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Distribution And Adsorption of Mercury in Abandoned Mines in The Laberinto - Tambopata -Puerto Maldonado Sector

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Abstract

The study was conducted in the Laberinto Sector. It determined the distribution and adsorption capacity of mercury in the soil, how the physical-chemical characteristics of the soil influence the adsorption, and the entry of mercury into the vegetation. An area of 20 km2 was studied, applying the Soil Sampling Guide of the Ministry of the Environment, using the Circular Grid sampling, obtaining 4 Quadrants (A, B, C, and D) with 8 sectors, extracting a total of 33 samples, with 17 samples for physical-chemical study. For the vegetation samples, it was based on the Inventory Guide of Flora and Vegetation of the Ministry of the Environment, obtaining a total of 21 samples. The concentration of mercury in soil and vegetation samples was analyzed in the laboratory by atomic adsorption analysis, and the adsorption capacity was obtained by the Langmuir Isotherm formula. As a result, the distribution of mercury concentration is not homogeneous in the study area, and the concentration of mercury in the soil does not exceed the Environmental Quality Standards of the Peruvian Ministry of the Environment but does exceed the standards of the United Nations Environmental Program (UNEP). The adsorption capacity of mercury decreases as the mercury concentration increases, being fundamental to the physical and chemical characteristics of the soil in the entry of mercury into the plants. The concentration of mercury in vegetation exceeds the maximum standards allowed by the European Union Commission by Regulation.

Keywords: *Mercury, Soil, Vegetation, Concentration, Ingress*

1. Introduction

In Peru, gold mining is a tangent problem, which produces exorbitant pollution in the ecosystem, as well as in the health of the population; it is the main source of income for the department of Madre de Dios, however, due to the lack of training and awareness on issues of management application and regulations of the authority in heavy metal pollution, it produces large-scale pollution since heavy metals enter the trophic chain by different means, where living organisms present biomagnification and biocumulation of metals in their organisms (Wang et al., 2009).

Mercury is a toxic element that is not essential in organisms and, due to its high density, is a heavy metal that, although toxic in small quantities, can damage the nervous system (Abollino et al., 2002). Mercury enters the trophic chain in the amalgam for gold extraction because it is the main element used for gold extraction. It is melted together with the gold to separate them and obtain the precious metal. In this process, vapors are generated that enter the atmosphere, and due to the lack of adequate biosafety in the process, miners are exposed to metallic mercury vapor that enters their bodies.

In water sources, 45% of mercury enters the water, which is transformed by the action of microorganisms into methyl mercury (MeHg); the remaining mercury enters the atmosphere in the form of ethyl mercury, accelerating precipitation in rainy regions (Veiga et al., 1995). This is the means by which mercury enters the soil. In ecosystems, mercury is transformed by biogeochemical processes and is distributed with different physicochemical characteristics, with two pathways: microbial metabolism (biotic process), where the methyl ion (CH_3^-) is transferred by sulfate-reducing bacteria, and chemical methylation (abiotic process) (Mahbub et al., 2017). Mercury is retained in the soil, or it can be mobilized by different chemical and biological means (Pagnanelli et al., 2004).

In vegetation, mercury enters through the substrate, allowing the metal to enter the food chain. The adsorption and accumulation of mercury, and the mobility of metals depend primarily on how the solution is found in the soil so that it can enter through the root of the plant. Depending on the species of plant, as well as its physiological and morphological characteristics, it will absorb the mercury from the soil, as well as the concentration of the metal in the soil, etc. Plants adapt and adopt different strategies when there is mercury in the soil (Barceló et al., 2003). In the population, mercury enters the diet of the population, directly or indirectly, due to mining activity. Organomercury compounds, by their nature, are easily absorbed and are neurotoxic; the maximum permissible level of mercury in the blood, according to WHO, is (0.3 ppm), an international reference in human health.

The distribution and adsorption of mercury in abandoned gold mining were studied, after the extraction activity in the sector of Laberinto - Tambopata - Madre de Dios, in the mining concession of "Kiara and Grecia Project"; the physical and chemical characteristics of the soil were determined, as well as the amount of mercury that entered the soil; and the proportion of mercury that entered the most representative vegetation in the study area was determined. The data obtained showed the mercury contamination in the soil, allowing to visualize the real extent of such contamination, as well as the mercury entering the vegetation of the jungle ecosystem; this information provides important data to promote the recovery of the altered ecosystem, using different technologies for its extraction and possible decontamination of the ecosystem.

2. Materials And Methods

Scope of Study

The present study was carried out in the Madre de Dios Region, Tambopata Province, Laberinto District, where soil and vegetation samples were obtained from the "Kiara y Grecia" concessionaire, in the sector called La Pampa. The study area is located at an average altitude of 200 masl, at 12° 52' 29" S South Latitude and 69° 59' 08" W West Longitude, concerning the Greenwich meridian; the total area of devastation caused by mining activity in the pampas sector is 34,875 km², the research work covered a surface area of 20 km² (Figure 1).

The study area has an average annual temperature of 24.95 °C, the average annual precipitation is 320.82 mm/year, and the average monthly relative humidity is 87.40%. This study area has two life zones, according to Holdrige's classification of life zones, which are: very humid premontane tropical forest transitional to tropical humid forest and very humid tropical forest.

Soil sample selection and data collection techniques

Determination of Sampling Points: The methodology used in the collection and determination of the sampling points were obtained by the guide for soil sampling of the Ministry of Environment of 2014, in a total area of 20 km^2, 4 directions were taken, north, south, east, and west; from which 8 sampling points were obtained from each direction, starting from the center of the Study area, obtaining a total of 32 soil samples, in two seasons of the year (dry and rainy), having a total of 64 soil samples plus 2 samples from the central part of the study area. The number of samples is representative because the statistical curve of operation was carried out employing MiniTab software, obtaining a 0.99 confidence level (Figure 2).

Soil sample collection and transport: The objective of the sample collection was to obtain the amount of mercury present in the soil contaminated by the mining activity, which was based on the Environmental Quality Standards, established in the D.S. N° 011-2017-MINAM in Peru, as well as by the United Nations Environment Program (UNEP) of 2002. Stratified and/or systematic (regular) random sampling was performed. The suspicion of mercury contamination in the soil was considered, so the sampling patterns were expanded. Circular grid sampling was used, with manual probing. Surface samples were obtained, and pits 20 cm wide by 40 cm long and 30 cm deep were made (Guide for Soil Sampling - MINAM 2014), obtaining per sampling point, 500gr of soil sample. The soil samples were sent to the laboratory, where the transport material was compatible with the soil materials and the contaminant under study, such material avoided chemical reactions with the soil sample and was resistant to breakage, avoiding losses of the metal under study by evaporation; according to the guide for soil sampling, glass containers with Teflon lids are compatible for the transport of samples with heavy metals.

Conversion from parts per million of mercury to moles of mercury: When obtaining the laboratory results of the mercury concentration in parts per million, to use the data in the Langmuir Isotherm, it must be converted to moles of mercury, thus obtaining the Adsorption Capacity of mercury in the soil. The following formula was used:

$M = mg/L\ X\ 1\ g/1000mg\ X\ 1mol\ de\ Hg\ /mol\ atomo\ gr\ (200.59gr)$

Sample selection techniques and vegetation data collection.

Determination of Sampling Points:_In the office, a preliminary legend of the detailed vegetation map was structured, which was adjusted after conducting the floristic inventory; the location method is Systematically stratified. That is, it implies the existence of vegetation, according to a systematic pattern within each stratum (Guía de Inventario de Flora y Vegetación, MINAM, 2015).

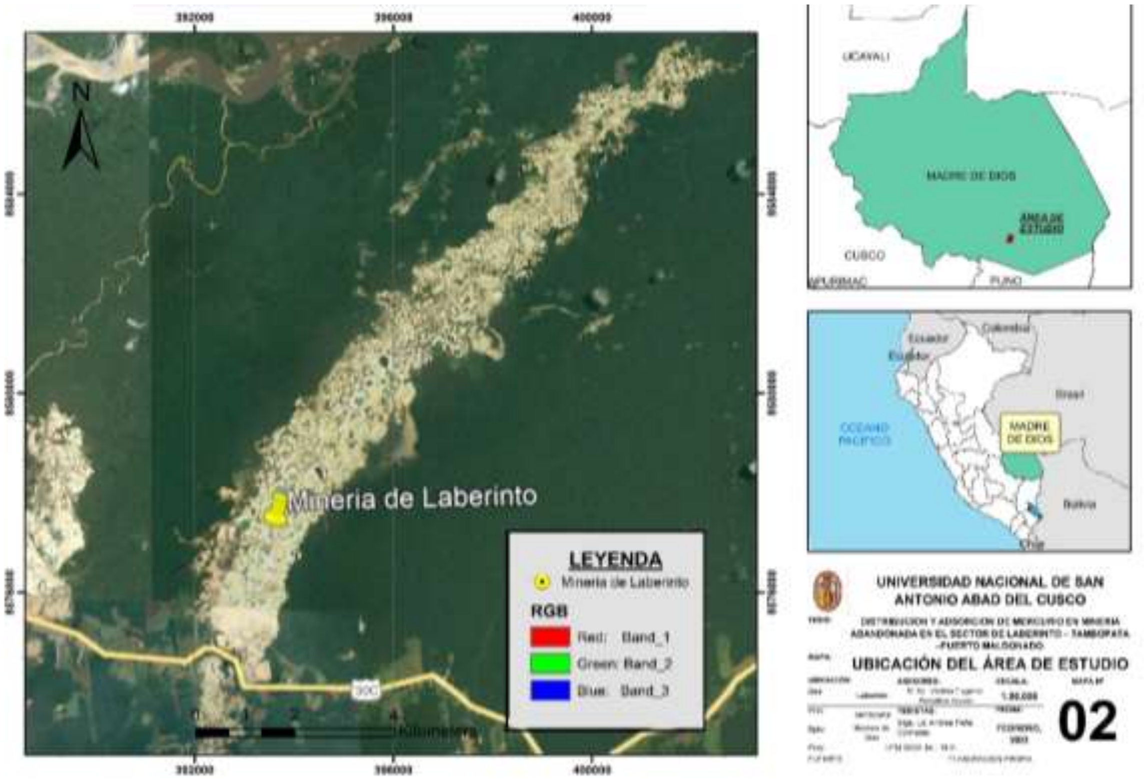

Figure 1 Map Of The Study Area

Collection and transport of vegetation samples: Samples were obtained by simple random sampling, which depended on the presence of vegetation in the study area. Sampling was of the "quadrant" type, which is based on whether there is herbaceous, shrub, or tree vegetation in the study area; measuring $1m^2$, in the case of herbaceous vegetation; $4m^2$ in shrub species and $25m^2$ in the case of tree vegetation; samples were taken from the root, stem, leaves, and fruits of the plant species found in the study area (Guía de Inventario de Flora y Vegetación, MINAM, 2015), obtaining a total of 500 gr of vegetation samples per sampling point; these were placed in hermetically sealed Ziploc bags to be taken to the laboratory. Because the study area is devastated, no vegetation samples were found in many of the sampling points.

Method of collection of vegetation samples for taxonomic identification: Taxonomic identification was carried out through the extraction of plant samples. These were taken to the Vargas Cuz Herbarium of the University of San Antonio Abad del Cusco for identification. The specimens, had as far as possible the vegetative parts, such as roots, stem, and leaves, and reproductive structures such as flowers and fruits (Manual of Curation and Preservation Techniques for a Weed Herbarium, SENASICA, 2019).

Atomic Absorption Analysis. To obtain the mercury concentration of the soil and vegetation samples, these were sent to the laboratory for their respective analysis, using atomic absorption spectrophotometry analysis, using the EPA METHOD 7471B method.

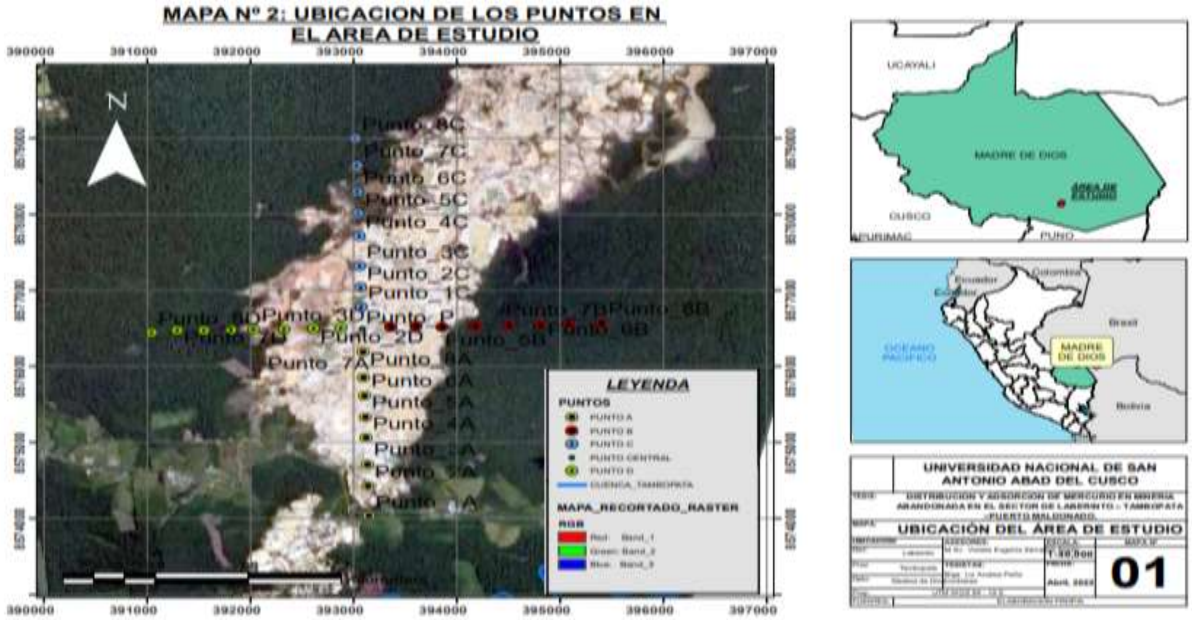

Figure 2 Location Of Sampling Points.

3. Results and Discussion

To evaluate the distribution and adsorption capacity of mercury in the soil impacted by mining activities in two seasons of the year in the Laberinto - Tambopata - Madre de Dios sector.

Soil mercury concentration. According to Peruvian regulations given by the Peruvian Ministry of Environment, the amount of mercury allowed in the soil is 6.6 mg/kg MS2, according to Ministerial Resolution No. 182-2017- MINAM; a comparison was also made with the quality standard of the United Nations Environment Programmed (UNEP) of 2002, where the maximum concentration of mercury allowed is 1.4 mg/kg MS2. These data allowed a comparison of the concentrations found in the samples. The results showed that the sample with the highest mercury concentration is 4.48 mg/kg at point C2 in the dry season, which according to Peruvian regulations does not exceed the quality standards, therefore, no sample exceeds the quality standards, i.e., the soil of the mining area does not present mercury contamination. While most of the samples obtained exceed the quality standard for soils according to the United Nations Program for the Prevention and Control of Mercury Contamination.

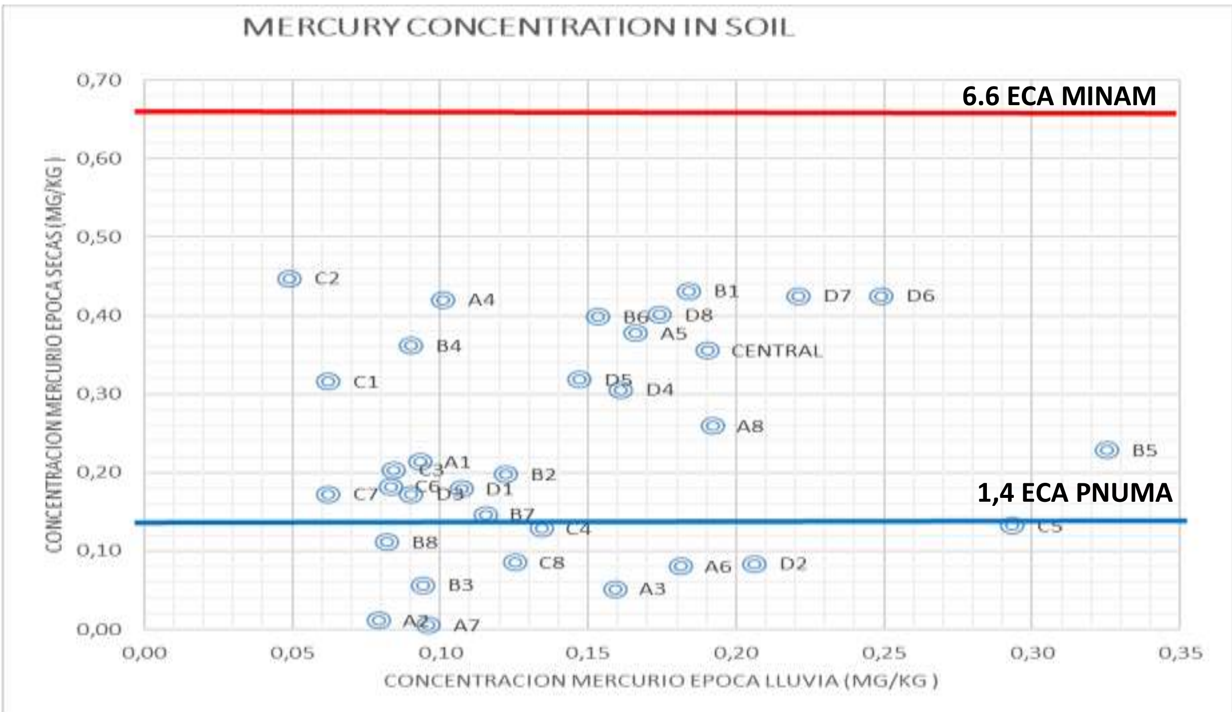

Figure 3 Mercury concentration at each soil sampling point in rainy and dry seasons.

Relationship between mercury concentration and adsorption capacity by epoch: Figure 3 shows the concentration of mercury in the two seasons of the year in mg/Kg. comparing the UNEP environmental quality standards with 1.4 mg/Kg and the Peruvian MINAM regulations with 6.6 mg/Kg. It is observed that most samples exceed the environmental quality standards, that is, more than 70% of soil samples are contaminated with mercury, according to UNEP, but not so for the environmental quality standards established by the Peruvian MINAM, where no sample exceeds these standards. When performing a Pearson correlation for mercury concentration in the soil, both in rainy and dry seasons, a non-significant value is obtained; that is, sectors contaminated in dry seasons will not necessarily continue to be contaminated in rainy seasons, because external factors intervene in mercury concentrations, where in the rainy season, it is strongly dispersed due to the washing of water coming from the rains.

Soil mercury adsorption capacity: To obtain the adsorption capacity, the Langmuir Isotherm formula was used, which was obtained from each of the soil sampling points. The mercury concentration was transformed from mg/kg to moles. The adsorption capacity (q) of the soil is closely related to the mercury concentration, finding a reciprocity, that for each mole of Hg/L, -7.13775 (q) is found at the 10^-9 scale. Indicating a relationship with a negative sign, i.e., the higher the mercury concentration, the lower the adsorption capacity. Proportionally, for each mole of mercury, the capacity of the soil to receive mercury decreases by 7.13775 of its mercury adsorption capacity. It was observed that the adsorption capacity decreases in the dry season at -8711 and in the rainy season at -5034.

Determine the distribution, concentration, and adsorption capacity of Mercury in the soil impacted by the mining activity in a range of 20 km^2 within the direct area of influence.

The mercury concentration presented an unusual distribution, i.e., the distribution of mercury does not decrease as it moves away from the central mining point. To adequately identify the mercury concentration, a heat map was generated with the samples by interpolating the points. Figure 4 of the heat map shows the approximate distribution of mercury concentrations in the labyrinth sector, which ranges from 0.006 to 0.45 mg/kg. 45 mg/kg, where the values of red tones present the highest mercury concentrations, and green tones the lowest; the red tone quadrants decrease notably during the rainy season, proving that there is a difference in mercury concentration during the rainy season because it is dispersed by the washing of rainwater. It was observed that the center of the mining exploitation of the study area does not contain the highest concentration of mercury. It was obtained that the reddest point is found in sectors 2C, 4B, and 6B, where there are mercury washing ponds, and the whole sector D presents an unusual behavior, because this area has vegetation, having concentrations of mercury in the soil in a slight shade of red.

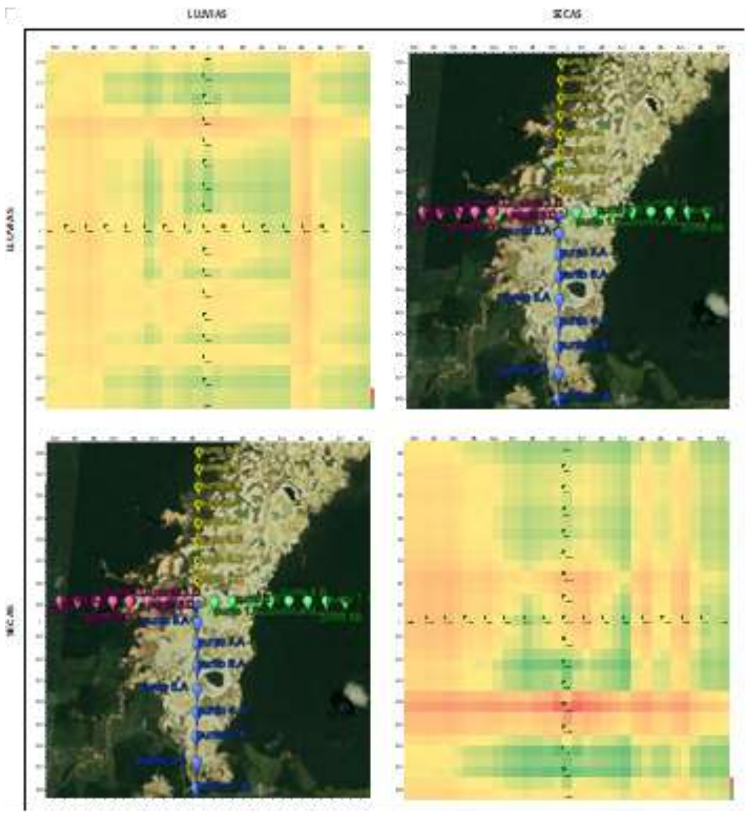

Figure 4 Mercury Concentration in Soil Impacted by Mining Activities.

Relate the physical and chemical characteristics to the concentration of soil mercury in the study area.

Physicochemical characteristics and mercury in soil. A total of 17 soil samples were taken for the evaluation of the physical and chemical characteristics, which were selected in an intercalated way. The most variable characteristic of the soil was the physical characteristic of the "clay" textural class, with a coefficient of variation of 1.14. The most homogeneous characteristics were real soil density with an average of 2.19, followed by pH, with a coefficient of variation of 0.10, presenting a low alkaline level in most of the soil studied. Pearson's correlation showed that the higher the real and apparent density, the higher the mercury concentration; the lower the pH, the higher the mercury concentration; the lower the percentage of sand in the soil, the higher the mercury concentration; the higher the concentration of silt in the soil, the higher the mercury concentration; soil moisture had a significant effect on the concentration of mercury in the soil, being more relevant in the dry season. In all the physical characteristics of the soil, water is an important factor in the spread of mercury.

Determine the concentration of mercury in plants in the study area.

Taxa Richness in the Study Area. A total of 21 vegetation samples were obtained; 11 samples were taken during the rainy season and 10 during the dry season. Taxonomic determination was carried out by the Vargas Cuz Herbarium, obtaining the following families: Urticaceae, Cyatheaceae, Zingiberaceae, Cannaceae, Euphorbiaceae, Fabaceae, and Poaceae. It was observed that many of the plant species persist both in the rainy and dry seasons, the most significant being the species of the following families: Fabaceae and Poaceae.

Mercury concentration in vegetation. The quality standard limit established for mercury in vegetation varies from 0.02 mg/kg to 0.9 mg/kg, according to the European Parliament of the European Union (Regulation (EU) 2018/73 of the Commission), which allowed a meaningful comparison. Peruvian regulations do not present a quality standard for mercury concentration in vegetation. The vegetation in the study area of the Laberinto sector presents average concentrations of 1.0 mg/kg in the rainy season and 2.8 mg/kg in the dry season, finding a high statistical significance for the two seasons of 0.99, which indicates that the concentration of mercury in the plants of the study area exceeds the environmental quality standards allowed by the European Union (Regulation (EU) 2018/73).

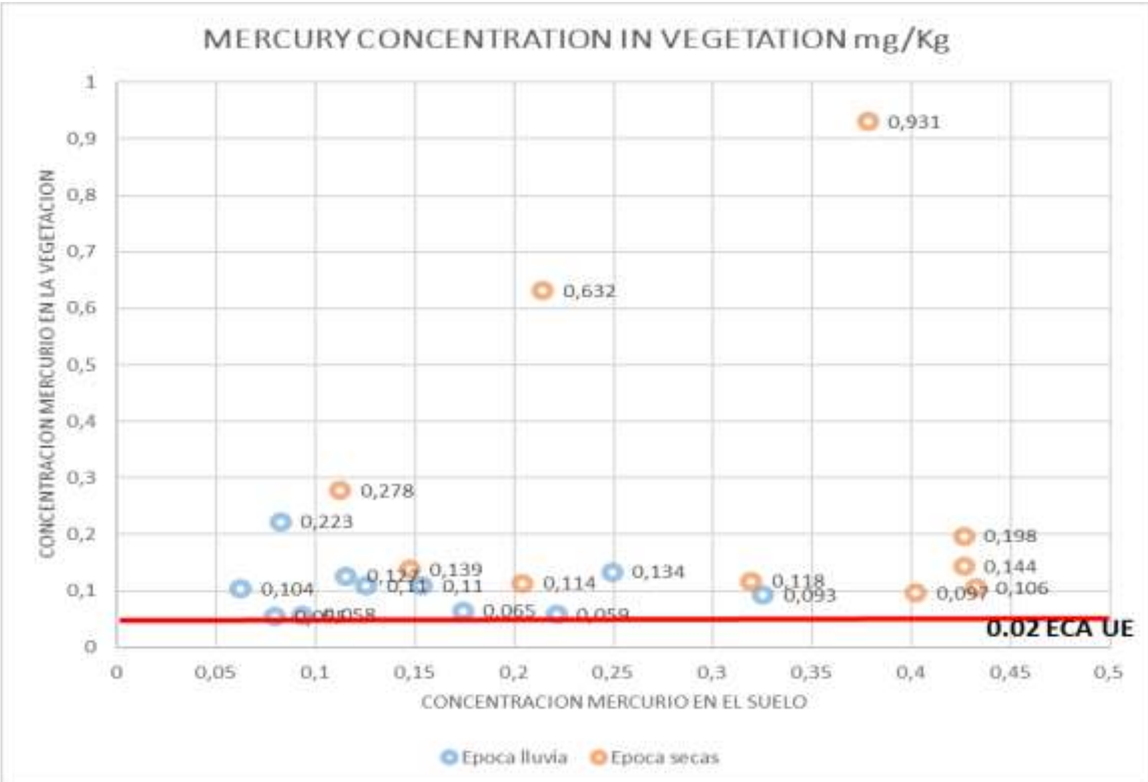

Figure 5 Mercury Concentration in Vegetation in Rainy and Dry Seasons

Relate the physical and chemical characteristics of the soil to the concentration of mercury in the vegetation in the study area.

Physicochemical characteristics and Mercury in plants. The physical-chemical results indicate that the higher the organic matter in the soil, the lower the mercury concentrations in the plants; the higher the soil conductivity, the lower the mercury concentration in the vegetation; the higher the potassium in the soil, the lower the mercury concentration in the plants excite relationship of mercury adsorption, by the physical and chemical characteristics of the soil.

4. Conclusion

The research conducted by Camargo in 2014 in Colombia obtained average Hg values of 7.1 mg/kg in soil, being higher in areas close to the assemblies as well as with increasing precipitation (Camargo et al., 2014). In the research work, it was obtained that the average concentration of mercury in the area of Laberinto - Tambopata - Madre de Dios in the dry season was 1.4 mg/kg, and in the rainy season was 2.3 mg/kg, such concentrations are lower than the environmental quality standards, according to Peruvian regulations; but not so for the regulations of the United Nations Environment Programme (UNEP). The higher the concentration of mercury in the soil, the lower the adsorption capacity of mercury, with a value of -7.13775 10^-9 of adsorption capacity. This is because mercury interacts with the physical and chemical factors of the soil, such as organic matter and clays, which due to different factors such as pH, electrical conductivity, etc., adsorb and absorb mercury. They adsorb and absorb them, thus generating organic and inorganic compounds, which decrease the adsorption capacity of the soil. Therefore, it is understood that any soil where gold mining activity is carried out is contaminated with mercury.

In the research conducted by Delgado in 2019, on the relationship between amalgamation with mercury for gold recovery in the Secocha sector, it was found that in places where gold amalgamation is carried out, there is a higher concentration of mercury at the surface, which decreases as it progresses deeper. It was obtained that, in the places where gold amalgamation is performed, there is a higher concentration of mercury at the surface level, which decreases as it advances in depth (Delgado, 2019). In the research work, the distribution of mercury in the study area does not decrease as it moves away from the central extraction point, unlike the work done by Delgado; that is, the concentration of mercury in the soil in the study area presents an irregular arrangement. This concentration varies at different times of the year, being lower in the rainy season due to the action of water, which leaches the mercury to the deep layers.

The study conducted by Muñoz in 2019 determined the levels of mercury in soils contaminated by illegal mining activity, in the community of San Jacinto, Tambopata Province - Madre de Dios. He determined that the levels of mercury were altered by illegal mining, chemical analysis was performed on the soil, comparing with environmental quality standards, which concluded that the soil texture influences the degree of mercury contamination. MUÑOZ. O.C. (2019). The physical-chemical characteristics of the soil are an important factor in the retention and adsorption of mercury; because, in the research work, the rainy season, is when the lowest concentration of mercury in the soil in the study area occurs, due to the high permeability in the soil texture, being this similar to the study mentioned by Muñoz. The relationship of the most important physical-chemical parameters in the concentration of mercury was obtained, obtaining that the characteristics of soil texture, pH, electrical conductivity, humidity, organic matter, and phosphorus are the most important parameters.

In the study conducted by Arostegui in 2017, the amount of mercury in soils, and plantain Musa cultivar AAB in the sector of Punkiri Chico and Iberia - Madre de Dios, reported values below detectable environmental quality standards; while in the sector of Punkiri Chico, the values were higher than the environmental quality standards according to the European Union - Codex Alimentarius Commission (Arostegui, 2017). When determining the concentration of mercury in the vegetation in the research work, it was found that the concentration of mercury exceeds the environmental quality standards, with average concentrations of 1.0 mg/ kg of mercury in the rainy season, and 2.8 mg/kg of mercury in the dry season, exceeding the standards according to the European Union, unlike the work done by Arostegui. It was not possible to make a comparison with Peruvian regulations because no document provides guidelines on environmental quality standards for mercury vegetation. The physical and chemical characteristics of the soil were related to the concentration of mercury in the vegetation in the study area, where it was obtained that organic matter, electrical conductivity, and potassium are the most important characteristics in the decrease of mercury concentration for the plants because these interact and retain mercury in their structures, thus generating little availability of mercury in solution to be absorbed by the plants.

Author's Contribution: The author contributed with conceptualization, formal analysis, fund acquisition, research, methodology, project management, supervision, validation, visualization, and writing.

Conflict of Interest: The author declares no conflict of interest

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About Research Ethics and Legal Standards: The research complied with all established ethical standards, the collection of plant samples was authorized by the regional government of Madre de Dios, because there is no vegetation in the area due to the dredging carried out by the mining activity, there being no endangered plant or animal species, so Sernamp did not intervene in the authorization.

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