A STUDY OF PHYSICOCHEMICAL PARAMETERS AND HEAVY METALS CONCENTRATION LEVELS IN ORIKUMI LAGOON, VLORA, ALBANIA

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Abstract

During this study we measured physicochemical parameters (T°C, pH, TDS, EC, Salinity) in situ by a multi parameter portable HI 9829 Hanna and also the concentration levels of heavy metals (cadmium, lead, iron and copper) were given by flame atomic absorption spectrometry in lagoon waters of Orikum, Vlora, Albania. On the basis of obtained data of the physico-chemical and spectrometric measured in water we found a slight variability in salinity, pH near neutrality with a low mobility of metals (except Fe) and elevated TDS and EC at stations mainly S_4 and S_5 subject to the direct influence of temperatures waters and discharges of wastewater from The Pashaliman Base (A Military Base of Vlora District). The contents of heavy metals concentrations in relation to maximum value are following this trend: Fe>Cd>Pb>Cu. Also, the values of standard deviations of Fe are highest which led to a totally heterogenous distribution.

Keywords

Lagoon Waters, Physico-Chemical Parameters, Heavy Metals, Flame Atomic Absorption Spectrometry

1. Introduction

Vlora, a southern district in the Western Adriatic Coastal Lowland, holds about 150 km of coastline. It borders on both the Ionian and the Adriatic coast. Along these a transitional coast continuum has been established extending from the Shkumbini delta in the north to the Vlora town in the south (A. Miho et al., 2013). The Orikumi lagoon, also called Pashalimani lagoon, is situated near the town of Orikumi, just at the south end of the Vlora bay. The lagoon is close to the military zone of Pashalimani that was heavily fortified after the Second World War and sheltered military submarines of the Warszawa Pact (UNEP, 2015). Like along the whole Albanian coast the climate is strongly influenced by the Adriatic Sea. Moreover, heavy urbanization is continuously spreading along the whole Vlora coastal zone from Zverneci to Orikumi. The growing number of wastewaters continues to be discharged directly into the sea, representing a great risk for the transitional habitats and the marine coastal zone. The lagoon represents now only the remaining coastal habitat reduced in size to about 4 km. Most of the lagoon area has been reclaimed around 1970 which altered the region drastically and decreased its natural values. The former Pallarengu alluvial forest that surrounded the lagoon was transformed into agricultural land while the freshwater brook of the Dukati and some freshwater springs were captured and pumped directly to the sea (A. Miho et al., 2013). This increased massively the salinity in the lagoon. The Orikumi

lagoon is of tectonic origin. It has a surface area of 1.5 km and relates to the sea by two channels, one of artificial construction and often is closed. The gravel coast is 6 km long and 10 to 80 m wide Figure 1 and has been formed by depositions of the Dukati torrent (Pano.N et al., 2014). The water exchange with the sea is rather poor and does not ensure optimal hydrological conditions. Consequently, the average water level in the lagoon may be 15 to 60 cm higher than the sea in winter, while in summer it decreases by 15 to 35 cm below sea level. There are only a limited number of studies that represent a completed pattern of lagoon's waters pollution. Anthropogenic activities have substantially increased trace metal concentrations in the atmosphere, pluvial precipitation and soil as well. These metals, which acting at the molecular scale, cause the effects that are propagated upto the ecological systems damaging both their structure and functions (Denaj, A. et al., 2015). During to the last decade it was observed that the pollution, especially with heavy metals, as well as the poor management of the profile agencies led to the degradation of the beneficial properties of lagoon. In this study were chosen seven sampling stations along the lagoon's perimeter, and the delta point with the sea, was analyzed in three depth levels in order to see the influence of depth maritime flows in the concentration levels of heavy metals.

2. Method and Data Analysis

Generalized method of sampler preparation and treatment are considered especially in the guide of the field of research (K. Danzer., 1996, Ponnada. S, 2013, Smith, R). From geographic point of view, we schematized the stations of measurement in order to represent total area of the lagoon, with some considerable anthropogenic sources mainly from the Pashaliman Base. Stations are situated in the lagoon's perimeter, distanced about 1km to each other.The first station is located near the delta zone and the others are situated along the perimeter (see Figure 1).

The measurements were realized in three different periods of years, during the winter, spring and summer. Except the delta sampling station, where were taken samples in three vertical points: at surface and close under-surface straits at 10 cm -60 cm largeness, and in a intermediate depth of -120 cm, in others stations samples were taken only in the subsurface in a quote of 10cm. The idea behind this measurement was to get known about direct surface situation where atmospheric or low discharges would be dominant factor and more homogenized part of the waters under this strait.

The sampling was performed by using a special dispositive (Van Dorn Water Sample, horizontal type) and by using appropriate procedures for evaluating the physicochemical

parameters and heavy metals. Based on the first goal of the study consisting in empirical evidence we have pursued standard rules in sampling and homogenization of the specimens. Practically a good level of homogenization is reached by taking samplers in 500 ml volume of water as usually applied in such measurement and recommended in standard guides. Regarding to the start of a more analytic view aimed in the analysis of the pollutant factors, we were based on appropriate methodology of sample preparation.
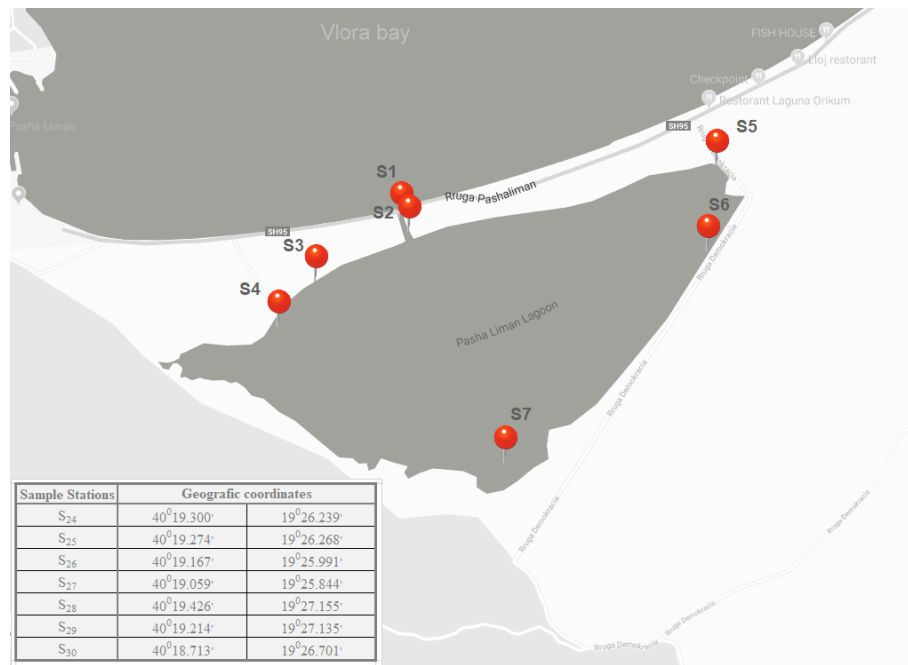

Sample Stations	Geografic coordinates	
S_{24}	$40^0 19.300'$	$19^0 26.239'$
S_{25}	$40^0 19.274'$	$19^0 26.268'$
S_{26}	$40^0 19.167'$	$19^0 25.991'$
S_{27}	$40^0 19.059'$	$19^0 25.844'$
S_{28}	$40^0 19.426'$	$19^0 27.155'$
S_{29}	$40^0 19.214'$	$19^0 27.135'$
S_{30}	$40^0 18.713'$	$19^0 26.701'$

Figure 1: *Positions of Sample Stations*

The collected samples were prepared in order to determination the concentration of heavy metals. In this respect it was achieved the mineralization of water samples by using the Standard Method 3015a (microwave assisted acid digestion of aqueous samples and extracts). After mineralization samples were analyzed using Flame Atomic Absorption Spectrometry (FAAS) as a very common and reliable technique for detecting metals and metalloids in environmental samples. In this study we used ContrAA 300 Analytic Jena, with an accuracy of ppb range (Çullaj A. et al., 2000). To estimate the analytical precision and accuracy and to assure the proper quality of analytical results (Lazo P, Bushati S, 2008), some necessary requirements for this technique was achieved. Analysis of duplicate samples was performed. Also, replication improves the quality of the results and provides a measure of their reliability.

3. Results and Discussions

Physico- chemical values during the three-time period and for each sampling stations are represented in following figures. In order to highlight the differences during sampling period each parameter is shown separately from the others.
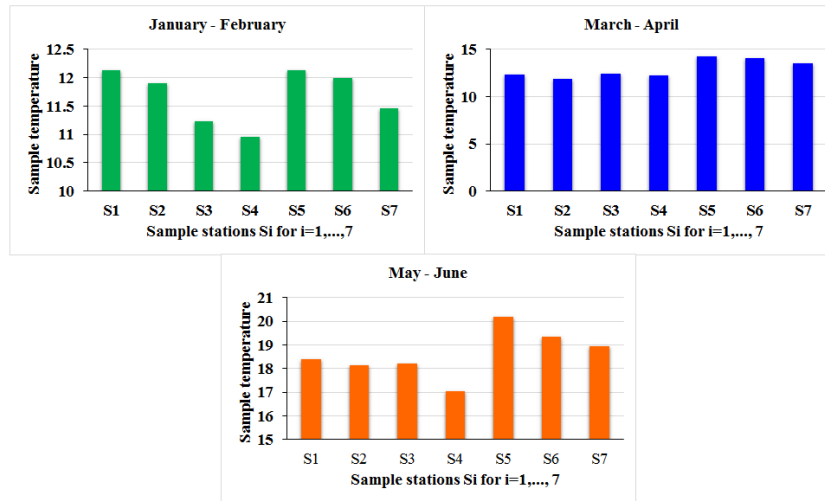

Figure 2: *Sample Temperature January – June 2019*

Water temperature is one of the most important environmental variables and a limiting factor in the aquatic environment. It affects metabolic activities, growth, feeding, reproduction, distribution and migratory behaviours of aquatic organisms (Suski et al, 2006). Figure 2 represents the values of water temperature during three periods of study. Here we can notice a notable variation of values at some of the sampling stations (mainly S3 and S4). From this we can expect correspondent variations on other physico-chemical parameters that are influenced form water temperature.

TDS is an indication of the potential buffering capacity of water and water hardness. TDS concentrations are equal to the sum of positively charged ions (cations) and negatively charged ions (anions) in the water. Water is tested for TDS because excessive amounts may be unsuitable for aquatic river life, it can affect the buoyancy of fish eggs and other organisms, and because of poor crop irrigation, in addition to being unsuited for drinking water (DRI, 2010, Phocaides A. 2000).The values of total dissolved solid (TDS) (as it shown in figure 3) were higher in the wet season than the dry season, and this might have contributed greatly to the low transparency experienced during the wet season.
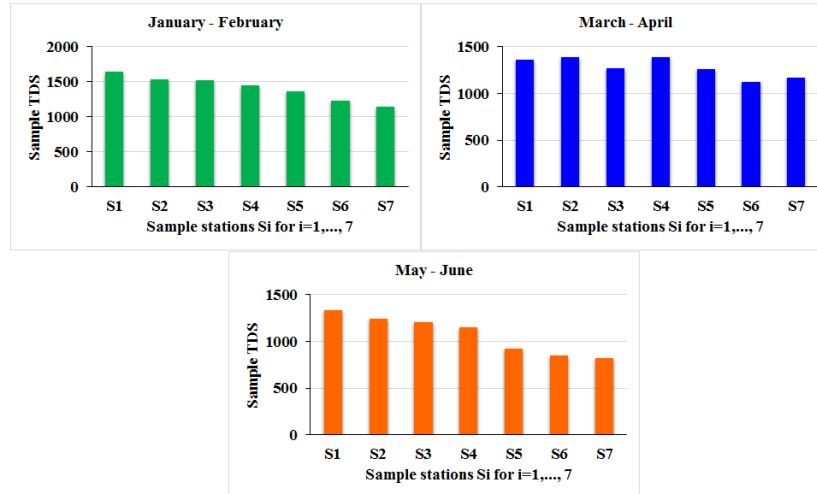
Figure 3: *Sample TDS January – June 2019*

pH is a measure of the acidity or basicity of an aqueous solution. An aqueous solution with pH value less than 7 is classified as acidic while the one with a pH value greater than 7 is said to be basic or alkaline. The pH varied between 8.00 and 8.24 with a mean of 8.1 ± 0.05 during the sampling period. This range falls within permissible range for fish culture. The lowest water pH was 8.03 and it was recorded in January-February period in S5 Station; while the highest pH reading (8.24) was recorded in May-June period, again in S5 Station. Seasonal pH variation was significant ($P < 0.05$) whereas there was no significant difference ($P > 0.05$) in the mean water pH among different Stations.
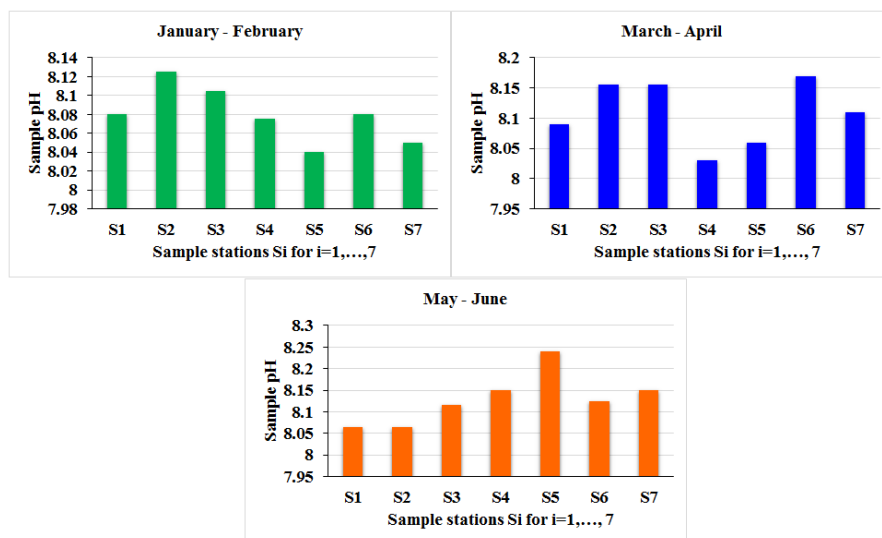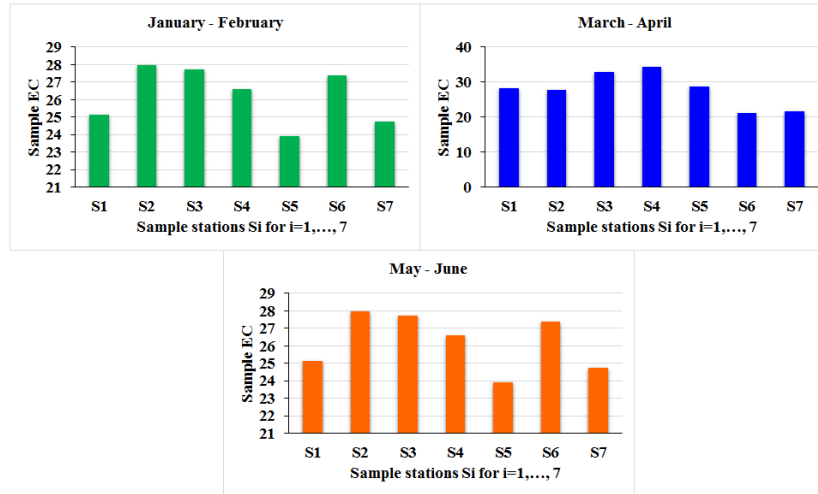

Figure 4: *Sample pH January – June 2019*

Figure 5: *Sample EC January – June 2019*

Low electrical conductivity is an indicator of pristine or background conditions but in the presence of low pH can indicate the removal of most salts, as it shown in S5 sampling station. High conductivity is an indicator of saline conditions caused by high evaporation, saline irrigation returns or runoff and caustic or alkaline industrial processes (DRI, 2010). Based on our data, we notice also a value range from 21.09 dS/m - 34.32 dS/m with a mean value of 26.75 ± 2.75.
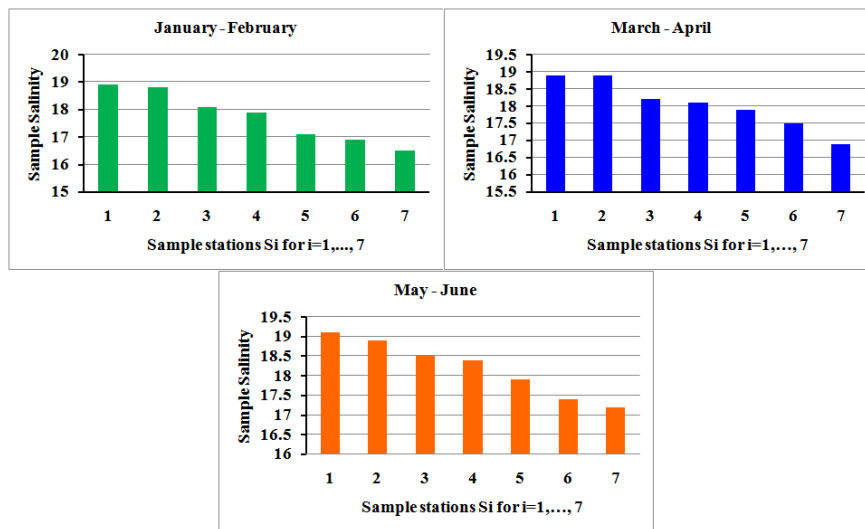

Figure 6: *Sample Salinity January – June 2019*

Salinity is the measurement of the Ionic composition of water and it varies depending on mixing of relatively fresh inland waters with saltier marine waters (Twomeu et al. 2010). It is an important factor that affects the density and growth of aquatic organism`s population (Powell et

al. 2001; Wuenschel et al. 2001; Ansa 2005; Jamabo 2008). From the data acquired, as it shown in figure 5, we noticed, firstly, a time depending variation by an approximate linear increasing coefficient and secondly decreasing almost linear according to the numbering range of the sampling stations S1-S7.

The descriptive statistic for all the physio chemical parameters is summaries in Table 1. According to the analyzed data, we noticed an increase of all values of Standard Deviations of all the physico-chemical studied parameters. During the May-June period, the standard deviations has a peak of the values compared to the other time periods. This may happen due to increasing of human activity in summertime.

Table 1: *Descriptive Statistics of Physic-Chemical Parameters, January - June 2019.*

Time Sampling Period	Chem.-Phys. Parameters	Statistical Parameters					
		Mean	St. Dev.	Kurtosis	Skewness	Min.	Max.
Jan. – Feb.	Temperature	11.69	0.47	-1.43	-0.62	10.96	12.14
	TDS	1411.93	176.95	-1.05	-0.39	1148	1640.5
	pH	8.08	0.03	-0.42	0.25	8.04	8.13
	EC	26.22	1.61	-1.85	-0.32	23.91	27.99
	Salinity	17.74	0.94	-1.7	-0.001	16.5	18.9
March - April	Temperature	12.94	0.97	-1.95	0.42	11.84	14.25
	TDS	1281.29	105.94	-1.49	-0.4	1126	1391.5
	pH	8.11	0.05	-1.39	-0.38	8.03	8.17
	EC	27.82	5.03	-1.08	-0.26	21.09	34.32
	Salinity	18.06	0.72	-0.39	-0.33	16.9	18.9
May - June	Temperature	18.61	1.003	0.36	0.06	17.04	20.18
	TDS	1077.21	207.41	-2.12	-0.18	823.5	1335.5

	pH	8.13	0.06	1.17	0.86	8.07	8.24
	EC	26.22	1.61	-1.85	-0.32	23.91	27.99
	Salinity	18.2	0.73	-1.49	-0.26	17.2	19.1

Another scope of our study was the assessment of same heavy metals concentrations, including Cu, Fe, Pb,Cd, by using flame atomic absorption spectrometry. Each of them shows specifics that we are referring shortly herein. The concentration of the heavy metals has been estimated with good certainty for all stations 1-7, specifically for three depth quotes surface (10m) undersurface (60 cm) and mid-depth at 120 cm, at first Station S1. Firstly, as it is shown in figure 6. the values taken in all stations were not like to be drawn from a give distribution. Therefore, the zone explored has not a representative value for concentration of all the analyzed heavy metal in statistical sense. It may be concerned of water currents, a heterogenicity of physico-chemical parameters, (as we explained above), unidentified or hidden sources which remained to be examined in the future by using more dense data points. From the figure 6, we obtained the maximum values of Fe, Cd and Pb in S7 sampling stations. While, the maximum value of Cu is obtained in S2 sampling station. We think that this is due to the fact that S7 sampling station is positioned near the Pashaliman Base with sheltered military submarines since in time of Warszawa Pact. Also, we can interpret the Fe data obtained in S1 sampling station with the influence of the water flows from the sea (S1-delta zone).
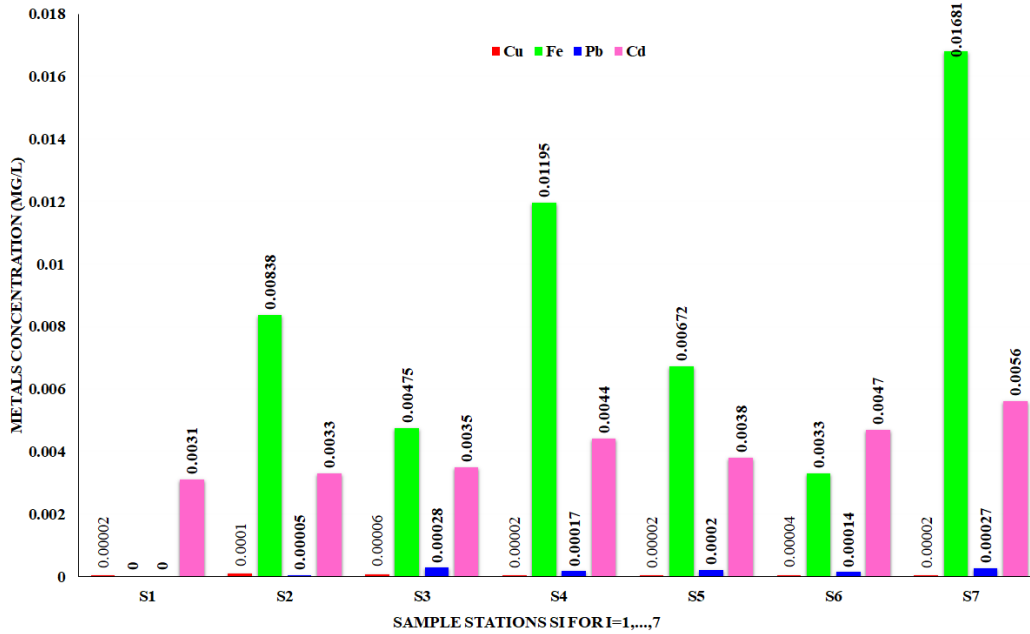
Figure 7: *Heavy Metals (Cu, Fe, Pb, Cd) Concentration Levels for Each Sample Stations*

Table 2: *Descriptive Statistics of Heavy Metals Concentrations*

Heavy Metals	Statistical Parameters					
	Mean	**St. Dev.**	**Kurtosis**	**Skewness**	**Min**	**Max**
Cu	0,00004	0,00003	1,97	1,57	0,00002	0,0001
Fe	0,0074	0,0056	0,028	0,56	0	0,0168
Pb	0,00016	0,0001	-1,02	-0,41	0	0,00028
Cd	0,004	0,00089	-0,16	0,81	0,003	0,0056

In table 2 is represented a decriptive statistics for the heavy metals studied. Here , we can point out that the stadart deviations for Cu values is too low compared with the others, so this might led to a homogenous distribution of this element in lagoon waters.It totally different the

pattern of Fe. Its values of standart deviations are highest which led to a totally heterogenous distribution.

4. Conclusion

In this study we focused in the lagoon water quality expressed by physico-chemical parameters and heavy metals concentration levels. We selected the sampling stations in order to cover all the hydrodynamical characteristics of the lagoon. From the obtained data we can state some conclusions as it follows. Based on horizontal grid (according to sampling stations) and time period, the distribution of physico-chemical parameters was heterogenous. This is indicated with high standart deviation values.

Concentration levels of heavy metals such as Cu, Fe, Cd, and Pb in Orikumi lagoon are in normal values for non-contaminated waters. The contents of heavy metals concentrations in relation to maximum value are following this trend: $Fe \succ Cd \succ Pb \succ Cu$. Also, the values of standard deviations of Fe are highest which led to a totally heterogenous distribution.

Due to the presence of a military base near the Orikumi lagoon (which serve also as a remounting area for the military naves), we suggest for the future some other researches on the concentration levels of heavy metals in soils. So, we can reveal the influence levels of the works in this base.

Based on research limitations, the measurements should be carrying out periodically in order to see how the physico-chemical parameters and also heavy metals concentration levels, alter during different periods of year.

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