Seasonal variation of heavy metals in surface water of the Ananea river contaminated by artisanal mining, Peru

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Abstract. The objective of this research work is to evaluate the effects of mining tailings leak on the water quality of the Ananea river, which contain heavy metals. For which techniques such as taking surface water samples were applied at five strategic points, programming two sampling campaigns; one in the rainy season (March) and the other in the dry season (June). Heavy metal concentrations were determined by the EPA METHOD 200.7 Atomic Emission Spectrometry method; The results show that the highest concentrations were recorded at the M-1 sampling point for both the dry season and the rainy season. These concentrations are well above the peruvian Environmental Quality Standards (WQS) for water. In the same way, point M-1 was identified as the most critical and vulnerable to contamination in the study area by heavy metals that are above WQS. Likewise, the survey technique was applied, for which a question sheet was prepared for the surrounding population according to the activities carried out in this part of the basin, obtaining data to determine the effects caused by mining pollution on the surrounding life. In conclusion, the quality of the waters of the Ananea River are contaminated by the presence of heavy metals and these have been causing negative effects to all the surrounding life found in the study area.

1. Introduction
Wastewater from surface and underground mining, mineral processing, and smelting in mines often contain many heavy metals, thus becoming sources of contamination in the water body. Many heavy metals are included in the "black list" of contamination, such as Pb, Zn, Cd, Cr, Cu and Ni, etc. [1]. Chemical leaching of metals occurs when precipitation from rain or snowmelt seeps through ore or waste materials and dissolves or desorbs metals from solid material. As a consequence, the streams carry high contents of toxic trace elements such as As, Cd, Pb, Zn, Cu, Sb and Se [2]. Most of the heavy metals that flow into rivers through a variety of forms change to the solid phase from the aqueous phase through physical sediments and chemical adsorption and are deposited in the sediment [3]. As a result, sediment is the main deposit of heavy metals in rivers and is the indicator of heavy metal pollution in the aquatic environment, which affects the effects of dredging and river governance. At the same time, heavy metals have toxicity or even poison (such as Cd, Hg, Pb and As), which cannot be degraded by microorganisms and will accumulate by concentration. The La Rinconada mining center (5000 meters above sea level) is located at the source of the Ananea river, where artisanal gold mining is carried out on a significant scale, its main impact being associated with the...
evacuation of mercury through rivers and streams [4], and other heavy metals [5] which finally drain through the Ramis river and then to Lake Titicaca. Along the way, the rivers receive different effluents from untreated wastewater.

The Ananea river, during its trajectory, crosses several areas whose priority development is made up of various human activities, possessing natural resources that allow mining exploitation (mostly gold). Throughout the riverbank there are populated centers that make population use of water, either for their consumption, for their animals and also for the irrigation of their crops and cultivated pastures, these systems fed in some areas by waters of the Ananea River.

The present study characterizes the effects of mining pollution on the quality of the waters of the Ananea river, through the use of techniques such as taking a water sample and conducting surveys of the surrounding population in different sectors of the same (five strategic points ), for their respective chemical analysis and determination of the degree of contamination by different components of heavy metals and their effects on surrounding life such as the flora and fauna of the place.

2. Method

The study area covers the districts of Ananea and Cuyocuyo; between the coordinates 69°25'38" W and 14°36'50" S from where the waters of the Ananea River are born, 70°01'54 "W and 14°21'40" S, the place where the last samples were taken of water near the city of Crucero.

![Location of sampling points (Ananea river)](image)

2.1. Determination of heavy metal concentration

To determine the concentration of heavy metals, the sampling protocol technique (Surface water sampling procedure) was applied, according to the methodology of the National Water Authority (ANA) [6] and subsequently taken to the laboratory.
2.2. Sampling design
Five sampling points were located along the Ananea River micro-basin. Which were strategically located according to the population, accessibility of the land and the activities carried out in the study area.
Plastic containers of 500 ml capacity were used, which were labeled according to the sampling point carried out, these were hermetically closed and protected from sunlight during transport to the laboratory.

2.3. Sampling
M-1 (446555E and 8376347N): taken at the source of the waters of the Ananea River, which is born in the Sillacunca lagoon. Sample taken at 9:20 a.m., about 4811 masl. This point was chosen because the waters of the Ananea River, which is the object of study, are born there (Figure 1).
M-2 (438131E and 8378792N): taken downstream from the city of Ananea, this area was chosen because the waters that were used by the mining activity of the mining cooperatives of the community of Pampilla (Ananea district) come together. Sample taken at 10:30 a.m., about 4585 masl.
M-3 (425472E and 8394898N): taken under the junction deviation bridge (Cuyocuyo district). This point was chosen because of its accessibility and because from this point on the Ananea River is called Rio Grande. Sample taken at 11:40 a.m., about 4373 masl.
M-4 (419222E and 8399106N): taken 50 meters from the peasant community of Huajchani. This point was chosen because of the existing surrounding population and because of the mining activities that took place a few years ago. Sample taken at 12:30 p.m., about 4336 masl.
M-5 (391645E and 8411128N): taken 100 meters upstream from the city of Crucero under the Crucero bridge. This point was chosen because of its proximity to the population of the Crucero district. Sample taken at 1:40 p.m., about 4142 masl.

2.4. Water analysis
The determination of the concentration of heavy metals (total metals) in both periods was carried out by the method of "Atomic Emission Spectrometry EPA METHOD 200.7" [7], in the Laboratory of Testing and Quality Control of the Catholic University of Santa Maria - Arequipa; laboratory accredited by the Peruvian accreditation body INACAL-DA with registration No. LE-070.
With the obtaining of the results, the degree of contamination by heavy metals in the waters of the Ananea River was evaluated, for which the established parameters of the Environmental Quality Standards (WQS) given by the Ministry of the Environment were taken into account. Environment (MINAM) of Peru [8].
Table 1 shows the updated parameters of the Environmental Quality Standards for water (WQS). category 1 destined for population and recreational use, in its subcategory A for surface waters destined to the production of drinking water and category 3, destined for the irrigation of vegetables (D1) and animal drink (D2).

3. Results and Discussions
With the obtaining of the results measured in the field and in the laboratory; we proceeded to the analysis and interpretation.

3.1. Concentration of heavy metals in the waters of the Ananea river
In this part of the study it is intended to determine the concentration of heavy metals, and to evaluate these according to the quality parameters of the WQS for water (human consumption, irrigation of crops and animal drinking).
From the data obtained in the laboratory, the analysis of heavy metals was obtained; of which seven elements exceed the WQS for waters at least in one sampling point carried out (Table 1).
Table 1. Heavy metal concentration vs WQS in dry and rainy season (mg/L)

| Analysis | Rainy season | Dry season | WQS          |
|----------|--------------|------------|--------------|
|          | M-1 | M-2 | M-3 | M-4 | M-5 | M-1 | M-2 | M-3 | M-4 | M-5 | Human consumption | Irrigation crops | Animal drink |
| Al       | 41.416 | 1.807 | 1.247 | 0.729 | 2.078 | 96.78 | 0.621 | 2.156 | 0.909 | 1.268 | 5 | 5 | 5 |
| As       | 0.331 | 0.014 | 0.006 | 0.004 | 0.009 | 0.765 | 0.006 | - | - | 0.012 | 0.15 | 0.1 | 0.2 |
| Cd       | - | - | - | - | - | 0.014 | 0.002 | 0.002 | 0.002 | 0.002 | 0.01 | 0.01 | 0.05 |
| Cr       | 0.019 | - | - | - | - | 0.067 | - | - | - | - | 0.05 | 0.1 | 1 |
| Fe       | 63.785 | 3.318 | 1.685 | 0.996 | 2.837 | 131.9 | 2.133 | 2.52 | 0.957 | 1.424 | 5 | 5 | - |
| Mn       | 0.743 | 0.319 | 1.047 | 0.418 | 0.529 | 1.43 | 0.565 | 0.251 | 1.167 | 0.17 | 0.5 | 0.2 | 0.2 |
| Pb       | 0.03 | - | - | - | - | 0.121 | 0.026 | 0.043 | 0.064 | 0.029 | 0.05 | 0.05 | 0.05 |

3.2. Chemical concentration of water

**Aluminum (Al):**

Al concentrations were recorded with maximum values of 41.416 mg/L in the rainy season and 96.78 mg/L in the dry season, both at the M-1 sampling point. These concentrations, both in the rainy season and in the dry season, exceed the parameters of the WQS for water at the M-1 sampling point, contrary to the other sampling points carried out where the Al concentrations are below the WQS quality parameters for water.

**Arsenic (As):**

As concentrations were recorded at the M-1 sampling point with maximum values of 0.331 mg/L in the rainy season and 0.765 mg/L for the dry season, which are above the WQS for human consumption, irrigation of crops and cattle drink at this point, otherwise for the other sampling points that their values are below the WQS for water. According to Salas-Urviola, [5] obtained As concentrations (6.55 mg/L) during the dry season, which is similar to the results obtained for the dry season but not to the results obtained during the rainy season. The studies carried out by Cornejo [9], affirm the increased risks of lung and bladder cancer, and of skin lesions, which were associated with the ingestion of water with As concentrations below 50 μg/L.

**Cadmium (Cd):**

The Cd concentration is with a maximum amount of 0.014mg/L at the M-1 sampling point during the dry season and there is no Cd concentration in the rainy season. Cadmium concentrations in the dry season exceed the WQS for human consumption and crop irrigation at sampling point M-1, while for the other sampling points the concentrations of this heavy metal are constant (0.002 mg/L) and are below the WQS for water. Cadmium concentrations were not recorded for the rainy season. Cd enters the human body through the digestive tract and respiratory tract, causing vascular hypertension, chronic poisoning, and other diseases [1].

**Chromium (Cr):**

Chromium concentrations are at maximum 0.019 mg/L in the rainy season and 0.067 mg/L in the dry season, both at the M-1 sampling point. These only exceed the WQS for human consumption during the dry season, downstream we note that there are no concentrations of this heavy metal, therefore they do not exceed the WQS quality parameters for water.

According to Salas-Urviola [5] in his study of the Ananea river, Chromium concentrations occurred only during the dry season (0.96 mg/L), which is fairly similar to the results obtained but with a considerable decrease in Cr in the results obtained.
Iron (Fe):
Iron concentrations are a maximum of 63.785 mg/L in the rainy season and 131.9 mg/L in the dry season, both at the M-1 sampling point, which exceed the WQS for human consumption and crop irrigation during the seasons. Two epochs, then downstream the concentrations of this heavy metal decrease considerably and at the same time show variables, which exceed the WQS for human consumption, but do not exceed the WQS for crop irrigation.

The high concentrations of Iron found at the M-1 sampling point (in both periods), contribute to the low concentrations of dissolved oxygen, since these waters were at rest shortly before (in the Sillacunca lagoon), are released and from from then on we have the source of the waters of the Ananea river.

Manganese (Mn):
Manganese concentrations are at a maximum of 1.43 mg/L at the M-1 sampling point during the dry season and maximum concentrations of 1.047 mg/L at the M-3 sampling point during the rainy season. In the rainy season, Mn concentrations exceed the WQS for crop irrigation and animal drinking throughout the entire route, and for human consumption the concentrations of this heavy metal only at the M-2 sampling point are below the WQS. For the dry season, Mn concentrations exceed the WQS for human consumption, crop irrigation, and animal drinking at sampling points M-1 and M-2, while for the other sampling points (M-3, M-4 and M-5), Mn concentrations are slightly below the WQS.

The Mn concentrations found during the dry season reflect the low concentrations of dissolved oxygen and the subsequent release of its waters. Meanwhile, the variable behavior during the rainy season is reflected in the higher concentration of the river flow and the continuous feeding of the wastewater from the mining activities carried out in the area.

Lead (Pb):
Lead concentrations are at maximum 0.03 mg/L in the rainy season and 0.121 mg/L for the dry season, both at the M-1 sampling point. Likewise, the concentrations of Pb in the rainy season are below the WQS for water in all the sampling points, with a minimum amount in the sampling point M-1 and with minimum concentrations (0.00 mg/L) in its route downstream.

For the dry season, the Pb concentrations are above the WQS for water in the sampling points M-1 and M-4, while the other sampling points (M-2, M-3 and M-5) have Pb concentrations below the WQS for water.

We can also note that there is a higher concentration of this heavy metal during the dry season, we assume a higher concentration of Pb at this time because in the area there are mining liabilities who make the most of the little water resource found in the area by reusing it (return) so many water is sometimes needed.

Mercury (Hg):
Hg concentrations were not recorded in all the sampling points carried out, during the two seasons. So we interpret that Mercury, being a liquid metal and having a specific weight much higher than that of water, tends to settle at the bottom of the river and it will not be possible to find Hg concentrations in surface water samples, otherwise it would happen in samples of sediments in the course of these waters, as indicated by [4], who found extremely high concentrations of mercury in sediments, exceeding the established limits.

3.3. Identification of critical points of contamination
The highest concentrations are mostly at the M-1 sampling point during the dry season. With heavy metals such as Aluminum with 96.78 mg/L and Iron with 131.9 mg/L. Figure 2 shows us a negative correlation for the analysis of heavy metals, this means that the concentration of these metals tends to decrease as their waters flow to the lower part of the basin.
Figure 2. Identification of the most critical point for heavy metals (A) rainy season and (B) dry season

Electric conductivity
The values obtained in the rainy season were from 226 uS/cm at sampling point M-1, to 724 uS/cm at sampling point M-5; while for the dry season there are values from 422 uS/cm at the M-1 sampling point, to 1220 uS/cm for the M-5 sampling point. (Figure 3). However, these values are below the WQS for waters issued by the MINAM.

According to Cornejo and Pacheco [9], in their study they show us that the behavior of electrical conductivity in the Azángaro sub-basin tends to increase (from 100 uS/cm to 900 uS/cm) as its waters flow through presence of salts, dissolved ions and dissolved organic matter. A similar case occurs in our study, so we can confirm that electrical conductivity tends to increase as its waters flow in this part of the basin (Table 2).

| Analysis | Rainy season | Dry season | WQS |
|----------|--------------|------------|-----|
|          | M-1 M-2 M-3 M-4 M-5 | M-1 M-2 M-3 M-4 M-5 | Human consumption | Irrigation crops | Animal drink |
| pH       | 4.9 5.3 8.2 8.4 8.3 | 6.7 8.5 9.9 10.2 10.1 | 9 | 8.5 | 8.4 |
| EC (uS/cm) | 226 268 252 304 724 | 422 488 460 585 1220 | 1500 | 2500 | 5000 |

Hydrogen potential (pH)
Results of pH in these waters indicate us in the rainy season as a minimum 4.9 in the sampling point M-1 and a maximum of 8.4 in the sampling point M-4, while the minimum values for the dry season show us in 6.7 in the sampling point M-1 and as maximum values of 10.2 at the sampling point M-4. (Table 2).

The pH in natural waters is between 6.00 and 8.50, although lower values can occur in diluted waters with a high content of organic matter, and higher values in eutrophic waters, underground brines and salty lakes. The pH is influenced by the content of salts and changes in the volume of water. In the dry season it increases due to the concentration of salts and decreases in the rainy season, as indicated [10].

3.4. Effects caused by the contamination of the waters of the Ananea river
With the elaboration of questions and answers obtained in-situ of the affected population, we proceed to the analysis and interpretation of the effects that have been caused by the contamination in this part of the micro-basin, as well as [11] it has been shown that artisanal mining has a significant impact on adjacent river ecosystems.
In people's health
Regarding the effects that pollution causes on people's diseases, based on surveys carried out with 252 families in the area, it is observed that 55.56% suffer from gastrointestinal and febrile diseases, 25.79% have skin diseases and infections and 18.65% have lung and respiratory diseases. Taking into account the laboratory results that indicate the presence of heavy metals such as As, Cd, Fe and Pb, and taking into account that most of the people who live near the Ananea river suffer from these ailments, which in part can be caused due to poor water quality.

In animals
With regard to the effects caused by contamination in animal diseases, it is observed that 63.49% present stomach and intestinal discomfort, 28.97% present infectious signs, while 7.54% present motor clumsiness, this indicates that the majority of animals suffer these ailments, similar to human beings living in the area around the Ananea river.

In fish
Most of the fish are in increasing extinction due to the effects of pollution with 55.95%, followed by sudden death that is 26.59%; therefore, pollution has an impact on the living standards of the fish that live in the Ananea river.

In aquatic plants
42.46% of aquatic plants do not develop properly and do not sprout; 65% present very weak roots and 31.75% present dryness due to substances adhered to the stem, and then they wither as a result of contamination; this effect has a negative and alarming impact on the flora of the area [11].

On farmland
Only 13.89% of the lands present normal fertility, 25.0% present complete infertility and 61.11% present progressive infertility, which affects the production of farmland. Laboratory results indicate the presence of heavy metals such as Aluminum and Chromium, and these cause negative effects on soils.

4. Conclusions
The high electrical conductivity values indicate the presence of particulate material and the presence of salts and minerals, it can be stated that there is a concentration of heavy metals in all the sampling points carried out, obtaining values well above the WQS for water for human consumption, irrigation of plants and cattle drink, therefore they are not recommended for consumption in general. It appears that there is a higher concentration of heavy metals at the M-1 sampling point, also the quality of the water in general tends to increase downstream in the path of the Ananea River. With the questions formulated and obtained from the population affected to the study area and the results obtained from the laboratory, the effects that have been causing adverse effects are affirmed, which has been alarmingly degrading life in this part of the micro-watershed and therefore the affected population is forced to leave their lands and seek other alternatives.

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