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Quality assessment of surface water associated with a copper mine in Peruusinggrey systems

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ABSTRACT

Locumba River Basin is characterized by its poor water quality due to its high concentrations of arsenic, boron and elevated electric conductivity, which has caused health problems related with the difficulty of a correct water treatment, especially in the Ite district, Peru. This study carries out a water assessment of surface waters using the Grey Clustering Method, based on the center-point triangular whitenization weight functions (CTWF), which are based on grey systems. In the present, eight points analyzed by DIGESA in 2019 along the basin are evaluated based on its values of pH, electric conductivity, dissolved oxygen and dissolved metals (being specifically arsenic, iron, cadmium and lead) according with the ranges established in the Peruvian ECA intended for human consumption. All points studied were classified within the subcategory A1, except the one located on the mouth of Locumba River (subcategory A3) due to its high electric conductivity and elevated iron and arsenic concentrations. These results could be used by authorities to evaluate better water sources to supply the human consumption, as well as supervise industrial activities nearby. Despite DIGESA's report is focused on inspecting Toquepala Mine impact, more parameters should be measured in future studies and additional intermediate points must be established at Pampa Sitana to determinate a current influence of the mining company in the area.

Key words: Grey systems, Grey Clustering, Locumba River Basin, Water Quality.

1. INTRODUCTION

Peru, particularly its southern part, is characterized by having several mining operations related mainly to cooper production. Despite of it, a Peruvian mining regulation has not been established until 1993 [1]. In the region of Tacna, due to the lack of regulations, Toquepala Mine had been dumping its tailings (40 Mm3) directly at Locumba River between 1960 and 1996, which used to transport those toxic compounds until Ite Bay [2].This pollution affected an area of more than 1600 hectares causing a variation of the coast line and damaging the sea coast. Nevertheless, in 2002, the Peruvian government approved the tailings remediation using an anaerobic wetland system. Thus, nowadays, Tacna people enjoy a tourist wetland with many species of birds as a result of the environment conditions improvements[3]. This wetland has neutralized the acidic and oxidizing conditions of the ancient tailings allowing the reduction of mobility and liberation of heavy metals such as Iron (Fe), Aluminium (Al), Manganese (Mn), Zinc(Zn), Cooper (Cu) and Nickel (Ni)[4]. Notwithstanding, the newspaper La República and the General Directorate of Health (DIGESA) have noticed some area that have not been remedied [2], [5]. As a result of these discrepancies, this study will be focused on analyzing the quality of the surface waters around the Toquepala Mine.

Many studies of water body analysis have applied the grey clustering method by means of the center-point triangular whitenization weight functions (CTWF), obtaining reliable results that lead to a great scientific interpretation [6], [7]. This is because the method is able to weight and classify the information from the sampling data according to standards known as grey classes [8]. These standards will qualify and classify the information from the sample data. In this case study, the dataobtained from OEFA's Technical Supervision Report (0391-2019-DSEM-CMIN) [9] will be gathered from the Peruvian law (D.S. 004-2017-MINAM) [10].

The main objective of this study is to characterize the quality of the waters surrounding Toquepala mine, located on Locumba River Basin. For which, each monitoring point is evaluated with the purpose of identifying contaminated areas and to assess the remediation carried out by Ite wetlands.

For this case study, 8 sampling points in 6 water bodies were considered to determine if the current and ancient activities of Toquepala mine have an impact on them. The first and second points belong to Suches lagoon at approximate 105 m from the shore of the Cuajone side at an altitude of 4461 m.a.s.l. and 472 m southeast of the ToquepalaBarcaza at an altitude of 4453 m.a.s.l., respectively. The third point is located at the exit of a catchment well on the northeast side of the Hacienda Matagroso at an altitude of 1689 m.a.s.l. The next two points are located at Aricota lagoon; the fourth, at approx. 270 m from the northeast end at an altitude of 2758; and the fifth, on the east side, between a public electric company (EGESUR) pumping station and floating trout cages at an altitude of 2734 m.a.s.l. The sixth and eighth points are found in watering holes, in the southern and northern sectors of the Ite tailings reserve, respectively. Lastly, the seventh point is located at Locumba River at approx. 100 m before the entry of the Ite tailings reserve.

The structure of the present study is as follows: In section 2 a literature review is given, then, in section 3 the grey clustering method based on CTWF is explained. Section 4 provides details and considerations needed for this particular case, while results and the discussion are presented in section 5. Finally, conclusions of both the method and the case analyzed are provided in section 6.

2. LITERATURE REVIEW

Wang [7] used the Grey Clustering methodology to highlight the differences in the impacts on surface water qualities (in periods of normal, abundant and poor water flow) of different indicators of water samples such as dissolved oxygen, permanganate index, five-day biochemical oxygen demand, ammonia nitrogen and total phosphorus. The evaluation was carried out in four sections of the Qingshui River in the Duyun city of China. Likewise, national water quality standards and the AHP method were used to establish the weighting of the values evaluated in the Grey Clustering. Therefore, it was concluded that the Grey Clustering method combined with the AHP method provides a more comprehensive and scientific assessment of water quality. In addition, they recommended the use of the Delphi method to obtain the weight of each parameter.

Likewise, considering 12 monitoring points in the Yellow River basin in China, a water quality assessment was carried out using the grey clustering method. Water quality monitoring data from the Ministry of Environmental Protection of China from May 2016 and the environmental quality standards of surface water that includes 5 levels (I, II, III, IV and V) were used. The parameters or indicators that were used for this study were OD (dissolved oxygen), CODMn (permanganate index) and NH3-N (ammonia). After the respective analysis using the grey clustering method, it was obtained that 9 out of the 12 monitoring points have a grade I of water quality, 2 of them belonged to grade V and 1 belonged to grade III of water quality. A fuzzy comprehensive evaluation method water quality study was also carried out to do a comparison between the methodologies; finally the results obtained were the same as for the grey clustering method. In conclusion, in the mentioned study of the Yellow River basin the grey clustering method demonstrated to be an optimal and efficient method [11].

Besides this, Delgado [12] carried out a study of six monitoring points in Challhuahuacho and Ferrobamba rivers, areas surrounding Las Bambas mine in Apurimac, south of Peru. Grey Clustering Method was used along with the water parameters established by Peruvian D.S. N° 004-2017-MINAM. The results of their study showed that The Ferrobamba River had a high-water quality, while the Challhuahuacho River presented a poor water quality, fact that could be associated with spills in the area.

In the same way, Diaby[4] carried out a study of the un-remediated and remediated parts of the tailings deposit at Ite Bay, Southern Peru, in order to understand the biogeochemical processes resulting from the construction of the Ite wetland. They used a solid and aqueous geochemistry, mineralogy, and microbiology methods. The results of their study showed that the oxidizing tailings have a low-pH oxidation zone (pH 1-4) with a strong accumulation of efflorescent salts at the surface due of the capillary transport of metal cations such as Iron (Fe), Cadmium (Cd), Manganese (Mn), Zinc (Zn), Cooper (Cu) and Nickel (Ni). Also, the authors mentioned that the alkaline waters (pH 8), that infiltrated into the Ite Bay tailings deposit, contained around 500ug/L of natural arsenic concentrations. However, in the shoreline samples, the arsenic concentrations in the pore water are below the detection limit, and the authors suggest a retention of As by Fe (III) hydroxide.

3. METHODOLOGY

In this section, the grey clustering method is explained as well as the parameters used for evaluating the surface water related with the mining activity at Toquepala Mine.

3.1 Grey Clustering Method

This method is a process at which the user can extrapolate few data of analyses to a whole component of interest in order to classify it and analyze a determined problem [8]. It is based on the center-point triangular whitenization weight functions (CTWF) and the steps followed were[6], [7], [11]–[13]:

First of all, a set of group of study $(i = 1, 2, 3, \dots, n)$, parameters$(j = 1, 2, 3, \dots, m)$, grey classes $(k = 1, 2, 3, \dots, z)$ and monitoring points for each group of study must be established for the case.

A. First Step

In order to compare the parameters that are measured in different units, it is necessary to establish non-dimension standard values (A_j^k) according to a regulation system, in this particular case, Peruvian law (D.S. 004-2017-MINAM) [10] was selected. This is carried out splitting the standard values on the average of them. Then, non-dimension monitoring data of each parameter (C_j^i) for each group of study (i) are calculated trough the average of standard values.

B. Second Step

The grey classes (k) are stablished with the non-dimension standard parameters obtained as detailed in the previous step. For this case, it will be stablished three criteria $(k = 1, 2, 3)$ according to water quality of the Peruvian law, a representation of this can be seen in Figure 1.

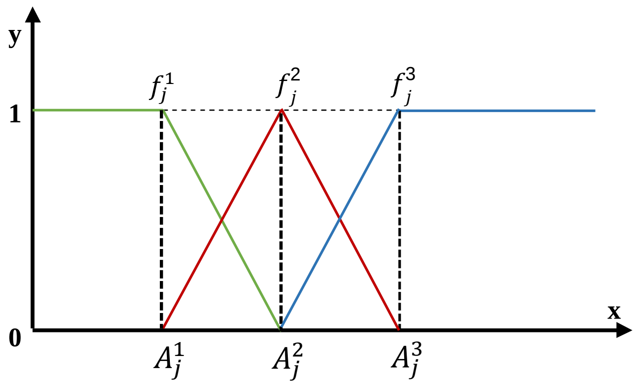

Figure 1: Grey Clustering Method based on CTWF

A_1, A_2 *and* A_3 Values are established according to Environmental Quality Standards for water for human consumption. Therefore, (1)-(3) are applied.

$$f_j^1(x_{ij}) = \begin{cases} 1, x \in \left[0, A_j^1\right] \\ \frac{A_j^2 - x}{A_j^2 - A_j^1}, x \in \left\langle A_j^1, A_j^2 \right\rangle \\ 0, \; x \in \left[A_j^2, +\infty\right\rangle \end{cases} \quad (1)$$

$$f_j^2(x_{ij}) = \begin{cases} \frac{x - A_j^1}{A_j^2 - A_j^1}, x \in \left\langle A_j^1, A_j^2\right] \\ \frac{A_j^3 - x}{A_j^3 - A_j^2}, \; x \in \left\langle A_j^1, A_j^2 \right\rangle \\ 0, \; x \in \left[0, A_j^1\right] \cup \left[A_j^3, +\infty\right\rangle \end{cases} \quad (2)$$

$$f_j^3(x_{ij}) = \begin{cases} \frac{x - A_j^2}{A_j^3 - A_j^2}, x \in \left\langle A_j^2, A_j^3 \right\rangle \\ 1, \; x \in \left[A_j^3, +\infty\right\rangle \\ 0, x \in \left[0, A_j^2\right] \end{cases} \quad (3)$$

Following this, the monitoring data is evaluated in its respective function.

C. Third Step

To avoid subjectivism, a weight of each parameter in each grey class is calculated using the following equation.

$$\eta_j^k = \frac{\frac{1}{A_j^k}}{\sum_{j=1}^{m} \frac{1}{A_j^k}} \quad (4)$$

This weight is calculated using the non-dimensional standard values (A_j).

D. Fourth Step

Afterward, the clustering coefficient is represented as the highest value obtained in the sum of each evaluated function multiplied per its weight, as is indicated by (5).

$$\sigma_i^k = \sum_{j=1}^{n} f_j^k(x_{ij}) \, . \, \eta_j \quad (5)$$

3.2 Parameters

The parameters used were obtained from the OEFA Technical Supervision Report (0391-2019-DSEM-CMIN) [9] and are listed below:

- Electric Conductivity (C1): It is the range for the subcategory A_3, however it is not specified in the law; therefore it was stablished as 1700 µS/cm assuming a continue succession.
- Dissolved Oxygen (C2): The values in the law were not modified.
- PH (C3): The law establishes a range at which its value is acceptable. However, in order to establish a fixed value, the variation of the highest boundary in the range respect to the neutral value (pH=7) was used.
- Total Arsenic (C4): The law does not contemplate different values for the subcategories $A_2$and A_3. For this reason, the limit of the subcategory $A_2$was calculated with the mean between the limits in the sub categories $A_1$and A_3.
- Total Iron (C5): The values in the law were not modified.
- Total Cadmium (C6): The values in the law were not modified.
- Total Lead (C7): The law does not contemplate different values for the subcategories A_2 and A_3. For this reason, the limit of the subcategory A_2 was calculated with the mean between the limits in the sub categories A_1 and A_3.

4. CASE STUDY

Water quality assessment in areas surrounding Toquepala mine was conducted through eight monitoring points. It is important to mention that Toquepala mine is in the middle of the area and it could be possible to cause a variation in the components of these waters.
Finally, the information to be used was obtained from Environmental Assessment and Control Agency (OEFA by its Spanish acronym). Data were collected from a public report N° 0391-2019-DSEM-CMIN, published on 2019 [9]. In this way, it is proposed to evaluate whether the water is suitable for human consumption or an advanced purification treatment is needed.

4.1 Context Description

The study area belongs to the Locumba river basin, located in the region Tacna, south of Peru (as seen in Figure 2).

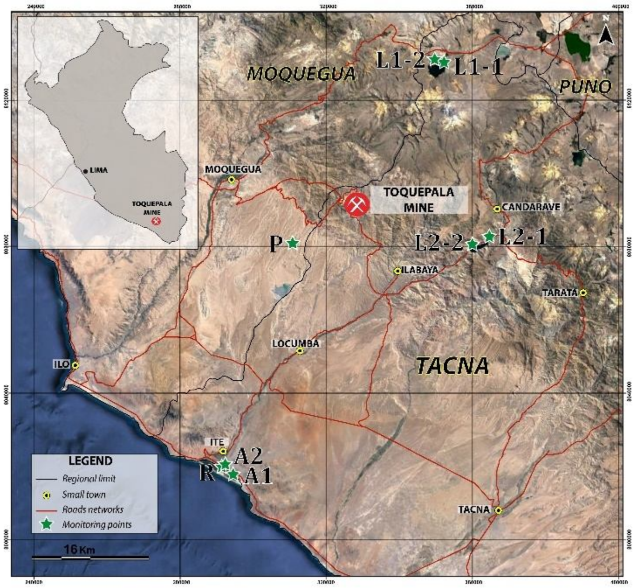

Figure 2: Areas surrounding Toquepala mine and monitoring points (modified from Google Earth)

Eight monitoring points were chosen to analyze the water quality in areas surrounding Toquepala mine. Table 1 details the monitoring points corresponding to the referring areas.

Table 1: Monitoring points in areas surrounding Toquepala mine

Body	Monitoring Points	Code	UTM coordinates	
			North	East
Suches Lagoon	ESP-AS-01(*)	L1-1	8 127 956	349 434
Suches Lagoon	ESP-AS-02(*)	L1-2	8 126 652	351 954
Catchment area	ESP-AS-03(*)	P	8 080 391	311 227
Aricota Lagoon	ESP-AS-04(*)	L2-1	8 081 335	364 376
Aricota Lagoon	ESP-AS-05(*)	L2-2	8 080 159	360 088
Southern Trough	ESP-AS-06(*)	A1	8 018 166	294 535
Locumba River	ESP-AS-07(*)	R	8 019 134	292 580
Northern Trough	ESP-AS-08(*)	A2	8 019 280	292 062

4.2 Toquepala Mine

Toquepala mine is located 150km from Tacna, in the south of Peru. The unit is between 1200 and 3600 m.a.s.l. The main commodities are copper and molybdenum which are processed in a concentrator plant of 12000 tons/day [14].
Two main areas of influence have been identified for the purpose of this study. First, the social influence involves the surrounding communities, such as Ilabaya and Locumba in Tacna and Moquegua district in Moquegua. Secondly, the environmental influence involves the change in water quality and the soils composition in the areas surrounding mine.

4.3 Calculations

The parameters used were defined based on the environmental and health problems that they produce. One set of parameters (see Table 2 for details) were defined for the CTWF analysis of each monitoring point.

Table 2: Parameters considered for the present study

Parameter	Symbol	Code
Electric conductivity	σ	C_1
Dissolved oxygen	O	C_2
Hydrogen Potential	pH	C_3
Arsenic	As	C_4
Iron	Fe	C_5
Cadmiun	Cd	C_6
Lead	Pb	C_7

These parameters were used as they provide the necessary information to determine the quality of the waters in which the Toquepala mine could have influence if gathered.Electrical conductivity is the measure of the ability of water to conduct an electric current. This property is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate anions or metal cations [15]. For this reason, conductivity is a general indication of quality.
Likewise, oxygen dissolved is a key factor for aquatic life and plant life, it is an indirect measure of the river or lake quality. Consequently, its concentration reflects the influence of other parameters that allow us to determine water quality. Furthermore, this parameter could be used for routine monitoring, since a study in Nepal showed that, only by analyzing dissolved oxygen, the quality results can be approximated in a large percentage to the quality results obtained with other parameters [16].
Ph is the measure of acidity of water. Water with more free hydrogen ions is acidic, meanwhile with more free hydroxyl ions is basic. The pH is altered when chemicals enter and change the composition of the water and therefore it is a good indicator of contamination. Additionally, it is an indicator of solubility and, for example, metals are more soluble at a lower pH, which can increase their toxicity [17].
On the other hand, arsenic is a highly toxic element and very harmful to human health. Its concentration depends on anthropogenic sources and natural sources; therefore, its analysis in water quality studies is crucial, especially if the water is evaluated to be potable [18].
Fe is one of the main components of acid mine drainage and is an indicator of this type of contamination [19]. For this reason, it is an important parameter for measuring water quality. Furthermore, in Peru one of the main problems caused by mining is the contamination of rivers by acid drainage [20]. Heavy metals like Cd and Pb belong to a group of metal and metalloid elements that have a high density between 3.5 and 7 g/cm3. These metals are toxic, poisonous and harmful to humans, even in low concentrations, mainly

because they are not biodegradable and can be concentrated in water [21]. They are found in the crust, but the most notable contamination has been from anthropogenic activities such as mining in the case of Pb [22]. Furthermore, Cd is not an important metal for biological systems and has almost no benefits for the ecosystem, highlighting its harmful effects [21].

These parameters will be evaluated in comparison with Peruvian law DS 004-2017-MINAM [10] in order to determinate if the quality of the water belongs to the category 1, subcategory A that indicates the level of the potability. Which, it also includes three categories itself: A_1, A_2 and A_3 which are defined by A_j^k $(k = 1, 2, 3)$.

A. First Step

Table 3 shows the non-dimensioned standard values and Table 4 the non-dimensioned values for the monitoring points.

Table 3: Non-dimensioned standard values

Parameters	Grey Classes		
	A_1	A_2	A_3
C_1	0.9375	1.0000	1.0625
C_2	1.2000	1.0000	0.8000
C_3	0.8571	1.0000	1.1429
C_4	0.1250	1.0000	1.8750
C_5	0.1429	0.4762	2.3810
C_6	0.5000	0.8333	1.6667
C_7	0.3333	1.0000	1.6667

Table 4: Non-dimensioned monitoring data values

Parameters	L2-2	A1	R	A2
C_1	1.1769	4.0063	1.5875	2.5375
C_2	2.0920	2.3100	1.6580	1.6960
C_3	0.9600	0.8286	0.8800	0.1543
C_4	8.7588	1.6669	8.3516	6.9644
C_5	0.0286	0.2190	4.0476	0.0190
C_6	0.0033	0.0050	0.0400	0.0233
C_7	0.0010	0.0023	0.4927	0.0010

B. Second Step

Using values from Table 3, the CTWF equations are calculated.

As example, equations of CTWF from parameter iron (C5) are show in (6) – (8).

$$f_5^1(x_{i5}) = \begin{cases} 1, x \in [0, 0.1429] \\ \frac{0.4762-x}{0.4762-0.1429}, x \in \langle 0.1429, 0.4762 \rangle \\ 0,\ x \in [0.4762, +\infty\rangle \end{cases} \quad (6)$$

$$f_5^2(x_{i5}) = \begin{cases} \frac{x-0.1429}{0.4762-0.1429}, x \in \langle 0.1429, 0.4762] \\ \frac{2.3810-x}{2.3810-0.4762},\ x \in \langle 0.4762, 2.3810 \rangle \\ 0,\ x \in [0.1429] \cup [2.3810, +\infty\rangle \end{cases} \quad (7)$$

$$f_5^3(x_{i5}) = \begin{cases} \frac{x-0.4762}{2.3810-0.4762}, x \in \langle 0.4762, 2.3810 \rangle \\ 1,\ x \in [2.3810, +\infty\rangle \\ 0, x \in \left[0, A_j^2\right] \end{cases} \quad (8)$$

Table 5 shows the values of the CTWF equation from all parameters in each one of the eight monitoring points.

Table 5: CTWF values of each monitoring point

L1-1	f_1	f_2	f_3
C_1	1.0000	0.0000	0.0000
C_2	1.0000	0.0000	0.0000
C_3	0.4000	0.6000	0.0000
C_4	0.9073	0.0927	0.0000
C_5	1.0000	0.0000	0.0000
C_6	1.0000	0.0000	0.0000
C_7	1.0000	0.0000	0.0000
Results	0.9375	0.0835	0.0000
L1-2	f_1	f_2	f_3
C_1	1.0000	0.0000	0.0000
C_2	1.0000	0.0000	0.0000
C_3	0.0000	0.0000	1.0000
C_4	0.8633	0.1367	0.0000
C_5	1.0000	0.0000	0.0000
C_6	1.0000	0.0000	0.0000
C_7	1.0000	0.0000	0.0000
Results	0.9020	0.0165	0.1676
P	f_1	f_2	f_3
C_1	0.0000	0.0000	1.0000
C_2	0.3400	0.6600	0.0000
C_3	1.0000	0.0000	0.0000
C_4	1.0000	0.0000	0.0000
C_5	1.0000	0.0000	0.0000
C_6	1.0000	0.0000	0.0000
C_7	1.0000	0.0000	0.0000
Results	0.9299	0.0795	0.1803
L2-1	f_1	f_2	f_3
C_1	0.0000	0.0000	1.0000
C_2	1.0000	0.0000	0.0000
C_3	0.7600	0.2400	0.0000
C_4	0.0000	0.0000	1.0000
C_5	1.0000	0.0000	0.0000
C_6	1.0000	0.0000	0.0000
C_7	1.0000	0.0000	0.0000
Results	0.5948	0.0289	0.2825
L2-2	f_1	f_2	f_3
C_1	0.0000	0.0000	1.0000
C_2	1.0000	0.0000	0.0000
C_3	0.2800	0.7200	0.0000
C_4	0.0000	0.0000	1.0000
C_5	1.0000	0.0000	0.0000
C_6	1.0000	0.0000	0.0000
C_7	1.0000	0.0000	0.0000
Results	0.5705	0.0867	0.2825
A1	f_1	f_2	f_3
C_1	0.0000	0.0000	1.0000
C_2	1.0000	0.0000	0.0000
C_3	1.0000	0.0000	0.0000
C_4	0.0000	0.2379	0.7621
C_5	0.7714	0.2286	0.0000
C_6	1.0000	0.0000	0.0000

C_7	1.0000	0.0000	0.0000
Results	0.5376	0.0865	0.2582
R	f_1	f_2	f_3
C_1	0.0000	0.0000	1.0000
C_2	1.0000	0.0000	0.0000
C_3	0.8400	0.1600	0.0000
C_4	0.0000	0.0000	1.0000
C_5	0.0000	0.0000	1.0000
C_6	1.0000	0.0000	0.0000
C_7	0.7610	0.2390	0.0000
Result	0.2643	0.0481	0.3630
A2	f_1	f_2	f_3
C_1	0.0000	0.0000	1.0000
C_2	1.0000	0.0000	0.0000
C_3	1.0000	0.0000	0.0000
C_4	0.0000	0.0000	1.0000
C_5	1.0000	0.0000	0.0000
C_6	1.0000	0.0000	0.0000
C_7	1.0000	0.0000	0.0000
Results	0.6069	0.0000	0.2825

C. Third Step

The weight of each parameter in each grey class is calculated using (4). The results obtained are shown in Table 6.

Table 6: Clustering weight values of each parameter

Parameters	**Weight of Grey Classes**		
	A_1	A_2	A_3
C_1	0.0462	0.1205	0.1803
C_2	0.0361	0.1205	0.2395
C_3	0.0506	0.1205	0.1676
C_4	0.3468	0.1205	0.1022
C_5	0.3035	0.2530	0.0805
C_6	0.0867	0.1446	0.1150
C_7	0.1301	0.1205	0.1150

D. Fourth Step

Using the clustering coefficient of each parameter and (5), the class of each monitoring point is defined. The results are presented in Table 7, in which we can appreciate the maximum value highlighted with the purpose to have visualization understanding regarding the class obtained.

Table 7: Coefficient and class category of each point

Monitoring points	**Subcategory A**			**Class**
	A_1	A_2	A_3	
L1-1	0.9705	0.0112	0.0000	A_1
L1-2	0.9566	0.0165	0.0000	A_1
P	0.9358	0.0795	0.1907	A_1
L2-1	0.6399	0.0000	0.2988	A_1
L2-2	0.6399	0.0000	0.2988	A_1
A1	0.5763	0.0865	0.2731	A_1
R	0.2032	0.0288	0.5035	A_3
A2	0.6399	0.0000	0.2988	A_1

5. RESULTS AND DISCUSSION

5.1 About the Case Study

After processing the data of each monitoring point, results are shown in Table 8 and will be analyzed in the following lines.

Table 8: Processed data results

Body	**Monitoring Point**	**Code**	**Class**
Suches Lagoon	ESP-AS-01(*)	L1-1	A1
Suches Lagoon	ESP-AS-02(*)	L1-2	A1
Catchment area	ESP-AS-03(*)	P1-3	A1
Aricota Lagoon	ESP-AS-04(*)	L2-1	A1
Aricota Lagoon	ESP-AS-05(*)	L2-2	A1
Southern Trough	ESP-AS-06(*)	A1	A1
Locumba River	ESP-AS-07(*)	R	A3
Northern Trough	ESP-AS-08(*)	A2	A1

From the results shown in the Table 8, it is obtained that points L1-1 and L1-2, which correspond to Suches lagoon, belong to subcategory A_1 according to Peruvian Law, since all the parameters analyzed show concentrations equal or lower than the limit established in it. In 2009, INGEMMET [23] carried out hydrochemical studies in the Locumba River Basin whose results are in agreement with the ones presented in this paper. According to the INGEMMET in 2009 and the results obtained in the present paper, the water from Suches lagoon could be used for the human consumption after a simple and regular disinfection process.

Likewise, point P1-3 is classified in the subcategory A_1 of the Peruvian law. However, it has high levels of electrical conductivity and intermediate concentrations (less than the proposed limit for A_1) of oxygen dissolved. Regarding the other parameters, it has been probed that they are found in an optymal state of quality. This point is located in the Quebrada Honda sub-basin of the Locumba River basin, which had relatively low levels of electrical conductivity (around 400 µS / cm, 2009 values) [23], compared to what was recorded in this study (2019 value); which indicates that the levels of electrical conductivity have increased over the last 10 years.

According to the hydrochemical analysis of the Quebrada Honda sub-basin by INGEMMET in 2009, Pampa Sitana presented high values of electrical conductivity (around 4800 µS/cm) with a pH greater than 8; this has indicated a high content of salts and gypsums in the underground levels and in the outcrops of that sector [3]. Likewise, in 2010, DIGESA detected high concentrations of heavy metals in the waters that filter from the Quebrada Honda Tailings Reservoir (north of Pampa Sitana) to the Pampa Sitana sector, where the water is used for agriculture [2]. Furthermore, according to the INGEMMET analysis of 2009, this sector does not have natural arsenic refills, but it was above the permitted values. However, point P1-3, which connects the mine with the reservoir, presents heavy metal values below standards that may indicate the remediation has already been carried out or there is underground infiltration of contaminated water of the tailings reservoir that resurfaces in the Pampa Sitana sector. According to chapter 2 of the Toquepala Closure Plan [14], the tailings of Quebrada Honda are mainly composed of copper, iron, sulfur, molybdenum sulfide, aluminum oxide and silica, so that in case that an analysis is carried out in the Pampa Sitana surface waters, these elements and compounds should be in high concentrations.

Points L2-1 and L2-2, which correspond to a natural waterbody (Aricota lagoon), show a similar pattern in the parameters analyzed above. On the one hand, oxygen dissolved, iron, cadmium and lead show concentrations inferior than the lower limit established in the subcategory A_1 (water that can be made drinkable with disinfection). On the other hand, values of arsenic and electric conductivity are considerably elevated, even higher than the upper limit of the subcategory A_3 (water that need an advanced treatment to be drinkable). These results agree with the ones obtained by the INGEMMET in 2009 [23], when the Locumba River Basin was characterized. They found high concentrations of arsenic and boron, as well as high conductivity in waters located in the southern part of Callazas River and Calientes Sub Basins due to the presence of the Yucamane and Tutupaca Volcanoes. Thus, the elevated arsenic concentration and conductivity values obtained in the lagoon might be explained by its effluent rivers, which flows through the basins previously mentioned.

Based on the results obtained by the grey clustering method, the sample taken from the Locumba River, which corresponds to point R of sampling, is the only one that is in subcategory A_3. This point is located 100 m from the entry of the Ite tailings deposit, which used to receive all the tailings from the Toquepala and Cuajone mines some years ago and, when deposited, expanded the coastal perimeter causing problems of contamination and ecosystem imbalance [2]. The low water quality at this point could be attributed to that fact since the filtration of contaminants in the old tailings deposit can affect the surrounding areas. Furthermore, a study in the area [4] showed that the part of the central delta, where the deposition of heavier and thicker sulfides took place, contains approximately 4% pyrite and traces of chalcopyrite, molybdenite and chalcocite-covelite. These results support the high Fe content of sample 7, which was taken nearby.

Points A1 and A2 (troughs) also belong to this ancient tailing area, reason for which it was expected to have a poor water quality; however, both of them belong to subcategory A_1. These results can be attributed to the fact that Southern Peru Copper Corporation (SPCC) carried out a remediation by installing a wetland cover on 80% of the affected area, with the exception of the central and near-shore areas [4]. These two points are in the north and south areas of the tailings deposit, so according to the results of these points this remediation would have been successful and beneficial.

The arsenic present at points L2-1 and L2-2 has a natural origin [23], which may be the explanation for the high content at points A1, R and A2. However, the 2009 INGEMMET analysis indicates that there is a high arsenic content in Pampa Sitana which is located in an area not influenced by high concentrations of arsenic indicating anthropogenic contamination. For this reason, it is possible that the arsenic in points A1, R and A2 is a product of the lack of remediation of the Ite wetland. Likewise, it is worth mentioning that the arsenic content decreases as the surface waters move away from points L2-1 and L2-2 [23], so the high content in Pampa Sitana, at points A1, R and A2 is unlikely to come from these sources rich in arsenic.

Despite the subcategories assigned in the present study using the grey clustering method, it has been identified that water in the Ite district needs an advanced treatment to be made drinkable (which makes it belongs to subcategory A_3) due to the elevated arsenic concentrations found in the area [23]. This discrepancy in the results might be caused due to the maximum weight to each parameter assigned according with Peruvian law.

Only based on DIGESA report, it is not possible to identify if current activities of the mining company have a negative impact on water quality of Ite district. Therefore, it is necessary to analyze intermediate points at Pampa Sitana in order to establish a causal relationship. Furthermore, more parameters as sulfate and total suspended solids should be measured in all points for this purpose. For example, sulfate concentrations have been successfully combined with other parameters to correlate the impact of acid mine drainage on water quality of nearby areas [24], [25].

5.2 About the Methodology

Grey Clustering is a useful mathematical method that enables us to classify and weight the sampling data according to the standards of the Peruvian law (and therefore its different subcategories A_1, A_2 and A_3). According to other authors such as [7], [11]it is an optimal method to study the environmental impact on the quality of surface waters. Furthermore, the method can detect negative anomalies as it was observed in the difference between the score of points L1-1, L1-2 and P with the rest of the monitoring points. Additionally, the pollutions caused by high concentrations of arsenic could be identified. However, it does not show a difference between values a little or slightly above the established by the lowest quality class, even if in the reality a different water treatment must be needed.

6. CONCLUSIONS

The results obtained in this study provide a broad overview of the effects of the Toquepala mine on water resources that are around it or under its influence. As a result, we could observe that the water from Suches lagoon (represented by points L1 and L2) can be used for human consumption, after the respective treatment. The Catchment area (point P1-3) that is between the mine and the current tailings deposit also complies with the A_1 standard but shows an increase in electrical conductivity over the last 10 years, which must be taken into consideration. The natural water of Aricota lagoon (points L2-1 and L2-2) is suitable for human consumption; however, treatment must consider the high values of arsenic and electrical conductivity, which are probably due to the influence of effluents from nearby volcanoes. Water of LocumbaRiver (point R), at least, in the location of the point studied, is not suitable for human consumption as the values analyzed did not meet the A_1 standard and its proximity to the Ite tailings deposit was not completely remedied. Finally, the troughs (points A1 and A2) belonged to the A_1 standard, but since they are in the Ite tailings area, other uses should be assigned for them.

Regarding the methodology, Grey Clustering method is very effective and practical to classify and weight the sampling data according to the standards of the Peruvian law. Also, despite the fact that most of the parameters are positive, the method is able to detect the negative anomalies presented. For this reason, despite the fact that points L2-1, L2-2, A1 and A2 belong to subcategory A_1 of Peruvian law, these presented a lower score than points L1-1, L2-2 and P indicating the presence of a parameter with values above the standards.

Based on the notable difference in quality at points P (near the nowadays mining operations) and R (near the ancient tailings), as well as the huge distance that separates them and contaminated upwelling at Pampa Sitana, intermediate sampling points should be considered in future analysis in order to determinate if an actual contamination caused by the mining company exists. Likewise, the same points could be reanalyzed measuring sulfate, since it is a strong indicator of the presence and evolution of acid mining drainage (AMD) in water bodies. Furthermore, due to water close to the informal agricultural area is polluted (point R), both the soil and agricultural products in this zone must be analyzed.

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