THE COMPARISON OF QUALITY WATER AND SEDIMENTS BETWEEN THE LAGOONS OF LEZHA

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ABSTRACT

The aim is to study the quality of surface water of these lagoons, analyzing the physicalchemical parameters, biological and toxicity in these waters, as well as sediment, spatial and temporal distribution of pollutants. The wetlands in the study have very precious values of biodiversity, and there is part of the Kune-Vain wetland ecosystem which lies on the Adriatic coast, on both sides of the Drini River delta. In the each lagoon, are defined and taken 4 points sampling, in which the samples were taken into the waters and sediments. The water samples, are taken during 4 seasons of 2012-2013, were analyzed for physical and chemical parameters: pH, T, EC, TDS, Salinity, DO (in situ), inorganic nutrients (NH₄, NO₂, NO₃, PO₄), COD and BOD₅, heavy metals. The sediment samples were taken in December 2011 and March 2013. The classification and comparison of water quality, is carried out according to the EC Directives (2000/60; 2006/44; UNECE; NIVA), and for sediments the comparison is used SQG (mg kg⁻¹) according to the ANZECC (ISGQ ISGQ low and high); NOAA (ERL and ERM); Standard of Florida (TEL instructions of PEL), WHO and EPA. It concluded that concentrations of heavy metals in water and sediments for the entire period in both lagoons are below the permitted values. The temperature values are almost similar in the two lagoons, the NO₃ values in all the surveyed period, resulted below the limit allowed. In the waters of the lagoon of Kune are found in higher average values of NH₄, TDS, EC, COD and BOD₅. In Vain Lagoon, they are easily found higher values of pH, DO, lower contents of heavy metals in water and sediments. The concentrations of heavy metals were found lower in the water than in sediments.

Keywords: Water quality, sediments, Lezha lagoons, classification.

INTRODUCTION

The process of eutrophication in water lagoon may be a result not only of increased nutrients but also by other factors, such as lack of communication of water, water exchange, through the use of agricultural practices and livestock inadequate, uncontrolled and untreated water discharge as urban as suburban and rural, climate change (extreme weather phenomena, low and high temperatures, heavy rains, floods, etc.).

Therefore deterioration of the surface water quality in enclosed coastal waters is strongly associated not only with the loading of nutrients, oxygen consumption, but also as a result of microbiological pollution, toxic, deterioration of habitat and livelihood creatures that live in them landing biodiversity to degraded ecosystem (Recknagel, et al., 1995).

The wetlands in the study are part of the wetland ecosystem Kune-Vain which lies on the Adriatic coast, on both sides of the Drini River Delta. In this wetland system includes marshes lagoon, marine waters and the coast, the land below sea level and typical coastal forests, shrubbery, water leakage and agricultural land and pastures. This lagoon system is closely connected with the coastal morphology, downloads Mat and Drin River, and hydrology of coastal waters.

This area is the first Protected Area of Albania declared as a Preserve since 1940. Actually, both these ecosystems are protected areas of the Albanian legislation, such as the Managed Natural Preserves (Category IV), as well as Emerald area network, important bird area (IBA), except Kune Island that belongs I, Strict Nature Reserve. The main species that give this status are Ardeidet and Phalocrocoridet. The most important values of the site are those of biodiversity, socio-economic (fishing) and recreational (tourism), which are conditional on ecological balance. The area is well known for its features recreational, educational and fascinating. But the region is distinguished for his historical values and archaeological sites. This legacy has unique features that are expressed in clothing, music, cooking etc. The water environment and aquatic habitat are the most important elements of the lagoons Kune-Vain. The surface waters are connected with the sea and the river Drin, and the groundwater.

Study area

The Lagoon Kune/Merxhani has the surface area of 360ha, with the average depth of 0.75-1.3m, is located in the northern part of the river Drin. The communication of waters between the Adriatic Sea through the canal becomes Kune/Merxhan, with a width of 22m, but is currently seriously reduced by the creation of the littoral arrows in the eastern part of the island.

The Vain Lagoon (Lagoon Ceka and Zajet, etc.), has an area of 9km², with 0.7-1.3m depth, Ceka lagoon consisting of 4.9km² and Zajet 2.4km², also and some other smaller lagoons and marshes. Realized through channel communication of waters between gravel/Drin after Matkeqe channel, is now closed, small channels, allow the exchange of water between the Zajet and Ceka lagoon.

This wetland system is in constant anthropogenic pressure from urban development and industrial areas (by a point and non point source pollution). Drin River flows into the sea between the lagoons of Kune and Vain. In the case of the atmospheric events, the river flooded by water pumped directly into the lagoon Vain.

MATERIALS AND METHODS

The selection and sampling is done based on the guidelines of the Institute of Environment, unified (Reference: Methodology the selection and design of samples, analysis of elements of Environmental pollutants in water monitoring, referring to the international standard method for sampling in Aquatic Environments). In figure 1, is presenting the satellite locations of sampling points of water and sediment.



Figure 1. Satellite Images of sampling points on the Kune and Vain Lagoons.

They are designed and defined four points sampling for each lagoon, sampling water and sediments are taken in the same geographical coordinates. The water samples are taken in the months March-July-October of 2012 and February-May-August and November of 2013, while for toxicological analysis, water samples and sediment are taken in the months December 2011 and March 2013.

At each sampling point, four samples are taken in the order to allow Statistical analysis attempting a normal value. The water samples are analyzed for physical and chemical parameters: pH; T; EC; TDS; Sal; DO; (In situ, with Parametric multi HANA probe instrument); soluble forms of N and P such as: NO_3^- , NO_2^- , NH_4^+ and PO_4^{-3} (were analyzed in model spectrophotometer HACH, DR/2000), COD, BOD₅, for toxicological parameters (heavy metal in water and sediments).

The water samples for physical-chemical analysis are taken into plastic bottles of pretreatment volume 0.5L, 0.3m at a depth; they are stored in temperature 4^{0} C and transported to the laboratory for analysis. For toxicological analysis, the samples are taken at 10-15cm water depth, in polyethylene bottle of the 1.5L volume. The collected samples are preserved by adding 2ml of nitric acid and stored in insulated cooler containing ice and brought on the same day to the laboratory and maintained at 4^{0} C $\pm 2^{0}$ C until processing and analysis is over as suggested in AOAC method.

The water and sediment samples for physical-chemical and toxicological evaluation, are analyzed in analytical chemistry laboratories of waters, Department of Environment and Health, IPH. The sediment samples taken at a depth of 0-10cm. The heavy metals are analyzed by Atomic Absorption Spectrometry (AAS), Varian SpectrAA 100, using flame and graphite furnace techniques (Cu, Pb, Cd, Cr, Ni), based on methodologies proposed by the AOAC, Official Method 974.27 (Determination of water Cd, Cr, Cu, Pb, Zn, Cap. 11, pg 16). The results are expressed as mg L⁻¹ for water, mg kg⁻¹ dry weight for sediments.

RESULTS

The graph 1, are presented variations of mean values, of physical-chemical parameters in the waters of lagoons (measured in situ), during the years 2012-2013.

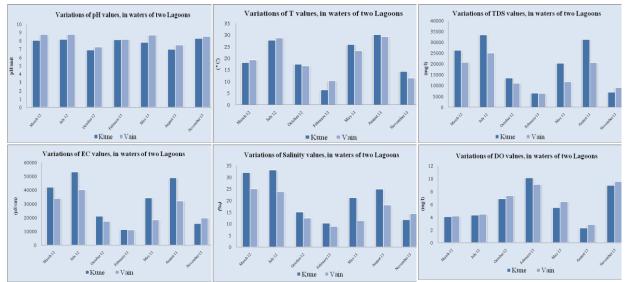
 $T^{0}C$. In the both lagoons, average values lower temperatures are found in February'13 whereas values higher average temperatures were observed in August '13.

pH. We Kune lagoon, lower values of pH are found in October'12 of August'13, while higher values of pH are found in November'13. We Vain lagoon, lower values of pH are determined October'12, while the highest values are found in March'12 pH of July'12. Referring to NIVA's classification, these waters belong to class I (very good environmental quality). While referring to Directive 2006/44/EC, pH values, they are within the limits required and recommended.

TDS and EC. In the Kune lagoon, the lowest values of TDS, are found in November'13 TDS, while the highest values are found in August'13. We Vain lagoon, the lowest values of TDS are found in November'13 TDS, while higher values of TDS are found in July'12 TDS. Average values lower of TDS are found in February'13 (Vain) and higher average values of TDS are found in July'12 (Vain).

In both lagoons, lower average values of the EC are found in February'13 whereas higher average values of the EC are found in July'12.

Salinity. In the Kune lagoon, the lowest values of salinity are found in February'13 (9.1‰), while the highest values of salinity are found in March'12 (34.2‰). In the Vain lagoon, lower values of salinity are found in August'13 (5.3‰), while the highest values of salinity are found in March'12 (30.1‰). Average values lower of salinity are found in February'13 (Vain), while the highest average values of salinity are found in July'12 (Kune).



Graph 1. Variations of mean values, for physical-chemical parameters in waters, in the both lagoons (in situ), during the period 2011-2013.

DO. In the Kune lagoon, lower values of DO are found in February'13 (2.14 mg L⁻¹), while the highest values of DO are found in February'13 (11.2 mg L⁻¹). In the Vain lagoon, lower values of DO are found in August'13 (1.88 mg L⁻¹), while the highest values of DO are found in November'13 (10.2 mg L⁻¹). Values lower average of DO, are found in August'13 and higher average values of DO are found in the lagoon of Kune February'12. Referring to the UNECE classification, waters of Kune Vain Lagoons for months (October'12-Vain), February '13 and November'13, belong to Class I; in the October'12 (Kune) and May'13

(Vain), belong to Class II; in the March'12 and July'12 (May'12-Kune) belong to Class III; while in August'13 waters belong to the Class V. Referring to NIVA classification, waters of Kune Vain Lagoons for months March'12, July'12 (and May'13-Kune) belong to Class III (environmental quality - average); in October'12 (May'13-November'13-Kune and Vain) belong to Class II (good environmental quality); in February'13 (November'13-Vain) belong Class I, the while waters belong to the Class IV (environmental quality - bad) in August'13. Referring to Directive 2006/44/EC, both surface water lagoons in October'12, February'13 and November'13 level in accordance with mandatory for quality of water Salmonid, while in October'12, February '13, May'13 and November '13 are in accordance with the level of mandatory for quality of water Cyprinid.

The graph 2, are presented variations of mean values, of soluble micro nutrients, BOD and COD in the waters of Kune-Vain Lagoons, during the years 2012-2013.

NH₄. In the both lagoons lower values of NH₄, are found in February'13 whereas the highest values of NH₄ are found in October'12 NH4. The contents of NH₄ compared with Directive 2006/44/EC has resulted over the mandatory for quality of water Salmonid and Cyprinid, in all series and samples taken in 2012 and in May'13. While during the months February, August and November'13, the water samples resulting in the level recommended within this directive Salmonid and Cyprinid waters. Referring to the UNECE classification, in March'12 (Kune) waters belonging to Class IV; (March'12 Vain), July'12, October'12, May'13, August'13 and November'13 (Vain) waters belonging to Class II; while in February'13 (Kune) waters belong to Class II; while in February'13 (Kune) waters belong to Class II.

 NO_3 . The values of NO_3 , at all stations sampled in all the surveyed period, resulted below the limit allowed, so the waters belonging to the class I, according to the classification of UNECE.

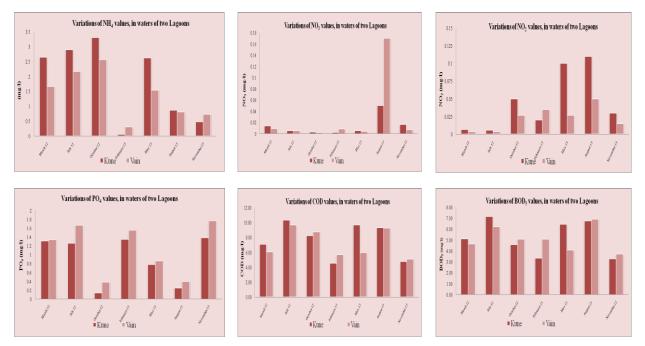
NO2. The contents of NO₂, compared with Directive 2006/44/EC, resulting in conformity with mandatory defined value for Salmonid waters in the two lagoons only in March of July'12, while conformity with mandatory defined value for Cyprinid waters in March'12, July'12, October'12, May'13 (Vain), February'13 (Kune) and November'13.

PO₄. The average values of PO₄ compared with Directive 2006/44/EC resulted in conformity with the value (level) required determining for only October'12 Salmonid waters (in Kune), while waters conform Cyprinid resulted at value (level) required in October'12 and August'13 months in both lagoons.

COD. Referring classification according to UNECE, the values of COD, the quality of water Kune Vain belongs to the class II and III (86% of samples taken in the lagoon of Kune and 93% of samples taken in the lagoon Vain belong class II, while 14% of water samples taken in Kune and 7% of the samples taken in Vain belonging to class III). Referred by NIVA's classification, quality of waters of the lagoon Kune, in 7% of samples of water taken belonging to class II, 29% of the samples belonging to class III, and 64% of samples belong to class IV). While in Vain lagoon, the quality of water, in 39% of samples are class III and 61% of samples are class IV.

BOD₅. The values of BOD5, compared with Directive 2006/44/EC, have resulted in conformity with the value required to Determine for the waters Salmonid, in the Kune Lagoon, only in November (in 21% of the sampling), the while for the waters Cyprinid, resulted conform almost all the required value Observed period (43% of the sampling). Taken in water samples in the lagoon of Vain, resulted not in conformity with the value recommended to Determine for the Salmonid waters, the while in 68% of the sampling are conform to the recommended value for the water cyprinid. Based on the classification of

waters according to UNECE, the waters of the lagoon of Kune in July'12, March and May of '13 August (spring and summer) Belonging to class III, and in the November of '13 February October'12 Belonging to class II (autumn and winter). Waters of Vain lagoon in March '12, May and November '13 belonging to class III, and in July of '12 October '13 and February of August belong to class II referred UNECE classification.



Graph 2. The variations of mean values, for the soluble forms of the nutrients in waters, in the both lagoons, during the period 2011-2013.

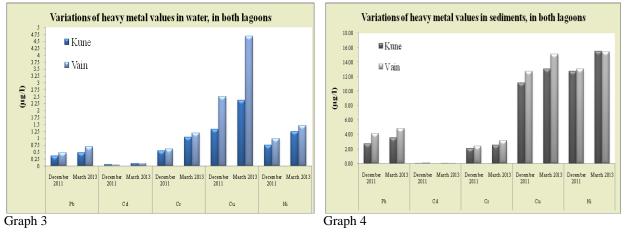
The relation N:P. The process of eutrophication, evaluated through the report Redfield Ratio (ratio of soluble forms of nutrients N and P expressed in μ mol L⁻¹). When this ratio approaches the number of Redfield's (C: N: P = 106:16:1), it is the process of eutrophication. Kune lagoon, in July'12, February and November'13, RR<10, then N is the limiting factor of eutrophication; we March'12, May and August'13, 10<RR<30, which is perfect for interval eutrophication processes; in October'12 and August'13 (point K3), RR>30, so P is a limiting factor, which controls eutrophication. Vain lagoon, in the months March and July '12, February, (May, August points V2, V3) and November '13, RR<10, N is the limiting factor of eutrophication; in May and August'13 (points V1, V4), 10<RR<30, which is perfect for interval for interval eutrophication processes; in October'12 and August'13 (points V1, V4), RR>30, so P is a limiting factor of eutrophication; which controls eutrophication processes; in October'12 and August'13 (points V1, V4), RR>30, so P is a limiting factor of eutrophication; which controls eutrophication processes; in October'12 and August'13 (points V1, V4), RR>30, so P is a limiting factor, which controls eutrophication processes; in October'12 and August'13 (points V1, V4), RR>30, so P is a limiting factor, which controls eutrophication.

Heavy metals. Were analyzed, in both lagoons, in two environments (water and sediments), in December 2011 and March 2013.

The concentration of heavy metals in the water. The metals concentration in water, for all survey period, belong to this sequence of Cu>Ni>Cr>Pb>Cd in both lagoons, as well referred to standards and norms of WHO standards, EPA and EC, average values to content of heavy metals in water were found lower than the guide values. Referring to the NIVA's, in Kune lagoon, the average values of Pb in water, classifies these waters to class I, for Cd, Cr and Ni belonging to class II, while for Cu belong to class III. In the Vain lagoon, referred NIVA's, the average values of Pb, Cd, Cr and Ni in water, classifies these waters to class II, while for Cu belong to class II.

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The concentration of heavy metals in the sediment. The metals concentration in sediments, for all survey period, belong to this sequence of Ni>Cu>Pb>Cr>Cd in both Lagoons. Referring NIVA's, the average values of Pb, Cd, Cu and Ni in the sediments it classifies to class I, concentrations of heavy metals in sediments are found lower than the guide values. Compared with the sediment quality guideline (mg kg⁻¹) according ANZECC (ISGQ ISGQ low and high); NOAA (ERL and ERM); Standard of Florida (TEL instructions of PEL), guidelines of WHO and EPA, the mean values of the concentration of heavy metals in sediments, in the monitored points are below the values quoted above standards.



Graph 3, 4. The variations of heavy metal values, in water and sediments, in the both lagoons.

Statistical Analysis

Data processing and statistical analysis is performed with SPSS ver.16. With the aim of testing the averages differences (for physical-chemical, micronutrients, heavy metals in water and sediment) is used statistical analysis ANOVA, Tukey's test (p<0.01dhe p<0.05).

For the physical-chemical measured in-situ: pH, T, EC, TDS, Sal and DO, is identified differences in the averages for the two lagoons, in the whole monitoring period showed that the difference, is statistically significant for elements pH, T, EC, TDS, and Salinity (table 1). For nutrients, in both lagoons, by ANOVA, Tukey's test (p<0.01dhe p<0.05 level), for the entire period of monitoring, it is noticed there is a difference statistically significant for NO2, PO4, COD and BOD₅ (table 2).

For heavy metals in water, the difference between the averages resulted in statistically significant for elements Pb, Cd, Cu, Ni, while in sediments there is a statistically significant difference for Cd (table 3).

ANOVA	pН	Т	EC	TDS	SAL	DO	ANOVA	NO ₂	NO ₃	PO ₄	COD	BOD ₅
Tukey's							Tukey's					
test		13		87	68)2	test	25	08	46	73	83
(p<0.01)	0.0	0.0	_	0.48).3(0.0((p<0.01)	0.02	0.0(70·C	0.20).48

Table: 1

ANOVA	Pb	Cd	Cu	ANOVA	Cd	
Tukey's test	water		Tukey's test	sediment		
(p<0.01)	0.577	0.876	0.014	0.287	(p<0.01)	0,112

Table: 2

Table: 3

Table 1,2,3. The results for ANOVA, Tukey's test (p<0.01dhe p<0.05).

Pearson correlation analysis showed that there are good correlations for some pairs of heavy metals (table 4). Correlation is significant at the 0.01 level for: Cr.W-Cr.S; Pb.W-Cu.W; negative correlation Cr.S-Cu.S; Pb.W-Cd.W; Cd.W-Cr.W; Cd.W-Cr.S; while Correlation is significant at the 0.05 level for: Cr.W-Ni.S; Cu.W-Cu.S; Pb.S-Ni.S; Cr.W-Ni.W; Ni.W-Ni.S; Cd.W-Ni.S; Pb.W-Cr.W; Pb.W-Cr.S; Cr.W-Cu.S and Pb.W-Pb.S.

Correlations										
	Pb_W	Cd_W	Cr_W	Cu_W	Ni_W	Pb_S	Cd_S	Cr_S	Cu_S	Ni_S
Pb_W	1	.675**	.529*	.692**	0.109	.500*	0.218	.509*	0.094	0.371
Cd_W	.675**	1	.644**	0.224	0.178	0.271	-0.084	.632**	-0.27	.511*
Cr_W	.529*	.644**	1	0.128	.584*	0.429	-0.15	.899**	507*	.585*
Cu_W	.692**	0.224	0.128	1	0.174	0.35	0.106	0	.613*	0.078
Ni_W	0.109	0.178	$.584^{*}$	0.174	1	0.355	-0.149	0.422	-0.114	.549*
Pb_S	$.500^{*}$	0.271	0.429	0.35	0.355	1	-0.08	0.352	0.215	$.580^{*}$
Cd_S	0.218	-0.084	-0.15	0.106	-0.149	-0.08	1	-0.011	-0.048	-0.241
Cr_S	$.509^{*}$.632**	.899**	0	0.422	0.352	-0.011	1	679**	0.468
Cu_S	0.094	-0.27	507*	.613*	-0.114	0.215	-0.048	679**	1	-0.104
Ni_S	0.371	.511*	$.585^{*}$	0.078	.549*	$.580^{*}$	-0.241	0.468	-0.104	1
**. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed).										

*. Correlation is significant at the 0.05 level (2-tailed)

CONCLUSIONS

The temperature values are found almost similar in the two lagoons, for the entire period surveyed. Values of pH, have fluctuated from 6.8 to 9.5, generally higher values of pH are encountered in Vain Lagoon. The values of TDS, EC and salinity are encountered higher, in the Kune lagoon. In the waters of the Kune lagoon, are found average values lower and higher of NH_4 , that in Vain lagoon waters. The NO_3 values, in the waters of the two lagoons in all the surveyed period, resulted below the limit allowed, the waters belonging to the class I, according to the classification of UNECE's. The average value of the DO is slightly higher in Vain lagoon. Lower average values of higher COD and BOD₅ are found in the Kune lagoon.

Concentrations of heavy metals are found lower in the water than in sediments. Lower contents of heavy metals in water and sediments are found in the Kune lagoon. The metals concentration in water, for all survey period, in two Lagoons, compared with Standards and norms of EC, WHO, EPA and NIVA, average values to content of heavy metals are found in water lower than the guide values. Compared with the sediment quality guideline (mg kg⁻¹) according ANZECC (ISGQ ISGQ low and high); NOAA (ERL and ERM); Standard of Florida (TEL instructions of PEL), NIVA's classification, the mean values of the concentration of heavy metals in sediments, are below the permitted values.

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