CHEMICAL QUALITY OF URBAN AND RURAL DRINKING WATER, IN TARAPACA, NORTHERN ARID AREA OF CHILE

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ABSTRACT

The population of Tarapacá, northern Chile, is supplied with drinking water of underground origin. The objective of this study was to evaluate the chemical quality of water for human consumption in nine urban and rural locations and its compliance with current norms (temperature, salinity, alkalinity, dissolved majority ions, As and B). Geochemical classifications were deduced to consider the origin and relationships between waters. Moreover, five water stability indicators were evaluated to estimate potential corrositivity (B/Cl^- ratio, Cl^-/SO_4^{2-} ratio and Larson ratio) and calcareous inlays formation (Langelier Saturation Index and Ryzman Stability Index). The samples analyzed were determined had mild temperatures, slightly alkaline, with a wide range of values of salinity (74.7 - 1287 mg L^{-1}). The hydrogeochemical results confirmed four water types: Na^+/HCO_3^--Cl^--SO_4^{2-}, Na^+/SO_4^{2-}, Na^+-Ca^{2+}/SO_4^{2-}, and Na^+-Ca^{2+}/Cl^--SO_4^{2-}. The 168 samples reached 100% of the degree of compliance of NCh409, except in the wells of Colonia Pintados, where As concentration exceeded 13 to 30 times the norm. Sulphate and B exceeded international standards. The water taste deterioration can be attributed to high concentrations of SO_4^{2-}, Cl^-, Ca^{2+}, and B. Finally, water stability indexes determined the capacity for severe corrosively potential and formation of light calcareous deposits. The internal regulations of the country must harmonize and admit substances suggested by the WHO.

Key words: water chemistry quality, geochemistry, stability indexes, regulations.

INTRODUCTION

For the population of the Tarapacá region (360000 inhabitants), located in the Atacama Desert of northern Chile, groundwater is the permanent main water resource, a common feature in many arid areas of the world[1]. The geomorphological and geological peculiarities of this zone have favored the accumulation of underground water volumes (27,000 Mm^3) at the Pampa del Tamarugal basin, whose age has been defined between recent and 10,000 years[2]. The local water utility, Aguas del Altiplano S.A. (the sanitary company), has several legally authorized water abstractions for the extraction of groundwater in this basin, with a total extraction of 2100 L s^{-1} and the subsequent production of drinking water from five treatment plants[1]. The extreme aridity of the zone conditions the abundance of inorganic compounds, finding groundwater enriched in dissolved majority ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- y CO_3^{2-}) and a variety of trace elements, mainly of geothermal and volcanic origin (Si, Li, B, As)[1].

The quality of groundwater as a source of supply for water utilities can significantly influence galvanic corrosion due to the increase of chloride and the formation of calcareous deposits on the piping surface of distribution networks or containers containing it[3,4,5]. To assess and explain this state or behavior, water stability indicators are used, such as meters of calcareous formations: Langelier Saturation Index (LSI), Ryzman Stability Index (RSI) or aggressiveness index[5]. For its part, an increase in the concentration of Cl^- ion in water promotes galvanic corrosion, and its evaluation considers the Cl^- and SO_4^{2-} mass ratio (CSMR) and the ratio of gram equivalents between Cl^- plus SO_4^{2-} and HCO_3^- ions, known as Larson ratio (LS)[3,5].

Water for public consumption must be free of any pollutant and legislation promotes legal protection of the resource from the point of capture until is supplied to consumers, a crucial issue that guarantees health assurances to access to water[6]. The World Health Organization (WHO) publishes quality guidelines and suggested maximum values of admissible concentrations for a variety of parameters[7] and have served as guidance for the development of the internal regulations globally. In Chile, at the Normalization Institute[8], the regularization of drinking water quality is in force by the Chilean Norm number 409 (NCh409), in order to provide satisfactory quality drinking water and minimize the risk of contamination.

The population of Tarapacá region consumes water of underground origin, however, there is not information available to date of its chemical composition. The objective of this study was to evaluate in the communes of Iquique, Alto Hospicio, Pozo Almonte and Pica and their surrounding rural towns: Caleta Los Verdes, La Tirana, La Huayca, Colonia Pintados and Matilla, the chemical quality of drinking water and its compliance with current norms. To this end, physicochemical characterizations of temperature, pH, salinity, dissolved majority ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- y CO_3^{2-}), As, and B concentrations were carried out. Geochemical classifications were deduced to consider the origin and relationships between waters. Furthermore, water stability indicators were evaluated to estimate potential corrosively (B/Cl^- ratio, Cl^-/SO_4^{2-} ratio and Larson ratio) and calcareous inlays formation (Langelier Saturation Index and Ryzman Stability Index) in a total of 168 representative samples.

EXPERIMENTAL

The study area in the Tarapacá region (42,226 km^2), the second northernmost part of Chile that extends between 18° 56' and 21° 36' South and 68° 24' West to the Pacific Ocean, comprised an extension of four communes of the Provinces of Iquique and Tamarugal (Table 1): that includes four cities (Iquique, Alto Hospicio, Pozo Almonte and Pica) and five rural towns (Caleta Los Verde, La Tirana, La Huayca, Colonia Pintados and Matilla).

Iquique is a port city and capital of the same name Province; it is located at 1.25 m above sea level (asl) on a rocky terrace. The Alto Hospicio commune is in the Cordillera de la Costa at 1000 m asl and is part of the Iquique Province, as well the rural town of Caleta Los Verdes, on the coast, located 50 Km south from Iquique. Both communes have a high demographic concentration and economic activities of services. Pozo Almonte is the capital city of the Province of Tamarugal, its extensions include the rural towns of La Tirana, La Huayca, Colonia Pintados, among others, at the Quebrada Guatacondo. The commune of Pica is located at 2,000 m asl, extending until the High Plateau. At present, the oasis of Pica (which includes the town of Matilla) has natural thermal springs and is one of the best places for the plantation of citrus fruits and tropical fruits in the region.

The field campaigns were carried out in June 2016, eighty-four sites were randomly selected to obtain water samples from the supply network and from wells (only in Colonia Pintados), distributed from the coastal edge to the pre-Cordillera (Table 1). The number of samples in each locality was determined according NCh409 in agreement with the number of inhabitants[8]. Authorizations were requested in schools, police stations, rural posts, restaurants, homes, and public squares. The tap water (3 L) was allowed to run for about 60 s before disposing of it in high-density polyethylene containers. In the wells of Colonia Pintados, the samples were collected directly from the extraction systems (pump) according to sampling protocols for groundwater[9].

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Table 1. Sampling localities (symbology used), number of sites and population by communes of the Tarapacá region.

Localities	N° of sites	Population	Communes	Province
Iquique (IQ)	20	183997	Iquique	**Iquique**
Caleta los Verdes (CV)	8			
Alto Hospicio (AH)	25	94254	Alto Hospicio	
Pozo Almonte (PA)	9	11466	Pozo Almonte	**Tamarugal**
La Tirana (LT)	6			
La Huayca (LH)	4			
Colonia Pintados (CP)	2			
Pica (P)	6	3498	Pica	
Matilla (M)	4			

In the samples obtained, temperature (T), electrical conductivity (EC) and pH were measured with a Hanna Instruments HI 9829 multisensor equipment.

The chemical analyzes in the laboratory were carried out in duplicate, following the APHA protocols[9]: samples were filtereded on a Merck membrane (<0.45 μm), analyzes were immediately developed to quantify HCO_3^- and CO_3^{2-} ions, by a volumetric acid-base method. The analysis of Total Dissolved Solids (TDS) were performed by the gravimetric method at 105° C. The determination of As concentration was carried out using Atomic Absorption Spectrometry coupled to a hydride generation mode (HG-AAS), in Perkin Elmer PinAAcle 900H equipment and a FIAS 100 hydride generator, at 193 nm, after pre-reduction from As (V) to As (III), with KI in the medium of Ascorbic acid and concentrated HCl. A sample (500 μL) was pumped simultaneously with 10% HCl and 0.2% $NaBH_4$ in 0.3% NaOH. For the determination of B concentration, the azomethine-H method was used and measured in the Lambda 25 UV-Vis spectrophotometer, using B-tritrisol solution (1000 mg L^{-1}, Merck). The analysis for Na, K, Mg and Ca metals were determined by Flame Atomic Absorption Spectroscopy (F-AAS), in Perkin Elmer PinAcle equipment and their corresponding hollow cathode lamps. For Na, KNO_3 2000 mg L^{-1} suppressor solution was used and measured at 589 nm; for K, Cs concentration at 10000 mg L^{-1} was used as a suppressor at 769.9 nm; for Ca and Mg, La 10000 mg L^{-1} solution was used as suppressor and measured at analytical wavelengths of 422.7 and 285.2 nm, respectively. Chloride determinations were carried out using the Mohr method and the quantification of SO_4^{2-} ion by a gravimetric method with $BaCl_2$ 10 % solution, as a precipitating reagent. The analyzes were done in duplicate and the quality of the results and validation of protocols by HG-AAS and HG-AAS were evaluated by graphite furnace-AAS Mixed Standard Solution (atomic spectroscopy standard PerkinElmer Pure).

The determinations of the indicators of potential corrosively and stability were calculated according to the following equations[3,4,5]:

Boron and Chloride mass ratio: $\frac{B}{Cl^-} = (Boron\ (\mu g/L))/(\text{Chloride}\ (mg/L))$

Chloride and Sulphate mass ratio: $CSMR = (\text{Chloride}\ (mg/L))/(Sulphate\ (mg/L))$

Larson ratio (LS): $LS = (\text{Chloride}\ (milieq/L) + (Sulphate\ (milieq/L))/(\text{Bicarbonate}\ (milieq/L))$

Langelier Saturation Index (LSI):

$$LSI = pH - pHs$$

$$pHs = (90.3 + (log10(STD) - 1)/10) + (130.12 * log(°C + 273) + 340.55)) - ((log(Ca\ como\ CaCO3) - 0.04$$

Ryzman Stability Index (RSI): $RSI = 2pHs - pH$

The statistical analysis included the statistical description of the water quality parameters (median, mean, standard deviation and range) and the correlation analysis. The geochemical relations and the multivariate analysis (hierarchical conglomerate) were used. All the analyzes were carried out through the program R 3.4.1, using VEGAN and STATS package (R Development Core Team 2018). To make comparisons of the physicochemical parameters and indicators of potential corrosivity and stability among all the sites, cluster analysis was carried out using Euclidean distance. The variables were combined with the unweighted average ligament grouping method (UPGMA)[11]. For the validation of the eight major ions, only those samples with an ionic balance error of less than ± 10% have been considered, although in Europe it is advisable only those with a lower error ± 5%[9,12].

RESULTS AND DISCUSSION

The characterization of basic statistics for the physicochemical parameters obtained in the field and the concentrations of TDS, As, and B in the water samples, of the nine localities under study, are summarized in Table 2. The average temperature records (21-26° C) indicated mild waters, with slight variation depending on the locality, being the highest in the supply network of the town of Matilla (28.8° C), followed by Colonia Pintados, Pozo Almonte, La Huayca and La Tirana, and the lowest in Pica (15.4° C), all these localities of the Province of Tamarugal. In Caleta Los Verde, Alto Hospicio and Iquique, water samples presented similar temperatures values. The water temperature can be influenced mainly by the temperature of the environment, solar radiation and the transfer of heat from the air that induces its increase. The water temperature also depends on the season of the year and the time of day, since the Tarapacá region is, in most of it, an arid zone with almost zero rainfall in its coast, Cordillera de la Costa or Central Depression. Although precipitations can increase gradually with the height at the pre-cordillera (50 - 250 mm year^{-1}) [1], the evaporation far exceeds the rainfall and reaches up to 3000 mm year^{-1}.

The pH in all water samples complies with both NCh409 and WHO standards, which established a normal value interval between 6.5-8.5 for natural waters[7,8]. The supply waters of Pica and Matilla and also those from Iquique, Caleta Los Verde and Pozo Almonte had similar pH values, a slightly alkaline waters reach the highest value in the groundwater of the wells of Colonia Pintados. The buffer capacity of carbonate rocks, the increase in the solubility of $CaCO_3$ in rocks and minerals, and the presence of borates and silicates explain the observed pH distribution[9].

The salinity of the water samples, expressed as EC and TDS, are relevant tools to express whether the waters are classified as freshwater or brackish[9,12], and the waters under study had a wide range values (113 to 1,589 µS cm^{-1} and 74.7 to 1,287 mg L^{-1}, respectively) and the correlation between both variables was positive and highly significant ($p < 0.005$) (Figure 1). The concentration of TDS is regulated by NCh409[8] to a maximum content in drinking water of 1,500 mg L^{-1} and by WHO[7] to 1,000 mg L^{-1}. All the samples tested reached 100% degree of compliance of NCh409, but only four localities (Alto Hospicio, La Huayca, Pica and Matilla) did it with the recommended by WHO. The commune of Iquique presented water with the highest salinity and classified as brackish, in contrast, the population from Pica consumes water with considerable lower salinity. The towns of Pozo Almonte, La Tirana, and Alto Hospicio presented water supply with values in the limit of the concentration recommended by WHO (1,000 mg L^{-1}), which separates those waters classified as freshwater from the brackish ones[9,12]. Only variations in the values of TDS were found in waters from La Huayca (40-90 mg L^{-1}) and Alto Hospicio (866-233 mg L^{-1}), probably due to water mixtures in the supply networks. In the rural town of Colonia Pintados, the groundwater used by the community from wells, corresponded to freshwater and relatively diluted.

Table 2. Basic statistics for the physicochemical parameters determined in the field and the concentrations of TDS, Arsenic and Boron**.**

Localities	Statistical	T (°C)	EC (µS/cm)	pH (U)	TDS (mg/L)	As (mg/L)	B (mg/L)
IQ	Median	24.1	1554	7.59	1214	0.013	5.31
	Mean	23.9	1554	7.60	1219	0.013	5.32
	SD	1.0	21	0.16	25	0.002	0.22
	Min	20.8	1508	7.23	1170	0.011	4.92
	Max	25.9	1589	7.88	1274	0.016	5.83
CV	Median	20.6	1557	7.50	1258	0.015	5.18
	Mean	20.5	1558	7.50	1252	0.014	5.09
	SD	0.1	7	0.04	27	0.002	0.22
	Min	20.4	1551	7.44	1211	0.011	4.76
	Max	20.6	1573	7.54	1287	0.016	5.31
AH	Median	20.7	1119	7.38	882	0.024	1.81
	Mean	20.7	1134	7.43	913	0.024	2.00
	SD	0.4	82	0.17	80	0.003	0.99
	Min	20.1	1103	7.20	866	0.012	1.73
	Max	21.6	1527	7.89	1233	0.029	6.76
PA	Median	24.3	1294	7.62	1005	0.007	4.25
	Mean	23.8	1275	7.63	1000	0.007	4.32
	SD	2.2	32	0.09	23	0.002	0.13
	Min	20.7	1200	7.49	945	0.005	4.13
	Max	26.6	1300	7.74	1024	0.011	4.53
LT	Median	21.3	1361	7.25	1067	0.010	4.69
	Mean	21.1	1347	7.32	1059	0.012	4.68
	SD	2.8	53	0.31	39	0.005	0.22
	Min	17.6	1248	7.06	994	0.007	4.34
	Max	25.6	1389	7.89	1097	0.019	5.00
LH	Median	22.9	893	7.34	699	0.019	1.95
	Mean	22.3	827	7.35	647	0.027	1.85
	SD	1.8	223	0.67	176	0.028	0.35
	Min	19.7	514	6.68	401	0.004	1.38
	Max	25.6	1389	8.04	790	0.067	5.00
CP	Median	24.4	611	8.12	455	0.642	2.23
	Mean	24.4	611	8.12	455	0.642	2.23
	SD	2.2	10	0.23	6	0.366	0.14
	Min	22.8	604	7.95	450	0.384	2.13
	Max	25.9	618	8.28	459	0.901	2.33
P	Median	20.3	166	7.87	117	0.004	0.67
	Mean	20.5	174	7.87	125	0.004	0.67
	SD	3.6	61	0.09	47	0.001	0.02
	Min	15.4	113	7.74	75	0.002	0.64
	Max	25.0	284	8.00	212	0.005	0.68
M	Median	27.2	583	7.88	452	0.017	1.70
	Mean	26.2	579	7.87	449	0.019	1.69
	SD	3.1	37	0.07	27	0.006	0.02
	Min	21.8	534	7.78	419	0.016	1.67
	Max	28.7	614	7.93	475	0.028	1.71

T: Temperature; EC: Electrical conductivity; TDS: Total Dissolved Solids

Table 3 shows the concentrations of eight major ions, indicating that dominated ions were SO_4^{2-}, Na^+, Cl^-, and Ca^{2+} in several of the water samples; with the exception of waters from the network supply in Pica and the groundwater from the wells from Colonia Pintados, where HCO_3^- ion was detected in greater proportion. Consequently, the geochemical classification by dominant ions in milliequivalent gram units made us established four types of water:1. Sodium/Bicarbonate Chloride Sulphate ($Na^+/HCO_3^- > Cl^- > SO_4^{2-}$) type, from the water supply network of Pica and the groundwater in Colonia Pintados, which may indicate waters of the same origin.

2. Sodium/Sulphate (Na^+/SO_4^{2-}) type, for waters from Matilla, La Huayca and Alto Hospicio networks. Since they exhibit the same predominance, a similar origin is likely.

3. Sodium Calcium/Sulphate ($Na^+ > Ca^{2+}/ SO_4^{2-}$) type, for waters from Iquique, Caleta Los Verdes and Pozo Almonte.

4. Sodium Calcium/Chloride Sulphate ($Na^+ > Ca^{2+} / Cl^- > SO_4^{2-}$) type, for waters from La Tirana, the increased chloride concentration is probably due to evaporation.

These differences in the chemistry are due to the dilution of groundwater sources by recharge in the pre-cordillera that composes HCO_3^- waters and supplies sectors of Pica, while in other sectors of the Pampa del Tamarugal basin, where water inputs are very scarce and high evaporation rates occur, where high concentrations of SO_4^{2-}, Na^+, and Cl^- ions are found[1,2]. These results are consistent with other studies in arid zones, establishing that the predominance of drinking water ions depends on the origin of the underground source, and in turn, this is influenced by hydrochemical processes that occur in the aquifer, as a consequence of leaching from rocks, evaporation, and recharge[13].

Currently, the maximum concentration for SO_4^{2-} and Cl^- ions allowed by NCh409 are 500 mg L^{-1} and 400 mg L^{-1}, respectively; while WHO suggested that for both anions the maximum concentration is 250 mg L^{-1}. The results obtained for the water samples established a wide range of values (63-469 mg L^{-1} and 53-283 mg L^{-1}, respectively), where the maximum concentration of SO_4^{2-} was detected in Iquique, meanwhile the maximum value for Cl^- was determined in the town of La Tirana.

The NCh409 does not specifically reference values for Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^- nor CO_3^{2-} ions in drinking water; WHO[7] established acceptable maximum values of 200 mg L^{-1} for Na, we determined that all the samples analyzed complied with this norm (133-187 mg L^{-1}). Calcium was detected with its highest value in Iquique (203 mg L^{-1}), this result, together with temperature and alkalinity detected in this water samples, favor conditions for the formation of calcareous deposits. The hardness degree in water acceptable by the population can vary greatly from one community to another, depending on the local conditions of aridity. For K and Mg ions, we determined a direct correlation in their concentrations in several samples, however, K in the analyzed groundwater from Colonia Pintados stands out, where its concentration was thirty times higher than Mg.

The taste deterioration of drinking water is attributed to high concentrations of major ions such as SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, and the nature of these associated ions[7,8]. Taste thresholds ranging from 250 mg L^{-1} and 1000 mg L^{-1} have been determined for Na_2SO_4 and $CaSO_4$ salts, respectively; for NaCl, KCl, and $CaCl_2$ salts thresholds range from 200 to 300 mg L^{-1}, at higher concentrations, it is likely that consumers will detect a salty taste in the water. It is important to emphasize that Na and the temperature of water have an influence on the taste perception thresholds of the samples[7,8].

Table 3. Basic statistics for the concentrations of the major ions (mg L^{-1}).

Localities	Statistical	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}
IQ	Median	186	26.9	172	21.8	193	470	128	ND
	Mean	187	26.9	173	21.4	193	469	128	
	SD	4	0.7	8	1.4	3	8	5	
	Min	182	25.3	164	17.2	189	444	120	
	Max	195	28.3	203	23.1	202	480	139	
CV	Median	163	28.9	159	21.0	194	461	126	ND
	Mean	164	28.7	159	21.1	194	461	127	
	SD	4	0.7	2	0.5	3	6	6	
	Min	156	27.7	156	20.7	189	449	121	
	Max	169	29,5	162	21.9	198	470	138	
AH	Median	177	17.0	68	7.94	113	338	84.8	ND
	Mean	176	17.4	72	8.46	116	342	86.3	
	SD	6	1.8	17	2.63	15	25	8.6	
	Min	154	16.5	63	7.46	110	318	79.4	
	Max	184	25.8	152	21.0	186	456	125	
PA	Median	162	27.0	167	22.5	204	456	130	ND
	Mean	163	24.5	166	22.5	211	449	130	
	SD	3	5.9	1	0.6	16	14	3	
	Min	158	13.7	164	21.2	201	424	125	
	Max	168	29.0	168	23.3	245	459	134	
LT	Median	145	29.3	173	24.0	283	450	158	ND
	Mean	146	30.2	171	23.7	283	445	158	
	SD	6	2.8	6	1.0	26	24	7	
	Min	138	27.7	161	21.8	253	407	150	
	Max	154	34.5	178	24.8	324	469	167	
LH	Median	145	20.7	85.7	6.85	150	336	86.6	ND
	Mean	136	20.7	85.0	6.71	142	319	86.2	
	SD	21	4.4	31.2	1.01	40	77	13.3	
	Min	105	15.4	55.6	5.48	89	220	69.8	
	Max	154	34.5	178	24.8	324	469	167	
CP	Median	144	33.3	20.3	0.83	53.1	111	101	ND
	Mean	144	33.3	20.3	0.83	53.1	111	101	
	SD	8	0.0	0.2	0.01	0.0	0	0	
	Min	139	33.3	20.2	0.83	53.1	111	101	
	Max	150	33.4	20.5	0.84	53.1	111	101	
P	Median	62	1.86	37.4	0.57	49.5	64.3	104	ND
	Mean	61	1.96	37.4	0.67	63.2	62.7	125	
	SD	2	0.43	0.7	0.24	23.1	3.6	36	
	Min	58	1.53	36.4	0.45	45.2	55.4	101	
	Max	64	2.72	38.4	0.97	93.7	64.4	183	
M	Median	158	7.76	67.0	1.32	89.1	253	74.4	ND
	Mean	159	8.06	67.1	1.33	89.0	250	74.4	
	SD	5	2.15	1.2	0.02	0.9	6	1.6	
	Min	155	5.75	66.0	1.32	88.0	241	72.7	
	Max	164	11.0	68.6	1.36	90.0	254	76.3	

ND: not detectable

The concentration of arsenic (Table 2) does not exceed the maximum value established by NCh409 (2006) for the Tarapaca region, since a sanitary resolution exists exclusively due to the high natural concentrations of the metalloid in the region (No. 2987 of the Ministry of Health of Chile, 2007) that granted a term of 10 years to Aguas del Altiplano SA to progressively decrease the permitted arsenic maxima from 0.03 mg / L (since 01.01.2012) to 0.01 mg / L (since01.01.2017) in waters for human consumption in the region. The town of Pica presented the lowest As concentration, confirming the superior quality of its drinking water, followed by Pozo Almonte, La Huayca and La Tirana; the water supply of Iquique had concentration near the maximum accepted. In Colonia Pintados, however, the groundwater used by the community exceeds the current regulations (0.383-0.901 mg L^{-1}), which confirms a potential health hazard for the population. The exposure and toxicity of As is a public health problem in many geographical areas and is determined by several factors, such as the size of the affected area, quantity and chemical speciation of the pollutant[14,15]. There are several records of the high and varied concentration of As in the scarce surface waters of Tarapacá region [1,16] and in the groundwater of the Pampa del Tamarugal basin that exceeds all current regulations[1,2]. Fuentes (2017)[17], reported As concentrations in water sources for sanitary treatment plants between 17 µg L^{-1} and 180 µg L^{-1} of the element.

The B concentrations (Table 2), stands out for its abundance and asymmetric distribution in the supply networks. The localities of Pica, Matilla, Colonia Pintados, and Alto Hospicio, presented lower levels of concentration for this element (0.70-2.2 mg L^{-1}). However, in Iquique and Pozo Almonte, they reached an average of 4.8 ± 0.4 mg L^{-1}. All drinking water in Tarapacá region is in breach of international standards for drinking water, considering that WHO[7] proposes a maximum concentration of 0.5 mg L^{-1} and for the European Union the limit concentration of B is 1.0 mg L^{-1}. In Chile, the NCh409 does not include reference value for this element, however, if there is a maximum admissible concentration for irrigation water, according to NCh1333[18], based on the damage that B causes in plants that are not tolerant to the element[18,19]. It is advisable to analyze the admission to current national regulations of chemical substances whose presence in drinking water can affect health[20]. Boron in water for public consumption in Chile, Germany, the United Kingdom, and USA, range from 0.01 to 15.0 mg L^{-1}, with most values under 0.4 mg L^{-1}. These values are consistent with the ranges and means observed for groundwater and surface waters of arid zones by two factors: firstly, the concentrations depend on B leaching from the surrounding geology and secondly, B is not removed by conventional methods of treatment from underground water[20,21].

The characterization of the basic statistics of water stability indicators is summarized in Table 4. The geochemical B/Cl^- ratio, presented a wide range of values (7.20 - 43.9 µg mg^{-1}) and had a positive linear correlation with salinity and B concentration (Figure 1), an enrichment of B was deduced in the groundwater that are extracted by the sanitary company[21]. The concentration of Cl^- ion, for its conservative nature, reflects with some approximation the initial conditions of the recharge water[21] and in Colonia Pintados, the geochemical relationship reached the highest value (42 ± 3 µg mg^{-1}), which is not related to the quality of freshwater and relatively diluted in Cl^- ion, therefore, it can be affirmed that the origin of B in this sector is due to leaching of the land through which the water circulates. The diluted waters of Pica, present a very low content of B (0.67 ± 0.02 mg L^{-1}), consequently, the geochemical relationship is reduced. In Iquique and Caleta Los Verde, as expected, due to the higher concentrations of B in the sample; similar B/Cl^- ratios values were obtained (27 ± 1 µg mg^{-1}), followed by the waters analyzed from Pozo Almonte, Matilla, Alto Hospicio and La Tirana (20 ± 2 µg mg^{-1}). The increase of B/Cl^- is associated with a greater geothermal intensity of the area[21].

Furthermore, the Cl^-/SO_4^{2-} mass ratio greater than 0.5 units (CSMR> 0.5) establishes that galvanic corrosion is promoted in the distribution systems at the networks due to the concentration of Cl^- in relation to SO_4^{2-} ion[3]. The highest values reached were in the supply networks in Pica (1.02 ± 0.43) and La Tirana (0.64 ± 0.03), which is due to similar concentrations of anions in the water samples from Pica and the increase in Cl^- concentrations in La Tirana water supply networks, respectively. The rest of the supply systems had values over 0.4 which is a value for early warning. There is a slight tendency to decrease the value of CSMR according to the As concentration (Figure 1).

The quantification of the Larson ratio is indicative of corrosion[3,5]. The waters from supply network of Pica and the groundwater of Colonia Pintados presented the lowest and similar LS values, supporting the deduction of a common origin of these. waters The other supply networks presented a similar behavior with LS values between 8-11 units, except those from Matilla supply system, which presented an intermediate condition. The increase in LS value represents anionic contaminants that are produced and concentrated in the water distribution systems, with an emphasis on the drinking water from underground sources with high concentrations of anions[13]. The positive Spearman correlation (Figure 1) was observed between LS values and concentration of B, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and Cl^- ions, in derivation, also with the increase in water salinity. The results are consistent with previous reports done by other authors in arid zones[13].

The values obtained from the Saturation Index of Langelier, presented negative values, except in the supply networks from the cities of Iquique and Pozo Almonte. If the value of the LSI is negative and less than -0.50 units, which is the case of waters from Alto Hospicio and La Huayca, where there is a severe potential of corrosion[3,5], in contrast, the other localities that presented a slight corrosion will could not have difficulties or costs, due to the formation of calcareous incrustations. The networks from Iquique and Pozo Almonte, showed a slight tendency to the formation of calcareous deposits and no correlations were observed with other parameters.

The calculated values for the Ryzman Stability Index, determine a significant corrosion[3,5] for most of the waters under study. The values of the Spearman correlation coefficients (Figure 1) established that the RSI has a direct relationship with salinity, B, Ca, Mg, SO_4^{2-}, Cl^-, and HCO_3^- ions. Usually, in natural waters of the Tarapacá region, the salinity increased with higher levels of Na and K[1,2,16].

The chemical quality and the stability indicators of urban and rural human consumption waters in the Tarapacá region showed clear divergences. This is probably due to that “Aguas del Altiplano SA” uses various points of sources for groundwater collection from the Pampa del Tamarugal aquifer (Canchones, El Carmelo, La Tirana, Chintaguay and Dupliza). Fuentes (2017)[17] noted that the very complex groundwater matrices of the Pampa del Tamarugal aquifer have high concentrations of TDS, SO_4^{2-} ion, hardness, silica, variable Fe/Mn ratio and As contents that exceed the national and international norms currently in force in our country. The chemical quality of the natural waters that are the source for the utility in the Tarapacá region, present a very heterogeneous condition at the level of major ions and trace elements; consequently, they condition the concentrations of the dissolved substances that are not admitted in the current norm in Chile. It is suggested to harmonize the discrepancies between the maximum limits suggested by WHO and those allowed by the NCh409 and also the inclusion of substances, such as B, Na and Ca.

Figure 1. Spearman correlation matrix for the physicochemical parameters and the stability indices of the waters under study (N = 168).

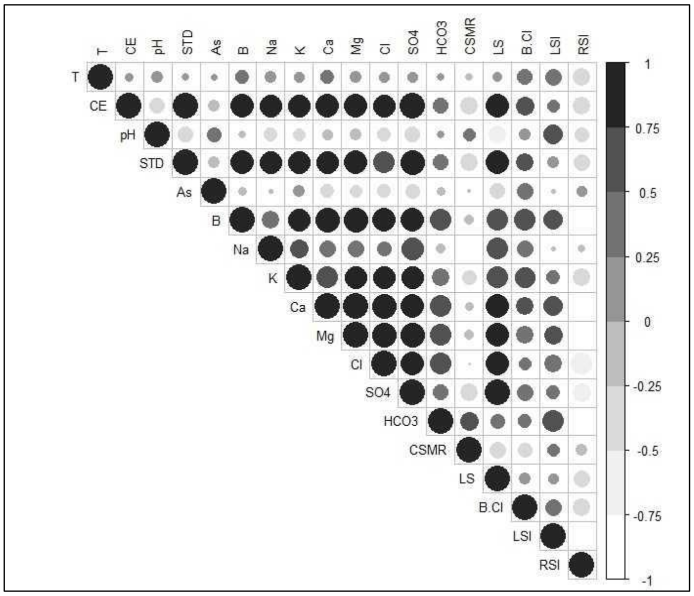

Table 4. Basic statistical for water stability indicators and calculated geochemical relationships.

Localities	Statistical	B/Cl^-	CSMR	LS	LSI	RSI
IQ	Median	27	0.41	10.1	0.13	7.3
	Mean	28	0.41	10.1	0.13	7.3
	SD	1	0.01	0.2	0.16	0.1
	Min	26	0.40	9.8	-0,20	7.0
	Max	30	0.43	10.5	0.45	7.6
CV	Median	27	0.42	10.1	-0,20	7.6
	Mean	26	0.42	10.1	-0,20	7.6
	SD	1	0.01	0.2	0.03	0.0
	Min	24	0.41	9.7	-0,12	7.6
	Max	28	0.43	10.3		7.7
AH	Median	16	0.34	8.3	-0,67	8.7
	Mean	17	0.34	8.3	-0,60	8.6
	SD	4	0.02	0.4	0.20	0.3
	Min	15	0.32	7.9	-0,89	7.7
	Max	36	0.41	9.9	-0,15	9.0
PA	Median	21	0.45	10.2	0.23	7.2
	Mean	21	0.47	10.3	0.21	7.2
	SD	1	0.04	0.5	0.08	0.1
	Min	18	0.44	9.8	0.08	7.1
	Max	22	0.54	11.2	0.29	7.3
LT	Median	17	0.63	11.7	-0,16	7.6
	Mean	17	0.64	11.5	-0,08	7.5
	SD	1	0.03	0.8	0.37	0.4
	Min	15	0.59	10.6	-0,40	6.7
	Max	18	0.69	12.7	0,62	7.9
LH	Median	12	0.44	9.3	-0,52	8.5
	Mean	14	0.44	8.9	-0,55	8.4
	SD	4	0.03	2.9	0.56	0.4
	Min	10	0.41	5.3	-1,10	8.0
	Max	20	0.69	12.7	0.62	8.8
CP	Median	42	0.48	2.9	-0,22	8.6
	Mean	42	0.48	2.9	-0,22	8.6
	SD	3	0.00	0.0	0.20	0.2
	Min	40	0.48	2.9	-0,36	8.4
	Max	44	0.48	2.9	-0,08	8.7
P	Median	13	0.77	2.2	-0,01	8.0
	Mean	12	1.02	2.5	-0,09	8.1
	SD	3	0.43	0.5	0.20	0.3
	Min	7	0.70	2.1	-0,36	7.7
	Max	15	1.69	3.1	0,08	8.5
M	Median	19	0.36	6.8	-0,06	8.0
	Mean	19	0.36	6.8	-0,04	8.0
	SD	0	0.01	0.2	0.07	0.1
	Min	19	0.35	6.6	-0,11	7.8
	Max	19	0.37	6.9	0,06	8.1

CSMR: Chloride and Sulphate mass ratio; LS: Larson ratio; LSI: Langelier Saturation Index; RSI: Ryzman Stability Index

CONCLUSION

The water for human consumption in the Tarapacá region presented a heterogeneous state of chemical quality and stability indicators, depending on different factors: its origin, mild temperature, increased salinity (TDS, SO_4^{2-}, and Ca^{2+}) and alkalinity. The drinking waters from the region were classified as freshwater, except those from Iquique. The potential taste deterioration from the analyzed waters was attributed to high concentrations of SO_4^{2-}, Cl^-, Ca^{2+}, and B, except in Pica. The geochemical classification determined four water types: $Na^+/HCO_3^- - Cl^- - SO_4^{2-}$ for Pica and Colonia Pintados; Na^+/SO_4^{2-} for Matilla, La Huayca and Alto Hospicio; $Na^+ - Ca^{2+}/SO_4^{2-}$ for Iquique, Caleta Los Verde and Pozo Almonte, and $Na^+ - Ca^{2+}/Cl^- - SO_4^{2-}$ for La Tirana. The concentration of As obtained from all the supply networks complied with current regulations. The town of Colonia Pintados had freshwater contaminated with As that exceeds the regulations values up to 30 folds, its population does not have safe drinking water. The B concentration does not meet international standards and reached values of 7 mg L^{-1}. The relatively mild temperatures, slightly alkalinity, and salinity promoted to slight calcareous incrustations, reaching high values the Ryzman Stability Index. There was a tendency to severe corrosion in Alto Hospicio and La Huayca, due to SO_4^{2-} and Cl^- concentrations, and slightly corrosive in Iquique and Pozo Almonte. The internal regulations of the country must harmonize and admit substances suggested by the WHO.

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