among others).

IV. Hydrogeological Characterization

The studied unconfined aquifer, formed by Neogene sediments, has a thickness of approximately 90 m. The depth of the water table varies between 5 and 15 m. From the hydrogeological point of view, and conditioned by the local geomorphology, two more important hydrogeological units were distinguished: one of fluvial origin (UHA) and another of fluvio-eolian origin (UHC). Towards the West and East of the studied area appear typical pure loessical formations that make up the hydrogeological unit UHB [12], which was not identified in the studied area. Taking into account the drilling information, noticeable aquifer heterogeneity must be highlighted in the studied sector, characterized by sediments of variable hydraulic conductivity (K). In the fluvial environment, the unconfined aquifer is formed by intercalations of sands, gravels and pelitic sediments although there is a domain of psefitic material (K = 5 to 70 m/d). The UHA was subdivided in two sub environments (UHAa and UHAb) being UHAb characterized by more abundance of fine sediments. In the fluvio-aeolian environment, fluvial sediments lie under the mentioned eolian sediments whose typical K is 0.8 to 2.5 m/d. Heterogeneities also appear in both units as a result of differential carbonate cementation of sediments. Fluvial sediments are characterized by a dominance of quartz grains (K feldspar and micas subordinated). Eolian sediments present a typical mineralogy dominated by volcanic glass and, in a subordinate way, pyroxenes, amphiboles, feldspars, Fe oxides and illites [11]. The groundwater flow direction is mainly Northwest-Southeast as is showed in the Fig. 2, where the lithological and topographical control is evident. The groundwater contributes to the Rio Cuarto River base flow, being the stream an obvious local hydrological discharge area. The largest hydraulic gradients (1%) and groundwater velocities (0.2 m /d) are related to the fluvial unit (UHA) and are affected by topographic changes, mainly conditioned by the presence of terrace levels linked to the Rio Cuarto River.

The Fig. 3 shows that in the whole area the groundwater is fresh, expressed by electrical conductivities values that cover a small range from 397 to 600 μS/cm (Table 1). The map also shows moderately fresher groundwater in the central sector with values between 397 to 450 μS/cm related to wells that have the screens in very coarse sandy-gravel materials.

Taking into account the total samples, 64.28% are of calcium bicarbonate geochemical type, 28.57% correspond to calcium-sodium bicarbonate type and 7.14% to sodium-calcium bicarbonate type. In the case of the UHA unit, HCO_3^- and Ca ions dominate due to the presence of coarse sediments with a high recharge rate [16] and higher groundwater flow velocity, which partially decreases the weathering processes that allow the passage of other ions and compounds to the solution. The calcium bicarbonate water types were also obtained in wells from the UHC hydrogeological unit, which extract water from very coarse sediment layers. Calcium-sodium and sodium-calcium bicarbonate water types are linked to the UHC unit, specifically to those sectors where thicker eolian layers appear. Thus groundwater has a longer interaction time with the solid phase of the aquifer which would explains processes of cation exchange (Ca x Na).

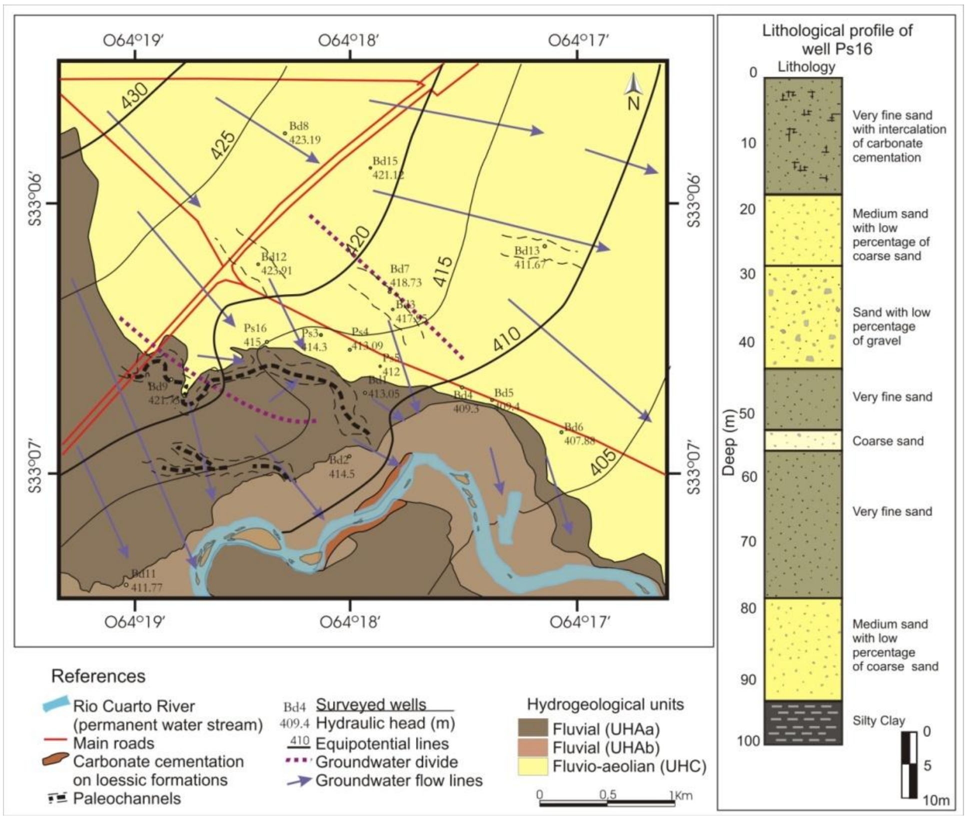

Fig. 2 Map of hydrogeological units and equipotential lines.

Table 1 Physico- chemical analysis of groundwater.

Date	**Nº Sample**	**pH**	**CE** [µS/cm]	**SDT** [mg/L]	**$CO_3^=$** [mg/L]	**CO_3H^-** [mg/L]	**$SO_4^=$** [mg/L]	**Cl^-** [mg/L]	**Na^+** [mg/L]	**K^+** [mg/L]	**Ca^{+2}** [mg/L]	**Mg^{+2}** [µg/L]	**As** [µg/L]	**F^-** [mg/L]	**NO_3^-** [mg/L]
29/09/17	BD1	8.2	419	293	0	145.0	60.77	17.14	18.2	6.15	45.6	5.85	5	0.18	11.5
29/09/17	BD2	7.6	571	400	0	197.5	43.27	17.14	18.2	7.03	57.6	5.85	5	0.15	27.0
23/08/17	BD3	8.0	453	317	0	240.0	22.81	8.57	42.4	8.50	54.4	7.80	8	0.40	30.0
23/08/17	BD4	7.8	460	322	0	247.5	14.95	11.43	38.4	8.06	56.8	4.88	8	0.26	15.0
23/08/17	BD5	8.1	557	390	0	300.0	10.62	14.29	55.6	8.94	60.8	6.34	3	0.24	28.0
23/08/17	BD6	8.0	509	356	0	297.5	14.55	11.43	69.7	7.62	51.2	7.32	6	0.20	5.0
29/09/17	BD7	8.3	440	308	2.4	162.5	5.51	11.43	16.6	6.45	45.6	3.90	4	0.35	13.2
03/10/17	BD8	7.9	536	375	0	212.5	83.45	8.57	32.8	7.62	51.6	10.0	6	0.26	9.0
03/10/17	BD9	7.0	437	306	0	150.0	56.24	11.43	13.1	7.33	51.2	9.76	4	0.15	21.0
03/10/17	BD11	7.4	501	351	0	162.5	42.87	14.29	35.3	8.06	60.0	3.90	3	0.12	32.0
03/10/17	BD12	8.1	397	278	0	145.0	56.24	8.57	26.2	6.59	48.0	4.39	3	0.13	13.0
03/10/17	BD14	8.2	431	301.7	0	177.5	105.14	8.57	36.4	7.03	44	10.2	1	0.14	1.5
01/03/17	P4	7.5	485	340	0	233.0	33.00	14.30	63.7	5.10	40.8	10.2	10	0.60	19.0
01/03/17	P5	7.6	410	287	0	215.0	37.00	14.30	45.5	5.60	40.0	8.80	8	0.40	10.5

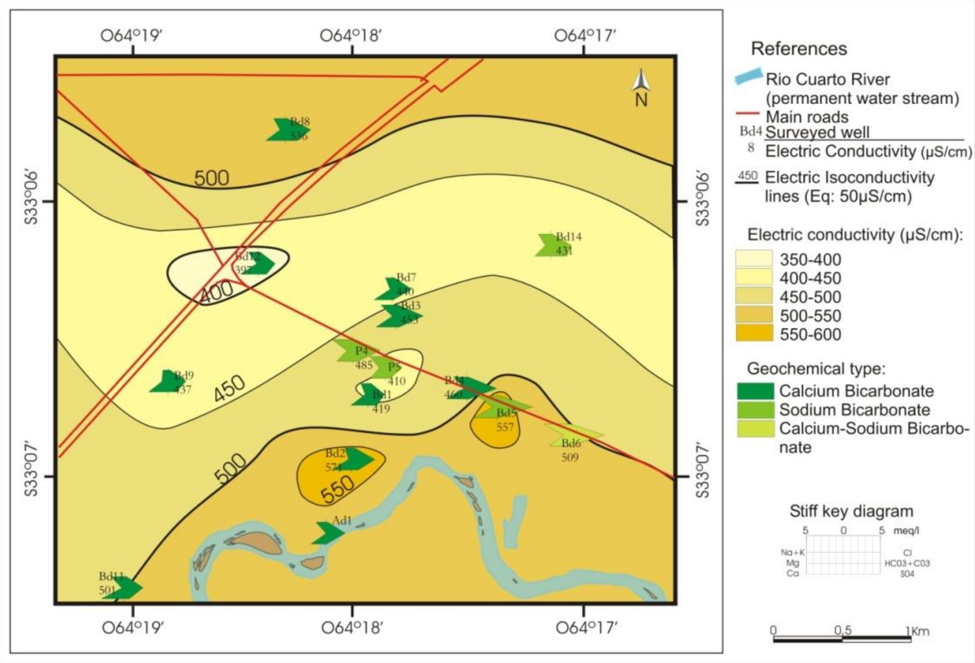

Fig. 3 Map of groundwater electric conductivity and groundwater geochemical types.

Trace elements: geochemistry of Arsenic and fluorides

The occurrence of As and F^- is often natural and controlled by the geological environment. Under certain geological conditions, the most important natural sources of As are the sulphurous minerals (orpiment (As_2S_3), arsenopyrite (FeAsS), realgar (AsS) and enargite (Cu_3AsS_4)). Arsenic can be a minor constituent of sulfides (pyrite, chalcopyrite, galena, pyrrhotite) and some oxides (iron mainly). In relation to other sources, some authors [18, 5] 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 [19] 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 can be desorbed from oxides under high pH and alkalinity and slow groundwater flow conditions. Indeed, and as was indicated by [19], 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). 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_2) and topaz (Al_2SiO_4 (F, $OH)_2$), but it is also found in accessory minerals such as cryolite (Na_3AlF_6) and apatite ($3Ca_3(PO4)$ 2Ca (F, Cl_2). 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 [20]. 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 source rocks [21, 22, 6]. Also, [23] indicate that alkaline conditions with pH between 7.6 and 8.6 are favorable for the dissolution of mineral fluorite. According to [18, 4, 24], the F^- contained in the volcanic glass could enter in solution, taking into account that volcanic glass is a reactive substance at high pH.

The distribution of As and F values in the studied area are shown in maps of Fig. 4. The studied trace elements show very low values in the groundwater. Arsenic values are in the range of 1 to 10 µg /L and fluoride values are between 0.12 and 0.6 mg/L. The spatial distribution (Fig. 4) shows that on the hydrogeological unit UHA the values are always very low, in agreement with the coarse fluvial sediments with a little reactive mineralogy. On the other hand, little higher As and F^- values are located in the UHC hydrological unit which exhibit, as already mentioned above, more abundance of eolian sediments, more propitious for the contribution of these elements.

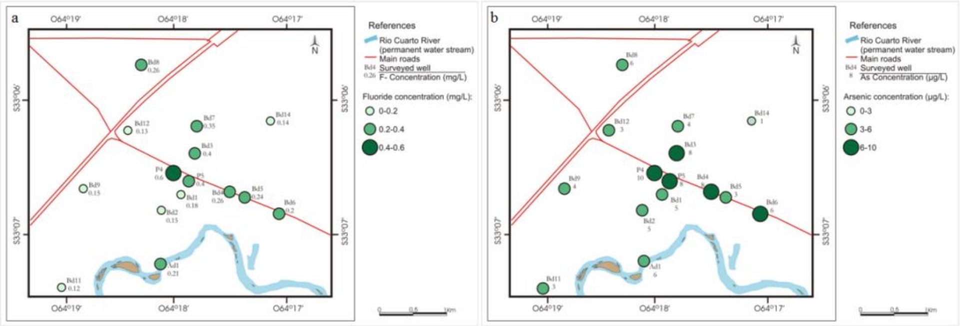

Fig. 4 Maps or spatial distribution of Fluoride (a) and Arsenic (b) in groundwater.

The linear correlation coefficient between As and F^- for all groundwater samples was r = 0.73. If the values of both elements are compared taking into account the hydrogeological units (UHA and UHC), even better correlations are obtained (r = 0.8 in both cases, Fig. 5a and 5b), which allows us to infer that these trace elements enter into solution for similar hydrogeological-geochemical conditions. From a multivariate statistical perspective, in cluster analysis in R mode, it is observed that As and F^- are linked to HCO_3^- and Na and more weakly to pH.

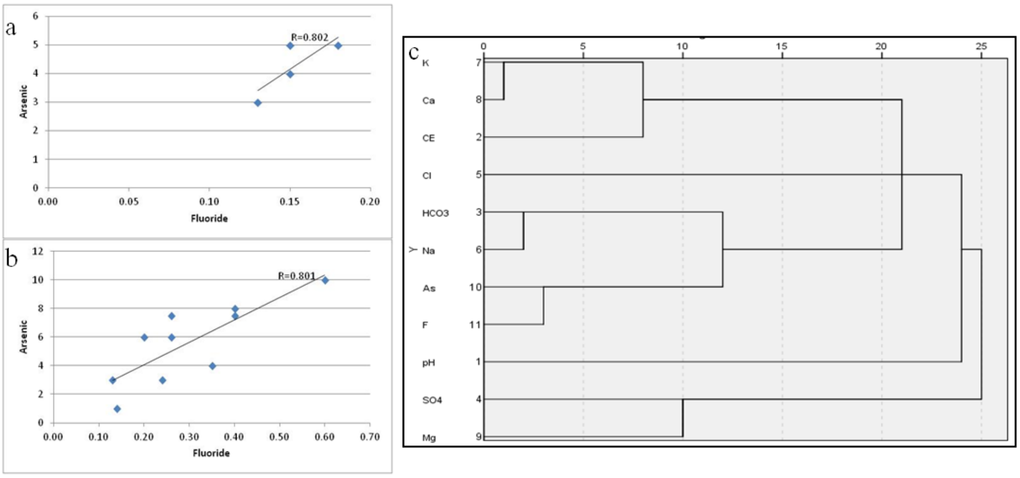

Fig. 5 a Correlation As–F^- for the hydrogeological unit UHA. **b** Correlation As-F^- for the hydrogeological unit UHC. **c** Cluster diagram in R mode for the chemical variables.

V. Conclusion

If the chemical composition of the water is taken into account, it is observed that there is an important geochemical homogeneity and all the water samples are fresh. Also, a 64.28% of the samples are calcium bicarbonate, aspect strongly related to the paleo-channels from which the groundwater is extracted, and independent of the hydrogeological unit in which the wells are located. As it can be observed, the samples represent scarcely evolved waters, mainly resulting from flows that circulate in very coarse sediments with very inert mineralogy, which decreases the weathering processes that contribute ions and chemical compounds to the solution.

With regard to the trace elements, the Arsenic and fluoride values show a good correlation in the different hydrogeological units, coinciding with the extensive bibliography that supports their similar behavior under given hydrogeological-geochemical conditions. The measured values of both ions are very low (1 to 10 µg/L and 0.12 to 0.6 mg/L respectively) due to the scarce estimated interaction time between the groundwater and the sediments. This condition is possible in an aquifer where the groundwater velocities are high and the source minerals are scarce, especially in the fluvial aquifer layers from which water is extracted.

The grouping and positive correlation between As and F^- with Na and HCO_3^- indicate that groundwater major ion chemistry plays a significant role in mobilizing these elements. In the studied zone the predominance of very low As and F^- values are related to the abundance of calcium groundwater whereas the little higher values appear in the eolian plain where sodium contents are higher. Taking into account the results and the regional antecedents it is interpreted that the mobilization likely occurs via desorption of As and F^- anions from hydrous metal oxides or dissolution of volcanic glass (which may release these ions) processes that are very inhibited in these coarse sediments. Moderate positive correlations between pH and As and F^- concentrations indicate that high pH may favor desorption, while it can be interpreted that HCO_3^- may act as a competitor in desorption sites. Higher Na contents likely result from cation exchange, while pH and HCO_3^- contents are predominantly controlled by carbonate weathering reactions.

All the chemical variables values, including As and F^-, indicate the high aptitude of groundwater to be used for human consumption in the Campus.

References

[1] J. Töth, Groundwater as a geologic agent: an overview of the causes, processes, and manifestations *Hydrogeology journal 7 (1),* 1999, 1–14.

[2] UNESCO, *Resumen del Informe de las Naciones Unidas sobre el Desarrollo de los Recursos Hídricos en el Mundo: Agua para todos, Agua para la vida* (Ediciones UNESCO - Mundi Prensa, Francia, 2003).

[3] V. K Saxena, and S. Ahmed. Dissolution of fluoride in groundwater: a water-rock interaction study. *Environmental Geology 40,* 2001, 1084–1087.

[4] M.A. Armienta. And N. Segovia, Arsenic and fluoride in the groundwater of Mexico, *Environmental. Geochem. Health*, *30(4),* 2008, 345-353.

[5] 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

[6] 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. In Roberto D. Martino y Alina B. Guereschi (Eds), *Relatorio del XIX Congreso Geológico Argentino: Geología y Recursos Naturales de la Provincia de Córdoba* (Asociación Geológica Argentina, Córdoba, 2014).

[7] 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.

[8] 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.

[9] A. Ayerza, Arsenicismo regional endémico (keratodermia y melanodermia combinadas). *Boletín de la Academia de Medicina, 2(3),* 1917, 11-24.

[10] M. Goyenechea. Sobre la nueva enfermedad descubierta en Bell Ville, *Revista Médica de Rosario,* 7, 1917, 485.

[11] M. Blarasin, A. Cabrera, E. Matteoda, *Aguas subterráneas de la Provincia de Córdoba* (Ebook, UniRío Editora, Universidad Nacional de Río Cuarto, 2014).

[12] 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.

[13] S. Degiovanni, M. Villegas, M. Blarasin y G. Sagripanti, *Hoja Geológica Río Cuarto-3263-III*. (Secretaría de Minería de la Nación – SEGEMAR, 2005).

[14] G. Chebli, M. Mozetic, C. Rossello and M. Bühler, Cuencas Sedimentarias de la Llanura Chacopampeana. In Ramos (Ed.), *Geología Argentina* (Instituto de Geología y Recursos Minerales, Buenos Aires, Anales 29 (20), 1999, 627-644).

[15] M. Cantú, Holoceno de la Provincia de Córdoba. Manual: Holoceno de la República Argentina. *Tomo I. (*Simposio Internacional sobre el Holoceno de América del Sur, Paraná, Argentina, 1992).

[16] D. Giacobone, Caracterización hidrogeológica y geoquímica del agua subterránea en el ámbito del campus de *la Universidad Nacional de Río Cuarto*, Universidad Nacional de Río Cuarto, Córdoba, Argentina, 2018.

[17] P. Smedley, Arsenic in rural groundwater in Ghana. *Journal of African Earth Sciences, 22 (4),* 1996, 459-470.

[18] 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.

[19] W. Stumm and J. J. Morgan, *Aquatic Chemistry*. Wiley, New York, 1996.

[20] S. Koritnig, *Fluorine*. In Handbook of Geochemistry. 2 (1), 9E1–9D11, (Springer-Verlag, 1972).

[21] G. Villalba, Estudio geohidrológico con énfasis en la geoquímica del flúor de la cuenca del arroyo El Talita. Dpto. Río Cuarto. Córdoba, Universidad Nacional de Río Cuarto, Córdoba, Argentina, 1999.

[22] 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.

[23] V. Saxena, and S. Ahmed, Dissolution of fluoride in groundwater: a water-rock interaction study, *Environmental geology*, *40*(9), 2001, 1084-1087.

[24] 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.

Giacobone D.1. " Arsenic And Fluoride In Groundwater of The Sedimentary Aquifer In The Campus of The National University of Rio Cuarto, Córdoba, Argentina." IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT) 12.4 (2018): 71-77