Research Article

Assessment of Heavy Metals Concentration in Arsenic Contaminated Groundwater of the Chaco Plain, Argentina

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The occurrence and distribution of arsenic and 23 other trace elements have been investigated in groundwater from Comandante Fernández Department in the Central region of Chaco Province, Northern Argentina. The arsenic concentrations samples ranged between 0.7 to 1990 $\mu\text{g L}^{-1}$; 91% ($n = 45$) exceeds the 10 $\mu\text{g L}^{-1}$ World Health Organization (WHO) provisional standard limits for drinking water. Fluorine was detected in 31% of groundwater samples. Furthermore, there was found a significant correlation between As and F ($r^2 = 0.50$), indicating an association in the prevalence of both elements. In addition, about 78%, 31%, 16%, 13%, and 4.5% of groundwater samples had, respectively, B, Fe, Al, Mn, and Sb exceeding Código Alimentario Argentino (CAA) guideline values. In contrast of the previously values descript, the corresponding to Cr, Be, Ni, Pb, Ag, Se, and Zn were found below the quantification limit. The presence of As and trace elements in groundwater represents an important issue because it can cause a public health problem.

1. Introduction

Among known pollutants, trace elements are widely recognized as being potentially toxic to living organisms. Water contamination with heavy metal (HM) are mainly determined by natural (i.e., weathering, erosion of bed rocks, and ore deposits) [1] and anthropogenic (i.e., mining, industries, and agriculture) processes [2].

Soils and water containing high levels of arsenic and other toxic trace elements can easily contaminate plants, animals, and human beings in contact with them, as they either produce toxic effects or accumulate in plants and thereby enter animal and human food chains [3].

Certain elements like sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), copper (Cu), cobalt (Co), and zinc (Zn) are essentially

required by living organisms in specific concentrations but may produce toxic effects in high concentrations [2]. The main threats to human health from HM are associated with exposure to lead (Pb), mercury (Hg), cadmium (Cd) and arsenic (As), which are extremely prejudicial owing to their toxicity, long persistence, and bioaccumulative nature [4]. Their toxic effects include headache, hypertension, irritability, abdominal pain, nerve damages, liver and kidney problems, sideroblastic anemia, intellectual disabilities, fatal cardiac arrest, and carcinogenesis. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO [5].

Long-term drinking of arsenic contaminated water can cause severe skin diseases including skin cancer; lung, bladder, and kidney cancers, and perhaps other internal tumors; peripheral vascular disease; hypertension; and diabetes [6, 7].

FIGURE 1: Geographical location of the study area and distribution of arsenic concentrations.

It also seems to have a negative impact on reproductive processes (infant mortality and weight of newborn babies) and cardiovascular diseases [8].

The occurrence of high concentrations of As and trace elements in drinking water has been recognized, over the past two or three decades, as a great public health concern in several parts of the world [6, 9]. The Chaco-Pampean plain is the largest one in Latin America and one of the largest geographic units in the world affected by As-contaminated groundwater [10]. In the Chaco plain (north of the Chaco-Pampean plain), the major source of arsenic in groundwater is chemical weathering of the rocks, and no anthropogenic sources of contamination have been reported [11].

Particularly, it has been identified that there are elevated As concentrations in groundwater and reported in different regions of Argentina such as La Pampa [1], Buenos Aires [9], Chaco [11], Córdoba [12], Santiago del Estero [13], Santa Fe [14], and Tucumán [15] Provinces. Detailed information of the arsenic concentration in the groundwater of the Central-West region of Chaco is available in recent publications; high fluorine (F) and As contents in drinking waters have also been reported [11, 16]. In addition, a positive correlation between As and F has been found ($r^2 = 0.66$).

In the study area, it is necessary to carry out the research on the presence of the trace elements in groundwater which are present in concentrations higher than the WHO reference values assigned for health reasons. These elements were selected taking in view the geology of the study area and possible leaching of As and other trace metals previously reported in other areas in Chaco-Pampean plain [14, 15, 17], like vanadium, strontium, barium, chromium, uranium, molybdenum, manganese, and selenium. The residents who live in As-contaminated areas and consume groundwater

are not only exposed to As concentrations but also to high concentration of multiple metals that can cause adverse health effects.

This paper presents an integrated study on the occurrence and the distribution of arsenic and heavy metals (HM) in groundwater in the area of Comandante Fernández in the Central region of Chaco Province, Northern Argentina. In addition, the relations between arsenic occurrence and these chemical components are discussed from a chemical point of view.

2. Materials and Methods

2.1. Location of the Study Area. The study area is located in the Department Comandante Fernández, Chaco Province, Northern Argentina (Figure 1). It covers an area of 1500 km², and approximately 0.10 million population [11]. Presidencia Roque Sáenz Peña (90000 inhabitants), located between 26°47'27" latitudes S and 60°26'29" longitudes W, is the most important town where we could find an economy based on agricultural and livestock exploitation.

This area is located within the geologic province known as the Chaco Pampean [11]. The aquifers are hosted in superposed sequences of aeolian and fluvial sediments of the tertiary and quaternary ages [18]. As there are no superficial sources of groundwater, recharge of the phreatic aquifer is produced from rainfalls, while deep aquifer recharge occurs from west to east and northwest-southeast, and it is supposed to be located in the higher parts of the sub-Andean outcrops [19, 20].

The studied zone has a semiarid and subtropical continental type climate, characterized by sultry summers and cold winters, receiving an annual precipitation of 900 mm, between November and March [21].

2.2. Sampling and Analysis. Forty-five groundwater samples were collected during May–October 2010 (a dry season), in rural and suburbs areas of the Comandante Fernández Department (Chaco Province), (Figure 1). Each sample has been collected from each tube well. Latitude and longitude of these tube wells were determined using a Garmin eTrex Legend, Global Positioning System (Garmin Ltd., UK). Specific well information, that is, the depth of the well was obtained from its owner. The sampling points were selected taking into account their spatial distribution in the area, in order to obtain an accurately representative hydrochemistry.

For all analyses, cleaning and sampling procedure involved deionized distilled water (DDW) produced by MilliQ water (Millipore Elix 5) and high-purity solvents. All glassware and polyethylene bottles were kept in 10% (v/v) HNO_3 (Merk 65%) for 24 hours, rinsed out with DDI, and dried in a stove. All tube-wells samples were collected after 3 min flushing, filtered through $0.45\ \mu\text{m}$ membrane filters and transferred to three different polyethylene bottles to undertake different analysis. Samples for major cations analysis (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) and total As were acidified with 0.06 M HCl. For trace metals analysis, samples were acidified to $\text{pH} < 2$ by addition of ultrapure nitric acid (Fluka). No acidified fractions were collected without headspaces in the sample bottles for measurements of anions such as Cl^- , SO_4^{2-} , NO_3^- , F, and alkalinity. All the samples were kept at 4°C until analysis.

2.3. Groundwater Analyses. The physical parameters like water temperature (T), pH, and electrical conductivity (EC) were measured *in situ* by using a HANNA HI991301 Portable PH/EC/TDS/Temperature Meter. Na^+ and K^+ were determined by emission flame spectrometry (JENWAY PFP7) and Ca^{2+} and Mg^{2+} concentrations were determined by complexometric titration using ethylenediaminetetraacetic acid (0.05N EDTA). Chloride, nitrate, and fluoride ionic activity were measured with ion-selective electrodes using OAKTON CE pH/ION Mod. 510. Alkalinity was analyzed by titration method with sulfuric acid, and sulfate was measured by turbidimetric method using Spectrophotometer UV-Visible Metrolab 1700. For a better detection limit, arsenic was analyzed by hydride generation atomic absorption spectroscopy method (HGAAS) using hollow cathode lamps at 193.7 nm wavelength. The instrument quantification limit for this system was $5\ \mu\text{g L}^{-1}$; an intermediate precision of less than $\pm 10\%$ was achieved. All these analyses were performed at the Laboratories of Química Analítica, Universidad Nacional del Chaco Austral, Argentina.

Total concentrations of 23 trace elements (Ag, Al, Ba, Be, B, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, S, Sb, Se, Si, Sr, Ti, V, and Zn) were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES), (PERKIN ELMER 5100 DV, axial, solid state detector, cross-flow nebulizer, associated with Scott Type chamber, and AS type auto sampler. The equipment was linearly calibrated from 1 to $100\ \mu\text{g L}^{-1}$ with custom certified standard solution (Merck ICP Multielement Standard Solution XIII). R^2 values of calibration curves were >0.995 , and no trend was observed

in the residuals for all analyzed metals. Linearity was checked after every 10 samples using *homemade* control solution. If the recovery was greater than $\pm 10\%$, the recalibration was performed for the concerned element. Accuracy of the procedure it has been tested by analyzing a certified reference material, NIST SRM 1643 c “Trace elements in water.” For the studied elements, bias ranged from 2 to 7%. Precision, expressed as intermediate precision was better than 9% for all analyzed elements.

2.4. Statistical Analysis. All statistical analysis of data, including maximum and minimums, means and medians, was performed using the program STATGRAPHICS 5.1 (Statistical Graphic Corporation. Manugistics Inc.; Rockville, USA). The software Rock Ware Aq.QA version 1.1.5.1 was used to construct the Piper diagrams that depicted the groundwater types.

3. Results and Discussion

3.1. Physicochemical Parameters. The physicochemical parameters determined in selecting 45 groundwater samples are shown in Table 1. Well depth ranged between 5 and 220 m, with average value of 23 m. The pH values of the assorted groundwater samples varied from 6.50 to 8.94 with average value of 7.54 indicating that the waters are generally neutral to slightly alkaline. The measured water temperatures vary from 22.6 to 27.5°C with an average of 23.8°C .

Major ion compositions of the analyzed groundwater samples and the major water types are shown in Table 1. High nitrate concentrations ($\text{max} = 200\ \text{mg L}^{-1}$) are present locally in some wells, probably due to anthropogenic influences, and a significant amount of NO_3^- is thought to be from evaporation. However, since the correlation between NO_3^- and Cl^- is weak ($r^2 = 0.04$), evaporation is unlikely to be the most important cause of the high NO_3^- concentrations.

Considerable spatial variation is observed for the distributions of major cations with dominance of Na^+ (132 to $5857\ \text{mg L}^{-1}$); K^+ (2.10 to $110\ \text{mg L}^{-1}$); Ca^{2+} (1.40 to $1100\ \text{mg L}^{-1}$), and Mg^{2+} (0.54 to $400\ \text{mg L}^{-1}$). The same variation is observed for distribution of major anions, with dominance of HCO_3^- (median value $679\ \text{mg L}^{-1}$), Cl^- (median value $269\ \text{mg L}^{-1}$), and SO_4^{2-} (median value $209\ \text{mg L}^{-1}$). Statistical parameters are shown in Table 2.

Major ion compositions plotted on a Piper diagram (Figure 2) indicate that bicarbonate and chloride were the dominant anions followed by sulfate, and that sodium was the prevalent cation. The major water types in the samples are presented in Table 1.

EC values vary from 0.69 and $24.9\ \text{mS cm}^{-1}$ with a median value of $2.50\ \text{mS cm}^{-1}$ and mean value of $5.27\ \text{mS cm}^{-1}$. This may be due to contribution of Na^+ , HCO_3^- , Cl^- , and SO_4^{2-} . In saline groundwater, chloride and sulfate are also important. The most saline groundwater samples are of Na-Cl type (maximum Cl^- concentration $8193\ \text{mg L}^{-1}$; Tables 1 and 2) although Na- SO_4^{2-} types are also important (maximum SO_4^{2-} concentration $3485\ \text{mg L}^{-1}$). The most significant correlations are those of chloride versus EC and sodium

TABLE 1: Major ions composition of groundwater from the Comandante Fernández Department, Chaco.

Sample ID	Depth (m)	pH	EC (mS cm ⁻¹)	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Water type
M1	30	7.53	2.62	656	269	351	23.1	644	7.10	3.54	1.65	Na-HCO ₃
M2	18	7.46	0.94	509	14.4	18.0	10.4	326	31.3	11.6	7.50	Na-HCO ₃
M3	13	8.08	7.07	860	510	3108	nd	1595	29.8	31.9	8.30	Na-SO ₄
M4	8	6.50	1.78	584	99.1	335	111	669	110	8.96	5.03	Na-SO ₄
M5	5	7.82	1.55	681	99.2	209	2.50	338	20.0	10.9	16.6	Na-HCO ₃
M6	20	7.11	0.83	408	21.1	159	12.2	132	13.9	24.5	11.4	Na-HCO ₃
M7	18	6.90	1.27	490	57.1	226	21.2	221	11.0	9.10	5.50	Na-HCO ₃
M8	20	7.68	2.69	497	427	369	49.3	1034	16.5	77.4	44.3	Na-Cl
M9	13	8.25	1.34	895	45.4	45.0	nd	257	2.10	7.39	5.43	Na-HCO ₃
M10	220	7.98	21.5	936	8193	2070	12.2	5857	32.2	206	44.7	Na-Cl
M11	50	7.89	2.44	135	135	480	nd	522	19.2	101	47.9	Na-SO ₄
M12	15	6.96	0.95	679	111	165	4.35	213	15.2	20.4	6.45	Na-HCO ₃
M13	12	7.29	1.36	722	140	107	2.10	382	9.10	1.40	0.54	Na-HCO ₃
M14	12	7.93	1.49	654	129	83.1	14.4	806	10.0	2.30	0.52	Na-HCO ₃
M15	12	7.61	2.37	769	512	412	107	531	17.2	18.9	12.8	Na-Cl
M16	35	7.51	0.69	198	89.2	136	2.30	200	6.87	28.5	7.54	Na-HCO ₃
M17	15	6.84	4.48	760	1447	431	20.1	825	23.2	14.9	46.4	Na-Cl
M18	8	6.91	3.36	448	1661	182	14.5	1161	12.1	122	56.9	Na-Cl
M19	12	6.78	1.75	302	408	335	200	132	12.9	6.46	2.18	Na-Cl
M20	13	7.78	4.41	751	1425	421	20.3	775	18.4	22.7	59.8	Na-Cl
M21	15	8.28	8.56	1017	908	3485	27.3	1814	19.4	63.4	78.7	Na-SO ₄
M22	17	7.36	0.88	251	140	49.2	24.5	216	18.4	12.5	0.92	Na-Cl
M23	10	7.24	1.59	980	28.0	113	13.4	309	16.3	9.37	3.50	Na-HCO ₃
M24	8	7.16	1.06	806	104	35.0	19.3	661	19.0	32.4	20.3	Na-HCO ₃
M25	14	7.31	23.3	835	5536	1486	19.5	3158	22.4	109	152	Na-Cl
M26	12	7.95	1.33	356	112	117	nd	877	21.2	71.6	32.6	Na-HCO ₃
M27	50	7.25	4.18	651	571	190	nd	836	23.3	50.1	22.3	Na-HCO ₃
M28	14	7.88	9.76	321	1142	804	nd	1969	69.8	432	147	Na-Cl
M29	15	7.06	5.35	405	1099	707	45.2	1065	57.7	319	120	Na-Cl
M30	10	7.64	1.41	864	110	164	12.2	320	15.2	33.2	22.1	Na-HCO ₃
M31	50	7.76	3.05	964	244	519	6.50	563	7.59	4.57	2.24	Na-HCO ₃
M32	12	7.29	8.05	1868	1300	43.2	10.1	489	3.12	355	92.2	Na-HCO ₃
M33	10	7.26	5.29	679	762	582	2.30	747	19.5	123	88.4	Na-Cl
M34	12	7.53	1.15	500	85.1	91.2	21.3	268	9.71	19.1	11.3	Na-HCO ₃
M35	8	8.17	2.98	1652	165	116	25.4	549	6.16	3.74	3.90	Na-HCO ₃
M36	10	7.17	11.8	1868	742	1506	2.25	2100	2.71	90.4	150	Na-SO ₄
M37	8	7.55	1.74	920	73.2	108	13.5	823	8.54	15.6	9.30	Na-HCO ₃
M38	20	8.94	6.33	214	1012	1350	nd	994	10.8	18.3	55.8	Na-Cl
M39	15	7.26	10.0	463	2634	1258	72.1	1029	67.8	498	202	Na-Cl
M40	52	7.00	19.4	764	4636	1520	23.4	200	54.2	183	182	Mg-Cl
M41	65	8.51	24.9	817	5121	1537	39.4	2100	67.9	67.0	144	Na-Cl
M42	12	8.92	1.43	668	26.0	35.5	21.2	244	11.5	8.06	3.37	Na-HCO ₃
M43	8	7.28	1.81	618	234	74.2	4.50	765	32.4	57.6	16.3	Na-HCO ₃
M44	11	7.07	2.50	723	450	90.1	56.1	223	30.3	132	64.6	Ca-Cl
M45	12	6.81	14.4	298	5674	26.3	42.4	459	28.6	1100	400	Ca-Cl

Nd: non detected. All concentrations are expressed as mg L⁻¹.

FIGURE 2: Piper diagram showing the chemical compositions of groundwater samples.

($r^2 = 0.91$; $r^2 = 0.69$) and sulfate versus EC and sodium ($r^2 = 0.62$; $r^2 = 0.61$), which is related to the predominance of sodium chloride types in groundwater with higher salinity. Sodium bicarbonate waters are related generally with low salinity samples; in analyzed groundwater samples the EC shows poor correlation with HCO_3^- ($r^2 = 0.21$).

Results of chemical analysis show large variations in chemical composition and also indicate the high salinity of many of the groundwater samples. According to Larroza and Fariña [19], the salinity of groundwater in the basin of the Chaco region is due to the previous existence of a shallow sea of restricted environment, which has left its salts; this geographical feature, called Paranaense Sea, has originated during the Middle and Upper Miocene. The extremely heterogeneous values of EC from groundwater could be explained by the local variation in sedimentary and hydrogeological characteristics [13]. Moreover, the evaporation in arid and semiarid zones favors the increase of salinity and alkalinity [15, 22].

3.2. Total Arsenic and Fluoride. Arsenic is classified as a human carcinogen (Type A) based on sufficient epidemiologic evidence linking increased mortality from liver, kidney, bladder, and lung cancers to drinking As-contaminated water [23]. The provisional guideline value recommended by the WHO [5] for this carcinogenic contaminant in drinking water is $10 \mu\text{g L}^{-1}$ and in Argentina this would be enforced in 2017 [24]. On the basis of this criterion, only 9% (4/45) of groundwater source is within levels recommended for consumption; whereas about 73% (33/45) of all analyzed samples showed As values above $50 \mu\text{g L}^{-1}$ (CAA) [25]. Mean concentration of total arsenic in groundwater was $213 \mu\text{g L}^{-1}$ and maximum was $1990 \mu\text{g L}^{-1}$ (Table 2). The highest As concentration was found in groundwater collected in sample M36. The presence of arsenic in the groundwater samples collected from this region of Argentina is natural; the local geology and rainfall have been shown to have major impact on the variations of As concentration in groundwater.

TABLE 2: Statistical summary of the chemistry of groundwater (major ions and trace elements; $n = 45$) from Comandante Fernández Department, Chaco, Northeast Argentina.

Parameter	Mean	Median	Range	10th percentile	90th percentile	Standard deviation
Depth (m)	22.0	13.0	5.00–220	8.00	50.0	33.1
pH	7.54	7.51	6.50–8.94	6.90	8.22	0.55
EC (mS/cm)	5.27	2.50	0.69–24.9	0.99	13.4	6.28
HCO ₃ [−] (mg L ^{−1})	699	679	135–1868	299	974	376
Cl [−] (mg L ^{−1})	1082	269	14.4–8193	50.1	3835	1832
SO ₄ ^{2−} (mg L ^{−1})	570	209	18.0–3485	43.9	1514	789
NO ₃ [−] (mg L ^{−1})	29.7	14	bdl–200	0.03	53.4	36.1
F (mg L ^{−1})	1.29	1.00	0.10–4.20	0.30	3.08	1.10
Na ⁺ (mg L ^{−1})	875	644	132–5857	214	1907	989
K ⁺ (mg L ^{−1})	23.6	18.4	2.10–110	6.96	56.3	21.5
Ca ²⁺ (mg L ^{−1})	101	28.5	1.40–1100	5.33	274	191
Mg ²⁺ (mg L ^{−1})	53.7	20.3	0.52–400	2.20	149	76.2
S (mg L ^{−1})	49.3	0.57	0.006–724	0.06	125	130
P (mg L ^{−1})	2.70	0.8	0.17–22.9	0.30	8.26	4.41
As (μg L ^{−1})	213	100	7–1990	17.0	500	347
Al (μg L ^{−1})	561	99.0	60.0–17380	60.0	257	2601
Ba (μg L ^{−1})	122	14.0	bdl–1400	2.00	135	211
B (μg L ^{−1})	4020	1970	156–21910	283	7896	5599
Cd (μg L ^{−1})	2.00	2.00	bdl–7.0	1.00	4.00	1.40
Cu (μg L ^{−1})	23.0	6.00	bdl–280	0.10	65.8	48.7
Co (μg L ^{−1})	27.2	3.00	bdl–280	1.40	82.6	6.20
Fe (μg L ^{−1})	276	81.0	bdl–2000	0.10	716	396
Mn (μg L ^{−1})	152	5.00	bdl–3740	0.10	327	574
Mo (μg L ^{−1})	23.9	21.0	bdl–160	3.00	42.0	30.8
Si (μg L ^{−1})	1057	150	bdl–16570	0.40	2415	2803
Sr (μg L ^{−1})	449	86	2.00–4871	15.0	873	873
Se (μg L ^{−1})	1.9	1.00	bdl–10.0	0.1	6.60	2.70
Sb (μg L ^{−1})	5.4	1.00	bdl–111	0.10	9.00	1.7
Ni (μg L ^{−1})	0.9	0.10	bdl–10.0	0.10	3.00	1.90
V (μg L ^{−1})	204	76.0	bdl–2646	11.4	416	431
Zn (μg L ^{−1})	83.8	3.00	bdl–2813	0.10	67.0	487

Different positive correlation were observed in groundwater between As versus HCO₃[−] and Na⁺ ($r^2 = 0.75$; $r^2 = 0.45$), and a negative correlation was found between As and Ca²⁺ ($r^2 = -0.05$). It could be assumed that As is associated with Na–HCO₃[−] system, related to feldspar dissolution [26]. Based on values of pH found in groundwater of this region of Chaco, including data reported from other sites of the region [1, 13, 27], it can be presumed that pH controls As mobility.

The study made by Smedley et al. [28] reveals that highly As(V)-contaminated groundwater in oxidizing environments throughout the world are characterized by high concentration of HCO₃[−] (>500 mg L^{−1}) and SO₄^{2−} (>250 mg L^{−1}) and pH > 7.50. Similar geochemical conditions occur in the Chaco-Pampean plain, like in the arid regions of Santiago del Estero, Córdoba y La Pampa [13, 14, 27]. High As concentrations are common and dominated by As(V), and the groundwater have correspondingly high F concentrations. These general characteristic are consistent with the analyzed

groundwater. However, arsenic speciation is not performed in the present study.

On the other hand, smaller quantities of fluoride ion in the order of 1 mg L^{−1} in ingested water are usually considered to have a beneficial effect by lowering the rate of occurrence of dental caries. Excessive intake (>1.5 mg L^{−1}) would results in pathological changes in teeth and bones, such as mottling of teeth or dental fluorosis, along with metabolic changes reported on soft tissues such as thyroid, reproductive organs, brain, liver, and kidneys [29].

The WHO guideline value for F concentration in drinking water is 1.5 mg L^{−1} [5], whereas the Código Alimentario Argentino (CCA) [25] establishes a limit that varies according to the average temperature of the place (1 mg L^{−1} for an average temperature of 21.5°C in the area under study). The distribution of F concentrations is heterogeneous and similar to As. A positive correlation was observed between As and F with $r^2 = 0.50$. The analyzed groundwater, 31% (14/45) of

the samples exceeded the WHO guideline value of 1.5 mg L^{-1} [5]. About 47% of all analyzed samples showed F values above 1 mg L^{-1} recommended by CAA (Table 4). Similar correlations between As and F were also observed in groundwater from neighboring Santiago del Estero [13], Santa Fe [14], and Salta Provinces [30].

In the same way as arsenic, the F rich water is characterized by high concentration of Na^+ and low concentration of Ca^{2+} and Mg^{2+} ($r^2 = 0.45$; 0.09 and 0.16 ; resp.). Fluoride is a highly reactive element that combines with other elements in covalent and ionic bonds. It is mainly found in alkaline rocks and alkaline soils, fluorite being the principal component. Gomez et al. [27] explain that the processes that could control the low relationship between F and Ca^{2+} and the positive relationship between F and bicarbonate ($r^2 = 0.24$) would be the balance equation relating calcite and fluorite when both are in contact with water.

As and other trace elements such as V, Mo, U, and minor elements such as B and F are presumed to have their original source in volcanic ashes originated from the volcanism in the Andes (5–25% in the loess-type sediments of the Chaco-Pampean plain) [9]. The main components of these sediments are feldspars, quartz, volcanic glass shards, and minor amounts of muscovite and calcite. The composition of volcanic glass is typically rhyolitic, containing a high concentration of F, As, V, and B among other trace elements [28].

3.3. Other Trace Elements. A series of various trace elements, including Ag, Al, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, S, Sb, Se, Si, Sr, Ti, V, and Zn were also determined in the studied groundwater. The concentrations of target elements are summarized in Table 3. Among all 23 target analytes, concentrations exceeding the WHO recommended drinking water limits (in parentheses) were found for B ($2400 \text{ } \mu\text{g L}^{-1}$), Ba ($700 \text{ } \mu\text{g L}^{-1}$), Cd ($3 \text{ } \mu\text{g L}^{-1}$), and Sb ($20 \text{ } \mu\text{g L}^{-1}$). Table 4 shows the percentage of groundwater samples exceeding these WHO and CAA elemental concentration guidelines. On the other hand, concentrations of Sn, Co, Cu, Ni, S, Se, Sr, V, and Zn were very low. Silver, beryllium, chrome, selenium, lead and titanium are not included in Tables 2 and 3 because these elements were never found above respective quantification limits.

From the samples investigated, only one (M45) showed elevated value of barium ($1400 \text{ } \mu\text{g L}^{-1}$) than in the WHO drinking water guideline ($700 \text{ } \mu\text{g L}^{-1}$) with an average value of $122 \text{ } \mu\text{g L}^{-1}$ (Table 2).

In small quantities, B is essential for healthy bones, joint function, and the metabolism of steroidal hormones. Boron deficiency seems to affect calcium and magnesium metabolism and affects the composition, structure, and strength of bone [31]. The concentrations of boron (B) ranged from 1560 to $21910 \text{ } \mu\text{g L}^{-1}$ with an average of $4020 \text{ } \mu\text{g L}^{-1}$ (Table 2). Boron concentration in the 44% (20/45) of the samples exceeds the WHO and 78% (35/45) of the samples exceeds the CAA standard limits for drinking water (Table 4). The highest concentration of boron was observed in sample M40 which is associated with the largest value

of EC ($19371 \text{ } \mu\text{S cm}^{-1}$). In general, the presence of boron in groundwater depends on its salinity (represented as EC), such that it increases with increasing salinity [32]. In this study, a positive correlation between EC and boron ($r^2 = 0.64$) suggests that boron might be associated with the salinity of these samples. Hence, the salinity mainly reflects the variation of Cl^- concentration, with a strong linear correlation ($r^2 = 0.91$) between EC and Cl^- , suggesting that the increase of Cl^- concentration contributes to increase in EC value. The hydraulic conductivity, salinity, type of clay sediments, pH and temperature are the crucial factors that determine boron mobility in the groundwater system [32]. Boron was strongly correlated with Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , and As, probably due to their common origin. The correlation between B and As is often observed in groundwater [1, 13].

Our results indicate that approximately 31% of the groundwater samples tested exceeded the CAA criteria of $300 \text{ } \mu\text{g L}^{-1}$ for total Fe in drinking water. The highest total Fe concentration ($2000 \text{ } \mu\text{g L}^{-1}$) appeared in sample M38. In general, Fe concentration was low in the studied groundwater samples; only fourteen samples had higher Fe with a mean value of $276 \text{ } \mu\text{g L}^{-1}$ and median value of $81 \text{ } \mu\text{g L}^{-1}$. On the other hand, weaker correlation is observed between Fe and As in groundwater ($r^2 = 0.17$). Moreover, almost all groundwater with high Fe concentration ($>300 \text{ } \mu\text{g L}^{-1}$) contained total As concentration over $10 \text{ } \mu\text{g L}^{-1}$ (Table 3).

The concentration of dissolved Al varied between 60.0 to $17380 \text{ } \mu\text{g L}^{-1}$ with a mean value of $561 \text{ } \mu\text{g L}^{-1}$ (Table 2). A 16% (7/45) exceeded the $200 \text{ } \mu\text{g L}^{-1}$ CAA drinking water guideline. However, the mean concentration of Al decreases significantly down to $178 \text{ } \mu\text{g L}^{-1}$ (median $98.5 \text{ } \mu\text{g L}^{-1}$), if the anomalous of sample M24 is excluded. Also Aluminum shows no correlation with As ($r^2 = -0.06$).

Manganese exceeded the $100 \text{ } \mu\text{g L}^{-1}$ CAA drinking water guideline value in 13% (6/45) of the samples (Tables 3 and 4). The highest Mn concentration ($3740 \text{ } \mu\text{g L}^{-1}$) was found in sample M32. However, the mean concentration of Mn decreases significantly from 152 to $70.0 \text{ } \mu\text{g L}^{-1}$ (median $5.00 \text{ } \mu\text{g L}^{-1}$), if the anomalous value of this sample is excluded. Manganese shows no correlation with As ($r^2 = -0.07$). Mn is known as an essential element for human survival, serves as a catalyst and cofactor in many enzymatic processes involved in the synthesis of fatty acids and cholesterol. The chronic ingestion of Mn in drinking water is associated with neurologic damage [33]. Moreover, manganese is a known mutagen [34].

Many samples have Fe, Al, and Mn concentrations below detection limits and most have below CAA guideline value. However, concentrations are higher in a few samples (Table 2). Smedley et al. [1] suggest that at the pH of the groundwater, the high concentrations for these elements trace are most likely due to presence of colloidal particles. As the groundwater are oxidizing, solubility of Fe, Al, and Mn oxides is low and concentrations of dissolved Fe, Al, and Mn are, therefore, mostly low.

The processes of dissolution and release from oxides and oxyhydroxides, mainly Al, Mn, and Fe, control the presence

TABLE 3: Trace element composition of groundwater samples from the Comandante Fernández Department, Chaco.

Sample ID	As _(tot)	F	Al	Fe	Mn	B	Ba	Mo	Si	V	Cd	Sr	Co	Ni	Zn	Cu	S	P _(tot)	Sb
QL	5.00	0.10	10.0	10.0	5.00	1598	10.0	126	bql	83.0	5.00	73.0	10.0	bql	bql	bql	0.025	0.10	2.50
M1	500	1.90	110	60.0	5.00	1598	bql	126	bql	83.0	5.00	73.0	bql	bql	bql	bql	11.0	0.80	bql
M2	25.0	0.50	120	40.1	bql	310	156	bql	309	45.0	bql	420	bql	bql	bql	bql	2.00	0.30	bql
M3	150.0	1.80	90.0	160	3.00	875	bql	bql	bql	10.0	bql	691	bql	bql	30.0	bql	107	2.90	bql
M4	15.0	0.30	100	bql	bql	206	bql	bql	bql	22.0	bql	290	bql	bql	bql	bql	7.00	0.30	bql
M5	127	0.74	220	bql	9.00	811	79.1	42.0	227	119	bql	594	bql	bql	41.0	bql	0.20	0.90	bql
M6	58.0	0.80	110	bql	bql	297	10.0	bql	bql	44.0	bql	498	bql	bql	bql	bql	7.00	0.50	bql
M7	24.0	0.40	100	bql	bql	275	48.2	12.0	bql	43.0	bql	230	bql	bql	bql	bql	8.00	0.30	bql
M8	120	1.00	100	bql	6.00	2654	79.0	bql	2099	90.0	3.00	2012	bql	bql	bql	bql	11.0	0.80	bql
M9	178	1.98	130	550	7.00	1550	10.1	99.0	549	163	7.00	81.1	bql	bql	bql	63.0	7.00	0.80	9.00
M10	500	2.60	80.0	220	870	15070	bql	160	16570	39.0	4.00	4871	bql	bql	bql	bql	725	1.90	bql
M11	250	2.24	100	bql	6.00	1387	bql	14.0	480	23.0	bql	641	bql	bql	bql	bql	132	0.50	bql
M12	11.0	0.44	100	bql	19.4	500	62.0	bql	114	53.0	bql	334	bql	10.0	bql	bql	13.0	0.60	bql
M13	95.2	1.10	110	bql	5.00	500	26.9	42.0	bql	76.0	4.00	68.3	bql	bql	bql	bql	10.0	0.30	3.00
M14	116	1.50	110	bql	5.00	665	bql	43.1	bql	65.0	5.00	54.0	bql	bql	bql	bql	7.00	0.70	bql
M15	31.0	0.50	102	50.0	5.00	2449	40.2	30.3	680	570	bql	521	bql	bql	bql	bql	49.0	0.60	bql
M16	29.0	0.40	130	150	5.00	255	51.8	bql	490	11.0	bql	362	bql	bql	bql	bql	26.0	0.30	bql
M17	83.0	1.20	100	bql	bql	1782	40.3	bql	3940	94.0	3.00	1427	bql	bql	bql	bql	113	0.20	3.00
M18	62.0	0.80	70.0	bql	18.2	734	bql	bql	2550	28.0	bql	2510	bql	bql	bql	bql	281	0.60	bql
M19	10.0	0.20	110	bql	5.00	298	14.4	bql	bql	30.0	bql	157	bql	bql	bql	bql	8.00	0.50	bql
M20	112	1.45	100	bql	bql	2316	22.0	10.9	4750	112	3.00	1390	bql	bql	bql	bdl	147	0.40	bql
M21	700	1.90	100	bql	25.4	2470	bql	11.2	353	28.0	bql	1361	bql	bql	bql	bql	415	8.90	bql
M22	10.0	0.20	100	bql	29.2	156	16.9	bql	bql	bql	bql	86.0	bql	bql	bql	bql	6.00	1.50	bql
M23	36.0	0.30	110	bql	bql	630	109	bql	bql	30.0	bql	225	bql	bql	bql	bql	5.00	0.70	9.00
M24	86.0	0.75	17380	310	296	21560	111	bql	1380	12.0	3.00	32.4	bql	bql	321	bql	0.10	0.80	bql
M25	770	1.20	2980	bql	521	6308	bql	bql	1647	22.0	Bql	bql.	bql	10.0	2831	32.0	0.10	2.50	4.00
M26	100	3.40	60.0	110	bql	1800	150	21.0	150	198	3.00	15.0	bql	bql	bql	bql	0.06	1.80	bql
M27	214	4.20	60.0	855	bql	6890	bql	21.3	150	560	3.00	213	280	bql	670	280	0.06	1.10	bql
M28	100	3.40	60.0	428	bql	8450	bql	21.4	150	219	3.00	15.0	22.0	bql	bql	22.0	0.06	6.70	bql
M29	100	0.60	60.0	660	bql	6850	bql	20.8	150	100	3.00	15.0	bql	bql	670	bql	0.06	7.70	bql
M30	244	0.90	60.0	81.0	33.0	3050	185	21.0	150	547	3.00	15.0	bql	bql	24.0	bql	0.06	1.30	25.0
M31	770	3.40	280	1013	23.0	7290	bql	21.0	150	2646	3.00	32.2	bql	bql	bql	bql	0.30	0.30	bql
M32	700	0.10	210	286	3740	5080	63.2	20.9	150	bql	3.00	164	64.0	bql	110	64.0	0.20	2.30	3.00
M33	174	1.70	60.0	734	32.1	2790	69.0	21.0	7540	266	3.00	15.0	bql	bql	270	bql	Bql	2.20	bql
M34	317	0.30	360	575	24.0	1970	11.8	21.4	150	436	3.00	15.0	bql	bql	bql	bql	0.40	0.60	bql
M35	1073	0.30	60.0	194	bql	6340	30.1	20.5	150	1249	3.00	15.0	120	bql	490	120	0.06	0.30	30.0
M36	1990	4.25	60.0	510	13	5580	bql	21.0	150	251	3.00	288	24.0	bql	13.0	bql	0.06	5.30	3.00
M37	200	0.30	570	606	13	1290	113	21.0	150	387	3.00	20.3	240	10.0	16.0	670	0.60	0.50	bql
M38	150	1.90	60.0	2000	bql	3710	bql	21.0	150	38.0	3.00	20.0	95.0	bql	bql	bql	0.06	0.30	3.00
M39	20.0	0.50	60.0	300	bql	4830	14.0	21.0	150	104	3.00	20.0	bql	bql	bql	670	0.06	9.90	14.0

TABLE 3: Continued.

Sample ID	As _(tot)	F	Al	Fe	Mn	B	Ba	Mo	Si	V	Cd	Sr	Co	Ni	Zn	Cu	S	P _(tot)	Sb
M40	20.0	0.50	60.0	689	bql	21910	bql	21.0	150	124	3.00	20.0	bql	bql	bql	24.0	0.06	1.30	3.00
M41	150	1.50	60.0	988	bql	21580	bql	21.0	150	176	3.00	30.2	bql	bql	bql	bql	0.06	1.10	3.00
M42	130	0.80	60.0	426	bql	1970	bql	21.0	150	345	3.00	369	180	bql	270	111	0.06	0.20	3.00
M43	150	1.40	60.0	70.0	431	1030	107	21.0	150	bql	3.00	bql	55.0	bql	22.0	27.0	0.06	0.80	bql
M44	100	1.20	60.0	80.0	bql	2600	289	21.0	150	191	3.00	bql	bql	bql	bql	bql	0.06	4.80	bql
M45	200	1.60	60.0	262	331	240	1400	21.0	150	35.0	3.00	bql	bql	bql	110	49.0	0.06	2.30	bql

QL: quantification limit; bql: below quantification limit; all concentrations are expressed as $\mu\text{g L}^{-1}$ excepted for F, S, and P expressed as mg L^{-1} .

TABLE 4: Risk-based drinking water criteria and the percentage of groundwater samples exceeding these criteria.

Element	Risk-based drinking water criteria		Percentage of groundwater samples exceeding these criteria	
	WHO*	CAA**	WHO	CAA
As ($\mu\text{g L}^{-1}$)	10***	50	91	73
Al ($\mu\text{g L}^{-1}$)	not established	200	NA	16
B ($\mu\text{g L}^{-1}$)	2400	500	78	78
Ba ($\mu\text{g L}^{-1}$)	700	None	2	NA
Cd ($\mu\text{g L}^{-1}$)	3	5	13	2
Cr ($\mu\text{g L}^{-1}$)	50***	50	0	0
Cu ($\mu\text{g L}^{-1}$)	2000	1000	0	0
Fe total ($\mu\text{g L}^{-1}$)	not established	300	NA	31
F (mg L^{-1})	1.50	1.00	31	47
Mn ($\mu\text{g L}^{-1}$)	not established	100	NA	16
Ni ($\mu\text{g L}^{-1}$)	70	20	0	0
Pb ($\mu\text{g L}^{-1}$)	10***	50	0	0
Sb ($\mu\text{g L}^{-1}$)	20	20	4.5	4.5
Se ($\mu\text{g L}^{-1}$)	10***	10	0	0
Zn ($\mu\text{g L}^{-1}$)	not established	5000	NA	0

NA: not applicable.

*WHO: World Health Organization, have not established risk-based drinking water criteria for Al, Ag, Be, Bi, Co, Fe, Mn, Mo, Si, Sr, Ti, V, and Zn.

**CAA: Código Alimentario Argentino.

***Provisional guideline value.

and mobility of As and F in groundwater [1]. Kim et al. [35] suggested that the cocontamination of As and F observed in oxidizing aquifers in many countries is associated with the desorption from the Fe-(hydr) oxides by the pH increases. The correlations between As and F are generally very high in those aquifers because the As released from Fe-(hydr) oxides does not readily precipitate again in the oxidizing alkaline condition. This is consistent with our observations, as many of the samples show high pH values and moderate coefficient correlation value between As and F ($r^2 = 0.50$). Also, solubility of Al minerals may be enhanced by the complex of dissolved Al with F that is also released from volcanic glasses.

Vanadium in groundwater ranged between <10.0 (QL) and $2646 \mu\text{g L}^{-1}$. The highest V concentration was found in sample M31 (Table 2). Vanadium shows a moderated positive correlation with As ($r^2 = 0.42$) and is likely to be derived from similar mineral sources (secondary Fe and Mn oxides) under the high pH conditions [1]. Our results also indicate that Mo in general appears in low concentrations (Table 3). Molybdenum is weakly correlated with As ($r^2 = 0.20$).

Gomez et al. [27] suggest that V, U, B, and Mo are enriched in volcanic materials and are mobilized as vanadate, molybdate, borate, and so forth, under oxidizing conditions. Alternatively, they are mobilized in alkaline solutions under

conditions of high pH and high HCO_3^- , controlled by carbonate reactions, (e.g., the F may be forming anionic complexes with B, Fe, and Al).

Antimony (Sb) is ubiquity a Group V of the periodic table and is similar to As in aspects as chemical behavior and toxicity to animals [5]. The Sb concentrations in studied samples exceeded $20 \mu\text{g L}^{-1}$, WHO and CAA drinking water guideline values in 4.5% (2/45) of the analyzed samples (Tables 3 and 4).

Cadmium reaches a maximum of $7.0 \mu\text{g L}^{-1}$ with most samples being less than $3.0 \mu\text{g L}^{-1}$. As this element forms cationic species in solution, its mobilization is not favored under the alkaline conditions of the groundwater [1].

The presence of arsenic and heavy metals in the samples collected from this region of Chaco in Argentina may be due to local geochemical conditions that facilitate the transfer of naturally occurring arsenic from soil and sediment to the water. The people in the Comandante Fernández Department may be overexposed not only to As, but also to B, Cd, Mn, and F. Adverse health effects may appear in coming years. This problem is a serious concern for the local population.

4. Conclusions

The results of the current study indicate that approximately 91% of the groundwater samples used for consumption by human and livestock, from the Comandante Fernández Department (Chaco province, Argentina), exceed the WHO provisional guideline value of $10 \mu\text{g L}^{-1}$ As, recommended as a maximum allowable level in potable water.

Evaporation, potentiated in arid, and semiarid zone, favors the increase of salinity and alkalinity, the results is a low quality of the resource but is not conditioning the concentration of As and F. Hence, factors other than evaporation, such as desorption from metal oxides and possibly silicate reaction, could be likely controlling As and F mobilization. Furthermore arsenic, associated trace elements may be absorbed on the surface of iron and aluminum oxides and oxyhydroxides (hematite, goethite, $\text{Fe}(\text{OH})_3$, and gibbsite), limiting the mobility of trace elements. Groundwater with high pH values and high concentration of bicarbonate would facilitate the dissolution of volcanic glass; thus, trace elements may enter groundwater cycles, forming anionic complexes in alkaline solutions and acquiring great mobility.

The hydrochemical trace in the region is characterized by high salinity and high As and F concentrations, which is related to volcanism and hydrothermal activity from the Andes. This association is often linked to presence of B, Cd, Mo, Mn, and V, indicating their common origin in the volcanic glasses.

Due to high As concentrations found in groundwater, serious health risk must be considered. The population in the area may be exposed to the chronic toxicological effects of hydro arsenicism and fluorosis, increasing the risks of contracting other diseases derived from them. Since the groundwater studied here constitutes the principal source of drinking water in the zone, mitigation efforts should not be limited to As health risks from other toxic elements present in drinking water must also be addressed in this region.

Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper. Its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

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