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RESEARCH ARTICLE

NUTRIENTS VARIATION IN THE COASTAL WATERS OF OUALIDIA LAGOON, MOROCCO, IN RELATION TO THE CONTRIBUTION OF WATERSHED AND HYDRO-CHEMICAL CHARACTERISTICS.

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Abstract

The aim of the present study is to investigate the hydrographic characteristics and nutrient salts in the Oualidia lagoon the period between July 2010 and June 2011. The results revealed that most of nutrients are concentrated upstream of the lagoon and decreased as it approaches the sea. The results showed that the impact of anthropogenic inputs was limited in the distribution of nutrient, the values of total phosphorus were below the Broadwater QWQG value (<25 µg L^{-1}), except during autumn period where the values reach 48 µg L^{-1}. Also, the relationships between the different nutrient concentrations and the other parameters (pH and suspended particulate matter) were discussed.

Introduction:-

The lagoons, interface between land and sea, congregate numerous habitats with very high biodiversity. Rich and diverse natural environments, they are places of life or passage for many plant and animal species and whose economic interest is recognized since ancient times. In addition, they provide an identity and landscape heritage that shapes the regional territory and represent a major important tourist attraction. In Oualidia lagoon this activity generates a significant economic flow especially in summer (Ministry of Interior, 2005).

So, the lagoons plays a directly and indirectly a capital socio-economic role, however, anthropic pressures and the development of multiple activities often create conflicts of interest that contribute to their vulnerability (Carruesco, 1989 ; Maanan, 2013).

The human pressure, concentrated on watersheds and areas near the lagoons such as domestic waste, industrial and agricultural activities, has consequences for these environments. In fact, it generates various types of inputs (nitrogen, phosphorus, pesticides, heavy metals, bacteria ...) which can lead to imbalances in the environment, harmful to traditional activities and the preservation of the quality of the lagoon environment.

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Study of the Oualidia lagoon was motivated by its importance as a biological reserve and its economic interest based on the exploitation of high-value resources (oysters). This lagoon is a RAMSAR wintering and stopover site for many migratory birds between Africa and Europe.

The Oualidia lagoon has been subject of several microbiological, hydrological, écological, geological, geochemical and sedimentary studies (Hassou *et al*., 2014 ; Hennani *et al*., 2014 ; Maanan and Robin, 2010 ; Farid *et al*., 2009 ; Chedad *et al*., 2007 ; Hilmi *et al*., 2005b ; Rharbi *et al*., 2003 ; Zourarah, 2002 ; El Attar and Assobhei, 2001 ; Sarf, 1999 ; Orbi *et al*., 1998 ; Bouchriti *et al*., 1992 ; Beaubrun, 1976) aiming to establish the current status of its functioning and characterize the different areas of this environment.

Continued population growth within coastal regions ensures there will be ongoing impacts on coastal wetland ecosystems (Lee *et al*., 2006). Within coastal waters, the primary point of entry for nutrients is from terrestrial sources (Pereira-Filho *et al*., 2001), for these high primary productivity and biological abundance are often observed in the lagoon (Alongi, 1998). In densely populated urban regions nutrient supply is greater due to the entry of both domestic and industrial waste and urban drainage (Lee *et al*., 2006).

The increase of nutrient concentrations within coastal waters can elicit either positive or negative responses in the ecological health of systems, including the alteration of species richness and abundance (Faulkner, 2004); productivity (Nixon, 1982); play an essential role in the biological productivities, ecosystem functions and biogeochemical processes in marine environments (Lin *et al*., 2012; Loh and Bauer, 2000) and fishing yields (Cederwall and Elmgren, 1980). Anthropogenic inputs of nutrients may lead to excessive eutrophication, especially where the circulation is restricted, such as in bays and coastal lagoons (Yu *et al*., 2012 ; Zhou *et al*., 2008 ; Lin *et al*., 2006., Trebini *et al*., 2005., Da Cunha and Wasserman, 2003).

The still incomplete knowledge of the geographical and spatial distribution of nutrients in the Oualidia lagoon was the origin of this work that uses the fluctuations in this element as pollution plotter.

This work has set the following objectives : (1) study of the spatial and temporal distribution of nutrient concentrations (nitrogen elements and total phosphorus) and the concentrations of chlorophyll-a according to usage activity and land use in the watershed; (2) relate the changes in these parameters with the variability of the activities and practices in the watershed using statistical methods ANOVA (analysis of variance) as well as the analysis of descriptive statistics SPSS Statistics 17.0.

However, it must be stressed that weather conditions encountered during this study, which took place from July 2010 to June 2011 correspond to a particular case : rainy period (autumn, winter and spring seasons) and dry season (summer season).

Material and Methods:-

Site description:-

The Oualidia lagoon (34°47'N - 6°13'W and 34°52'N - 6°14'W) is located on the Moroccan Atlantic coast in the province of Sidi Bennour, 168 km south of the city of Casablanca, and extends parallel to the coast for a distance of about 8 km long and 0.5 km wide.

The hydrological regime of the lagoon is primarily subject to the rhythm of the tides. During spring tides, the water flow has an average speed of about 0.46 m/s and a maximum speed of around 0.77 m/s; the filling time during the flow is 7 h 25 min and that of emptying is 5 h during the backflow. During neap tides, flow velocities are lower, in the range of 0.1 to 0.2 m s^{-1} and the times of filling and emptying are 4 h 25 min for the flow and 8 h in the ebb, respectively (Orbi *et al*., 2008). In addition, the hydrological regime of Oualidia lagoon is subject to the action of upwelling which affects the whole area, especially in summer (Makaoui *et al*., 2005).

The lagoon is shallow, the channel depth is not uniform and decreases upstream. During a low tide mark of spring tides, it varies depending on the location from 0.20 m to 1.80 m (Shafee and Sabatie, 1986).

The supply of fresh water to the lagoon occurs only upstream by means of a freshwater effluent, which maintains a certain gradient of desalting at low tide, while downstream it occurs via small resurgences. Because of its position between two hills forming its watershed, the Oualidia lagoon is a confluence of runoff water during rainfall in the region. On the other hand, faecal contamination (during the spreading of animal manure) and wastewater infiltration from septic tanks are the major mainland inputs to the lagoon (El Himer *et al*., 2013).

Shafee (1989) had cited that the water of the lagoon showed a richness in nutrients, particularly inorganic nitrogen. Indeed high levels are registered mainly in the upstream part of the lagoon. These levels were partly due to drainage of fertilizers used in agricultural activities, which causes intense development of macrophyte algae and phanerogams during the summer.

Sampling and methods of analysis:-

This study was carried out at 9 sampling sites distributed across the Oualidia lagoon (Fig. 1). The sampling points have been distributed as follows: Points representing the watershed in its agricultural area: EM5, EM6, EM7 and EM8; Points representing the watershed in its urban and touristic area : EM2, EM3, EM4 ; Points representing a reference of the sea located at the pass of the lagoon (EMT) and a point very close to it (EM1) and one point representing the situation at the salt marshes (EM9).

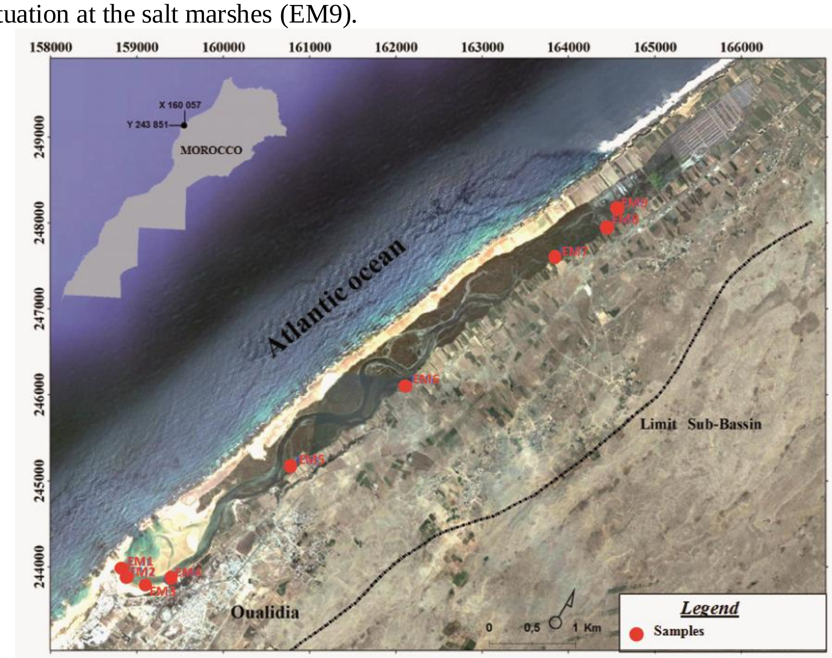

Figure 1:- Sampling sites in Oualidia lagoon (Cadastre Morocco, 2010)

The water samples were collected monthly at low tide during spring tides for an annual cycle (July 2010-June 2011) in ethanol-rinsed high density polyethylene bottles, which were washed with ambient water before sampling to prevent ethanol related die-off. The water samples were collected near the edge at 20 cm from the surface for the sampling sites located in the lagoon. They were collected in sterile glass bottles previously rinsed with water from the sampling site. They were then stored at 4 °C. The rainfall data for 2010-2011 were obtained from the local weather station. The physico-chemical analyses were performed by direct measurements on the surface, namely, the temperature and pH using a field pH meter Consort C931 and the salinity using a field salinometer Consort C861.

Depending on the rainfall data, the study period was divided into rainy period from September 2010 to May 2011 and a dry period including the months July-August 2010 and June 2011.

Nutrient Analysis:-

Total phosphorus (TP):-

Total phosphorus (TP) is measured after mineralization in acidic medium in presence of potassium persulfate followed by analysis of orthophosphates. Orthophosphates ($P\text{-}PO_4^{3-}$) are determined by a colorimetric measurement of the complex phosphomolybdic formed (AFNOR, T90-023).

Total Kjeldahl Nitrogen (TKN):-
Total Kjeldahl Nitrogen (TKN) is dosed by AFNOR method T90-110. It is a mineralization of organic nitrogen into ammoniacal nitrogen with sulfuric acid in the presence of a catalyst (copper sulphate, potassium sulphate). The ammonium obtained is dosed by acidimetry after distillation.

After mineralization, nitrogen is found in the mineral deposit in the form of NH_4^+. Total Nitrogen Analysis is an acid-base titration. Ammonium ions of the mineral deposit are in an excess of sulfuric acid and can't be dosed directly. In a first stage, we transform the ammonium ions of the mineral deposit into NH_3 (ammonia), then we will recover only ammonia in order to dose it with a calibrated solution of strong acid by distillation (Leeuwen van C *et al.,* 2000).

Nitrate (NO3-):-
After filtration, the determination of nitrate is expressed in mg L^{-1} by colorimetric method using sodium salicylate according to AFNOR T 90-012.

Results and Discussion:-

Physico-chemical water quality:-
The parameters measured within the lagoon system showed significant seasonal variations with the influence of tides and contribution of watershed. pH values are alkaline at all sampling points during both rainy and dry periods. It varies between 8.13 recorded during the rainiest months and 8.03 noted for dry months. This, implies a clear marine influence and absence of a significant seasonal variation. Mean pH values complied with the Broadwater values within the QWQGs of 8.0-8.4.

The turbidity of the lagoon waters is higher in the dry season than in the rainy period, medians of 5.62 and 4.40 NTU, respectively complying with the Broadwater values within the QWQGs <8 NTU.

During the rainy period season (spring, winter, autumn), when the waters are more turbid upstream of the lagoon, turbidity reaches a maximum value greater than 9 NTU. The observed turbidity is due to leaching of the watershed (Göransson *et al*., 2013). During the dry period (summer), the turbidity is very significant downstream of the lagoon with a maximum value of 10 NTU, which is due to tourism activity. This shows that the turbidity generated by tourism activity is higher than that caused by rainfall inputs.

Total phosphorus:-
Analysis of phosphorus data shows highly significant variations in the study sites (Fig. 2). Concentrations vary between 3.01 and 48.71 µg L^{-1} in autumn; 3.04 and 17.87 µg L^{-1} in the spring; 3.93 and 13.17 µg L^{-1} in winter and 2.75 and 11.62 µg L^{-1} in summer (Table 1). The peak concentrations of phosphorus observed in autumn at stations EM2 and EM3 (68.4 and 59.7 µg L^{-1}) can be attributed to overflowing of septic tanks for EM2 station and oyster farming activity at the oyster park (Park 01) for EM6 station.

The results of the variance analysis (ANOVA) regarding seasonal variations of total phosphorus shows a highly significant station and seasonal variation ($p = 0.000$).

The spatiotemporal monitoring of total phosphorus in the water lagoon (Fig. 2) showed that during the rainy period (spring, winter, autumn), the phosphorus concentration is the most important upstream and especially in the middle of the lagoon. This concentration is mainly observed in autumn with a maximum concentration of 48.67 µg L^{-1} coinciding with the first rains causing general leaching of agricultural land.

This increase can be explained by the important mobilization and release of this element by vegetation and silt, but also by waters rich in phosphates coming from sources (Duan *et al*., 2016 ; Hassou, 2014).

However, during the dry season (summer), the highest concentrations of phosphorus are observed in the in downstream part of the lagoon. During the same period, the levels decrease comparing to autumn, due to an important consumption of this element by algae.

During winter and spring times, that have registered heavy rainfalls, the high concentration downstream of the lagoon is mainly due to overflow of septic tanks. During the summer, the strong activity of upwilings causes the overthrust of phosphorus (Makaoui *et al*., 2005).

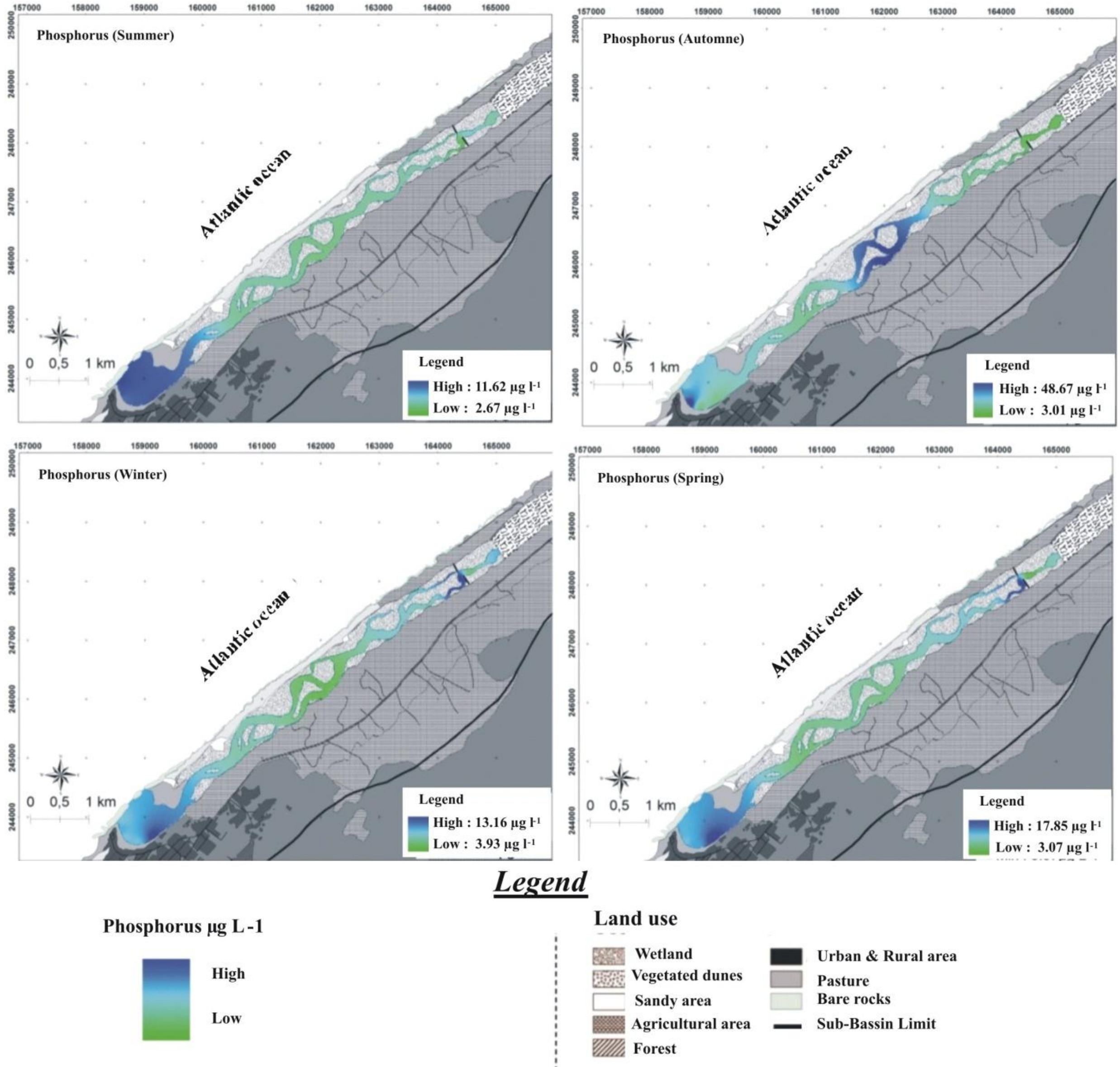

Figure 2:- Seasonal mapping of phosphorus concentration in waters of the Oualidia lagoon during the period between July 2010 and June 2011.

Mean concentrations of total phosphorus were below the Broadwater QWQG value (<25 µg L^{-1}), except during autumn period where the values reach 48 µg L^{-1} coinciding with the first rains causing a general leaching of agricultural land (Department of Environment and Resource Management, 2010).

Total Kjeldahl Nitrogen (NTK):-

The variance analysis ANOVA of kjeldhal nitrogen shows highly significant variations between study stations ($p = 0.000$) as well as for the season effect ($p = 0.000$). Concentrations vary between 8.89 and 21.34 mg L^{-1} in summer; 3.70 and 9.11 mg L^{-1} in autumn; 4.20 and 12.83 mg L^{-1} in winter; 8.05 and 14.45 mg L^{-1} in spring (Table1).

The spatiotemporal monitoring kjeldhal nitrogen in lagoon waters shows that during the rainy season (spring, winter, autumn), the Kjeldahl nitrogen concentration is the greatest upstream of the lagoon. This is due to the general leaching of agricultural land (Fig 3). However , during the dry season (summer), the highest concentrations of kjeldhal nitrogen are observed in the in downstream part of the lagoon

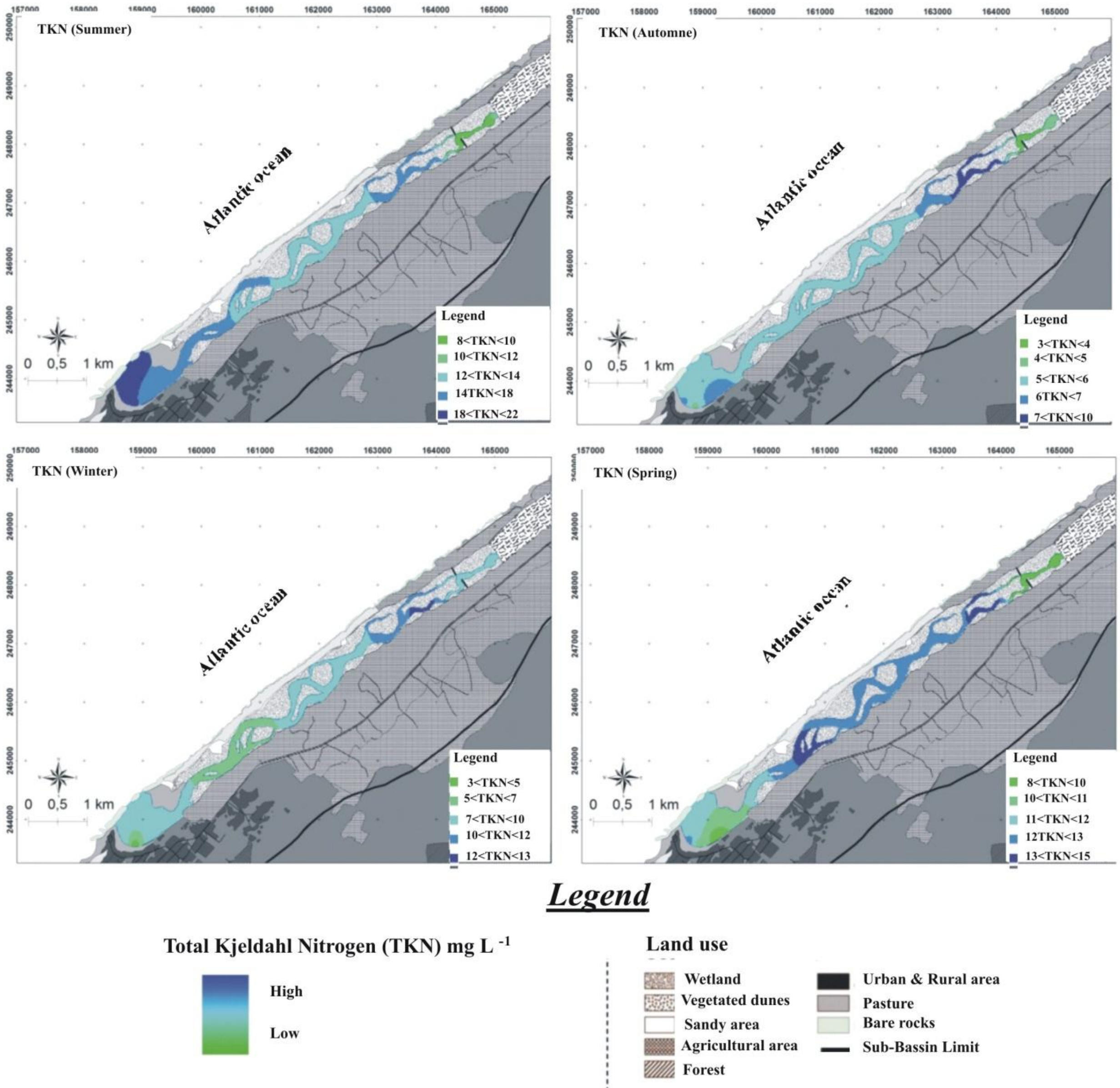

Figure 3:- Seasonal mapping of Kjeldahl Nitrogen concentration in the waters of the Oualidia lagoon during the period between July 2010 and June 2011

The strong concentartion downstream of the lagoon which is higher than that recorded during the rainy seasons is due to high concentrations of organic matter. The Seasonal variation shows an increase in nitrogen levels during the month of August on all sampling stations.

The potential sources nitrogen input in the waters of the lagoon are the leaching of nitrogenous fertilizers from farmlands, wastewater and organic matter. High levels of nitrogen in the lagoon provides a favorable factor in triggering the eutrophication phenomena.

Tableau 1:- Seasonal concentrations of nutrients in the waters of the Oualidia lagoon.

		Nitrate (µg L^{-1})	Phosphorus (µg L^{-1})	TKN (mg L^{-1})
Summer	Min-Max	120-946.67	2.75-11.62	8.89-21.34
	Median	431.67	8.75	15.77
	Mean ± Standard deviation	445.67± 224.53	8.04 ± 3.28	15.87 ± 4.74
Autumn	Min-Max	160-913	3.01-48.71	3.70-9.11
	Median	418.33	12.89	5.62
	Mean ± Standard deviation	436.3± 233.8	19.90 ± 15.49	5.66 ± 1.53
Winter	Min-Max	83.3-833.3	3.93-13.17	4.20-12.83
	Median	395	7.22	7.82
	Mean ± Standard deviation	420.3± 266.7	7.37 ± 2.63	7.96 ± 2.40
Spring	Min-Max	90-1193.3	3.04-17.87	8.05-14.45
	Median	220	9.5	11.7
	Mean ± Standard deviation	443± 391	9.35 ± 4.24	11.22± 2.22

Nitrate:-

The analysis of nitrates in the lagoon brings up fairly significant levels in the overall lagoon. The concentrations fluctuates between 90 and 1193.3 µg L^{-1} in the spring; 120 and 946.6 µg L^{-1} in the summer; 160 and 913 µg L^{-1} in autumn and 83.3 and 833.3 µg L^{-1} in winter (Table 1).

The results of the analysis of variance (ANOVA) concerning seasonal variations in nitrates show no significant seasonal variation ($p > 0.05$). However, the station effect is highly significant ($p = 0.000$).

In fact, during rainy period, nitrates are distributed according to an increasing gradient from the communication area with the ocean toward the upstream area, with the exception of an increase in downstream part in autumn due to overflowing of septic tanks. However, in summer, the highest concentration downstream and upstream of the lagoon is due to the intense tourist activity.

The origin of nitrates in the lagoon comes from the interaction between water and sediments by the remineralization phenomenon of organic matter, household waste dumped into septic tanks and inputs by fresh water from sweet water resurgences that constitute discharge points of groundwater.

In this framework the analyzes carried out on the main springs and wells identified in our work shows the presence of important levels of nitrate with concentrations ranging between 22.85 and 32.07 mg L^{-1} for the sources (Table 1), and between 16.38 and 32.66 mg L^{-1} for the wells. The arrival of ocean waters at rising tide relatively poor in nitrates, EMT and EM1 causes a decrease in levels across the lagoon.

Furthermore, the high levels recorded upstream in rainy period show that the essential contribution comes from the watershed. The spatio-temporal variation shows that high levels (1.19 mg L^{-1} upstream of the lagoon) are recorded in the spring following the leaching of vegetable crops particularly upstream of the lagoon. However, the levels decrease considerably in summer (0.3 mg L^{-1}) upstream, which shows the important role of rainfall during the rainy period and drainage from the watershed. Low value contents of seawater nitrate (0.09 mg L^{-1} or 90 µg L^{-1}), taken as a witness, confirms the enrichment of the lagoon, with nitrates by groundwater

The highest concentrations of nitrate are found during rainy periods (usually in winter and spring) and at the stations with the highest freshening, meaning the innermost. However, this relationship is not the same according to geographic areas. Indeed, it should be noted an elevation, downstream of the lagoon during the summer period, due to urban inputs.

The downstream area, made up of coarser sandy substrate, shows quite low levels. But in this part of the lagoon, the water-sediment exchanges are important, thereby reducing the nitrification time by bacterial activity. In the upstream portion where the bottom is sandy mud and muddy sand, the nitrification is more pronounced bringing up high concentrations such as the case of EM9 station (at the first artificial dike). The increase in nitrate levels in waters of the Oualidia lagoon (upstream part) during the rainy season compared to the dry period may be due to leaching of fertilizers used in agricultural soils located on the banks of the lagoon. However the values recorded during the dry season could be attributed to the waste water discharges which have undergone any treatment especially in EM2 and EM3 stations in addition of tourism activities.

It appears from these observations that nitrate levels recorded in surface waters of the Oualidia lagoon are below the limit values suggested by Moroccan and international standards (50 mg L^{-1}). This indicates that the studied waters are not subject to a risk of nitrate pollution.

The lagoon waters are characterized by high levels of nutrients, especially nitrates and phosphates in ionic form. Their evolution in space and over time follows an increasing gradient from downstream to upstream (rainy season), site of intense use of fertilizers used in vegetable crops. These variations are governed by three main phenomena that are primary production, bacterial regeneration and exogenous inputs. The highest concentrations are generally in the middle and upstream of the lagoon. The lowest are recorded downstream, especially in the open sea where dilution of lagoon waters is done by the massive rise of marine waters of good quality and the pressure of the masses of polluted water upstream.

Conclusion:-

This study allowed us to make a diagnosis of the status of the quality of the Oualidia lagoon. This diagnosis includes an evaluation of the nutrient content of surface waters of the Oualidia lagoon. The results showed that there is a deterioration of the quality of the water marked by the increase of these elements.

We conclude that the variation in nutrients varies according to a downstream-upstream gradient decreasing in summer and increasing in the rainy season. However, these variations could be due to the influence of environmental factors. Indeed, these elements are affected by the tide and hydrodynamics. However the sediment compartment is influenced by the nature of facies.

Also, the study of major sources bordering the continental shore of the lagoon shows, moreover, that significant levels of phosphates and, in particular, nitrates are brought into the lagoon, despite the lack of rainfall during the summer period. Freshwater resurgences which are groundwater discharge points are located in a watershed with size, topography and soil type explain the richness of the resurgences and the water masses (according to data resurgences Hassou (2014) : 36.12 µg L^{-1} nitrate, 4.76 µg L^{-1} total phosphorus and 15.4 mg L^{-1} Total Kjeldhal Nitrogen). Another exogenous contribution is due to the presence of a non-functional sewage treatment plant in the region and the lack of a sewerage system, therefore, the use of septic tanks. By infiltration, these discards of human origin, more or less well mineralized are directed to the groundwater and added to the previously mentioned contributions. In addition, the use of fertilizers in agriculture and topography of the field cause leaching of these fertilizers. Nutrient concentrations were influenced tidally and contributions of watershed, with increased concentrations occurring upstream of the lagoon during the rainy period which are added to the previous contributions, especially during the winter period (Hassou, 2014).

The phosphorus concentration exceeded Broadwater QWQG values excepted in autumn.

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