Geologica Acta, Vol.15, Nº 3, Decembre 2017, pgs-pgs
DOI: 10.1344/GeologicaActa2017.15.3.3

Arsenic, fluoride and other trace elements in the Argentina Pampean plain

R.S. BARRANQUERO[1] M. VARNI[2] M. VEGA[3] R. PARDO[3] A. RUIZ DE GALARRETA[1]

[1]Centro de Investigaciones y Estudios Ambientales, Facultad de Ciencias Humanas, Universidad Nacional del Centro de la Provincia de Buenos Aires (UNICEN)
Paraje Arroyo Seco s/n Campus Universitario Tandil, Tandil, 7000, Buenos Aires, Argentina.
Barranquero E-mail: rosario0405@gmail.com Ruiz de Galarreta E-mail: agala@live.com.ar

[2]Instituto de Hidrología de Llanuras 'Dr Eduardo J. Usunoff', UNICEN
República de Italia 780, Azul, B7300, Buenos Aires, Argentina. Varni E-mail: marcelovarni@gmail.com

[3]Departamento de Química Analítica, Facultad de Ciencias, Universidad de Valladolid
Campus Miguel Delibes, Valladolid, E-47011, España. Vega E-mail: solvega@qa.uva.es Pardo E-mail: rpardo@qa.uva.es

ABSTRACT

The contents of arsenic (As), fluoride (F) and other trace elements (B, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn, Ba, Si and Sr) have been determined in groundwater samples from the Langueyú creek basin, in the Argentina Pampean plain. This research aims to establish the baseline concentration and geographical distribution of trace elements in this basin. This aim has particular interest to public health in the city of Tandil where groundwater is the principal source of water for human supply. The baseline concentrations of elements in the Langueyú creek basin are in good agreement with published data from other locations of the Pampean aquifer. The arsenic limit of 10µg/L, established as provisional limit by the World Health Organization (WHO), was exceeded in 78% of the sampled wells, with As concentration increasing in the direction of groundwater flow. Concentrations of B, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn regulated by the Argentinian Food Code (CAA) do not exceed the maximum limit for drinking water, although concentrations of Ni, Zn or Pb peaked up at some wells, probably due to pipeline corrosion. The strong correlation observed between As, F, V, Cr and B has been related to their anionic character at the groundwater natural alkaline pH that is likely associated with similar mobilization (adsorption/desorption) processes. Worst consequences for human health have arisen in areas with the highest arsenic concentration in drinking water. The conclusions of this study contribute to understand the provenance and mobilization processes of some trace elements in groundwater. It enables the decision making regarding the public health priorities and the technological treatments of water resources in urban and rural areas.

KEYWORDS **Groundwater quality. Trace elements. Sedimentary basin. Langueyú creek basin. Argentina Pampean plain.**

INTRODUCTION

The drinking water supply for human development is a worldwide issue (WHO/UNICEF, 2012). Monitoring the chemical quality of water is fundamental because the occurrence of certain elements can cause health problems. Since groundwater is the main water resource in many regions, the presence of toxic elements in groundwater is a serious concern as they can originate not only from anthropogenic sources, but more frequently from natural sources due to natural processes.

Research on the occurrence of toxic trace elements in groundwater has increased worldwide in recent years (Silva Busso and Santa Cruz, 2005; Khan *et al*., 2010; Haloi and Sarma, 2011; Li *et al*., 2014; Ullah *et al*., 2015). These authors investigated the presence of trace elements in groundwater due to natural and anthropogenic sources and evaluated the risk to human health if used for drinking water supply. In Argentina, studies on trace elements in soil, surface and groundwater, at different scales, have been carried out in Buenos Aires province (Hernández *et al*., 2002; Kruse and Ainchil, 2003; Martinez *et al*., 2003; Bonorino *et al*., 2008; Navoni *et al*., 2012; Dietrich et al., 2016; Zabala *et al*., 2016), Córdoba (Gómez *et al*., 2009; Matteoda *et al*., 2010; Matteoda and Blarasin, 2013), La Pampa (Smedley *et al*., 2002; Smedley *et al*., 2005), Santiago del Estero (Bhattacharya *et al*., 2006), Tucumán (Nicolli *et al*., 2010) and in several provinces of the Chaco-Pampean plain (Farías *et al*., 2003; Blanco *et al*., 2006; Nicolli *et al*., 2012). Arsenic is an extremely toxic metalloid that can be incorporated by humans through diet, inhalation and dermal contact, but especially through drinking water. It is transported by the bloodstream, accumulating in lungs, liver, kidneys, skin, teeth, hair and nails (WHO-Executive Council, 2006).

Arsenic is often found in groundwater, thus restricting water use. There have been numerous attempts to elucidate the sources and mobilization mechanisms that regulate the occurrence of As in ground water and surface water. These investigations have focused on hydrogeochemical processes, climatic factors, geomorphology, geological/tectonic setting, groundwater-surface water interactions and groundwater exploitation (Smedley and Kinniburgh, 2002; Mukherjee *et al*., 2006; Bundschuh *et al*., 2012; Alarcon-Herrera *et al*., 2013; Giménez-Forcada *et al*., 2017). Arsenic in groundwater is mainly derived from natural sources often linked to geological materials of volcanic origin. It is necessary to investigate not only the potential sources of high As concentration in groundwater, but also the factors controlling its geographical distribution (Giménez-Forcada *et al*., 2017).

In Latin America, the population exposed to As concentrations in water above 10µg/L is estimated to be about 14 million. In Argentina between 3 and 8 million people consume water with As concentration over 10µg/L (Bundschuh *et al*., 2012). Consequences of long-term consumption of water with high As concentration have been described and include diseases like Endemic Regional Chronic Hydroarsenicism (HACRE) that is characterized by skin lesions and cancerous and noncancerous systemic disorders (Ministerio de Salud de la Nación Argentina, 2001; Bocanegra *et al*., 2002; Ng *et al*., 2003; WHO, 2004; Gaioli *et al*., 2009; Litter, 2010; Bundschuh *et al*., 2012; McClintock *et al*., 2012; Alarcon-Herrera *et al*., 2013).

In urban areas, technological advances for As mitigation in drinking water have been implemented. They are mainly based on coagulation-flocculation-filtration and reverse osmosis, although in some cases fouling and scaling problems have occurred (Fernández and Ingallinella, 2010). In contrast, no progress has been made on solutions for rural and peri-urban populations that are not connected to a centralized water supply system. A few local-scale experiences have been described for household methods to remove As from drinking water by treating flows for daily consumption (Bundschuh *et al*., 2012).

The Chaco-Pampean plain, that covers about one million square kilometres in Argentina, is the largest area in the world identified with high As concentration in groundwater. It is assumed that in this region As and other trace elements (*e.g*. V, Mo, U) and minor elements (*e.g*. B and F) have their primary source in volcanic ash (Bundschuh *et al*., 2012), and minerals contained in loess materials and outcropping or subsurface cemented-limestone layers, locally known as tosca, which contribute to the decrease in regional permeability. The antecedents referred to these sectors, especially those that also share geomorphological and/or climatic characteristics with the study area, are those that have been considered more relevant for the work: Salado river basin (Galindo *et al*., 1999), North of La Pampa province (Smedley *et al*., 2002), several provinces of the Pampean plain (Farías *et al*., 2003), Southwest of Buenos Aires province (Bonorino *et al*., 2008), Southwest of Córdoba province (Gomez *et al*., 2009) and Del Azul creek basin (Zabala *et al*., 2016).

In Argentina, the limit established for As in water for human consumption is 50µg/L. In 2007, it was proposed to lower this limit to 10µg/L in accordance with the WHO water quality guidelines for human consumption (WHO, 2004). The proposal was strongly debated, highlighting three concerns: i) the difficulty of finding water resources in wide regions of Argentina, such as the Chaco-Pampean plain, with As concentration below 10µg/L; ii) the limited effectiveness of the existing treatment processes to remove As from water and the difficulties of implementing these processes in rural areas and iii) the scarcity of epidemiological studies for low As concentrations in Argentina and countries with similar diet patterns, in order to assess the suitability of the 10µg/L limit because the WHO guideline for As was based on epidemiological studies carried out in Taiwan (Steinmaus *et al*., 2006, 2007; Gerstenfeld *et al*., 2012; Palacios *et al*., 2012; Villaamil Lepori, 2015). Accordingly, a transitional period of five years (extended for a further five years) was set to adapt to the new maximum threshold of 10µg/L, and the project "Hydroarsenicism and Basic Sanitation in Argentina: basic studies for the establishment of health priorities" was approved. At the end of the adaptation period (2017), the Federal Water Council decided that a limit of 50µg/L should be valid until all scientific doubts about the risks of low water As concentrations are cleared. The results of the aforementioned project would be fundamental for this purpose.

The main aim of the present study is to evaluate the occurrence of As, F and other minor elements in the groundwater of the Langueyú creek basin in the Pampean plain (Fig. 1). The city of Tandil, with a population of 116,916 inhabitants (National Institute of Censuses and Statistics, INDEC, 2010) and a rapid population growth, faces occasional problems in quality and quantity of water supply due to an inadequate planning and mismanagement of basic sanitation services. In Tandil, groundwater is the principal water resource for human supply and for a variety of socio-economic activities such as agriculture, cattle raising, and food and metallurgical industries. A second aim of this study is to contribute to the knowledge of the composition and quality of the groundwater in this region and to understand the hydrogeochemical processes that are responsible for trace element mobilization and dispersion.

The main limitation of this study is the scarcity of economic resources for research. Therefore, there is no monitoring network *ad hoc*, in which the depth and drilling conditions can be chosen, and the sampling frequency and type of determinations are limited. Despite this, considering the lack of background studies in the basin, this research will contribute to the establishment of the baseline concentrations and geographical distribution of trace elements in the Langueyú creek basin. These advances will be useful for decision making, contributing to the prioritization of the more demanding situations, in terms of the availability of safe water for different uses, and to the selection of adequate technologies for water treatment.

STUDY AREA

The Chaco-Pampean plain covers an area of over 10 million square kilometres in the South American plain and includes part of Argentina, Bolivia, Brazil, Uruguay and Paraguay. The Argentinian sector of the Chaco-Pampean plain is an extensive region that limits to the North with Paraguay and with the Patagonian Plateau to the South. The boundaries are marked by the great orographic piedmont masses to the West and the rivers Aguapey, Uruguay, La Plata and the Atlantic Ocean to the East.

One of the greatest obstacles for the socioeconomic development of the area is the quality of the water resources available for the rural population (Nicolli *et al.*, 2010). Salinity and/or hardness, high As concentration and the occurrence of other minor and trace elements, such as F, 235U, B, Mo, and V, are the fundamental constraints limiting water use. The sources of these trace elements are the volcanic and the hydro-geothermal areas of the Andes Range in the Northern sector of the Chaco-Pampean plain whereas in the central areas the main sources are the Quaternary loess that fills the basins. The dominant sediment fraction corresponds to clayey silt and in some zones to silty clay (Nicolli *et al.*, 2010; Bundschuh *et al.*, 2012; Nicolli *et al.*, 2012; Alarcon-Herrera *et al.*, 2013).

The Pampean plain is in the South sector of the Chaco-Pampean region and is characterised by a less extreme climate regime, with four well defined seasons and average mild temperatures, unlike the rest of the region that has two marked climatic seasons (dry and wet) and higher average temperatures. The ecological characteristics (vegetation and soils) are also different.

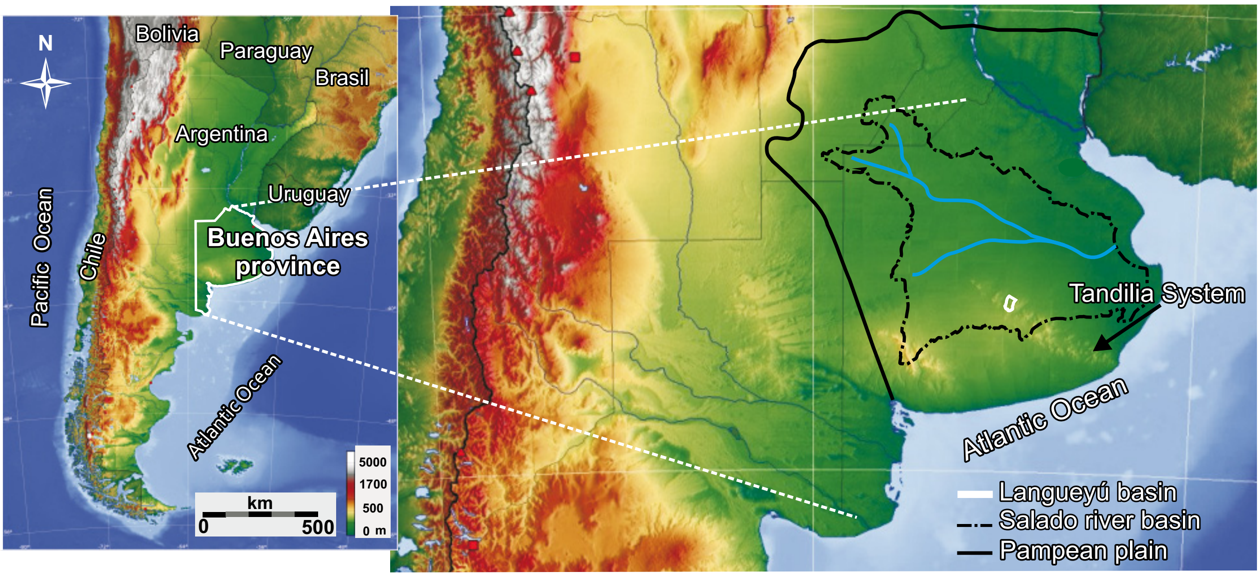

FIGURE 1. Location of the Langueyú creek basin in Buenos Aires, Argentina

In the Pampean basin, the Langueyú creek basin (600km^2) is located in the Centre-Southeast of Buenos Aires province with headwaters in the Tandilia hilly system and regional groundwater discharge in the Salado river basin.

The Tandilia System consists of a crystalline basement of Precambrian age and a sedimentary cover that is mainly composed of Pampean sediments of Pliocene-Middle Pleistocene age. Postpampean sediments of top-recent Pleistocene age are represented in smaller proportions in the sedimentary cover (Teruggi and Kilmurray, 1975).

The Pampean sediments are composed of loessial materials rich in weatherable minerals (*e.g.* calcite, dolomite, some silicates as plagioclase and mica) with conspicuous amounts of calcium, potassium, phosphorus and microelements, as well as amorphous materials of volcanic origin (ash, dust, etc.). In the region, these sediments are known as "Pampean loess" that are compositionally similar to loess deposits in other parts of the world (Frenguelli, 1955; Teruggi, 1957), but showing different granulometries. The Pampean loess are massive, compact and include calcrete horizons. The matrix is silty with subordinate fractions of sand and clay. A basal unit, composed of sandstones with gravel levels, is identified at the foothills (upper basin) and disappears in the runoff direction to the Northeast (Fidalgo *et al.*, 1975) (Fig. 2). The mineralogical composition of the sand and coarse silt fractions is dominated by an assemblage of volcanic phases (plagioclase, orthoclase, quartz and volcanic glass; Teruggi and Kilmurray, 1975).

The multi-unit phreatic aquifer that is recharged by precipitation is mainly located in the hilly area (Figs. 1; 2). Groundwater flow direction is Southwest-Northeast in accordance with the topographic surface (Barranquero *et al.*, 2014). Groundwater hydrochemistry is characterized by low contents of Total Dissolved Salts (TDS), and the chemical composition varies from calcium and/or magnesium bicarbonate to sodium bicarbonate (Barranquero *et al.*, 2014).

Tandil city has a subhumid to humid mesothermal climatic regime with little or no water deficiency (Thornthwaite and Mather, 1957).

METHODS

An inventory of private drilled wells was carried out between December 2006 and May 2007 to define a monitoring network (Fig. 3). Twenty-eight representative wells homogeneously distributed across the basin were selected for groundwater sampling. The selection was also made on wells that were used regularly and not intensively to avoid hydrodynamic alterations. Therefore, wells for domestic use were prioritized over wells devoted to crop irrigation.

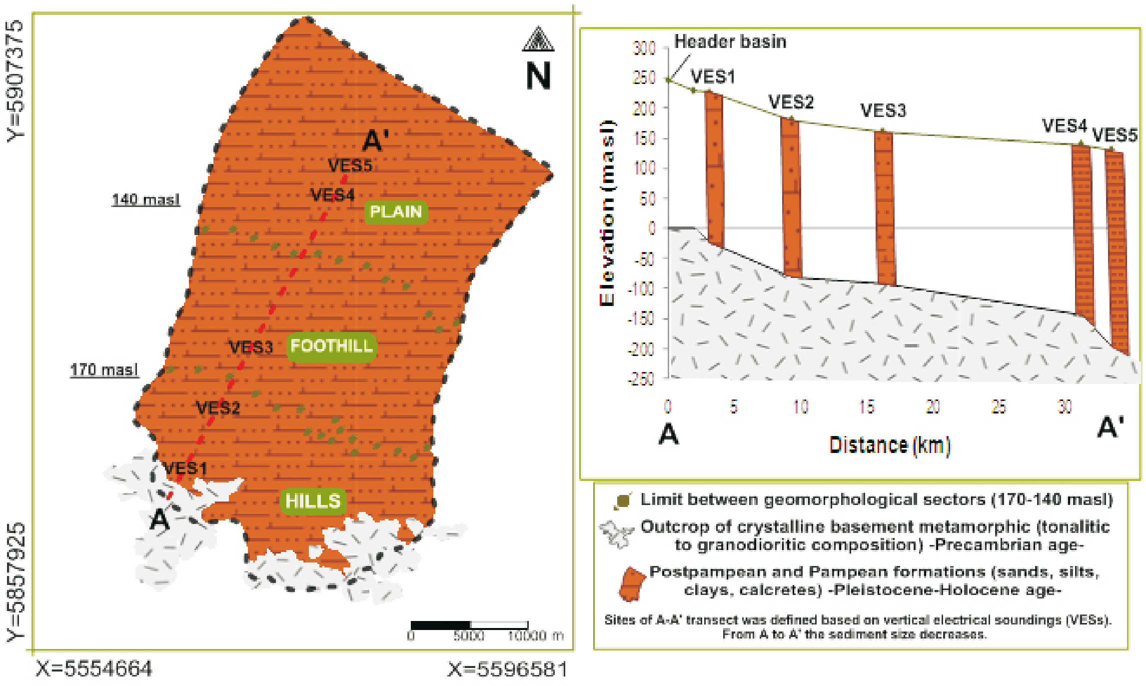

FIGURE 2. General geological characteristics and SW-NE cross section of the Langueyú creek basin

The depths of the sampled wells ranged between 2m and 3m below the water table of the phreatic aquifer. These shallow wells were either hand or machine excavated, and all had a pumping system (hand pumps, mills or electrical submersible pumps) and a well cap. Groundwater samples were collected from the installed pumps after at least 4 minutes of well purging. The sampling was carried out in June 2011, coinciding with the dry season. Since it was also the coldest period, evapotranspiration decreased and yielded a positive hydric balance.

UTM coordinates of the sampled wells were registered using a GPS system. At each well, two groundwater samples were filtered through 0.45µm membrane filters and collected in PET (polyethylene terephthalate) bottles. The sample intended for the determination of trace elements and major cations was acidified with nitric acid (1µL of 65% nitric acid per mL of water) whereas the sample devoted to the analysis of F was kept at its natural pH. Samples were refrigerated at 4ºC from collection to analysis, except during the transport from Tandil to the University of Valladolid, Spain, where trace elements were analysed. Samples were collected cautiously to avoid cross-contamination and loss of analytes. Duplicate samples were collected from some wells to check the precision of the results. Repeatability was better than 10% for each analyte.

Electrical conductivity, pH and water temperature were measured on-site with a multiparametric probe. Alkalinity was measured by acid-base titration. Although these parameters have not been included in the results, they have been used to interpret the origin and behavior of minority elements.

The aqueous concentrations of As, F, Ba, B, Sr, Fe, Si, V, Zn, Cd, Cu, Cr, Mn, Ni and Pb in the groundwater samples were analysed at the Laboratory of Instrumental Techniques (LTI, University of Valladolid, Spain). F was measured by HPLC using a Metrohm792 IC BASIC ion chromatograph equipped with a Metrosep A Supp4 column, guard precolumn and chemical suppression unit. B, Ba, Si and Sr were determined by ICP-OES using a Varian 725-ES instrument. The remaining trace elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) were analysed using a 7500c Agilent ICP-MS equipped with Octopole Reaction System (ORS) and collision-cell interface. Detection limits (see Table 1) were calculated from the respective lineal calibration plots as $3.29s_e/b_1$, where s_e symbolizes the square root of the residual variance and b_1 is the slope of the calibration line (Miller and Miller, 2010). To assess the trueness and precision of the results, duplicates and control samples (standard solutions and certified reference materials) were measured every 10 samples, and the instruments were recalibrated when bias was larger than 10%.

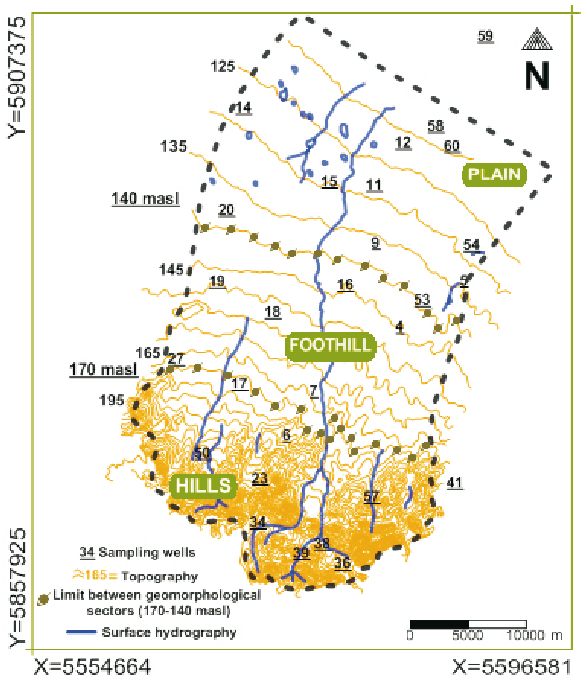

FIGURE 3. Monitoring network of private wells

The results were interpreted using univariate statistical techniques, assessing the relationship with hydrogeological processes. They were compared with the limits for drinking water (CAA, 2012). The maximum values established for The aqueous concentrations of As, F, Ba, B, Sr, Fe, Si, V, Zn, Cd, Cu, Cr, Mn, Ni and Pb in the groundwater samples were analysed at the Laboratory of Instrumental Techniques are listed in Table 1.

For F, Argentinian Food Code (CAA) establishes the minimum and maximum concentrations according to local average and maximum annual temperatures, decreasing the recommended concentration as temperature increases, because higher temperatures are associated with an increment of drinking water consumption. For the annual average temperature registered in the Tandil area (14.4ºC, Ruiz de Galarreta and Banda Noriega, 2005), F concentration must range between 0.8 and 1.3mg/L. Note that the As limits established by CAA and WHO are 50µg/L and 10µg/L, respectively.

Some elements (*e.g.* As, F, B and Si) that originate from natural sources are considered geogenic elements. For these elements, the considered baseline level ranges between the minimum and maximum values found in published studies of other locations with geological characteristics similar to those dominating in the Langueyú creek basin. The baseline levels (Reference Value in Table 1) were taken from Bonorino *et al.* (2008), except for boron and fluoride that were from Smedley *et al.* (2002).

TABLE 1. Descriptive statistics of 15 trace elements in 28 groundwater samples, detection limits, maximum allowable concentration in Argentinian drinking water, reference or baseline values, anomaly threshold and modified baseline range proposed for the Langueyú creek basin

Element	Units	Mean	Tr. Mean[b]	Median	Min.	Max.	p-value[d]	Detection limit	Max. Conc.[e]	Ref. value	Anomaly threshold	Proposed range
B	mg/L	0.28	0.29	0.31	0.06	0.44	0.021	0.03	0.5	0.5 - 14	0.49	
Ba	mg/L	0.14	0.13	0.14	0.04	0.43	<0.005	0.05		0.006 - 0.141		
Sr	mg/L	0.49	0.49	0.45	0.22	0.95	0.338	0.1		0.084 - 1.280	0.77	0.22 - 0.73
Si	mg/L	31.2	31.4	31.2	24.0	34.1	<0.005	0.5		3.5 - 69.7		
F	mg/L	0.88	0.86	0.88	0.44	1.68	0.669	0.2	1.3	0.03 - 29		
Fe	µg/L	38.0[a]	36.8	34.4	8.8	99.9	<0.005	0.5	300	18 - 1268	90	10 - 73
Mn	µg/L	4.3[a]	0.9	0.2	n.d.[c]	95.2	<0.005	0.5	100	1.2 - 33	5	0.004 - 1
Ni	µg/L	0.52[a]	0.25	0.04	0.01	8.21	<0.005	0.1	20	0.5 - 14.4	1	0.01 - 0.99
Cu	µg/L	11.3	7.2	4.5	0.7	129.4	<0.005	0.5	1000	1.1- 41.5	30	0.7 - 25.4
Zn	µg/L	437[a]	298	57	3	4475	<0.005	0.5	5000	0.01 - 0.19	2.09	10 - 260
As	µg/L	22.7	21.5	20.9	1.0	78.2	0.067	0.5	50	2 - 270		
Cd	µg/L	0.10	0.05	0.02	n.d.[c]	1.29	<0.005	0.1	5	0.01 - 0.2	0.2	0.01 - 0.19
Cr	µg/L	0.55	0.54	0.53	n.d.[c]	1.24	0.93	0.2	50	2.0- 9.3	1.2	
Pb	µg/L	0.44[a]	0.22	0.02	n.d.[c]	6.53	<0.005	0.2	50	0.1 - 1.3	5	0.1 - 3
V	µg/L	106.2	104.3	100.1	10.8	251.1	0.483	0.2		13 - 1380	200	20 - 165

[a], [b]For elements with some large outliers[a] the trimmed mean[b] has been preferred over the mean. Trimmed mean has been calculated removing 5% of values in tails.
[c]No detected with this decimal numbers.
[d]Anderson-Darling normality test. Variables with a posteriori p-value < 0.005 are very asymmetrical.
[e]Maximum allowable concentration in drinking water according to CAA (Argentinian Food Code).

As for the remaining elements (B, Sr, Fe, Mn, Ni, Cu, Zn, Cd, Cr, Pb and V), background studies of Argentinian groundwater do not evidence a natural origin. However, some studies attribute the occurrence of these elements to anthropogenic sources (Silva Busso and Santa Cruz, 2005; Huang *et al.*, 2007; Haloi and Sarma, 2011; Li *et al.*, 2014; WHO and UNICEF, 2015). Therefore, the baseline value of this second group was defined using the anomaly threshold, which was calculated as the mean plus twice the standard deviation of the population considered "uncontaminated" (Mazadiego Martinez, 1995). Values are reported in Table 1. The baseline concentration of the trace elements in the Tandil region was estimated as the range recalculated after removing the values above the anomaly threshold. The obtained modified range ("proposed range" column in Table 1) is proposed as the baseline concentration for the investigated elements in the Langueyú creek basin. Therefore, it is considered that the concentrations above the modified range are from anthropogenic pollution.

RESULTS AND DISCUSSION

Table 1 shows some statistical parameters describing the distribution of trace elements in the analysed samples. Some elements show large variations in the groundwater samples from the Langueyú creek basin, with mean values generally lower than the median ones, thus pointing to the existence of large upper tails. The Anderson and Darling test was applied to identify departures from normality, and variables with *p*-value<0.005 were considered very asymmetrical. As, B, Cr, F, Sr and V were normal or close to normal parameters. It must be noted that this group comprises most elements considered of natural origin. For the elements showing very large outliers, the trimmed or truncated mean, obtained after discarding 5% of values at the upper and lower tails, was preferred over the mean to show central tendency of the variable.

Bivariate correlations between trace elements were estimated using the Pearson's correlation coefficient, r. Table 2 shows the correlation matrix in which significant correlations at the 95% confidence limit have been underlined. As, F, B, V and Cr are strongly and positively correlated. These elements have in common that they occur in anionic form at the natural alkaline pH of groundwater, thus suggesting a similar hydrochemical behaviour in the aquifer and probably a common source. Most elements in this anionic group show negative significant correlation with Sr and Fe. Several studies found a significant correlation between As and Fe, suggesting that desorption of As from Fe oxyhydroxides under oxic and alkaline conditions was an important source of As in groundwater (Bhattacharya *et al.*, 2006; Bundschuh *et al.*, 2012; Smedley *et al.*, 2002). However, this correlation cannot be inferred from our results. A lack of correlation or negative correlation between As and Fe has been also observed for the arid Duero basin in Spain (Carretero, 2016; Giménez-Forcada *et al.*, 2017).

Bhattacharya *et al.* (2006) found the same correlations for As, F, B, V and Cr, concluding that volcanic ash in a distinct layer and also in dispersed form in sediments

TABLE 2. Pearson's bivariate correlation coefficients between 15 trace elements. Critical r value is 0.374 for 26 (n-2) degrees of freedom and 95% confidence level. Significant correlations are underlined

	F	B	Ba	Si	Sr	Fe	V	Zn	Cr	Mn	Ni	Cu	Cd	Pb
B	0.656													
Ba	-0.390	-0.251												
Si	0.187	0.389	-0.641											
Sr	-0.628	-0.555	0.360	0.158										
Fe	-0.752	-0.695	0.631	-0.526	0.650									
V	0.881	0.701	-0.312	0.156	-0.555	-0.671								
Zn	-0.155	0.206	0.184	-0.087	-0.135	0.187	-0.212							
Cr	0.642	0.490	-0.373	0.134	-0.554	-0.535	0.590	0.280						
Mn	0.025	0.211	0.176	-0.083	0.070	0.000	0.236	0.091	-0.058					
Ni	-0.284	-0.151	0.367	-0.318	0.218	0.317	-0.181	-0.249	-0.167	0.421				
Cu	-0.258	-0.332	0.774	-0.795	0.108	0.633	-0.263	0.050	-0.355	-0.054	0.263			
Cd	-0.014	0.077	0.058	-0.052	-0.097	0.001	-0.076	0.572	0.288	0.256	-0.032	-0.139		
Pb	-0.239	-0.061	-0.020	-0.146	-0.073	0.087	-0.226	0.412	0.295	-0.053	0.136	-0.021	0.328	
As	0.894	0.609	-0.348	0.067	-0.623	-0.679	0.954	-0.191	0.657	0.145	-0.178	-0.229	-0.059	-0.209

seems to be the primary source of these elements in the Pampean plain. Nicolli *et al.* (2010) also found a strong positive correlation between As and V, indicating that these elements may be mobilized in environments with high pH and high HCO_3^- concentrations, which are the conditions occurring in the Langueyú creek basin.

Some trace elements (*e.g.* Cd, Pb, Ni, Zn and Mn) showed weak significant correlations with other trace elements. This could be caused by the low concentrations found (hardly above the instrumental detection limit for Ni, Pb or Cd) and by the contamination of Zn, Pb and Mn in a few samples due to pipe corrosion.

The Box and Whisker plots of the trace elements analyzed in the 28 groundwater samples are displayed in Figure 4. The lower and upper limits of the box represent the first and third quartiles, and the line inside the box is the median. The whiskers extend to ±1.5IQR (interquartile range) from the respective quartile. Symbols represent outlying values. The dashed lines in the F box plot represent the range of recommended concentrations of F in drinking water (0.8 to 1.3mg/L) for the Tandil area according to CAA; dashed lines in the As box plot indicate maximum allowable concentration of As in drinking water according to CAA (50mg/L) and WHO (10mg/L). For the rest of elements, the maximum allowable concentrations are further above the maximum values found in groundwater samples and were not represented.

The plots were calculated after removing the most extreme values: concentrations of Fe, Zn, Mn and Ni in sample 23 and Zn and Pb in samples 9 and 34. These atypical high concentrations suggest corrosion of the pipelines and pumping systems installed in the wells. This phenomenon was visually noticed.

The Box and Whisker plots show the distribution of values for each element in the studied area. Tailed distributions are observed for most elements, especially Ni, Zn or Pb, which are supposed to originate from human activities. It must also be emphasized that, for most trace elements, the concentrations observed are below the maximum allowable or recommended limits established for drinking water by CAA (see Table 1). Only As and F reached concentrations above their respective limits.

The As concentration was higher than 10µg/L in 78% of the samples and above 50µg/L in sample 59. According to the current CAA normative, only this last sample is not suitable for human consumption. F also exceeded the upper limit indicated by CAA (1.3mg/L) in sample 59. In 39% of the analyzed samples the concentration of F was below the lower limit recommended for the area of Tandil according to its climate patterns (0.8mg/L).

The spatial distribution of As and F is depicted in Figures 5 and 6, respectively. It shows that the occurrence of both elements increases towards the North of the basin in agreement with the more abundant occurrence of thin loessial materials.

Arsenic values found in the area of study are within the range that is defined in the background studies in Buenos Aires and Córdoba provinces (Bonorino *et al.*, 2008; Gomez *et al.*, 2009), but are higher than those reported by Hernandez *et al.* (2002) for the quarry mining area of Tandilia. The origin of As in these waters can be attributed to the high content of volcanic glass in the silty loess deposits accumulated in this region.

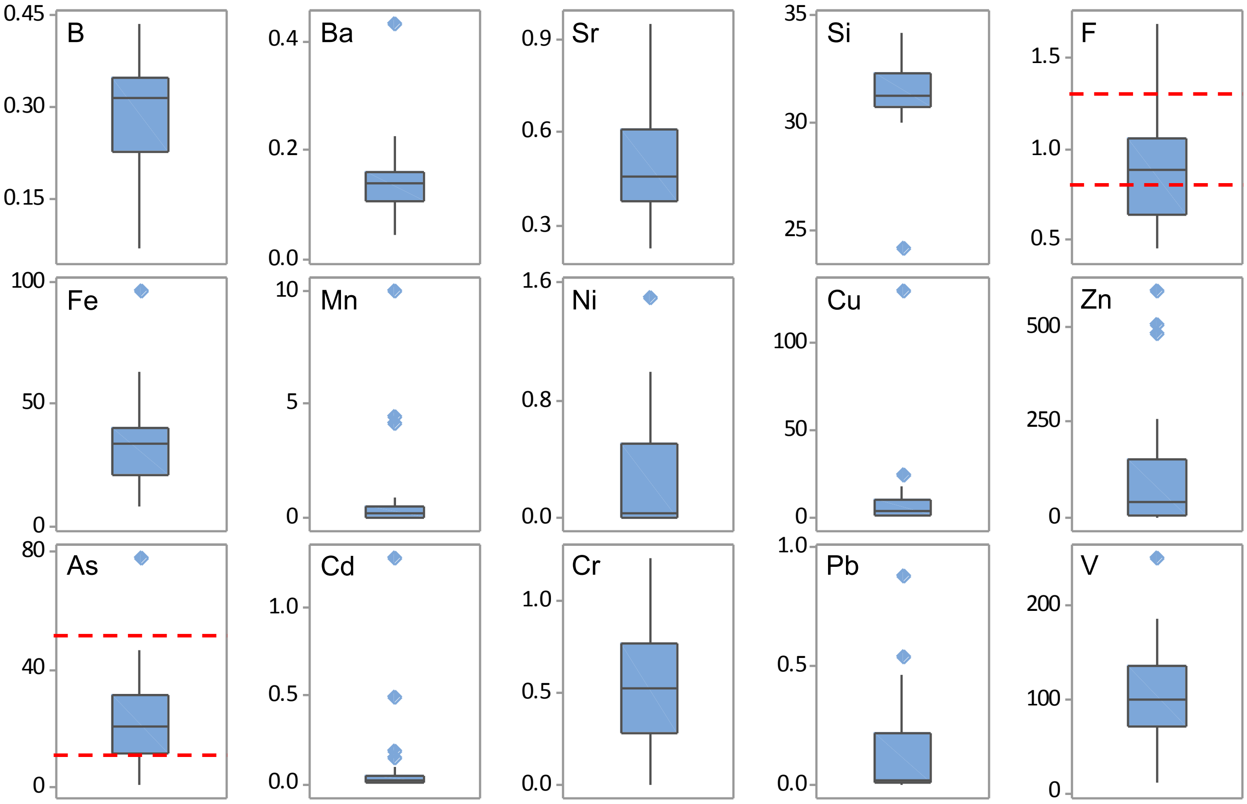

FIGURE 4. Box and Whisker plots of trace elements in 28 groundwater samples. Variable units as in Table 1.B, Ba, F, Si and Sr are expressed in mg/1; the rest of elements, in µg/1. Red lines symbolize maximum allowable concentrations according to CAA

F concentrations are located in the lower portion of the reference range (Smedley *et al.*, 2002) and are similar to those found by Hernandez *et al.* (2002) and Massone *et al.* (2005).

All elements, except silicon, are considered trace components of groundwater, with concentrations below 10mg/L (Foundation International Center of Groundwater Hydrology, FCIHS, 2009).

The mean concentration of Ba coincides with the upper limit of an aquifer in the Southwest of Buenos Aires province (0.14mg/L). According to Bonorino *et al.* (2008) this element has preference to move to the solution during loess weathering processes, thus justifying its occurrence in groundwater.

Zn concentration exceeds by several orders of magnitude the reference values found by Bonorino *et al.* (2008) and Hernandez *et al.* (2002). The maximum value (4.47mg/L in well 9) is probably caused by corrosion of the pipeline system, which has been identified in the literature as the most common source (Haloi and Sarma, 2011; WHO, 2015).

Pb exhibits maximum values, higher than those found by Bonorino *et al.* (2008), in wells 34 (2.2µg/l) and 9 (6.5µg/l), exceeding the anomaly threshold. WHO (2015) states that this element comes primarily from domestic water facilities containing Pb in pipelines, solder, fittings and service connections. Assuming an anthropic source of Pb for the mentioned wells, the proposed range was calculated after removing these two values from the dataset.

The other elements (B, Cd, Cu, Cr, Sr, Fe, Mn, Ni, Si, and V) are below or in the range of regional background studies. Regarding these elements, the anomaly threshold was exceeded in the following cases: for Cd in wells 5 and 18, for Cu in well 34, for Sr and FE IN in well 50, for Mn in well 58, for nickel in wells 6 and 23, and for V in well 59. Again, the proposed range was calculated after discarding the values above the anomaly threshold.

Si cannot be strictly considered a trace element since it is present at concentrations of several milligrams per litre (average concentration 31.2mg/L). Its maximum and minimum values are within the range established by Bonorino *et al.* (2008). These authors related the Si content in the Pampa aquifer located in the Southeastern area of Tandilia to the weathering of silicate minerals, especially plagioclase and montmorillonite. In the Langueyú creek basin, within the silicates group, plagioclase, orthoclase and quartz are abundant and could also cause the high levels of Si. Moreover, the presence of volcanic glass is important in the basin.

B showed values above 0.1mg/L in 97% of the groundwater samples and peaked up at 0.44mg/L, which is very close to the maximum value of 0.5mg/L allowed by Argentinian legislation for drinking water. Its source in groundwater is related to the presence of volcanic glass in the parent materials of the aquifer.

The spatial distribution of B, Fe, Si, Sr and V in some groundwater samples from the Langueyú creek basin is depicted in Figure 7. V and B show a positive correlation with As whereas Sr and Fe are expected to follow a different pattern as they are negatively correlated with the As group. In addition, despite the limited number of plotted samples, the different distribution patterns of the selected elements are observed. Fe and Sr peak up at the South of the basin in the hilly area of the Tandilia system, decreasing towards the North. On the contrary, V and B concentrations increase from South to North, in the groundwater flow direction, like As and F. Si shows a steady concentration in the Langueyú creek basin.

The results obtained by Galindo *et al.* (1999) in the Salado river basin are much higher for all the elements than the concentrations found in the Langueyú creek basin. Therefore, for all elements except As and Cr, the proposed range has been based on results from the Langueyú creek basin after removing individual values associated with anthropic contamination. The higher concentrations of trace elements found in the Salado river basin could be attributed to the longer water-sediment contact time caused by the larger sediment thicknesses in the central region of the Salado basin.

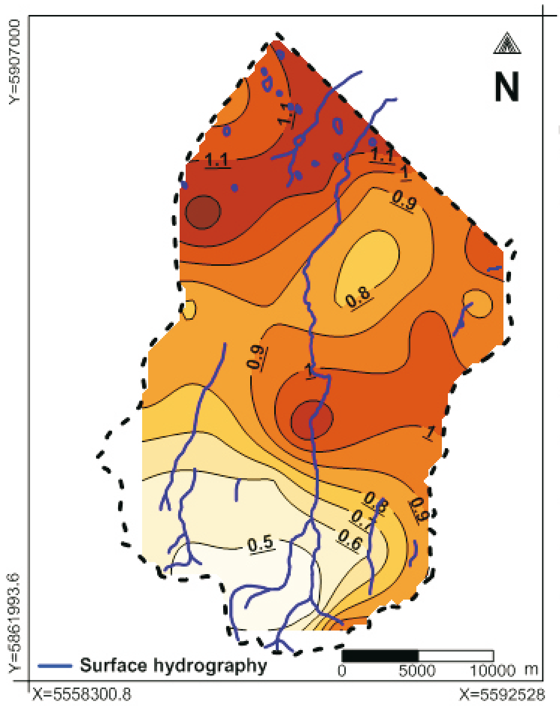

FIGURE 6. Fluoride spatial variation in the June 2011 sampling campaign

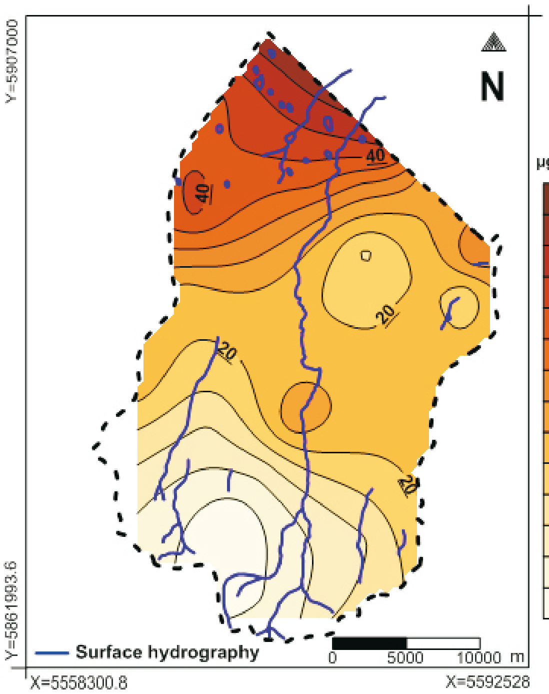

FIGURE 5. Arsenic spatial variation in the June 2011 sampling campaign

The maximum concentrations reported by Smedley *et al.* (2002) for groundwaters from the North of La Pampa province are also much higher than those found in the Langueyú creek basin. Contents of Si are similar in both studies, suggesting that weathering of silicate minerals and subsequent supersaturation are the common limiting factors that control the occurrence of Si in groundwater. The concentration of Ba is slightly higher in the Langueyú creek basin, but coherent with the values found by Bonorino *et al.* (2008) in the Southwest of Buenos Aires province.

For most trace elements, the results reported by Farías *et al.* (2003) are higher than those reported in our study. These authors argued that the average particle size decreases from West to East of the Pampean plain, increasing the contact surface between sediments and water. Moreover, the volcanic glass shards are considerably more abundant than quartz in the fractions of sand and silt sized particles of the sediments, resulting in higher amounts of extractable elements. Therefore, both factors, the abundance of volcanic minerals and smaller particle sizes can explain that the concentrations of elements are higher than in the Langueyú area. Barium is the exception, showing higher concentration in the Langueyú basin.

TABLE 3. Overview of the occurrence of concentrations of trace elements in groundwater of different areas of the Argentinian Chaco-Pampean plain

Element	Units	Concentration range		Location and area covered	Reference
		Langueyú creek basin (this study)	Other studies in the Chaco-Pampa		
As	µg/L	1.0 - 78.2	12.8 - 797.3	Salado river basin (25,000 km^2)	Galindo *et al.*, 1999
Cd	µg/L	0.01 - 0.19[a]	0.06 - 0.69		
Cr	µg/L	0.01 - 1.2	0.01 - 57.0		
Cu	µg/L	0.7 - 25.4[a]	1.9 - 90.3		
Fe	µg/L	10.0 - 73.0[a]	5.0 - 499.6		
Mn	µg/L	0.004 - 1.0[a]	0.6 - 1997.2		
Pb	µg/L	0.1 - 3.0[a]	0.1 - 65.5		
Si	mg/L	24.0 - 34.1	17.9 - 36.3		
V	µg/L	20.0 - 165.0[a]	55.0 - 671.5		
Zn	µg/L	10.0 - 260.0[a]	6.5 - 1394.7		
As	µg/L	1.0 - 78.2	4.0 - 4900	North of La Pampa province (7,700 km^2)	Smedley *et al.*, 2002
B	mg/L	0.06 - 0.44	1.9 - 14.0		
Ba	µg/L	40.0 - 430.0	21.6 - 259.0		
F	mg/L	0.44 - 1.7	0.03 - 28.4		
Fe	µg/L	10.0 - 73.0[a]	6.0 - 618.0		
Mn	µg/L	0.004 - 1.0[a]	0.2 - 77.0		
Pb	µg/L	0.1 - 3.0[a]	0.2 - 1.6		
Si	mg/L	24.0 - 34.1	22.0 - 35.0		
Sr	mg/L	0.2 - 0.73[a]	0.2 - 13.3		
V	µg/L	20.0 - 165.0[a]	90.0 - 4400		
As	µg/L	1.0 - 78.2	10.0 - 593.0	Several provinces of the Pampean plain (50.000 km^2)	Farías *et al.*, 2003
Ba	µg/L	40.0 - 430.0	30.0 - 170.0		
Cr	µg/L	0.01 - 1.2	20.0 - 230.0		
Cu	µg/L	0.7 - 25.4[a]	10.0 - 240.0		
Fe	µg/L	10.0 - 73.0[a]	10.0 - 7600		
Sr	mg/L	0.22 - 0.73[a]	0.09 - 11.0		
V	µg/L	20.0 - 165.0[a]	10.0 - 670.0		
Zn	µg/L	10.0 - 260.0[a]	20.0 - 1030		
As	µg/L	1.0 - 78.2	0.0 - 250.0	Southwest of Córdoba province (400 km^2)	Gómez *et al.*, 2009
F	mg/L	0.4 - 1.7	0.5 - 12.0		
Si	mg/L	24.0 - 34.1	13.7 - 70.0		
As	µg/L	1.0 - 78.2	5.0 - 121.0	Del Azul creek basin(6.237 km^2)	Zabala *et al.*, 2016
F	mg/L	0.44 - 1.7	0.34 - 2.9		
Si	mg/L	24.0 - 34.1	50.3 - 81.8		

[a] The “Proposed range” has been used for comparative purposes when available (see Table 1)

The concentrations of As, Si and F reported by Gómez *et al.* (2009) in groundwater from a small area of Córdoba province are only slightly higher than those in the Langueyú creek basin. They are attributed to dissolution of amorphous silica (*e.g.* volcanic glass) and calcite in the prevalent $NaHCO_3$ type waters. However, the minor groundwater-sediment contact in the Langueyú basin yields lower concentrations.

Finally, Zabala *et al.* (2016) found very similar concentrations of As and F in the vicinity of Del Azul creek basin, increasing from South to North, in the direction of groundwater flow. Nevertheless, concentrations of Si are slightly higher in Del Azul basin. The authors argue that silicate dissolution must occur at least during recharge because rain water is undersaturated with respect to all minerals.

CONCLUSIONS

In summary, the baseline concentrations of As, F, Si and other trace elements in the Langueyú creek basin are in good agreement with levels found in background studies carried out in neighbouring basins belonging to the Pampean aquifer. The most relevant differences were found in the maximum concentrations of most trace elements, which were lower in the Langueyú creek basin. This is due to the shorter time of the groundwater-sediment contact that is associated with the smaller sedimentary thickness and is restricted to approximately 250m at the NE limit of the study area. In addition, the contact with volcanic glass particles can be shorter than in the western areas of the Pampean plain, where the sand and silt fractions in the sediments are more abundant. Nevertheless, the observed correlations amongst elements are similar to those found in other sectors of the Chaco-Pampean plain, suggesting common sources and similar mobilization pathways.

According to the current maximum concentration of As in drinking water allowed by the Argentinian legislation (50µg/l), all analysed groundwater samples, except that collected in well 59, would be suitable for human consumption. Note, however, that epidemiological studies on the consequences of continuing ingestion of water with low As concentration on health are lacking in Argentina. Therefore, further studies of the Chaco-Pampean plain are necessary to assess the suitability of the maximum concentration of 10µg/L recommended by WHO.

With the exception of As, none of the other trace elements regulated by CAA (B, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn) has exceeded the maximum limit for drinking water in the investigated area.

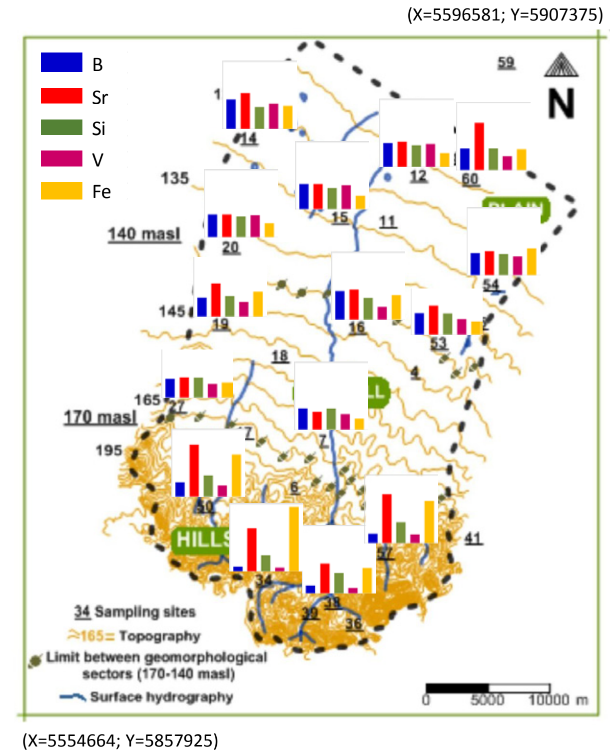

FIGURE 7. Spatial distribution of V, B, Si, Sr and Fe in the Langueyú creek basin. Given the different orders of magnitude of the concentrations of the elements, the values have been scaled by using the following factors: 0.02 (V), 0.1 (Fe and Si) and 10 (B and Sr)

ACKNOWLEDGMENTS

Rosario Soledad Barranquero participated in this project thanks to the support of a CONICET fellowship (Resolution No. 4936/2014). The authors gratefully acknowledge the reviews and comments provided by two anonymous reviewers and the corrections made by the Editorial Office, which helped to improve the quality of this paper.

REFERENCES

Argentinian Food Code, CAA. Código Alimentario Argentino, Ley 18.284, reglamentada por el Decreto 2126/741 del Poder Ejecutivo Nacional. [Last access: 2016/12/22] http://www.anmat.gov.ar/alimentos/codigoa/Capitulo_XII.pdf

Alarcon-Herrera, M.T., Bundschuh, J., Nath, B., Nicolli, H., Gutierrez, M., Reyes-Gomez, V.M., Nuñez, D., Martín-Dominguez, I.R., Sracek, O., 2013. Cooccurrence of arsenic and fluoride in groundwater of semi-arid regions in Latin America: genesis, mobility and remediation. Journal of Hazardous Materials, 262, 960-969.

Barranquero, R.S., Pardo, R., Varni, M., Ruiz de Galarreta, A., Vega, M., 2014. Modelling of the groundwater hydrological behaviour of the Langueyú creek basin by using N-way multivariate methods. Hydrological Processes, 28, 4743-4755.

Bhattacharya, P., Claesson, M., Bundschuh, J., Sracek, O., Fagerberg, J., Jacks, G., Martin, R.A., Storniolo, A.R., Thir, J.M., 2006. Distribution and mobility of arsenic in the Río Dulce alluvial aquifers in Santiago del Estero Province, Argentina. Science of the Total Environment, 358, 97-120.

Blanco, M.del C., Paoloni, J.D., Morra's, H.J.M., Fiorentino, C.E., Sequeira, M, 2006. Content and Distribution of Arsenic in Soils, Sediments and Groundwater Environments of the Southern Pampa Region, Argentina. Environmental Toxicology, 21(6), 561-574.

Bocanegra, O. C., Bocanegra, E. M., Alvarez, A. A., 2002. Arsénico en las aguas subterráneas: su impacto en la salud. In: Bocanegra, E., Martínez, D., Massone, H., (eds.). XXXII Congreso AIH y VI Congreso ALHSUD "Aguas Subterráneas y Desarrollo Humano". AIH-ALSHUD, Mar del Plata, 21-27.

Bonorino, A.G., Limbozzi, F., Albouy, R., Lexow, C., 2008. Movilidad de metales pesados y otros elementos en el acuífero loéssico regional del suroeste bonaerense. Geoacta, 33, 31-42.

Bundschuh, J., Litter, M.I., Parvez, F., Román-Ross, G., Nicolli, H.B., Jean, J-S., Liu, C-W., López, D., Armienta, M.A., Guilherme, L.R.G., Gómez Cuevas, A., Cornejo, L., Cumbal, L., Toujaguez, R., 2012. Review. One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries. Science of the Total Environment, 429, 2-35.

Carretero, M.C., 2016. Hidrogeoquímica de aguas subterráneas de un sector de la Cuenca del Duero con altos niveles de arsénico. PhD Thesis. University of Valladolid, Spain, 279pp.

Dietrich, S., Bea, S.A., Weinzettel, P., Torres, E., Ayora, C., 2016. Occurrence and distribution of arsenic in the sediments of a carbonate-rich unsaturated zone. Environmental Earth Sciences, 75:90. DOI: 10.1007/s12665-015-4892-7

Farías, S.S., Casa, V.A., Vazquez, C., Ferpozzi, L., Pucci, G.N., Cohen, I.M., 2003. Natural contamination with arsenic and other trace elements in ground waters of Argentine Pampean plain. Science of the Total Environment, 309(1-3), 187-199.

Foundation of the International Centre for Groundwater Hydrology (FCIHS), 2009. Hidrogeología. Comisión Docente Curso Internacional de Hidrología Subterránea. Escuder, R., Fraile, J., Jordana, S., Ribera, F., Sánchez-Vila, X., Vázquez-Suñe, E. (eds.), Barcelona, Artes Gráficas Torres, 768pp.

Fernández, R.G., Ingallinella, A.M., 2010. Experiencia argentina en la remoción de arsénico por diversas tecnologías. In: Litter, M.I., Sancha, A.M., Ingallinella, A.M. (eds.). Tecnologías económicas para el abatimiento de arsénico en aguas. Ciencia y Tecnología para el Desarrollo del Programa Iberoamericano (CYTED), Santiago de Chile, 155-167.

Fidalgo, F., De Francesco, F., Pascual, R., 1975. Geología superficial de la Llanura Bonaerense. In: Angelelli, V., De Francesco, F., Etchevehere, P.H., Fidalgo, F., Kilmurray, J.O., Llambias, E.J., Pascual, R., Prozzi, C.R., Rolleri, E.,O., Sala, J.M., Teruggi, M.E., Turner, J.C., Yrigoyen, M.R. (eds.). Relatorio Geología Provincia de Buenos Aires, VI Congreso Geológico Argentino., Asociación Geológica Argentina, Imprenta CONI, Bahía Blanca, 104-106.

Frenguelli, J., 1955. Loess y Limos Pampeanos. In: Serie Técnica y Didáctica 7, Facultad de Ciencias Naturales y Museo de la Universidad Nacional de La Plata, La Plata, 88pp.

Gaioli, M., González, D.E., Amoedo, D., 2009. Hidroarsenisismo crónico regional endémico: un desafío diagnóstico y de prevención. Archivos Argentinos de Pediatría, 107(5), 459-473.

Galindo, G., Herrero, M.A., Flores, M., Fernández-Turiel, J.L., 1999. Correlación de metales trazas en aguas subterráneas someras de la Cuenca del Río Salado, Provincia de Buenos Aires, Argentina. In: In: Hidrología Subterránea, II Congreso Argentino de Hidrogeología y IV Seminario Hispano Argentino sobre temas actuales de la Hidrología Subterránea. Serie Correlación Geológica 13: 251-261.

Gerstenfeld, S., Jordán, A., Calli, R., Farías, P., Malica, J., Gómez Peña, M.L., Aguirre, L., Salvatierra, M., Leguizamón, E., Coronel, C., Flores Ivaldi, E., 2012. Determinación de zonas de riesgo al agua arsenical y prevalencia de HACRE en Villa Belgrano, Tucumán, Argentina. Revista Argentina de Salud Pública, 3(10), 24-29.

Giménez-Forcada, E., Vega-Alegre, M., Timón-Sánchez, S., 2017. Characterization of regional cold-hydrothermal inflows enriched in arsenic and associated trace-elements in the southern part of the Duero Basin (Spain), by multivariate statistical analysis. Science of the Total Environment, 593-594, 211-226.

Gómez, M.L., Blarasín, M.T., Martínez, D.E., 2009. Arsenic and fluoride in a loess aquifer in the central area of Argentina. Environmental Geology, 57, 143-155.

Haloi, N., Sarma, H.P., 2011. Heavy metal contaminations in the groundwater of Brahmaputra flood plain: an assessment of water quality in Barpeta District, Assam (India). Environmental Monitoring Assessment, 184(10), 6229-6237. DOI: 10.1007/s10661-011-2415-x

Hernández, M., Giaconi, L.M., González, N., 2002. Línea de base ambiental para las aguas subterráneas y superficiales en el área minera de Tandilia, Buenos Aires, Argentina. In: Bocanegra, E., Martínez, D., Massone, H. (eds.). Groundwater and human development. Mar del Plata, IAH (International Association of Hydrogeologists) and VI ALHSUD (Latin-American Association of Groundwater Hydrology for Development), 336-343.

Huang, S.S., Liao, Q.L., Hua, M., Wu, X.M., Bi, K.S., Yan, C.Y., 2007. Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China. Chemosphere, 67, 2148-2155.

Khan, S.D., Mahmood, K., Sultan, M.I., Khan, A.S., Xiong, Y., Sagintayev, Z., 2010. Trace element geochemistry of groundwater from Quetta Valley, western Pakistan. Environmental Earth Sciences, 60, 573-582.

Kruse, E., Ainchil, J., 2003. Fluoride variations in groundwater of an area in Buenos Aires Province, Argentina. Environmental Geology, 44, 86-89.

Li, J., Li, F., Liu, Q., Zhang, Y., 2014. Trace metal in surface water and groundwater and its transfer in a Yellow River alluvial fan: Evidence from isotopes and hydrochemistry. Science of the Total Environment, 472, 979-988.

Litter, M.I., 2010. Actualización. La problemática del arsénico en la Argentina: el HACRE. Revista Sociedad Argentina de Endocrinología Ginecológica y Reproductiva (SAEGRE), XVII(2), 5-10.

Martinez, D.E., Massone, H.E., Ceron, J.C., Farenga, M., Ferrante, A. 2003. Hidrogeoquímica del área de disposición final de residuos de Mar del Plata, Argentina. Boletín Geológico Minero de España, Número Monográfico Iberoamericano Hidrología Subterránea, 114(2), 237-246.

Massone, H., Martinez, D.E., Tomas, M.L. 2005. Caracterización hidroquímica superficial y subterránea de la cuenca superior del arroyo Grande (Prov. de Buenos Aires). In: Actas del II Seminario Hispano-Latinoamericano sobre Temas Actuales de la Hidrología Subterránea, Río Cuarto: 47-56.

Matteoda, E., Blarasin, M., 2013. Fondo natural de cadmio en aguas subterráneas. Vinculación con usos del territorio. Valle de La Cruz, Córdoba, Argentina. In: González, N., Kruse, E.E., Trovatto, M.M., Laurencena, P. (eds.). Actas del VIII Congreso Argentino de Hidrogeología, Editorial de la Universidad Nacional de La Plata (EDULP), La Plata, II: 70-77.

Matteoda, E., Blarasin, M., Damilano, G., Cabrera, A., 2010. Manganeso en aguas subterráneas y superficiales. Relación con valores de fondo natural y actividades antrópicas. Córdoba, Argentina. Unpublished. https://doi.org/10.13140/2.1.4783.6964

Mazadiego Martínez, L.F., 1995. Autocorrelación espacial y criterios de reconocimiento de anomalías. In: López Santiago, F., Ayala Carcedo, F.J. (eds) Contaminación y Depuración de suelos, Instituto Tecnológico Geominero de España, Madrid, ISBN: 84-7840-236-5. 330pp.

McClintock, T.R., Chen, Y., Bundschuh, J., Oliver, J.T., Navoni, J., Olmos, V., Villaamil, E., Habibul Ahsan, L.H., Parvez, F., 2012. Arsenic exposure in Latin America: biomarkers, risk assessments and related health effects. Science of the Total Environment, 429, 76-91.

Miller, J.N., Miller, J.C., 2010. Statistics and Chemometrics for Analytical Chemistry. Sixth edition, Pearson Education Limited, Edinburgh Gate Harlow Essex, England, 221-250.

Ministerio de Salud de la Nación Argentina, 2001. Programa nacional de prevención y control de las intoxicaciones. Hidroarsenicismo crónico regional endémico. Módulo de capacitación, 3, 1-68.

Mukherjee, A., Sengupta, M.K., Hossain, M.A., Ahamed, S., Das, B., Nayak, B., 2006. Arsenic contamination in groundwater: A global perspectivas with emphasis on the Asian scenario. Journal of Health, Population and Nutrition, 24, 143-63.

National Institute of Censuses and Statistics (INDEC), 2010. http://www.censo2010.indec.gov.ar/resultadosdefinitivos.asp Last access: 2015/07/29.

Navoni, J.A., De Pietri, D., Garcia, S.Y, Villaamil Lepori, E.C., 2012. Riesgo sanitario de la población vulnerable expuesta al arsénico en la provincia de Buenos Aires, Argentina. Revista Panamericana de Salud Pública, 31(1), 1-8.

Ng, J., Wang, J., Shraim, A., 2003. A global health problem caused by arsenic from natural sources. Chemosphere, 52, 1353-1359.

Nicolli, H.B., Bundschuh, J., García, J.W., Falcón, C.M., Jean, J.-S., 2010. Sources and controls for the mobility of arsenic in oxidizing groundwaters from loess-type sediments in arid/semi-arid dry climates – evidence from the Chaco – Pampean plain (Argentina). Water Research, 44(19), 5589-5604.

Nicolli, H.B., Bundschuh, J., Blanco, M.delC., Tujchneider, O.C., Panarello, H.O., Dapeña, C., Rusansky, H.E., 2012. Arsenic and associated trace-elements in groundwater from the Chaco-Pampean plain, Argentina: Results from 100 years of research. Science of the Total Environment, 429, 36-56.

Palacios, S.V., Moron Guglielmino, C., Verea, M.A., Pecotche, D.M., 2012. HACRE: Hidroarsenicismo Crónico Regional y Endémico. Presentación de un caso clínico y breve reseña bibliográfica. Archivos Argentinos de Pediatría, 62, 233-238.

Ruiz de Galarreta, A., Banda Noriega, R., 2005. Geohidrología y evaluación de nitratos del Partido de Tandil, Buenos Aires, Argentina. In: Galindo, G., Fernández Turiel, J.L., Parada, M.Á., Torrente, D.G. (eds.). Actas del IV Congreso Argentino de Hidrogeología y II Seminario Hispano-Latinoamericano sobre temas actuales de la Hidrología Subterránea. Río Cuarto, Universidad Nacional de Córdoba (UNCR), 99-108.

Silva Busso, A., Santa Cruz, J., 2005. Distribución de elementos traza en las aguas subterráneas del Partido de Escobar, Buenos Aires, Argentina. Ecología Austral, 15, 31-47.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, 17, 517-568.

Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J., Tullio, J.O., 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Applied Geochemistry, 17, 259-284.

Smedley, P.L., Kinniburgh, D.G., Macdonald, D.M.J., Nicolli, H.B., Barros, A.J., Tullio, J.O., Pearce, J.M., Alonso, M.S., 2005. Arsenic associations in sediments from the loess aquifer of La Pampa, Argentina. Applied Geochemistry, 20, 989-1016.

Steinmaus, C., Bates, M.ND., Michael, N., Yuan, Y., Kalman, D., Atallah, R., Rey, O.A., Bigss, M.D., Mary, L., Hopenhayn, C., Moore, L.E., Hoang, B.K., Smith, M.D., Allan, H., 2006. Arsenic methylation and bladder cancer risk in case–control studies in Argentina and the United States. Journal of Occupational and Environmental Medicine, 48, 478-88.

Steinmaus, C., Moore, L.E., Shipp, M., Kalman, D., Rey, O.A., Biggs, M.L., Hopenhayn, C., Bates, M.N., Zheng, S., Wiencke, J.K., Smith, A. H., 2007. Genetic polymorphisms in MTHFR 677 and 1298, GSTM1 and T1, and metabolism of arsenic. Journal of Toxicology and Environmental Health, Part A, 70(2), 159-70.

Teruggi, M.E., 1957. The nature and origin of Argentine Loess. Journal of Sedimentary Petrology, 27, 322-332.

Teruggi, M., Kilmurray, J., 1975. Tandilia. Relatorio Geología Provincia de Buenos Aires. In: Angelelli, V., De Francesco, F., Etchevehere, P.H., Fidalgo, F., Kilmurray, J.O., Llambias, E.J., Pascual, R., Prozzi, C.R., Rolleri, E.,O., Sala, J.M., Teruggi, M.E., Turner, J.C., Yrigoyen, M.R. (eds.). VI Congreso Geológico Argentino, Asociación Geológica Argentina, Imprenta CONI, Bahía Blanca, 55-77.

Thornthwaite, C.W., 1957. Instructions and tables for computing potential evapotranspiration and the water balance (Number 551.57 T515i). Drexel Institute of Technology, Centerton, New Jersey. Laboratory of Climatology, 10(3).

Ullah, K., Arif, M., Tahir Shah, M., Abbasi, I.A., 2015. Geochemistry and Provenance of the Lower Siwaliks from southwestern Kohat, western Himalayan Foreland Basin, NW Pakistan. Geologica Acta, 13(1), 327-343.

Villaamil Lepori, E.C., 2015. Hidroarsenicismo crónico regional endémico en Argentina. Acta Bioquímica Clínica Latinoamericana, 49(1), 83-104.

WHO (World Health Organization), 2004. Guidelines for Drinking-Water Quality, 1: Recommendations. Geneva, WHO, 668pp.

WHO (World Health Organization)-Executive Council, 2006. Mitigación de los efectos del arsénico presente en las aguas subterráneas: informe de la Secretaría. Official document Consejo Ejecutivo, 118. Issue Date: 2006, code: EB118/14, May 24th.

WHO (World Health Organization), UNICEF (Fondo de las Naciones Unidas para la Infancia), 2012. Trends in maternal mortality: 1990 to 2010. WHO, UNICEF, Francia, ISBN: 978 92 4 150363 1.

WHO (World Health Organization), UNICEF (United Nations Children's Fund), 2015. Progress on sanitation and drinking water: 2015 update and MDG (Millennium Development Goals) assessment. WHO, UNICEF, United States, ISBN: 978 92 4 150914 5.

Zabala, M.E., Manzano, M., Vives, L., 2016. Assessment of processes controlling the regional distribution of fluoride and arsenic in groundwater of the Pampeano Aquifer in the Del Azul Creek basin (Argentina). Journal of Hydrology, 541, 1067-1087.

Manuscript received December 2016;
revision accepted May 2017;
published Online July 2017.