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High fluorine and other associated trace elements in waters from the south of the Pampean plain

Altas concentraciones de flúor y oligoelementos asociados en aguas del sur de la llanura Pampeana

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Abstract. We investigated the levels of F and its relationship with As, B and V in ground and surface waters of the southern Pampas, where cases of dental and skeletal fluorosis, and arsenic in hair and urine samples have been detected in the rural population. Eating vegetables and cereals grown in irrigated areas with excessive fluoride may increase the risk of fluorosis due to the addition of the extra F contributed from other sources such as drinking water. Moreover, if these elements exceed the tolerance of crops produce toxicity and, like salinity, they decrease the potential crop yield. Within an area of 2300 km^2, 81 samples were taken from surface and groundwaters to determine F, As, B and V. Fluoride was detected in 86% of the sampled groundwaters, and in 65% of the surface waters reaching maximun concentrations of 7.12 mg/L and of 6.5 mg/L, respectively. Risk areas were determined based on the distribution of F in the unconfined aquifer; the highest concentrations were observed towards the S-SW, in the central and SE sectors. On the surface flow, the highest concentrations were found at the west with sampling points remarkably prominent. These waters are classified as sodium-sulfate, C3 and with high concentrations of F, B and V that could produce toxicity and reduce yields on irrigated crops. Fluoride correlated significantly ($p<0.01$) with As ($r=0.75$), B ($r=0.57$) and V ($r=0.53$) in groundwater; it also associated with As ($r = 0.65$) in surface waters, and showed higher levels of association with boron ($r=0.88$) and vanadium ($r=0.81$), which showed highly significant linear regressions ($p<0.01$).

Keywords: Fluoride; Trace elements; As; B; V; Surface and groundwaters; Toxicity; Irrigation; Crops and human consumption.

Resumen. Se investigaron los niveles de F y su relación con As, B y V en aguas freáticas y superficiales del sur de la Llanura Pampeana, donde se detectaron casos de fluorosis dental, esquelética y presencia de arsénico en muestras de cabello y orina, en la población rural. El consumo de vegetales y cereales cultivados en áreas irrigadas con excesivo flúor podrían incrementar el riesgo de fluorosis a raíz de la adición de F suplementario al aportado desde otras fuentes como el agua de bebida. Por otra parte, si estos elementos sobrepasan la tolerancia de los cultivos producen toxicidad, y al igual que la salinidad disminuyen el rendimiento potencial. Sobre un área de 2.300 km^2, se tomaron 81 muestras de aguas subterráneas y superficiales, de cuyo análisis se determinó la presencia de F, As, B y V. Se detectaron concentraciones de F de hasta un máximo de 12.7 mg/L en 86% de las muestras de agua freática, y valores de hasta 6.5 mg/L en 65% de las muestras de aguas superficiales. Se determinaron áreas de riesgo en función de la distribución del F en el acuífero freático, observándose las mayores concentraciones hacia el S-SO, en el centro y SE. En el flujo superficial, las mayores concentraciones se encontraron sobre el sector oeste, con puntos de muestreo notablemente destacados. Estas aguas se clasifican como sódicas-sulfatadas, C3 y con elevadas concentraciones de F, B y V que podrían producir toxicidad en los cultivos cuando son regados, disminuyendo los rendimientos. En las aguas freáticas el F se correlacionó significativamente ($p<0,01$) con As ($r=0,75$), B ($r=0,57$) y V ($r=0,53$); en aguas superficiales también se asoció con As ($r=0,65$) y se registraron mayores niveles de asociación con boro ($r=0,88$) y vanadio ($r=0,81$), que presentaron regresiones lineales altamente significativas ($p<0,01$).

Palabras clave: Flúor; Oligoelementos; B; As; V; Agua superficial y subterránea; Toxicidad; Riego; Cultivos y humanos.

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INTRODUCTION

Groundwater represents approximately 30% of all the fresh water distributed in our planet, and it is only 2.5% of the world's total (Shiklomanov & Rodda, 2003). If we consider within that percentage the presence of a group of natural contaminants, and other ones caused by anthropic actions, we could infer that water quality, and therefore its quantity, are very risky from the point of view of human consumption. Nearly the entire rural population of our country consumes groundwater simply because it is the most readily accessible resource and, in addition, it does not normally require any purification process. Therefore, we find that a large percentage of this population is consuming water with high contents of certain natural contaminants such as F, As, B and V, among others, which represents a considerable threat to their health. Drinking water is the most important source of F, As, V and other associated trace elements to humans. Moreover, the development of irrigation projects aimed to plant production, such as grains and vegetables, applying surface or groundwater affected by natural, high concentrations of one or more of these contaminants, might give rise to their accumulation in plant tissues, which can impair the normal development of crops. At the same time, the daily consumption of these products also contributes to their incorporation into the human body. This might increase the potential risks in population health when contaminant contents exceed guidance levels indicated by the regulations for food quality control (CAA).

Fluoride is a member of the halogen family naturally present in the Earth's crust that is usually found in soils and waters (Wright, 2003). The presence of F in superficial and groundwaters, with concentration values surpassing the guidelines suggested by the World Health Organization (WHO, 2004), has been reported in different parts of the world such as India, Sri Lanka, China, Senegal, Ghana, Ivory Coast, Tunisia, Libya, Sudan, Uganda, Kenya, Tanzania, Ethiopia, Mexico, Argentina (Pauwels & Ahmed, 2007; Choubisa, 2007), Malawi, Czech Republic (Zemek et al., 2006), Nigeria, Papua New Guinea, Egypt, Thailand, India/Pakistan (Ayoko et al., 2007), the USA (Boulding & Ginn, 2004) and the UK (Neal et al., 2003). In Argentina, most of the Provinces located within the great Chaco-Pampean Plain, namely Chaco, Córdoba, La Pampa, Buenos Aires, Santiago del Estero and Santa Fe, among others, show areas with high concentrations of F in groundwaters.

Consuming waters with elevated concentrations of F, accumulated in crops and animals, put human health at risk. The most common symptom in human communities exposed to the ingestion of waters with excess F is dental fluorosis, which produces mottled tooth enamel, decay and even tooth loss in severe cases (Pauwels & Ahmed, 2007). Since F causes calcifications and increases bone mass, another very common diagnosis is skeletal fluorosis. The most severe form is skeletal crippling, responsible for ligament calcification, immobility, emaciation and neurological disorders (Puche & Rigalli, 2007).

In accord to Jha et al. (2011), consumption of cereals and crops cultivated in irrigated areas with excessive F in waters could increase fluorosis risk, owed to supplementary F addition from sources other than drinking water or those used for food cooking. Some vegetal species accumulate F without developing toxicity symptoms even at high concentrations (up 4000 μg/g); several others evidence toxicity at lower concentrations, whilst some are extremely sensitive at concentrations < 20 μg/g. Lettuce (*Lactuca sativa*), spinach (*Spinacea oleracea*) and potato (*Solanum tuberosum* subsp. *Tuberosum*) are recognized to be high fluoride providers to the daily diet. Meanwhile, accumulation is most noticeable for wheat (*Triticum aestivum*) than for rice (*Oryza sativa)*. Onion crops (*Allium cepa*) have lower F accumulation in bulbs than in roots (Jha et al., 2009).

The Argentine Food Code (CAA, 2007) suggests a table of values with the recommended limit contents of fluoride according to mean and maximum temperatures in the consumption area; the highest limit (for medium and maximum temperatures of 10 °C and 12 °C) is 1.7 mg/L, because concentration values decrease as temperature increases (Gray, 1996). The WHO (2004) states a reference guideline value for drinking water of 1.5 mg/L, adopted by many countries as the national standard value.

Associated to F, the presence of As, B and V in waters constitute a pool of elements that have harmful effects on human health when their concentrations exceed the reference guideline values suggested for drinking waters by the WHO (2004), CAA (2007) and US EPA (1997). They might be additional contaminants of the water resources. They produce toxicity when surpassing the tolerance criteria indicated by Ayers & Wescot (1987), and like salinity, they might potentially decrease yield. Their effects directly occur on plants through accumulation in leaves via transpiration (Rhoades, 1972; Maas, 1984).

Moreover, clear symptoms appear in older leaves with elevated B. There is a progressive yellowing with wilting and necrosis from the border towards the centre of the leaves with a gradual increase in concentration (Montiel, 1984; Prieto et al., 1996; Vargas, 2009). In relation to As, it is also hosted in leaves and grains, although high concentrations may appear in roots (Prieto García et al., 2005). It was demonstrated a close correlation between the high levels of F and As in water resources. Irrigation of edible vegetables with high F and As determines their transfer from water, and their accumulation in plant tissues at levels that in some cases may be excessive and harmful to human health. The subsequent integration into food chains exposes population to contamination through food intake (Nriagu, 1994).

Considering that vegetables are fundamental in diet, investigation of the maximum amounts of As that could reach human body is needed; the normal values in vegetal tissues range from 0.08 to 2 mg/kg (Warren & Alloway, 2003). The maximum acceptable level is 1 mg/kg in fresh weight (Warren & Alloway, 2003; CAA, 2007). There are some studies of As contents for soya (*Glycine max*: Bustingorri y Lavado, 2011), rice (*Oryza sativa*: Soro et al., 2011), lettuce (*L. Sativa)* and carrot (*Daucus scarota*): (Cao & Ma, 2004), cauliflower (*Brassica oleracea var. Botrytis*: Kim et al., 2002) and arugula (*Eruca vesicaria cavanilles*: Franco et al., 2012).

Recent studies also demonstrated that irrigation water with high V might contaminate grasses and vegetables with this ion and impact in cattle and humans (Khan et al., 2011). Vanadium contents exceeding the maximum recommended level (2 μg/g) may cause chlorosis and restrictions to plant development, affecting also cattle food. Constant consumption of grasses and vegetables with high V leads to concentration in cells and, in the long term, could induce symptoms of poisoning. The presence of V in irrigation waters affects plants to a degree depending on concentration and pH. The potential replacing of PO_4^{3-} by V in bones of mammals including cattle when consuming grasses has been reported in the scientific literature. Water and foods (cereals, vegetables and fresh fruits) are the main sources of human exposure to V for most of the populations (Barceloux, 1999). Nevertheless, the biological behaviour of V is not completely understood. Its image faces a great contradiction from toxic to essential, with antidiabetic and anticarcinogenic effects (Mukherjee et al., 2004). We report excessive V levels in waters in the present study.

In typical agriculture-cattle breeding regions, rural populations are pressed by the need of water for human, crop and cattle use thus depending on the exploitation of hydric resources, particularly groundwater. They mostly ignore the risk imposed by its ingestion. This research work aimed at providing information on the levels of F, As, B, and V, and their distribution in the waters of the south of the great Pampean Plain. This is a region where rural and peri-urban populations are exposed to a potential risk of hydroarsenicism (Paoloni et al., 2005), and cases of dental and skeletal fluorosis have been detected (De La Sota et al., 1997).

MATERIALS AND METHODS

The cartography made by the Instituto Geográfico Militar (IGM-Military Geographical Institute) in scales of 1:100000 and 1:50000, and Landsat images, provided the basis for developing our research. In the southern most sector of the Great Chaco-Pampean Plain (1200000 km^2), a 2300 km^2 area, where some endemic cases of fluorosis have been diagnosed (De La Sota et al., 1997), was selected for study. In this area lies Bahía Blanca municipality, with a population of approximately 320000 inhabitants. The municipality, whose southern boundary corresponds to the Atlantic Ocean coast, is located between latitudes 38° 22' S and 38° 45' S and longitudes 61° 46' W and 62° 28' W, of Greenwich Meridian (Fig. 1).

Our study area is included in a temperate climate region, whose annual rainfall varies between 550 and 600 mm, with mean temperatures ranging between 8.9 °C and 21.9 °C and well-defined thermal seasons. Quaternary loess sediments constitute an undulating relief in the southern extreme of the Pampean Plain, where agriculture and farming are the main regional activities. These result in the strong presence of a residing and stable rural population. Soil and water resources are the components governing the production systems mentioned above. They have been abused during almost a century, and degraded as a result. Attempts to employ conservation techniques have been scarce and/or limited, while anthropic action has been pronounced at the same time. All these productive activities are largely dependent on the quantity and the quality of water provision sources.

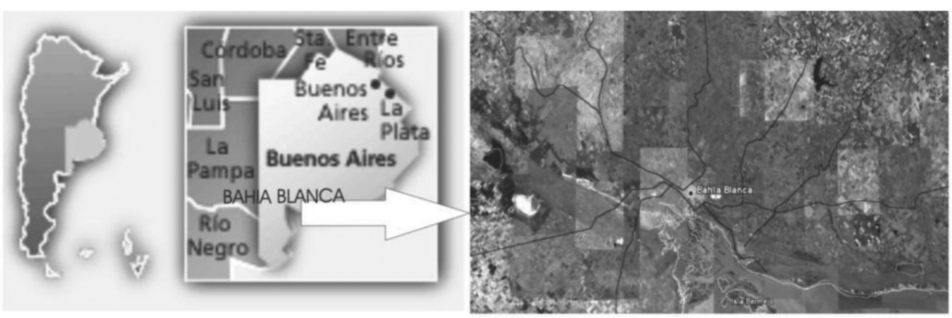

Fig. 1. Geographical location of the study area.
Fig. 1. Ubicación del área de estudio.

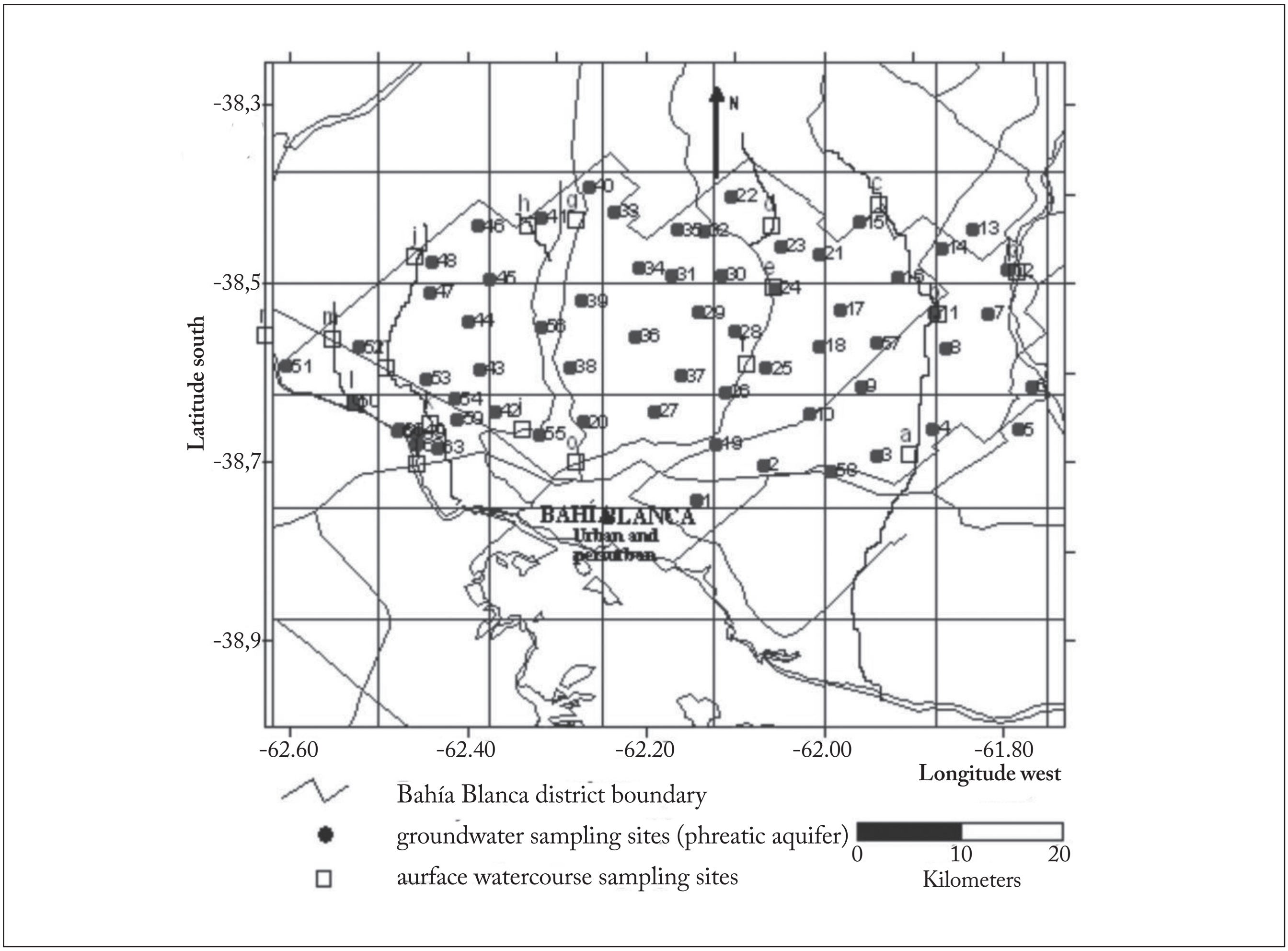

Fig. 2. Bahía Blanca district. Location of sampling sites in the phreatic aquifer and in surface watercourses.
Fig. 2. Partido de Bahía Blanca – Ubicación de los lugares de muestreo en cauces superficiales y acuífero freático.

A selective and precise sampling of water from superficial and ground water sources was made. Water sampled was that more easily accessible to users (i.e., phreatic aquifers). An adequate flow rate for meeting their demands can be obtained from these water sources by using low-capacity centrifugal or piston pumps. A Global P*ositioning* System (GPS) was employed in the survey to determine the geographical location of the 63 groundwater samples and the 18 superficial ones (Fig. 2). Temperature and depth of water level were recorded for all wells and perforations.

A HI 98401 meter was used to determine F concentrations. This instrument measures values from 0.05 mg/L to 1.9 g/L in five different scales, automatically choosing the range that provides the best resolution. Measurements were performed using a specific F electrode and a reference electrode to ensure maximum accuracy. A temperature probe automatically compensated the results by means of an incorporated microprocessor. In addition, the following supplementary analyses were carried out: pH (potentiometer); electrical conductivity (EC meter); hardness; dissolved solids (evaporation); $Ca^{+}Mg$ (versenate method); Ca, Na and K (photometry); Mg (EDTA complexometry); sulfates (turbidimetry); carbonates and bicarbonates (volumetry with H_2SO_4); nitrates (specific electrodes) and phosphates. B, Cr, V and other toxic elements were analyzed according to specific electrodes and Inductively Coupled Plasma (ICP). Arsenic was analyzed with a Hydride Generator and by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

The hydrodynamics of the phreatic levels are presented as an isohypsic chart, and the geographical distribution of the concentrations of total soluble salts and F is illustrated in isoconcentration maps performed with Surfer V.8 software. Moreover, statistical analysis on surface and groundwater concentrations of F, As, B and V was performed using Infostat (Di Rienzo et al., 2009).

RESULTS AND DISCUSSION

Tables 1 and 2, respectively, show the results of hydrochemical analyses and the statistical treatment of the samples from the phreatic aquifer and superficial watercourses. This is together with the guidelines values for the inorganic component set for drinking water suitability by the CAA (2007 amendment). Chemical data from the phreatic level are representative of the rural environment. With the exception of particular cases of contamination, it represents the chemical baseline or regional background level of phreatic groundwaters.

The phreatic aquifer acts as an active system; it is exclusively recharged by infiltration of excess rainfall in the area of the basins involved in our research. The morphology of the area determines the hydrodynamics of the phreatic surface, which is/are exhibited (Fig. 3) by the significant parallelism between the isohypses. The distribution pattern of isohypses defines a clear orientation of the discharge towards lower positions at the maritime coast, with a hydraulic gradient of 4.5‰ in the western sector, which coincides with the end of the lower basin of Sauce Chico river, and 2.8‰ in the eastern sector of the study area.

Groundwater hydrochemistry showed a strong presence of F, found with an irregular and asymmetric frequency distribution, so that 86% of the samples exceeded the WHO reference guideline value (1.5 mg/L) (Fig. 4). Minimum concentrations were of 0.4 and maximum levels reached 12.7 mg/L (Table 1), with a modal interval ranging from 2.5 to 3.5 mg/L, which corresponded to 22.2 % of the free aquifer samples.

Regarding surface waters, 67% of the sampling points exceeded WHO limits (Fig. 5), with most concentrations in the range of 0.5 - 1.5 mg/L, a minimum of 0.6 and a maximum of 6.5 mg/L (Table 2).

Generally speaking and considering the major ions, both the superficial and groundwater resources could be classified as sodium-sulfate, and a water aptitude for irrigation of C3 owing to salinity. Taking into account the mean concentrations of F, B and V, utilization of this water in irrigation projects could produce toxicity and accumulation in summer (sunflower, *Heliantus annuus*; soya, *G. Max;* grain sorghum, *Sorghum bicolor*) and winter crops (wheat, *T. Aestivum;* barley, *Hordeun vulgare;* oats, *Avena sativa)*. Our study indicates that As does not affect water quality for irrigation, although it is not suitable for human consumption. Figure 6 shows a highly-irregular distribution pattern in the phreatic waters by means of isoconcentration curves, and according to the dimensions of the sampling points in the form of nuclei. Highest values are exhibited in the southwestern and south-

Table 1. Results of phreatic water analyses.
Tabla 1. Resultados de los análisis de las aguas del nivel freático.

Hydrochemical Parameters -Limit Value (AFC)	Minimum Value	Maximum Value	Medium Value	Standard Deviation	Median
HCO_3 (600 mg/L)	148	764	374	132	347
Cl^- (350 mg/L)	6	1688	198	277	132
$SO_4^=$ (400 mg/L)	5	2539	308	499	148
$N\text{-}NO_3^-$ (45 mg/L)	1	155	15	27	5
Na^+ (920 mg/L)	64	1944	428	346	339
Mg^{++} (60 mg/L)	0	130	22	27	12
Ca^{++} (400 mg/L)	4	577	40	74	25
PO_4^{3-} (0.2 mg/L)	0.15	1.74	0.19	0.22	0.15
Cr (0.05 mg/L)	0.001	0.012	0.005	0.002	0.005
Cd (0.01 mg/L)	0.001	0.007	0.003	0.001	0.003
Ba (1 mg/L)	0.05	0.07	0.06	0.01	0.07
As (0.01 mg/L)	0.007	0.302	0.081	0.060	0.070
V (0.05 mg/L)	0.05	2.453	0.608	0.459	0.512
B (0.30 mg/L)	0.15	5.33	1.11	0.82	0.94
F^- (1.5 mg/L)	0.4	12.7	3.9	2.4	3.4
pH (6.5 – 8.5)	6.6	8.1	7.6	0.2	7.6
Ce (dS/m)	0.3	8.1	1.9	1.6	1.4
Depth (m)	1.2	55.8	16.7	12.2	14.1

Table 2. Results of superficial watercourse analyses.
Tabla 2. Resultados de los análisis de las aguas de los cauces superficiales.

Hydrochemical Parameters -Limit Value (AFC)	Minimum Value	Maximum Value	Medium Value	Standard Deviation	Median
HCO_3 (600 mg/L)	234	944	518	219	452
Cl^- (350 mg/L)	13	416	177	132	116
$SO_4^=$ (400 mg/L)	25	693	342	263	233
$N\text{-}NO_3^-$ (45 mg/L)	0	128	19	36	2
Na^+ (920 mg/L)	73	852	483	301	343
Mg^{++} (60 mg/L)	10	51	27	12	22
Ca^{++} (400 mg/L)	9	89	47	17	43
PO_4^{3-} (0.2 mg/L)	0.15	0.16	0.15	0.00	0.15
Cr (0.05 mg/L)	0.002	0.041	0.005	0.009	0.004
Cd (0.01 mg/L)	0.001	0.071	0.002	0.020	0.003
Ba (1 mg/L)	0.05	0.06	0.06	0.00	0.06
As (0.01 mg/L)	0.005	0.130	0.048	0.038	0.039
V (0.05 mg/L)	0.050	1.064	0.543	0.351	0.383
B (0.30 mg/L)	0.18	2.56	1.15	0.79	0.65
F^- (1.5 mg/L)	0.6	6.5	3.6	2.2	2.7
pH (6.5 – 8.5)	7.6	8.3	8.0	0.2	7.9
Ce (dS/m)	0.5	3.4	1.9	1.0	1.7

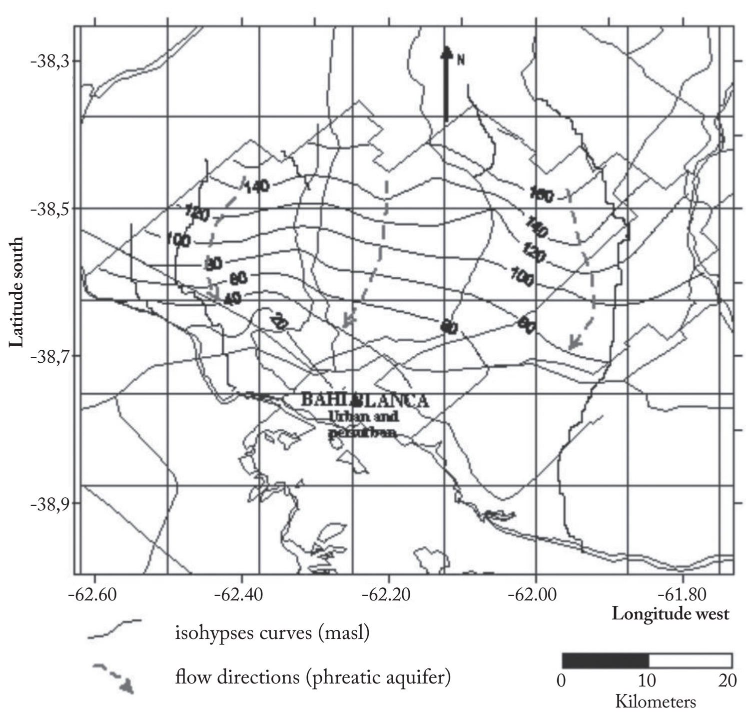

Fig. 3. Isohypsic map.
Fig. 3. Mapa de isohipsas.

ernmost sectors of the studied area, and lowest values were found in the northern sector. This arrangement is typical not only for F but also for As, B and V in the large region adjacent to the study area in the south of the great Pampean Plain (Paoloni et al., 2003; Paoloni et al., 2005). Regarding the behaviour of the superficial flow, the highest concentrations were found in watercourses from the western sector, with significantly-marked sampling points, while values were considerably low in the eastern sector reaching up to 0.6 mg/L (Fig. 7).

Thus, concentrations of F and other trace elements may depend mainly on hydrogeological and geochemical characteristics of the saturated medium of the phreatic aquifer and upper unsaturated section that includes sediments, and soil forms the top of the aquifer, besides the depth and temperature of perforations and wells.

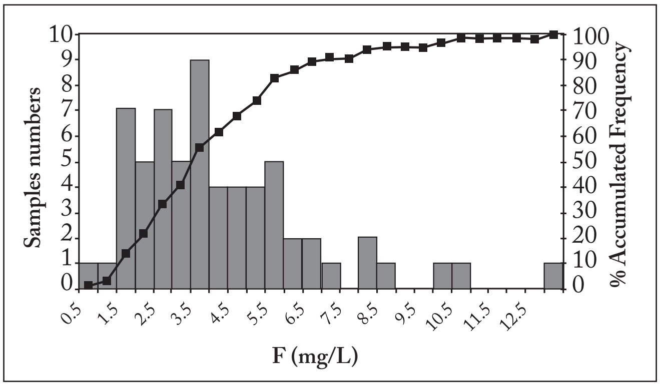

Fig. 4. Distribution of relative and accumulated frequencies of F concentrations at the phreatic level.
Fig. 4. Distribución de frecuencias relativas y acumuladas de las concentraciones de flúor en el nivel freático.

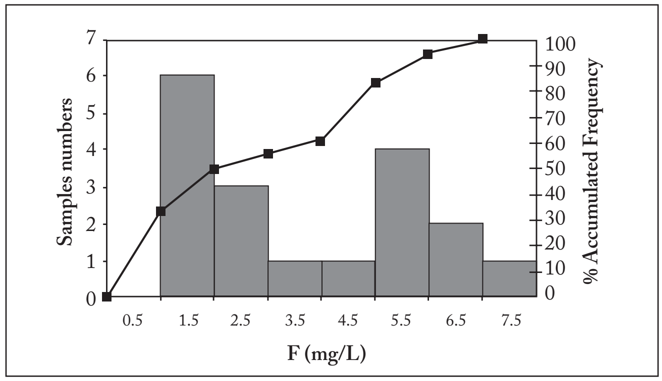

Fig. 5. Distribution of relative and accumulated frequencies of F concentrations in surface watercourses of the study district.
Fig. 5. Distribución de frecuencias relativas y acumuladas de las concentraciones de flúor en los cursos superficiales en el distrito estudiado.

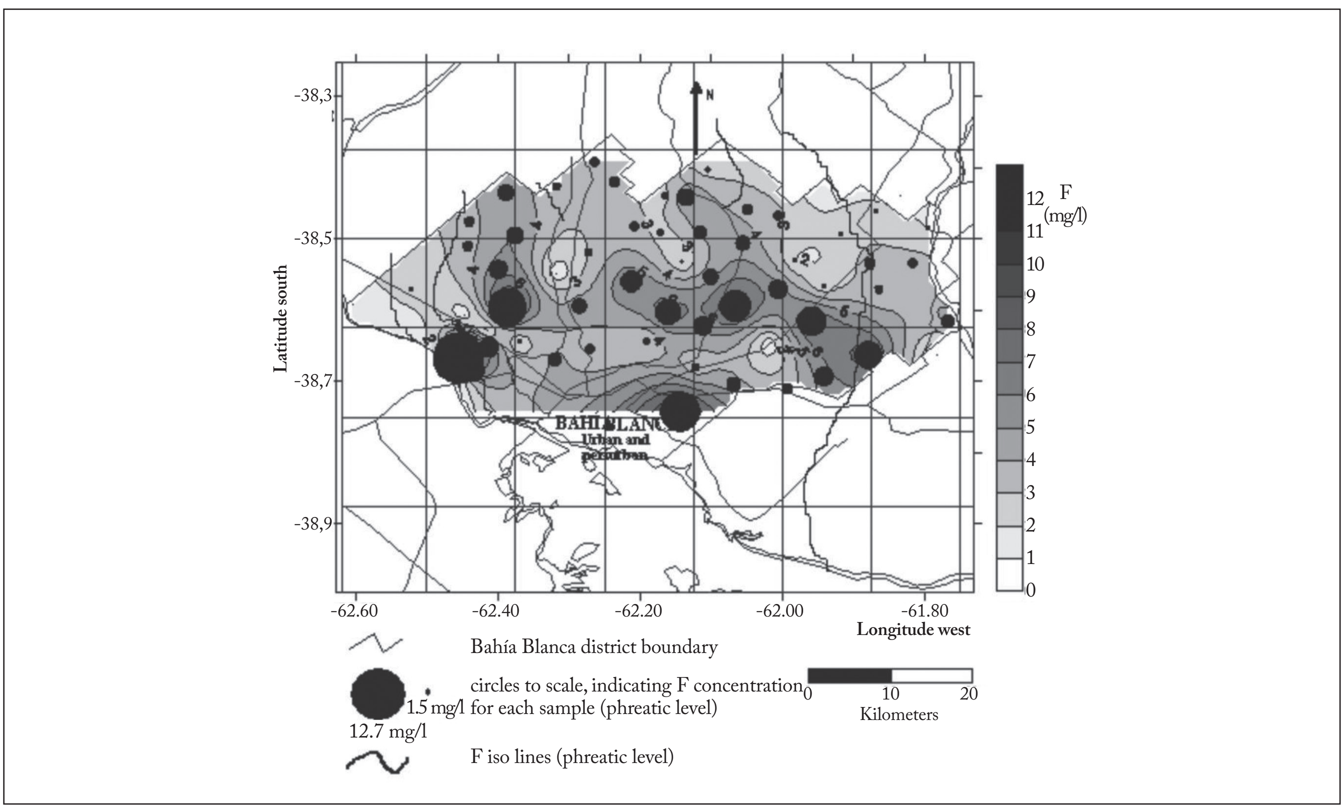

Fig. 6. Fluorine – Isoconcentrations at the phreatic level. Circles size indicate levels in every sample (phreatic level).
Fig. 6. Flúor – Isoconcentraciones en el nivel freático. Los círculos indican, a escala, los valores en cada muestra (nivel freático).

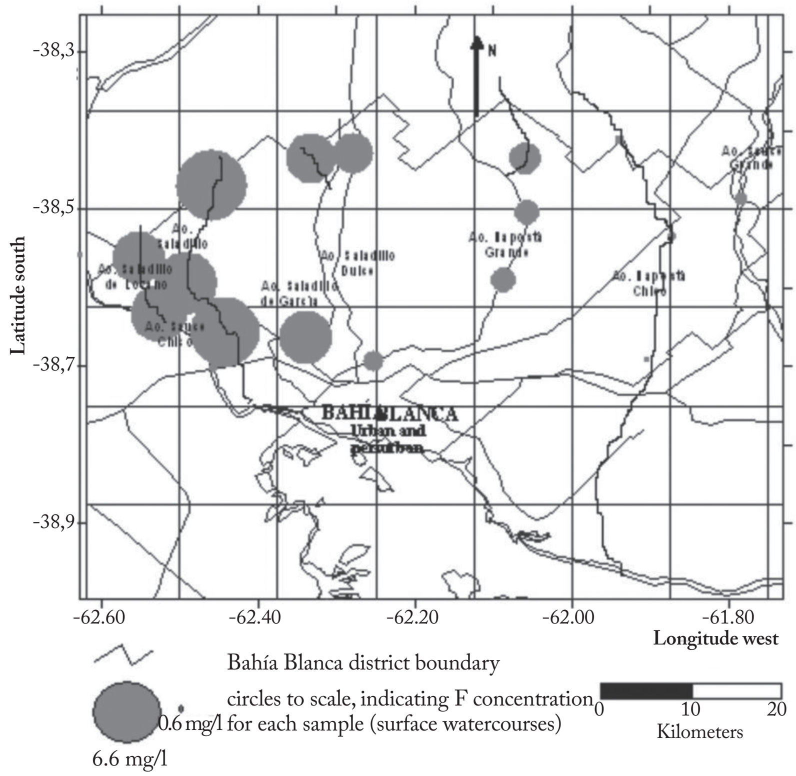

Fig. 7. Fluorine concentrations in surface watercourses.
Fig. 7. Concentraciones de Flúor en cursos superficiales.

Figure 8 shows the results of the linear correlation analysis between F *versus* As ($p<0.01$) (correlation coefficient $r=0.75$), B ($r=0.57$) and V ($r=0.53$) in phreatic waters (63 samples), and those with As ($r= 0.65$), B ($r=0.88$) and V ($r=0.81$) in superficial waters (18 samples). Linear equations and coefficients of determinations (R^2) are included. Results demonstrated positive and highly significant relationships between F and the other trace elements (As, B and V). This is indicative of that high F levels are associated to high concentrations of the other studied ions. Moreover, linear positive regressions between F-B and F-V were found in surface waters, which suggests that concentrations of B and V can be estimated from those of F.

CONCLUSIONS

F-contour maps enabled the identification of areas (1) with F levels exceeding the standards accepted for drinking water, (2) at risk of fluorosis, and (3) with levels of exposure to F. The highest concentrations in phreatic waters were found in the south-southwestern, south-southeastern, and central sectors of the southern Pampean region. Only 14% of the groundwater samples, found in reduced sectors from the north of the study area, showed no risk for drinking water. In the superficial water resource, the risk increased from the central sector towards the west limit of Bahía Blanca district, where the highest concentrations were measured.

Linear correlation analyses indicated that a rise in F-concentration was associated to unacceptable concentrations of As, B and V. All of them increase the danger of consuming affected waters during long periods of time. Even though F *versus* As correlations were lower for superficial waters, their quality was equally affected by concentrations higher than those recommended. This is particularly the case for the watercourses of the western sector, and in locations close to the discharge points on the Atlantic coast.

The high degree of association between F and As in the phreatic aquifer is related to the geoavailability from the aquifer lithology. It is constituted by loess layers that include F and As bearers in the mineral suite and to analogous environments, comparable from the geochemical point of view, which are of the oxidizing type and have a low-rate flow.

Our results presented as maps designed for the southern pampean region could be an efficient tool for preventive medicine in the area of Bahía Blanca district. They facilitate not only the identification but also an early diagnosis of dental or skeletal fluorosis, and hydroarsenicism. In addi-

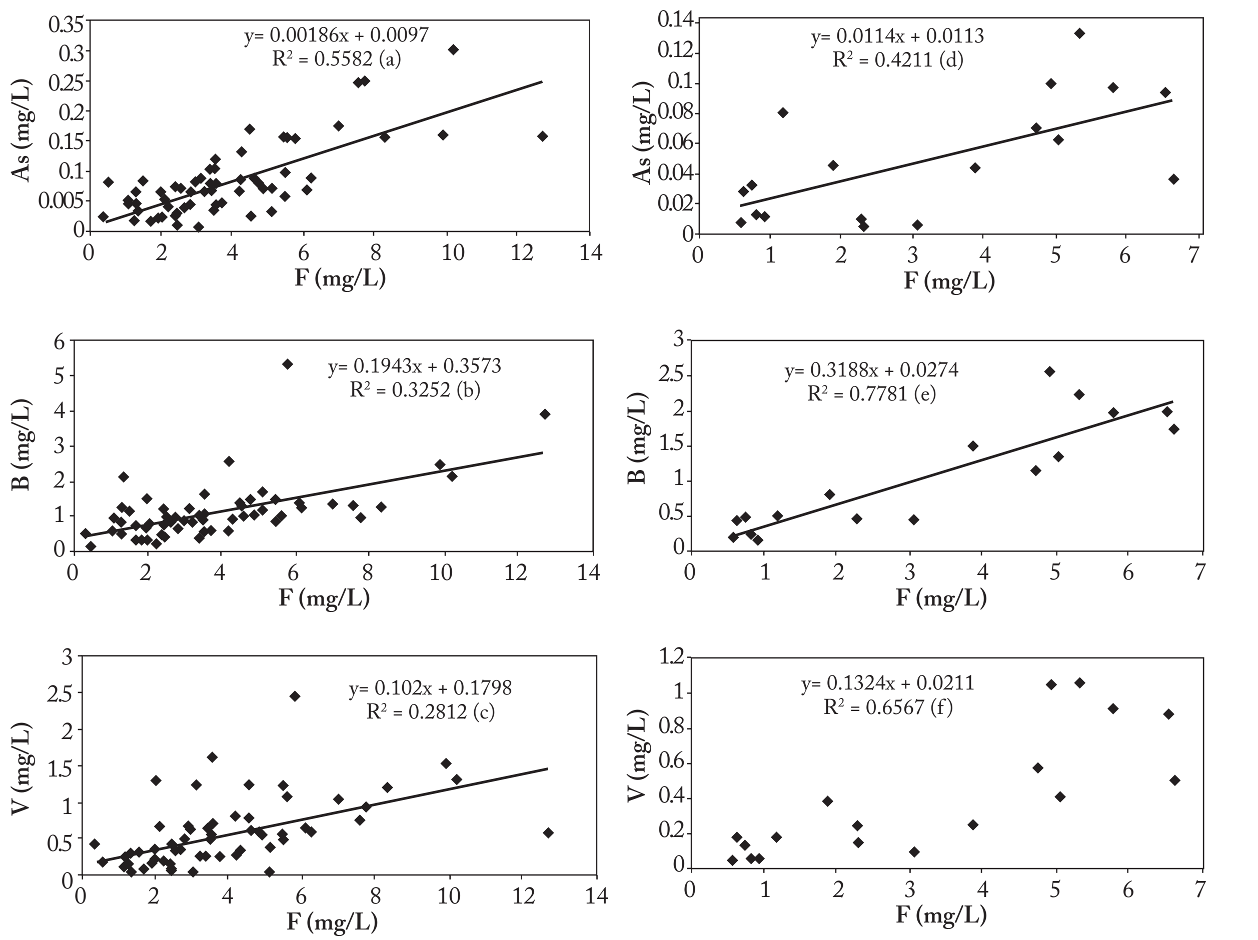

Fig. 8. Correlation of F with As, B and V in groundwater [(a), (b) and (c)] and in surface waters [(d), (e) and (f)].
Fig. 8. Correlación del Flúor con Arsénico, Boro y Vanadio en el agua subterránea [(a), (b) y (c)] y en el agua superficial [(d), (e) y (f)].

tion, they contribute to the identification of the risk factors for the population health, particularly in the peri-urban and rural sectors, where people have no access to piped water. Moreover, evaluation of water quality for irrigation projects in horticulture, and cereal and forage production (for cattle breeding) is essential to (1) choose crop types, and (2) select, plan and develop irrigation systems. The natural contamination investigated causes not only a potential reduction of crop yields, but also its transference to humans through drinking water and food consumption, thus constituting a strong risk for public health.

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