

Hydro-chemical characteristics, water quality assessment and water relationship (HCA) of the Amuyo Lagoons, Andean Altiplano, Chile

Lorena Cornejo^{a,b,*}, Hugo Lienqueo^b, Patricia Vilca^b

^aFacultad de Ingeniería, Departamento de Ingeniería Mecánica, Universidad de Tarapacá, Avda. General Velásquez 1775, Arica, Chile, Phone: (56) (58) 2 205075, (56) (58) 2 205406, email: lorenacp@academicos.uta.cl (L. Cornejo) ^bLaboratorio de Investigaciones Medioambientales de Zonas Áridas, LIMZA, Universidad de Tarapacá, Avda. General Velásquez 1775, Arica, Chile

Received 9 November 2018; Accepted 24 February 2019

ABSTRACT

This study was carried out to assess the water quality in the Amuyo Lagoons, Arica & Parinacota Region, Chile. 19 variables were monitored bi-monthly over the period of 12 months by monitoring standardized in situ and laboratory analysis, compared to Chilean regulations. One of the main characteristics of the waters in the Red, Yellow and Green Lagoons is having high total Arsenic content, above 10 mg L⁻¹, which is more likely related to naturally occurring biogeochemical processes associated with the activity of volcanoes. The Wilcox diagram was classified that these waters as C4-S4 indicating high salinity and sodium absorption rate and advises against their use in irrigation. The Stiff and Piper diagram shown an important analogy between the three lagoons, although the HAC analysis demonstrates a greater similarity between the characteristics of the Red and Yellow Lagoon with the Green Lagoon showed some differences. In the PCA analysis, the concentrations of yellow and green lagoons were indicated the following arsenic parameter (13.65 mg L⁻¹ and 15.77 mg L⁻¹, respectively). Although, for the red lagoon concentration is high (18.91 mg L⁻¹). Nevertheless, the untreated water is not suitable for drinking and agriculture purpose. In our knowledge, this is first time we reported that the water characteristics in the area of the Amuyo Lagoons in Chile.

Keywords: Amuyo Lagoon; Water; HCA; PCA; Hydro-chemical

1. Introduction

Environmental problems related to water in arid and semi-arid regions have evolved into an international problem as water is a key factor in satisfying both human requirements and those of productive activities such as mining, livestock and agriculture [1,2]

Thus, to study the composition of hydric resources in order to know their potential use has become essential. Furthermore, a monitoring program is needed to provide a representative and reliable estimation of the quality of surface water bodies [3]. Irrigation of water quality is usually related to salinity and sodium, which are probably the most common indicators, [4] while Wilcox classification [5] and sodium absorption ratio (SAR) are the probed methods for evaluating the most irrigated water [6].

On the other hand, when studying the general water quality, multivariate statistical analysis is a tool which allows adequate studying and interpreting of the physical and chemical information obtained by water characterization techniques. Among these statistical assays, cluster analysis (HCA) is widely used to evaluate surface water quality as it allows relationships to be obtained between parameters and sample zones, thus identifying the possible factors and sources that influence the quality of hydric systems [7] and determining if samples can be grouped into hydrochemical groups [8]. In this way, it is possible to obtain valuable information that can be efficiently used to find rapid solutions to tackle pollution problems [9]. Hydro-chemical diagrams can also be used to compliment the analysis and allow the main characteristics of water source to be sum-

^{*}Corresponding author.

^{1944-3994 / 1944-3986} $\ensuremath{\mathbb{C}}$ 2019 Desalination Publications. All rights reserved.

marized, thereby facilitating classification. Another good option to reduce the number of water parameters when a large number of variables are studied without loosing too much of the information is to apply principal components analysis (PCA) [8].

In this way, a large number of studies that make use of these techniques have been reported. For instance, [10] Junxia et al. studied the enrichments of arsenic and fluoride in groundwater from the Northern China using HCA and [11] Güller et al. assessed the impact of anthropogenic activities on groundwater by means of PCA and clustering.

On the other hand, also water quality dynamics information is valuable. Water quality parameter values vary in space, but in time too and, therefore, monitoring is a key aspect to capture the system dynamics. In this way, it is possible to find many time-related publications about water quality [12–14].

In this sense, in the north of Chile, particularly the Atacama Desert that is considered the most arid area worldwide, the hydric resources are extremely scarce. In the region of Arica and Parinacota, transverse channels are located with a view to the high plateau and with access to the sea. The aquifers are constituted by fluvial quaternary filling in the riverbeds. These unconfined aquifers have thicknesses of not more than 200 m and their feeding is directly related to the rivers. In these sectors, the presence of arsenic (apparently due to volcanic activity) and boron have been detected, both in surface water and groundwater. These systems of closed surface runoff would be interconnected underground through the said aquifers [15]. Many studies have been carried out on water quality in rivers and estuaries in the region. Nevertheless, there is very little knowledge about the water quality in lakes, lagoons and wetlands and the potential to use the water as a resource for human consumption and/or agriculture and livestock activities is unclear. In the recent times, the removal of arsenic was done by several methods such as chemical oxidation (fenton), microbiological oxidation, coagulation-flocculation, photocatalyst, activated carbon, ion exchange, membrane processing, zero valent, adsorption, electrocoagulation and so on [16–31].

The present study deals with the assessment of the water quality in the Amuyo Lagoons, since no previous scientific study of this area has been published. During a 12 month period, 19 variables were monitored bi-monthly by means of standardized in situ and laboratory analysis and an in depth analysis was carried out on the data using different tools.

2. Study area

This work considers a study area, the Amuyo sector in the Andean foothills in the north of Chile that belongs to the Camarones region (Arica & Parinacota), where the Red lagoon (19K 0473441 UTM 7892761), the Green Lagoon (19K 0473382 UTM 7892664) and the Yellow lagoon (19K 0473336 UTM 7892830), also known as the Amuyo lagoons, are located close to the Chuquicamata (5590 m above sea level) and Anocarire (5050 m above sea level) volcanos [32]. These lagoons, which can be seen in Fig. 1, are close to the Caritaya reservoir (19K 0464651 UTM 7897375, 3700 m over sea level). The Red lagoon, 130 m and 116 m away from Yellow and Green lagoons respectively, flows into the Caritaya River. This region is characterized by a cold tundra climate, with a tropical influence which concentrates rainfall in summer, and a high dryness level which increases from south to north [33,34]. The temperature does not normally exceed 5°C with a high diurnal range, while the annual precipitation is low [34]. The Amuyo lagoons correspond to hydro-



Fig. 1. Map Lagoons Amuyo, Región de Arica y Parinacota, Chile, South America.

thermal outcrops, whose temperature ranges from 24.5° C on the surface and rising to 57° C at 11 m depth for the red lagoon. The yellow lagoon has 25° C in the surface and 28° C in the bottom of the lagoon (estimated depth of 6.5 m). For the green lagoon, its temperature is 33° C throughout its depth (depth estimated 3.5 m) [15]. The access to this region is difficult, even more from January to March, while heavy summer rains are present.

3. Methods

3.1. Monitoring parameters and analytical methods

Samples were taken bi-monthly in the four seasons between August 2012 and August 2013, collecting seventeen samples of surface water from the Amuyo Lagoons. Each sample consists of equal volumes collected from 3 locations of the lagoons, which were always the same ones. Temperature, conductivity, pH and total dissolved solids (TDS) were measured in situ by means of a multi-parameter device (HI 9828 model, HANNA Instruments, USA). The instrument was calibrated every day.

Afterwards, the samples were divided into two sets. One set was acidified with HNO₃ to pH < 2 in order to be later analyzed for heavy metals. The other was used to determine cations (Na⁺, K⁺, Ca²⁺, Mg²⁺), anions (Cl⁻, SO₄^{2-,} HCO₃⁻, CO₃⁻, NO₃⁻), total hardness and some other elements such as Zn, Mn, Fe, Cu, As and B. The total arsenic was determined in an atomic absorption spectrophotometer (Spectr AA-200 Varian) with a cathode lamp such as Hole (Varian), according to the methodology used by Cornejo [35]. The remaining physico-chemical parameters of the samples of River Camarones was recollected and were analyzed according to international standards as APHA [36], in the Environmental Research Laboratory of Arid Zones, LIMZA, at the University of Tarapacá (Arica, Chile).

3.2. Data processing and multivariate statistical analyses

The accuracy of the chemical analysis done in the LIMZA laboratory (ionic equilibrium – summation of cationic charge and summation of anionic charge) was validated by means of ROPRO 8.05 software [37].

AquaChem software [38,39] was used to plot the Piper and Stiff hydro-chemical diagrams. The latter, also called a polygonal diagram, gives the primary qualitative information about mineralization levels. This study uses the concentration values for anions (right) and cations (left) to construct polygons using parallel straight half lines. The concentration values are expressed in meq L⁻¹. The Stiff diagram is usually plotted without the labeled axis and is useful while making visual comparisons of water characteristics. The patterns tend to maintain their shape upon concentration or dilution, thus visually allowing the flow paths to be traced on maps [40].

The Piper diagram is probably the method most commonly used to identify similarities between different water resources. It allows the proposing mixtures happened between different water systems, which can be classified attending to their position in the diagram [41].

Finally, Wilcox classification [5] is carried out to study the possibility of using water from the lagoons for irrigation. This analysis is mainly based on electrical conductivity and Sodium Adsorption Ratio (SAR).

3.2.1. Hierarchical Cluster Analysis (HCA)

Cluster analysis is a statistical tool used to classify data groups based on their similarities. It provides intuitive resemblance relationships between any simple variable or sample and the whole data set and it is usually plotted in a dendrogram, a tree diagram frequently used to illustrate the arrangement of the clusters [42]. Hierarchical cluster analysis (HCA) is the most common approach in which clusters are formed sequentially, by starting with the most similar pair of objects and forming higher clusters step by step. The Euclidian distances (dxy) between the two samples represented by the difference between the analytical values of the samples (x_j and y_j) [Eq. (1)] were used as the similarity measurements [43].

$$dxy = \sum_{j=1}^{p} (\mathbf{x}_j - \mathbf{y}_j) \tag{1}$$

Thus, the hierarchical cluster analysis (HCA) was used to test the water quality data and to determine if the samples can be grouped into hydro-chemical clusters [8]. This procedure was carried out by means of Pirouette 3.11 software and applied to every sample collected in the study.

3.2.2. Principal Component Analysis (PCA)

The principal component analysis (PCA) [44] provides a way to reduce dimensionality of the data by finding lineal combinations of independent variables. PCA express a matrix X as a product of the other two matrices, the score matrix T and the transpose of the score loadings matrix L according to Eq. (2):

$$X = TL^{T}$$
⁽²⁾

The columns of L are the principal components (PC's), the m elements of the first column of loadings indicate the contribution of the original variables to the first principal component (PC1) and the matrix of scores T is the projection of the samples over the axes defined by the loadings. Associated with each factor is a PC, which expresses the magnitude of variance captured by each factor.

PCA methods were performed by using Piruette 4.5 [45]. The computation of PC's was developed using Nonlinear Iterative Partial Least Squares (NIPALS) algorithm [46,47] over the data, because it finds the first k PC's without computing all factors. The optimal number of PC's was determined based on the cumulative variance percentage of PC's.

4. Results and discussion

4.1. Monitoring parameters and analytical methods

The statistical analysis resulting from in situ measurements as well as the ion concentrations of the waters of the Amuyo Lagoons can be found in Table 1. The dominant cat-

Parameter	Red Lagoon	toon				Yellow Lagoon	agoon					Green Lagoon	goon			
	(n = 6)					(9 = 0)						(n = 5)				
	Min	Max	Median Mean	Mean	SD	Min	Max	Median	Mean		SD	Min	Мах	Median	Mean	SD
Hd	7,15	8,00	7,67	7,66	± 0,30	6,57	7,90	7,50	7,43	+1	0,47	6,25	8,86	7,02	7,28	± 0,98
T° (°C)	18,85	24,74	23,70		± 2,37	20,13	25,71	23,99	23,28	+1	2,45	20,85	35,90	33,02	31,35	± 6,15
EC (mS/cm)	14,14	14,90	14,54	14,50	± 0,31	11,25	14,72	14,36	13,70	+1	1,38	12,02	25,04	14,49	16,12	± 5,11
TDS (mg/L)	7095,00	10772,00	7409,00	8261,17	± 1565,85	6164,00	10633,00	7185,50	7494,83	+1	1610,66	6389,00	10378,00	7249,00	7697,60	± 1547,43
Cl (mg/L)	3800,00	3800,00 4303,03	3945,50	3979,17	± 191,03	2800,00	4050,00	3987,50	3737.50	+1	487.75	3990,00	4098,00	4002,00	4023,13	± 45,84
NO_{3}^{-} (mg/L)	10,22	24,40	23,00	19,44	± 6,50	9,08	25,60	17,57	18,19	+1	6,43	8,78	27,70	17,37	17,77	± 8,64
$SO_4^{2-}(mg/L)$	965,00	1113,52	1005,00	1023,42	± 62,79	865,00	1080,00	975,00	971,67	+1	77,24	723,16	1075,26	1001,00	964,28	± 138,17
HCO ₃ ⁻ (mg/L)	204,00	504,59	303,50	337,60	± 114,22	258,03	524,70	320,00	350,17	+1	102,00	137,00	544,73	437,25	402,72	± 155,35
As total (mg/L)	18,32	20,18	18,61	18,91	± 0,71	11,54	14,88	13,75	13,65	+1	1,19	14,82	16,80	15,76	15,77	± 0,73
B total (mg/L)	298,00	486,70	334,05	356,83	± 71,41	190,00	341,93	305,17	280,03	+1	68,72	283,00	352,35	309,70	314,59	± 29,33
Na ⁺ (mg/L)	2025,00	2025,00 2381,86	2256,45	2240,59	± 131,17	1787,00	2256,16	2185,00	2118,03	+1	182,03	2129,45	2375,14	2250,00	2253,92	± 88,38
K^{+} (mg/L)	216,00	321,00	269,52	270,41	± 33,82	160,00	285,00	248,53	240,62	+1	41,48	194,10	273,36	253,13	245,55	± 30,41
$Ca^{2+}(mg/L)$	460,00	739,33	719,01	644,85	± 130,51	360,00	729,28	680,49	620,84	+1	141,29	678,00	729,44	710,00	705,68	± 19,04
$Mg^{2+}(mg/L)$	36,07	45,20	39,93	40,55	± 3,23	33,42	44,80	38,62	38,78	+1	4,21	33,21	38,72	37,41	36,69	± 2.40

ion was Na⁺, corresponding to 2041 ± 131, 2118 ± 182 and 2254 ± 88 mg L⁻¹ for the Red, Yellow and Green Lagoons, respectively. The order of prominence of cations in the waters, from most abundant to least was: Na⁺ > Ca²⁺ > K⁺ > Mg²⁺. This pattern was the same for all the three Lagoons. On the other hand, the most abundant anion in the lagoons was Cl⁻ with 3979 ± 191, 3733 ± 488 and 4023 ± 46 mg L⁻¹, again for the Red, Yellow and Green Lagoon. It is worth noting that there is a high concentration, around 1000 mg L⁻¹, of sulfate in each of the lagoons while the micronutrients Cu, Fe, Mn and Zn were below the detection limit, 0.1 mg L⁻¹. The order of prominence of anions in the waters from most abundant to least was: Cl⁻ > SO₄²⁻ > HCO₃⁻ > NO₃⁻ with this order also being repeated in all the three lagoons.

One of the main characteristics of water in the Amuyo Lagoons is their high total As content, which is more likely related to naturally occurring biogeochemical processes associated with mineral solubilisation and volcanic activities due to the proximity of the Chuquicamata and Anocarire volcanos [48]. The Red, Yellow and Green Lagoons have 18.91 \pm 0.71; 13.65 \pm 1.19 and 15.77 \pm 0.73 mg of As L⁻¹ respectively; concentrations much higher than those allowed by Chilean regulations [49,50] which are not limited to Chile, but are effective worldwide. For instance, in the European Union (EU) elemental As and As compounds are classified as toxic and dangerous for the environment directive 67/548/EEC [51]. This directive lists arsenic trioxide, arsenic pentoxide and arsenate salts as category 1 carcinogens and we should be noted that the concentration of this element found in the Amuyo lagoons is considerably higher than those reported in northern Chilean rivers, which range from 1 to 3 mg L⁻¹ [48], or in natural spring waters from which people living in small villages, far from potable water treatment plants take their drinking water [52]. Consequently, the use of the waters in the Amuyo Lagoons as a drinking water source or even for irrigation is highly dangerous if untreated.

Different processes have been described as the potential technologies for As removal: membrane processes [25,53,54], ion exchange [24,55], adsorption [27–31,56], SORAS (Solar oxidation and removal of As) [57] or zero valent technologies [26].

High concentrations of B were also found, with 357 ± 71 ; 280 ± 69 and 315 ± 29 mg L⁻¹ for the Red, Yellow and Green Lagoons, respectively. Again, the presence of this element is more likely related to the volcanic activity of the region. The WHO has estimated that the maximum acceptable B level in water is 2.4 mg L⁻¹ [58] while, in the EU, local standards establish a concentration limit of 1 mg L⁻¹ [59]. The applicable Chilean regulation [49] does not include any concentration limit for B in drinking water, although the highest concentration allowed in water irrigation is 0.75 mg L⁻¹ [50]. Nevertheless, the values in the Amuyo Lagoons exceed the WHO recommendations by more than 7000%. Consequently, the use of these waters is not advisable, especially considering that conventional water treatments (coagulation, sedimentation and filtration) do not remove boron to any appreciable extent and, although some special treatments have been proven to remove boron, the authors could not find any study which dealt with the appropriate or higher concentration range.

The pH in the Green Lagoon demonstrated a large variation ranging from 6.3 to 8.8. The Red Lagoon (7.2–8)

and the Yellow Lagoon (6.6–7.9) show far less variation. A similar pattern can be seen regarding temperature, where the Green Lagoon ranges from 20.8 to 35.9° C and the Red and Yellow Lagoons range from 18.8 to 24.7° C and from 20.1 to 25.7° C, respectively. The temperature was found to be almost identical in the Red and Yellow Lagoons during sampling. Finally, it is worth noting that the total hardness of these waters can be classified as very hard with a higher level of Ca²⁺ (approximately 600–700 mg L⁻¹) than Mg²⁺ (approximately 30–40 mg L⁻¹).

As revealed by the relative standard deviation, nitrates, bicarbonates, total hardness and presence of TDS afford the highest seasonal variability. On the other hand, the lowest variations are much more dispersed and depend on each lagoon.

4.2. Hydrochemical characteristics

Using the EC and the SAR, the Wilcox diagram is presented in Fig. 2. It can be observed that all the samples correspond to water with very high salinity (C4), which is not suitable for irrigation under ordinary conditions, but may be used occasionally under very special circumstances. In order to use the water for irrigation, the soil must be permeable, drainage must be adequate, irrigation water must be applied in excess to provide considerable leaching and much more salt-tolerant crops must be selected [5]. Similarly, the water in the lagoons is considered to have very high sodium levels (S4) and is generally unsatisfactory for irrigation purposes except at low and perhaps medium salinity [5]. Consequently, considering the complete Wilcox classification (C4–S4), it can be deduced that these waters are not recommendable for irrigation due to an excess of salinity and sodium. Nevertheless, it is worth commenting that some vegetal species such as moss or lichen, in addition to animal tracks can be found in the vicinity of the lagoons.

The Piper diagram (Fig. 3) shows that Na^+ is the main cation present in the lagoon waters, while chloride is the most abundant anion species. It can be clearly seen that all the samples are located next to each other indicating almost equal characteristics. This is also reflected in Table 2, where a water composition classification given by AquaChem

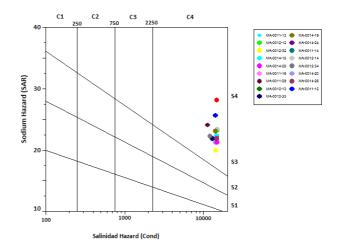


Fig. 2. Wilcox diagram where RL, YL and GL stands for Red, Yellow and Green Lagoons, respectively.

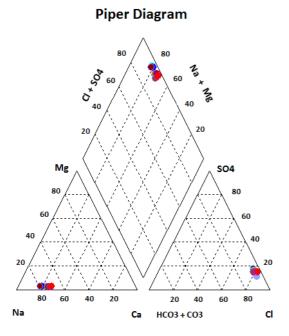


Fig. 3. Piper diagram.

Table 2 Hydro-chemical classification of the Amuyo Lagoons waters

Lake	Sample	Type of Water "AquaChem"	CE µS/ cm	Sodium Adsorption Ratio (SAR)
Red	MA-0011-13	Na-Cl-B	14660	28.13
Lagoon	MA-0011-28	Na-Cl-B	14140	25.62
	MA-0012-12	Na-Ca-Cl	14900	23.21
	MA-0012-32	Na-Ca-Cl	14170	19.33
	MA-0014-18	Na-Ca-Cl	14410	22.28
	MA-0014-25	Na-Ca-Cl-B	14740	21.27
Yellow	MA-0011-16	Na-Cl-B	14590	22.35
Lagoon	MA-0011-29	Na-Cl	11250	24.08
	MA-0012-13	Na-Ca-Cl	14720	22.18
	MA-0012-33	Na-Ca-Cl	12880	21.85
	MA-0014-19	Na-Ca-Cl-B	14120	23.06
	MA-0014-24	Na-Ca-Cl-B	14610	21.81
Green	MA-0011-14	Na-Ca-Cl	25040	23.09
Lagoon	MA-0012-14	Na-Ca-Cl	14930	23.36
	MA-0012-34	Na-Ca-Cl	12020	22.27
	MA-0014-20	Na-Ca-Cl-B	14140	21.27
	MA-0014-26	Na-Ca-Cl	14490	21.86

software is presented. The samples can be divided into four water faces: Na-Ca-Cl (9 samples, 53%), Na-Ca-Cl-B (4 samples, 23%), Na-Cl-B (3 samples, 18%) and Na-Cl (1 sample, 6%). Again, some type of relationship can be observed between the Red and Yellow Lagoons as 4 out of 6 samples have the same classification. The Green Lagoon water is also similar to the other waters, but with a lower coincidence.

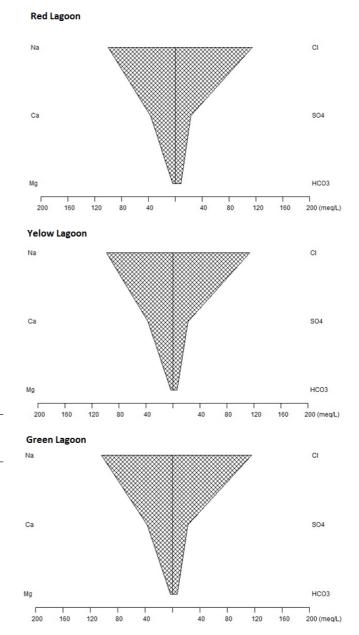


Fig. 4. Stiff diagram.

All the polygons shown in the Stiff diagram (Fig. 4) resemble each other, once more indicating that the lagoon characteristics are analogous. The species with the highest concentrations present in the diagram are chloride and sodium plus potassium; sulphate and calcium are present in medium concentrations and bicarbonate and magnesium in low concentrations.

4.3. Principal Components Analysis (PCA)

By PCA, the samples were separated in three non-overlapping classes, corresponding RL, YL, and GL (Fig. 5A). Using auto-scaling as a preprocessing, the cumulative vari-

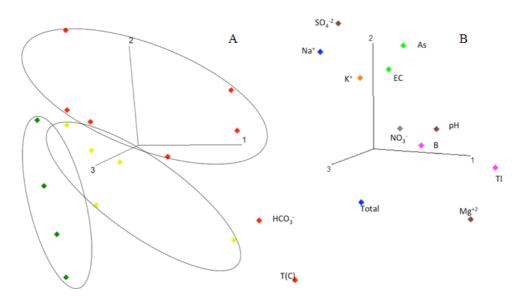


Fig. 5. PCA scores plot (A) and PCA loading plot (B) for the samples collected from the Amuyo Lagoons (red data – Red Lagoon, yellow – Yellow Lagoon, green data – Green Lagoon). These data were autoscaled and the PCA has been validated by cross validation. The variance for PC1, PC2 and PC2 are 29.7%, 16.3% and 15.4% respectively.

ance explained by the first three PCs is 61.5%. The data classification in Lagoons by the scores plot allows identifying significant differences between the physicochemical properties of the lagoons. The loading plot (Fig. 5B) shows the role of the physicochemical variables by the differences showed in the scores plot. In this way, the Green Lagoon shows higher values for HCO_3^- and T and lower values for As and EC. On the other hand, the Yellow Lagoon is classified mainly for its lower values of SO_4^{-2} , Na⁺, EC and As.

4.4. Hierarchical Cluster Analysis (HCA)

In order to determine the composition and physicochemical property patterns in the studied samples, HCA was used. The first analysis was carried out (figure not shown) including all the variables studied (see Table 1). This analysis showed an important temporal relationship between the samples, but no important information regarding the lagoons. Thus, the analysis was repeated using only general parameters (pH, T, EC, total hardness and TDS) plus *As* and *B* as key components. All the cations and anions were excluded from this analysis and the results are shown in Fig. 6. Primary outcomes still show an important analogy between the consecutive samples of the same lagoon (GL-5 and GL4; YL-6 and YL-5; RL-6 and RL-5; RL-3 and RL-4). On the other hand, it is noted that the Subgroup I displays a correlation between Green Lagoon samples (4 out of 5 Green Lagoon total samples). In a similar way, Subgroup IV shows parallelism between all the Yellow Lagoon samples, all the Red Lagoon samples and subsequently, between Red and Yellow Lagoon samples. This is in accordance with the data previously expressed which intimately related these lagoons. Subgroup III shows that the first sample of the three Lagoons, corresponding to the samples collected in spring presents an important relation between them, especially in respect to Red and Yellow Lagoons. It

should be commented that the second Yellow Lagoon sample is a subgroup by itself (Subgroup II) which is probably caused by EC and TDS values, which are the lowest of their respective series. Subgroups I and II form the Group I which includes all Green Lagoon samples except GL-1. Subgroups III and IV form Group II which includes all the Red Lagoon samples, the first Green Lagoon sample and all the Yellow Lagoon samples except YL-2, show once again the great resemblance between the Red and Yellow Lagoons. Finally, the figure shows how Groups I and II do not correspond, indicating that the Green Lagoon demonstrates some general differences from the other two lagoons. This connection may be related to rain, the total volume of the lagoons and their relative position. The Green Lagoon is the furthest from the river and is the highest, the Red Lagoon is located in the middle (position and height) and the Yellow Lagoon is the closest to the Caritaya River and is the lowest. In the Andean foothills, there can be significant rainfall meaning that, due to the height difference, water from the Green Lagoon may flow to the Red Lagoon and in the same way, from the Red Lagoon to the Yellow Lagoon (see Fig. 1). However, the Red Lagoon is probably not influenced by this fact, because its volume is much greater than that of the Green Lagoon. On the contrary, the Yellow Lagoon receives water from the Red Lagoon and due to its lesser volume, this effect might be more noticeable as it has been seen throughout this paper.

5. Conclusions

In this study, the first time we successfully reported the quality assessment and characteristics of the waters in the Amuyo Lagoons, Chile. The annual averages of the studied parameters show a very high concentration of As (18.91 \pm 0.71; 13.65 \pm 1.19 and 15.77 \pm 0.73 mg of As L⁻¹ for the Red, Yellow and Green Lagoons, respectively) and B (357 \pm 71;

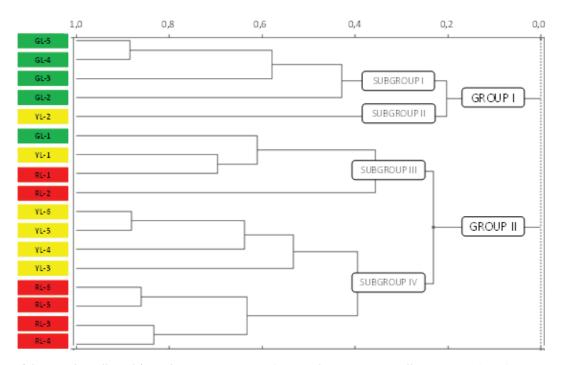


Fig. 6. HCA of the samples collected from the Amuyo Lagoons (RL – Red Lagoon, YL – Yellow Lagoon, GL – Green Lagoon).

 280 ± 69 and 315 ± 29 mg L⁻¹, following the same order). Both values are clearly above both the Chilean and international regulations for drinking and irrigation water. Due to their high salinity and SAR, these waters are classified as C4 and S4 in the Wilcox diagram which advises against their use for irrigation. The Piper diagram and the Stiff diagram show a high similarity among the lagoon water characteristics. However, the HCA revealed a higher analogy between the Red and Yellow Lagoons and some differences with the Green Lagoon characteristics. In the PCA, it is observed that the arsenic concentration in the three lagoons differ between them, with the green and yellow lagoons being the most similar and differing from the red lagoon.

Acknowledgements

The authors wish to thank the FONDECYT Proyect N°1120881, Proyecto de Investigación Científica y Tecnológica UTA 2017 N° 8721-12.

References

- L. Cornejo, J. Acarapi, U. Mella, Cuenca de Camarones: identificación y caracterización de fuentes que condicionan la calidad de las aguas superficiales: rol del Tranque Caritaya. Gobierno de Chile, Ministerio de Obras Públicas Dirección General de Aguas, Chile, 2009.
- [2] J. Bundschuh, B. Nath, P. Bhattacharya, C-W. Liu, M.A. Armienta, M.V. Moreno, D. Lopez, J.-S. Jean, L. Cornejo, L.F. Lauer, A. Tenuta, Arsenic in the human food chain: the Latin American perspective, Sci. Total Environ., 429 (2012) 92–106.
- [3] B.D. Bhattrai, S. Kwak, W. Heo, Assessment of water quality variations under non-rainy and rainy conditions by principal component analysis techniques in Lake Doam watershed, Korea, J. Ecol. Environ., 38 (2015) 145–156.

- [4] S.C. Nishanthiny, M. Thushyanthy, T. Barathithasan, S. Saravanan, Irrigation water quality based on hydrochemical analysis, Jaffna, Sri Lanka, American-Eurasian J. Agric. Environ. Sci., 7 (2010) 100–102.
- [5] V. Chaudhary, S. Satheeshkumar, Assessment of groundwater quality for drinking and irrigation purposes in arid areas of Rajasthan, India, Appl. Water Sci., 8 (2018) 218.
- [6] A.M. Al-Bassam, Y.A. Al-Rumikhani, Integrated hydrochemical method of water quality assessment for irrigation in arid areas: application to the Jilh aquifer, Saudi Arabia, J. African Earth Sci., 36(4) (2003) 345–356.
- [7] K.P. Singh, A. Malik, D. Mohana, S. Sinhab, Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India)—a case study, Water Res., 38 (2004) 3980–3992.
- [8] B. Zhang, X. Song, Y. Zhang, D. Han, Ch. Tang, Y. Yu, Y. Ma, Hydrochemical characteristics and water quality assessment of surface water and groundwater in Songnen plain, Northeast China. Water Res., 46 (2012) 2737–2748.
- [9] K.D. Brahman, T. Gul Kazi, H.I. Afridi, S. Naseem, S.S. Arain, N. Ullah, Evaluation of high levels of fluoride, arsenic species and other physicochemical parameters in underground water of two sub districts of Tharparkar, Pakistan: A multivariate study, Water Res., 47 (2013) 1005–1020.
- [10] J. Li, Y. Wang, X. Xie, C. Su, Hierarchical cluster analysis of arsenic and fluoride enrichments in groundwater from the Datong basin, Northern China, J. Geochem. Explor., 118 (2012) 77–78.
- [11] C. Güller, M.A. Kurt, M. Alpaslan, C. Akbulut, Assessment of the impact of anthropogenic activities on the groundwater hydrology and chemistry in Tarsus coastal plain (Mersin, SE Turkey) using fuzzy clustering, multivariate statistics and GIS techniques, J. Hydrology, 414–415 (2012) 435–451.
- [12] J.S. Horsburgh, A.S. Jones, D.K. Stevens, D.G. Tarboton, N.O. Mesner, A sensor network for high-frequency estimation of water quality constituent fluxes using surrogates, Environ. Modell. Soft., 25 (2010) 1031–1044.
- [13] C. Neal, B. Reynolds, P. Rowland, D. Norris, J.W. Kirchner, M. Neal, D. Sleep, A. Lawlor, C. Woods, S. Thacker, H. Guyatt, C. Vincent, K. Hockenhull, H. Wickham, S. Harman, L. Armstrong, High-frequency water quality time series in precipi-

tation and streamflow: From fragmentary signals to scientific challenge, Sci. Total Environ., 434 (2012) 3–12.

- [14] L.K. Pandey, J. Park, D.H. Son, W. Kim, M. Saifullslam, S. Choi, H. Lee, T. Han, Assessment of metal contamination in water and sediments from major rivers in South Korea from 2008 to 2015, Sci. Total Environ., 651 (2019) 323–333.
- [15] Ministerio de Agricultura, CNR, Diagnóstico de la subcuenta aportante al Embalse Caritaya Región de Arica y Parinacota, Informe Final, 2014, Vol 1 págs: 1–234.
- [16] L. Cornejo-Ponce, J. Acarapi-Cartes, M. Arenas-Herrera, Development and validation of a method for simultaneous arsenic, antimony, selenium and mercury determination in plants by energy dispersive X ray fluorescence spectrometry, Interciencia., 43 (2018) 426.
- [17] H. Lan, J. Li, M. Sun, X. An, Ch. Hu, R. Liu, H. Liu, J. Qu, Efficient conversion of dimethylarsinate into arsenic and its simultaneous adsorption removal over FeCx/N-doped carbon fiber composite in an electro-Fenton process, Water Res., 100 (2016) 57–64.
- [18] S. Ghosh (Nath), A. Debsarkar, A. Dutta, Technology alternatives for decontamination of arsenic-rich groundwater—A critical review, Environ. Technol. Innov., (2018) 9–34.
- [19] Z.A. ALOthman, R. Ali, M. Naushad, Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies, Chem. Eng. J., 184 (2012) 238–247.
- [20] R. Saravanan, S. Agarwal, V.K. Gupta, M.M. Khan, F. Gracia, E. Mosquera, V. Narayanan, A. Stephen, Line defect Ce³⁺ induced Ag/CeO₂/ZnO nanostructure for visible-light photocatalytic activity, J. Photochem. Photobiol. A: Chemistry, 353 (2018) 499– 506.
- [21] R. Saravanan, J. Aviles, F. Gracia E. Mosquera V.K. Gupta, Crystallinity and lowering band gap induced visible light photocatalytic activity of TiO₂/CS (chitosan) nanocomposites, Int. J. Bio. Macromol., 109 (2018) 1239–1245.
- [22] M. Naushad, T. Ahamad, B.M. Al-Maswari, A.A. Alqadami, SM. Alshehri, Nickel ferrite bearing nitrogen-doped mesoporous carbon as efficient adsorbent for the removal of highly toxic metal ion from aqueous medium, Chem. Eng. J., 330 (2017) 1351–1360.
- [23] M. Naushad, Surfactant assisted nano-composite cation exchanger: Development, characterization and applications for the removal of toxic Pb²⁺ from aqueous medium, Chem. Eng. J., 235 (2014) 100–108.
- [24] R. Šaravanan, D. Manoj, J. Qin, Mu. Naushad, F. Gracia, A.F. Lee, M.M. Khan, M.A. Gracia-Pinilla, Mechanothermal synthesis of Ag/TiO₂ for photocatalytic methyl orange degradation and hydrogen production, Process Safe. Environ. Protect., 120 (2018) 339–347.
- [25] M. Naushad, Z.A. Alothman, Separation of toxic Pb²⁺ metal from aqueous solution using strongly acidic cation-exchange resin: analytical applications for the removal of metal ions from pharmaceutical formulation, Desal. Water Treat., 53 (2015) 2158–2166.
- [26] M. Naushad, T. Ahamad, G. Sharma, M.M. Alam, Z.A. ALOthman, S.M. Alshehri, A.A. Ghfar, Synthesis and characterization of a new starch/SnO₂ nanocomposite for efficient adsorption of toxic Hg²⁺ metal ion, Chem. Eng. J., 300 (2016) 306–316.
- [27] G. Sharma, Mu. Naushad, D. Pathania, A. Mittal, G.E. El-Desoky, Modification of Hibiscus cannabinus fiber by graft copolymerization: application for dye removal, Desal. Water Treat., 55 (2015) 3114–3121.
- [28] A.B. Albadarin, M.N. Collins, Mu. Naushad, S. Shirazian, Activated lignin–chitosan extruded blends for efficient adsorption of methylene blue, Chem. Eng. J., 307 (2017) 264–272.
 [29] E. Daneshvar, A. Vazirzadeh, A. Niazi, M. Kousha, M. Naushad,
- [29] E. Daneshvar, A. Vazirzadeh, A. Niazi, M. Kousha, M. Naushad, A. Bhatnagar, Desorption of Methylene blue dye from brown macroalga: Effects of operating parameters, isotherm study and kinetic modeling, J. Cleaner Prod., 152 (2017) 443–453.
 [30] K. Deepa, C. Prasad, N.V.V. Jyothi, Mu. Naushad, S. Rajendran,
- [30] K. Deepa, C. Prasad, N.V.V. Jyothi, Mu. Naushad, S. Rajendran, S. Karlapudi, S. Himagirish Kumar, Adsorptive removal of Pb(II) metal from aqueous medium using biogenically synthesized and magnetically recoverable core-shell structured

AM@Cu/Fe $_3{\rm O}_4$ nanocomposite, Desal. Water Treat., 111 (2018) 278–285.

- [31] A.A. Al-Kahtani, S.M. Alshehri, M. Naushada, T. Ruksana, Ahamad, Fabrication of highly porous N/S doped carbon embedded with ZnS as highly efficient photocatalyst for degradation of bisphenol, Int. J. Bio. Macromol., 121 (2019) 415–423.
- [32] E. Tréllez, M. Mamani, F. Valenzuela, C. Vera, Guía educación y sensibilización ciudadana para la conservación y uso sustentable de los humedales de la región de Tarapacá, Centro de Estudios de Humedales (CEH) 2011 págs: 49–53.
- [33] M. Ahumada, L. Faundez, Guía descriptiva de los sistemas vegetacionales azonales hídricos terrestre de la Eco región Altiplánica (SVAHT). Ministerio de Agricultura de Chile, Servicio Agrícola y Ganadero, Santiago 2009 pág: 118.
- [34] G. Henríquez, Antecedentes climáticos de la XV Región de Arica y Parinacota: Caracterización de humedales alto andinos para una gestión sustentable de las actividades productivas del sector norte del país. Centro de Información de Recursos Naturales (CIREN) Biblioteca Digital. 2013. Available: http:// bibliotecadigital.ciren.cl/bitstream/handle/123456789/6800/ CIREN-HUMED035.pdf.
- [35] L. Cornejo, H. Lienqueo, M. Arenas, J. Acarapi, D. Contreras, J. Yáñez, H. Mansilla, In field arsenic removal from natural water by zero-valent iron assisted by solar radiation, Environ. Pollut., 156 (2008) 827–831.
- [36] APHA, AWWA, and WEF. Standard Methods for the Examination of Water and Wastewater, 23 rd edition. American Public Health Association, American Water Works Association, Water Environment Federation. 2017.
- [37] ROPRO software reaches version 8.0. Membrane Technology. 12 (2008) 3–4.
- [38] M. Ormachea, J.L. Garcia, P. Bhattacharya, O. Sracek, M. Garcia, C. Kohfahl, J. Quintanilla, J. Hornero, J. Bundschuh, Geochemistry of naturally occurring arsenic in groundwater and surface-water in the southern part of the Poopó Lake basin, Bolivian Altiplano, Groundwater Sustain. Develop., 2(3) (2016) 104–116.
- [39] A.M.S. Abd El-Gawad, A.S. Helaly, M.S.E. Abd El-Latif, Application of geoelectrical measurements for detecting the ground-water seepage in clay quarry at Helwan, southeastern Cairo, Egypt, NRIAG J. Astron. Geophys., 7 (2018) 377–389.
- [40] C. Güller, G. Thyne, J. McCray, K. Turner, Evaluation of graphical and multivariate statistical methods for classification of water chemistry data, Hydrogeology J., 10 (2002) 455–474.
- [41] P. Ravikumar, R.K. Somashekar, Assessment and modelling of groundwater quality data and evaluation of their corrosiveness and scaling potential using environmetric methods in Bangalore South Taluk, Karnataka State, India, Water Resour., 39 (2012) 446–473.
- [42] K. Nosrati, M. Van Den Eeckhaut, Assessment of groundwater quality using multivariate statistical techniques in Hashtgerd Plain, Iran. Environ Earth Sci., 65 (2012) 331–344
- [43] E.J.K. Singh, A. Gupta, N.R. Singh, Groundwater quality in Imphal West district, Manipur, India, with multivariate statistical analysis of data, Environ. Sci. Pollut. Res., 20 (2013) 2421–2434.
- [44] K. Zeinalzadeh, E. Rezaei, Determining spatial and temporal changes of surface water quality using principal component analysis, J. Hydrology: Regional Studies, 13 (2017) 1–10.
- [45] Piruette 4.5, Comprehensive chemometrics modeling software, Infometrix Inc.
- [46] H. Wold, Estimation of principals components and related models by iterative least squares, in P. R. Krishnaiah (Ed.), Multivariate Analysis New York, (1966) 391–420.
- [47] Y. Miyashita, H. Katsumi, Sasaki, Shin-Ichi, Comments on the NIPALS algorithm, J. Chemometrics, 4 (1990) 97–100.
- [48] L. Figueroa, Arica inserta en un ambiente arsenical: el arsénico en el ambiente que la afecta y 45 siglos de arsenicismo crónico. Ediciones Universidad de Tarapacá, Chile, 2001 págs. 5–25.
- [49] INN. NCh409/1:2005. Drinking water Part 1: Requirements. Instituto Nacional de Normalización. Santiago, Chile.
- [50] INN. NCh1333:1987. Water quality requirements for different uses. Instituto Nacional de Normalización. Santiago, Chile.

- [51] Council Directive 67/548/EEC. On the approximation of the laws, regulations and administrative provisions relating to the "Classification, packaging and labelling of dangerous substances. Official Journal of the European Communities. 2015.
- [52] F. Queirolo, S. Stegen, J. Mondaca, R. Cortés, R. Rojas, C. Contreras, Total arsenic, lead, cadmium, copper and zinc in some salt rivers in the northern Andes of Antofagasta Chile, Sci. Total Environ., 255 (2000) 85–95.
- [53] M. Walker, R.L. Seiler, M. Meinert, Effectiveness of household reverse-osmosis systems in a Western U.S. region with high arsenic in groundwater, Sci. Total Environ., 389 (2008) 245–252.
- [54] A. Figoli, A. Cassano, A. Criscuoli, M. Salatul, I. Mozumder, M. Uddin, M. Islam, E. Drioli, Influence of operating parameters on the arsenic removal by nanofiltration, Water Res., 44 (2010) 97–104.
- [55] A.M. Donia, A.A. Atia, D. Mabrouk, Fast kinetic and efficient removal of As (V) from aqueous solution using anion exchange resins, J. Hazard. Mater., 191 (2011) 1–7.
- [56] J. Giménez, J. de Pablo, M. Martínez, M. Rovira, C. Valderrama, Reactive transport of arsenic (III) and arsenic (V) on natural hematite: Experimental and modeling, J. Colloid Interface Sci., 348 (2010) 293–297.
- [57] F. Lara, L. Cornejo, J. Yáñez, J. Freer, H. Mansilla, Solar-light assisted removal of arsenic from natural waters: effect of iron and citrate concentrations, J. Chem, Technol. Biotechnol., 81 (2006) 1282–1287.
- [58] Guidelines for Drinking-Water Quality. 4th ed. World Health Organization. Geneva, Switzerland, 2011, 178 p.
- [59] Council Directive 98/83/EC, 1998.The quality of water intended for human consumption, Official Journal of the European Communities.