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Physico chemical characteristics and heavy metal contents of water from Butrinti lagoon, Albania

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Abstract:

A study was conducted between May 2010 and January 2011 in the Butrinti Lagoon, an important ecological and economical area in the south of Albania. The study aimed to determine (i) the water quality in the lagoon of Butrint using physico-chemical parameters and 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 multiparameter portable instrument. Surface and bottom water of the lagoon were analyzed for heavy metals: Pb, Cr, Cu, Cd, Hg. The results showed that water temperature varies depending on the seasons. The highest temperatures were in August from 26 to 27.3 ^{0}C depending on the sampling station. pH in the water of the lagoon is basic, its values ranged from 8.12 to 8.49, and were optimal for the production of mussels. The values of salinity in the lagoon of Butrint are smaller than those of the Ionian sea influenced by rivers Bistrica, Pavlo and groundwater resources. Lower values of DO in the depth of the lagoon were recorded in August at stations SS2 (1.4 mg L^{-1}) and SS5 (1.9 mg L^{-1}), and therefore a damage was noticed in the growth of mussels in the lagoon. The heavy metals Cr, Pb, in some stations are found in higher levels than the values allowed by the EU and pose a potential health risk to humans and the aquatic life of the lagoon's ecosystem.

Key words: Heavy metals, Butrinti Lagoon, physico-chemical parameters, aquatic life.

1. Introduction

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, 10]. The quality of lagoon water changes with seasons and geographical areas, even when there is no evident pollution. Water quality guidelines insure basic scientific information on quality parameters and toxicological values for specific uses of water. Some important physical and chemical parameters that influence the aquatic environment are temperature, pH, salinity, dissolved oxygen, conductivity and heavy metal contaminants. 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 [7].

Temperature is a limiting factor in the aquatic environment [6]. 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. It is expressed as the total concentration of electrically charged ions in water in part per thousand (‰). Salinity is expressed either as a mass of these ions per unit volume or as milli-equivalent of the ions per volume of water. This 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.

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.

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

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Their presence in the aquatic ecosystem, mainly due to anthropogenic influences, has direct implications to the biota and indirectly to men. Trace metals have been referred to as common contaminants, widespread in the environment with sources mainly from the weathering of minerals and soils [11].

In the past few years, levels of heavy metals have increased due to human inputs and activities [11]. They are extremely dangerous economically as far as fishing, agriculture, farming, ecological tourism and scientific research and education are concerned. Therefore, the exact determination of heavy metals and other physico-chemical parameters in aquatic environments are important to control their pollution levels. 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 Butrinti 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

The Butrinti lagoon lies within the Mediterranean Climatic Zone, Central Sub-zone. The average rainfall is 1200 –1300 mm during 95 – 100 days of the year. The winter is mild, and January is considered to be the coldest month of the year (average temperature 11.9°C), while the hottest month is July (average temperature 27°C). The average annual temperature is 20°C.

2.2 Sampling

Water samples were collected from the Butrinti Lagoon at seven selected sites between May 2010 and January 2001. The sampling sites were strategically selected to see the impact of all potential contamination sources. The sampling points were counted as follows: Point 1 (N: 39^0 48 '556" and E: 20^0 01'808") was set 100m away from Bistrica River to see its impact, as a pure and sweet water with a volume of about 5 m^3 sek-^{1}, in the ecosystem of the lagoon; Point 2 (N: 39^0 47 '540', E: 20^0 02'885") in front of Cimikos hill and near the gorge flow of Pavllo River; Point 3 (N: 39^0 46’ 880’’, E: 20^0 02'723’’) in front of a small valley between two low and soft hills, which were used for grazing. Point 4 (N: 39^0 45’ 370’’,E: 20^0 02'788’’) the connection spot between the Butrinti lagoon and Bufi lake ; Point 5 (N: 39^0 45’ 311’’,E: 20^0 02'175’’) i south of the lagoon; Point 6 (N: 39^0 46’ 695’’ E: 20^0 01'054’’) in Pallavraq; and Point 7 (N: 39^0 48’ 332’’, E: 20^0 01'240’’) near the Cleaning and Package center of mussels. The water samples were taken from the surface and from the bottom of the lake (50 cm under the surface and 50cm over the lagoon bed).

Water sampling 'Ruttner' is used for sampling of the lagoon water. In order to analyze the heavy metals in the water of lagoon, plastic bottles of 1,5 liters were used. There is an exception only for Hg, for which we used glass bottles in order to analyze it. At Water samples were taken 50 cm below the water surface and 50 cm above the bed of the lagoon in depth.

All samples were stored in refrigerator boxes (+4 ° C) and transported to the laboratory within a day. To determine the level of heavy metals in the lagoon’s water (Cd, Cr, Cu, Pb, Hg) the AOAC Official Method; 974.27 and 977.22 was used. Metals in solution were determined directly by Graphite Furnace AAS.

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

Measuring physical and chemical parameters of the water of the lagoon is done in situ in four seasons using multiparameter portable instrument. The parameters which were measured in-situ were: Temperature, Salinity, pH, DO at the surface of lagoon water and DO at the batton of lagoon water.

3. Results and Discussion

3.1 Physical and chemical characteristics

Water temperature varies according to the seasons, the highest temperatures are recorded in August varying according to the sampling site from 26 to 27.3 0C. The lowest temperatures are recorded in January and they vary from 13.4 to 14.7 degrees. 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. Temperature can have both positive and negative effects on the growth of organisms. Temperatures that exceed 30 degrees Celsius can slow down growth. It can be seen (Fig. 1) that through all the seasons, the highest temperatures have been recorded in station 4 where the influence of cool waters is less evident. The water temperature in the lagoon is typically Mediterranean. Temperature and other physical and chemical parameters are affected significantly by the quality of water streams communicating with the Butrinti Lagoon, rivers that flow into it (10m^3/sec) and precipitations.

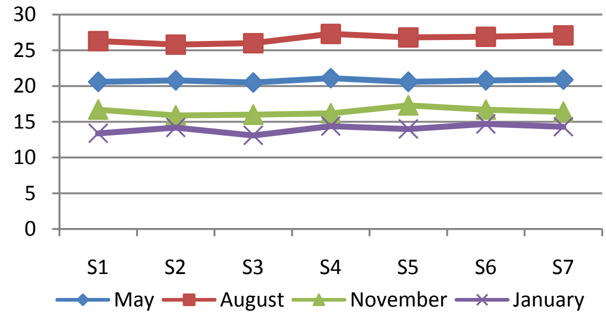

Figure 1: Temperature (°C) of water in the lagoon

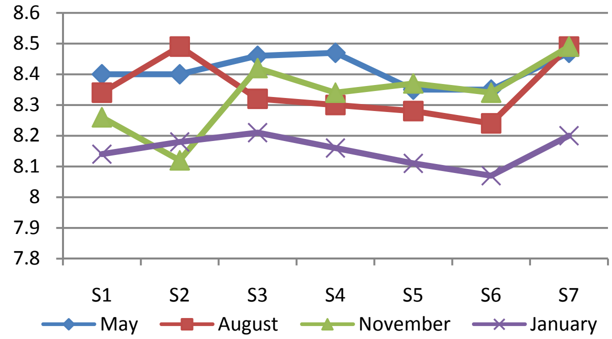

Figure 2: pH of water in the lagoon

pH in the lagoon water is determined to be mainly basic. Every season and in all the sample sites it exceeds 8. pH varies from 8.12 to 8.49, its highest values are recorded at site number 7 throughout all the seasons. Ramanathan et al [13] recommends as optimum pH values 6.8-8.7 to ensure maximum growth and reproduction of mussels and fish. High pH levels increase carbonate levels in the water. The minimum value of pH was recorded in sampling site 6 (8.07) in January and the maximum values were recorded in August in sampling site 2 and 7 respectively 8.12 and 8.49. High pH could be the result of a high photosynthesis rate from dense phytoplankton.

A pH between 7 and 8.5 according to Abowei, 2010 [4], is ideal for biological productivity and a pH lower than 2 is found to be harmful for the aquatic life.

pH values (Fig. 2) and temperatures, 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. [5]

Salinity values in the Butrinti Lagoon are lower than those of the Jon Sea (approximately 37 ppt) influenced by the Bistrica and Pavlo rivers and underground sources. The maximum values of salinity were recorded in August, 24.8-28.3 and the minimum values in November, 10.7-14.7 (Fig. 3).

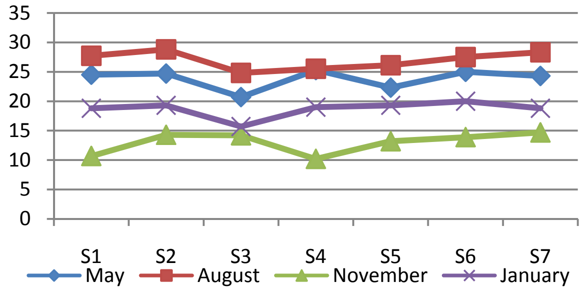

Figure 3:. Salinity (ppt) of water in the lagoon

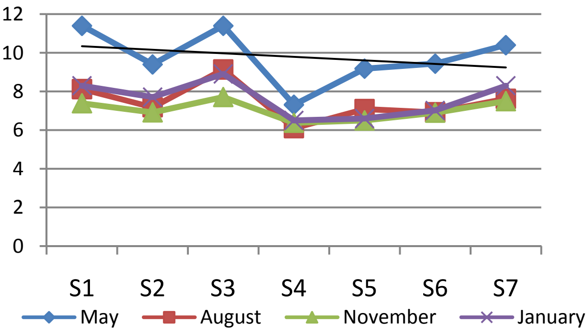

Figure 4: DO in surface water (mg L^{-1})

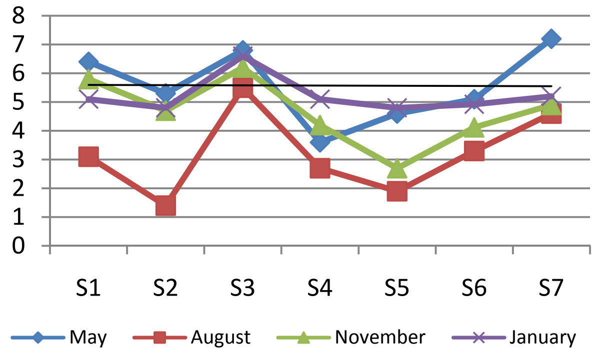

Figure 5. DO in the bottom of water (mg L^{-1})

The medium value of the dissolved oxygen on the surface (approximately 30 cm below the surface) of the lagoon water (Fig. 4) reached its highest peak during May, 9.79±1,4 mg L^{-1}. The minimum values of DO have been recorded during November, 7±0,5 mg L^{-1}. These minimum values on the surface of the lagoon water have been recorded in site number 4 (6,5 mg L^{-1}), the furthest from the influence of fresh waters. The collected values nevertheless encourage biological productivity because when DO levels are under 2 mg L$_{-1}$, some aquatic organisms could get damaged [8].

Medium values of DO in depth of the lagoon (50 cm above the lagoon floor) are considerably smaller than the value of DO on the surface, DO is approximately 2 times smaller (Fig. 5). The highest medium value of DO in depth was measured in May and it varies from 5,57± 1.2 mg L^{-1} which is relatively high for the aquatic ecosystem. The lowest DO values in depth of the lagoon were recorded in August in sites 2 (1,4 mg L^{-1}) and 5 (1,9 mg L^{-1}) mainly because of the increase in temperatures and salinity. These values were not regarded as encouraging for the biological productivity of the lagoon. In the Butrinti Lagoon the increase in temperatures and salinity is associated with the decrease of DO levels [10]. This phenomenon as a result was accompanied with the damaging or the decrease in mussel growth rate.

3.2 Heavy metals in the water samples of Butrinti lagoon

We have sampled and measured the heavy metal values on the surface and in depth of the lagoon water to observe the effects of the soil, sediments and/or other factors that may have influenced the release and transportation of heavy metals (Table 6,7). The average level of Pb on the surface is higher mainly throughout winter (2,65±1,26 μg L-1) while the lowest medium level was measured in August (0,58±0,23 μg L^{-1}). Throughout sites the highest levels of Pb on water surface have been recorded in the sampling site SS6 almost throughout all seasons. The highest value of Pb on the water surface was recorded in August in the sampling site SS6 (4,6 μg L^{-1}). Its value on the surface was smaller than the referenced standards (EU-2008 - 7.2 μg L^{-1}) [9]. As far as Pb in depth is concerned, the average values are higher than on the surface. The highest Pb medium value in depth was recorded in May 6,98 μg L^{-1} with a maximum value in SS1. Nevertheless there are no statistically proven changes as far as Pb concentration between sites is concerned. In August the value measured in SS6 (7,61 μg L^{-1}) is higher than the European standard. With a security level 0.05 there are statistically proven changes as far as Pb concentration is concerned in depth, throughout different seasons of sampling. We can argue that Pb in the water comes from urban Ksamili discharges before it is deposited in the in depth sediments[14]. Pb is a non-essential component for plants and animals and it is often an accumulative poison toxic for living organisms. Average Cd values on the surface vary according to the seasons. The highest values were measured in November 0,153±0,23 μg L^{-1}, with maximum values in SS4 0,18 μg L^{-1}.

The lowest average Cd values have been recorded in May 0,04 ±0,03 μg L^{-1}. For the water sampled in depth the highest values have been recorded in August 0,1± 0,06, the highest have been recorded in sampling site 2 (0,2 μg L^{-1}). The average concentration of Cd on the surface and in bottom of the lagoon water is constantly under the allowed standards (<1 μg L^{-1}) (Table 6,7,8). There are no important changes as far as the concentration of this element in depth, between sampling sites, according to the seasons, is concerned. The average maximum value of Cr in botton water of lagoon is recorded in August, exactly 20,5±16,5 μg L^{-1}, slightly higher than the required values from EU standards. In the sampling stations SS2 and SS3, the concentration of Cr in the botten water of lagoon results to be twice higher than the EU standard values, whereas in the SS6 and SS7 stations the values are higher than those of EU standards and as well higher than WHO and EPA standards (Table7,8).

Nevertheless, there are no important changes in terms of concentration of this element in the depth water of lagoon between the sampling stations. The season is the one who affects the change in the concentration of Cr in the depth water of lagoon (level of security 0,05). World Health Organization (WHO) 1998[15]. recommends the limit of Cr in the drinking water to be 50 μg /L. In all the surface water samples the level of Cr results to be lower than this limit but in depth water samples (SS6, SS7) the level of Cr is higher than the EU standart-2008. Furthermore, Cr is found to be in higher levels in the stations where the sediments are rich in Cr and are influenced by the flow of rivers that flow into the lagoon[14]. The highest average concentration value of copper in the surface of the water was noticed in august, exactly 15.87±10,6 μg L^{-1}. The highest value recorded on SS4 and SS6 are respectively 27,4 and 30,8 μg L^{-1}.The surface water highest values were generally recorded on SS4 station, who is affected by the contribution of Bufi's soils, which due to historical data were regularly treated with copper-based pesticides.

The highest average concentration value of copper in the bottom of lagoon was recorded on august as 24.56±13 μg L^{-1} and the highest value of it was recorded on SS6 station as 47,8 μg L-1. This value is close to the standards of EU, nevertheless it should be monitored. The change in the concentration of Cu in the botton water of lagoon is not important between the stations (level of security 0.05). The lowest concentrations were recorded during the month of November, exactly 2,9±2,16 μg L^{-1} and they should be monitored.

Table 6: Heavy metals in the surface of water ((µg L-1) in Butrinti lagoon.

Sampling stations	*Pb*				*Cd*				*Cr*				*Hg*			*Cu*			
	May	August	Nov	January	May	August	Nov	January	May	August	Nov	January	May	August	Nov	May	August	Nov	January
SS1	1,15	0,78	2,6	1,42	0,03	0,049	0,14	0,066	2,04	0,64	0,2	1,76	0,01	0,09	0,12	9,7	10,4	3,2	4,1
SS2	1,25	0,68	2,4	2,04	0,02	0,075	0,12	0,087	0,87	1,84	0,4	1,83	0,01	0,26	0,12	8,3	6,2	2	3,9
SS3	1,01	0,44	0,97	2,62	0,03	0,047	0,13	0,077	1,3	0,54	0,2	1,5	ND	0,27	0,08	2,3	4,8	2,1	3,2
SS4	0,98	0,29	3,9	2,12	0,06	0,022	0,18	0,079	0,7	1,45	0,21	2,06	ND	ND	0,18	14,6	27,4	7,7	4,4
SS5	1,48	0,52	2,6	1,26	0,03	0,041	0,14	0,066	0,6	3,77	0,53	2,77	ND	ND	0,16	11,9	22,1	2,2	1,9
SS6	1,53	0,93	4,6	1,33	0,09	0,068	0,17	0,08	0,7	1,51	0,71	3,53	ND	ND	0,61	18,7	30,8	4,99	5,6
SS7	0,64	0,39	1,5	1,22	0,01	0,039	0,16	0,02	0,7	1,66	0,16	5,35	ND	ND	0,19	6,3	9,4	1,14	2,3
Average	1,15	0,58	2,65	1,72	0,04	0,05	0,153	0,07	0,99	1,63	0,34	2,69	0,01	0,21	0,25	10,3	15,8	3,37	3,6
STDEV	0,31	0,23	1,26	0,54	0,03	0,02	0,23	0,02	0,52	1,07	0,21	1,37	0	0,1	0,16	5,42	10,6	2,24	1,27
Max	1,53	0,93	4,6	2,62	0,09	0,075	0,18	0,09	2,04	3,77	0,71	5,35	0,01	0,27	0,161	18,7	30,8	7,7	5,6
Min	0,64	0,29	0,97	1,12	0,01	0,022	0,12	0,02	0,6	0,54	0,16	1,15	0,01	0,09	0,08	2,3	4,8	1,4	1,27

Table 7: Heavy metals in the botten water (µg L-1) of Butrinti lagoon.

Sampling stations	*Pb*				*Cd*				*Cr*				*Hg*			*Cu*			
	May	August	Nov	January	May	August	Nov	January	May	August	Nov	January	May	August	Nov	May	August	Nov	January
SS1	10,78	1,68	0,95	1,02	0,03	0,055	0,073	0,02	2,1	19,8	0,53	1.3	ND	0,23	0,19	10,4	23,1	3,09	4,9
SS2	7,87	1,3	1,17	0,94	0,02	0,204	0,076	0,08	2,22	49,2	0,7	1,26	ND	0,26	0,12	15,6	9,9	4,99	6,2
SS3	8,97	1,95	0,97	2,41	0,03	0,164	0,054	0,04	2,58	36,5	0,35	1,1	0,07	0,26	0,19	8,3	16,7	2,64	3,6
SS4	3,46	3,78	1,07	0,96	0,07	0,076	0,081	0,03	1,5	12,9	0,34	1,56	0,05	0,29	0,23	12,8	32,3	2,65	4,7
SS5	8,48	3,17	0,55	2,7	0,06	0,032	0,038	0,15	0,9	12,4	0,29	1,82	ND	ND	0,24	24,2	28,9	2,16	2,1
SS6	4,06	7,61	0,55	2,44	0,1	0,097	0,038	0,04	0,8	54,6	0,27	2,85	ND	ND	0,22	16,5	47,8	2,28	4,25
SS7	5,25	1,46	0,41	1,37	0,1	0,092	0,028	0,07	0,7	56,6	0,43	3,45	ND	ND	0,29	9,7	13,2	2,65	3,65
Average	**6,98**	**2,99**	**0,81**	**1,6914**	**0,06**	**0,1**	**0,055**	**0,06**	**1,54**	**20,5**	**0,41**	**1,72**	**0,26**	**0.26**	**0,21**	**13,9**	**24,5**	**2,92**	**4,2**
STDEV	2,75	2,24	0,29933	0,7903	0,03	0,06	0,02	0,045	0,77	16,5	0,15	0,93	0	0,02	0,052	5,45	13	0,95	1,28
Max	**10,78**	**7,61**	**1,17**	**2,44**	**0,1**	**0,204**	**0,081**	**0,104**	**2,58**	**56,6**	**0,7**	**3,45**	**0,29**	**0,29**	**0,29**	**24,2**	**47,8**	**2,16**	**6,2**
Min	3,48	1,3	0,41	0,96	0,02	0,032	0,028	0,02	0,7	12,4	0,27	1,1	0,23	0,23	0,12	8,3	9,9	4,99	2,1

So, we found changes statistically proven (level of security 0.05), regarding the concentration of copper in the depth water of lagoon as a function of the season. Copper results to be lower than the standards of EU. The components of copper are used as fungicide, algaecide, insecticide and fertilizers in the soils of Vurgu and Bufi's hills, but the absence of Cu can be explained from its mobility.

Table 8: The heavy metals concentration guidelines (µg L-1)

Guidelines	*Cd*	*Cr*	*Cu*	*Pb*	*Hg*
WHO	1	50	200	50	
EPA	1	50	130	50	
EU	1	20	50	7.2	0.05

4. Conclusions

The study showed that physico-chemical parameters measured in the lagoon should be monitored carefully. Increased temperature and salinity in August 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 mussels in the lagoon.

In August, the measured values of Pb in sampling station SS6 (7.61 µg L-1), were higher than the European standard. It can be explained that Pb is found in deep water of Lagoon because of the urban emissions of Ksamilis. The distribution of heavy metals in the deep water of lagoon varies depending on the season, with the exception of Cd. The elements Cr, Pb, in some stations are found to be higher than the values allowed by the EU standards and represent a potential contamination risk.

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