

Abundance and distribution of fluoride concentrations in groundwater: La Ballenera catchment, southeast of Buenos Aires Province, Argentina

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Abstract High concentrations of fluoride have negative effects on human health, and it is one of the most widespread contaminants in groundwater, having been found in high concentrations in different countries over the entire world. Fluoride concentrations exceeding the drinking water levels are very frequent in the region known as Pampa Plain in Argentina, associated with loess-like sediments bearing volcanic shards and calcium carbonate concretions. In this study, the behavior of fluoride in the catchment of La Ballenera creek is performed to contribute to the understanding of the processes controlling its distribution at catchment scale. The catchment is around 100 km², mostly in a flat landscape, outflowing into the Atlantic Ocean. The concentration of major ions, silica and fluoride was measured on 34 groundwater and 9 surface water samples obtained in October 2013. All the samples, both streamwater and groundwater, were sodium bicarbonate type with an average pH of 8 and 7.3, respectively. The fluoride concentrations in groundwater ranged between 1.1 and 2.5 mg/L with an average value of 1.9 mg/L.

Fluoride concentrations in streamwater were close to groundwater concentrations indicating the predominance of baseflow on surface water composition. The variations in the contents of fluoride are due to two main factors, one geological–geomorphological and the other geochemical. The first one is related to the dominance of loess-like sediments formed by minerals bearing fluoride, and the second one is related to the control resulting on calcite precipitation adsorbing fluoride ions.

Keywords Fluoride · Saturation index calcite · Hydrogeochemistry · La Ballenera creek

Introduction

Fluoride is one of the oligoelements which ingest causes both harmful and beneficial effects for health. The use of water for human consumption having F⁻ above the standard of the World Health Organization (1.5 mg/L) results in health problems as dental and skeletal fluorosis endemic causes (WHO 2004). Fluorosis causes discoloration and deterioration of the teeth and bones, and in severe cases can lead to loss of mobility. The presence of high contents of fluoride in groundwater has been studied by many researchers (Rao 2003; Edmunds and Smedley 2005, 2013; among others). There is no a single reason that explains the presence and behavior of this oligoelement; however, there is a link between the mineralogical composition of the sediments that form the aquifer and the concentrations of F⁻ present in the water. Fluorite (CaF₂) and fluorapatite (Ca₅(PO₄)₃F), and in a subordinate manner, to amphibole, pyroxene and biotite are cited as probable sources of this element in groundwater (Edmunds and Smedley 1996; Villalba 1999). The Chaco-Pampeana plain of Argentina is

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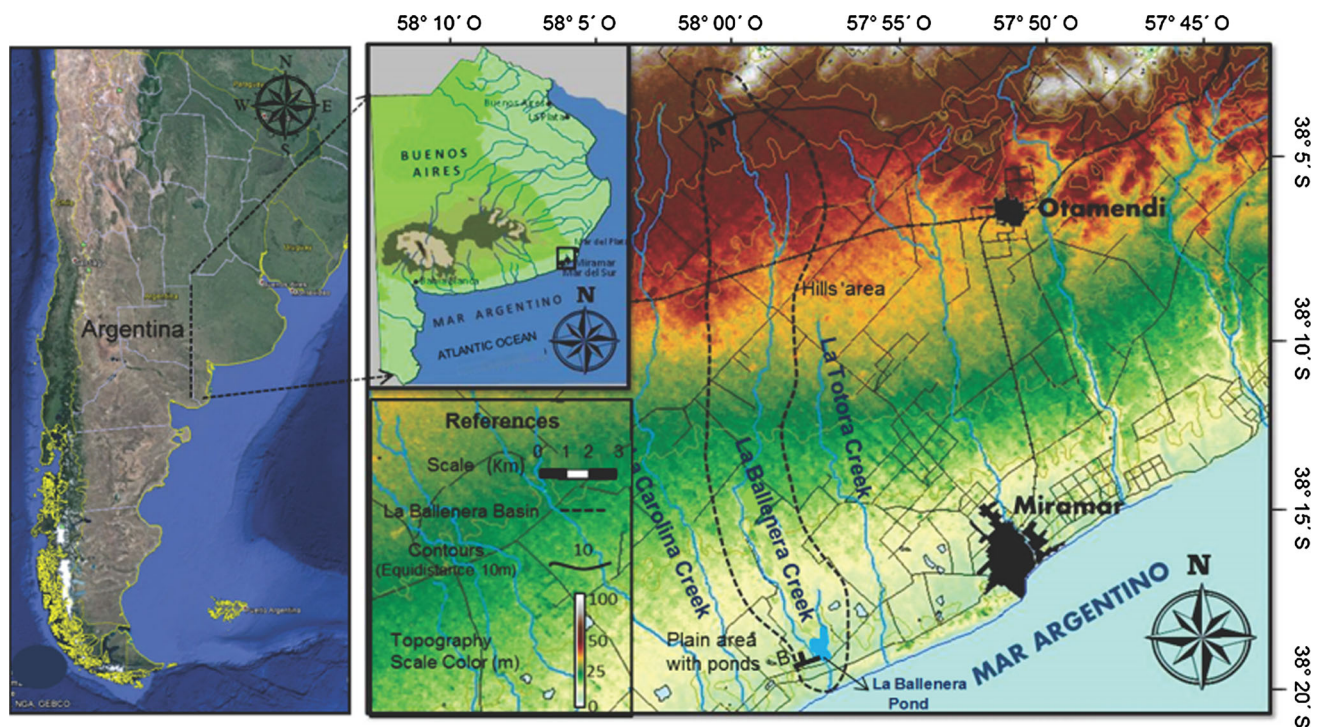


Fig. 1 Location map of the study area

one of the world's regions where the fluoride concentrations are of concern for its impact on the quality of water (Kruse and Ainchil 2003; Gómez et al. 2009; Garcia et al. 2009, 2012; Rosso et al. 2011; Martinez et al. 2012). In this area, the origin of fluoride due to the dissolution of volcanic glass shards present in the composition of the sediments has been generally accepted (Nicolli et al. 1989, 2012; among others). Volcanic glass is extremely reactive and weatherable, at high pH may dissolve and make minor elements and traces. Researches in other parts of the world (Armienta and Segovia 2008; Ayenew 2008; Viero et al. 2009) determined that the fluoride is released into water through the dissolution mechanism of volcanic glass and fluoride containing minerals, like fluorite among others.

La Ballenera creek catchment in the province of Buenos Aires, Argentina, is a typical small basin that drains the flat landscape toward the Atlantic Ocean. There, the loess-like sediments form the main phreatic aquifer and evidences of dental fluorosis can be easily observed in the population. Land use in the area is agriculture, and livestock to a lesser extent. The main towns in the basin are Miramar and Comandante Nicanor Otamendi with 30,000 and 7000 inhabitants, respectively. The goal of this paper is to analyze the abundance and distribution of fluoride concentrations in La Ballenera Creek basin in order to contribute to a better comprehension of the behavior of this natural contaminant at catchment scale.

Characterization of the area and geological background

La Ballenera creek catchment is located between Tandilia and Ventania mountain ranges in the area denominated Interserrana plain, in the southeast of the Buenos Aires province. The sources of the creek are in the Tandilia system and its outlet into the Atlantic Ocean. The area presents a characteristic network of narrow drainage floodplains, with orientation north–south and perpendicular to the coastline. The creek has a total length of 30 km and feed La Ballenera pond near to the outlet (Fig. 1).

Weather is humid—wet with little or no water deficiency and mesothermal with concentration of thermal efficiency in summer. The annual rainfall for the period 1944–2013 is 900 mm and the average annual temperature is 13.5° C (CHEM 2013).

Hydrogeology

The hydrogeological region sequence was described by Rossi (1994) for the area of the La Tigra and La Carolina catchment next to La Ballenera basin (Fig. 1). In the area, it is possible to identify two large units: a hydrogeological basement formed by Precambrian and early Paleozoic rocks, and an aquifer section formed by the Cenozoic cover.

The hydrogeological basement consists of two main groups of rocks. The first one is the Complex Buenos Aires (Marchese and Di Paola 1975) formed by granites, migmatites and gneisses of Precambrian age. These rocks are the oldest in the country, reaching an age of 2700 millions of years (Rapela et al. 2011), and they are covered by a sequence of sedimentary rocks. The sedimentary sequence includes a set of Precambrian–Cambrian dolomites, limestones and orthoquartzites forming the Sierras Bayas Group (Poiré 1993). An important set of orthoquartzites of Early Paleozoic age included in the Balcarce Formation (Dalla Salda e Iñiguez 1979) is outcropping in most of the range, and especially close to the study zone (Fig. 2). This group of rocks constitutes a discontinuous and heterogeneous system, without primary porosity, in which only the presence of weakness as stratification surfaces, joints and fractures, can give a secondary porosity.

The Cenozoic sequence lies on the hydrogeological basement represented in the study zone by the Complex Buenos Aires and the Balcarce Formation. It is a thick deposit (between few meters to 200 m) of loess-like silt and silty-sand sediments, frequently including precipitated CaCO₃ layers, called Pampeano sediments (Fidalgo et al. 1975). Holocene is present in restricted zones being formed

by sand deposits forming dunes corresponding to the *Post-pampeano* sediments. *Pampeano* and *Post-pampeano* deposits constitute together the hydrogeologic unit designed as Pampeano Aquifer. It is the main and only exploited aquifer in the zone. This is dominated on the bottom by sandy sediments, while on the top is mostly silt-sandy, silt-clayed and loess-like sediments having degrees of cementation and interbedded nodules of banks of calcareous material (Kruse 1986; Rossi 1994; CFI 1994, 1995). The mineralogical composition of these sediments was described in a relevant work on Pampas loess and silt by Teruggi (1957), and in a more close local study by Martínez and Osterrieth (2013).

In this study, the data of drilling records obtained through 20 holes located in the neighboring cities of Miramar and Mar del Sur (CFI 1995) are integrated, which allowed to make a correlation of wells to better fit the conceptual hydrogeological model of the basin (Figs. 2, 3). Quartzites outcrops can be found next to the head of the basin, while the middle and distal sectors of the catchment are dominated by thick levels of silt and calcrete deposits.

Geomorphology

The study catchment is located nearby to the southern spurs of Balcarce mountain range, which altitude in the area is around 130 masl. There is a smooth transition to the plain environment through a gentle slopes fringe. La Ballenera creek catchment can be divided into two geomorphological units, based on previous classifications that consider land use and soil associations (INTA 1989) and general descriptions (Kruse 1986; del Rio et al. 2004). These units are: Hilly area to the northern sector, and Plain area with ponds in the distal part of the catchment (Fig. 1).

The hilly unit is irregular and has large forms with notches of different magnitude and its slope is in the order of 1–0.6 %. The Plain unit with ponds is characterized by slopes lesser than 0.6 %, reaching values as low as 0.01 %. The presence of shallow circular ponds in the flat area is due to a deflation process during arid period of the Upper Pleistocene–Holocene. They are shallow and they receive temporary flooding from the higher surrounding areas. In many cases, these ponds are arranged in a parallel line to the creek canal (del Rio et al. 2004).

Methods

Streamwater samples were collected at 9 sampling points along the course and groundwater samples were taken on 34 wells, mostly shallow wind mill boreholes about 25 m deep, and irrigation wells about 50 m deep during October 2013. The standard methods used (APHA-AWWA-WPCF

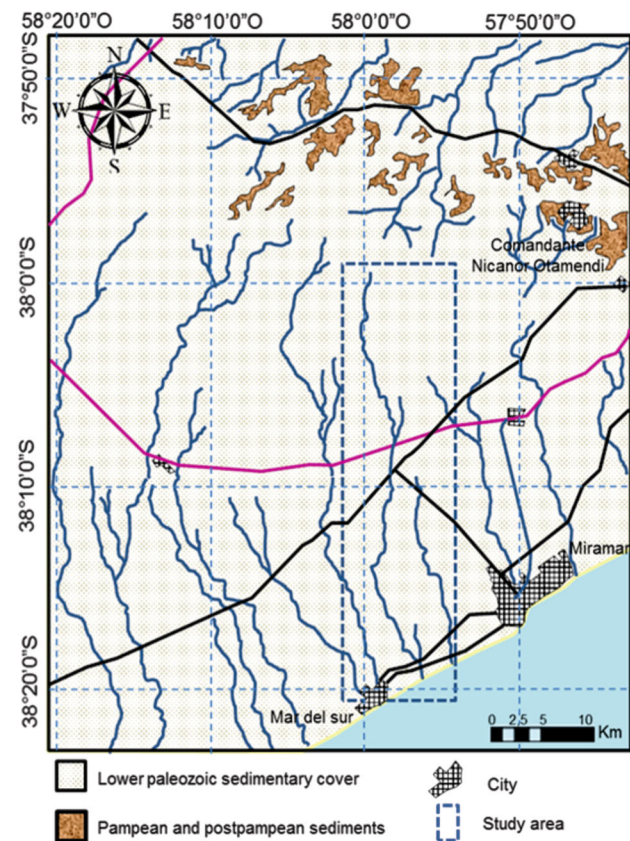
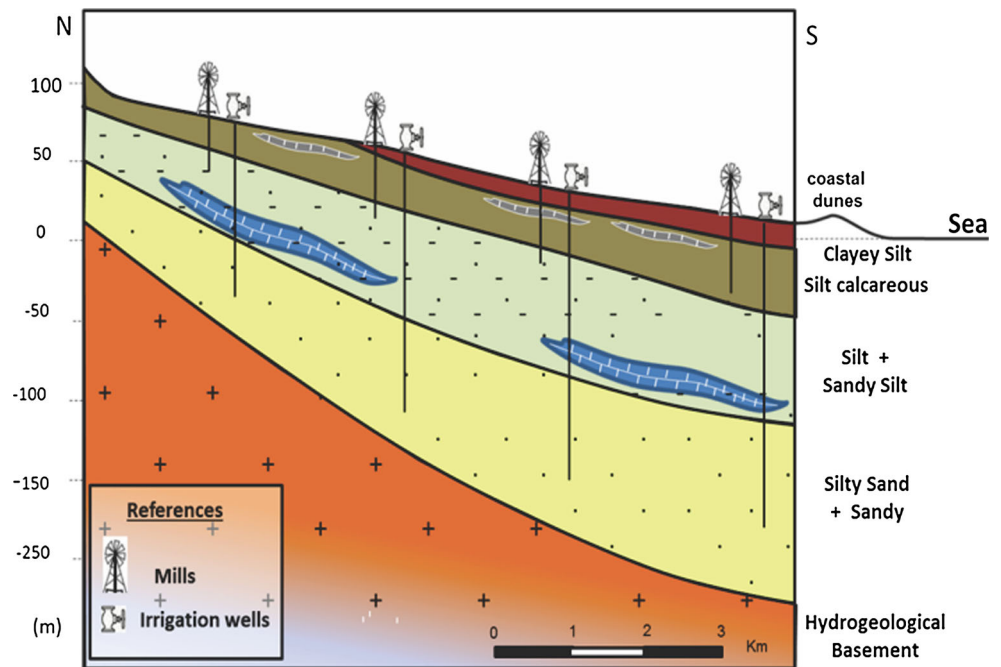


Fig. 2 Geological map of the area

Fig. 3 Hydrogeological model of the study area (vertical scale is enlarged)



1989) were as follows: chloride following Mohr method, sulfate by turbidimetry, calcium and magnesium by complexometric titrations with EDTA, sodium and potassium by flame spectrometry, silica by means of silicomolybdate method, nitrate by the brucine method and bicarbonate-carbonate by potentiometric titration. Furthermore, fluorine by the zirconyl chloride method and total iron by spectrophotometry (HachDrel 2800 Ferrover1 method) were done.

Hydrochemical results have been analyzed emphasizing fluoride geochemistry by using conventional hydrochemical diagrams (Piper and Stiff). The PHREEQC2.0 code (Parkhurst and Appelo 1999) was used for calculation of saturation indexes. A GIS developed with ArcGIS code was used for graphical purposes and spatial distribution analyses.

Results

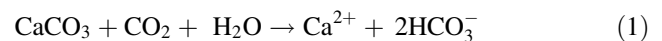
Hydrogeochemistry

The statistical parameters that characterize the contents of the major components for both, streamwater and groundwater are shown in Tables 1 and 2. From the hydrochemical point of view, all the samples are classified as sodium bicarbonate type (Fig. 4). pH is lightly alkaline in groundwater, and alkaline in surface waters, with mean values of 7.3 and 8.0, respectively (Table 1, 2). Groundwater samples show a higher variability in the cationic

composition (Fig. 4). The cationic composition of surface water is sodium type for all samples, although they correspond to different sectors along the drainage network. The anionic composition is mostly constant, but has some more chlorinated groundwater terms. Stiff diagrams of mills and irrigation wells are represented in Fig. 5; where a moderate increase of salinity in the flow direction can be observed.

In order to clarify the geochemical behavior of the study zone some binary graphs have been performed (Figs. 6, 7, 8, 9, 10). Groundwater and surface water contents of Na^+ expressed as meq/L are higher than Cl^- values (Fig. 6), diverging from the 1:1 ratio assigned to halite dissolution and suggesting other source of Na^+ , typically interpreted as released from silicate weathering reaction (i.e. Meybeck 1987). Silicate dissolution is one of the probable source of Na^+ but another one is the reactions of exchange (Na^+ for Ca^{2+} and Mg^{2+}) as was observed in other places of the Pampean Plain (i.e. Miretzky et al. 2000; Martínez and Bocanegra 2002; Fernández Cirelli and Miretzky 2004).

Alkalinity in most natural waters is mainly derived from the equilibrium with atmospheric CO_2 and CO_2 in the soil above the water table, and also from the dissolution of carbonate minerals. The plot Ca^{2+} vs. HCO_3^- (Fig. 7) also shows an excess of HCO_3^- or Ca^{2+} deficit from the expected rate according to the equation



HCO_3^- excess can result from other reactions involving

Table 1 Statistical parameters of chemical composition of streamwater in La Ballenera creek catchment

Aguas superficiales <i>n</i> = 9									
Parameter	Unit	Min	Max	Average	St. dev.	Dev. coef %	Q25	Q50	Q75
Temp	°C	15.5	19.1	16.9	1.0	6.0	16.3	16.7	17.0
pH		7.7	8.3	8.0	0.3	3.1	7.8	8.1	8.3
Cond	mS/cm	877.0	1894.0	1364.7	286.8	21.0	1151.3	1311.5	1498.3
Ca	mg/L	28.0	42.0	35.3	4.2	11.8	31.3	36.0	36.8
Mg	mg/L	21.2	45.6	32.7	7.3	22.2	25.3	33.2	35.8
Na	mg/L	270.0	420.0	315.6	51.7	16.4	270.0	300.0	330.0
K	mg/L	3.0	22.0	13.8	6.3	45.9	8.5	12.5	17.8
HCO ₃	mg/L	554.0	892.0	744.1	99.0	13.3	680.3	743.0	786.8
SO ₄	mg/L	30.0	66.0	50.8	11.0	21.6	40.5	53.0	56.8
Cl	mg/L	109.0	283.0	164.7	54.8	33.3	117.3	142.0	183.7
Si	mg/L	11.7	56.4	27.8	14.4	51.8	15.7	22.4	32.7
F	mg/L	1.1	2.1	1.5	0.3	22.9	1.2	1.4	1.7

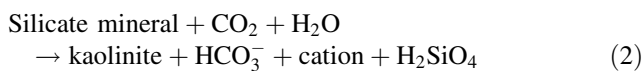
Number of samples: 9

Table 2 Statistical parameters of chemical composition of groundwater in La Ballenera creek catchment

Aguas subterráneas <i>n</i> = 34									
Parameter	Unit	Min	Max	Average	St. dev.	Dev. coef %	Q25	Q50	Q75
Temp	°C	15.1	21.6	16.3	1.1	6.8	15.6	16.1	16.6
pH		6.8	8.0	7.3	0.3	4.1	7.3	7.4	7.6
Cond	mS/cm	893	1848	1363.0	253.7	18.6	1156.0	1329.0	1540.5
Ca	mg/L	27	86	40.3	11.6	28.6	33.0	36.0	43.5
Mg	mg/L	13.5	61.6	38.0	11.8	31.0	29.8	37.0	47.2
Na	mg/L	150	400	261.2	58.1	22.2	220.0	250.0	300.0
K	mg/L	6	30	15.4	5.9	38.4	10.5	14.0	19.0
HCO ₃	mg/L	520	946	643.3	91.6	14.2	591.5	628.0	675.0
SO ₄	mg/L	21	80	44.8	14.6	32.6	32.0	41.0	55.5
Cl	mg/L	65	294	143.8	49.2	34.2	109.5	136.0	164.0
Si	mg/L	7.1	70.0	35.3	20.6	58.3	14.0	27.0	53.7
F	mg/L	1.1	2.5	1.9	0.4	19.2	1.7	1.8	2.1

Number of samples: 34

CO₂, such as the hydrolysis the most abundant minerals, the silicates, according to a general equation:



The excess of HCO₃⁻ and Na⁺ could be released by minerals weathering (Stallard and Edmond 1983; Fisher and Mullican 1997) but a higher increase of Na⁺ compared to HCO₃⁻ concentration suggests another source like ionic exchange or anthropogenic activities.

The plot of Ca²⁺ vs. SO₄²⁻ shows waters with a rCa²⁺/rSO₄²⁻ ratio higher than 1, which is the value expected from gypsum dissolution and indicating another sources of calcium (Fig. 8). Calcium concentration is also controlled by calcite precipitation–dissolution equilibrium, cationic

exchange process and probably in minor extend by the weathering of calcium plagioclases.

In order to explain the origin of the excess of Na a plot Ca²⁺ + Mg²⁺ – SO₄²⁻ – HCO₃⁻ vs. Na–Cl⁻ was performed (Fig. 9). Results indicated a good linear correlation (*r*² = 0.68) and a slope (–0.97) that tends to the theoretical value of –1. This behavior may be explained considering an ion exchange reaction in the hydrochemical evolution (Fisher and Mullican 1997). Therefore, a cation exchange process took place in the sediments. This fact was described by other authors in the Pampean loess (Rossi and Bonorino 1996; Miretzky et al. 2000; Martínez and Bocanegra 2002; Fernández Cirelli and Miretzky 2004).

From the previous observations, it is possible to identify the main processes determining the bulk hydrochemistry in the area. As the considered aquifer is an unconfined aquifer,

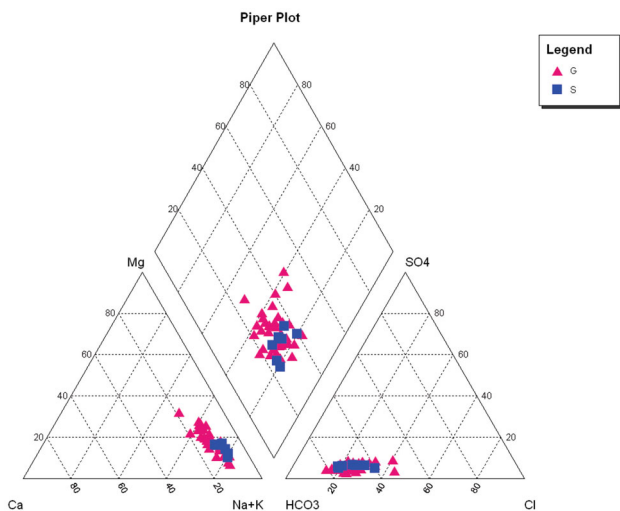


Fig. 4 Piper diagram showing groundwater (*G*) composition and streamwater (*S*) at the La Ballenera catchment

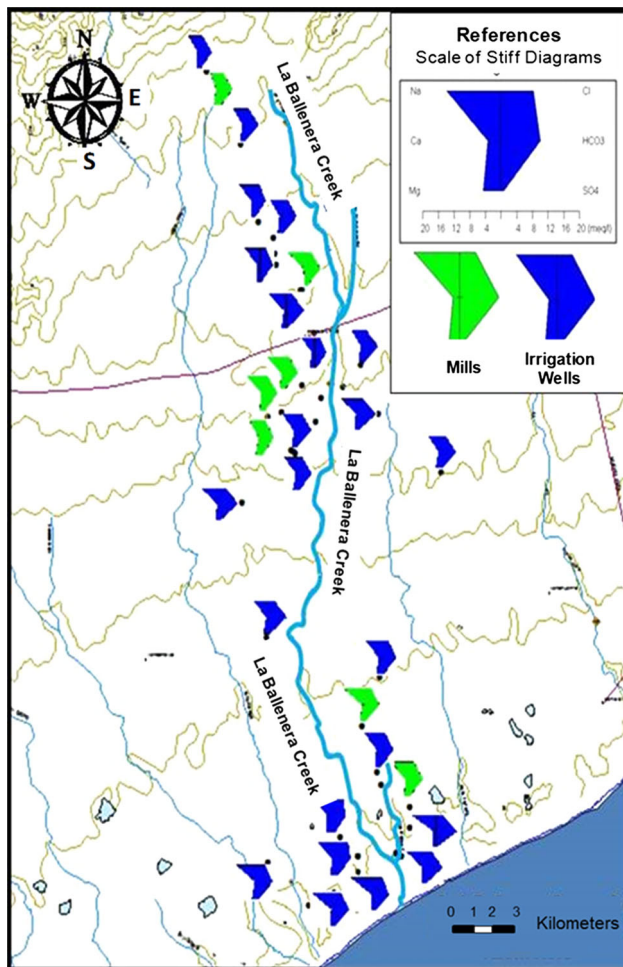


Fig. 5 Stiff Diagrams groundwater (mills and irrigation wells)

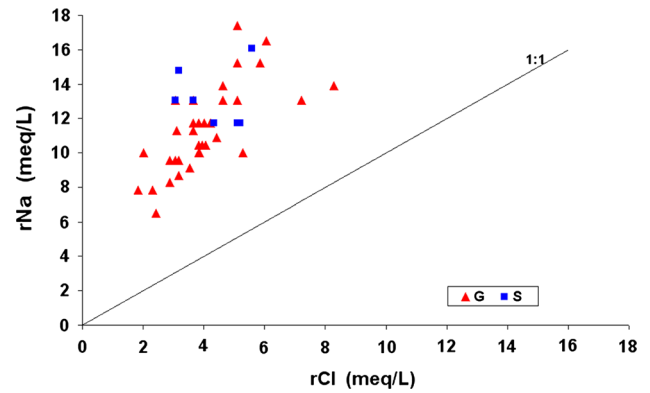


Fig. 6 Relation between Na^+ and Cl^- in groundwater and surface water. *G* groundwater, *S* surface water

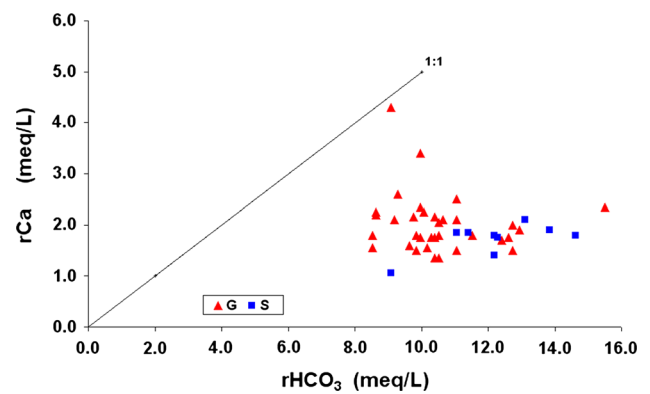


Fig. 7 Relation between Ca^{2+} and HCO_3^- in groundwater and surface water. *G* groundwater, *S* surface water

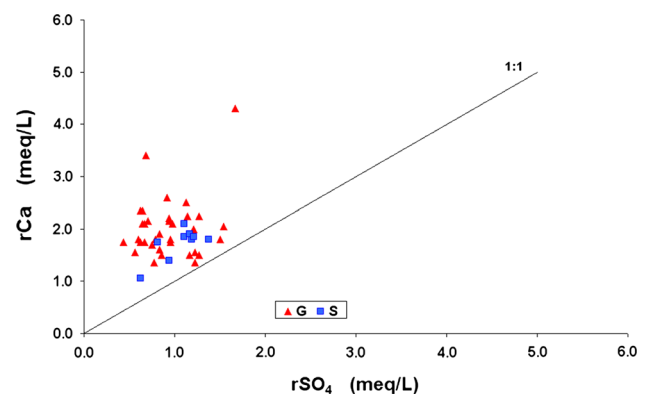


Fig. 8 Relation between Ca^{2+} and SO_4^{2-} in groundwater and surface water. *G* groundwater, *S* surface water

groundwater is equilibrated with atmospheric CO_2 which reacts dissolving carbonates and hydrolyzing silicates, giving to the water its bicarbonate anionic type. The sodium dominant cationic type is mostly the result of cation exchange at the abundant montmorillonite clay in the sediments.

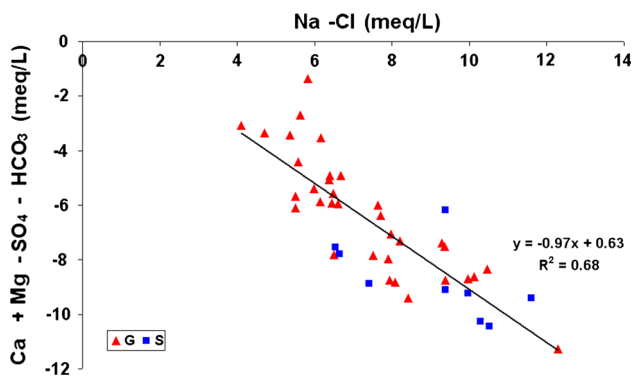


Fig. 9 Relation between $Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^-$ vs. $Na^+ - Cl^-$ in groundwater and surface water. *G* groundwater, *S* surface water

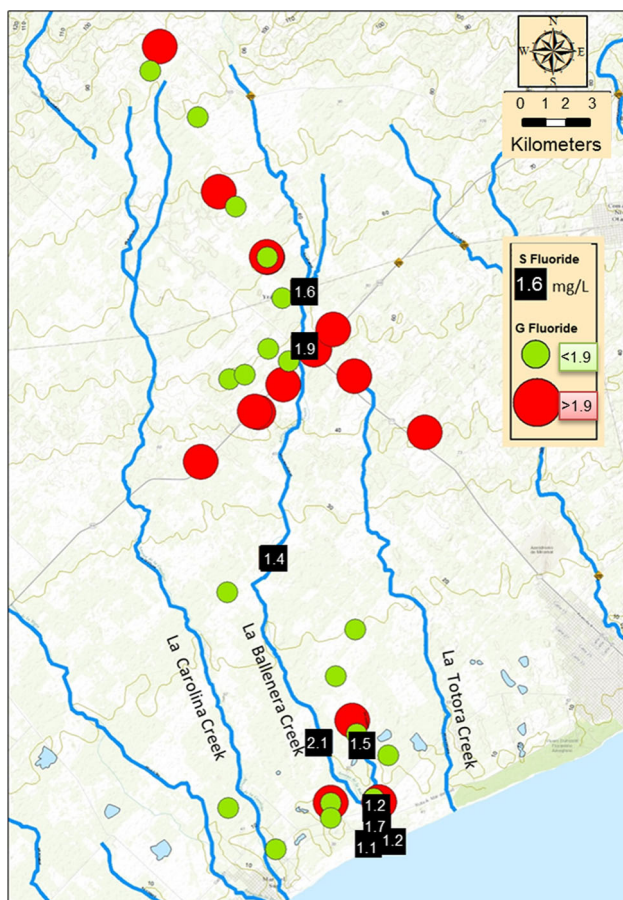


Fig. 10 Fluoride concentrations in stream and groundwater

Dissolved silica is an important component in waters of aquifer Pampeano (Martinez and Osterrieth 1999). In the case of study, the silica content of groundwater has a great variation, with values between 7 and 70 mg/L (Table 2). In general, higher values (>40 mg/L) are found in deep wells (50–70 m).

The concentration of fluoride in the streamwater of the Ballenera creek ($n = 9$) shows ranges between 1.1 and 2.1 mg/L (average 1.5 mg/L) with 55.5 % of samples with values higher than 1.5 mg/L (Table 1; Fig. 10). Fluoride concentrations in groundwater ($n = 34$) range between 1.1 and 2.5 mg/L (average 1.9 mg/L), showing 93.4 % of the sample values higher than 1.5 mg/L (Table 2; Fig. 12). Fluoride concentrations in streamwater have the same behavior than groundwater, indicative of the predominance of baseflow in surface water composition.

The distribution of fluoride contents in groundwater considering the geological–geomorphological units previously described, shows a higher frequency of values between 2.1 and 2.5 mg/L in the Hilly area (Fig. 11a), while in the Plain area with ponds, dominated by thick levels of silt and calcrete deposits, the fluoride concentrations range from 1.5 to 2 mg/L (Fig. 11b).

Fluorite is the most common mineral containing fluoride, and equilibrium condition could be a limit to the dissolved concentration of F^- . In order to determine the role played by fluorite in controlling maximum fluoride concentration in waters, the saturation index of this (SI_{CaF_2}) was calculated and defined as:

$$SI_{CaF_2} = \log ([Ca^{+2}][F^-])/K_{CaF_2} \tag{3}$$

where $[Ca^{+2}]$ is the calcium dissolved concentration, $[F^-]$ is the fluoride dissolved concentration. Calculations were performed using PHREEQC2.0 code (Parkhurst and Appelo 1999).

The saturation indexes (SI) of fluorite calculated for surface and groundwater indicate that the saturated condition is not achieved by any sample, and most of them are unsaturated, especially for streamwater. These results are shown in a graph relating SI_{CaF_2} vs. F^- concentration (Fig. 12).

The presence of calcium carbonate is very common in the catchment, as concretions, grid, and mantles with different degree of compaction and development. As calcium is a common ion for calcite and fluorite minerals, the conditions of equilibrium of those minerals are important in the local hydrochemistry of fluoride.

The saturation index of calcite (SI_{CaCO_3}) is defined as:

$$SI_{CaCO_3} = \log ([Ca^{+2}][CO_3^-])/K_{CaCO_3} \tag{4}$$

where $[Ca^{+2}]$ is the calcium dissolved concentration, $[CO_3^-]$ is the carbonate dissolved concentration and is K_{CaCO_3} the calcite equilibrium constant. Also, calculations were performed using PHREEQC2.0 code (Parkhurst and Appelo 1999). Considering the SI_{CaCO_3} values for groundwater it is possible to identify two sectors: one of them in equilibrium, and the other oversaturated (Fig. 13).

In general, there is a correspondence between fluoride concentrations lower than 1.9 mg/L and the zones where

Fig. 11 **a** Histograms of hilly area, **b** histograms of plains with ponds area

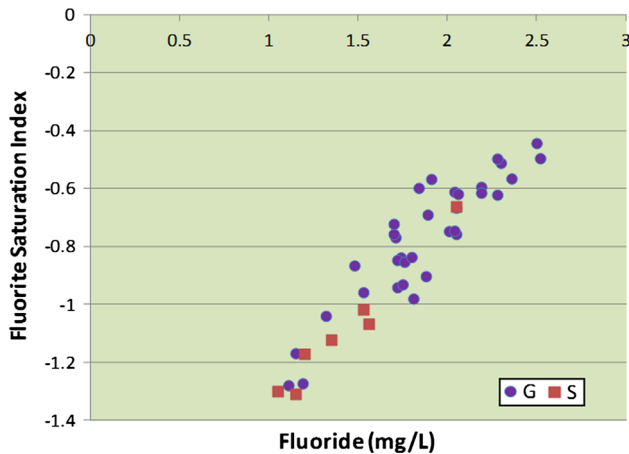
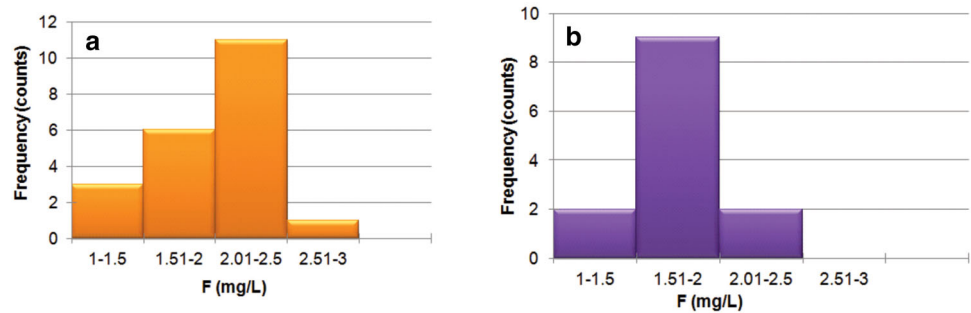


Fig. 12 Saturation index of fluorite for surface water (S) and groundwater (G)

groundwater is oversaturated in calcite. In the sector where groundwater is close to calcite equilibrium, the fluoride concentrations are above and below 1.9 mg/L. In the equilibrium dominated zone, the fluoride concentrations are mostly above 1.9 mg/L in the shallow wells (<25 m) and below 1.9 mg/L in the deeper (50–70 m) irrigation wells.

Electrical conductivities (EC), in surface and groundwater, are very similar and vary between 880 and 1894 $\mu\text{S}/\text{cm}$. EC of groundwater shows a moderate increase in regional flow direction to the southeast while fluoride concentrations do not follow this trend (Fig. 14a).

Discussion

The 93.4 % of all groundwater samples in La Ballenera basin have high fluoride concentrations above the admissible water drinking level of 1.5 mg/L. Groundwater composition is sodium bicarbonate type and pH is lightly alkaline. The relationship between sodium bicarbonate waters, alkaline pH and high content of fluoride has been

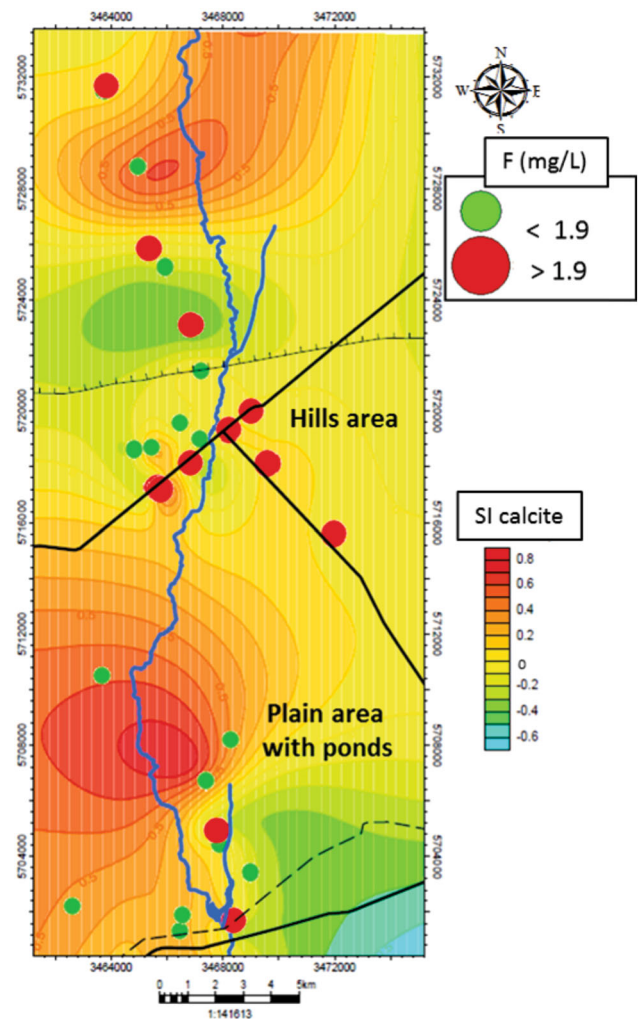


Fig. 13 The map shows SI Calcite areas and groundwater fluoride values compared to the average 1.9 mg/L (higher or lower)

shown by many authors (Kruse and Ainchil 2003; Edmunds and Smedley 2005, 2013; Gómez et al. 2009; Blarasin et al. 2011) and it is the main behavior in this catchment.

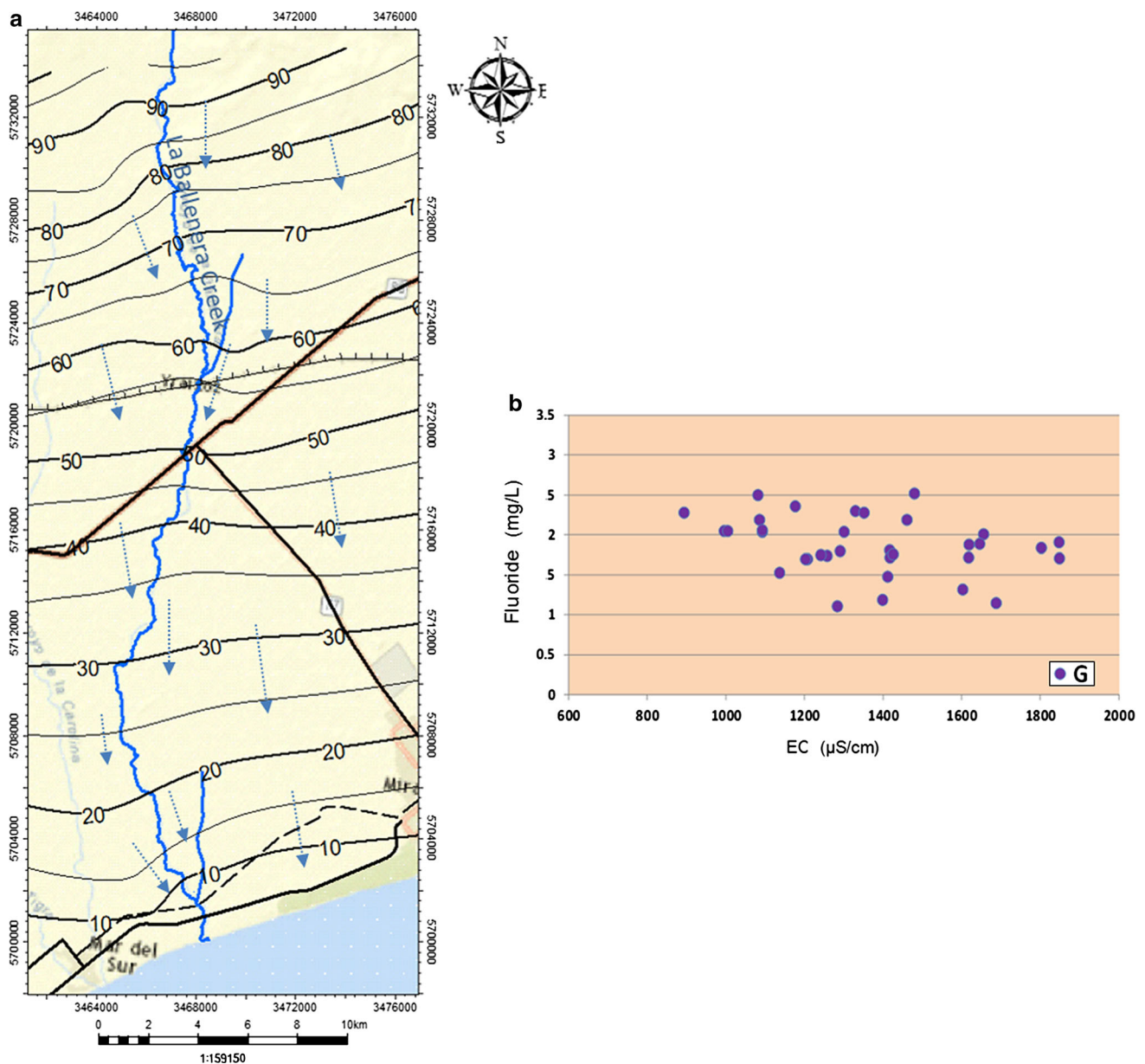


Fig. 14 a Flow line map of groundwater. b F^- vs EC in groundwater

A general increase of all the dissolved ions in the main flow direction can be observed in the distribution of the electrical conductivity (EC) (Fig. 14b). However, this behavior is not observed for fluoride, which is indicating that other factors like geological–geomorphological and geochemical conditions are determining the contents distribution in the catchment.

From the geological point of view, the source of fluoride in groundwater of the Pampa plain has been generally attributed to dissolution of volcanic glass shards disperse in loess sediments (Nicolli et al. 1989, 2012; Borgnino et al. 2013). In addition, fluoride has been associated with

minerals of crystalline rocks as biotite, fluorapatite, amphiboles and piroxenes (García et al. 2012; Borgnino et al. 2013) and granitic rocks (Chae et al. 2007; Martinez et al. 2012).

In La Ballenera basin, the Plain area with ponds is characterized by relative fluoride lower concentrations, lower than the average value (1.9 mg/L) (Fig. 13). This area is dominated by the Pampeano loess-like sediments, bearing important proportions of volcanic glass shards, and fluoride in groundwater can be related to the dissolution from these materials. The Hilly area includes the maximum fluoride levels (higher than 1.9 mg/L) probably due to an

additional source. The weathering of the Precambrian bedrock and Paleozoic cover (Poiré et al. 2003; Dalla Salda et al. 2006) could be assumed to be another supply for the higher concentrations of fluoride, as it has been appointed in the Quequén river catchment, about 100 km from the study zone (Martinez et al. 2012).

Geochemical factors control the other main aspects of fluoride distribution. As mentioned before, a correspondence can be observed between calcite oversaturation area and low fluoride concentrations. Carbonated minerals are known to be very reactive with respect to dissolution/precipitation processes and are strongly involved in the sorption processes of trace elements (Tertre et al. 2012). Many authors (Foxall et al. 1979; Fenter et al. 2000; Tertre et al. 2012; Heberling et al. 2014; among others) have been interested in the surface reactivity of these minerals and particularly into investigate their surface charges when analyzing the removal of trace elements by calcite precipitation. Additionally Stipp's model proposes that along any cleavage point on the calcite surface, the calcium and carbonate ions can also react with any other ions in solution as fluoride (Stipp 1999). The presence of the adsorption reaction has been confirmed by experiments where fluorite precipitation does not occur ($SI_{\text{fluorite}} < 0$) (Fan et al. 2003; Turner et al. 2005). The described effect of fluoride adsorption by calcite precipitation is possibly significantly affecting its concentration in this catchment. Vital et al. (2015 this issue) demonstrated through batch dissolution experiments on sediments taken close to the study zone, that fluoride release is maximum when calcite dissolves, obtaining fluoride concentrations around 0.12 mmol/l after 1200 min of water–sediment contact.

In areas where the SI of calcite is close to equilibrium, the concentrations of fluoride are variable. The permanent dissolution and precipitation of calcite in the balance could remove fluoride for adsorption during the precipitation or release fluoride during the dissolution of calcite. In the areas where oversaturation of calcite is the dominant condition, calcite precipitation adsorbs fluoride from the solution, being a sink for this ion and then reducing the dissolved concentration. Calcite oversaturation does not correspond to the thermodynamic equilibrium, and some over-imposed process can be affecting the geochemical behavior. Some kinetic effect can explain oversaturation, such as simultaneous cation exchange or ion common effect. The ion common effect can also result in fluoride decrease leading to fluorite precipitation because of calcite dissolution (Coetsiers et al. 2008). Nevertheless, in La Ballenera catchment, the saturation indexes of calcite and fluorite are saturated and subsaturated, respectively; so that process should not be influencing fluoride in solution.

Conclusions

About 93.4 % of fluoride contents in the groundwater samples in La Ballenera basin exceed maximum admissible levels. There is no correlation between the fluoride concentrations and the electrical conductivity (EC), and the fluoride content has not increased on the same way of the regional flow. Then, other constraints must be regulating fluoride concentrations.

The variations in the concentrations of fluoride are due to two main factors, one geological–geomorphological and other geochemical. The first geological–geomorphological factor is related to the proximity in the hilly area of basement rocks, granites, quartzites, gneisses and migmatites, including fluoride bearing minerals. The geochemical factor is linked to the saturation state of calcite. A correspondence between areas with waters with fluoride concentrations less than 1.9 mg/L and calcite oversaturation has been observed. This could indicate that fluoride in solution decreased while calcite precipitates. On the other hand, the fluoride content varies in the calcite equilibrium area. Fluoride removal may be produced by adsorption during precipitation, or release of fluoride in the dissolution of calcite.

Finally, the predominance of baseflow in stream water composition has been also demonstrated by the coincidence pattern in fluoride distribution for groundwater and stream water.

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