

## **Arsenic contamination of natural waters in San Juan and La Pampa, Argentina**

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## Abstract

Arsenic (As) speciation in surface and groundwater from two provinces in Argentina (San Juan and La Pampa) was investigated using solid phase extraction (SPE) cartridge methodology with comparison to total arsenic concentrations. A third province, Río Negro, was used as a control to the study. Strong cation exchange (SCX) and strong anion exchange (SAX) cartridges were utilised in series for the separation and preservation of arsenite ( $\text{As}^{\text{III}}$ ), arsenate ( $\text{As}^{\text{V}}$ ), monomethylarsonic acid ( $\text{MA}^{\text{V}}$ ) and dimethylarsinic acid ( $\text{DMA}^{\text{V}}$ ). Samples were collected from a range of water outlets (rivers/streams, wells, untreated domestic taps, well water treatment works) to assess the relationship between total arsenic and arsenic species, water type and water parameters (pH, conductivity and total dissolved solids, TDS). Analysis of the waters for arsenic (total and species) was performed by inductively coupled plasma mass spectrometry (ICP-MS) in collision cell mode. Total arsenic concentrations in the surface and groundwater from Encon and the San José de Jáchal region of San Juan (north-west Argentina within the Cuyo region) ranged from 9 – 357  $\mu\text{g l}^{-1}$  As. Groundwater from Eduardo Castex (EC) and Ingeniero Luiggi (LU) in La Pampa (central Argentina within the Chaco-Pampean Plain) ranged from 3 – 1326  $\mu\text{g l}^{-1}$  As. The pH range for the provinces of San Juan (7.2 – 9.7) and La Pampa (7.0 – 9.9) are in agreement with other published literature. The highest total arsenic concentrations were found in La Pampa well waters (both rural farms and pre-treated urban sources), particularly where there was high pH (typically > 8.2), conductivity (> 2600  $\mu\text{S cm}^{-1}$ ) and TDS (> 1400  $\text{mg l}^{-1}$ ). Reverse osmosis (RO) treatment of well waters in La Pampa for domestic drinking water in EC and LU significantly reduced total arsenic concentrations from a range of 216 – 224  $\mu\text{g l}^{-1}$  As to 0.3 – 0.8  $\mu\text{g l}^{-1}$  As. Arsenic species for both provinces were predominantly  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$ .  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  concentrations in San Juan ranged from 4 – 138  $\mu\text{g l}^{-1}$  and < 0.02 – 22  $\mu\text{g l}^{-1}$  for surface waters (in the San José de Jáchal region) and 23 – 346  $\mu\text{g l}^{-1}$  and 0.04 – 76  $\mu\text{g l}^{-1}$  for groundwater, respectively. This translates to a relative  $\text{As}^{\text{III}}$  abundance of 69 – 100 % of the total arsenic in surface waters and 32 – 100 % in groundwater. This is unexpected because it is typically thought that in oxidising conditions (surface waters), the dominant arsenic species is  $\text{As}^{\text{V}}$ . However, data from the SPE methodology suggests that  $\text{As}^{\text{III}}$  is the prevalent species in San Juan, indicating a greater influence from reductive processes. La Pampa groundwater had  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  concentrations of 5 – 1332  $\mu\text{g l}^{-1}$  and 0.09 – 592  $\mu\text{g l}^{-1}$  for EC and 32 – 242  $\mu\text{g l}^{-1}$  and 30 – 277  $\mu\text{g l}^{-1}$  As for LU, respectively. Detectable levels of  $\text{MA}^{\text{V}}$  were reported in both provinces up to a concentration of 79  $\mu\text{g l}^{-1}$  (equating to up to 33 % of the total arsenic). Previously published literature has focused primarily on the inorganic arsenic species, however this study highlights the potentially significant concentrations of organoarsenicals present in natural waters. The potential for separating and preserving individual arsenic species in the field to avoid transformation during transport to the laboratory, enabling an accurate assessment of in-situ arsenic speciation in water supplies is discussed.

## Keywords

Argentina · Arsenic · Speciation · Organoarsenicals · ICP-MS · Groundwater · Surface water

## Introduction

In 1993, the World Health Organisation (WHO) revised its guideline level for arsenic in drinking water from 50 to 10  $\mu\text{g l}^{-1}$  As (WHO 1993). Argentina still adopts the former WHO limit of 50  $\mu\text{g l}^{-1}$  As as its national drinking water standard (Frisbie et al. 2005). The new WHO recommended value came in as a direct result of the increased awareness of the toxicity of arsenic, particularly its carcinogenicity (Jong and Parry 2005). Human exposure to arsenic can occur through a variety of pathways, including air, water, soil and food (Mandal and Suzuki 2002). Arsenic exposure through food poses a substantial risk to humans in certain parts of the world, particularly in Asia from the consumption of staple foods such as rice and vegetables, which have been irrigated with As-rich groundwater (Meharg et al. 2009; Mondal and Polya 2008; Kile et al. 2007; Smith et al. 2006). However, drinking water is seen to pose the most significant risk to human health in Argentina, primarily through consumption and cooking, this is due to the various potential sources of arsenic present in the region, such as in groundwater and surface water (Nguyen et al. 2009; Asante et al. 2007; Ning et al. 2007; Ohno et al. 2007).

In recent years various studies have highlighted that countries such as Argentina, Bangladesh and Chile were experiencing high total concentrations of natural and anthropogenic (man-made) arsenic in drinking water from newly identified sources (Halim et al. 2009; Bhattacharya et al. 2006; Oyarzun et al. 2004; Ng et al. 2003; Smedley et al. 2002). The most common sources of arsenic in the natural environment are volcanic rocks (specifically their weathering products and ash), marine sedimentary rocks, hydrothermal ore deposits and associated geothermal waters, and fossil fuels, including coals and petroleum (Wang and Mulligan 2006; Smedley and Kinniburgh 2002). Anthropogenic activity, such as gold mining, has contributed to a sharp rise in natural arsenic concentrations reported for many artesian water supplies, often exceeding 600  $\mu\text{g l}^{-1}$  As (Duker et al. 2005; Farias et al. 2003; Plant et al. 2003). Local communities use these water supplies for drinking, cooking (Tseng 2009; Roychowdhury et al. 2005), cattle watering (Nriagu et al. 2007) and crop irrigation (Bhattacharya et al. 2007; Hossain 2006; Bundschuh et al. 2004), creating a possible pathway for the arsenic to enter both the animal and human populations.

The chemical species of arsenic, which can exist in the natural environment heavily influence its mobility, adsorptivity and toxicity (Ascar et al. 2008). In solution, arsenic primarily occurs as the inorganic arsenate ( $\text{As}^{\text{V}}$ ) species ( $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ ) and the uncharged arsenite ( $\text{As}^{\text{III}}$ ) species ( $\text{H}_3\text{AsO}_3^0$ ), as shown in Figure 1 (Gault et al. 2005a; Kumaresan and Riyazuddin 2001). The organic species monomethylarsonic acid ( $\text{MA}^{\text{V}}$ ), and dimethylarsinic acid ( $\text{DMA}^{\text{V}}$ ), have also been measured in surface and groundwater at the sub  $\mu\text{g l}^{-1}$  level (Smedley and Kinniburgh 2002). Variations in redox potential and pH will affect species predominance and the distribution between aqueous and solid phases. The mobility of inorganic arsenic ( $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$ ) under reducing conditions in aquifers has been widely reported (Nath et al. 2008; Bhattacharya et al. 2007). Arsenic mobilisation under oxidising conditions is also recognised as an important process, especially in the contamination of water affected by oxidation of sulphide minerals (Schreiber et al. 2000). Very high concentrations of aqueous arsenic are achievable under these conditions, however its mobilisation is heavily restricted due to the strong adsorptive capacity of metal oxides in soils/sediments, especially in the presence of iron (Fe) oxides (Scanlon et al. 2009; Smedley et al. 2002). Although, under oxidising conditions and high pH ( $\sim 8.5 - 9.5$ ), arsenic is often less strongly bound to Fe oxides than at lower pH ranges,

allowing for an enhanced mobility (Verplanck et al. 2008). If these conditions persist in aquifer environments, elevated aqueous arsenic concentrations may be a widespread occurrence. The shallow groundwater aquifers in the Chaco-Pampean Plain of Argentina are a good example (Gomez et al. 2009; Mukherjee et al. 2008; Bundschuh et al. 2004). High concentrations of total arsenic and other trace elements (B, F, Mo, V, U) have been reported to cause water-quality problems in aquifers from the provinces of Córdoba, Santa Fe and Buenos Aires, as well as La Pampa (Gomez et al. 2009; Smedley et al. 2005).

Arsenic has long been recognised as a toxic and carcinogenic element, with widespread health problems from contaminated groundwater reported in South America. Chronic long-term arsenic exposure thought to be a result of contact with inorganic arsenic (iAs) from drinking water sources, typically above  $50 \mu\text{g l}^{-1}$  As are symptomatic of skin, cardiovascular, renal, haematological and respiratory disorders (Bertolino et al. 2007; Hughes 2002). Documented evidence of illnesses from oral exposure to elevated arsenic is commonly seen in a pattern of skin changes including hyperpigmentation, hypopigmentation and hyperkeratosis lesions of the skin and the appearance of small “corns” or “warts” on the palms, soles, and torso. A small number of corns may develop into skin cancer (Chou and De Rosa 2003). Ingestion of arsenic causes peripheral vascular diseases and is associated with carotid atherosclerosis (Chiou et al. 2005; Wang et al. 2002). Ingesting iAs has also been reported to increase the risk of cancer in the bladder, lung, liver, and kidney (Ferreccio and Sancha 2006). It is becoming increasingly more important to identify arsenic species (particularly iAs) in drinking water sources due to the variability in their metabolic pathway in humans (reduction of  $\text{As}^{\text{V}}$  to  $\text{As}^{\text{III}}$ , followed by oxidative methylation of  $\text{As}^{\text{III}}$ ) and the potential toxicological effects (Suzuki 2005).

The main objective of this study was to determine the concentration of both total dissolved arsenic and its individual chemical species ( $\text{As}^{\text{III}}$ ,  $\text{As}^{\text{V}}$ ,  $\text{MA}^{\text{V}}$  and  $\text{DMA}^{\text{V}}$ ) using novel solid phase extraction (SPE) technology in relation to different geographical regions of Argentina; water types; and physical parameters (pH, conductivity and TDS). The SPE cartridges utilised in this study (500 mg SCX and SAX Varian Bond Elut<sup>®</sup> Junior) have been shown to be highly effective in preserving the four arsenic species under investigation in the field, with little influence from external factors such as pH (Watts et al. [THIS ISSUE]). This technique allows for greater specificity and accuracy in the determination of arsenic species. Comparison of arsenic concentrations (total and species) from various water sources (surface water, groundwater and tap) provides an insight into characteristic features of arsenic mobility and the potential toxicity in these regions of Argentina.

## **Materials and methods**

### **Study sites**

Surface and groundwater samples were collected from two provinces in Argentina, San Juan and La Pampa (Fig. 2). The sites were selected based on their direct interaction with human exposure pathways, via drinking water, crop production (irrigation) and animal grazing (cattle, goat, horse and sheep). Sites were also selected based on known high total arsenic concentrations in natural waters (Smedley et al. 2002) and evidence of arsenic related health problems within the population cited by local medical practitioners, with symptoms ranging from keratosis and skin

lesions to several reported cases of cancer. Additional water samples were collected from the province of Río Negro as a control to the arsenic study (Fig. 2).

### *San Juan*

San Juan Province is located in western Argentina on the border with Chile within the Cuyo region, approximately 280 km east of the Pacific coastline. Average rainfall in the region is very low ~ 100 mm per year, creating a semi-arid environment (de Salmuni et al. 2007). The province covers an extensive area of over 89,000 km<sup>2</sup> (Dilks 2004). Water samples were principally collected from river/stream systems (surface waters), used for irrigation and cattle watering purposes, groundwater sources as well as untreated domestic tap supplies. Study sites comprised surface waters from the Río Blanco near Angualasto (ANG) [30°3'0S, 69°9'0W]; the Río Jáchal (RJ) in and around San José de Jáchal [30°14'0S, 68°45'0W]; the Cuesta del Viento dam (CU) on the Río Jáchal; the Río Colola (CO), a tributary that feeds into CU; Agua Negra (AN), a freshwater spring flowing into the Río Jáchal and the Río Huaco in Huaco (HU) [30°09'17S, 68°28'46W] as shown in Figure 3. Surface waters were collected at a range of depths (0 – 30 cm below the water level). Domestic (untreated) tap supplies were collected from Niquivil (NQ) [30°24'2S, 68°41'47W] and San Juan (SJ) [31°32'03S, 68°31'34W] the provincial capital of San Juan Province (Figs. 3, 4). Tap water samples were taken after allowing the water to run for a minimum of 30 – 60 seconds through the pipes, in order to flush the pipeline of any potential adsorbed-As deposits. Artesian well and untreated residential tap waters were taken from the community of Encon (EN) [32°12'0S, 67°47'0W] on the San Juan – Mendoza border (Fig. 4). Water samples (groundwater) collected from the community of Encon originate from two different sources, the main community well supply and a blended combination of this well with a rural farm (finca) well, (which is located approximately 30 km away and the extracted water is piped to Encon where it is blended and stored in tanks for community distribution and usage).

Sampling elevations ranged from 1635 m above sea level (a.s.l.) at Angualasto in the north to 507 m a.s.l. at Encon in the south. Water collection from San Juan (San José de Jáchal and San Juan areas) amounted to 23 surface water samples and 5 domestic tap supply samples, as well as 15 samples from the community of Encon (5 urban well; 4 finca (rural farm) well; 3 blended untreated tap supplies; 3 school water supplies).

### *La Pampa*

La Pampa Province is located in central Argentina covering an approximate area of 140,000 km<sup>2</sup> within the Chaco-Pampean Plain, at a distance of 450 km west of the Atlantic coastline (Nicolli et al. 1989). Rainfall is greatest in the north and north-east of the province, which experiences between 500 – 700 mm per year (Michelena and Iruña 1995). The study was focused to the north of the province in the towns of Eduardo Castex [35°53'60S, 64°17'60W], 80 km north of Santa Rosa, the provincial capital, and Ingeniero Luiggi [35°25'0S, 64°28'60W], 130 km northwest of Santa Rosa, at elevations of 166 – 206 m a.s.l. Well waters (groundwater from Quaternary loess aquifers), used predominantly for drinking and irrigation were sampled from individual farmsteads (rural wells), urban wells and from two reverse osmosis water treatment works in Eduardo Castex (EC) and Ingeniero Luiggi (LU) (Fig. 5). Water flow-rates at the private farmsteads (fincas) were dependent on wind conditions, because wind turbines are used to draw up the groundwater into untreated open-air storage tanks. Flow-rates varied from between 1 – 19 l min<sup>-1</sup> at the time of sampling

and between sites. Tap water samples were taken after allowing the water to run for a minimum of 30 – 60 seconds through the pipes. A total of 157 water samples (60 urban wells; 52 rural wells; 15 untreated domestic tap supplies; 30 water treatment works) were collected from the province (Fig. 5).

### *Río Negro*

Río Negro Province lies within Patagonia (encompassed in the Monte Desert), extending westward from the Atlantic Ocean to the Cordillera of the Andes to the north of 42°S and the border with Neuquén Province (Abraham et al. 2009) (Fig. 2). The province covers an area of 203,013 km<sup>2</sup> (Zárate 2003). Water samples were collected from surface waters (Río Colorado (RC) and Río Negro (RN)), domestic tap supplies from the local school and residences and groundwater well supplies in the province (Fig. 6). Sampling was primarily focused to the north of the province in the town of General Roca (GR) [39°02'S, 67°35'W] approximately 418 km north-west of the provincial capital, Viedma, at typical elevations of 227 – 362 m a.s.l. Water samples collected from the province consisted of 40 surface waters, 6 groundwater well supplies and 31 domestic tap waters.

### **Water sampling**

Water samples for total arsenic determination were collected in opaque 30 ml Nalgene<sup>®</sup> bottles (Thermo Fisher Scientific, UK). Prior to collection, each Nalgene<sup>®</sup> bottle was rinsed three times with the filtered water sample, to minimise potential elemental contamination from the bottle during storage. Filtered/acidified (F/A) water samples for total arsenic analysis were drawn up in clean/rinsed disposable 20 ml BD<sup>™</sup> plastic syringes (Becton Dickinson Ltd, UK), injected into each bottle through a 0.45 µm membrane filter and preserved to an acidity of 1 % v/v HNO<sub>3</sub> (not accounting for potential neutralisation from carbonates/bicarbonates/phosphates) to prevent arsenic precipitation during transportation (Pandey et al. 2004; Bednar et al. 2002a; Garbarino et al. 2002). A further 30 ml water sample was passed through the SPE cartridge set-up for arsenic speciation. A filtered/unacidified (F/UA) aliquot of water was also taken for arsenic speciation analysis by HPLC-ICP-MS, as an inter-analytical method comparison with the SPE cartridges. All samples were stored at 4 °C during field sampling using a Tropicool 14 Litre Thermoelectric Cool Box TC-14 (Waeco<sup>®</sup>, Dorset, UK) connected to a powered car cigarette lighter socket. All water samples were subsequently transferred to a refrigerator (4 °C) on return to the laboratory. The analysis of waters for arsenic species by HPLC-ICP-MS was carried out within 2 weeks of sample collection. It has been shown in the literature that organoarsenicals remain stable in waters for at least 2 weeks when stored at 4 °C and in dark conditions (Francesconi and Kuehnelt 2004; Bednar et al. 2002a; Gong et al. 2002; Roig-Navarro et al. 2001).

Physical water parameter measurements (pH; conductivity, µS cm<sup>-1</sup>; total dissolved solid (TDS), mg l<sup>-1</sup>) were recorded at the time of sampling (prior to filtration/acidification) using a fully calibrated Hanna HI 98129 Digital Combo Meter (Hanna Instruments Ltd, UK). A GPS reference and elevation was also taken at each sampling site using a Garmin<sup>™</sup> Geko 201 (Garmin Ltd., UK).

### **Field-based arsenic speciation methodology**

On-site arsenic speciation was carried out utilising pre-conditioned Varian 500 mg Junior Bond Elut<sup>®</sup> strong cation exchange (SCX) and strong anion exchange (SAX) cartridges (Varian, UK) as described by Watts et al. [THIS ISSUE]. Conditioning of the SCX cartridge was undertaken using 15 ml of 50 % methanol (CH<sub>3</sub>OH; BDH; HPLC Grade, UK) followed by 15 ml of 1 M phosphoric acid (H<sub>3</sub>PO<sub>4</sub>; BDH; Aristar<sup>®</sup>, UK) and 5 ml of de-ionised water. The SAX cartridge was preconditioned using 15 ml of 50 % methanol and 5 ml of de-ionised water. Following the conditioning process, the cartridges were connected in series with a 0.45 µm filter (Fig. 7). A known volume of water (typically 30 ml) was then passed through the assembled kit using a clean/rinsed disposable 20 ml BD<sup>™</sup> plastic syringe (Becton Dickinson Ltd, UK). The effluent retained the As<sup>III</sup> species, the SCX cartridge retained DMA<sup>V</sup> and the SAX cartridge captured the MA<sup>V</sup> and As<sup>V</sup> species. Subsequent elution of the species captured on the cartridges was achieved using 5 ml of 1 M HNO<sub>3</sub> for DMA<sup>V</sup> on the SCX cartridge. MA<sup>V</sup> was firstly eluted from the SAX cartridge with 5 ml of 80 mM acetic acid (CH<sub>3</sub>COOH; BDH; Aristar<sup>®</sup>, UK) into a 15 ml bottle followed by 5 ml of 1 M HNO<sub>3</sub> to elute the As<sup>V</sup> species also retained on the SAX cartridge, which was eluted into a separate 15 ml bottle (Fig. 7).

Verification of the SPE methodology was achieved using synthetic As solutions (As<sup>III</sup>, As<sup>V</sup>, MA<sup>V</sup> and DMA<sup>V</sup> each at 10 µg l<sup>-1</sup>), with recoveries of 94 – 105 % (n = 25). The influence of pH on the recovery of the individual arsenic species was investigated over the pH range 4 – 10, As<sup>III</sup> and DMA<sup>V</sup> exhibited recoveries of 95 – 104 %, whilst As<sup>V</sup> and MA<sup>V</sup> showed slightly elevated recoveries of 109 – 117 %. A series of matrix components (Br, F, Fe, Cl, Mn, NO<sub>2</sub>, NO<sub>3</sub>, PO<sub>4</sub> and SO<sub>4</sub>) were also tested to investigate the performance of the SPE cartridges, as outlined by Watts et al. [THIS ISSUE]. Validation of the SPE field-based arsenic speciation method was undertaken using HPLC-ICP-MS as described in the literature (Button et al. 2009; Watts et al. 2007), to confirm the presence of the individual arsenic species in their respective fractions, as reported by Watts et al. [THIS ISSUE].

### Standards and reagents

All chemical reagents were of analytical reagent grade. Aqueous solutions were prepared using de-ionised water (18.2 MΩ; Millipore, UK). Water samples (30 ml) were filtered (0.45 µm; Millex, UK) and preserved on collection with nitric acid (HNO<sub>3</sub>; BDH; Aristar<sup>®</sup>, UK) for the analysis of total arsenic.

### Instrumentation

Filtered and acidified (F/A) water samples for total arsenic analysis and fractionated water samples from the SPE field-based speciation method were analysed using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500 Series, Agilent Technologies, UK) at the British Geological Survey (BGS), Keyworth, Nottinghamshire. The standard operating conditions were as follows: RF power 1550 W; reflected power < 20 W; coolant gas flow 15 l min<sup>-1</sup>; auxiliary gas flow 0.8 l min<sup>-1</sup>; nebuliser gas flow 0.8 l min<sup>-1</sup>; spray chamber temperature 4 °C. The ICP-MS instrument was fitted with a Micromist concentric nebuliser and PTFE Scott-type spray chamber. Arsenic detection was performed in collision cell mode using 4 l min<sup>-1</sup> <sup>1</sup>He to minimise polyatomic interferences at *m/z* 75 such as <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup>.

Optimisation of the ICP-MS was performed daily for arsenic and tuned using a 100  $\mu\text{g l}^{-1}$  dilution of Claritas PPT<sup>®</sup> multi-element tune solution 1 (SPEX CertiPrep<sup>®</sup>, UK). A 50  $\mu\text{g l}^{-1}$  solution of tellurium (SPEX CertiPrep<sup>®</sup>, UK) in 1 % v/v  $\text{HNO}_3$  was used as an internal standard for arsenic to correct for signal drift ( $< \pm 1$  % signal change) through addition to the sample solution via a T-piece. Calibration standards were prepared from a multi-element standard (SPEX CertiPrep<sup>®</sup>, UK) over the calibration range 0.1 – 100  $\mu\text{g l}^{-1}$  As. The instrumental limit of detection (LOD) for arsenic by the Agilent ICP-MS represented as the mean blank ( $n > 10$ ) signal + 3 x standard deviation (SD) was 0.1  $\mu\text{g l}^{-1}$  As. The instrumental LOD (mean blank ( $n > 10$ ) signal + 3 x SD) for each of the arsenic species by the field-based SPE method (using ICP-MS detection) was  $\text{As}^{\text{III}}$ : 0.12  $\mu\text{g l}^{-1}$ ,  $\text{As}^{\text{V}}$ : 0.02  $\mu\text{g l}^{-1}$ ,  $\text{MA}^{\text{V}}$ : 0.02  $\mu\text{g l}^{-1}$  and  $\text{DMA}^{\text{V}}$ : 0.03  $\mu\text{g l}^{-1}$ . A preconcentration factor of x6 (30 ml water sample passed through cartridge set-up, followed by arsenic species removal with 5 ml eluting solution) was applied to the eluted fractions of  $\text{As}^{\text{V}}$ ,  $\text{MA}^{\text{V}}$  and  $\text{DMA}^{\text{V}}$  from the SPE cartridges. A subsequent x2 dilution was performed prior to ICP-MS analysis, resulting in a final preconcentration factor for  $\text{As}^{\text{V}}$ ,  $\text{MA}^{\text{V}}$  and  $\text{DMA}^{\text{V}}$  of x3.

Validation of the ICP-MS for arsenic was achieved using certified reference waters TMDA-54.4 (National Water Research Institute, Ontario, Canada) and SRM<sup>®</sup> 1643e (National Institute of Standards and Technology, Maryland, USA). Mean total arsenic concentrations ( $\pm$  SD) over a series of 10 analytical runs ( $n = 36$ ) for TMDA-54.4 was  $45.3 \pm 2.3 \mu\text{g l}^{-1}$  As (certified:  $43.6 \pm 0.8 \mu\text{g l}^{-1}$  As) and  $58.3 \pm 3.3 \mu\text{g l}^{-1}$  As for SRM<sup>®</sup> 1643e (certified:  $60.5 \pm 0.7 \mu\text{g l}^{-1}$  As). The HPLC-ICP-MS procedure was monitored using the certified reference material CRM No. 18 Human Urine (National Institute for Environmental Studies, NIES, Ibaraki, Japan). A mean total arsenic value of  $131.1 \pm 1.2 \mu\text{g l}^{-1}$  As ( $n = 8$ ) was achieved (certified:  $137 \pm 11 \mu\text{g l}^{-1}$  As).

A comparison of the mean arsenic species concentrations from the SPE field-based method and the HPLC-ICP-MS laboratory based method showed no statistically significant difference between the two techniques at  $P < 0.01$  (Watts et al. [THIS ISSUE]). The relationship between the sum of the arsenic species ( $\text{As}^{\text{III}}$ ,  $\text{As}^{\text{V}}$ ,  $\text{MA}^{\text{V}}$  and  $\text{DMA}^{\text{V}}$ ) by the SPE method and the total arsenic concentration in the F/A water samples reported a strong positive correlation ( $R^2 = 0.9874$ ).

## Results

### Water parameter results

Physical water parameter (pH, conductivity, total dissolved solids (TDS)) measurements for surface, ground and domestic tap waters show clear variations both within and between the provinces of San Juan and La Pampa, Argentina (Table 1).

Different pH ranges were observed between the surface and domestic tap waters from the San Juan (SJ) sampling locations (Figs. 3, 4), namely 7.8 – 8.9 and 7.2 – 7.7, respectively (Table 1). Conductivity levels ranged from 1295 – 2506  $\mu\text{S cm}^{-1}$  in the surface waters and 1126 – 1837  $\mu\text{S cm}^{-1}$  in the domestic tap supplies. Conversely, TDS levels in surface waters ranged from 527 – 1245  $\text{mg l}^{-1}$  and 922 – > 2000  $\text{mg l}^{-1}$  in domestic tap supplies (Table 1).

The two different water sources in Encon, as well as their blended supply demonstrated similar parameter measurements. The pH conditions ranged from 9.3 –

9.7 for the urban well, 9.4 – 9.7 for the rural well and 9.1 – 9.4 for the blended tap supply (Table 1). Conductivity levels ranged from 972 – 1603  $\mu\text{S cm}^{-1}$  for the urban well, 1387 – 1552  $\mu\text{S cm}^{-1}$  for the rural well and 1047 – 1534  $\mu\text{S cm}^{-1}$  for the combined tap water supply (Table 1). Similar levels were also reported for TDS, 526 – 1346  $\text{mg l}^{-1}$  for the urban well, 690 – 1405  $\text{mg l}^{-1}$  for the rural well and the combined water supply exhibited 997 – 1267  $\text{mg l}^{-1}$  (Table 1). Treatment of the drinking water by ion-exchange in the local school - Escuela Albergue Dr Juan Carlos Navarro, reduced pH levels from 9.6 (untreated) to 8.0 (treated), conductivity levels from 1387  $\mu\text{S cm}^{-1}$  (untreated) to 743  $\mu\text{S cm}^{-1}$  (treated) and TDS levels from 1107  $\text{mg l}^{-1}$  (untreated) to 561  $\text{mg l}^{-1}$  (treated). Conductivity measurements showed little variability between water types in Encon, with the urban well displaying the greatest range (Table 1). TDS results for Encon were comparable with those exhibited in the surface waters from the province, ranging from 526 – 1405  $\text{mg l}^{-1}$  and 527 – 1245  $\text{mg l}^{-1}$ , respectively (Table 1).

Water parameter measurements for La Pampa demonstrate a much wider range of pH, conductivity and TDS than those from San Juan (Table 1). Urban well samples from Eduardo Castex (EC) reported higher pH values compared to similar waters taken in Ingeniero Luiggi (LU), with ranges of 7.9 – 9.3 and 7.4 – 8.7, respectively (Table 1); somewhat lower than San Juan. Rural well supplies, showed pH ranges of 7.4 – 9.9 and 7.5 – 9.0 for EC and LU, respectively. Tap water pH values from EC were 7.7 – 8.8. Water samples collected from the two reverse osmosis water treatment works (WTWs) in EC and LU exhibited the lowest pH levels with 7.0 – 8.6 in EC and 7.4 – 8.7 in LU (Table 1). Both EC and LU displayed similar conductivity levels for the urban and rural well water samples with ranges of 399 – > 3999  $\mu\text{S cm}^{-1}$  and 940 – > 3999  $\mu\text{S cm}^{-1}$ , respectively (Table 1). Conductivity measurements reported in the tap waters in EC displayed levels of 1446 – > 3999  $\mu\text{S cm}^{-1}$  (Table 1). The introduction of the water treatment works in both towns notably lowered all water parameter values, with conductivities as low as 79  $\mu\text{S cm}^{-1}$  in EC and 9  $\mu\text{S cm}^{-1}$  in LU (Table 1). This trend was also seen in TDS measurements, with EC displaying a reduction in the low end TDS range from 87  $\text{mg l}^{-1}$  to 39  $\text{mg l}^{-1}$  and for LU from 242  $\text{mg l}^{-1}$  to 4  $\text{mg l}^{-1}$  (Table 1). With the exception of the water treatment works in LU, all water types, namely ground (rural and urban wells) and tap, collected from La Pampa reported conductivity and TDS ranges to maximum recordable values of 3999  $\mu\text{S cm}^{-1}$  and 2000  $\text{mg l}^{-1}$ , respectively. No statistically significant relationship was observed between pH and either conductivity or TDS in San Juan (conductivity:  $R^2 = - 0.0321$ ; TDS:  $R^2 = - 0.0333$ ) or La Pampa (conductivity:  $R^2 = 0.0523$ ; TDS:  $R^2 = 0.0181$ ).

Water parameter measurements for the control province of Río Negro (RN) exhibited a pH range of 6.9 – 9.2 for Río Colorado and Río Negro surface waters; 7.1 – 8.0 for well waters and 7.0 – 8.8 for domestic tap supplies (Table 1). Conductivity and TDS measurements for surface waters ranged from 987 – 3149  $\mu\text{S cm}^{-1}$  and 219 – 1994  $\text{mg l}^{-1}$ , respectively. Well waters had conductivity levels of 1109 – 2129  $\mu\text{S cm}^{-1}$  and TDS levels of 1258 – 1853  $\text{mg l}^{-1}$ , whereas domestic tap supplies showed lower levels, reporting 908 – 1574  $\mu\text{S cm}^{-1}$  and 470 – 1620  $\text{mg l}^{-1}$  for conductivity and TDS, respectively (Table 1).

### **Total arsenic**

Total arsenic concentrations in all surface, ground and some tap waters from San Juan and La Pampa (Tables 2, 3) determined by ICP-MS were elevated in comparison to

the control province of Río Negro (Table 4) in almost all study locations. In San Juan, surface waters, primarily used for irrigation and livestock, exhibited the lowest concentrations of arsenic (mean: 67; median: 74; range: 11 – 133  $\mu\text{g l}^{-1}$  As) measured in natural waters in this study (Figs. 8, 9). The highest concentrations of arsenic in these surface waters were found in the Río Blanco near Angualasto (47 – 133  $\mu\text{g l}^{-1}$  As), the uppermost sampling location at 1635 m a.s.l. and the closest to the Andes and sites of local gold mining activities. The lowest total arsenic concentrations were found in the Río Huaco - a separate river system north of San José de Jáchal (Fig. 3). Arsenic in the man-made lake of the Río Blanco/Río Jáchal, namely, Cuesta del Viento dam (CU1) was 78  $\mu\text{g l}^{-1}$  As (Fig. 9), compared to the Río Colola inflow (52  $\mu\text{g l}^{-1}$  As). A raised arsenic concentration was measured at the outflow of the Pachimoco dam (RJ1) of the Río Jáchal with a value of 116  $\mu\text{g l}^{-1}$  As (Fig. 9), which is in agreement with a previously reported value (Hill 2009).

Total dissolved arsenic remained relatively constant along the Río Jáchal (mean: 78; median: 74; range: 55 – 116  $\mu\text{g l}^{-1}$  As), with minimal addition of arsenic from the freshwater spring at Agua Negra (Fig. 9). Arsenic concentrations in untreated domestic tap water samples from the same area ranged from 9 – 100  $\mu\text{g l}^{-1}$  As, with a mean of 38  $\mu\text{g l}^{-1}$  As (Tables 1, 2), almost all of which exceed the WHO drinking water limit for arsenic with a maximum measured concentration of 10x that value.

The different sources of water in the community of Encon (in the south of San Juan Province) displayed significantly different total arsenic concentrations in comparison to the main provincial sampling sites in the north. Encon (EN) rural well waters (n = 4) had a more limited range of arsenic concentrations (mean: 59; range: 25 – 76  $\mu\text{g l}^{-1}$  As) as shown in Figure 8. However, the EN urban well waters (mean: 254; range: 31 – 357  $\mu\text{g l}^{-1}$  As) (Tables 1, 2), are all well above the WHO recommended limit of 10  $\mu\text{g l}^{-1}$  for arsenic in drinking water (WHO 1993). Untreated domestic tap waters composed of the two different well supplies blended together is the main drinking water source for the community; these had a mean total arsenic concentration of 253  $\mu\text{g l}^{-1}$  As. A reduction in total arsenic was seen after treatment by ion exchange at the local school from 66 to 21  $\mu\text{g l}^{-1}$  As (Table 1). The distribution of total arsenic in the rural well and surface waters were comparable, with median values of 68  $\mu\text{g l}^{-1}$  As and 74  $\mu\text{g l}^{-1}$  As, respectively (Fig. 8). The Encon urban well and domestic tap supply waters showed a similar arsenic concentration range, however the distribution of the results were different with median arsenic concentrations of 324  $\mu\text{g l}^{-1}$  As and 270  $\mu\text{g l}^{-1}$  As, respectively (Fig. 8).

Total arsenic in La Pampa for EC and LU displayed distinct variability and overall had a greater range in arsenic concentrations compared to San Juan. Urban well waters in EC had total arsenic concentrations of 39 – 290  $\mu\text{g l}^{-1}$  As, whilst LU were 115 – 327  $\mu\text{g l}^{-1}$  As (Table 1). The rural well waters from both towns had the highest concentrations of total arsenic found in this study, with EC (n = 29) having a maximum of 1128  $\mu\text{g l}^{-1}$  As and LU (n = 23) 1326  $\mu\text{g l}^{-1}$  As (Table 1 and Fig. 8); with overall means of 484  $\mu\text{g l}^{-1}$  As (EC) and 212  $\mu\text{g l}^{-1}$  As (LU). Tap water samples from EC were also above the WHO guideline levels, with a range of 41 – 747  $\mu\text{g l}^{-1}$  As (mean: 379  $\mu\text{g l}^{-1}$  As) (Table 1). Groundwater values reported in the literature for the town of Eduardo Castex ranged from < 4 – 5300  $\mu\text{g l}^{-1}$  As (Smedley et al. 2002). The rural well waters displayed the broadest concentration range in La Pampa with arsenic values of 3 – 1326  $\mu\text{g l}^{-1}$  As (Fig. 8). The urban well and domestic tap supply samples yielded narrower ranges of 39 – 327  $\mu\text{g l}^{-1}$  As and 41 – 747  $\mu\text{g l}^{-1}$  As, respectively

(Fig. 8). Little similarity was seen in the range of total arsenic concentrations for each water type from the provinces of La Pampa and San Juan.

Total arsenic in the control province of Río Negro displayed concentrations well below the WHO drinking water limit of  $10 \mu\text{g l}^{-1}$  As in the majority of samples (surface waters:  $0.8 - 16.4$ ; well waters:  $1.5 - 5.2$ ; tap supplies:  $0.5 - 2.5 \mu\text{g l}^{-1}$  As) (Table 1). Surface water arsenic concentrations in Río Negro were on average 10-fold lower than those reported in San Juan; well waters were approximately 100-fold lower than in Encon and as much as 500-fold lower than corresponding samples in La Pampa. Tap water samples from Río Negro displayed a 150-fold reduction in total arsenic concentrations in comparison to the two impact areas of San Juan and La Pampa.

### Arsenic species

The individual arsenic species ( $\text{As}^{\text{III}}$ ,  $\text{As}^{\text{V}}$ ,  $\text{MA}^{\text{V}}$  and  $\text{DMA}^{\text{V}}$ ), separated in the field using the SPE cartridge methodology, displayed varying concentrations and percentage contributions between the two main study provinces in Argentina.

#### *San Juan*

Dissolved arsenic in waters (surface and tap) collected from the main San Juan study sites (San José de Jáchal region) was largely composed of  $\text{As}^{\text{III}}$ . Surface waters had an  $\text{As}^{\text{III}}$  concentration range of  $4 - 138 \mu\text{g l}^{-1}$  ( $n = 19$ ), contributing 69 – 100 % of the total arsenic (Table 2). The highest  $\text{As}^{\text{III}}$  concentrations in surface waters were found near Angualasto (ANG) (mean: 98; range:  $51 - 138 \mu\text{g l}^{-1}$ ), with little contribution from  $\text{As}^{\text{V}}$ ,  $\text{MA}^{\text{V}}$  or  $\text{DMA}^{\text{V}}$ . This trend was observed in the Río Colola (CO1), with values of  $45 (\text{As}^{\text{III}}) > 3.7 (\text{MA}^{\text{V}}) > 2.4 (\text{As}^{\text{V}}) > 0.03 (\text{DMA}^{\text{V}}) \mu\text{g l}^{-1}$  (Table 2). A similar relative abundance at lower arsenic concentrations was found in the Cuesta del Viento dam and Río Jáchal samples. The freshwater stream at Agua Negra and the Río Huaco had some of the lowest concentrations of arsenic species in the surface waters with mean values for the Río Huaco of  $7.6 \mu\text{g l}^{-1}$  ( $\text{As}^{\text{III}}$ ),  $0.3 \mu\text{g l}^{-1}$  ( $\text{As}^{\text{V}}$ ),  $0.6 \mu\text{g l}^{-1}$  ( $\text{MA}^{\text{V}}$ ) and  $0.2 \mu\text{g l}^{-1}$  ( $\text{DMA}^{\text{V}}$ ). Tap water samples from San Juan city and Niquivil ( $n = 5$ ) showed an 85 % mean contribution of  $\text{As}^{\text{III}}$  (mean: 31; range:  $6 - 90 \mu\text{g l}^{-1}$ ), as highlighted in Table 2.

Tap water samples from Encon exhibited a high concentration of  $\text{As}^{\text{III}}$  (mean: 153; range:  $68 - 201 \mu\text{g l}^{-1}$ ), equating to a 53 % average contribution with the remainder principally composed of  $\text{As}^{\text{V}}$  (25 %) and  $\text{MA}^{\text{V}}$  (22 %). Encon urban well waters contained 80 %  $\text{As}^{\text{III}}$  (mean:  $219 \mu\text{g l}^{-1}$ ) and 8 %  $\text{As}^{\text{V}}$  (mean:  $16 \mu\text{g l}^{-1}$ ). However, the arsenic species composition in the rural well waters from Encon ( $n = 4$ ), consisted of 99 %  $\text{As}^{\text{III}}$  (mean: 54; range:  $23 - 78 \mu\text{g l}^{-1}$ ), with the remaining 1 % made up of the three other species (Table 2). These findings show a substantial increase in  $\text{As}^{\text{III}}$  concentrations in Encon well waters (urban and rural) in comparison to the untreated domestic tap waters.

Low concentrations of organoarsenicals were found in the main San Juan (surface waters) region, with values of  $< 0.02 - 8.4 \mu\text{g l}^{-1}$  for  $\text{MA}^{\text{V}}$  and  $< 0.03 - 0.7 \mu\text{g l}^{-1}$  for  $\text{DMA}^{\text{V}}$  (Table 2). These low concentrations are indicative of low microbial activity, such as algae growth, which has been noted to metabolise arsenic into these organoarsenicals in surface waters during summer months (Smedley and Kinniburgh

2002). The lack of farming activity around the sampling locations also leads us to believe there is no input from agrochemicals by surface run-off. In contrast, the high concentrations of the organoarsenic species  $MA^V$ , in Encon tap supplies (mean: 57; range: 23 – 79  $\mu\text{g l}^{-1}$ ) and urban well water (mean: 26; range: 10 – 45  $\mu\text{g l}^{-1}$ ) suggests possible microbial activity leading to methylation of iAs, which is worthy of follow-up in future studies.

### *La Pampa*

The loess groundwater of EC exhibited a very high proportion of  $As^{III}$ , as was evident in the community of Encon in San Juan Province. Urban well waters in EC had a mean ( $n = 3$ )  $As^{III}$  concentration of 158  $\mu\text{g l}^{-1}$  (range: 46 – 226  $\mu\text{g l}^{-1}$ ), equating to 93 % of the total arsenic. The highest contribution of iAs species in rural well waters was in EC, with  $As^{III}$  accounting for 68 % of the total arsenic (mean: 466; range: 5 – 1332  $\mu\text{g l}^{-1}$ ), compared with 26 % (mean: 132; range: 3 – 592  $\mu\text{g l}^{-1}$ ) for  $As^V$ , as reported in Table 3. Tap waters from EC had mean iAs concentrations of 141  $\mu\text{g l}^{-1}$  (range: 131 – 151  $\mu\text{g l}^{-1}$ ) and 13  $\mu\text{g l}^{-1}$  (range: 2 – 23  $\mu\text{g l}^{-1}$ ) for  $As^{III}$  and  $As^V$ , respectively (Table 3). Urban well waters in LU had a mean  $As^{III}$  concentration of 100  $\mu\text{g l}^{-1}$  (range: 32 – 163  $\mu\text{g l}^{-1}$ ), accounting for 48 % of total arsenic (Table 3). A large proportion of the arsenic recorded in the individual LU urban well waters consisted of  $As^V$  (18 – 60 % of total arsenic), with a mean concentration of 88  $\mu\text{g l}^{-1}$  (42 % of total arsenic), which was not observed in the EC samples. Inorganic arsenic concentrations in the LU rural well waters paralleled those measured in the urban wells, consisting predominantly of  $As^{III}$  (56 %) and  $As^V$  (39 %) at mean concentrations of 130  $\mu\text{g l}^{-1}$  and 109  $\mu\text{g l}^{-1}$ , respectively. Comparison of the arsenic species within the province of La Pampa shows a slight variability between inorganic and organic species.

Organoarsenicals were present throughout the province within a range of 1.2 – 59  $\mu\text{g l}^{-1}$  and  $< 0.03$  – 11.4  $\mu\text{g l}^{-1}$  for  $MA^V$  and  $DMA^V$ , respectively (Table 3). The dominant species was that of  $MA^V$ , with the highest concentrations in the EC rural well waters (mean: 26; range: 1.2 – 57  $\mu\text{g l}^{-1}$ ). This pattern was not found in the LU waters, which saw the highest  $MA^V$  concentration (10 %) in urban well waters (mean: 21; range: 5 – 59  $\mu\text{g l}^{-1}$ ), compared with a 5% mean contribution in rural well waters (mean: 12; range: 6 – 23  $\mu\text{g l}^{-1}$ ) (Table 3). The lowest  $MA^V$  concentrations were found in the domestic tap supplies (mean: 6; range:  $< 0.02$  – 11  $\mu\text{g l}^{-1}$ ) and urban well waters (mean: 6; range: 4 – 8  $\mu\text{g l}^{-1}$ ) in EC.

### *Río Negro*

The control province of Río Negro is characterised by sandy plains of Quaternary fluvial, lacustrine and aeolian origin (Abraham et al. 2009). Mean iAs species concentrations for the surface waters ( $n = 8$ ) were 4.3  $\mu\text{g l}^{-1}$  for  $As^{III}$  (range: 0.1 – 8.6  $\mu\text{g l}^{-1}$ ) and 7.5  $\mu\text{g l}^{-1}$  for  $As^V$  (range: 3.6 – 13.3  $\mu\text{g l}^{-1}$ ) (Table 4). Mean concentrations of  $As^{III}$  and  $As^V$  in the urban well waters ( $n = 2$ ) were 1.0 and 0.7  $\mu\text{g l}^{-1}$ , respectively and for the tap supplies ( $n = 2$ ) 3.4 and 0.1  $\mu\text{g l}^{-1}$ , respectively (Table 4). Detectable levels of organoarsenicals were seen in all water types with the highest concentrations in the surface waters, 3.3  $\mu\text{g l}^{-1}$  ( $MA^V$ ) and 1.2  $\mu\text{g l}^{-1}$  ( $DMA^V$ ).

## **Water Treatment Works**

Two water treatment works in La Pampa, namely Eduardo Castex (EC) and Ingeniero Luiggi (LU), were also investigated. Both treatment plants were built in the 1980s, as a potential remediation method for the high concentrations of arsenic in the domestic drinking water. At both locations the raw water originates from a mixture of underground urban well supplies, which are extracted at various depths (20 – 90 m). Firstly, raw well water undergoes a filtration step, which removes any mud/solid particulates (Fig. 10). The filtered water then enters a two-stage reverse osmosis (RO) process using iron (Fe) oxide. Residual (waste) water is removed from the system at two outlets during the RO phase, and is subsequently pumped back into the underground urban well supply. The addition of sodium carbonate to the system is required to help stabilise the pH (Fig. 10). The final ‘cleaning’ process uses UV radiation and ozone (O<sub>3</sub>) or chlorination to sterilise the water. Constant monitoring of the water is then undertaken to ensure a minimal bacterial presence. The final drinking water is housed in a water tower (approximate capacity 10,000 litres) or in 10 litre individual containers.

Total arsenic concentrations from water samples taken at 8 different stages along the water treatment process in EC and LU (Fig. 10) show a substantial decrease in arsenic concentrations at the outflow. Initial total arsenic concentrations reported from the mixed raw well water sources in EC and LU displayed concentrations of 216 µg l<sup>-1</sup> As and 224 µg l<sup>-1</sup> As, respectively (Table 5). From Stage 5 (outflow after RO) onwards there was a significant reduction in arsenic with the concentrations in the samples from the final drinking water supplies of 0.8 µg l<sup>-1</sup> As and 0.3 µg l<sup>-1</sup> As for EC and LU, respectively (Table 5). These total arsenic concentrations, following treatment of the drinking water are below the WHO limit of 10 µg l<sup>-1</sup> As (WHO 1993). A difference was noted in total arsenic between both water treatment works at Stage 6 (RO + Na<sub>2</sub>CO<sub>3</sub>), with EC reporting 30.1 µg l<sup>-1</sup> As and LU 0.1 µg l<sup>-1</sup> As. This difference in total arsenic concentration may be due to dissimilarity in construction or operation between the two treatment plants. A higher concentration of total Fe was also seen at Stage 6 in the EC water treatment works (387 µg l<sup>-1</sup>) compared to an undetectable level at LU (< 7 µg l<sup>-1</sup>), which may support this theory.

The arsenic speciation studies at both of these treatment works found that the inflow water had a relative abundance of As<sup>III</sup> > As<sup>V</sup> > MA<sup>V</sup> > DMA<sup>V</sup> (Table 6). Treated drinking water from EC (Stage 8) showed the only measurable alteration to this trend with the greatest contribution (0.6 µg l<sup>-1</sup>) coming from As<sup>V</sup>. Due to the effective nature of the water treatment process, speciation analysis was undetectable at most post-treatment stages, with species concentrations reported < 0.12 µg l<sup>-1</sup> for As<sup>III</sup>, < 0.02 µg l<sup>-1</sup> for As<sup>V</sup> and MA<sup>V</sup>, and < 0.03 µg l<sup>-1</sup> for DMA<sup>V</sup> (Table 6).

## Discussion

Total arsenic concentrations reported from San Juan and La Pampa (Argentina) were shown to be elevated well above the control province of Río Negro, the WHO recommended drinking water limit of 10 µg l<sup>-1</sup> As and in some cases above the 100 µg l<sup>-1</sup> As limit set by the FAO for irrigational waters (FAO 1994). Total arsenic concentrations for surface waters and groundwater (San Juan) are in good agreement with previously reported values, namely, 140 – 260 µg l<sup>-1</sup> As (Cáceres et al. 2005; WHO 2001; Williams 2001). Total arsenic concentrations for La Pampa groundwater (median: 164; range: 3 – 1326 µg l<sup>-1</sup> As) are notably lower than those reported by

others, namely, as high as 5300  $\mu\text{g l}^{-1}$  As (median: 150  $\mu\text{g l}^{-1}$  As) (Smedley et al. 2002; WHO 2001).

The elevated total arsenic concentrations in San Juan surface waters (11 – 133  $\mu\text{g l}^{-1}$  As) could be classified from either natural or anthropogenic sources and will be discussed further. The main river system in the north of the province is the Río Blanco, a third or fourth order river (Rawlins et al. 1997), which feeds the subsequent river systems that were sampled, with the exception of the Río Huaco (Fig. 3). The source of the Río Blanco comes from the periphery of the Andes mountain range. The geology of the area is dominated by marine sedimentation from the Carboniferous, which also experienced periods of localised volcanism in the Permian (Limarino et al. 2006). The input from natural processes (leaching/weathering) and anthropogenic activity (base metal and gold mining) in the area may both contribute to the measured arsenic in these river systems (Williams 2001; Rawlins et al. 1997). The semi-arid nature of San Juan would tend to suggest a limited interaction between As-rich mine waste and drainage water. However, Rawlins et al. (1997) reported 150  $\mu\text{g l}^{-1}$  dissolved arsenic in the Río Blanco system, which if used as potable water could provide a regional source of arsenic that could potentially have health implications for the local population. It was noted, by Rawlins et al. (1997) that water samples collected further downstream did display smaller arsenic concentrations, suggesting the possibility of a dilution effect or a higher presence of Fe oxides acting as arsenic binders preventing mobilisation. This trend was also seen in the current study. The total arsenic concentration at the uppermost sampling site (1635 m a.s.l.) along the Río Blanco/Río Jáchal system (ANG1a) was 133  $\mu\text{g l}^{-1}$  As compared with the lowest sampling location (1001 m a.s.l.) along the same river system (RJ6) at 55  $\mu\text{g l}^{-1}$  As (Table 2). These results suggest the effect of downstream arsenic dilution, consistent with increasing distance from mining activity and run-off from the Andes. Low concentrations of Al, Fe and Mn in the surface waters downstream indicates a lack of arsenic binding to metal oxides (Table 2).

The lower concentrations of arsenic (11 – 16  $\mu\text{g l}^{-1}$  As) reported from the Río Huaco (HU) system may be attributed to a distinct difference in the geology of the river basin. The Río Huaco is primarily located within Tertiary continental marine deposits. There is also little evidence to suggest the recent involvement of volcanic or mining activity in the area (Jenchen and Rosenfeld 2002). The Río Huaco is also not as strongly influenced by seasonal climatic effects that are more apparent in the Río Blanco, such as snowmelt from the Andes, as it is a smaller more localised system. This would tend to suggest that the input of arsenic into the Río Huaco from natural and anthropogenic sources is on a much smaller scale to that seen in the Río Blanco and Río Jáchal. High concentrations of boron (3.92  $\text{mg l}^{-1}$ ) and sodium (1020  $\text{mg l}^{-1}$ ) were also found in the Río Jáchal, which have been associated with the rivers high salinity (Adamo and Crews-Meyer 2006). High levels of salinity have been shown to correlate well with high arsenic concentrations (Smedley and Kinniburgh 2002).

Concentrations of arsenic in domestic tap water supplies from the San José de Jáchal region of San Juan ranged from 9 – 100  $\mu\text{g l}^{-1}$  As within a pH range of 7.2 – 7.7 (Table 1). This range in pH is indicative of conditions that enable the mobility of arsenic under both oxidising and reducing environments (Smedley and Kinniburgh 2002). It is thought that in oxidising conditions, the dominant arsenic species in surface waters is that of  $\text{As}^{\text{V}}$ , as shown in Figure 1 (Impellitteri and Scheckel 2006). However, SPE methodology from this study suggests that  $\text{As}^{\text{III}}$  was the prevalent

species at the time of collection in these San Juan samples (relative abundance: 69 – 100 %) (Figs. 11, 12). This is potentially due to a greater influence from reductive processes and also, with a pH lower than 9.2, the predominant species is likely to be the uncharged As<sup>III</sup> species H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> (Fig. 1), aiding desorption of arsenic from metal oxides such as Al, Fe and Mn (Smedley and Kinniburgh 2002). However, redox potentials (Eh) for San Juan have reported ranges of 197 – 230 mV (Rawlins et al. 1997), suggesting the presence of As<sup>V</sup> in the form HAsO<sub>2</sub><sup>2-</sup> (Fig. 1). This suggests that the prevalence of As<sup>III</sup> at the time of collection was generated within the soil-aquifer strata and could essentially be a relic feature of the surface water environment.

Concentrations of total arsenic (159 – 331 µg l<sup>-1</sup> As) in untreated water samples from Encon (southern San Juan) which originate from a different water source to the San José de Jáchal region highlights the potential increase in arsenic concentrations due to variation in physical and geochemical conditions. Encon has a different geology to the north of the province. The community is predominantly set upon Quaternary continental deposits of sand and loess (Lloret and Suvires 2006; DNGM, 1964). The geological composition of the sampling area may lead us to expect similar arsenic concentrations to those found in La Pampa (3 – 1326 µg l<sup>-1</sup> As), due to the environmental development of both regions during the Quaternary age (Smedley et al. 2005; Bundschuh et al. 2004; DNGM, 1964). However, the apparent variation in total arsenic between the two regions may be ascribed to differences in the natural environment. Encon displays a greater expanse/diversity of vegetation in comparison to La Pampa, which may indicate a difference in the geochemistry of the two areas or potentially a greater uptake of arsenic by plants in Encon leading to lower total arsenic concentrations.

Arsenic speciation suggests the presence of the organoarsenical, MA<sup>V</sup>, in both San Juan (< 0.02 – 79 µg l<sup>-1</sup>) and La Pampa (< 0.02 – 59 µg l<sup>-1</sup>), which was measured in up to 97 % of water samples from both San Juan and La Pampa. Organoarsenicals can arise through anthropogenic activity (Cowen et al. 2008; Vaclavikova et al. 2008; McSheehy et al. 2003). The community of Encon is principally an arid semi-desert rural community with local goat farming being the main agricultural activity. Surface and groundwater collected from isolated farm areas have been shown to contain methylated arsenicals, such as MA<sup>V</sup>, due to the use of arsenic-containing herbicides (Bednar et al. 2004; Bednar et al. 2002b) and pesticides (Choong et al. 2007). However, agrochemicals containing high levels of NO<sub>3</sub> and PO<sub>4</sub> in waters have been shown to enhance/suppress MA<sup>V</sup> levels from the SPE methodology utilised in this study by as much as 13 – 21 % (Watts et al. [THIS ISSUE]). Previous studies on the levels of arsenic in waters have mainly reported only inorganic species (As<sup>III</sup> and As<sup>V</sup>), in which As<sup>V</sup> was deduced from the subtraction of As<sup>III</sup> from the total arsenic level (Sigrist and Beldoménico 2004; Smedley et al. 2002; Edwards et al. 1998). This subtraction method does not account for organoarsenicals and may provide apparently elevated concentrations for As<sup>V</sup>. The use of SPE cartridges that have the ability to separate and retain the individual aqueous arsenic species (inorganic and organic) in the field affords an opportunity to detect and measure arsenic in environmental samples.

The concentrations of organoarsenicals (MA<sup>V</sup> and DMA<sup>V</sup>) in both San Juan and La Pampa were greater in groundwater (< 0.02 – 79 µg l<sup>-1</sup>) than surface waters (< 0.02 – 8 µg l<sup>-1</sup>). This suggests that due to the lack of farming activity around surface water sampling locations, little input of organoarsenicals is seen from agrochemical use

(herbicides and pesticides), therefore the main source of the organoarsenicals must be attributed to algae formation. In contrast, high concentrations of organoarsenicals in groundwater from Encon (farming community) in San Juan and La Pampa (rural farmsteads) may have arisen as a result of anthropogenic input from agrochemical use, for example nitrate fertilisers (Tables 2, 3). The presence of phosphate (potentially from herbicides and pesticides) has been shown to substantially suppress arsenic adsorption by soils (Smith et al. 2002). However, arsenic methylation to  $\text{MA}^{\text{V}}$  and  $\text{DMA}^{\text{V}}$  may increase arsenic mobility, as these organoarsenicals are less strongly adsorbed than  $\text{iAs}$ , leading to highly measurable concentrations (Deutsch 1997).

High  $\text{As}^{\text{III}}$  species concentrations were also measured in the groundwater (aquifer) systems within Encon from the community and rural farm well supplies. The difference in  $\text{As}^{\text{III}}$  concentrations between the two water sources may be due to variability in redox conditions at different well depths impacting on the geological influence, which would require further investigation. The community or urban well was built in 1963 and is in continuous use, it is approximately 15 m deep, the rural well however (called the Manantial de Cuyo well), was built in the 1950s and is 300 m deep. It is assumed that both wells are open for much of their length, as no reported screening processes have been undertaken. As there is no significant variation in the pH of both water types, it may be considered that a difference in the sedimentation of the aquifer systems or the residence time of the groundwater as a consequence of well depths, may influence the mobility of the arsenic (Gault et al. 2005b; Polizzotto et al. 2005; Kinniburgh and Kosmus 2002).

Groundwater arsenic concentrations from the province of La Pampa have been reported in the literature to be elevated due to weathering processes/volcanic activity (Smedley et al. 2002). These natural processes have subsequently created a soil strata composed of Quaternary deposits of loess sedimentation (Smedley et al. 2005). The pH conditions within the province (7.0 – 9.9) demonstrate ideal conditions in which arsenic can become mobilised. Elevated concentrations of total arsenic ( $> 1300 \mu\text{g l}^{-1}$ ) have been observed, with the most contribution (7 – 97 %) coming from  $\text{As}^{\text{III}}$  (Table 3 and Fig. 11). This implies reducing conditions in the aquifer; however, with a high probability of mobilisation, the groundwater seems to exhibit both reducing and oxidising characteristics, which is demonstrated by the presence of  $\text{As}^{\text{V}}$  in the region,  $0.09 - 592 \mu\text{g l}^{-1}$  ( $< 1 - 82 \%$ ) (Figs. 11, 12). Typically the highest concentrations of  $\text{As}^{\text{III}}$  were reported from groundwater aquifer systems in Eduardo Castex (EC), with a range of  $5 - 1332 \mu\text{g l}^{-1}$  (Table 3), demonstrating the potential stability of these arsenic species in the environment prior to extraction and use by humans. Since the reporting of data from previous studies in Argentina, it has come to light that  $\text{As}^{\text{III}}$  species in water are unstable in the presence of high concentrations of  $\text{Fe}^{\text{III}}$ , causing oxidation of  $\text{As}^{\text{III}}$  to  $\text{As}^{\text{V}}$  (Gault et al. 2005a; Gong et al. 2002; Le et al. 2000). This process can also occur from the photolytic reduction of nitrate to nitrite, which has been shown to convert up to 50 % of the  $\text{As}^{\text{III}}$  to  $\text{As}^{\text{V}}$  within 3 hours of collection (Hug et al. 2001; Sharpless and Linden 2001). The use of opaque polyethylene bottles for water collection is one method to eliminate the effect of photochemical oxidation by omitting light exposure (Garbarino et al. 2002). This provides a more representative sample, in terms of arsenic species composition, in order to verify the SPE method. Local populations that rely solely on As-rich groundwater supplies exhibit symptoms that parallel those of arsenic exposure, such as skin lesions and pigmentation changes (Choong et al. 2007; Bhattacharya et al. 2006; Hopenhayn-Rich et al. 1998).

The implementation of a water treatment works in two towns in La Pampa has addressed the issue of reducing the arsenic concentrations in raw well water supplies. Treatment of the raw water with a series of RO, UV radiation and ozone/chlorination processes reduces overall arsenic levels by almost 100 %, from the initial concentrations of 216  $\mu\text{g l}^{-1}$  As (EC) and 224  $\mu\text{g l}^{-1}$  As (LU) to 0.8  $\mu\text{g l}^{-1}$  As and 0.3  $\mu\text{g l}^{-1}$  As, respectively (Table 5). Reverse osmosis filters containing Fe oxide reduces the mobility of the arsenic, adhering it to the surface of the solid packed material. The resultant drinking water achieves arsenic concentrations well below the WHO recommended limit of 10  $\mu\text{g l}^{-1}$  As, and predominantly in the less toxic As<sup>V</sup> form.

The main limitation to the use of SPE methodology for the assessment of arsenic species in the field is the effect on the ion exchange efficiency of the cartridges from high matrix components and competing ions in the waters. The presence of fluoride, chloride (25  $\text{mg l}^{-1}$ ) and phosphate (1  $\text{mg l}^{-1}$ ) has been shown to inhibit MA<sup>V</sup> retention on the SAX cartridge, with recoveries of 75, 68 and 79 %, respectively (Watts et al. [THIS ISSUE]). However, enhancements were seen in the subsequent As<sup>V</sup> fraction eluted from the SAX cartridge effluent. Conversely, for sulphate (25  $\text{mg l}^{-1}$ ), enhancement was seen in the MA<sup>V</sup> fraction (113 %) and a reduction in As<sup>V</sup> (79 %), as reported by Watts et al. [THIS ISSUE]. Measurement of water conductivity is one way to address this problem. A ceiling value of 1500  $\mu\text{S cm}^{-1}$  was established at which conductivity remained relatively constant with varying percent differences between total arsenic measurements in filtered/acidified (F/A) water and the sum of arsenic species measured using the SPE method (Watts et al. [THIS ISSUE]). Therefore, in order to overcome high matrix effects, a dilution factor of x2 or higher should be applied to a water sample that exceeded the 1500  $\mu\text{S cm}^{-1}$  limit, using de-ionised water (pH 6.8) immediately prior to speciation through the SPE cartridges. This reduces the potential for saturating the ion-exchange cartridges, as reported in other studies (Bednar et al. 2004; Garbarino et al. 2002).

## Conclusions

Water samples collected from San Juan and La Pampa Provinces in Argentina showed elevated total dissolved arsenic compared to Río Negro (control) and natural background concentration ranges in uncontaminated water of 1 – 10  $\mu\text{g l}^{-1}$  As (Smedley and Kinniburgh 2002; Williams 2001). Surface waters exhibited arsenic concentrations of 11 – 133  $\mu\text{g l}^{-1}$  As in San Juan with tap, rural well and urban well levels in the range 9 – 357  $\mu\text{g l}^{-1}$  As. Arsenic levels in groundwater from La Pampa ranged from 39 – 327  $\mu\text{g l}^{-1}$  As in urban wells; 3 – 1326  $\mu\text{g l}^{-1}$  As in rural wells; and 41 – 747  $\mu\text{g l}^{-1}$  As in domestic untreated tap water supplies. Drinking water concentrations greatly exceed the WHO limit of 10  $\mu\text{g l}^{-1}$  As, recommended as a maximum allowable level in potable waters (WHO 1993). Additionally, many surface water samples were shown to surpass the FAO irrigational limit of 100  $\mu\text{g l}^{-1}$  As (FAO 1994). Not only do both provinces experience higher arsenic concentrations in the waters compared to typical background levels, but the majority of the dissolved arsenic resides as the more toxic inorganic species (percent contributions: San Juan, As<sup>III</sup>: 32 – 100 % and As<sup>V</sup>: < 1 – 35 %; La Pampa As<sup>III</sup>: 7 – 97 % and As<sup>V</sup>: < 1 – 82 %). However, a high presence of organoarsenicals were also found in both provinces. Monomethylarsonic acid (MA<sup>V</sup>) was seen in the range < 0.02 – 79  $\mu\text{g l}^{-1}$  in San Juan and < 0.02 – 59  $\mu\text{g l}^{-1}$  in La Pampa (Tables 2, 3). The presence of organoarsenicals has rarely been reported in the literature due to the limitations in certain analytical

techniques, such as the lack of hydride formation from  $\text{MA}^{\text{V}}$  and  $\text{DMA}^{\text{V}}$  (Sigrist and Beldoménico 2004).

Higher concentrations of  $\text{As}^{\text{III}}$  were apparent in high alkaline and high TDS environments, particularly in groundwater (aquifer) systems (Figs. 11, 12). Concentrations of the individual arsenic species in these waters were generally of the order:



which also represents the order of arsenic species toxicity (Francesconi and Kuehnelt 2004). Individual arsenic species concentrations reported in the literature for La Pampa have reported higher levels of  $\text{As}^{\text{V}}$  (Smedley et al. 2005; Smedley et al. 2002), based on a subtraction method ( $\text{As}^{\text{V}} = \text{Total As} - \text{As}^{\text{III}}$ ). However, based on the high levels of organoarsenicals reported in some samples in this study by SPE methodology, the subtraction method may inadvertently provide a more elevated concentration for  $\text{As}^{\text{V}}$  than is actually the case.

The identification of individual arsenic species provides increased understanding of the likely toxicity of arsenic in the environment. Total arsenic concentrations in San Juan were in good agreement with other literature sources (Cáceres et al. 2005; Williams 2001). However, total arsenic reported in La Pampa showed lower maximum concentrations than other reported cases (Smedley et al. 2002). Smedley et al. (2002) reported a maximum of  $5300 \mu\text{g l}^{-1}$  As in groundwater supplies throughout the province, compared to a maximum of  $1326 \mu\text{g l}^{-1}$  As seen in this study (Table 3). Differences in reported concentrations could be based on the geology of the province, the time of sampling and the different wells visited. This may also explain the difference in arsenic species contribution between the two studies. The Quaternary loess that predominates in La Pampa is not uniformly spread throughout the soil strata. Therefore large variations in arsenic concentrations can be seen at sampling sites only a few metres apart, due to differences in depth and the open-interval of individual wells. However, this study primarily focused on a small sampling radius and did not reflect the same scale as that undertaken by Smedley et al. (2002). Although sampling was localised to the main towns of Eduardo Castex and Ingeniero Luiggi, the study does highlight the need for arsenic mitigation strategies to be employed for the wider community allowing for greater accessibility to clean drinking water sources.

Arsenic exposure from these water sources is highly achievable via numerous direct (drinking) and indirect pathways (crops, meat, washing, cooking). Consequences of arsenic exposure to humans are evident when levels surpass  $50 \mu\text{g l}^{-1}$  As (the current Argentine drinking water limit) (Bhattacharya et al. 2006; Frisbie et al. 2005). Health problems observed in the Argentine population are symptomatic of arsenic exposure (Steinmaus et al. 2006; Tchounwou et al. 2003). The most common manifestation is from skin disorders (lesions, keratosis, hyperpigmentation), but other more chronic conditions have been reported such as cancers (Steinmaus et al. 2006; Bates et al. 2004; Farías et al. 2003; Hopenhayn-Rich et al. 1998). Remediation and mitigation strategies have been adopted in the provinces. The introduction of water treatment works in La Pampa highlighted the significant contribution they provide in relieving the arsenic contamination problem, providing the local population with clean uncontaminated drinking water. Full-scale known remediation methods for arsenic

are not viable options in the more rural areas of the provinces due to economic constraints, therefore cheaper, more sustainable alternatives are needed to lessen the effects of arsenic contamination.

This research consolidates work undertaken by Smedley et al. (2005 and 2002) to highlight the extent of the arsenic contamination problem in Argentina, with particular emphasis on the provinces of San Juan and La Pampa. The SPE method utilised for the determination and identification of arsenic species in water samples in this study provides a safe, simple and robust field-based technique, allowing for greater specificity and accuracy. It allows for a prolonged time period between sampling and analysis due to the stable preservation of the arsenic species on the SPE cartridges. The method also enables a greater flexibility in the transportation of samples, requiring a minimal volume (typically 30 ml) and no addition of chemicals. It provided a method for arsenic species identification, to aid the understanding of arsenic exposure through drinking water and the need for biomonitoring in the regions due to the possible exposure pathways (particularly drinking water), which is being investigated by the authors.

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Tables and Figures

**Table 1** Total arsenic (range) and physical parameters (range) for surface, tap and groundwater collected from San Juan, La Pampa and Río Negro, Argentina

	n	Total As range $\mu\text{g l}^{-1}$ (F/A) <sup>#</sup>	pH	EC* ( $\mu\text{S cm}^{-1}$ )	TDS** (mg l <sup>-1</sup> )
<b>San Juan (SJ)</b>					
Surface waters	23	11 – 133	7.8 – 8.9	1295 – 2506	527 – 1245
Domestic tap supplies	5	9 – 100	7.2 – 7.7	1126 – 1837	922 – > 2000
<b>Encon (EN)</b>					
Community well	5	31 – 357	9.3 – 9.7	972 – 1603	526 – 1346
Rural well	4	25 – 76	9.4 – 9.7	1387 – 1552	690 – 1405
Blended tap supplies	3	159 – 331	9.1 – 9.4	1047 – 1534	997 – 1267
School (treated/untreated)	3	21 – 66	8.0 – 9.6	743 – 1387	561 – 1107
<b>Eduardo Castex (EC)</b>					
Urban wells	40	39 – 290	7.9 – 9.3	399 – > 3999	87 – > 2000
Rural wells	29	33 – 1128	7.4 – 9.9	767 – > 3999	383 – > 2000
Domestic tap supplies	15	41 – 747	7.7 – 8.8	1446 – > 3999	118 – > 2000
WTWs***	21	0.8 – 216	7.0 – 8.6	79 – > 3999	39 – > 2000
<b>Ingeniero Luiggi (LU)</b>					
Urban wells	20	115 – 327	7.4 – 8.7	1015 – > 3999	242 – > 2000
Rural wells	23	3 – 1326	7.5 – 9.0	940 – > 3999	345 – > 2000
WTWs***	9	0.3 – 370	7.4 – 8.7	9 – 2145	4 – 1182
<b>Río Negro (RN)</b>					
Surface waters	40	0.8 – 16.4	6.9 – 9.2	987 – 3149	219 – 1994
Well supplies	6	1.5 – 5.2	7.1 – 8.0	1109 – 2129	1258 – 1853
Domestic tap supplies	31	0.5 – 2.5	7.0 – 8.8	908 – 1574	470 – 1620

<sup>#</sup> F/A: filtered/acidified (1 % v/v HNO<sub>3</sub>)

\* EC: electrical conductivity

\*\* TDS: total dissolved solids

\*\*\* WTWs: water treatment works

**Table 2** Total arsenic and arsenic species concentrations for a selection of sampling sites in the province of San Juan, Argentina

Study site *	Total As $\mu\text{g l}^{-1}$ (F/A)**	Arsenic species concentrations by SPE / $\mu\text{g l}^{-1}$				Sum As species $\mu\text{g l}^{-1}$	Al $\mu\text{g l}^{-1}$	Fe $\mu\text{g l}^{-1}$	Mn $\mu\text{g l}^{-1}$	Mo $\mu\text{g l}^{-1}$	SO <sub>4</sub> mg l <sup>-1</sup>	NO <sub>3</sub> mg l <sup>-1</sup>	PO <sub>4</sub> mg l <sup>-1</sup>
		As <sup>III</sup>	As <sup>V</sup>	MA <sup>V</sup>	DMA <sup>V</sup>								
<b>San Juan (SJ)</b>													
ANG1 (S)	77.9	69.7	14.6	8.4	0.7	93.3	< 0.8	< 7	55.2	8.3	233	2.3	< 1
ANG1a (S)	133	138	< 0.02	< 0.02	n.d.	138	< 0.8	286	< 0.8	4.0	224	1.6	< 1
ANG1b (S)	132	124	n.d.	3.8	n.d.	128	< 0.8	676	< 0.8	4.3	218	1.6	< 1
ANG1c (S)	131	129	n.d.	3.0	< 0.03	132	< 0.8	85	< 0.8	3.9	219	1.6	< 1
ANG1d (S)	116	110	n.d.	2.8	n.d.	113	< 0.8	179	< 0.8	4.2	219	1.5	< 1
ANG4 (S)	46.7	50.8	0.2	1.9	0.4	53.4	< 0.8	559	< 0.8	3.1	203	0.9	< 1
ANG5 (S)	78.7	62.7	22.1	6.0	0.1	90.9	< 0.8	< 7	55.4	3.9	244	2.3	< 1
CO1 (S)	52.0	45.2	2.4	3.7	< 0.03	51.3	< 0.8	< 7	402	14.0	1091	2.1	< 1
CU1 (S)	77.5	92.9	6.7	1.3	0.12	101	1302	2064	65.3	2.3	303	1.8	< 1
RJ1 (S)	116	51.8	14.8	2.5	n.d.	69.3	< 0.8	< 7	< 0.8	118	166	1.1	< 1
RJ2 (S)	75.7	86.0	2.0	2.2	< 0.03	90.2	< 0.8	< 7	3.4	4.4	270	1.6	< 1
RJ3 (S)	73.9	85.0	0.9	3.3	n.d.	89.2	< 0.8	< 7	1.0	4.2	307	1.7	< 1
RJ4 (S)	73.8	86.2	1.7	2.6	0.1	90.7	< 0.8	< 7	22.1	4.4	292	1.8	< 1
RJ5 (S)	74.1	60.4	18.8	4.8	0.1	84.1	< 0.8	< 7	8.7	4.4	300	1.6	< 1
RJ6 (S)	54.5	59.2	1.4	1.2	0.1	61.9	< 0.8	< 7	26.3	4.1	395	2.6	< 1
AN1a (S)	23.9	20.1	2.3	1.2	0.1	23.7	< 0.8	< 7	< 0.8	3.3	475	10	< 1
AN1b (S)	23.1	11.1	0.3	0.5	n.d.	12.0	< 0.8	< 7	< 0.8	3.1	475	10	< 1
HU2a (S)	11.6	4.2	0.3	0.8	0.1	5.4	8.7	4	602	8.3	380	6.1	< 1
HU2b (S)	10.6	10.9	0.2	0.3	0.2	11.6	8.3	2	541	7.9	380	6.1	< 1
NQ1 (T)	17.0	13.9	0.9	1.7	0.13	16.6	< 0.8	422	4.0	4.5	21.3	1.6	< 1
NQ2 (T)	9.2	5.8	1.8	1.6	< 0.03	9.3	< 0.8	312	5.2	23.5	23.7	1.8	< 1
NQ3 (T)	21.3	18.6	0.8	1.1	0.06	20.5	1.2	335	12.4	26.3	15.4	0.9	< 1
SJ1 (T)	43.3	28.9	0.7	2.3	0.04	31.9	< 0.8	189	13.2	12.1	33.3	2.2	< 1
SJ2 (T)	99.8	89.8	1.1	1.9	< 0.03	92.8	0.9	263	1.4	9.1	29.9	1.2	< 1
<b>Encon (EN)</b>													
EN1 (U)	31.2	25.3	6.1	9.5	< 0.03	40.9	18.7	< 7	1.8	18.4	162	0.1	< 1
EN2 (U)	324	253	38.2	32.6	0.09	323	< 0.8	104	15.0	8.8	209	0.1	< 1
EN3 (U)	357	346	8.4	45.1	n.d.	399	< 0.8	387	1.2	20.8	211	0.8	< 1
EN4 (U)	205	204	13.6	12.3	< 0.03	230	< 0.8	798	1.4	15.7	114	1.3	< 1
EN5 (U)	353	268	14.5	32.5	n.d.	315	< 0.8	947	< 0.8	20.7	213	1.1	< 1
EN6 (R)	65.6	46.3	0.04	0.1	< 0.03	46.5	< 0.8	< 7	2.1	6.3	113	32	< 1
EN7 (R)	76.0	78.2	0.17	0.6	0.2	79.2	< 0.8	799	2.7	8.7	221	35	< 1
EN8 (R)	24.6	22.7	0.09	0.1	0.05	22.9	< 0.8	51	5.0	8.7	216	30	< 1
EN9 (R)	69.4	70.4	0.14	0.1	0.04	70.7	< 0.8	351	0.9	8.5	112	27	< 1
EN10 (T)	270	189	70.1	22.8	0.07	282	< 0.8	397	3.1	8.2	118	6.5	< 1
EN11 (T)	331	201	46.1	79.2	< 0.03	327	10.5	79	4.8	21.1	201	4.9	< 1
EN12 (T)	159	68.3	75.5	70.2	< 0.03	214	8.5	39	4.0	20.1	154	1.8	< 1

(R) = rural well; (S) = surface water; (T) = domestic tap supply; (U) = urban well

SPE = solid phase extraction; MA<sup>V</sup> = monomethylarsonic acid; DMA<sup>V</sup> = dimethylarsinic acid

\* Refer to Figures 3 and 4

\*\* F/A = filtered/acidified (1 % v/v HNO<sub>3</sub>)

(Sample codes refer to study sites)

**Table 3** Total arsenic and arsenic species concentrations for a selection of sampling sites in the province of La Pampa, Argentina

Study site *	Total As $\mu\text{g l}^{-1}$ (F/A)**	Arsenic species concentrations by SPE / $\mu\text{g l}^{-1}$				Sum As species $\mu\text{g l}^{-1}$	Al $\mu\text{g l}^{-1}$	Fe $\mu\text{g l}^{-1}$	Mn $\mu\text{g l}^{-1}$	Mo $\mu\text{g l}^{-1}$	SO <sub>4</sub> mg l <sup>-1</sup>	NO <sub>3</sub> mg l <sup>-1</sup>	PO <sub>4</sub> mg l <sup>-1</sup>
		As <sup>III</sup>	As <sup>V</sup>	MA <sup>V</sup>	DMA <sup>V</sup>								
<b>Eduardo Castex (EC)</b>													
EC6 (U)	209	202	0.09	6.1	0.1	208	1.2	< 7	n.d.	148	760	9.2	< 1
EC24 (U)	290	226	2.2	7.8	0.4	236	< 0.8	< 7	n.d.	98.8	598	10	2.1
EC33 (U)	61.2	46.3	2.2	4.1	0.4	53.0	< 0.8	< 7	n.d.	113	564	7.5	1.1
EC41 (R)	1117	547	37.2	15.6	0.8	601	< 0.8	< 7	< 0.8	1037	901	82	< 1
EC42 (R)	1063	951	n.d.	43.6	< 0.03	994	n.d.	544	n.d.	46.1	46.5	52	< 1
EC44 (R)	1128	1332	11.8	42.1	0.3	1387	< 0.8	< 7	< 0.8	697	4.5	81	< 1
EC45 (R)	476	251	114	3.8	11.4	380	< 0.8	2614	92	22.0	52.2	75	1.3
EC47 (R)	546	370	16.5	45.3	n.d.	432	3.8	2678	93	30.8	66.8	55	2.3
EC50 (R)	639	277	359	18.1	< 0.03	654	n.d.	223	n.d.	95.1	171	159	< 1
EC65 (R)	68.6	4.7	51.8	12.0	0.1	68.7	3.6	11	n.d.	15.3	23.3	8.2	< 1
EC66 (R)	86.5	46.0	3.2	1.2	0.1	50.5	< 0.8	34	2.2	22.6	1879	87	< 1
EC68 (R)	1125	416	592	56.5	0.1	1065	6.9	< 7	< 0.8	205	147	57	< 1
EC81 (T)	92.9	131	23.2	< 0.02	0.04	154	n.d.	623	n.d.	8.2	159	121	< 1
EC84 (T)	150	151	2.4	11.3	< 0.03	165	1.3	59	n.d.	13.3	270	53	< 1
<b>Ingeniero Luiggi (LU)</b>													
LU1 (U)	149	32.3	98.5	32.0	0.2	163	4.5	121	n.d.	5.8	369	13	< 1
LU2 (U)	115	78.9	32.9	4.5	0.1	116	< 0.8	954	n.d.	13.7	470	345	< 1
LU5 (U)	293	163	120	12.3	0.1	295	1.4	< 7	n.d.	6.0	426	12	< 1
LU9 (U)	293	156	54.9	12.4	0.1	223	< 0.8	954	n.d.	13.7	645	119	< 1
LU10 (U)	255	136	106	12.1	0.2	255	< 0.8	606	n.d.	7.5	380	20	1.2
LU13 (U)	156	38.0	93.8	30.4	0.2	162	1.3	984	36.0	3.5	57.7	2.9	< 1
LU14 (U)	224	127	98.1	15.9	0.3	241	< 0.8	702	n.d.	6.3	264	76	1.1
LU17 (U)	305	92.6	150	59.1	0.2	302	< 0.8	634	2.1	3.3	55.4	0.6	< 1
LU19 (U)	167	131	29.7	6.5	0.3	167	< 0.8	819	n.d.	9.3	885	20	< 1
LU20 (U)	182	42.9	97.0	28.8	0.2	169	< 0.8	< 7	1.4	3.1	86.2	5.3	< 1
LU24 (R)	133	101	29.7	5.7	1.2	137	< 0.8	297	13.3	12.2	114	22	< 1
LU25 (R)	217	130	68.2	8.6	0.05	207	1.2	1041	23.9	13.5	3.6	39	< 1
LU29 (R)	208	138	65.6	8.1	0.4	212	< 0.8	1041	23.1	13.5	3.0	38	< 1
LU34 (R)	269	37.6	277	23.1	0.1	338	1.4	634	2.7	3.3	52.6	46	< 1
LU38 (R)	276	242	105	13.6	0.04	360	n.d.	977	n.d.	8.0	384	15	< 1

(R) = rural well; (T) = domestic tap supply; (U) = urban well

SPE = solid phase extraction; MA<sup>V</sup> = monomethylarsonic acid; DMA<sup>V</sup> = dimethylarsinic acid

\* Refer to Figure 5

\*\* F/A = filtered/acidified (1 % v/v HNO<sub>3</sub>)

(Sample codes refer to study sites)

**Table 4** Total arsenic and arsenic species concentrations for a selection of sampling sites in the province of Río Negro, Argentina

Study site *	Total As $\mu\text{g l}^{-1}$ (F/A) **	Arsenic species concentrations by SPE / $\mu\text{g l}^{-1}$				Sum As species $\mu\text{g l}^{-1}$	Al $\mu\text{g l}^{-1}$	Fe $\mu\text{g l}^{-1}$	Mn $\mu\text{g l}^{-1}$	Mo $\mu\text{g l}^{-1}$	SO <sub>4</sub> mg l <sup>-1</sup>	NO <sub>3</sub> mg l <sup>-1</sup>	PO <sub>4</sub> mg l <sup>-1</sup>
		As <sup>III</sup>	As <sup>V</sup>	MA <sup>V</sup>	DMA <sup>V</sup>								
<b>Río Negro (RN)</b>													
RC1 (S)	5.7	0.1	3.9	0.8	1.1	5.9	10.1	<7	1.4	3.7	18.4	<0.2	<1
RC2 (S)	11.7	5.2	4.5	0.5	0.6	10.8	4.8	<7	0.4	3.6	19.0	<0.2	<1
RC3 (S)	13.1	8.6	7.2	1.2	1.2	18.1	193	<7	1.8	3.6	18.6	26	<1
RC4 (S)	8.5	n.d.	6.6	1.6	1.2	9.3	<0.8	12	0.4	2.7	15.8	<0.2	<1
RC5 (S)	16.4	n.d.	13.0	3.3	1.0	17.2	n.d.	10	24.0	310	19.2	0.8	<1
RN1 (S)	14.2	n.d.	13.3	3.0	1.2	17.4	27.8	10	1.4	2.8	19.8	3.1	<1
RN2 (S)	13.7	3.2	7.8	1.8	1.1	13.9	<0.8	<7	472	7.0	18.3	2.1	<1
RN3 (S)	6.3	n.d.	3.6	0.8	1.0	5.5	<.08	<7	246	6.7	20.6	<0.2	<1
GR1 (U)	1.3	0.6	0.5	0.2	n.d.	1.3	13.2	3	4.2	3.2	14.6	0.9	<1
GR2 (U)	2.5	1.4	0.9	0.1	0.1	2.4	9.8	4	4.0	1.1	26.1	1.4	<1
GR3 (T)	3.2	2.8	0.1	n.d.	0.6	3.5	<0.8	6	6.6	1.3	18.9	<0.2	<1
GR4 (T)	4.4	3.9	n.d.	0.03	0.1	4.0	1.4	2	2.0	2.2	25.3	<0.2	<1

(S) = surface water; (T) = domestic tap supply; (U) = urban well

SPE = solid phase extraction; MA<sup>V</sup> = monomethylarsonic acid; DMA<sup>V</sup> = dimethylarsinic acid

\* Refer to Figure 6

\*\* F/A = filtered/acidified (1 % v/v HNO<sub>3</sub>)

(Sample codes refer to study sites)

**Table 5** Total arsenic concentrations throughout the treatment stages of two reverse osmosis water treatment works (WTWs), La Pampa, Argentina

Treatment stage <sup>#</sup>	Description of treatment	n	Arsenic concentration ( $\mu\text{g l}^{-1}$ )	
			EC* WTW	LU** WTW
1	Mixed well water	1	216	224
2	Pre-treated water	1	n.s.	5.8
3	Inflow before RO	1	72.2	213
4	Residual outflow water	1	76.4	370
5	Outflow after RO	1	0.8	< 0.1
6	RO + Na <sub>2</sub> CO <sub>3</sub>	1	30.1	0.1
7	Water tower	1	13.1	n.s.
8	Drinking water	1	0.8	0.3

n.s. not sampled

<sup>#</sup> Treatment stages relate to WTW schematic in Figure 10

\* EC: Eduardo Castex

\*\* LU: Ingeniero Luiggi

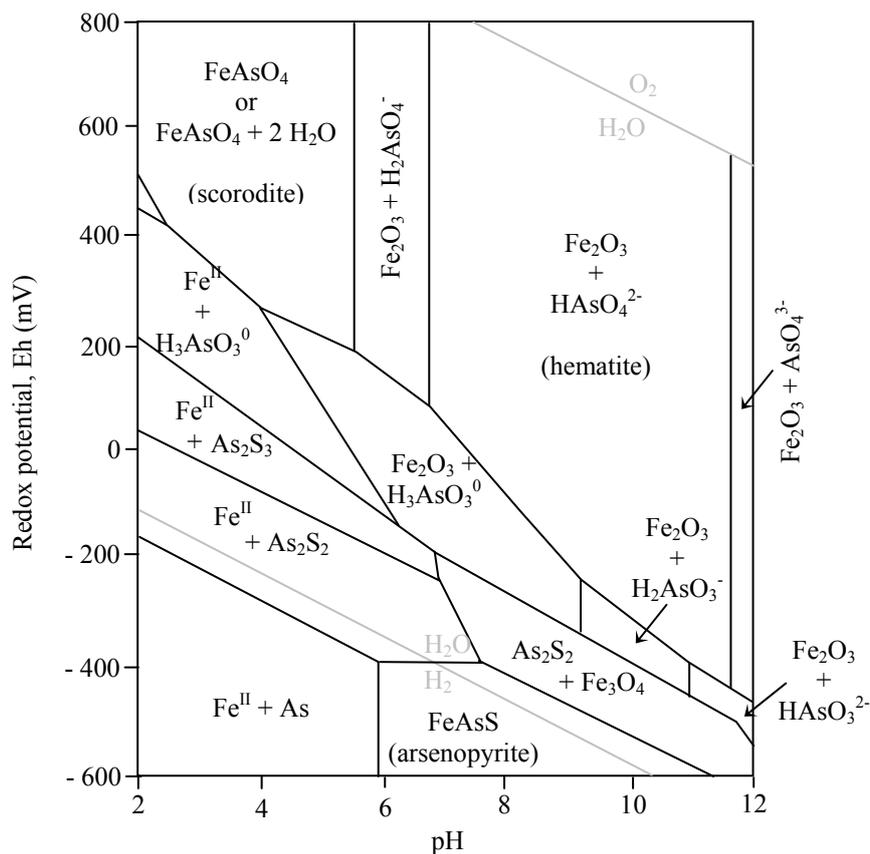
**Table 6** Arsenic species concentrations determined by SPE throughout the treatment stages of two reverse osmosis water treatment works (WTWs), La Pampa, Argentina

Treatment stage <sup>#</sup>	Description	Arsenic species concentrations by SPE / $\mu\text{g l}^{-1}$				Sum As species $\mu\text{g l}^{-1}$	Al $\mu\text{g l}^{-1}$	Fe $\mu\text{g l}^{-1}$	Mn $\mu\text{g l}^{-1}$	Mo $\mu\text{g l}^{-1}$	SO <sub>4</sub> $\text{mg l}^{-1}$	NO <sub>3</sub> $\text{mg l}^{-1}$	PO <sub>4</sub> $\text{mg l}^{-1}$
		As <sup>III</sup>	As <sup>V</sup>	MA <sup>V</sup>	DMA <sup>V</sup>								
<b>EC* WTW</b>													
3	Inflow before RO	73.1	4.1	2.1	0.3	79.6	13.6	< 7	2	4.5	953	66	< 1
5	Outflow after RO	0.1	0.4	0.2	< 0.03	0.7	3.3	< 7	< 0.8	0.9	3.3	5.2	< 1
8	Drinking water	0.1	0.6	0.2	< 0.03	0.9	2.9	< 7	< 0.8	0.7	7.6	6.3	< 1
<b>LU** WTW</b>													
1	Mixed well water	196	2.8	6.0	1.7	207	6.7	1	< 0.8	0.1	< 0.5	3.7	< 1
2	Pre-treated water	2.2	0.7	1.2	0.2	4.3	< 0.8	< 7	7	65.8	273	24	< 1
5	Outflow after RO	< 0.12	< 0.02	0.02	< 0.03	0.02	34.1	18	1	< 0.04	< 0.5	3.1	< 1
6	RO + Na <sub>2</sub> CO <sub>3</sub>	< 0.12	0.02	< 0.02	< 0.03	0.02	< 0.8	< 7	< 0.8	< 0.04	< 0.5	3.4	< 1

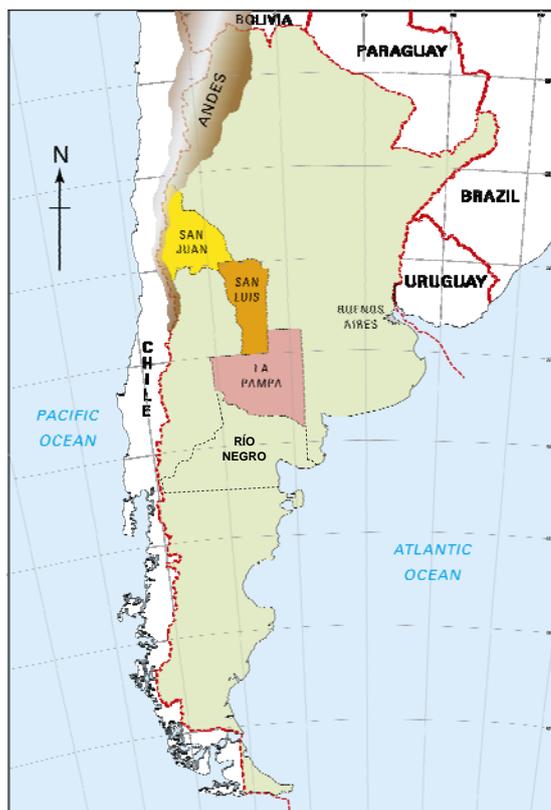
<sup>#</sup> Treatment stages relate to WTW schematic in Figure 10

\* EC: Eduardo Castex

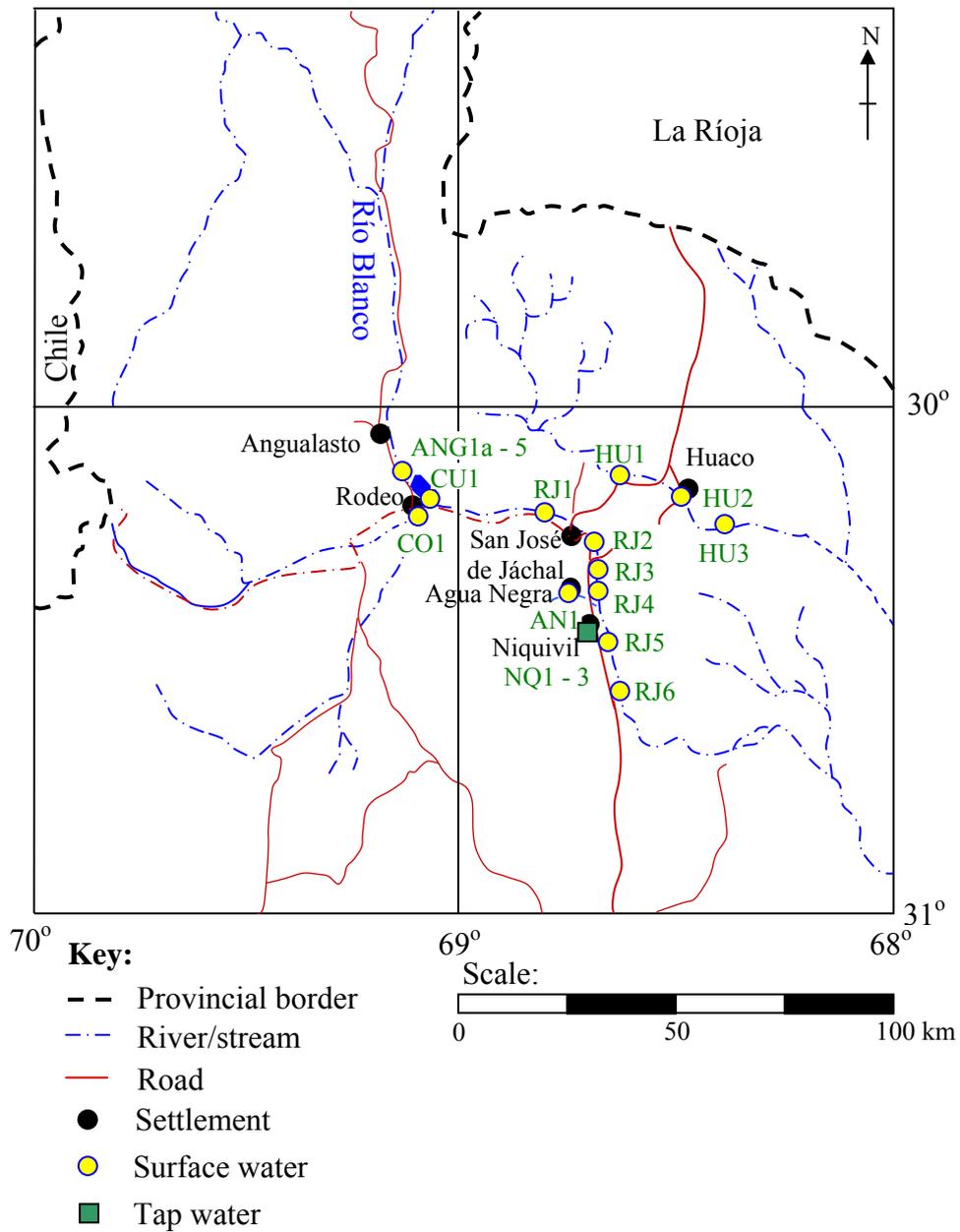
\*\* LU: Ingeniero Luiggi



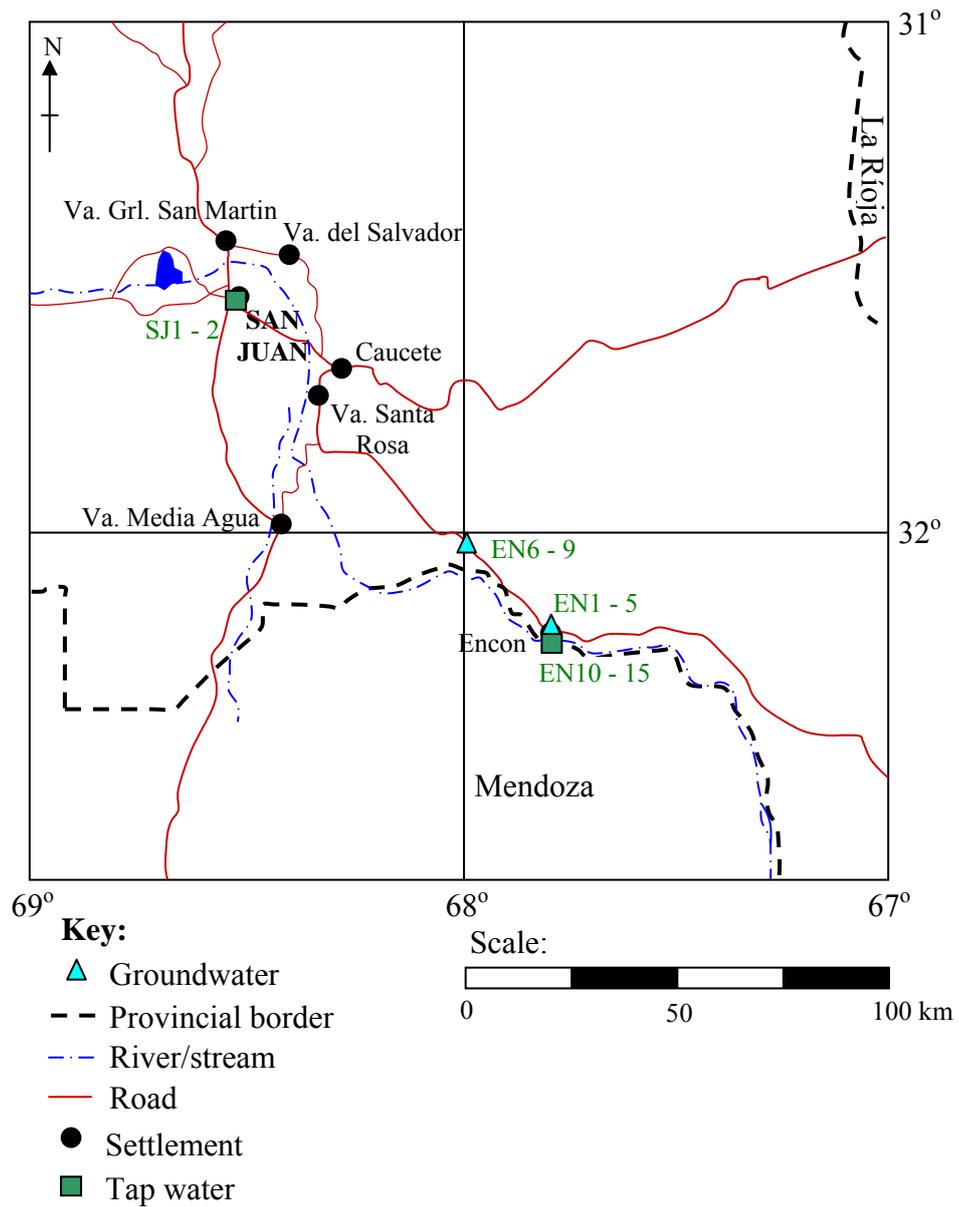
**Fig. 1** Eh-pH diagram for aqueous arsenic species in the system As-Fe-O-H-S in water at 25°C, 1 bar pressure with total arsenic  $10^{-6} \text{ mol l}^{-1}$  (Daus et al. 2002)



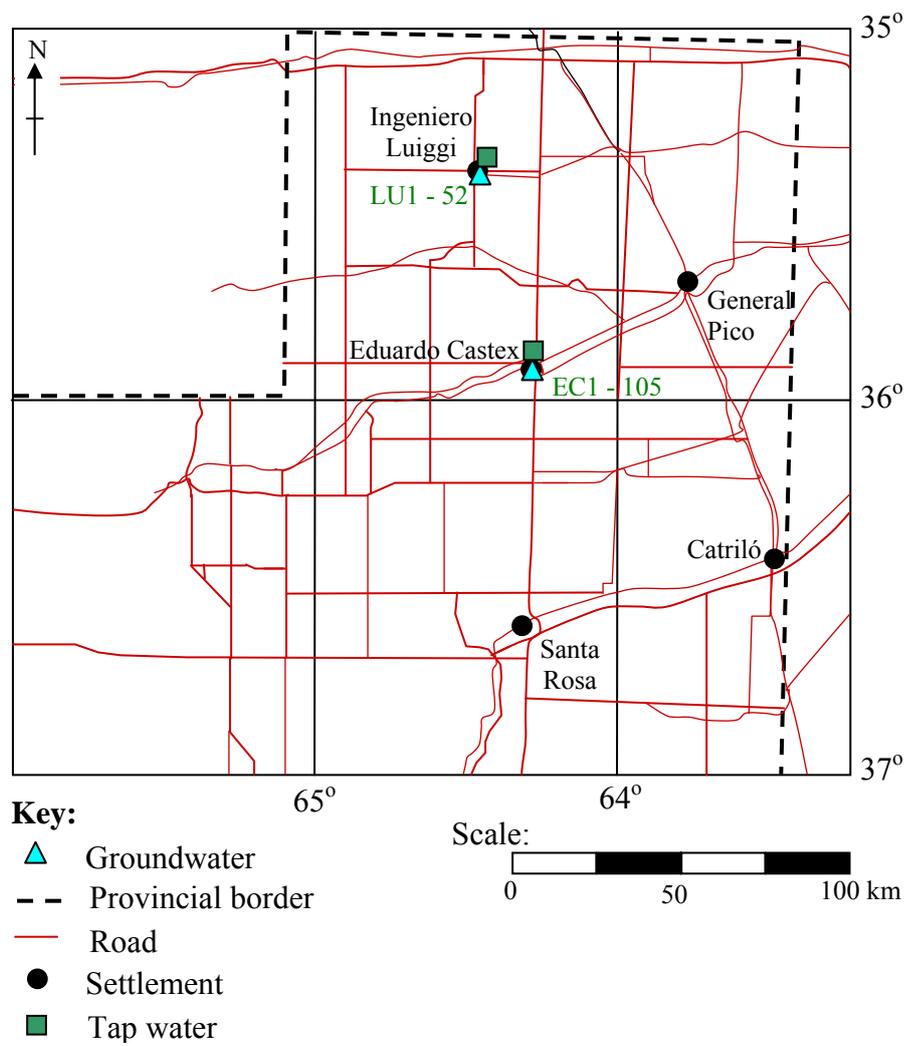
**Fig. 2** Study sites of La Pampa, San Juan and Río Negro provinces, located in Argentina (prepared courtesy of Paul Lappage, British Geological Survey, 2008)



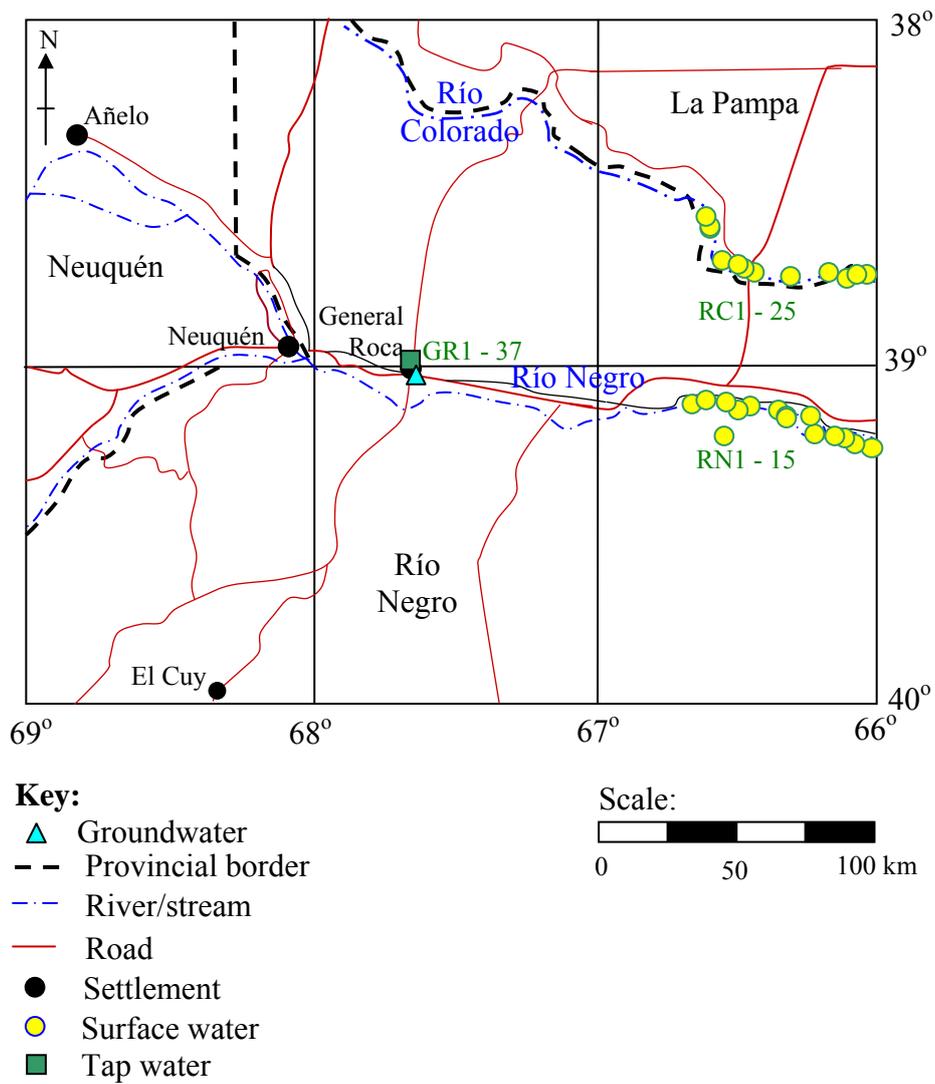
**Fig. 3** Map of sampling locations in northern San Juan Province, Argentina (Sample codes refer to study sites)



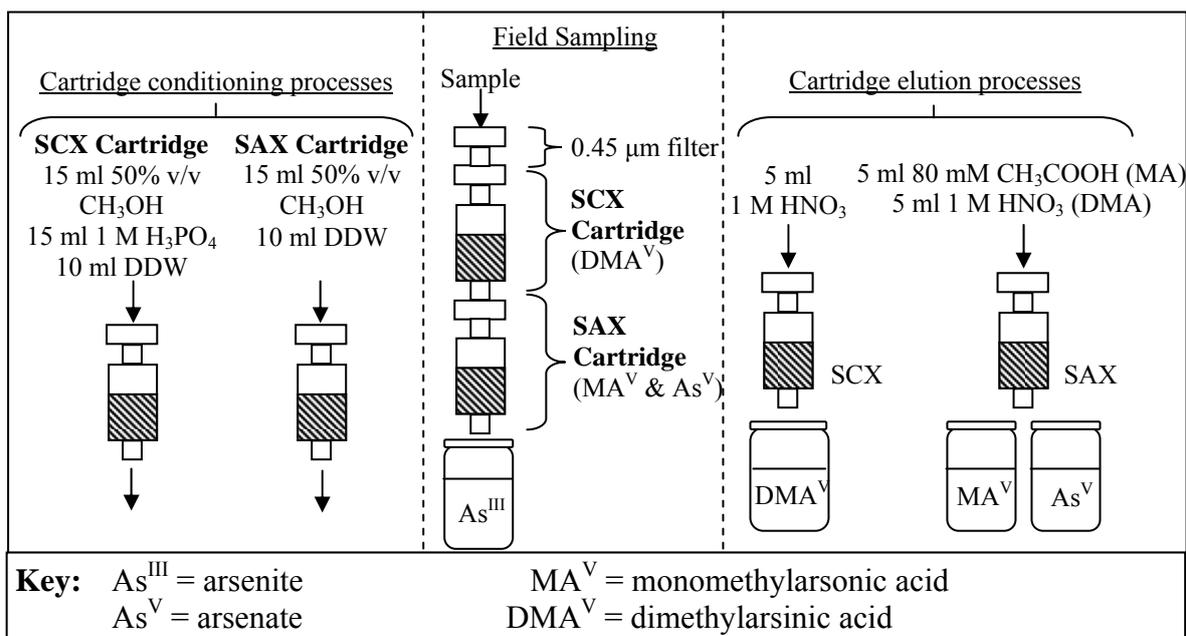
**Fig. 4** Map of sampling locations in southern San Juan Province, Argentina (Sample codes refer to study sites)



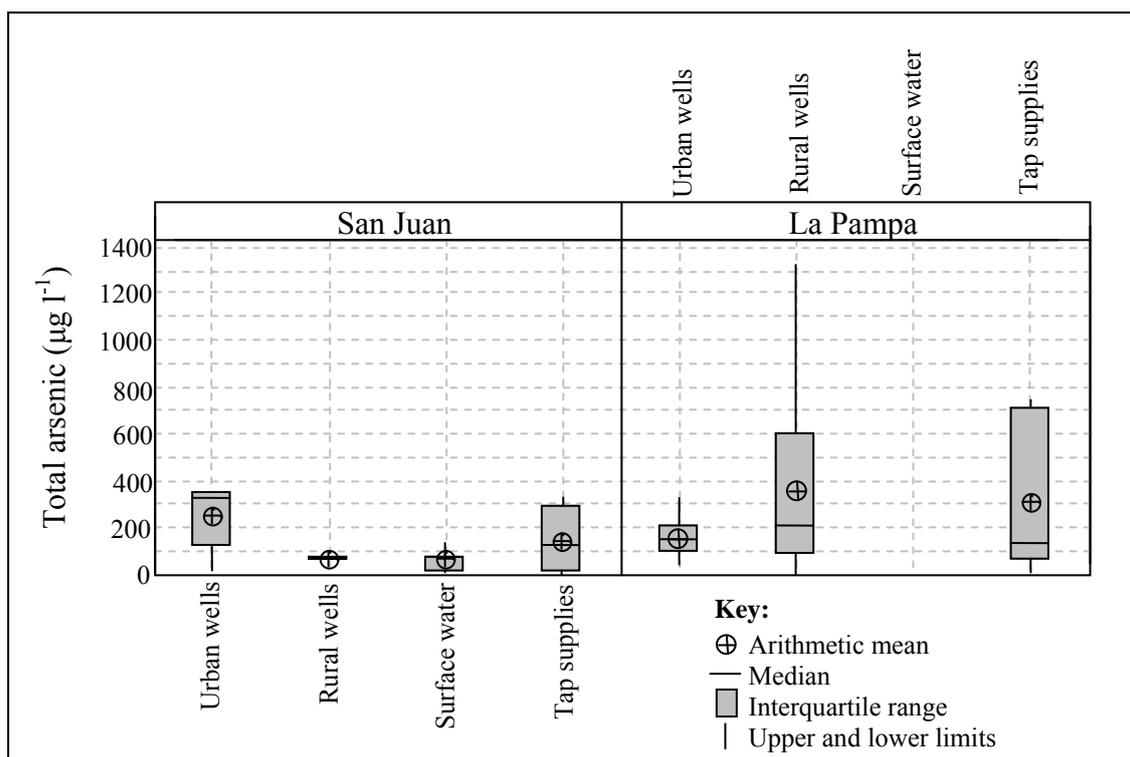
**Fig. 5** Map of sampling locations in north-east La Pampa Province, Argentina (Sample codes refer to study sites)



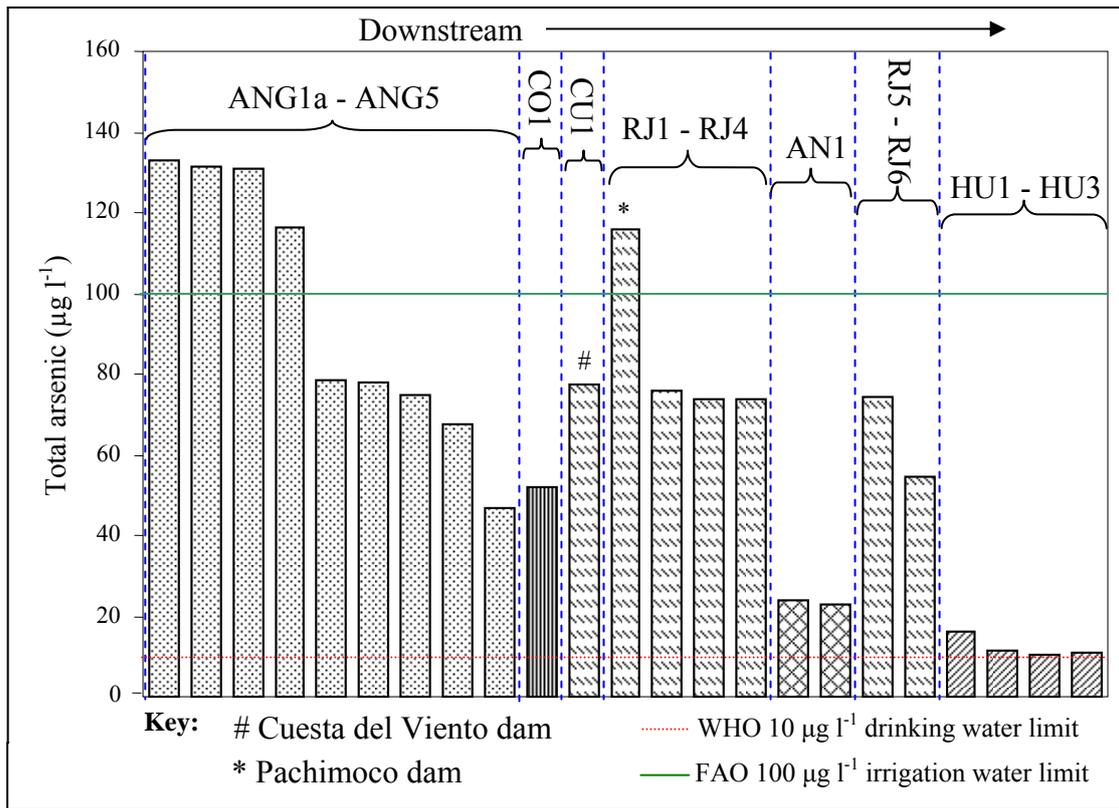
**Fig. 6** Map of sampling locations in Río Negro Province (control), Argentina (Sample codes refer to study sites)



**Fig. 7** Field-based arsenic speciation methodology (preservation and separation)

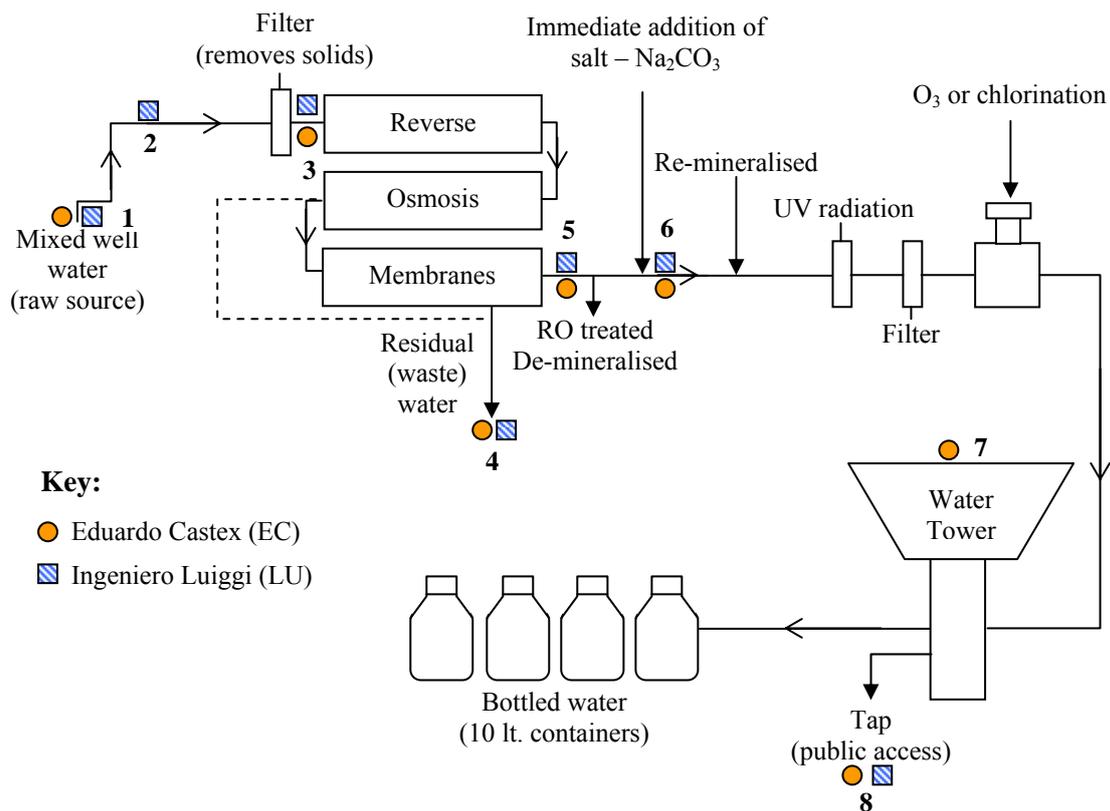


**Fig. 8** Total arsenic concentrations in waters from San Juan and La Pampa, Argentina (no surface waters in La Pampa)

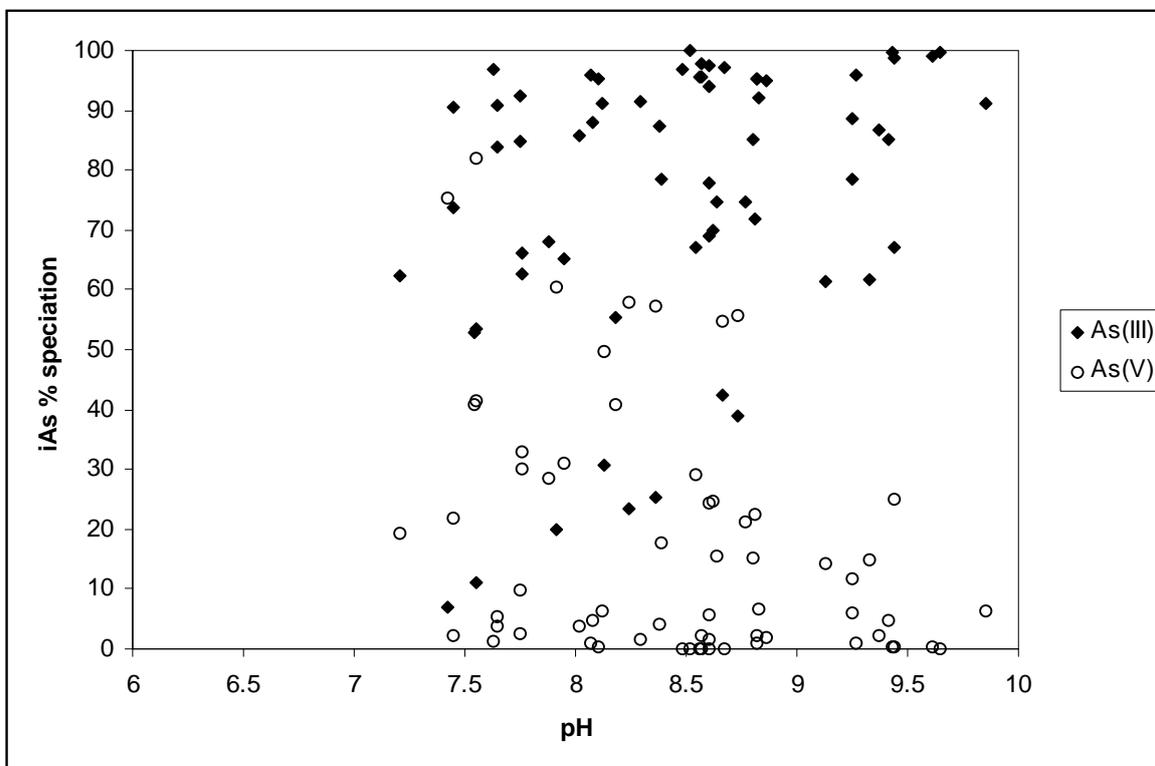


**Fig. 9** Total arsenic concentrations reported downstream from the surface waters in San Juan, Argentina

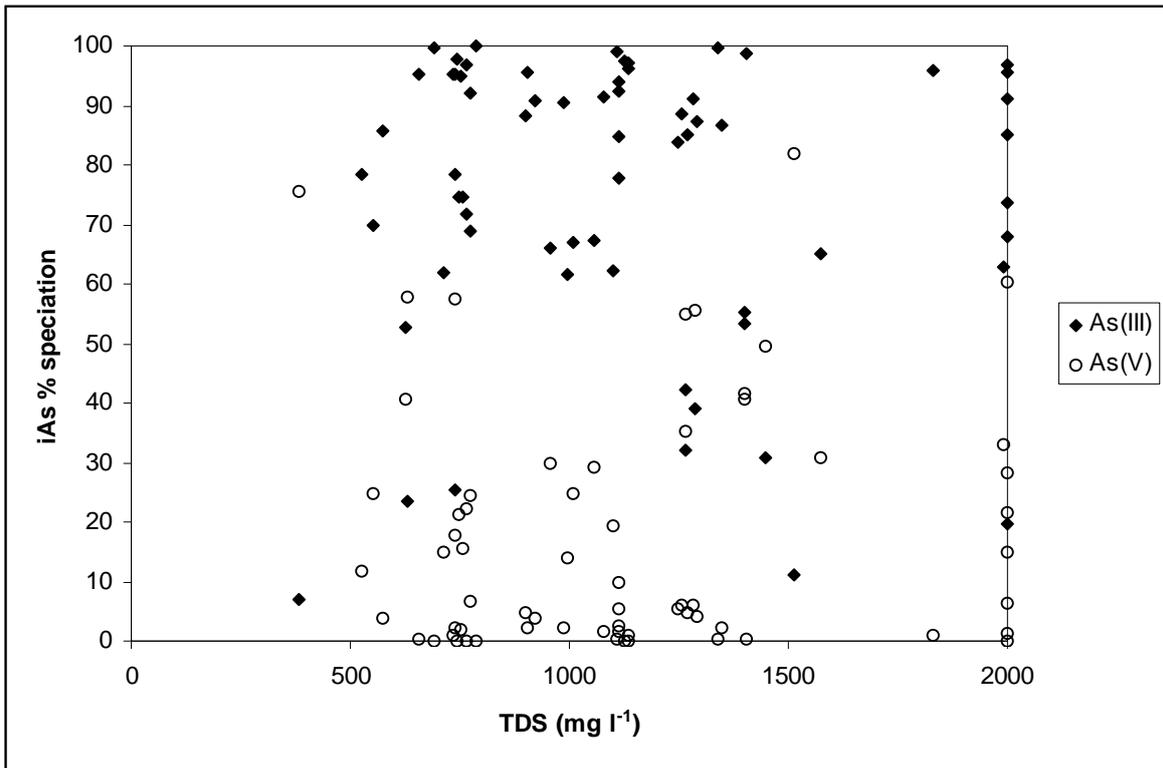
Río Blanco (ANG1a – ANG5)  ; Río Colola (CO1)  ; Río Jáchal (CU1, RJ1 - RJ6)  ; Agua Negra (AN1)  ; Río Huaco (HU1 – HU3) 



**Fig. 10** Schematic of the water treatment works process in EC and LU, La Pampa, Argentina



**Fig. 11** Correlation between inorganic arsenic (iAs) % speciation and the pH of the waters for La Pampa and San Juan



**Fig. 12** Correlation between inorganic arsenic (iAs) % speciation and the TDS levels of the waters for La Pampa and San Juan