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# GROUNDWATER CONTAMINATED WITH ARSENIC AND FLUORIDE IN THE ARGENTINE PAMPEAN PLAIN

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*The phreatic aquifer of the Los Jagüeles basin is made up principally of Quaternary loessic sediments. It has sodium bicarbonate (high and middle basin) and sodium sulfate (lower basin) water, with fluoride and arsenic concentrations that exceed the permissible limits for human consumption. The major contents of fluoride and arsenic are found in the middle basin, where the predominance of loess, bicarbonate waters, and the highest $Na^+/Ca^{++}$ index values coincide. The fluoride is derived from the main components of loess, with anion exchange being the most important release mechanism. Arsenic is derived from the alteration of volcanic glass and, although it is generally related to reducing conditions, it occurs in the basin under oxidizing conditions. In this paper, some appropriate techniques to lower the concentrations of fluoride and arsenic are suggested.*

## INTRODUCTION

A hydrogeochemical investigation was carried out in the phreatic aquifer of a typical basin of the Argentine Pampean plain. The investigation is connected with the presence of fluoride (F) and arsenic (As), since they are considered natural pollutants of the plain. In the study basin, phreatic groundwater is the main source of supply for human consumption, and all the activities that take place there. These two elements are present in the groundwater at very high concentrations, which constitutes a very important risk for the health of inhabitants that consume it. Even though the World Health Organization (WHO) and the institutions of every country have set drinking water limits for these elements, very few studies have linked the concentrations of F and As and the health problems associated with them, an aspect which may also vary from one region to another. This deficiency of studies lies mainly in the lack of specific statistics from hospitals or in physicians' ignorance about the quality of the water their patients consume. In this paper, it is considered appropriate, instead of establishing fixed norms for the entire world, to adapt them to the conditions of every region. In this way, this investigation fits into a completely new study area termed "Geomedicine" (Låg, 1990). Within this framework, some correlations will be sought in the future between the contents of F and As and their effects on health, which will permit corroboration or modification of the existing groundwater quality guidelines for this region.

## RESULTS

### Study Area

The Los Jagüeles basin (40,000 ha), includes the rural and urban areas of three locations: Las Vertientes, Los Jagüeles and Malena, and it is situated in the South of Córdoba province, Argentina, between 33°10' and 33°40' south latitude and 65°00' and 64°15' west longitude (Figure 1). The drainage system is scarcely developed, with a main channel of perennial regime. The study area has a sub-humid mesothermal climate, with an annual mean rainfall of 793 mm, 85 percent of which is concentrated in spring-summer. The annual mean evapotranspiration is 711 mm, which gives a mean rainfall excess of 82 mm.

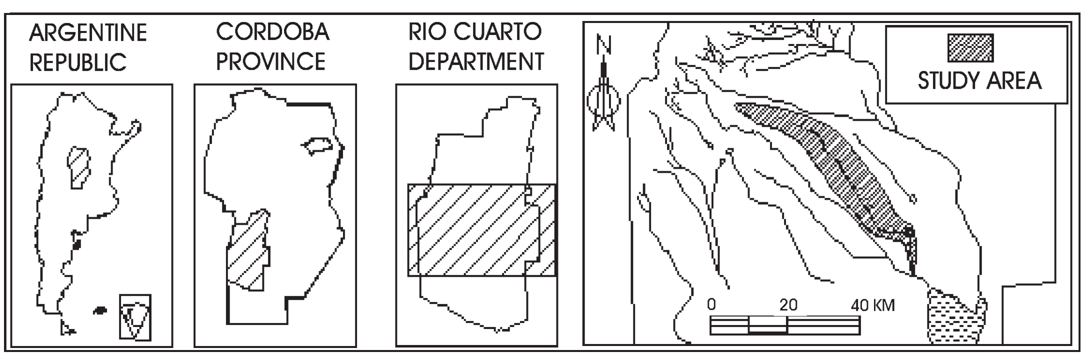


Figure 1. Relative location of Los Jagüeles basin

### Geology and Geomorphology

The basin is situated adjacent to the Comechingones Mountains. The igneous-metamorphic bedrock, which is upper Precambrian-middle Paleozoic, is present in small outcrops only in the high basin. In the rest of the area, Quaternary sediments exist (upper Pleistocene-Holocene), mainly of eolian and subordinately fluvial origin, which were deposited in this region during a succession of dry and humid climate periods. The main geologic structures of the basin, some of

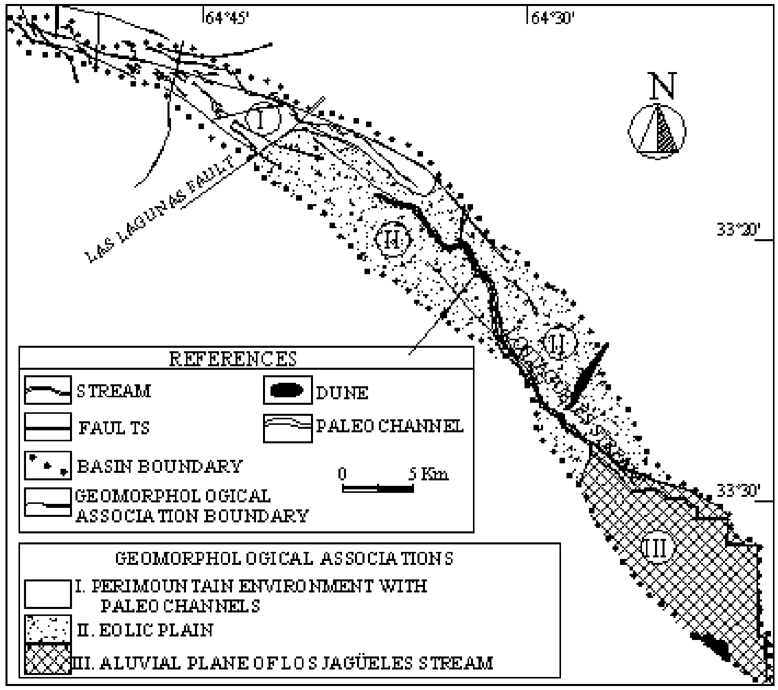


Figure 2. Geomorphological map.

which show relatively recent activity, have NW-SE and NE-SW orientation. Differential vertical movements have produced a morphology of east dipping blocks.

Three geomorphologic associations were determined (Figure 2). I) A perimountain environment with paleochannels. It is characterized by numerous fluvial paleofeatures with different levels of preservation and is covered by a more modern eolian mantle. Psammitic and psefitic sediments occur in paleochannels, and psammitic and pelitic sediments are found in the rest of the area. The soils are Haplustols and Argiustols. II) An eolian plain. It possesses a significant eolian cover, made of sandy fine-silt materials that cover the oldest features and deposits, with the presence of numerous longitudinal dunes. The soils are Haplustols. III) The alluvial plain of the Los Jagüeles stream. It includes the present channel and its overflow area. It is controlled partly by the structures of the area. It flows in a large paleochannel except for its downstream section where it is a man-made channel. The soils are Entisols and Haplustols.

## Hydrogeology

The phreatic aquifer has two different environments. I) a sector related to the perimountain environment with paleochannels, with fine, medium and coarse sand, and gravel sediments. In this area the aquifer is heterogeneous and anisotropic; the more permeable facies are represented by the paleochannels. II) The eolian plain sector, which includes the area where the stream overflows, with silts, fine sands, clays and calcretes, and subordinately, medium and coarse sands. In this section, the aquifer is more homogeneous and isotropic. In the high basin, the base of the aquifer is formed by bedrock; in the rest of the area, the base is a mantle of clays located at a depth of approximately 80 meters. In the high and medium basin the water table is slightly undulating, with a 1.6 percent hydraulic gradient. It is almost flat in the low basin, with a 0.5 percent hydraulic gradient. The groundwater flow direction is mainly west to east in the high basin and northwest to southeast in the middle and lower basin. The net area of regional recharge of the aquifer is the area surrounding the hills, although the entire basin is recharged by infiltrating rain water. The stream origin is a phreatic outcrop (discharge area). Water table elevations in the basin are in the range 0-40 m below ground surface.

Total dissolved solids in groundwater ranges from 250 mg/l to 3,500 mg/l. A normal geochemical evolution is observed, caused by an increase in the concentration of salts and a change in the anion facies in the direction of flow. The most important cause of this evolution is the distance traveled, even though there are local variations due to lithological changes and relief of the area. Groundwater is young, fresh, and of a geochemical sodium bicarbonate type in the high and middle basin, while it is more mature, brackish, and of a sodium sulfate type in the lower basin. The most important reactions that determine the chemical quality of groundwater are mainly the dissolution of salts, as a function of the solubility product (*Ks*), and redox reactions. Ion exchange

Table 1: Chemical Analysis of Some Typical Samples of the Los Jagüeles Basin

| Sample | pH | TDS [mg/l] | $CO_3^{=}$ [mg/l] | $HCO_3^-$ [mg/l] | $SO_4^{=}$ [mg/l] | $Cl^-$ [mg/l] | $Na^+$ [mg/l] | $K^+$ [mg/l] | $Ca^{++}$ [mg/l] | $Mg^{++}$ [mg/l] | $As^{+3/+5}$ [μg/l] | $F^-$ [mg/l] | $NO_3^-$ [mg/l] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| J4 | 7.94 | 1,053 | 0 | 625.0 | 115.6 | 18.0 | 256.8 | 7.6 | 4.8 | 4.9 | 100 | 10.6 | 10 |
| J6 | 8.38 | 392 | 4.9 | 230.0 | 29.1 | 6.4 | 81.4 | 5.9 | 8.8 | 3.9 | 20 | 1.4 | 20 |
| J19 | 8.07 | 1,093 | 0 | 462.5 | 217.8 | 87.4 | 265.9 | 15.5 | 21.6 | 10.7 | 50 | 3.5 | 8 |
| J48 | 8.14 | 805 | 0 | 520.0 | 45.2 | 18.0 | 193.1 | 10.4 | 4.8 | 4.9 | 500 | 8.2 | 0 |
| J50 | 7.42 | 1,125 | 0 | 590.0 | 132.3 | 77.1 | 289.2 | 12.2 | 10.0 | 7.3 | 300 | 6.8 | 0 |

reactions are also occur (Na-Ca, OH-F) which depend mainly on the sediments. The main characteristic of the groundwater is the presence of high concentrations of F and As, the behavior of which will be explained later. The samples analyzed correspond to wells that take water from the upper part of the aquifer. The chemical results that were obtained from five samples considered representative from the 68 analyzed are presented in Table 1.

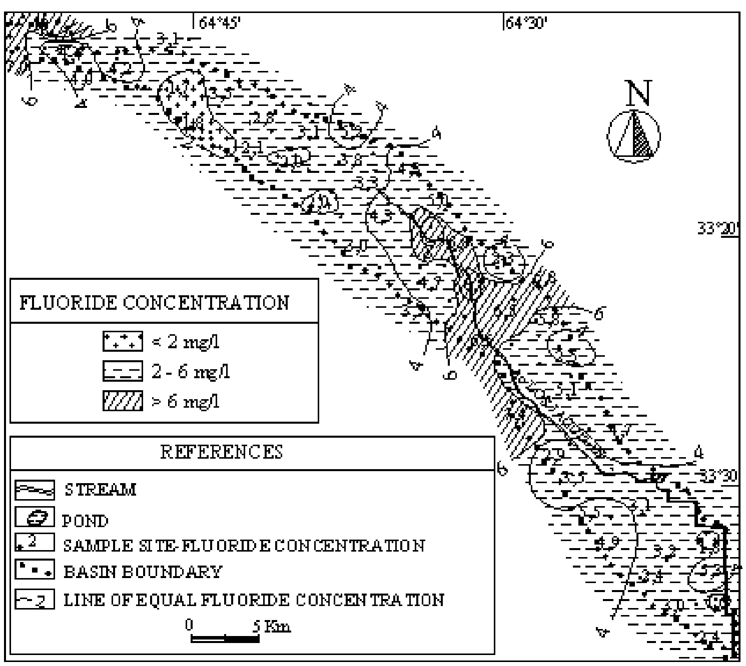


Figure 3. Fluoride concentration in groundwater.

- Fluoride

Epidemiological studies have shown that in order to produce symptoms of chronic toxicity, it is required to ingest daily and continually water with more than 10 mg/l F. The most evident symptom in the inhabitants of the studied area is dental fluorosis. The established limit for human consumption is set at 1.3 mg/l for the mean environment temperature of the region (16°C). In the basin, contents of F between 1.4 and 10.6 mg/l were determined, in all cases exceeding the established limit (Figure 3).

Previous studies of the behavior of this element show that it appears in the water by mineral dissolution or is released to the environment by anion exchange in minerals that give up F and bind other ions, OH and Cl (Zack, 1980). Thus, fluorapatite ($Ca_5(PO_4)_3F$) (Zack, 1980), mica and hornblende (Robinson, 1946), titanites and fluorites (Villalba, 1999), and volcanic glass (Nicolli et al., 1997) are considered possible sources of F. In addition, it is believed that the dissolution of $CaCO_3$ is responsible for the presence of F, since it allows the anion OH-F and the cation Na-Ca to exchange in clays (illites dominate), and it releases $HCO_3$ to the environment through the reactions (1) and (2). This hypothesis can be applied to the basin if it is considered that the groundwater is a sodium bicarbonate type with a high percentage of F.

$$CaCO_3 + H_2O = HCO_3^- + Ca^{++} + OH^- \quad (1)$$

$$CaCO_3 + Na_2\,(clays) + CO_2 + H_2O = 2\,Na^+ + 2\,HCO_3^- + Ca\,(clays) \quad (2)$$

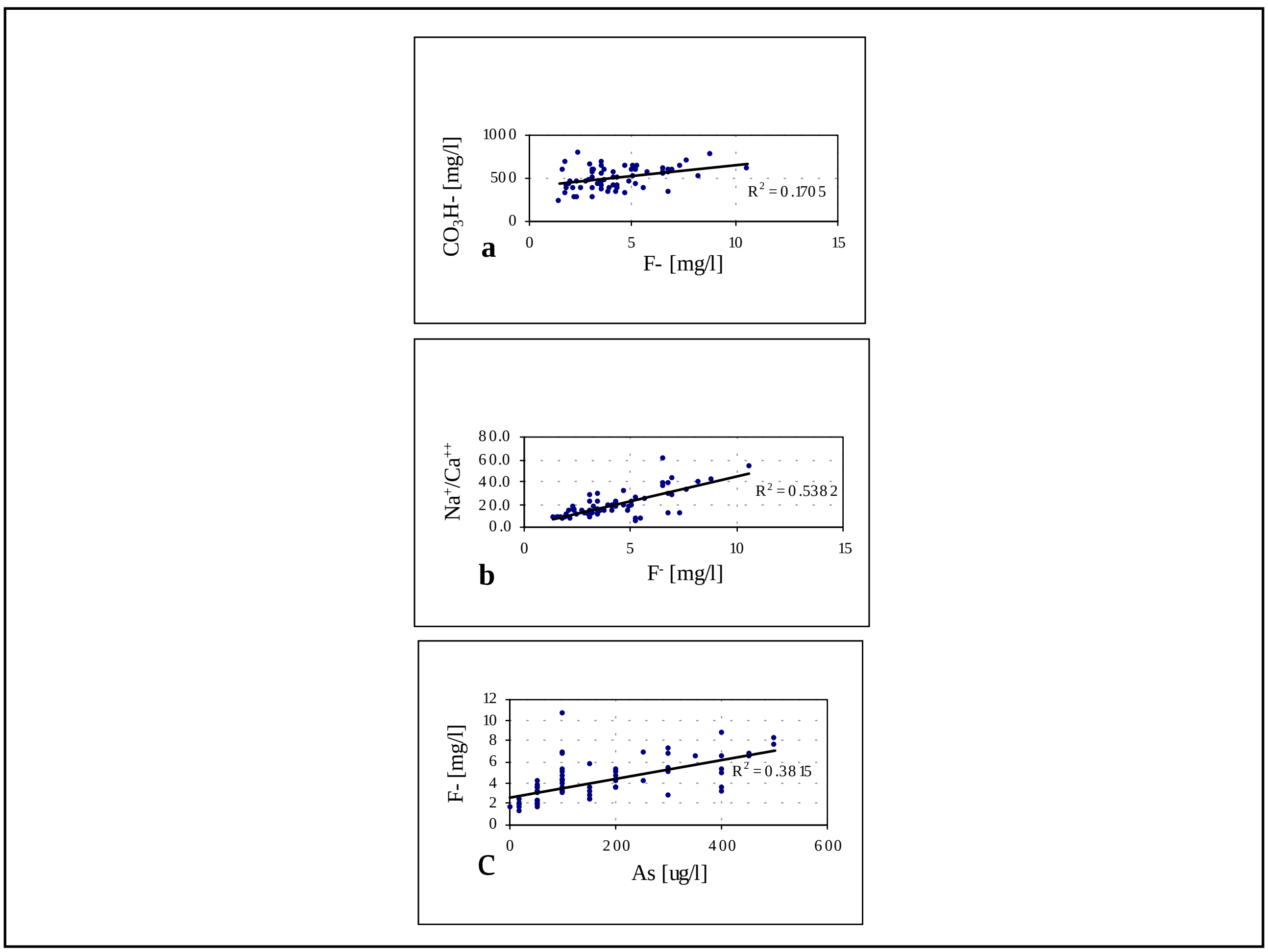


Figure 4. Relation between (a) $F^-$ and $HCO_3^-$, (b) $F^-$ and $Na^+/Ca^{++}$, (c) and $F^-$ and As.

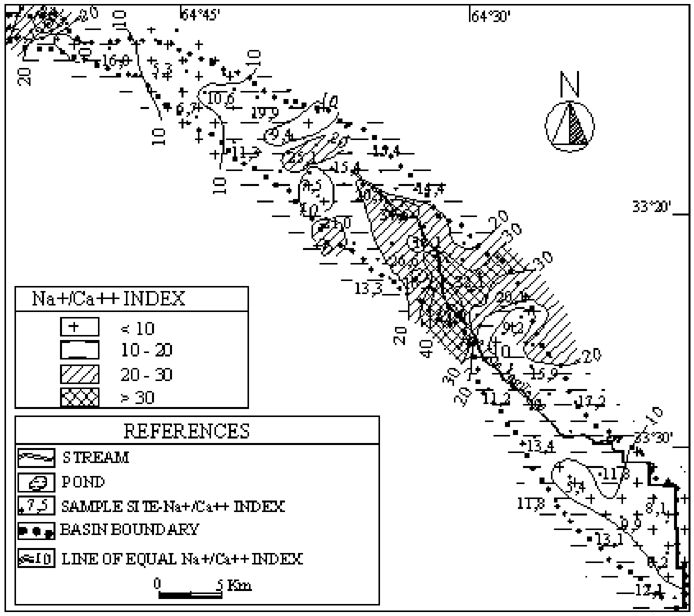


Figure 5. $Na^{+}/Ca^{++}$ index in groundwater.

The comparisons made among the different chemical elements analyzed do not show good correlations. The results found between F and $HCO_3$ and between F and Na/Ca are shown in Figures 4a and 4b. Even though the correlation coefficients are very low, the results of the hypothesis tests ($p < 5$ percent) allow a possibility of a linear relationship among these variables. In spite of the low correlations found, it is observed from the maps that the sectors that present the highest contents of F (Figure 3) are related to the highest Na/Ca index (Figure 5), to the presence of water of a geochemical bicarbonate type, and to the predominance of loessic materials. These materials present a high percentage of fluorapatite and volcanic glass, and are partially cemented with $CaCO_3$ (Blarasin, 1984), which would indicate the availability of carbonates for reactions (1) and (2). The conjunction of all these factors is present in the middle basin. Even though there exists a low positive correlation between F and As (Figure 4c), it can be interpreted from the maps that the spatial distribution of these two elements also have a high coincidence in the middle basin.

- Arsenic

The daily and continual consumption of high doses of As produces a chronic arsenic poisoning as the main effect on man. In Argentina, it is an endemic disease known as HACRE (Chronic Endemic Regional Hydroarsenicism) and the main symptoms are the thickening of the epidermis, ulcers in the mouth, intestinal tract disorders, melanosis and arsenic cancer. The limit for human consumption established in Córdoba province by the DAS (Sanitary and Water Direction) is 100 µg/l, while the WHO has recently established it at 10 µg/l. The As components vary in their toxicity, $As^{+3}$ (arsenites) being more toxic than the $As^{+5}$ (arsenates). The most important chemical species in natural water are $As^{+3}$, $H_3AsO_3$, $H_2AsO_4^{-}$, $HAsO_4^{=}$, which are highly soluble and stable under a wide range of Eh and pH. The $As^{+3}$ is more common under reducing conditions and in a wide range of pH, while $As^{+5}$ is more common in oxidizing environments and for the same pH. In other words, as As is present at different Eh levels, its occurrence depends mainly on the availability of As in the aquifer materials or on the introduction of As by pollutant sources (Smedley, 1996). In the study basin, in 99 percent of the analyzed samples, As varies between 20 and 500 µg/l (Figure 6). Even though in general As is associated to reducing conditions, in the basin it is present in oxidizing conditions. According to Nicolli et al. (1997), As would come from volcanic glass, which is the

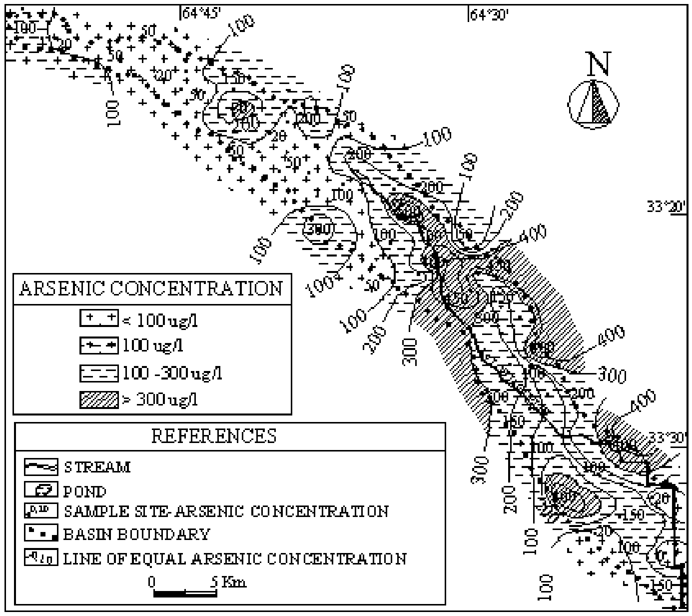


Figure 6. Arsenic concentration in groundwater.

main component of the loessic sediments of the area (Blarasin, 1984). From the relation between As and the chemical variables that were analyzed, a low positive correlation is observed with F, as has been shown. The correlation is low and positive between As and $HCO_3$ (Figure 7a) and between As and the Na/Ca index (Figure 7b). However, in this case also the maps show a high coincidence in the middle basin, where loessic materials, bicarbonate waters and the highest Na/Ca index predominate.

Multivariate analysis

A cluster treatment was applied to the data, resulting in a dendrogram (Figure 8) with two main hydrochemical groups. Group 1 is defined by the nucleus (TDS, Na) and the variables Cl and $SO_4$ and the nucleus (Ca and Mg) associated with the variables K and $NO_3$. Group 2 is defined by a nucleus (As and F) and the variable $HCO_3$ and the nucleus (pH, $CO_3$). These results support the interpretations made from the maps.

- Lowering of F and As in drinking water

Due to the problems discussed, special techniques to mitigate the levels of F and As are

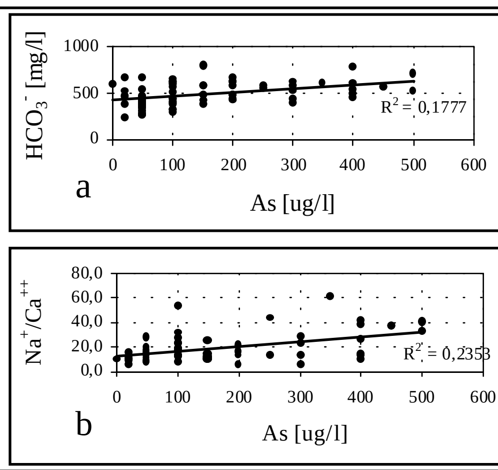


Figure 7. Relation between (a) As and $HCO_3^-$ and (b) $Na^+/Ca^{++}$.

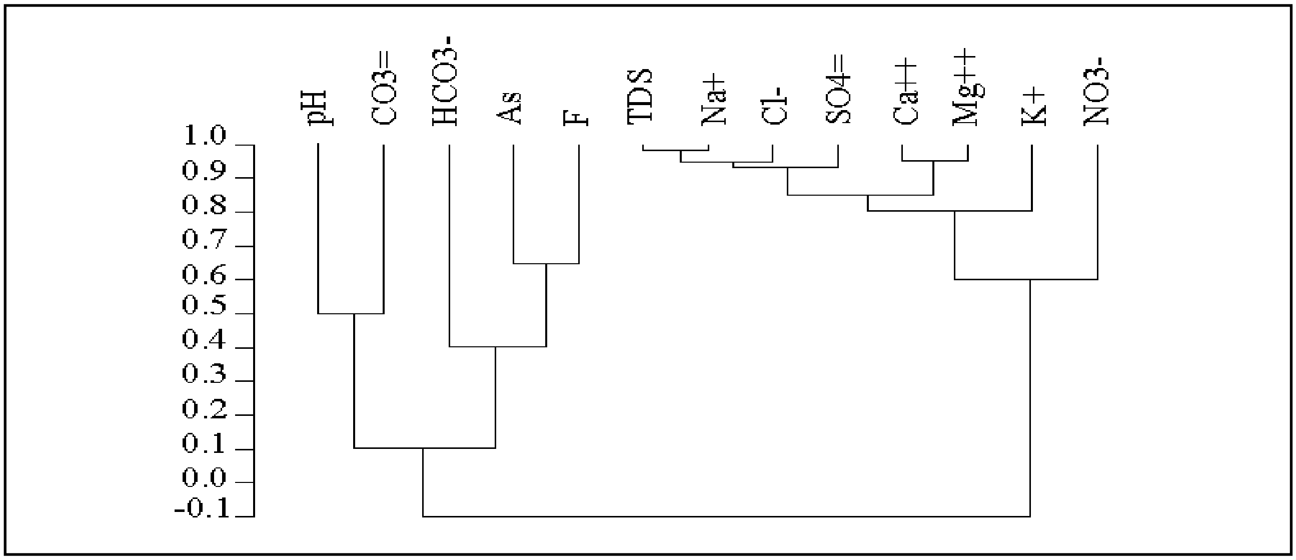


Figure 8. Cluster analysis.

required. There are different methodologies based on chemical and physical-chemical reactions that produce the adsorption, oxidation, coagulation-flocculation, or physical separation by processes of filtration-sedimentation of these ionic species. Nowadays, some effective and low cost methods are being applied (Castro, 1999), which have been developed in Argentina since the ‘70s. In Figure 7 an up-to-date summary of those techniques is presented

## CONCLUSIONS

1. The phreatic aquifer is made up of Quaternary sediments, mainly of loessic and subordinate fluvial origin.

2. Groundwater presents a normal geochemical evolution, produced by an increase in the salt concentrations and by a change in the anionic facies in the regional NW-SE flow direction. The most important factor in its evolution is the distance traveled, even though there are local variations due to lithological changes and relief of the area.

3. The main characteristic of groundwater is the presence of high concentrations of F and As which are derived from the main components of loess. Fluoride is derived from volcanic glass with fluorapatite, mica, hornblende and titanites with F in its chemical composition. The most important mechanism of release of F is ion exchange facilitated by the presence of calcium carbonate and clays in the aquifer. The processes of dissolution, that tend to be very slow, are of lesser importance. Arsenic would come from the alteration of volcanic glass, and although it is generally related to reducing conditions, in the studied basin it is related to oxidizing conditions.

4. The highest concentrations of F and As are in the middle basin, where three factors coincide: the predominance of loessic materials, bicarbonate waters and the highest Na/Ca index values.

5. Due to the fact that groundwater is the most used resource, domestic techniques for the lowering of As and F are recommended in rural areas with low population density. For the lowering of As the recommended techniques are the adsorption and coprecipitation with salts of Fe and Al, while for F the suggested technique is adsorption by hydroxyapatite. For urban areas the recommended technique is reverse osmosis accompanied by the mixture of waters of different quality. Table 2 summarizes the most widely used methods to mitigate F and As in Argentina.

Table 2. Summary chart of the most widely used methods to mitigate fluoride and arsenic in Argentina.

| Method | Physical-chemical principle | Obtained results | Advantages | Disadvantages | Place of application |
|---|---|---|---|---|---|
| Adsorption by hydroxyapatite | Adsorption of F and As by hydroxyapatite of calcinated, powdered bones | Very good: 95% of F and 90% of As. | Low cost | Interference due to the complex composition of bones. Some use synthetic hydroxyapatite | Chaco-Pampeana Plain |
| Reverse Osmosis | Flow of water through an acetate cellulose membrane under certain flow conditions | Very good (> 90%) | Practically total removal of F and As. Small plants of solar energy | High cost. Reconditioning of water for human consumption. Disposal of the effluents | Pampean Plain Santiago del Estero Salta. |
| Adsorption and coprecipitation of $As^{+5}$ with salts of F and Al | Oxidation of As with Cl; adding of activated clay to provide colloids to the water; adding of $Al_2(SO_4)_3$ or $FeCl_3$, to produce coagulation, precipitation and adsorption of $As^{+5}$. Decantation/filtration | Very good: (95% of $As^{+5}$). | Low cost. Easy domestic application. Removal of As and improvement of the bacteriological quality | Disposal of effluents | Salta Tucumán |
| Oxidation followed by filtration | Acidification with $H_2SO_4$ to pH 6.5; oxidation of As with NaOCl; flocculation and adsorption of As with $FeCl_3$; flocculation in anthracite and filtration on sand | Very good: reduction of 90% | Simple, low cost, easy maintenance technology | Necessity of mounting a cylinder of great capacity with a filtrating mantle of anthracite, gravel and sand | Santa Fe |

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