



Geochemical processes regulating F^- , As and NO_3^- content in the groundwater of a sector of the Pampean Region, Argentina



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HIGHLIGHTS

- The Pampean Region in Argentina presents serious water potability problems.
- The chemistry of the water depends on natural and anthropogenic processes.
- F^- , NO_3^- and As are the main ions limiting water quality in the phreatic aquifer.

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ABSTRACT

The presence of F^- and As in groundwater is common in volcanic aquifers. Excessive concentrations of these ions affect the quality of drinking water and can be harmful to health. When there is an anthropogenic source in phreatic aquifers, NO_3^- is incorporated to the groundwater components, deteriorating its quality. The objective of this work is to assess the geochemical processes that regulate the contents of F^- , As and NO_3^- of the groundwater in a sector of the Pampean Region in Argentina. This area is supplied with water by exploiting a multilayer aquifer, composed of a phreatic aquifer occurring in loess sediments and a fluvial semi-confined aquifer, separated by an aquitard. The results obtained show that the phreatic aquifer has a higher concentration of F^- , As and NO_3^- than the semi-confined aquifer. Fluoride derives from the dissolution of volcanic glass at a slightly alkaline pH and from anion exchange; however, it may also be absorbed by the reprecipitating carbonates. The As is released by desorption, with the main source being the glass and lithic fragments of the loess. The NO_3^- originates from the decomposition of organic matter, mainly in the septic tanks of the peri-urban areas. Meanwhile, the As and F^- content in the semi-confined aquifer is lower and its origin is the result of water inflow by vertical downward infiltration from the phreatic aquifer through the aquitard. The Pampean Region is one of the areas with the largest volume of agricultural exports in the world and at present it is undergoing a strong social and economic growth. Understanding the geochemical processes that regulate the quality of drinking water is of vital importance to generate water management guidelines aiming at minimizing the deterioration of drinking water sources.

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1. Introduction

Long-term consumption of water with high concentrations of F^- and/or As brings about negative effects on human health. Concentrations of F^- above 1.5 mg/L may cause an endemic disease called fluorosis (Handa, 1975; World Health Organization, 2004; Tennakoon, 2004; Chae et al., 2007; Cordeiro et al., 2012). The identification of this pathology varies with its severity, showing from stained teeth in less advanced

degrees to a crippling fluorosis in the most serious cases (World Health Organization, 2004). It is estimated that about 200 million people worldwide are supplied with water containing high concentrations of F^- (Edmunds and Smedley, 2004). Some of the countries where high contents of F^- in groundwater used for drinking have been reported are India (Ramamohana Rao et al., 1993; Karthikeyan et al., 1996; Viswanathan et al., 2009), Serbia (Mandinic et al., 2010), Korea (Chae et al., 2007), China (Zhang et al., 2003; Binbin et al., 2005), Cameroon (Fantong et al., 2010), Nigeria (Gbadebo, 2012), Pakistan (Shah and Danishwar, 2003), Spain (Sanz Pérez and Sanz, 1999), Italy (D'Alessandro et al., 2008), Portugal (Cordeiro et al., 2012), Mexico

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(Grimaldo et al., 1995), Chile (Mella et al., 1994), Brazil (De Souza et al., 2013), Argentina (Kruse and Ainchil, 2003; Paoloni et al., 2003), etc.

Moreover, according to public health researchers, As exposure leads to an increase in infant mortality rates (Rahman et al., 2010), reduced intellectual function in children (Wasserman et al., 2004; Wang et al., 2007), and an increase in adult mortality rates (Argos et al., 2010) as a result of cardiovascular disease (Chen et al., 2011), as well as lung, liver and bladder cancer (Smith et al., 2000). At present, over 100 million inhabitants in Bangladesh, Pakistan, India, Nepal, Vietnam, Cambodia and China are thought to be chronically exposed to As due to drinking groundwater that fails to meet the guideline set by the World Health Organization (0.01 mg/L; Ravenscroft et al., 2009).

In phreatic aquifers, where oxidizing conditions predominate, NO_3^- is a common ion in groundwater and its origin is usually associated with sources external to the aquifer system, such as septic tanks (Canter and Larry, 1996), cattle (Sankaramakrishnan et al., 2008), agriculture (Datta et al., 1997; Bijay-Singh and Singh, 2004; Kundu and Mandal, 2009), etc. A high level of NO_3^- (50 mg/L) in the drinking water can cause methemoglobinemia or 'blue baby syndrome' in infants and gastrointestinal cancer in adults (McDonald and Kay, 1988).

In aquifers of volcanic origin, F^- and As are usually natural elements of groundwater that sometimes exceed the potability limit (Ashley and Burley, 1995; Tekle-Haimanot et al., 2006; Vivona et al., 2007; Rango et al., 2009; Cordeiro et al., 2012). In phreatic aquifers with NO_3^- contributions of anthropogenic origin, this ion is added to the components of groundwater, deteriorating its quality (Datta et al., 1999; Sankaramakrishnan et al., 2008; Kundu et al., 2009; Kundu and Mandal, 2009).

The objective of this work is to assess the geochemical processes that condition the water chemistry, in particular the contents of F^- , As and NO_3^- in a sector of a multilayer aquifer occurring in the Pampean Region in Argentina. This aquifer constitutes the only source of drinking water in the area, which is why the study of the different aquifer layers that constitute it is of interest for the development and management of the water resources in the region.

2. Materials and methods

2.1. Study area

The Pampean Region is one of the areas with the highest volume of agricultural exports in the world, and at present it is undergoing a strong social and economic growth. It extends over an area of 420,305 km², covered by volcanic sediments of loess type where the phreatic aquifer occurs. This aquifer, which is part of a multilayer aquifer together with the underlying semi-confined aquifer, has serious quality problems in some areas in relation to the high concentrations of F^- and As, as well as of NO_3^- sometimes (Smedley et al., 2002, 2005; Bundschuh

et al., 2004; Warren et al., 2005; Gomez et al., 2009). Arsenic- and fluoride-related diseases potentially affect 2 to 8 million inhabitants in Argentina (Bundschuh et al., 2012).

The study area includes a sector of the Pampean Region located in the northeast of the Province of Buenos Aires (Fig. 1). The region is covered by a thick mantle of loess, with an approximate thickness of 54 m in the study area. This material of volcanic origin contains plagioclase, quartz, orthoclase, volcanic glass and carbonate concretions among its main components, and the systematic absence of apatite is noteworthy (Teruggi, 1957). Glass is always present but its proportion is variable; the finer fractions are represented by montmorillonite and illite (Teruggi, 1957). This fine fraction becomes more abundant towards the base of the sequence, where a 10-m-thick clay layer can be found. The underlying fluvial-deltaic deposits are composed by fine to medium sands of quartz composition (Santa Cruz, 1972) with an average thickness of 20 m. The set of loess and fluvial sediments form a multilayer aquifer, composed of a phreatic aquifer hosted in the loess, with a basal clay layer acting as an aquitard and a semi-confined aquifer occurring in river sands (Fig. 1). These are underlain by a clay layer (aquiclude), and all of the underlying aquifer formations contain saline water unfit for human consumption (Sala, 1983). The recharge of the phreatic aquifer is by rainwater infiltration, while the semi-confined aquifer in the study area is recharged by the downward vertical seepage from the phreatic aquifer through the aquitard layer (Sala, 1983). This is due to the fact that the sand composing the semi-confined aquifer does not crop out, so its recharge is indirect at the sites where the phreatic aquifer has a larger hydraulic potential than the semi-confined one (Auge, 1986). The discharge of the phreatic aquifer occurs locally into surface watercourses, whereas the discharge of the semi-confined aquifer is towards the phreatic aquifer at the sites where the hydraulic potentials are reversed (Auge, 1986). At a regional level, the discharge of the semi-confined aquifer occurs towards the littoral of the Province of Buenos Aires (Río de la Plata) and towards a depressed region (Salado Basin) located to the southwest of the study area, in the centre of the abovementioned province (Fig. 1; Auge et al., 2002).

The source of the water supply in the study area is the exploitation of the multilayer aquifer. In the urban area, there is a sewage network, the water extraction wells are generally in the semi-confined aquifer and the supply is by means of water mains. In suburban areas, due to the lack of sewers, wastewater is discharged into septic tanks and there are private water wells whose drillings are mostly in the phreatic aquifer (Fig. 1). These septic tanks constitute sources of contamination that may supply NO_3^- into the phreatic aquifer. Although the water quality of the semi-confined aquifer is better, the cost of drilling causes this aquifer to be exploited only by organisms that supply the urban centres.

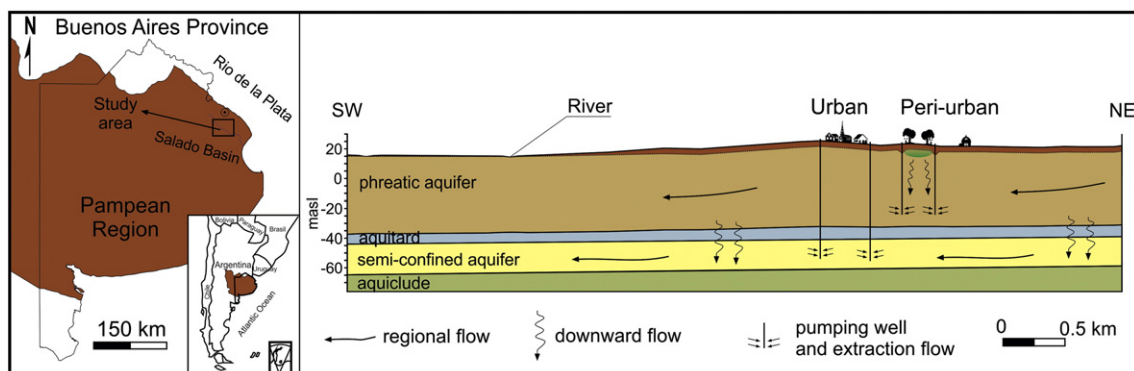


Fig. 1. Geographical location of the study area and hydrogeological profile showing the dynamics of the phreatic and semi-confined aquifers.

2.2. Methodology

A study of the geological characteristics and the thickness of the formations that compose the multilayer aquifer were undertaken on the basis of the lithological records of water wells existing in the study area. The data analysed in this paper correspond to private water wells drilled in the phreatic aquifer or to the drinking water supply pumped from the semi-confined aquifer. These data come from the drill logs and quality monitoring carried out by the Servicio Provincial de Agua Potable y Saneamiento Rural (Potable Water and Rural Sanitation Service of the Province of Buenos Aires; SPAR) and the Autoridad del Agua (Water Board; ADA) in that location. The collection, preservation and chemical analysis of the water samples were carried out in accordance with the standard methods proposed by the American Public Health Association (APHA, 2012). Sodium (Na^+) and potassium (K^+) were determined by flame photometry. Hardness as calcium carbonate (CaCO_3), calcium (Ca^{2+}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and chloride (Cl^-) were determined by volumetric methods. Magnesium (Mg^{2+}) was calculated on the basis of the data on calcium and total hardness. Sulfate (SO_4^{2-}) was measured by nephelometry, nitrates (NO_3^-) by spectrophotometry, F^- by selective electrode, As by silver diethyldithiocarbamate and the amount of total dissolved solids (TDS) was assessed by gravimetry. A characterization of the water type was carried out by means of a Piper-Hill-Langelier diagram (Fig. 2; Piper, 1944) and the relationships between the components were analysed using bivariate plots. An analysis of the correlation between the physical and chemical parameters determined was carried out for each aquifer studied by means of correlation matrices.

3. Results

The water classification diagram based on major ions shows that the water from the phreatic aquifer is Na-HCO_3 with a slight tendency to Ca-HCO_3 , while in the semi-confined aquifer it is Na-HCO_3 with a tendency to Na-Cl . TDS content in the phreatic aquifer varies between 500 and 1218 mg/L and in the semi-confined aquifer, between 693 and 1469 mg/L (Table 1). The correlation matrix constructed shows that in the phreatic aquifer the TDS positively correlates mainly with hardness and Cl^- , with a correlation coefficient close to 0.60 (Table 2, Fig. 3a), whereas in the semi-confined, it does with the Cl^- , with a correlation coefficient of 0.89 (Table 2, Fig. 3b).

High concentrations of F^- and As are the main limiting factors for human consumption in the phreatic aquifer, which is not the case in the semi-confined aquifer. Concentrations in the phreatic aquifer reach values of 1.95 mg/L of F^- and 0.13 mg/L of As, while in the semi-confined aquifer the values are 1.2 mg/L and 0.09 mg/L, respectively (Table 1). The WHO recommends a maximum limit of F^- in drinking water of 1.5 mg/L (depending on the average temperature of each locality), taking into account the volume of water consumed and the intake from other sources. The results obtained for this ion show that 22% of the samples of the phreatic aquifer are above the maximum limit. The suggested limit for As is 0.01 mg/L, although it should be noted that this benchmark is provisional, since there is evidence of the dangers of As even if the effects on health are poorly documented for this value. The results recorded in the phreatic aquifer show that 100% of the samples exceeded this value. The increase in F^- concentration shows that mainly in the phreatic aquifer there is a direct relationship

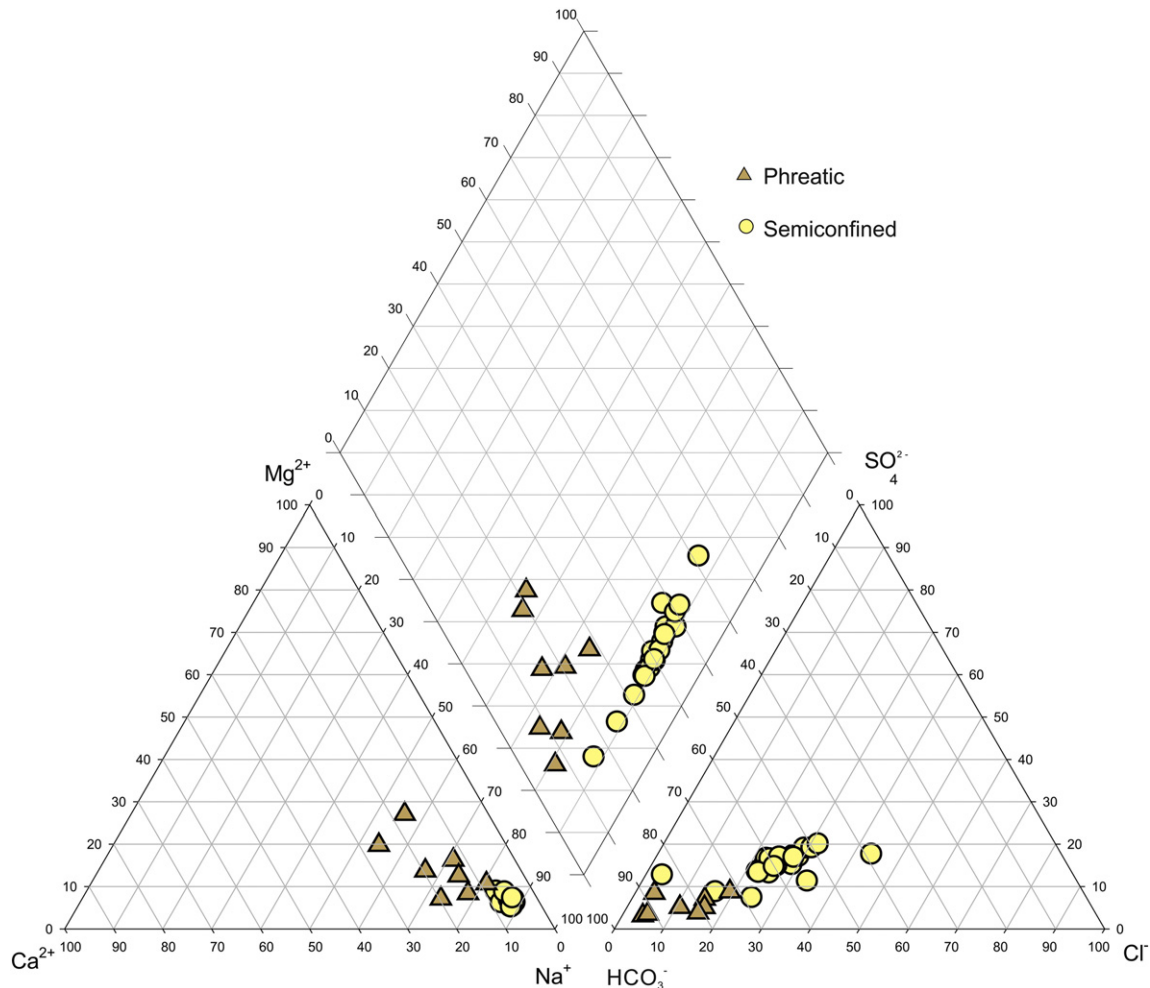


Fig. 2. Piper-Hill-Langelier water classification diagram.

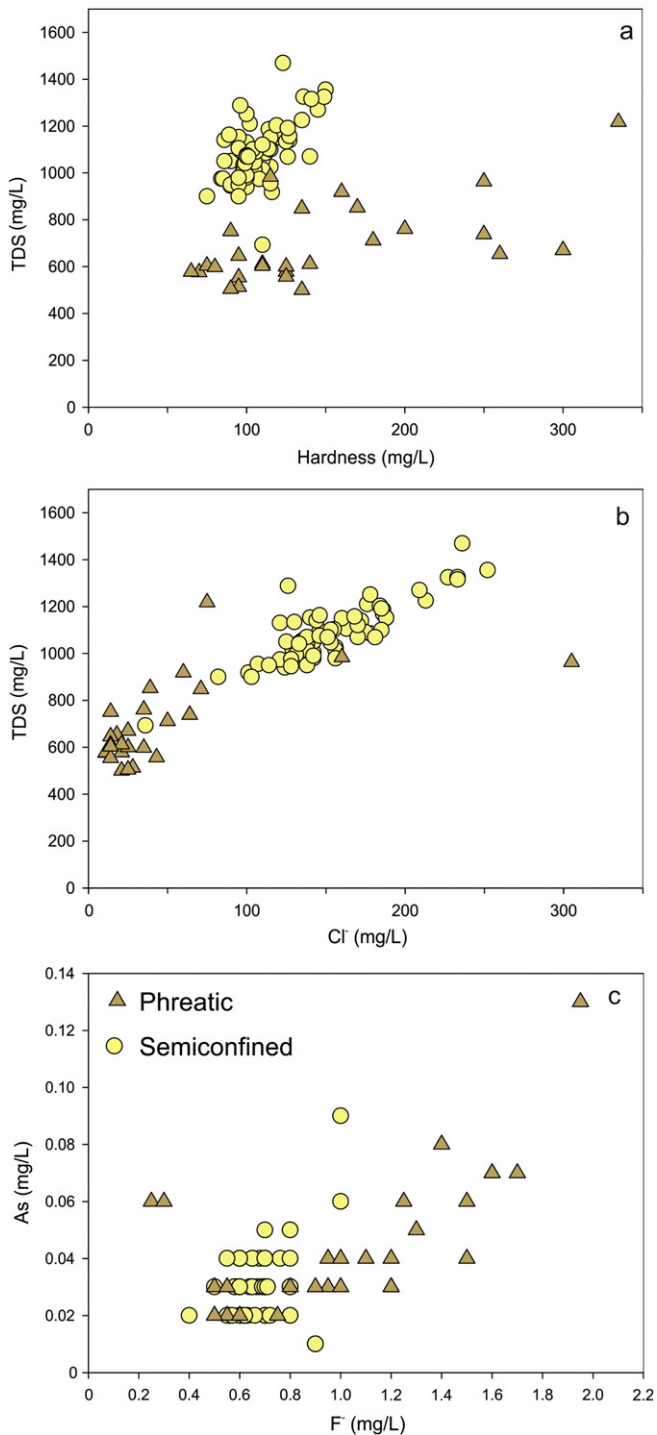


Fig. 3. Relationship between the concentrations of Cl^- vs. TDS and F^- vs. As in the phreatic and semi-confined aquifers.

7 mg/L (Table 1), showing low correlation coefficients with pH and hardness (Fig. 5c and d, Table 2). Even though the low NO_3^- concentrations prevent the observation of a trend regarding F^- and As concentrations (Fig. 5e and f), a positive correlation of 0.57 and 0.39, respectively, was registered between these parameters.

4. Discussion

The dissimilarities observed in the facies types, concentrations and ion relations indicate that different geochemical processes regulate the water chemistry of both the phreatic and semi-confined aquifers.

As regards the phreatic aquifer, part of the ions is acquired as rainwater infiltrates the unsaturated zone (UZ), owing to the fact that a reaction occurs between rainwater and the $\text{CO}_{2(g)}$ present in the atmosphere and in the sediment pores, which in turn generates HCO_3^- and H^+ . The hydrogen ion acidifies water, which dissolves the carbonates. Carbonate dissolution causes a decrease in acidity, which in turn is recovered in the UZ by the further dissolution of $\text{CO}_{2(g)}$ mostly originating in the roots and in the decomposition of soil organic matter, as well as by the atmosphere. Below the water table, as carbonate dissolution consumes H^+ and $\text{CO}_{2(g)}$, the water loses acidity due to the fact that it cannot incorporate $\text{CO}_{2(g)}$ to the system, which decreases its capacity to dissolve and attack minerals (Hem, 1985; Appelo and Postma, 2005). Once within the aquifer and in the deeper sector, the pH tends to increase. This increase and the predominance of bicarbonate facies cause the Ca^{+2} ions dissolved in water to precipitate as calcium carbonate, forming aggregates in the matrix or concretions in the loess sediments. As a consequence of the precipitation of carbonates, hardness tends to decrease as the pH becomes more alkaline. Similarly, Ca^{2+} precipitation determines a decrease in such ions in solution, with Na^+ becoming the dominant cation, which causes the predominance of Na-HCO_3 facies.

The volcanic glass occurring in the loess begins to dissolve as groundwater reaches slightly alkaline pH values. The correlation observed between the concentrations of F^- and As in the phreatic aquifer is the result of the interaction between groundwater and the loess sediments. One of the main components of these sediments is volcanic glass, which usually contains such trace elements (Tricart, 1973). The lithic components and rhyolitic volcanic ashes are also possible sources for these ions (Nicolli et al., 1997). Elevated concentrations of F^- and As are recorded in loess aquifers in several Argentine provinces, such as La Pampa (Smedley et al., 2002), Buenos Aires (Kruse and Ainchil, 2003), Tucumán (Warren et al., 2005), Santiago del Estero (Bundschuh et al., 2004), Santa Fe and Córdoba (Nicolli et al., 1989, 2009; Gómez et al., 2009). In every case, their origin is mainly explained on the basis of the dissolution of the volcanic glass occurring in the loess. However, the concentrations of F^- and As observed vary due to the natural compositional heterogeneities of volcanic glass (Tricart, 1973).

If the increase in pH dissolves the volcanic glass, the F^- and As ions are released into solution, the Ca^{2+} reprecipitates and the Na-HCO_3 facies predominate. Therefore, it is logical to expect a strong positive correlation between pH and the increase in F^- , As and Na^+ concentrations and a negative correlation between the last two and Ca^{2+} . However, the correlation between such parameters is low, which is why there must be another process regulating the mobility of F^- and As (Table 2). The release of F^- from the aquifer matrix by anion exchange favoured by the presence of carbonates is another process that could also occur in the phreatic aquifer (Zack, 1980). The CaCO_3 in an aqueous medium is dissolved, originating HCO_3^- , Ca^{2+} and $(\text{OH})^-$ ions, where the Ca^{2+} is exchanged by Na^+ , favouring the dominance of Na-HCO_3 facies and the $(\text{OH})^-$ is exchanged by F^- , increasing the concentration of the latter in groundwater. Also as regards F^- , high concentrations of Ca^{2+} may lead to the precipitation of fluorite (Martinez et al., 2012), or the presence of apatite could also condition the concentrations of that ion. However, in the loess sediments, the presence of minerals that may have F^- in their structure (e.g., apatite, fluorite; Teruggi, 1957) has not been reported. The adsorption in reprecipitated carbonates is a possible explanation, since—as mentioned in detailed studies—calcite precipitation can decrease F^- concentrations by adsorption (Gaciri and Davies, 1993; Turner et al., 2005).

Regarding As, it is known that Fe minerals, such as magnetite, ilmenite, biotite, goethite and hematite, and Mn oxides may retain or release As by desorption (Smedley et al., 2000; Hasan et al., 2008; Reza et al., 2010). At a pH between 7.3 and 8.6 and a high alkalinity, the As may derive from the desorption of Fe–Mn oxides. Even though there are no data on Fe and Mn to compare these ion relations, this process is feasible since it has been studied in other sectors of the loess aquifer (Smedley et al., 2000). It should be noted that the As desorption process requires

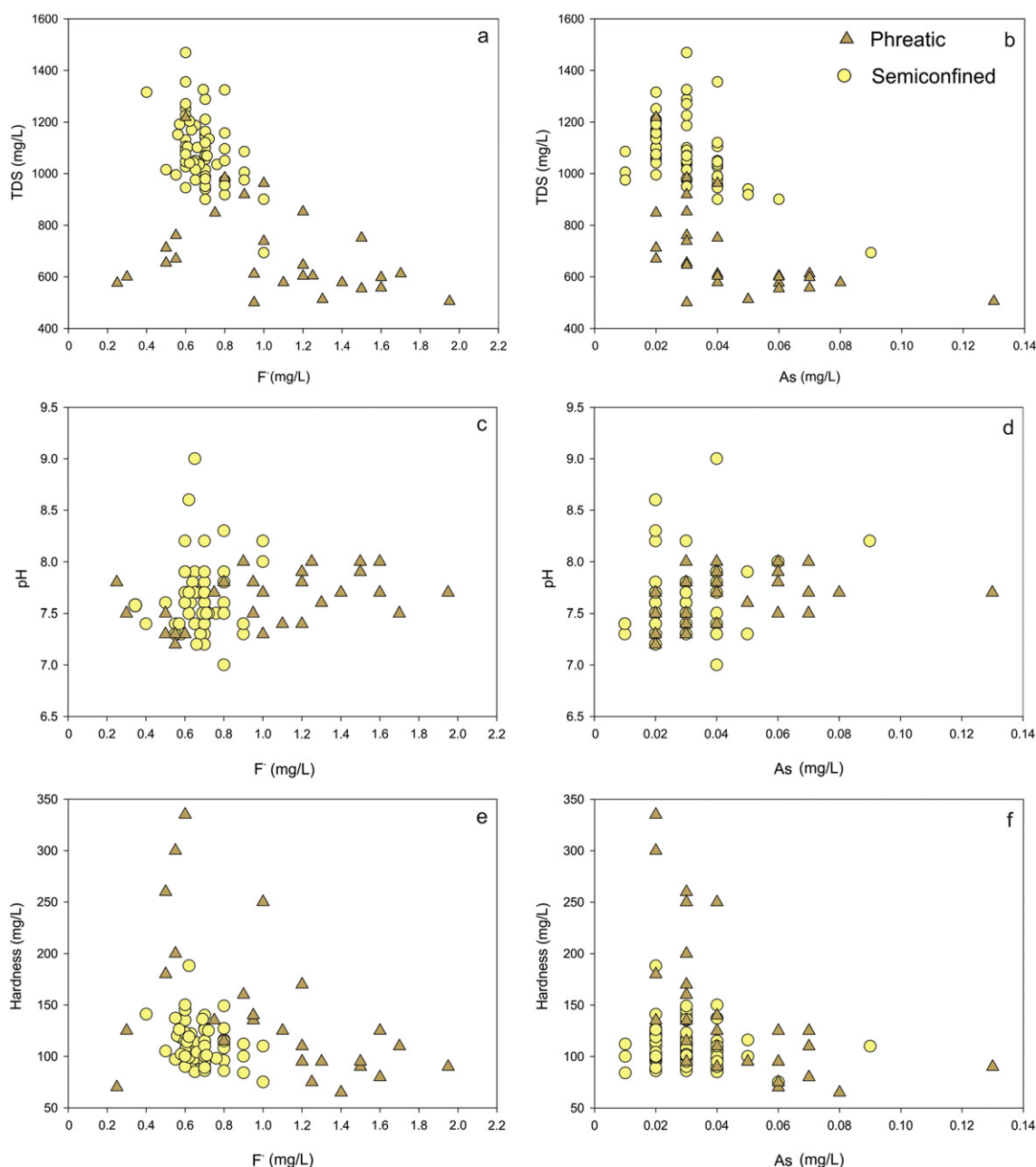


Fig. 4. Relationship between the concentrations of F^- and As vs. hardness, pH and TDS in the phreatic and semi-confined aquifers.

a slow groundwater flow, which occurs in the study area due to the low hydraulic gradient of the plain (10^{-4}) and the medium to low permeability of the loess (Sala, 1983). In the desorption process, the anions of the As species may compete with the HCO_3^- (Su and Suarez, 1997; Appelo et al., 2002), V (Smedley et al., 2000; Fiorentino et al., 2007) and P (Hingston et al., 1971; Manning and Goldberg, 1996). Out of such ions, the present work verifies the importance of the HCO_3^- , which may condition the adsorption of As. The presence of $Na-HCO_3$ facies and high Na^+/Ca^{2+} ratios, such as the ones observed in the study area (with values close to 10), are conditions that favour the desorption of As and the consequent increase in its concentration in groundwater (Smedley et al., 2000).

The inverse relation observed between F^- and As, and TDS is due to the fact that in the phreatic aquifer the TDS mainly derives from the increase in hardness (high positive correlation between TDS and hardness), which occurs in slightly acidic pH levels where volcanic glass is more stable.

The set of hydrogeochemical characteristics observed regarding F^- and As have also been registered in aquifers in other regions worldwide (e.g., Meenakshi and Maheshwari, 2006; Saxena and Ahmed, 2003; Chae et al., 2007; Viswanathan et al., 2009; Guo et al., 2014).

In turn, as regards the NO_3^- sources, it can be observed that the samples with higher concentrations correspond to the urban area in the periphery of the inner city, which has no sewer system. In peri-urban areas, the presence of septic tanks that are badly built or that intersect the water table are the main source of the NO_3^- entering the phreatic aquifer (Borzi and Carol, 2014). The N_{org} that composes the organic matter reacts with the dissolved O_2 , generating NH_4^+ and HCO_3^- ions. Subsequently, the NH_4^+ is transformed first into NO_2^- and then into NO_3^- by means of a series of reactions in which nitrifying bacteria—which also contribute H^+ to groundwater—intervenes. In this way, the anthropogenic contribution of NO_3^- , associated with the decomposition of organic matter of faecal origin, causes a decrease in pH and, consequently, a

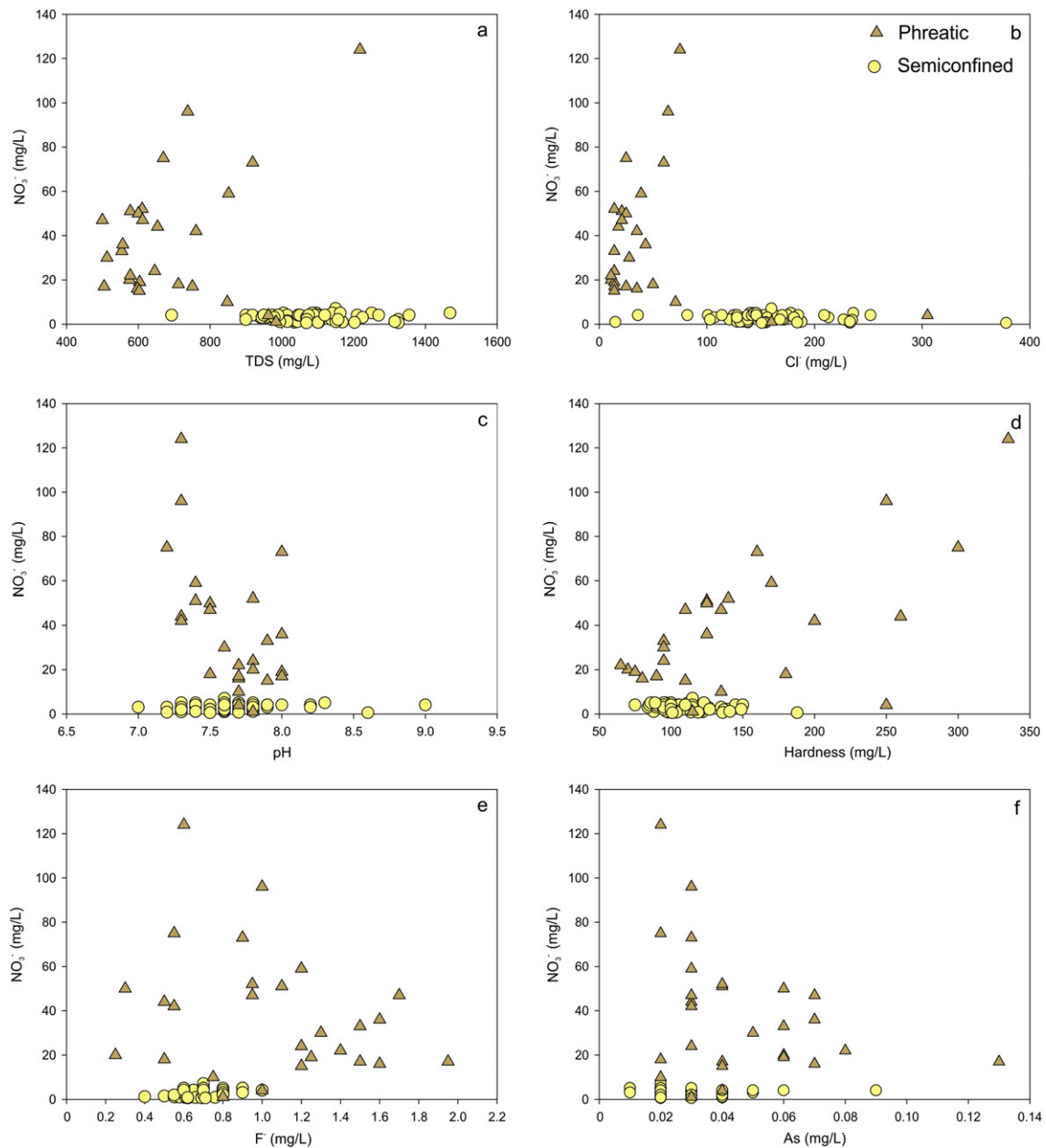


Fig. 5. Relationship between the NO_3^- concentrations depending on F^- , As, hardness, pH, Cl^- and TDS in the phreatic and semi-confined aquifers.

decrease in the dissolution of volcanic glass. This process explains the inverse relationship observed between the concentrations of F^- and As and the NO_3^- content. Besides, in the areas with NO_3^- contamination, lower pH values favour the dissolution of carbonates, an increase in water hardness and the trend towards Ca- HCO_3 type water.

All of the processes registered in the geochemical analysis of the phreatic aquifer cannot be observed in the semi-confined aquifer. The quartz sands that compose this aquifer do not contribute components in solution to the groundwater. Apart from this, there are no sources of anthropogenic contributions, which indicates that the saline enrichment observed in this aquifer depends on the regional evolution of the groundwater flow, where the more conservative components, such as chlorides, tend to dominate. At a regional scale, the Cl^- and TDS concentrations tend to decrease towards the northeast and to increase towards the southwest, showing a relationship between the path of the groundwater flow and the increase in the TDS and Cl^- concentrations (Auge, 2002). This explains the correlation observed between TDS and Cl^- , as well as the trend towards Na-Cl facies.

Regarding the NO_3^- , there is no direct connection with the contribution by anthropogenic sources, and the low values recorded are typical of the background (Canter and Larry, 1996). The presence of F^- and As is caused by the contribution of water from the phreatic aquifer. In the study area, the position of the water level in the phreatic aquifer is higher than in the semi-confined aquifer, which generates a downward flow through the aquitard. This downward flow causes the ions that are dispersed all over the thickness of the phreatic aquifer (among them, F^- , As and NO_3^-) to flow towards the semi-confined aquifer. Out of these ions, it can be expected for NO_3^- —whose source is associated with septic tanks—to have a higher concentration in the most superficial sectors of the aquifer near the source; however, its conservative characteristics determine its presence all over the aquifer thickness. Besides, due to the hydraulic connection occurring in the multilayer aquifer, the intensive exploitation of the semi-confined aquifer lowers the levels and generates a greater hydraulic gradient difference between the phreatic and semi-confined aquifers, increasing the downward flow. Even though the clay components of the aquitard may protect the semi-confined

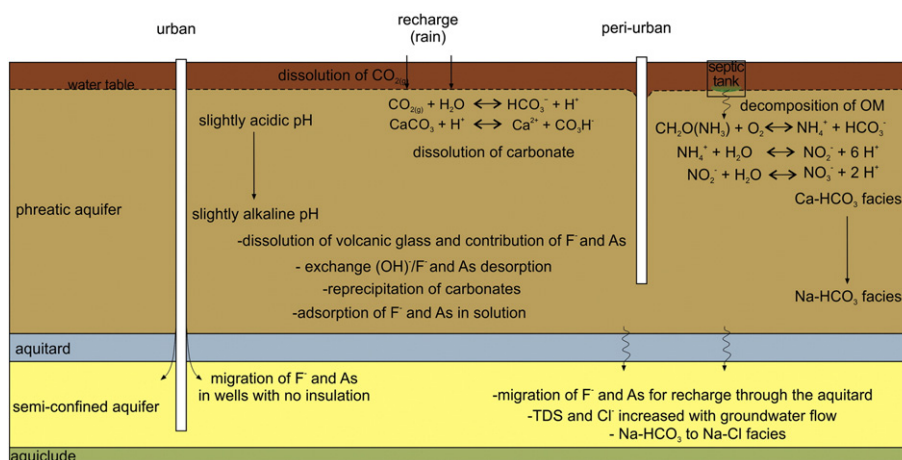


Fig. 6. Scheme showing the geochemical processes that regulate water quality in each aquifer.

aquifer against the inflow of pollutants from the phreatic aquifer (by adsorption, ion exchange, etc.), the existence of wells lacking an insulating seal favours the direct water inflow from the phreatic aquifer, as observed in other areas of the Pampean Region (Auge, 2005). An upward flow from the semi-confined aquifer to the phreatic aquifer is mainly registered in the littoral zone of the Province of Buenos Aires but not in the study area (Sala, 1983; Auge, 2005), which is why the migration of ions from the semi-confined aquifer to the phreatic aquifer would not be possible. However, should there be an upward flow, the sand composing the semi-confined aquifer is quartzose and has no mineral components that may release F^- and As into the groundwater (Santa Cruz, 1975).

Since the phreatic aquifer is less saline, and considering that the contributions of F^- and As enter the semi-confined aquifer by downward flow, in the semi-confined aquifer the higher concentrations of F^- and As are expected to be associated with lower saline contents, as observed in the negative correlations obtained between these parameters. All of the geochemical processes determined for the phreatic and semi-confined aquifers are summarized in Fig. 6.

5. Conclusions

The mobility and presence in solution of F^- and As in the phreatic aquifer are related to both natural and anthropogenic processes. Natural processes are associated with the interaction of groundwater with the loess components. At a slightly alkaline pH, the volcanic glass in the loess starts to dissolve, contributing F^- and As ions. In such pH conditions, the F^- may also be released into solution by anion exchange, although it may also be adsorbed by the reprecipitating carbonates. Similarly, the desorption of the As in volcanic glass and lithic materials in the loess is favoured by the slightly alkaline pH, the presence of $Na-HCO_3$ water and the slow groundwater flow.

The supply of NO_3^- of anthropogenic origin, the degradation of organic matter in septic tanks and the incorporation of $CO_{2(g)}$ occurring in the most superficial sectors regulate these processes. Even though the interpretation of chemical data shows that higher concentrations of NO_3^- are associated with low concentrations of F^- and As, NO_3^- is not directly responsible for the existence of a lower solubility of volcanic glass, but rather the pH is. In these slightly acidic pH conditions, the dissolution of carbonates is the dominant process. Subsequently, pH tends to increase with the groundwater flow, the volcanic glass is dissolved, releasing F^- and As, and the carbonates reprecipitate, adsorbing part of the F^- in solution.

Even though the semi-confined aquifer has limitations regarding As, its water is the most suitable for human consumption. This is due to the fact that its mineral components have no elements that may dissolve and affect their potability, as well as to the fact that the clay in the

aquitard layer tends to capture ions during the vertical recharge of the semi-confined aquifer from the phreatic aquifer.

Understanding the geochemical processes that regulate the quality of drinking water is of vital importance, not only to control its quality for the inhabitants, but also to generate guidelines for water management that aim at minimizing the deterioration of its sources.

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