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Geochemistry of As-, F- and B-bearing waters in and around San Antonio de los Cobres, Argentina, and implications for drinking and irrigation water quality

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Abstract

Spring, stream and tap waters from in and around San Antonio de los Cobres, Salta, Argentina, were sampled to characterize their geochemical signatures, and to determine whether they pose a threat to human health and crops. The spring waters are typical of geothermal areas world-wide, in that they are Na-Cl waters with high concentrations of As_{tot}, As(III), Li, B, HCO₃, F and SiO₂ (up to 9.49, 8.92, 13.1, 56.6, 1250, 7.30 and 57.2 mg L⁻¹, respectively), and result from mixing of deep Na-Cl brines and meteoric HCO₃-rich waters. Springs close to the town of San Antonio have higher concentrations of all elements, and are generally cooler, than springs in the Baños de Agua Caliente. Spring water chemistry is a result of mixing of deep Na-Cl brines and meteoric HCO₃ waters. Stream waters are also Na-Cl type, and receive large inputs of all elements from the springs near San Antonio, but concentrations decrease downstream through the town of San Antonio due to mineral precipitation. The spring that is used as a drinking water source, and other springs in the area, have As, F and B concentrations in excess of WHO and Argentinian drinking water guidelines. Evaluation of the waters for irrigation purposes suggests that their high salinities and B concentrations may adversely affect crops. The waters may be improved for drinking and irrigation by dilution with cleaner meteoric waters, mineral

precipitation or by use of commercial filters. Such recommendations could also be followed by other settlements that draw drinking and irrigation waters from geothermal sources.

Keywords: water, San Antonio de los Cobres, Argentina, geothermal, arsenic, boron, fluoride, environmental analysis, wáter quality

Introduction

In volcanic areas, drinking water sources often have inputs from geothermal activity related to volcanic and/or hydrothermal processes (Hedenquist and Lowenstern, 1994). These waters can contain high concentrations of As that arises from dissolution of As gas or As-bearing minerals in magmatic and hydrothermal waters and subsequent mixing of these waters with meteoric waters (Ellis and Mahon, 1977; Welch et al., 1988; Webster and Nordstrom, 2003). In these waters, As generally occurs either as As(III) or As(V), depending on pH, redox potential and the availability of As(III)-oxidising bacteria (Langner et al., 2001; Webster and Nordstrom, 2003). Other elements that are concentrated in geothermal brines and related meteoric waters, such as B and F, may also pose a threat to human health should they be ingested (Webster, 1999; Katsoyiannis et al., 2007).

San Antonio de los Cobres (24°13'32"S, 66°19'9"W) is a town of 5000 inhabitants (Bennett, 1947) who are mostly indigenous. It lies in the northwest of Argentina, in the arid Puna region of the middle Andes, at an altitude of 3775 m (Concha et al., 1998; Fig. 1), lying SE of the Tocomar geothermal region and 5486 m Tuzgle volcano (Sainato and Pomposiello, 1997). The town is underlain by Quaternary sediments, and the surrounding area, by Precambrian to Palaeozoic high-grade metamorphic rocks, Ordovician orthogneiss and granitoids and Cenozoic volcanics (Reutter et al., 1994; Blasco et al., 1996). Temperature varies from about -26°C in July to +30°C in December. Annual precipitation in the Puna region averages 100 mm per annum (Argentinean National Meteorological Service; www.meteofa.mil.ar), falling to less than 5 mm during the dry winter season (May-October). The Tuzgle-Tocomar area has been evaluated as having a capacity for < 0.1 MWt of geothermal energy (Pesce, 2005).

Previous studies on the San Antonio area have shown that the waters are highly enriched in As. Thermal springs in the area are reported to contain up to 10,000 µg L⁻¹ As, stream waters up to 1360 µg L⁻¹ As and drinking waters, between 200 and 500 µg L⁻¹ As (De Sastre et al., 1992; Vahter et al., 1995;

Concha et al., 1998, 2006, 2010; MRA-UGAN, 2005). The As is thought to be of geogenic (geothermal) origin, since there are no reported industrial sources in the area. Recent studies have been carried out to evaluate the factors influencing the metabolism and toxic effects of drinking water As (Vahter et al., 1995; Concha et al., 2006) and the concentrations of As in breast milk in San Antonio (Concha et al., 1998). Vahter et al. (1995) reported elevated concentrations of As in drinking water ($179\text{-}219\ \mu\text{g L}^{-1}$), soup (average $336\ \mu\text{g kg}^{-1}$), polenta ($58\ \mu\text{g kg}^{-1}$), blood ($2.7\text{-}18\ \mu\text{g L}^{-1}$) and urine ($109\text{-}405\ \mu\text{g L}^{-1}$). These authors also found relatively high dimethylarsinic acid (DMA; the more readily excreted and less toxic metabolite of As) and low inorganic As in the urine samples compared to women with lower drinking water As exposure in three other Argentinian villages, and suggested that this was due to efficient methylation of inorganic As to DMA, as a result of favorable genetic factors. Concha et al. (1998) also reported high blood and urine As (10 and $320\ \mu\text{g L}^{-1}$, respectively), and elevated concentrations in breast milk (range $0.83\text{-}7.6\ \mu\text{g kg}^{-1}$). Two measurements were made of As in urine of nursing babies; these were both low (17 and $47\ \mu\text{g L}^{-1}$) and were attributed to the breast feeding mothers not secreting inorganic arsenic. Concha et al. (2006) demonstrated that As concentrations in drinking water correlated well with As in women's urine, and that some water-based foodstuffs (soup and polenta) had high As concentrations ($400\ \mu\text{g kg}^{-1}$). Elevated concentrations of other potentially toxic elements including Li, B and Cs in San Antonio drinking water were also recorded by Concha et al. (2010).

The studies of Vahter et al. (1995) and Concha et al. (1998, 2006, 2010) identified water as an important pathway for As and other toxic element exposure to the residents of San Antonio. Although studies have been carried out to examine regional patterns in As and ore deposit pathfinder element patterns (MRA-UGAN, 2005), none have been undertaken to evaluate the source(s) of As or other potentially toxic elements in potential drinking or irrigation water sources for the town, and whether natural attenuation processes occur in the area to reduce element concentrations to less hazardous

levels. Such information will underpin future health-related studies in the area. To this end, the aim of this study was to characterise the geochemistry of As and other potentially toxic elements in and around San Antonio de los Cobres, to evaluate element sources, possible natural attenuation mechanisms and health implications. This information will be of use in evaluating other areas affected by geothermal activity, in terms of water quality and element sources.

Methods and Materials

Sampling of 46 waters took place between the 23rd and 27th of March, 2006. Samples of spring waters were taken from three major sources (Fig. 1): near the town of San Antonio (samples SPR1-6), at the town's drinking water source at Agua de Castilla (SPR7) and at Baños de Agua Caliente (SPR8-12). Stream waters were taken from the Rio Tocomar – San Antonio de los Cobres (samples STR2-4, 6-8, 10, 11) and its tributaries (STR1, 5, 9). Sample STR1 is taken from a tributary that drains all of the springs in the SPR1-6 sample area (Fig. 1). Drinking waters (CHNF, TAP1-6) were taken from taps from public and private residences in the town of San Antonio. Taps were allowed to run freely for three minutes prior to sample collection. At each sample site water was collected in a clean syringe previously rinsed three times with water from that sample location. A total sample quantity of 120 mL was then divided between four acid-washed sample bottles as follows:

- type 1: 30 mL for anion analysis; collected filtered and unacidified,
- type 2: 30 mL for cation analysis; collected filtered and acidified,
- type 3: 30 mL for cation analysis after digestion; collected unfiltered and acidified.
- type 4: 30 mL for type 3: 30 mL for As speciation analysis; collected filtered through both 0.2 μm and As speciation cartridges (Meng and Wang, 1998) and acidified.

Sample types 1 and 2 were filtered through clean 0.2 μm filters and types 2, 3 and 4 were preserved with approximately 0.6 mL of 8 N HNO_3 to $\text{pH} < 2$. All water samples were stored cool in acid-washed

30 ml HDPE bottles with HDPE lids (VWR, Poole, UK, 215-7504). Field blanks were opened and acidified in the same manner as samples in each location. Conductivity, pH and dissolved oxygen content were determined in the field using a Hanna DIST conductivity meter, Hach sension1 pH meter and Hach sension1 DO₂ meter, respectively. Titration using a Hach kit was used to determine concentrations of HCO₃⁻.

To determine the concentrations of As and B in waters used for drinking (type 3 water sample), the tap waters were digested in order to dissolve their suspended particulates, since both the water and particulates would be ingested by those who drank the waters. For the digestions, 18 mL of unfiltered sample was digested in 3 mL concentrated HNO₃ (AR grade) and then made up to 25 mL (method based on EPA Method 200-2, 2011). A blank was added to each digestion batch to enable the data quality to be assessed and ensure that preparation and analysis was consistent for each batch.

Concentrations of As and B in the blanks were below detection limits, and for reference material TMDA-64 (National Water Research Institute) and Ion-96.3 (both were from the National Water Research Institute, Environment Canada), were within the reported certified concentration ranges.

A DIONEX ICS-2500 series ion chromatograph using an Ionpac AS17 analytical column and an Ionpac AG17 guard column were used to measure the concentration of F, Cl, NO₃ and SO₄ in all water samples. Reference material Ion-96.3 (National Water Research Institute) was used to test the accuracy of this method, and concentrations were within reported ranges. Analysis of Ca, Na, K, Mg, Rb, Li, Fe, Mn, B, Ag, Al, Cd, Cr, Cu, Ni, Sb, Sr, Tl, V and Zn was carried out using a JY Ultima 2 ICP-OES. Results for Ag, Al, Cd, Cr, Cu, Ni, Sb, Sr, Tl, V and Zn were below detection limits of, on average, < 0.5 mg L⁻¹. Determined values of trace and major cations were within reported certified concentration ranges for reference materials TMDA-64 and Ion-96.3, respectively (National Water Research Institute). Dissolved silica was analysed by spectrophotometry, and reference material Ion-96.3 was used to test the accuracy of this method. Determined values were within the reported certified

concentration ranges. Blank concentrations for all elements were low, and precisions were within 10%, except for two duplicate pairs for Li, for which concentrations were low ($< 1 \text{ mg L}^{-1}$).

The computer program Excel was used to manipulate the water data and produce graphs to examine downstream trends (for the stream samples). The software package AqQA™ (Rockware) was used to assess the ion balance of the water analyses, delineate groundwater types and assess the irrigation and drinking water quality of the samples. Equilibrium speciation modeling and mineral saturation index calculations were carried out using the React program within The Geochemist's Workbench® package, version 8.0 Standard.

Results and Discussion

Characteristics of spring waters

All of the spring waters are Na-Cl type, except STR9, which is Ca-Cl type. The pHs are slightly acid to near-neutral (6.42-7.39), and the waters have high concentrations of Na, Li, B, HCO_3 , Cl, F and SiO_2 , which are typical of spring waters in geothermal areas (Hem, 1985; Aiuppa et al., 2006). The three groups of spring waters (SPR1-6, near the town of San Antonio; SPR7, the town's drinking water source and SPR8-12 at Baños de Agua Caliente) have distinct major and trace element compositions (Table 1, Figure 2). SPR1-6 waters are the most concentrated in all elements except F of the springs sampled (SPR8-12 waters have higher F than SPR1-6), and SPR7 the least.

Springs in geothermal areas have chemical signatures arising from mixing of meteoric waters, deep aquifer Na-Cl brines and interactions with hydrothermal vapours (Ellis and Mahon, 1977, Aiuppa et al., 2006). In Figure 2 these possible sources with respect to the San Antonio waters are explored. Springs 1-6 are closest in composition to Na-Cl brines, which plot near the Cl and Na+K axes on the two triangular plots in Figure 2 (cf., Aiuppa et al., 2006). The compositions of SPR7 and SPR8-12 move away from the brine axes and towards the HCO_3 axis on the SO_4 - HCO_3 -Cl plot, suggesting

mixing with meteoric waters rather than with steam-heated, hydrothermal acid sulphate groundwaters, which would plot at the SO_4 axis. The degree of mixing for SPR1-6 may be limited, however, since these waters are extremely enriched in all elements and, particularly, the brine elements Na and Cl, compared to the other springs (Table 1). SPR7 plots furthest away from the NaCl brine axes, suggesting that it is the most diluted by meteoric waters of the springs sampled. This is supported by its lower element concentrations (Table 1), temperature and conductivity (13.1°C , $712 \mu\text{S cm}^{-1}$) compared to the other springs ($21.9\text{-}45.7^\circ\text{C}$, $2240\text{-}6810 \mu\text{S cm}^{-1}$).

Arsenic concentrations in the springs SPR1-6 range from 7390 to 9490 $\mu\text{g L}^{-1}$, and in SPR8-12, from 274-366 $\mu\text{g L}^{-1}$. The SPR1-6 concentrations are higher than those found by Vahter et al. (2000) for the same area. The concentration in SPR7 (208 $\mu\text{g L}^{-1}$, also discussed below in the drinking water section) is slightly lower than those of SPR8-12. In the El Tatio system in the Antofagasta region of Chile, As concentrations of 45,000-50,000 $\mu\text{g L}^{-1}$ are recorded (Ellis and Mahon, 1977). While the San Antonio spring water concentrations are not as high as this, they are on the order of those reported for other geothermal areas, such as California (up to 7500 $\mu\text{g L}^{-1}$, Coso Hot Springs, Imperial Valley, Welch et al., 1988) and Kyushu, Japan (500-4600 $\mu\text{g L}^{-1}$, Yokoyama et al., 1993).

The ratios of As/Cl and As/Na are not consistent for the three spring groups (2.5-3.3 and 2.4-3.0 for SPR1-6, 0.9 and 0.8 for SPR7 and 0.3 and 0.2 for SPR8-12) and As does not correspond only moderately well to Cl and Na (Figure 3), in contrast to other geothermal areas (Welch et al., 1988). Ballantyne and Moore (1988) pointed out, however, that such correlations should be examined with caution, since they reflect the common behavior of As and Cl in geothermal areas rather than common sources or chemical associations: Cl is generally derived from magmatic gaseous HCl, whereas As is derived from host-rock leaching (Webster and Nordstrom, 2003). The San Antonio ratios suggest enrichment of As relative to Cl in SPR1-6, which has also been documented in Yellowstone National Park (Nordstrom et al., 2001), and was attributed to high CO_2 concentrations in the source waters. This

may also be possible for SPR1-6, given their high HCO_3 concentrations (Table 1), although these may also at least partly be due to dilution with meteoric waters, as discussed above (Figure 2). Further H and O isotopic analysis is required to further delineate the relative contribution of meteoric waters to these springs.

Arsenic concentrations in the springs do not correlate well with any of the other parameters examined, including pH, T, As(III) and As(III)/As(tot). Arsenite concentrations and percentage As(III) of total As in the spring waters are highly variable (Table 1), as in other geothermal areas (Ballantyne and Moore, 1988), and probably reflect the degree to which the spring waters have been oxidized upon ascent to the surface by abiotic and biotic processes (cf., Langner et al., 2001). As(III) concentrations are highest in the highest temperature SPR1-6 group, and these are the lowest pH spring waters sampled (pH = 6.42-6.75). At this pH, the As(III) will likely occur as the species H_3AsO_3 (Brookins, 1988).

Fluoride concentrations in the springs are 4.96-5.35 mg L^{-1} in SPR1-6, 2.38 mg L^{-1} in SPR7 and 6.66-8.04 mg L^{-1} in SPR8-12. Like As, F concentrations do not correlate well with any other ion or measured parameter within or between spring groups. Positive saturation indices (SI) for fluorite [CaF_2] were calculated for all of the spring waters using Geochemist's Workbench, suggesting saturation with this mineral, and that dissolution of this mineral gave rise to the F concentrations observed. The relative SIs for the spring groups (+0.11-0.40 SPR1-6; +0.001 SPR7; +0.50-0.72 SPR8-12) correspond well to the aqueous F concentrations, and give an indication of the relative amounts of weathering of fluorite that took place. It should be noted, however, that these SIs are not conclusive evidence of fluorite weathering; the high aqueous F could be due to weathering of other F-bearing minerals, including apatite and amphiboles (Deer et al., 1992). Further work is required to determine the exact sources of F.

Boron spring water concentrations are 50.0-56.6 mg L⁻¹ in SPR1-6, 6.33 mg L⁻¹ in SPR7 and 26.5-28.5 mg L⁻¹ in SPR8-12. Boron concentrations correspond well to Na, Cl and HCO₃ (Figure 3), reflecting the common behavior of B to these ions and possibly a common geothermal source.

Characteristics of stream waters and downstream trends in element concentrations

The stream waters are also Na-Cl waters, but have variable major and trace element chemistries (Table 1; Hudson-Edwards and Archer, 2008). All elements follow the same pattern as those shown in Figure 4 for As(tot) (except As(III) and As(V), discussed below). In most cases, the concentrations are relatively low in samples taken upstream of the SPR1-6 area. Contributions from these springs and the tributary STR1 appear to cause a significant increase in concentrations of the main river elements downstream of these inputs. In Figure 5 the significance of dilution from these inputs is examined by plotting the concentrations of some of the dissolved constituents versus the concentrations of Cl. Mixing lines represent concentration trends expected through simple dilution of the most Cl-rich water (the tributary STR1, which drains the element-rich SPR1 to 6 samples; Fig. 1) and the Cl-poor water just upstream of the point where STR1 enters the main Tocomar-San Antonio de los Cobres river (STR3). In this analysis, Cl is used as a conservative tracer since, as in other geothermal areas (Mroczek, 2005) it is highly concentrated in the waters and behaves in a conservative manner. Speciation modeling of the river waters using Geochemist's Workbench suggests that chloride minerals are unlikely to precipitate from river waters or, if they do, they remove no more than a very small fraction of the total dissolved Cl. Water compositions that fall on the mixing lines indicate a mechanism of simple dilution, those that fall above indicate addition of dissolved species through dissolution or desorption and those that fall below indicate the removal of species through precipitation or adsorption processes (cf. Berger et al., 2000; Hudson-Edwards et al., 2005).

Figure 5 shows that the downstream decreasing trends in Na, F, SiO₂, As, B and Li (and K and Rb, not shown on the figure) can be explained by mineral precipitation, and removal of these elements and compounds on or within the mineral structures. These trends are supported by speciation modeling, which suggests that fluorite [CaF₂], chalcedony [SiO₂] and the clay mineral sepiolite [Mg₄Si₆O₁₅(OH)₂·6H₂O] are at or near saturation in the waters (although we acknowledge that saturation and/or precipitation of other Na-, F-, SiO₂-, As-, B-, Li-, K- and Rb-bearing minerals may also explain the trends). Potassium and Li are known to substitute in sepiolite (Mayayo et al., 1998; de la Fuente et al., 1999). Only one sample (STR4, just downstream of the junction of the tributary STR1 and the main trunk of the river), falls very near or on the dilution line, suggesting that at this point downstream, no mineral precipitation has yet occurred to remove constituents. Calcium and Mg concentrations fall above the line, suggesting that they are added to the river water. Equilibrium speciation modeling with Geochemist's Workbench suggests that halite [NaCl], gypsum [CaSO₄·2H₂O], magnesite [MgCO₃] and calcite [CaCO₃] are among the minerals being dissolved to produce the river water.

The mixing plots in Figure 5 also suggest that As(III) is removed from the stream water, and As(V) added to the stream water. This may not be a function of mineral precipitation but, rather, oxidation of the As(III) to As(V). In the SW USA, Wilkie and Hering (1998) recorded a fast rate (as low as 0.3 h) of oxidation of As(III) in geothermal waters to streams, and suggested that this was due to biotic oxidation of the As(III). The lack of a significant increase in As(V) downstream (Fig. 4) may be due to its removal by sorption onto stream particulates such as Fe oxides (cf., De Vitre et al., 1991).

The downstream natural attenuation of As, F and B concentrations and plots in Figure 5 suggest that mineral precipitation may be a viable mechanism for removal of these elements from stream waters. The farthest downstream sample taken (STR11), however, has concentrations of As (476 µg L⁻¹), F (2.36 mg L⁻¹) and B (7.46 mg L⁻¹) that exceed recommended guidelines for drinking and irrigation

(see below). This suggests that if waters from the San Antonio de los Cobres river are to be considered for these purposes, they should be exploited much further downstream where mineral precipitation may have removed even more As, F and B, or treated prior to use.

Drinking water quality

The Argentinian drinking water standard for As (CAA, 1994; Fiorentino et al., 1998; www.anmat.gov.ar accessed 30 April 2009; Argentinian Alimentary Code, http://www.unep.org/hazardoussubstances/Portals/9/Lead_Cadmium/docs/submissions/ARGENTINA-Pb_Cd-INFORMATION-revised.pdf, accessed 15 April 2011) and World Health Organization (WHO) guideline and recommended guideline concentrations for As and all the other elements (WHO, 1998, 2002a, b) are used for all drinking water assessments. Only the filtered and unfiltered tap samples and drinking water source spring sample SPR7 are included in this assessment. All concentrations of Na, Fe, Mn, Cl, SO₄ and NO₃ fall below their respective guidelines and standards. There are no guidelines and standards for K, Ca, Mg, HCO₃, SiO₂, Li or Rb.

Arsenic concentrations for filtered samples SPR7, CHNF, and TAP1 to TAP6 range between 151 and 236 $\mu\text{g L}^{-1}$. There is little difference between the source SPR7 As concentration and those of the tap waters (Table 1), suggesting that the metal piping used to transport the water to the town (Concha et al., 2006) does not remove As. These concentrations exceed the Argentinian drinking water limit for As and WHO recommended guideline for As concentrations in drinking water of 10 $\mu\text{g L}^{-1}$ (CAA, 1994; WHO, 1996, 1998; Fiorentino et al., 1998) by a factor of 15 to 24. The concentrations are in the same range as those reported by Concha et al. (1998; 157-219 $\mu\text{g L}^{-1}$; 2010, 202-214 $\mu\text{g L}^{-1}$). Concentrations of unfiltered As concentrations in tap and the source spring water (SPR7) (157 – 235 $\mu\text{g L}^{-1}$) are similar to the filtered waters (and in some cases, are lower than the corresponding filtered water sample, which may be due to errors associated with the digestion method), suggesting that the tap

waters have few particulates or, if they do, they do not contain As. The values are in the same range as those reported by Concha et al. (1998, 2006, 2010), and also exceed the WHO and Argentinian drinking water limits for As. These elevated As concentrations may pose a hazard to human health in San Antonio. The species of As in the San Antonio drinking waters, however, is mainly As(V) (Table 1) rather than the more toxic As(III) (cf., Jain and Ali, 2000), which may be a contributing factor to the low As uptake in babies observed previously (Concha et al., 1998).

Boron concentrations in all San Antonio filtered tap waters and the drinking water source (SPR7) range from 4.63 to 5.33 mg L⁻¹, and thus exceed both the WHO and Argentinian Alimentary Code recommended guidelines for B concentrations in drinking water of 500 µg L⁻¹ (0.5 mg L⁻¹) (WHO, 1998), and the USEPA health advisory guideline for long-term exposure of 900 µg L⁻¹ (0.9 mg L⁻¹) (USEPA, 1996; Rowe, 1999), by a factor of between 5.1 and 10.6. The unfiltered B concentrations for these samples range from 5.27 to 5.89 mg L⁻¹, and thus also exceed the recommended guidelines. Excessive concentrations of B in drinking water can cause nausea, vomiting, diarrhea and degenerative effects on the liver and kidneys (Parks and Edwards, 2005). The source SPR7 has a higher amount of B (6.33 mg L⁻¹) than the taps (4.63-5.18 mg L⁻¹), suggesting some removal of B during transport from the spring to the taps.

Fluoride concentrations in the San Antonio filtered tap waters and the drinking water source (SPR7) range from 2.03 to 2.72 mg L⁻¹, and exceed the WHO recommended guideline for F concentrations in drinking water of 1.5 mg L⁻¹ (WHO, 1998) by a factor of 1.3 to 1.8. It was not possible to determine the unfiltered concentrations of F, but, based on the unfiltered concentrations of As and B reported above, it is likely that they will be higher than the filtered concentrations of F, and thus also higher than the WHO recommended guideline value. Excessive intake of F from drinking water can cause dental and skeletal fluorosis, arthritis, decreased thyroid function and detrimental effects on the brain (Carton, 2006). In other parts of Argentina (Cordoba, Santa Fe and Buenos Aires),

high concentrations of F have given rise to dental fluorosis (Smedley et al., 2002). Like B, the source SPR7 has a higher amount of F (2.38 mg L^{-1}) than the taps ($2.03\text{-}2.44 \text{ mg L}^{-1}$), suggesting some removal of B during transport from the spring to the taps.

The studies of Vahter et al. (1995) and Concha et al. (1998, 2006) suggest that elevated As in drinking water may be linked to elevated As in urine and breast milk. The high concentrations of F and B, in addition to As, in drinking water suggest that further epidemiological study is required, as also recommended by Concha et al. (2010).

Irrigation water quality

Irrigation waters in rural areas are often drawn from natural springs or streams. These waters, however, may not always be suitable for crop growth. For example, high concentrations of exchangeable (soluble) sodium (Na) and high levels of salts in soils negatively affect plant growth. Soils with high exchangeable Na have poor tillage qualities and low permeability. To determine the exchangeable Na for the San Antonio spring and stream waters, the Na adsorption ratio (SAR), which compares the concentrations of Na^+ , Ca^{2+} and Mg^{2+} in irrigation waters, since Ca and Mg moderate the negative effects of Na, was calculated using AqQA (Table 1). A SAR value above 15 suggests that plants grown on these soils will not adsorb water very easily (Lloyd and Heathcote, 1985; Munshower, 1994). Most of the spring SARs are greater than this recommended value, suggesting that, based only on the SAR values, these waters should not be used for irrigation. The stream SARs are all less than 15, except for STR1, which drains springs SPR1 to 6, so these are more suitable for irrigation.

Salinity is another measure of irrigation water quality, and the measured conductivity in the field can be used as a measure of salinity. Lloyd and Heathcote (1985) suggest that a conductivity measurement of $< 250 \mu\text{mho cm}^{-1}$ is of low salinity, with no detrimental effects on crops expected, 250 to $750 \mu\text{mho cm}^{-1}$ represents medium salinity, with detrimental effects to sensitive crops expected, 750

to 2250 $\mu\text{mho cm}^{-1}$ represents high salinity, with adverse effects on many crops expected, and 2250 to 5000 $\mu\text{mho cm}^{-1}$ represents very high salinity, suitable only for salt-tolerant plants. Salinity was calculated for the San Antonio waters with AqQA using the measured conductivity values in Table 1. The salinity values (Table 1) for almost all of the spring waters are very high and for the stream waters are high. These results suggest that, although the SARs for the streams are acceptable, the overall salinity of the waters may be adverse to crop growth.

In the absence of Argentinian irrigation water guidelines, Australian irrigation water quality guidelines are used to assess the stream waters and spring sample SPR7 for exposure of crops to B and As from irrigation water. Excessive B in irrigation water is a particular hazard (Leyshon and Jame, 1993), as many crops have a narrow tolerance range for the element (Maas, 1986; Gupta, 1993). The Australian irrigation guideline for B is 0.5 mg L^{-1} (Water Quality Guidelines Online, 2006), and all of the stream samples, and the SPR7 sample, exceed this by a factor of 10, suggesting that B may pose a threat to crops. However, the plot in Figure 5 suggests that B is removed from the river waters by precipitation, suggesting that given time or inducement, B may be removed in solid form and made unavailable to crops. The Australian irrigation guideline for As for long-term use is 2,000 $\mu\text{g L}^{-1}$ (Water Quality Guidelines Online, 2006). All of the stream samples except STR1 fall below this guideline, suggesting that, over the long-term, As concentrations in these waters may not pose a threat to crops. Because our samples were taken during the dry season, the concentrations reported are likely to represent the higher end of the range of stream concentrations expected, so the conclusions above likely also apply to the wet season.

Conclusions and Recommendations

Concentrations of As, B and F in spring, stream and drinking waters in and around San Antonio de los Cobres exceed World Health Organization guidelines, and the Argentinian drinking water guideline for

As. Assessment of the waters for irrigation purposes also suggests that their high B concentrations and salinities may adversely affect crops. The geochemical signatures of spring and stream waters, and modeling of mixing with meteoric waters, suggest that As, B and F concentrations may be reduced by dilution of geothermal Na-Cl brines with cleaner meteoric waters or by mineral precipitation. Sources of dilute meteoric waters are scarce around San Antonio, however, and rainfall is also low, suggesting that these techniques may not be cost-effective or feasible. Ideally, technologies to remove excess concentrations of As, F and B should be developed to reduce concentrations of these elements in drinking waters.

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Figure Captions

Figure 1. Location of San Antonio de los Cobres and of water sampling sites.

Figure 2. Major dissolved ion composition of San Antonio de los Cobres spring waters. (a) $\text{SO}_4\text{-HCO}_3\text{-Cl}$ anion triangular plot; (b) Na+K-Mg-Ca cation triangular plot. NaCl brines and meteoric mixing arrows based on those in Figure 2 of Aiuppa et al. (2006).

Figure 3. Scatter plots showing co-variation of As and B with Na, Cl and HCO_3 .

Figure 4. Variation of total As, As(III) and As(V) in Rio de San Antonio de los Cobres and tributary stream waters and springs with distance downstream of the single spring 10 km from San Antonio de los Cobres, Argentina. Spring groups SPR1-6, SPR7 and SPR8-12 are indicated.

Figure 5. Mixing plots for San Antonio de los Cobres waters.

Figure 1

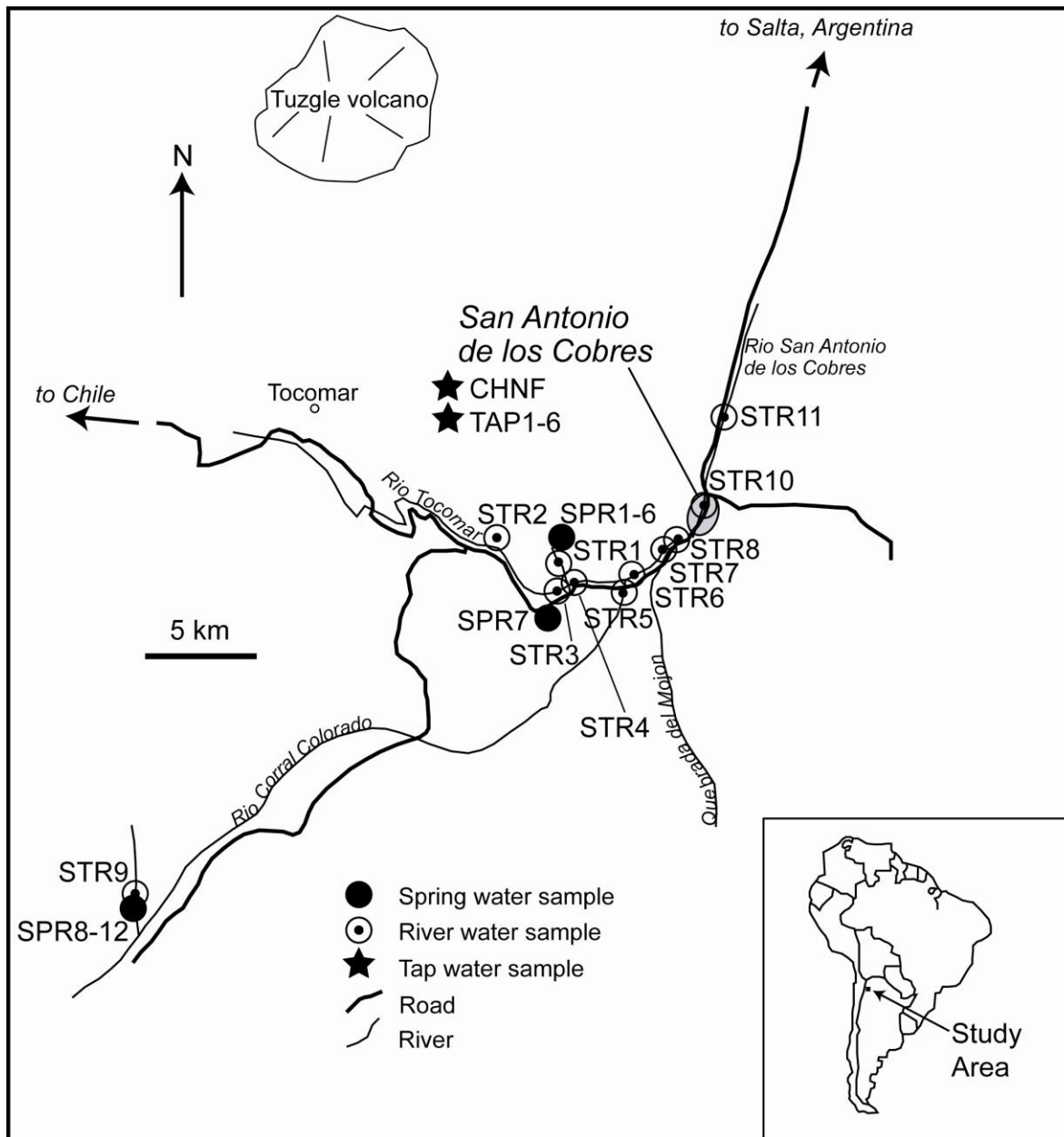


Figure 2.

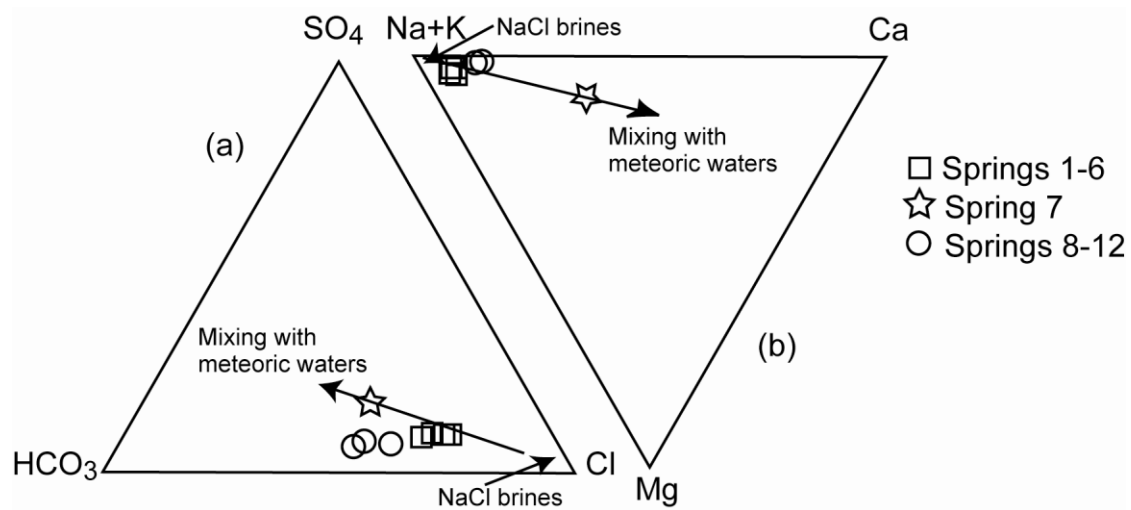


Figure 3.

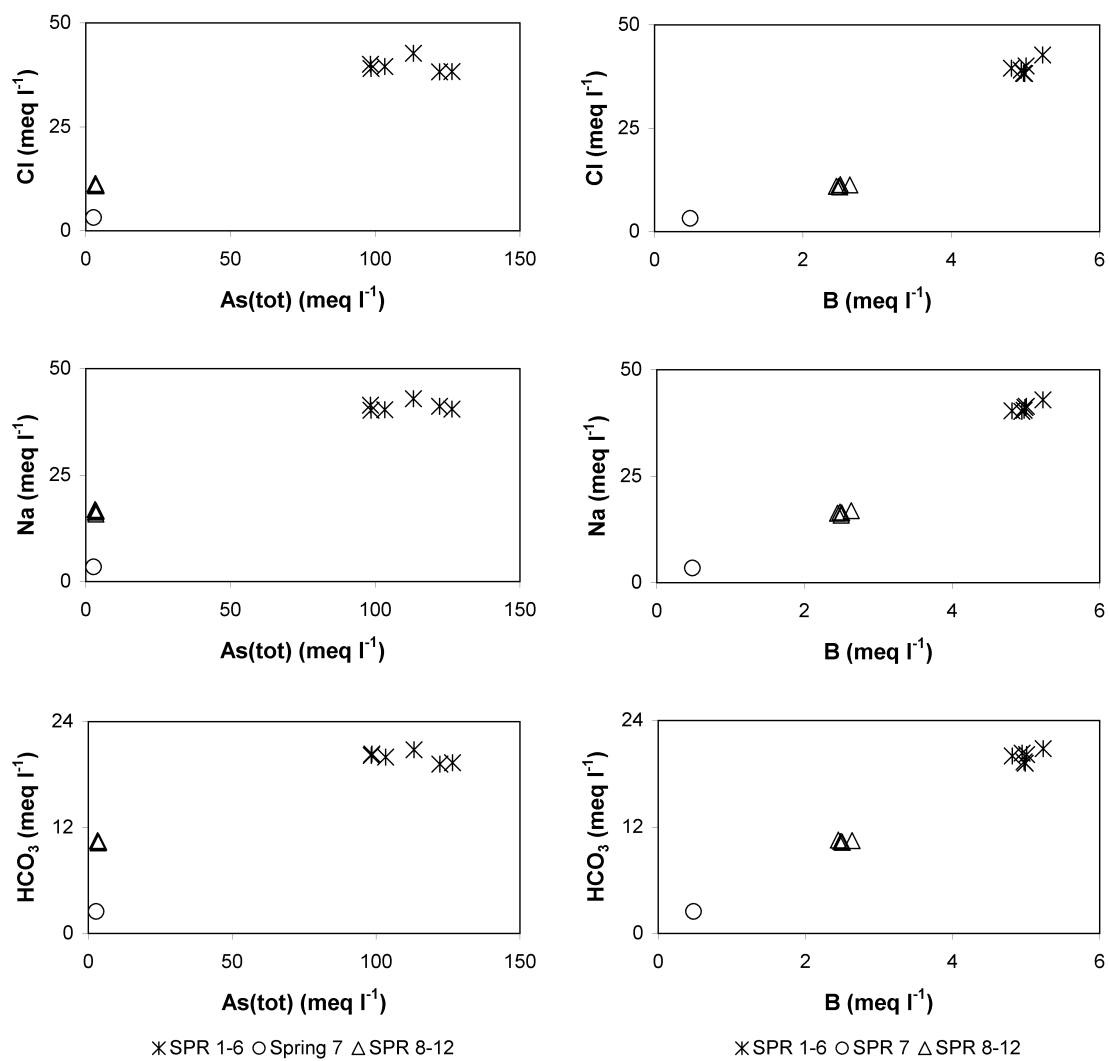


Figure 4

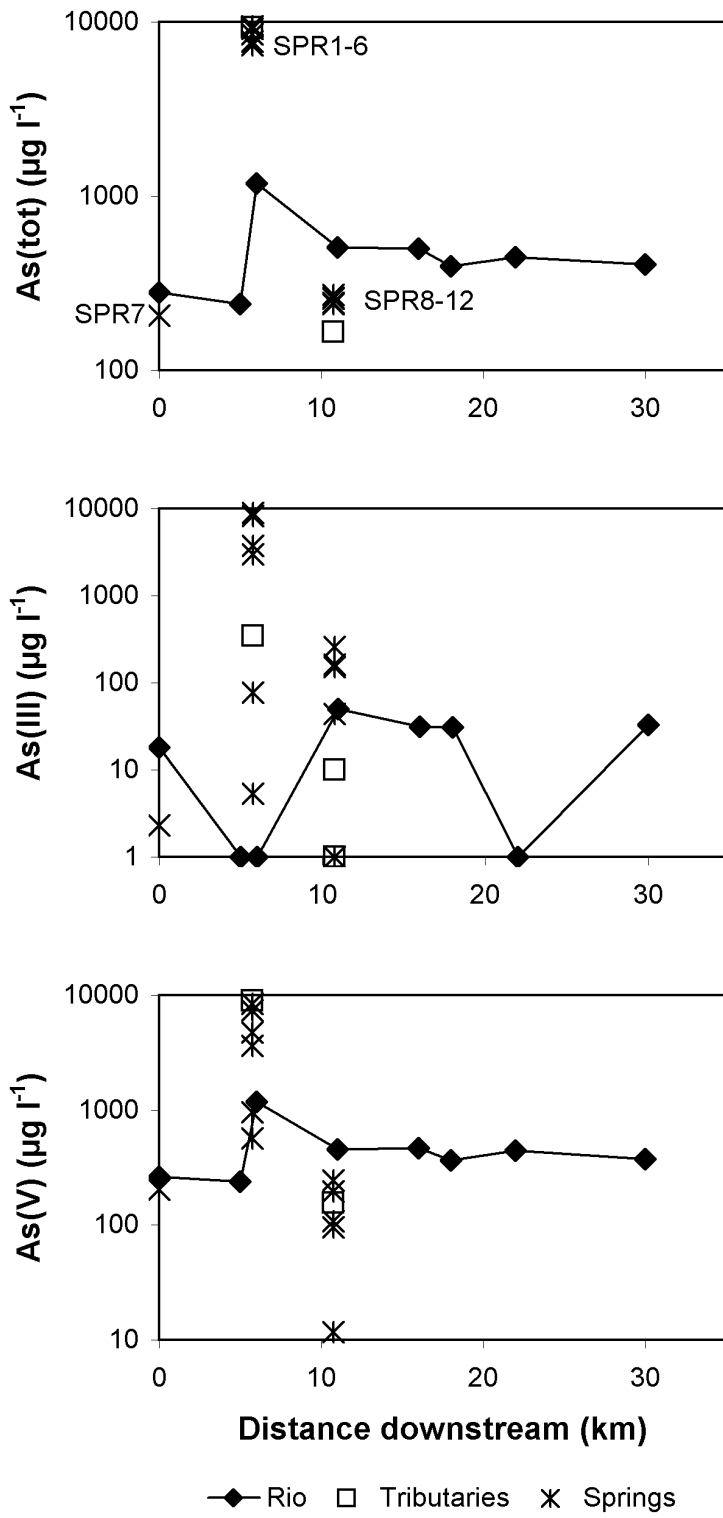


Figure 5.

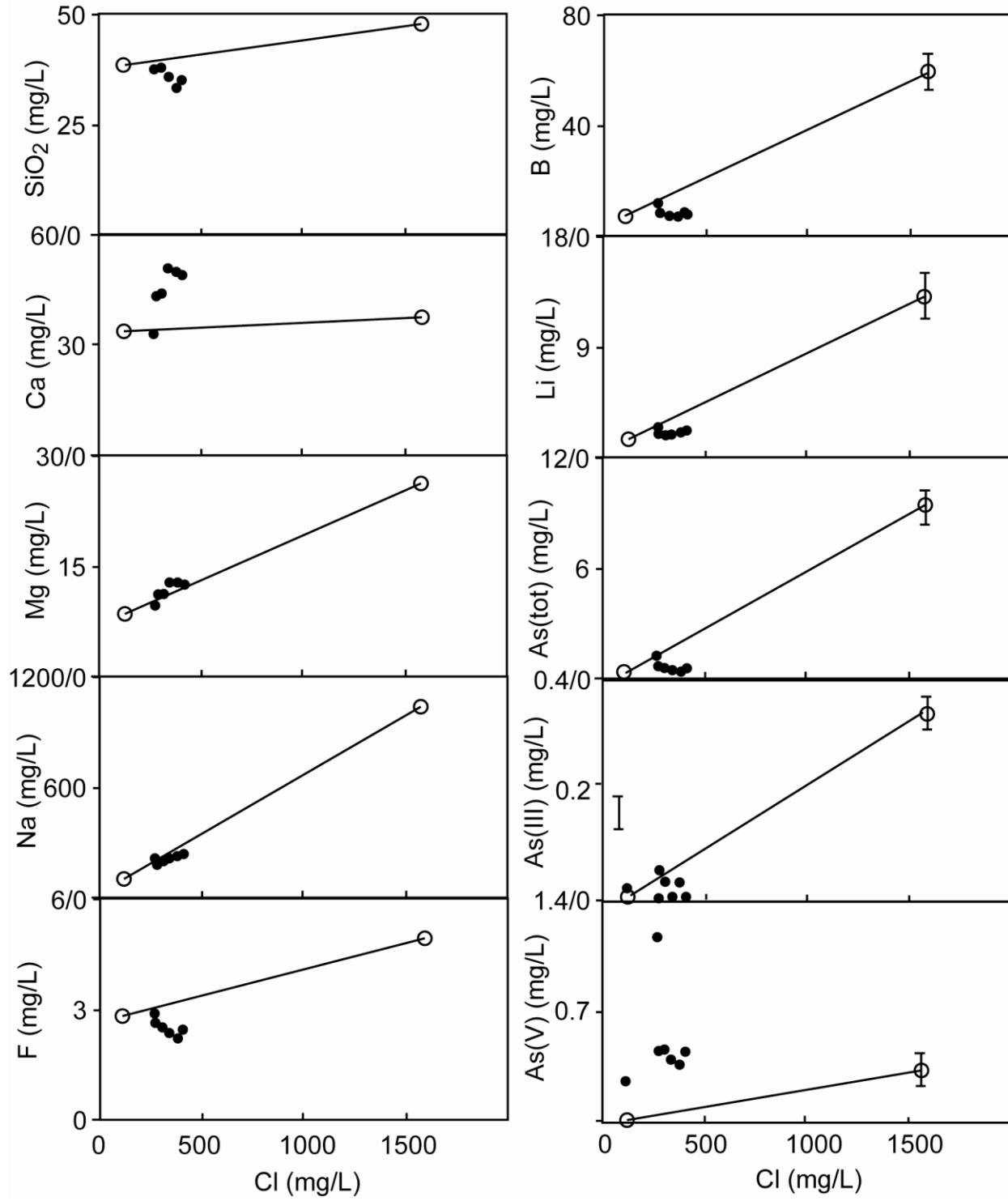


Table 1. Composition of filtered waters from San Antonio de los Cobres area, Argentina. Analyses in bold exceed WHO recommended drinking water guidelines. All concentrations are given in mg L⁻¹ except where indicated. Percentage AsIII of total As for samples below detection limits are calculated using the maximum detection limit value of 9 µg L⁻¹ for AsIII.

Sample	Temp °C	EC µScm ⁻¹	pH	DO %	As µg L ⁻¹	AsIII µg L ⁻¹	AsV µg L ⁻¹	AsIII *100// As	Na	K	Ca	Mg	Rb	Li	Fe	Mn	B	HCO ₃	Cl	SO ₄	F	NO ₃	SiO ₂	SAR	Salinity Hazard	
SPR1	39.6	6810	6.60	38.1	9170	8210	955	90	947	250	56.0	25.5	0.89	11.4	0.16	0.08	53.9	1170	1360	241	5.22		47.9	26	VH	
SPR2	43.2	6680	6.56	22.0	9490	8920	569	94	930	237	56.2	25.6	1.13	11.3	0.48	0.09	53.8	1170	1360	241	4.96		47.3	26	VH	
SPR3	21.9	6080	7.03	106	7390	5.3	7380	0.1	925	258	65.3	26.4	1.11	12.1	0.04	0.14	51.5	1200	1350	239	4.97		50.2	24	VH	
SPR4	38.5	6360	6.42	39.9	7370	3760	3610	51	953	268	69.6	25.7	1.15	11.9	<0.04	0.18	54.1	1230	1420	246	5.30		57.2	25	VH	
SPR5	30.4	6760	6.81	200	8490	77	8420	1	988	282	60.6	27.0	1.00	13.1	0.04	0.12	56.6	1250	1480	262	5.35		44.0	26	VH	
SPR6	26.3	6150	6.75	43.2	7750	3000	4750	39	928	261	58.5	24.4	1.00	11.7	<0.04	0.09	50.0	1200	1380	250	5.14		56.6	26	VH	
SPR7	13.1	712	7.39	96.2	208	2.3	206	1	78.7	6.52	37.1	7.61	0.13	0.41	<0.04	<0.05	6.33	151	114	50.8	2.38	1.4	38.5	3	M	
SPR8	40.9	2440	6.53	24.7	366	260	106	71	381	50.7	49.7	4.03	0.53	6.94	0.26	0.17	26.8	632	389	59.6	8.04		97.1	14	VH	
SPR9	44.0	2320	6.48	30.3	313	152	161	49	364	49.0	49.8	4.17	0.45	6.60	0.21	0.16	27.0	628	384	57.4	6.68		18.4	13	VH	
SPR10	31.8	2240	7.23	90.8	330	<9	c. 330	<3	375	49.3	49.0	4.28	0.61	5.45	<0.04	0.07	26.5	642	390	60.1	6.92		36.0	14	H	
SPR11	40.9	2320	6.95	82.6	274	44	230	16	389	51.4	50.2	4.12	0.52	7.11	<0.04	0.20	28.5	639	402	69.4	7.30		98.1	14	VH	
SPR12	45.7	2300	6.57	25.5	341	162	179	48	376	51.2	47.9	3.96	0.38	6.82	0.21	0.18	27.1	626	403	68.5	6.66		98.0	14	VH	
STR1	25.8	6570	8.43	104	9310	346	8960	4	1030	298	72.9	26.2	1.18	13.1	<0.04	<0.05	56.6	1200	1480	275	4.96		47.3	26	VH	
STR2	10.0	730	8.02	95.7	278	18	c. 260	6	94.2	7.09	33.3	8.21	0.04	0.95	<0.04	<0.05	6.75	163	117	31.5	2.47		36.2	4	M	
STR3	15.6	728	8.35	106	284	<9	c. 284	<3	95.2	7.25	33.3	8.16	0.06	0.95	<0.04	<0.05	6.73	165	121	37.4	2.77		38.4	4	M	
STR4	18.3	1410	8.51	106	1240	<9	c.1240	<1	213	27.2	32.8	9.64	0.16	2.17	<0.04	<0.05	11.9	305	268	62.7	2.90		37.4	8	H	
STR5	21.5	1780	6.87	110	202	10	192	49	234	18.6	66.5	16.3	0.18	1.45	<0.04	<0.05	7.11	151	452	81.5	2.14		38.2	7	H	
STR6	21.1	1340	7.38	111	510	49.8	460	10	179	16.9	43.5	11.2	0.04	1.39	<0.04	<0.05	7.60	179	279	60.0	2.62		37.7	6	H	
STR7	21.9	1380	8.40	109	625	31.5	594	5	189	20.8	43.7	11.2	0.17	1.52	<0.04	<0.05	7.60	183	303	61.6	2.54		37.7	7	H	
STR8	19.8	1700	8.26	97.0	424	30.7	393	7	219	32.8	49.5	12.7	<0.01	1.78	<0.04	<0.05	7.02	187	378	62.0	2.22		33.3	7	H	
STR9	20.1	250	6.32	97.4	13	<9	c. 13	<69	9.39	0.51	34.9	11.6	0.11	0.01	<0.04	<0.05	0.21	110	55.8	14.1	0.74		18.4	0.003	M	
STR10	24.7	1610	8.23	102	518	<9	c. 518	<2	229	35.5	48.8	12.6	0.15	1.97	<0.04	<0.05	7.71	165	405	67.2	2.43		35.1	8	H	
STR11	10.7	1440	6.54	84.4	476	32.7	443	7	205	25.9	50.6	12.7	0.10	1.48	<0.04	<0.05	7.46	178	339	76.9	2.36		35.8	7	H	
CHNF	15.2	526	6.87	99.0	225	10.3	215	5	80.7	6.06	38.0	7.88	<0.01	0.40	<0.04	<0.05	5.10	154	112	49.8	2.08	3.6	38.2			
TAP1	16.4	720	7.50	98.3	209	<9	c. 209	<4	80.8	5.92	37.8	7.71	0.10	0.48	<0.04	<0.05	4.66	146	117	51.6	2.72	0.6	38.3			
TAP2	17.5	709	7.26	98.2	233	19	214	12	78.4	5.74	38.2	7.88	0.01	0.50	<0.04	<0.05	4.63	159	112	49.8	2.03	0.6	38.1			
TAP3	17.9	688	6.86	96.6	235	23	212	18	78.3	5.60	37.3	7.63	0.08	0.46	<0.04	<0.05	4.67	163	117	51.8	2.44	4.0	37.9			
TAP4	15.8	707	6.86	98.7	236	<9	c. 236	<4	74.9	5.28	36.0	7.23	0.13	0.46	<0.04	<0.05	4.66	143	111	51.0	2.05	4.6	38.2			
TAP5	18.3	648	7.48	78.3	151	<9	c. 151	<6	80.2	5.91	37.9	7.90	<0.01	0.50	<0.04	<0.05	4.72	165	115	50.7	2.38	0.4	36.3			
TAP6	17.4	709	7.85	102	220	10	210	5	75.8	5.39	37.2	7.46	0.08	0.46	<0.04	<0.05	4.65	127	112	48.5	2.39	0.4	37.3			
<i>WHO Drinking water Guidelines (^</i>					10*				200**	-	-	-	-	-	0.3*	0.4#	0.5^	-	250**	250**	1.5^	50^	-			
<i>WHO, 1998 – limit; *WHO, 2002a –</i>																										
<i>provisional limit; **WHO, 2002b –</i>																										
<i>complaints from customers, #2004-</i>																										
<i>limit)</i>																										
<i>Argentinian drinking water guideline</i>					10									-	0.3	0.1	0.5				0.4					
<i>and Alimentary Code(CAA, 1994;</i>																										
<i>Fiorentino et al., 1998)</i>																										

SAR = Sodium adsorption ratio. Salinity hazards: VH = very high; H = high; M = mediu

Table 2. Composition of unfiltered drinking waters from San Antonio de los Cobres area, Argentina. Analyses in bold exceed recommended WHO (2004) recommended drinking water guidelines.

Sample	Description	As $\mu\text{g l}^{-1}$	B mg L^{-1}
<i>Spring and Tap Waters</i>			
SPR7	Drinking water spring source for San Antonio de los Cobres	223	5.44
CHNF		219	5.38
TAP1		235	5.89
TAP2		219	5.34
TAP3		205	5.30
TAP4		217	5.31
TAP5		157	5.27
TAP6		214	5.39
<i>WHO Drinking water guidelines</i>		10	0.5