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Determination of the concentration of heavy metals and oils in seawater in the port of Ilo, Peru

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Abstract:
Industrialization and population growth on our planet has led to a greater emission of pollutants into ecosystems. The coastal marine area of Ilo is the most important aquatic ecosystem on the southern coast of Peru, receiving effluent discharges from the Osmore River, urban wastewater and from industries near the coast. Therefore, studies are necessary to determine the level of heavy metals in the marine environment and to determine potentially dangerous levels for hydrobiological resources and humans. The concentration of heavy metals (Pb, Cu, As) and oils and fats in seawater were determined in parallel at four beaches located in the port of Ilo, Peru, which is an industrial and tourist place. During a period of 9 months in three different seasons and in low and high biological productivity. The concentration of heavy metals and oils and fats in seawater has a marked variation during the periods of sampling and seasonal stability, the sampling was carried out according to the National Water Resources Quality Monitoring Protocol (Headquarters Resolution 010-2016-ANA), Atomic Absorption Spectrophotometry (AAS). According to the methodology by AAS and AWWA method. The concentration of lead and oils and fats exceeds the limits established in each of the stations and very marked in the spring season of 0.74 mg / L for lead and for oils and fats also exceeds 108.5 mg / L. For copper in summer there is the proximity to what is established in environmental regulations with 0.048 mg / L and the arsenic is the closest at 0.0042 mg / L in summer.
***Key Word**: Seawater; oils; concentration; heavy metals; lead; quality.*

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I. Introduction

The strip of the Peruvian coast has 2,815 km, where we find beaches and bays, experiencing local variations in some areas. The land area adjacent to the sea does not have a precise limit that has been marked by a single topographic feature, the use of these terms being variable according to the geographical or economic factor. Other authors consider the coastal zone as the strip limited by the emerged part close to the high tide line and the line located in the sea below which the effect of the waves still persists or is noticeable. This corresponds to an isobath of 25 to 35 m.

The Peruvian coastline has a varied morphological aspect, characterized by desert plains and high hills. The coastal surface geonorphology is due to subaerial and fluvial erosion. There are large areas like buckets caused by wind deflation that eliminates products of mechanical weathering (as occurs in the Ica desert). In other regions, huge masses of fine sand accumulate developing large sandy areas and dune fields [16].

Geomorphological aspect of the coastal area; the climatological, edaphological, phytogeographic and other factors depend mainly on the three-dimensional development of the morphological structure of Peru. These forces have given rise to a multitude of forms of the country that require a detailed and general ordering to achieve an interpretation of the dominant features of the land's relief. The coast of Peru shows changes that define the coastline in three geographic zones northwest, center and south. These features have been acquired in the Pliopleistocene, the tertiary paleography extended north to 5º S and south to 16º S [15].

The Peruvian coastline is characteristic because it is divided into three zones; north, center and south. Of the three segments, broadly speaking, the southern margin has a perennial tendency to emersion, the central margin has a tendency to subsidence, this explains the presence of denser material in the cortical structure and the northwestern margin, anomalous and whose development would be linked to the tectonic phenomena of the Gulf of Guayaquil[18].

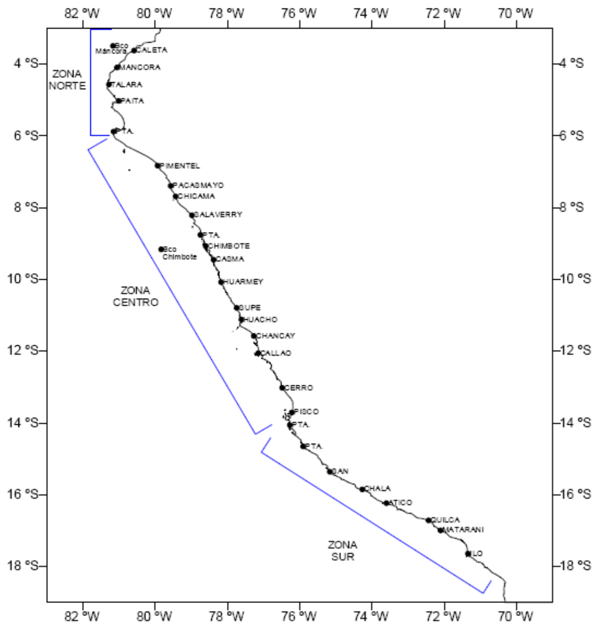


Figure 1. Distribution of the north, center and south coast, according to Schweigger.

The northern zone that includes from the border with Ecuador to Punta Aguja, characterized by its aridity. Constituted by tertiary tablazos that emerged and are exposed from the extreme north to the south of Máncora, the course of the coastline is northeast, between Mancora and the south of Talara where Punta Pariñas is located is almost north-south except for the mentioned point, which extends west throughout the South American continent. Towards the south the course changes in the bays of Paita and Punta Falsa.

The central area that includes the coast between Punta Aguja and Isla San Gallán, this area is crossed by some valleys, in front of its coasts there are islands. The course is generally northwest.

The southern zone that includes from Pisco to Morro Sama, presents an arid coast with steep hills and cliffs close to the coast that are made up of older metamorphic rocks that have been called the Cordillera de la Costa, this area is sporadically cut by some valleys. In the southern zone there are two geological sectors, one known as the northern sector (located from the Paracas Peninsula to Caravelí (it is rising) and the southern sector from Caravelí to Arica (an area experiencing a subsidence).

The South sector starts specifically from Atico, some terraces are exposed in the Ilo region, where four of them are distinguished behind the town and at the northernmost point of the Port of Ilo, three stages are also recognized.

The direction of the coastal strip in the southern zone is predominantly northwest, varying locally towards east-west at the height of Punta; Sama, Yerba Buena, Islay and others. Gradually going from northeast to northwest. At Punta Coles there is a southwestern setting.

The coastal mountain range known as the structural high that separates the basins, in southern Peru is formed by a Precambrian and Paleozoic basement locally covered by Mesosoan volcano-sedimentary rocks. These lands outcrop continuously from Paracas (14ºS) to the vicinity of the border (17ºS) with Chile.

Bathymetry and morphology; From the structural point of view, the morphostructural units of the Peruvian continental margin are described. Below the current sea level are the oceanic trench and part of the forearc region. The forearc region extends between the trench and the western ridge (magmatic arc). In this region morphologically, four elongated and parallel sectors to the trench are distinguished (Fig. 2 and 3), such as: Continental Platform, the cartographic High Structural, the Upper Slope and the Middle and Lower Slope[15].

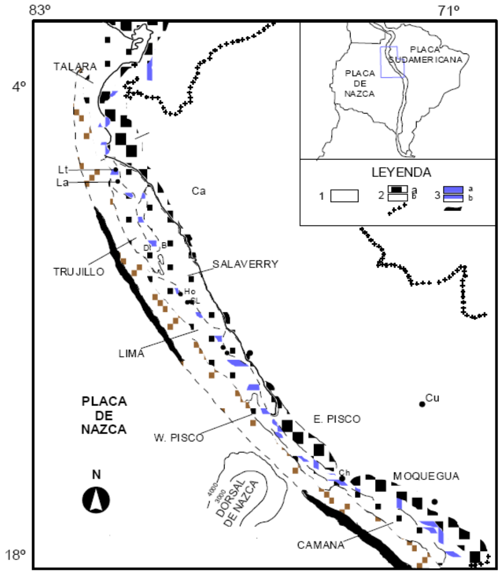


Figure 2. Morphostructure of the Peruvian coast

a) The continental shelf develops between 07ºS and 14ºS, with variations in the platform that are related to the geodynamic evolution of this margin.
b) The High Structural that separates the external and internal ante-arc basins. South of 14ºS, this Alto is represented by the Cordillera de la Costa. Between 14ºS and 06ºS it is submerged and forms the outer edge of the continental shelf; here it was mapped by Thorburng and Kulm, who gave it the name Outer Shelf High (OSH). The central margin formed by the islands Chincha, Hormigas, Lobos de Tierra, have similar metamorphic rocks. North of 06ºS this structure reappears on the coast forming the Illescas massifs, according to Caldas (1979) they belong to the same group.
c) Upper slope, with more regular relief;
d) The middle and lower slope, which is bounded upward by a slope break named after Thorburng and Kulm. Upper Slope Ridge Threshold (USR).

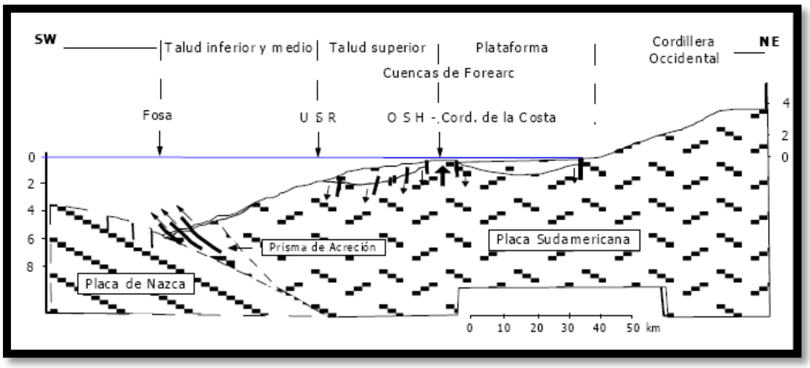


Figure 3. Cross section showing the morphostructural characteristics of the Peruvian coast

The current coastal geomorphology is the reflection of the interrelation processes between the coast and the ocean, also due to the influence of the climate, which have occurred over time. The physical and chemical characteristics of the formations that are in contact with the sea are also an important factor depending on their degree of resistance to the action of this. The oceanographic context on a larger scale also has great influence on these processes.

The outcrops of coastal waters cause the cooling of the surface waters that in turn favor the formation of intense fogs that, when reaching the coastline, deeply weather the outcropping rocks, facilitating marine erosion. The Peruvian current has a coastal branch that runs towards the coastline favoring erosion and determining symmetry in the extreme north of many bays. The rough or storm surge produce strong erosion of beaches and cliffs The predominant direction of the wave crests is from the southwest, originating coastal erosion due to the effect of the blow of the waves and wave refraction phenomena on promontories and projections, the Studies and observations on the convergence or divergence of the waves, there are also possibilities of Tsunamis related to earthquakes, which contribute to the change in the morphology of the coastline [8].

The Peruvian Current system is made up of the Peruvian Coastal Current, the Oceanic Current, the Peruvian-Chilean Subsurface Current and the Peruvian Countercurrent. The Peruvian Coastal Current is influenced by the Peruvian coastal outcrop that runs parallel to the coast with a north direction up to the height of Punta Aguja, where it continues southwest, presenting an average speed of 20.6 to 25.7 cm / sec; its maximum activity is in winter and minimum in summer due to the weakening of the trade winds.

Marine aquatic ecosystems are being deteriorated and/or contaminated by landings, fishing boats and anthropogenic influence on the Peruvian coastline and in particular the port of Ilo and is also influenced by the presence of an industrial area. The presence of heavy metals and oils and fats in seawater cause dangerous impacts on marine organisms and indirectly on human health. The increase in the concentration levels of heavy metals and oils and fats in seawater is a very serious problem today. Especially in the last four decades, the fishing industry (extractive and flour), urban waste and mining (Southern Peru) have severely polluted the marine areas where they dumped their waste; Because before the reduction of this contamination was minimal or null[20].

In the port of Ilo there have been many times fuel spills from marine vessels of smaller and larger tonnage whose content is highly toxic to marine life, many times artisanal fishermen dump oils, detergents or other chemical products that they use to the cleaning of the boats themselves. They also collaborate with pollution, gradually generating the destruction of plankton (the basis of the food chain), the destruction of the marine flora and fauna of the beach "La Glorieta", "Playa el Diablo" and the loss of the tourist potential of our Port of Ilo.

The port of Ilo is located in the district of Ilo, Ilo Province, Moquegua Region which limits to the north with the Mariscal Nieto province; to the east with the Province of Jorge Basadre (Tacna); to the south with the Pacific Ocean and; to the west with the Province of Islay (Arequipa) and in the southern part of Peru. Of its economic activity, it is worth highlighting the industry and fishing. The industry focuses on copper smelting and fishmeal factories. In terms of fishing, the fleet dedicated to catching anchovy stands out.

Heavy metals constitute a serious environmental problem due to their toxicity and their physiological repercussions both on humans and on hydrobiological species such as fish, as well as causing dangerous impacts on marine flora and fauna. There are a number of toxic metals such as Cd, Cr, Pb, As, Cu, Hg and Zn, and the high concentrations of these metals in seawater is a very serious problem for aquatic life and society[21].

According to White & Rainbow (1987), this situation is attributed to the existence of various sources that produce pollutants in the coastal zone, mainly represented by liquid and solid industrial waste, and discharges of urban sewage directly into the sea. Due to this fact, the contamination of the coastal environment has risen and, in many cases, has exceeded critical points, creating extensive areas harmful to marine flora and fauna[2,3]. The study of the presence of heavy metals in seawater and sediments constitutes a contribution to the provision of environmental information on these waters, which will contribute to a final diagnosis and therefore facilitate decision-making on this impact. Heavy metals constitute a serious environmental problem due to their toxicity and their physiological repercussions on both humans and animals, such as fish, as well as causing dangerous impacts on marine flora and fauna.

The investigation of the presence of heavy metals in certain waters allows to know the possible routes of pollutants such as effluent discharges from industries, or through nearby domestic wastewater and their interaction with other substances present in the waters. Therefore, the present study deals with heavy metals such as (Pb, Cu and As), as well as with Oils and Fats in seawater from the coasts of Ilo, in the department of Moquegua.

According to the environmental regulations in force in our country, water is an essential element for living beings. In this study we take as a reference the Standards of Environmental Quality of Water, (S.D. No. 004-2017-MINAM), General Environmental Law No. 28611.

II. Material And Methods

For the present investigation it was proposed to study the beaches of; Ilo Craft Landing, Media Luna Beach, beach in front of Southern Foundry and apply the methodology of the National Protocol for the Quality of Water Resources Monitoring (Headquarters Resolution 010-2016-ANA), the water samples were taken at the surface level and the respective parameters indicated in this standard as dissolved oxygen, T (° C), pH, salinity and conductivity respectively. In the determination of heavy metals (Pb, As, and Cu), Atomic Absorption Spectrophotometry (AAS) was used. According to the AAS methodology and the AWWA method for oil and grease. The study is descriptive, comparative and correlational and the work was done in 10 months, from November 2018 to September 2019.

Sampling area location

The project was carried out on three beaches belonging to the district of Ilo located in the province of Ilo, also known as "Puerto de Ilo", it is located on the southern coast of Peru, between coordinates 17º14'48" and 17º49'16" South latitude and 71º29'15" and 70º54'50 " West longitude; 1,280 km from the city of Lima. Located in three specific points on the coast of Ilo, as can be seen in Table 1.

Table 1: Location of sampling points.

Beaches	Sample points	Code	Coordinated Location DATUM WGS89			
			UTM		Greenwich	
			East	North	South	West
Desembarcadero Artesanal	P1	P1-DA1 AYG P1-DA2 MET. PES.	19 k 0250854	8047651	17°38'06.1"	71°20'49.2"
Media Luna	P2	P2-ML1 AYG P2-ML MET. PES.	19k 0248683	8063292	17°36'052"	71°21'030"
Frente a Fundición Southern	P3	P3-FF1 AYG P3-FF2 MET. PES.	19k 0250338	8062370	17°29'941"	71°21'762"

Sample size:

The type of sampling of the present investigation is of the probabilistic method for convenience according to W. Creswell, (2008). Since the main sampling points are critical areas where there is an industrial presence and maritime trade in the port of Ilo. The sampling period was carried out during the summer, winter and spring season between 2018 and 2019. Surface water samples of 1000 ml were collected at each sampling point and the field physicochemical parameters were measured. The frequency is quarterly the four seasons, carried out the same day. The sample was taken in the marine ecosystem using a boat.

Instruments:

For the determination of the concentration of heavy metals such as Pb, As and Cu in mg / L and it was carried out through atomic absorption spectrophotometry (EAA), PERKIN ELMER "AANALYST 3100". Which is an analytical method of choice for the analysis of traces of heavy metals and metalloids in various matrices. The AWWA method by Soxhlet extraction for the determination of oils and fats is applicable to determine biological lipids, hydrocarbons, whether heavy or relatively polar fractions of petroleum and when the levels of non-volatile fats can alter the solubility limit of the solvent. The instrumental analysis of the samples was carried out in the SEVILAB laboratories of the Universidad Nacional San Agustín de Arequipa.

III. Results

Surface marine circulation in the port of Ilo varies between 7 to 27.5 cm/s, with an average of 19.8 cm/s. Speeds of greater intensity are registered south of Ilo, with predominant directions towards the north, south of Pinta Picata, while between Punta Coles and Punta Icuy there are flows towards the south, southwest, which could be due to the convergence of the waters in Punta Coles, the same trend of current flows was found during the work carried out. From Ilo to the north, flows with a north direction predominate and at a depth of one meter in front of the smelter the flows go south. The intensities vary between 7 and 17 cm/s.

The sea surface temperature (SST) varied between 13 ° C and 18 ° C, with the average of 15.5 ° C, the temperatures increased in front of smelting approximately 17.9 ° C.

At the surface level, dissolved oxygen and salinity vary between 2.5 to 5 mg/L and 33 to 35.4% respectively at our sampling points.

The port of Iloport has a typical coastal climate where its atmosphere is humid and the difference between the spring and summer seasons with respect to autumn and winter is very marked. During winter, low temperatures occur, giving rise to the outcrop of the coastal hills. Meanwhile, in spring and summer, the weather is sunny and dry between the months of October to March. The maximum annual average temperature is 17 °C. Being a minimum temperature of 9 °C and a maximum temperature of up to 32 °C

1. Result of the seawater quality conditions in spring time from the sampling points in table 2 and 3.

Table 2: Physicochemical parameters of seawater quality.

Code	Sampling points	Unit	Pb	Cu	As	Oils and Fats
P1-DA1 MET. PES. P1-DA1 AYG	Desembarcadero	mg/L	0.501	0.043	0.0012	39.5
P2-ML1 MET. PES. P2-ML1 AYG	Media Luna		0.497	0.048	0.0034	17.25
P3-FF1 MET. PES. P3-FF1 AYG	Fundición Southern		0.527	0.046	0.0042	15.02

Table 3: Physic parameters of seawater quality.

Physic parameters of seawater in situ			
PARAMETERS	**P1**	**P2**	**P3**
Temperature	16.2 °C	15.7 °C	17.1 °C
pH	7.35	7.36	7.28
ORP	-35 mV	-32 mV	-34 Mv
Humidity	65 %	71%	67%
T° environment	18.4°C	20.3°C	21.5°C

2. Result of the seawater quality conditions in the autumn-winter season at the sampling points in table 4 and 5.

Table 4: Physicochemical parameters of seawater quality.

Code	Sampling points	Unit	Pb	Cu	As	Oils and Fats
P1-DA1 MET. PES. P1-DA1 AYG	Desembarcadero	mg/L	0.565	0.040	0.0028	45.00
P2-ML1 MET. PES. P2-ML1 AYG	Media Luna		0.517	0.033	0.0028	51.50
P3-FF1 MET. PES. P3-FF1 AYG	Fundición Southern		0.546	0.029	0.0028	31.50

Table 5: Physic parameters of seawater quality.

Physic parameters of seawater in situ			
PARAMETERS	**P1**	**P2**	**P3**
Temperature	13.8 °C	13.4 °C	13.6 °C
pH	7.56	7.90	7.78
ORP	-32 mV	-53 mV	-45 mV
Humidity	75 %	77%	78%
T° environment	16.1°C	16.5°C	16.7°C

3. Result of the seawater quality conditions in the summer season at the sampling points in table 6 and 7.

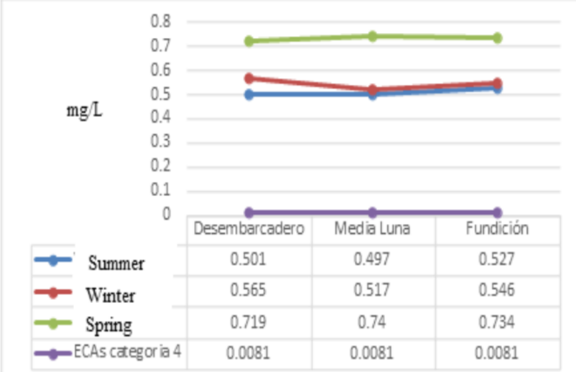
Table 6: Physicochemical parameters of seawater quality.

Code	Sampling points	Unit	Pb	Cu	As	Oils and Fats
P1-DA1 MET. PES. P1-DA1 AYG	Desembarcadero	mg/L	0.719	0.039	0.0028	39.5
P2-ML1 MET. PES. P2-ML1 AYG	Media Luna		0.740	0.027	0.0028	108.50
P3-FF1 MET. PES. P3-FF1 AYG	Fundición Southern		0.734	0.026	0.0029	24.50

Table 7: Physic parameters of seawater quality.

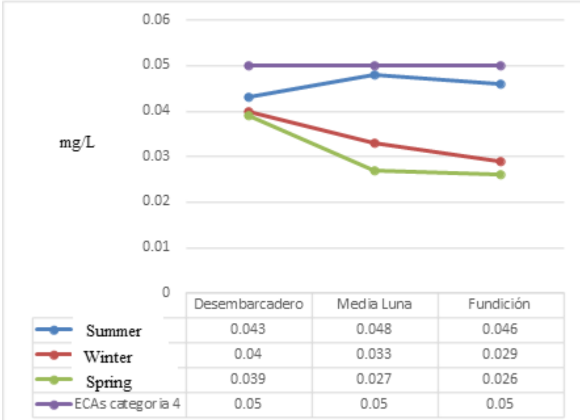
Physic parameters of seawater in situ			
PARAMETERS	**P1**	**P2**	**P3**
Temperature	16.8 °C	18.3 °C	17.9 °C
pH	7.51	7.62	7.50
ORP	-51.9 mV	-55.9 mV	-55.9 mV
Humidity	62 %	72%	70%
T° environment	22.1°C	23.0°C	22.5°C

Figure 4: Concentration levels of lead (Pb) of the seawater samples vs. ECAs at the three seasons.



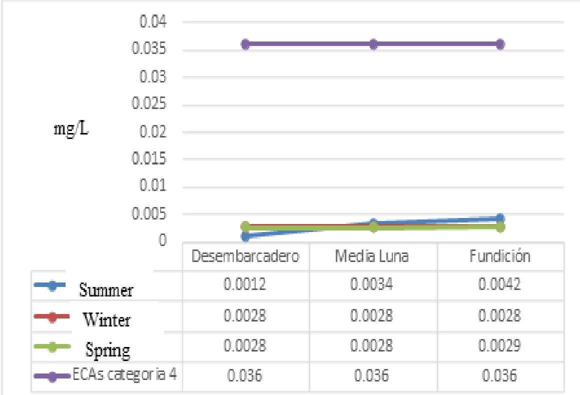
We can clearly differentiate in figure 1 that the level of lead concentration in seawater exceeds the limits established in the ECAs in all seasons and is very marked in the spring season at 0.74 mg/L.

Figure 5: Concentration levels of Copper (Cu) of the seawater samples vs. ECAs at the three seasons.



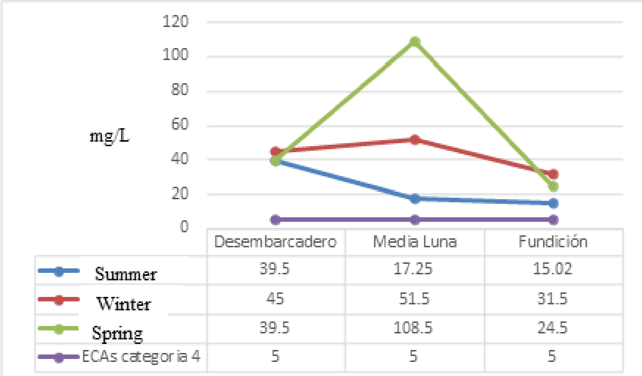
For the case of copper in figure 5 it is noticeable that no seawater sample exceeds the limits established by the ECAs of Peru, it should be noted that there is proximity to the ECAs and with greater representation it is possible to see in the summer season with a concentration of 0.048 mg/L.

Figure 6: Concentration levels of Arsenic (As) of the seawater samples vs. ECAs at the three seasons.



In figure 6 the arsenic in seawater and in all the seasons the concentration levels are very low compared to the ECAs.

Figure 7: Concentration levels of Oils and Fats of the seawater samples vs. ECAs at the three seasons.



As can be seen in figure 7, the concentration levels of oils and fats in the three stations exceed the levels allowed by the ECAs and in each monitoring station, the most representative is 108.5 mg/L in spring.

IV. Discussion

The population of the port of Ilo is established in the district of Pacocha, a part of the District of Algarrobal and a large part of the coastline is from the district of Ilo, approximately almost 70 thousand inhabitants in the province of Ilo, the majority of families They live from fishing and commerce and a minority from the mining industry and other activities.

According to the evaluations, the concentration levels of Lead exceed the Environmental Quality Standards (DS004-2017-MINAM) for category 4 seawater: in the three monitoring points, having a high content of this heavy metal being significant in the spring season is 0.74 mg/L in excess, being a risk to benthic species and in the trophic chain of the aquatic ecosystem.

In relation to arsenic concentrations, results of 0.0028 mg/L were obtained on average, placing them below the established environmental quality standard, and for copper, results of 0.048 mg L were obtained, being very close to the limit of the environmental quality standard for seawater which is 0.05 mg/L.in patients with diabetes plays an important role in development of atherogenesis.

The quality of sea water in relation to the concentration of oils and fats was evidenced in a specific way and by physicochemical analysis that our results are above the ECA's of sea water established for category 4. Which is harmful to life Aquatic speaking of the flora and fauna, which form like mirrors and do not let sunlight pass through for the respective photosynthesis and it is not suitable for the landscape of the Ilo city.

V. Conclusion

The results obtained during the 3 seasons (summer, winter and spring) show that the concentration levels of lead and Oils and fats Exceed the Environmental Quality Standards (ECAs) for seawater, category 4, while copper and arsenic They are within the allowed limit of ECAs. Having an alert regarding copper that is close to the limit concentration designated by the Peruvian standard.

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