

# Hydrogeochemistry of fluoride in the Quequen river basin: natural pollutants distribution in the Argentine pampa

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**Abstract** Fluoride pollution is a widespread problem in Argentina, as it is in many areas of the World. Former investigations have demonstrated that the dissolution of volcanic glass disseminated in the loess-like sediments is the main source of fluoride in the Argentine pampas. Nevertheless, fluoride distribution is erratic and the factors controlling it are not yet well-known. A large amount of hydrochemical data collected in the Quequen Grande river catchment is used in order to contribute to the understanding of fluoride distribution and mobility in groundwater in the Argentine pampas. The Quequen Grande river catchment is 10,000 km<sup>2</sup>. It extends between two low hills ranges of Precambrian metamorphic rocks and sedimentary Paleozoic rocks, filled by a thick sequence of Cenozoic sediments, mainly silts and silt-clayed, with sand layers. These sediments form a multilayer phreatic aquifer, which is recharged from precipitation infiltration, discharging through streams directly into the sea. Fluoride concentration in surface water ( $n = 353$ ) ranges between 0 and 6.5 mg/l, with an average value of 2.14 mg/l. Groundwater concentration ( $n = 135$ ) is from 0 up to 5.7 mg/l, with an average of 1.84 mg/l. Considering the statistic distribution of fluoride, two groups of samples can be determined. A dominant group between 0 and 3 mg/l, with a mean value

around 1.5 mg/l, corresponding to samples widely distributed in the catchment; and a second one group with fluoride contents between 3 and 6 mg/l, corresponding to a smaller area in the central-west border. Two different sources are proposed. Volcanic glass dissolution is responsible for dominant values in the catchment, while the weathering of biotite from the Paleozoic bedrock can be assumed to account for the higher concentrations in the second group.

**Keywords** Argentine pampas · Quequen Grande river · Fluoride · Hydrogeochemistry

## Introduction

Fluoride is a pollutant of natural waters. Main adverse effects on human health have been synthesized by Dissanayake (1991) and Ozvath (2008). The World health Organization (WHO) established a maximum admissible level of 1.5 mg/l for drinking water. In Argentina, the local legislation stated a temperature dependent admissible level for drinking water (CAC 1994), which is of 1.3 mg/l at 20°C. However, concentrations exceeding admissible levels are quite frequent and widely spread over all the continents. Some of the most recent contributions on the subject correspond to studies carried out in China (Guo et al. 2007), Pakistan (Rafique et al. 2008), India (Handa 2006), Africa (Gaciri and Davies 1993, Edmunds 1994), etc. In Latin-America, the problem regarding fluoride water is also widely distributed and high concentrations have been reported in Chile, Peru, Mexico, etc., (Armienta and Segovia 2008).

In the earth crust geochemical cycle, fluoride appears initially related to igneous alkaline rocks and to hydrothermal minerals like fluorite (CaF<sub>2</sub>) and fluorapatite

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(Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F) (Rao 2003; Edmunds and Smedley 2005). Field and Laboratory studies demonstrated that the weathering of some accessory minerals like biotite is enough to result in concentrations as higher as 4 mg/l in water (Chae et al. 2006a, b; 2007).

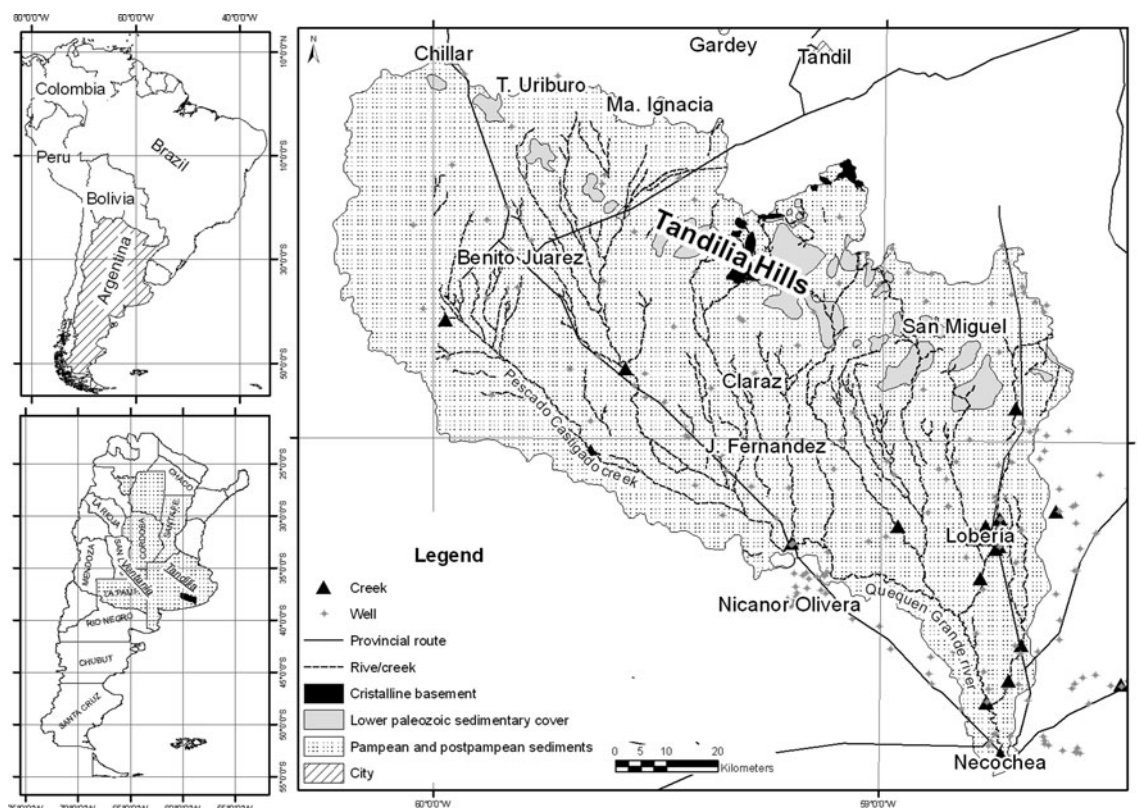
Fluoride problem in Argentina is also widely spread all over the country. High concentrations can be found in the provinces of La Pampa (Smedley et al. 2002), Buenos Aires (Kruse and Ainchil 2003), Tucuman (Warren et al. 2005), Santiago del Estero (Bundschuh et al. 2004), Santa Fe and Cordoba (Nicolli et al. 1989; Blarasin 2003; Gómez et al. 2009; Franco and Carro 2009) (Fig. 1). Reported values are as high as 7.2 mg/l (Gómez et al. 2009) or 10 mg/l (Nicolli et al. 1989). An important issue in the studies of fluoride in waters in the Argentine Pampas is the relationship found in many studies (Nicolli et al. 1989; Gómez et al. 2009; Franco and Carro 2009) with a more dangerous natural pollutant, arsenic. The correlation between arsenic and fluoride in groundwater in the Pampa region has been attributed to a common origin. The study performed by Nicolli et al. (1989) is one of the most important contributions on the issue. It demonstrated that volcanic glass shards, widely dispersed in sediments of the Pampa, is probably the most important (or only) source of natural arsenic and fluoride in groundwater. An alternative source of as and F proposed by Smedley et al. (2002, 2005)

is the adsorption process on the surface of Mn and Fe oxides.

The presence of fluoride as a result of the dissolution of volcanic glass in which F is included as impurity, allows for an explanation for the wide distribution of fluoride all over the Pampa plain. Most of the region is covered by a thick deposit of loess-like sediments (Teruggi 1957); in which volcanic glass constitutes an important fraction (Tricart 1973). Nevertheless, fluoride distribution is rather erratic, and processes determining observed concentrations need to be better understood. The purpose of this article is to use the large amount of hydrochemical information obtained in the catchment of the Quequen Grande river (QGR), in the province of Buenos Aires, Argentina, to analyze the possible hydrogeological factors that determine abundance and distribution of fluoride in groundwater. The results are expected to contribute to a better comprehension of the geochemical cycle of fluoride and, consequently, to the water quality management in the Pampa plain.

### Characterization of the area and geological background

The study area is a great basin (10,000 km<sup>2</sup>) filled by a thick sequence of Cenozoic sediments, mostly silt-sandy



**Fig. 1** Location map of the study area, showing main hydrological elements and sampling sites

and silt-clayed, which forms a multilayered unconfined aquifer. Recharge is from infiltration of precipitation excess and discharge takes place through streams in the catchment. The climate of the area is sub-humid temperate. The average annual temperature is 14°C, being July the month of lowest temperatures with an average of 7.3°C, and January the hottest month with an average temperature of 21°C. The mean rainfall for the period 1958–2009 was about 902 mm/y.

Over the last 10 years, the annual precipitation values have ranged from 703 to 1400 mm/y, with an average of 943 mm/y. The highest precipitation values are recorded between September and March. As regards evapotranspiration potential values, they have been calculated for the same period using Thornthwaite method and they have been estimated at between 750 and 833 mm/y, with an average of 786 mm/y. The catchment is drained by a series of streams with a general trend North–South, which are intercepted by the Pescado Castigado Creek (Fig. 1), with a Northwest to Southeast trend. The Quequen Grande River at its outlet into the Atlantic Ocean has an average flow rate in the order of 11 m<sup>3</sup>/s with peaks reaching to 300 m<sup>3</sup>/s, and a maximum historical record of 1942 m<sup>3</sup>/s during September 1998.

The Cenozoic sequence lies on Paleozoic rocks that constitute the hydrogeologic basement in the zone (Llambías and Prozzi 1975). Early Paleozoic orthoquartzites outcrop to the north and northeast of the catchment, forming a low-altitude range (510 m a.s.l.) known as Tandilia Range. Apart from this, the basement in the Southwestern area is formed by rocks belonging to the Ventania Range, being represented by sandstones with calcareous cementation and micaceous sandstones of Lower Carboniferous age (Llambías and Prozzi 1975).

The mineralogical composition of the loess-like sediments was described in an important work on the Pampean Loess by Teruggi (1957), which analyzes samples taken near the study area, and reports a constant composition in all the considered samples. The sand fraction is composed mainly by plagioclases that constitute at least a 30% of the light minerals, reaching until a 65% in some samples. The most common specie is labradorite, followed by oligoclase and andesine. Quartz is not very abundant, ranging between 2 and 30%. Potassium feldspars are present in rounded grains, usually strongly weathered. Volcanic glass is always present in proportions between 1 and 25%. Organic opal is presence ranges between 1 and 5%. Heavy minerals form between 0 and 6% of the samples. The composition of the silt fraction is similar to that described for the sand fraction, while the clay fraction is mainly composed by montmorillonite. The content of calcite in this loess and loess-like sediments is about 2 and 4% (Tricart 1973).

A study carried on Pampean sediments in the Southeast the Province of Cordoba (Nicolli et al. 1989) assign the major composition of sand and silt fractions to feldspars (40–75%), followed by volcanic glass (25–50%), and decreasing proportions of quartz, calcite, muscovite, and rock debris. Illite is the dominant specie in the clay fraction. Bundschuh et al. (2004) highlighted quartz (35%), plagioclase (20%), and volcanic glass (25%) as the major mineralogical component of Pampean sediments in an area of Santiago del Estero.

A grain size analysis performed on drilling samples from four wells in the area (Quiroz et al. 2008) yields clayey silt-sands prevalence, while the psammitic fraction accounts for more than 60% in all cases. Very fine sands between 0.125 and 0.062 mm prevail. Mineralogical analyses carried out with a binocular loupe revealed abundance of quartz, as well as the presence of calcium carbonate concretions and some lithoclast fragments. Occasionally, plagioclase, obsidian, biotite, and gypsum fragments were observed; while ferromagnesian minerals were frequently detected in sandy fractions. The silt fraction contained disseminated CaCO<sub>3</sub> in 95% of all samples. The upper outcropping sediments are formed by Plagioclase (65%), quartz (30%), orthoclase, volcanic glass shards (1–25%), and organic opal are the main components of this sandy fraction. Other minerals, such as chalcedony, chert, sanidine, and gypsum are found occasionally. Even some heavy minerals, especially iron ores (mainly magnetite), amphiboles and pyroxenes and, rarely, pyrite are found. In the silt fraction, volcanic glass shards are usually detected, followed by plagioclase, quartz, orthoclase, and, more rarely, by gypsum fibrous crystals, in this particular case, antigenic. Finally the clayey fraction is essentially made up of montmorillonite.

An exploration well has been recently drilled in the central western area on the right margin of the Quequén Grande river, reaching the bedrock at 69 m depth. A homogeneous sequence of medium sand sediments characterizes most of the sedimentary section. A preliminary mineralogical survey was carried out on this sequence. Quartz makes up over a 50% of the sediment. Feldspars and opaque minerals are the other constituents of the aquifer in the area. These sands probably result from the weathering process of the outcropping sandstones in the area.

## Methods

During the development of different research projects in the catchment of the QGR a lot of groundwater and stream-water samples were taken and analyzed. Stream-water samples were collected at five sampling points weekly or

bimonthly during four consecutive years (2005–2008). Groundwater samples were taken in about 100 wells (mostly shallow wells between 25 and 40 m deep) several times along these 4 years. Major chemical composition was analyzed on all the samples by standard methods (APHA-AWWA-WPCF 1989), nitrate by colorimetric brucine method, silica by spectrometry molybdenum blue method and F<sup>-</sup> by spectrometry zirconil chloride method.

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

## Results

### Main characterization

Fluoride concentration in streamwater of the QGR catchment ( $n = 353$ ) ranges between 0 and 6.5 mg/l, with an average value of 2.1 mg/l (Fig. 2a). In groundwater ( $n = 135$ ) fluoride concentration is between 0 and 5.7 mg/l, showing the higher frequency of data in the range 0.6–2.4 mg/l and an average of 1.84 mg/l (Fig. 2b). In both cases fluoride histograms show an approximately normal distribution and a tail of anomalous high values. The statistical parameters of major chemical composition for both, streamwater and groundwater, are shown in Tables 1 and 2.

From the hydrochemical point of view, streamwater and groundwater are bicarbonate type, mostly composed sodium bicarbonate, but also some calcium-magnesium members can be observed. pH is lightly alkaline in groundwater, and alkaline in surface waters, with mean values of 7.58 and 8.14, respectively, (Tables 1 and 2). Major groundwater composition has been plotted in two

different Piper diagrams in order to observe the relationship between hydrochemical facies and fluoride concentration. In the first one (Fig. 3a) the composition of all the samples containing less than 1.2 mg/l have been represented, and in the second one (Fig. 3b), the samples with fluoride higher than 1.2 mg/l can be observed. All the samples containing more than 1.2 mg/l are a bicarbonate sodium type, while low fluoride concentration waters (less than 1.2 mg/l) correspond to a bicarbonate type, including sodium, calcium, and magnesium water types. The difference is not as visible as the correlations already mentioned in other areas (Nicolli et al. 1989; Gómez et al. 2009).

A graph designed in order to observe the behavior of fluoride against sodium and calcium concentrations (expressed in mmol/l) (Fig. 4) shows a general trend to increase fluoride concentration together with sodium concentration increases. Unlike wise, calcium concentration against fluoride concentration results in a negative slope of the regression line. A gap between the major group of samples up to 0.2 mmol/l of F<sup>-</sup> and the group of samples above 0.2 mmol/l of F<sup>-</sup> can be observed.

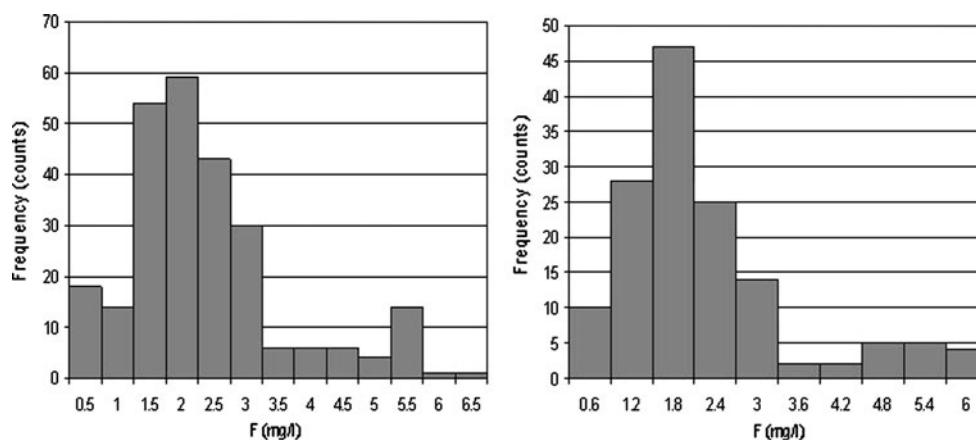
### Limitations of fluoride solubility

As mentioned above, fluoride concentration varies from 0 mg/l to more than 6 mg/l. Fluorite is the mineral species mostly considered in equilibrium with dissolved fluoride, mainly because of its abundance and high probability of having been formed during the sedimentary cycle. In order to determine the role played by fluorite precipitation in controlling maximum fluoride concentration in waters, the saturation index of this (SI<sub>CaF<sub>2</sub></sub>) was calculated and defined as

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

where [Ca<sup>+2</sup>] is the calcium dissolved concentration, [F<sup>-</sup>] is the fluoride dissolved concentration. Calculations were

**Fig. 2** Frequency histograms of fluoride distribution. **a** Streamwater. **b** Groundwater



**Table 1** Statistical parameters of chemical composition of streamwater in the Quequén Grande river catchment

Number of samples: 658

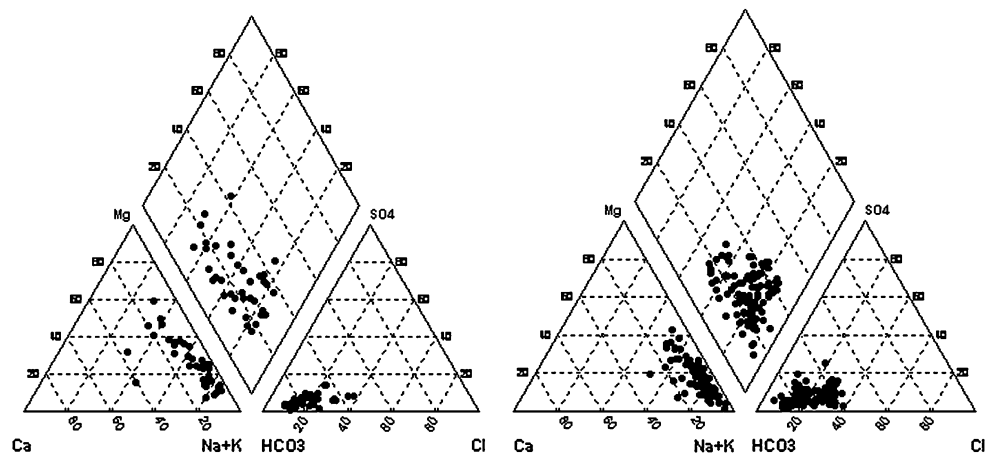
Parameter	Unit	Min	Max	Average	St. dev.	Dev. coef	Q25	Q50	Q75	Sample num
Ca	mg/l	5.18	236	23.57	17.37	73.70	15.4	20.6	28.3	360
Mg	mg/l	1.51	138.7	25.47	13.81	54.22	16.6	23.8	34	360
Na	mg/l	24.1	2722.4	314.02	249.29	79.39	226.5	277.9	346.25	359
Cl	mg/l	10	2115.7	169.78	185.89	109.49	89.1	129	190	360
F	mg/l	0.0	6.5	2.14	1.25	58.66	1.38	2.0	2.68	353
HCO <sub>3</sub>	mg/l	185.4	4410	641.85	338.53	52.74	484	610	738.63	360
SO <sub>4</sub>	mg/l	1.35	550	91.82	80.91	88.11	43	69.1	116.75	357
TEMP	°C	5	29.2	15.72	4.69	29.84	11.55	15.8	19.5	126
pH		7	9.8	8.14	7.99	98.16	0	0	0	357
Cond	uS/cm	158.3	12885	1185.09	955.78	80.65	780	1085	1307	356

**Table 2** Statistical parameters of chemical composition of groundwater in the Quequén Grande river catchment

Number of samples: 221

Parameter	Unit	Min	Max	Average	St. dev.	Dev. coef	Q25	Q50	Q75	Sample num
Ca	mg/l	4.03	172.8	23.85	16.58	69.53	14.95	20.05	28.80	215
Mg	mg/l	1.44	130	33.55	20.74	61.82	18.08	30.05	44.60	215
Na	mg/l	22.62	626	206.66	113.30	54.82	118.72	185	280	212
Cl	mg/l	21	673.1	124.63	98.34	78.91	63.45	94.35	147.85	215
F	mg/l	0	5.69	1.84	1.18	64.05	1.11	1.56	2.2175	135
HCO <sub>3</sub>	mg/l	328.6	1357.5	679.25	180.79	26.62	555.75	666	793.50	215
SO <sub>4</sub>	mg/l	5.53	470	62.06	55.21	88.96	28.30	50	78.10	214
TEMP	°C	11.4	20.4	16.28	1.31	8.04	15.30	16.20	17.03	107
pH		6.92	8.96	7.58	7.66	101.10	0	0	0	211
Cond	uS/cm	500	3040	1014.46	390.10	38.45	774	930	1165	214

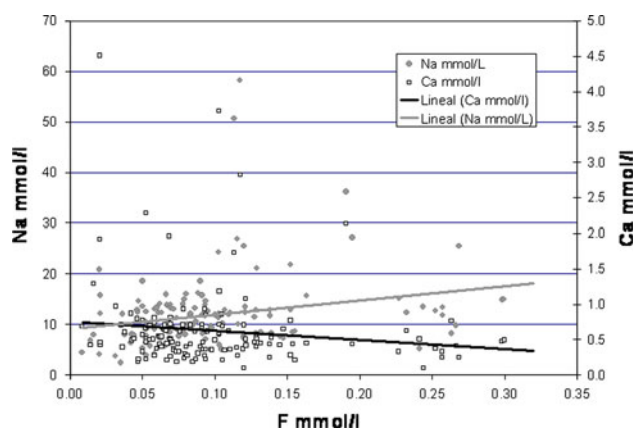
**Fig. 3** Piper diagram showing groundwater composition at the QGR catchment. **a** Samples containing less than 1.2 mg/l of fluoride. **b** Samples containing more than 1.2 mg/l



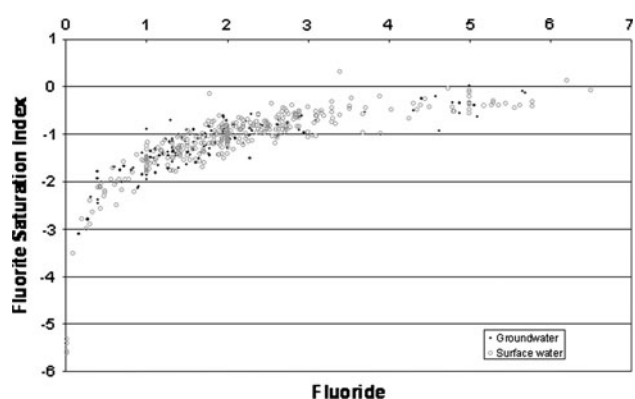
performed using PHREEQC2.0 code (Parkhurst and Appelo 1999). Results are shown in a graph relating F<sup>-</sup> concentration versus SI<sub>CaF<sub>2</sub></sub> (Fig. 5). As expected, SI values increase as fluoride concentration increases tending to the equilibrium value (SI = 0), but few samples reach this state.

Fluoride distribution in groundwater

Fluoride content in the QGR catchment increases in some concordance (not total) with the groundwater flow direction. The zone with the highest values (between 3.1 and 3.7 mg/l) is located in the southwestern section of the



**Fig. 4**  $F^-$  concentration against  $Na^+$  and  $Ca^{+2}$  concentrations in groundwater samples



**Fig. 5** Fluorite saturation index versus fluoride concentration

catchment. On the other hand, the eastern belt of the catchment shows an area with ranges 1.1–2.0 mg/l (Fig. 6).

#### Fluoride distribution in surface water

Fluoride concentrations in surface water have the same behavior as groundwater, confirming the predominance of baseflow in surface water composition (Martínez et al. 2007). Figure 6 also shows the average value of fluoride concentration at different sampling points.

## Discussion

Fluoride concentration in the catchment of the QGR is high, such as in many areas of the Pampa plain in Argentina. Mean values exceed the drinking water admissible levels established by the local regulations. More than 70% of the total amount of samples exceeds the regulation value (1.2 mg/l).

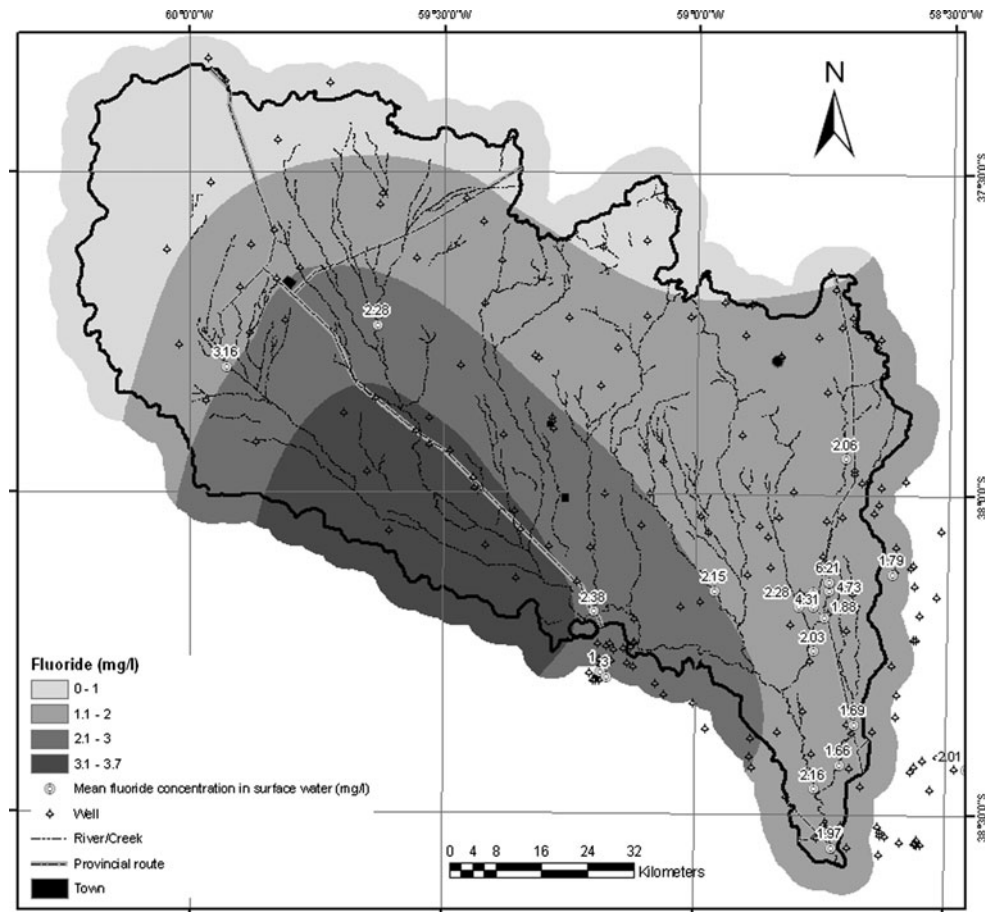
A natural origin for fluoride pollution is a logical conclusion taking into account the lack of any human source.

As mentioned above, the typical mineralogy of loess-like sediments in the Argentine Pampa does not include main fluoride bearing mineral. However, the presence of biotite has been reported in the study area (Quiroz et al. 2008). Volcanic glass shards scattered in the loess-like sediments have been considered to be the main source of fluoride in groundwater of the Pampa from the work of Nicolli et al. (1989). Because of the presence of volcanic glass all over the Pampa's area and the random distribution of fluoride contents, the processes controlling the shards dissolution and the fluoride mobility must be identified. Another possible fluoride source is biotite weathering as has been already said. In the catchment it is possible to expect the presence of biotite in the hydrogeologic basement, which is formed by micaceous sandstones of the Ventania range, outcropping to the western border.

Surface water has an average and a maximum value higher than those of groundwater. Previous studies in the catchment (Martínez et al. 2007; Quiroz et al. 2008) indicate that streams are mostly gaining streams all along the basin, and consequently their compositions correspond to that of groundwater discharge. The highest values are consequence of being groundwater discharge the main component of streamflow, and it is dominated by sodium bicarbonate water types. The correlation between  $F^-$  and  $Na-HCO_3$  waters has been already mentioned in many works (Rafique et al. 2008; Coestiers et al. 2008; Fantong et al. 2009), some of them of the Pampa plain (Gómez et al. 2009; Kruse and Ainchil 2003). Then, the dominance in the composition of streamflow of groundwater discharge that is  $Na-HCO_3$  type can explain the higher mean and peak contents of fluoride in this kind of water.

The causes of the good correlation between fluoride content and  $Na-HCO_3$  type waters found in groundwater have been assigned in some reviews (Edmunds and Smedley 2005) to the effect of high Ca contents that can result in lowering the fluoride concentration in solution through fluorite precipitation and also through calcite precipitation, as proposed by Turner et al. (2005). Another reason for the  $F^-$  versus  $Na-HCO_3$  water type correlation in the Pampas is the higher solubility of silica, volcanic glass shards in this case, under alkaline pH and sodium waters (Marshall and Warakomski 1980). The Piper diagrams (Fig. 3) have been designed in order to relate  $F^-$  concentration against major ion composition of groundwater, in a similar way of that previously used by Nicolli et al. (1989). They show some relationship between  $F^-$  contents and  $Na-HCO_3$  water type. The direct correspondence between  $F^-$  and  $Na^+$  increase is more clearly shown in Fig. 4, indicating a general trend to increase  $F^-$  as  $Na^+$  increase. The correlation coefficient between F and Na is not so high (0.236), but it is over the theoretical value for a 99% of confidence (0.198), indicating a significant

**Fig. 6** Fluoride distribution in groundwater. Fluoride distribution in streamwater is indicated including average values for each sampling point are shown



correlation (Merodio 1985). This observation suggests that, while the higher solubility of silica under alkaline conditions is important to determinate fluoride contents, other processes overlap, which must be discussed.

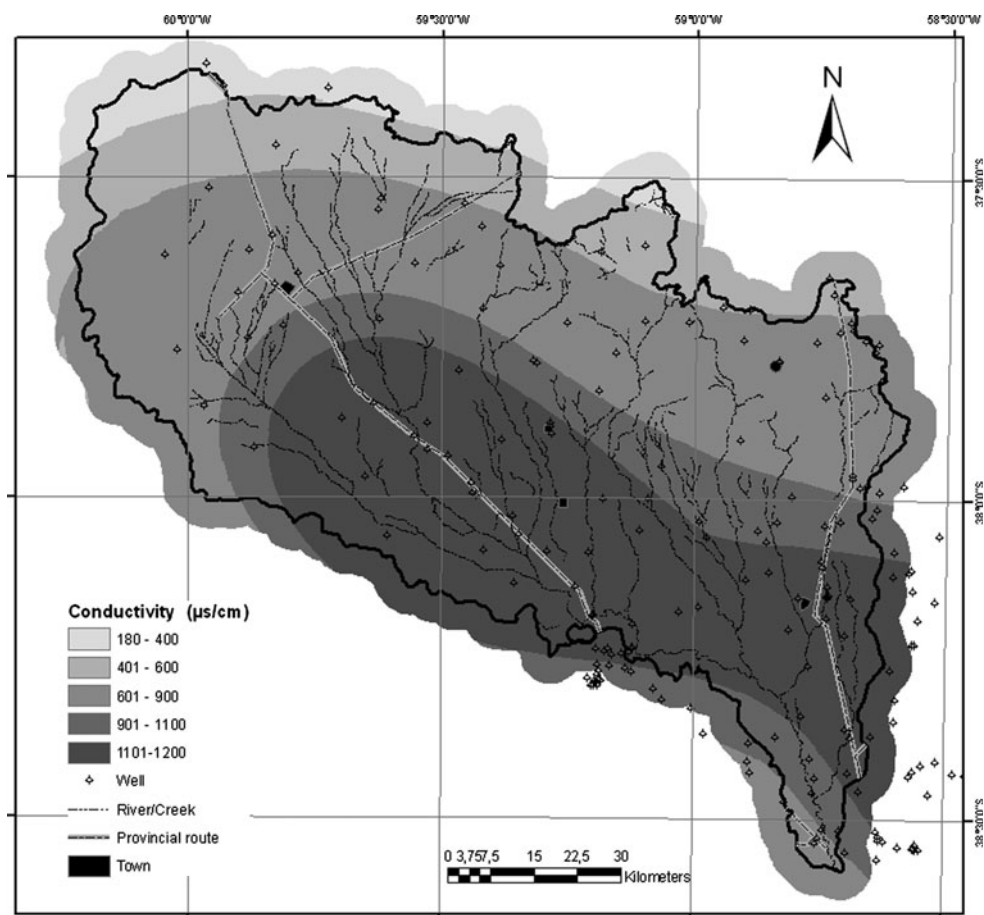
In few samples  $SI_{CaF_2}$  calculations show that maximum fluoride contents can be controlled by fluorite saturation and precipitation. Then other processes affecting fluoride sources, solubility and mobility should be addressed. The distribution map (Fig. 6) suggests two main factors controlling fluoride contents, one hydrological and the other geochemical. There is a general increase of all the dissolved ions in the main flow sense as the natural consequence of the higher residence times, which can be observed in the distribution of the electrical conductivity (EC) (Fig. 7). Nevertheless, the fluoride concentration is not well correlated with EC at the outlet of the basin into the Atlantic Ocean. The occurrence of the higher values of EC, and also of fluoride in the SW area do not exactly correspond to the final discharge point and can be attributed to geological conditioning.

It is interesting to observe that the group of samples forming the tail of high values exceeding 3.5 mg/l of  $F^-$  in Fig. 2b, is obviously those defining the high values zone in Fig. 5. One normal distribution corresponds to the main

portion of the histogram with a mean value around 1.5 mg/l, and the other minor distribution is the tail with a mean value around 4.8 mg/l. Smirnov (1963) stated that the normal distribution is the statistical result of chemical equilibrium. The important issue is that the existence in the histogram of two superposed normal distributions can be interpreted as two different sources of fluoride under equilibrium conditions.

The fluoride normal distribution occupying the larger area, with maximum values around 3.0 mg/l can be the result of the most common process in the pampas plain, volcanic glass dissolution. On the other hand, other fluoride source can be responsible for higher concentrations. Analyzing the particular conditions in the area of the second population of samples, two distinctive types of features can be recognized. The first one is a geological feature. As already said, outcrops of rocks have been identified in the area, and in this contribution the basement rocks have been detected at 69 m. Being the outcropping basement formed by micaceous sandstones (Llambías and Prozzi 1975), the presence or higher percentages of biotite in the sediments can be expected. Moreover, this basement block constitutes an impermeable barrier which also affects groundwater flow, leading to the upward flow of deeper and more saline

**Fig. 7** Distribution of electrical conductivity values in groundwater



waters, resulting in the higher EC zone. Deeper groundwater in the area is more saline as a consequence of a larger contact time with the aquifer materials, as it has been demonstrated by CFCs age dating. Water age in wells deeper than 60 m is older than 50 years, while it is about 25–30 years for shallow wells (Martínez et al. 2009).

Geochemical factors control the other minor aspects of fluoride distribution. The map of saturation index in fluorite in groundwater (Fig. 5) is quite similar to that of fluoride concentration (Fig. 6), being the area of maximum contents near to the saturation. This is indicating that maximum fluoride levels are poorly conditioned by fluorite precipitation. As mentioned before, calcite precipitation can decrease fluoride concentrations by adsorption (Turner et al. 2005). Apart from this, Coestsiers et al. (2008) pointed out that calcite dissolution can also result in fluoride decrease because of the ion common effect, leading to fluorite precipitation. Groundwater in the QGR catchment is saturated in calcite (Fig. 8) and then that process should not be influencing fluoride in solution. No correspondence can be observed between calcite oversaturated areas and low fluoride areas. This suggests that the effect of fluoride adsorption by calcite precipitation does not affect dissolved fluoride significantly.

## Conclusions

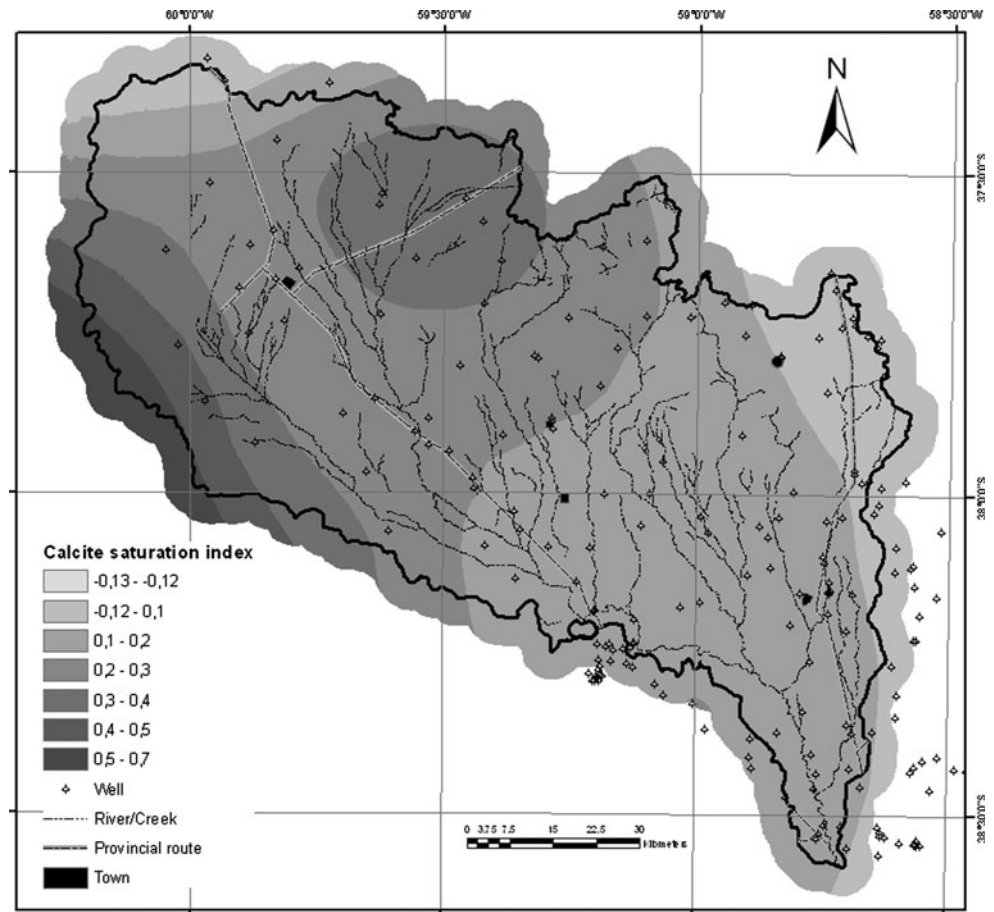
From the former observations, it can be concluded that about 70% of fluoride in the groundwater samples in the QGR basin exceed maximum admissible levels. This observation is also true for stream water. Fluoride concentration distribution in the catchment shows a zone of higher values toward the western-central area.

Analyzing the statistical distribution of fluoride in groundwater, a bi-modal distribution appears and it seems to be the combination of two normal populations. The group of samples of relative lower concentrations is dispersed on the major area of the catchment, with a mean value around 1.5 mg/l of  $F^-$ . This area is dominated by the silt-sand Pampero deposits, bearing important proportions of volcanic shards. The origin of  $F^-$  because of volcanic glass dissolution has been generally accepted in the Pampa plain environment. In this environment, the relationship between higher salinity sodium waters and volcanic glass dissolution can be due to the higher solubility of silica under alkaline conditions.

The western areas of outcrops of Paleozoic rocks bearing biotite determine the existence of a second group of samples which include the maximum fluoride levels. If



**Fig. 8** Distribution of values of saturation index calcite in groundwater



well it is also possible to expect some contribution from volcanic glass source in the area, the cutting from drilled wells in the zone reveals a dominance of sands instead of silt sediments. The lower proportion of the silt fraction in the area involves a lower volcanic glass proportion and probably a lower contribution from this source to  $F^-$  contents.

No specific adsorption processes have been identified. The maximum fluoride concentration zone coincides with the calcite equilibrium area, and then, the removal of fluoride by calcite precipitation, as proposed by Turner et al. (2005), is not probably taking place at the QGR catchment. Some limit to maximum fluoride concentration can be stated by fluorite equilibrium, but this study shows that very few samples are supersaturated in fluorite, involving samples with concentrations higher than 6 mg/l of  $F^-$ . Ion common effect in calcium by its removal during calcite precipitation contributes to increase fluoride solubility, decreasing fluorite ionic activity product.

The existence of two different fluoride sources, one related to volcanic glass dissolution, and the other assigned to the weathering of minerals in the bedrock sandstones, probably biotite, appears to be the most noticeable findings in this study case.

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