RESEARCH ARTICLE **(Open Access)**

Physico-Chemical Characteristics and Heavy Metal Contents of Water from Karavasta lagoon, Albania

ROMINA KOTO[1,2], AIDA BANI[1,2*], NAJADA SKUKA[3]

[1]Agro-Environmental Department, Faculty of Agronomy and Environment, Agricultural University of Tirana, Koder-Kamez, Tirane, Albania
[2]Agro-Environmental & Economic Management-Center
[3]Faculty of Economics, University of Tirana, Rr. Arben Broci, Tirana, Albania

Abstract:

A study was conducted on physico-chemical parameters and heavy metal contents of water from the Karavasta Lagoon(40º56' N and 19º29' E). Karavasta Lagoon is one of the largest lagoons in the Mediterranean Seaand one of the most important economic and ecological areas in the southern part of Albania. The overall complex is composed of four lagoons, sand dunes, and a river mouth has a surface of 10000 ha. It is situated in the central part of western region, between Shkumbini River in the north and Semani River in the south, 40 km west of the city of Lushnja, by the Adriatic coast. The study aimed to determine (i) the water quality in the lagoon of Karavasta using physico-chemical parameters and the level of heavy metals, (2) its status to support living life in the aquatic ecosystem. Data on temperature, pH, salinity, dissolved oxygen were obtained in-situ using Hanna multi-parameters instruments. Surface water of the lagoon was analyzed for heavy metals: Pb, Cr, Cu, Cd, As.The results showed that water temperature varies depending on the seasons. The highest temperatures were in July from 26 to 28.6 ºC depending on the sampling station.The results showed that water temperature varies depending on the seasons. Highest values of pH in the water of the lagoon are verified in December from 10.72 to11.98. The values of salinity in the lagoon of Karavasta are higher in Dajlani station SS1 ranging 42.31% in July to 40.83 %in December, depending from the connection with Adriatic Sea. Also it varies considerably from one area to another, and between seasons, depending on the degree of isolationThe heavy metals Cr, Pb, Cu in some stations are found to be close or higher than the values allowed by the EU and pose a potential health risk to humans and the aquatic life of the lagoon's ecosystem.

Keywords: Heavy metals, sediment, water quality, Karavasta Lagoon, physico-chemical parameters

1. Introduction

The quality of lagoon water changes with seasons and geographical areas, even when there is no evident pollution. The physical and chemical characteristics of the lagoon water are considered to have a great importance in identifying the nature, the quality and type of water for an aquatic system [1, 12, 13]. These parameters are the binding factors for the survival of aquatic organisms notably flora and fauna. Poor water qualities may be the result of municipal effluents, agricultural activities in the area, industrial and urban discharges [5]. Temperature is a limiting factor in the aquatic environment [12]. Water temperature is probably the most important environmental variable affecting metabolic activity, growth, feeding and reproduction. pH is a vital environmental characteristic that affects the survival of aquatic organisms, their metabolism and growth. Salinity is a dynamic indicator of the nature of the exchange system. Salinity determines the distribution of organisms in aquatic environments. The dissolved oxygen impacts the solubility and the availability of nutrients. Its low levels can result in damages to the oxidation state of substances. The dissolved carbon dioxide increases, in aquatic environment, with decreased dissolved oxygen [12]. This is an important parameter in primary production and phytoplankton biomass. Water acidity increases with the increasing of dissolved carbon dioxide levels. High rates of dissolved carbon dioxide are harmful to the physiology and metabolic activities of aquatic animals, including mussels and fish [3]. Elements such as industrial development, mines, agriculture, forestry and urban activities affect significantly water quality. Agriculture increases the concentration of nutrients, pesticides, suspended sediments which

*Corresponding author: Aida Bani; E-mail: aida_alushi@hotmail.com
(Accepted for publication September 25, 2014)
***ISSN**: 2218-2020, © Agricultural University of Tirana*

bring heavy metals in the water[5]. Consequently they increase water temperature and decrease levels of dissolved oxygen[13].

Besides its importance as a natural heritage, Karavasta Lagoon is threatened by several factors. Increase in population, human activities, industries and agriculture around the coastal environment are greatly affecting the neutrality of the water system. Lagoon pollution has been increasingly significant over the recent years and this has been found to contribute significantly to environmental problems[10]. Due to intensive agricultural activities in the surrounding area of lagoon, the soils could be subjected to non-point pollution as for relevance to Lagoon environments[10]. Karavasta is subject to different factors that would damage its biodiversity and eco-touristic values such as: eutrophication, urban pollution, illegal constructions, illegal hunting and fishing, weak participation of local communities in decision-making etc. Shkumbini River was strongly impacted by the Metallurgic Complex of Elbasan: about 30 to 35 million m^3 $year^{-1}$ of liquid waste with a high content of toxic compounds were discharged directly into the river, and about 300,000 tonnes $year^{-1}$ of solid waste were disposed on its riverbanks [10]. Even if Divjaka urban area is not drained to the lagoon, part of its polluting load discharging from Terbufi Canal may reach the lagoon because its plume is directed mainly southward and close to the coast during spring and summer [11]. In this context, assessment of physico-chemical parameters and the concentration of heavy metals in the lagoon water stand important at first for measuring the state of pollution of Karavasta Lagoon, and secondly it contributes on designing and implementing scientifically sound based conservation policies and actions.

The main purpose of this study is to provide information on lagoon water quality and the heavy metal levels in the surface as well as in depth of the water. The study serves to determine (i) water quality in the Karavasta Lagoon using physico-chemical parameters, (ii) its status for the support of living organisms in it, and also to compare with lagoon ecosystem standards.

2. Material and Methods

2.1 Study area

Karavastalagoon lies within the Mediterranean Climatic Zone, Central Sub-zone. The average rainfall is 950 – 1200mm during 85 – 100 days of the year, being one of the lowest levels in Albania [11]. Two thirds of this occurs in November to March, with peaks in October and November. The winter is mild, with January the coldest month of the year (average temperature 8.5°C). Days of temperature under 0°C are very rare. The mean annual temperature is 19.8°C. The temperature remains > 10°C up to about 9 months. The wind has two main directions southeast during autumn and winter and northwest during spring and summer. The average wind speed varies 2.5 m/s to 3.3 m/s[11].

2.2 Sampling

Water samples were collected at eight sites in the Karavasta Lagoonon December 2013 and July 2014. The sampling sites were strategically selected to see the impact of all potential contamination sources. Sampling station 1 was at Dajlan Center (N: 40° 55' 507"and E: 19° 28' 264") 200 m from the quay where fish is processed in order to see the influence of such activity; sampling station 2 was among “Grykederdhje 3” and Bedat village (N: 40° 54’ 287” and E: 19° 27' 489"); sampling station 3 in front of Bedat village, closed to Lena channel (N: 40° 53' 451" and E: 19° 28' 247"); sampling station 4 was closed to Mucias village (N: 40° 54' 164"and E:19° 30' 255"); sampling station 5 closed to the villages of Kamenice and Gur (N:40° 55' 421"and E: 19° 31' 396"); sampling station 6 is set in a distance of 100m from Kryekuq channel, at the pumping station (N:40° 55' 242"and E:19° 30' 562"); sampling station 7 at Kryekuq outlet (N:40° 55' 421" and E:19° 31' 396"), and the last one sampling station(8) at drainage outlet of Zharnec village (N: 40° 56' 421"and E: 19° 31' 68").

Water sampling 'Ruttner' is used for the sampling of the lagoon water. The water samples for the physico-chemical analysis were taken from the surface of the lagoon (50 cm under the surface) at each sampling location using 1.5 liters polyvinyl bottles and labeled according to the sampling sites. The samples for the trace metal analysis were acidified to pH <2 using 10% analytical grade HNO3. This was to keep the metals in dissolved state and to prevent bacteria action on them. The samples were placed in refrigerator boxes (+4 °C) and transported to the laboratory of Faculty of Science, University of Tiranawithin a day.

Fig 1 *- Map of the location of the study area (Karavasta Lagoon)*

2.3 In-situ measurement of physico-chemical parameters of the water of the lagoon

Measurement of the physical and chemical parameters of the lagoon water is done in situ in four seasons using Hannamultiparameter portable instrument. The parameters measured in-situ are: Temperature, Salinity, Conductivity, Dissolved Solids (TDS), pH, DO at the surface of lagoon water [1].

2.4 Heavy metals analyses

To determine the level of heavy metals in the lagoon's water (Cd, Cr, Cu, Pb, Hg) was usedthe EPA Method No. 1637. The water samples were treated with nitric acid to reach pH = 2. A volume of 100 ml of sample was put in a 400 ml volume chemical cup and treated with 3 ml of concentrated nitric acid. In addition, the chemical cup was heated without reaching the boiling level in order to evaporate until reaching the 20 ml volume. Then 3 ml of concentrated nitric acid is added again, covering crystal glasses and heating temperature is regulated, so that an acid reflux can be created until the complete digestion of the sample. The samples then evaporated until they almost dried up and were left to cool down. After cooling, nitric acid 1:1 is added and the samples heated until complete dissolution of any residue or precipitation. Samples were centrifuged to remove any insoluble residue and then diluted up to 25 ml volume [8]. The concentration of metals in this fraction was calculated by the method calibration curve and converted to lagoon water (ppb) concentration according to the formula: $C_m = C_{l.kal.} \frac{25}{100}$. Metals in solution were determined directly by Graphite Furnace AAS.

3. Results and Discussion

3.1 Physical and chemical characteristics

Water temperature varies according to seasons; the highest temperatures are recorded in July varying according to the sampling site from 26.9 to 28.57ºC. The lowest temperatures are recorded in December and they vary from 8.9 to 10.36 ºC. The recorded values are within the acceptable limits for the survival, metabolism and physiology of aquatic organisms. Water temperature is a highly important component of the aquatic ecosystem as it affects the living organisms and the physical and chemical characteristics of water. In the cause of Karavasta lagoon can be seen (Fig. 2) that through both seasons, the highest temperatures have been recorded in station 7, 8 where the influence of cool waters is less evident. The water temperature in the lagoon is typically Mediterranean [11]. Temperature and other physical and chemical parameters are affected significantly by

the quality of water streams communicating with the Channel and the water pumping station.

The conductivity in Karavasta Lagoon water is higher in July than in Decemberdue to evaporation. The water fluctuate in July from28.4 ms/cm to 66,32ms/cm. The maximum values were recorded in July (Dry Season) in station 7, 8 respectively 64.41 and 66.32 ms/cm, which indicates higher level of evaporation and lower influence of the freshwater. In December the water fluctuate from 41.4 ms/cm in Ss7 and a maximum 43.65 ms/cm in Ss 1 which correspond to Dajlan Center. The TDS, the index of the amount of dissolved solids in water, which also determines the degree of salinity, would also be high [10]. So the TDS of the water samples ranged from 28.5 inSs 2 to 62, 65 ppt in Ss1 in July and from 29.53 to 30.72 ppt in December. Salinity values in the Karavasta Lagoon measured in winter 2013 and summer 2014 reflect high values. The maximum values of salinity were in Ss1 ans Ss2 respectively39.31% and 39.95 (in July) and (30.83 % and 29.36 in (December), due to the connection of these stations with the sea (Fig. 5). pH values, recorded from the lagoon water samples, are good indicators for the lagoon because they constitute 2 of the main parameters that affect aquatic life there [2]. The Karavasta lagoon samples during winter 2013 and summer 2014 reflect a high pH level (Fig. 2) which means the increase carbonate levels in the water. The pH varies from 8.33 to 9.1 with an average of 8.7 in July, its highest values are recorded in December varies from 8.2 to 11.98 with an average of 10. High pH could be the result of a high photosynthesis rate from dense phytoplankton in those sampling stations. A pH between 7 and 8.5 according to Abowei, 2010 [2], is ideal for biological productivity and a pH lower than 2 is found to be harmful for the aquatic life.

The medium value of the dissolved oxygen on the surface (approximately 30 cm below the surface) of the lagoon water (Fig. 7) reached its highest peak in the sampling stations 6 (11.57ppm) in December. The minimum values of DO in December have been recorded in sampling station 1 and 7, 8 respectively 7.18, 8, 45and 3,11ppm influenced by fishing activities or by the drainage flow. The collected values for July didn't encourage biological productivity since when DO levels are under 2 mg L^{-1}, some aquatic organisms could get damaged.

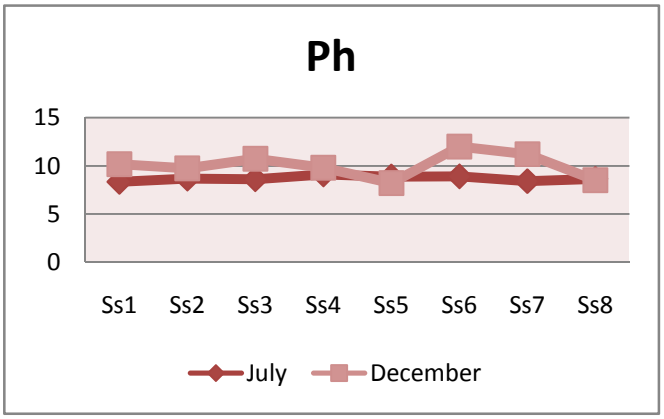

Fig 2, pH of water in Karavasta lagoon

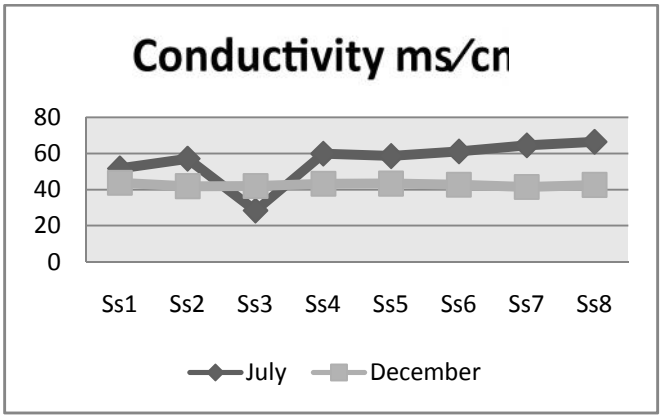

Fig.4 Conductivity ms/cm) in the water of Karavasta lagoon

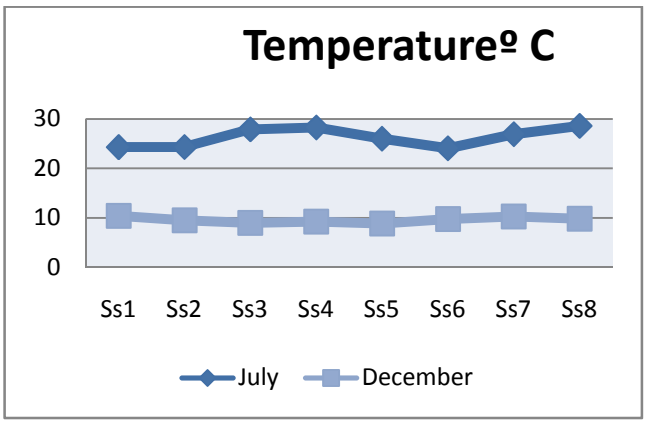

Fig 3. Temperature (°C) of water in Karavasta lagoon

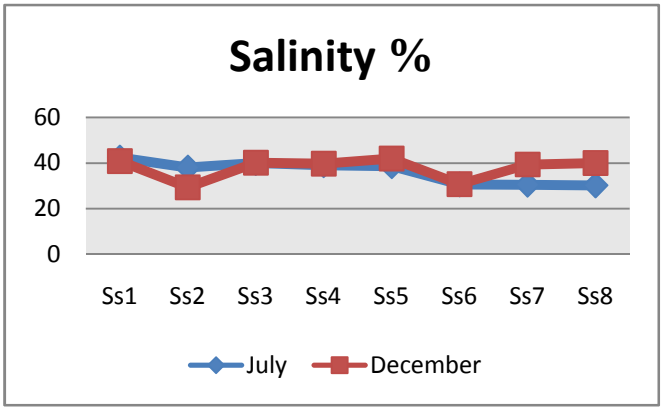

Fig. 5 Salinity (ppt) in the water of Karavasta lagoon

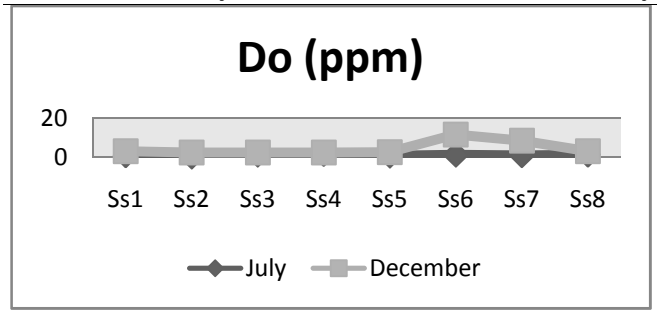

Figure 6. DO (ppm) in the water of Karavasta lagoon.

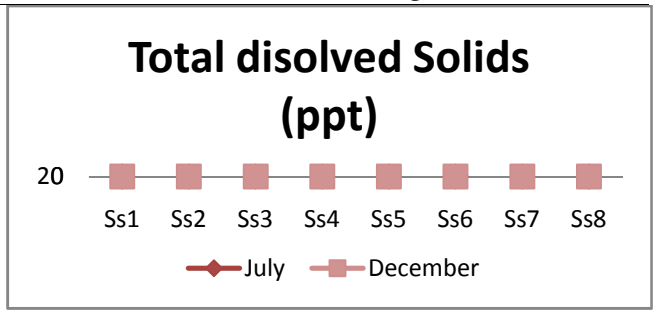

Figure 7 Total dissolved Solids (ppt) in the water of Karavasta lagoon.

3.2 Heavy metals in the water samples of Karavasta lagoon

We have analyzed the heavy metal values concentration on the lagoon water to know the effects all factors that may have influenced the status of heavy metals in the lagoon (Table 1). The average level of Cu in the water samples ranged from 13.5 to 24.1µg L^{-1}depending of the season of the sampling. The highest average concentration value of copper in the water for both seasons was measured in sampling stations 3, 7 and 8 affected by contribution of Lena andZharnecchannel that pass along agricultural fields of these village, that were regularly treated with copper-based pesticides. Cu levels in Karavasta lagoon were higher than surface water of Butrinti Lagoon [13] due to the intensive agriculture activities in the field around the Karavasta Lagoon, but close to the standards of EU (Table 1), so it should be monitored. Cd values on the water of Karavasta vary according to the sampling stations and seasonsbut Cdvalues in the lagoon water was under the allowed standards (<1 µg L^{-1}) (Table 1). The average level of Pbin the lagoon's water ranged from 0.72 to 4.95 µg L-1 in December and from 0.33 to 2.9µg L-1in July while highest value of Pb on the water surface was measured in December and in the sampling stations 1 and 8 respectively influenced by fishing activities and Zharnec channel. Pbvalue in water lagoon was smaller than the referenced standards (EU-2008 -7.2 µg L^{-1}). Results of this study told that Pb values have to be monitored because Pb it is an accumulative poison toxic for living organisms[9].

The average value of Cr in sampling sample of water inKaravasta lagoon ranged depending of sampling stations but had not big differences between seasons. Table 1told usthat theaverage values and in some stations Cr values were higher than the required values from EU standards. In the sampling stations 3, the concentration of Cr in the water of lagoon results to be about twice higher than the EU standard values, whereas in the 4 and 8 stations the values were higher than those of EU standards influenced by alluvium brought by Shkumbini river which passes through areas rich in Cr (Albanian ultramafic sites) ([6]) (Table 1).

Table 1: Heavy metals concentration in water of Karavasta Lagoon in Winter 2013 and Summer 2014 (µg L^{-1})

Sampling station	Cu		Cd		Pb		Cr	
	December	July	December	July	December	July	December	July
1	12.2	27,4	0.050	0.032	4.95	2.90	16.5	19.0
2	2.98	6.8	0.010	0.001	0.72	0.40	12.1	14.3
3	16.9	48.2	0.010	0.001	1.36	1.10	40.2	45.0
4	12.2	24.0	0.040	0.004	0.65	0.33	22.5	23.5
5	8.5	16.0	0.019	nd	1.61	1.41	10.2	12.5
6	4.5	14.5	0.023	0.01	0.70	0.40	13.5	15.6
7	17.7	28,4	0.064	0.039	0.68	0.34	16.3	14.5
8	33.2	55.4	0.010	0.001	2.66	2.02	31.5	32.0
Average	13.5	24.1	0.028	0.011	1.65	1.11	20.35	22.05
STDEV	9.5	16.6	0.020	0.01	1.40	0.95	10.5	11.2
Max	33.2	55.4	0.050	0.039	4.95	2.9	40.2	45
Min	2.98	6.8	0.019	0.001	0.72	0.33	10.2	12.5
EU *Guidelines*	**50**		**1**		**7.2**		**20**	

4. Conclusions

The study showed that physic-chemical parameters measured in the lagoon should be monitored. Increased temperature and salinity in July is accompanied by the reduction of dissolved oxygen in the depth of the lagoon and therefore this phenomenon leads in damaging or reducing the rate of growth of living organisms in the lagoon. The physic-chemical parameters have to be monitored in the sampling stations 1, 7 and 8 influenced by fishing activities and by the flow of drainage channel. The distribution of heavy metals in the water of the lagoon varies depending on the season and sampling stations. The elements Cu, Pb in some stations are found to be closeto the allowablevalues by the EU standards and represent a potential contamination risk [7]. The average values of Cr in water of Karavasta lagoon in both seasons were higher than the European standards.This can be explained by the flow of Shkumbini River, which runs in ultramafic areas [6] of the country, or passes through the metallurgical site.

Considering this study for the state of heavy metals in the lagoon of Karavasta, as a conclusion it could be said that continuous monitoring has to be carried out in order to prevent its pollution.

Acknowledgments

The authors wish to thank the Critical Ecosystem Partnership Fund (CEPF) for the support provided in the frame of project “Ecological and economical assessment of ecosystem services in the Karavasta Lagoon’’.

5 References

[1] Abdo MH, (2005): Physico-chemical characteristics of Abu Za’baal pond. Egypt. Egypt. J. Aquatic Res., 31(2): 1-15.

[2] Abowei JFN (2010) : Salinity, dissolved oxygen, pH and surface water temperature conditions in Nikoro River, Niger Delta, Nigeria. Adv. J. Food Sci. Technol, 2(1): 16-21.

[3] Addo MA, (2002): An assessment of aspects of environmental impacts of the proposed ‘West African gas pipeline project in Ghana’. Thesis, Department of Environmental Science Programme, University of Ghana, Legon-Ghana, pp: 115-116.

[4] Abulude FO, Fapohunda OO, Awanlenhen (2006): Determination of some heavy metals in Procambaris clakii, Paleanon sp., Macrobrahium vollenhovenii and Penaeus notalis from the coastal water of Ondo State, Nigeria. J. Anim. Vet. Adv., 5(1): 38-41.

[5] Binning K, Baird D, (2001): Survey of heavy metals in the sediments of the Swartkops River Estuary, Port Elizabeth South Africa. Water, 27 (4): 461-466.

[6] Bani A, Imeri A, Echevarria G, Pavlova D, Reeves RD, Morel JL, and Sulçe S, (2013): Nickel Hyperaccumulation in the serpentine flora of Albania. *Fresenius Environmental Bulletin. Vol 22*.Nr. 6 *Factor impact 0.7.*

[7] EU Framework Water Directive on: environmental quality standart. 2008, 39.

[8] Environmental Protection Agency Inductively coupled plasma-atomic emission spectrometry: Method 6010B. EPA, Washington D.C, USA.

[9] Christophoridis A, Stamatis N, and Orfanidis S, (2007): Sediment heavy metals of a Mediterranean coastal lagoon. Agiasma, Nestos Delta, Eastern Macedonia (Greece), Transitional Waters Bulletin TWB, Transit. Waters Bull, 4: 33-43.

[10] Cullaj A, Hasko A, Miho A, Schanz F, Brandl H, Bachofen R, (2005) : The quality of Albanian natural waters and the human impact. Environment International 31, 133-146.

[11] Chauvelon P, (2004): Hydrological functioning and hydraulic management of the Karavasta lagoon system, Albania. FAO, World Bank, Ministry of Environment of Albania, Report 27p.

[12] Lord DA, Thompson GA, (1988): The Swartkops estuary, Pollution status. In: Baird D, Marias JFK, Marin AP (eds.) Proc. Symp. Held on the 14 and 15 September 1988 at the Univ.of Port Elizabeth. S. Afr.Nat. Sci. Programmes Rep. 156: 16-24.

[13] Topi T, Bani A, Sulce S, (2012): Heavy metals in soil, sediments, mussels, and water from Butrinti lagoon (Albania). Fresenius Environmental Bulletin. Vol, 21.