Water Quality Analysis in Mantaro River, Peru, Before and After the Tailing's Accident Using the Grey Clustering Method

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Abstract—**Problems with environmental accidents are increasing worldwide, which generates great damage to the environment. In fact, in July 2019, a tailing spill occurred that flowed into the Mantaro River, contaminating it with thousands of liters of waste. This had environmental consequences and social ones since there were people for and against mining, which is the principal economic activity in the area. In this way, this study proposes to quantify the damage caused by the tailing spill using the grey clustering method, which is based on grey systems theory. For this purpose, two sampling points were chosen for data collection and evaluation both before and after the accident, which allowed to measure the impact of metal concentrations and other physical-chemical parameters caused by accident. The results obtained from the study revealed increases in the concentration levels of metals such as aluminum, arsenic, among others, in some cases very high that exceeded the maximum permitted limits. Such findings could help local and national government authorities, people living and transiting near the river, and activities related to the use of the water in this river; since the quality of the river water can be lethal if the necessary measures are not taken. In addition, the method used in this study showed to be very practical and efficient during its application. Finally, it is advised that future research investigate each point along the Mantaro River and show the areas where the disaster had the most impact to develop some mitigating techniques.**

Keywords— **Environmental accident; grey clustering method; Mantaro river; mining project; water quality.**

I. INTRODUCTION

The department of Huancavelica, Peru, has a small and medium-scale mining activity. Likewise, it is the seventh producer of silver at a national level, eighth at a national level in the lead, ninth in zinc at a national level, among others [1]. Among its mining projects, the Cortiza project provides 30% of the copper concentrate processed by the Metallurgical Complex of La Oroya. Although we have found out that mining is essential, it is not an environmentally friendly activity [2], [3], either directly or indirectly [4]; as has been observed on July 10, 2019, in the district of San Pedro de Colis (Huancavelica), when more than 67,400 cubic meters of tailings fell from their treatment area and affected a large area until they reached the Mantaro River. This had consequences, reported by the citizens in the surrounding areas, on their fruits, plants. Likewise, this caused a social separation between those who support mining, since they recognize the vitality and economic influence that the Cobriza mining unit, owned by the Doe Run Peru SRL company, has on their daily lives, and those who prefer that this project be stopped as soon as possible [5].

In addition, tailings, and their management, are the greatest environmental concern in mining [2]. Since these are mixtures of crushed rocks and mill processing fluids, washing machines or concentration left over after the extraction of metals, minerals, mineral fuels, or economic coal from the mining resource [6]. Another definition is that tailings are fine-grained, particulate solids consisting of ground rock slurry, water, and chemical residues that remain after the minerals or commercial elements have been removed from the ore [7]. Thus, mine tailings and associated accidents have been identified as one of the most dangerous environmental problems worldwide [8]. Therefore, they are controlled by the mining companies because when there is a problem related to them, they can generate a negative and harmful environmental impact, which can be both immediate and long-term [9]. In addition, the quantification of the damage is controlled by national entities, as in the Peruvian case the National Water Authority (ANA in its Spanish initials).

Nevertheless, during the last decades, due to the growing awareness of the quality of water resources by the scientific community and the scarcity of water in all parts of the world [10], river basins are being evaluated by international organizations considering the existing water crisis. Therefore, it is important to recognize the influence of water on life on earth, such as its presence in the life cycle of all plants and animals, in the preservation of the various ecosystems, in the control of climate, and in the continuous remodeling of the Earth [11], [12].

In turn, the objective of this study is to carry out a quantitative analysis that can determine the possible existence of risk. To achieve this, different methodologies have been considered as fuzzy comprehensive evaluation [13], Unascertained measure [14], or grey clustering method [15]. It was decided to use Grey Clustering Methodology since traditional methods cannot solve the complicated nonlinear relationship between evaluation indicators and water quality grade [16]. Since the monitoring data provided by finite monitoring points are limited and ignored in assessing the water environment, it may be considered a grey system [17].

As previously mentioned, the National Water Authority (ANA) has constantly evaluated water quality, including the Mantaro River. Thus, two of these points (RMant1 and RMant2) were chosen to analyze the present study considering the records obtained before and after the tailing slide, which allow the measurement of the most opportune contrast that consents to catalog the water quality for each evaluation parameter under the provisions of Peruvian legislation [18]. This study evaluated nine among six parameters are chemical elements such as Aluminum, Arsenic, Manganese, Copper, Iron, and Lead. Additionally, the OD, pH, and Conductivity parameters were evaluated.

II. MATERIALS AND METHOD

The grey system theory is a method of systems analysis, which could make full use of known information to diminish unknown information, and finally reflect impersonally and truly the essence of the system [19]. Grey system theory was developed by Deng in 1985, studying the problems of small samples and limited and true information. For this reason, it has served as the basis for the method of grey clustering, a widely used methodology, since in the real world, there are various problems with the characteristics mentioned; this influences its application to various fields such as water, air, soil, or social aspect evaluations, among others. The Grey Clustering procedure is detailed below.

First, the variables that depend on the analysis performed are defined as follows.
- The objects of analysis are defined (in this case, they were defined as $(P_1, P_2, ..., P_n)$).
- The evaluation criteria or parameters to be measured of the objects of analysis are defined $(C_1, C_2, ..., C_n)$.
- The grey classes in our studio are defined $(A_1, A_2, ..., A_n)$.

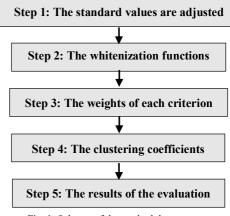Then, the steps of the methodology process are presented in Fig. 1.

Fig. 1 Schema of the methodology

After defining these variables, we proceed to the following steps:

Step 1: The standard values are adjusted, according to the Peruvian legislation, and the values of the information obtained from ANA, due to the different units that have the analysis criteria.

Step 2: The triangle graphic functions of the Whitenization are assembled based on the number of classes of Grey, as seen in Fig. 2.
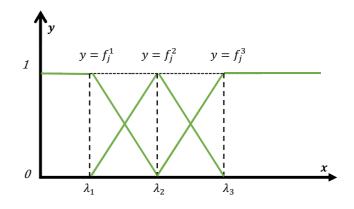

Fig. 2 Center-point Triangular Whitenization Weight Functions (CTWF) [20]

Where:

$f_j^1 = A_1$: Waters that can be purified with disinfection.

$f_j^2 = A_2$: Waters that can be treated with conventional treatment.

$f_j^3 = A_3$: Waters that can be treated with advanced treatment.

Next, the Whitenization functions of the study method are applied as presented on the equations 1-3.

$$f_j^1 = \begin{cases} 1 & ; x \in [0; \lambda_j^1] \\ \frac{\lambda_j^2 - x}{\lambda_j^2 - \lambda_j^1} ; & x \in \langle \lambda_j^1; \lambda_j^2 \rangle \\ 0 & ; x \in [\lambda_j^2; \infty \rangle \end{cases} \quad (1)$$

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$$f_j^2 = \begin{cases} \frac{x - \lambda_j^1}{\lambda_j^2 - \lambda_j^1}; & x \in \langle \lambda_j^1; \lambda_j^2] \\ \frac{\lambda_j^3 - x}{\lambda_j^3 - \lambda_j^2}; & x \in \langle \lambda_j^2; \lambda_j^3 \rangle \\ 0; & x \notin [\lambda_j^3; \infty] \end{cases} \quad (2)$$

$$f_j^3 = \begin{cases} 0 & ; x \in [0; \lambda_j^2] \\ \frac{x - \lambda_j^2}{\lambda_j^3 - \lambda_j^2}; & x \in \langle \lambda_j^2; \lambda_j^3 \rangle \\ 1 & ; x \in [\lambda_j^3; \infty \rangle \end{cases} \quad (3)$$

Step 3: The determination of the weights of each criterion is calculated objectively by using equation 4.

$$n_j^k = \frac{1/\lambda_j^k}{\sum_{j=1}^{m} 1/\lambda_j^k} \quad (4)$$

Step 4: The clustering coefficients are defined in accordance with equation 5 for each point studied or object of study.

$$\sigma_i^k = \sum f_j^k (x_{ij}) n_j \quad (5)$$

Where $f_j^k(x_{ij})$ are the functions of whitenization and n_j are the weights.

Step 5: Finally, the results of the evaluation are analyzed. The maximum values are considered and associated with their respective Grey classes in order to determine the classification.

III. RESULTS AND DISCUSSION

On July 10, 2019, in the district of San Pedro de Coris (Huancavelica, Peru), more than 67,400 cubic meters of tailings fell from their treatment area and affected a considerable area until they reached the Mantaro River itself. According to the mining official, contingency and emergency systems were developed in the environmental implications of the project cycle [21]. The protocols were activated immediately after the tailing slide. The provincial prosecutor was informed of the incident and coordinated with the Environmental Evaluation and Inspection Agency (OEFA in Spanish), the National Police, municipal authorities, and representatives of the mining company to carry out the investigation [5]. However, according to the OEFA, the spill affected 41,574 square meters and damaged the Cobriza II electrical substation and the mining unit's maintenance workshop, leading to one of the most important rivers in the center of the country, which was already mentioned Mantaro River.

Finally, the tailings slide, coming from the collapsed tailings storage facility, were discharged at two different points. First in a surrounding area that affected the electrical substation; and then, on the cliff, where the rapeseed flowed dragging gravel-sand material, discharging into the Mantaro River and settling on its bank, making an alluvial fan and a dam of diverse material, blocking the water flow and causing a 1200-meter long spillway. It is estimated that after this event, the Mantaro River in the affected area had a flow of $2 \ m^3/(s)$, a width of 30 m and a slope of 0.4%.

On the other hand, the dam was 5m high and 40m long. Fortunately, there was no reference to existing populations or water users of the Mantaro River in the vicinity of the lower part that could have been affected first hand. As a result, the Mantaro River was classified as "Category N°1: population and recreational" according to the Environmental Ministry [18]. It was evaluated that category comparing the values obtained with the Environmental Quality Standards of the Waters of the D.S N° 004-2017-MINAM [18]. The ANA carried out two sampling points, RMant1 (upstream) and RMant2 (3700m downstream of the tailings discharge) would give us the values we need for the present work. For a better appreciation of their locations, see Fig. 3.

Fig. 3 Location of the case study in a global map

In the following, the applied steps of the methodology in the case study is shown:

Step 1: Standardized, non-dimensional values are presented for each evaluation parameter under the provisions of Peruvian legislation [18]. The size data for each parameter at each monitoring point collected by the government from the National Water Authority (ANA), both before and after tailings spill, are displayed in Table I.

TABLE I
SAMPLED VALUES NON-DIMENSIONED BEFORE AND AFTER TAILINGS SPILL

Parameter		Before Tailings Spill		After Tailing Spills	
		RMant1	RMant2	RMant1	RMant2
Aluminum	C_1	0.117	0.146	0.012	3.220
Arsenic	C_2	0.131	0.237	1.536	12.478
Manganese	C_3	0.363	0.707	0.037	2.782
Copper	C_4	0.011	0.017	0.001	0.160
Iron	C_5	0.329	0.565	0.010	13.738
Lead	C_6	0.667	1.287	0.013	4.980
OD	C_7	1.294	1.350	1.140	1.142
pH	C_8	1.433	1.438	1.430	1.367
Conductivity	C_9	0.200	0.218	0.504	0.479

The data presented in Table I are substituted in the equations that describe the triangular functions to obtain the values of each grey class. Based on equations 1, 2, and 3, the following Whitenization functions for the first parameter are developed as an example of its application.

$$f_j^1 = \begin{cases} 1 & ; x \in [0; 0{,}305] \\ \frac{1-x}{1-0{,}305} & ; x \in \langle 0{,}305; 1 \rangle \\ 0 & ; x \in [1; \infty \rangle \end{cases} \quad (6)$$

$$f_j^2 = \begin{cases} \frac{x-0{,}305}{1-0{,}305} & ; x \in \langle 0{,}305; 1] \\ \frac{1{,}695-x}{1{,}695-1} & ; x \in \langle 1; 1{,}695 \rangle \\ 0 & ; x \notin [0{,}305; 1{,}695] \end{cases} \quad (7)$$

$$f_j^3 = \begin{cases} 0 & ; x \in [0; 1] \\ \frac{x-\lambda_j^2}{\lambda_j^3-\lambda_j^2} & ; x \in \langle 1; 1{,}695 \rangle \\ 1 & ; x \in [1{,}695; \infty \rangle \end{cases} \quad (8)$$

The same procedure is performed for the remaining eight parameters. With these Whitenization functions, the values for each function are determined.

Step 2: Whitenization values were calculated at each sampling point (RMant1 and RMant2). The results of before tailings spill are provided in Table II.

TABLE II
CENTER-POINT TRIANGULAR WHITENIZATION FUNCTIONS OF THE DATA BEFORE THE TAILING SPILL

RMant1	f_j^1	f_j^2	f_j^3	RMant2	f_j^1	f_j^2	f_j^3
C_1	1	0	0	C_1	1	0	0
C_2	0.56	0.44	0	C_2	0	0.98	0.02
C_3	1	0	0	C_3	1	0	0
C_4	1	0	0	C_4	1	0	0
C_5	0.44	0.56	0	C_5	0	0.95	0.05
C_6	0.5	0.5	0	C_6	0	0.57	0.43
C_7	1	0	0	C_7	1	0	0
C_8	1	0	0	C_8	1	0	0
C_9	1	0	0	C_9	1	0	0

Likewise, the results of after tailings spill are shown in Table III.

TABLE III
CENTER-POINT TRIANGULAR WHITENIZATION FUNCTIONS OF THE DATA AFTER THE TAILING SPILL

RMant1	f_j^1	f_j^2	f_j^3	RMant2	f_j^1	f_j^2	f_j^3
C_1	1	0	0	C_1	0	0	1
C_2	0.47	0.53	0	C_2	0	0	1
C_3	1	0	0	C_3	0	0	1
C_4	1	0	0	C_4	1	0	0
C_5	1	0	0	C_5	0	0	1
C_6	1	0	0	C_6	0	0	1
C_7	0.7	0.3	0	C_7	0.71	0.29	0
C_8	1	0	0	C_8	1	0	0
C_9	1	0	0	C_9	1	0	0

Step 3: For all previously obtained data, the weight must be calculated for each parameter, a weight is obtained, which is shown in Table IV.

TABLE IV
PARAMETERS WEIGHTS

Parameter	Category 1		
	λ_j^1	λ_j^2	λ_j^3
C_1	0.112	0.068	0.083
C_2	0.376	0.375	0.051
C_3	0.041	0.071	0.117
C_4	0.037	0.069	0.128
C_5	0.239	0.143	0.059
C_6	0.102	0.068	0.084
C_7	0.028	0.068	0.175
C_8	0.029	0.068	0.168
C_9	0.035	0.068	0.136

Step 4: With the previously calculated data, the clustering coefficients were calculated. These results can be visualized in Table V.

TABLE V
CLUSTERING COEFFICIENTS BEFORE AND AFTER THE TAILINGS SPILL

	Before Tailings Spill			After Tailings Spill		
	A_1	A_2	A_3	A_1	A_2	A_3
RMant1	**0.651**	0.278	0.000	**0.792**	0.219	0.000
RMant2	0.283	**0.543**	0.040	0.122	0.020	**0.393**

Step 5: Finally, the maximum value in each scenario was considered, which is the grey class category. The results revealed that the water in RMant1 was of category $A_1(\lambda_1)$, meaning water that can be purified with disinfection, both before and after the tailings spill. Nevertheless, before the accident, the water at RMant2 was category $A_2(\lambda_2)$, namely, Waters that can be treated with conventional treatment; a situation that changed after the accident, according to the results, since it became $A_3(\lambda_3)$ Waters that can be treated with advanced treatment.
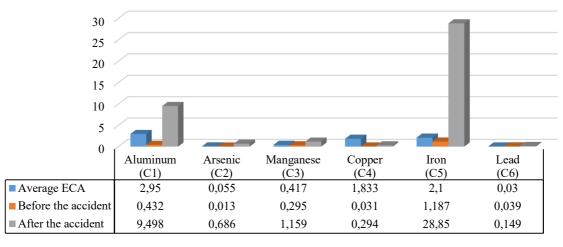
A. About the Case Study

After analyzing the results obtained and summarized in Table V, it was observed that there were changes concerning water quality, with the most likely cause of contamination being the tailings slide from the Cobriza mining unit, owned by the Doe Run Peru SRL company, that occurred in the Mantaro River.

On the one hand, at point Rmant1 it was observed that its initial category is A_1 (water that can be treated with disinfection) and after the accident, it maintained its initial category. However, it should be noted that the analysis point of the Rmant1 is upstream, so it has not been significantly impacted by accident, but it provides a monitoring point for future comparison.

On the other hand, it was observed at point Rmant2 that there was a change, as it went from category A_2 (water that can be treated with conventional treatment) to category A_3 (water that can be treated with advanced treatment). In addition, it was noted that the content of metals such as aluminum, arsenic, manganese, copper, iron, and lead increased and even surpassed the values of water quality

standards and maximum permissible limits defined by D.S. 055-2010-EM of the Ministry of Energy and Mines [22].

Furthermore, it can be seen that the increase in metal content was only more pronounced at point Rmant2, which, as indicated in Fig. 2, is downstream of the river under analysis, which helped us to determine the contamination produced by the waste slides.

Finally, a comparative graph (Fig. 4) with the six chemical elements (Aluminum, Arsenic, Manganese, Cooper, Iron and Lead) was developed, in which the values obtained before and after the accident are shown for point RMant2, since this is the area where the variation in content occurred with a higher average of the values concerning the three scenarios. Finally, it was observed that the most critical metal contents are aluminum and iron, which greatly exceed the Maximum Allowable Limit or MPL; at the same time, all the criteria were increased and exceeded the proposed limits, except for the case of Cooper C_4, where there was an increase, but the limits were not exceeded.

	Aluminum (C1)	Arsenic (C2)	Manganese (C3)	Copper (C4)	Iron (C5)	Lead (C6)
■ Average ECA	2,95	0,055	0,417	1,833	2,1	0,03
■ Before the accident	0,432	0,013	0,295	0,031	1,187	0,039
■ After the accident	9,498	0,686	1,159	0,294	28,85	0,149

■ Average ECA   ■ Before the accident   ■ After the accident

Fig. 4 Metal content at the RMant2 sampling point

B. About the Methodology

Regarding the Grey Clustering methodology, its usefulness and versatility against the development of analysis with limited amounts of data were confirmed. This was particularly beneficial as the existing results were for two sampling points that were very well located as these enabled the analysis before and after the tailings spill into the Mantaro River. This feature differentiates it from other methodologies that could have been applied in the study, such as Delphi, Shannon entropy, and AHP, since the objective of the investigation was to determine the contamination of the Mantaro River quantitatively due to the accident that occurred on July 2019. Some of the advantages of the methodology are described below.

- Since environmental conflict is a fickle and subjective social issue, one of the criteria for its evaluation must be its cost [23]; in this regard, it should be noted that an approach of the Grey Clustering methodology fully covers this need since it would have a lower cost than the statistical approach, as the sample size influences the research field expense [24].
- It has been demonstrated that the predictive accuracy of the Grey Model is generally superior to that of the regression model by contrasting the mistakes in the predictions of both models and the real sightings [20].
- Compared to other methodologies, the theory of Grey Systems highlights the exploration of those objects that handle clear expansions and uncertain intent [20].

IV. Conclusions

In the case study, two points from Mantaro River, RMant1 and RMant2, were determined as good and moderate-quality water respectively before the accident, and the point after the accident, Rmant2 showed a poor quality. In addition, the information of this study is highly recommended to be made known to the Peruvian citizens, especially those who reside or circulate in the affected area, and their local authorities for them to take the necessary precautions and measures.

Finally, for future studies, it is suggested to analyze each point of the Mantaro River and show the points where the accident had more impact on creating some mitigation technique. This analysis can be done when the respective authorities display all the results of every point of the Mantaro River before and after the accident. In addition, the grey clustering method could be tested on other environmental accidents.

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