JOURNAL OF
ENVIRONMENTAL HYDROLOGY

The Electronic Journal of the International Association for Environmental Hydrology
On the World Wide Web at http://www.hydroweb.com

VOLUME 19 2011

FLUORIDES IN THE PHREATIC AQUIFER OF THE LOESS PLAIN, CORDOBA PROVINCE, ARGENTINA

M. Blarasin[1]
A. Cabrera[1]
F. Hildmann[2]
E. Matteoda[1]
F. Becher[3]
J. Giuliano[3]
L. Maldonado[4]

[1]Dpto. Geología, Univ. Nacional de Río Cuarto, Argentina
[2]Dpto. Geografía, Univ. Nacional de Río Cuarto, Argentina
[3]CONICET, Argentina
[4]FONCyT, Argentina

The natural occurrence of excessive quantities of dissolved fluorides in water has affected people's health for centuries. The aim of this paper is to assess fluoride contents and the geochemical environment that determines their presence and distribution in the unconfined aquifer in Malena town and its surrounding rural area (Córdoba, Argentina). The area presents two hydrogeologic environments: one composed by loess sediments and another where fluvial and aeolian sediments are interstratified. The F^- *levels range between 1.53 mg/L and 8.75 mg/L, the lowest contents being related to paleochannels. The statistical multivariate analysis (cluster and principal components) showed two groups: one is composed of the majority of main ions, with a high correlation nucleus formed by electrical conductivity and* Na^+*, which explains water mineralization. The other group is composed by* F^-*-As-pH-*HCO_3^-*, which validates the affinity of these two trace elements to high pH, alkaline solutions. The negative high correlation (R -0.82) found between* F^- *and* Ca_2^+ *corroborates that in groundwater with low levels of* Ca_2^+*, high concentrations of* F^- *in solution are stable. The results show the geomorphological and lithological control over the dissolved* F^- *levels. The highest levels of* F^- *are related to: textural characteristics of the aquifer in the aeolian environment (very fine sands-silts) that generate slow groundwater flow; the mineralogy (volcanic glass, amphibole, pyroxene, apatite, all possible fluorine sources); and the bicarbonate sodium groundwater type and high pH of the solution (>7.80). Numerous cases of dental fluorosis were found in children, youngsters, and adults from the study region.*

INTRODUCTION

Fluoride has a significant mitigating effect against dental caries if the concentration is approximately 1 mg/L. However, continuing consumption of higher concentrations can cause dental fluorosis and in extreme cases even weakening of bones or skeletal fluorosis (Adriano 2001). High fluoride concentrations are especially critical in developing countries, largely because of lack of suitable infrastructure for treatment. The World Health Organization (WHO 1993) sets the limit for F concentration in drinking water between 0.5 and 1.2 mg/L whereas the Argentine law *Código Alimentario Argentino* (CAA 1994) establishes a limit that varies according to the average temperature of the region (1.3 mg/L for an average temperature of 16ºC in the area presented in this paper).

Fluoride is a common constituent of groundwater. Natural sources are associated to various types of rocks and volcanic activity. Agricultural (phosphatic fertilizers) and industrial activities (burning of coals) also contribute to high fluoride concentrations in groundwater (Brunt et al. 2004). During weathering and flow of water in rocks and soils, fluorine can be leached out and dissolved in groundwater. The fluoride content of groundwater varies significantly depending on the geological settings and type of rocks. The most common fluorine-bearing minerals are fluorite, apatite and micas (Brunt et al. 2004). Thus, fluoride problems tend to occur in places where these minerals are most abundant in the host sediments and rocks. Due to the presence of important fluoride levels in the groundwater of the Argentine Pampean Plain, the Malena town and the surrounding rural area (southern Córdoba province, Argentina, Figure 1) were studied with the purpose of providing an answer to the problem of groundwater quality, which worries the entities in charge of water distribution as well as the inhabitants of the region. The aim of this paper is to present the results obtained in relation to fluoride contents and the geochemical conditions that determine their presence and distribution in the unconfined (or phreatic) aquifer, which is used to provide all type of activities in the studied area.

MATERIALS AND METHODS

A hydrogeological survey (1:50.000 scale) was carried out with the aim of assessing the hydrogeochemical characteristics of the unconfined aquifer in an area of 200 km^2. The geological-hydrogeological features of the region were identified in the field and information was obtained from 40 different wells, most of them penetrating the first 20 m of the unconfined sedimentary aquifer. Twenty (20) groundwater samples were obtained and field parameters were measured in situ: pH (Electrode Orion 9104), conductivity (Hanna Instrument, HI 9033) and dissolved oxygen and temperature (YSI Model 95 Handheld Dissolved Oxygen and Temperature System). The samples were collected in 1 L plastic bottles and were analyzed within a period of the 24 h since collection. The following parameters were analyzed in the laboratory: Na^+, K^+ (flame photometric method), HCO_3^-, Cl^-, Mg^{2+}, Ca^{2+}, SO_4^{2-}, [Standard methods APHA (American Public Health Association), AWWA (American Water Works Association), WPCF (Water pollution Control Federation) 1995], NO_3^-, F- (Ion-Selective Nitrate and Fluoride Electrodes, Orion Models 9307 and 9609) and As (total) (Atomic absorption spectroscopy analyst 300 Perkin-Elmer). In order to be able to define more precisely the hydrogeological characteristics, information obtained from deeper wells (up to 350 m) was used. Finally, the data were treated statistically by means of multivariate analysis (cluster and principal components, using *SPSS v11 s*oftware).

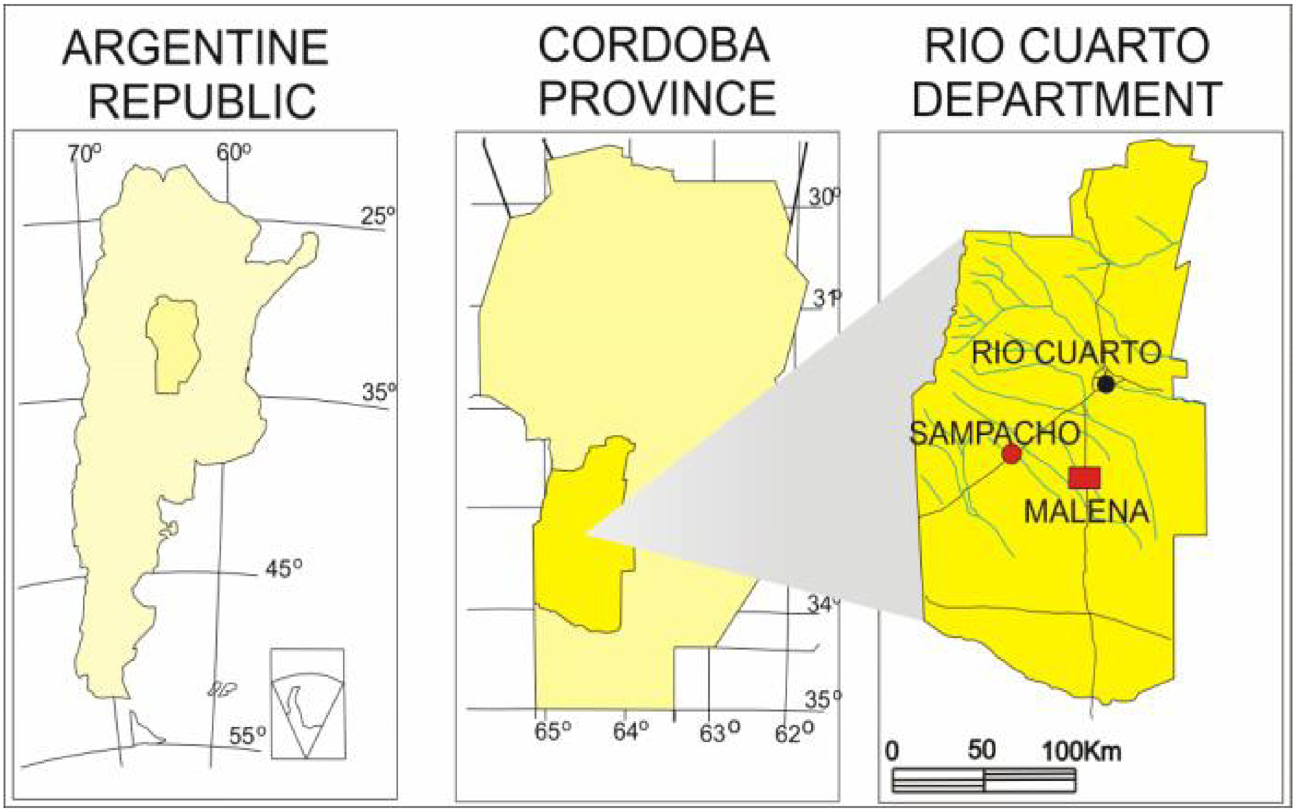

Figure 1. Location of study area.

RESULTS AND DISCUSSION

At present, the study area has a subhumid climate with a mean annual precipitation of 840 mm. Climatic changes that occurred in South America during the Quaternary provoked erosion and deposition of large masses of silt, which formed loess and loess units of regional extension in several areas of the continent. The winds from the Patagonian ice field during the Last Glacial Maximum, transported to the NE silt and fine sand formed by frost action in the Andean Cordillera (Iriondo 1997). The area studied in this work is situated in the typical loess plain of southern Cordoba Province. It shows a very slightly undulating topographic surface with gradients which are generally lower that 1%. The outcropping sediments of the Quaternary period (Cabrera et al. 2001) are very fine sands-silts (Pampa loess type, Iriondo 1997), constituting longitudinal, discontinuous, dissipated dunes with a NNE-SSW orientation. Locally, there are also fluvial sand-coarse sediments related to the Del Gato stream, the main watercourse that crosses the study area (Figure 2). The phreatic aquifer was divided in two principal hydrogeological units: an extended aeolian environment of a loess type and another where aeolian and fluvial sediments (fine, medium and coarse sands corresponding to the paleochannels of Del Gato stream) are interstratified. Calcrete layers at different depths and disseminated calcium carbonate are common features of the regional sediments. The phreatic aquifer thickness ranges between 40 and 70 m of depth. Hydraulic conductivities in the dominant aeolian environment range between 0.2 to 1.0 m/day (Blarasin et al. 2005). The equipotential map (Figure 2) shows a NW–SE groundwater flow direction and a very slightly undulating water table. The mean hydraulic gradient was 0.4% whereas the groundwater flow velocities were between 0.01-0.04 m/day (considering porosities between 5 and 10%). The low velocity values are associated with the flat relief of the area and essentially with the fine sediments in the aeolian environment.

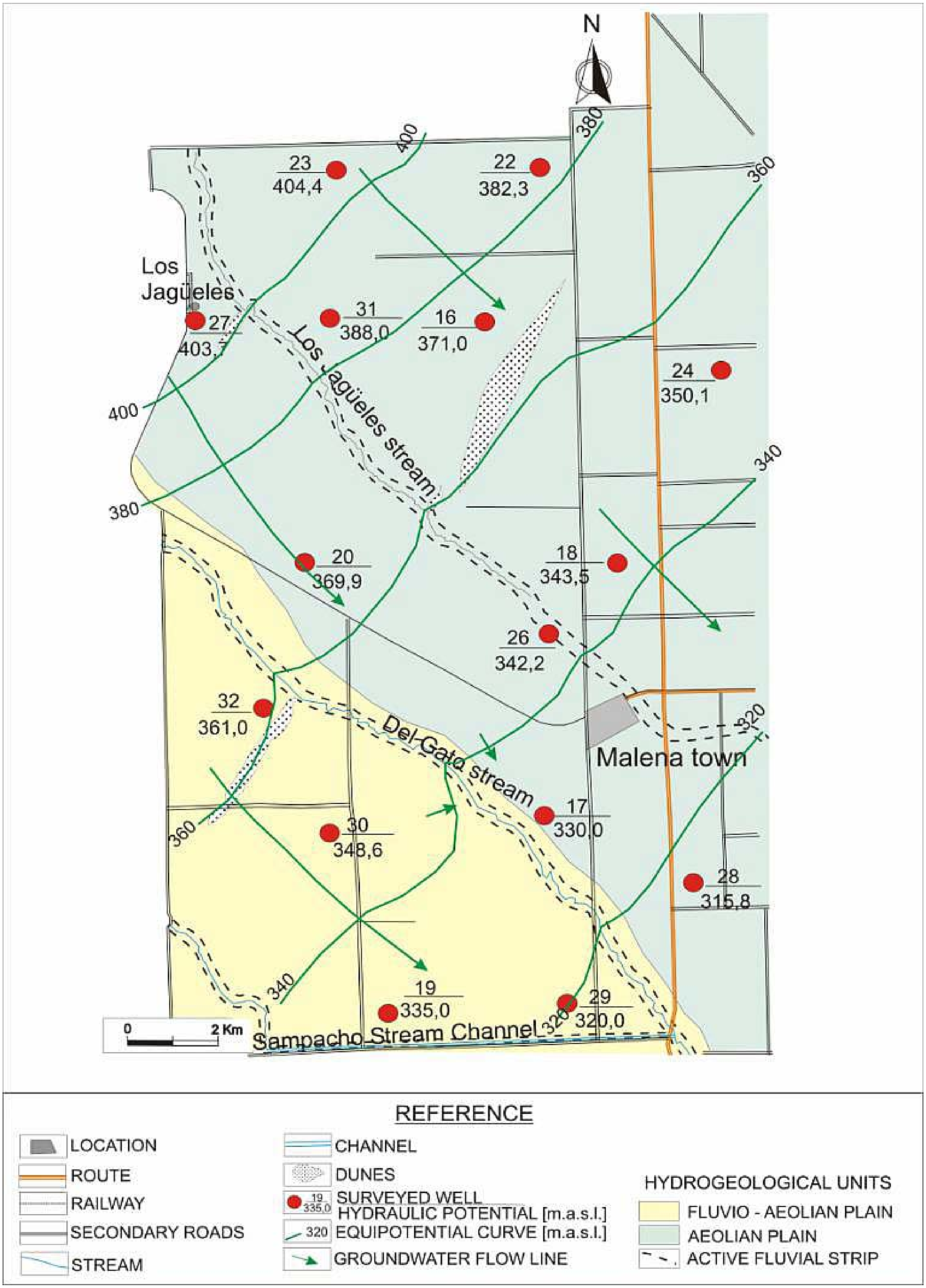

Figure 2. Hydrogeological units and groundwater flow lines.

Concordantly with the smooth dominant relief and slow groundwater flow, the groundwater total dissolved salts contents are between 1,000 and 3,500 mg/L. The geochemical composition of groundwater is of sodium bicarbonate type (35%), sodium bicarbonate-sulfate type (55%), sodium sulfate type (5%) and sodium sulfate-chloride type (5%). In Figure 3 the distribution of main cations and anions (meq/L) is shown in box plots.

In relation to loess textural characteristics, a dominant grain size of very fine sands could be found, with a weight percentage of 50–60%, followed in the order of importance by silts and clays (illite dominant). Mineralogical studies of loess in southern Córdoba province (Blarasin 1984) have determined that the main components are light minerals, the heavy ones being highly subordinated (<10%). Among the light minerals, potassic feldspar dominates followed in order of importance by quartz, volcanic glass (up to 24% of weight percentage) and plagioclase. Pyroxenes and amphiboles predominate among the heavy minerals, with tourmaline, zircon, apatite and opaque minerals subordinate. In this region, ferromagnesian minerals such as ilmenite and magnetite are altered into clay minerals and Fe and Ti oxides (Smedley et al. 2002). The average chemical composition of these loess sediments closely resembles the dacite, and the composition of volcanic glasses is similar to that of the rhyolite (Nicolli et al. 1989). According to Nicolli et al. (1989, 2004), As and F are part of the main trace elements of the pampean loess geochemical composition, with medians in the order of 16 and 908 ppm, respectively.

Brunt et al. (2004) establish that clastic sediments have high fluorine concentrations as the fluorine is concentrated in micas and illites in the clay fractions. Many hydrochemical studies of F and its origin in Argentina have been associated with the alteration of the volcanic glass, present in Pampean loess sediments (Nicolli et al. 1989; Carrica and Albouy 1999; Carrica et al. 2002; Smedley et al. 2002; Cabrera et al. 2001).

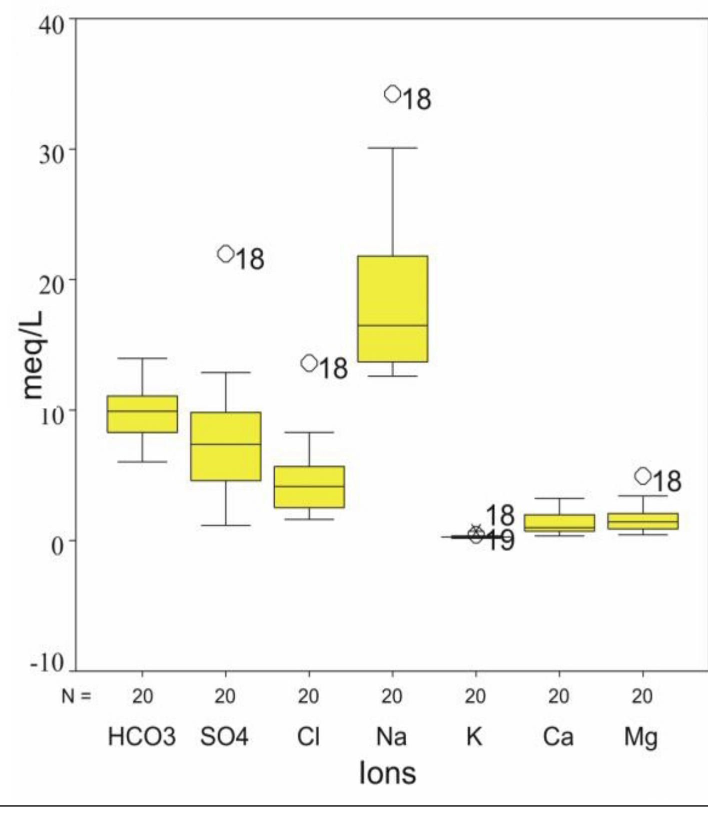

Figure 3. Box plots for main groundwater ions.

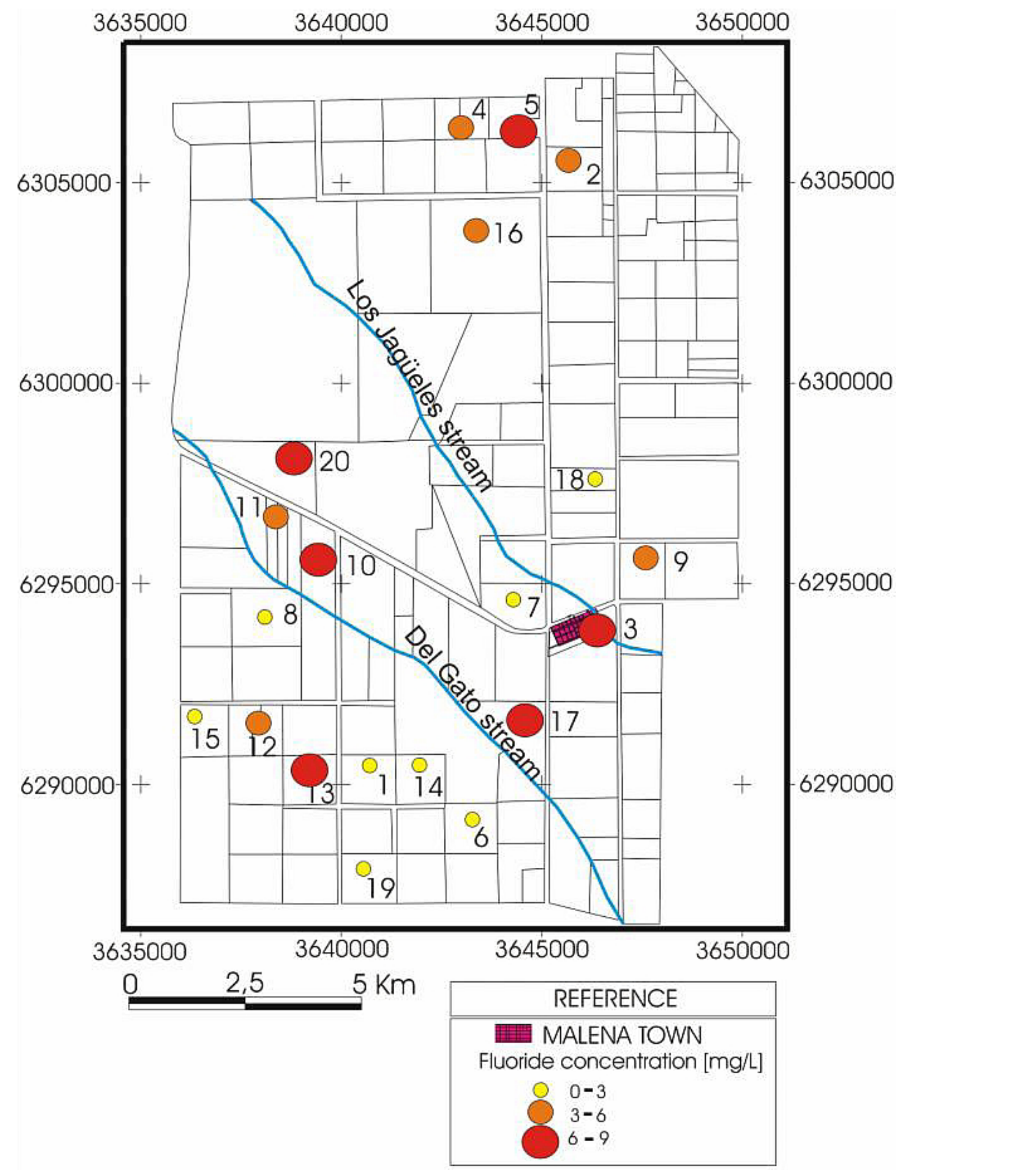

Figure 4. Areal distribution of fluoride in groundwater (unconfined aquifer).

The measured F^- levels in Malena town and rural area (Figure 4) range between 1.53 and 8.75 mg/L (mean: 4.6 mg/L and median: 5.5 mg/L). High levels of As, between 30 and 350 µg/L (mean: 191 µg/L and median: 220 µg/L) were determined also. The correlation between the two chemical elements was high (R=0.90, Figure 5a). The pH values of groundwater were between 6.80 and 8.20 and it was found that, in general, high levels of F and As were related to higher pH (> 7.80).

According to Frencken (1992) arid regions are prone to high fluoride concentrations. In these areas, groundwater flow is slow and the reaction times with rocks and sediments are therefore long. The fluoride contents of water may increase during evaporation if solution remains in equilibrium with calcite and alkalinity is greater than hardness. In the subhumid study area the low groundwater flow is basically controlled by relief and lithology, favoring in the loess environment high contents of As and F (Figure 5a). In addition, an important negative correlation was found (R=-0.82)

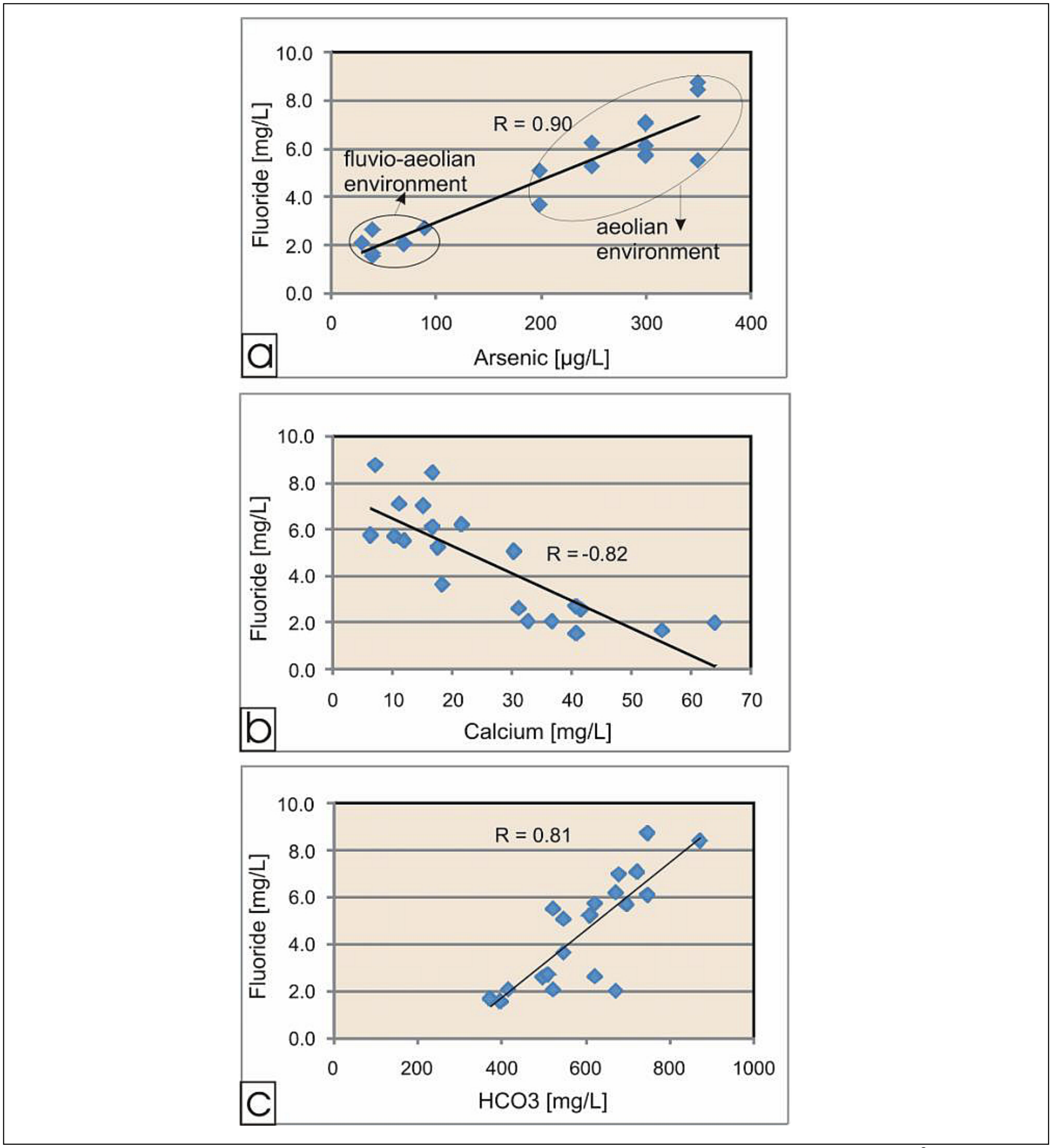

Figure 5. Relationship between chemical variables - a. fluoride vs. arsenic. b. fluoride vs. Ca^{+2}. c. fluoride vs. HCO_3^-.

between F^- and Ca^{2+} (Figure 5b) and a high positive correlation was found between F and HCO_3^- (Figure 5c). As was established by Frencken (1992) and Brunt et al. (2004), information on chemical composition of groundwater can be used as an (proxy) indicator of potential fluoride problems. Thereby, high-fluoride groundwaters are mainly associated with a sodium-bicarbonate water type and relatively low calcium and magnesium concentrations. Such water types usually have high pH values (above 7).

The multivariate statistical analysis (cluster, Figure 6a) showed 2 groups: the first one composed of variables that explain water mineralization, with a high correlation nucleus: EC-Na^+,

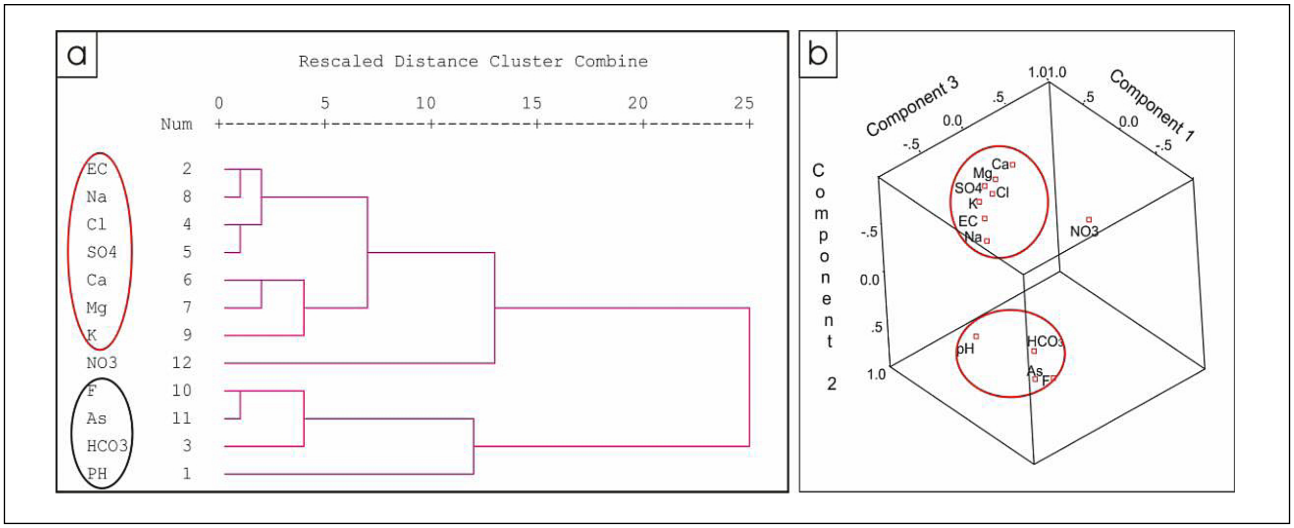

Figure 6. .Statistical multivariate analysis - a. Cluster diagram. b. Principal components.

related to Cl^- and SO_4^{2-} associated to the remaining cations. In this group, NO_3^- stayed isolated, which is linked to its anthropogenic origin. The second group, composed by F^--As-pH-HCO_3^-, corroborates the affinity of these elements to alkaline solutions and the connection to pH. Similar results were found with main component analysis, validating the conceptual model (Figure 6b).

In relation to As, the oxidant aquifer environment (dissolved oxygen in the order of 6 mg/L) would favor the predominance of As^{5+}, and the geochemical conditions previously described would collaborate in its desorption from the Fe oxide surfaces (Smedley et al. 2005). According to Smedley and Kinninburg (2002) the As content of the aquifer materials in major problem aquifers does not appear to be exceptionally high, being normally in the range 1–20 mg kg^{-1}. There appear to be distinct “triggers” that can lead to the release of As on a large scale. One of them is the development of high pH conditions in semi-arid environments usually as a result of the combined effects of mineral weathering and high evaporation rates. This pH change leads either to the desorption of adsorbed As (especially As (V) species) and a range of other anion-forming elements (V, B, F, Mo, Se and U) from mineral oxides, especially Fe oxides, or it prevents them from being adsorbed (Smedley and Kinninburg 2002).

Although high levels of As were detected in the study area, there are no official records of hydro arsenic poisoning in health institutions. However, it was detected that there are dental fluorosis problems in children, youngsters and adults, which is understandable, taking into account the easy recognition by non-specialists (Figure 7). Recent toxicological studies (Torti et al. 2011) using biomarkers have shown high fluoruria (fluoride/creatinine ratio in urine) in these exposed inhabitants.

In this study, and looking for a new water source, the chemical analysis of a groundwater sample from a confined aquifer (300 m deep) shows that fluoride and arsenic are below human consumption limits. The low concentration of As and F in deep confined aquifers was demonstrated in a neighboring area, after the analysis of more than 20 groundwater samples (Cabrera et al. 2010).

CONCLUSIONS

The statistical results validate the conceptual geochemical model, which, in conjunction with hydrogeological information allow us to state that fluorides are part of the baseline groundwater quality and that geomorphologic and lithological features control the dissolved amounts of this

Figure 7. .Dental fluorosis in children (Malena town and rural area).

chemical element. The highest levels of F^- in the solution are related to the textural characteristics of the aeolian aquifer (very fine sands-silts that favor slow groundwater flow); mineralogy (volcanic glass, amphiboles, pyroxenes, apatite; all possible sources of Fluoride); and the sodium type and high pH of groundwater. The high pH could collaborate either to the desorption of adsorbed As (especially As (V) species) and F from mineral oxides, especially Fe oxides, or it prevents them from being adsorbed. The important negative correlation between F^- and Ca^{2+} corroborates that in groundwater with low levels of Ca^{2+}, high concentrations of F^- in solution are stable otherwise it could precipitate fluorite. The high correlation found between F^- and As shows their geochemical relation and similar origin (lithological and aquifer conditions).

It is necessary to replace the present water sources. The water abstracted from a confined aquifer could be the best possible alternative of water supply to further study, especially for the urban area, since the analysis carried out revealed that it is suitable for human consumption.

ACKNOWLEDGMENTS

This is an extended version of the paper presented in the International Conference on the Biogeochemical trace elements (Mexico 2009). The authors would like to thank the comments of the anonymous reviewers on that occasion. This research work has been supported by the National University of Río Cuarto (UNRC) and ANPCYT-PICT 562/06 and PID 35/08 Investigation Projects.

REFERENCES

Adriano, D. 2001. Trace elements in terrestrial environments. Sec. Edit. Springer. USA.

APHA, AWWA, WPCF. 1995. Standard methods for the examination of water and wastewater, 17th edn. Washington.

Blarasin, M. 1984. Hidrología subterránea de la zona de Laguna Oscura. Córdoba. Tesis de Licenciatura. UNRC. Inédito.

Blarasin, M., A. Cabrera, E. Matteoda and M.L Gomez. 2005. Ascenso del nivel freático y cambios ambientales:

diagnóstico hidrogeológico y propuesta de manejo en Coronel Moldes, Córdoba. En Aguas Superficiales y Subterráneas en el Sur de Córdoba: una perspectiva geoambiental. Ed. UNRC.

Brunt, R., L. Vasak, and J. Griffio. 2004. Fluoride in groundwater: Probability of occurrence of excessive concentration on global scale. Report SP 2004-2, International Groundwater Resources Assessment Centre (IGRAC).

CAA Código Alimentario Argentino. 1994. Resolución 494/94. Boletín Oficial Nº. 27.932, 1ra sección. Art. 982 modificado.

Cabrera, A., M. Blarasin, and G. Villalba. 2001. Groundwater contaminated with arsenic and fluoride in Chaco-Pampeana Plain. Journal of Environmental Hydrology, Vol 9 Paper 6.

Cabrera, A., M. Blarasin, and E. Matteoda. 2010. Análisis hidrodinámico, geoquímico e isotópico de base para la evaluación de sistemas hidrotermales de baja temperatura en llanura cordobesa (Argentina). Boletin Geológico y Minero. Vol.121 (4) pp 387-400.

Carrica, J., and R. Albouy. 1999. Variaciones hidroquímicas en el agua subterránea en localidades del partido de Púan, provincia de Buenos Aires. Hidrología Subterránea. Serie Correlación Geológica. Nº 13, 221-230.

Carrica, J., A. Bonorino, and D. Delpino. 2002. Fluoruros en el agua de Manantiales en la zona de Zapala, provincial de Neuquén. Argentina. XXXII IAH & VI ALHSUD Congress. Mar del Plata. Argentina.

Frencken, J.E. 1992. Endemic Fluorosis in developing countries, causes, effects and possibility solutions. Publication number 91.082, NIPG-TNO, Leiden, The Netherlands.

Iriondo, M. 1997. Models of deposition of loess and loessoids in the Upper Quaternary of South America. Journal of South American Earth Sciences, 10(1), 71-79.

Nicolli, H., J. Suriano, M. Gómez Peral, L. Ferpozzi, and O. Balean. 1989. Groundwater contamination with Arsenic and other trace elements in an area of the province of Córdoba, Argentina. Enviromental Geology and Water Sciences, 14(1), 3-16.

Nicolli, H., A. Tineo, C. Falcon, J. García, M. Merino, M. Etchichury, M. Alonso, and O. Tófalo. 2004. Aguas subterráneas con alto contenido en arsénico en el área de Los Pereyra, Tucumán, Argentina. XXXIII Congress IAH & VII Congress ALHSUD. Zacatecas México.

Smedley, P., and D. Kinniburgh. 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, Vol 17 paper 5 pp 517-568.

Smedley, P., D. Kinniburgh, D. Macdonald, H. Nicolli, A. Barros, J. Tullio, J. Pearce, and and M. Alonso. 2005. Arsenic associations in sediments from the loess aquifer of La Pampa, Argentina. Applied Geochemistry, Vol 20 paper 5 pp 989-1016. Elsevier

Smedley, P., H. Nicolli, D. Macdonald, A. Barros, and O. Tullio. 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Applied Geochemistry, Vol 17 paper 3, 259–284.

SPSS for Windows, Rel. 11.0.1. 2001. Chicago: SPSS Inc.

Torti, S., M. Defacci, M. Blarasin, and A. Cabrera. 2011. Análisis de la incidencia del consumo de agua con arsénico y flúor en pobladores rurales de la colonia Sampacho. Informe Pasantía Profesional. Inédito. Universidad Nacional de Río Cuarto. Argentina.

WHO World Health Organization. 1993. Guidelines for drinking water quality. 2nd edn. 1. 188 p.

ADDRESS FOR CORRESPONDENCE
M. Blarasin
Department of Geology
National University of Río Cuarto
Rio Cuarto
Cordoba
5800 Argentina

E-mail: mblarasin@exa.unrc.edu.ar