ORIGINAL ARTICLE

Arsenic and fluoride in a loess aquifer in the central area of Argentina

M. L. Gomez · M. T. Blarasin · D. E. Martínez

Abstract The objective of this study is to analyze the geochemical conditions associated with the presence of arsenic (As) and fluoride (F) in the phreatic aquifer of Coronel Moldes, in the central sector of the Argentine Chacopampean plain. The studied aquifer is composed of silty sand sediments of aeolian origin, typically loess-like sediments. The geochemical composition of water varies from sodium bicarbonate to sodium sulfate-chloride water. As contents range from low concentrations, below detection level, to 250 µg/l. High values of F (up to 12 mg/l) were recorded. A high As–F correlation was found ($R^2 = 0.84$). The pH varied from 7.31 to 8.85 and the nitrates reached concentrations up to 200 mg/l, indicating an oxidant environment. The highest values of As and F agreed with sodium bicarbonate waters as well as with the highest values of pH recorded. There was a high correlation between As and F^- as well as between As and the Na/Ca ratio. The composition and texture of loess, low permeability and hydraulic gradients together with the geochemical features of sodium bicarbonate waters are proper conditions for the mobilization of As and F in groundwater in the central area of Argentina.

Keywords Groundwater · Arsenic · Fluoride · Pampa Argentina · Loess aquifer

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Introduction

Drinking water supply is a basic need and has thus worldwide issue. Moreover, not only the supply but also the quality and composition of this resource has became the focus of attention. It is well known that high values of total dissolved solids (TDS) can restrict human, livestock, agricultural and industrial water use, while elements such as arsenic (As) and fluoride (F) can cause health problems among the population (Smedley et al. 2002).

Arsenic contamination of groundwater is a widespread phenomenon, affecting for example areas in Bangladesh, Taiwan, China, Hungary, Mexico, United States, Chile and Argentina (Smedley et al. 2002). Because of the global character of this phenomenon, there exist numerous epidemiologic studies on the effects of As consumption on health, even in concentrations as low as 50 µg/1. Some of the clinical manifestations of chronic hydroarsenism discussed in these studies are hyper- and hypo-pigmentation, keratosis, cardiovascular disorders, diabetes, and cancer (Buchet et al. 1981). As a result of these findings and in attempt to establish safe standards, the World Health Organization (WHO 1993) has set the limit for arsenic in drinking water at 10 µg/1 in 1993.

The origin of arsenic in water can be natural as well as anthropogenic. Natural sources are related to geothermal sources or derived from the meteorization of arsenic-bearing minerals, mainly arsenopyrite (Sracek et al. 2004).

Smedley et al. (2002) pointed out that As is the main component of more than 200 mineral species, and it can be found in different concentrations, especially in sulfide minerals, pyrite being the most abundant among them.

The highest concentrations of minerals rich in arsenic occur in mineralized areas associated with basement rocks and active volcanic areas (Smedley et al. 2002). Arsenic is a singular metalloid because it is mobilized at the pH values usually found in groundwater, and also in a wide range of redox conditions, both in reduced (Hossain et al. 2004; Smedley et al. 2002) or oxidant environments (Smedley et al. 2002; Nicolli et al. 1989; Blarasin 2003).

A comprehensive analysis of arsenic sources in water has been published by Smedley and Kinniburgh (2002). Nicolli et al. (1989) and Smedley et al. (2002) showed that the ashes and volcanic glasses contained in loess sediments in the Pampa region are the principal natural source of arsenic in groundwater in Argentina. The term Pampean sediments is a generic denomination which included a wide range of Cenozoic silt and thin sands from aeolian or fluvio-aeolian origin, extending along the Argentine Chaco-Pampean plain for more than 1,500,000 km^2 (Teruggi 1957).

Arsenic values in volcanic glasses range from 2.2 to 2.12 mg/kg (Smedley and Kinniburgh 2002). High concentrations of As and F in waters from different areas within the Chaco Pampean Plain have been reported earlier. Blanco et al. (1999) stated that even though the origin of both ions in solution is natural and derived from Pampean sediments, it is not solely due to the dissolution of volcanic glass dissolution but also due to other components. However, Fernández Turiel et al. (2005) suggested a different origin for these ions, mainly related to volcanic emissions occurring in northeastern Argentina.

The presence of high F concentrations in groundwater has also prompted many scientific studies around the world. The most common fluoride minerals found in the Earth's crust are fluorite and apatite (Valenzuela and Ramírez 2004). Fluoride is a highly reactive element that combines with other elements in covalent and ionic bonds. It is mainly found in alkaline rocks and alkaline soils, fluorite being the principal component (Saxena et al. 2004).

Insufficient or excessive intake of F will bring about problems to the human organism. Studies carried out in Southeast (Korea Kim and Young Jeong 2005) have shown that the concentrations above 1.5 mg/l will predictable lead to both dental and bone fluorosis. However, due to chemical affinity between F and the hydroxyapatite in bones F accumulates in the skeleton and might lead to conditions similar to osteoporosis. The WHO sets the limit for F concentration in drinking water between 0.5 and 1.2 mg/l whereas the Código Alimentario Argentino (CAA 1994) establishes a limit that varies according to the average temperature of the place (1.3 mg/l for an average temperature of 16°C in the area under study).

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; Blarasin 2003). Health problems related to the consumption of water with high As and F concentrations in Argentina have been registered mostly in the Chacopampean area, particularly in the provinces of Córdoba, Santa Fe, Santiago del Estero, Buenos Aires, Chaco and La Pampa (Biagini et al. 1978; Besuschio et al. 1980).

The study area, Coronel Moldes town and the surroundings, is located in the center of |the Chacopampean plain. Rural and urban activities rely exclusively on the exploitation of groundwater. Water supply is provided by a phreatic aquifer with high concentrations of As and F$^-$ (up to 300 µg/1 and 7.2 mg/1 respectively, Blarasin et al. 2004), whereas Coronel Moldes obtains its water supply from a confined aquifer located at 150 m in depth. These aquifers are mainly composed of thin or remobilized aeolian materials which, as explained, constitute the main natural source carrying As and F$^-$ in groundwater. The objective of this study is to establish the geochemical conditions associated with the presence and mobilization of As and F$^-$ in the groundwater of the phreatic aquifer located in Coronel Moldes and its surroundings. In this way, this study will enhance the knowledge of the geochemical distribution and behavior of As and F in the Argentine Chacopampean plain contributing to more efficient management policies.

Methodology

A geologic–geomorphologic study of the basin was carried out, identifying outcropping materials, and those that make up the subsoil from deep wells carried out by the Dirección Provincial de Aguas y Saneamiento (DIPAS) and shallow bore holes. A topographic map in a 1:50,000 scale from the Instituto Geográfico Militar (IGM) 1969 Hoja 3366-30-4 ·Coronel Moldeš, was taken as the cartographic base. Aerial |photographs from 1970 were also used (1:50,000 scale) and satellite images: LANDSAT ETM+ 229/83 2000 digital format (1:50,000 scale).

About 40 samples were taken during the period December 2004 to March 2005. Field parameters were measured in situ, pH (using Electrode Oryon 9104 and potentiometer 710 A), conductivity and temperature (using Hanna Instrument, HI 9033). The samples were collected in 1 l plastic bottles and were analyzed within a period of the 24 h since collection. When this was not possible, they were stored and refrigerated, below 5°C, in a styrofoarm box until analysis was performed. The ions measured in

Fig. 1 Location map and main geomorphologic units in Coronel Moldes and surrounding area
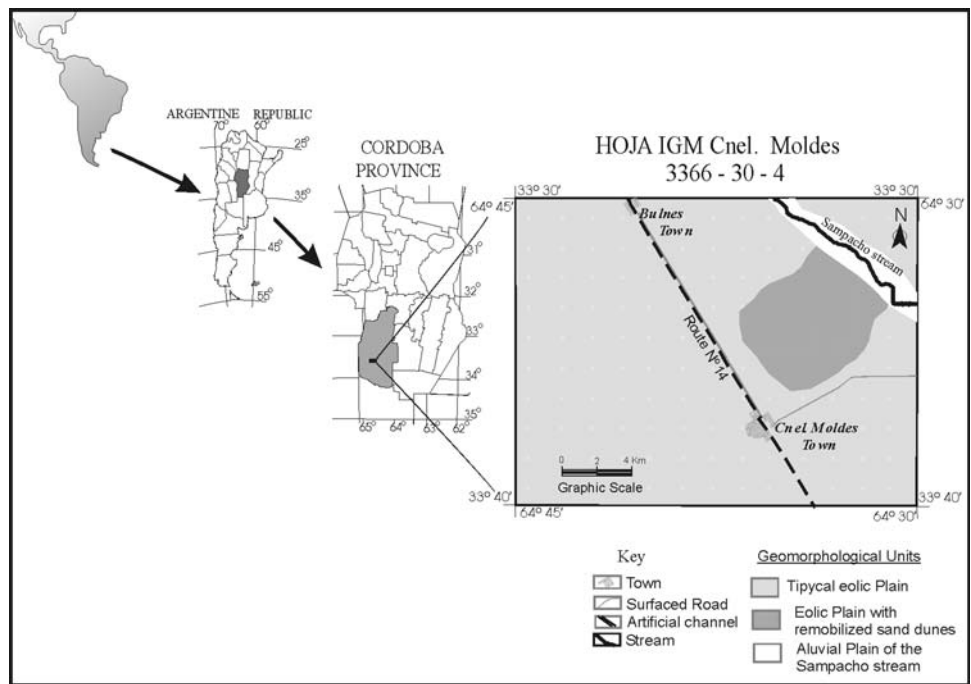
water samples were, Na^+, K^+ (flame photometric method), HCO_3^-, Cl^-, Mg^{2+}, Ca^{2+}, SO_4^{2-}, SiO_2 [Standard methods APHA (American Public Health Association), AWWA (American Water Works Association), WPCF (Water pollution Control Federation) 1995], F^-, NO_3^- (Ion-Selective Fluoride and Nitrate Electrode, Orion Models 9609 and 9307) and As (total) (Atomic absorption spectroscopy Analyst 300 Perkin-Elmer).

For the hydrometeorologic analysis, information on precipitation and temperature corresponding to automatic stations settled in the region was gathered. The information underwent to a statistical descriptive analysis. A system of perforations to measure groundwater levels and to take samples was defined for the hydrogeological characterization, taking into account the scale employed (approximately 1 hole/16 km^2). The selected holes correspond to rural inhabitants who obtain water from the aquifer's top (first 15–20 m). Information referring to the details of the well, lithologies, water lflows and so on was observed in each of these points. The phreatic aquifer levels were measured by using a piezometric probe. Water samples were taken with appropriate equipment to measure pH in situ, conductivity, total dissolved salts and temperature.

The equilibrium conditions of the solution regarding different mineral species were analyzed from the saturation rates obtained with the program PHREEQC2.0 (Parkhurst and Appelo 1999). Furthermore, inverse models of the hydrochemical evolution were developed with the program NETPATH (Plummer et al. 1991). Arsenic speciation was calculated with the program WATEQF (Truesdell and Jones 1974).

Location and general features of the study area

The study area is located in the south of the province of Cordoba, between latitude 33°30′ and 33°40′ south and longitude 64°30′ and 64°45′ west (Fig. 1). It comprises 400 km^2 and the mean altitude is 400 m above sea level (masl). The average precipitation for the area is 878 mm, with a noticeable seasonality, as 85% rainfalls take place between October and April. Coronel Moldes (8,850 inhabitants) is the most important town in the area, which bases its economy on agricultural exploitation.

The area is poorly drained and rainwater surplus usually drains into lowlands. The drainage pattern has been modified by human activity. As an example, the rural road network became an important part of the drainage network. Parallel to route No. 14, which connects the towns of Bulnes and Coronel Moldes, there is an artificial channel which carries the water of Suco creek during rainy season. The northeastern angle of the area is surrounded by a permanent stream, the Sampacho creek.

Geologic and geomorphologic features

The study area is part of the Chacopampean plain, a big basin that received sediments coming from the Andes and that today constitutes the main transit place of those materials toward the Atlantic continental platform and slope (Chebli et al. 1999). The outcropping sediments in the study area are mainly aeolian of Holocene age. These materials were locally remobilized by the dominant NE

winds, and deposited forming sand dunes, which constitute a geomorphic region called as the loess plain of the south of Cordoba (Cantú and Degiovanni 1987). The relief presents homogeneous features, and only 3 geomorphologic units can be differentiated (Fig. 1): the *Typical aeolian plain* unit comprises the greatest part of the study area and presents a nearly plain relief. The general topographic slope is low and uniform toward the SE, with an average of 0.55% and a minimum of 0.4%. In certain places, the remobilized sand dunes are erased because of parceling and soil management. The effects of hydric erosion processes can be clearly seen in the roads, which have become the main network of surface drainage during storms. Two units were defined in the northeastern: the *Aeolian plain with remobilized sand dunes* and the *Aluvial plain of Sampacho stream*. The Aeolian plain with remobilized sand dunes̈ unit corresponds to the most pronounced slopes (2% in the sand dune area), resulting in a slightly sloped relief. This unit is characterized by sand dunes stabilized by vegetation and spread out ponds. The *Aluvial plain of Sampacho stream* unit has a width between 1,000 and 2,000 m and includes the river-bed with a terrace level and also old overflown areas. The river-bed has a rather winding design, width between 1 and 2 m and a bed made up of thin alluvial and aeolian remobilized sediments.

Hydrogeology

The materials that make up the phreatic aquifer correspond to Quaternary deposits, mainly very thin sands and silts of aeolian origin (loess) with carbonate cementation (Fig. 2). The homogeneity of this sedimentary package is interrupted by thin sandy levels that do not exceed 7–10 m thickness. There are also some thin layers of calcium carbonate concretions locally known as *tosca* at 1.5 m and a more important one at 16 and 21 m depth.

The phreatic aquifer thickness ranges between 49 and 60 m of depth. Hydraulic conductivities ranges between of 0.2 to 1 m/day and transmisivities between 10 and 60 m^2/day (Blarasin et al. 2004). The confined aquifer exploited in Coronel Moldes city is located between the 154 and 161 m below the surface (Fig. 2).

The thickness of the non-saturated zone shows the highest values, 10–14 m, to the NW part of the study area. These values decrease toward the SE, up to values of 5 m, and they vary locally (between 3 and 1 m) in the central and eastern sector, where phreatic outcrops in ponds of small extension. The bedrock was found toward the north, in Bulnes town, at 131 m depth. It is made up of metamorphic and granitic rocks, biotitic gneisses from the Precambrian-low Paleozoic era. However, another
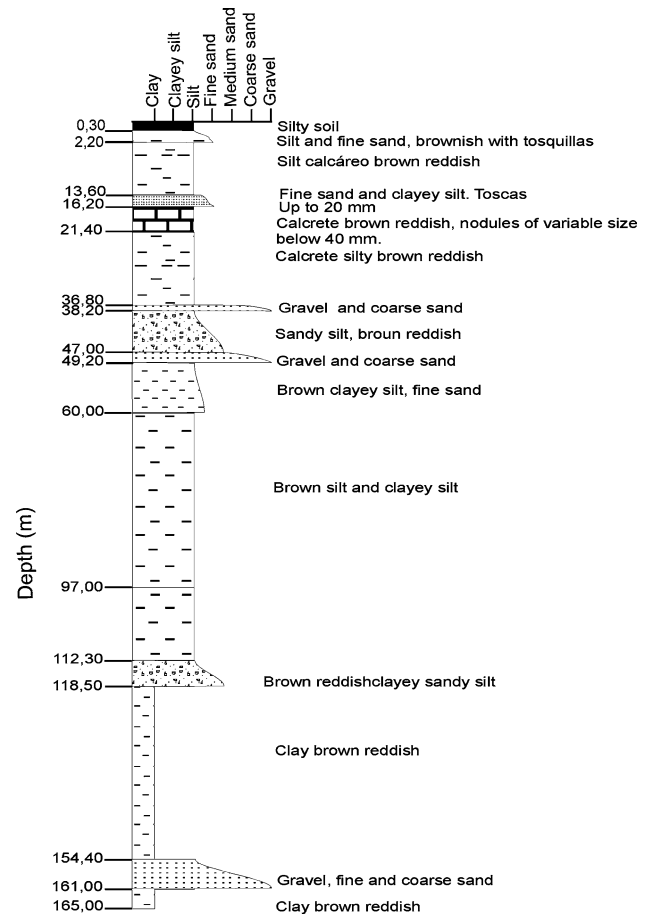

Fig. 2 Lithological log of DIPAS borehole. Coronel Moldes town (33°38′ S–64°36′ W)

perforation drilled in Coronel Moldes reached 165 m without hitting bedrock.

Loess texture and geochemical features

A texture analysis was carried out on five selected samples from perforations drilled in the first six meters of the subsoil. A dominant grain size mode of very thin sands could be found, with a weight percentage of 52–60%, followed in the order of importance by silts and clays.

Petrographic studies of loess in South Córdoba (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 the order of importance, by quartz, volcanic glass (up to 24% of weight percentage) and plagioclase, making up the rock fragments between 6 and 10%. Pyroxenes and amphiboles predominate among the heavy minerals, being tourmaline, zircon, apatite and opaque minerals subordinated. Ferromagnesian minerals,

Table 1 Chemical date of trace elements in loess samples of the Chaco-Pampean plain in Argentina (Nicolli et al. 1989, 2004)

Trace elements	SW Sector of Córdoba province			NE Sector of Tucumán province		
	Min[a]	Max[a]	Average[a]	Min[a]	Max[a]	Average[a]
As	5.51	37	16.7	6	25	11
F				534	3,340	908
Se	1.1	2.3	1.53			
U	1.25	8	2.99	3.34	16.0	6.04
Sb	0.25	0.88	0.55	0.3	1	0.8
Mo	2.2	5.2	3.4	<2	5	–

[a] The corresponding units of constituents are ppm

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). Geochemical analyses of loess from different parts of the Chacopampean plain carried out by Nicolli et al. (1989, 2004) show the maximum, minimum and geometric mean concentrations of the main trace elements in loess sediments (Table 1). All these trace elements are found in the loess in high concentrations and thus constitute a potential source of contribution to groundwater, especially in the case of As.

Results

Hydrodynamics

The potentiometric map (Fig. 3) shows a NW–SE groundwater flow direction and a slightly winding to plain phreatic level morphology. The hydraulic gradient was determined at 0.4% for the area, reaching 1.6% locally, whereas the drainage velocities measured were between 0.01 and 0.4 m/day. They were calculated considering porosities between 1 and 7%. The low velocity values are associated with the flat relief of the area, which also results in the impossibility to define groundwater divides.

Recharge of the phreatic aquifer from rainfall is produced in the whole surface of the area. Human contribution to recharge in the urban area is very important. Calculations made in Coronel Moldes indicate that about 70% of recharge water is from sewage systems, while a 30% is from rainwater. Groundwater flow shows a relationship of influence on the creek's upper and lower stretch whereas on the middle stretch, it evidences a relation of indifference (Fig. 3).

Hydrogeochemistry

Groundwater is mostly alkaline, with pH values ranging from 7.31 to 8.85. The presence of high concentrations of nitrate evidences contamination anthropogenicsources and the prevalence of an oxidant environment.

A geochemical classification was carried out using the methodology of Custodio and Llamas (1983), taking into account the dominant anion and cation. Hydrochemical facies are mostly sodium bicarbonate to sodium bicarbonate sulfate, with a predominance of sodium bicarbonate and sodium bicarbonate sulfate water (Fig. 4). Saline content distribution does not increase in the groundwater flow direction. Likewise, there is not a defined pattern for the distribution of the different geochemical types. Sodium bicarbonate water corresponds, in general, with low salinity samples. As water mineralization increases and due to the high solubility of sulfate and chloride salts, the hydrochemical facies become dominated by those anions.

Fig. 3 Potentiometric contour map. Unconfined aquifer of Coronel Moldes and its surroundings
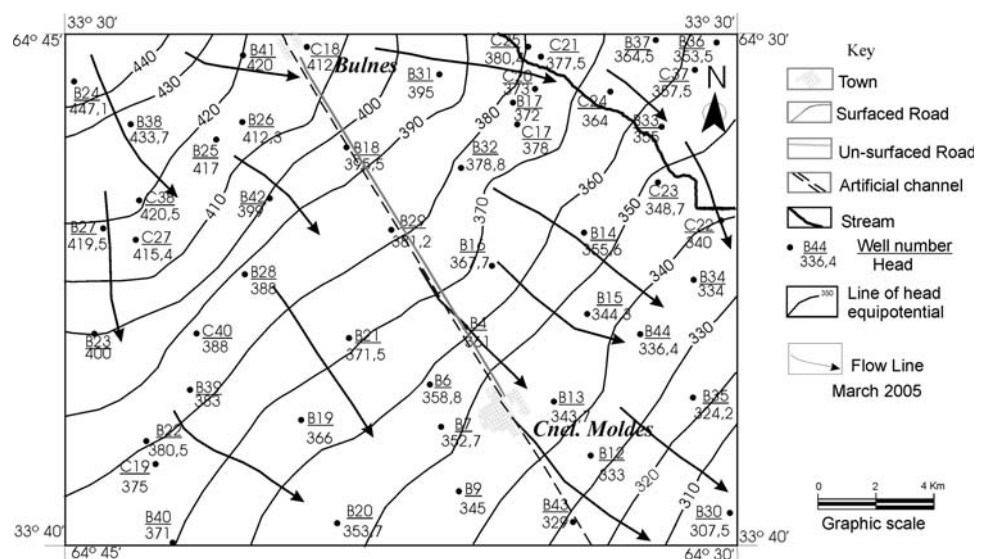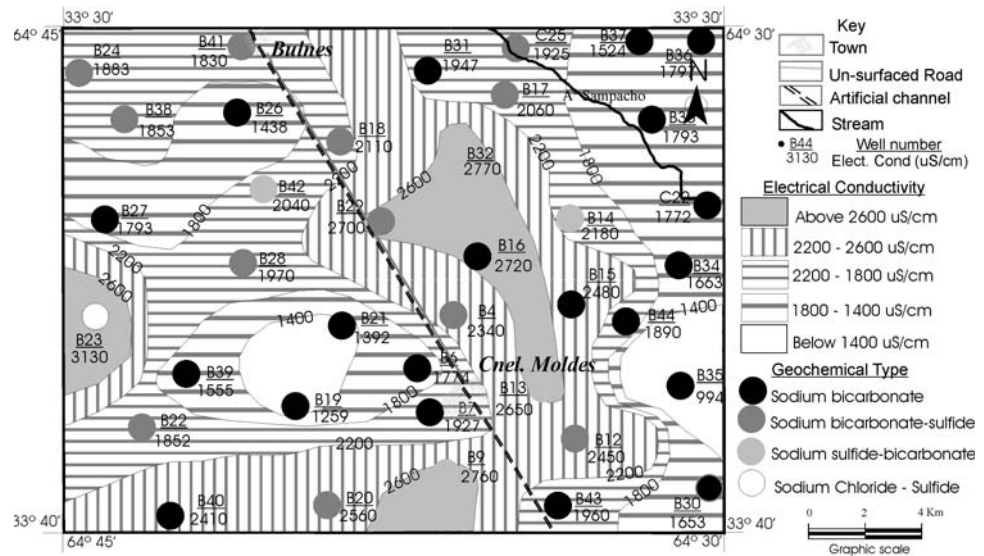
Fig. 4 Groundwater conductivity and geochemical composition map. Unconfined aquifer of Coronel Moldes and its surroundings

The table of correlation coefficients (Table 3) shows that the more significant correlations are those of sulfate and chloride against electric conductivity and sodium, which is related to the predominance of sulfate and sodium chloride facies in waters of higher salinity.

Statistical parameters of these hydrochemical determinations are presented in Table 2. Electric conductivity values in groundwater vary from 994 to 3,130 µs/cm (Table 2) resulting 97% of the samples in fresh water (<2,000 mg/l), and the remaining 3% in salt water. The highest values were found in the central part (up to 2,770 µs/cm), central south (2760 us/cm) and west of the area (3,130 µs/cm), whereas the lowest values were identified in the central west sector (1,392 µs/cm) and east of the study area (994 µs/cm) (Fig. 4).

A general evolutionary trend from sodium bicarbonate waters to sulfate and sodium chloride waters can be observed in the Piper diagram (Fig. 5). The hydrochemical facies distribution does not follow a pattern which can be related to the geomorphologic features or to the groundwater flow system. This might be conditioned by evaporation processes resulting from the proximity of the phreatic level to the surface, and by the presence of *tosca* layers at different depths, which would produce differential rates of recharge in local flow systems. In the urban area, fresher water perched on tosca layers of 50-cm thick was identified at 1.5 m depth (Blarasin et al. 2004).

Sodium is the dominant cation, with concentrations from 200 to 600 mg/l (Table 2). This is related to cationic exchange processes, resulting from the interaction between

Table 2 Groundwater statistic parameters of the analyzed samples

Parameter	Unit	Min	Max	Average	St. dev.	Dev. coeff.	Sample num
pH		7.31	8.85	7.87	8.00	101.70	40
Cond.	µS/cm	994	3130	1,985	484.77	24.42	40
Temp.	°C	12.5	23.7	20.45	2.22	10.86	40
Na^+	mg/l	235	687	455	120.55	26.47	40
K^+	mg/l	5.7	18.0	10.2	2.5	24.10	40
Ca^{2+}	mg/l	3.2	50.4	22.5	11.8	52.42	40
Mg^{2+}	mg/l	3.9	62.9	15.1	10.1	66.73	40
HCO_3^-	mg/l	460.0	912.5	629.1	115.8	18.40	40
CO_3^{2-}	mg/l	0.0	46.1	4.9	10.7	213.83	40
Cl^-	mg/l	28.6	368.6	152.6	80.4	52.68	40
SO_4^{2-}	mg/l	35.4	601.5	262.6	166.9	63.55	40
NO_3^-	mg/l	5.0	200.0	91.0	68.3	75.10	40
Si	mg/l	13.7	70.0	34.2	16.1	47.19	34
F	mg/l	0.5	12.0	3.5	2.3	66.65	40
As	µg/l	0	250	70	60	89.48	38
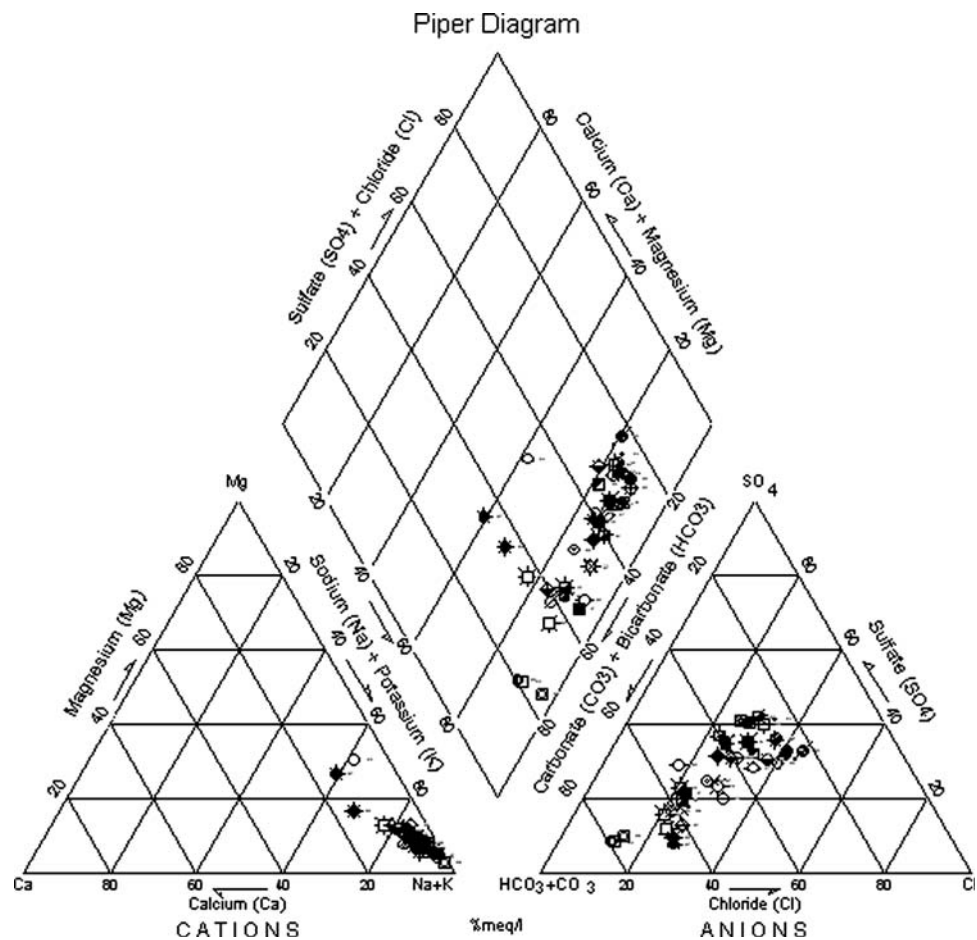
water and clay minerals (mainly illite in the loess of the area), although a great amount of sodium is brought by the hydrolysis of the silicate minerals. The concentration of Ca ion is governed by the equilibrium reaction of calcite dissolution and by the cationic exchange. The saturation index (SI) in aragonite and calcite is between 0.01 and 0.28, indicating equilibrium conditions.

High dissolved silica concentrations are observed, between 13.7 and 70 mg/l, as it has been mentioned in other loess aquifer in the Pampa (Martínez and Osterrieth 1999). These concentrations can in general be attributed to the dissolution of amorphous silica minerals, such as volcanic glass, whose reaction velocity is faster. Chalcedony and quartz are under oversaturation conditions. SI values in amorphous silica are slightly subsaturated or close to equilibrium conditions (SI between −0.2 and −0.8), which indicates that it is possible to assume its dissolution.

Arsenic and fluoride

The concentrations of As in groundwater are between 0 and 250 µg l^{-1} (Table 2). Eighty-eight percent of the samples present concentrations above 10 µg l^{-1} (WHO admissible level for drinking water) and 54% exceeds the Argentine national regulation of 50 µg l^{-1}. Under oxidizing conditions of the aquifer, as indicated by the presence of NO_3^-, As is mainly found as As $^{(5+)}$. The dominant ionic species in solution (90% of the total As) is $HAsO_4^{2-}$, and in subordinated form as $H_2AsO_4^{1-}$ (10% of the total As) (Smedley and Kinniburgh 2002).

There is a correspondence between high As contents (>200 µg l^{-1}) and sodium bicarbonate water facies, while a weak positive correlation was found between As and bicarbonates. Those samples with As concentrations below 40 µg l^{-1} do not show a correlation with pH, electric conductivity, level depth or even with bicarbonates. The distribution of As contents (Fig. 6) shows a significant spatial variation. The observed distribution does not respond to changes in sampling depth, flow water directions, total salinity, pH and thickness of the non-saturated zone. A moderate positive correlation ($R^2 = 0.43$) between As and pH was found only if sodium bicarbonate waters are considered in isolation (Fig. 7), whereas in sodium sulfate bicarbonate and sodium bicarbonate sulfate water, these correlations are not evident. As expected, the highest pH (>8) is more frequent in sodium bicarbonate water.

Fig. 6 Distribution of pH, As and F concentrations in groundwater of unconfined aquifer of Coronel Moldes and its surroundings
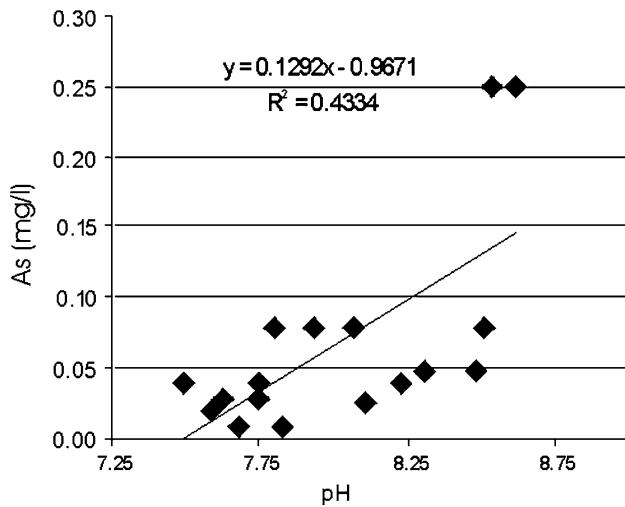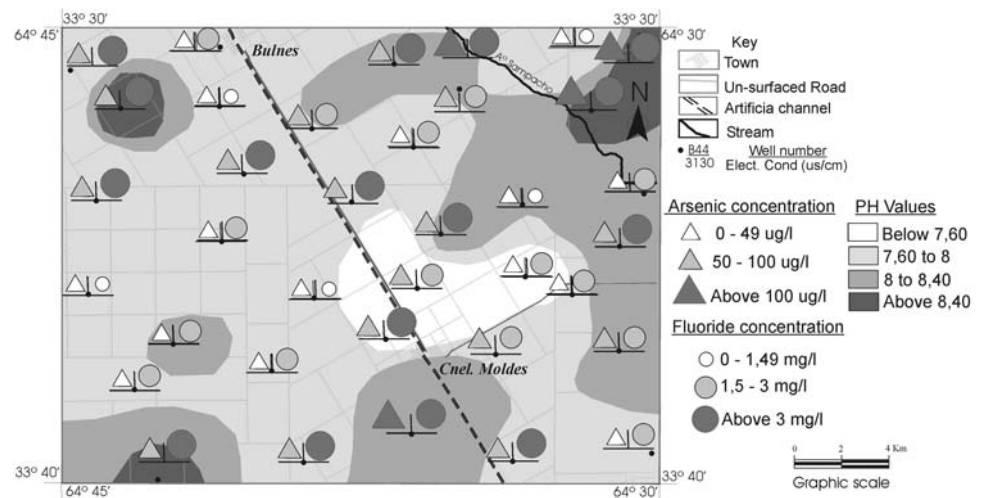

Fig. 7 Correlation between As and pH to the sodium bicarbonate waters

Fig. 8 Correlation between As and F of the groundwater of unconfined aquifer in Coronel Moldes and surrounding area

About 90% of the analyzed samples show F values above 1.3 mg/l (CAA limit). The distribution of F^- concentrations in groundwater was heterogeneous, similar to that of As (Fig. 6). There is a significant correlation between As and F^- ($R^2 = 0.814$) showing the possible common of both variables (Fig. 8). Furthermore, a moderate positive correlation between As and F^- with the relationship Na/Ca ($R^2 = 0.55$ and $R^2 = 0.61$, respectively) was found. This correlation is highlighted if bicarbonate water is solely considered, observing $R^2 = 0.73$ for As and the relationship Na/Ca, and $R^2 = 0.77$ for F^- and the same relationship (Figs. 9, 10).

The highest F^- concentrations (>5 mg/l) correspond with sodium bicarbonate water. For this type of water, a positive correlation of $R^2 = 0.35$ for F^- and pH was observed.
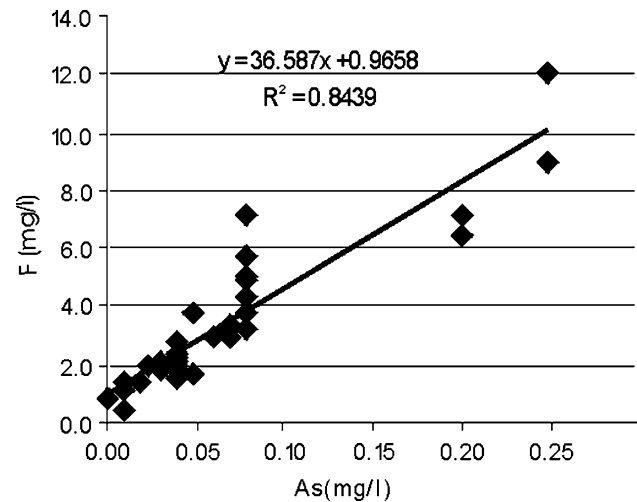
A negative correlation (Table 3), considering all the samples, was observed between As and F^- with Ca and Mg. Other authors previously have identified small affinity between As and F^- with calcium and magnesium in groundwater (Cabrera and Blarasin 2001; Smedley et al. 2002; Blarasin 2003; Bundshchuh et al. 2000; Valenzuela and Ramírez 2004). The processes that could control the negative relationship between F and Ca, and the positive relationship between F and bicarbonate would be the balance equation relating calcite and fluorite (Valenzuela and Ramírez 2004), when both are in contact with water

$$CaCO_{3(s)} + H^+ + 2F^- = CaF_{2(s)} + HCO_3^-$$
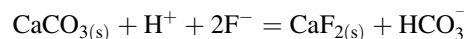
The samples in which F^- concentrations are over 5 mg/l are oversaturated with regarding fluorite. Once the fluorite equilibrium is reached, $CaCO_3$ removal due to calcite
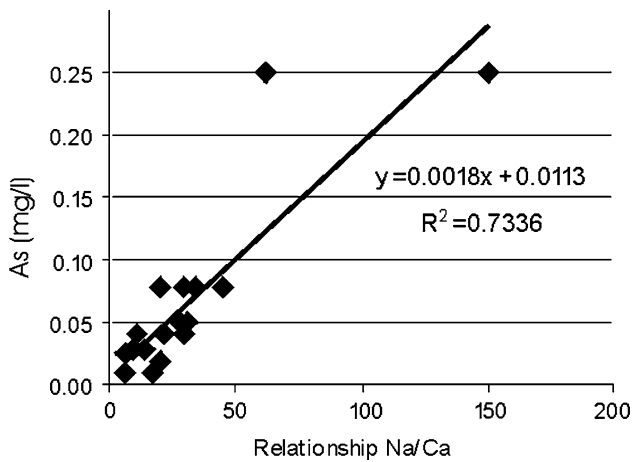
Fig. 9 Correlation between As and relationship Na/Ca for sodium bicarbonate waters
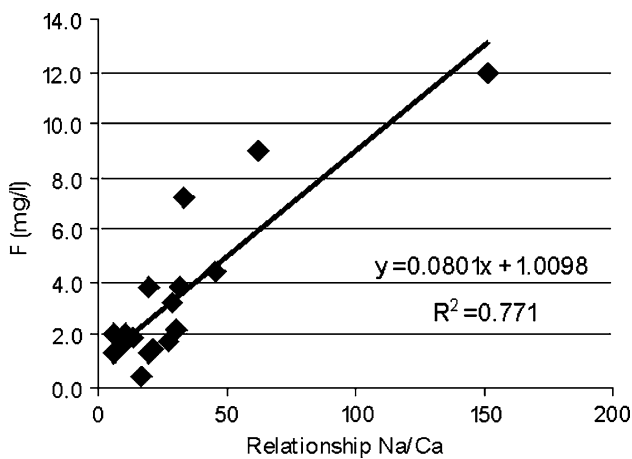

Fig. 10 Correlation between F and relationship Na/Ca for sodium bicarbonate waters

precipitation allows F^- concentration to increase (Kim and Young Jeong 2005).

Hydrogeochemical modeling

The distribution of water salinity and hydrochemical facies is heterogeneous and does not correspond with normal groundwater evolution in a flow system (Chevotarev II 1955) based on thermodynamic concepts (Garrels and Christ 1965). Then, a conceptual approach is proposed to explain the observed features.

An understanding of the hydrochemical evolution of the main components is important to analyze the causes of the observed relationships between As and F concentrations and specific water types. Inverse modeling for three different evolutionary scenarios was done using NETPATH (Plummer et al. 1991):

(a) To explain the composition of sodium bicarbonate water from the composition of rain water and its interaction with the solid phase in the non-saturated zone.

(b) To explain the composition of sodium sulfate water from the composition of rain water and its interaction with the solid phase in the non-saturated zone.

(c) To determine the chemical changes in the evolution from bicarbonate water to sodium sulfate.

Sodium chloride sulfate water types were not included in the models since it was observed in only one sample. The evolution of the main ions (HCO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}), F and Si was studied in all the models. The reactive phases considered were equilibrium with calcite, gypsum and amorphous silica, cationic exchange and dissolution or loss of CO_2 in open system, which have been previously mentioned in the Pampean sediments (Martínez and Bocanegra 2002; Martínez and Osterrieth 1999). Fluorite and fluorapatite phases have also been considered because of their participation in the contribution and mobility of F. The composition of rainwater was determined and F concentration was measured in several samples in Coronel Moldes.

The evolution of sodium bicarbonate water from rainwater can be explained by two different models. The first model considers that salinity increases by means of an evaporation factor using Cl^- as a conservative ion. The second model explains the evolution by including the dissolution of NaCl which might be dispersed in the non-saturated sediment. The model that explains the sodium bicarbonate composition from rainwater through an evaporation factor is considered to be the most appropriate hydrochemical evolutionary model (Table 4).

This model explains the composition of sodium bicarbonate water as the result of: (a) calcite dissolution in an open system, (b) cationic exchange with adsorption of Ca and release of Na, and low rates of Mg/Na exchange, (c) amorphous silica dissolution and, (d) gypsum precipitation. If the minimum F value of the analyses carried out in Coronel Moldes rainwater water is used (0.08 mg/l), the models include the dissolution of fluorapatite. This mineral is included as F source because of the impossibility of simulating impurities in volcanic glasses. However, if the maximum determined value of 0.11 mg/l is used for precipitation, concentration can be explained only by the evaporation factor. In this evolutionary phase, the dissolution of amorphous silica (volcanic glass) at a value of 0.00481 mg/l is included.

The modeling carried out to explain the composition of the sodium sulfate facies from rainwater is included in the second column of Table 4. An extremely high evaporation factor should be considered to justify the increase in

Table 3 Correlation coefficients matrix foe the measured parameters in groundwater in Coronel Moldes and its surroundings

	pH	Cond.	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	HCO$_3^-$	SO$_4^{2-}$	Cl$^-$	NO$_3^-$	Si	F$^-$	As
pH	1.000	−0.281	−0.204	−0.048	−0.304	−0.361	−0.219	−0.138	−0.257	−0.453	−0.071	0.406	0.366
Cond.		1.000	0.931	0.483	0.178	0.426	0.187	0.827	0.888	0.493	−0.089	0.070	0.194
Na$^+$			1.000	0.392	−0.021	0.206	0.249	0.857	0.818	0.412	−0.024	0.200	0.329
K$^+$				1.000	0.360	0.388	−0.328	0.551	0.543	0.155	−0.055	−0.295	−0.106
Ca^{2+}					1.000	0.706	−0.199	0.055	0.277	0.448	−0.123	−0.533	−0.513
Mg^{2+}						1.000	0.103	0.234	0.424	0.444	−0.239	−0.305	−0.224
HCO$_3^-$							1.000	−0.155	−0.186	0.369	−0.172	0.345	0.293
SO$_4^{2-}$								1.000	0.851	0.170	0.046	0.037	0.255
Cl$^-$									1.000	0.297	−0.010	−0.096	0.001
NO$_3^-$										1.000	0.011	−0.261	−0.192
Si											1.000	−0.016	0.077
F$^-$												1.000	0.814
As													1.000

chlorides, which leads to the introduction of processes like fluorite precipitation, or fluoropatite. These are not very likely processes, and the increase in F would only be explained by the concentration by evaporation of the contents in rainwater.

Finally, samples B19 and B9 were taken as extremes to obtain an evolutionary model from sodium bicarbonate water to sodium sulfate bicarbonate waters. Several models were obtained, but it was chosen these presented in the third column of Table 4. Concentration because of evaporation was discarded because this evolution took place in a saturated zone. The observed processes in this evolution are weak calcite dissolution, cationic exchange involving adsorption of Ca and release of Na and of Mg in a smaller proportion, and a very important dissolution of gypsum and NaCl. A greater dissolution of a fluorine-bearing phase is necessary, represented here by fluorapatite, although it could be represented by volcanic glass.

Table 4 Processes and mol transference in the inverse geochemical models from selected wells in Coronel Moldes and surrounding area

Phases [a]	Rain water to B19	Rain water to B9	B19 to B9
Calcita	0.39097	0.06501	0.22096
CO2 Gas	−0.06676	−0.46480	−0.43895
Exchange	0.44156	0.14031	6.47758
Gypsum	−0.04881	−0.00719	5.84143
Fluorar	0.00357	−0.00275	0.09510
SiO2	0.04380	0.00326	−0.30124
Mg/Na exchange	0.02493	0.03167	−0.52382
Evaporation factor	13.123	83.967	–
NaCl	–	–	5.65551

[a] Values in moles/l

Discussion

As and F concentrations in groundwater in the Chaco-pampean plain are conditioned by natural sources in the like loess sediments (Nicolli et al. 1989; Smedley et al. 2002; Blarasin 1984, 2003). The processes of dissolution and release from oxides and oxyhydroxides, mainly Fe and Mn, integrate the processes that control the presence of As and F in groundwater. Smedley et al. (2002) also highlight that the mobilization of As in water increases if oxidant conditions and high pH prevail in the aquifer. Two features of the geochemical behavior of these elements have been found in Coronel Moldes and they coincide with other records in the region (Nicolli et al. 1989; Smedley et al. 2002; Blarasin 1984, 2003): a high correlation between them and a good correlation with the distribution of sodium bicarbonate water.

It has also been observed that the most important source of As and F in the phreatic aquifer of Coronel Moldes and its surroundings is the Quaternary sediment of aeolian origin. These loess sediments hold important quantities of volcanic glass, volcanic minerals and volcanic lithic fragments. High pH and high bicarbonate concentrations would facilitate the dissolution of volcanic glass, passing As and F into groundwater cycle, where they constitute anionic complexes. The processes of sorption and release over the surface of Fe and Al (gibbsite, hematite and goethite) would also be responsible for As distribution in groundwater (Nicolli et al. 2004).

Other minerals, from the rocks that form the crystalline bedrock of the Sierras de Córdoba, and its derived sediments, are also considered probable sources of F (Villalba 1999). Biotites, present in biotitic gneisses, could be responsible for part of F present in water. On the other

hand, F^- in the solution could also be derived from the exchange of ions from bearing minerals (apatite, pyroxene, hornblende and titanite among others). Zack (1980) highlights that F^- would be released to the environment by an anionic exchange with OH^-, more than by the dissolution of source minerals. In this way, dissolution processes, which tend to be very slow, would be subordinated. In alkaline environments, F^- is desorbed from clay minerals (Valenzuela and Ramirez 2004), and in high pH conditions, F dissolution from bearing minerals, in this case volcanic glass, would be more favorable (Saxena et al. 2004). Laboratory experiments carried out by Turner et al. (2005) in calcite solutions and F^- concentrations between 3 and 2,100 mg/l showed that together with CaF_2 precipitation processes, F^- adsorption processes on the surface of calcite also occur. In this manner, $CaCO_3^-$ precipitation processes would also decrease the concentration of F in the solution.

The high correlation between As and F^- in the groundwater of Coronel Moldes supports the hypothesis of a common source for these elements, which could be the dissolution of volcanic glass. The highest solubility of amorphous silica is related to sodium bicarbonate water (Marshall and Warakomski 1980). Moreover, the correlation between As and F^- with pH and the association between the higher concentrations of both elements in sodium bicarbonate water evidence the dissolution process of amorphous silica.

Inverse hydrogeochemical models are useful to explain the origin of sodium bicarbonate water from processes that take place during the recharge from rainwater, including the concentration due to evaporation, but not the origin of sulfate bicarbonate water or chloride bicarbonate. Only an evaporation factor of 83.96 would account for the latter, which is considered most unlikely. Blarasín et al. (2004) determined recharge values, by different methods, of 10%, which discard such a high evaporation values. In this way, the accepted evolutionary model is that of the origin of sodium sulfate water from the transit of sodium bicarbonate water. From a hydrological viewpoint, this explanation requires the existence of local flow systems defined in very short distances, as it seems to occur in this loess aquifer. These local flows could be conditioned by geological heterogeneities.

This evolution is useful to explain the correlation between As and F with bicarbonate water. As observed in Table 4, the characteristic processes in the genesis of bicarbonate water are cationic exchange (adsorption of Ca and release of Na and Mg), dissolution of small quantities of gypsum, and dissolution of calcite and amorphous silica. However, in its evolution toward sulfate water, the processes are also the cationic exchange (adsorption of Ca and release of Na and Mg) and a dissolution of small quantities of gypsum, but a smaller dissolution of calcite and amorphous silica precipitation.

Conclusions

In the study area, the outcropping materials and those that constitute the phreatic aquifer correspond to Quaternary sediments of aeolian origin (loess). The most abundant size fraction is very thin sands, followed, in the order of importance by slit-clay fractions. Important quantities of volcanic glass, volcanic minerals and volcanic lithic fragments are included in the loess sediment. Volcanic glasses contain As and F in its chemical composition, thus being considered the main source of As and F in groundwater.

The chemical composition of the water in the aquifer is dominantly sodium bicarbonate and sodium sulfate bicarbonate, resulting 97% of the samples in fresh water. The most mineralized samples are the sulfate and sodium chloride sulfate, even though they are subordinated.

There is a good correlation between As and F^- ($R^2 = 0.84$, which is interpreted as an indicator of the common natural origin of these elements which, due to the subsaturation in amorphous silica, is attributed to the dissolution of volcanic glass.

Despite of the very homogeneous geomorphologic and lithologic features at a regional scale, the distribution of As and F^- concentrations in groundwater is heterogeneous. This is attributed to the lower scale heterogeneities in the materials that constitute the phreatic aquifer, which would bring about the resulting changes in the geochemical conditions required for the mobilization of those elements.

The higher contents of As and F are related to the presence of NaHCO3 water type, in which amorphous silica (e.g., volcanic glass) dissolves, together with the dissolution of calcite. Calcite dissolution could also contribute to supply absorbed F^-, according to the experiments of Turner et al. (2005). In non-bicarbonate water, there is no dissolution of glass, and when calcite precipitation occurs, the adsorption of As and F would take place (Turner et al. 2005). Thus, the proposed geochemical models explain the association of As and F between themselves and with sodium bicarbonate water.

It can therefore be assumed that the composition and texture of loess, low permeability, low hydraulic gradients, low velocities of water circulation and geochemical characteristics, are proper conditions for the mobilization (dissolution and release) of the high contents of As and F. In agreement with the negative correlation between As and F^- with Ca and Mg, and with the positive correlation with Na, the highest values were associated with the geochemical environment of sodium bicarbonate water and high pH.

References

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

Besuschio SC, Desanzo AC, Perez A, Croci M (1980) Epidemiological associations between arsenic and cancer in Argentina. Biol Trace Elem Res 2:41–55

Blanco MC, Paoloni JD, Morrás H, Florentino D, Sequeiro M (1999) Variabilidad espacial del paisaje pampeano sudoccidental y su influencia en la distribución del ion arsénico en suelos y aguas. I Congreso Argentino de Cuaternario y Geomorfología, La Pampa, Argentina. Actas, pp 25–26

Biagini R, Rivero M, Salvador M, Córdoba S (1978) Hidroarsenisismo crónico y cáncer de pulmón. Arch Argent Dermatol 48:151–158

Blarasin M (1984) Hidrología subterránea de la zona de Laguna Oscura. Córdoba, Argentina. Trabajo final de Licenciatura. U.N.R.C. 50 páginas

Blarasin M (2003) Geohidrología ambiental del Sur de Córdoba, con énfasis en la ciudad de Río Cuarto y su entorno rural. Ph.D. thesis, UNRC. 300 páginas

Blarasin M, Cabrera A, Matteoda E, Gomez ML (2004) Estudio hidrogeológico para el diagnóstico y propuesta de solución del problema ocasionado por el ascenso del nivel freático en la ciudad de Coronel Moldes, Córdoba, Informe técnico. Municipio de Coronel Moldes, 20 páginas

Buchet J, Lauwerys R, Roels H (1981) Comparison of urinary excretion of arsenic metabolites after a single oral dose of sodium arsenite, monomethylarsonate, or dimethylarsinate in man. Int Arch Occup Environ Health 48(1):71–79

Bundschuh J, Bonorino G, Viero AP, Albouy R, Fuertes A (2000) Arsenic and other trace elements in sedimentary aquifers in the Chaco-Pampean Plain, Argentina: 31st International Geol. Cong., Río de Janeiro, Brazil, 2000, pp 27–32

Cabrera A, Blarasin M (2001) Geoquímica de Flúor y Arsénico en el agua subterránea del Sur de Córdoba, Argentina. En Las Caras del agua subterránea. Edit. Instituto Geológico Minero de España, Barcelona ISBN 84-7840-427-9-1

Cantú M, Degiovanni S (1987) Génesis de los sistemas lagunares del Centro Sur de la Prov. de Córdoba. X Congreso Geológico Argentino. San Miguel de Tucumán II, 120–129

Carrica JC, Albouy ER (1999) Variaciones hidroquímicas en el agua subterránea de localidades del Partido de Puán, Provincia de Buenos Aires (Groundwater hydrochemical changes in towns of Puán District, Buenos Aires province). Hidrología Subterránea. II Congreso Argentino de Hidrogeología. Santa Fe, Argentina. Ser Correl Geol 13:221–230

Carrica JC, Bonorino G, Delpino D (2002) Fluoruros en el agua de manantiales en la zona de Zapala, provincia del Neuquén. Argentina. XXXII AIH and VI ALHSUD CONGRESS, Agua Subterránea y Desarrollo Humano, Mar del Plata, Argentina

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

Custodio E, Llamas MR (1983) Hidrogeología subterránea. Seg. Edición (ed) Omega, S. A. Barcelona

Chebli G, Mozetic M, Rossello C, Bühler M (1999) Cuencas Sedimentarias de la Llanura Chacopampeana. Instituto de Geología y Recursos Minerales. Geología Argentina. Anuales 29(20):627–644

Chebotarev II (1955) Metamorphism of Natural Waters in the Crust of Weathering. Geochim Cosmochim Acta 8(22–48):137

Fernández Turiel JL, Galindo G, Parada MA, Gimeno D, García-Valles M, Saavedra J (2005) Estado actual del conocimiento sobre el arsénico en el agua de Argentina y Chile: origen, movilidad y tratamiento. Workshop Arsénico en aguas: origen, movilidad y tratamiento, Río Cuarto, Argentina. Actas, pp 1–22

Garrels RM, Christ CL (1965) Solutions, minerals and equilibrio. Harper & Row, New York, 450 pp

Hossain MA, Jungi A Sakugawa H (2004) Mobilization of arsenic from subsurfase by effect of bicarbonates ions in groundwater. Chemosphere 54(6):753–762

Kim K, Young Jeong G (2005) Factors influencing natural occurrence of fluoride-rich groundwaters: a case study in the southeastern part of the Korean Peninsula. Chemosfere 58(10):1399–1408

Marshall W, Warakomski M (1980) Amorphous silica solubility. II: Effect of aqueous salt solutions at 25°C. Geochim Cosmochim Acta 44:915–924

Martínez DE, Bocanegra E (2002) Hydrogeochemistry and cationic exchange processes in the coastal aquifer of Mar del Plata, Argentina. Hydrogeol J 10(3):393–408

Martínez DE, Osterrieth M (1999) Geoquímica de la Sílice Disuelta en el Acuifero Pampeano en la Vertiente Sudoriental de Tandilia. II Congreso Argentino de Hidrogeología, San Miguel de Tucumán, Argentina Ser Correlac Geol 13:241–250. ISSN 1514-4186

Nicolli H, Suriano JM, Gómez Peral MA, Ferpozzi LH, Baleani O (1989) Groundwater contamination with Arsenic and other trace elements in an area of the La Pampa province of Córdoba, Argentina. Environ Geol Water Sci 14(1):3–16

Nicolli HB, Tineo A, Falcon CM, García JW, Merino MH, Etchichury MC, Alonso M S, Tófalo O (2004) Aguas subterráneas con alto contenido en arsénico en el área de Los Pereyra, Tucumán, Argentina. XXXIII Congress IAH & 7° Congress ALHSUD. Zacatecas México. ISBN: 970-32-1749-4

Parkhurst DL, Appelo CAJ (1999) Useŕs guide to PHREEQC (Version 2): a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. U.S.G.S. Water-Resources Investigations Report 99-4259, pp 1–312

Plummer LN, Prestemon EC, Parkhurst D (1991) An Interactive Code (NETPATH) for Modelling NET Geochemical Reactions Along a Flow PATH. U.S.G.S. Water Resources Investigations, 4078, 227 pp

Saxena VK, Sanjeev Kumar, Singh V (2004) Occurrence, behaviour and speciation of arsenic in groundwater. Curr Sci 86(2):281–284

Smedley PL, Kinniburgh D (2002) A review of the source, behaviour and distribution of arsenic in natural waters. Appl Geochem 17:517–568

Smedley PL, Nicolli HB, Macdonald DMJ, Barros AJ, Tullio O (2002) Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Appl Geochem 17(3):259–284

Sracek O, Bhattacaharya P, Jacks G, Gustafsoon JP, von Brömssen M (2004) Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments. Appl Geochem 19(2):169–180

Teruggi M (1957) The nature and origin of the Argentine loess. J Sediment Petrol 27(3):322–332

Truesdell AH, Jones B (1974) WATEQ, a computer program for calculating equilibria in natural waters. USGS J Res 2(2):233–248

Turner B, Binnig P, Stipp L (2005) Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption. Environ Sci Technol 39(9):9561–9568

Valenzuela VL, Ramírez HJ (2004) Análisis del comportamiento del Flúor en el acuífero que abastece a Hermosillo, Sonora, México. XXXIII Congress IAH & 7° Congress ALHSUD. Zacatecas México. ISBN: 970-32-1749-4

Villalba G (1999) Estudio geohidrológico con énfasis en la geoquímica del Flúor de la cuenca del Río Talita, Dpto. Río Cuarto, Córdoba. Trabajo final de Licenciatura. URC. Inédito 200 pág

WHO (World Health Organization) (1993) Guidelines for drinking-water quality. 2nd edn, vol 1. 188 p

Zack A (1980) Geochemistry of fluoride in the Black Creek aquifer system of Horry and Georgetown counties, South Carolina and its Physiological implications. Washington, D.C.; Geological Survey water-supply Paper 2067