Title: Distribution of inorganic arsenic species in groundwater from Santa Fe Province, Argentina

Corresponding Author: Dr Mirna Sigrist,

Corresponding Author's Institution: Universidad Nacional del Litoral

First Author: Mirna Sigrist

Order of Authors: Mirna Sigrist; Antonela Albertengo; Lucila Brusa; Horacio Beldoméncio, Prof.; Mabel Tudino, PhD

Abstract: The distribution of inorganic arsenic species in groundwater used as drinking water supply by the peri-urban and rural population from central-western area of Santa Fe Province, Argentina, was studied. An analytical methodology based on an online system of atomic absorption spectrometry with hydride generation and flow injection (FI-HGAAS) was used for total inorganic arsenic determination. For speciation purposes, the distinction between As(V) and As(III) was performed through the on line coupling of FI-HGAAS to a solid phase system based on an anionic exchanger able to retain As(V) as oxyanion, allowing As(III) to be selectively determined. The concentration of As(V) was calculated as the difference between total arsenic and As(III) concentrations. Effects of matrix interference due to the nonselective behavior of the exchange resins were carefully laid. Results for 59 samples collected from 27 localities showed an almost exclusive predominance of pentavalent forms.

Santa Fe, March 14, 2013

Cover letter

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We are submitting the electronic version of the manuscript "Distribution of inorganic arsenic species in groundwater from Santa Fe Province, Argentina" by Mirna Sigrist (corresponding author), Antonela Albertengo, Lucila Brusa, Horacio Beldoménico and Mabel Tudino to be considered for publication in Applied Geochemistry. The work has approximately 4,000 words without references.

Our work is focused on the study of the distribution of inorganic arsenic species in groundwater used as drinking water by the peri-urban and rural population from central-western area of Santa Fe Province, Argentina, without water supply services. Although the presence of an oxidizing environment suggests the predominance of As(V), arsenic speciation analysis has not been reported in the groundwater of the region. An analytical methodology based on an online system of atomic absorption spectrometry with hydride generation and flow injection (FI-HGAAS) was used for total inorganic arsenic determination. For speciation purposes, the distinction between As(V) and As(III) was performed through the on line coupling of FI-HGAAS to a solid phase extraction (SPE) system based on an anionic exchanger able to retain As(V) as oxyanion, allowing As(III) to be selectively determined. The SPE-FI-HGAAS system provides a simple, sensitive, easy to operate, fast and inexpensive strategy for speciation analysis of inorganic arsenic in water samples at trace level using an accessible instrumentation to routine analytical laboratories. Results for 59 samples collected from 27 localities showed an almost exclusive predominance of pentavalent forms which are the lower toxic species, with As(III) values bellow 2.5 $\mu g\ L^{-1}$ (LOQ). Nonetheless, total As concentrations ranging between 25.8 and 400.4 $\mu g\ L^{-1}$ greatly exceeded the maximum contaminant level (MCL) of 10 $\mu g\ L^{-1}$ for arsenic in drinking water. The moderate clinical status in ratio to HACRE (the Spanish acronym for Endemic Regional Chronic Hydro Arsenicism), better than expected by the epidemiologists, possibly could be associated to the oxidation state of the arsenic.

Thanking you in advance, I remain sincerely yours.

Dra. Mirna Sigrist
msigrist@fiq.unl.edu.ar
Programa de Investigación y Análisis de Residuos y Contaminantes Químicos
PRINARC-Facultad de Ingeniería Química
Universidad Nacional del Litoral
Santa Fe ARGENTINA

Highlights

- Study on inorganic arsenic species in groundwater for drinking in Santa Fe Argentina
- This information is currently scarce or absent in the region
- An analytical methodology based on SPE-FI-HGAAS coupling was used for speciation
- Information is given for a more accurate interpretation of the toxicological impact

Distribution of inorganic arsenic species in groundwater from Santa Fe Province, Argentina

*Mirna Sigrist[a], Antonela Albertengo[a], Lucila Brusa[a], Horacio Beldoménico[a], Mabel Tudino[b]

[a] Programa de Investigación y Análisis de Residuos y Contaminantes Químicos, PRINARC,

Facultad de Ingeniería Química, Universidad Nacional del Litoral,

Santiago del Estero 2654 Piso 6, (3000) Santa Fe Argentina

[b] Laboratorio de Análisis de Trazas, Departamento de Química Inorgánica, Analítica y Química

Física / INQUIMAE, Facultad de Ciencias Exactas y Naturales, Pabellón II, Ciudad Universitaria

(1428), Buenos Aires Argentina

*Corresponding author. Tel/fax: +54-342-457-1161

E-mail address: msigrist@fiq.unl.edu.ar

Abstract

The distribution of inorganic arsenic species in groundwater used as drinking water supply

by the peri-urban and rural population from central-western area of Santa Fe Province, Argentina,

was studied. An analytical methodology based on an online system of atomic absorption

spectrometry with hydride generation and flow injection (FI-HGAAS) was used for total inorganic

arsenic determination. For speciation purposes, the distinction between As(V) and As(III) was

performed through the on line coupling of FI-HGAAS to a solid phase system based on an anionic

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concentration of As(V) was calculated as the difference between total arsenic and As(III)

concentrations. Effects of matrix interference due to the nonselective behavior of the exchange

resins were carefully laid. Results for 59 samples collected from 27 localities showed an almost exclusive predominance of pentavalent forms.

1. Introduction

Arsenic is a natural component of the Earth's crust distributed in soils, sediment, water, air and living organisms in four oxidation states: -III, 0, III and V. Natural waters usually contain low concentrations of arsenic (1-2 μg L^{-1} or even below), nonetheless higher concentrations (up to 12 mg L^{-1}) may be found in areas containing natural sources of this element (Smedley and Kinniburgh, 2002; Mandal and Suzuki, 2002; WHO, 2011). This becomes a subject of great concern in groundwater, mainly if they are used as drinking water sources. More than 20 countries in the world suffer natural contamination of their aquifers, affecting the quality of drinking water of more than 150 million people. Leaving aside occupational exposure, the most important routes of arsenic exposure are food and drinking water. Nonetheless, in those cases where the concentration of arsenic in drinking water is 10 μg L^{-1} or greater, it becomes the dominant source of intake (FAO/WHO, 2011).

In the underground aquatic environment, arsenic arises mainly from weathering of the arsenic-containing minerals. The prevalent forms are inorganic As(III) and As(V) and their distribution depends mainly on pH, redox potential and salinity of the water body. In oxidizing environments, pentavalent forms (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{-3}) are usually predominant while trivalent forms (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-}) are found in reducing environments. At typical pH values of groundwater (6.5-8.5), As(V) occurs as oxyanions while

As(III) as uncharged species (Smedley and Kinniburgh, 2002). Organoarsenicals are usually absent but they may exist in fresh and marine water systems as consequence of bacterial-biotransformation of inorganic forms (Francesconi and Edmonds, 1998).

Biochemical and toxicological behavior of different forms of arsenic widely varies (Leermarkers et al., 2006; Sharma and Sohn, 2009; Jain and Ali, 2000). Generally inorganic arsenic forms are more toxic than organoarsenicals and As(III) more toxic than As(V), presumably due to As(III) interference on enzymatic processes by bonding to –SH and –OH functional groups. Recent studies showed even that trivalent methylated arsenicals are more acutely toxic and more genotoxic than inorganic pentavalent arsenicals (Styblo et al., 2010). Thus, the different toxicities between inorganic As(III) and As(V), in addition to a higher removal efficiency of As(V) from water (Walker et al., 2008; Chen et al., 1999) make that both toxicological and technological aspects, generate a great interest in the individual species determination.

Inorganic arsenic compounds are classified by IARC in Group 1 (carcinogenic to humans) (IARC, 1987). Although there is available vast information on the association between the exposure to arsenic in drinking water and the increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin changes as hyperkeratosis and pigmentation changes (IPCS, 2001), considerable uncertainty still remains on the actual risks at low concentrations. Available data on the mode of action of the arsenic in human body do not provide a biological basis for using either linear or non-linear extrapolation. Thus, WHO provisional guideline value of 10 µg L^{-1} has been established on the basis of removal treatment performance and analytical achievability (WHO, 2011). In recent years, it has been observed a global trend to adopt as maximum contaminant level (MCL) the value proposed by the WHO. Argentina legislation also reduced the MCL for arsenic in drinking water from 50 to 10 µg L^{-1} while recommended to achieve this value throughout the country by 2017 (CAA, 2012).

A major area of Argentina, the Chaco-Pampean plain (over 1×10^6 km^2), is partially affected by high arsenic concentrations in groundwater (ranging between <10-5300 µg L^{-1}), in addition to other associated trace elements (F, U, V, B, Se, Mo, etc) and high levels of salinity and/or hardness. This region extends from Paraguay border in the North to the Patagonian Plateau in the South and, from the Pampean Hills in the West to the Paraná and de la Plata rivers in the East (Smedley et al., 2002; Bundschuh et al., 2011; Nicolli et al., 2012). In the central-east area of the region is placed the province of Santa Fe (Fig. 1), which suffers the natural arsenical pollution of its aquifers along the west side (about 60% of the province) in mostly concentrations up to 1000 µg L^{-1} (Nicolli et al., 2009).

Recently, an epidemiological study from populations exposed to arsenic levels in drinking water above 50 µg L^{-1} was conducted in the province by the Pan American Health Organization in localities with water supply services. Results showed that the incidence of arsenic on health problems regionally known as HACRE (the Spanish acronym for Endemic Regional Chronic Hydro Arsenicism) was estimated in 2.5%. The moderate clinical status was better than expected by the epidemiologists, situation possibly associated to the oxidation state of the arsenic and other factors of uncertainty not evaluated by the study (Corey et al., 2005).

Different arsenic speciation methodologies in aqueous solution have been reported mainly from the 1970´s. Earlier literature on this subject was devoted mostly to off-line methodologies involving the species separation and/or pre-concentration and further detection by discontinuous steps (Irgolic, 1994). Later, on-line speciation analysis using hyphenated techniques became preferred due to lower detection limits, minor sample manipulation, easiness of operation and faster determination of the different species (Das et al., 2001). Nowadays, the coupling between liquid chromatography and high sensitivity detectors as mass spectrometry is the more powerful tool in elemental speciation (I. Komorowicz and D. Barałkiewicz, 2011) but the instrumentation is

still expensive and sophisticated. Nevertheless, if the objective is the individual determination of the most toxic species in addition to the total element concentration, non-chromatographic procedures involving selective extraction steps coupled to atomic spectrometry for detection could be an excellent alternative. Hydride generation atomic absorption spectrometry (HGAAS) with a heated quartz tube atomizer is a very widely used technique for the ultratrace determination of arsenic and other hydride forming elements (Dedina and Tsalev, 1995). This technique allows an increase of sensitivity and selectivity of the analytical determination. It employs the reduction of arsenic to its hydride, the arsine (AsH_3), by means of sodium borohydride ($NaBH_4$, the most common reducing agent) in acid media. The different reaction rates of inorganic As(III) and As(V) to form AsH_3 by $NaBH_4$ under suitable acidic conditions, have been often used for the speciation analysis. Literature on arsenic speciation in environmental samples using hydride generation have been recently reviewed (Anawar, 2012). Nevertheless, the use of diluted or weak acid medium (Anderson et al., 1986; Coelho et al., 2002) and /or low $NaBH_4$ concentration (Sigrist and Beldoménico, 2004) to selectively reduce As(III) into AsH_3 with no significant interferences of As(V) can produce a low efficiency on arsine generation and thus, a significant loss of sensitivity. In this sense, a good alternative is to remove As(V) from samples prior to hydride generation reaction. The different first acid dissociation constants (pK_a) of H_3AsO_4 and H_3AsO_3 (2.3 and 9.2, respectively) allow the separation of As(III) and As(V) by means of ionic exchange mechanisms since, at typical pH range of groundwater, As(V) forms are retained onto an anion exchange resin whereas the As(III) neutral form pass through. This can be carried out with a very good performance using solid phase extraction (SPE). Flow techniques as flow injection (FI) are particularly advantageous to make easier the coupling for on-line separation of species.

The main aim of the present work is to study the distribution of the inorganic arsenic species in groundwater from province of Santa Fe. An analytical methodology based on a FI-HGAAS

system was employed for the determination of total inorganic arsenic whereas an on-line SPE-FI-HGAAS coupling was used for the selective As(III) determination. The locations included in the study are sited in the west-central area of the province. This region is highly affected by arsenic occurrence in its aquifers and additionally, the peri-urban and rural population uses residential wells as a source of water supply for drinking.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Model 3110 flame atomic absorption spectrometer (Connecticut, USA) equipped with an arsenic hollow cathode lamp Photron (Victoria, Australia) was used as detector. A Perkin-Elmer FIAS 100 flow injection hydride generation system (Connecticut, USA) with a heated quartz tube atomizer (10 mm i.d. x 160 mm length) was used for hydride generation and coupled to the AAS. An anion-exchange cartridge was placed before the injection valve to produce a SPE-FI-HGAAS system with on-line separation of the inorganic arsenic species. The flow rates and the time of the process were programmed and automatically controlled through the software AA WinLab version 3.2 provided by Perkin Elmer. The sample solution flowed into a 500 μL sample loop. Polytetrafluoroethylene (PTFE®) tubing of 1.0 mm id was employed for the movement of the fluids through the manifold. Flexible polyvinylchloride peristaltic pump tubing was used to transport the HCl carrier and the $NaBH_4$ reducing reagent. Peak height was used for the measurement of the analytical signal.

2.2. Reagents and chemicals

All reagents were of high purity or at least of analytical reagent grade. Deionized-distilled water (DDW, resistivity 18 MΩ.cm) was used to prepare all solutions. As(III) stock solution 1000 mg L^{-1} was prepared from 1.3204 g of As$_2$O$_3$ (Riedel-de Haën, Germany) dissolved in 20 ml of 1 mol L^{-1} NaOH, neutralized with 2 mol L^{-1} HCl and diluted to 1000 ml with 0.6 mol L^{-1} HCl. Working solutions were prepared daily by appropriate dilution of the stock solution in DDW. As(V) stock solution of 1000 mg L^{-1} was obtained from Merck (Darmstadt, Germany). For the determination of total inorganic arsenic, working solutions were prepared by pre-reduction of the As(V) standard stock solution with 5% potassium iodide (KI) Merck (Darmstadt, Germany) - 5% ascorbic acid (C$_6$H$_8$O$_6$) Merck (Darmstadt, Germany) in HCl 1.2 mol L^{-1}. The same was employed for pre-reduction of As(V) to As(III) in the water samples. Reference material NIST 1643e (trace elements in water) was used to evaluate the analytical method for determining total inorganic As.

Hydrochloric acid solutions 1.2 mol L^{-1} and 3.5 mol L^{-1} prepared from concentrated HCl Carlo Erba (USA) were used as carrier solutions for determining total inorganic As and As(III), respectively. Sodium tetrahydroborate solution (NaBH$_4$) 0.2% (m/v) was used for determining total inorganic As whereas NaBH$_4$ 0.35% (m/v) for As(III). Both were prepared daily by dissolving NaBH$_4$ Merck (Darmstadt, Germany) in 0.025% (m/v) sodium hydroxide Merck (Darmstadt, Germany). Nitrogen 99.998 % purity, obtained from Linde (Argentina) was used as carrier gas to transport the generated hydride to the atomizer.

Silica-based chloride-form strong anion exchange (SAX) resin with trimethylaminopropyl functional groups (500 mg sorbent of 40 μm particle size and 60 Å pore size) packed in Bond Elut cartridges of 10 ml were obtained from Varian (Harbor City, USA). Cartridges were preconditioned with 1 ml methanol and DDW before use. The cellulose acetate membrane filters (0.45 μm pore size) were obtained from Microclar (Argentina).

2.3. Methodology

The SPE-FI-HGAAS and FI-HGAAS methodologies used for determining As(III) and total inorganic As, respectively, were reported by Sigrist et al. (2011). Chemical and operational parameters for As(III) were optimized using a multivariate approach. In the SPE-FI-HGAAS system, an anion exchange cartridge was incorporated to the FI-HGAAS before the injection valve by means of a simple coupling with a flexible polyvinylchloride coil of 10 cm length and 2 mm i.d. As(V) was retained onto the ion exchange resin whereas the eluent containing As(III) was transported to the chemifold where it was mixed with the reductant in the reaction coil to produce arsine. The gaseous hydride was transported by the nitrogen carrier stream to the quartz atomizer heated with an air-acetylene flame. A scheme of the SPE-FI-HGAAS system is shown in Figure 2.

Total inorganic arsenic concentration was determined on 10 ml sample aliquots acidified with concentrated HCl (5ml) and pre-reduced with 5% (m/v) KI - 5% (m/v) $C_6H_8O_6$ solution (5 ml) in 50 ml volumetric flask. As(V) concentration was calculated from the difference between total inorganic arsenic and As(III). The instrumental and operating parameters are shown in Table 1.

Limits of detection and quantification were 0.8 μg L^{-1} and 2.5 μg L^{-1} for As (III), and 0.6 μg L^{-1} and 2.0 μg L^{-1} for total inorganic As, respectively. Results obtained from the analysis of the certified reference material NIST 1643e for total inorganic As was 60.7 ± 2.6 μg L^{-1} (95% confidence level; $n = 3$) which was in good agreement with the certified value of 60.45 ± 0.72 μg L^{-1}. Validation of As(III) measurements was made by means of spike assays as no certified material for the different species are available in the market. Recoveries between 98-106% were found from spiked real samples with As(III) at 10 μg L^{-1} level.

2.4. Sampling and sample preservation

Several studies have been reported on arsenic species stability in water samples, but conclusions are usually contradictories or confusing (McCleskey et al., 2004; Bednar et al., 2005). There is still no a standard preservation strategy that becomes effective for all water samples. Also, it should be noted that most preservation assays use deionized water as background matrix and not real water samples. The photochemical reactions between Fe(II)/Fe(III) redox system and As(III)/(V), dissolved oxygen and microbial activity are the major causes of arsenic species interconversion. Field filtration, refrigeration at 4º C and storage in the dark have been recognized as prerequisites for the analytes stabilization (Kumar and Riyazuddin, 2010). The use of membrane filters with pore size 0.45 μm allows standardizing the dissolved fraction of metals, acting as a barrier for microorganisms and particulate materials as well. In presence of low concentrations of metals able to form hydroxides, the refrigeration at 4-5 °C was reported as an effective way to preserve the species distribution in filtered natural water samples for a period of up 30 days (Hall et al., 1999). In addition, several preservatives (e.g. HCl, H_2SO_4, EDTA) have been tested although its efficiency varies on sample matrix and microbial activity (McCleskey et al., 2004).

Preservation also depends on the analytical techniques to be used. HCl is better suited for measurements by HGAAS because the sample matrix is similar to the carrier stream. However, high Cl^- concentrations could interfere on the separation procedure of As(III)/As(V) if anionic exchangers are used. Some authors have reported the separation of As(III) and As(V) species on site using ion-exchange resins (Edwards et al, 1998; Yalcin and Le, 1998). However, the lack of a

priori knowledge of the sample matrix such as high competitive anion concentrations (e.g. SO_4^{2-}, Cl^-) can led to erroneous results (Miller et al., 2000; Sigrist et al., 2011).

In this work, the water samples were collected from the first point of the extraction pipe ascent of well water. In those sites where it was possible, extraction was performed by a homemade immersion sampling device constructed in Delrin ® and polypropylene in order to minimize contact with metallic components and atmospheric oxygen. Characteristics and operation of the sampler are detailed in Sigrist et al. (2011). Finally, the water samples filtered were stored in 100 mL high density polythene bottles and kept refrigerated at 4-5 °C until the analysis. No preservatives were added as the metals concentrations were low enough to prevent metal hydroxides production.

3. Results and discussion

3.1. Groundwater sample composition from center-western area of Santa Fe Province

The aquifer system of the study region shown in Fig.1 comprises a semi confined alluvial aquifer known as "Puelches sands" which usually hosts good quality groundwater, predominantly of the Na-bicarbonate type, with moderate arsenic concentrations (19.5-53.6 µg L^{-1}). Nonetheless the aquifer can be affected by saline intrusion of deep water and, upwards, by Quaternary aeolian loess deposits of the "Pampean Formation" that include a shallow aquifer of variable water quality, usually carbonated and with higher As concentration (17.9-780 µg L^{-1}) (Nicolli et al., 2012). The latter are universally oxidizing waters with high dissolved O_2 concentrations and pH values from neutral to alkaline (Smedley et al., 2002). The increase of the arsenic concentration and other associated trace elements is favored by the evapotranspiration process occurring in

shallow unconfined groundwater from predominantly semi-arid climates and high pH values that favor desorption process from mineral phases (Nicolli et al., 2010). Although the presence of an oxidizing environment suggests the predominance of As(V), arsenic speciation analysis has not been reported in the groundwater of the region. Since Pampean aquifer is usually used by the peri-urban and rural population as a source of water supply for drinking from residential wells, the study becomes of social relevance. Physicochemical parameters and ions measured in the samples collected are shown in Table 2.

3.2. Effects of interferences on As(III) and As(V) separation

The uptake of As (V) on the SAX exchange resin can be affected by the presence of competitive anions of natural occurrence in waters such as Cl^-, SO_4^{2-}, NO_3^-, HPO_3^{2-}, HCO_3^-. The sulfates showed to be the more important interference by decreasing the retention efficiency of As(V) to 95%, 32% and 19% for 1000 mg L^{-1}, 1200 mg L^{-1} and 2000 mg L^{-1} sulfate concentrations, respectively. A sample dilution of 3:5 was enough to minimize the matrix effect in waters containing up to 1500 mg L^{-1} sulfate (Sigrist et al., 2011). Dilution was thus selected as a compromise between sensitivity and matrix interference. From 62 samples collected, arsenic speciation analysis was not possible for 3 samples due to higher sulfate concentrations.

3.3. Speciation analysis in groundwater samples

The sampling was conducted in 27 localities placed between latitudes 30º 46´S and 32º 0´S and between longitudes 60º 34´O and 62º 3´ O. Results obtained are shown in Table 3. In all samples, the concentration of total arsenic was above the MCL of 10 µg L^{-1} set by national

legislation (CAA, 2012) and even a 85% of the samples was above the maximum limit of 50 µg L^{-1}, provisionally allowed in the Santa Fe Province (ENRESS, 2011). The speciation analysis showed the prevalence of As(V) forms so that a lower toxicological impact would be consistent with previous epidemiological studies (ENRESS, 2005). Nevertheless, MCL is defined in terms of the total arsenic concentration and, in this sense, the groundwater of the region becomes highly risky for drinking. From a technological viewpoint, it is important highlight that the dominance of As(V) species leads to enhance the arsenic removal from water if are used strategies suitable for home scale, such as those based on adsorption or coagulation/precipitation processes.

Conclusions

The natural contamination of groundwater with arsenic compromises the quality of drinking water in many regions of the world. In this work we conducted the study of the distribution of inorganic arsenic species in groundwater for drinking in the province of Santa Fe (Argentina).

The incorporation of an ion exchange stage by SPE to FI-HGAAS system provides a simple, sensitive, easy to operate, fast and inexpensive strategy for speciation analysis of inorganic arsenic in water samples at trace level using an accessible instrumentation to routine analytical laboratories. The most important limitation of the methodology is attributable to the interferences caused by high concentrations of sulfate in the retention process of As(V). Results showed an almost exclusive dominance of the pentavalent forms in groundwater samples of the center-western area of Santa Fe Province with As(III) values bellow 2.5 µg L^{-1} (LOQ). Nonetheless, total As concentrations ranging between 25.8 and 400.4 µg L^{-1} greatly exceeded the MCL of 10 µg L^{-1} for arsenic in drinking water. Finally, results obtained will provide information for a more

accurate interpretation of the toxicological impact of contaminant in studies related to the adoption

of criteria regarding allowable regulatory level of arsenic in drinking water in Argentina.

Acknowledgements

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Table

Table 1

Instrumental and operating conditions used for As(III) and total inorganic As determinations

Wavelength	193.7 nm
HCL current	11 mA
Slit width	0.7 nm
Integration time	15 s
Read time	20 s
Carrier solution flow rate	10.0 mL min^{-1}
Reductant solution flow rate	5.0 mL min^{-1}
Carrier gas flow-rate (N_2)	75 mL min^{-1}
Sample loop volume	500 μL
Prefill time	15 s
Fill time	10 s
Injection time	15 s

Table 2

Chemical characterization of the groundwater samples ($n = 62$).

Parameter/Ion	Units	Minimum	Maximum	Media
pH		7.2	8.0	7.6
Dissolved oxygen	mg O_2 L^{-1}	2.8	5.6	4.2
Hardness	mg L^{-1}	38	1245	189
Alkalinity	mg $CaCO_3$ L^{-1}	375	1333	729
Chlorides	mg L^{-1}	< 5	1333	230
Sulfates	mg L^{-1}	< 20	1807	396
Nitrates	mg L^{-1}	< 5	743	98.4
Nitrites	mg L^{-1}	< 0.03	0.92	0.06
Ammonium	mg L^{-1}	< 0.05	0.64	0.07
Calcium	mg L^{-1}	4.5	200	25.8
Magnesium	mg L^{-1}	2.2	155	19.2
Iron	mg L^{-1}	< 0.05	0.53	0.14
Manganese	mg L^{-1}	< 0.03	0.50	0.04
TDS	mg L^{-1}	672	6077	1971

TDS: Total dissolved solids

Table

Table 3

Results from inorganic speciation analysis of groundwater samples ($n = 59$).

Locality *Nº Sample*	As(III) ($\mu g\ L^{-1}$)	Total inorganic As ($\mu g\ L^{-1}$)	Locality *Nº Sample*	As(III) ($\mu g\ L^{-1}$)	Total inorganic As ($\mu g\ L^{-1}$)
Lehmann Lat 31° 7' S; Long 61° 27' O			**Colonia Bigand** Lat 31° 4' S; Long 61°43' O		
1	< LC	111.7 ± 0.4	1	< LC	128.5 ± 0.6
2	ND	79.4 ± 0.3	2	ND	32.2 ± 0.1
3	< LC	91.4 ± 0.6	3	ND	128.1 ± 0.4
Castellanos Lat. 31°12' S; Long 61°43' O			**Ramona** Lat 31°5' S; Long 61°54' O		
1	ND	40.0 ± 0.1	1	< LC	104.1 ± 1.1
2	< LC	191.4 ± 0.6	2	< LC	28.4 ± 0.2
Bauer y Sigel Lat 31°16' S; Long 61°57' O			**Felicia** Lat 31°15' S; Long 61°13' O		
1	< LC	139.6 ± 1.2	1	< LC	45.4 ± 0.7
2	< LC	162.2 ± 1.8	2	< LC	77.1 ± 0.4
Bella Italia Lat 31°17' S; Long 61°25' O			**Nuevo Torino** Lat 31°21' S; Long 61°14' O		
1	< LC	76.9 ± 0.1	1	< LC	56.8 ± 0.7
2	< LC	73.8 ± 0.3	2	< LC	91.4 ± 1.0
Egusquiza Lat 31° 6' S; Long: 61°38' O			**Presidente Roca** Lat 31°13' S; Long 61°37' O		
1	ND	66.3 ± 0.2	1	ND	71.1 ± 0.5
2	ND	91.6 ± 0.4	2	ND	126.4 ± 1.6
3	ND	82.9 ± 0.1	3	ND	25.8 ± 0.4
4	< LC	68.4 ± 0.5	4	ND	58.5 ± 1.0
Humberto Primo Lat 30°52' S; Long 61°21' O	< LC	65.3 ± 0.5	**Pilar** Lat 31°26' S; Long 61°16' O	< LC	115.2 ± 0.1
Susana Lat 31°21' S; Long 61°31' O			**Grutly** Lat 31°16' S; Long 61° 4' O		
1	ND	90.6 ± 0.6	1	< LC	92.8 ± 0.3
2	ND	111.4 ± 0.4	2	< LC	59.7 ± 1.5
3	ND	80.3 ± 0.1	3	ND	65.2 ± 0.2
Santo Domingo Lat 31° 7' S; Long 60°53' O	ND	87.1 ± 0.7	**San Jorge** Lat 31°54' S; Long 61°52' O	ND	216.0 ± 4.2
Progreso Lat 31° 8' S; Long 60°59' O	ND	29.1 ± 0.2	**Cañada Rosquín** Lat 32° 3' S; Long 61°36' O	< LC	177.8 ± 0.1
San Antonio Lat 31°13' S; Long 61°43' O			**Sarmiento** Lat 31° 4' S; Long 61°10' O		
1	ND	122.3 ± 1.6	1	< LC	181.3 ± 2.3
2	ND	113.2 ± 0.5	2	< LC	101.9 ± 1.0
Rafaela Lat 31°15' S; Long 61°29' O	< LC	78.8 ± 0.4	**Casas** Lat 32° 8' S; Long 61°32' O	ND	119.9 ± 5.0
Pueblo Marini Lat 31° 2' S; Long 61°53' O			**Eusebia** Lat 30°57' S; Long 61°51' O		
1	ND	186.5 ± 0.3	1	ND	59.8 ± 0.2
2	ND	400.4 ± 3.1	2	< LC	183.3 ± 2.0
Sunchales Lat 30°57' S; Long 61°34' O			**Vila** Lat 31°11' S; Long 61°50' O		
1	< LC	45.5 ± 0.4	1	< LC	135.2 ± 0.4
2	ND	177.9 ± 4.4	2	ND	20.0 ± 0.0
3	ND	90.7 ± 1.0	3	ND	118.2 ± 0.7
4	ND	34.4 ± 3.4	4	ND	86.1 ± 1.9
5	ND	82.3 ± 4.2	**Coronel Fraga** Lat 31°10' S; Long 61°55' O	ND	50.8 ± 0.3
6	ND	55.2 ± 2.0			

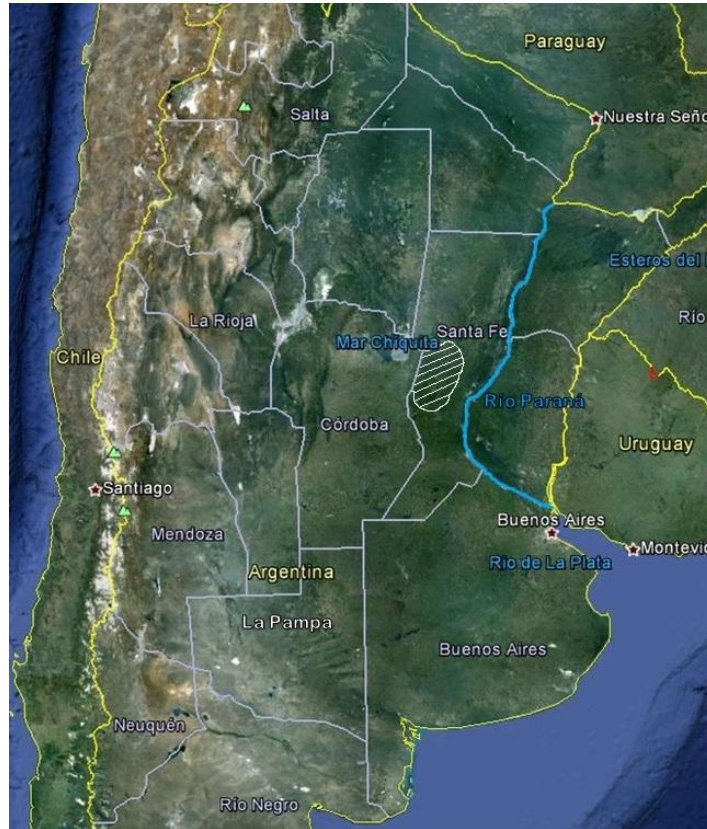ND: 0.8 $\mu g\ L^{-1}$; LC: 2.5 $\mu g\ L^{-1}$

Fig. 1. The Chaco-Pampean plain with location of the study area. ©2012 Google Earth digital image
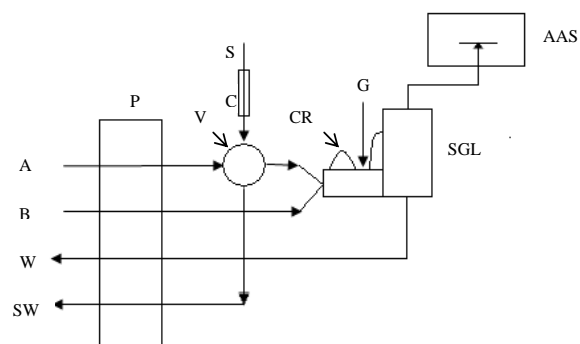
Fig.2. SPE-FI-HGAAS configuration for selective As(III) determination. A, carrier acid solution; B, reductant solution; W, waste; SW, sample waste; P, peristaltic pump; S, sample; C, anion exchange column; V, injection valve; G, carrier gas; CR, reaction coils; SGL, gas-liquid separator; AAS, atomic absorption spectrometer with quartz tube atomizer.